FOREWORD

This report was prepared by Battelle Memorial Institute on Contract No. AF 33(657)-10988 under Project No. 6373, "Equipment for Life Support in Aerospace", and Task No. 637302, "Respirator Support Equipment". The work was performed under the direction of the 6570th Aerospace Medical Research Laboratories, Aerospace Medical Division, Wright-Patterson Air Force Base, Ohio, and was administered by Richard E. Bennett and Clyde G. Roach, Respiratory Equipment Branch, Biotechnology Division, Biomedical Laboratory. The work reported here was done between 1 April 1963 and 28 February 1964.

The principal investigators for Battelle Memorial Institute were: E. S. Kolic, Electrochemist; J. E. Clifford, Senior Chemical Engineer; and J. T. Gates, Mechanical Engineer. The work was done under the direction of Dr. Charles L. Faust, Chief, Electrochemical Engineering Division.

ABSTRACT

The experimental investigation has demonstrated that a static water electrolysis cell with a palladium-silver alloy hydrogen-diffusion cathode is technically feasible. The best result was obtained with an experimental cell constructed with a 1/4-inch-diameter palladium-silver alloy tube of 5-mil wall thickness (0.5-inch effective length), a matrix of Teflon threads and calcium hydroxide impregnated with an electrolyte of 50 weight percent sodium hydroxide, and a platinum screen anode. The cell was operated satisfactorily independently of gravity for a minimum of 24 continuous hours with 97-100 percent hydrogen transmission at 75 amp/ft^2 and 2.0 volts at 145°C with water supplied as vapor (1 atmosphere partial pressure). Preliminary design estimates for a cell to supply breathing oxygen for 3 men (6 pounds O_2 per day) indicate a very small cell (25 pounds, 0.2 ft^3) with low power consumption (760 watts).

PUBLICATION REVIEW

This technical documentary report is approved.

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Technical Director
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RESEARCH ON A GRAVITY-INDEPENDENT WATER-ELECTROLYSIS CELL WITH A PALLADIUM-SILVER ALLOY CATHODE

by

John E. Clifford, Edwin Kolic, and Charles L. Faust

INTRODUCTION

This project was initiated to investigate a method of accomplishing electrolysis of water for use under weightless conditions on protracted space missions (up to 2 years). Specific investigation covered a static cell using a palladium-silver cathode. The term static is used in the sense of nonrotating to differentiate from electrolysis cells investigated on prior projects: a rotating electrolysis cell (conventional electrolysis principle) (Ref. 1), and a rotating cell with a palladium-silver cathode (Ref. 2).

Prior related studies at Battelle on the hydrogen-diffusion cathode (Ref. 2) demonstrated that 100 per cent hydrogen transmission was possible through a palladium-silver cathode at high current densities (up to 265 amp/ft^2). However, the few satisfactory runs of about 1-hour duration were not readily reproduced and further study of the palladium-silver cathode was recommended. To eliminate the need for cell rotation, it was necessary to develop an oxygen anode. The research program covered herein was conducted in three phases: cathode studies, anode studies, and cell-design studies.

SUMMARY OF EXPERIMENTAL RESULTS

In the first phase of the program in which the PdAg cathode was studied alone, it was shown that satisfactory operation could be readily obtained with vacuum-annealed foil. Satisfactory operation (95 ± 5 per cent hydrogen transmission) was maintained for 70 hours at 40 amp/ft^2 with 1-mil foil. Also, 5-mil PdAg in the form of 1/4-inch-diameter tubes was operated at practically 100 per cent hydrogen transmission at current densities up to 100 amp/ft^2 for periods of at least 6 hours.

In the second phase of the program in which oxygen anodes were studied alone, satisfactory operation was obtained independent of gravity at current densities up to 245 amp/ft^2. However, the biporous anodes (i.e., double-pore layer electrode similar to the type first developed for fuel cells) required careful pressure control.

In the third phase of the program on static cell design with a PdAg cathode, it was found that a matrix-type cell construction was better for an electrolysis cell. The advantages of a matrix-type cell with a platinum screen anode relative to a biporous-anode-type cell appear to be:

(1) Ability of the PdAg cathode to function without polarization at less than 100 per cent hydrogen transmission independent of gravity (weightlessness)

(2) Simplicity of operation (careful gas pressure control not necessary)

(3) More reliable and shock-resistant electrode construction (flexible platinum screen versus sintered metal plaque of controlled pore size)

(4) Simplicity of water addition as water vapor absorbed by matrix according to electrolysis need

(5) Tolerance for electrolyte concentration increase and associated electrolyte volume decrease (e.g., about 35 per cent volume decrease for change from 60 to 70% KOH).

The objective of the project was attained with the demonstration of the technical feasibility of continuous operation of a static electrolysis cell with a PdAg cathode with satisfactory performance for 24 hours. The experimental apparatus, shown in Figure 1, consisted of a matrix fabricated from Teflon threads and relatively insoluble calcium hydroxide. The anode was 8-mesh platinum screen and the cathode was a PdAg tube (1/4-inch diameter by 5-mil wall) of which about 1/2 inch was used to give an effective cathode electrolysis area of 0.38 $in.^2$. Operation at 0.193 ampere supplied from a constant current source (for accurate measurement of hydrogen transmission by Faraday's Law) resulted in a cathode current density of about 75 amp/ft^2 which is practical for cell design. During the run, the hydrogen transmission measured 97-100 per cent for 24 continuous hours while the cell voltage was 2.05 volts ±0.05 volt at a cell temperature of 145°C.

Time did not permit a study of other current densities or operating conditions with this cell. However, it is logical to conclude that satisfactory performance would also be attained at any lower current density than 75 amp/ft^2. Limited extrapolation of cell performance to higher current density of at least 100 amp/ft^2 is reasonable for the matrix cell, whereas use of even higher current densities appears possible based on the proven performance of PdAg cathodes alone.

Water for electrolysis was supplied to the cell from a water-vapor generator operating at 100°C (760 mm Hg abs). Since no pumps were used to feed liquid water to the cell and no blowers were required to circulate water vapor, the electrolysis concept is truly a static cell that operates independently of gravity with no moving parts.

The cell was initially impregnated with about 0.3 ml of 66 wt per cent sodium hydroxide so that the contained water was only 0.25 ml. During 24 hours of operation at 0.193 ampere, 1.6 ml of water was electrolyzed which indicates that a steady-state condition was established between the vapor supplied and the water consumed by electrolysis. Ideally, the water vapor could be supplied at the equilibrium vapor pressure over the electrolyte (about 200 mm Hg for 66 wt per cent NaOH at 145°C). However, at the operating current density of 75 amp/ft^2, it was necessary to supply water vapor at 760 mm Hg. The amount of water removed with the oxygen stream that would have to be recycled is proportional to the ratio of partial pressures of water vapor and oxygen. The ratio could be reduced by operating at a lower water-vapor pressure (i.e., anode/matrix design for improved absorption) or by operating the cell at a higher oxygen partial pressure.

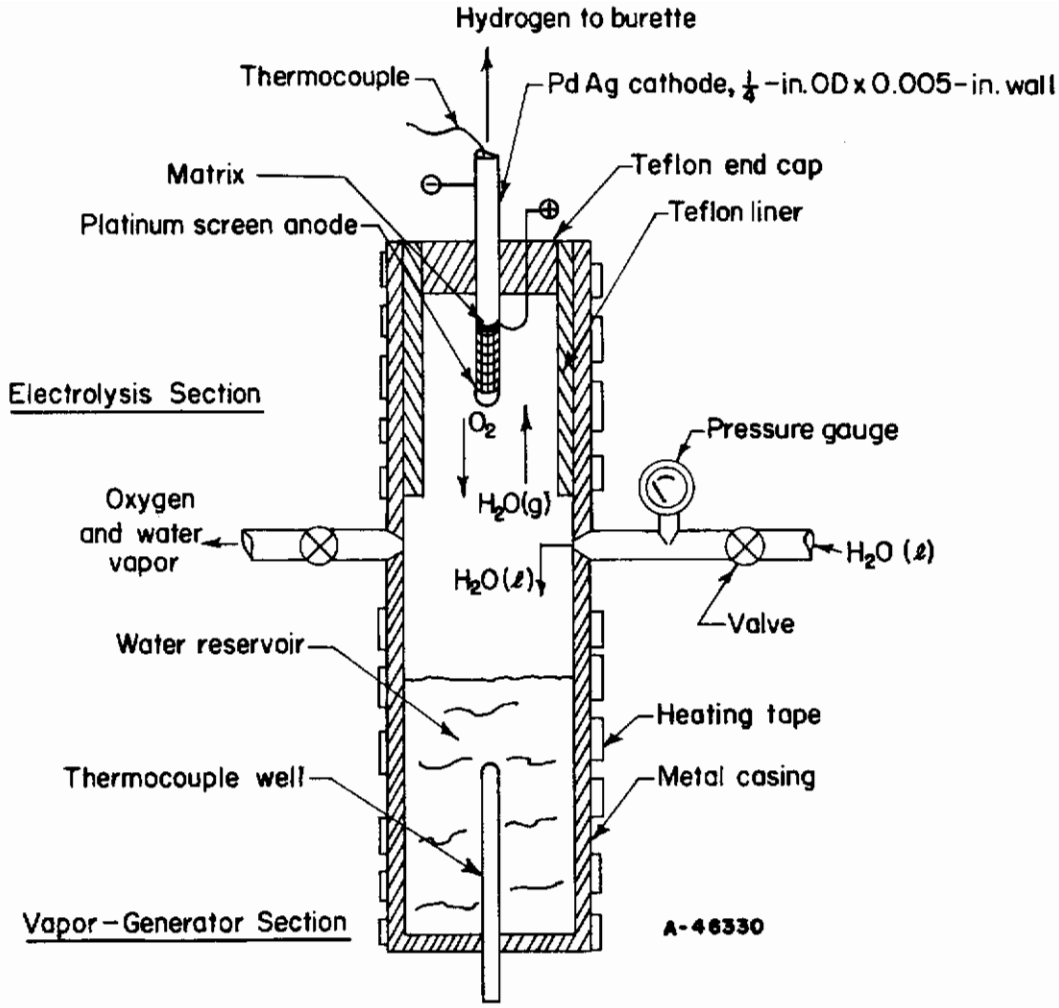

FIGURE 1. SCHEMATIC OF EXPERIMENTAL APPARATUS FOR EVALUATION OF STATIC CELL FOR GRAVITY-INDEPENDENT OPERATION WITH A WATER-VAPOR FEED

The cell voltage of 2 volts at 75 amp/ft^2 demonstrated in the 24-hour run is characteristic of the Teflon/$Ca(OH)_2$ matrix and is higher than for some other matrix materials. For example, the current-voltage curves of Figure 2 for a static cell with an asbestos matrix indicate about 1.6 volts at 75 amp/ft^2. Furthermore, at lower current densities the cell voltage approaches the calculated theoretical reversible cell potential of 1.17 volts. The use of an asbestos matrix was studied more extensively than the Teflon/$Ca(OH)_2$ matrix but at the present time asbestos is not considered satisfactory. The asbestos matrix contaminated the electrolyte (presumably with iron) which in time reduced hydrogen transmission. With acid-leached asbestos, satisfactory operation at greater than 90 per cent hydrogen transmission lasted only 2-5 hours.

