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September 1985

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OPTICAL AND ELECTROCHEMICAL STUDY OF

MODEL ZINC ELECTRODE PORES IN ALKALINE ELECTROLYTE

by

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ABSTRACT

A computer-controlled model single-pore cell has been developed to study zinc electrode discharge behavior in alkaline electrolytes. The cell design allows for simultaneous microscopic and potential performance observations. A quartz-supported, thin-film cadmium reference microelectrode was designed, fabricated and installed in the cell to provide pore potential distribution and hydroxyl-ion concentration information. The thin-film cadmium reference microelectrode was designed to be stable in strong alkaline electrolyte without interfering significantly with transport processes in the pore. Reference microelectrode fabrication involved the use of microelectronic metal deposition and photolithographic techniques. The cell was designed to create model pores of dimensions comparable to those in commercial zinc electrodes. Zinc electrode discharge behavior was studied in pores of effective radii between 14 and 20 microns at 7 mA/cm$^2$, 30 mA/cm$^2$ and 1250 mA/cm$^2$ rates of discharge in 7.7M KOH electrolyte. Results are consistent with a dissolution-precipitation discharge reaction mechanism. SEM studies showed significant variations in electrode surface morphology with location in the pore and rate of discharge. Significant pore $[\text{OH}^-]$ gradients, with slow relaxation times, were found to exist within the pore at the 30 mA/cm$^2$ rate. There was no evidence of electrode passivation at 30 mA/cm$^2$ and 7 mA/cm$^2$ rates, but passivation was observed at the 1250 mA/cm$^2$ rate. Zinc electrode discharge behavior in 3.5M KOH-3.4M KF showed a similar discharge reaction mechanism. However, earlier surface film formation in 3.5M KOH-3.4M KF was found to occur, which is consistent with reduced zinc solubility. Earlier film formation may decrease zinc redistribution rates by decreasing the residence time of soluble zinc species in the electrolyte. Initial reaction penetration depths in 7.7M KOH and 3.5M KOH-3.4M KF electrolytes were found to be 0.11 cm and 0.10 cm, respectively.
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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

The alkaline zinc-nickel oxide (Zn/NiOOH) battery is a promising candidate for use as a power source of electric vehicles. The Zn/NiOOH battery, however, is not able to meet life-cycle requirements for electric vehicle batteries. The porous zinc negative electrode limits the cycle life of the Zn/NiOOH battery. Four primary failure modes have been linked to the zinc electrodes' short cycle life in alkaline electrolyte: zinc redistribution, zinc densification, shorting by zinc dendrite growth, and zinc passivation. The goal of the work described here is to obtain fundamental information about zinc electrode behavior in alkaline electrolytes to improve understanding of the electrode failure modes. This information may eventually lead to improvements in Zn/NiOOH cell design.

The Zn/NiOOH battery typically consists of a series of alternating porous zinc and nickel oxide electrodes spaced by a cellophane separator and electrode-wetting wick material, and contained in aqueous KOH electrolyte. The overall chemical reaction for the Zn/KOH/NiOOH system is:

\[ 2\text{NiOOH} + \text{Zn} + \text{H}_2\text{O} = 2\text{Ni(OH)}_2 + \text{ZnO} \]  

(1)

The electrochemical half-reaction at the positive electrode is:

\[ 2\text{NiOOH} + 2\text{H}_2\text{O} + 2e^- = 2\text{Ni(OH)}_2 + 2\text{OH}^- \]  

(2)

The electrochemical half-reaction at the negative electrode is:

\[ \text{Zn} + 2\text{OH}^- = \text{ZnO} + \text{H}_2\text{O} + 2e^- \]  

(3)
1.2 ZINC ELECTRODE FAILURE MODES

Zinc redistribution, commonly referred to as shape change, results in a loss of cell capacity over cycle life. Zinc redistributes across the face of the electrode, which leads to uneven zinc deposit thickness and exposure of the current collector. Cell capacity is reduced because: (a) zinc-depleted or zinc-bare sections reduce charge and discharge reactions at corresponding sections on the nickel electrode, and (b) there is a loss of projected surface area of the zinc electrode. Zinc redistribution becomes progressively worse with cycling, and thus is a serious barrier to increasing zinc electrode cycle life. 5

The problem of zinc redistribution can be traced to the movement of soluble zinc species in alkaline electrolyte by various transport mechanisms: forced convection, free convection, diffusion and migration. The causes and mechanisms of zinc redistribution still are not well understood. However, recent work on the problem by Choi has suggested that zinc redistribution is caused by convective flows induced by membrane "pumping" which preferentially distribute soluble zincate \((\text{Zn(OH)}_2\text{OH})\). Previous work by McBreen related zinc redistribution to non-uniform current density distribution at the zinc electrode surfaces. 7

Zinc densification results in a loss of active material surface area, which also leads to a loss of capacity. Zinc densification is associated with a loss of porous structure within the electrode. In the worst cases, pores may actually become blocked at the pore entrance, thus preventing electrode reactions within those pores. 8 Zinc densification may be related to zinc redistribution.

Shorting by zinc dendrite growth to the nickel oxide electrode leads to catastrophic failure of the cell. Zinc dendrite growth results from locally high overpotentials and inadequate hydroxyl-ion concentration. During cycling, local regions of the electrolyte may become starved of hydroxyl ions, which causes a growth of zinc from high \([\text{OH}^-]\) to low \([\text{OH}^-]\) region. 9,10 The zinc preferentially grows in needle-like formations, perpendicular to the electrode surface. The growth of zinc dendrites during the charge half-cycle has been associated with the
formation of hydrogen bubbles on the zinc electrode surface, which causes local, non-uniform current density distribution. This phenomenon can cause a local increase in overpotential in the spaces between bubbles, which leads to growth of dendrites between hydrogen bubbles. Various microporous polymer membranes, placed between the zinc and nickel oxide electrodes, help prevent dendrites from bridging to the nickel oxide electrode.

The condition that occurs when the zinc electrode rapidly polarizes on discharge, because of inability to carry out normal electrode reactions, is termed passivation. Studies of passivation have been carried out on planar zinc electrodes by many investigators. Liu suggests that passivation is caused by the inability of hydroxyl ions (OH⁻) to transport and react at the electrode surface because of zinc oxide film formation on the surface. Near the beginning of the discharge, a "Type I" porous ZnO film slowly forms and achieves a critical thickness, which prevents OH⁻ transport to the surface sufficient to sustain the reaction. At a later point in the discharge, a "Type II" compact ZnO film forms which completely prevents transport of OH⁻ ions to the electrode surface. It has been found experimentally that the time required for the onset of passivation of planar electrodes is related to current density by the following equation:

\[(i - i_e)t^{1/2} = k\]  (4)

where:

\[i\] = electrode current density (mA/cm²)
\[i_e\] = diffusion-excluded convective current density (mA/cm²)
\[t\] = time until onset of passivation (seconds)
\[k\] = correlation constant (mA·sec⁻¹/²·cm²)

Hampson found that passivation of porous electrodes occurs more slowly and less abruptly than in planar electrodes. Passivation was indicated by a gradual increase in electrode potential was associated with penetration of the reaction into the depth of the zinc electrode as pore surfaces became passivated with oxide.
1.3 PHILOSOPHY OF SINGLE-PORE STUDIES

All four previously-described failure modes are related to microscopic processes occurring with the confines of the pores. Microscopic morphological changes can occur as a result of variations in local current densities and both zincate and hydroxyl ion concentrations, and they are strongly manifested by transport processes that are a function of pore dimensions. Thus, it is useful to study the behavior of zinc in single pores of dimensions similar to those of actual pores within zinc electrodes.

Because of statistical variations of pore configuration and dimensions, one cannot expect to exactly replicate actual pores. Rather, idealized model pores with adjustable dimensions can be useful in deriving approximate qualitative and quantitative information about zinc behavior in actual pores. It is important to design a model single pore which both replicates important pore dimensions is experimentally accessible with electrical and optical instruments. Methods of zinc behavior observation must not interfere with zinc behavior, such as restricting or enhancing transport of species within the pore.

The model single pore used in this study is based on a design originally created by T. Katan, modified to permit simultaneous electrical and optical performance observation. A side view of the pore is shown in Figure 1.1, and Figure 1.2 shows schematically the model pore derivation, indicating how the model single pore relates to actual pores in electrodes. Three significant improvements on Katan's cell have been made to increase the quality and quantity of information obtained from the pore. First, reference microelectrodes, which are used to obtain potential distribution information throughout the pore, are deposited on a thin, clear, quartz cover slide which allows simultaneous visual observation through a microscope. Secondly, the pore length has been reduced from 6.0 mm to 1.5 mm to better replicate pore dimensions. Finally, a computerized experiment control and data-acquisition system has been implemented to accurately record potential and visual information over time. This is necessary to resolve small potential differences over short periods of time.
Figure 1.1 Side view of Model Single Pore Cell.
A. Commercial zinc electrode consisting of bonded particles with interconnected pores.
B. An idealized abstraction of a commercial electrode retaining tortuous pores, but pores are no longer connected.
C. A further abstraction where pores pass through the electrodes (tortuosity factor = 1).
D. A section through the cell, shown in abstraction and as the model single-pore electrochemical cell. Dashed box outlines the same section in Figures C and D. Thus, the coverslide passes through the centerline of the idealized pore.

Figure 1.2 Model Single Pore Derivation from Commercial Porous Electrode.
1.4 PREVIOUS POROUS ELECTRODE SIMULATION STUDIES

Previous porous electrode simulation studies fall into one of two categories: 1) construction of actual or idealized macroscopic porous structures resembling actual porous electrodes; and 2) construction of microscopic model single pores resembling typical single pores in a porous electrode. Both approaches have certain advantages and drawbacks. The first approach provides the best replication of porous structure and gives information concerning the behavior of pores in aggregate.

The second method allows for microscopic, in-situ observation of single pores, which the first method cannot provide. Unfortunately, the model single pores are not as representative of actual pores as are pores fabricated by the first approach. This section will summarize the methods and results of previous porous electrode simulations utilizing both approaches. For brevity, not all studies will be reviewed; only studies making important contributions to porous electrode simulation techniques or understanding of zinc electrode behavior will be mentioned.

