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WATER-ELECTROLYSIS CELLS USING HYDROGEN-DIFFUSION CATHODES

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FOREWORD

This investigation was made by the Columbus Laboratories of Battelle Memorial Institute on Contract No. AF 33(615)-2954 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 Aerospace Medical Research Laboratories, Aerospace Medical Division, Wright-Patterson Air Force Base, Ohio 45433, and was administered by Richard E. Bennett, contract monitor, Biotechnology Branch, Life Support Division, Biomedical Laboratory. The work reported here was done between 1 June, 1965, and 20 January, 1967.

The principal investigators for Battelle Memorial Institute were: J. E. Clifford, Project Leader, and E. S. Kolic, Electrochemist. The work was done under the direction of Dr. C. L. Faust, Chief, Electrochemical Engineering Division.

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ABSTRACT

The feasibility of extended operation of palladium-silver alloy hydrogen diffusion cathodes was demonstrated by essentially 100 percent hydrogen transmission for 486 days of operation at the following experimental conditions: 6.35-mm-OD x 0.13-mm-wall Pd-25Ag cathode tube at 37 ma/cm²; free electrolyte cell with 22 ml of 60 percent NaOH at 145 C; cell voltage of 1.74 ± 0.03 volts with solid cylindrical platinum anode. The determination of the maximum efficient current density (MECD) as a function of temperature indicated that satisfactory operation in the above run could have been obtained at temperatures as low as 112 C; 53 C with new cathode-activation treatments; or 30 C with a rhodium treatment of the cathode. In addition to platinum, platinum-10 rhodium alloy was shown to be a satisfactory anode material, but not gold. The feasibility of producing hydrogen gas at a pressure 15 psi higher than oxygen with only a slight decrease in MECD was demonstrated. New electrolyte preelectrolysis procedures were developed to counteract apparent purity variations in reagent-grade NaOH pellets. Of a number of possible matrix materials investigated, the longest satisfactory operation was obtained with fuel-cell asbestos: 281 hours at 70 C and 37 ma/cm², but only 15 hours at 135 C. The feasibility of using a free electrolyte of phosphoric acid was demonstrated in a 4-hour run at 37 ma/cm² and 60 C.

Contrails

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SECTION I

INTRODUCTION

This program described in this report was a fundamental study of the use of a palladium-silver hydrogen-diffusion cathode in a water-electrolysis unit designed for aerospace application. The hydrogen-diffusion cathode provides a unique water-electrolysis unit for gravity-independent operation with several potential advantages in addition to small size and power consumption. A potential advantage is the possibility of operating a matrix-type cell at large differential pressure without crossleak of oxygen and hydrogen. The production of pure, dry hydrogen at positive pressure in an electrolysis cell that can operate at temperatures up to 200 C are features of interest for integration into advance oxygen-recovery systems that utilize hydrogen for subsequent reduction of carbon dioxide (e. g. , Sabatier or Bosch systems).

Two earlier studies by Battelle Memorial Institute^(1,2) successfully demonstrated the technical feasibility of a hydrogen-diffusion technique using a palladium - silver-alloy cathode. The second of these studies demonstrated the technical feasibility of a matrix-type cell for gravity-independent operation with a water-vapor feed. This program is a continuation of that experimental work, with emphasis on a fundamental study of the hydrogen-diffusion cathode to define the operational capabilities and demonstrate reliability. Since the overall objective of this work is a matrix-type electrolysis cell, studies of matrix materials and operating conditions were directed toward demonstration of satisfactory performance of a matrix-type cell for more than the 24 hours shown in prior studies.⁽²⁾

SECTION II

EXPERIMENTAL PROCEDURE AND APPARATUSIntroduction

The experimental program was designed to study the important factors that affect operation of the Pd-25Ag hydrogen-diffusion cathode. All of the data are pertinent to the potential application of the Pd-25Ag cathode in a matrix-type cell. Data primarily related to the cathode, but including the effect of the anode and electrolyte (exclusive of a matrix), are applicable to potential applications of the Pd-25Ag cathode in a free-electrolyte-type cell. The factors investigated fall into two general categories: (1) time-dependent factors, and (2) design or initial-performance factors.

Time-dependent factors (e. g. , contamination occurring from electrolyte, matrix, or anode) were evaluated in extended operational tests. Results were compared on the basis of satisfactory operational hours (>95 percent H₂-transmission efficiency).

Factors affecting design or initial performance of the cathode (e. g. , cathode activation or pretreatment, electrolyte concentration, or composition) were evaluated in terms of maximum efficient current density (MECD). The MECD is defined as the maximum current density that can be applied while diffusing hydrogen at essentially 100 percent efficiency under steady-state conditions. The MECD or rate constant is temperature dependent. Thus, the results for specific experimental conditions could be described and compared by the temperature dependence of the rate constant.

Determination of Maximum Efficient Current Density

The rate constants were experimentally derived by a technique of extrapolation from cathode-potential - current-density curves. The unique procedure developed involves application of a high current density (hydrogen evolution) on a cathode under investigation, followed by incremental decreases in the applied current until a break is obtained in the recorded voltage-current curve. Rate-constant values, found rather quickly by this procedure, were verified as steady-state values in 15-hour runs. Figure 1 illustrates a typical cathode-potential - current-density curve from which an MECD rate constant of approximately 230 ma/cm² was determined. Conditions for the test were: 66% NaOH electrolyte at 147 C and 6.35-mm-OD Pd-25Ag tube given Activation Treatment CA-1. The latter cathode treatment is described in detail in Section IV.

In evaluating factors influencing initial performance described above, the rate constant, as affected by the variable under consideration, was determined at several selected temperatures. A resulting temperature-dependence curve was then established by plotting the logarithm of rate constant against reciprocal of the absolute temperature at which the rate constant was determined. Since the resulting relationship is linear, only a few rate constants were required to establish the curve.

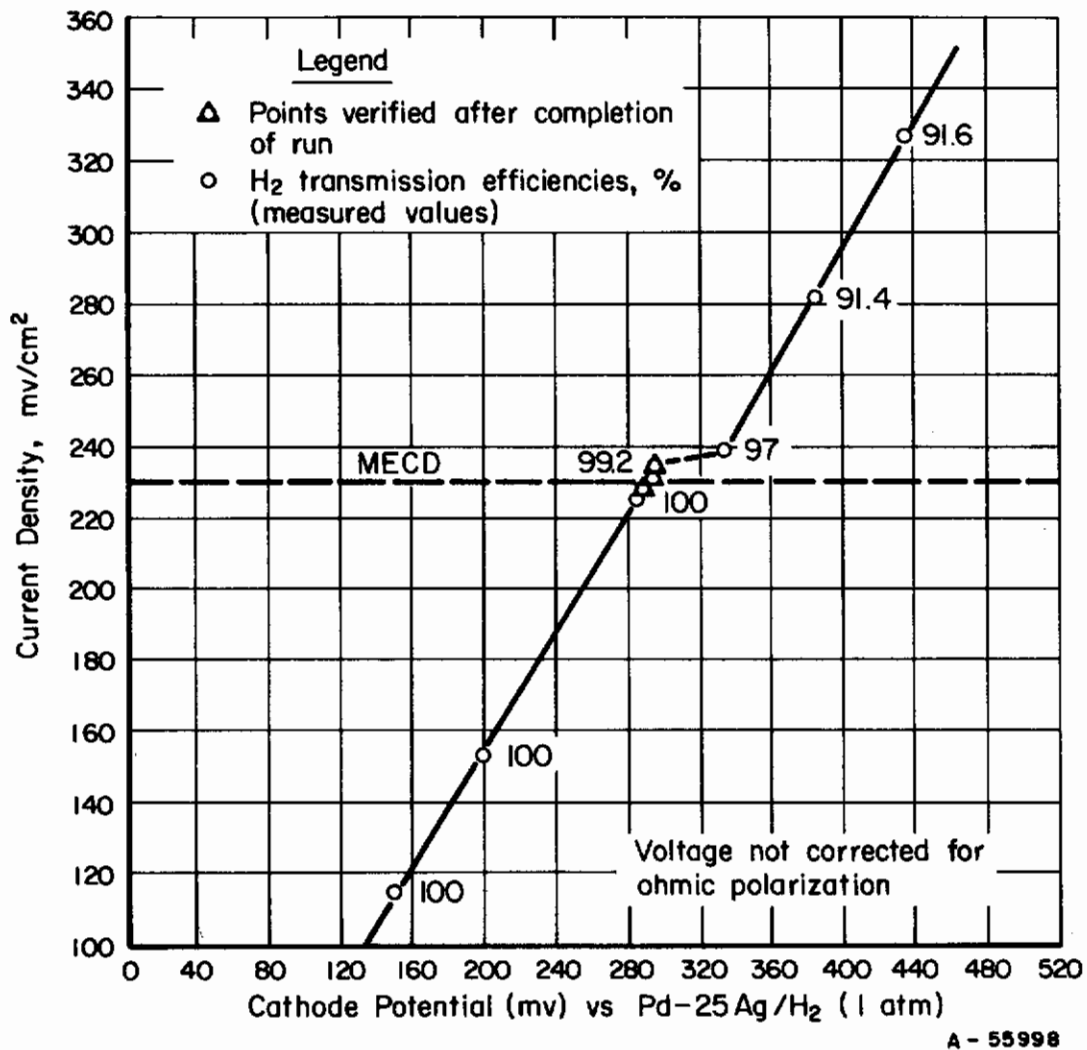


FIGURE 1. DETERMINATION OF MECD FROM VOLTAGE-CURRENT CURVE

Determination of H₂-Transmission

Hydrogen gas diffusing through the cathode was collected in a burette containing dibutyl phthalate (low vapor pressure). H₂-transmission efficiency was calculated from the ratio of gas-collection rate to the corrected theoretical rate:

$$\% \text{H}_2\text{-transmission} = \frac{\text{gas-collection rate} \times 100}{\text{corrected theoretical rate}},$$

where the corrected theoretical rate:

$$\frac{(22,400) (60) (T) (760) (I)}{(96,000) (2) (273) (P)} = \frac{19.6 T I}{P}.$$

T = absolute temperature of collected gas, K

P = barometric pressure, mm Hg

I = electrolysis-cell current, amperes.

EXPERIMENTAL APPARATUS

In the experimental program, six types of electrolysis cell were designed and fabricated for obtaining experimental data. Each cell was constructed with special features, according to the need and requirements of the particular objective investigated.

Experimental Cell A

Experimental Cell A, shown in Figure 2, is a static vapor-feed free-electrolyte cell designed for use in the extended operational-evaluation run. The principal feature of the cell is the vapor-feed section located at the top of the unit. This section was designed for automatic operation to provide makeup water to the cell (lower section) during long periods when the unit was left unattended. Automatic regulation of the vapor feed is accomplished by a temperature controller, which regulates the heat input to the water reservoir (vapor pressure). The temperature controller is activated by a thermocouple sensor positioned at the desired electrolyte level.

Initially, the cell performed satisfactorily. However, 6 days after startup, the cell polarized during a period when the electrolyte level was too low. Polarization was due to an increase in electrolyte concentration and subsequent solidification. The problem resulted from not taking into consideration the void volume of the electrolyte (increase in electrolyte level) caused by entrained oxygen gas. The electrolyte-level sensor was subsequently adjusted to a slightly higher, calculated level (0.8 cm, corresponding to an increase in volume of about 2.3 cm³), which resolved the polarization problem.