Figure 3 shows a proposed design for a static cell with a PdAg cathode using tubular cathodes.

DISCUSSION OF EXPERIMENTAL RESULTS

Phase 1. Cathode Studies

Background

This phase of the program was a continuation of the study of the palladium-silver alloy hydrogen diffusion cathode. The objective was to define the conditions under which satisfactory cathode performance could be reproduced in extended runs of 8 to 24 hours.

Previous research (Ref. 2) demonstrated the technical feasibility of 100-per cent hydrogen transmission at high-current density. Table 1 indicates the status at the beginning of the research covered herein. Several attempts to reproduce the results of Table 1 were unsuccessful in the previous research. Possible differences in the metallurgical characteristics of the 1-mil-thick palladium-silver foil used in various experiments was suspected. The effect of annealing the "as received" foil was the first variable covered herein.

Experimental Apparatus

The electrolytic cell (Cell A) used in the early work on cathode studies is shown in Figure 4. The Teflon-lined cell contained three palladium-silver alloy tubes, two of which acted as hydrogen reference electrodes for measurement of the cathode voltage (so as to exclude the anode voltage, although a small ohmic drop through the electrolyte was included in the measurement). The third tube was used as a thermocouple well for measuring the electrolyte temperature and was platinum clad to function as an anode. The 1-mil-thick palladium-silver foil was positioned in the bottom of the cell exposing a 3/4-inch-diameter cathode area to electrolysis.

Cell A was also used for anode studies discussed later. As shown in Figure 4, the biporous anode could be positioned at the bottom of the cell in place of the PdAg foil and either the PdAg tube or platinum-clad tube used as the opposing cathode.

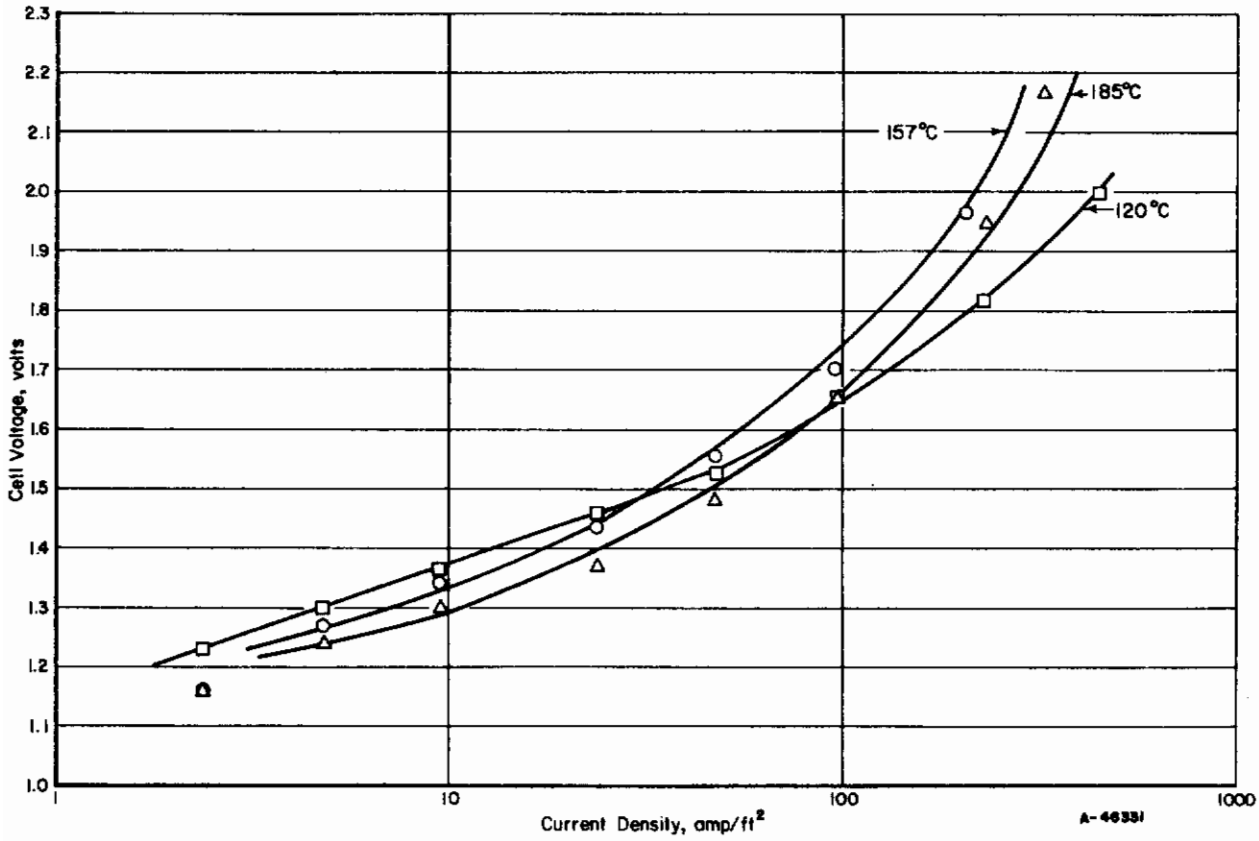

FIGURE 2. VOLTAGE CHARACTERISTICS AT VARIOUS CELL TEMPERATURES FOR A STATIC CELL WITH AN ASBESTOS MATRIX

Impregnated with 65% NaOH electrolyte; 48-mesh platinum screen anode; water-vapor feed at a partial pressure of 760 mm Hg (100°C); H_2-transmission averaged 70%.

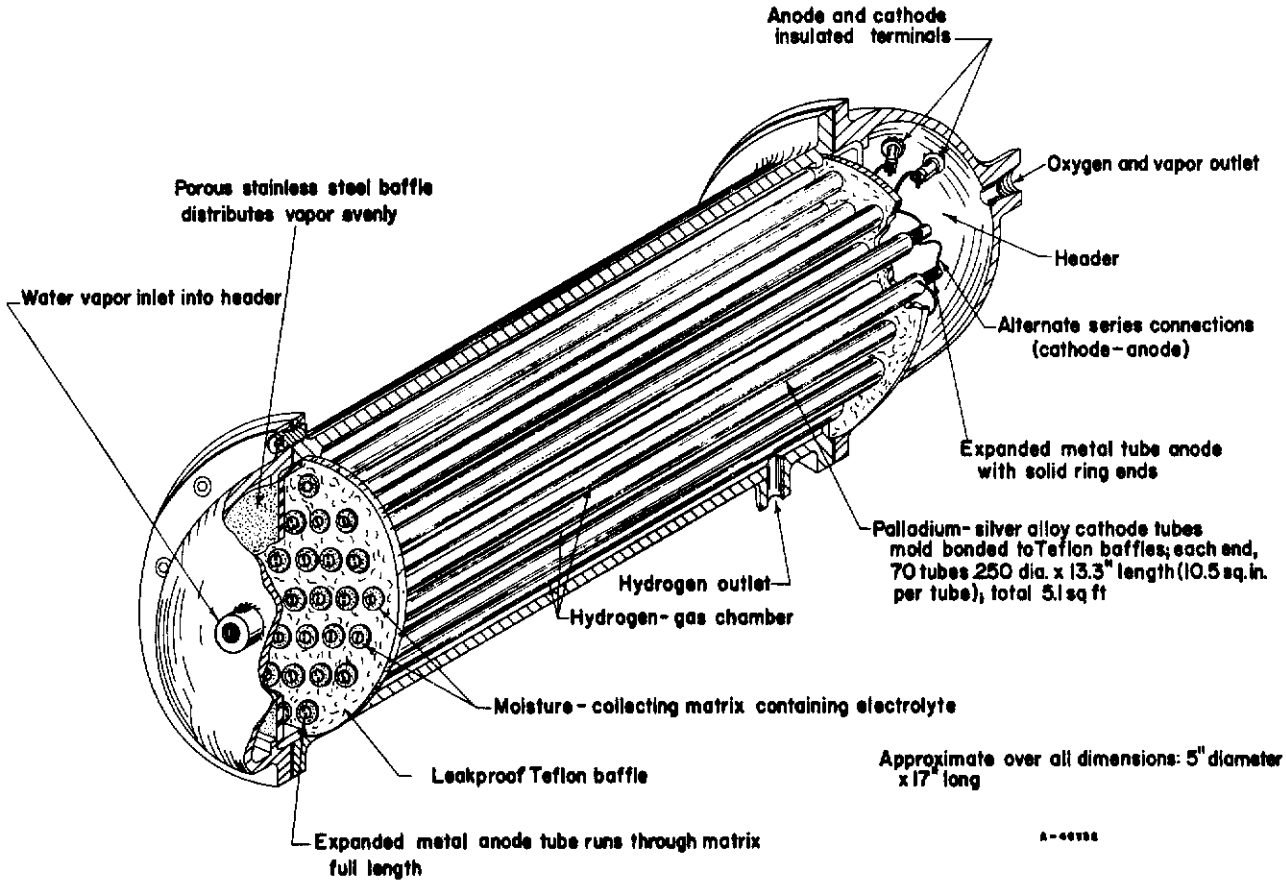

FIGURE 3. SCHEMATIC OF PROPOSED TUBULAR CELL DESIGN OF STATIC ELECTROLYSIS CELL TO SUPPLY OXYGEN FOR THREE MEN

TABLE 1. SUMMARY OF BEST EXPERIMENTAL RESULTS IN PRIOR STUDY OF HYDROGEN-DIFFUSION CATHODES (REF. 2)

(Palladium-silver alloy, 0.001 inch thick.)

