

FOREWORD

This report was prepared by Battelle Memorial Institute on Contract No. AF 33(616)-8431 under Project No. 6373, "Equipment for Life Support in Aerospace," and Task No. 637302, "Respiratory Support Equipment." The work was performed under the direction of the 6570th Aerospace Medical Research Laboratories, Aerospace Medical Division, Wright-Patterson AFB, Ohio, and was administered by Richard E. Bennett and Clyde G. Roach, Respiratory Equipment Section, Sustenance Branch, Life Support Systems Laboratory. The work reported here was done between June 1, 1961, and May 31, 1962.

The principal investigators were John E. Clifford, Senior Chemical Engineer, John C. Matthews, Principal Chemical Engineer, and Edwin S. Koglikowski, Senior Laboratory Technician. The work was under the direction of Charles L. Faust, Chief, Electrochemical Engineering Division.

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ABSTRACT

The experimental investigation has shown that the concept of a hydrogen-diffusion cathode is technically feasible for potential use in a water-electrolysis cell for production of breathing oxygen under weightless conditions. The best result was a cathode current density of 265 amp/ft² at a cell voltage of 1.76 volts while maintaining for about 1 hour 100 per cent transmission of hydrogen through a cathode of palladium-silver alloy foil (3/8-inch diameter x 0.001-inch thickness). The pure, dry hydrogen gas that permeated the cathode foil was collected at atmospheric pressure during electrolysis of a potassium hydroxide electrolyte (50 weight per cent KOH) at 230 C and 15 to 25 psig in a Teflon-lined cell with a platinum anode. The laboratory experiments with a stationary cell indicated the importance of designing for minimum electrolyte contamination and the need for further study of activation of the cathode foil. To supply breathing oxygen for 3 men (6 lb of oxygen/day), preliminary design estimates for a rotating cell (to provide an artificial gravity field for separation of oxygen from the anode and electrolyte) indicate an electrolysis cell (exclusive of motor, controls, etc.) of 4-3/4-inch diameter x 4-3/4-inch height, weighing about 10 pounds and consuming an electrolysis power of 670 watts.

PUBLICATION REVIEW

This technical documentary report has been reviewed and is approved.

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RESEARCH ON THE ELECTROLYSIS OF WATER WITH A HYDROGEN-DIFFUSION CATHODE TO BE USED IN A ROTATING CELL

by

John Clifford and Charles Faust

INTRODUCTION

The objective of this project was to investigate a method of accomplishing electrolysis of water for use under weightless conditions on space missions of extended duration (2 days to 2 years). Consideration of man's respiratory function and water intake-output had indicated that a system should be designed for electrolyzing water at rates of from 0.7 to 2.25 lb/man/day (ref. 1*). The lower rate is a minimum based on the excess of man's total output of water over his intake. The higher water rate is based on the average requirement of 2.0 lb of oxygen/man/day in a closed ecological system. Although not a direct concern of this project, it is generally known that the other product of water electrolysis, namely hydrogen, could be used in the reduction of carbon dioxide to carbon and water. The latter would be returned to the electrolysis cell (ref. 2).

The requirements of the electrolysis method can be defined as follows with reference to the ultimate system design anticipated:

- (1) The system shall be designed to provide oxygen for three men and shall be capable of electrolyzing water at rates from 0.7 to 2.25 lb/man/day (i. e. , 2.1 to 6.75 lb of water/day, the higher rate corresponding to 381 amperes).
- (2) Weight, space, and power requirements shall be kept as low as possible in accordance with sound engineering design and consistent with other requirements.
- (3) The device shall employ gravity-independent principles, so that it will operate when weightless. The equipment shall be capable of operating in accelerations from 0 to 1 G and capable of withstanding 15 G without damage.
- (4) The oxygen evolved from the cell shall be hydrogen-free, but may be saturated with water vapor since it can be assumed that moisture will be removed by cabin dehumidifiers.
- (5) The system shall be capable of operating in a capsule environment of from 7.2 to 14.7 psia and 0 F to 100 F.

The first part of the prior investigation at Battelle (ref. 1), considered various methods of accomplishing electrolysis of water that would be operable under weightless

*References are listed on page 24.

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conditions. One of the methods proposed in the paper study of feasibility was the rotating cell with a palladium cathode. Centrifugal force produced by the rotation of an electrolytic cell would be used to establish an artificial gravity field so that electrolysis could proceed at the anode to evolve oxygen, which would be simultaneously separated from the electrolyte. Separation of gaseous hydrogen and oxygen would be accomplished by a hydrogen-diffusion cathode that would permit generation of hydrogen into a gas phase on the side of the cathode opposite the side on which hydrogen would be deposited by electrolysis of water.

The idea on which the method was based was a combination of the better features of several systems. There was no published information on the practicability of a hydrogen-diffusion cathode in electrolysis of water. The experimental work on this project was concerned principally with the cathode reactions involving hydrogen. Non-rotating "beaker-scale" experimental cells were used for convenience. The principle of separating oxygen from the anode and electrolyte during electrolysis in a rotating cell has been demonstrated previously in the laboratory model evaluated in prior work (ref. 1).

The immediate objective of the experimental feasibility and design study was to investigate the use of a palladium cathode or other hydrogen-diffusion metal (or alloy) to determine the feasibility of the electrolysis method with reference to the project objectives. It was recognized that any radically new electrolysis system would involve years of development to establish a basis of reliability for space application. Therefore, a new system such as a hydrogen-diffusion cathode cell must offer significant prospects for reduction in size, weight, or power of the life support system either as a unit or when integrated with other system components. Thus, presentation of the important experimental results and their evaluation in terms of design estimates for a proposed electrolysis cell is considered the main function of this report. A discussion of postulated reaction mechanisms and the experimental details are included in Appendixes to this report.

DISCUSSION OF EXPERIMENTAL RESULTS

The experimental investigation has shown that an electrolysis cell using a hydrogen-diffusion cathode is technically feasible for production of breathing oxygen by electrolysis of water under weightless conditions. A rotating cell design would provide the artificial gravity field to separate evolved oxygen from the anode and electrolyte. Hydrogen deposited at the opposite electrode diffuses through the thin-metal-foil cathode (0.001-inch-thick palladium-silver alloy) and emerges on the back side as pure and dry hydrogen, ideally suitable for any subsequent use such as for catalyzed reaction with carbon dioxide.

The demonstration of electrolytic production of hydrogen at practical rates with simultaneous transport of hydrogen from a liquid through the metal cathode to a gas phase is believed to be new. No description of an exactly comparable process was found in the published literature. Various other examples of hydrogen permeation through palladium have been reported (i. e. , gas phase to gas phase, electrolyte to electrolyte, gas phase to electrolyte) but not electrolyte to gas phase. Of particular importance for a practical cell for this project was the requirement that nearly complete transmission

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of hydrogen be attained at reasonably high cathode current densities. Thus, the demonstration of the technical feasibility of the concept originally proposed is considered significant even though the present state of knowledge did not permit ready duplication of results in a limited number of subsequent experiments toward the end of the project.

The three significant experiments using a PdAg cathode (0.001 inch thick), a platinum anode, and a potassium hydroxide electrolyte are summarized in Table 1.

TABLE 1. SUMMARY OF BEST EXPERIMENTAL RESULTS IN STUDY OF HYDROGEN-DIFFUSION CATHODES

(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 1 is a schematic drawing of an experimental cell used to study hydrogen-diffusion cathodes. A Teflon coating sprayed on the metal surfaces of the electrolysis chamber was believed to be the important feature in minimizing contamination of the electrolyte by corrosion. Figure 2 shows the data obtained in the first run in which practically 100 per cent hydrogen transmission was maintained for a significant period. While 100 per cent transmission is desirable, it is not essential. For the experimental work, hydrogen transmission above 90 per cent was considered practical. For extended runs, it can be assumed that the 10 per cent of the total hydrogen not collected would evolve on the polarization side of the cathode and would be mixed with the oxygen stream. The hydrogen impurity in the oxygen stream could be subsequently removed in a catalytic burner. The net result of less than 100 per cent transmission would be an energy inefficiency that would not be serious if small. The following examples based on the data in Figure 2 assume a cathode area sufficient to allow current for a three-man oxygen supply at 15 amp/ft²:

$$\text{Electrolysis Power} = \frac{\text{Volt amperes (100)}}{\text{Per cent hydrogen transmission}}$$

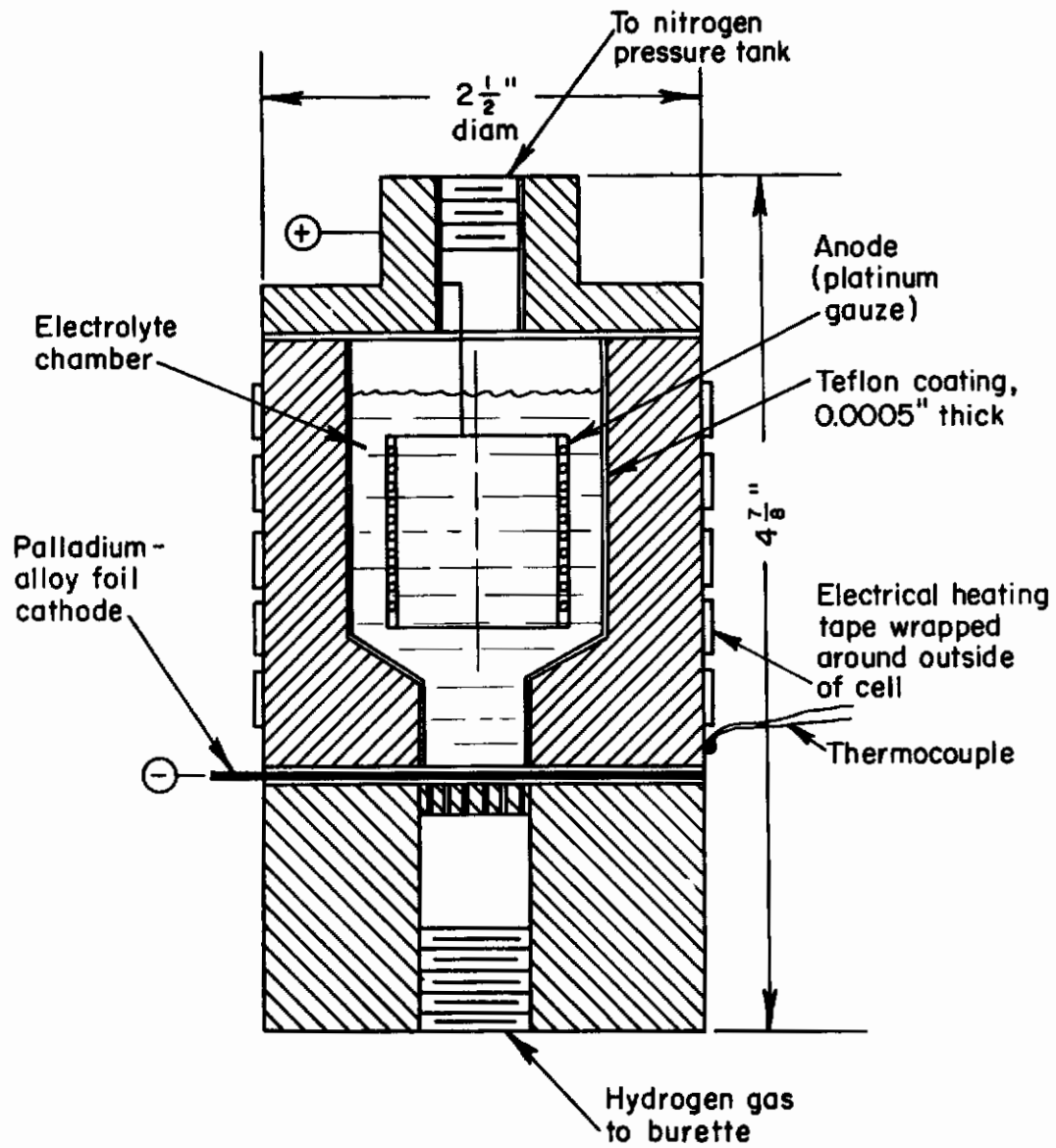


FIGURE 1. DESIGN OF EXPERIMENTAL CELL D

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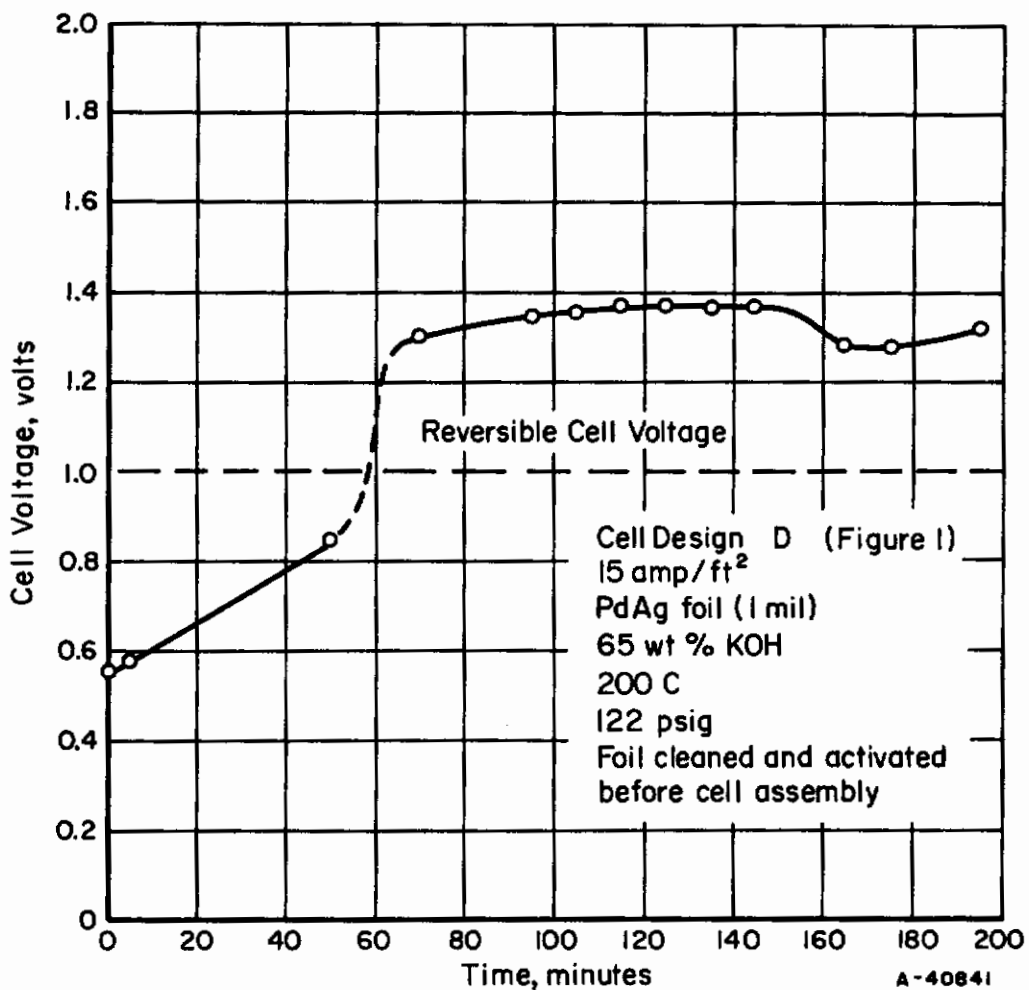
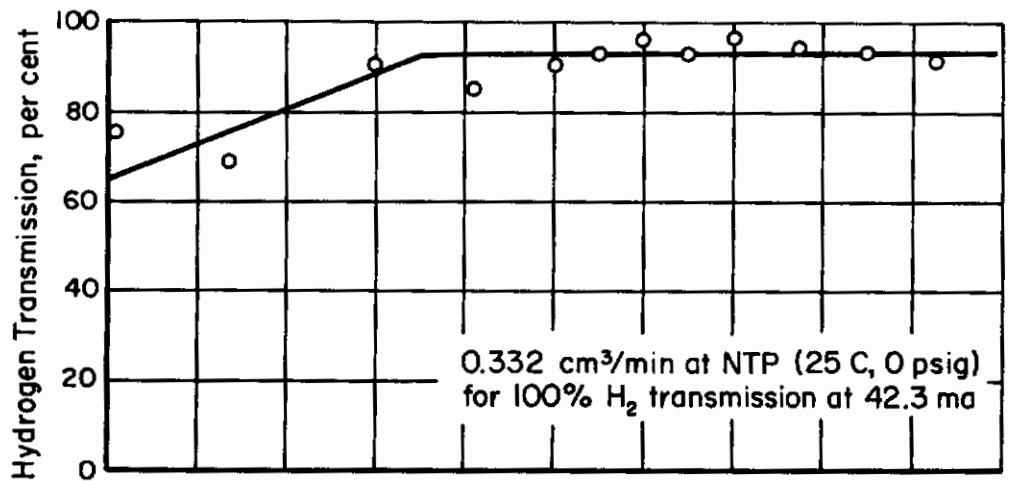


FIGURE 2. RUN 2-34 SHOWING SATISFACTORY OPERATION AT 15 AMP/FT²

First demonstration of practically 100 per cent hydrogen transmission for about 2 hours.

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Theoretical power based on a reversible cell potential of 1.0 volt at 200 C:

$$\frac{(1.0)(381)(100)}{100} = 381 \text{ watts.}$$

Estimated power based on average cell voltage of 1.34 volts and 93 per cent hydrogen transmission of Figure 2:

$$\frac{(1.34)(381)(100)}{93} = 549 \text{ watts.}$$

An important feature of the run shown in Figure 2 is the low cell voltage. The average cell voltage of 1.34 volts is only 0.34 volt above the theoretical minimum voltage of 1.0 volt for electrolysis of water shown by the reversible cell voltage calculated for 200 C. The low cell voltage is the result that was expected for a hydrogen-diffusion cathode where cathodic overvoltage and polarization are at a minimum.

In Figure 2, the low voltage during the first hour is believed to represent a period during which the deposited hydrogen is absorbed by the PdAg foil to build up the equilibrium hydrogen concentration in the PdAg. Thus, the indication of less than 100 per cent transmission during the first hour (based on hydrogen collected on the diffusion side) does not mean that hydrogen gas was evolved on the polarization side into the oxygen stream.

It appears significant that the equilibrium voltage value of 1.34 volts and the equilibrium percentage hydrogen transmission of 93 per cent were approached at about the same time (i. e., at the end of 1 hour). The results suggest a change in the electrochemical mechanism of hydrogen deposition at the cathode as the surface concentration of hydrogen in the palladium-silver alloy increases to establish the concentration gradient for diffusion.

For extended cell operation additions of water were necessary to make up for the water consumed by electrolysis and water lost with the evolved oxygen stream. A technique was devised for adding water from a steam generator connected to the electrolyte chamber to maintain the electrolyte concentration. Figures 3 and 4 provide the data on which such a scheme might be based for a practical cell.

Figure 3 shows the boiling point and solubility (freezing point) curves for potassium hydroxide solutions. One advantage of using concentrated potassium hydroxide solutions as the electrolyte is that high temperatures can be obtained without excessive pressure. For example, Figure 3 shows that, at 200 C, the highest electrolyte concentration that would still be liquid is about 84.5 weight per cent KOH. A concentration of 64.5 weight per cent is at the boiling point at 200 C (i. e., partial pressure of water vapor above potassium hydroxide solution is 1 atmosphere absolute or 0 psig). At a room temperature of 20 C, the maximum solubility of potassium hydroxide in water and thus the highest concentration of solution that can be prepared at room temperature is 52.5 weight per cent KOH. Such a solution boils at 153 C; at 200 C the partial pressure of water vapor above the solution is 40 psig.