1.4.1 MACROSCOPIC POROUS ELECTRODE SIMULATION

Actual commercial porous electrodes have been studied by several investigators.\textsuperscript{21-24} The electrodes are usually cycled and then examined post-situ by sectioning the electrode. Sections of the electrodes can be examined for chemical composition and changes in porous structure.

Bro and Kang sliced cadmium electrodes into sections after discharge and analyzed each section for \(\text{Cd}^{2+}\) to reconstruct reaction profiles.\textsuperscript{21} Nagy and Bockris similarly examined the alkaline zinc electrode, supplemented by SEM examination to determine electrode micromorphology.\textsuperscript{22} Sunu and Bennion compared in-situ electrode overpotential measurements with predicted results from a complex mathematical model in order to obtain information on zinc redistribution.\textsuperscript{23} McBreen examined lateral current density and overpotential distribution over a sectioned zinc electrode face to elucidate causes of zinc redistribution.\textsuperscript{24}
Studies have been done with ordered, idealized porous structures to provide a reproducible structure. The well-defined geometry of the porous structure lends itself to mathematical modeling, in addition to quantitative characterization of morphological changes. Porous structures have been constructed from uniformly-packed spheres, cylinders and wires of varying dimensions. For example, Katan and Grens carried out in-situ measurements of the effect of increasing porous electrode thickness of an oxygen gas electrode by dropping uniform silver spheres onto a silver grid. Chopped silver wire electrodes were used to study the Ag/AgO electrode, and the results confirmed experimental knowledge that optimum silver electrode performance is obtained with silver particles ranging from 1-10 µ in diameter. Liu, et al used a segmented porous electrode consisting of 265µ-diameter pores to determine current distribution profiles in alkaline zinc electrodes. Katan and Bauman's work on relating structural variables, such as pore diameter, specific surface area and porosity, to ordered structures constructed with various particle shapes is useful in characterizing ordered porous structures.

1.4.2 ELECTRODE SIMULATION WITH MODEL SINGLE PORES

Model single pores have been utilized to study battery electrode processes for almost twenty years. Simon and Damjanovic demonstrated that in-situ optical microscopy of electrode surfaces in model single pores could provide useful information about transient electrode processes and morphology variations. In this manner, morphological studies of zinc electrodes have been performed by several investigators. These morphological studies were aided by post-mortem SEM studies. Results from the studies were useful in understanding the alkaline zinc electrode discharge mechanism.

More recently, model single pores containing reference electrodes have been utilized to obtain more quantitative information about the electrochemical behavior of electrode material. Reference electrodes are useful in determining potential and current distributions at the electrode and can yield information about local species concentration with suitable modeling. Katan studied alkaline zinc electrodes at
high current densities and correlated the movement of sequential ZnO precipitation fronts with polarization of the electrode. Gu and Bennion determined post-mortem reaction profiles in the Ag/AgCl system through use of an electron microprobe.

Segmented electrodes have been applied to determine current density distribution in model single pores. Szpak and Katan used a 60μ-wide pore containing isolated segments of vapor-deposited zinc to determine current distribution and reaction penetration depth as a function of time in the alkaline zinc system. Katan's work was pioneering in several ways: his model pore design allowed pores with diameters on the order of actual pore dimensions to be studied; and he was the first to implement a multiple reference electrode to obtain potential distributions within the pore over very short distances.

In summary, porous electrode simulation studies have advanced understanding of electrode behavior significantly over the years. Specifically, techniques have been developed to microscopically study behavior in idealized pores whose dimensions are of the order of those in actual pores. However, more sophisticated analysis of aggregate porous electrodes and model single pores is necessary to accurately apply information obtained from model single pores to commercial porous electrodes.

1.5 OBJECTIVES

The goal of work described in this thesis is to obtain quantitative and qualitative fundamental information from the study of a model single pore which will aid in understanding behavior in zinc porous electrodes. This information may subsequently help understand zinc electrode failure modes. Recommendations concerning electrolyte properties, electrode properties, and porous electrode design needed to reduce zinc electrode capacity-loss in alkaline electrolyte will be made.

The first objective was to determine zinc behavior during discharge in aqueous electrolytes of two compositions: 31 wt% KOH-1 wt% LiOH; and 15 wt% KOH-15 wt% KF. Electrolyte of composition 31 wt% KOH-1 wt% LiOH has been found to provide good performance characteristics in Zn/NiOOH batteries with regard to conductivity and nickel electrode utilization.
Unfortunately, the high solubility of oxidized-zinc species in this electrolyte exacerbates the problem of zinc redistribution.

It has been proposed that an alkaline-fluoride electrolyte could reduce the problem of zinc redistribution by reducing zinc solubility.\(^{38}\) (Zinc solubility increases non-linearly with potassium hydroxide concentration).\(^{39}\) Unfortunately, reduction of KOH concentration reduces both conductivity and nickel electrode utilization.\(^{40}\) Potassium fluoride is added as a supporting electrolyte to improve electrolyte conductivity. Study of zinc behavior in this electrolyte will improve understanding of the potential beneficial effects of this electrolyte in a Zn/NiOOH system.

A second objective was to determine the effects of rate of discharge on zinc behavior. Typically, an electric-vehicle battery is subjected to varying load requirements, reflecting transient accelerations or decelerations. The EPA urban driving profile is representative of the typical transient power required from a battery. Unfortunately, this driving profile cannot be implemented for discharge of the model zinc single pore at this time. A study of different rates of discharge can provide qualitative information about the effects of transient power requirement on zinc electrode behavior, and ultimately, battery performance.

The final objective was to determine the reaction penetration depth within the pore, which will be useful in determining an optimum electrode thickness. Of course, all electrode design parameters will be determined by performance and cost considerations.

The following chapter describes a simple mathematical model of the experimental model single pore. As mentioned previously, a model is necessary to relate reference microelectrode potential measurements to events occurring within the pore.
REFERENCES


17. Liu, Ibid, p.3.


CHAPTER 2

ALKALINE ZINC ELECTRODE SINGLE PORE THEORY

2.1 INTRODUCTION

Simple electrochemical concepts can be applied to the alkaline zinc electrode model single pore to derive useful information about the pore's behavior. For example, it is necessary to make certain assumptions about the cell behavior to obtain usable information from the reference microelectrodes, e.g. measured potential distributions can be translated into useful current density distributions. Section 2.3 describes the equations used to interpret information obtained from the microreference electrodes. The derived current density distributions can be combined with pore behavior assumptions to predict pore concentration profiles as a function of time. The reaction penetration depth, which is a measure of electrode utilization, can also be determined from measured potential distributions.

Comparison of experimentally-measured data to applicable theoretical models serves two purposes: validation of experimental data; and determination of plausible explanations for experimental observations. Specifically, two published theories which predict current distributions in idealized porous electrode are analyzed with respect to the alkaline zinc electrode model single pore.

The discharge behavior of the zinc electrode has been examined in this study, although the cell design does not prohibit studies of charge or cycling behavior of the zinc electrode. The discharge behavior is of special interest because of the high solubility of the zinc discharge products in KOH, which is linked to zinc redistribution, and the complex reaction mechanism. A description of the zinc electrode discharge behavior is presented in the next section to provide a basis for subsequent experimental and theoretical analysis.
2.2 ALKALINE ZINC ELECTRODE DISCHARGE BEHAVIOR

The overall half reaction at the zinc electrode is:

\[ \text{Zn} + 2\text{OH}^- = \text{ZnO} + \text{H}_2\text{O} + 2\text{e}^- \]  

(1)

A variety of reaction mechanisms have been proposed to explain the discharge process, including the dissolution-precipitation, adsorption, and nucleation and two-dimensional growth of crystal theories. Common to all theories is a zinc dissolution step whereby the zinc electrochemically reacts to form a soluble zinc species, known as zincate ion \((\text{Zn(OH)}_4^{2-})\).

Studies of the effect of concentration of soluble species on the exchange current density, \(\text{i}_0\), have led to the following two-step mechanism for zinc dissolution:  

\[ \text{Zn} + 2\text{OH}^- = \text{Zn(OH)}_2 + 2\text{e}^- \]  

(2)  

\[ \text{Zn(OH)}_2 + 2\text{OH}^- = \text{Zn(OH)}_4^- \]  

(3)

Zinc mono-, di-, tri-, and tetrahydroxide species are all soluble in KOH solution. However, a comparison of the complex formation constants of each hydroxide indicates that zincate, zinc tetrahydroxide, is the predominant species in concentrated (>1M) KOH solutions. The equilibrium constant for the formation of zincate has been determined to be \(1 \times 10^{15.38}\).

In the adsorption model, the zincate dissolution product is adsorbed onto the zinc surface to form a monolayer of \(\text{Zn(OH)}_2\). The hydroxide layer releases water to form a passive \(\text{ZnO}\) film, which retards diffusion of the hydroxyl ion to the electrode surface. In contrast, the nucleation and two-dimensional growth model postulates the formation of zinc oxide nuclei on surface nucleation sites by adsorption.