Run	2-34	2-77	2-95
Electrolyte, weight per cent KOH	65	55	50
Temperature, °C	200	200	230
Pressure, psig			
Electrolysis side	122	20	13-25
Diffusion side	0	0	0
Current density, amp/ft^2	15	150	265
Average Cell Voltage, volts	1.34	2.0	1.76
Average Hydrogen Transmission, per cent	93	100	100
Satisfactory Operating Period, hours	2	1.5	0.85

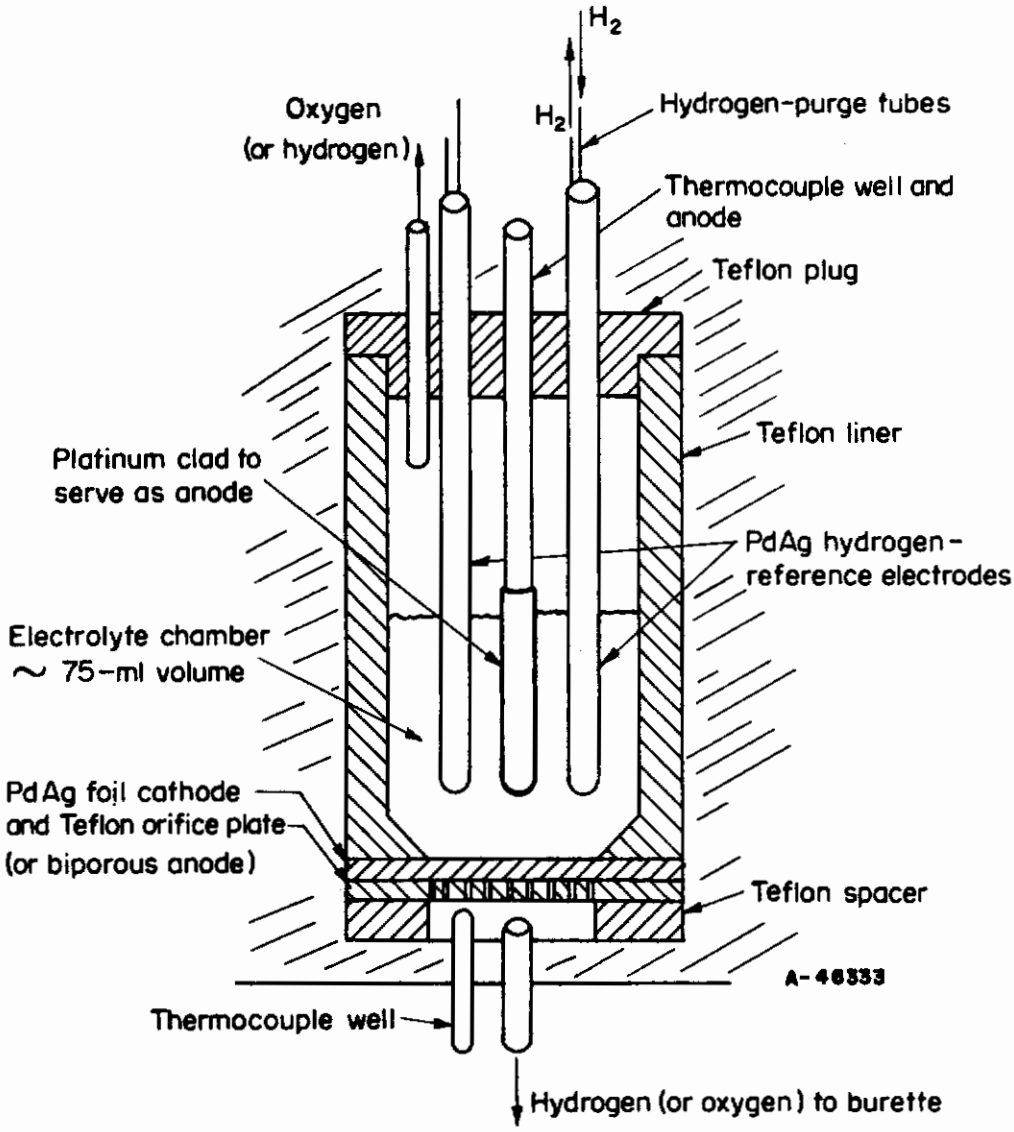

FIGURE 4. SCHEMATIC OF EXPERIMENTAL ELECTROLYSIS CELL USED FOR STUDY OF PdAg FOIL CATHODES (OR BIPOROUS ANODES)

A new supply of palladium-silver foil and tubes was obtained* at the beginning of this research. No analysis of the alloy was made, but both, the foil and tubes, were reported by the manufacturer as containing 25 per cent silver by weight and the balance palladium. The 1-mil-thick foil was obtained in strips 2 inches wide by 6 inches long. The tubes were 1/4-inch OD by 6 inches long by 5-mil wall. One end of the tube was pinch closed and electrically welded.

A low-voltage, 50-ampere rectifier** and a high-voltage, constant current (193 ma max) rectifier*** were used in the experimental work as the direct-current sources. The cell and electrode voltages were measured with a vacuum-tube recorder.**** Temperatures were recorded with a 2-point millivolt recorder***** operating with Chromel-Alumel thermocouples.

Hydrogen gas diffusing through the foil was collected over water in a burette. The per cent hydrogen transmission is defined as the ratio of the rate of gas collected (time 100) to the theoretical rate of gas expected based on Faraday's Law and the amount of current passed. The theoretical rate was corrected for temperature and vapor pressure:

$$\%H_2 = \frac{\text{gas collection rate} \times 100}{\text{corrected theoretical rate}},$$

where corrected theoretical rate $= \frac{(22{,}400)\ (60)\ (298)\ \ (760)}{(96{,}500)\ (\ 2)\ (273)\ (760\text{-}25)} = 7.85\ (I)$ ml/min

I = electrolysis cell current, amperes.

Effect of Annealing

Palladium-Silver Foil. The "as received" palladium-silver foil was vacuum-annealed for 1 hour at 650°C prior to evaluation in Cell A (Figure 4). The results of this experiment (Run 17-2) are summarized in Table 2. Continuous operation for nearly 70 hours at 40 amp/ft^2 with an average hydrogen transmission of 95 per cent was a substantial improvement over prior results (Ref. 2), and the improvement was attributed to the annealing. At the beginning of the run after anodic activation, essentially 100 per cent hydrogen transmission was maintained for 10 hours. When the hydrogen transmission had slowly decreased to 90 per cent (after 40 hours), it was shown that 100 per cent transmission could be restored by anodic activation at 40 amp/ft^2 for 3 minutes. The hydrogen transmission was 91 per cent when the run was terminated after 68-1/2 hours.

At a temperature of 200°C the total cell voltage was about 1.6 volts. The cathode voltage was 0.135 volt ± 0.025 volt versus the reference electrode. Thus, the anode voltage was about 1.46 volts for oxygen evolution at about 40 amp/ft^2 on the smooth platinum-clad anode.

*J. Bishop and Company, Malvern, Pennsylvania.
**Selenium Rectifier, Model 50 C, Rapid Electric Company, New York, New York.
***Coulometric Current Source, Model IV, E. H. Sargent Company, Chicago, Illinois.
****Volt-Ohm Millamp Recorder, Bausch and Lomb, Inc., Rochester, New York.
*****"Micromax" 2-Point Recorder, Leeds and Northrup Co., Philadelphia, Pennsylvania.

TABLE 2. SUMMARY OF DATA FROM PdAg CATHODE STUDIES

Run	Experimental Cell Used	Electrode Description		Electrolyte, KOH		Cathode Current Density, amp/ft^2	Cell Voltage, volts	Hydrogen Transmission, per cent	Electrolysis Time	Remarks
		Cathode	Anode	Conc., wt per cent	Temp, °C					
17-2	A	PdAg foil	Pt-clad tube	70	185-220	40	1.6	95	68 hr – 30 min	Foil vacuum annealed for 1 hour at 1200 F; foil was transmitting at 91 per cent when run was terminated
17-18	A	PdAg tube	Pt-clad tube	62	185	40	1.65	98	2 hr – 30 min	As-received tube
						40	1.65	100	1 hr	
						50	1.92	100	40 min	
						60	2.02	100	30 min	
						70	2.07	100	25 min	
						80	2.12	100	1 hr	
						100	2.17	100	2 hr – 25 min	Oxygen analyzed pure; tube was transmitting at 100 per cent when run was terminated
17-56	B	PdAg foil	Pt strip	70	190	70	1.80	98	3 hr – 45 min	Make-up water was added to the cell dropwise during run; for continuation of this run with an asbestos matrix, see Run 17-56, Table 4.
						140	1.91	100	45 min	

The favorable operation with an electrolyte of high concentration (70 wt per cent KOH) and low equilibrium water-vapor pressure was a feature desired for a practical cell to minimize loss of water with the oxygen stream. While operation of a practical cell at a positive pressure (i.e., 15 psig on the oxygen side) might be desirable to further minimize water loss, the extended run at 0 psig showed that a positive pressure was not essential to operation of the hydrogen-diffusion cathode. [The few good results in prior research had indicated that a positive pressure on the electrolysis side might be required for 100 per cent transmission (Table 1)]. Most of the subsequent experimental work on this contract was performed at atmospheric pressure which simplified experimental cell design and operation.

Experimental Cell B was a simple cell used in later experiments with a matrix (Figure 6 shown later). However, in Run 17-56 (Table 2) Cell B was used to study the PdAg cathode foil alone positioned at the bottom of the cell, which was filled with 3 ml of electrolyte. Make-up water was added dropwise. The PdAg foil was vacuum annealed at 650°C for 1 hour prior to use. A platinum-strip anode of small area was used as the opposing electrode so the cell-voltage values are not representative. During the first 4-1/2 hours, 98-100 per cent hydrogen transmission was demonstrated at current densities up to 140 amp/ft^2. The results indicated that there was no problem in achieving satisfactory performance of the hydrogen-diffusion cathode when the palladium-silver foil was annealed. Although not directly proved by experiment, the inference is that the difficulties previously encountered (Ref. 2) related to use of "as received" foil. Apparently the metallurgical changes associated with physical reduction to 1-mil foil adversely affect the permeability of the foil to hydrogen. Further evidence of metallurgical factors was the satisfactory performance of palladium-silver tubes in the as-received condition which were not annealed at Battelle prior to use. Presumably, the tubes were annealed during fabrication.

Palladium-Silver Tubes. One disadvantage of using palladium-silver in the form of thin flat foil was the tendency for the foil to crinkle in the electrolysis zone through expansion when hydrogen was added. The tubes expanded uniformly on the circumference when charged with hydrogen and the surface did not crinkle. For this and other reasons related to cell design, the use of palladium-silver tubes appears preferable to flat foil as the cathode.