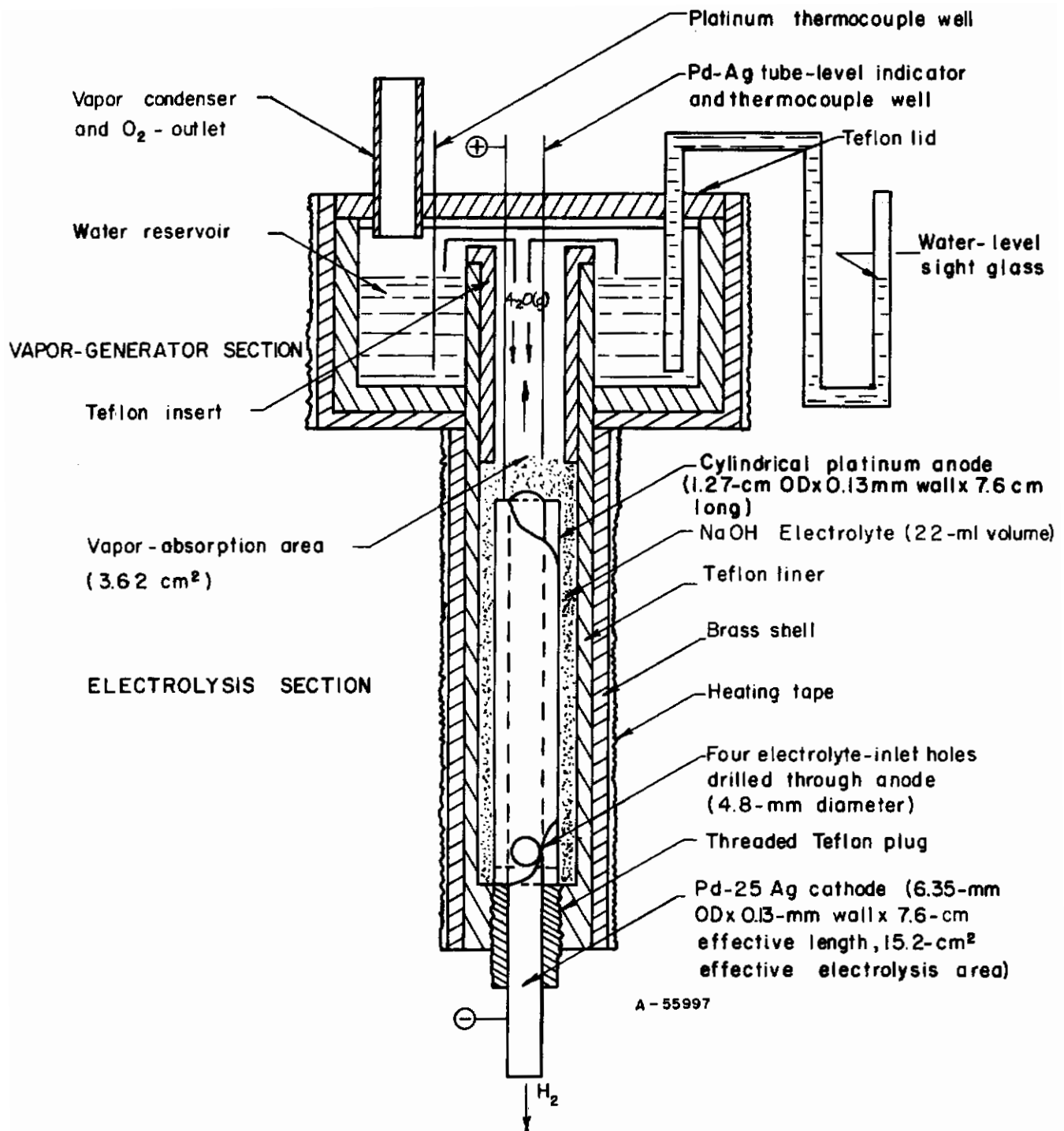


FIGURE 2. EXPERIMENTAL CELL A

Experimental Cell B

MECD rate-constant data were obtained in Experimental Cell B, shown in Figure 3. The Pd-25Ag tube reference electrode was maintained with pure, dry hydrogen at a pressure of 1 atmosphere. Hydrogen was stored in a burette reservoir equipped with a level bottle containing dibutyl phthalate.

Experimental Cell C

Experimental Cell C is shown in Figure 4. The unit was designed for use in anode studies, electrolyte studies, and for screening matrix materials. The principal feature of this unit is that five individual (and possibly different) tests can be performed concurrently while equivalent temperature and current density are maintained. Current density can be maintained by electrically connecting the cells in a series arrangement.

Typical experimental conditions were: 37 ma/cm² cathode current density, 50 weight percent NaOH electrolyte, 70 C electrolyte temperature, cylindrical platinum or platinum-rhodium alloy anode, and a 1.6-mm-OD cathode tube (activated by a vacuum-annealing procedure discussed in Section IV).

When Experimental Cell C was employed in matrix-screening tests, the matrix was applied to the cathode, and a piece of platinum wire was then spiraled around the matrix to hold it in place. A platinum-foil cylinder was used as the anode in testing and not the platinum wire.

Experimental Cell D

Experimental Cell D, shown in Figure 5, was designed and fabricated for evaluating matrix materials at high temperature and pressure. The electrolysis unit was originally designed for a static water-vapor feed from a separate water-vapor generator. After preliminary experiments, the system was modified for a dynamic water-vapor feed. For convenience, nitrogen gas was used as the water-vapor carrier in the experimental studies. It was bubbled through the water-vapor generator in a one-pass feed. A practical system would use a recirculated oxygen stream as the water-vapor carrier. Components for water-vapor feed and water-vapor separation from gas streams were not designed for gravity-independent operation. The cell was designed to accept three 6.35-mm-OD cathode tubes (e.g., three different matrices could be evaluated concurrently). However, only one cathode position was used in a subsequent matrix-evaluation run.

Experimental Cell E

Experimental Cell E is a matrix-type cell having a static vapor feed. The cell is shown in Figure 6. The vapor feed that provided makeup water to the matrix was regulated manually by controlling the temperature (vapor pressure) of the vapor generator located above the cell.

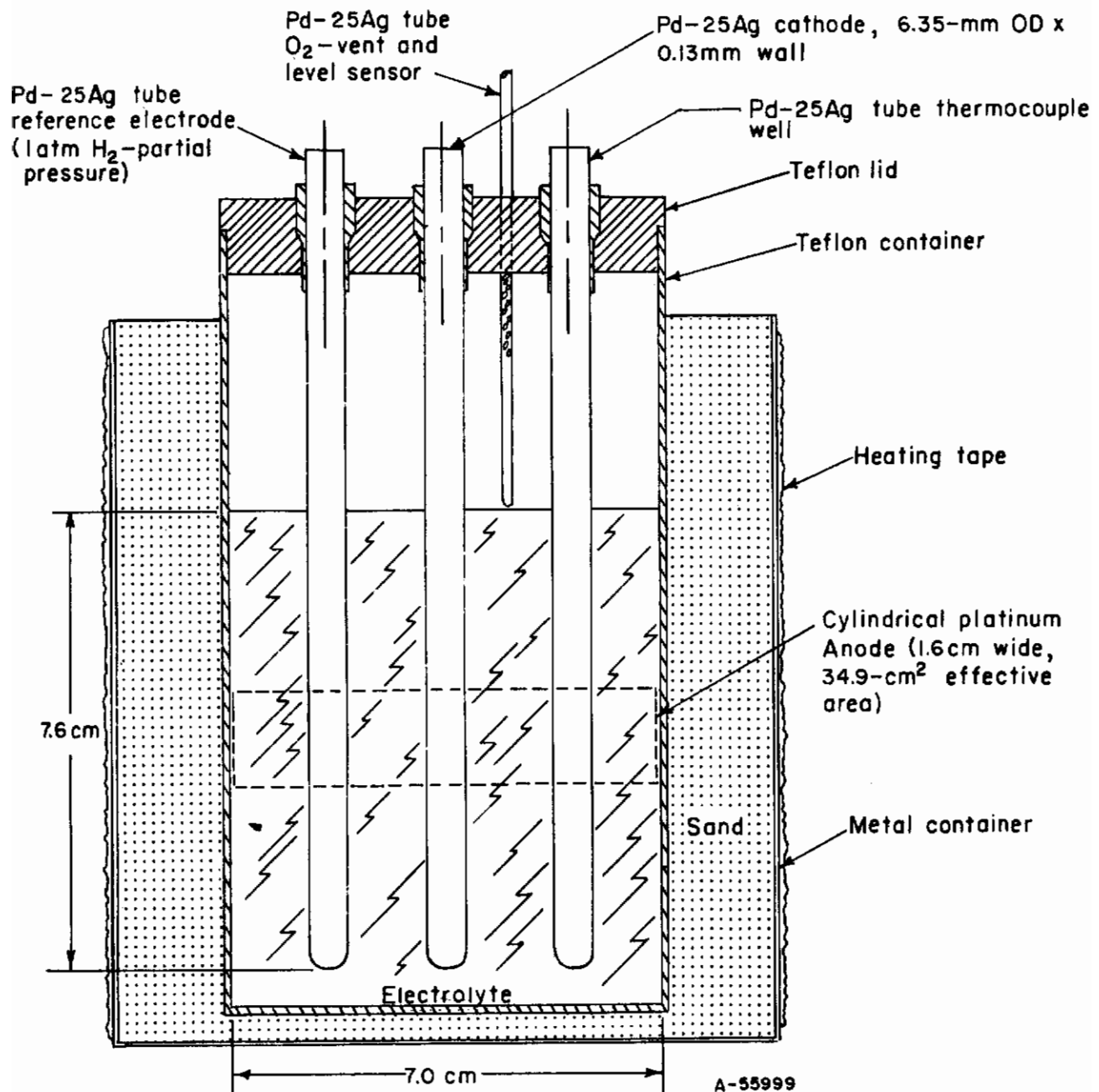
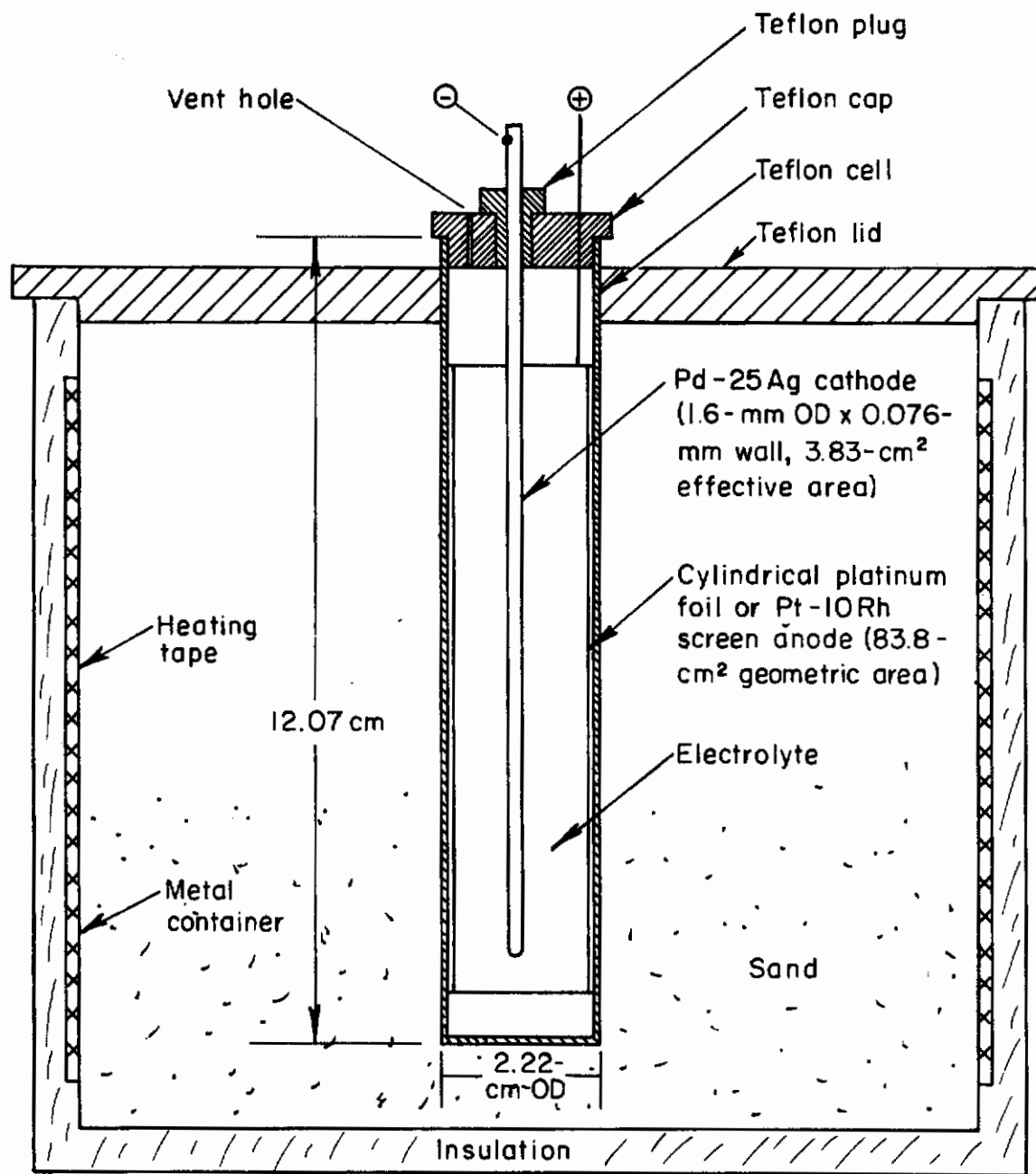


FIGURE 3. EXPERIMENTAL CELL B



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FIGURE 4. EXPERIMENTAL CELL C

