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PORE SIZE, ZINC PENETRATION, AND ZINC DIFFUSION STUDIES ON PPQ/CA SEPARATORS

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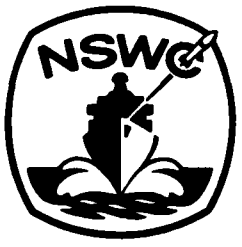

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(U) Studies were performed of some properties of co-polymeric polyphenylquinoxaline/cellulose acetate (PPQ/CA-60/40) membranes that are candidate separator materials for secondary alkaline batteries. Pore size measurements were obtained by bubble pressure, mercury porosimetry and electron microscopy methods. Zinc penetration measurements and measurements of zinc ion diffusion through the membrane were obtained in aqueous potassium hydroxide media using standardized electrolysis methods. For comparison purposes,

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dendrite penetration and zinc diffusion measurements were also obtained for two conventional cellulosic separator materials. It was concluded that the methods chosen are valid and useful for assessing the quality of separator materials. It was also concluded that PPQ/CA-60/40 membranes compare favorably with conventional separator materials.

FOREWORD

This report documents the results of studies of the properties of a new membrane separator material for aqueous alkaline secondary batteries, a co-polymer of polyphenylquinoxaline and cellulose acetate. The studies were undertaken as a part of the development of improved separators for secondary silver oxide-zinc and nickel oxide-zinc batteries. The studies described are a significant contribution to the basic technology of secondary batteries for Navy applications. Funding support was provided by NAVSEASYSCOM, Task Number 62543N/SF43431302/1R33JE701.

J. R. DIXON
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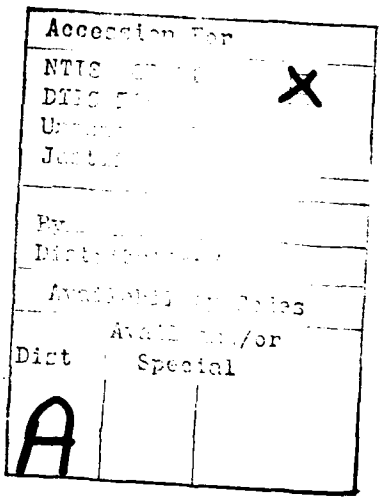

PREFACE

The development of improved separators for alkaline battery systems requires that the new membranes be fully characterized by investigating their properties under certain conditions. In this technical report, we describe pore size, zinc penetration, and zinc diffusion studies on polyphenylquinoxaline/cellulose acetate (PPQ/CA) separators for the purpose of establishing a data base on their physical characteristics.

The characteristics of the new separator material are compared to state-of-the-art materials to determine whether or not it has the desirable properties for use as a separator in secondary alkaline batteries.

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CHAPTER 1

PORE SIZE DETERMINATION

BACKGROUND

In the process of characterizing separator materials, pore size determinations are one of the most important because pore size could be an effective factor in determining migration rates on large ion and colloidal particles. Both ions and colloidal particles can exist in the electrolyte of the silver-zinc battery due to the limited solubility of zinc oxide and silver oxide.

There are several independent methods for obtaining data concerning the nature of membrane pores[1]:

1. The bubble - pressure (Blasendruck) technique.
2. The Hagen - Poiseuille or solvent permeability method.
3. Direct observation with standard and scanning electron microscope.

In this chapter we will concentrate on methods 1 and 3.

1. The Bubble - Pressure (Blasendruck) method

Bechhold[2] first evaluated pore size by measuring the pressure necessary to blow air through a water-filled membrane. He employed Cantor's relationship[3]

$$r = \frac{2\sigma}{P} \qquad (1\text{-}1)$$

where r = radius of capillary
σ = surface tension (water/air)
P = pressure

[1]Kesting, R. E., Synthetic Polymeric Membranes (New York: McGraw-Hill Book Co., Inc., 1971).

[2]Bechold, H., "Porosity of Ultra Filters," Z. Physik. Chem., Vol. 64, 1908, pp. 328-42.

[3]Cantor, M., "Surface Tension Effects on Capillary Radius," Ann. Physik. (N.F.), Vol. 47, 1892, pp. 399.

In practice a filter apparatus is placed upside down so that air can impinge on the membrane from beneath. Bubbles of air are then observed as they penetrate the membrane into an overlying layer of water.

Because the larger pores open at lower pressures, this method tends to yield high values. This weakness, however may be used to advantage in qualitatively estimating the pore-size distribution. If the number of pores which are permeable to air increases substantially with only a small increase in pressure, a narrow pore-size distribution is indicated. On the other hand, a gradual increase in the number of air-permeable pores is indicative of a broad pore-size distribution. The bubble-pressure method is strictly valid when the imbibed medium completely wets the membrane and when the ratio of the pore diameter to that of the permeant species is large. As this ratio diminishes, the validity of Eq(1-1) decreases particularly when there is interaction between the permeant species and the membrane. Moreover, because of the high water/air surface tension of 73 dynes/cm, narrow pores require a relatively high pressure before air will permeate. High pressures in turn cause plastic flow in the membranes which results in pore-size shrinkage in a time dependent manner. In recognition of these difficulties Bechhold, Schlesinger and Silbereisen[4] modified Bechhold's original bubble-pressure method by reducing the interfacial tensions between the imbibed and penetrating media. While the earlier system consisted of water as the imbibed and air as the penetrating medium, a new system using an isobutyl alcohol-water interface was chosen (for application to collodion membranes) in which the surface tension varied from 1.61 dynes/cm at 3°C to 1.80 dynes/cm at 37°C. This new system permitted the measurement (at a given pressure) of pores which were smaller by a factor of 40 than those measured by the original bubble-pressure technique. The concept is, of course, applicable to other than nitrocellulose membranes. In general, it is preferable to utilize as the imbibed medium that liquid which exhibits the lower contact angle with the membrane, i.e., that which more rapidly wets the membrane. To render observation of the droplets of the penetrating liquid possible, there should also be a substantial difference between the indices of refraction of the two liquids.

A weakness of the bubble-pressure method is that the r values obtained vary with the rate of pressure increase.[4-6] The values of the largest pore, i.e. those which become permeable first and at the lowest pressure, decrease with increasing rate of pressure. Furthermore, those values decrease with

[4]Bechhold, H. et al, "Pore Diameters of Ultrafilters," Kolloid-Z., Vol. 55, 1931, pp. 172-98.

[5]Knoll, H., "Capillary Systems at the Boundary Surface Gas-Liquid," Kolloid-Z., Vol. 86, 1939, pp. 1-11.

[6]Knoll, H., "Method for Determining the Maximum Pore Size of Filters," Kolloid-Z., Vol. 90, 1940, pp. 189-94.

increasing capillary length, increasing viscosity and decreasing interfacial tension. To eliminate these possible sources of error, Schlesinger[4] developed the relationship:

$$r = \frac{20}{P}\left(1 + \frac{21}{\sigma}\right) A \frac{n_1 + n_2}{2} \qquad (1\text{-}2)$$

where l = length of capillary
$A = dP$
n_1 = viscosity of imbibed phase
n_2 = viscosity of penetrating phase

Therefore, for a given system, by varying the rate of pressure increase both pore radius and length can be determined. The pore radii which are determined by this method lie between the maximum and the average values.