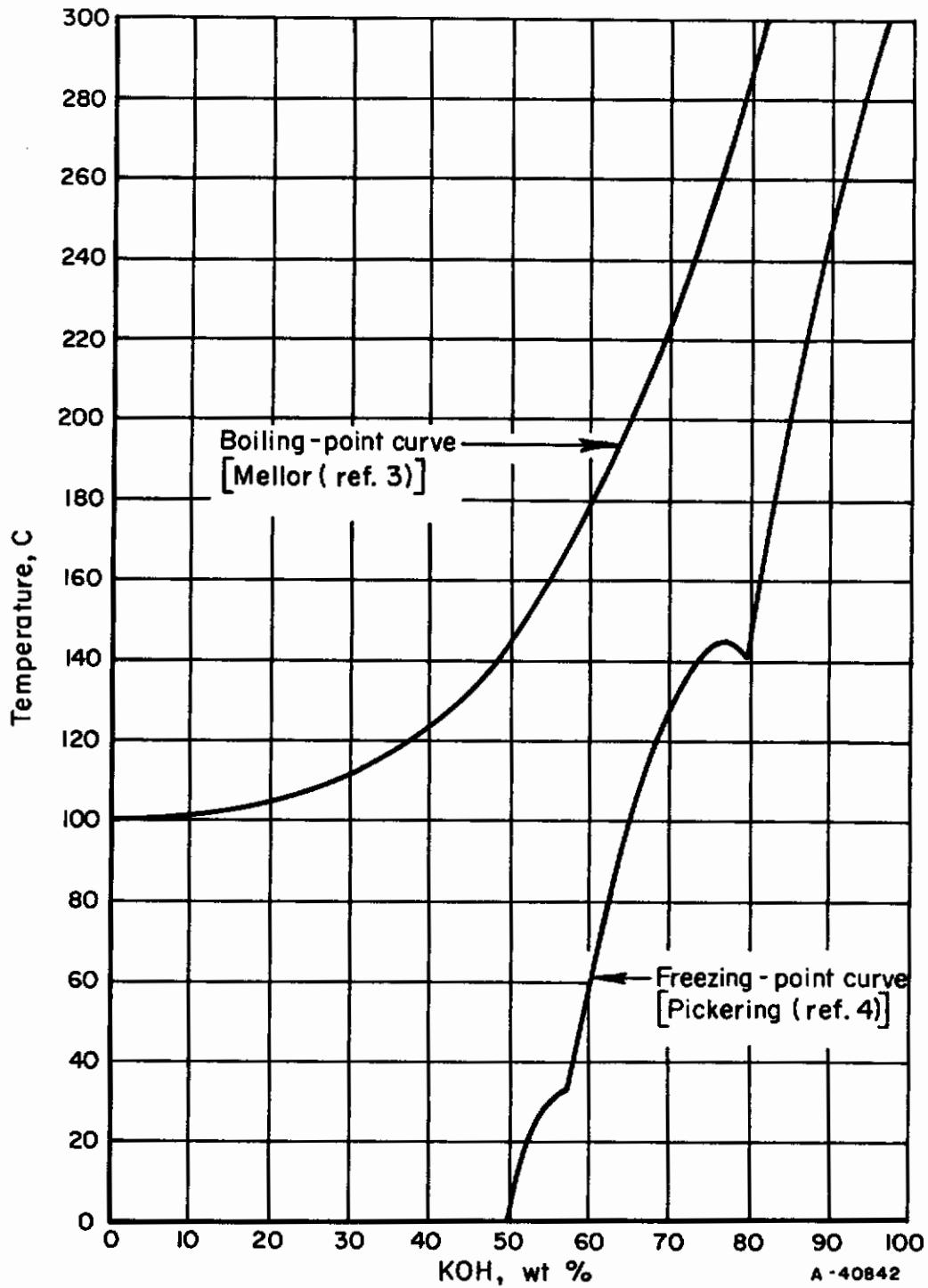


FIGURE 3. SOLUBILITY AND BOILING-POINT CURVES FOR POTASSIUM HYDROXIDE SOLUTIONS AT 1-ATMOSPHERE PRESSURE

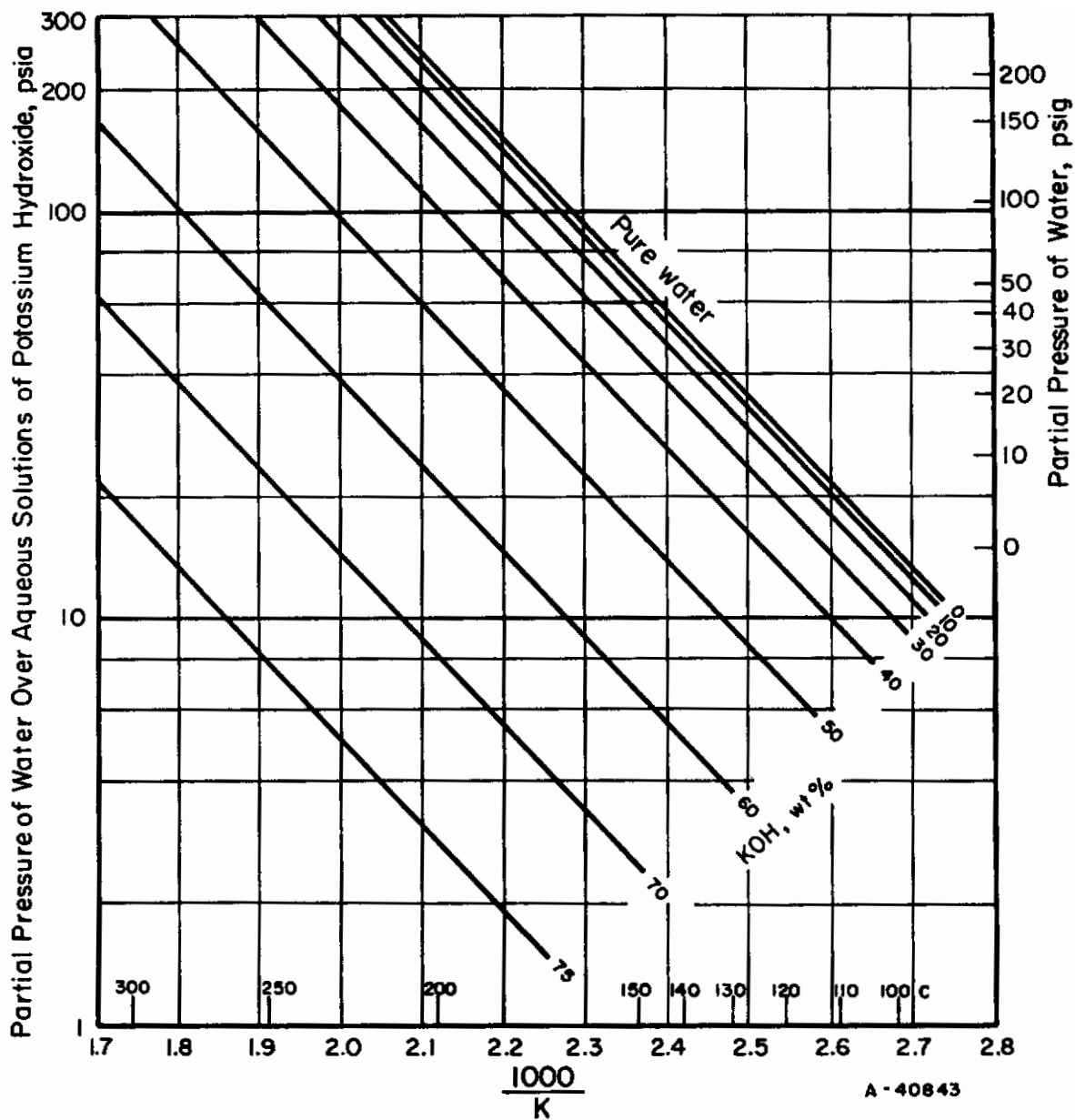


FIGURE 4. PRESSURE-TEMPERATURE EQUILIBRIUM FOR WATER VAPOR ABOVE AQUEOUS SOLUTIONS OF POTASSIUM HYDROXIDE AND PURE WATER

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The partial pressure of water vapor above aqueous solutions of potassium hydroxide is shown in Figure 4. Figure 4 was constructed by plotting the log of the vapor pressure of water above pure water as a function of the reciprocal absolute temperature. The partial pressure of water above aqueous solutions of potassium hydroxide for various concentrations was identified at a known pressure (14.7 psia or 0 psig) from the boiling-point curve of Figure 3 and plotted in Figure 4.

With reference to Figure 4, if it is desired to maintain an electrolyte concentration of 55 weight per cent KOH at 200 C (partial pressure of water vapor above electrolyte is 35 psia), the steam generator is set for a temperature of 127 C, at which temperature the partial pressure of water vapor above pure water is 35 psia (20 psig).

A cell as shown in Figure 1 with the outlet from the electrolysis chamber connected to a steam generator rather than a nitrogen tank was run continuously for 9 days at about 200 C, 20 to 30 psig, about 15 amp/ft², with the percentage hydrogen transmission ranging from 40 to 85 per cent. While the combination of conditions for attaining 100 per cent transmission were not found during this run (Run 2-66, Appendix II), the extended duration of the run was indicative of the durability of the PdAg foil to pass hydrogen continuously without deterioration.

When it was desired to investigate higher pressure (up to 120 psig), a nitrogen tank connected to the steam generator provided the added pressure while the steam generator was maintained at the temperature required to provide the partial pressure of water vapor to maintain the electrolyte concentration.

In practice, the added system pressure could be provided by the evolved oxygen and an adjustable pressure-relief valve. There might be some advantage to operating with high oxygen pressure and low partial pressure of water vapor (high electrolyte concentration) to minimize loss of water from the electrolyte.

Also, both hydrogen and oxygen might be generated at high pressure (i. e. , 100 psig or higher) with only a small differential pressure (i. e. , 15 to 20 psig) across the foil cathode. For the added advantage of direct charging of storage cylinders, the added cell weight and complexity for high-pressure cells might be justified.

During the extended run for 9 days, reversal of the electrical connections to make the PdAg foil anodic usually increased the percentage of hydrogen transmission when the foil was returned to cathodic. Superimposed alternating current on the direct current also increased the percentage transmission. This was evidence that electrochemical factors at the cathode surface were controlling.

During an anodic treatment of the foil by reversal of the electrical connections, the previously collected hydrogen in the burette could be passed back through the foil from the gas phase to the electrolyte with the hydrogen consumed by anodic oxidation on the electrolyte side of the PdAg-alloy foil. At current densities from 15 to 30 amp/ft², the consumption of hydrogen was 100 per cent (based on the current) but the percentage decreased with time.

Toward the end of the extended run, the cathodic current density on the PdAg foil was increased to 1466 amp/ft², while the percentage of hydrogen transmission did not decrease below 19.5 per cent. Therefore, while hydrogen was evolving on the cathode side of the foil at a rate corresponding to 1163 amp/ft², the rate of hydrogen permeating

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the foil was equivalent to 303 amp/ft². Thus, the ability of the palladium-silver foil to pass hydrogen did not appear to be the limiting factor up to 300 amp/ft². The problem was to prevent hydrogen evolution on the cathode side to attain 100 per cent hydrogen transmission.

Metal contamination of the electrolyte was suspected, so a new cell was designed as shown in Figure 5 with a smaller outlet from the electrolysis chamber. Only palladium-silver, platinum, and Teflon were in contact with electrolyte and electrolyte vapor to minimize electrolyte contamination.

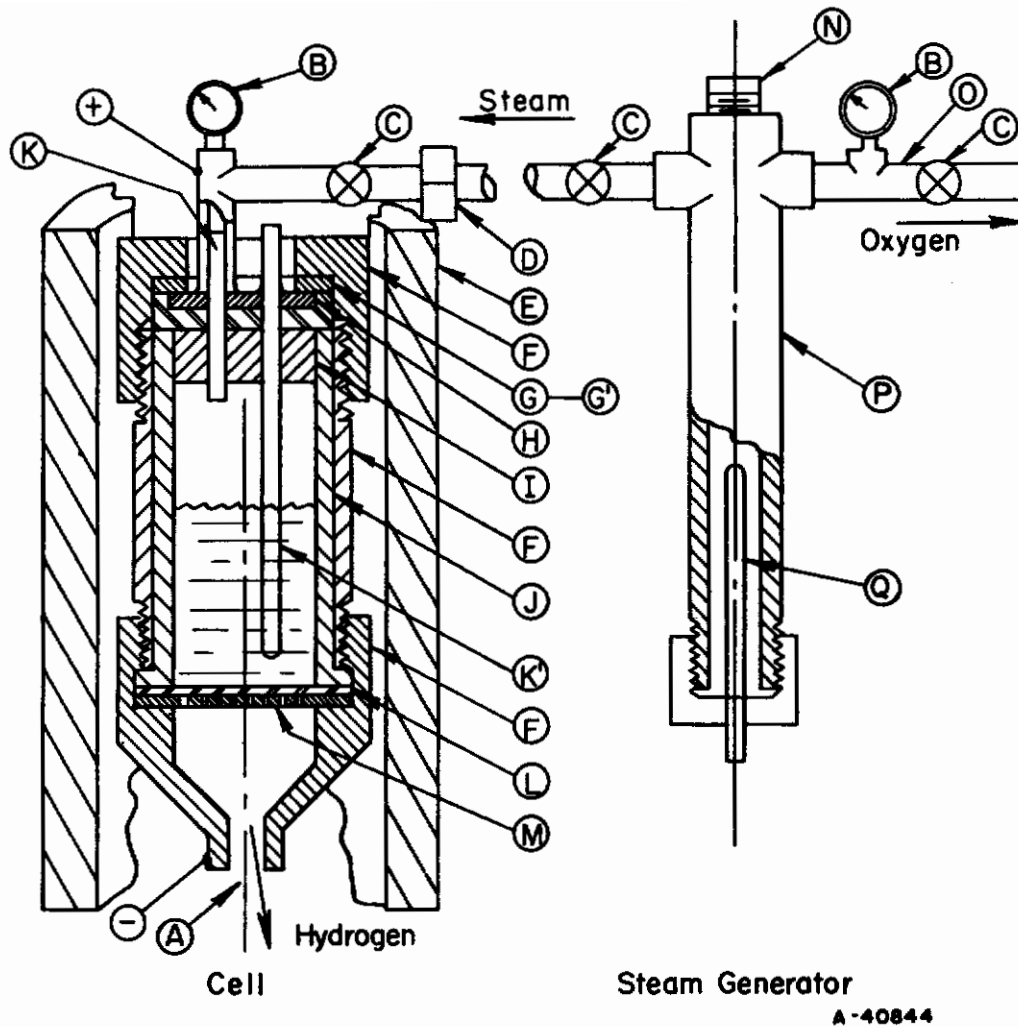
Figure 6 shows the data from the first run in which 100 per cent hydrogen transmission was obtained at 150 amp/ft² for about 1 hour, using the cell shown in Figure 5. There was no activation of the PdAg foil prior to cell assembly. The as-received foil was cleaned by wiping with tissue soaked in methyl ethyl ketone. During cell assembly, 2 grams of potassium hydroxide (KOH) pellets were added to the electrolyte chamber. After cell assembly, the unit was heated to 200 C. The valve connection to the steam generator was opened and water vapor went over to the electrolyte chamber to dilute the KOH to the desired concentration. After 30 minutes the equilibrium concentration of 55 weight per cent KOH was obtained as determined by the vapor pressure in the electrolysis chamber with the valve to the steam generator closed.

Figure 6 shows the results from the first time the current was turned on. No hydrogen was collected for the first 7 minutes at 20 amp/ft². The leads were reversed to make the foil anodic for 5 minutes at 20 amp/ft². When the foil was again made cathodic, the voltage was 1.76 volts, lower than before activation, but no hydrogen was collected in the next 7 minutes.

The current density was increased to 150 amp/ft² and the voltage increased to 2.8 volts. After anodic activation of the foil for 5 minutes at 150 amp/ft², the cell voltage decreased to 2.0 volts and hydrogen began to permeate the foil.

The steady voltage of 2.0 volts from 50 to 145 minutes and 99 to 100 per cent hydrogen transmission from about 75 to 145 minutes was considered a real demonstration of satisfactory operation. The relatively low voltage of 2.0 volts for 150 amp/ft² is another indication of voltage reduction at the cathode when hydrogen gas is not being evolved. A comparison of voltage before and after activation at 150 amp/ft² shows a decrease of 0.8 volt.

It is not known how long the satisfactory operation at 150 amp/ft² would have continued. At 145 minutes higher current densities were explored. At 380 amp/ft² and 2.5 volts, about 90 per cent hydrogen transmission was obtained for 10 minutes, then the cell polarized and the percentage transmission dropped to about 10 per cent. Apparently, the cell ran out of water. The small outlet in the top of the cell was plugged, probably with solidified KOH. After the outlet was unplugged and the cell again sealed, the low pressure (0 psig) on the electrolysis chamber indicated a very high electrolyte concentration (>65 weight per cent KOH, Figure 4). The valve to the steam generator was opened and the water vapor diluted the electrolyte. After about 10 to 15 minutes, the foil was still active and 90 per cent transmission was obtained for 40 minutes at 150 amp/ft² and 2.1 volts before the cell polarized again.