The most widely-accepted theory is the dissolution-precipitation mechanism. Dissolved zincate collects in a solution layer near the electrode surface until a critical supersaturation of zinc species is reached locally. The maximum supersaturation concentration of zincate
has been reported to be between two and three times the zinc saturation concentration. Once supersaturation has been reached, a combination of ZnO and Zn(OH)$_2$ will precipitate out of solution onto the electrode surface. Thus, the overall dissolution-precipitation reaction can be described by the following equations:

$$Zn + 4OH^- = Zn(OH)_4^{2-} + 2e^- (4)$$

$$Zn(OH)_4^{2-} = ZnO + H_2O + 2OH^- (5)$$

The precipitate will form a type I, porous white film on the surface. Diffusion of hydroxyl ions through the film to the electrode surface permits continuation of the dissolution reaction. Liu, et al propose that two factors can lead to electrode passivation. They conclude that the primary cause of passivation is the depletion of hydroxyl ions near the electrode surface, which limits the dissolution reaction. Transport of hydroxyl ions to the surface becomes increasingly slow as the Type I film thickens. Passivation can also be caused by the formation of a Type II compact film on the electrode surface; this film also blocks the dissolution reaction. It is postulated that zinc on the surface underneath the Type I film reacts directly to form ZnO once the Zn/ZnO standard potential on the surface is reached (1.2 volts versus Hg/HgO). Liu's results are in accordance with ellipsometry studies of alkaline zinc processes performed by Smith. 13

Many authors have discussed anodic zinc processes only in terms of formation of a ZnO film on the electrode surface. In fact, studies have shown that Zn(OH)$_2$ is also present. 14,15 The electrode surface films typically do not have an overall stoichiometric composition equivalent to ZnO. Films are usually zinc-rich and dark in appearance, especially at discharge current densities typically found in Zn/NiOOH cells for electric vehicle applications. 14,15
2.3 INTERPRETATION OF REFERENCE ELECTRODE MEASUREMENTS

Three types of differential electrode potential measurements are made during model single pore experiment runs: (1) zinc working electrode potential versus individual reference electrode potentials positioned throughout the pore; (2) individual reference electrode potential versus another individual reference electrode potential, and (3) zinc working electrode potential versus zinc counter electrode potential. Measurements are made with and without current flow through the cell. Each type of differential electrode potential measurement yields different information about zinc pore behavior. The following sections discuss some of the information that can be obtained from differential electrode potential measurements, including determination of the initial current density distribution and the concentration profile in the electrolyte.

2.3.1 EXPERIMENTAL DETERMINATION OF CURRENT DENSITY DISTRIBUTION

Sequential measurement of the potential of the working electrode versus each reference electrode will yield a plot of potential distribution in the pore. The initial potential distribution can be used to estimate the initial current density distribution. This estimation is simplified by assumptions that can be made at short time periods, including uniform electrolyte composition and electrode surface composition. Two methods of estimating initial current density distribution will be presented in order of increasing complexity.

The working electrode versus the reference electrode measurements provide the electrode potential minus the potential in the electrolyte adjacent to the electrode. Thus, at short times, the potential difference between the two electrodes with current flow is composed of an ohmic-loss term, proportional to current, and an activation energy term:

\[ \phi = \eta_A + A_i + E^\circ_{\text{ref}} - E^\circ_{\text{working}} \]  

If linear polarization is assumed, which is a valid assumption at low current densities, then the electrode surface overvoltage \( \eta_A \) is directly proportional to the local current density. In addition, if the
current flux lines are assumed to be parallel, then the ohmic-loss term coefficient, $A$, would be the same for each differential potential measurement. Of course, the potential differences must be corrected for the difference in the reversible thermodynamic potentials, $E^\circ$, of the Cd and Zn electrodes. With the above assumptions, the measured potential differences are equivalently proportional to the local current density, $i$. Thus, the following expression holds:

$$\frac{\phi(y)}{\phi_{avg}} = \frac{i(y)}{i_{avg}}$$  \hspace{1cm} (7)

and can be used to calculate the current distribution. Individual local current densities can then be calculated by observing that $i_{avg}$ equals the total current passed through the cell divided by the electrode surface area. Equation (7) contains some crude simplifying assumptions, but it serves as a good starting point for calculations.

By eliminating the assumption that the current lines are parallel, and accounting for dependence of electrolyte potential on current flow, a better approximation of the current density distribution can be obtained. A more realistic representation of the current lines in the model pore is given in Figure 2.1. Wagner gives an expression for the dependence of electrolyte potential adjacent to the surface in a slot pore, similar in geometry to the pore studied here.\(^{17}\) If the dependence of the potential on $x$ is disregarded, the solution potential, measured by the reference electrode, is related to the current density by Ohm's law:

$$I_y = -\kappa \cdot \frac{d\phi}{dy}$$  \hspace{1cm} (8)

where $I_y$ is the current density flowing coplanar to the electrode, and $\kappa$ is the electrolyte conductivity, as shown in Figure 2.2. Owing to the high conductivity of metals, the potential inside the electrode $E_w$ can be assumed to be uniform. Thus, the local electrode potential $E_a$ increases as the potential, $\phi$, in the electrolyte decreases. This can be expressed by equation (9):

$$\phi(y) + E_a(y) = \text{constant}$$  \hspace{1cm} (9)
Figure 2.1 Representation of current lines in model single pore.
Figure 2.2 Model single pore cell showing thin lateral section with model variables.
Utilizing the above information, equation (8) can be rewritten as:

\[ I_y = \kappa \cdot \frac{d(E_w - \phi)}{dy} \]  

(10)

Note that \( E_w - \phi \) is equal to the potential of the working electrode versus reference electrode. The local current density, \( J(y) \), can be obtained from the local electrolyte current \( I_y \) by doing a shell balance on a finite differential volume taken through the cross-section of the pore (Figure 2.2). By this analysis:

\[ J(y) = \frac{(I_y - I_y + \Delta y) \cdot d}{\Delta y} \]  

(11)

In the limit of an infinitely-thin volume element, equation (11) becomes:

\[ J(y) = \frac{dI_y}{dy} \cdot d \]  

(12)

Substituting eq. (10) into eq. (12) gives the final expression for the local electrode current density, \( J \), as a function of the measured potentials:

\[ J(y) = d \cdot \kappa \cdot \frac{d^2(E_w - \phi)}{dy^2} \]  

(13)

Linear polarization of the electrode surface is a reasonable assumption at low current densities. Thus, the local electrode current density, \( J \), is related to the overpotential, \( E_w - \phi \), by the following relationship:

\[ J = \frac{i_o(\alpha + \alpha_c)F}{RT} \frac{E_w - \phi}{(E_w - \phi)} \]  

(14)

Eq. (14) can be solved simultaneously with Eq. (13) to determine the expected local electrode current density, \( J \), and the overpotential, \( E_w - \phi \). Substitution of eq. (14) into eq. (13) gives a second-order differential equation, which can be solved analytically for the measured potential. The boundary conditions are:

at the pore entrance \( (y=0) \)

\[ I_{tot} = -w \cdot d \cdot \kappa \cdot \frac{d(E_w - \phi)}{dy} \]  

(15)
at the pore root \((y=L)\)

\[
\frac{d(E_w-\phi)}{dy} = 0, \text{ or } I_y = 0 \tag{16}
\]

Non-dimensionalizing the resulting equation and boundary conditions gives the following equations:

\[
\eta = p^2 \frac{d^2 \eta}{dY^2} \tag{17}
\]

B.C. 1 \[ I^* = \frac{dn}{dY} \tag{18} \]

B.C. 2 \[ \frac{dn}{dY} = 0 \tag{19} \]

where:

\[
\eta = \frac{(E_w-\phi) \cdot F}{RT} \tag{20}
\]

\[ Y = y/L \tag{21} \]

\[
p^2 = \frac{d \cdot \kappa \cdot RT}{i_0 (\alpha_a + \alpha_c) FL^2} \tag{22}
\]

\[
I^* = \frac{-I_{tot} \cdot F \cdot L}{R \cdot T \cdot \kappa \cdot w \cdot d} \tag{23}
\]

The solution to eq. (17) is:

\[
\eta = I^* \left[ \frac{P \exp(Y/P)}{(1-\exp(2/P))} + \frac{P \exp(-Y/P)}{\left(\frac{1}{\exp(2/P)} - 1\right)} \right] \tag{24}
\]

The current density is given by:

\[
J = i_0 (\alpha_a + \alpha_c) \cdot \eta \tag{25}
\]
The current density distribution is found by noting that:

\[
\frac{J(y)}{J_{avg}} = \frac{w \cdot L}{I_{tot}} \tag{26}
\]

Thus, the above expressions calculate the actual current density, \( J \), as a function of distance, \( y \), into the pore. Some error is inherent in eq. (26) because of the necessity to numerically differentiate the experimental data in eq. (13). By continuity, the total current flowing through the pore is related to the local current density by the expression:

\[
I_{tot} = \frac{1}{L} \int_0^L J(y)dy \tag{27}
\]

Thus, there is an implicit check on the validity of the data and the applicability of the above analysis to a set of data.

For any given set of data, the differential reference electrode potential measurements can be used to check the validity of the data. At short times, the electrolyte composition can be assumed to be constant. Thus, all reference electrode measurements without current flow in the cell should be equal. In addition, the difference between one reference electrode measurement and another should be given by Ohm's law according to the equation:

\[
\phi_i - \phi_j = i\rho \Delta y \tag{28}
\]

where

\( \phi_i, \phi_j \) = electrolyte potential measurement at points \( i \) and \( j \)

\( i \) = current density between points \( i \) and \( j \)

\( \rho \) = electrolyte resistivity

\( \Delta y \) = distance between points \( i \) and \( j \)

The error in equation (28) increases as the distance, \( \Delta y \), increases because the current density is not constant from point \( i \) to point \( j \) in the pore. The current flow through the pore, \( I_y \), can be obtained by multiplying the current density \( i \), (calculated by eq. (28)) by the pore...
cross-sectional area. Thus, eq. (12) can again be used to obtain the current density distribution. However, the current density distribution is approximate because there are only six reference electrode potential measurement points through the pore.

2.3.2 THEORETICAL PREDICTION OF CURRENT DENSITY DISTRIBUTION IN THE PORE

Experimentally-obtained current density distributions, determined by one of the methods described in Section 2.3.1, can be compared to theoretical predictions of current density distributions in similar geometries. Two theories will be discussed: Euler and Nonnemacher's theory of idealized porous electrodes, and Wagner's theory of idealized slot pores.

These theories must be applied with caution because neither the geometries nor the boundary conditions apply exactly to the model single pore.

