RLO-2434-8

RESEARCH ON ALKALINE ZINC SECONDARY ELECTRODES
WITH EMPHASIS ON MODEL TESTING

MASTER

Final Report

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June 15, 1976 - August 31, 1979

PREPARED FOR THE U.S. DEPARTMENT OF ENERGY

UNDER CONTRACT NO. EY-76-S-06-2434

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ABSTRACT

The goal of this work was to obtain information which will be useful in the improvement of life and performance of alkaline secondary cells which utilize porous zinc electrodes. Toward this end, experiments designed to test predictions of the most sophisticated mathematical models of the porous zinc electrode, i.e., those developed by Choi, Sunu, Bennion and Newman (1, 2), have been done. This approach is based on our conviction that the surest way to realize a significantly longer lived zinc electrode is through better understanding of the electrode gained through the interaction between modeling and model revision based on feedback resulting from experimental testing of the models.

Experiments performed have emphasized determination of the potential distribution over the surface of a flat rectangular porous zinc electrode operated under conditions of severely limited convective flow, the determination of potential distribution and concentration variations over the surface of similar electrodes when operated under "normal" flow conditions and the evaluation of OH^- depletion as a failure mode in zinc electrodes operated under conditions of severely limited convective flow.¹ Results of the experiments and interpretations of them in terms of the appropriate models are included in this report and its appendices.

1. Normal flow refers to flows similar to those described previously (8) and observed in some commercial cells.

1. INTRODUCTION

The goal of a large fraction of the effort being expended in secondary battery research is to learn how to construct long-lived cells which are economical and have appreciably higher energy densities than available lead-acid batteries. Alkaline cells which utilize porous zinc electrodes have, for several years, been accepted as the system most likely to provide an intermediate solution to achieve the desired goal. Several problems continue to stand in the way of production of such cells; these are commonly categorized under headings such as dendrite control, shape change, passivation, capacity retention, separator problems, problems associated with choice of positive, and problems with charge control (3, 4, 5, 6, 7). The fact that the reproducibly long-lived zinc secondary battery, designed and constructed in such a manner as to retain the high energy density capability of the zinc electrode, continues to elude manufacture is evidence of the need for further research and improved understanding of "how" the porous zinc electrode and its closely associated (i.e. the separator) parts function together in a working cell.

Our approach to contributing to the understanding of the zinc electrode has been to do experiments designed to test predictions based on mathematical models of the electrode (1, 2). The modelers use their best efforts to construct tractable models which include the essential aspects of the physical processes occurring in the electrodes. The modeling efforts yield predictions of physically observable quantities related to electrode performance; thus, the predictions serve, in a sense, as roadmaps for the experimentalist to use in making laboratory work more effective. Agreement between predictions based on a model and experiment serves to reinforce one's conviction that essential processes are understood and properly incorporated into the model; disagreement defines limits of applicability of the model and/or calls for changes in the model which might involve fine tuning of an approximation or major changes such as inclusion of factors previously believed negligible but indicated, by experimental evidence, to be of greater importance.

The two models which have been used in this work are those developed by Choi, Sunu, Bennion and Newman. The experiments described are extensions of

or complementary to those previously reported (8). They deal with potential distributions over the surface of a working porous zinc electrode under limited convective flow conditions, with potential distributions and concentration variations over the surface of a working zinc electrode with "normal" convective flow, (convective flow similar to that previously described (8) and observed in cells which use ion exchange membranes and have head space) and with OH^- depletion as a failure mode in zinc electrodes operated under conditions of limited convective flow. Data from these experiments support the basic convective flow theory of shape change developed in Choi's model; however, other evidence from the same experiments indicated disagreement between experiment and other assumptions or predictions based on the two models. The particulars of the agreements and the disagreements are detailed below.

Since much of the work to be included in this report has been published we summarize it briefly and include the publications as part of the report in the appendices. Work which has not been published is described in greater detail.

Fig. 2.1 Labeling of axes for the flat, rectangular porous zinc electrode. The Y axis is parallel to the membrane separator surface, the X axis is perpendicular to the separator.

2. SUMMARY OF ACCOMPLISHMENTS

2.1 Theoretical Basis, The Models

The work done under Subject Contract originated at UCLA during the year 1974-75 under Air Force Contract No. F33615-74-C-2004(2) and has been continued here since 1976. Two papers were published which summarized work completed at UCLA (1, 8) and two papers have resulted from the work done here (9, 10). Copies of the latter two papers are attached to this report as Appendix A.

The first paper published by Prof. Bennion's group on the porous zinc electrode was theoretical in nature and described a one dimensional (Y dimension, see Figure 2.1) model, developed by Dr. King Choi, of the zinc-silver oxide secondary cell. This model was based on the hypothesis that zinc electrode shape change in cells utilizing certain types of membrane separators is caused by membrane pumped convective flows in the electrode compartments coupled with electrode processes (1). Experiments demonstrating the existence of the volumetric flows in the electrodes and quantitative agreement between predicted and measured flow rates as well as evidence of the relationship of the flows to the development of shape change were presented in the second paper (8).

The predictive successes of the initial model as described in the second paper were considerable; however, several predictions, e.g., regarding concentration changes, metallic zinc distribution and development of resistive overpotentials in cells with convective flow, remained untested at that time and important questions relative to zinc electrode performance were not addressed by the Y dimension model. In work that continued at UCLA, Prof. Bennion's student, Dr. Won Sunu, developed an X demension model of the electrode (see Figure 2.1) operated under conditions of severely limited convection and carried out an experimental evaluation of that model. The work is described in Dr. Sunu's dissertation (2). Both models have been used to guide experiments in this laboratory as explained below.

2.2 Year Ending June 15, 1977

Emphasis during the year ending June 15, 1977 was on the behavior of the flat, rectangular 12 A-hr AFAPL porous zinc electrode operated under conditions in which convective flow through the electrode was severely

restricted. Most of this work has been published (9) and is included as Appendix A-1. The work was selected because of the promise of reduced rate of development of shape change in electrodes operated under limited convective flow conditions and the desire to identify problems which might be associated with this mode of operation. Accomplishments included:

2.2.1 The development of a Hg-HgO in stainless steel, flooded, non-vented reference electrode that performs well in the system of interest.