- | | |
|---|--|
| <p>A. Dry hydrogen gas to burette</p> <p>B. Pressure gages</p> <p>C. Valves</p> <p>D. Union</p> <p>E. Tube furnace</p> <p>F. Standard 3/4" brass fittings</p> <p>G. Teflon washer; G', Teflon cap</p> <p>H. Copper disk</p> <p>I. Teflon plug</p> | <p>J. Teflon liner, 1/2" ID x 2" long</p> <p>K. Platinum tubes, 0.070" OD; K', platinum tube serves as an anode and thermocouple well</p> <p>L. Palladium-silver foil, 0.001" thick</p> <p>M. Teflon orifice plate, 0.010" thick</p> <p>N. Brass plug, water inlet to steam generator</p> <p>O. Standard 1/8" brass pipe nipples</p> <p>P. Standard 1-1/4" x 10" brass pipe nipples, heated by electrical tape</p> <p>Q. Stainless steel thermocouple well</p> |
|---|--|

FIGURE 5. DESIGN OF EXPERIMENTAL CELL H

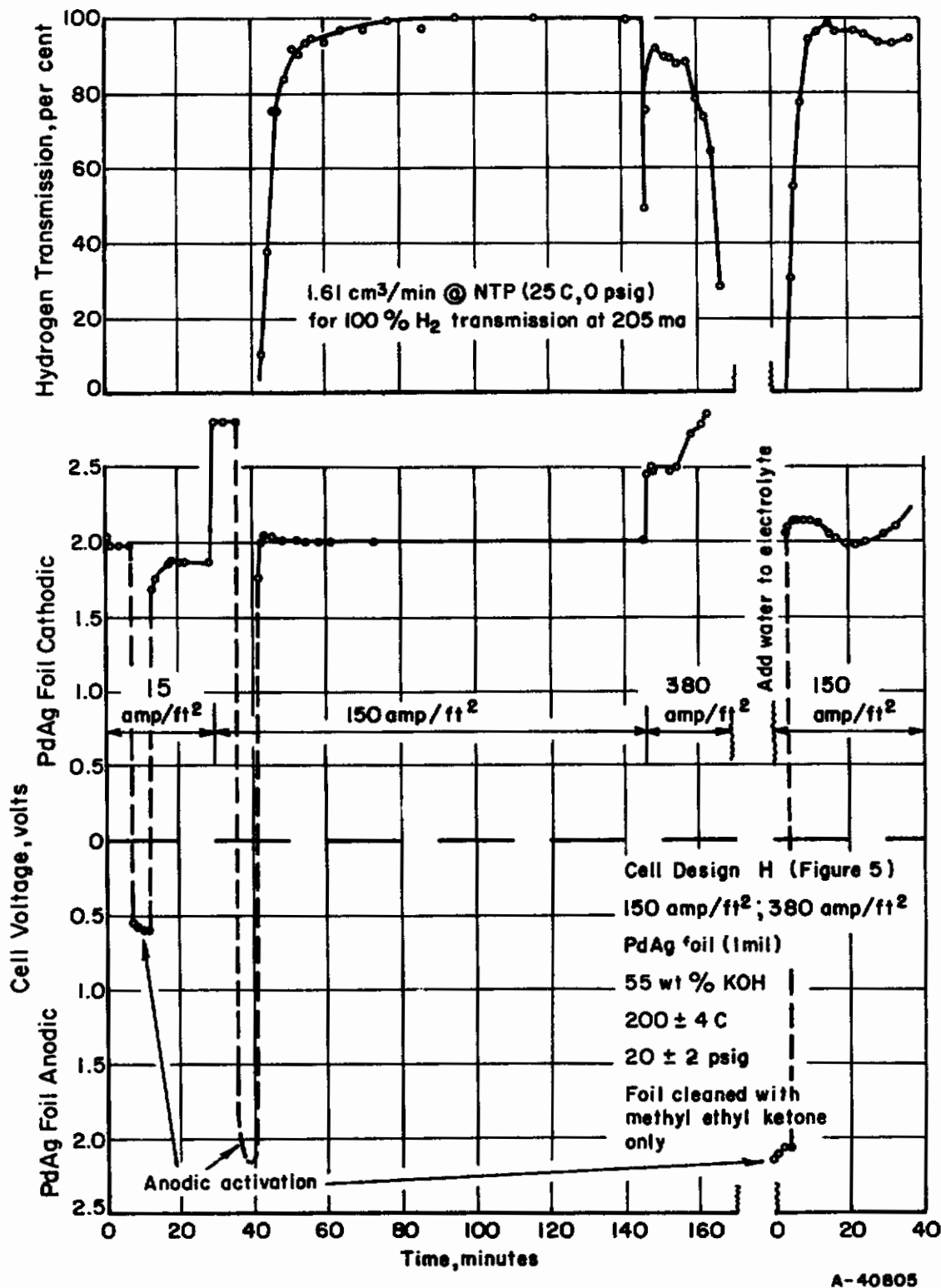


FIGURE 6. RUN 2-77 SHOWING SATISFACTORY OPERATION AT 150 AMP/FT²

First demonstration of 100 per cent hydrogen transmission at high current density for 1-1/2 hours.

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The indicated problem was lack of water in the electrolyte. The cell design with a small oxygen outlet appeared to be unsatisfactory at 150 amp/ft² since the volume of oxygen issuing prevented water vapor from reaching the electrolyte. Therefore, new cell designs were devised involving reflux condensers to minimize water loss with the oxygen stream. Figure 7 shows a typical cell design in which the upper portion of the tall Teflon electrolysis chamber acted as a reflux condenser. The steam generator was not used with this design to eliminate contact of hot vapor with metal pipe and to minimize possible sources of electrolyte contamination. A greater volume of electrolyte could be used in Cell I, and additions of water or electrolyte were made by inserting a hypodermic needle through the Teflon wall near the top of the tube.

Figure 8 shows data from the last successful run in which 100 per cent hydrogen transmission was obtained at 265 amp/ft² for nearly 1 hour. The entire run (Run 2-95, Appendix II) involved numerous anodic activations until about 87 per cent hydrogen transmission was obtained at 265 amp/ft². The cell was shut off and allowed to cool to room temperature over a weekend. Figure 8 shows the results from the time that the run was resumed.

Following anodic activation at 265 amp/ft², hydrogen transmission increased rapidly to 100 per cent from the 70 per cent value prior to activation. Again, the voltage was lower when the process was operating correctly at 100 per cent transmission. Figure 8 shows a lower voltage of 1.76 volts in Run 2-95 at a higher current density of 265 amp/ft² compared with Run 2-77 (2.0 volts at 150 amp/ft²) (Figure 6). The lower cell voltage is probably attributable to reduction in electrolyte resistivity and polarization at the higher temperature of 230 C compared with 200 C, and to the use of a platinum-wire anode in Cell I (Figure 8) compared with the platinum-thermocouple well as anode in Cell H (Figure 6).

The termination of satisfactory operation at about 70 minutes appears related to slight changes in operating conditions. Teflon begins to char at about 250 C. The cell temperature which had reached 240 C was reduced at 70 minutes. The pressure in the electrolysis chamber had increased to 25 psig from evolved oxygen, and the pressure was bled to 15 psig at 74 minutes. The effect of pressure reduction on increasing the cell voltage is evident in Figure 8. This might be expected because of a nearly twofold increase in the oxygen-bubble size which could increase the electrolyte resistance. Two subsequent pressure reductions at 132 minutes and 162 minutes also caused sharp reductions in hydrogen transmission. This indicates that pressure influences the electrochemical reactions at the cathode too.

In Figure 8, the plot of pressure readings with time shows a marked change in slope at 20 minutes when 100 per cent hydrogen transmission was obtained. This indicates that some gaseous hydrogen was being evolved in the electrolyte prior to the activation and was contributing to the pressure increase. During the time that 100 per cent hydrogen transmission was obtained, the increase in pressure is solely attributed to the oxygen evolved. After the hydrogen transmission decreased below 100 per cent, gaseous hydrogen contributed to the total pressure of the oxygen stream as indicated by the increased slope of the pressure-time curves. The results are indirect evidence that the measured loss of per cent hydrogen transmission results in evolved hydrogen gas on the cathode rather than a mechanism involving interaction of dissolved hydrogen at the anode to form water.

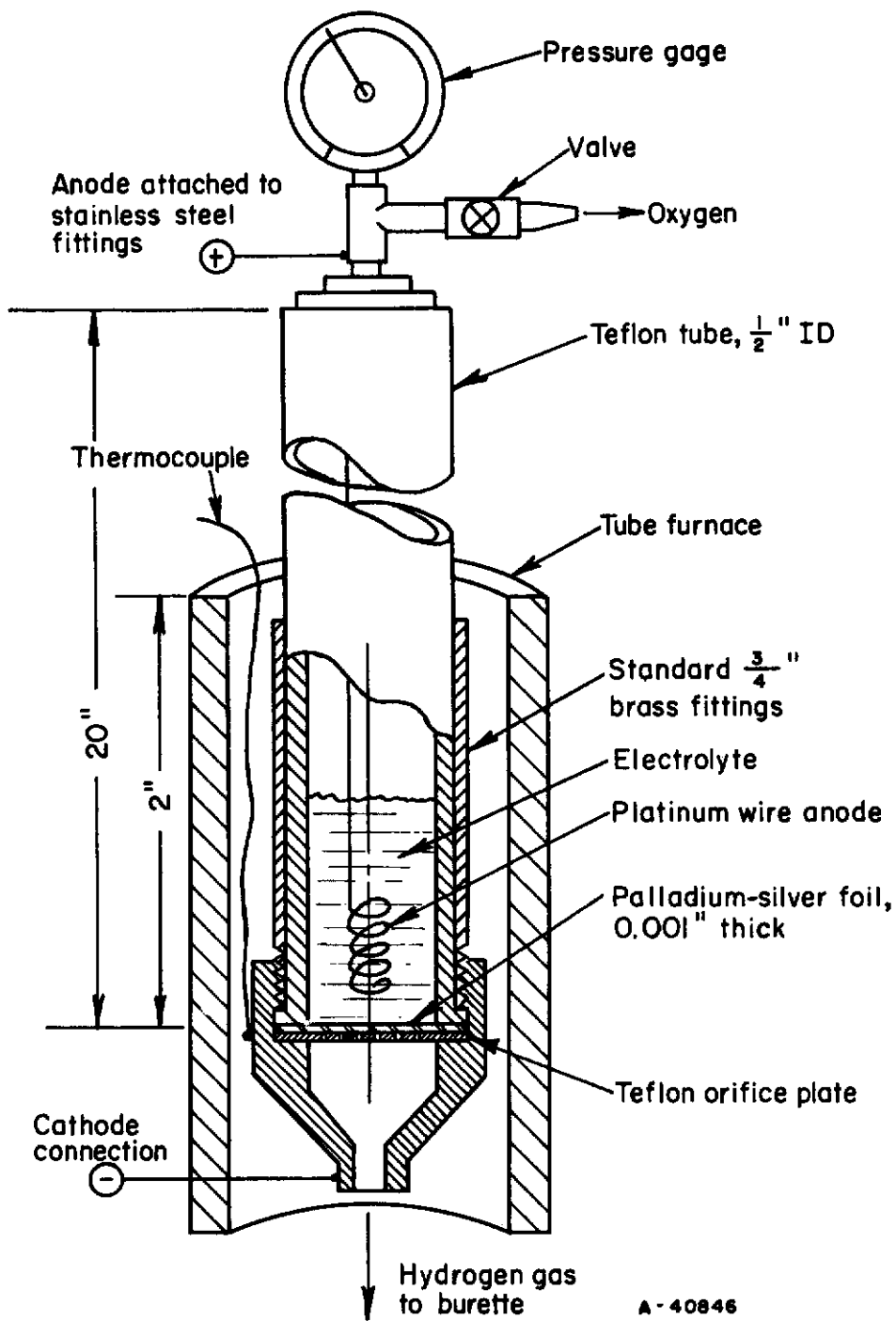


FIGURE 7. DESIGN OF EXPERIMENTAL CELL I

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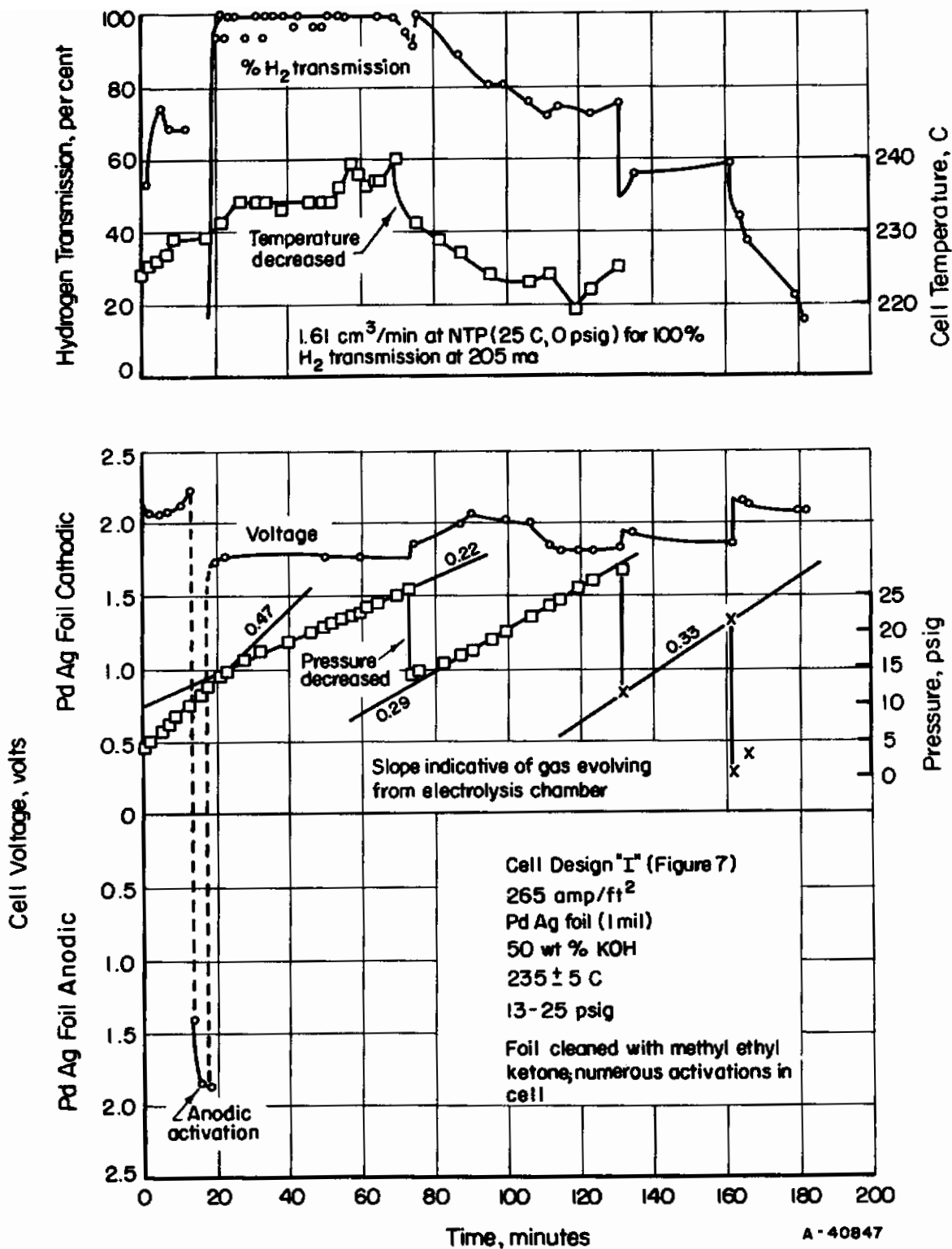


FIGURE 8. RUN 2-95 SHOWING SATISFACTORY OPERATION AT 265 AMP/FT²

Termination of operation at 100 per cent hydrogen transmission appears to be related to changes made in temperature and/or pressure.

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No direct measurements of oxygen-stream purity were made during the periods of indicated 100 per cent hydrogen transmission. The purity of the oxygen stream can be inferred by collecting all of the hydrogen formed, based on the current used and Faraday's Law of electrolysis. Individual measurements of hydrogen transmission were accurate only within about ± 6 per cent (± 0.1 ml reading of gas-collection burette). However, cumulative readings over periods of 10 minutes or more were accurate to about ± 1 per cent hydrogen transmission, so that the evolved oxygen stream was probably at least 99 per cent pure when the process was operating correctly.

The technical accomplishments considered important and their relation to the project objectives are:

- (1) Attainment of 100 per cent transmission of the hydrogen generated (within experimental accuracy of ± 1 per cent) based on Faraday's Law and the cell current used which indirectly implies relatively pure breathing oxygen. The small amount of hydrogen that might have to be removed by catalytic burning to produce a pure oxygen stream would result in a negligible reduction in the energy efficiency of water electrolysis.
- (2) The high current density demonstrated will allow design of a small, lightweight cell.
- (3) The relatively low voltage obtained verifies the low power consumption originally predicted for a hydrogen diffusion cathode. The low cell voltage obtained when the process is operating correctly (no gaseous hydrogen evolved on electrolyte side of the cathode) is the combined result of reduction in cathode polarization, hydrogen overvoltage, and electrolyte resistance. The elimination of gaseous hydrogen from the electrolysis zone represents a two-thirds reduction in gas volume in the electrolyte which could restrict current flow. With 100 per cent hydrogen transmission there is no need for a diaphragm which normally contributes to electrolyte resistance.

The electrolytic conditions for satisfactory performance obtained towards the end of the project were not far different from the principal conditions originally proposed and studied throughout the project (i. e. , potassium hydroxide electrolyte, 200 C, PdAg alloy). Optimum performance was finally obtained by a combination of the following features that were incorporated as the experimental work progressed:

- (1) A satisfactory cell design to prevent electrolyte and/or gas leakage at high temperature and pressure.
- (2) Minimum electrolyte contamination from corrosion products by use of Teflon in contact with electrolyte and vapors.
- (3) Optimum pressure and temperature. The data are inconclusive concerning the optimum conditions but satisfactory operation at high current density was obtained only when the temperature was above about 190 C and the pressure at least 13 psig.

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- (4) Proper activation of the cathode foil is required for satisfactory operation when the first three conditions are met. The successful runs at high current density were always preceded by a reversal of the electrical connections to make the PdAg foil anodic at the operating current density for 2 to 5 minutes.

The most important area for future research is a study of cathode foil activation. Several attempts to duplicate the results of the high-current-density runs were unsuccessful.

In spite of the difficulty experienced in reproducing the good experimental results, the results obtained are considered real and not transient. In each case, the satisfactory operation was maintained for at least 1 hour and the cause of termination of satisfactory operation appears to have been identified.

- (a) Run 2-34 was voluntarily interrupted and resumed the following day at higher current density. However, the thin Teflon coating on the cell had failed, allowing corrosion and electrolyte contamination.
- (b) Run 2-77 was proceeding smoothly and unvarying at 150 amp/ft², so operation at 380 amp/ft² was checked. About 80 per cent transmission was obtained for 10 minutes before polarization occurred. The cause of polarization was identified as a loss of water from the electrolyte which solidified at the higher concentration. An improved cell design is needed for high-current-density operation.
- (c) Run 2-95 was proceeding satisfactorily until the temperature was lowered slightly about the same time the pressure was sharply reduced. Either reduction in temperature or pressure or a combination of both precipitated a decrease in transmission of hydrogen. The cause was identified as a change in operating conditions but the reason for the failure is not clear at this time.

While the experiments in which 100 per cent hydrogen transmission was obtained were few in number, the results in terms of current density are encouraging. At the time that the hydrogen-diffusion cathode was first proposed and preliminary design estimates were made, it was not known that the concept was technically feasible. More reliable estimates can be made now of the important factors of cell size, weight, and power consumption on which to base a recommendation for further study of the hydrogen-diffusion-cathode cell.

DESIGN ESTIMATES FOR A ROTATING CELL

Basis of Comparison

On a previous project at Battelle, a laboratory-model rotating cell designed for electrolysis of water under weightless conditions was built and evaluated (ref. 1). The cell design used principles found in industrial electrolytic cells for producing hydrogen

and oxygen (steel cathodes and nickel anodes separated by asbestos diaphragms in 28 weight per cent potassium hydroxide electrolyte). The method featured a relatively high degree of reliability by analogy to industrial cells with operating experience indicating 5 to 10 years of operating life with low maintenance.

The laboratory model was large and bulky but was surprisingly economical of power. As intended, the laboratory-model rotating cell provides a basis of comparison and will be referred to as a "conventional cell" with regard to the principle of electrolysis. The cell proposed on this present project is also a rotating cell but is differentiated as a "hydrogen-diffusion-cathode cell" for purposes of discussion.

As pointed out in the "Introduction", any new concept of generating hydrogen and oxygen that departs from established principles of electrolysis of water should offer great improvement (mainly weight reduction for the integrated life-support system) to justify the expense of development to the status of reliability required for life-support systems in space. The purpose of this section of the report is to provide a basis for evaluating the further development of the "hydrogen-diffusion cathode" in relation to other oxygen recovery methods being considered.

Advantages and Disadvantages

On the basis of the experimental work reported in the previous section of this report, the following features must be considered potential disadvantages of the hydrogen-diffusion-cathode cell with regard to reliability:

- (1) The high operating temperature of 200 to 230 C presents problems with stability of materials of construction, resistance to corrosion, and electrolyte purity.
- (2) The mechanism of hydrogen permeation through metals is complex, involving surface activation, catalytic reaction, metallurgical structure, etc., susceptibility to poisoning or change. This is evidenced by the lack of agreement in the published literature on values for hydrogen diffusion through palladium and other features of the hydrogen-palladium system.
- (3) At the present time, the absence of data on extended operating time beyond a few hours with 100 per cent hydrogen transmission must be listed as a disadvantage.