Instruments are now commercially available which utilize a variation of the bubble-pressure technique known as the MERCURY-intrusion Method. Equation (1-1) is modified to take into account the contact angle θ (mercury/membrane).

$$r = \frac{-2\sigma \cos\theta}{P} \qquad (1\text{-}3)$$

A membrane is placed in a porometer chamber, and pressure is applied, thereby forcing mercury into the pores. It is assumed that all void space is full at the highest pressure (usually about 75 atm). This assumption of course is valid only for cases in which all the voids are of the open-cell variety. From the weight of the membrane at the lowest and higher pressures, bulk densities are obtained from which the void volume (porosity) can be obtained by difference.

ELECTRON MICROSCOPY

The first two attempts to study membrane ultrastructure by electron microscopy were those of von Ardenne and Pietsch.[7-8] Helmcke[9-10] subsequently developed the carbon and metal shadowing techniques which made more exact studies possible. His studies showed that commercially available cellulosic membranes (e.g., Gelman, Millipore and Sartorius) are cohesive systems consisting of open celled foams, i.e. vacuoles with breached walls.

[7]Pietsch, H., "Membrane Ultrastructure Using Electron Microscopy," Naturwiss., Vol. 36, 1949, p. 250.

[8]Ardenne, M. V., Elektronen Ubermikroskopie, Physik-Technik-Ergebnisse (Berlin: J. Springer, 1940).

[9]Helmcke, J. G., "Metal Shadowing in Electron Microscopy," Zentr. Bakterial, Vol. 159, 1953, p. 308.

[10]Helmcke, J. G., "Carbon Shadowing in Electron Microscopy," Optik, Vol. 10, 1953, p. 147.

Electron microscopy and recently scanning electron microscopy[11] have provided the physical basis for understanding the causal relationships between cellular structure and resistance to material transport. Besides providing otherwise inaccessible information about membrane structure, electron microscopy can furnish more detailed and unequivocal pore statistics than any other method. With the advent of electron microscopy, the assumption that pores consist of cylindrical capillaries was shown to be the exception rather than the rule. The void structure of most polymer membranes must be visualized on the colloidal level where "pores" are seen as irregular passages through openings between neighboring cells.

EXPERIMENTAL

The mercury porosimetry study was done on a MICROMERITICS Model 905-2, 0-50,000 psia porosimeter. The bubble-pressure and electron microscope determinations were done by Nuclepore Corporation at Pleasanton, California. The membranes were prepared according to our previous report.[12]

RESULTS AND DISCUSSION

The results of all determinations are summarized in Table 1-1.

TABLE 1-1. PORE DIAMETERS OF PPQ/CA SEPARATORS

METHOD	SOLVENT	PORE DIAMETER, MICRONS
Bubble pressure	Water	0.34
Bubble pressure	Isopropanol	0.38
Mercury porosimetry	N/A[a]	0.23

a. N/A = Not Applicable

Using equation (1-3) one can calculate the pore diameter with water and isopropanol as the solvent. The bubble point measurements were 32 psi with isopropanol and 62 psi with water. The contact angle with water was 58-63°, and with isopropanol was assumed to be zero. The pore diameters are then calculated:

For isopropanol σ = 21 dynes/cm

$$d = \frac{(4)\ (21)\ (1)}{(32)\ (68947)} = 3.8 \times 10^{-5} \text{cm}$$

[11] Kesting, R. E., "Role of Formamide in the Preparation of Cellulose Acetate Membranes by the Phase Inversion Process," Kolloid-Z. Z. Polymere, Vol. 230, 1969, pp. 341-6.

[12] Angres, I., "Battery Separator from Polyphenylquinoxaline Polymer Blends," NSWC/WOL TR 78-56, April 1978.

$$d_{isopropanol} = 0.38\mu$$

For water

$$\sigma = 72 \text{ dynes/cm}$$

$$d = \frac{(4)(72)\ (0.5)}{(62)\ (68947)} = 3.4 \times 10^{-5} \text{cm}$$

$$d_{water} = 0.34\mu$$

The mercury porosimetry determination is shown in Fig. 1-1. The graph shows pore volume (cc/gm) penetrated versus absolute pressure (curve A), which is related to the pore diameter

$$D = 176.8/P$$

assuming a contact angle of 130°.

The pore size distribution (curve B) is plotted on the same graph and illustrates where the porosity exists. The average pore diameter is taken at 50% of the pores with greater than indicated diameter and by extrapolation is found to be 0.23 .

The pore diameter determinations using bubble pressure and mercury porosimetry compare favorably as shown in Table 1-1. The lack of exact agreement may be attributed to the assumption of zero tortuosity in the calculation and to the difference in the state of the separator in the two tests, namely dry in the mercury porosimeter method while wet in the bubble pressure method. Also, in comparing these values, one cannot expect perfect agreement because all measurements are not through pores with zero tortuosity. Also the pores may be distended during measurement at relatively high pressures under either method.

The electron micrographs in Fig. 1-2 show uniformity of the pores and are given for purposes of illustration.