Further experimental studies relating to palladium-silver cathodes were carried out with tubes having a 5-mil wall. Run 17-18, Table 2, was made with a tube previously used as a hydrogen-reference electrode in Cell A of Figure 1. After anodic activation, 98 per cent hydrogen transmission was obtained at 40 amp/ft^2 for 2-1/2 hours, after which time the hydrogen transmission increased to 100 per cent where it remained for the next 6 hours. During this last 6 hours of the run, the cathode current density was increased stepwise from 40 to 100 amp/ft^2, with the higher current density being maintained for a 2-1/2-hour period with 100 per cent hydrogen transmission. The sample of oxygen evolved from Cell A was collected over a 40-minute period, and analysis indicated 100 per cent O_2 within ±0.1 per cent on a dry basis.

The per cent hydrogen transmission and cell voltage at 40 amp/ft^2 with a PdAg tube (Run 17-18) compares favorably with annealed foil (Run 17-2). The increase in cell voltage at higher current density in Run 17-18 reflects the anode overvoltage on smooth platinum rather than the overvoltage of the PdAg tube.

Current densities greater than 100 amp/ft^2 were not investigated in Run 17-18 because less need appeared for high-current densities with a static-cell design. However, in beaker-type studies with Cell D, Figure 5, 100 per cent hydrogen transmission was maintained for 45 minutes at 230 amp/ft^2 in 66 per cent KOH electrolyte at only 125°C. Assuming that the limiting diffusion rate of hydrogen through palladium-silver foil is a linear function of its thickness (which appears logical under conditions for 100 per cent transmission), a current density of 1150 amp/ft^2 might be possible with an active 1-mil-thick foil, based on the 230 amp/ft^2 through the 5-mil wall.

Cathode Activation

General Activation Procedure. In the early part of the program there was no difficulty in initially activating palladium-silver for 100 per cent hydrogen transmission when the alloy was in the annealed condition. The procedure used for activation in the cell electrolyte at operating temperature was as follows:

For annealed foil (1 mil)

(1) Cathodic for 5 minutes at 200 amp/ft^2

(2) Anodic for 1 minute at 200 amp/ft^2

(3) Cathodic at operating current density

For tubes (5 mils)

(1) Cathodic for 7 minutes at 200 amp/ft^2

(2) Anodic for 1 minute at 200 amp/ft^2

(3) Cathodic at operating current density.

The activation procedure was adequate for annealed foil in Runs 17-2 and 17-56 where new foil was used for each run and for virgin palladium-silver tubes (i.e., as-received tubes used for the first time in electrolysis) as in Run 17-18, Table 2. The activation procedures are known to be satisfactory for potassium hydroxide electrolytes of 62 to 75 wt per cent KOH at temperatures from 126° to 200°C. In a few instances with tubes it was necessary to repeat the activation procedure to achieve 100 per cent transmission of hydrogen. Because the tubes were expensive, they were often reused in the experimental studies. New activation problems became apparent during the study of matrix cells due to the introduction of contamination from the matrix materials. Because of the limited volume of electrolytes in the matrices compared to the large excess of electrolyte used in cathode studies, the cathode-poisoning rate was accelerated and special activation procedures were required before the tubes could be reused.

Reactivation of Poisoned Cathode. Reactivating the surface of palladium-silver tubes which became poisoned during the experimental work was a special problem that does not appear pertinent to practical cells made with the preferred matrix. However, the special activation procedures developed were sometimes informative regarding the nature of the poisoning and the factors affecting attainment of 100 per cent hydrogen

transmission. These studies were carried out in Cell D (Figure 5) where it was possible to observe directly the effectiveness of activation.

For an active tube, no hydrogen gas bubbles were discharged from the cathode surface and the measured hydrogen transmission was 100 per cent. Sometimes small isolated areas of the tube remained inactive and hydrogen bubbles could be observed to discharge from the inactive sites (hydrogen transmission of 97 per cent or less). Similar visual observations were used to verify contamination of tubes from disassembled matrix cells. Copious amounts of hydrogen could be seen discharging from poisoned cathodes which gave less than about 80 per cent hydrogen transmission because of the high current densities used (40-200 amp/ft^2).

Hydrogen-diffusion cathodes which became poisoned during experimental work with asbestos matrices responded to two treatments: (1) repeated anodic activations at current densities of 800-1200 amp/ft^2 until oxygen evolved for 30-60 seconds, and (2) soaking the poisoned cathode in 37 per cent hydrochloric acid for 10-15 minutes at 25°C. Apparently, the contaminant common to asbestos was acid soluble (probably iron). In the first reactivation procedure (1), the contaminate is probably deplated from the surface of the PdAg tube by the anodic treatment. Of the two procedures, the hydrochloric acid soak was the procedure most frequently used to avoid contaminating the electrolyte of Cell D used for cathode studies. All asbestos-poisoned tubes which were treated with acid responded to the normal 200 amp/ft^2 anodic activation and, in some cases, no anodic activation was required at all.

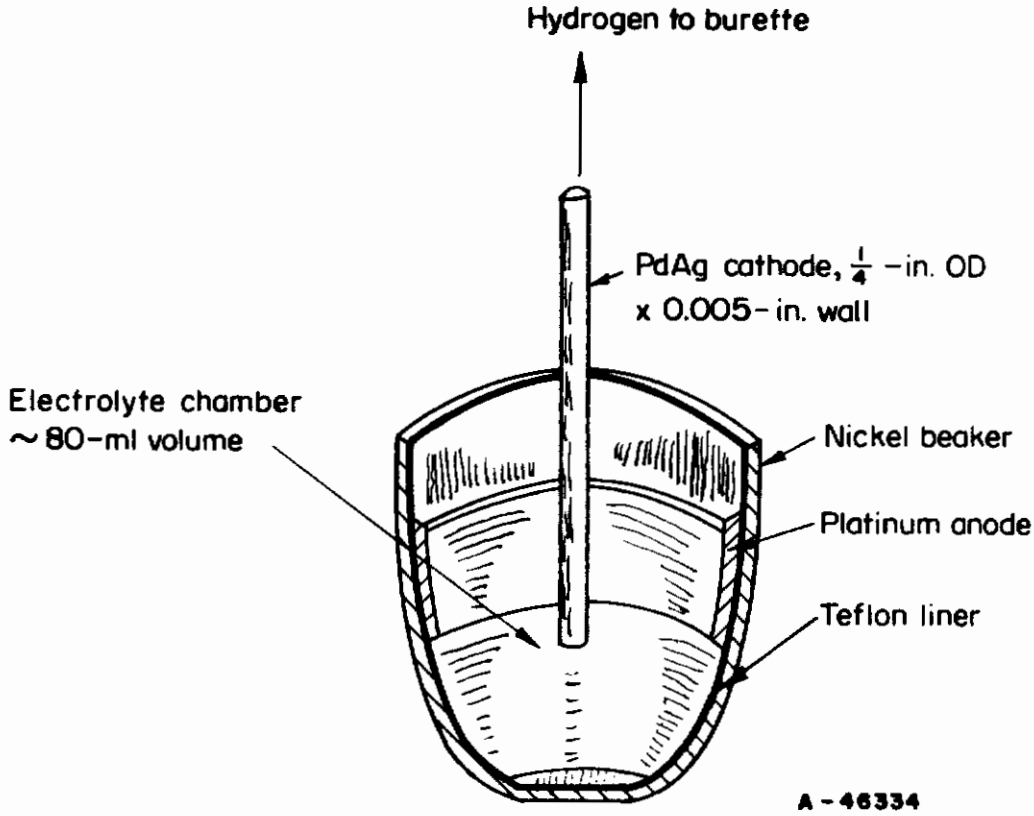

FIGURE 5. SCHEMATIC OF EXPERIMENTAL ELECTROLYSIS CELL D (OPEN BEAKER) USED FOR STUDY OF PdAg TUBE CATHODES

Hydrogen-diffusion tubes which became poisoned during experimental runs with magnesium oxide matrices responded to the hydrochloric acid treatment.

The most difficult tubes to reactivate were those tubes used in experimental runs employing matrices of nylon, Orlon, and Dacron. Hydrogen-diffusion cathodes poisoned by these matrices did not respond to acid treatment, nor did they respond to anodic activations at excessive current densities (800-1200 amp/ft^2). However, after the tubes were cathodically charged with hydrogen and heated to redness in the oxidizing flame of a Bunsen burner, 100 per cent hydrogen transmission could be obtained. The normally bright palladium-silver tubes which were treated in this manner had a dull surface in the treated area. A tube reactivated in this manner gave 100 per cent hydrogen transmission at 220 amp/ft^2 in 66 wt per cent KOH at 120°C using Cell D (Figure 5). At 375 amp/ft^2 the hydrogen transmission was 95 per cent. This activation procedure was developed toward the end of the experimental work and was not compared directly with other activation methods. However, it is noteworthy that two of the better results with matrix cells discussed later (Runs 78-27, Table 4, and 78-32, Figure 8) were obtained with tubes which had been pretreated by the heating procedure.

Activation of Effusion Side. During the course of the cathode studies in Cell D, moisture on the gas-phase side of cathode tube was found to be detrimental to hydrogen transmission. Drying the inside of moisture-poisoned tubes did not restore good transmission. However, washing the inside of these tubes with 37 per cent hydrochloric acid at 50°C followed by a water rinse and drying at room temperature before reuse restored activity. As a precaution, the palladium-silver tubes were treated in this manner before each experimental run to assure that any low hydrogen-transmission values obtained were not due to the surface of the gas-phase side being inactive.

Electrolyte Component Purity. During the first part of the experimental program covered herein, the potassium hydroxide pellets were obtained from the remainder of a 25-pound supply purchased and used on a prior project (Ref. 2). No difficulty was experienced with electrolytes made from these pellets and distilled water (4×10^5 ohm-cm) and pre-electrolysis of the electrolyte was not a standard procedure. However, when a new supply of potassium hydroxide was used, there was difficulty in obtaining and maintaining 100 per cent hydrogen transmission. Apparently there was some contaminant affecting the cathode, but surprisingly the visible evidence of electrolyte contamination was a black deposit which slowly formed on the platinum anode (in Cell D, Figure 5) during continued electrolysis.

Potassium hydroxide produced by three different suppliers (including the source of the good batch) and chemicals packaged in glass bottles and polyethylene (as with the good batch) all gave similar results. Sodium hydroxide considered as a substitute for potassium hydroxide also caused a similar result with regard to the black anodic deposit. Use of a small amount of potassium hydroxide remaining from the initial good batch did not result in a black anodic deposit, which ruled out introduction of any new variable in the experimental procedure.