The above disadvantages are not of a fundamental nature but rather are the type that could be eliminated or minimized by further research and knowledge of the process.

Certain features of the hydrogen-diffusion-cathode cell indicated by the experimental work are neither advantages nor disadvantages but rather encouraging results or possibilities relative to the knowledge of the system at the beginning of the study.

- (1) No signs of physical deterioration of the palladium-silver alloy foil were detected during extended use, temperature cycling, or charging and discharging with hydrogen.

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- (2) The ability to use a relatively high concentration of potassium hydroxide electrolyte offers a means of stopping the rotating cell without removal of the electrolyte. For example, solidification of the electrolyte by rapid decrease in cell temperature (from 200 C to 100 C for 65 weight per cent KOH) and resumption of operation by heating. Low vapor pressure of high electrolyte concentrations minimizes water removal with oxygen.
- (3) The techniques devised for adding water as steam might control electrolyte concentration and liquid level in the cell with less complexity than water pumps and electronic circuitry involving liquid-level indicators. Water supplied as steam from a well-designed steam generator would approach the purity of distilled water and minimize electrolyte contamination.
- (4) The indication that the pressure over the electrolyte can be on the order of 15 psig means that the cell does not have to be rotated at high speed or designed for high gas pressures, with consequent problems in sealing and providing added structure strength.

The potential advantages of the hydrogen-diffusion-cathode cell are the same as those originally proposed:

- (1) Production of pure breathing oxygen. Even if a catalytic burner were required to remove at most 10 per cent hydrogen from the oxygen stream, the over-all energy efficiency still would be better than other electrolysis methods.
- (2) Production of pure hydrogen for subsequent catalytic reactions with carbon dioxide.
- (3) Production of dry hydrogen so that water vapor is not cycled to the water-producing reaction and back to the electrolysis cell.
- (4) Reduced electrolysis power consumption for comparable cell sizes.
- (5) Reduced cell size and weight for comparable electrolysis power consumption.

Weight, Size, and Power Comparisons

The weight, size, and power consumption of a proposed electrolysis cell are the only features susceptible to quantitative comparison. The current density that the cell can be designed for is a measure of the size of the electrolysis portion of the cell on which to base estimates of weight of the electrolysis portion. The cell voltage is a measure of the electrolysis power consumption which is a large percentage of the total power consumed in operating a rotating cell. Estimation of size and weight of various components that must be added to the electrolysis portion to make a complete cell is difficult. It was reasoned that, if the electrolysis portion could be made small and light, there would be sufficient justification for study and effort to miniaturize the remaining components.

Contrails

For appraising the desirability of further study of the hydrogen-diffusion-cathode cell, it was reasoned that the estimates should reflect the most optimistic values possible based on the available experimental data, on the assumption that all of the apparent technical problems could be resolved by further research. In other words, the following estimates indicate the present foreseeable goal.

The first comparison shown in Table 2 is limited to the electrolysis portion of the cell and excludes the superstructure (base, motor, valves, lines, etc.). Approximate calculations of electrolysis cell size with a hydrogen-diffusion cathode were made for the three current densities demonstrated and for both parallel and bipolar (series) electrical connection.

For parallel operation at high amperage-low voltage, the palladium-alloy cathode was considered to be the outer surface of a cylinder of diameter equal to height. Because of the electrical losses in supplying high amperage through brushes in a rotating cell design, a series-connected bipolar cell is probably preferable.

A special bipolar-electrode design would be required for a bipolar rotating electrolysis cell containing hydrogen-diffusion cathodes. One design example is a circular plate of porous metal (i. e. , porous stainless steel) bonded on one side to a thin fold of palladium alloy and on the other side to a thin foil of platinum. The metallic electrode would provide electronic conduction from the palladium-alloy surface acting as cathode in one cell to the platinum surface acting as anode in the adjoining cell. Hydrogen formed at the cathode would permeate through the palladium alloy and collect in the porous interior of the electrode. Hydrogen would not permeate through the platinum, and hydrogen gas would be removed from the porous stainless steel interior of the electrode. Oxygen evolved on the platinum surface in contact with electrolyte would be removed by the centrifugal action of the rotating cell. A sufficient number of bipolar electrodes could be assembled (with electrical insulation between) to obtain the desired electrode area, similar to a "conventional" bipolar cell.

For a bipolar design of the hydrogen-diffusion-cathode cell, the electrodes were assumed to have an effective area defined by a concentric ring of 3-inch inside diameter and outside diameter equal to the total cylinder height. To allow for the volume of oxygen gas per unit cell, the individual cell widths were taken as 1/8 inch for 15 amp/ft² and 1/4 inch for 150 and 265 amp/ft². In view of the measured value of 1.76 volts at 265 amp/ft², the assumed voltage of 1.7 volts (rather than the measured value of 2.0 volts) appears more representative of operation at 150 amp/ft².

From Table 2 it can be seen that, for a hydrogen-diffusion-cathode cell connected in parallel, a practical-size cell requires a current density greater than 150 amp/ft². However, a bipolar cell designed for 15 amp/ft² would be smaller than the "conventional" cell because of the closer electrode spacing assumed, which appears justified when the diaphragm is eliminated and two-thirds of the normal gas volume (hydrogen) is absent. The hydrogen-diffusion-cathode cell appears very attractive for a bipolar design at 265 amp/ft², where a tenfold reduction in electrolysis-cell volume is estimated in comparison with the volume of the "conventional" cell.

In view of the small cell size of 0.05 ft³ estimated for bipolar operation at 265 amp/ft², relatively little reduction in volume could be achieved by having a higher current density to use as a design basis. Thus, the principal advantage of achieving higher current densities in the 1000 to 2000 amp/ft² range would be to increase the capacity from a 3-man cell to a 10- or 20-man cell, while maintaining a small cell size.

TABLE 2. COMPARATIVE ESTIMATES OF THE SIZE AND POWER CONSUMPTION OF THE ELECTROLYSIS PORTION OF A ROTATING CELL BASED ON THE EXPERIMENTAL RESULTS

[Basis: 3-man cell (6 lb of O₂/day).]

	Dimensions ^(a) , inches	Volume, ft ³	Current, amperes	Electrolysis Cell Voltage, volts	Electrolysis Power, watts
Conventional Cell					
Parallel	10-3/4 x 10-1/16	0.53	381	2.1	800
Bipolar	10-3/4 x 10-1/6	0.53	23.8	33.5	800
Hydrogen-Diffusion Cathode Cell					
Parallel					
15 amp/ft ²	34 x 34	17.8	381	1.34	510
150 amp/ft ²	10-3/4 x 10-3/4	0.56	381	1.70	639
265 amp/ft ²	8 x 8	0.23	381	1.76	671
Bipolar					
15 amp/ft ²	8-3/4 x 8-3/4	0.30	5.4	93.8	510
150 amp/ft ²	5-1/2 x 5-1/2	0.08	17.1	37.4	639
265 amp/ft ²	4-3/4 x 4-3/4	0.05	20.1	33.4	671

(a) First dimension given in each case is diameter.

In estimating designs for a rotating cell with a hydrogen-diffusion cathode, it must be pointed out that the "beaker-scale" cells used in the experimental work approximated the condition assumed for a "parallel" connected rotating cell when the rotation is sufficient to provide at least a normal gravitational field of 1G in the electrolyte at the cathode. There is little doubt that, in such a design for a rotating cell, the results would be equivalent to those obtained in the laboratory experiments.

In the bipolar-cell design assumed, the artificial gravity field acts parallel to the plane of the cathode. Thus, there is a differential hydrostatic pressure on the cathode, decreasing from outer radius to inner radius of the cathode. At the present time, there is no reason to believe that the operation of the hydrogen-diffusion cathode would be affected by orientation in a gravity field, since, presumably, at 100 per cent transmission there are no hydrogen-gas bubbles on the cathode surface. However, this would have to be verified by laboratory experiments in which the cathode is mounted vertically.

For space applications, equipment size is important but weight may be more important. In the following comparison, estimates of weight of a hydrogen-diffusion-cathode cell have been based on the volume and probable density of such structures. The laboratory-model cell used as a basis of comparison was larger and heavier than necessary to allow for electrolysis experiments at high pressure. The estimates based on improved redesign for lower pressure are included in Table 3 for a better comparison.

TABLE 3. BEST PRESENT ESTIMATE OF TOTAL SIZE, TOTAL WEIGHT, AND ELECTROLYSIS POWER OF A ROTATING-CELL DESIGN WITH A HYDROGEN-DIFFUSION CATHODE

[Basis: 3-man cell (6 lb of O₂/day).]

	Volume, ft ³	Weight, lb	Electrolysis Power, watts
Conventional (ref. 1)			
Electrolysis Portion Only	0.53	108	800
Total (Actual)	4.4	284	
Estimated Redesign Total	2.2	200	
Hydrogen-Diffusion Cathode (265 Amp/Ft ²)			
Electrolysis Portion Only	0.05	10	670
Estimated Total	0.2	20	

At the present time, there is no other water-electrolysis system designed for operation under weightless conditions that is known to offer the prospects for size and weight reduction indicated by the estimates for the hydrogen-diffusion-cathode cell shown in Table 3. While a weight of about 10 pounds for the estimated size of the electrolysis portion appears attainable, the main design problem is in miniaturizing the superstructure (which includes the motor, housing, valves, lines, etc.) to avoid more than doubling the total weight.

The important factor is the total weight of the integrated life-support systems, which should include the proportionate share of the power-supply weight. By the time

that advanced chemical oxygen-recovery systems are used, it is expected that the weight of power supplies will be reduced considerably from present values (in the range of 100 to 1000 lb/kw).

The specific weight of power supplies decreases as the power output increases. According to Beller (ref. 5), the estimated electric power requirements for space missions will reach 10 kw by 1966. Extrapolation of Beller's estimates indicates a need for 1000 kw by 1970. Estimates of 10 to 20 lb/kw for nuclear-reactor-type power supplies are given for the 1000-kw level (ref. 5). Thus, optimistically, the proportionate share of the power-supply weight estimated for the 3-man hydrogen-diffusion-cathode cell would be in the range of 7 to 14 pounds, or the same order of magnitude as the estimated weight of the electrolysis cell.

More realistically, a SNAP-8 nuclear power supply of 60 kw would have a specific weight of no better than 100 lb/kw when shielded for man (ref. 5). If SNAP-8 is introduced in 1965, it might have sufficient reliability for use on manned space flights by 1970. At 100 lb/kw for the power supply, the optimum design of electrolysis cell for minimum system weight might require a lower design current density and a larger cell to reduce power consumption.

The low power consumption of the hydrogen-diffusion-cathode cell in relation to estimated cell size makes it appear ideally suited for even the most optimistic planning of future power supplies.

CONCLUSIONS

These results have shown that the concept of 100 per cent hydrogen transmission through a palladium-silver cathode at high current density is technically feasible. The high current density demonstrated would permit design of a rotating cell for generation of breathing oxygen that is estimated to be smaller and lighter, and to consume less electrolysis power than any other known system for electrolyzing water.

There is insufficient knowledge available, at the present time, of the various factors involved, particularly cathode activation, to specify the optimum conditions for attaining satisfactory performance. To determine whether the hydrogen-diffusion-cathode cell is technically practical will require at least a demonstration of extended satisfactory operation for days or weeks compared with the hours demonstrated in the present experimental work.

RECOMMENDATIONS

In view of the orders of magnitude of reduction in system weight and other advantages that might be realized with a successful cell based on a hydrogen-diffusion cathode, further study is recommended along the following lines:

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- (1) A continuation of the present type of study of palladium-alloy cathodes with experimental nonrotating cells to investigate cathode activation. The apparently interrelated variables of temperature, pressure, and electrolyte composition should be investigated, directed toward satisfactory operation for periods of at least 8 to 24 hours.
- (2) Design, construction, and evaluation of a laboratory-model rotating cell with a hydrogen-diffusion cathode to produce pure breathing oxygen for 3 men during continuous operation for evaluation periods of from 1 to 5 days.

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DISCUSSION OF HYDROGEN PERMEATION THROUGH
PALLADIUM AND PALLADIUM ALLOYS

Introduction

The palladium-hydrogen system has been the subject of many studies because of the unique property of palladium to occlude large volumes of hydrogen without disintegration (i. e, 700 volumes of hydrogen in 1 volume of palladium). There are fewer data available on the palladium-silver alloy which was mainly used on this project. All of the published information on hydrogen diffusion through cathodes and all electrolysis studies of interest deal with pure palladium. In many respects the palladium-hydrogen (Pd-H) system is similar to the palladium silver-hydrogen (PdAg-H) system. Therefore, the discussion of hydrogen permeation, diffusion, electrolytic reactions, etc., can best be made with reference to pure palladium. Finally, the differences between PdAg and palladium will be discussed.

Review of the Published Literature

Part of the doctoral dissertation of Andrus (ref. 1*) on "Hydrogenation With Palladium Diaphragms" is devoted to a fairly comprehensive review (70 pages, 100 references) of the diffusion of hydrogen through palladium, covering both gaseous permeation of hydrogen through palladium and diffusion of electrolytically generated hydrogen through a palladium bielectrode. Unfortunately, this book (341 pages) did not become available until near the end of the project. The literature review covers most of the pertinent articles through about 1959. The references listed at the end of this Appendix include pertinent articles subsequent to 1959.

A shorter review of the literature on gaseous-hydrogen permeation through palladium is included in the report by Rowlette (ref. 2).

A fairly detailed study of permeation of hydrogen through palladium (gas phase to gas phase) is covered in a series of four reports (1954-1956) on work done at the Knolls Atomic Power Laboratory, operated for the AEC by the General Electric Company (refs. 3, 4, 5, 6). Of particular interest are the studies by Davis (ref. 4) relating to poisoning and activation of palladium. The values of hydrogen diffusion coefficient obtained by Davis for clean active palladium are considered to be the most reliable of those reported in the literature:

$$D_0 = 4.3 \times 10^{-3} \text{ cm}^2/\text{sec}, E_0 = 5620 \text{ calories.}$$

Figure 9 shows some of the data on hydrogen permeation through palladium and palladium-silver obtained from the published literature. The permeation rate is shown as the equivalent current density for 100 per cent hydrogen transmission to indicate the

*References mentioned in this Appendix are listed on p 36.

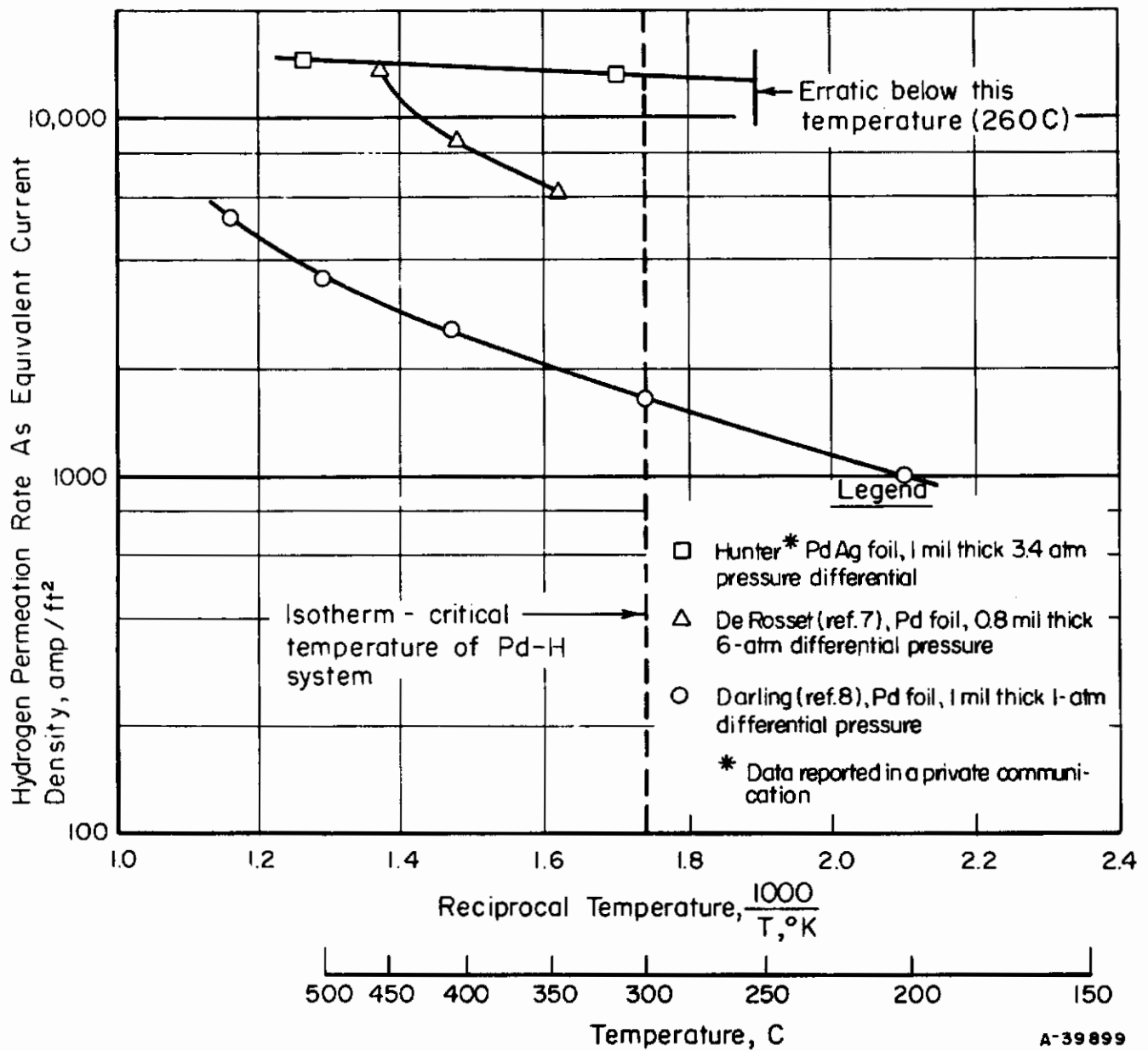


FIGURE 9. HYDROGEN PERMEATION RATES REPORTED FOR Pd AND PdAg

order of magnitude of current densities that might be obtained. Unfortunately, there are relatively few data available at temperatures below about 300 C, the critical temperature for the Pd-H system. Most gas purification using palladium or PdAg alloys is done above 300 C in order to obtain appreciable rates. Below 300 C, there is a two-phase region in the Pd-H system as shown in Figure 10.

The palladium-hydrogen phase diagram shown in Figure 10 was prepared from three sources of literature data (refs. 9, 10, 11) in order to cover the temperature range of interest in the present work. A logarithmic pressure scale was used to emphasize the low-temperature region.

Extrapolation of permeation rates from high temperature to the low temperature region of interest on this project (230 C and less) can give erroneous results if, in the low temperature region, two phases are present at the pressures to be used.

In Figure 9, the data of Darling (ref. 8) applies to 1-atmosphere pressure differential across the palladium foil from 14.7 psia to 0 psia. Thus at 200 C, both sides of the palladium are in the α phase at equilibrium.

In Figure 9 the data of de Rosset (ref. 7) for a differential pressure of 6 atmospheres (i. e., 105 psia to 15 psia) could not be extrapolated directly, since at 200 C and 105 psia the front side of the foil would be in the β phase (Figure 10) and the back side at 15 psia would be in the α phase at equilibrium. Thus, somewhere within the foil there would be an α/β interface or discontinuity which appears to seriously affect diffusion rates. The effect of phase discontinuities is discussed by Ash and Barrer (refs. 12, 13) and van Swaay and Birchenall (ref. 14).