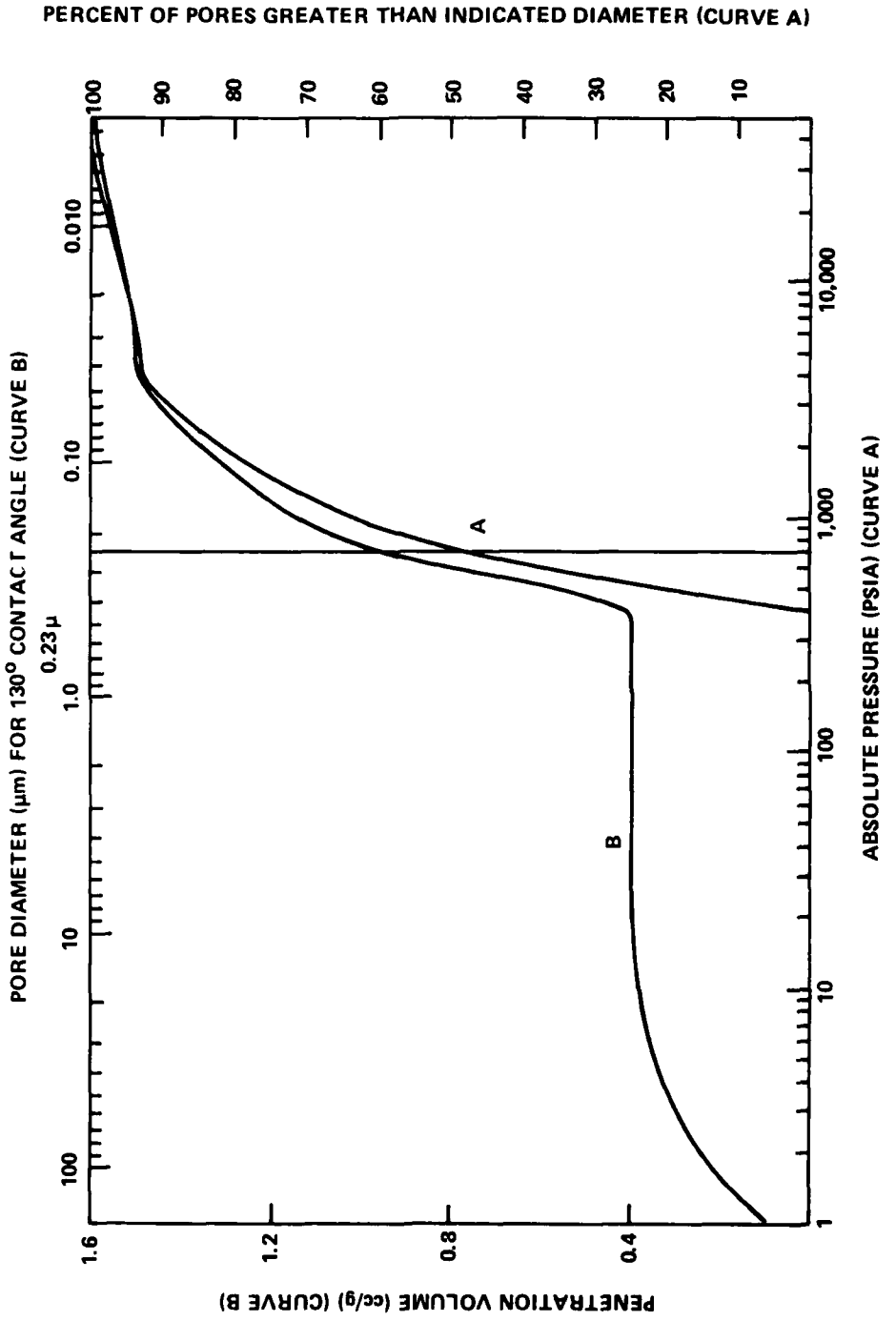


FIGURE 1-1 MERCURY POROSIMETRY ON PPQ/CA

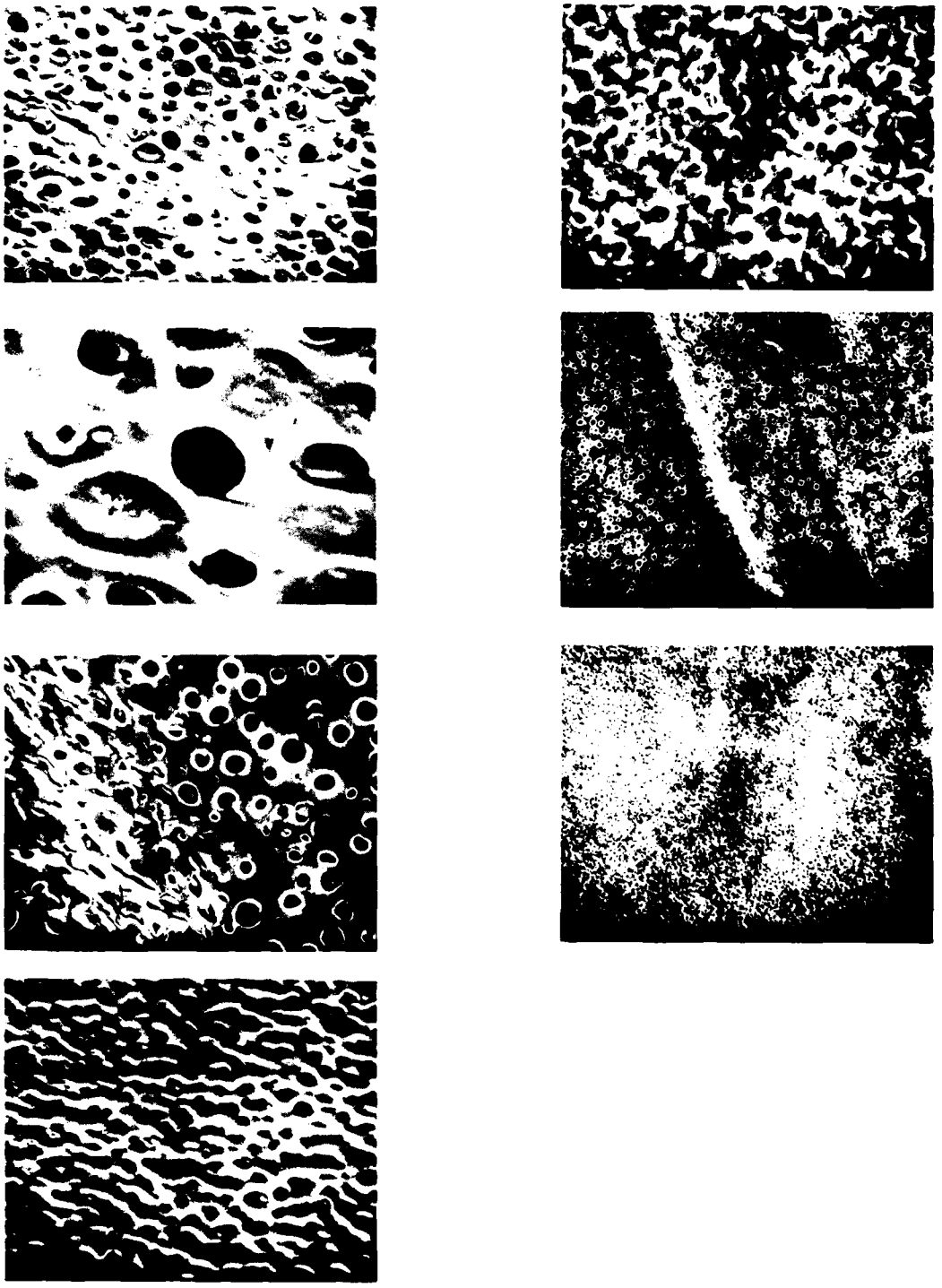


FIGURE 1-2 ELECTRON MICROGRAPHS OF PPO/CA (60/40) MEMBRANES

CHAPTER 2

ZINC PENETRATION

BACKGROUND

Zinc dendrites have traditionally been the headache of the alkaline systems. When zinc is plated out of alkaline solution the product is dendritic and spongy. In an alkaline cell the spongy deposit would rapidly grow across to the positive electrode and short out the cell if it were not for the separator. A principal function of the separator, therefore, is to retard the growth of the zinc sponge between the negative and the positive electrodes.

Cellophane has been the landmark in separator materials. Whereas, a cell without separator will usually fail on the first recharge, a cell with one turn of 1 mil cellophane around the positive electrode will last for several cycles, and a cell with six or eight turns will last up to several hundred, depending on cycling conditions. Cycle life can be increased by additional separator turns but the cost in increased volume and weight, and in decreased voltage and capacity is serious.

Attempts to escape penalties of the above kind led to research efforts directed toward an understanding of failure mechanisms. The most important aspect of the failure mechanism is the conversion of zinc to a soluble form during discharge. If zinc oxide is formed, via the reaction

$$Zn + 2OH^- \longrightarrow ZnO + H_2O + 2e^- \qquad (2\text{-}1)$$

it can dissolve in the alkaline electrolyte as $Zn(OH)_4^{2-}$, up to saturation, with the excess remaining on the zinc electrode as a solid deposit.