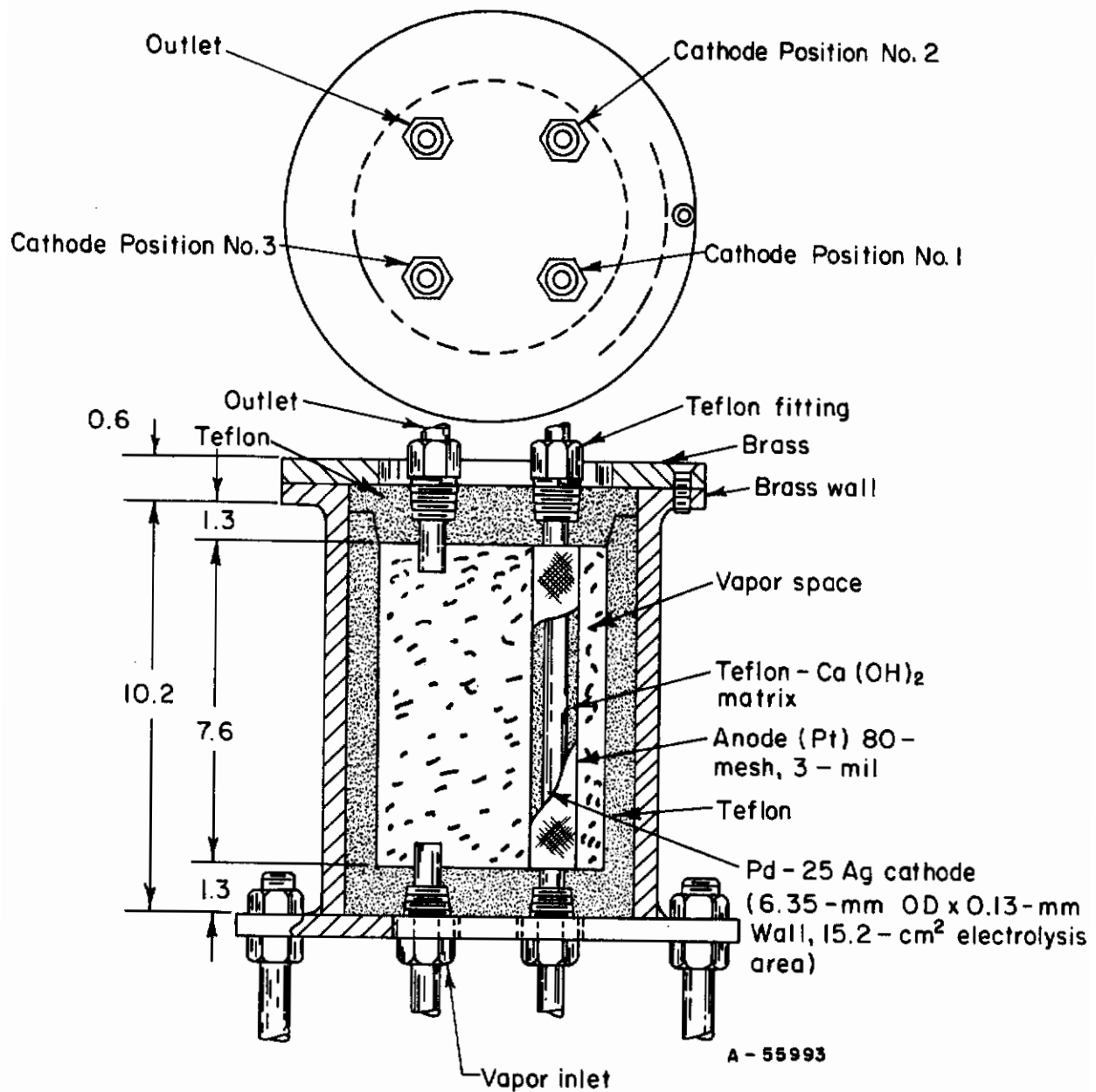


FIGURE 5. EXPERIMENTAL CELL D

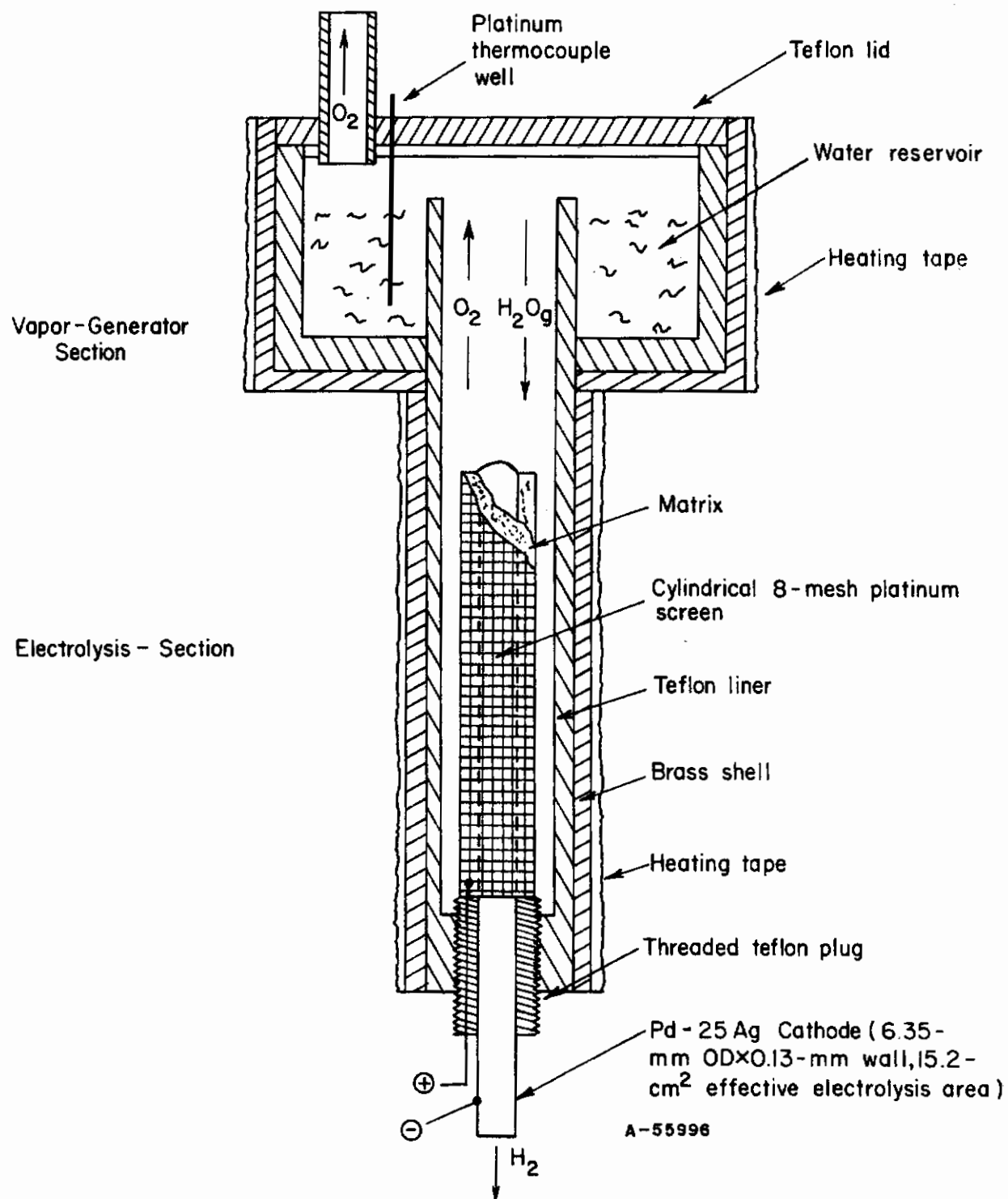
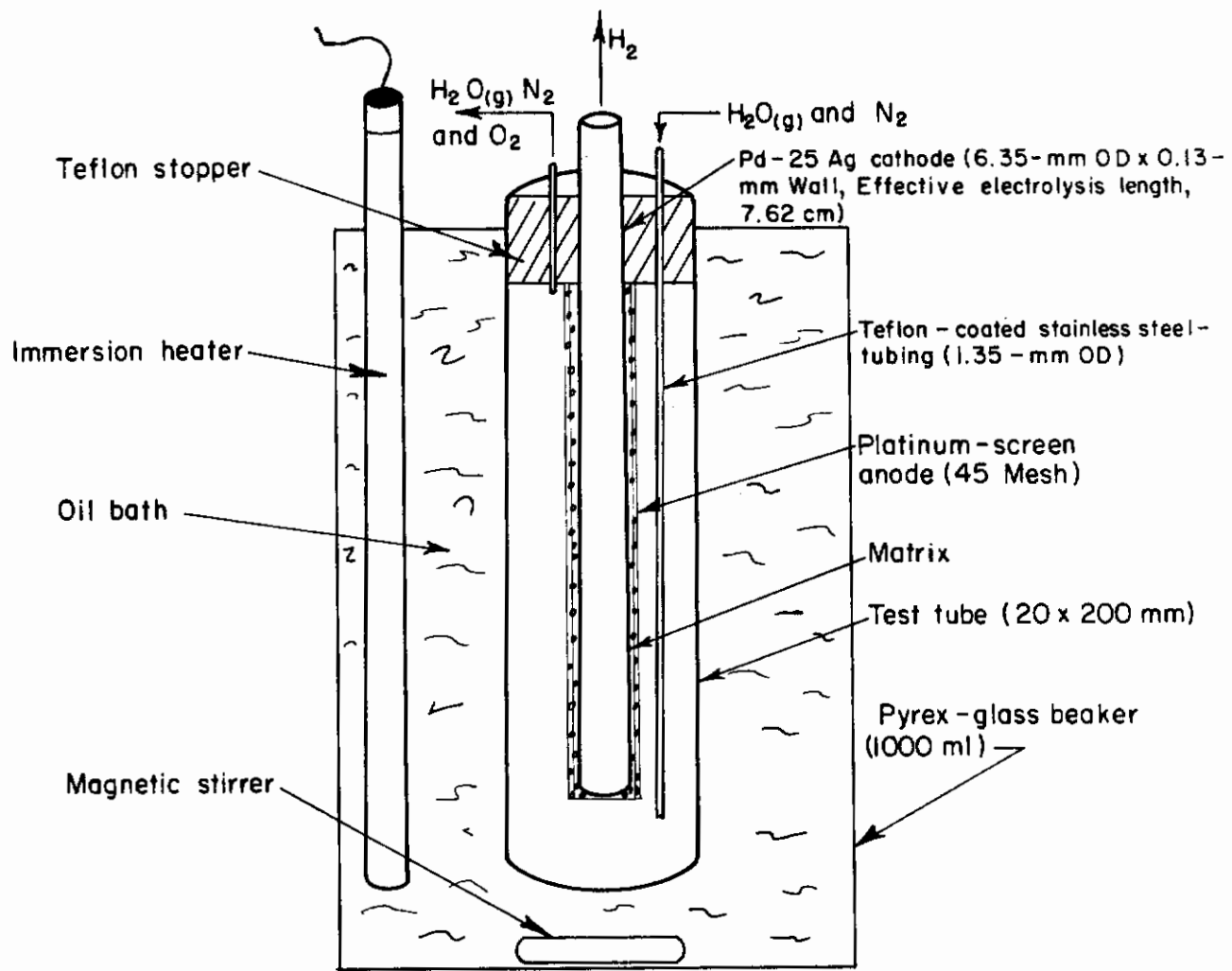


FIGURE 6. EXPERIMENTAL CELL E

Experimental Cell F

Experimental Cell F is shown in Figure 7. This matrix-type cell was designed to operate on a dynamic water-vapor feed system that used nitrogen gas as the water-vapor carrier. In most instances, the nitrogen was metered to a flow rate of 300 ml/min, STP. The vapor generator, through which the nitrogen gas was bubbled, was operated at about 45 C. This temperature resulted in a vapor-feed partial pressure to the cell of 75 mm Hg. Experiments were carried out at 65 C with matrices impregnated with 50 percent NaOH electrolyte (equivalent to an equilibrium vapor pressure of 33 mm Hg). Thus, the driving force for water-vapor absorption in the tests was approximately 42 mm Hg. Since the cell was constructed from glass, the wetted condition of the matrix could be visually inspected.



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FIGURE 7. EXPERIMENTAL CELL F

SECTION III

EXTENDED OPERATIONAL EVALUATIONIntroduction

In the first experimental test of the program, a small, free-electrolyte electrolysis cell with a water-vapor-feed system (shown in Figure 2) was designed for extended, continuous operation. Prior studies at Battelle^(1,2) suggested that sufficient knowledge was available to construct a free-electrolyte cell having a vapor feed that should operate for an extended period, provided no contamination was introduced into the system. One objective of an extended operational run was to verify that 100 percent H₂-transmission could be maintained with a Pd-25Ag cathode for at least 1000 hours, and, hopefully, for the duration of the program. A second objective was to provide a base line for comparing results of subsequent investigation of variables that are expected to affect the performance of a palladium-silver diffusion cathode. Thus, the first experimental cell was designated a "control" cell, and was designed and operated with the best available knowledge obtained from prior experience.