Thereafter, it was found necessary to pre-electrolyze the electrolytes using platinum anodes and cathodes in Cell D. The contaminant could not be removed by

electrolysis at room temperature with diluted solutions, and it was necessary to pre-electrolyze at the normal operating conditions (>50 wt per cent KOH, >100°C). Pre-electrolysis was continued until no visible black deposit formed on the anode during a 1-hour period at about 50 amp/ft^2 anode current density.

The dark anodic deposit removed on the anode was soluble in hydrochloric acid and gave a positive test (blood-red color) with potassium thiocyanate indicating the presence of ferric iron.

Experimental runs designated 17- (Tables 2 and 3) used electrolytes that did not require pre-electrolysis, whereas runs designated 78- (Table 4) were made with pre-electrolyzed electrolyte and include some of the best results.

Whereas sodium hydroxide electrolytes were similar to potassium hydroxide electrolytes with regard to black anodic deposit, the effect on cathodic hydrogen transmission was not detrimental for sodium hydroxide. In an experiment with a fresh electrolyte (75 wt per cent NaOH, not pre-electrolyzed) at 140°C in Cell D (Figure 5), 100 per cent hydrogen transmission was maintained at 150 amp/ft^2 for 2 hours with no indication of cathode poisoning when the run was terminated, but the platinum anode had a black deposit. In a comparable test with potassium hydroxide electrolyte, the 100 per cent hydrogen transmission lasted for only about 15 minutes after which the per cent transmission slowly decreased; therefore a change was made to sodium hydroxide electrolyte toward the end of the experimental program. However, pre-electrolysis was used with sodium hydroxide electrolytes also as a standard procedure. Some of the better runs in the static vapor cell discussed later (Runs 78-27, 78-32, and 78-39) were made with matrices impregnated with pre-electrolyzed sodium hydroxide electrolyte.

Activation of Matrix Cells. In the early study of matrix cells (Phase 3), the cell was assembled and impregnated with electrolyte at operating temperature before the palladium-silver cathode was activated by anodic treatment. The result was the formation of a gray deposit on the side of matrix that was in contact with the palladium-silver cathode. A spectrographic analysis indicated that the deposits were palladium-silver products formed by the anodic activation. It was not determined whether the deposits were detrimental to hydrogen transmission, nevertheless, an investigation was made in Cell D of preactivation of the PdAg cathode prior to cell assembly. The investigation disclosed that an active palladium-silver tube that had been anodically activated to give 100 per cent hydrogen transmission could be removed from electrolysis, water rinsed, dried, and replaced without loss of activity, i.e., would diffuse hydrogen at 100 per cent transmission without further anodic activation. As a result of these studies, the PdAg cathode of Runs 78-27, -32, and -39 with matrices was preactivated in Cell D before cell assembly. The preactivated cathode performed satisfactorily without further anodic activation, and no palladium-silver deposits were noted in the matrices of these runs after experimental testing.

Preferred Activation Procedure. The following preferred activation procedure, developed at the end of the program, includes all beneficial effects noted during the course of cathode studies. The procedure was successfully used to activate the surface of a virgin palladium-silver tube in 65 per cent sodium hydroxide electrolyte at 130°C. The activation step of heating the tube to redness after being charged with hydrogen was not incorporated in the procedure since it was not established that the treatment offered any particular advantage.

(1) Pre-electrolyze the electrolyte in a Teflon-lined beaker with platinum electrodes at current density of about 50 amp/ft^2 until contaminates are plated out, e.g., no formation of a black film on the anode. The black anode film is soluble in hydrochloric acid.

(2) Charge palladium-silver tube (tube cathodic) at 200 amp/ft^2 using platinum anode.

(3) Remove tube after electrolysis. Wash gas-phase side (inside) of tube with hydrochloric acid solution (37 wt per cent HCl) at 50°C, water rinse, and dry thoroughly.

(4) Replace tube for electrolysis and electrolyze anodically (tube anode) at 200 amp/ft^2 until oxygen is evolved for 1 minute.

(5) Make tube cathodic at a current density of 100 amp/ft^2. Active tube will be noted by absence of hydrogen evolution on the surface and 100 per cent hydrogen transmission after the tube is saturated with hydrogen.

(6) If tube is not fully active, e.g., evolution of hydrogen gas or less than 100 per cent transmission, repeat Steps (4) and (5).

Phase 2. Anode Studies

Introduction

This phase of the program consisted of an investigation of different anode designs which would preclude the use of centrifugal techniques for separating oxygen from the electrolyte (i.e., allow design of a static cell rather than a rotating cell to use the palladium-silver hydrogen-diffusion cathode). Three concepts were considered: the oxygen-diffusion anode and the oxygen-permeable anode and a matrix-type cell defined below.

An oxygen-diffusion anode would be the counterpart of the hydrogen-diffusion cathode. Oxygen would be selectively transmitted through a nonporous anode by a diffusion process whereas water vapor and electrolyte would not.

An oxygen-permeable anode is defined as a porous electrode which would pass oxygen and water vapor but not liquid electrolyte. Such electrodes have been used in fuel-cell technology and there are various types (i.e., waterproofed electrodes, biporous electrodes, etc.). In general, such electrodes are used with a free volume of electrolyte and simultaneously serve to retain the electrolyte within the cell by capillary forces and act as an electronic conductor at which the electrochemical reactions occur.

A distinction is made between an electrolysis cell with an oxygen-permeable anode as defined above and an electrolysis cell with a matrix. In a matrix-type cell there is no free volume of electrolyte. The electrolyte is completely retained in the matrix by capillary and/or physico-chemical attractive forces. The anode (i.e., platinum screen) used with a matrix serves only as an electronic conductor for the electrochemical

reactions. Therefore, a matrix relates to cell construction and is discussed later in relation to Phase 3 "Cell Design Studies". Phase 2 studies related only to oxygen-diffusion anodes and oxygen-permeable anodes (specifically a biporous anode) which can be studied alone in a large excess of electrolyte independent of the cathode used.

Oxygen-Diffusion Anode

A literature survey revealed little data on the diffusion of oxygen through metals and all data were based on initially gaseous oxygen. Silver appeared to have the highest oxygen-diffusion coefficient although relatively low compared to the hydrogen-diffusion coefficient for palladium. The variation in reported oxygen-diffusion coefficients suggested that surface activity and other factors associated with diffusion from a gas phase might be involved. Since no reference was found to diffusion of anodically generated oxygen through silver, an exploratory experiment was planned.

A 1-mil silver foil was made anodic at 10 amp/ft^2 in an electrolyte of 70 wt per cent potassium hydroxide at 190°C. A brown precipitate, probably silver oxide (AgO), which formed on the anode appeared to be insoluble but was readily dispersed in the electrolyte. Since the silver anode did not appear to be stable for the electrolytic conditions expected for a PdAg cathode, the study of oxygen-diffusion anodes was not continued.

Oxygen-Permeable Anodes

At the beginning of the Battelle investigation of water-electrolysis methods for weightless conditions several years ago, a paper study recommended a fuel cell operated in reverse as one of several possibilities for further study (Ref. 1, Appendix II). One example used was a Bacon-type fuel cell characterized by the use of biporous electrodes (i.e., two layers of different-size nickel powders pressed and sintered together to form a plaque). With the smaller pore layer on the electrolyte side and the larger pore layer on the gas side, the gas-liquid-metal interface is maintained within the electrode by a delicate balance of capillary forces and gas pressure. One feature of the Bacon fuel cell was that the electrodes were developed for use in potassium hydroxide solutions at high temperature (200°C). Only the oxygen electrode was of interest on this project for use with the PdAg cathode.

There is little doubt that a biporous metal oxygen electrode is satisfactory when operated in the fuel-cell direction. However, for reverse operation as an electrolyzer there is the problem of oxygen evolution from the conducting fine-pore layer on the electrolyte side. Such a problem has been reported particularly for the oxygen electrode of a Bacon cell used as an electrolyzer. One solution is to make the smaller pore layer on the electrolyte side of a nonconducting material. A second problem associated with the use of a porous nickel oxygen electrode is the tendency for anodic dissolution of nickel. This can be minimized by special treatment of the electrode to form a more resistant oxide film which is still conductive. However, there was a question of the long-term corrosion resistance of a nickel anode for use with a PdAg diffusion cathode which appears to be sensitive to electrolyte contamination. The problem might be avoided by use of porous platinum electrodes. Prior studies had indicated that platinum and Teflon were compatible with a PdAg cathode at high caustic concentration and temperature.

Biporous Anodes

For the initial feasibility study of an oxygen-permeable anode, a biporous electrode was fabricated from Teflon powder (small-pore layer on electrolyte side) and an 80-mesh platinum screen (large-pore layer, on the gas-phase side).

The biporous anode was positioned in the bottom of Cell A of Figure 4 to demonstrate that the evolved oxygen could be separated from the electrolyte independently of gravity. A slight positive pressure of 2-4 inches of water maintained at the oxygen-collection burette was required to prevent electrolyte from passing through the platinum screen without forcing oxygen back through the porous Teflon.

Satisfactory operation of the biporous anode with 100 per cent separation of oxygen from 75 wt per cent KOH electrolyte at 100°C was obtained for 7-1/2 hours at anode current densities of 120 to 245 amp/ft^2 (based on geometric area). Thus, the primary objective of the experiment was achieved in demonstrating the performance of the biporous anode with regard to oxygen evolution.

The secondary objective of experiments related to compatibility of the biporous anode with the PdAg cathode and electrolyte contamination was a problem as shown by low hydrogen transmission for Run 17-33, Table 3. The PdAg tube cathode had operated satisfactorily for 8-1/2 hours in a prior run (Run 17-18, Table 2). The electrolyte contamination in Run 17-33 was attributed to residual organic wetting agents left in the porous Teflon layer after its fabrication. The Teflon powder from which the porous electrode was constructed was filtered from a colloidal Teflon dispersion used in the spraying of Teflon coatings. Although much care was taken in washing the Teflon layer with water and hot KOH solution, apparently not all of the wetting agent was removed. After the run the electrolyte was noted to have a green color.

A typical effect of electrolyte contamination was the increase in per cent hydrogen transmission with increase in current density as shown for Run 17-33, Table 3.

A second type of biporous electrode was made from chemically-pure asbestos fibers on a platinum screen and evaluated in Run 17-76, Table 3. Again the oxygen was separated from the electrolyte effectively independently of gravity. However, after 2 hours of operation at 115 amp/ft^2, the effect of electrolyte contamination by the asbestos was evident in the decrease in hydrogen transmission by the PdAg tube.