Alternatively, the mechanism could be

$$Zn \longrightarrow Zn^{2-} + 2e^- \qquad (2\text{-}2)$$

followed immediately by

$$Zn^{2-} + 4(OH)^- \longrightarrow Zn(OH)_4^{2-} \qquad (2\text{-}3)$$

The zincate in excess of saturation would deposit ZnO on the zinc electrode, since it is formed in contact with this plate. The zincate ion, during discharge and during stand, diffuses through the separator, thus introducing zincate ions into the separator layers, into the spaces between the layers, and into the region occupied by the positive electrode.

At the start of charging, the zinc which is first deposited comes from the zincate ion in the immediate vicinity of the plate, causing a drop in zincate concentration at the face of the plate, and within the pores. Simultaneously,

under the driving force of the concentration difference, zincate diffuses from the vicinity of the positive electrode toward the negative electrode. This latter rate has been measured, and is sufficiently low so that solid zinc oxide, until it is exhausted or can no longer react, must be the principal source of the deposited metal.

When the zinc oxide at the negative electrode no longer supplies metal, the rate of diffusion of the zincate ion through the separator becomes paramount in importance. In those cases where the charging rate is high, or where the temperature during charging is low, the rate of replenishment by diffusion of zincate ions will be lower than the deposition rate. Zincate is then depleted in the region between the cathode and the separator. As a result, the locale of the reduction process crosses the separator surface to the separator interior where the zincate concentration is higher and therefore more favorable for plating. In this process, a zinc trail is started within the first separator layer. The continuation of this process extends the zinc trail through successive layers until eventually the cell short-circuits.

This is thought to be the mechanism of failure; it is generally referred to as failure by zinc penetration. Separators of different origin display greater or less resistance to such penetration.

The main purpose of the zinc penetration test is to establish a reliable and meaningful test for alkaline zinc separators which provides a quantitative measurement of the rate at which zinc dendrites penetrate the separator under controlled conditions.

EXPERIMENTAL

Two tests are described below, the Hull procedure and the Wagner procedure.

A. HULL TEST OPERATING PROCEDURE

Size of Cathode Plate: 3-7/8" x 2-1/2"
Anode Plate: 2-1/2" x 2-1/2"

Electrolyte: 45% KOH in a 1 molar ZnO solution

Current: 1 Ampere

Size of Film: 6" x 5"
Cleaning Steps for Film:
Hot KOH H_2O Methanol (CH_3OH)

I. PREPARATION OF ZINC PLATES

The larger plate must have its edges and corners sanded smooth to prevent any punctures or tears in the film. After the sanding, both plates are washed in a solvent, such as acetone, to remove any surface dirt. The smaller plate is connected to the positive terminal (red). The larger plate will be discussed in Part III.

II. PREPARATION OF FILM FOR TEST USE

A piece of film measuring 6" x 5" should be cut from the desired sample to be tested. Cuttings should be taken from a clean area of the film and should always be handled carefully, by the edges, in order to avoid a puncture or a tear.

III. FITTING FILM ON PLATE

The prepared piece of film must now be fitted to the larger (3-7/8" x 2-1/2") plate. The film is first folded in half along its length covering the plate evenly. The film extending beyond the sides of the plate is folded backwards and securely taped. The film remaining above the plate is then cut, so that the film fits tightly around the plate with no excess. This plate is then placed in the Hull Test Unit and connected to the negative terminal (black). The connection (lead) must be in contact with the zinc plate; therefore, it is slipped under the film. The connecting clip should clamp onto the cell wall. After this is done, the 45% KOH-ZnO solution is poured to the filling line on the test cell. The current is then turned on and kept at 1 ampere. A timer should be used and set at 15 minute intervals. The test for dendrite formation is a visual one with most of the films showing formation at the closest distance between the plates. The time when the dendrites just penetrate the film should be recorded; this completes the test. WARNING: SAFETY GLASSES MUST BE WORN WHILE PERFORMING THIS TEST!!

B. THE WAGNER PROCEDURE

The zinc penetration cell design is illustrated in Figure 2-1. The cathode was a Pellon clad zinc sheet. The anode was a partially charged nickel hydroxide ($Ni(OH)_2$) electrode clad with one or more layers of the test separator material. The approach was to determine the time required for zinc dendrites to form and penetrate the test separator causing a short circuit.

The following test conditions were selected to render the zinc penetration test as reproducible and simple as possible:

a. State of charge of the Ni $(OH)_2$ reference electrode - 0.0005 Ah

b. Working current density - 100 $mA/inch^2$

c. Electrolyte - 42% KOH saturated with zincate

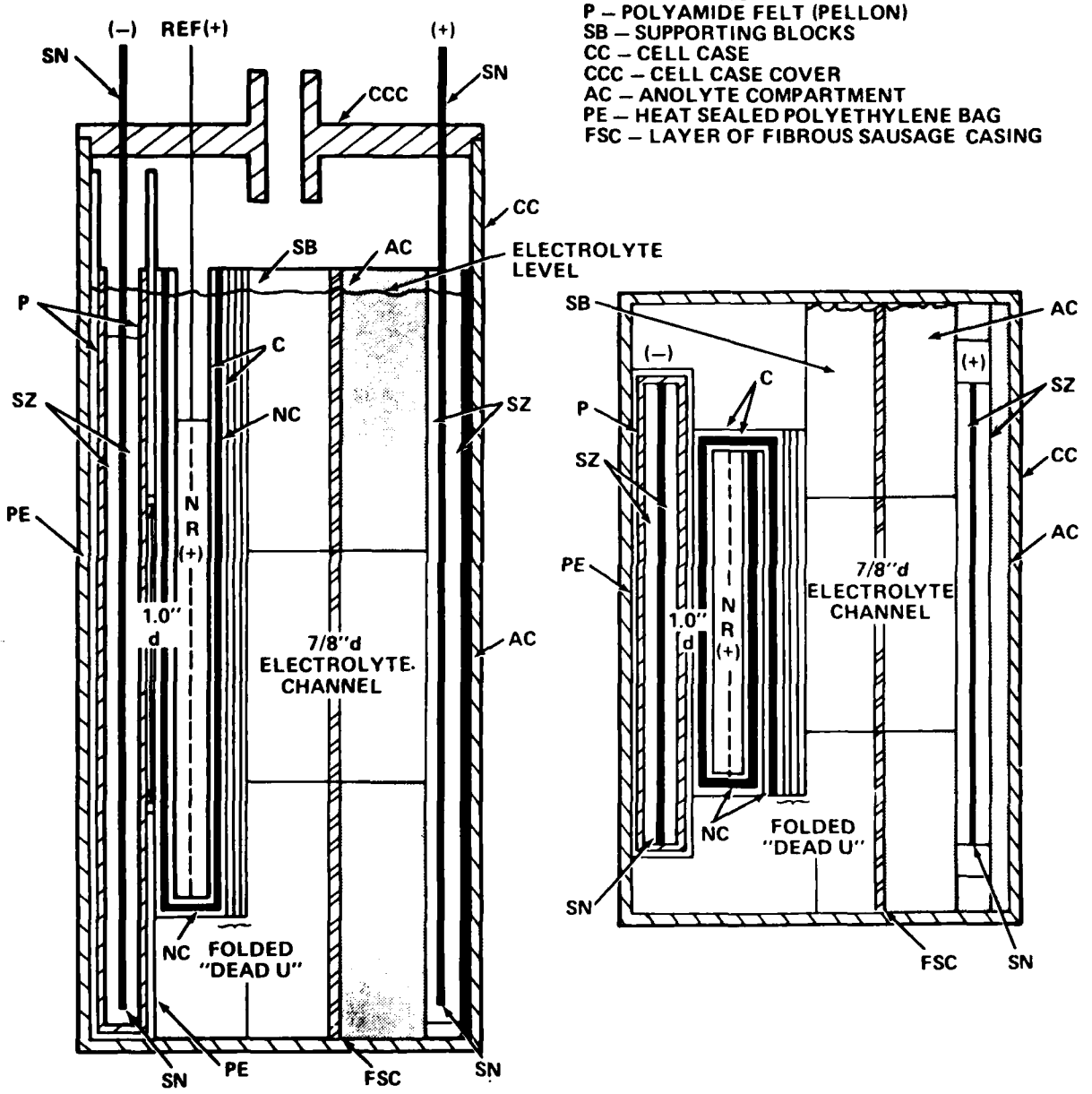
d. Soak time - overnight for single layered, and 2 to 3 days for multi-layered separators.