Experimental Procedure

A description of the experimental cell and the water-vapor feed-control system is shown in Figure 2. Electrolyte treatment, cathode activation, and operating conditions used in testing were based on a successful 24-hour run made with a vapor-feed matrix-type cell in prior experimental work (Run 78-27)⁽²⁾. The treatment procedures used to activate the cathode and purify the electrolyte are discussed in Sections IV and V, respectively, of this report. The experimental conditions for operation of the cell were as follows:

Electrolyte	66 wt % NaOH
Cell temperature	145 C
Cathode	Pd-25Ag tube with one end closed; 6.35-mm OD x 7.62 cm long x 0.13-mm wall
Cathode current	560 ma
Cathode current density	37 ma/cm ²
Anode material	Pure platinum
Cell material	Teflon.

Ideally, a vapor-generator feed system providing makeup water to a 66 percent NaOH electrolyte at 145 C would operate at a temperature of about 66.5 C (200 mm Hg, equilibrium vapor pressure over the electrolyte). However, a driving force of about 65 mm Hg was experimentally found to be required for mass transfer of water vapor during steady-state operation. Thus, the vapor generator, instrumented for automatic regulation, operated at an average temperature of 73 C (equivalent to a vapor pressure of about 265 mm Hg).

Results and Discussions

The essential results of the extended evaluation run are summarized in Table I. The cell was operated for a period of 1 year and 121 days (11,600 hours), during which time essentially 100 percent H₂ transmission was obtained. The run is considered a satisfactory demonstration of the electrochemical reliability of the hydrogen-diffusion cathode, in the present state of the art of water-electrolysis cells.

TABLE I. SUMMARY OF EXTENDED EVALUATION

Days of Continuous Operations	Accumulative Operational Days	Cause of Interruption in Operation	Duration of Interruption	Average Measured Values ^(a)	
				Cell Voltage, volts	H ₂ Transmission, percent
6	6	Level sensor set too low	2 hours	1.64	99.3
108	114	Power failure	30 seconds	1.73	99.8
61	175	Power failure	5 minutes	1.76	99.5
61	236	Performed voltage analysis	5 minutes	1.75	100.3
5	241	Control setting too low	1 hour	1.77	100
104	345	Power failure	64 hours	1.72	100
141	486	Terminated test	--	1.73	100

(a) Refers to average values up to the time of either polarization, power failure, or termination. Other values were constant throughout the experimental run: current, 560 ± 8 ma; cell temperature, 145 ± 5 C; and vapor-generator temperature, 73 ± 5 C.

During the run, electrolysis was interrupted six times because of either polarization caused by vapor-feed problems or power failures. However, after all interruptions, satisfactory operation was resumed without any adjustments to the cathode. In one interruption, which occurred 345 days after startup, the electrolysis cell was down for a 64-hour period (longest interruption) when electrical power to the laboratory was interrupted. During this period, both d-c power, supplying current for electrolysis, and a-c power, supplying current for the heating units, were turned off. The relatively long down period, however, did not affect the subsequent performance of the cell. After electrical power was restored, satisfactory electrolysis continued after the cell had attained operational temperature. No mechanical or electrochemical adjustments were required to attain successful operation again.

After 236 days, a current-voltage curve was obtained for the cell. From rapid cell-voltage measurements at selected current densities of 1, 10, and 37 ma/cm², the voltage equation was determined to be of the form $E = a + b \log i + ci$ and, specifically, $E = 1.499 + 0.113 \log i + 0.00143 i$ (where E is in volts and i is in ma/cm²). The latter current/voltage relationship is characteristic of the operating conditions of 37 ma/cm², 66 percent caustic electrolyte at 145 C, and platinum-foil anode spaced 0.3 cm from the cathode. The equation predicts a cell voltage of 1.73 volts at 37 ma/cm² compared to 1.74 ± 0.03 volts obtained throughout the operating life of the cell.

The apparent voltage component due to ohmic resistance (ci term in the equation) is 0.053 volt at 37 ma/cm², compared to about 0.009 volt calculated from published values of electrolyte resistivity. The difference is attributed to entrained oxygen gas in the electrolyte. The value of the constant " a ", minus the reversible cell potential ($E_0 \cong 1.15$ volts at 145 C), gives a comparative value of overvoltage at 1 ma/cm² of

0.35 volt. This value of overvoltage (presumably at the anode) is higher than expected and indicates the need for further study of overvoltage: anode material and configuration (i. e. , screen) with and without a matrix.

A hydrogen-permeation rate constant established for a palladium-silver cathode under conditions which can be related to the "control" cell showed that the cell was operated about 140 ma/cm^2 below the limiting current density for 100 percent H_2 -transmission. The temperature dependence of the rate constant is discussed in the next section.

CATHODE TREATMENTS

Introduction

The studies in Section IV of the experimental program include investigation of various techniques of activating and pretreating Pd-25Ag cathodes to attain better diffusion characteristics, e. g. , higher MECD values. The term "cathode activation" means physical or chemical treatment of the surface of a cathode without introduction or application of catalytic materials, whereas "cathode pretreatment" means the application of a catalyst, such as a metal oxide or a metal black. In the investigation, three cathode-activation procedures and one pretreatment procedure were evaluated.

Cathode Activation Treatment CA-1

Cathode Activation Treatment CA-1 was developed in prior experimental work and was used to activate the cathode tube for the extended operational run. The resulting temperature-dependence data of this activation treatment served as a base line for comparing and evaluating the effectiveness of the other cathode treatments.

- (a) The cathode was made cathodic in 60 percent NaOH electrolyte for 15 minutes at a current density of 115 ma/cm^2 and an electrolyte temperature of 100 C. Pure platinum foil was used as anode material.
- (b) The cathode was flamed to cherry-red in the flame of a Bunsen burner for approximately 1 minute.
- (c) Step (a) was repeated.
- (d) The cathode was electrolyzed anodically for 10 minutes at conditions given in Step (a).
- (e) Step (a) was repeated.
- (f) After water rinsing, the gas-phase side (inside) of the tube was filled with warm ($\sim 32 \text{ C}$) 37 percent HCl solution.
- (g) After about a 3-minute period, the HCl solution was removed, and the cathode tube was thoroughly rinsed with distilled water and dried with hand tissues.
- (h) Step (b) was repeated.

Cathode Activation Treatment CA-2

Cathode Activation Treatment CA-2 was developed as the result of experimental indications that the surface reaction occurring on the gas-phase side of cathodes was rate limiting. The hypothesis was based on an apparent relationship between the temperature-dependence results of Treatment CA-1 and anodic-diffusion results, which were obtained in a related AMRL sponsored project at Battelle.⁽³⁾

In the latter experimental work, the activation energy (slope of temperature-dependence curve) of a Pd-25Ag tube made anodic with a feed of pure, dry hydrogen was found to be essentially the same as the cathodic temperature-dependence slope obtained with Cathode Activation Treatment CA-1. Since both tubes were activated by the same procedure and tested under similar conditions, the same rate-limiting reaction was probably common to both diffusion processes. Further experimental work with the anodic tube indicated that the gas-phase side was rate limiting when a change in activation energy (lower value) was obtained after the inside surface was pretreated with rhodium.

- (a) The inside of the tube was filled with an aqueous solution of 37 weight percent hydrochloric acid.
- (b) The inside of the tube was then electrolyzed anodically at 37 ma/cm^2 for 75 seconds at 23 C. A platinum rod 1.2 mm in diameter was used as the cathode.
- (c) The inside of the tube was rinsed with distilled water.
- (d) The tube was then cathodically electrolyzed at 37 ma/cm^2 in 60 percent NaOH electrolyte at 130 C.
- (e) If 100 percent H_2 -transmission was not obtained in Step (d), Steps (a), (b), and (c) were repeated.

Cathode Activation Treatment CA-3

Cathode Activation Treatment CA-3 (vacuum annealing) was also developed in prior experimental studies at Battelle⁽²⁾, but its effectiveness was never determined. In this investigation, an evaluation of the treatment was made by comparing the results of two treated cathode tubes with two as-received cathode tubes. The experimental work was carried out with 1.6 mm diameter Pd-25Ag tubes (6.35 mm diameter Pd-25Ag tubes were used in all other cathode-treatment investigations). Principally, the treatment was investigated in lieu of Cathode Activation Treatment CA-2, which was too difficult to perform on the smaller diameter tubing. A need for an activation procedure for the smaller diameter tubes existed since they appeared to be more suitable for use in electrolyte contamination studies and matrix screening tests discussed in subsequent sections of this report.

- (a) The as-received tubes were held in a tantalum crucible, 8.9-cm OD by 15 cm long.
- (b) The crucible was positioned in the heated zone of a high-vacuum - heat-treating furnace. The furnace contained a tantalum element and had a heated zone 11 cm in diameter by 18 cm long.
- (c) After the furnace was closed, the atmosphere was decreased to about 5×10^{-5} mm Hg.
- (d) The controller was then set for 650 C, and about 12 minutes were required to attain temperature.
- (e) The tubes were maintained at the 650 C temperature and 5×10^{-6} mm Hg pressure for a period of 1 hour.
- (f) The tubes were allowed to cool to 28 C while under vacuum for a period of about 6 hours.
- (g) After cooling, the unit was pressurized to atmospheric conditions, and the tubes were then removed.

Cathode Pretreatment CP-1

Cathode Pretreatment CP-1 consisted of applying a rhodium deposit on the surface of the gas-phase side (inside) of Pd-25Ag tubes. The procedure, obtained from a literature survey⁽⁴⁾, was found to be beneficial for the anodic reaction of consuming hydrogen (e. g. , the reverse of cathodic diffusion) in prior experimental work at Battelle⁽³⁾. However, electrodes treated with rhodium in the latter experimental work developed hairline cracks. The cracks were suspected to be due to embrittlement caused by alloying of the rhodium and palladium-silver during a heat-treatment cycle that was part of the procedure. In the present investigation, only 0.1 mg/cm^2 of rhodium (one-tenth suggested amount of rhodium deposit) was applied on the inside surface of a cathode tube. The objective of this change was to eliminate the embrittlement problem while, hopefully, maintaining the better diffusion characteristics displayed by rhodium treatment.

- (a) A 6.35-mm-OD Pd-25Ag tube was annealed in argon at 850 C for a 2-hour period.
- (b) The inside of the tube was electroplated with a rhodium deposit from a 0.001 M solution of RhCl_3 adjusted to pH 1 with HCl. Conditions for plating were: a current density of 70 ma/cm^2 , 24 C, 5-second time period, and a platinum-rod anode. It is estimated that about 0.1 mg/cm^2 of rhodium-black was deposited.
- (c) The tube was given two heat treatments in an atmosphere of air:
(1) 2 hours at 850 C and (2) 2 hours at 700 C.

The cathode tube given Cathode Pretreatment CP-1 was tested for embrittlement by electrolyzing for 72 hours prior to evaluating. Testing conditions were: 20 ma/cm² cathodic current density, 60 percent NaOH electrolyte, and 110 C cell temperature. No visible cracks in the surface of the tube could be detected after testing. Apparently, the thinner rhodium deposit reduced the degree of embrittlement to a tolerable level.

Results of Evaluation of Cathode Treatments

The essential results of the investigation of cathode treatments are summarized by the temperature-dependence curves shown in Figures 8 and 9. The rate constants (MECD values) resulting from the various treatments were determined experimentally with techniques, apparatus, and procedures discussed in Section II. As can be seen in Figure 8, when the logarithms of the MECD values were plotted against the reciprocal of the absolute temperature, a straight line was obtained. For ease in reading, the ordinates of the latter values have been translated so that temperature (in degrees Centigrade) can be read directly.

The data shown in Figure 8 were obtained in comparable tests with 6.5-mm-OD x 0.13-mm-wall Pd-25Ag tubes. The data for vacuum annealing in Figure 9 were obtained with 1.3-mm-OD x 0.07-mm-wall Pd-Ag tubes. The differences in electrolyte concentration used in the evaluation of the cathode treatments is not considered a principal influencing factor (66, 60, 50, and 40 percent NaOH for evaluation of Treatments CA-1, CA-2, CA-3, and CP-1, respectively). The small effect of electrolyte concentration is discussed in the next section. A change to lower electrolyte concentration was necessary to avoid electrolyte solidification at the lower temperatures.

Figure 8 shows that the rate constant of Treatment CA-2 (anodic treatment with HCl) was appreciably increased with respect to Cathode Activation Treatment CA-1 ("control" cathode), whereas the effect on the slope (activation energy) was negligible. Apparently, the same rate-limiting reaction is common to both cathodes, and the relative displacement of the curves is due to differences in active surface caused by the treatments. That is, Cathode Activation Treatment CA-2 merely made available more active sites than did Cathode Activation Treatment CA-1, thus increasing the rate constant. The data suggest the possibility that MECD values would be displaced still farther to the left (increased) if the surface (gas-phase side) of the cathode were treated with Pd-black. This possibility will be explored in future work.