2.2.2 Demonstration that cycling of the flooded, non-vented AFAPL (actually fabricated by Eagle-Picher Co., but supplied by AFAPL) zinc electrode at constant current in cells with severely limited convective flow results in the development of average anodic overpotentials which increase with number of cycles and vary from point to point over the surface of the zinc electrode, a fact which was not foreseen as a result of prior modeling work. No corresponding changes in average cathodic overpotential were observed.

2.2.3 Identification of potential causes of the observed anodic overpotentials developed in electrodes cycled under conditions of severely limited flow (See list below in Section 2.4.1).

2.2.4 Reinforcement of our conclusions concerning the relationship between the rate of active material redistribution and the presence of convective flow; i.e., the rate of lateral shape change is reduced by limiting convective flow parallel to the apparent electrode surface and material redistribution in cells with flow may be drastically altered by changing cell design in such a manner as to alter convective flow patterns (See Figure 2.2) (11).

2.3 Year Ending June 15, 1978

During the year ending June 15, 1978, emphasis was placed on testing assumptions involved in the convective flow theory (Choi Model) regarding concentration changes which occur within cycles and predictions made on the basis of the theory concerning cumulative concentration changes at the ends of cycles as cycling proceeds in cells with normal convection. In this phase of the project, cells with normal convection having multiple reference electrodes and solution sampling ports were cycled. Data obtained included overpotentials as functions of position (Y) and time as cycling proceeded, volume average fluid flow rates for selected cycles, and concentrations as functions of position (Y) and time in the cell compartments

during selected cycles. Active material distribution over the zinc electrode after cycling was also determined. This work has also been published (10) and is included as Appendix A.2. Our findings included:

2.3.1 Certain features of the concentration variations postulated in the Choi model, in particular periodic concentration changes in the zinc compartment within cycles were confirmed; however, the drastic cumulative concentration changes predicted at the ends of cycles were not observed, indicating a need for revision of the model to better reflect the actual construction of the real cell and concentration changes developed during cycling. (These observations, also indicate the need for reinterpretation of the behavior of the flow cell on cycling as described in reference 8.)

2.3.2 Analysis of electrodes subsequent to cycling in these cells confirmed the kind of active material redistribution predicted and observed by Choi et.al, for similar cell design, flow rates, and current densities. The data also indicated a movement of active material from the sides toward the middle of the electrode, i.e., the classical shape change pattern, an effect not predicted by the convective flow model.

2.3.3 Extensive potential vs. time and concentration data were taken during flow cell operation. These are discussed in some detail in the published paper. It was found that observed anodic overpotentials were larger than could be rationalized on the basis of observed changes in solution concentration. Possible reasons for these discrepancies are discussed in the paper.

2.4 Year Ending August 31, 1979

2.4.1 Introduction

Late in the second year work was initiated on porous zinc electrode fabrication and the testing of these electrodes in small cells with limited convection. Our purpose was to define more clearly which of several possible problems were the greatest contributors to the deterioration in anodic performance of the zinc electrode under limited flow conditions. For convenience and in an attempt to better define superficial average current densities, we began by fabricating small, 1 cm^2 electrodes. Both uncharged, pressed ZnO plates and charged, pressed amalgamated zinc plates were fabricated. The cell used for initial electrode testing was equipped for observation of electrode overpotential behind and in front of the test electrode, across

Fig. 2.2 Photographs of a pair of rectangular zinc electrodes after cycling in a cell in which convective flow patterns were directed by unusual cell design. Flow patterns were conditioned by baffles in the solution reservoirs behind the electrodes (11).

the cell membrane, and for micro-sampling of the zinc compartment fluid with a 10 μ l syringe through a rubber wall as had been done successfully with the larger flow cell. In our initial experiments we used the pressed, ZnO electrodes which were doped with HgO. Clear evidence of OH⁻ concentration depletion during discharge as predicted by Sunu (2) was sought (21).

The problems encountered with the initial cell and electrodes involved gassing at the negative, especially on charge, and difficulty in drawing samples from the small, tightly closed zinc electrode compartment. Failure to obtain concentration data with this cell led to the development of a new cell and the electrode construction and analysis techniques which are described below. Since this work has not been published it is described in detail.

Dr. Sunu's one dimensional model of the porous zinc electrode deals with the electrode in a cell which is designed to severely limit convective flow through the electrode. His model is commonly referred to as the X dimension model (See Figure 2.1).

Failure modes which have been suggested for zinc electrodes operated with limited convection are summarized as follows:

Short Time Failure During Discharge

- *a. pore plugging, reaction product deposition in electrode pores (2)
- b. thin film passivation (12)
- c. OH⁻ depletion (2)
- d. H₂ evolution

Short Time Failure During Charge

- *a. depletion of zincate
- b. zinc dendrite formation and short circuiting
- c. H₂ evolution

Long Time Failure on Cycling

- a. zinc dendrite formation and short circuiting (20)
- *b. active material redistribution in the X direction (2)
- c. accumulated gas evolution
- d. detrimental changes in the conducting matrix as cycling continues, including separation of metallic zinc from the current collector and changes in matrix structure as a

result of cell cycling (8, 9, 13)

- e. changes in ZnO crystal morphology and the kinetics of the dissolution-precipitation process for this material (19)
- f. loss of active material from the zinc electrode compartment to the positive compartment (8, 5)

Those failure modes emphasized in Sunu's thesis are marked with the symbol *. The mode of interest in the work described below is that of short time failure due to OH^- depletion in the electrode during discharge. Our intention was to initially observe volume average concentration changes in a small cell with severely limited convection, to compare these data with Sunu's predictions, and to correlate the determinations with simultaneous observations of cell overpotentials and hydrostatic pressure variations. This work was considered to be preliminary to a more detailed study of concentration gradients established perpendicular to the membrane surface (X direction) in the electrode during electrolysis.