2.3.2.1 Model Porous Electrode

Euler and Nonnemacher studied a model porous electrode containing rectangular pores. The boundary conditions are slightly different in that there is a conductor (not an insulator) at the root of the pore (y=L). In addition, a full pore is studied, i.e. there is not an insulator at the midplane of the pore and coplanar to the electrode surface. Euler applies an equivalent-resistance analysis to a small segment taken through the cross-section of the pore. Upon solution of the differential equation, Euler obtains the following expression for the secondary current density distribution, assuming linear polarization:

\[ i(y) = \frac{Y \cdot \kappa}{(\kappa + \sigma)} \cdot \sinh \gamma \left[ \frac{\sigma}{\kappa} \cosh \gamma \left( \frac{1}{L} y \right) + \cosh \left( \frac{Y \gamma}{L} \right) \right] \]

where \( Y \) is the polarization parameter given by:

\[ Y = L \sqrt{\frac{a_1 nF(\kappa+\sigma)}{RT\kappa\sigma}} \]

where
L is the length of the pore
κ = is the electrolyte conductivity
σ = is the conductivity of the solid phase, and
a = is the specific surface equal to the electrode area divided by the electrolyte volume (cm⁻¹).

The approximate forms of eq. (29) and eq. (30), assuming κ/σ approaches 0, are:

\[
\frac{i(y)}{I_{\text{avg}}} = \frac{\gamma \cosh \gamma (1 - \frac{y}{L})}{\sinh \gamma} \quad (31)
\]

and

\[
\gamma = \frac{a \cdot i_0 \cdot nF}{RT\kappa} \quad (32)
\]

The polarization parameter, γ, is a dimensionless group related to the penetration depth. As γ becomes smaller, the penetration becomes larger.

2.3.2.2 Model Single Pore

Wagner studied current distribution in a slot pore, similar in geometry to that employed here. The only differences between the two applications occur in the boundary conditions. The Wagner slot pore has a conducting wall at the root of the pore (y=L), whereas the model single pore has an insulating wall. The Wagner slot pore has conducting electrolyte between the working electrode and the counter electrode, whereas the present model single pore has an insulating block, in the form of a mylar spacer, between working and counter electrodes. Finally, Wagner studied the full pore, without an insulator at the midplane of the pore. However, if it is assumed that the model single pore resembles a half-pore, and that the pore behavior is symmetric about the midplane, then the last difference between model single pore and idealized slot pore characteristics is minimized. The Wagner slot is the closest approximation discussed in the literature to the model single pore.
In his analysis, Wagner solves Laplace's equation for the primary current distribution and solves for the secondary current distribution for the two cases of linear and Tafel polarization. Linear polarization is an appropriate assumption at low current densities, whereas Tafel polarization is an appropriate assumption at very high current densities. For the secondary current distribution, with linear polarization, Wagner gives the following expression:

\[ J(y) = J_{\text{edge}} \cdot \exp \left[ -\frac{y}{(dK_a/2)^{1/2}} \right] \]  

(33)

where \( K_a \) is the polarization parameter given by:

\[ K_a = \frac{kRT}{F_i_o(a_a + a_c)} \]  

(34)

and \( J \) is the average electrode current density far away from the pore, \( J_{\text{edge}} \) is the current density at the mouth of the pore, and \( d \) is the pore diameter. Equation (33) is valid when \((K_a/d)^{1/2} \gg 1\) and \( L \gg (dK_a/2)^{1/2} \).

The secondary current distribution with Tafel polarization is given by:

\[ J(y) = \frac{J_{\text{edge}}}{\left[ 1 + \frac{y}{[aK_a(\text{edge})]^{1/2}} \right]^2} \]  

(35)

where

\[ K_a(\text{edge}) = \frac{kRT}{a_a \cdot z \cdot F J_{\text{edge}}} \]  

(36)

Equation (35) is valid when \((K_a(\text{edge})/d)^{1/2} \gg 1\) and \( L \gg (dK_a(\text{edge}))^{1/2} \).

The current density at the mouth of the pore, \( J_{\text{edge}} \), must be known in order to apply equations (22) and (24). Wagner gives a plot of \( J_{\text{edge}}/J \) versus \( \log(K_a/d) \) for both linear and Tafel polarization cases.
from which $J_{\text{edge}}$ can be determined. For typical values of $K_a$ and $d$:

$$J_{\text{edge}} = (0.7-0.9) \cdot J$$ (37)

Applications of both Euler's and Wagner's equations to the model single pore will be discussed in Chapter 5.

2.3.3 DETERMINATION OF CONCENTRATION PROFILES IN THE PORE

Two methods to obtain approximate concentration profiles in the pore are described in this section. Both methods focus on determination of the hydroxyl ion concentration. The concentration profiles of other species can be estimated from a hydroxyl-ion concentration profile by assuming the overall stoichiometry of the dissolution-precipitation mechanism. The first method described is an experimental determination of $[\text{OH}^-]$. This method is more exact than the second method: calculation of the concentration profile from the initial current density distribution.

2.3.3.1 Experimental Determination of Concentration Profiles

Reference-electrode potential measurements can be used to elucidate information of the concentration profile in the pore. In the absence of cell current flow, the difference in potential between one reference electrode and another reference electrode will be indicative of a difference in hydroxyl-ion concentration. The cadmium reference electrode is sensitive to changes in hydroxyl-ion concentration. The seventh reference electrode is located at a point midway between the working and counter electrodes. During short experiments (<1 hour) it can be assumed that the hydroxyl-ion concentration is roughly unchanged from the initial hydroxyl-ion concentration at the seventh reference electrode. Given the relationship for dependence of the cadmium reference electrode on $[\text{OH}^-]$, the $[\text{OH}^-]$ can be determined by subtracting any reference electrode potential from the seventh reference electrode potential. The dependence of the cadmium electrode on hydroxyl-ion concentration can be calculated from theory and is given by:

$$E = -0.809 - 0.059 \log a_{\text{OH}^-}$$ (38)
Falk measured the potential of the cadmium electrode in solutions of varying hydroxyl-ion activity and found the theoretical predictions matched the experimental observations.\(^{21}\)

Calculation of the \([\text{OH}^-]\) by this method is most accurate over short time periods. Substantial concentration gradients which form over time will provide the driving force for small internal currents in the absence of cell current flow. The internal currents will add an unknown ohmic contribution term to the differential reference electrode potential readings, causing improper determinations of hydroxyl-ion concentration. Current will flow from regions of high \([\text{OH}^-]\) to low \([\text{OH}^-]\) because the zinc dissolution reaction will be preferred in areas of high \([\text{OH}^-]\) to relax the concentration gradient.

2.3.3.2 Calculation of Concentration Profiles

The second method for determining \([\text{OH}^-]\) uses the initial current density distribution and the dissolution-precipitation mechanism to estimate the hydroxyl-ion concentration. The extent of dissolution and precipitation reaction in each segment of the pore can be calculated by Faraday's Law, given the local current density in each segment. Unfortunately, this method requires many assumptions: (1) that the current density distribution does not vary significantly over time; (2) that transport of electrolyte-soluble species by migration, diffusion and convection is negligible; and (3) that the dissolution-precipitation reaction occurs and the supersaturation concentration of zincate is uniform throughout the pore with a value between two and three times the zincate saturation concentration.

Despite these crude approximations, this method is useful in determining qualitative information about pore behavior. For instance, the time when precipitation of a film on the electrode surface should occur can be estimated and compared with visual microscopic observations. This provides a qualitative check on the applicability of various discharge mechanisms, including the dissolution-precipitation mechanism.
2.4 APPLICATIONS TO POROUS ELECTRODES

2.4.1 REACTION PENETRATION DEPTH

Determination of the initial potential distribution within the model single pore can be useful in estimating the reaction penetration depth within a porous electrode. The distance into the electrode to which the reaction penetrates determines the electrode thickness that can support substantial utilization of the active material. Electrodes much thicker than the penetration depth are not fully utilized, and thus they are both uneconomical and impractical, especially where specific energy considerations are important. Electrodes much thinner than the penetration depth are fully utilized but can result in higher cell costs. Thus, penetration depth information is useful in commercial porous electrode design calculations.

Experimental data using segmented electrodes and theoretical predictions have shown that current distributions typically exhibit exponential decay behavior as distance into the pore increases. The reaction penetration distance measures the point at which there is an appreciable reduction in current density. The reaction penetration depth can be estimated from a plot of pore potential versus distance into the pore. The penetration depth can be obtained from the initial potential distribution by drawing a line tangent to the potential curve, reflecting the initial slope. The penetration depth is the distance at which the tangent line intersects the X-axis (the distance axis).\(^{22}\)

Newman gives an expression for the penetration depth, \(L\), in commercial porous electrodes as:\(^{23}\)

\[
L = \frac{RT}{Y} \left(\frac{1}{\alpha + \alpha_c} \right) \frac{1}{F} \left(\frac{k_o}{\kappa + \sigma} \right)^{1/2} \left(\frac{1}{A} \right)^{1/2} 
\]

(39)

where \(Y\) is the dimensionless exchange current given by:

\[
Y = \sqrt{\frac{(\alpha + \alpha_c)F \cdot A \cdot i_o L^2}{RT} \left(\frac{1}{\kappa} + \frac{1}{\sigma} \right)} 
\]

(40)

This expression can be rearranged to give equation (41), assuming that the effective conductivity of the solid matrix, \(\sigma\), is much greater than
the effective conductivity of the solution, \( \kappa \).

\[
L = \left( \frac{RT}{nF_i_0 \rho} \right)^{1/2} \left( \frac{\epsilon}{A} \right)^{1/2}
\]  

(41)

Thus, the penetration depth is a function of electrolyte properties, (resistivity, \( \rho \)), electrode reaction kinetics (exchange current density, \( i_0 \)), and porous electrode structure. Equation (41) has been shown to be in good agreement with experimental data.