The beneficial results obtained with Cathode Pretreatment CP-1 (rhodium-black pretreatment) can be seen in Figure 8. The rate constants are the highest obtained in the low temperature range of 28 C to about 90 C. A linear relation assumed indicates a different slope caused by a change in activation energy (lower value) associated with the rhodium treatment. The change in activation energy correlates well with other literature data. The result with rhodium treatment verifies the assumption that the rate-limiting reaction was on the gas-phase side, since the activation energy was changed by treatment of the gas-phase side of the cathode.

The practical significance of the rhodium treatment is the lower operational temperature possible at a practical current density of 37 ma/cm²: 30 C for the Cathode Pretreatment CP-1 compared to 55 C for Cathode Activation Treatment CA-2

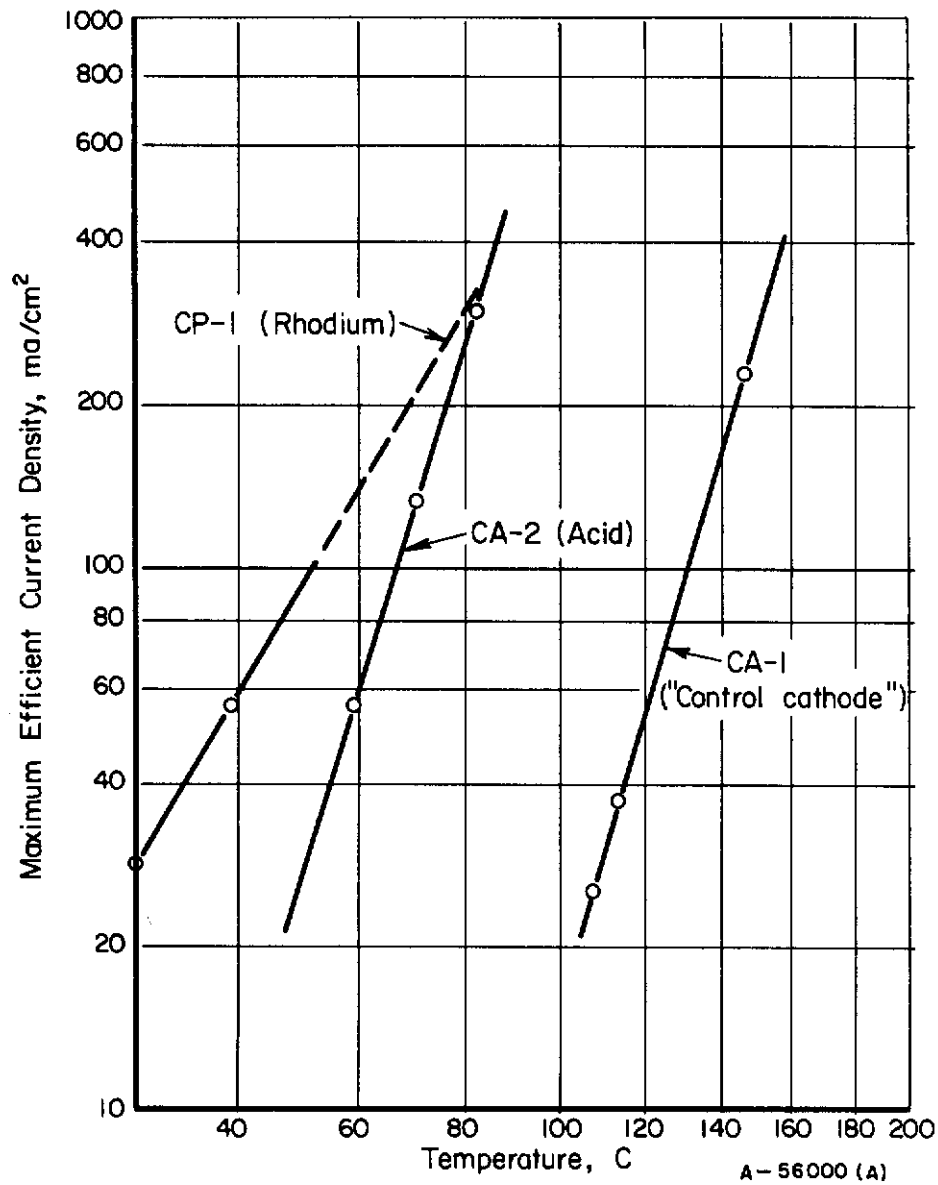


FIGURE 8. INFLUENCE OF SURFACE TREATMENTS ON THE PERFORMANCE OF Pd-25Ag CATHODES

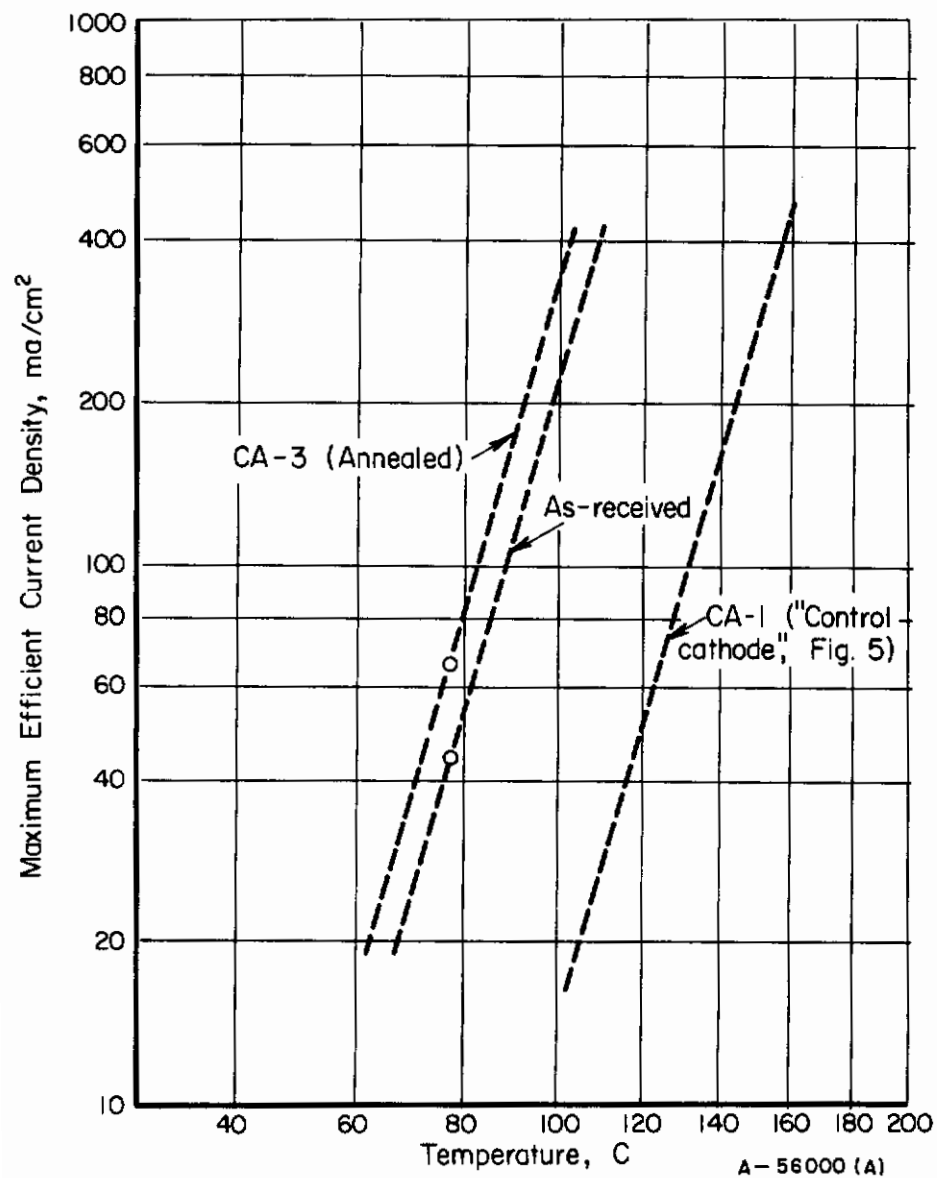


FIGURE 9. INFLUENCE OF VACUUM ANNEALING ON THE PERFORMANCE OF Pd-25Ag CATHODES

and 117 C for Treatment CA-1. Further evaluation of cathode pretreatments is required to verify that the initial performance can be maintained in extended operation. Cathode Pretreatment CP-1 involves heat treatment in air, and presumably would convert rhodium black to rhodium oxide. The latter might not be stable for long periods in the presence of hydrogen, or, alternatively, good performance might be obtained without oxidation of the rhodium black.

Figure 9 shows that vacuum annealing resulted in a small but definitive increase in rate constant (each MECD value represents duplicate tests).

A significant result shown by Figure 9 is that the small-diameter, as-received tubes performed well without any cathode treatment. Their performance was better than that of the large-diameter control cathode with Cathode Activation Treatment CA-1, as shown for reference in Figure 9. In the latter comparison, the difference in tube diameter (1.3 mm versus 6.3 mm) and difference in wall thickness (0.07 mm versus 0.13 mm) might be factors. However, the variation in the as-received tubes (i. e. , surface cleanliness) is believed to be an important factor. Thus, vacuum annealing might be considered a surface-cleaning treatment. Possibly, all as-received tubes should be vacuum annealed by Cathode Activation Treatment CA-3 to provide a reproducible base line for evaluating additional cathode treatments in future research.

ELECTROLYTE STUDIES

Introduction

The principal experimental efforts described in this section were directed toward resolving an electrolyte-contamination problem caused by impurities associated with the NaOH pellets used. Also, the influence of electrolyte concentration on H₂ transmission was investigated in the range of 50 to 60 percent NaOH. In addition to the NaOH-electrolyte studies, the feasibility of using phosphoric acid as electrolyte for a palladium-silver electrolysis unit was explored.

Electrolyte Purity

Six electrolyte preelectrolysis treatments were evaluated in the electrolyte-purity investigation. They are described below.

Treatment E-1. Preelectrolysis of 66 percent NaOH solution at 100 C for 24 hours at 60 ma/cm² (3 amperes), using platinum-gauze electrodes

Treatment E-2. Preelectrolysis of NaOH electrolyte at 70 C for 24 hours at 200 ma/cm² (5 amperes), using platinum-foil electrodes, and at the electrolyte concentration to be used in the subsequent evaluation

Treatment E-3. Preelectrolysis of 70 weight percent NaOH solution at 500 ma/cm² (5 amperes) and 150 C for 48 hours, using platinum-foil electrodes, followed by dilution to 50 weight percent concentration

Treatment E-4. Treatment E-3, plus further preelectrolysis for 24 hours at 500 ma/cm² and 50 C, using platinum-foil electrodes

Treatment E-5. Treatment E-4, plus further preelectrolysis for 72 hours at 40 ma/cm² (5 amperes) and 50 C, using Pt-10Rh-screen electrodes (80 mesh, 3-mil wire)

Treatment E-6. Treatment E-5, plus further preelectrolysis for 72 hours at 300 ma/cm² (5 amperes) and 50 C, using Pt-10Rh-screen electrodes (80 mesh, 3-mil wire).

Results and Discussion

Initially, chemical purity of electrolyte made up from reagent-grade NaOH pellets had not been a problem, since preelectrolysis was adopted as a standard procedure in electrolyte preparation. The usual procedure consisted of Treatment E-1, which was applied successfully to the electrolyte used in the "control" cell of the Extended Operational Run. In the early stages of the program, when it became desirable to work with other electrolyte concentrations (i. e. , Section IV, Cathode Treatments),

electrolyte Treatment E-1 was modified to Treatment E-2 for convenience. Treatment 2 saved a dilution step required by Treatment 1. Before the electrolytes treated by Treatment E-2 in the experimental work were introduced, the treatment was evaluated for effectiveness in a 24-hour test period on 50 percent NaOH solution. Conditions for the test were: 70 C, 6.35-mm-OD Pd-25Ag cathode tube given Cathode Activation Treatment CA-2, and a current density of 37 ma/cm². During the testing period, essentially 100 percent H₂ transmission was obtained, indicating that Treatment E-2 was satisfactory for use in the experimental work. Consequently, this preelectrolysis treatment procedure was applied to electrolytes throughout the major portion of the program. There was no adverse effect attributable to the electrolyte in extended operational tests of over 200 hours at 65 C.

However, in the last stages of the experimental work (i.e., Anode Studies, discussed in the next section), Treatment 2 was found to be inadequate for purifying electrolytes formulated from a new supply of NaOH pellets. Therefore, an investigation was initiated to establish a treatment procedure that would compensate for an apparent variation in purity.