For a number of years, there have been fundamental studies relating to electrochemical reactions at a palladium cathode at the U. S. Naval Research Laboratory (refs. 15-24). The work has been primarily directed towards a better understanding of electrode reactions, hydrogen overvoltage, etc. Schuldiner and Hoare (ref. 16) describe the deposition of hydrogen on a palladium-foil cathode from a 2N H_2SO_4 solution whereby they obtained 100 per cent hydrogen transmission at current densities up to 17 amp/ft² (33 C). The hydrogen that diffused through the foil was removed from the back side by chemical reaction with ceric sulfate in 2N H_2SO_4 . The rapid chemical reaction maintained practically a zero concentration of hydrogen in palladium on the back side, giving a large concentration gradient for diffusion.

Elmore and Tanner (ref. 25) used palladium foil as an electrode of a fuel cell. Hydrogen permeated through the foil from the gas phase to the electrolyte side where it was oxidized electrolytically. The highest current density reported was about 100 amp/ft² using a sodium hydroxide electrolyte at 150 C. With reference to Figure 10, it can be seen that the gas-phase side of the foil might have been in the β phase ($\sim 0.5H/Pd$) at 1 atmosphere and 150 C. The electrolysis side would have a low concentration of hydrogen, giving a large concentration gradient. Experiments by Andrus (ref. 1) utilized a palladium bielectrode with sulfuric acid electrolyte on both sides. Hydrogen was electrolytically deposited on the cathode side of the bielectrode and removed from the opposite side by anodic oxidation. The best result reported was 93 per cent hydrogen transmission at 238 amp/ft² at about 110 F with 0.008-inch vacuum-annealed palladium diaphragm. The technique of anodic removal of hydrogen that diffused through the foil did not allow attainment of 100 per cent transmission because of oxygen poisoning on the anodic side of the foil. A similar experiment at 150 amp/ft² with 90 to 95 per cent hydrogen transmission was run continuously for 21 days.

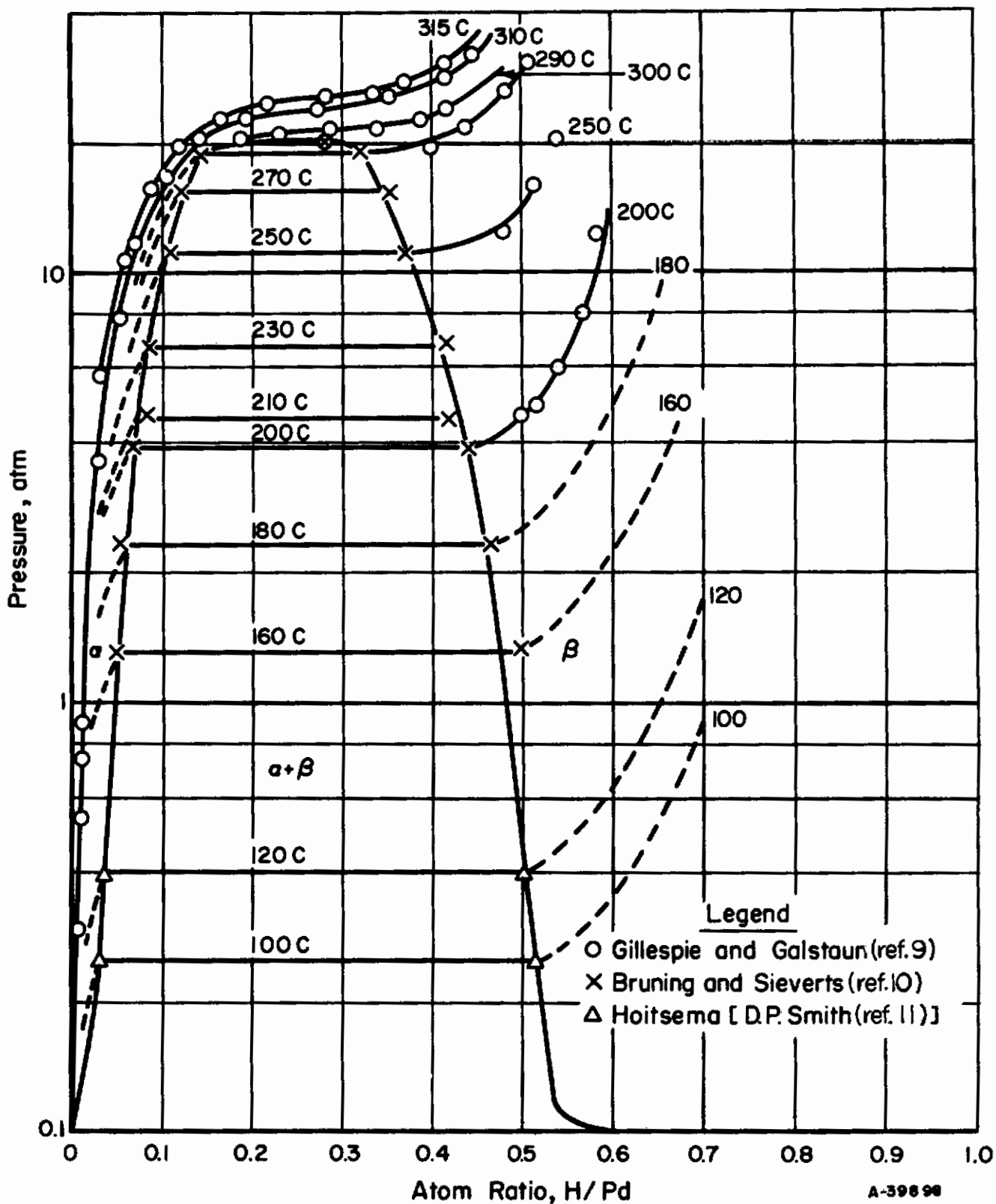


FIGURE 10. Pd-H PHASE DIAGRAM

Hoare and Schuldiner (ref. 17) also studied a palladium bielectrode in which one side of the foil was cathodic and the opposite side anodic.

In general, most previous investigators using a palladium diffusion cathode have used acid electrolytes. No work was reported in which the cathodically deposited hydrogen was removed from the back side into a gas phase as on this project.

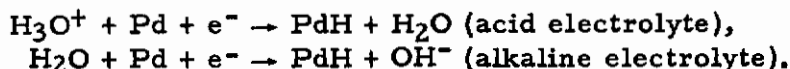
The work of McGraw et al. (refs. 26, 27) with steel suggests the use of poisons such as arsenic compounds in the acid electrolyte to increase the hydrogen diffusing through the palladium by poisoning the catalytic decomposition reaction of the Pd-H alloy on the cathode surface. The use of poisons was not studied on this project since 100 per cent transmission of hydrogen was obtained by use of alkaline electrolyte and pressure.

Other miscellaneous references are the studies of Carson et.al. (refs. 28, 29) dealing with palladium electrodes. Levine and Weale (ref. 30) presented data on the Pd-H system at high temperature and pressure.

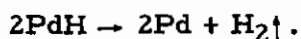
Proposed Mechanism of Hydrogen Transport

Figure 11 is a schematic diagram of palladium cathode foil with reactions showing the proposed mechanism of a hydrogen-diffusion cathode. It is postulated that transport of hydrogen through the palladium takes place in the following manner:

- (1) Hydrogen is deposited on the palladium surface by the following reactions:



- (2) Hydrogen diffuses through palladium as a proton.
- (3) Hydrogen gas is liberated on the gas side of the foil by the following reaction:



The rate of diffusion of hydrogen is governed by the following equation:

$D = D_0 e^{-E_0/RT} \frac{dc}{dx}$,

where

D = hydrogen diffusion rate, cm/sec or cm³/cm²/sec

D₀ = diffusion coefficient of hydrogen through palladium, cm²/sec

E₀ = activation energy, cal

R = gas constant, 1.986 cal/g-mole/K

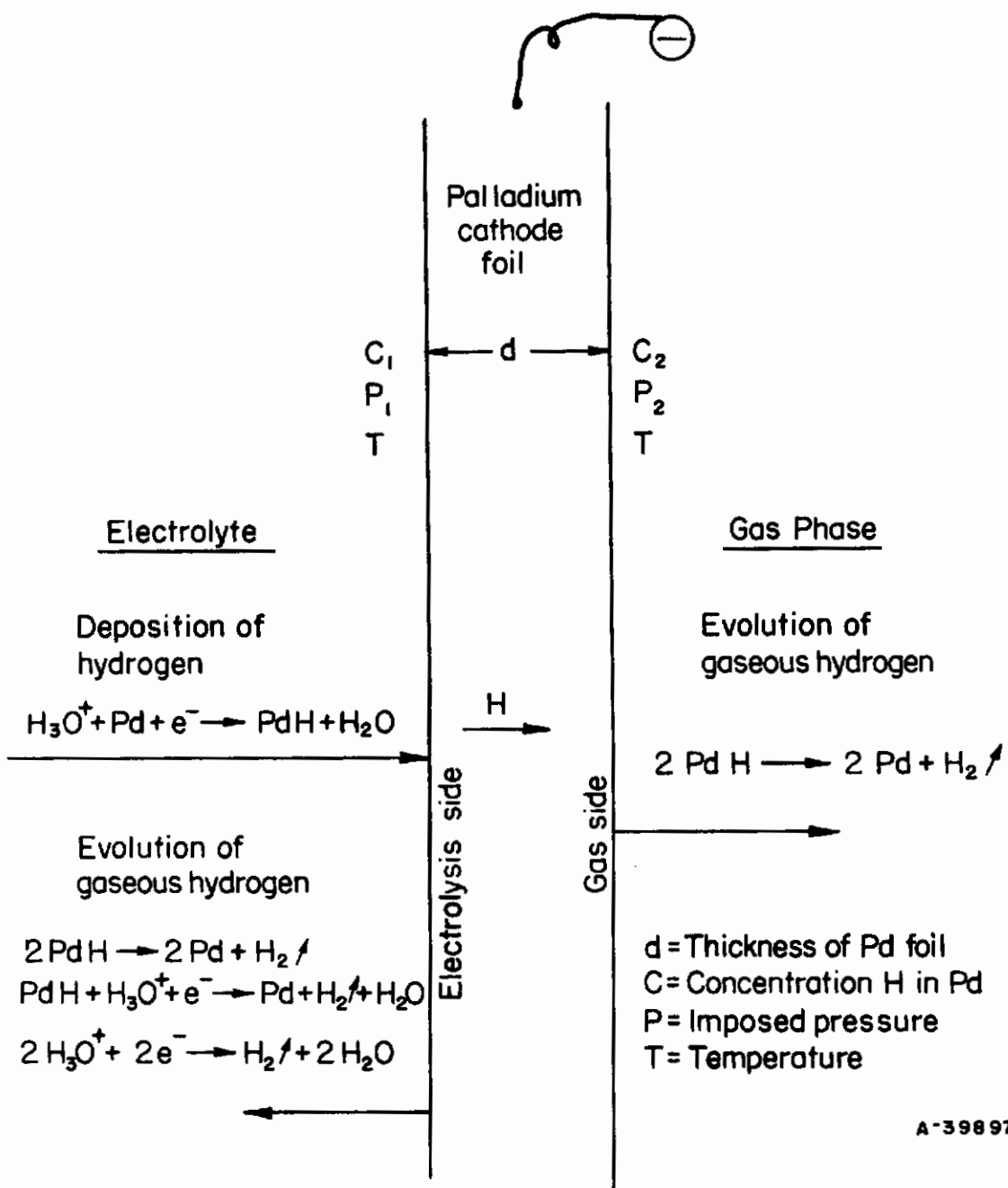


FIGURE 11. PROPOSED MECHANISM OF HYDROGEN PERMEATION THROUGH A PALLADIUM FOIL CATHODE

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T = temperature, K

e = base of natural logarithm

$\frac{dc}{dx}$ = concentration gradient of hydrogen across foil.

For a single phase at equilibrium

$$D = D_0 e^{-E_0/RT} \left[\frac{C_1 - C_2}{d} \right],$$

where

C = concentration of hydrogen in palladium, $\frac{\text{gram-atoms}}{\text{cm}^3}$

d = foil thickness, cm.

Diffusion is the process whereby hydrogen is transported across the foil because of a difference in hydrogen concentration existing between a point just inside the front surface of the PdH alloy and the hydrogen concentration existing just inside the back surface. Permeation is the transfer of hydrogen through a metal by the combination of surface adsorption, dissociation, solution, diffusion, desolution, association, and desorption. The term permeation is applicable to transfer of hydrogen through palladium from gas phase to gas phase. Permeation involves surface phenomena in addition to diffusion. For the purpose of discussion of the hydrogen-diffusion cathode, it might be assumed that the permeation rate is equivalent to the rate at which hydrogen is collected on the back side of the cathode. For the case where neither the front-side reaction (cathodic deposition of hydrogen) nor the back-side reaction (desolution of H from PdH, association of H to form H₂, and desorption of H₂ from the surface) is limiting, then the permeation rate (P) equals the diffusion rate (D).

The values of D₀ and E₀ given by Davis (ref. 4) for most active palladium are D₀ = 0.0043 cm²/sec and E₀ = 5620 cal. The maximum current density with 100 per cent hydrogen transmission can be calculated for 200 C and 0.001-inch-thick foil by assuming a concentration gradient. For example, if the difference in atom ratio of H/Pd at the front and back sides is 0.1, then for a density of 12.02 g/cm³ for palladium and a molecular weight of 106.7:

$$C_1 - C_2 = \frac{0.1}{106.7} \frac{12.02}{\text{cm}^3} = 0.0113 \text{ g-atom H/cm}^3$$

$$P = D = 0.0043 e^{-5620/(1.986)(473)} \left[\frac{0.0113}{(0.001)(2.54)} \right]$$

$$= 4.9 \times 10^{-5} \text{ g H/cm}^2/\text{sec}$$

$$4.9 \times 10^{-5} \frac{\text{g H}}{\text{cm}^2/\text{sec}} \quad 96,500 \frac{\text{amp-sec}}{\text{g H}} \quad 929 \frac{\text{amp/ft}^2}{\text{amp/cm}^2} = 4380 \text{ amp/ft}^2.$$

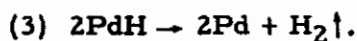
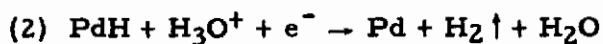
The value of current density depends on the values of D₀ and E₀ used. A similar calculation was made for values reported by a few other investigators:

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	$D_o,$ cm^2/sec	$E_o,$ cal	<u>Current Density,</u> <u>amp/ft²</u>
Davis (ref. 4)	0.0043	5620	4380
Van Swaay and Birchenall (ref. 14)	0.00013	5000	225
Barrer (ref. 13)	0.015	6800	4320

Assuming that the values of Davis are correct for active palladium, the maximum current density is a linear function of the hydrogen-concentration gradient. The probable gradient that can be established for satisfactory operation with 100 per cent transmission depends on the solubility of hydrogen and the mechanisms of hydrogen evolution on the front and back side of the foil.

Hydrogen gas can be evolved from the electrolysis surface of a palladium cathode in acid electrolyte by either of three mechanisms,



The first two mechanisms are "electrochemical" mechanisms; the last is a "catalytic" mechanism. Because of the great affinity of palladium for hydrogen, Reaction (1) is assumed to take place only when the palladium is saturated with hydrogen.

The second reaction is a function of the hydrogen-ion concentration of the electrolyte. In strongly alkaline solutions it is assumed to be negligible.

The extent to which the catalytic reaction [Reaction (3)] takes place is not known. It is assumed that the formation of gaseous hydrogen by this method can be effectively reduced by increasing imposed pressure.

For highly alkaline electrolytes, there might be an electrochemical reaction analogous to Reaction (2) above:



Very little is reported on the decomposition of PdH in highly alkaline electrolytes. The evidence of 100 per cent hydrogen transmission in the present experimental work indicates that Reaction (4) does not proceed to any appreciable extent.

The experimental work thus far has been based on the hypothesis that pressure on the electrolysis side of the foil is sufficient to prevent the "catalytic" back reaction and allow 100 per cent hydrogen transmission. The concept can be visualized with reference to Figure 11. On the gas side of the foil, the equilibrium H/Pd ratio or concentration C_2 is determined by the temperature and pressure, and a value of C_2 can be determined from the phase diagram, Figure 10. If by some means the concentration C_2 is increased above the equilibrium value for the temperature and pressure, the palladium-hydrogen alloy will decompose according to the reaction shown in Figure 11.

Conclusions

The transport of hydrogen from the front side to the back side of the palladium foil requires a concentration gradient (i. e., $C_1 > C_2$). Since the system is at a constant temperature T , a greater pressure is needed on the front side (i. e., $P_1 > P_2$ and $C_1 > C_2$). When electrolysis begins, hydrogen is deposited as PdH on the electrolysis side according to the reaction shown in Figure 11. The concentration C_1 increases until a gradient ($C_1 - C_2$) is reached such that, at the temperature T , the rate of diffusion of hydrogen through the palladium just equals the rate at which hydrogen is deposited at the cathode and 100 per cent hydrogen transmission is obtained. If the current density is increased, the concentration C_1 increases and the system equilibrates at a new concentration gradient $C_1 - C_2$ such that the hydrogen transmission again equals the hydrogen deposition rate.

As the current density is increased, C_1 continues to increase until such time as the value of C_1 reaches an unstable condition for the pressure and temperature conditions on the electrolysis side. In other words, C_1 reaches a value at which there is more hydrogen in the palladium that can be retained at that temperature and pressure, and the PdH on the front side begins to lose hydrogen at a rate equal to the rate at which excess hydrogen is being deposited. This results in less than 100 per cent transmission based on the total hydrogen being deposited.

The loss of hydrogen from the electrolysis side can proceed by several mechanisms. In acid electrolytes, the electrochemical mechanism involving reaction of PdH and H_3O^+ probably proceeds fastest. In alkaline electrolyte the catalytic decomposition mechanism probably proceeds fastest.

If the current density is increased beyond the value for 100 per cent transmission, an unstable concentration of PdH is formed on the electrolysis side. A slightly higher diffusion rate is obtained at less than 100 per cent transmission because of the increase in C_1 , the concentration on the electrolysis side.

If the current density is increased considerably, the PdH on the electrolysis side becomes saturated and a new mechanism of hydrogen deposition occurs involving direct reduction of hydrogen ions or water on the cathode surface.

Most of the data reported in the literature on diffusion of hydrogen through palladium have been obtained with a hydrogen-gas phase on both sides of the palladium. Diffusion data are usually of interest at temperatures from 300 C to 500 C, where palladium is most often used for industrial and laboratory purification of hydrogen. Some of the available hydrogen-diffusion data were shown previously in Figure 9. The reported permeation rates are related to equivalent current density to indicate that, at temperatures from 300 C to 600 C and differential pressures from 1 to 14 atmospheres across the foil (0.001 inch thick), sufficient hydrogen would diffuse through to more than meet the objectives of this project in terms of current density.

However, for an electrolytic process it would be desirable to work at temperatures below 300 C if possible and preferably as low as 200 C or 100 C. The temperature range of interest lies below the critical temperature of the palladium-hydrogen system, indicated at 300 C by the vertical dashed line in Figure 9.