Katan and Szpak have shown that the characteristic geometric group for porous electrodes, \( \epsilon/A \), is equivalent to the characteristic geometric group for model single pores of the type utilized in this study, \( c/P \), where \( c \) is the pore cross-sectional area, and \( P \) is the pore perimeter. Substitution of the group \( c/P \) into eq. (41) gives the final equation for prediction of penetration depth in the model single pore cell:

\[
L = \left( \frac{RT}{nF_i_0 \rho} \right)^{1/2} \left( \frac{c}{P} \right)^{1/2}
\]  

(42)

Application of equation (42) to the model single pore will be discussed in Chapter 5. It is important to note that the reaction penetration depth will increase with time due to various factors, including broadening of the current distribution curve by kinetic factors and precipitation of \( \text{ZnO/Zn(OH)}_2 \) near the mouth of the pore, that will force the reaction zone further into the pore.
### NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tr>
<td>a, A</td>
<td>specific surface, cm(^{-1})</td>
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<tr>
<td>c</td>
<td>pore cross-sectional area, cm(^2)</td>
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<td>d</td>
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REFERENCES


11. Powers and Breiter, op. cit..


CHAPTER 3

EXPERIMENTAL DESIGN AND PROCEDURES

3.1 BACKGROUND

A complete description of the electrochemical cell design and experiments will be given in this chapter, with the exception of the cadmium reference microelectrode fabrication procedures (discussed in Chapter 4). The electrochemical cell was designed to model the dimensions of a pore in a porous zinc electrode of the type used in Zn/NiOOH cells. Porous zinc electrodes for use in Zn/NiOOH cells are typically manufactured by combining ZnO and other minor species with granular PTFE (teflon) to form a paste, dough or slurry. The ZnO and binder are combined with a metal mesh current collector, and pressed to the desired porosity and thickness.

The porous structure consists of macropores between ZnO particles and micropores within ZnO particles. Because important failure modes, e.g. zinc redistribution, involve the macroscopic movement of soluble zinc species, it is appropriate to examine behavior in macropores. Studies have shown that the majority of electrochemically-active zinc is contained in macropores. Other investigations indicate that alkaline zinc electrodes typically have macropore diameters ranging from one to 40 μm and pore lengths ranging from 0.01 to 2 millimeters. The average tortuosity of pores is about two. 

The model zinc electrode pore is a rectangular parallelepiped, having on one side a lucite-mounted zinc electrode surface. Katan has illustrated the analogy between such a parallelepiped geometry and that of an actual electrode pore. A teflon spacer creates the model pore's effective radius, assuming a radially-symmetric pore. A quartz slide lies on the teflon spacer to complete the model pore. The behavior of the zinc electrode surface is then studied simultaneously by electrochemical and optical methods. Cadmium reference microelectrodes deposited on the quartz surface provide qualitative and quantitative information. Figure 3.1 shows a side view of the assembled model zinc pore with reference microelectrodes in place. The model pore length is
1.57-mm, and pore radii (i.e. the separation between the zinc electrode and the quartz cover slide) between 5 and 20 μ can be easily studied. Conceivably, pores of diameter between 0.5 and 5 μ could be studied if thin film deposition techniques were used to deposit the spacer that creates the effective pore radius.

Sections 3.2-3.3 describe in detail the zinc pore electrochemical cell and computerized system designed to simultaneously obtain optical and electrochemical information from the cell. Section 3.4 discusses the types of experiments and typical procedures performed.

3.2 HARDWARE CONFIGURATION

3.2.1 PURPOSE

The hardware for these experiments includes a potentiostat/galvanostat, a potentiostat-reference electrode multiplexer (PREM) and a host Digital Equipment LSI-11/23 computer. The hardware was designed and configured such that the computer could control the course of an experiment in real time and simultaneously record potential and photographic data.

3.2.2 HARDWARE COMPONENTS

The potentiostat/galvanostat serves to pass a constant current through the cell and monitor potentials at the counter and working electrodes. A PAR model 173 potentiostat/galvanostat was used in this study. The galvanostat has the ability to pass currents to the cell with accuracy to 0.1% of full scale. One channel is programmed to output the desired current, while another channel is programmed to output zero current. In addition, the potentiostat sends voltage signals to the PREM where the working vs reference and working vs counter electrode potentials are amplified.

The computer controls the progress of the experiment, data acquisition and processing, and timing. The computer is comprised of an LSI-based processor, analog-to-digital (A/D) cards to receive output from the peripheral hardware, digital-to-analog (D/A) cards and parallel input/output (P-I/O) cards to send input and to control peripheral
Figure 3.1 Model zinc pore with cadmium reference microelectrodes.
hardware, and a programmable real-time clock. In addition, magnetic disks, CRT terminals, a line printer and an X-Y plotter are available to facilitate data storage, input/output functions and data processing. The computer system was developed by M. Katz. An additional DRV-11 P-I/O card was installed to allow the computer to control the various functions of the PREM.

The versatility of the computer system allows program software to control and monitor progress of the experiment. By sending a signal to the PREM, current from either channel of the potentiostat/galvanostat can be imposed on the cell. Thus, intermittent momentary open-circuit potential measurements can be made without significantly disrupting the electrode discharge process. Similarly, a digital signal to the PREM logic can initiate a photographic exposure through the camera attached to the microscope. Current to the cell is monitored from a port on the potentiostat. Figure 3.2 shows a block diagram of the system configuration.

3.2.3 POTENTIOSTAT - REFERENCE ELECTRODE MULTIPLEXER (PREM)

The potentiostat-reference electrode multiplexer (PREM) is a custom-built potentiostat-cell-computer interface unit. A photograph of the PREM is shown in Figure 3.3, and a more detailed description of the operation and specifications of this unit is given in Appendix A. The following paragraphs discuss general characteristics and performance of this unit.

The PREM receives all electrode and reference electrode potential signals from the cell and potentiostat, computes and amplifies the differences, and transmits them to the computer via the A/D card. Because only one potential reading can be monitored at a time, a multiplexer in the PREM allows the computer to digitally select the desired potential, through the P-I/O card. In addition, a digital signal from the multiplexer can control a relay to open and close the camera shutter and advance the film through a camera motor drive. This allows precise control and recording of the camera and reduced vibration of the cell. Two other signals from the multiplexer can initiate TTL logic-generated
SYSTEM CONFIGURATION

Figure 3.2 Block diagram of data acquisition system.
Figure 3.3 Potentiostat—Reference Electrode Multiplexer, showing variable gain amplifiers, zero-offset amplifiers, variable precision voltbox and PC cinch card connector.
pulses to the potentiostat/galvanostat such that either channel can be selected.

The primary function of the PREM is to generate amplified differential electrode potentials from the cell's counter and working electrodes and the cadmium reference electrodes. The reference electrode potentials are obtained through a "cinch" card, which is a printed-circuit board connector that attaches to the quartz cover slide. The seven differential working vs reference electrode potentials and single differential working vs counter electrode potential are each amplified through variable gain (1-1000) operational amplifiers. Amplification is necessary to improve the signal-to-noise ratio in the system. Each amplifier is connected to a zero offset amplifier to compensate for internal ohmic and voltage offsets.

A series of precision voltages ranging from zero to two volts are available for amplifier calibration within the PREM. Given the input reference voltage to the amplifier and output voltage from the amplifier, the computer can determine the exact amplification of the signals and adjust amplifier output continuously to obtain the actual measured potentials.

3.3 ZINC ELECTRODE FABRICATION

3.3.1 DESIGN CONSIDERATIONS

The mounted zinc electrodes serve as the working and counter electrode pore surfaces. The pore dimensions are determined by the dimensions of the mounted zinc electrodes and the distance between the zinc electrode and the quartz cover slide. Planar-mounted electrodes can be polished to obtain a smooth, reproducible surface for each run. This is important in making comparisons between the effects of different operating conditions.
3.3.2 DESIGN CONFIGURATION

The pore design was chosen to simulate actual pore dimensions and the corresponding counter-electrode pore is identical to the model pore. The pore design is based on a model pore design developed by T. Katan. In order to better replicate actual zinc electrode pores, the dimensions of the pore are smaller than those used by Katan. In addition, the design has been altered to allow for simultaneous visual and potential observation of the zinc behavior in the pore.

Each zinc electrode is 0.157-cm deep and 0.635-cm (± 0.002 cm) wide. They are mounted directly opposite one another, separated by 0.025 cm. Figure 3.4 shows the dimensions of the zinc electrodes, which are mounted in lucite (polymethylmethacrylate).

3.3.3 FABRICATION PROCEDURE

There are three basic steps in fabricating the mounted zinc electrodes: 1) sizing and squaring the zinc electrodes; 2) mounting the zinc in lucite; and 3) making electrical connection to each electrode.

Slightly oversize zinc electrodes are prepared from 99.99% pure zinc sheet that is 0.157-cm thick. Electrodes are cut using an abrasion saw, to reduce surface distortion, and a squaring guide, to insure rectangular geometry. Slugs are then ground to the desired dimensions, 0.157-cm X 0.635-cm X 0.350-cm, using silicon carbide abrasion papers and a micrometer. Finally, the electrodes are degreased in acetone, followed by soap and water, and dried before mounting.

The electrodes are mounted in lucite using a standard hot mounting press. A 0.025-cm X 0.157-cm X 0.350-cm mylar spacer is then placed between the electrodes on the press surface to provide a uniform spacing between the electrodes. Ball-milled lucite powder is used as the standard mounting material. After mounting, excess lucite is cut off to achieve a lucite thickness of 1 cm.
Figure 3.4 Zinc electrode mounted in lucite.
Electrical connection is made by press-fitting a drill bit stud into a pre-drilled hole until it contacts the electrode. Holes are drilled through the lucite from the bottom surface using a number 68 drill bit and microdrill. A small amount of gold foil is placed in the hole at the electrode surface to improve contact between zinc and drill stud. Sharpened drill bit studs, slightly larger in diameter than the hole, are press-fitted into the holes until contact is made with the electrode. Finally, tinned-copper wire leads are soldered to the base of the studs. Electrical contact from the wire to the electrode surface is checked with a point-probe ohmmeter.