The investigation was carried out in small-volume free-electrolyte cells of Experimental Cell C, using standardized conditions described in Section II. Electrolytes were treated in 1-liter batches in a large Teflon cell. After treatment, 40-ml samples of electrolyte were measured out for testing in Experimental Cell C. Treatments were evaluated by the number of continuous hours of satisfactory H₂ transmission obtained. Treatments were considered to have failed the tests when less than 95 percent H₂-transmission efficiency was recorded.

Table II summarizes the essential results of electrolyte-treatment investigation. In general, the results show (Tests 3B, 4D, and 5A) an apparently wide variation in purity of NaOH pellets that were obtained from three lots of two distributors (Allied Chemical Corporation and J. T. Baker Company).

TABLE II. SUMMARY OF ELECTROLYTE-PURITY EVALUATION

Test	Source of Pellets(a)	Electrolyte Treatment	Anode Material	Duration of Satisfactory H ₂ Transmission, hours
1A	A-Z080	E-2	Pt-10Rh screen	1
2A	A-Z080	E-3	Pt foil	27
2B	A-Z080	E-3	Pt-10Rh screen	1
3A	A-Z080	E-4	Pt foil	113
3B	A-Z080	E-4	Pt-10Rh screen	1
4A	A-V016	E-4	Pt foil	690
4B	A-V016	E-4	Pt screen	68
4C	A-V016	E-4	Pt-10Rh foil	234
4D	A-V016	E-4	Pt-10Rh screen	6
5A	B-32217	E-4	Pt-10Rh screen	64
5B	B-32217	E-5	Pt-10Rh screen	68
5C	B-32217	E-6	Pt-10Rh screen	2225

(a) Prefixes A and B designate source of pellets: Allied Chemical Corporation and J. T. Baker Chemical Company, respectively. The remaining figures are the lot numbers assigned by the manufacturer.

The most significant result noted was a substantially longer satisfactory H₂-transmission time for tests performed with foil anodes than for tests performed with anodes fabricated from screen. The duration of satisfactory H₂ transmission of test 4A (Pt foil) was 10 times longer than that of test 4B (Pt screen). The same results can be seen for other sets of comparable tests: 2A and 2B, 3A and 3B, and 4C and 4D. These results led to the conclusion that screen anodes accelerated the rate of cathodic deposition of contaminants that were apparently not removed in the preelectrolysis treatment. Thus, in further experimental work (Treatment E-5 and E-6), preelectrolysis was carried out with Pt-10Rh-screen anodes.

The effectiveness of preelectrolyzing with screen anodes can be seen by comparing Tests 5A and 5C, where the duration of satisfactory performance was increased from 64 hours to 2225 hours (and probably longer if the test had been continued). A comparison of Tests 5A and 5B shows that the additional preelectrolysis step with screen anodes at 40 ma/cm² (Treatment E-5) was not sufficient. The added step (Treatment E-6) of high-current-density preelectrolysis (300 ma/cm²) produced the significant improvement.

It is not known at this time whether all the consecutive steps involved in Treatment E-6 are necessary. In the experimental approach, the same batch of electrolyte for a given series was used for all tests in that series, the only difference being an additional electrolyte treatment. Preelectrolysis of a 1-liter batch of 50 weight percent solution at 300 ma/cm² (5 amperes) with Pt-10Rh-screen electrodes for 72 hours at 50 C is believed to be a sufficient treatment for caustic electrolytes. The experimental work also indicated that, in addition to a high current density, a low temperature and high solution concentration are desirable for deposition of some contaminants that are probably charged particles (i.e., slightly soluble contaminants that are organic in nature or are metal oxides). The suggested combination of conditions cause a high potential gradient to exist between the electrodes, thus facilitating their removal by electrophoretic deposition.

Electrolyte Concentration

In the investigation of electrolyte concentration, a new 6.35-mm-OD Pd-25Ag tube was activated by Cathode Activation Treatment CA-2 (anodically treated with HCl). After activating, MECD values were determined at temperatures of 61 C (77.5 ma/cm²) and 53 C (45 ma/cm²). The experimental work was carried out in Experimental Cell B, using 50 percent NaOH electrolyte and procedures discussed in Section II.

The temperature dependence of the determined rate constants is shown in Figure 10. The curve is compared with results obtained in the evaluation of Cathode Activation Treatment CA-2 (Section IV; shown in Figure 8). In the latter evaluation, 60 percent NaOH solution was used for electrolyte.

As can be seen in Figure 10, the rate constant was not affected significantly by the electrolyte concentration in the range of 50 to 60 percent. Further experimental work over a wider concentration range would be required to definitely rule out electrolyte concentration as a variable affecting MECD.

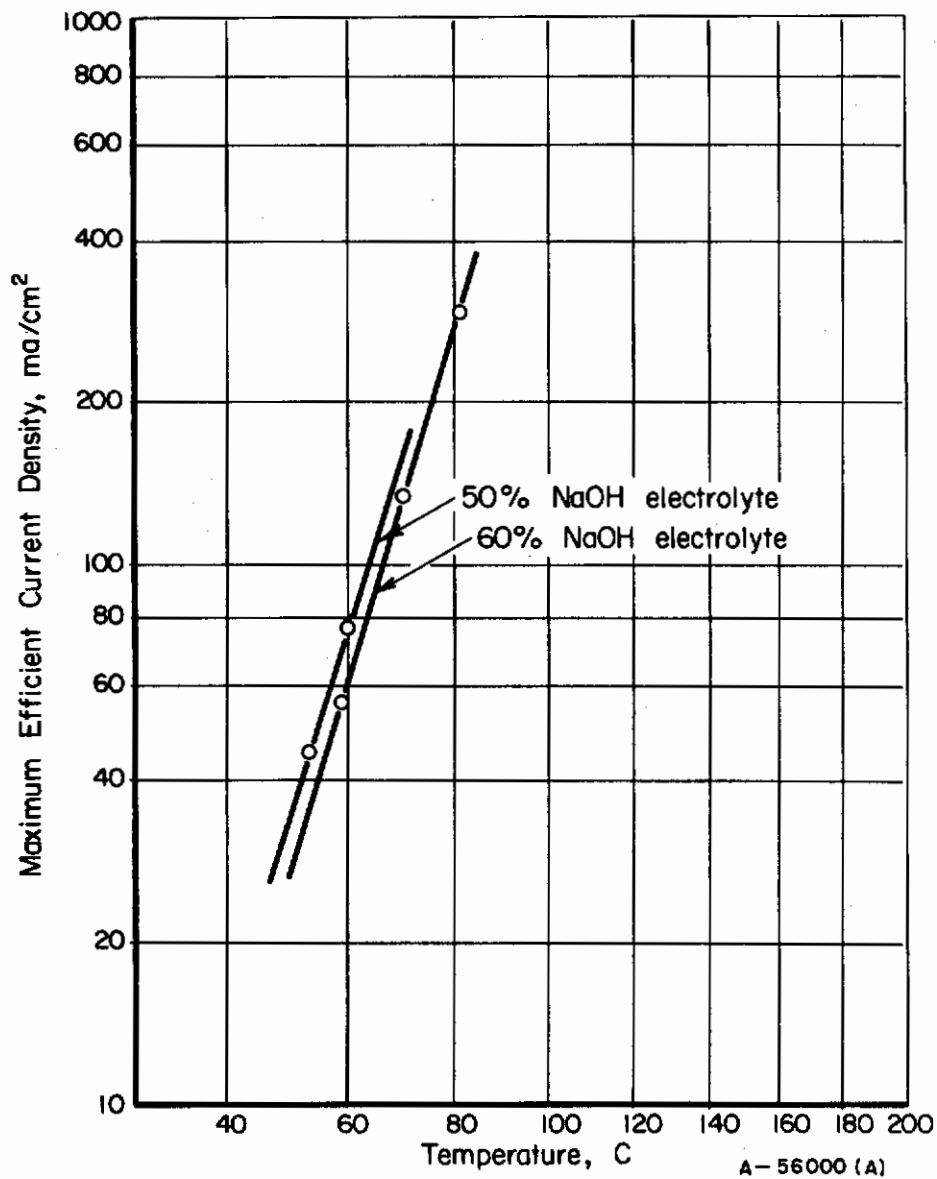


FIGURE 10. INFLUENCE OF ELECTROLYTE CONCENTRATION ON THE PERFORMANCE OF Pd-25Ag CATHODES

Electrolyte Composition

In the feasibility studies of phosphoric acid electrolyte, the experimental work was performed using untreated 85 percent solution (Baker reagent grade) in Experimental Cell B (Section II) at 60 C. A new palladium-silver tube (6.35-mm-OD) given Cathode Activation Treatment CA-2 was employed in the investigation. Prior to being electrolyzed in the acid electrolyte, the cathode tube was tested for H₂-transmission characteristics in 50 percent NaOH electrolyte at 37 ma/cm² and a cell temperature of 60 C. Essentially 100 percent transmission was obtained for a 1-hour period.

After the cathode was tested for activity, the tube was rinsed with water and electrolyzed in the phosphoric acid electrolyte for a 2-hour period. The applied current density was 37 ma/cm² (560 ma on a 7.6-cm length). Best H₂ transmission obtained during the run was about 73 percent, which actually was a steady-state value. The tube was subsequently removed from testing and the inside surface (gas-phase side) was palladized after which the cathode tube was again electrolyzed under the same conditions. The results obtained after palladizing were essentially the same as before pretreatment. A steady-state transmission value of about 73 percent was obtained in a 2-hour run.

After the above test, the outside surface (electrolyte side) was palladized and the cathode was again returned to testing under the same conditions. The second pretreatment resulted in obtaining essentially 100 percent H₂ transmission for a 4-hour period, after which time the run was terminated.

The run is considered a satisfactory demonstration of the feasibility of using phosphoric acid electrolytes with the palladium-silver hydrogen-diffusion cathode. The low initial H₂-transmission values obtained were suspected to be due to electrolyte contamination and that palladizing the outside surface of the cathode made available more active sites. In future experimental work, an electrolyte-purity program will be carried out on phosphoric acid solutions.

SECTION VI

ANODE-MATERIAL EVALUATIONIntroduction

Almost no effort was made in this program to find the anode material and configuration that would give the greatest reduction in anode overvoltage. To facilitate the experimental work, anode material was limited to bright-platinum screen, wire, or foil, which were shown in prior work to be adequate for avoiding electrolyte and cathode contamination. The use of pure platinum in the control cell of the extended operational run has shown that the metal is satisfactory for cell operations that exceed a year. However, pure platinum has the disadvantages of being expensive, not readily available in large quantities, relatively low in electrical conductivity, and characterized by a high oxygen overvoltage. This section describes experimental work initiated to uncover other possible anode materials that are compatible with the palladium-silver cathode in caustic electrolytes. Pure-gold screen and Pt-10Rh screen were investigated in Experimental Cell C using standardized testing procedures and conditions described in Section II. Efforts were directed toward establishing compatibility in relation to cathode contamination. In future work, in addition to screening other possible anode materials, consideration will be given to characterizing the overvoltage of promising anodes that are uncovered.

Platinum-10 Rhodium Alloy

Platinum-10 rhodium screen (80 mesh, 3-mil wire) was shown to be a satisfactory anode in the electrolyte purity investigation discussed in Section V (Test 5C, Table II). Under the standardized test conditions, the material performed satisfactorily for 2225 continuous hours. Anodes fabricated from this alloy were expected to be dependable in cells designed for extended operations. As compared to pure platinum, Pt-10Rh screen is more readily available (because of wide use in nitric acid manufacture) and is less expensive. However, it has a slight disadvantage of lower electrical conductivity (i. e., about half that of pure platinum).

Pure Gold

Results of the standardized test with pure-gold, 80-mesh screen anode showed anodic dissolution with subsequent cathodic deposition as evidenced by a gold deposit on the surface of the palladium-silver cathode. In the tests, a H₂ transmission efficiency of only 44 percent was obtainable 6 hours after initiating electrolysis. The run was terminated 14 hours later when no H₂ transmission could be detected at all. Thus, gold is ruled out as an anode material in palladium-silver electrolysis cells using caustic electrolytes.

MATRIX-MATERIAL EVALUATIONIntroduction

In prior work⁽²⁾ satisfactory operation of the Pd-25Ag cathode had been demonstrated in the temperature range of about 140 to 230 C. Considerable effort had been devoted to finding a suitable matrix for use in that temperature range. The best result demonstrated was a 24-hour run at 80 ma/cm² and 145 C with the "Teflon/Ca(OH)₂" matrix. The matrix consisted of a mechanical mixture of Teflon threads (machined from a solid block of Teflon) and Ca(OH)₂^{*}, initially impregnated with 76 percent NaOH and wrapped around the cathode tube with a 45-mesh, 7.5-mil-wire platinum-screen anode.