RESULTS AND DISCUSSION

The results of zinc penetration studies on PPQ/CA compared to other separators are given in Table 2-1. In evaluating the results presented in Table 2-1, two points must be considered:

1. Can the test distinguish between different materials?; and

SZ – SHEET ZINC
SN – SHEET NICKEL
NR(+) – NICKEL REFERENCE ELECTRODE
C – CELGARD
NC – NICKEL COATED CELGARD
P – POLYAMIDE FELT (PELLON)
SB – SUPPORTING BLOCKS
CC – CELL CASE
CCC – CELL CASE COVER
AC – ANOLYTE COMPARTMENT
PE – HEAT SEALED POLYETHYLENE BAG
FSC – LAYER OF FIBROUS SAUSAGE CASING



SIDE VIEW

TOP VIEW

FIGURE 2-1 ZINC PENETRATION CELL DESIGN

TABLE 2-1 ZINC PENETRATION RESULTS ON PPQ/CA MEMBRANES

Sample #	Hours to Short	Thickness (mils)	hrs/mil	Resistivity $m\Omega\text{-inch}^2$	$\frac{m\Omega\text{-inch}^2}{mil}$
[a]					
PPQ/CA 27	1.28	1.0	1.28	20	20
PPQ/CA 28	0.68	1.0	0.68	17	17
PPQ/CA 29	1.00	1.0	1.00	18	18
PPQ/CA 30	1.45	1.0	1.45	17	17
[b]					
C-19-1	7.45	3.0	2.48	14	4.7
C-19-2	6.13	3.0	2.03	13	4.3
[c]					
FSC-1	12.1	7.5	1.62	38	5.0
FSC-2	13.2	7.5	1.76	38	5.0
FSC-3	13.9	7.5	1.85	38	5.0

a. PPQ/CA (60% PPQ and 40% cellulose acetate)

b. Cellophane treated with silver. (YEC treatment)

c. FSC = Fibrous sausage casing.

2. Is there a correlation between the zinc penetration data and cell performance?

Taking point number one first, it can be seen that the range of measured results, as given in Table 2-1 for PPQ/CA, extends from 0.68 to 1.45, a ratio greater than two. The variation is so great as to warrant examination of the cause. From measurements of the resistivity at different regions of the separator, it does not appear that variation in current density on a macroscopic scale over the surface of the separator is responsible.

On the microscopic scale it seems likely that resistivity or porosity may vary from point to point within the separator. Such variations would favor the formation of isolated zinc trails rather than massive deposition on an advancing front. It is evident from the examination of shorted separators that penetration always occurs at isolated points; therefore, it seems likely that some type of variation in the separator structure is included. On this basis, the shorting time for a specific test sample is a measure of the zinc stopping factor of the weakest point in the sample. (See photographs illustrating Dendrite Growth, Figure 2-2).

The second point will be considered in a forthcoming publication.