3.3.4 ELECTRODE POLISHING

Prior to polishing, the electrodes are screw-mounted into a machined teflon holder and belt-sanded with 240 silicon carbide paper to insure a flat surface for polishing. The electrodes are then fine-ground using slab-mounted silicon carbide papers, of grit sizes 240, 320, 400, and 600, and water as a lubricant. After completing a particular grit polish, the electrodes are rinsed in water and turned 90 degrees clockwise. Because of zinc's inherent softness, polishing must continue far beyond the point at which prior scratches are no longer visible. This procedure will remove sub-surface deformations.7

The lucite-mounted electrodes are polished using standard metallurgical apparatus to achieve a flat, reproducible surface. The polishing procedure involves use of sequential decreasing size grits with lubricants to achieve a sub-micron smooth finish. The electrodes are rough-polished using 6-μ diamond paste compound with a lapping-oil lubricant on a nylon-covered rotating wheel. The electrodes are then fine-polished using 1-μ diamond paste compound until microscopic observation reveals no remaining deep scratches. The final electrode polishing step requires ten to fifteen minutes using 0.05-μ chromium oxide (CrO) polishing compound with distilled-water lubricant on a felt-covered wheel. Electrodes are then washed and rinsed in a distilled water and dried in nitrogen. The electrodes are ready for use in pore experiments after being polished by this method.
3.4 EXPERIMENTAL RUN PROCEDURES

Prior to initiating a run, the zinc working and counter electrodes and the cadmium reference microelectrodes must be fabricated (discussed in section 3.3 and Chapter 4, respectively). There are six steps necessary to complete a run: 1) hardware set-up; 2) electrochemical cell assembly and alignment; 3) software initialization; 4) cell operation; 5) cell disassembly; and 6) data reduction and analysis.

3.4.1 HARDWARE SET-UP

Hardware set-up includes making the proper electrical connections between the potentiostat, PREM and the computer, and setting individual working vs reference electrode amplifications on the PREM unit. The electrical connections are described in detail in Appendix A.

The first step in setting the seven individual potential amplifiers is to zero the amplifiers by adjusting a matching zero offset variable gain trim amplifier. The built-in voltbox is set to zero volts and the cinch card cable is plugged into the reference voltage printed circuit card (Figure 3.5). Each trim amplifier is then adjusted until the digital voltmeter reads $0 \pm 0.00002$ volts. The amplifications are established in a similar fashion by first setting the voltbox to an appropriate reference voltage, and then adjusting each amplifier until its output (monitored by the digital voltmeter) gives the desired amplification. The amplification is calculated by equation (1):

$$\text{Amplification} = \frac{\text{Output Voltage}}{\text{Input Voltage}}$$  (1)

The amplification appropriate for each reference electrode depends on the particular run conditions and are determined by trial and error. Since reference electrode seven is closest to (and reference electrode one is farthest from) the counter electrode, one would expect reference electrode seven to have the lowest amplification and reference electrode one to have the highest amplification. It is desirable to set amplifications such that output voltages from the PREM are close to, but not in excess of, five volts. Voltages above five volts exceed the limit of the A/D cards and thus, would result in a loss of information.
Figure 3.5 PREM Cinch Card Connector plugged into built-in amplifier calibration voltbox.
3.4.2 ELECTROCHEMICAL CELL ASSEMBLY

The cell assembly consists of the mounted zinc electrodes, a teflon spacer to establish the separation between the zinc electrodes and the quartz cover slide, and the quartz cover slide containing the deposited cadmium reference microelectrodes. Top and side views of the cell are shown in Figures 3.6 and 3.7. The electrochemical cell is mounted on an X-Y translation microscope stage, and cables provide electrical contact to the potentiostat and PREM.

The mounted zinc-electrode assembly is placed on a steel plate which is attached to a glass microscope slide with modeling clay. This configuration provides a stable mount for the cell, and allows the flexibility necessary to finely adjust the plane of the electrode surface such that it is coplanar with the reference microelectrode.

A teflon spacer mask, cut from teflon film of the desired thickness, is placed on the mount surface and can be aligned within 0.001 cm of the electrode edges. Figure 3.8 shows the zinc electrodes with the teflon mask in place. The spacer establishes the working electrode/cover slide separation, which is the effective "pore radius". The measured separation may be slightly larger than the film thickness due to the presence of wrinkles or deformations in the teflon film. Teflon films of thicknesses 4.8, 6.4, 9.5, 12.7 and 25.4 microns were used in this study. The film was cut using a precision coordinatograph (discussed in Chapter 4), which permitted a precisely-defined cut with a minimal amount of film distortion.

The reference microelectrode is placed in the cinch card connector and electrical connection to each of the electrodes is checked with a point-probe ohmmeter. The reference microelectrodes and cable are screw-mounted onto a Y-Z translation stage to allow for proper alignment over the zinc electrode surface. Alignment is performed by adjusting the X-Y position of the microelectrodes such that the tips (0.1 X 0.01 cm) of the reference electrodes lie along the centerline of the working electrode (0.315 cm from the electrode edge), and reference electrode six registers exactly with the edge of the working electrode nearest to the counter electrode (Figure 3.9). This alignment is performed by assembling the cell (without electrolyte) under the microscope.

-45-
Figure 3.6 Top view of model single pore cell.
Figure 3.7 Side view of model single pore cell.
Figure 3.8 Cell prior to assembly.
ALIGNMENT OF REFERENCE MICROELECTRODES

Figure 3.9 Alignment of reference microelectrodes over the electrode surface.
The electrolyte is placed on the electrode surface using a microliter syringe. An excess (double the amount required) of electrolyte was applied to insure complete filling of the cell. Cell assembly is completed by lowering the quartz cover slide onto the teflon spacer surface until a snug fit is achieved. Excessive pressure can cause the quartz cover slide to break. Figure 3.10 shows the assembled cell.

The electrical connections between the cell, computer, potentiostat, and PREM are completed and checked. The amplified output of the working vs reference electrodes and working minus counter electrodes are checked at open circuit to check the stability of the rest potentials.

3.4.3 SOFTWARE INITIALIZATION

Experimental run conditions are set both in the software experiment-controlling routine (POREST) and the potentiostat/galvanostat. The experiments are run in the galvanostatic mode, and the current is set on a channel of the potentiostat and monitored by the computer. The other potentiostat channel is set to open circuit to allow for periodic IR-free potential measurements.

Experiments are initiated by running the POREST program, inputting parameters, starting the current flow to the cell, and starting the data-acquisition portion of the program. The program POREST has three basic functions: control of optical and potential data acquisition, experiment control, and storage of results in a usable format. Appendix B contains a complete listing and description of POREST. The initialization section of the program allows the user to input the data acquisition rate parameters appropriate to the specific experiment. In addition, the software directs the computer to measure actual amplifications of the working vs counter and working vs reference electrodes signals. There are provisions to re-zero or recalibrate the electrodes at this point in the program, if necessary.
Figure 3.10 Assembled model single pore cell.
3.4.4 CELL OPERATION

Just before the current is turned on, a photograph of the zinc electrode surface is taken manually. Figure 3.11 shows the entire experimental setup prior to a run. The electrode/cover slide separation is measured by determining the microscope adjustment necessary to focus on the zinc electrode surface and on the reference microelectrodes. Then, the "experiment" run section of the program is started, and the potentiostat provides current to the cell. The experiment run section reads in amplified potential measurements and periodically places the cell on open circuit to take transient potential data. Automatic camera control is also provided by the program. All data-acquisition rates are set by the user in the initialization section.

3.4.5 CELL DISASSEMBLY

Current flow to the cell is manually terminated at the end of the experiment. The cell can be left on open circuit while FOREST is running in order to obtain data on potential decay (electrolyte concentration gradient relaxation), if desired. Once the program is stopped, potential versus time data and photograph-time information are logged into a data file for later reduction and analysis. The cell is then immediately disassembled. The mounted zinc electrodes are washed in 0°C deionized water and stored under nitrogen until an SEM examination can be completed. The reference microelectrodes are washed and stored under nitrogen for later use.

3.4.6 DATA REDUCTION

Various programs, described in Appendix B, analyze, reduce, and format data such that plots of overpotential versus time, overpotential versus distance, and current density versus distance can be generated. In addition, data can be adjusted in an appropriate manner if conditions necessitated changes in electrode amplifications during a run.
Figure 3.11 Data acquisition system, showing assembled cell, microscope and camera, PREM, and potentiostat/galvanostat.
SEM examination of the discharged electrode followed each run to obtain microstructure and morphology information on the effects of various discharge conditions. Mounted electrodes were coated with a very thin film (approximately 100 Å) of 10% gold/90% palladium prior to SEM examination, using a vacuum-sputter deposition unit. This metallization of the electrode surface is required to reduce charge accumulation on non-conducting oxide surfaces. An aqueous silver dispersion was applied to the lucite surface to reduce charge accumulation near the zinc-lucite interface.
REFERENCES


FOOTNOTES

A. Digital Equipment Corporation, Maynard, MA.
C. Burr-Brown Research Corporation, Tucson, AZ.
D. A.D. MacKay, Darien, CT.
E. Dielectrix Corporation, Lockport, N.Y.
CHAPTER 4

MULTIPLE REFERENCE MICROELECTRODE

4.1 DESIGN

Combined with optical microscopy, potential distribution information is useful in resolving time-dependent electrochemical phenomena. To obtain this data, a multiple cadmium reference microelectrode was developed for the single-pore experiment. The microelectrode is prepared using standard microelectronic processing techniques. It consists of three metallic thin films, titanium, copper and cadmium, which are sequentially deposited onto a quartz substrate and patterned into the desired configuration. The completed cadmium reference microelectrodes deposited on the quartz cover slide are shown in Figure 4.1. A close-up, cross-section view of a single cadmium reference microelectrode is shown in Figure 4.2.

The quartz cover slide contains seven microelectrodes, spaced such that potential measurements can be obtained at seven points along the entire pore length. The first microelectrode lies directly above the midpoint between the working and counter electrode and serves as an overall reference. The remaining six reference electrodes, each 0.100-mm wide, are spaced 0.195 mm apart throughout the length of the pore as shown in Figure 4-3.