The development of a satisfactory matrix for extended high-temperature operation is a difficult problem. Some compromise between high-temperature operation (favored for low cell voltage) and long operating life appeared possible, depending on the application of the matrix-type cell. Two potentially different applications were recognized from concurrent projects at Battelle on integrated oxygen-recovery systems.

One study⁽³⁾ involved integration of the matrix-type electrolysis cell with the Sabatier reaction (i.e., CO₂ hydrogenation catalyst inside Pd-25Ag tube). Operation at about 200 C was required, and the only matrix available for consideration was Teflon/Ca(OH)₂. The evaluation of this matrix for the first time at 200 C was conducted in conjunction with these studies⁽³⁾ and is reviewed in this section of this report under "High-Temperature Matrix Evaluation", covering the temperatures above approximately 150 C.

The other concurrent study at Battelle involved integration of the matrix-type electrolysis cell with the Bosch reaction for CO₂ reduction. Operation of the matrix-type cell at high temperature was not essential. Also, consideration of the matrix cell as a water-electrolysis cell independent of the source of water used for vapor did not indicate any absolute requirement for high-temperature operation. Therefore, as knowledge was gained that would permit satisfactory operation of the Pd-25Ag cathode at lower temperatures, the evaluation of matrix materials was carried out at lower temperatures to enlarge the scope of materials that could be considered. The results of the matrix evaluations are covered in this section under "Low Temperature Matrix Evaluation", covering the temperatures under 150 C and as low as 60 C.

The immediate objective of the research was a matrix that at any temperature would provide reasonable life. A tentative goal of 1000 hours of satisfactory operation of a matrix-type cell was adopted. Future experimental goals were to be directed toward matrices with reasonable life for operation at higher temperature or with favorable physical properties that would result in lower cell voltage and/or more stable operation with water-vapor feed. The latter goals remain for future research, since the best matrix developed during this program indicates an operational life only one-quarter of the way to the 1000-hour goal, but a tenfold improvement over prior results.

^{*} Prepared by mixing CaO with Teflon threads, and presumed to form relatively insoluble Ca(OH)₂ when impregnated with electrolyte.

High-Temperature Matrix Evaluation

A high-temperature experimental run (200 C) with a Teflon/ $\text{Ca}(\text{OH})_2$ matrix was performed in Experimental Cell D, described in Section II. The matrix was fabricated from a Teflon-wool mat and reagent-grade $\text{Ca}(\text{OH})_2$ powder. Application of the matrix consisted of spreading a thin layer of $\text{Ca}(\text{OH})_2$ powder (~ 0.5 mm thick) over a pad of matted Teflon threads (~ 1.5 mm thick), and rolling the mat around a 6.35-mm-OD Pd-25Ag tube that was previously activated by Cathode Activation Treatment CA-2. Application of an 80-mesh, 3-mil platinum-screen anode held the matrix together and in place. (The use of 80-mesh, 3-mil wire, platinum screen rather than 45-mesh, 7.5-mil wire was not considered a significant design change.)

Matrix-cell operation at about 200 C had not been attempted previously. A water-vapor feed at a partial pressure above 760 mm Hg was required for operation at 200 C. The electrolysis unit was designed for study of total pressure (oxygen plus water vapor) up to 1500 mm Hg (gage). A high pressure on the anodic side minimizes the amount of water removed with the product oxygen that would have to be separated and recycled.

In the experimental run, a current of 750 ma provided a current density of 37 ma/cm² on a 10-cm length of the cathode. The electrolysis unit was maintained at 200 C, and water vapor was supplied initially by a static system. With the water-vapor generator set at 100 C, the water-vapor pressure was 1075 mm Hg (absolute). The electrolyte concentration in the matrix that exists at steady-state conditions is not known. If the concentration remained at the value of initial impregnation (76 percent NaOH), the water-vapor pressure of the electrolyte would be 975 mm Hg at the cell temperature of 200 C, which would mean a driving force of about 100-mm Hg differential water-vapor pressure.

During the first 3 hours of operation, 100 percent H_2 transmission was obtained with the total electrolysis-unit pressure at 1065 mm Hg (mostly water-vapor pressure). The expected increase of cell pressure as oxygen accumulated was not obtained because the unit leaked. Overnight, the pressure decreased to 812 mm Hg because of leakage, and the H_2 transmission decreased to 89 percent because of drying out of the matrix and possible solidification of the electrolyte.

After the fittings around the cathode tube were tightened, the unit pressure increased from 1020 to 1380 mm Hg, and the H_2 transmission increased to a value of 100 percent, which was maintained for the next 7 hours.

Operation was continued over a weekend, and measurement 64 hours later showed the H_2 transmission to be about 50 percent, with the unit pressure at 960 mm Hg because of leakage. The fittings were again tightened so that the unit pressure increased to 1065 mm Hg, and the H_2 transmission increased to 100 percent, which was maintained for 4 hours. The run was then terminated to modify the water-electrolysis unit.

The total operating time for the above run of the water-electrolysis unit was 100 hours, and there was no evidence of permanent poisoning of the Pd-25Ag-tube cathode with the Teflon/ $\text{Ca}(\text{OH})_2$ matrix. A total of 14 hours of satisfactory operation at 100 percent H_2 transmission was obtained when adequate water-vapor pressure was maintained (i.e., 1050-mm Hg partial pressure of water for electrolysis-cell operation at 200 C and 37 ma/cm²). The cell voltage was 1.9 to 2.1 volts during periods of normal

operation. Polarization to 2.5 to 3.0 volts and partial loss of H_2 transmission occurred when the matrix was deficient in water. Normal operation of the electrolysis cell was resumed when adequate water-vapor feed was restored.

The electrolysis unit was modified to incorporate a dynamic water-vapor feed. Nitrogen was used as the carrier gas for experimental studies. With nitrogen bubbled through the water-vapor generator, both the nitrogen flow rate and water temperature could be used to control the water-vapor feed to the electrolysis unit.

During a subsequent checkout of the water-electrolysis unit, a leak developed at the connection to the Pd-25Ag tube cathode so that nitrogen and water vapor entered the inside of the tube with hydrogen. Further modification of the electrolysis unit is required to provide pressure-tight seals for operation at 200 C with a positive pressure on the water-vapor-feed circuit.

Further study of the Teflon/ $Ca(OH)_2$ matrix at 145 C is covered below.

Low-Temperature Matrix Evaluation

Introduction

Low-temperature matrix evaluations were performed in Experimental Cells C (free-electrolyte cell), E, and F (vapor-fed cells). Techniques of operating the cells and descriptions of them appear in Section II. Experimental Cell C was introduced to the program to devise a screening-type testing procedure that would emphasize matrix contamination while being independent of a separate design problem of water-vapor feed to the matrix. The latter problem was experienced in a few tests made in both vapor-fed cells Experimental Cells E and F).

In the experimental work following a cathode treatment (identified in Table III for each test and discussed in Section IV), the cathode tube was tested for activity by electrolyzing it cathodically for a 2-hour period under the same conditions to be used in the matrix-evaluation test (also given in Table III). The matrix and anode screen were then applied, after which the unit was soaked in electrolyte at the testing conditions for a 1-hour period to saturate the matrix.

The results of tests with matrices evaluated at low temperature are listed (in Table III) in chronological order and are discussed below.

Teflon/ $Ca(OH)_2$

The Teflon/ $Ca(OH)_2$ matrix was operated successfully in Experimental Cell E for 100 continuous hours at 37 ma/cm² and 145 C. After this time, H_2 -transmission efficiency began to decrease. Satisfactory H_2 transmission could be restored by lowering the current density. The run was subsequently extended an additional 44 hours with satisfactory operation at 20 ma/cm², after which the run was terminated. Termination was caused by loss of electrolyte by dilution of the electrolyte- $Ca(OH)_2$ mixture, which flowed down from the Teflon mat under the influence of gravity.

TABLE III. SUMMARY OF MATRIX-EVALUATION TEST

Material	Matrix Classification and Source	Thick- ness, mm	Cathode Treat- ment(a)	Conditions(b)			Testing Time, hour		Suspected Cause of Failure
				Experimental Cell	Electrolyte Impregnation, wt % NaOH	Temperature ±5 C	Current Density ma/cm ²	Cell Voltage, volts	
Teflon/ CaOH ₂	Machined teflon threads (0.08 mm diameter), reagent grade calcium oxide	1.5	CA-1	E	66	145	32/20	2.0-2.7	Overdilation of electrolyte in matrix
								Total	
								168	
								100 (37 ma/cm ²) 44 (20 ma/cm ²)	
Fuel-cell asbestos, Test A	Type SL-15, Johns-Manville	0.5	CA-1	E	66	135	37	2.1	Matrix deterio- ration
								17	
								15	
Al ₂ O ₃ -Foam ALSIMAS No. 614, Style 0.013, Ameri- can Lava Corporation		1.5	CA-1	E	66	135	37	3.1	Catalytic burn- ing in void areas in matrix
								48	
								3	
Cotton	Style M1165, Webull	0.4	CA-1	E	66	130	37	1.8	Matrix deteri- oration
								6	
								4	
Al ₂ O ₃ - Sapphire, Test A	"Sapphire Whisker Paper" Type 1-C, Thermo- kinetic Fiber	0.3	CP-1	E	40	65	37	2.2	Matrix deteri- oration
								500	
								32	
Al ₂ O ₃ - Sapphire, Test B	Ditto		CA-2	F	50	65	7-37	2.3	Matrix deteri- oration
								432	
								240	
PVC, Test A	Microporous polyvinyl- chloride, Electric Storage Battery Company	0.3	CA-2	F	50	65	37	2.4	Matrix deteri- oration
								228	
								216	
PVC, Test B	Ditto		CA-3	C	50	70	37	2.2	Matrix deteri- oration
								197	
								185	
Fuel cell asbestos, Test B	Same as Test A		CA-3	C	50	70	37	2.1	Matrix deteri- oration
								310	
								281	

(a) Used 6.35-mm-OD Pd-25Ag cathode tube in tests performed in Experimental Cells E and F; in tests performed in Experimental Cell C, a 1.6-mm-OD cathode tube was employed.

(b) An 80-mesh, 3-mil wire, platinum screen was used for anodes in tests performed in Experimental Cells E and F; a solid, cylindrical platinum anode was used in tests performed in Experimental Cell C.

A check of the cathode tube made after the run indicated that the tube was capable of transmitting hydrogen satisfactorily at 37 ma/cm² and at 145 C in 66 percent electrolyte. Thus, the problem of a Teflon/Ca(OH)₂ matrix appears to be of a physical nature (nonwettability of Teflon and absence of sufficient capillary forces to hold electrolyte).

Since the Teflon/Ca(OH)₂ matrix is the only one found that does not appear to poison the cathode at temperatures up to 200 C for several hundred hours and possibly longer, it remains a prime candidate. Future study of this type matrix, with emphasis on more precise water-vapor-feed control, is warranted.

Fuel-Cell Asbestos

Test A (135 C). High-purity white asbestos (designed for fuel-cell use) was successfully run for 15 continuous hours at 37 ma/cm² and a cell temperature of 135 C in Experimental Cell E. After this period, H₂-transmission efficiency began to decrease, and the run was terminated 2 hours later. Testing of the cathode tube after the run indicated that the surface of the cathode was poisoned. Also, a visual inspection of the matrix showed that it was deteriorating, as evidenced by a reddish-green substance dispersed throughout the matrix.

Fuel-Cell Asbestos

Test B (70 C). The second fuel-cell-asbestos evaluation was performed in Experimental Cell C using the standardized conditions. Satisfactory H₂ transmission was obtained for 281 continuous hours at the 70 C electrolyte temperature and 37 ma/cm². Examination of the cathode after the run showed that failure was due to cathode contamination. The run represents the best results obtained for continuous operation in low-temperature testing at the desired current density of 37 ma/cm².

Polyvinylchloride

Test A. The best results obtained at the desired current density and under water-vapor-feed conditions was with a microporous polyvinylchloride (PVC) matrix tested in Experimental Cell F. Satisfactory H₂ transmission was obtained for 216 continuous hours at a current density of 37 ma/cm² and 65 C. The run was terminated when the cell was inadvertently flooded by a high partial pressure of water-vapor feed. When this situation was corrected and the matrix was reimpregnated with electrolyte, further electrolysis did not result in satisfactory H₂ transmission. Testing of the cathode tube after termination of the run indicated that the surface (electrolysis side) of the cathode was poisoned.

As received, the PVC matrix material had already been treated with an amine reagent to improve wettability. The posttreatment reagent may have caused the poisoning, and the flooding may have been coincidental to loss of transmission. However, because of the mode of failure, and in view of the fact that the duration of transmission obtained with the PVC matrix was a milestone for matrix-type cells operating at 37 ma/cm², the PVC matrix material was evaluated further in Experimental Cell C.