The electrolytic solution in the cells of interest is assumed to consist of four species: K^+ , OH^- , $\text{Zn}(\text{OH})_4^{2-}$, and H_2O (3). The overall discharge reaction at the zinc electrode is commonly written as the sum of the two overall reactions:

However, there is evidence that the second equilibrium is not attained rapidly (14, 10) and that supersaturated zincate solutions formed on discharge persist for many hours after cell current termination. Since OH^- is consumed during discharge, its concentration in the zinc compartment is expected to decrease during discharge if the supply of OH^- being transported from the counter electrode compartment is inadequate. Sunu has provided an approximate equation based on the membrane being the supply limiting barrier from which this concentration effect can be estimated.

$$\frac{C_3}{C_3^0} = 1 - \frac{(\xi - t_3) I}{F L C_3^0} \left(1 - \epsilon^- \frac{LA t_3}{V \epsilon} \right) \quad [3]$$

$V \equiv$ volume of zinc electrode compartment

$A \equiv$ cross sectional area of the electrode

$\epsilon \equiv$ electrode porosity, assumed constant in this approximation.

$I \equiv$ apparent current density

$C_3 \equiv$ volume average OH^- concentration in the zinc electrode compartment

$F \equiv$ Faraday Constant

$C_3^0 \equiv$ initial volume average OH^- concentration in the zinc electrode compartment and at all times in the counter electrode compartment

$L \equiv$ mass transfer coefficient for KOH across two layers of RAI P2291 40/30, 1.5×10^{-5} cm/sec (15).

$t_3 \equiv 0.5$, transference number of OH^- across the membrane (15)

$\xi \equiv$ a constant. $\xi = 1$, Case A, an amount of zinc equivalent to that going into solution is precipitated. $\xi = 2$, Case B, no zinc is precipitated.

A similar equation may be derived for potassium ion.

$$\frac{C_1}{C_1^0} = 1 - \frac{t_1 I}{F L C_1^0} \left(1 - e^{-\frac{A L t}{V \epsilon}} \right) \quad [4]$$

$C_1 \equiv$ potassium ion concentration

$C_1^0 \equiv$ initial potassium ion in the electrode compartment and at all times in the counter electrode compartment.

$t_1 \equiv$ transference number for K^+ , 0.5 (15)

Assumptions made in obtaining equations 3 and 4 include: for $\xi = 1$, complete conversion of zincate produced on discharge to ZnO ; that OH^- inside the zinc electrode is completely mixed; that KOH provides the only current carrying species, and neglect of additional driving forces and fluxes involved in a more exacting analysis of membrane transport under the given conditions. Values of C_3/C_3^0 based on equation 3 as well as values of C_1/C_1^0 based on equation 4 are plotted in Figure 2.3 for the parameters given above and in the Figure caption.²

2.4.2. Experimental

The experiment which has been carried out involves placing a porous zinc electrode in an electrolysis cell with several reference electrodes, carrying out a discharge half cycle at constant current, then removing the whole electrode intact from the cell, leaching the fluids from the electrode and analyzing them.

2. Constancy of C_2 was also assumed, as well as constancy of ϵ .

2.4.2.1 The cell design for this experiment is shown in Figures 2.4, 2.5, 2.6, 2.7. Two photographs of the cell are shown in Figures 2.8 and 2.9. The electrode holders are machined from Lucite plastic sheet. The zinc electrode is 1.00 cm^2 apparent surface area, 0.100 cm thick. Allowance is made for a .001" Dynel separator between the zinc electrode and the two layers of RAI P2291 40/30 membrane. Spaces for two Hg-HgO reference electrodes, R-1 and R-2, which have been described previously (9) are also provided in the holder. The channels which join the reference electrodes to the test electrode chamber were drilled as small as possible, 0.013" diameter, in order to cut down accessible solution reservoir volume in the test electrode compartment. As shown in Fig. 2.5 the capillary channel for R-1 enters the test electrode chamber behind the test electrode while the capillary channel for R-2 communicates with the fluid in front of the test electrode. In order to prevent de-wetting of the small capillary entrances to the reference electrodes, strips of RAI P2291 membrane material are placed in these holes. The electrical lead to the test electrode is a 0.020" silver wire flattened at the contact surface. It is not welded to the electrode but simply makes pressure contact with it in order to allow for quick removal of the electrode from the cell after electrolysis. Three quarter-inch holes are provided for bolts which are used only during cell assembly for alignment. The counter electrode compartment is shown in Figure 2.6. The cell is designed so that when the two halves are clamped together references R-2 and R-3 are positioned directly opposite one another on either side of the cell membrane.

The position of R-1 was selected to allow measurement of test electrode overpotential with minimal contribution due to IR drop. The difference of potential measured between R-1 and R-2 provides information on the potential drop through the zinc electrode and the difference between R-2 and R-3 allows one to monitor potential drop across the membrane.

The counter electrode in the cell is a circular piece of expanded silver metal attached to the counter electrode compartment filling port.

An O ring which surrounds the test electrode seals the cell when it is clamped together with three De-Sta-Co plier type quick release clamps, No. 462, as shown in Figures 2.8 and 2.9.

Fig. 2.3 Concentration ratios for potassium ion and hydroxyl ion as functions of time under different assumptions regarding zincate equilibration with solid species. ————Calculated values for C_1/C_1^0 (potassium ratio) vs. time applicable to both cases A and B. -----Calculated values for C_3/C_3^0 (Hydroxyl ratio), case A. - - - - -Calculated values for C_3/C_3^0 , case B. For definitions of cases A and B see equation 3, ξ . $C_1^0 = 10.0$, $C_3^0 = 7.4$, $C_2^0 = 1.15$. Experimental points, ●, are also described in Table 2.3.

Fig. 2.4 Schematic design of the zinc electrode holder. Top and one side view are shown. The side view, SF-1, emphasizes the electrode chamber and filling port opening. Dimensions are given in inches.

Fig. 2.5 Additional side views of the zinc electrode holder showing electrode chamber and (1) position of Reference Electrode #2 capillary, SR-2; (2) position of Reference Electrode #1 capillary, SR-1; and (3) position of the lead capillary, SL-1. Dimensions are given, in inches.

Fig. 2.7 Illustration and dimensions of (from top to bottom) an electrical lead plug, a stainless steel container for a Hg-HgO reference electrode, and a filling port attachment. Dimensions are given in inches.