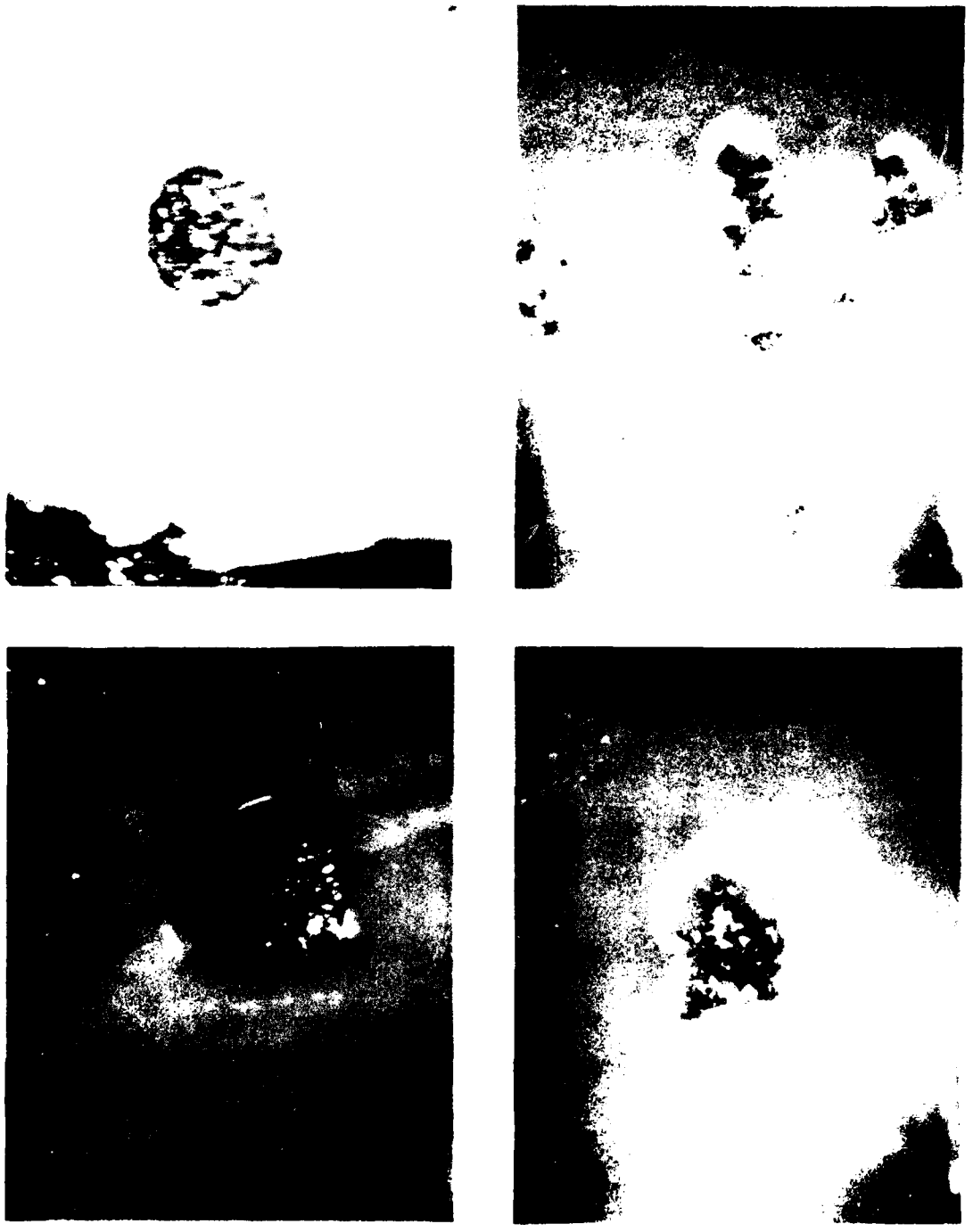


FIGURE 2-2 ZINC DENDRITES ON PPO/CA

CHAPTER 3

ZINC DIFFUSION

BACKGROUND

During the discharge of a zinc anode, zinc can go into solution as a soluble ion,[13] most likely according to the following reaction:

$$Zn + 4OH^- \longrightarrow Zn(OH)_4^{2-} + 2e^- \qquad (3\text{-}1)$$

There seems to be no particular harmful effect of soluble zinc on the positive plate. In fact, soluble zinc distribution throughout the cell would be innocuous, except its presence in and in between the separator layers provides a large enough supply of zinc to feed the growth of a metallic zinc path (dendrite formation) through the separator during charging of a cell. Thus, a mechanism for failure by electrical short-circuiting is provided and such failures in fact occur. Electrical short-cicuiting occurs rapidly when highly porous materials are used as separator membranes. Therefore, the successful development of the silver-zinc cell as a rechargeable system with appreciable cycle life is dependent on the use of multiple layers of semi-permeable membranes having pore diameters on the order of molecular diameters.[14]

Rates of diffusion of zincate ion (soluble zinc) are still of interest. If materials can be found which will retard diffusion of zincate ion, failure by metallic zinc penetration would be retarded. Such materials might also provide thinner separator designs with consequent gains in energy yields per unit weight and volume.

Diffusion is a process in which the transport of molecules takes place in the absence of bulk flow. The flux J (quantity of substance diffusing per second through a unit area) of a substance through a plane perpendicular to the direction of diffusion is directly proportional to the concentration gradient, according to Fick s first law

$$J = - D \frac{dC}{dx} \qquad (3\text{-}2)$$

---

[13] Dirkse, T. P., "The Nature of the Zinc-Containing Ion in Strongly Alkaline Solutions," J. Electrochem. Soc., Vol. 101, 1954, pp. 328-31.

[14] Cooper, J. E., and Fleischer, A., ed., "Characteristics of Separators for Alkaline Silver Oxide Zinc Secondary Batteries," AD-447301, AF AERO Propulsion Lab, Wright-Patterson AFB, Ohio, 1964, p. 93.

where D is the diffusion coefficient, $(\frac{dC}{dx})$ is the concentration gradient, C is the concentration and x is the distance.

Experimentally, the molecular flux, J, is obtained by measuring the average time rate of change of concentration. Mathematically, the requirements and conditions for the experimental application of Fick's first law have been described by Jost[15]. By maintaining uniform concentrations on each side of the diffusion layer or barrier with stirring and by varying the concentrations only slowly with time, the concentration gradient may be expressed as follows:

$$\frac{dC}{dx} \approx \frac{C_1 - C_2}{l} \tag{3-3}$$

where C_1 is the concentration on the dilute side, C_2 is the concentration on the concentrated side, and l is the thickness of the diffusion layer. If C_1 is zero when only the solvent is present and C_2 is a concentrated solution, the change of $(C_1 - C_2)$ during an experimental determination becomes small and negligible so that the concentration gradient is constant. Under this condition, the flux J can be used to characterize the membrane.

In practice the concentration of the diffusion constituent on the low concentration side of the membrane is plotted as a function of time. Where the change in concentration with time represents the slope of the line.

$$m = \frac{\Delta C}{\Delta t} \tag{3-4}$$

The concentration on the dilute side of the membrane yields a linear plot.

$$m = \frac{\Delta C}{\Delta t} = K \tag{3-5}$$

If the measured volume, V, of liquid on the dilute side does not change, the rate of material transfer (M) through the membrane is

$$\frac{\Delta M}{\Delta t} = \frac{\Delta C}{\Delta t} \times V \tag{3-6}$$

Since the area through which the mass change takes place is known, the rate of mass transfer or flux can be expressed in terms of area and time as:

$$\frac{\Delta M}{A\Delta t} = \frac{\Delta C}{\Delta t} \times \frac{V}{A} \tag{3-7}$$

The latter equation is a special case of Fick's first law, involving a constant concentration gradient. That is to say, where the concentration gradient is constant, the flux J (or $\Delta M/A\Delta t$) is constant and if the diffusing material passes into an unchanging volume on the dilute side of the membrane, the concentration will change linearly with time. Use of the linear portion of the diffusion curve makes the data somewhat easier to handle, and by standardizing the techniques comparison of many samples of separator material can be simplified.

[15]Jost, W., Diffusion in Solids, Liquids, and Gases (New York: Academic Press, Inc., 1952), pp. 437-8.

EXPERIMENTAL

Two methods were used to determine the diffusion of zincate. Method I uses a titration technique, while Method II makes use of potentiometry.

METHOD I

The diffusion cell used is similar to the one described in Reference 14. The diffusion of Zn species occurred from a solution approximately 5M in KOH and 0.1M in ZnO through the membrane to a 5M KOH solution containing no ZnO.

KOH and ZnO were "Reagent Grade" (Fisher Scientific). They were used without further purification. Deionized and deaerated water were used to make the required solutions. The solutions were kept in well-stoppered polyethylene bottles, but no special precautions were taken to prevent CO_2-uptake during storage, transfer and experimentation. Hydroxide ion (OH^-) concentrations of the experimental solutions were always redetermined shortly before an experiment, but in no case did we find significant changes due to CO_2-uptake. The presence of a relatively small amount of carbonate ions would not interfere with the transport measurements. KOH concentrations were determined by titration with standard HCl solutions using phenolphthalein indicator. In KOH solution containing ZnO, the titration was ended when the solution was colorless. A $Zn(OH)_2$ precipitate remained; the pH of the final solution was found to be around 7. Thus only the "free" OH^- was determined by first neutralizing the solution sample with 1M or 5M HCl and subsequent titration with E.D.T.A. using a pH 10 buffer and Eriochrome Black as indicator. Accuracy of the concentration determinations is extremely important because of the relatively small concentration changes that have to be detected. Repeatability of the OH^- determinations is estimated at 0.1% when no Zn is present in the solution, and at 0.1 - 0.2% for solutions containing ZnO. Repeatability of Zn determinations using a 0.01N E.D.T.A. solution was better than 0.2% when more than 10 ml E.D.T.A. was used, but this uncertainty became propotionally higher when smaller quantities of E.D.T.A. were needed.