Test B. In the second test of a PVC matrix, satisfactory H_2 transmission was obtained for 185 continuous hours at the standardized conditions used with Experimental Cell C (i.e., 37 ma/cm², 70 C, and 50 percent electrolyte). Testing of the cathode tube after termination of the run indicated that failure was caused by poisoning of the cathode surface. The experimental data are considered to be in good agreement with PVC Test A (216 hours of satisfactory electrolysis at 65 C, performed in vapor-fed Experimental Cell F). The correlation indicates that matrix-screening results in the small-volume, free-electrolyte test are indicative of results that can be expected in a water-vapor-fed cell.

Al₂O₃-Foam

Since the Al₂O₃-foam matrix was hand shaped from a solid block, it was difficult to obtain a close fit. However, the matrix was run satisfactorily for a 3-hour period at 37 ma/cm² and 132 C in Experimental Cell E, after which time H_2 transmission efficiency began to decrease. The run was terminated 45 hours later. No cathode poisoning could be detected when the tube was tested after the run. Low H_2 transmission was probably due to catalytic burning in exposed areas on the surface of the cathode.

Al₂O₃-Sapphire

Test A. The Al₂O₃ "sapphire-whisker paper" matrix did not cause poisoning of the cathode after 500 hours of experimental testing in Experimental Cell E at 65 C and with 40 percent electrolyte. However, during the extended run, acceptable H_2 transmission could be obtained only in 2- to 8-hour continuous periods (total 32 hours). Control of electrolyte volume in this matrix was difficult with a water-vapor feed (some flooding conditions, but mostly undersaturation with subsequent loss of H_2 -transmission efficiency). The material was readily wettable by electrolyte, and the apparent stability encouraged further evaluation in Experimental Cell F.

Test B. The second Al₂O₃ sapphire-whisker paper matrix evaluation was performed in Experimental Cell F at 65 C. Satisfactory H_2 transmission was obtained for 240 continuous hours; the cell current was gradually increased toward 37 ma/cm² during the run while water-vapor feed was controlled. However, after satisfactory H_2 -transmission had been obtained for only 8 hours at the desired current density of 37 ma/cm², H_2 -transmission efficiency gradually began to decrease, and after 432 hours the experimental run was terminated. During the 240 hours of acceptable H_2 transmission, the average current density was about 20 ma/cm². Failure was attributed to cathode poisoning caused by chemical attack of the caustic electrolyte on the sapphire-whisker paper (Al₂O₃) matrix. Subsequent testing of the cathode showed that acceptable H_2 transmission could be obtained only after the surface of the cathode was abraded with crocus cloth.

Cotton

A matrix fabricated from cotton was successfully run for a 4-hour period in Experimental Cell E, after which the run was terminated because of loss of

H₂-transmission efficiency. Testing conditions were 37 ma/cm², 66 percent electrolyte, and 130 C. Visual inspection of the matrix after the run showed that the cotton matrix was disintegrating. Also, a test of the cathode tube for H₂ transmission indicated that its surface was poisoned.

ADDITIONAL DESIGN FEATURESIntroduction

The experimental efforts described in this section of the report concern an investigation of some unique features of the palladium-silver hydrogen-diffusion cathode that are pertinent to the design and operation of a laboratory-model electrolysis cell. The investigation includes: a measure of the dimensional change that occurs when a Pd-25Ag cathode is charged with hydrogen; the effect that a Pd-25Ag cathode would have on overall cell operation if the cathode were operated above the maximum efficient current density; and the influence of hydrogen partial pressure (gas-phase side) on the diffusion process of a Pd-25Ag cathode.

Dimensional Change of Charged Cathode

The expansion of cathodically charged Pd-25Ag tube was investigated for cell-design purposes. The work was directed toward establishing the dimensional change of small-diameter tubes which appeared suitable for use in constructing experimental laboratory-model electrolysis cells. In the experimental work, two 1.6-mm-OD by 0.076-mm-wall by 13.3-cm-long Pd-25Ag tubes were measured before and after electrolysis. Electrolysis was performed at 37 ma/cm^2 for a 2-hour period in Experimental Cell B using 50 percent NaOH electrolyte at 60 C. The tubes were activated by Cathode Activation Treatment CA-3 (vacuum annealing). Essentially 100 percent H_2 transmission was obtained during the 2-hour electrolysis period.

The experimental results showed that the small-diameter tube elongated about 0.2 mm/cm length (~ 2.6 mm total) and swelled 0.04 mm on the diameter. Electrolysis units designed with Pd-25Ag tubes must allow for cathode expansion to prevent buckling (i. e. , one free end with sufficient clearance).

 H_2 Transmission Above the MECD

The relationship of applied cathode current density and percent H_2 transmission above the MECD was investigated with a small-diameter Pd-25Ag cathode. The objective of the investigation was to establish the effect that a Pd-25Ag cathode would have on overall cell operation if the current density for 100 percent H_2 transmission were exceeded. The investigation was carried out with Experimental Cell B at 77 C and with 50 percent NaOH electrolyte, and was performed with one of the small-diameter tubes used to evaluate Cathode Activation Treatment CA-3 of the vacuum-annealing studies (Section IV). After the MECD of the annealed tube was established in the vacuum-annealing studies, a current density of 270 ma/cm^2 was applied, and the H_2 transmission was measured until two equivalent 5-minute hydrogen collections were recorded. Subsequent H_2 -transmission values were obtained at incremental decreases in current density until 100 percent H_2 transmission was measured (the MECD value for 77 C).

Results of the experimental test showed that H_2 -transmission efficiency decreased slowly for up to a twofold increase in current density over the MECD. Thereafter, the efficiency decreased at a faster rate as the applied current density was increased. This is shown in Table IV. The data suggest that operation of a small-diameter cathode slightly above the MECD might not have an adverse effect on overall cell operation.

TABLE IV. HYDROGEN TRANSMISSION ABOVE THE MECD

Conditions: 50% NaOH electrolyte; 77 C

Applied Current Density, ma/cm ²	H ₂ Transmission, percent
65 (MECD)	100
123	97.3
147	95.8
172	94.0
196	91.6
221	89.3
270	84.3

Influence of H₂ Partial Pressure

In investigating the influence of H_2 partial pressure on the diffusion process of a palladium-silver cathode, the temperature dependence of a large-diameter cathode given Cathode Activation Treatment CA-2 was established for the conditions 50 percent NaOH electrolyte and 1-atmosphere H_2 partial pressure. The effluent hydrogen of the cathode tube was then restricted through a valve arrangement until a constant pressure of about 1.8-atmospheres absolute pressure was obtained. A rate constant of 44 ma/cm² was then determined for a 56 C electrolyte temperature at the applied pressure.

The result of the investigation is illustrated in Figure 11. At the 56 C temperature and 1.8-atmospheres pressure, the MECD was lowered only about 6 ma/cm². Operation was continued to verify that 100 percent H_2 transmission can be maintained under steady-state conditions while a pressure is applied on the gas-phase side of a palladium-silver cathode. A satisfactory 3-hour run was made at 37-ma/cm² current density with 2.1-atmospheres absolute H_2 pressure while an electrolyte temperature of 58 ± 2 C was maintained (conditions slightly below the MECD). During the run, essentially 100 percent H_2 transmission was obtained. Recent specifications for the water-electrolysis unit for the Integrated Life Support System at NASA Langley Research Center require delivery of product gases at 1 atmosphere (presumably to feed the Bosch reactor). With a hydrogen-diffusion cathode, pure, dry hydrogen can be delivered by the electrolysis cell at up to 1 atmosphere (gage) for metering directly to the Bosch reactor without a pump and relatively independent of O_2 pressure.

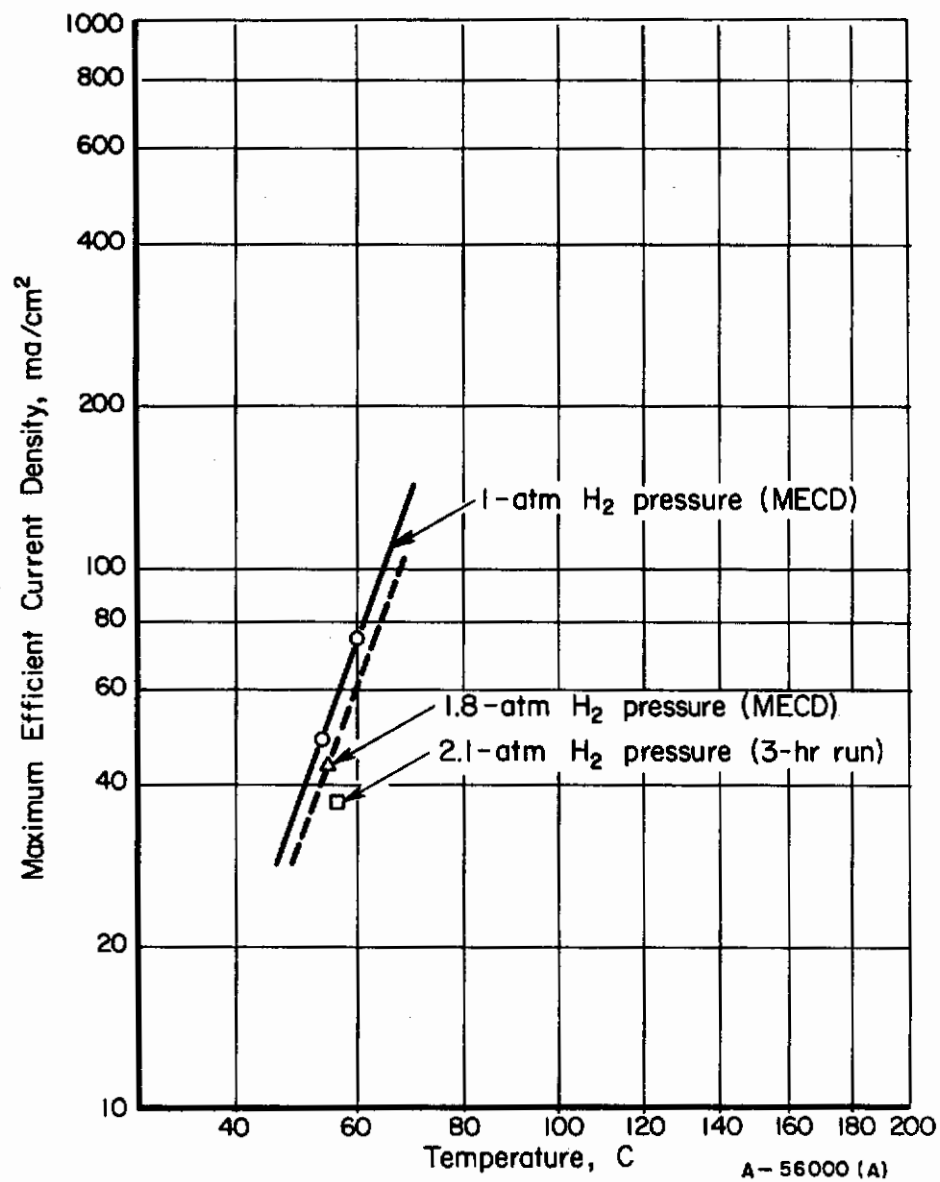


FIGURE 11. INFLUENCE OF HYDROGEN PARTIAL PRESSURE ON THE PERFORMANCE OF A Pd-25Ag CATHODE

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13. ABSTRACT <p>The feasibility of extended operation of palladium-silver alloy hydrogen-diffusion cathodes was demonstrated by essentially 100 percent hydrogen transmission for 486 days of operation at the following experimental conditions: 6.35-mm-OD x 0.013-mm-wall Pd-25Ag cathode tube at 37 ma/cm²; free electrolyte cell with 22 ml of 60 percent NaOH at 145 C; cell voltage of 1.74 ± 0.03 volts with solid cylindrical platinum anode. The determination of the maximum efficient current density (MECD) as a function of temperature indicated that satisfactory operation in the above run could have been obtained at temperatures as low as 112 C; 53 C with new cathode-activation treatments; or 30 C with rhodium treatment of the cathode. In addition to platinum, platinum-10 rhodium alloy was shown to be a satisfactory anode material, but not gold. The feasibility of producing hydrogen gas at a pressure 15 psi higher than oxygen with only a slight decrease in MECD was demonstrated. New electrolyte preelectrolysis procedures were developed to counteract apparent purity variations in reagent-grade NaOH pellets. Of a number of possible matrix materials investigated, the longest satisfactory operation was obtained with fuel-cell asbestos: 280 hours at 70 C and 37 ma/cm², but only 15 hours at 135 C. The feasibility of using a free electrolyte of phosphoric acid was demonstrated in a 4-hour run at 37 ma/cm² and 60 C.</p>			

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