Fig. 2.8 Photograph of the porous zinc test electrode holder before cell closure. Reference electrodes and filling ports are visible through the plastic.

Fig. 2.9 Photograph of the assembled cell ready for vacuum filling. The clamps which hold the cell together can be released quickly so that the electrode can be removed within seconds after termination of cell current.

The cell is vacuum filled with electrolytic solution through rubber filling tubes shown in Figure 2.9. After filling the cell, the filling ports in the zinc compartment are plugged. The cell is discharged with the test electrode positioned horizontally below the counter electrode. The counter electrode is vented to atmospheric pressure during cell operation.

2.4.2.2 Electrolyte Preparation and Tests

The solution used for filling the cell is prepared from singly deionized distilled water and reagent grade chemicals. KOH is first dissolved in water to prepare a concentrated solution. This solution is diluted to a specific gravity of 1.40 at 20° C. Fine grained reagent grade ZnO is then added in excess of the amount required to saturate the solution and magnetic stirring is carried out over a period of several days. The solution is stored in a capped polyethylene bottle and filtered before use.

The quantity of CO₂ absorbed from the atmosphere by the solution during preparation and storage has been of concern. We have, therefore, determined the quantity of carbonate in the solution after preparation and then periodically thereafter. The method described by Reid for determination of hydroxide and carbonate with indicators in the presence of zinc was used (16). Results are shown in Table 2.1.

Table 2.1

Electrolyte preparation date, 2/1/79

Results of analysis on 2/15/79 before addition of ZnO.

$$[\text{OH}^-] = 9.82 \text{ M}$$

$$[\text{CO}_3^{=}] = 0.11 \text{ M}$$

Results of analysis on 3/7/79 after addition of ZnO.

$$[\text{OH}^-] = 10.83 \text{ M}$$

$$[\text{CO}_3^{=}] = 0.17 \text{ M}$$

Results of analysis on 3/20/79.

$$[\text{OH}^-] = 12.03 \text{ M}$$

$$[\text{CO}_3^{=}] = 0.16 \text{ M}$$

It is concluded that most of the carbonate is picked up during electrolyte preparation. The rate of carbonate uptake during solution storage is small and could probably be made smaller by using a container cap with a better seal. Although the amounts of carbonate are measurable and appreciable, it is not clear at this time that carbonate at these levels is so serious a problem that more elaborate preparation procedures which would exclude the carbonate are warranted. We are continuing to prepare our electrolyte in the same manner, attempting to seal storage containers better, and continuing to monitor carbonate levels in the electrolyte used in experiments.

2.4.2.3 Electrode Preparation

Our electrodes have been prepared by procedures similar to those described by Morrel and Smith (17) and Sunu(2). Zinc metal powder of high purity and particle size between 250 and 325 mesh (sieve openings between 6.1 and 4.3×10^{-3} cm.) is obtained from Plasmadyne Co., Santa Ana, Calif. The powder is amalgamated by immersion in a dilute (1.0%) acetic acid solution which contains an amount of mercuric acetate such that the weight of mercury present is equal to 7.5 weight percent of the zinc powder. Reduction of the mercury in the stirred solution is found to be complete after one hour according to a negative qualitative test for Hg^{++} in the solution with 1:1 NH_4Cl , NH_4OH . The $Zn(Hg)$ powder is rinsed, vacuum dried and stored in a vacuum desiccator until used. It is mixed with sized $NaCl$ crystals (250 to 325 mesh as determined with standard sieves for electrodes up to number 72; 150 to 250 mesh for electrodes numbered 73 and above). The $Zn(Hg)$ and $NaCl$ is hand mixed with spatula and glass rod to avoid procedures such as ball mixing which might change the $NaCl$ grain size. A weight-weight ratio of $Zn(Hg)$ to $NaCl$ of 10/4 has been found to yield a satisfactory electrode. Electrodes with a 6/4 ratio were found to be unsatisfactorily fragile.

The desired quantity of mix is weighed out and poured into a hardened stainless steel die over a weighed circular piece, 1.0 cm^2 , of expanded metal screen (Exmet Corp., 5 Ag5-4/0). The electrode is pressed for ten minutes (20,000 psi for electrodes up to number 67; 40,000 psi for electrodes numbered 68 and above). Mechanical strength of the electrodes was found to improve if the pressure was left on for 10 minutes as opposed to simply

bringing the electrode up to pressure and then releasing.

After removal from the die, each electrode is successively leached in several portions of distilled water over a 24-hour period. Complete removal of Cl^- is checked by addition of AgNO_3 to the last electrode rinse water. The electrode is then vacuum dried, weighed, and stored in a desiccator for later use.

Electrode thickness tolerances (applied after electrode 27) were 0.038" to 0.040". The electrodes have been subjected to simple porosity tests which are described below (See Table 2.4).

2.4.2.4 Electrode Solution Analysis

The following symbols are defined and used to describe the electrode and its analysis:

$A \equiv$ apparent electrode surface area

$\delta \equiv$ electrode thickness = depth of the electrode holder

$V \equiv$ volume of the electrode = volume of the zinc electrode chamber in the Lucite holder

$$= A\delta$$

$$= \pi r^2 \delta = 3.15 (0.56 \text{ cm})^2 (0.100)$$

$$= 0.100 \text{ cm}^3 \text{ (constant)}$$

$\epsilon^i \equiv$ initial electrode porosity

$\epsilon^f \equiv$ final electrode porosity, after single discharge electrolysis

$m_{\text{Ag}} \equiv$ mass of expanded silver metal screen (constant)

$\rho_{\text{Ag}} \equiv$ density of silver metal

$m_{\text{Zn(Hg)}}^i \equiv$ mass of amalgamated zinc used to form the electrode

$\rho_{\text{Zn(Hg)}} \equiv$ density of amalgamated zinc used to form the electrode

$v_{\text{Zn(Hg)}}^i \equiv$ initial volume of zinc amalgam

$\alpha \equiv$ weight-weight fraction of zinc in the zinc amalgam used to form the electrode

$\beta \equiv$ weight-weight fraction of mercury in the zinc amalgam used to form the electrode

$m_{\text{Zn}} \equiv$ mass of zinc reacted electrolytically, based on Faraday's Law and assumed 100% current efficiency

$m_{\text{ZnO}} \equiv$ mass of zinc oxide formed electrolytically, based on Faraday's Law and assumed equilibration of solution species with solids.