METHOD II

This technique is described in Reference 14. The technique allows accurate determination of zinc in strong electrolyte at concentrations of 10^{-3}M or less without sample withdrawal and enables the determination of diffusion rates in about two hours depending on permeability of the membrane.

The method is potentiometric and is based on the fact that the potential of the zinc-zincate couple at constant hydroxyl ion concentration varies by 0.0295 volts for each 10-fold change in concentration of the zincate ion. Because it is potentiometric, a zinc electrode may be used to sense the zincate ion concentration. The logarithmic dependence of the voltage change on concentration makes it especially sensitive at low concentrations where sensitivity is most desired.

The diffusion cell is designed to allow a test membrane to be introduced between cell halves. On one side of the membrane, the zinc-rich solution of potassium hydroxide is introduced, while on the other, a zinc-free solution of potassium hydroxide of the same concentration is introduced. Thereby, a

[14] See footnote 14 on page 3-2.

concentration gradient of zincate ion is set up across the membrane, and zincate ion will diffuse to the zinc-lean side of the cell at some rate controlled by the membrane thickness, area, total porosity, and pore size. Instead of the zinc-free solution, a 10^{-4}M zinc solution may be used to establish an initial gradient (and the zinc electrode potential) rapidly. Gradients as large as those allowed by the solubility limit of zinc oxide in the zinc-rich side can be provided.

Into the zinc-lean side of the cell, two electrodes are placed. The reference electrode is a Hg/HgO electrode which is filled with potassium hydroxide of the same strength as that used in the cell. It is convenient to use electrolyte of the same strength to avoid the problem of a liquid junction potential. The second electrode is a heavily amalgamated zinc strip electrode (the zincate ion concentration measuring electrode), the potential of which changes as zincate ion diffuses into the zinc-lean half of the cell. It is amalgamated because an ordinary strip of zinc will self-discharge in potassium hydroxide at rates sufficient to supply some zinc to the solution according to the reaction:

$$Zn + 2OH^- + 2H_2O \longrightarrow H_2 + Zn(OH)^{2-} \qquad (3\text{-}8)$$

It is important that all of the zinc in solution on the zinc-lean side come from diffusion through the membrane. Amalgamation results in an electrode which is very stable. Potential drifts of only 5 millivolts downward over a 15 hour period have been measured. This value is acceptable because the membranes tested allow sufficient zincate ion to diffuse in approximately two hours to establish accurate rates of diffusion.

The change in potential of the zinc electrode is measured against the Hg/HgO reference with time and the concentration corresponding to the potential is read from a calibration curve. The calibration curve was established by making up 45% potassium hydroxide solutions with known concentrations of zinc over the range of 10^{-4} to 1.0M and by measuring their potential against the Hg/HgO reference electrode. The curve is linear with a slope of approximately 0.030 volts as illustrated in Figure 3-1.

If the concentration of zinc on the zinc-rich side of the cell is 1.0M and diffusion into a similar volume is allowed to continue until the concentration in the zinc-lean side is 10^{-3} to 10^{-2}M, an essentially constant concentration gradient will be driving the diffusion.

The apparatus used was the same as the one used in METHOD I. It was fitted with a port on the top of each side for the introduction of solutions. The port on the zinc-lean side was also used to support the reference electrode, the amalgamated zinc electrode and a tube for the introduction of inert gas. An inert gas cover was provided to reduce corrosion of the zinc sensing electrode at the solution-gas interface because the corrosion rate is promoted by oxygen at the interface. The circuitry used was as described in Reference 14.

[14]See footnote 14 on page 3-2.

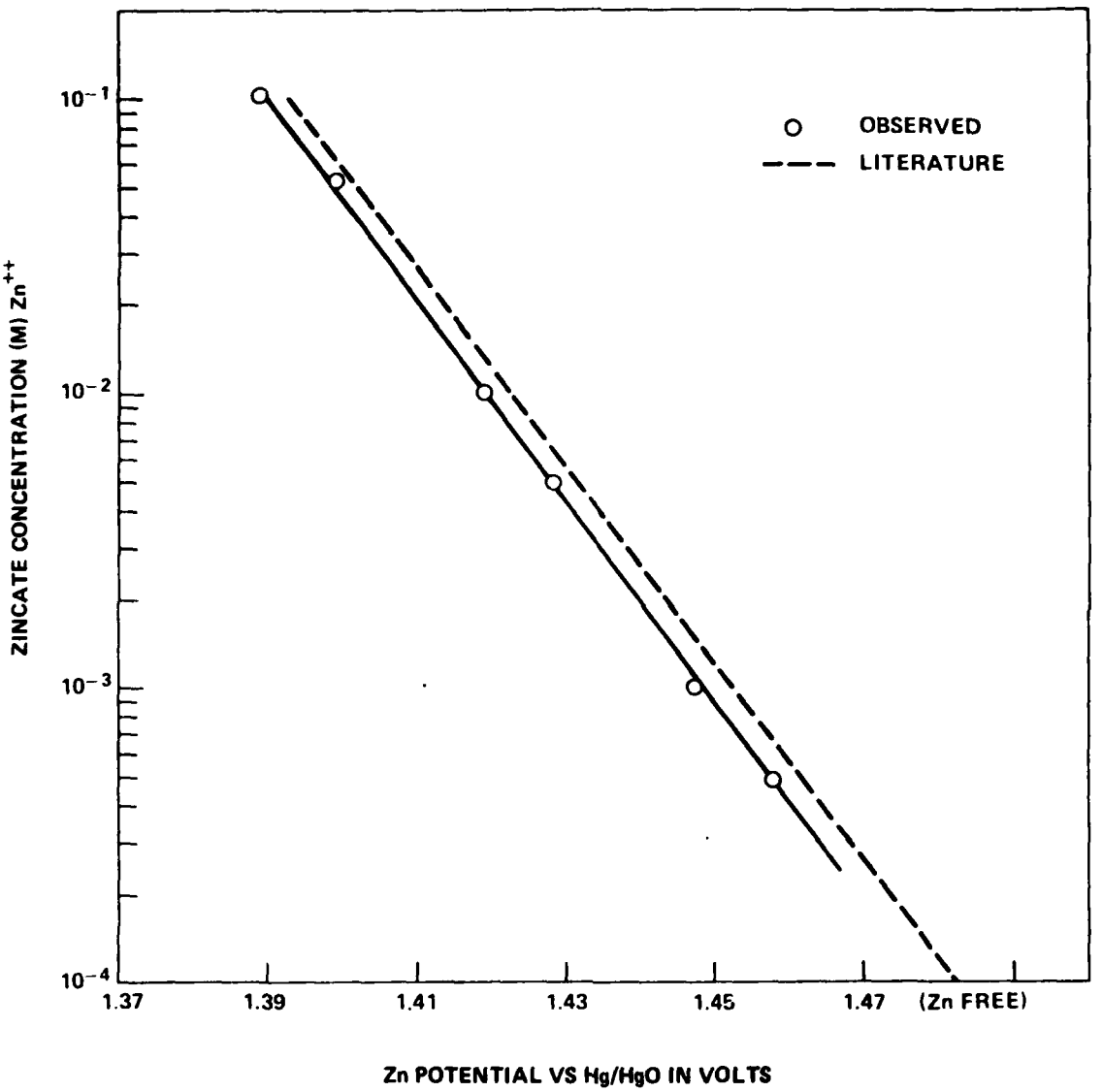


FIGURE 3–1 CALIBRATION CURVE FOR Zn CONCENTRATION AND POTENTIAL IN 45% KOH

RESULTS AND DISCUSSION

The results of Zn diffusion tests using the potentiometric method are summarized in Table 3-1 and Figure 3-2[16] where the results are compared to standard commercially available samples.