Apart from the electrolyte contamination problem encountered in the above experiments, it became apparent that there would be cell-design problems with biporous anodes when used with a PdAg cathode. Extended operation with precisely 100 per cent hydrogen transmission at the cathode did not appear to be an attainable goal. While greater than 95 per cent hydrogen transmission would be acceptable from the standpoint of power efficiency in electrolysis, a cell with a biporous anode used with free electrolyte did not offer any simple means of handling the small amount of hydrogen that did not pass through the cathode, particularly under weightless conditions. For this and other reasons, a matrix-type cell construction was preferred and oxygen-permeable anodes were not investigated further.

TABLE 3. SUMMARY OF DATA WITH OXYGEN-PERMEABLE ANODES

Run	Experimental Cell Used	Electrode Description		Electrolyte, KOH		Current Density, amp/ft^2		Cell Voltage, volts	Average Separation Efficiency, per cent		Electrolysis Time	Remarks
		Cathode	Anode	Conc., weight per cent	Temp, °C	Cathode	Anode		H_2	O_2		
17-33	A	PdAg tube	Porous Teflon; 80-mesh Pt screen	75	180	120 150 245	120 150 245	2.33 2.30 2.43	55 78 80	100 100 100	4 hr – 30 min 1 hr – 42 min 1 hr	Low transmission due to electrolyte contamination; note how per cent transmission increases with increased current density
17-76	A	PdAg tube	Porous asbestos; 80-mesh Pt screen	70	190	115	115	2.7	95	100	2 hr	Electrolyte contaminated by asbestos, H_2 transmission was decreasing when run was terminated

Phase 3. Cell-Design Studies

Introduction

During this phase of the program consideration was given to practical cell designs and it became apparent that a matrix-type cell construction would have many advantages over a cell construction based on a biporous anode. The cell-design factors are discussed in this section. The remainder of the experimental work on this contract related to finding a suitable matrix material. Many matrix materials and variations of cell construction were screened.

Satisfactory operation for the first 5 to 15 minutes was not difficult to obtain because the principal problem of electrolyte contamination and influence on hydrogen transmission was time dependent. Satisfactory operation for 1-5 hours was more difficult to obtain and the more favorable results are summarized in Table 4.

The tentative goal of 24 hours of satisfactory cell operation was obtained near the end of the experimental program and this was considered a sufficient demonstration of technical feasibility. However, further study of matrix materials is needed to find the optimum construction and further data on cells operated for weeks or months is needed to establish reliability.

Experimental Apparatus

Figure 6 shows a schematic of an experimental cell with a matrix-type construction. As mentioned previously the distinguishing feature of a matrix cell is that there is no free electrolyte; the matrix is in contact with the PdAg cathode. For the example shown in Figure 6, the asbestos used as matrix has a very small pore size relative to the platinum screen anode. However, in contrast to a biporous anode, the cell shown in Figure 6 could be operated in an inverted position in the laboratory without concern for the pressure in the oxygen compartment since the electrolyte is retained in position in the cell by absorbency of the matrix.

While a matrix-type cell construction could be used with flat PdAg foil, many advantages appeared for cell construction in using a PdAg tube (i.e., sealing, structural stability, etc.). Also, the PdAg tube appeared to have greater dimensional stability than foil when charged with hydrogen, as mentioned previously. Figure 3 is a schematic sketch of a proposed tubular cell construction for a matrix cell. Most of the experimental work on matrix cells used a small section (about 1/2 inch long) of a tubular element and extrapolation of results to the full-size cell of Figure 3 would appear to be direct.

Figure 1 is a schematic of the experimental apparatus used to study matrix cells. The experimental unit is referred to as a static vapor cell, because the water for electrolysis was supplied as vapor from the water vapor generator which formed the bottom of the experimental apparatus. The upper and lower sections of the apparatus were heated independently by heating tapes. The vapor generator was generally maintained at 50°-120°C, whereas the upper electrolysis cell section could be varied from 120°-220°C.

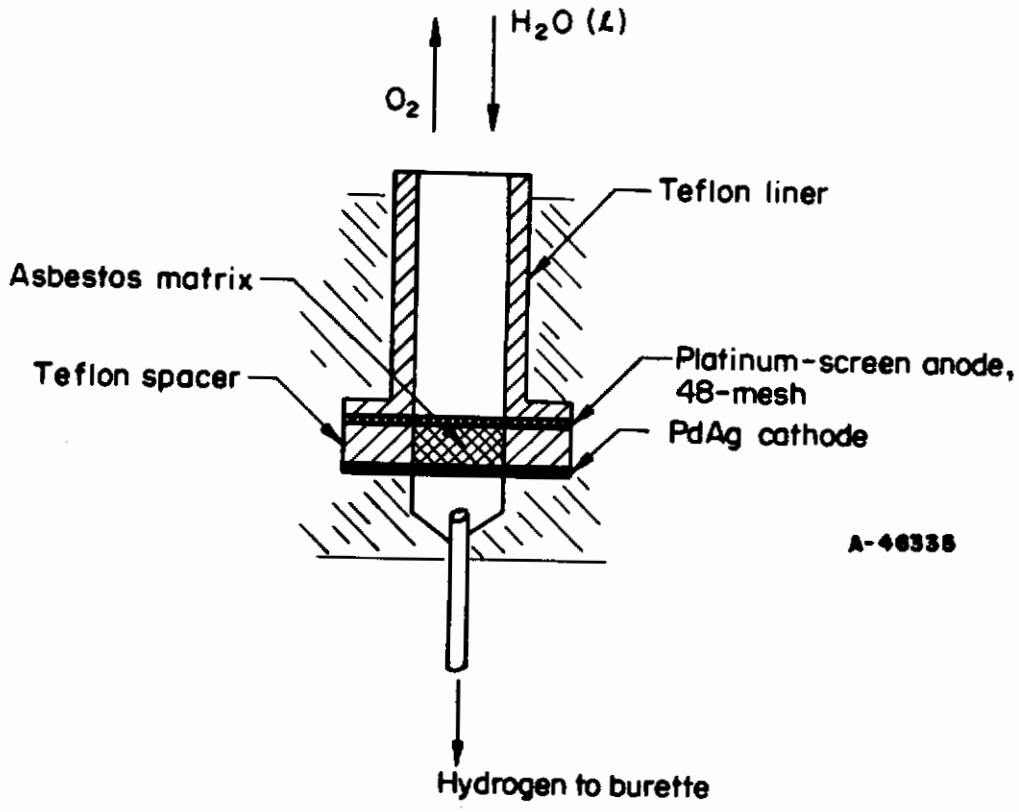

FIGURE 6. SCHEMATIC OF EXPERIMENTAL ELECTROLYSIS CELL B USED FOR STUDY OF MATRICES

The use of a vapor generator for controlling the electrolyte concentration while supplying water for electrolysis was described in previous work (Ref. 2). Curves showing the pressure-temperature equilibrium for water vapor above aqueous solutions of potassium hydroxide and pure water from previous work (Figure 4, p 8, Ref. 2) were used for most of the experimental work with potassium hydroxide electrolytes. A similar relation is shown in Figure 7 for sodium hydroxide electrolyte. The preferred operation of the vapor generator is illustrated by the following example with reference to Figure 7.

With the vapor generator at 90°C, the water-vapor pressure is 525 mm Hg (pure water). With the electrolysis cell at 152°C, the electrolyte concentration would be maintained at 60 wt per cent NaOH (525 mm Hg water-vapor pressure above electrolyte). This method of electrolyte control is independent of the total pressure on the system and oxygen can be generated at various partial pressures. Since no moving parts are involved and no liquid level sensors are required, the method is simpler than direct addition of liquid water to the electrolyte.

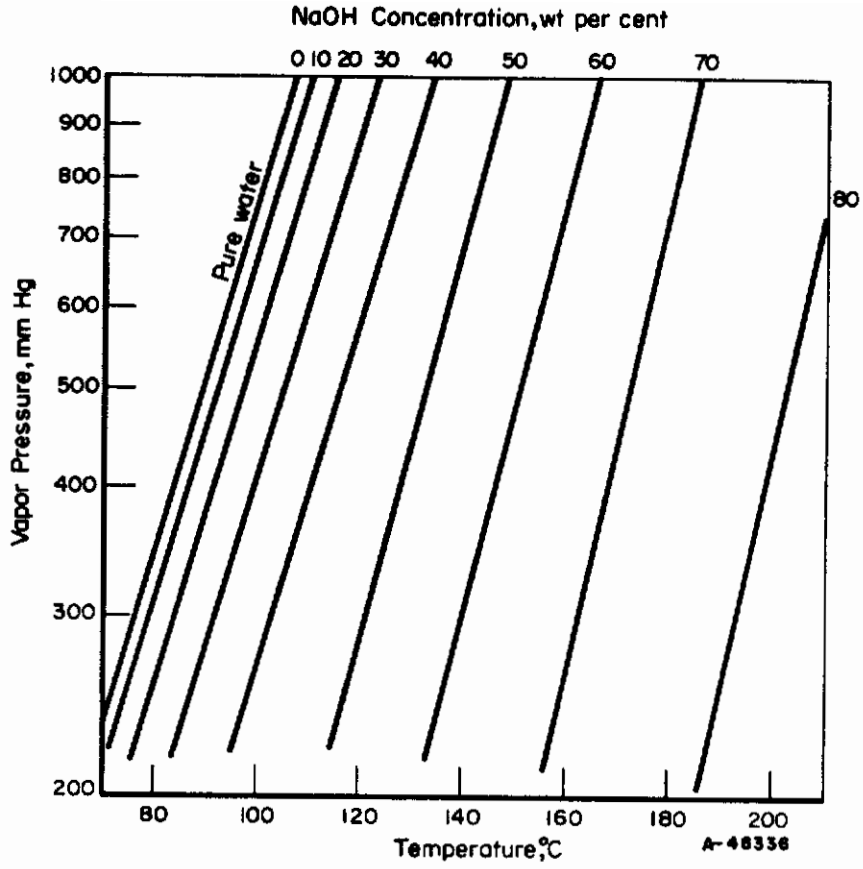

FIGURE 7. PRESSURE-TEMPERATURE EQUILIBRIUM FOR WATER VAPOR ABOVE AQUEOUS SOLUTIONS OF SODIUM HYDROXIDE AND PURE WATER

Matrix Evaluation

Asbestos. Table 4 summarizes the better results with matrix-type cells for which about 1 hour or more of satisfactory operation was demonstrated. Proportionally more effort was devoted to asbestos as a matrix material because of the good water-vapor adsorption which allowed high current densities at relatively low voltage (Figure 2).