The microelectrodes consist of three regions: microelectrode active area, transmission area, and printed-circuit contact region. The microelectrode active region is 1-mm long and is the only metallic portion in contact with electrolyte. The transmission region serves to bring the electrical signals from the microelectrode region to the printed circuit contact region. The copper and titanium thin-film traces in the transmission region are protected by a thin layer of sputtered quartz. Finally, the traces expand to a printed-circuit region which transmits signals from the pore to the potentiostat reference electrode multiplexer (PREM) for processing. The titanium and copper traces in the region are 0.254-cm wide and separated by 0.143 cm.
Figure 4.1 Multiple cadmium reference microelectrode.
Figure 4.2 Cross-section view of a cadmium reference microelectrode, showing titanium, copper and cadmium thin films.
Figure 4.3 Locations of reference microelectrodes within the pore.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Distance into pore (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.525</td>
</tr>
<tr>
<td>2</td>
<td>1.230</td>
</tr>
<tr>
<td>3</td>
<td>0.935</td>
</tr>
<tr>
<td>4</td>
<td>0.640</td>
</tr>
<tr>
<td>5</td>
<td>0.345</td>
</tr>
<tr>
<td>6</td>
<td>0.050</td>
</tr>
<tr>
<td>7</td>
<td>-0.139</td>
</tr>
</tbody>
</table>
The quartz substrate allows microscopic observation of the single-pore cell. A very thin film of titanium is necessary to promote adherence to the quartz (SiO₂) plate. It is the low free energy of formation TiO₂ (compared with the free energy of formation of SiO₂) that gives titanium a quartz-adhering character.

A thin film of copper deposited onto titanium both protects the titanium from passivation and provides the conductivity necessary to electroplate cadmium onto the electrode. Prevention of titanium passivation is necessary to avoid peeling at the titanium-copper interface when contacted with alkaline solutions. The following sections provide more detail on the steps involved in fabricating the multiple reference microelectrode.

4.2 FABRICATION PROCEDURE

The steps involved in fabricating the microelectrode include quartz substrate preparation, metal deposition, pattern-mask preparation, photolithography, and cadmium reference electrode electroplating.

4.2.1 QUARTZ SUBSTRATE PREPARATION

Quartz was chosen as the microelectrode substrate because of its optical transparency and resistance to attack by strong alkaline solutions. Thorough cleaning of the quartz substrate is necessary to promote strong adhesion of the microelectrode to the substrate, prevent microelectrode contamination, and ensure a smooth, uniform metallic deposit.

One-sixteenth inch thick ground and polished quartz plates were cut into rectangles 5.08-cm X 4.35-cm (to within 0.01 cm). The plates are thoroughly cleaned with glass cleaner to remove dirt particles and quartz dust. After rinsing with deionized (DI) water, the plates are degreased by ultrasonic agitation at 60°C in 1-1-1 trichloroethane. A two-minute rinse in acetone removes the trichloroethane and any residual organics. A one-minute rinse in DI water then removes the acetone. Finally, the plates are dipped in a 5% (by volume) hydrofluoric acid/95% DI water solution for three minutes. The hydrofluoric acid removes the
surface oxide layer. Following a two-minute rinse in DI water, the quartz substrates are ready for processing.

4.2.2 METAL DEPOSITION

Titanium\(^\text{A}\) of 99.3% purity is deposited on the clean quartz substrate by vacuum evaporation. Approximately 500 Å of titanium are deposited at a rate of 5 Å/s at a pressure of 5 \( \times 10^{-7} \) Torr. This low pressure prevents incorporation of contaminants into the deposited film. Next, 2500 Å of 99.999% pure copper,\(^\text{B}\) is deposited at a rate of 15 to 40 Å/s, without interrupting the vacuum after titanium deposition. It is necessary to immediately deposit the copper onto the titanium to avoid titanium oxidation.

4.2.3 PATTERN MASK GENERATION

The deposited metals are cut into the desired pattern by a photolithographic process. The photolithographic process requires the use of a pattern mask to imprint the pattern onto the photoresist-covered substrate. The pattern mask is a developed 5.10 cm \( \times \) 5.10 cm High-Resolution Plate (HRP).\(^\text{C}\)

The first step in mask generation is to cut an oversize pattern on Rubylith,\(^\text{D}\) which is a red plastic film with a polyester backing. Cutting is performed on a coordinatograph, which consists of a precision drafting table with a rack-mounted knife capable of cutting oversize patterns accurate to 0.003 cm. Cut portions of the Rubylith are stripped of the red plastic film, leaving a clear area capable of transmitting light. The pattern is then transferred onto the High-Resolution Plate by photographing the Rubylith pattern with a photoreduction camera, using 23X reduction. Uncut Rubylith material prevents exposure of the corresponding area on the HRP negative, which is insensitive to red light. Development of the HRP negative leaves the actual-size pattern on the mask.\(^1\)
4.2.4 PHOTOLITHOGRAPHY

The process of transferring the pattern onto the metallized substrate (photolithography) consists of the following steps: photoresist application, pattern exposure and development, photoresist baking, metal etching, and photoresist stripping.\(^2\) An outline of the process is diagrammed in Figure 4.4. Because of the small dimensions and light-sensitive materials involved, clean-room conditions (less than 100 particles greater than 0.5 µm in diameter per cubic foot) are required during this procedure.

The photoresist coating provides a method to generate a pattern by selectively protecting portions of the metallized substrate during photolithography. A positive photoresist, Shipley AZ1350J,\(^E\) was used to develop the reference electrode. Positive photoresist is an organic dispersion containing a low molecular-weight polymer and a photosensitizer. Upon exposure to ultraviolet light, the non-polar photosensitizer is converted into a polar molecule, which is soluble in an aqueous organic developer. Unexposed portions are insoluble in the developer and protect underlying thin films during the metal etching step. Removal of the photoresist then leaves the final pattern of metal on the substrate.

4.2.4.1 Photoresist Application

Before the photoresist application, a hexamethyldisilizane (HMDS) primer is deposited from the gas phase onto the substrate at room temperature in a flow chamber. The primer promotes adherence of the photoresist to the substrate. Photoresist is then applied to the mounted substrate using a vacuum chuck spinner, which is spun at 6000 r.p.m. for thirty seconds to achieve a desired resist thickness of 1.35 µm. The coated substrates are then dried under an infrared lamp for five minutes and prebaked for twenty minutes at 90°C. Drying and prebaking removes the solvent from the photoresist coating.
Figure 4.4 Overview of photolithographic process used to fabricate cadmium reference microelectrodes.
4.2.4.2 Pattern Exposure and Development

The coated substrate is exposed to ultraviolet light through the pattern mask. Mask alignment and exposure take place on a 1:1 mask aligner.\textsuperscript{F} Because of mask defects resulting from contact between mask and photoresist during exposure, it was necessary to replace masks after ten to fifteen exposures. Developed areas on the mask prevent exposure of the same areas on the coated substrate.

The photoresist is developed by treating the substrate with a 1:1 solution of Shipley AZ developer and water for one minute. The developer rinses away exposed areas, leaving only the microelectrode pattern on the photoresist. Substrates are examined under a yellow-light microscope to determine if any defects exist in the photoresist pattern.

4.2.4.3 Photoresist Baking

The photoresist-covered substrate is postbaked at 120°C for fifty minutes. Postbaking hardens the photoresist by promoting thermal cross-linking of the polymer. In addition, postbaking improves photoresist adhesion to the thin metallic films, and postbaked photoresist is resistant to attack by various metal etchants.

4.2.4.4 Metal Etching

The unprotected portions of the copper and titanium films are removed by a wet-chemical etch process, one of several available etch processes. Copper was removed by treatment with a 5:1 solution of deionized water/nitric acid (HNO\textsubscript{3}) for three minutes. The etch rate is roughly 800 Å/min. After rinsing the etchant away with water, the titanium is then etched in a 50:1:1 solution of deionized water/hydrogen peroxide (H\textsubscript{2}O\textsubscript{2})/hydrofluoric acid (HF) for ninety seconds, which provides an etch rate of roughly 350 Å/min. The substrate is finally rinsed in deionized water for two minutes to remove all etchants and dried in a nitrogen stream.
4.2.4.5 Photoresist Stripping

Stripping of the photoresist is the final step in the photolithographic process. Photoresist is removed in a 1:1 solution of Shipley 1112A remover and water for two minutes at room temperature. The substrate is rinsed, dried, and stored under nitrogen. A slight undercutting of the copper can be observed, but it is not deleterious to microelectrode performance.

4.3 CADMIUM REFERENCE ELECTRODE PLATING

A thin layer of cadmium is electroplated onto the patterned copper to form the reference microelectrode. A proprietary cyanide cadmium plating solution is used in conjunction with a cadmium sheet counter electrode. A current density of 2 mA/cm² for 10 minutes provides a cadmium coating 2500 Å. Film thicknesses were determined with a stylus profilometer. Figure 4.5 shows a close-up photograph of a portion of the cadmium-plated reference microelectrode region.

The deposited copper metal in the printed circuit contact region at the edge of the quartz substrate is built up to a thickness of approximately 50 μ by zinc electroplating in an acid zinc solution (no. 245) at a current density of 50 mA/cm² for forty minutes. The printed circuit contacts are then gold plated to provide a reusable and reliable electrical contact. The substrates are then dipped in an Atomex immersion gold plating solution (8 grams of gold per liter of solution) and electroplated at a temperature of 60°C for six minutes. This provides a 200-300 Å gold deposit.

In order to protect the circuit from chemical attack, the area between the reference microelectrode and the printed circuit contacts is coated with a layer of quartz approximately 1.4-μ thick. The quartz coating is applied by RF sputtering of a quartz target in a vacuum chamber backfilled with 80% argon/20% oxygen. Sputtering is done at a rate of approximately 40 Å/min for 6 hours. In addition, the coating serves to limit the region of the microelectrode (to one millimeter from the center of the electrode) from which potential measurements are taken, thus minimizing edge effects (Figure 4.6). The potential should
Figure 4.5 Close-up view of cadmium reference microelectrode.
QUARTZ MASKING OF REFERENCE MICROELECTRODE

Electrolyte

Working electrode

0.1 cm

Reference microelectrode

Quartz

0.635 cm

Figure 4.6 Quartz masking of reference microelectrode.
not vary substantially across 1-mm perpendicular to primary current flow. This completes the preparation of the multiple reference microelectrode, and it is ready for use in a cell.
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2. Ibid, pp. 39-49.