$C_1 \equiv$ volume average potassium concentration in the solution in the zinc compartment

$C_2 \equiv$ volume average zinc concentration in the solution in the zinc compartment

$C_3 \equiv$ volume average hydroxyl concentration in the solution in the zinc compartment

$\rho_{\text{ZnO}} \equiv$ density of ZnO

The initial electrode porosity is calculated as follows:

$$v_{Zn(Hg)}^i = \frac{m_{Zn(Hg)}^i}{\rho_{Zn(Hg)}} = \frac{\alpha m_{Zn(Hg)}^i}{\rho_{Zn}} + \frac{\beta m_{Zn(Hg)}^i}{\rho_{Hg}} = m_{Zn(Hg)}^i \left(\frac{\alpha}{\rho_{Zn}} + \frac{\beta}{\rho_{Hg}} \right) \quad [5] *$$

$$v_{Ag} = \frac{m_{Ag}}{\rho_{Ag}} \quad [6]$$

$$V = v_{Zn(Hg)}^i + v_{Ag} + \epsilon^i V \quad [7]$$

$$\epsilon^i = 1 - \left(v_{Zn(Hg)}^i + v_{Ag} \right) \frac{1}{V} \quad [8]$$

$$\epsilon^i = 1 - \frac{m_{Zn(Hg)}^i}{V} \left(\frac{\alpha}{\rho_{Zn}} + \frac{\beta}{\rho_{Hg}} \right) - \frac{m_{Ag}}{\rho_{Ag}} \frac{1}{V} \quad [9]$$

Final electrode porosity is calculated from:

$$V = v_{Zn(Hg)}^f + v_{Ag} + v_{ZnO} + \epsilon^f V \quad [10]$$

$$\epsilon^f = 1 - \frac{m_{Zn(Hg)}^i}{V} \left(\frac{\alpha}{\rho_{Zn}} + \frac{\beta}{\rho_{Hg}} \right) - \left(\frac{m_{Zn}}{\rho_{Zn}} + \frac{m_{Ag}}{\rho_{Ag}} + \frac{m_{ZnO}}{\rho_{ZnO}} \right) \frac{1}{V} \quad [11]$$

$$\epsilon^f = 1 - \frac{m_{Zn(Hg)}^i}{V} \left(\frac{\alpha}{\rho_{Zn}} + \frac{\beta}{\rho_{Hg}} \right) - \left(\frac{It(65.4)}{\rho_{Zn} 2F} + \frac{m_{Ag}}{\rho_{Ag}} + \frac{It(81.4)}{2F \rho_{ZnO}} \right) \frac{1}{V} \quad [12]$$

*This approximation could be improved if partial molar volumes of zinc amalgams were available.

After electrolysis is completed the electrode is removed from the cell as quickly as possible (less than 1.0 minute) and transferred to a special centrifuge test tube and crushed with a glass rod under 10 ml of ethanol; the mixture is shaken vigorously for one minute and then centrifuged at 21,000 RPM for 5 minutes. The fluid is decanted into a 25.0 ml volumetric

flask and the ethanol leach, centrifuging and decantation repeated. The volumetric flask is then brought to volume and the fluid is analyzed for total potassium by FES (Flame Emission Spectroscopy) and for total hydroxide by volumetric titration. It is assumed that during the leaching process all $K_2Zn(OH)_4$ present in the electrolytic solution yields precipitated ZnO and KOH in solution. All KOH is assumed to be leached out by the ethanol (8).

To the solids remaining in the test tube, approximately 10 ml of potassium hydroxide of specific gravity 1.40 is added and the contents shaken vigorously. The tube is centrifuged and the fluid decanted into a 25.0 ml volumetric flask. This process is repeated once after which the fluid in the flask is brought to volume and the contents are analyzed for Zn by AAS (Atomic Absorption Spectroscopy) and EDTA titration. During this procedure it is assumed that all ZnO present in the electrode residue is leached out and determined.

To the solids remaining in the test tube concentrated HCl is added, time is allowed for complete reaction of all zinc metal, and the fluid is decanted into a 100 ml volumetric flask, made to volume and determined for zinc by both AAS and EDTA titration.

We define:

$n_K \equiv$ total moles of potassium found in the alcohol rinse solutions

$n_{OH} \equiv$ total moles of hydroxide found in the alcohol rinse solutions

$n_{ZnO} \equiv$ total moles of zinc found in the KOH rinse solutions

$n_{Zn} \equiv$ total moles of zinc found in the HCl rinse solutions

Concentrations may then be calculated from:

$$C_1 = \frac{n_K}{V \epsilon} \quad [13]$$

$$C_3 = \frac{n_{OH}}{V \epsilon} \quad [14]$$

C_1 and C_3 should be nearly the same and the extent of their disagreement may be taken as one measure of experimental uncertainty. True OH^- concentration in the electrode at the end of electrolysis is less than C_3 , i.e., the alcohol rinse is believed to cause;

[15]

To test the analytical technique described above, known mixtures were prepared and analyzed. Measured volumes of stock solution containing potassium and zinc at known concentrations were added to 95% ethanol and carried through the procedure. The results for four samples are shown in Table 2.2.

TABLE 2.2

Sample #	Moles of zinc added	Moles of zinc found in KOH extract	Moles of potassium added	Moles of potassium found in ethanol extract
1	3.77×10^{-5}	3.78×10^{-5}	4.79×10^{-4}	4.70×10^{-4}
2	"	3.80×10^{-5}	"	4.76×10^{-4}
3	"	3.72×10^{-5}	"	4.76×10^{-4}
4	"	3.77×10^{-5}	"	4.80×10^{-4}

On the basis of these results it was concluded: that the zinc present in the original stock solution was quantitatively precipitated in the 95% ethanol; that the potassium in the stock solution was dissolved into the alcoholic solution; and that the zinc precipitated was redissolved in the KOH rinse solution.