The principal objection to using palladium as the diffusion metal is the dimensional change caused by introducing hydrogen into the crystal lattice. Two distinct palladium-hydrogen alloys are recognized. The transition α -PdH to β -PdH is accompanied by about

10 per cent volume change up to 300 C, where only one phase exists. Both repeated charging and discharging of hydrogen and temperature cycling in a hydrogen atmosphere cause complete disintegration of the palladium. As can be seen from Figure 10, the above procedures result in repeated transformations of phase α -PdH to β -PdH and vice versa. The resulting dimensional changes eventually cause disintegration of the palladium.

M. van Swaay and Birchenall (ref. 14) conducted gas-phase experiments in which pure electrolytic hydrogen at 1 atmosphere was allowed to diffuse through palladium foil to a vacuum. They found that, at a temperature of 155 ± 2 C or below, the permeability slowly decreased with time, eventually becoming too small to measure. The permeability recovered slowly by evacuation or heating in hydrogen at temperatures near 200 C.

The pressure and temperature conditions for loss in permeability correspond so closely to those observed for the formation of the β phase (see Figure 10) that this is considered to be the cause of the permeability change.

M. van Swaay and Birchanall suggest that the α - β interface is the locus of a slow transport step. At 200 C and 200-psig gaseous pressure on the palladium surface, the palladium-hydrogen alloy will be in the β phase at equilibrium. The back side of the foil will be in the α phase since it is at atmospheric pressure. Hence, there will be an α - β interface at some point within the foil. Extrapolation of diffusion data taken in the α phase will suggest erroneous diffusion rates if applied to a system in which α and β phases are present simultaneously.

Hunter (ref. 31) described a palladium-silver alloy which does not undergo dimensional changes upon repeated absorption-desorption of hydrogen. This alloy is reported to be more than two times as permeable to hydrogen as pure palladium. (ref. 12) The reason that the palladium-silver alloy does not undergo a phase change is extremely important because the postulation relates to the mechanism of hydrogen permeation.

Smith (ref. 11) discussed the palladium-silver-hydrogen ternary alloy in detail. Palladium-silver alloys, like pure palladium, absorb hydrogen without loss of the fcc symmetry of the lattice, which is nevertheless gradually distended by the entering hydrogen, until at a certain concentration it suddenly expands to a new β lattice, which is still fcc, while additional absorption produces further distention of the β phase. In all this, the alloys with the smaller silver content show an entire qualitative similarity to the palladium-hydrogen alloy.

For higher percentages of silver, the system palladium-silver-hydrogen shows, at ordinary temperatures, but one solid phase, a condition realized in the binary palladium-hydrogen alloy at temperatures of 300 C or above.

According to Kruger and Gehm (ref. 32), the two phases of the palladium-silver-hydrogen alloy approach each other both in respect to lattice constants and to saturation limits as the silver content grows, until at a composition near 45 per cent silver the two become identical in both regards.

The observations of Rosenhall (ref. 33) indicate a lower value for the silver content at which the two phases become identical, ~25 per cent instead of ~45 per cent.

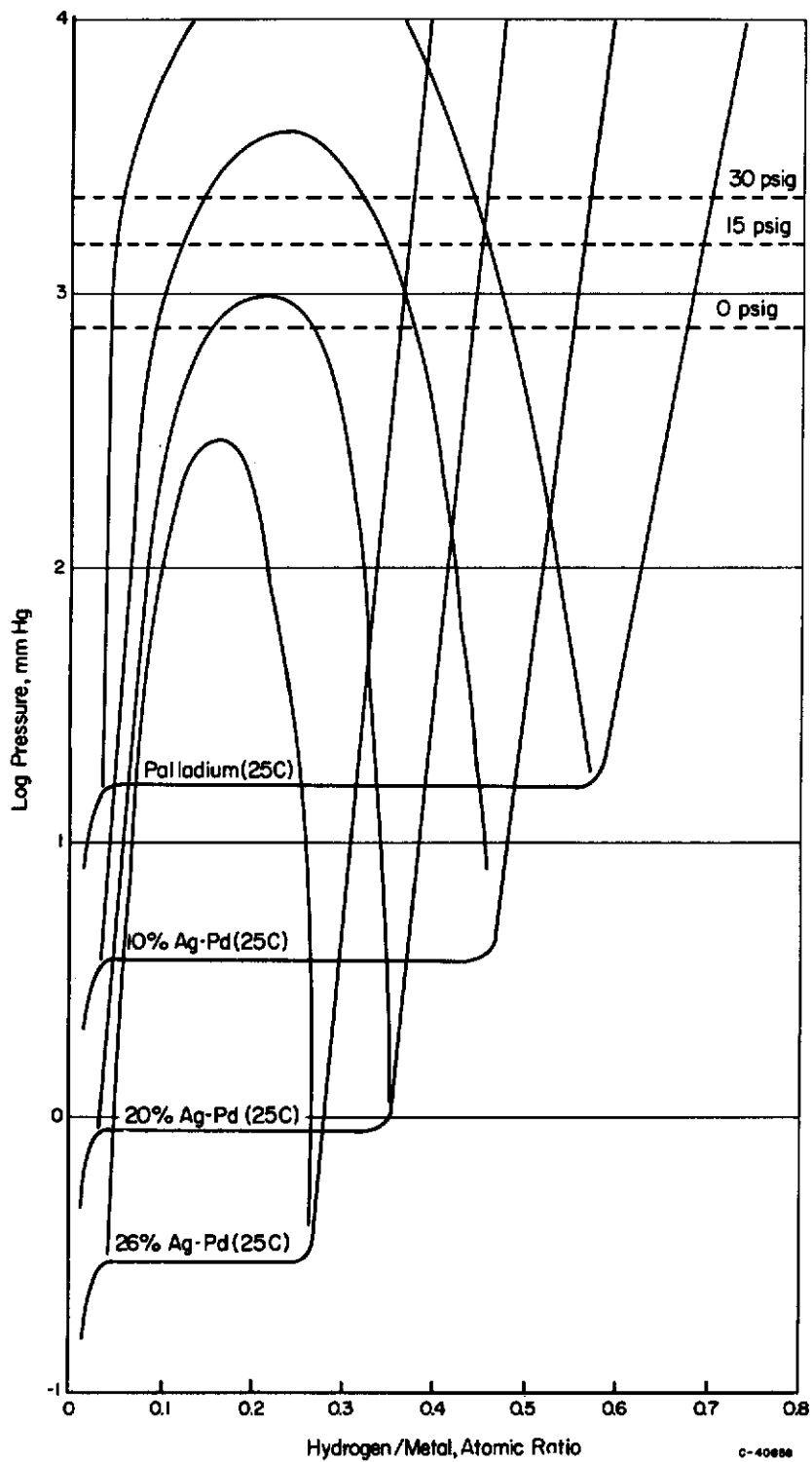


FIGURE 12. ESTIMATED LIMITS OF TWO-PHASE REGION FOR Ag-Pd-H SYSTEM

Isotherms for Ag-Pd-H system at 25 C from Lewis (ref. 34).

Figure 12 shows some isotherms for the H-PdAg system at 25 C reported by Lewis (ref. 34). The line outlining the two-phase region for pure palladium was sketched in accordance with Figure 10 to show a hypothesis used on this project. The lines outlining the two-phase region were not shown in the reference by Lewis, but were sketched in for the various PdAg alloys, using as a guide the limits of the two-phase region at 25 C. If the estimate is approximately correct, then there would be no two-phase region at atmospheric pressure (0 psig) for 25 per cent Ag-Pd. Thus, no α/β interface would be encountered across the foil.

The absence of a two-phase region would be in accordance with the ability of 25 per cent Ag-Pd to withstand repeated temperature cycling and not disintegrate as does palladium. For higher temperatures, the near-vertical isotherms would be displaced to the left toward lower hydrogen/metal ratio.

The lines shown in Figure 12 represent the solubility of hydrogen in the β alloy that is stable for the pressure and temperature indicated. More hydrogen can be put into the foil by cathodic charging, possibly up to a hydrogen/metal ratio of 1. It is postulated that this excess hydrogen above that required to form the β phase H-PdAg alloy readily decomposes by a catalytic mechanism on the cathode surface, resulting in less than 100 per cent transmission. Thus, for satisfactory operation, the concentration of hydrogen on the alloy must be along the isotherm and defined by the pressure on the front and back of the foil. As can be seen in Figure 12 the isotherm for 26 per cent Ag-Pd between 15 psig and 0 psig allows only a 0.01 concentration gradient. On the basis of the previous calculations of 4380 amp/ft² for a 0.1 concentration gradient, 0.01 would allow only 438 amp/ft² which is the order of magnitude obtained experimentally. If the reasoning is correct, it might explain the apparent sensitivity of the cathode to slight changes in pressure and temperature. Also, without a clean, activated surface the limiting current density might be less than predicted.

It would appear that the limiting current density could be increased by increased pressure.

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APPENDIX II

DISCUSSION OF EXPERIMENTAL DATA AND RESULTS

Exploratory Experiments

Table 4 summarizes the results of the early exploratory runs on the project. All electrolytes were prepared with cp-grade chemicals and distilled water.

The palladium (or palladium-silver) foil was pretreated in six steps:

- (1) Wiped with methanol
- (2) Rinsed with cold tap water
- (3) Anodic alkaline clean at 70 amp/ft²*
- (4) Rinsed with cold tap water
- (5) Dipped in 10 volume per cent sulfuric acid
- (6) Rinsed with cold distilled water.

The palladium** was obtained in strips 1 inch wide x 18 inches long and 1 mil thick. The palladium-silver alloy*** was obtained in strips 1 x 9 inches and 1 mil thick. A separate foil was used in each experiment. The palladium-silver alloy is reported by the manufacturer to contain 25 weight per cent silver. No analysis was made on the project.

A direct-current rectifier**** and a variable resistance in series with the cell were used to control the voltage applied to the cell.

Cell A

Figure 13 shows the design of the Teflon cell used in the earliest experiments. Visual observation of the cathode indicated that all of the hydrogen would not pass through the foil at current densities of 5 amp/ft² when the electrolyte was at atmospheric pressure.

Cell B

Cell B, as shown in Figure 14, differed from Cell A in that a steel cap allowed pressurization of the electrolyte chamber. The Teflon cell fit inside a brass pipe (2-1/2-inch ID) closed at one end and provided with a threaded cap which was tightened to seal the cell. Openings in the brass container were provided for the hydrogen-gas outlet, pressure inlet, and electrical connection to the palladium alloy foil. Electrical tape wrapped around the brass was used to heat the cell.

*Enthone 808, 6 oz/gal, 180 F.

**From Baker Platinum Division, Englehard Industries.

***From J. Bishop & Co.

****Selenium rectifier, Rapid Electric Co., Model 50C.

TABLE 4. RESULTS OF BEAKER-SCALE EXPERIMENTAL STUDY OF HYDROGEN-DIFFUSION CATHODES
All cathodes 1 mil thick

Run	Cell	Electrolyte	Cathode	Circular Cathode Diameter ^(a) inch	Temperature, C	Pressure ^(b) psig	Current Density, amp ft ²	Per Cent Transmission	Duration, minutes	Current ma	Voltage, volts
2-1	A	28% wt KOH	Pd	5.8	25	0	<.5	~100 ^(c)	~5	<11	
2-3	A	18% wt H ₂ SO ₄	Pd	5.8	25	0	<.5	~100 ^(c)	~5	<11	
2-4	A	18% wt H ₂ SO ₄	Pd	5.8	90	0	<.5	~100 ^(c)	~5	<11	
2-5	A	18% wt H ₂ SO ₄	Pd	5.8	25	0	2.5	~100 ^(c)	~20	5.3	
2-6	A	18% wt H ₂ SO ₄	Pd	5.8	70	0	3.3	~100 ^(c)	~20	7.0	
2-8	A	60% wt KOH	Pd	5.8	200	0	3	~100 ^(c)	~20	6.4	
2-9	B	9% wt H ₂ SO ₄ + 20% wt Na ₂ SO ₄	Pd-Ag	5.8	25	90	3.3*	100 ^(d)	~40	7*	
2-11A	B	9% wt H ₂ SO ₄ + 20% wt Na ₂ SO ₄	Pd-Ag	9.16	25	90	7.8	45 ^(d)	~40	13.5	
2-11B	B	9% wt H ₂ SO ₄ + 20% wt Na ₂ SO ₄	Pd-Ag	9.16	25	90	16	41 ^(d)	~40	27.2	
2-11C	B	9% wt H ₂ SO ₄ + 20% wt Na ₂ SO ₄	Pd-Ag	9.16	25	90	11	19 ^(b)	~40	19.2	
2-12A	B	75% wt KOH	Pd-Ag	7.16	200	90	29	100 ^(d)	50	30	
2-12B	B	75% wt KOH	Pd-Ag	7.16	200	90	20.4	31 ^(d)	35	21.3	
2-14A	B	75% wt KOH	Pd-Ag	7.16	200	90	29	100 ^(d)	55	30	
2-14B	B	75% wt KOH	Pd-Ag	7.16	200	90	10.2	45 ^(d)	20	10.7	
2-16	C	65% wt KOH	Pd-Ag	7.16	125	90	16.7	(e)	1	175	2.3
2-18	C	65% wt KOH	Pd-Ag	7.16	170	90	19	(e)	1	20	2.8
2-19	C	65% wt KOH	Pd-Ag	7.16	170	120	86	(e)	1	90	2.6
2-20	C	65% wt KOH	Pd-Ag	7.16	170	100	76	(e)	1	80	2.9
2-35	C	18% wt H ₂ SO ₄	Pd-Ag	7.16	70	10	29	(e)	1	30	1.5
2-34A	D	65% wt KOH	Pd-Ag	23.32	200	122	15	100 ^(d)	195	42.3	1.3
2-34B	D	65% wt KOH	Pd-Ag	23.32	200	122	20	45 ^(d)	200	56.4	1.26

(a) The nominal diameter of the Teflon cells was 5/8 inch. The recorded diameter is the actual diameter measured on the foil after each run. The decrease in exposed cathode area was caused by the deformation of Teflon under the operating conditions of high temperature and pressure.

(b) Pressure on the electrolysis side; gas side at 1 atmosphere.

(c) For Cell A visual observation of the cathode was used to determine when transmission of hydrogen through palladium was 100 per cent.

(d) Actual hydrogen-diffusion rates were measured with Cell B and Cell D by collecting the hydrogen gas that permeated the cathode.

(e) With the inverted cell, Cell C, the maximum current density attainable without polarization was assumed to be the highest current density with 100 per cent transmission.

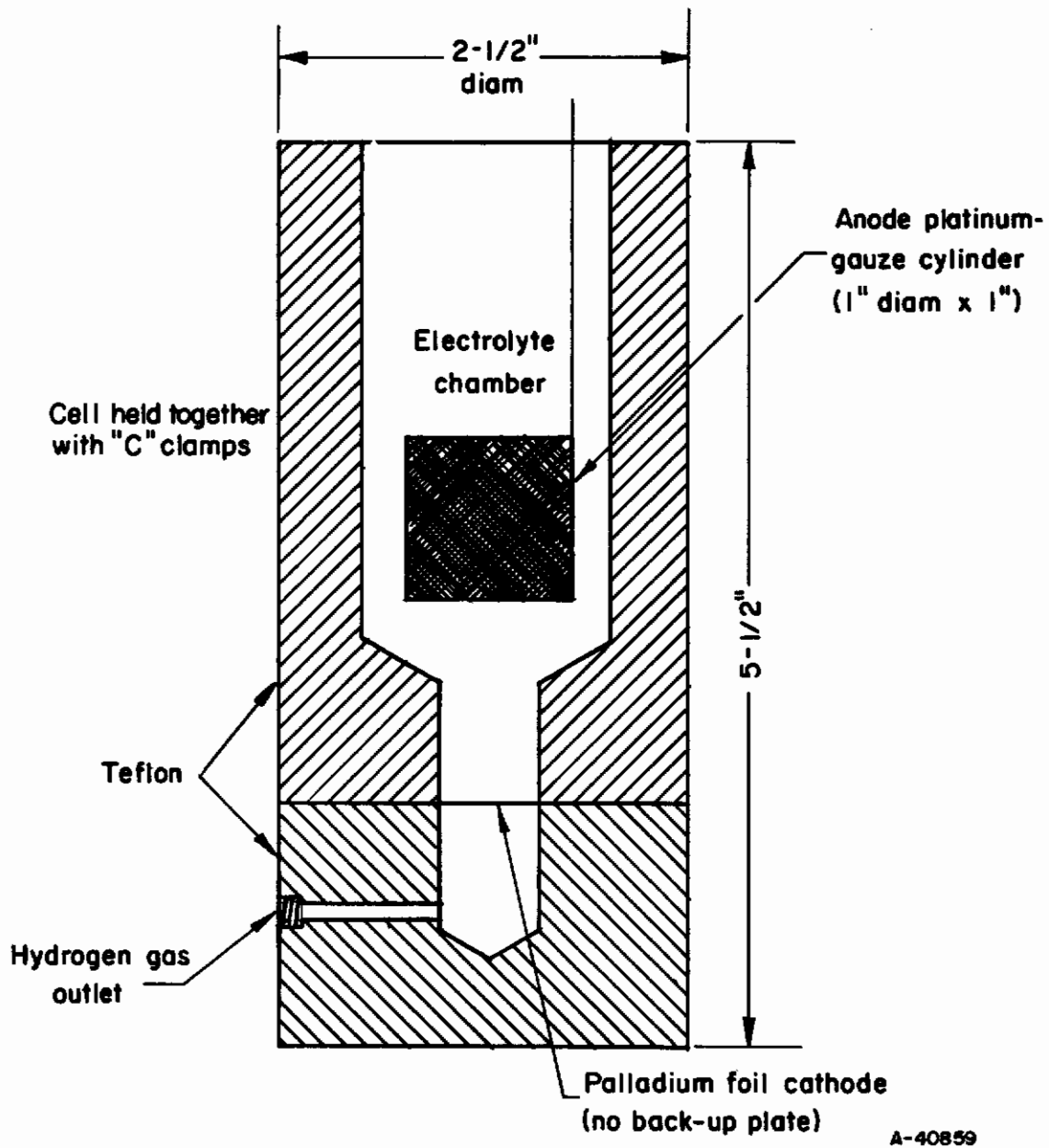
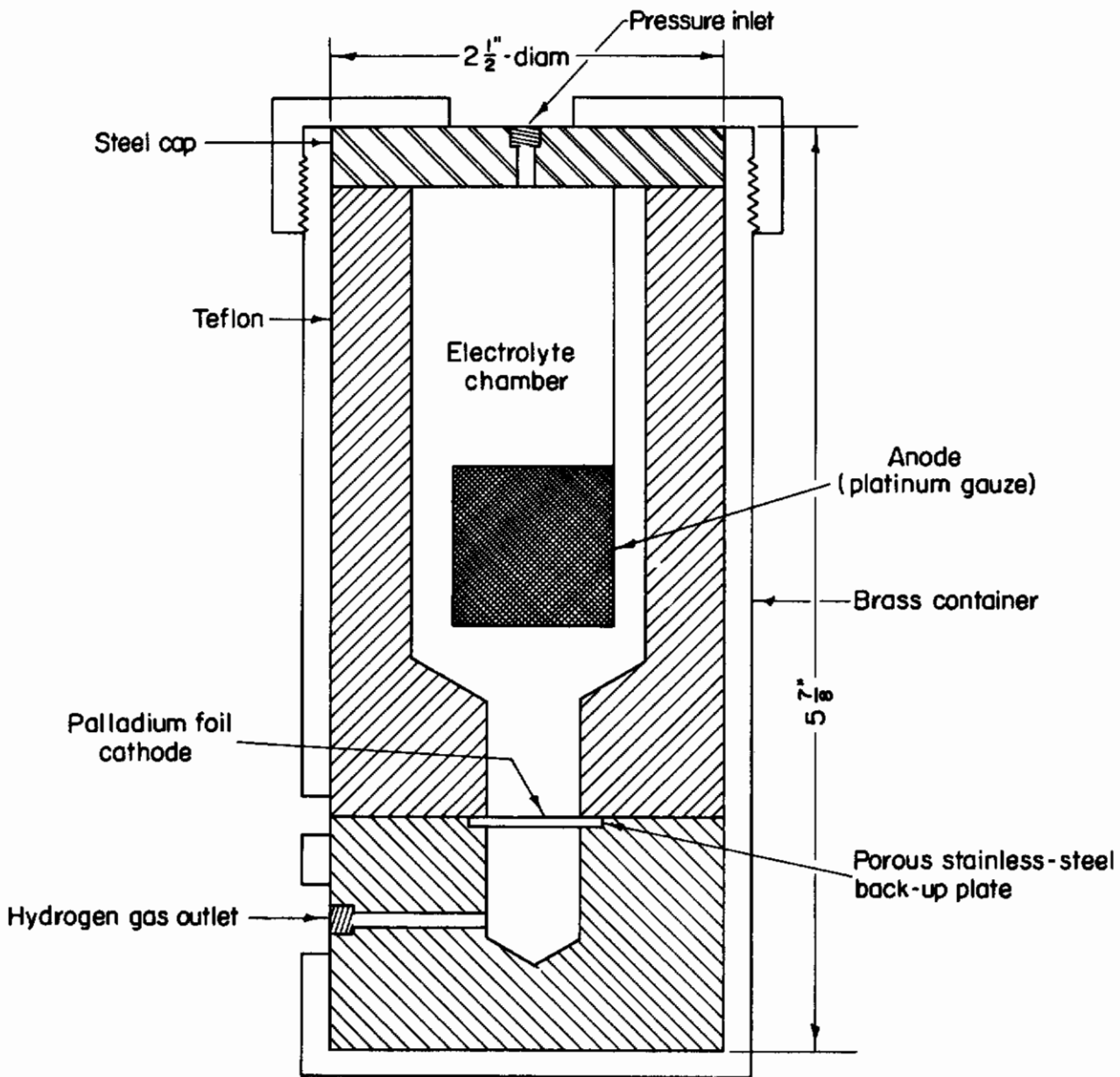


FIGURE 13. CELL DESIGN A



A-40860

FIGURE 14. CELL DESIGN B

Teflon was desired for general chemical resistance to acid and alkali. The temperature limit for Teflon is about 250 C (begins to char). At 200 C, Teflon flows a little under pressure, which made sealing of the cell difficult. With use, the area of the cathode became smaller because of the swelling of the Teflon.