TABLE 3-1
Zn DIFFUSION FLUXES USING POTENTIOMETRIC METHODS

Membranes	Sample	V_i	V_f	C_i	C_f	K (mole/in^2-min.)
PPQ/CA 60/40	32	1.445	1.439	0.0012	0.0020	7.9×10^{-7}
PPQ/CA 60/40	48	1.437	1.434	0.0023	0.0030	7.2×10^{-7}
PPQ/CA 60/40	63	1.442	1.437	0.0016	0.0023	7.7×10^{-7}
Sausage casing	1	1.447	1.438	0.0010	0.0021	1.2×10^{-6}
Sausage casing	2	1.447	1.430	0.0010	0.0035	2.10×10^{-6}
Cellophane	3	1.456	1.429	0.0005	0.0045	2.81×10^{-6}
Cellophane	4	1.464	1.428	0.0003	0.0048	2.73×10^{-6}

The results using the titration technique are summarized in Table 3-2. Comparing the flux data obtained by both methods, it is seen that the results are somewhat variable.

[16]Kilroy, W. P., and Laughlin, L., "Diffusion Studies on a PPQ-CA Membrane--A Comparison with Standard Membrane Materials," NSWC/WOL TR 78-174, Dec. 1978.

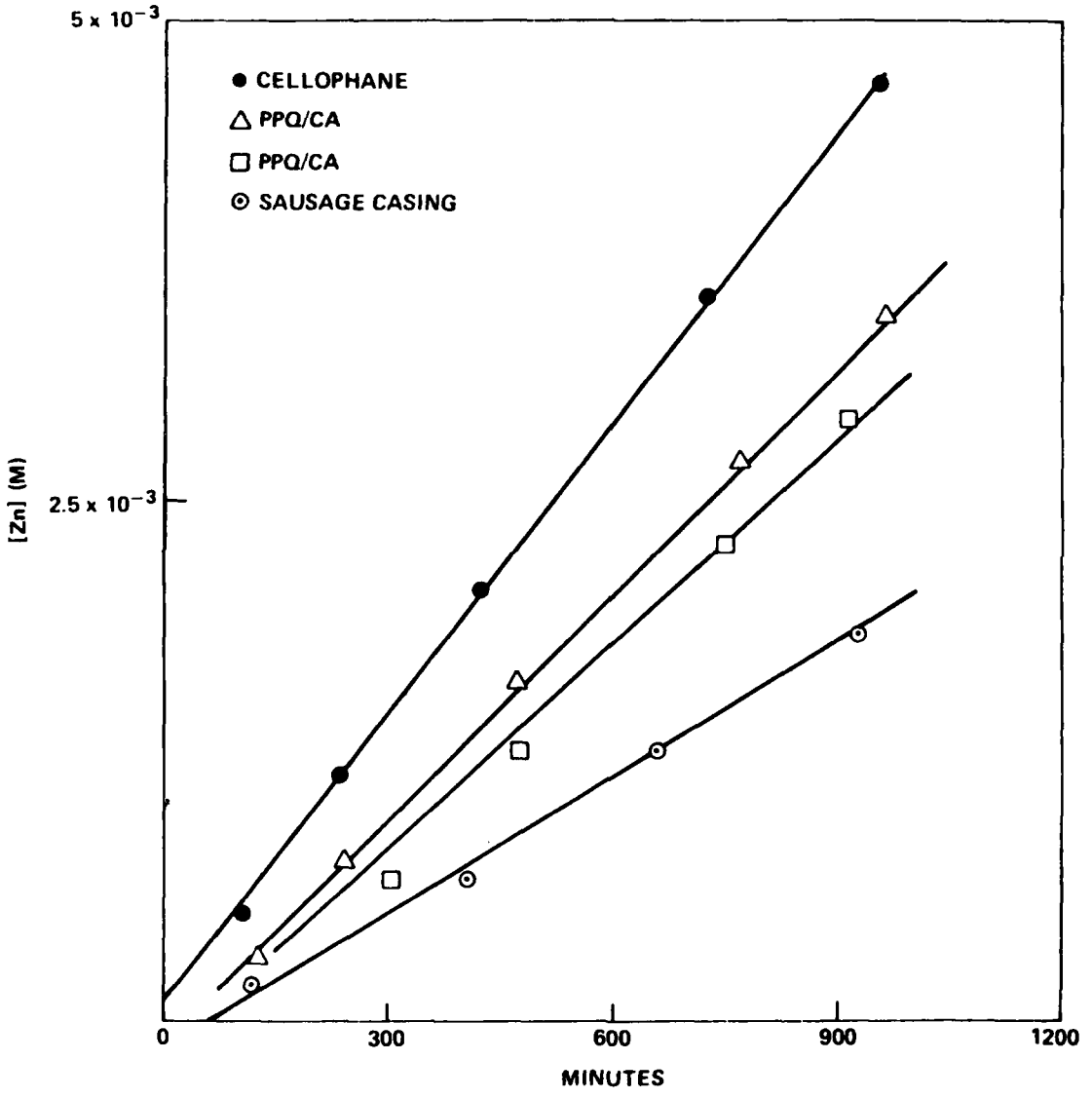


FIGURE 3-2 DIFFUSION OF Zn USING POTENTIOMETRIC TECHNIQUE

TABLE 3-2

Zn DIFFUSION DETERMINATION USING TITRATION TECHNIQUE

Membranes	Sample	K (mole/in^2-min.)
PPQ/CA 60/40	32	6.5×10^{-7}
PPQ/CA 60/40	48	5.9×10^{-7}
PPQ/CA 60/40	63	6.2×10^{-7}
Sausage casing	1	2.2×10^{-6}
Sausage casing	2	2.9×10^{-6}
Cellophane	3	3.0×10^{-6}
Cellophane	4	2.7×10^{-6}

The variability can be attributed to the experimental error within each technique. The results also indicate that none of the materials tested were non-permeable to zincate-ion. The rate of diffusion of the zincate does not appear to correlate with the zinc penetration data (See Chapter 2).

The experimental data also indicates that zinc diffuses faster through cellophane and sausage casing than through PPQ/CA. This was unexpected because the pore diameters of cellulosic materials are on the order of 20-30 Angstroms, while those of PPQ/CA are on the order of 23000 Angstroms (See Chapter 1). Therefore, it appears that PPQ/CA membranes have a higher tortuosity than cellulosic membranes.

CONCLUSIONS

It has been shown that the tests described in this technical report can be used to characterize the PPQ/CA separator membrane. The results indicate that PPQ/CA compares favorably with commercially available materials.

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