One of the first experiments with asbestos was carried out in Cell B, Figure 6, and is summarized as Run 17-56 in Table 4. The earlier part of the run was discussed previously (Table 2) in relation to cathode studies in which the PdAg electrode had operated satisfactorily for over 4 hours at current densities up to 140 amp/ft^2 with only 3 ml of electrolyte in the cell of Figure 6. After the asbestos (purified fiber) was added, the cell continued to operate satisfactorily for another hour after which the hydrogen transmission began to decrease.

Subsequent experiments in the open Teflon-lined beaker (Figure 5) verified that the asbestos was causing contamination of the electrolyte. In one experiment at 90 amp/ft^2 in potassium hydroxide electrolyte (66 wt per cent KOH) at 173°C, the addition of an asbestos matrix (commercial grade) to a previously activated PdAg tube resulted in a decrease of hydrogen transmission from 100 to 88 per cent. After the matrix was removed, hydrogen transmission was increased to 93 per cent after several anodic activations. The asbestos-contaminated electrolyte was a green color suggesting iron

TABLE 4. SUMMARY OF DATA FROM STUDY OF MATRIX CELLS(*)

Run	Matrix	Anode	Impregnating Electrolyte			Vapor-Generator Temp, °C	Cell Temp, °C	Current Density, amp/ft^2	Cell Voltage, volts	Hydrogen Transmission, per cent	Electrolysis Time	Remarks
			Type	Conc., per cent	Temp, °C							
17-56	Asbestos (purified fiber)	Pt screen, 48 mesh	KOH	70	190	–	190	140	2.15	97	1 hr	Electrolyte contaminated by asbestos, cell polarized and run was terminated
17-98	Asbestos (grade, commercial)	Spiraled Pt wire, 24 gage	KOH	66	133	100	130	180	2.0	91	1 hr – 35 min	Asbestos leached in KOH solution before use; H_2 transmission decreasing when run was terminated
78-17	Asbestos (grade, AAAA)	Pt screen, 8 mesh	KOH	66	155	86	155	165	2.0	96	50 min	Electrolyte contaminated by asbestos, H_2 transmission decreasing when run was terminated
78-27	Asbestos-$Ca(OH)_2$ (grade, AAAA)	Pt screen, 8 mesh	NaOH	75	145	100	140	65	1.71	97	5 hr – 30 min	Asbestos leached in H_2SO_4 solution before use; H_2 transmission decreasing when run was terminated
78-39	Asbestos-$Ca(OH)_2$ (purified fiber)	Pt screen, 48 mesh	NaOH	70	130	100	140	155	1.95	96	40 min	Asbestos leached in both H_2SO_4 and NaOH solution before use; PdAg surface was palladized
										100	>20 min	Cell was performing at these values when left running overnight, the next morning (13 hr later) the H_2 transmission measured 30 per cent, failure was attributed to electrolyte contamination by the asbestos
78-19	Magnesium oxide	Spiraled Pt wire, 24 gage	KOH	66	150	95	160	180	2.0	98	2 hr	H_2 transmission decreasing when run was terminated

(*) With the exception of Run 17-56 with PdAg foil cathode in Cell B (Figure 6) other runs were made with PdAg tube cathodes and water vapor feed in apparatus of Figure 1.

contamination; when replaced by fresh electrolyte it was possible to increase the hydrogen transmission to 100 per cent after anodic activation of the PdAg tube.

Subsequent experiments with asbestos matrix were carried out in the static vapor cell of Figure 1. Preleaching of the asbestos (commercial grade) to remove the contaminant prior to cell assembly appeared to offer a limited improvement. The cell operating temperature was reduced to 130°C to minimize chemical attack on the asbestos. Satisfactory operation was obtained at relatively high current density of 180 amp/ft^2 at first, but hydrogen transmission decreased after about 1 hour (Run 17-98, Table 4).

The same problem was encountered with Grade AAAA, asbestos cloth (purest commercial grade used for electrolysis cells) as a matrix (Run 78-17, Table 4). A spectrographic analysis of the asbestos cloth showed the presence of iron (1 to 10 per cent). Preleaching of the Grade AAAA asbestos cloth with a sulfuric acid solution (50 wt per cent H_2SO_4) before cell assembly appeared to give improved results (Run 78-27, Table 4). Part of the improvement might have resulted from the use of a layer of calcium hydroxide between the asbestos and PdAg tube or the use of sodium hydroxide in place of potassium hydroxide. For the first 2 hours, the hydrogen transmission was 99 per cent, but had decreased to 90 per cent by the end of the seventh hour. For 5-1/2 hours, the hydrogen transmission averaged 97 ±2 per cent, which was the best result demonstrated with an asbestos matrix. The failure was attributed to incomplete removal of the iron contaminant by leaching.

Another experiment with preleached asbestos was repeated in Run 78-39, Table 4, with the added feature of using a palladized surface on the PdAg tube. A palladized surface should offer more active sites for electrolysis and minimize the effect of contamination. The initial performance of the cell was good at 155 amp/ft^2, but the expected extended operation was not obtained (less than 13 hours). The matrix was made from asbestos (purified fiber) which was leached for 2 hours in sulfuric acid solution (50 wt per cent H_2SO_4 at 30°C) and for 2 hours in sodium hydroxide solution (60 wt per cent NaOH at 150°C). The PdAg tube was palladized in a palladium chloride solution for 30 seconds at a cathodic current density of 150 amp/ft^2. The matrix was assembled over a thin layer (~5 mils) of calcium hydroxide on the palladized surface.

The per cent hydrogen transmission gradually increased during the early minutes of operation: average of 89 per cent for first 10 minutes, average of 96 per cent during the next 10 minutes, and practically 100 per cent for the next 20 minutes. Throughout the initial period, oxygen was collected at a rate corresponding to 100 per cent based on Faraday's law. Thus, the initial period of less than 100 per cent measured hydrogen transmission resulted from loss of hydrogen that was retained in the PdAg tubes until an equilibrium hydrogen concentration was attained.

Magnesium Oxide. Magnesium oxide powder which can be sintered to form a porous nonconducting matrix is reasonably resistant to caustic electrolyte at high temperature and offered prospects of avoiding electrolyte contamination problems. The first result with a cell containing a magnesium oxide matrix was encouraging in that satisfactory operation was obtained for 2 hours at 180 amp/ft^2 (Run 78-19, Table 4). The matrix (about 1/8 inch thick) had been shaped from an available piece of flat stock sintered at 1425°-1480°C.

Subsequent studies were related to making a more practical matrix of magnesium oxide (about 10 mils thick). Magnesium oxide powder was hydrostatically pressed on to

one side of a platinum screen anode and sintered at temperatures of 1000° to 1260°C. At these sintering temperatures brittleness and shrinkage were minimized, and the resultant matrix was physically satisfactory. However, the results with cells using these matrices were unsatisfactory (30 to 70 per cent hydrogen transmission). Since the better result with the thin matrices was obtained with those sintered at the higher temperature, hydration of the magnesium oxide in the cell electrolyte was suspected of affecting hydrogen transmission. Possibly, thin matrices sintered at temperatures of 1425°C and above would perform better based on the initial result with magnesium oxide (Run 78-19, Table 4).

Other Matrix Materials Investigated. Some preliminary experiments on using zirconium oxide as a matrix material were unsuccessful. Nylon, Orlon, and Dacron were investigated as matrix materials. However, even at relatively low temperatures of 120°-130°C, these materials were not physically stable in the caustic electrolyte.

Teflon was investigated as a matrix material. Teflon had been used extensively in cell construction in the experimental studies and was known to be stable in all concentrations of caustic used up to 230°C. Extended satisfactory operation of PdAg cathodes in electrolyte in contact with Teflon indicated a minimum of electrolyte contamination.

Various forms of Teflon such as powder and woven cloth were investigated. The available Teflon powder contained a dispersant which appeared to act as a contaminant. The woven Teflon cloth did not have absorbent properties to hold the electrolyte. A matrix made by matting fibers from Teflon cloth appeared to be better, but satisfactory performance was not obtained in the static vapor cell. Threads of Teflon were made by machining a solid block of white Teflon used in cell construction. A matrix of Teflon threads on a PdAg tube allowed practically 100 per cent transmission in the open-beaker cell (Figure 5) with excess electrolyte. When the same matrix cells were transferred to the static cell (Figure 1) for operation on a water-vapor feed, the results were poor. While Teflon appeared to have the chemical resistance required of a matrix, the poor wettability characteristics of Teflon prevented its use alone as an absorbent matrix.

Teflon-Calcium Hydroxide. The best result during the experimental program was obtained with a matrix of Teflon threads and calcium hydroxide. The relatively insoluble calcium hydroxide provided the absorbency to hold the electrolyte but was not coherent itself and required the Teflon threads for support. The significant period of 24 hours of continuous satisfactory operation is described in the "Summary" of this report and the data for the complete experiment (Run 78-32) are shown in Figure 8.

As shown in Figure 8, there was an unusual procedure and result that preceded the satisfactory operating period. For the first hour the average per cent hydrogen transmission was 78 per cent. When the inside of the PdAg tube was packed with dry asbestos fiber, the average hydrogen transmission increased to 95 per cent and was satisfactory for the next 24 hours (i.e., >97 per cent hydrogen transmission).