In another similar set of tests known quantities of stock solution containing potassium and zinc were added to ethanol in the presence of known quantities of zinc metal. In this case the potassium results were as good as before; however, the zinc analyses for zinc dissolved by KOH rinse indicated that some zinc originally present as zinc metal was finding its way into the rinse solution. The extent of this effect was as great as 25% of the zinc expected. However, provided electrolyses times in the cell are long enough (e.g. 0.020 amps for 30 minutes) the zinc expected to be present as oxide at the end of electrolysis is approximately five times that present in solution at the beginning of the experiment. The fractional analytical error in moles of zinc oxide found due to non-electrolytic metal oxidation should be smaller.

Assumptions recognized in the analytical method and associated

calculations are (a) equality of electrode thickness and holder depth, (b) simple volume additivity in the case of the zinc amalgam and related approximation in equation 11, (c) the assumption that total pore volume of the electrode is filled with fluid and retained during extraction of the electrode from the cell. Point (a) is a mechanical matter which involved learning to make the electrodes within desired thickness tolerances. Point (b) is not believed to be a critical matter within the limits of uncertainty we are seeking, i.e., a relative uncertainty of $\pm 10\%$. Point (c) is a problem which we have investigated by simply placing electrodes in the cell, vacuum filling them with solution of known concentration, then removing and analyzing the electrodes without electrolysis. The degree of agreement between analytical results and the known initial concentrations has been used as an additional means of evaluating the assumptions on which the method is based (See Table 2.5). A final, and perhaps most critical, assumption in the experiments is related to cell design and involves additional reservoir volume accessible to the electrode. We are speaking here of a comparison of fluid volume in the porous electrode with "excess" or "nuisance" fluid volume trapped in the capillaries and tubes which join the reference electrodes to the cell and those which are used for vacuum filling of the cell. It was assumed that the use of the small capillary openings, 0.013" diameter, of length 0.10", would effectively prevent transfer of species between the fluid in the electrode and excess fluid in the connecting capillary tubes. No special experimental method has been devised to test this assumption and we will make further comments about it below in our discussion of experimental results. The information in section 2.4.3.1, Cell Relaxation Time, is also pertinent.

2.4.2.5. Pressure Measurements--Equipment Description

Late in the report year the cell was modified to allow static pressure measurements during electrolysis. A Miniature Pressure Transducer, Model 147, from Precision Measurement Co., was flush mounted in the back of the zinc compartment and calibrated. A few pressure measurements, as described below were made before the seal on the transducer failed allowing KOH solution to penetrate and destroy it.

2.4.2.6 Hydrogen Permeability of the RAI P2291 40/30 Membrane

A small cell was designed and constructed which allowed a constant pressure of hydrogen gas to be applied to one side of a layer of membrane. The other side of the membrane was flooded with electrolytic solution and provision was made to trap the hydrogen which crossed the membrane. From measurements of membrane area, hydrogen pressure, amount of hydrogen transferred and time, rate of transfer of hydrogen as a function of pressure difference was obtained.

2.4.3 Results

2.4.3.1 Cell Relaxation Time

The time necessary for concentration changes due to electrolysis to relax after termination of cell current was of interest. Assuming overpotential between R-1 and the zinc electrode is primarily due to concentration changes, decrease of the overpotential with time is one measure of the rate of relaxation of concentration changes built up due to electrolysis. An electrode was discharged for 60 minutes at 25 mA after which cell current was terminated. Total overpotential as indicated by reference electrode R-1 is plotted vs. time in Fig. 2.10. Overpotential rose to about 79 mV and was not effected immediately by cell current termination indicating that overpotential was not some simple resistive effect related to current passage. The initial rate of decay of overpotential was observed to be about 1.5 mV/min. Percent decay of overpotential after current termination, $t = 60$ min., was: 4%, 2.5 min.; 9%, 5.0 min.; 12%, 7.5 min. Since the design of the cell allows removal of the electrode within one minute after current termination, it was felt that natural relaxation of concentration differences would not seriously effect the results. This conclusion seems valid whether one is considering relaxation by movement of species through the cell membrane or by movement of species from "nuisance" volumes in the capillaries of the Lucite holder. This point is considered further below.

2.4.3.2 Initial Experimental results

The results from six initial experiments including values of C_1/C_1^0 are given in Table 2.3 and Figs. 2.3, 2.11, and 2.12.

In Fig. 2.11 and 2.12, overpotential data for the electrode pairs R-1 to Test and R-2 to Test are plotted as a function of time for the

cells described in Table 2.3.

2.4.3.3 Additional Testing of Analytical Method

The failure of the initial experimental potassium concentration to agree even approximately with theory (Fig. 2.3) led us to check other aspects of our experimental method and inquire more closely into potential sources of experimental errors. One concern was whether porosity as calculated was realistic. A number of electrodes were filled with distilled water or the stock electrolytic solution of known density and concentration under different conditions and the void volume, *i.e.*, porosity, determined by weight differences. Representative results are shown in Table 2.4. After a large number of tests, it was concluded that calculations of initial porosity on the basis of equation 9 were commonly in agreement with the gravimetric porosity (based on weight of water necessary to fill the pores) to within $\pm 10\%$. However, it was also discovered that considerable error could be incurred by different methods of handling the fluid filled electrodes. In particular, it was found that large fractions of cell fluid could be lost during removal of electrodes from the cell. Apparently a partial seal is formed under and around the electrode when it is seated in the cell; attempts to simply lift the porous electrode from the holder causes loss of fluid due to a suction effect (this would cause low results). We found (electrodes 77-80) that this effect could be partially alleviated by holding the RAI membrane material tightly down on the top of the electrode as it was being removed from the cell. The potassium data for electrodes 77 through 80 (Table 2.4) which were simply vacuum filled in the cell with stock solution and then removed and analyzed is believed to be representative of the uncertainty of the method. With care, accuracy of the potassium results with standard solutions are commonly better than 5% but an occasional large error (electrode 80) occurs, probably due to loss of fluid during handling of the electrode.

Fig. 2.10 Overpotential vs. time data for the couple R-1 to Test electrode at the conclusion of a 0.025A electrolysis of the test cell for one hour. The rate of relaxation of overpotential after cell current was terminated (60 min.) is shown.