The hydrogen gas that had diffused through the cathode was collected in a gas-measuring burette*. The aqueous solution used in the burette contained 20 weight per cent Na₂SO₄ and 5 volume per cent H₂SO₄ rather than pure water to minimize errors due to solubility of hydrogen gas. The hydrogen gas (although dry as it left the palladium cathode) was assumed to be saturated with water vapor at the temperature of measurement (25 C) in the burette.

The per cent hydrogen transmission was determined by the ratio of the gas-collection rate to the theoretical rate expected based on Faraday's Law and calculated as follows:

$$\text{Theoretical rate, cm}^3/\text{min} = \frac{\text{Amperes} \left| \begin{array}{c|c|c|c} 22,400 & 60 & 298 & 760 \\ \hline 96,500 & 2 & 273 & 760-23 \end{array} \right.}{}$$

$$= 7.83 \times (\text{current in amperes}).$$

Figure 15 shows the results obtained with Cell B in Runs 2-9 through 2-14 (Table 4). The decrease in per cent transmission beyond some limiting current density (for 100 per cent transmission) was similar to observations made by Schuldiner (ref. 16, Appendix I), using chemical oxidation on the back side to consume the hydrogen diffusing through the foil.

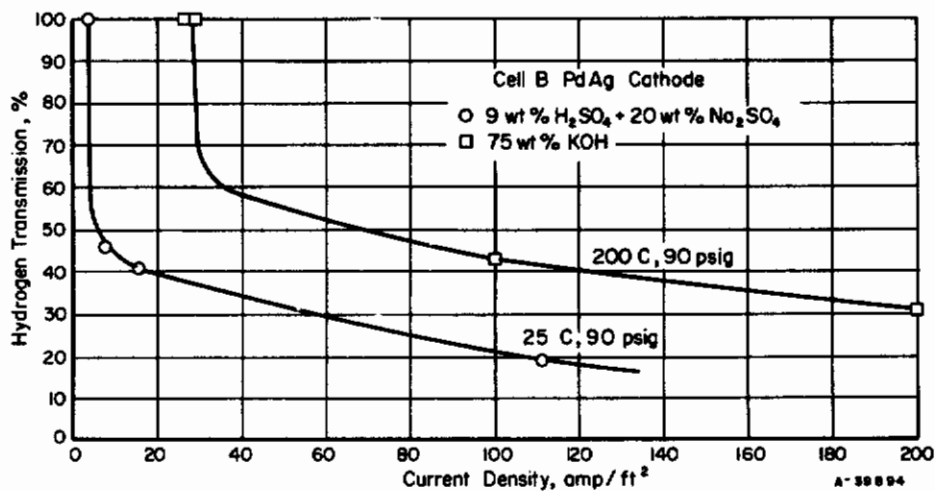


FIGURE 15. PER CENT HYDROGEN TRANSMISSION CURVES FOR RUNS 2-9 THROUGH 2-14 IN CELL B (FIGURE 14) TABLE 4

*Burrell portable Type 10, Model 39-980.

Contrails

The product of the current density and per cent transmission (divided by 100) is a measure of the effective hydrogen permeation; for example, see the following tabulation (for Runs 2-12 and 2-14):

Current Density, amp/ft ²	Hydrogen Transmission, %	Effective Hydrogen Permeation, amp/ft ²
28.7	100	29
102	45	46
204	31	63

Thus, the amount of hydrogen permeating the foil increases with increased current density. However, the concentration of hydrogen in the palladium-alloy surface on the electrolysis side required to establish the concentration gradient for diffusion was not stable and a competing reaction evolved hydrogen on the electrolysis side of the foil. The increase of permeation rate with current density was also shown in Schuldiner's work (ref. 16, Appendix I).

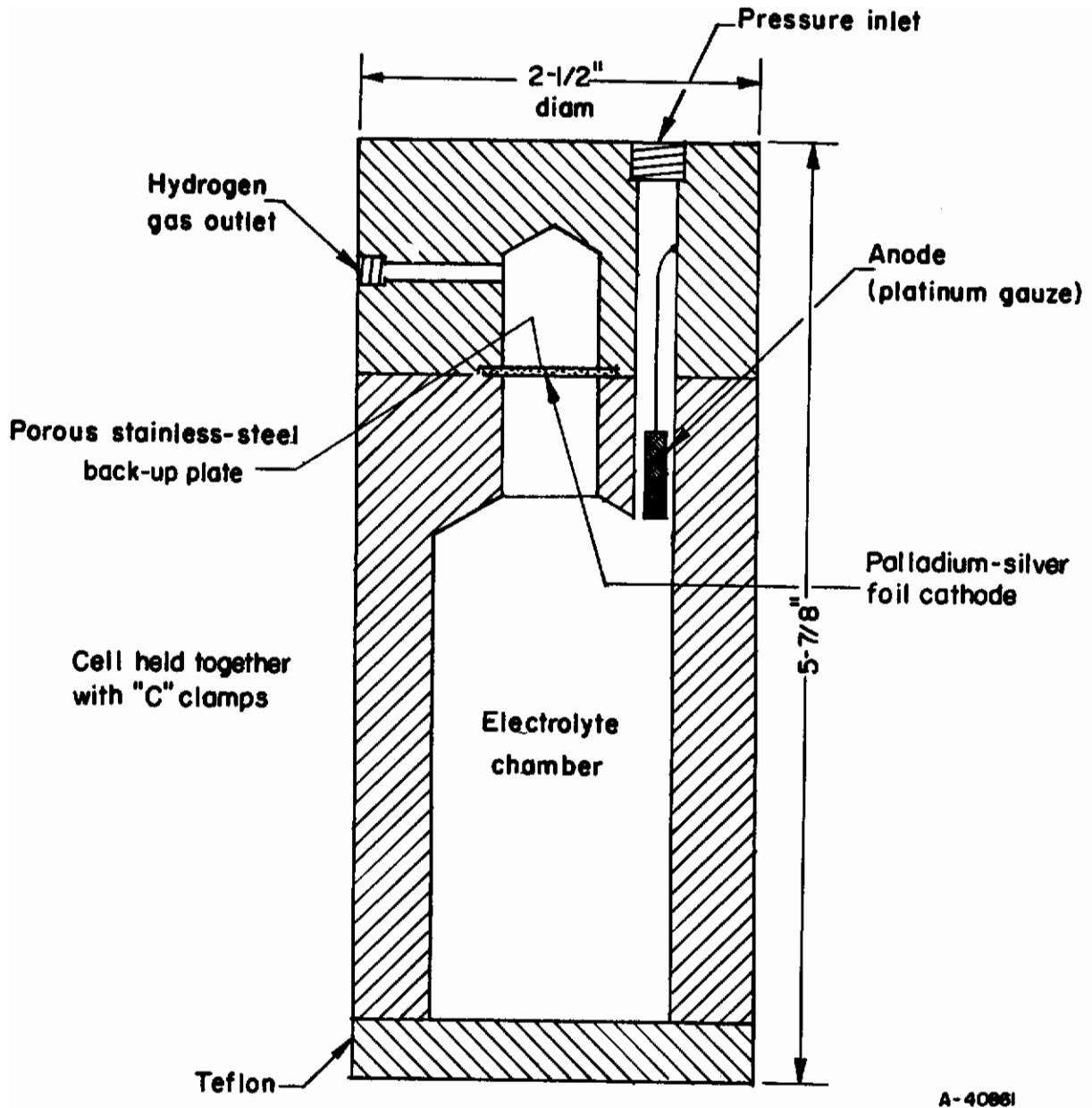
The main data of interest to the project objectives are the maximum current densities that can be obtained at or near 100 per cent hydrogen transmission. The highest value that had been demonstrated (29 amp/ft²) was much lower than had been predicted considering the temperature and pressure used.

In retrospect, it is of interest to note that anodic activation of the foil in the cell was used in Runs 2-12 and 2-14. This was not a standard procedure but was later found to be the best technique for obtaining high current densities at 100 per cent hydrogen transmission. Prior to Run 2-12A the electrical connections were reversed to make the foil anodic at 8 amp/ft² for 5 minutes. When the foil was next used cathodically 100 per cent transmission was obtained. It was noted that when the temperature was decreased from 200 C the per cent transmission decreased, but was restored to 100 per cent when the temperature was returned to 200 C. The current density was increased directly from 29 amp/ft² to 204 amp/ft² without any anodic activation.

In Run 2-14A, the palladium-alloy foil was made anodic at 29 amp/ft² for 4 minutes before the run at that current density. The per cent transmission increased with time and reached 100 per cent after 55 minutes. The foil was made anodic at 102 amp/ft² for 1 minute before the run at that current density. For the first 5 minutes an average of 98 per cent transmission was obtained, decreasing to 45 per cent after 20 minutes.

Cell C

Cell C shown in Figure 16 was an inverted version of Cell B with an extra hole drilled in the Teflon to provide a separate compartment for the anode so that evolved oxygen gas would not be collected under the palladium-silver foil. Small current densities were obtained with 100 per cent hydrogen transmission compared with the very high current densities predicted on the basis of gas-phase permeability of palladium alloys. It was reasoned that, in the inverted cell design (Cell C), if all of the hydrogen evolved did not pass into the cathode then a hydrogen gas layer should collect on the electrolysis



A-40861

FIGURE 16. CELL DESIGN C

side of the cathode. Thus, for the temperature and pressure imposed, any gaseous hydrogen evolved should permeate the foil in accordance with reported permeation rates. Presumably, an inability to achieve high current density would indicate a limited permeability rather than an instability of the PdH at the cathode surface.

If hydrogen collected on the cathode side, the blocking effect would cause polarization, indicated by a voltage rise at constant current density.

In Table 4 the current density listed is the maximum current density obtained without polarization. No further work with the inverted cell was done, because of problems of sealing. From the extended use of the Teflon cell at high temperature and pressure, it became deformed. Subsequent cells were made predominantly of metal both with and without a Teflon coating or liner to obtain the necessary rigidity for sealing.

Cell D

The design of Cell D was shown primarily in Figure 1, and the results of Run 2-34A (Table 4) were shown previously in Figure 2. Run 2-34A, in which satisfactory operation was obtained for over 3 hours at 15 amp/ft², was considered the first meaningful result that demonstrated the technical feasibility of the concept of using a hydrogen-diffusion cathode.

For Run 2-34A, the internal walls of the electrolysis chamber were coated with Teflon by spraying and baking. Several coats with intermediate baking at 450 F for 15 minutes were used. The total thickness of coating was estimated to be about 0.0005 inch.

In view of the fact that after Run 2-34B at 20 amp/ft² the Teflon coating failed allowing contamination of the electrolyte, the indicated 45 per cent transmission was questioned as being representative. Thus, the value of 15 amp/ft² in Run 2-34A was not considered to be the highest current density that might have been obtained in the absence of electrolyte contamination.

Figure 17 summarizes the runs from Table 4 in which 100 per cent transmission was obtained. The indication was that satisfactory operation was obtained with a combination of high temperature and pressure.

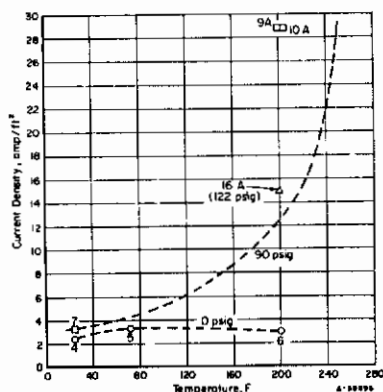


FIGURE 16. EFFECT OF TEMPERATURE AND PRESSURE ON CURRENT DENSITY

FIGURE 17. EFFECT OF TEMPERATURE AND PRESSURE ON CURRENT DENSITY FOR 100 PER CENT HYDROGEN TRANSMISSION

Continued Experimental Runs in the Study of Hydrogen-Diffusion Cathodes

Table 5 gives a partial summary of the data obtained in the more important experimental runs in the continued study of the hydrogen-diffusion cathode. The more important information in Table 4 is discussed below for each run.

Run 2-38

The electrolysis chamber of Cell D (Figure 1) was nickel plated after the Teflon coating failed. During the run, the insulation between the cap and the electrolysis chamber failed so that the latter became anodic (low cell voltages were an indication). Finally, the cell became short circuited. Loss of nickel and stainless steel by anodic dissolution contaminated the electrolyte.

Runs 2-41A and B and Run-2-42

Since Type 316 stainless steel is reported to be resistant to chemical attack in alkaline electrolytes, several attempts were made to operate at lower temperature (100 C) and high pressure. Palladium foil cathodes were used instead of palladium-silver. By operating at temperatures below about 150 C at any pressure from 0 psig to 120 psig and higher, both sides of the foil should have the β Pd-H phase. The results were indefinite with regard to β -phase operation, since corrosion of the stainless steel cell was suspected even at 100 C.

Run 2-43

This run was an attempt to duplicate the previous good run (2-34A) at 15 amp/ft². The inability to achieve higher than about 70 per cent transmission was attributed to cell contamination. Apparently the stainless steel electrolyte chamber had to be protected from corrosion at 100 to 200 C.

Run 2-45

This room-temperature run did not allow attainment of as good results as had been obtained earlier (Table 4) with a Teflon cell. Thus, electrolyte contamination was suspected. Some form of Teflon liner was used in subsequent cell designs.

Run 2-48

A new cell (G) was designed similar to Cell D (Figure 1) except that a 1/8-inch thick Teflon liner was machined to fit inside the electrolyte chamber so that the liquid electrolyte contacted only the palladium-alloy cathode, palladium anode, and Teflon. The failure to achieve better than about 80 per cent transmission at 15 amp/ft² was attributed to electrolyte contamination by vapor corroding the top part of the cell.

TABLE 5. SUMMARY OF DATA FROM EXPERIMENTAL

Run	Cell	Cathode		Electrolyte, KOH, wt %	Cathode Current Density, amp/ft ²	Cell Conditions			
		Foil	Diameter, inch			Temperature, C	Pressure, psig	Voltage, volts	
2-38	D	Pd	0.72	65	5.0	200	25	0.52-0.64	
				65	5.0	200	25	0.42-0.50	
				65	5.0	200	30		
2-41A	D	Pd	0.72	20	10.0	100	120	1.58	
2-41B	D	Pd	0.72	20	10.0	100	120	1.75	
2-42	D	Pd	0.72	20	10.0	100	120	1.78	
2-43	D	Pd-Ag	0.72	65	15.0	200	120	1.62	
					15.0	200	120	1.50-1.65	
					15.0	200	120	1.75	
2-45	D	Pd-Ag	0.72	20	5.0	25	50	1.65	
2-48	G	Pd-Ag	0.50	65	11.0	200	120	1.0	
					11.0	200	120	1.0	
					11.0	200	120	1.0-1.4	
					14.7	200	120	1.4	
					18.3	200	120	1.41	
					22.0	200	120	1.43	
					25.7	200	120	1.45	
					to	26.7	200	120	1.45
					26.7	200	120	1.55	
					29.4	200	120	1.55	
					36.6	200	120	1.57	
					44.0	200	120	1.62	
					44.0	200	120	1.61	
					44.0	200	120	1.65	
83	200	120	1.36						
59-65	11.0	200	120	0.68-1.34					
2-64	G'	Pd-Ag	0.50	55	11	200	20	1.5-1.8	
					11	200	20	1.7	
					4	200	20	1.6	
2-66	G'	Pd-Ag	0.50	55	11	202	23-26	1.5	
					11	200	30-35	1.6	
					11	201	27	1.6	
					20	199	28	1.8	
					40	187-204	27-31	1.8	
					11	210	28	1.6	
					5	187-200	22-38	1.5	
					11	200	26	0.5	
					20	197	27	0.6	
					39	197	29	0.8	
48	195	31	1.7						

RUNS WITH HYDROGEN-DIFFUSION CATHODES

Transmission, % H ₂	Duration of Run		Remarks
	Interval, min	Accumulative, min	
00	50	-	Cell was contaminated; foil contained a dark powdery deposit
46	305	355	
21	60	415	
12	2,765	-	Cell was contaminated; foil contained a dark powdery deposit
20	210	-	Cell was contaminated; foil contained a dark powdery deposit
9	1,000	-	Cell was contaminated; foil contained a dark powdery deposit
00	10	-	Cell was contaminated; foil contained a dark powdery deposit
67	70	80	
16	675	755	
28	450	-	Foil contained a film at end of run
0	15	-	
25	20	35	
74	1,105	1,140	
81	150	1,290	
81	210	1,500	
77	65	1,565	
78	60	1,625	
69	15	1,640	
38	1,030	2,670	
34	60	2,730	
38	265	2,995	
40	1,035	4,030	
25	60	4,090	
30	60	4,150	
30	240	4,390	Electrolyte solidified after 4,390 min; added make-up water to cell Electrolyte was found to be contaminated with iron
62	4,410	8,800	
5	105	-	
21	220	325	Electrolyte leaked around the foil
30	920	1,245	
46	85	-	
73	80	165	
83	135	300	
78	20	320	
51	40	360	
40	15	375	
46	1,305	1,680	
124	33	1,713	Reversed electrical leads to cell, making foil anodic; the hydrogen gas diffused through the foil from the burette
101	22	1,735	
89	20	1,755	
53	10	1,765	