Several possible explanations for the effect of the asbestos such as removing water vapor from inside the tube or in some way favoring the release of hydrogen from the effusion side of PdAg tube do not appear likely since there was no change in cell voltage as might normally be expected for a more active tube. It is postulated that the low hydrogen transmission measured during the first hour was due to a loss of hydrogen which diffused back through the tube at the exposed portions above and below the

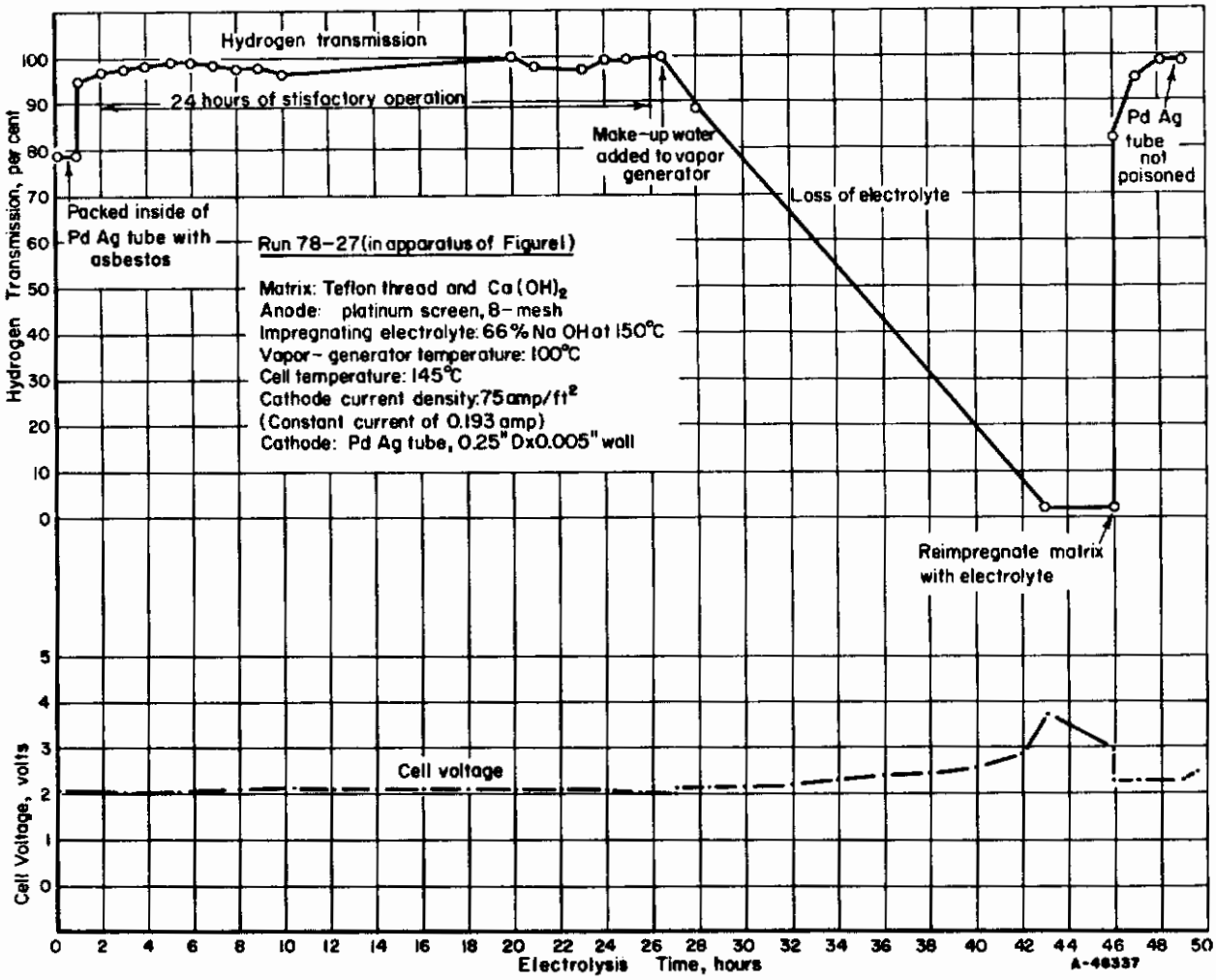

FIGURE 8. DATA SHOWING SATISFACTORY OPERATION OF STATIC CELL WITH PdAg CATHODE FOR A 24-HOUR PERIOD

electrolysis zone shown in the schematic of the experimental apparatus in Figure 1. It is further postulated that the asbestos on the inside of the tube inactivated the tube for back diffusion from the gas phase and allowed all of the electrolytically generated hydrogen to be collected from inside the tube. If this is true, then the effect of the asbestos would not be important for a practical cell in which there would be no portions of PdAg tube not covered by the matrix. In contrast to the experimental cell in which only a portion of the PdAg tube was used for electrolysis, practically all of the tube would be used for electrolysis in a practical cell design as in Figure 3.

After the second hour of operation, 97 per cent hydrogen transmission was obtained and satisfactory operation was maintained for the next 24 hours, at which time the hydrogen transmission was practically 100 per cent. This type of operation would probably have continued except that make-up water was added to the vapor generator. Apparently, this caused flooding of the matrix, loss of electrolyte and eventually complete loss of hydrogen transmission. The fact that satisfactory operation was restored by reimpregnating the matrix with electrolyte and without any activation indicates that the PdAg tube was not inactivated by contamination.

The run demonstrated that with a matrix that does not cause contamination of the electrolyte, extended operation of the PdAg cathode in a static cell can be expected with satisfactory hydrogen transmission. Thus, the technical feasibility of a static cell was demonstrated. However, the run also indicated the need for further improvement in matrix design to achieve reliable operation.

A matrix-type cell appears to operate satisfactorily with careful control of water-vapor addition as during the 24-hour period shown in Figure 8. While some control of water-vapor addition appears necessary for a practical cell design, a matrix less susceptible to failure under adverse conditions would increase the system reliability. One advantage of the matrix-type construction appears to be the ability to operate under conditions where the electrolyte concentration increases from the value at the time of impregnation.

The increase in electrolyte concentration is accompanied by a decrease in electrolyte volume and apparently a matrix cell continues to operate with the matrix unsaturated (i.e., 50-75 per cent of the voids in the matrix filled with electrolyte). Such operation would be more difficult for a cell with a biporous anode. On the other hand, an oversaturated condition would be detrimental to biporous anodes and matrix cells of any type. For example, if the matrix is completely saturated at the time of impregnating with electrolyte, overdilution of the electrolyte with water vapor increases the volume of electrolyte beyond the capacity of the matrix and electrolyte would be permanently lost.

In the experimental work thus far, the impregnating electrolyte concentration was known but the operating electrolyte concentration could only be estimated. Further study is required on water-vapor absorption by the matrix and the relation between the vapor pressure feed, the cell temperature, the initial electrolyte concentration and operating electrolyte concentration with various electrolysis rates.

Throughout the experimental program, there was a steady improvement in cell performance with improvement in matrix. It is logical to expect that further improvement could be obtained by continued investigation leading to an optimum matrix. There

is much information yet to be learned about PdAg cathodes and further research should be directed toward operational runs of experimental static cells for periods of weeks or months. The favorable estimates of size, weight, and power for the static cell appear to warrant the additional development to increase reliability.

CELL-DESIGN ESTIMATES

Figure 3 shows a proposed design for a static cell with a PdAg cathode using tubular cathodes. Designs using flat sheets of PdAg foil are possible. The tubular design is preferred, and it appears that the matrix could be on the inside of the PdAg tube as shown in Figure 3 or on the outside of the PdAg tube as shown in Figure 1.

Preliminary cell-design estimates were made based on the experimental matrix cell which gave 24 hours of satisfactory performance. For a tubular construction, a number of unit cells would be constructed from lengths of palladium-silver tubing. A unit cell might consist of a 13.3-inch length of palladium-silver cathode (0.25-inch diameter by 0.005-inch wall) wrapped with a 1/16-inch layer of matrix containing electrolyte and covered with a cylindrical platinum screen anode (0.375-inch diameter by 0.005 inch thick). For a cell potential of 2 volts at a cathode current density of 75 amp/ft^2 (demonstrated to be feasible), 14 unit cells would be connected in series in a bank to operate on 28 volts. Five banks of cells would be provided for 6 lb O_2/day (three-man cell) or a total of 70 unit cells. Each unit cell 13.3 inches long would weigh about 0.1 pound, or a total of 7 pounds for 70 unit cells.

Arranged on 1-inch centers (0.5-inch diameter for each cell), the 70 unit cells would occupy a cross-sectional area of 13.7 in.^{2} (i.e., about 0.1 ft^3 of cylindrical volume: 4.2-inch diameter by 13.3 inches long). Allowing for a cylindrical container (5-inch diameter by 17 inches long), tube headers, electrode connections, etc., should not add more than 18 pounds to the 7 pounds of electrolysis-cell components. The preliminary estimates for a three-man unit are:

Weight	25 pounds
Volume	0.2 ft^3
Electrolysis power	762 watts.

The proposed cell is well matched to advanced power-supply penalties of about 30 lb/kw. For power-supply penalties of 300 lb/kw or higher, there might be advantage in designing for lower current density to reduce the cell voltage and power consumption or in further research to reduce the cell voltage at 75 amp/ft^2. Possibly the power consumption could be reduced to 610 watts at 1.6 volts and 75 amp/ft^2 with an improved matrix comparable to asbestos as indicated by the possible voltage characteristics of Figure 2.

CONCLUSIONS

The original study of the PdAg hydrogen-diffusion cathode (Ref. 2) and the continued study of a static cell design in this report were directed toward an order-of-magnitude reduction in cell size and weight without increase in power consumption compared to other electrolysis cells. That this objective could be achieved is shown by the following comparison based on a three-man cell (6 lb O_2/day):

	Weight, pounds	Size, ft^3	Power, watts
Laboratory-Model Rotating Electrolysis Cell (Reference 1)	284	4.4	760
Estimate for Optimum Rotating Cell*	125	2.0	650
Estimate for Phosphorus Pentoxide Cell (Reference 3)	150	1.0	1580
Estimate for Static PdAg Cell	25	0.2	760

A static cell with a PdAg hydrogen-diffusion cathode is technically feasible and the most promising of several different electrolysis methods studied. It is difficult to conceive of any other type of electrolysis cell for zero-gravity operation that could be designed more compactly and weigh less, or, alternatively, that could be operated at lower cell voltage for practical current densities. The system is ideal because rotating parts are not needed and the hydrogen produced is pure and dry, hence is ideally suitable for subsequent catalytic reactions. Further research is needed to prove system reliability over long periods.

RECOMMENDATIONS FOR FUTURE WORK

Lack of knowledge of the many factors influencing operation of a PdAg cathode at 100 per cent hydrogen transmission and the limited satisfactory operating time (one 24-hour run) presently prevents an engineering estimate of the reliability of the system. Therefore, it is recommended that the research be continued to provide the knowledge for optimum cell design and to increase the reliability confidence level by extension of satisfactory operating time. Further research is needed to develop improved anode/matrix combinations that will tolerate variation in operating conditions while minimizing electrolyte contamination and providing good adsorption of water vapor. Evaluation of anode/matrix combinations requires study of the effect of operating variables or design variables such as temperature, electrolyte concentration, pressure, and current density. In the quest for improvement beyond 24 hours of satisfactory operation, consideration should be given to devising accelerated evaluation programs.

*Unpublished results of design study at Battelle relating to proposed redesign of rotating electrolysis cell (Ref. 1) for optimum size, weight and power consumption.

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