TABLE 2,3

Elec- trode #	Cell Current i	Dis- charge Time	Initial Concentrations (Molar)				Final Experimental Concentrations (Molar) Based on Alcohol Extract		Moles Zn found as ZnO	Theoretical Zn as ZnO **
			$[K^+]_1 = C_1^0$	$[OH^-]_1 = C_3^0$	$[CO_3^{--}]_1$	$[Zn(OH)_4^{--}]_1 = C_2^0$	$[K^+] = C_1$	$[OH^-] + 2[CO_3^{--}]$		
6	0.20A	30 min.	10.1	7.5	0.16	1.14	8.8	8.7	1.96×10^{-4}	1.87×10^{-4}
7	"	"	"	"	"	"	10.5	10.7	1.98×10^{-4}	1.87×10^{-4}
8	"	60 min.	"	"	"	"	10.6	10.6	3.92×10^{-4}	3.73×10^{-4}
9	"	60 min.	"	"	"	"	10.2	10.2	4.34×10^{-4}	3.73×10^{-4}
10	"	90 min.	"	"	"	"	9.2	9.11	5.75×10^{-4}	5.60×10^{-4}
11	"	150 min.	"	"	"	"	14.3*	14.0		
12	0.050	30 min.	"	"	"	"	7.6	8.42	5.19×10^{-4}	4.66×10^{-4}

* Large discrepancy in final porosity.

** Based on Coulombs of charge passed through the cell.

Fig. 2.11 Overpotential vs. time (R-1 to Test) data for six cells discharged at 0.020A for different times. Electrode numbers correspond to those in Table 2.3.

Fig. 2.12 Overpotential vs. time (R-2 to Test) data for six cells discharged at 0.020A for different times. Electrode numbers correspond to those in Table 2.3.

TABLE 2.4

electrode #		ϵ_c^i	$\epsilon_{H_2O}^i$	ϵ_{KOH}^i	$[K^+]$, molar stock solution	$[K^+]$, molar, calc.,
20	vac. filled in cell	0.63	0.70		9.5	8.3
21	vac. filled bell jar	0.63		0.56	9.5	8.9
22	vac. filled bell jar	0.65		0.59	9.5	9.4
23	vac. fill	0.68	0.64	0.70		
24	not vac. fill	0.64	0.70			
25	"	0.65	0.63			
26	"	0.66	0.80			
27	"	0.68	0.72		9.5	9.3
28	vac. filled in cell (KOH only)	0.68	0.69	0.55		
29	"	0.67	0.67	0.52		
30	"	0.69	0.77	0.51		
31	"	0.66	0.62	0.57		
34	vac. filled in cell	0.67	0.68			
35	"	0.68	0.66			
36	"	0.68	0.62			
37	"	0.68				
38	"	0.68	0.62			
77		0.63	0.69	0.59	9.5	9.7
78		0.63	0.65	0.55	9.5	9.4
79		0.63	0.65	0.61	9.5	9.5
80		0.63	0.74	0.49	9.5	8.4

ϵ_c^i = calculated porosity, see equation 8.

$\epsilon_{H_2O}^i$ = experimental porosity based on weight measurement involving H_2O uptake of the electrode.

ϵ_{KOH}^i = experimental porosity based on weight measurement involving uptake of stock KOH solution.

$[K^+]$ = molar potassium concentration, stock solution

$[K^+]*$ = calculated potassium concentration using moles of K^+ found in the electrode by FES and the porosity value ϵ_c^i from equation 9.

2.4.3.4 Second Series of Experimental Results

The results of a second series of tests are shown in Table 2.5 and in graphs in Figs. 2.13 and 2.14. Some additional tests on the cell operated without RAI membranes or with diluted electrolytic solution were carried out. The data are summarized in Figs. 2.15 and 2.16 which also repeats the data of Figs. 2.13 and 2.14 for comparison. Thus, in Figure 2.15 several "normal" sets of data are shown for the potential difference R-1 to Zn test electrode for discharge of the cell at 0.020 mA/cm^2 with the RAI membranes in place; in addition, data are shown for discharge at the same rate but without membrane, and, data for discharge at the same rate but at lower initial electrolyte concentration. Figure 2.16 shows corresponding data for the electrode pair R-2 and the zinc test electrode.

2.4.3.5 Pressure Measurements

In Figure 2.17 some very limited data concerning pressure variations in the cell during discharge are shown.

2.4.3.6 Hydrogen Permeability Measurements

A few measurements were carried out which indicated a rate of hydrogen transfer through the RAI P2291 40/30 membrane of 1×10^{-11} moles/cm² (lb/in²) sec. This may be compared with 1×10^{-9} moles/cm² sec of hydrogen generated at 1% current efficiency at 0.020 A/cm^2 .

2.4.4 Discussion of Results

2.4.4.1 OH⁻ Depletion as a Failure Mode.

Given (a) the large magnitude of the predicted concentration effects (according to eqs. 3 and 4) during cell discharge, (b) the magnitude of the apparent concentration overpotentials observed, (c) the average degree of uncertainty associated with the concentration data, and (d) the fact that Dr. Sunu assembled an impressive list of evidence, both theoretical and experimental, for OH⁻ depletion as a failure mode under conditions of discharge similar to those used in these experiments, it is surprising that our data do not show significant OH⁻ depletion during discharge.

Two avenues are clearly open for further consideration: (a) Sunu's theory of OH⁻ depletion is correct and something in our experimental method is preventing our detection of the large predicted concentration changes; and (b) Sunu's simplified theory concerning OH⁻ depletion is incorrect due to neglect of important transport related driving forces.