TABLE 5. SUMMARY OF DATA FROM EXPERIMENTAL

Run	Cell	Cathode		Electrolyte, KOH, wt %	Cell Conditions			
		Foil	Diameter, inch		Cathode Current Density, amp/ft ²	Temperature, C	Pressure, psig	Voltage, volts
					20	193	33	1.6
					30	193	33	1.7
					20	194	35	1.6
					11	196	30	1.6
					11	199	27	1.5
					11	200	15	1.6
					11	198	20	1.6
					11	196	30-37	1.6
					11	195	18-26	1.6
					11	195	10-15	1.6
				70-80	5	190	0	1.6
				70	5	200	120	1.5
					20	210	120	1.7
					40	210	120	1.7
					80	211	120	1.8
					160	210	120	2.0
					366	210	120	2.4
					11	217	120	1.6
					11	210	120	1.7
					11	210	120	1.7
					11	210	120	1.7
					11	210	120	1.7
					11	210	120	1.7
					160	201	118	2.2
					366	203	118	2.8
					733	220	118	3.4
					1466	262	118	4.5
2-77	H	Pd-Ag	0.50	55	15	195	19	1.9
					150	204	18	2.8
					150	204	19	1.6-2.1
					150	200	20	2.1
					150	198	20	2.0
					380	203	22	2.5-2.9
					380	182-200	23	3.0-3.6
					150	213	23	2.1
					150	188	23	2.1
					150	199-288	20	2.1
2-81	I	Pd-Ag	0.50	40	11	28	00	2.2
					11	36-51	00	0.85-2.3
					11	51-75	00	2.2
					11	75-115	00	1.9
					11	115	00	1.8

RUNS WITH HYDROGEN-DIFFUSION CATHODES (Continued)

Transmission, % H ₂	Duration of Run		Remarks
	Interval, min	Accumulative, min	
95	15	1,780	
66	10	1,790	
68	31	1,821	
94	36	1,857	
54	60	1,917	Reversed electrical leads to cell, making foil cathodic
72	840	2,757	
64	1,680	4,457	
67	1,260	5,717	
61	16	5,733	
59	352	6,086	
37	3,803	9,889	
31	469	10,358	
59	70	10,428	
55	25	10,553	
42	15	10,568	
39	15	10,583	
28	15	10,598	
48	2,655	13,253	
67	70	13,323	Superimposed ac on dc: ac = dc
73	21	13,344	Superimposed ac on dc: ac = 1.3 x dc
75	34	13,378	Superimposed ac on dc: ac = 2.5 x dc
50	17	13,395	Superimposed ac on dc: ac = 0.5 x dc
40	18	13,415	
33	10	13,425	Equivalent to 54 amp/ft ² at 100% transmission
25	10	13,435	Equivalent to 98 amp/ft ² at 100% transmission
20	10	13,445	Equivalent to 143 amp/ft ² at 100% transmission
20	10	13,455	Equivalent to 303 amp/ft ² at 100% transmission
00	29	-	After 8 min foil was made anodic for next 4 min at 15 amp/ft ²
3	7	36	
-	6	42	Foil anodic during this period
63	10	52	
98	93	145	Actually transmitted 100% H ₂ for 64 min
87	14	159	
17	28	187	Electrolyte solidified; cell polarized; shutdown to break through solid KOH which had plugged the vapor line
-	4	183	Foil anodic during this time interval
73	6	189	
95	31	220	Electrolyte solidified and cell polarized after this time interval; run was terminated
00	8	-	
-	7	15	Foil anodic during this period
24	78	33	
145	21	54	Greater than 100% transmission believed due to foil discharging absorbed hydrogen because of temperature increase and subsequently a new equilibrium
100	22	76	Electrolyte leaked around foil; run was terminated

TABLE 5. SUMMARY OF DATA FROM EXPERIMENTAL

Run	Cell	Cathode		Electrolyte KOH, wt %	Cell Conditions			
		Foil	Diameter, inch		Cathode Current Density, amp/ft ²	Temperature, C	Pressure, psig	Voltage, volts
2-83	I	Pd-Ag	0.38	33	39	55-63	00	2.1
					130	63-94	00	2.6
					130	98	00	1.2-2.4
					130	100-112	00	2.3
					267	112	00	2.4
					20	111	00	1.6
2-87	I	Pd-Ag	0.38	50	150	185	00	2.95
					195	190	00	1.4-2.0
					150	205	00	2.75
					182	209	00	1.2-2.07
					150	209	00	2.8
					390	208	00	3.1
2-90	I	Pd-Ag	0.38	50	265	204	00	2.6
					265	119-166	20	2.2
					265	166-189	20	1.0-1.8
					265	189-226	20	2.4
					265	226	20	-
					265	231	20	1.7
					265	234	20	1.8-2.1
					265	231	13	2.4
					265	228	20	2.4
					265	226	20	0.85-2.0
					265	224	20	1.9
					265	224-140	00	2.3
2-95	I	Pd-Ag	0.38	50	265	200	00	2.7
					265	200	00	2.0
					265	202	00	2.5
					265	202	00	1.0-2.1
					265	203	00	2.4
					265	203	00	-
					265	203	00	2.4
					265	204	00	-
					265	183-204	0-6	2.2-2.4
					265	183	6	-
					265	192	1-4	2.1
					265	200	4	-
					265	212	4-11	2.1
					265	215	13	0.9-1.7
					265	223	14-17	1.8-2.1
					510	226	20	-
					265	226	22	1.8-2.1
					00	28	00	00
					265	226	4-10	2.1
					265	229	9-12	1.4-1.9
265	229-239	12-25	1.8					
265	224	17-24	1.9					

RUNS WITH HYDROGEN-DIFFUSION CATHODES (Continued)

Transmission, % H ₂	Duration of Run		Remarks
	Interval, min	Accumulative, min	
30	3	-	
22	11	14	
-	2	16	Foil anodic during this period
20	15	31	
1	15	42	
29	3,600	3,642	Cell contaminated with copper; run was terminated
00	7	-	
-	7	14	Foil anodic during this period
4	77	91	
-	4	95	Foil anodic during this period
2	21	116	
5	13	129	Cell was contaminated; foil contained dark deposit
4	84	-	
00	17	101	
-	3	104	Foil anodic during this period
21	14	124	
-	6	130	Foil anodic during this period
39	2	132	
84	11	143	
78	10	144	
73	12	156	
-	4	160	Foil anodic during this period
86	7	167	
54	15	182	Cell polarized; run was terminated
9	10	-	
-	5	15	Foil anodic during this period
25	21	36	
-	2	38	Foil anodic during this period
39	57	95	
-	4	99	Foil anodic during this period
45	21	120	
-	6	126	Foil anodic during this period
44	68	194	
-	3	197	Foil anodic during this period
49	11	208	
-	2	210	Foil anodic during this period
60	8	218	
-	4	222	Foil anodic during this period
68	9	231	
-	2	233	Foil anodic during this period
88	8	241	
00	3,600	3,841	Cell was not electrolyzed during this period
67	13	3,854	
-	5	3,859	Foil anodic during this period
97	69	3,928	Actually 100% transmission for 55 min
77	27	3,955	

TABLE 5. SUMMARY OF DATA FROM EXPERIMENTAL

Run	Cell	Cathode		Electrolyte KOH, wt %	Cell Conditions			
		Foil	Diameter, inch		Cathode Current Density, amp/ft ²	Temperature, C	Pressure, psig	Voltage, volts
					265	190-225	5-26	2.0
					265	200	8	1.2-1.9
					265	204-229	8-19	2.1
					265	230	12	-
					265	233	13-17	2.0
					510	235	8	-
					265	236	8-13	2.0
7-9	I	Pd-Ag	0.38	40	67	21-167	5-11	2.8
					67	173	12	1.5-1.9
					67	175-213	14	2.4
					392	220	15-22	-
					65	222	15-22	1.6-2.3
					392	222	15-20	-
					67	222	15-20	1.7
					266	222	20	3.0
					1,170	222	18	3.8
					266	222	17-21	2.7
7-12	I	Pd-Ag	0.38	40	67	33-105	5-9	2.6-3.2
					67	106	9	-
					67	107	9	2.0-2.5
					265	108	9	1.6-2.6
					265	108-126	12	2.5-3.0
7-14	I	Pd-Ag	0.38	40	27	202	20	1.6
					265	202	20	3.0
					265	206	23	-
					265	209	20-24	2.8-3.4
					150	209	20	0.5-1.95
					265	209	20	2.3-3.5
7-16	I	Pd-Ag	0.38	55	15	200-210	19	1.6
					150	204	19	2.0
					150	203	19	0.3-2.0
					150	203	19	2.0

RUNS WITH HYDROGEN-DIFFUSION CATHODES (Continued)

Transmission, % H ₂	Duration of Run		Remarks
	Interval, min	Accumulative, min	
51	68	4,023	
-	5	4,028	Foil anodic during this period
63	17	4,045	
-	5	4,049	Foil anodic during this period
80	8	4,057	
-	5	4,062	Foil anodic during this period
68	5	4,067	Run was terminated
48	40	-	
-	5	45	Foil anodic during this period
6	49	94	
-	6	100	Foil anodic during this period
62	31	131	
-	5	136	Foil anodic during this period
50	14	150	
39	15	165	
-	3	168	Foil anodic during this period
26	15	183	A pin hole developed in the foil after this period and the run was terminated
18	40	-	
-	3	43	Foil anodic during this period
33	9	52	
-	3	55	Foil anodic during this period
13	8	63	Run was terminated; foil contained a dark deposit
00	29	-	After 8 min foil was made anodic for next 4 min at 27 amp/ft ²
1	7	36	
-	6	42	Foil anodic during this period
2	12	54	
-	6	60	Foil anodic during this period
6	19	79	Run was terminated
00	29	-	After 8 min foil was made anodic for next 4 min at 15 amp/ft ²
00	7	36	
-	6	42	Foil anodic during this period
3	13	55	Four additional attempts to activate the foil (anodic treatment) at temperature from 203 to 245 C, and current densities of 150 and 522 amp/ft ² , did not increase the per cent hydrogen transmission

Contrails

Palladium foil anodes were used for the first time because they could be wedged between the Teflon liner and the top of the cell. After the run it was found that a considerable amount of palladium had dissolved anodically. Platinum anodes were used for all subsequent runs.

During the run (after 1,625 minutes), the pressure was decreased from 120 psig to 0 psig and the hydrogen transmission decreased from about 70 per cent to 40 per cent.

Because of the extended time of the run and lack of provision for continuously adding water the electrolyte solidified. The cell was disassembled, water added, and the cell reassembled; the hydrogen transmission increased from 30 to 60 per cent.

After the water was added some unusual cell voltages were obtained. For the first 5 hours at 15 amp/ft², the cell voltage was 0.69 ± 0.01 volt. The per cent transmission increased gradually to 62 per cent after 2-1/2 hours but never exceeded 80 per cent during the 5-hour period. The run was continued overnight, and in the morning the voltage was found to be 1.3 volts with about 62 per cent transmission. Sometime between 10:45 a.m. and 12:30 p.m. of that day, the voltage decreased from 1.27 volts to 0.73 volt. By 3:45 p.m. the voltage was 0.66 volt and transmission was down to 57 per cent. By the following morning, the voltage was back up to 1.32 volts and transmission was 50 per cent when the run was terminated. The electrolyte was found to be black and gave a positive test for iron.

The unusually low voltage is difficult to explain. It may have been the result of contamination. In retrospect, this was the only run in which palladium was used as anode. Possibly, the anodically dissolved palladium deposited on the cathode and caused the unusually low voltages, or the low voltage may have occurred because the anodic reaction was palladium dissolution rather than oxygen evolution.

Run 2-64

Cell G was modified to minimize contamination. A Teflon plug was used in the top of the cell to fit tightly around the platinum wire connected to a platinum-gauze anode. An automotive spark plug was used in the top of the cell, with the platinum anode lead brazed to the insulated center electrode of the spark plug.

A small hole of about 1/16-inch diameter drilled in the Teflon plug was the only exit from the Teflon-lined electrolysis chamber and the hole connected to the oxygen exit pipe. The latter was connected to a steam generator to supply water to control the electrolyte concentration as discussed previously.

Run 2-64 was unsuccessful because electrolyte leaked around the cathode foil. A new cathode foil was used for the next attempt (Run 2-66).

Run 2-66

This run lasted for 9 days and demonstrated the usefulness of the steam generator in maintaining the electrolyte concentration. The highest hydrogen transmission was 83 per cent. During this extended run various factors affecting the per cent transmission were explored.

Contrails

During the time interval from 1,713 to 1,857 minutes, the electrical connections were reversed and hydrogen previously collected in the burette was passed back through the foil from gas phase to electrolyte to be anodically consumed at high rates.

Continuation of the run with the foil cathodic indicated that the anodic treatment resulted in increased per cent transmission. Varying the pressure from 0 to 120 psig had little effect. Superimposed ac on dc increased transmission. Toward the end of the run high current densities were explored and equivalent transmission of 300 amp/ft² was reached, indicating that the cathode could still pass considerable hydrogen after 9 days.

Run 2-77

This was one of the best runs in which 150 amp/ft² was demonstrated. The total cumulative time of satisfactory operation was 93 minutes. This run was described previously (Figure 6). A new cell design was used (Figure 5) which incorporated most of the features of Cell G (Runs 2-64 and 66) but was a much smaller version made of standard fittings for easy assembly and disassembly. Pretreatment of the foil before cell assembly consisted of wiping with methyl ethyl ketone.

Runs 2-81, 2-83, and 2-87

In these runs various types of reflux condensers were tried. There was no pressure on the electrolyte and very poor results were obtained.

Run 2-90

In this run the reflux condenser was fitted to take pressure, and transmission was increased to about 85 per cent.

Run 2-95

This was the run in which satisfactory operation at 265 amp/ft² was demonstrated. It has been discussed in detail previously (Figures 7 and 8) and involved a considerable history prior to the satisfactory operation as shown in Table 5. Particularly noteworthy is the indication that the anodic activations had more effect as the pressure and temperature were increased, reaching 88 per cent at 226 C and 20 psig after 233 minutes.

Pretreatment of the foil before cell assembly consisted of wiping with methyl ethyl ketone.

Run 7-9 and 7-12

In these runs, anodic treatment of the foil in place in the cell at various current densities, temperatures, and pressures did not result in activating the foil. Possibly the sequence of events preceding the attainment of 100 per cent transmission was critical. It would be difficult to duplicate run Run 2-95, and since Run 2-77 had involved fewer steps, it was selected for the pattern of the following runs.

Run 7-14

This run was supposed to duplicate Run 2-77 (Figure 6) in which 100 per cent transmission was obtained. Temperature, pressure, and time cycle of activation were the same. The 100 per cent transmission sought was not obtained. The current was the same as that for Run 2-77 but the current density was higher because the foil area was smaller. The electrolyte concentration was lower than in Run 2-77.

Run 7-16

Run 7-16 repeated the following procedure, used in Run 2-77, to the extent that the variables that were known were controlled:

- (1) The palladium-silver foil "as received" was cleaned by wiping with methyl ethyl ketone and assembled in the cell.
- (2) The electrolyte was 55 weight per cent KOH solution. The potassium hydroxide pellets (3.2g KOH) were added dry to the cell, which was then heated to 200 C and water (2.3g) added [by injection with a hypodermic needle at top of Teflon tube (Cell I, Figure 7).]
- (3) A pressure of 19 psig was maintained by connection to a nitrogen tank.
- (4) With the temperature in the range of 200 ± 5 C and the pressure at 19 ± 1 psig the following sequence was used:

Foil cathodic at 15 amp/ft² for 8 minutes
Foil anodic at 15 amp/ft² for 4 minutes
Foil cathodic at 15 amp/ft² for 17 minutes
Foil cathodic at 150 amp/ft² for 7 minutes
Foil anodic at 150 amp/ft² for 6 minutes
Foil cathodic at 150 amp/ft² (should increase to over 90 per cent transmission in 10 minutes).

As can be seen in Table 5 practically no hydrogen transmission was obtained in Run 7-16. Four additional attempts to activate the foil at temperatures up to 245 C and current densities up to 522 amp/ft² were unsuccessful in increasing per cent transmission.

The run was continued overnight at 23 amp/ft² with only 5 per cent transmission. Subsequent anodic activations had no effect.

The reason for not being able to duplicate Run 2-77 in Run 7-16 was puzzling. The cell design was different but it is difficult to see how this could be a factor. Figure 5 shows the cell design for Run 2-77 with connection to the steam generator. Figure 7 shows the cell design for Run 7-16 with no steam generator used. The latter cell design had already been shown capable for attaining 100 per cent transmission in Run 2-95.

After Run 7-16, the cell design of Figure 7 was modified by replacing the metal at the top of the Teflon with an inverted glass U-tube with the platinum anode lead wire sealed through the glass wall. The metal pressure gage was attached to an arm of the

Contrails

glass U-tube so that any condensate which might contain metallic corrosion products would not fall back into the cell electrolyte as was possible with the design shown in Figure 7

Cell Design I (Figure 7) modified as discussed above represented the cell design that was least susceptible to contamination with corrosion products. Yet with all the runs made with this cell, (7-9, 7-12, 7-14 and 7-16) there was negligible transmission of hydrogen. It appeared that, as efforts to prevent electrolyte contamination succeeded, poorer results were obtained in terms of per cent transmission. Possibly, a degree of electrolyte contamination was needed. It is possible that anodic oxidation of palladium alloy during activation provides a small amount of palladium in solution which is beneficial.

Since the successful Run 2-77 had been made with connection to the brass pipe of the steam generator, a possible contaminating metal ion might be copper which was not present in subsequent runs. At the end of Run 7-16 the electrolyte was purposely contaminated with copper by adding 0.5 milliliters of 40 weight per cent KOH which had been electrolyzed with a copper anode and platinum cathode until the solution was faint blue. The contamination did not change the per cent transmission at 150 amp/ft² which was practically 0 per cent.

When the cell was disassembled, the cathode foil had a dark reddish-brown deposit, the reddish color from the cathodically deposited copper. Surprisingly there was a reddish hue on the back side of the palladium-silver foil.

Summary

Pretreatment of the foil including activation appears to be an important factor in obtaining 100 per cent transmission at high current density, provided other conditions are also met. Based on the successful runs (2-77 and 2-95) the other conditions appear to be: > 50 weight per cent KOH electrolyte, > 190 C, > 13 psig. Pretreatment of the foil consisting of simple wiping with methyl ethyl ketone to remove grease and oil is adequate when followed by the proper anodic activation treatment in the cell electrolyte at operating current density, temperature, and pressure.

When the activation is successful, practically 100 per cent hydrogen transmission is obtained. When activation is unsuccessful, practically no hydrogen passes through the foil. Where the preassembly treatment of the foil consisted of only cleaning with MEK, hydrogen transfer from the gas phase to the electrolyte side of the foil during anodic treatment was never observed.

Where transfer of hydrogen back through the foil to the electrolyte side was observed during anodic treatment in Run 2-66, the preassembly treatment of the foil had included: degreasing, anodic activation in alkaline cleaner, and acid dip in which both sides of the foil were treated before cell assembly. Where the above treatment of the foil was given prior to assembly it was always possible to obtain some hydrogen transmission at high current density immediately. Anodic activation in the cell increased the transmission, but 100 per cent transmission was not obtained.