TABLE 2, 3

Elec- trode #	Cell Current	Dis- charge Time	Initial Concentrations (Molar)				Final Experimental Concentrations (Molar) Based on Alcohol Extract		Moles Zn found as ZnO	Theoretical Zn as ZnO **
			$[K^+]_{I=C_1^0}$	$[OH^-]_{I=C_3^0}$	$[CO_3^{=}]_1$	$[Zn(OH)_4^{=}]_{I=C_2^0}$	$[K^+]_{=C_1}$	$[OH^-] + 2[CO_3^{=}]$		
73	0.025A	30 min.	9.9	7.3	0.16	1.14	7.3	7.0	2.32×10^{-4}	2.33×10^{-4}
74	0.025A	30 min.	"	"	"	"	6.8	6.5	2.34×10^{-4}	"
81	0.050A	30 min.	"	"	"	"	9.5	9.0	4.08×10^{-4}	4.69×10^{-4}
93	0.050A	30 min.	"	"	"	"	9.0	8.2	3.72×10^{-4}	"
96	0.75A	30 min.	"	"	"	"	9.5	8.8	6.98×10^{-4}	7.00×10^{-4}
97	0.075A	22.5 min.	"	"	"	"	8.8	7.9	5.79×10^{-4}	5.25×10^{-4}
98	0.100A	22.5 min.	"	"	"	"	8.0	7.6	6.05×10^{-4}	7.00×10^{-4}
99	0.100	16.02 min.	"	"	"	"	7.9	7.4	5.22×10^{-4}	4.98×10^{-4}

C_1 = final observed potassium concentration

Fig. 2.13 Overpotential vs. time (R-1 to Test) for eight cells discharged at constant apparent current densities of 25 to 100 mA per cm² for various times as indicated in Table 2.5. Test electrode numbers correspond to those in Tables 2.4 and 2.5.

Fig. 2.14 Overpotential vs. time (R-2 to Test) for eight cells discharged at constant apparent current densities of 25 to 100 mA per cm^2 for various times as indicated in Table 2.5. Test electrode numbers correspond to those in Tables 2.4 and 2.5.

Fig. 2.15 Comparative overpotential vs. time data, reference electrode R-1 vs. the test zinc electrode. Solid lines are as in Figure 2.11 for the electrodes indicated. ●, data for two electrodes operated with no membrane separators in the cell. ■, data for an electrode discharged in the cell with membrane in place but stock solution diluted by 1:1 with distilled water.

Fig. 2.16 Comparative overpotential vs. time data, reference electrode R-2 vs. the test zinc electrode. Solid lines repeat Figure 2.12 for the electrodes indicated. ●, data for an electrode operated for 30 min. at 0.020A with no membrane separators in the cells.

Fig. 2.17 Pressure variation in the zinc compartment of the cell during a 30 min. discharge. — 0.020A cell current.
----- 0.050A cell current.

Under category (a), problems in experimental method, we tend to suspect problems with nuisance volumes in the cell. However, the rate of decay of overpotential after termination of cell current (Fig. 2.10) indicates that relaxation is not fast; if it is concentration differences which cause the observed overpotentials they are not being rapidly returned to their original values by influx of species across the membrane or from nuisance volumes. The poor reproducibility and lack of regularity of overpotential data indicated for the second series of experiments (Fig. 2.13 compared to Fig. 2.11) indicate that there are parameters which we are not adequately controlling and/or not understanding in the experiment. Concentration overpotentials in cells of this type have been discussed previously (10) and values of 60 mV are clearly within the realm of possibility--if zincate concentrations rise well above equilibrium levels as they are known to do (10).

Other evidence which needs to be considered relative to the existence of the predicted large OH^- depletion is related to osmotic and electro-osmotic effects observed in cells with "normal" convective flow which use the same membrane material (10). In such cells, volumetric flows established during electrolysis are observed to decay and change direction within a few minutes after termination of cell current. These observations have been interpreted as indicating a rapid decay of electroosmotic effect as well as an osmotic effect associated with potassium and hydroxyl ions but a slow decay of an osmotic effect associated with zincate (8). According to this interpretation overpotentials being observed (R-1) in the present experiments would be attributed primarily to slowly decaying non-equilibrium zincate concentrations.

Under (b) above, we believe that there may be a problem in treatment of the flux of water across the membrane under the given physical circumstances (discharge of the zinc electrode with severely restricted convective flow). It is possible that the development of large concentration differences across the membrane as predicted by the simplified theory is not physically realistic in that a water flux may develop which tends to transfer solute in such a direction that expected concentration imbalance does not develop. The observed hydrostatic pressure difference,

as shown in Fig. 2.16, is in such a direction as to support this view.

The regularity and reproducibility of the overpotential data in Fig. 2.11 were encouraging; however, even with this set of data we must note that overpotentials shown in Fig. 2.12 for the same cells by the pair R-2 to test electrode, which should all be the same at the same times, differ widely. It is strongly suspected, from observations of the electrodes after electrolysis, that current densities were not uniform over the zinc electrodes. It is possible that the overpotential differences shown in Figure 2.12 are a result of such non-uniformity in current density. The same could be said of the data in Figures 2.13 and 2.14. However, in the latter case additional effects seem to be present. For electrodes 93 through 99 rapid increases in overpotential (R-1) near the end of electrolysis were noted. Large fractions of these increases decayed within fractions of a second upon termination of cell current (Fig. 2.13) indicating simple resistive overpotential. Neither of these effects was noticed at lower current densities.

In our opinion, the questions which we have raised about OH^- depletion as a failure mode based on the work described above are important to zinc electrode technology; in addition, since our data raise questions concerning some of Dr. Sunu's interpretations of zinc electrode discharge data, we feel a responsibility to continue experimental work along this line until a clear result emerges. Additional experiments are, therefore, currently being carried out under subcontract 4506910, LBL which are designed to provide further information on the topic.

2.4.4.2 Conducting Permanent Matrix for the Zinc Electrode.

We have suggested that one avenue for improvement of the zinc secondary electrode is provision of a permanent conducting porous matrix or substrate for the electrode. Such a matrix would: (a) allow periodic stripping of zinc without matrix destruction, (b) help prevent detachment of active material from the current collector, (c) help provide a more reproducible surface area as cycling proceeds. One approach which we have investigated under subject contract is a porous nickel body as a matrix material. We have fabricated nickel structures of favorable porosity and structural strength and have investigated the feasibility of uniformly electroplating onto these structures materials of high

hydrogen overvoltage. This very limited work with nickel as substrate has not been successful and has been rather severely criticized by industrial technologists. The work is described in detail in the thesis of Mr. John Pfeffer (20). Although the initial choice of Ni as a porous substrate was probably a mistake electrochemically, we still suggest that a permanent conducting matrix would be beneficial in the electrode body and are continuing our search for a suitable material.

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