FOOTNOTES

A. Cerac/Pure Incorporated, Menomonee Falls, WI.
B. Alfa Products, Danvers, MA.
C. Kodak Corporation, Rochester, NY.
D. ULANO Corporation, Brooklyn, NY.
E. Shipley Corporation, Newton, MA.
F. Quintel Corporation, San Jose, CA.
G. M&T Chemicals, Pico Rivera, CA.
H. Tencer Instruments, Mountain View, CA.
I. M&T Chemicals, Pico Rivera, CA.
J. Engelhard Industries, Newark, NJ.
RESULTS AND DISCUSSION

5.1 INTRODUCTION

The experiments described in this chapter were conducted to obtain optical and electrochemical information to improve understanding of alkaline zinc electrode discharge behavior. A goal of these experiments is to evaluate zinc electrode behavior in pores of realistic dimensions at typical rates of discharge encountered in electric vehicle applications. Zinc behavior was studied in two electrolytes: one of composition 31% KOH and another of composition 15.3% KOH-15.0% KF. Better understanding of alkaline zinc electrode behavior will ultimately lead to improvements in cell design which can alleviate problems due to various failure modes. The alkaline-fluoride electrolyte is of interest because of its potential beneficial effect of reducing zinc redistribution by decreasing zinc species solubility.

Zinc behavior was studied at several rates of discharge because zinc electrodes will experience widely varying rates of discharge in electric vehicle applications. Three experiments, performed at constant discharge current densities of 1250 mA/cm$^2$, 30 mA/cm$^2$ and 7 mA/cm$^2$, are meant to give qualitative information about changes in zinc electrode behavior as a result of changes in discharge rate.

Table 5.1 contains a summary of the experiments performed in this study. Included in the summary are the discharge conditions, electrolyte compositions, and effective pore radii. Current densities were calculated on the basis of pore cross-sectional area as shown in Figure 5.1. It is assumed that the model single pore represents one-half of a parallelepiped pore perpendicular to the porous electrode face. It is assumed also that the electrode porosity ($A_p/A_e$) is 50%. Electrodes were all discharged at constant current to 20 mAh.
Table 5.1: Model Single Pore Screening Experiments

<table>
<thead>
<tr>
<th>Aqueous Electrolyte</th>
<th>Pore Radius (μm)</th>
<th>Current Density (mA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>31% KOH-1% LiOH</td>
<td>19</td>
<td>1250</td>
</tr>
<tr>
<td>31% KOH-1% LiOH</td>
<td>18</td>
<td>30</td>
</tr>
<tr>
<td>31% KOH-1% LiOH</td>
<td>14</td>
<td>7</td>
</tr>
</tbody>
</table>

* Rate of Discharge Effects *

| 31% KOH-1% LiOH     | 18               | 30                      |
| 15.3% KOH-15% KF    | 18               | 30                      |

* Electrolyte Effects *

A Current density as calculated in Figure 5.1

5.2 ZINC ELECTRODE BEHAVIOR IN STANDARD ALKALINE ELECTROLYTE - 31% KOH

Experiments performed at an average rate of discharge of 30 mA/cm² in 31% KOH (corresponding to a C/0.75 discharge rate) served as the basis for zinc studies. Complete pore potential and optical observations were made throughout the discharge. Experiments were also performed at average rates of discharge of 1250 mA/cm² and 7 mA/cm² (C/0.02 and C/3 rates of discharge, respectively). Complete pore potential and optical information data were not obtained for the entire discharge because of either cell or reference electrode failure. Hydrogen bubbles, evolved at the zinc counter electrode, or electrolyte leaks caused by improper gasketing of the cell led to cell failures. Slow attack of the copper-titanium interface, eventually leading to peeling, sometimes led to reference electrode failure.

The following paragraphs discuss the electrochemical and optical observations of the zinc electrode during discharge along with interpretations of the observations. Included are experimental determinations of the initial electrode current distribution, pore concentration profile as a function of time, reaction penetration depth, and surface morphology as a function of position in the pore.
CURRENT DENSITY DETERMINATION

\[ C. \ D. = \frac{1}{w \cdot d \cdot \left( \frac{A_t}{A_p} \right)} \]

\[ \frac{A_p}{A_t} = 0.5 \]

WHERE

C.D. = CURRENT DENSITY (mA/cm²)
I = CURRENT PASSED (mA)
\( A_p \) = CROSS-SECTIONAL PORE AREA (cm²)
\( A_t \) = CROSS-SECTIONAL PORE AND ELECTRODE AREA (cm²)
w = PORE WIDTH (cm)
d = PORE DIAMETER (cm)

Figure 5.1 Determination of cell current density.
5.2.1 ELECTROCHEMICAL AND OPTICAL OBSERVATIONS

Typical cell potential and potential distribution behavior over time are shown in Figure 5.2. The cell potential, reflecting the difference between working and counter electrode potentials, rises slowly over time. This behavior is associated with changes in overall electrolyte composition and electrode surface-layer changes caused by the formation of \( \text{ZnO/Zn(OH)}_2 \) species. The most significant changes in potential occur at the mouth of the pore, nearest to the counter electrode. This is not surprising given that the initial current density is highest at the mouth of the pore and decreases exponentially as distance into the pore increases. Initially, there is an increase in potential at the mouth of the pore \((y/L = 0.03)\) followed by a sharp decrease in potential. The experimentally-determined concentration profile indicates that the maximum in the potential versus time curve reflects the start of \( \text{ZnO/Zn(OH)}_2 \) film formation, presumably by precipitation.

The behavior at the mouth of the pore is mirrored at the middle of the pore \((y/L = 0.60)\), only at a later time. In addition, the magnitude of the potential change is smaller. This is expected because of the slower rate of the dissolution reaction as distance into the pore increases. Thus, zincate concentration rises more slowly at the middle of the pore, resulting in precipitation occurrence later.

The combination of potential distribution information and experimentally-derived concentration information indicates the passage of a precipitate "front" on the surface of the electrode through the pore. This observation is in accordance with results from similar experiments at very high current densities \((750-3000 \ \text{mA/cm}^2)\).\(^1\) It is important to note that the initial reaction mechanism does not appear to change as current density changes significantly. The lack of change of potential at the root of the pore \((y/L = 0.79 \text{ and } y/L = 0.97)\) indicates little electrochemical activity. This indicates that current flow to the root of the pore is not sufficient to drive electrode reactions to an appreciable extent.
Figure 5.2 Cell potential and potential distribution behavior over time at 30 mA/cm².
The cell potential and potential distribution information show no evidence of passivation of the working electrode. Passivation would be evidenced by a sharp, unbroken rise in potential. Inferences about pore behavior made from potential information are confirmed by simultaneous microscopic optical observations of the electrode surface. The upper three pictures in Figure 5.3 show typical zinc electrode behavior over time at a discharge current density of 30 mA/cm². The mouth of the pore, closest to the counter electrode, is located in the upper portion of all in-situ photographs. Initially, the polished zinc surface appears black and uniform, as shown by the upper-left picture. The upper-middle picture shows changes that have occurred after 10 minutes. The zinc surface is preferentially etched at various sites on the electrode, indicated by the bright-white grain regions. Sequential pictures show that the etch pattern extends further into the pore and becomes more fully developed as time increases. The upper-middle picture shows the appearance of a thin, light-gray film extending about 0.25 millimeters into the pore. Katan et al,² observed that Type I ZnO films appeared light-gray in color and Type II ZnO films appeared dark gray in color under the microscope.

Well-defined etch and film fronts, as reported by Katan, were not observed optically. Rather, the photographs show a diffuse movement of the dissolution and precipitation reactions from the mouth of the pore toward the root of the pore. In addition, observation of the zinc surface at low discharge current densities was made difficult by the slow rate of reaction. Studies of thin oxide films show that film thicknesses of several hundred angstroms must be reached before films become visible under direct light.³ This can explain why optical observations show precipitation starting after 10 minutes, whereas potential measurements indicate precipitation starting after 5 minutes. Because of the slow rate of reaction, it takes time for a surface film to build to thicknesses which allow the film to be observed under the microscope.

The lower three photographs in Figure 5.3 are SEM pictures of the electrode surface, taken at different positions in the pore. Clearly, there are differences in surface morphology as position in the pore changes. The lower-left, lower-middle, and lower-right pictures show
OPTICAL MICROSCOPE and SEM PHOTOGRAPHS

of a ZINC ELECTRODE DISCHARGED AT 30 mA/cm² in 15% KOH, 15% KF

Figure 5.3
surface morphology at the mouth (y/L = 0.03), middle (y/L = 0.50) and root (y/L = 0.98) of the pore. After discharge at 30 mA/cm² for forty minutes, the deposit at the mouth of the pore is carpet-like and porous. The deposit is filamentary and porous at the middle of the pore. There is an abrupt change from the carpet-like morphology to the filamentary morphology which occurs at the middle of the pore. The surface morphology at the root of the pore (y/L = 0.98) has the appearance of fibers laid down on a smooth surface. The morphology indicates that some reaction has occurred at the root of the pore. There is no optical evidence of a compact, passivating film. This observation is in agreement with electrode potential observations. This confirms Liu's results which show that passivation is an unlikely failure mechanism for the alkaline zinc electrode at rates of discharge typical for electric vehicle applications.⁴

5.2.2 INITIAL CURRENT DENSITY DISTRIBUTION

An approximate initial current density distribution can be determined from the initial potential distribution by assuming linear polarization and no mass-transfer limitations at low current densities, as discussed in Chapter 2. Determination of the current density distribution serves as a starting point for developing an understanding of system behavior. Figure 5.4 shows the initial current density distribution at the zinc electrode at 30 mA/cm² discharge current density in 31% KOH. There is roughly a four-fold difference between the local current density at the mouth of the pore and the local current density at the root of the pore.

Calculations of the secondary current density distributions given the cell geometry were made on the basis of the three theories, Euler and Nonnemacher, Wagner, and the Section 2.3.1 model, all of which were described in Chapter 2. Calculations were performed for several values of the exchange current density, iₒ. Values of iₒ from 8.4 to 250 mA/cm² for the alkaline zinc electrode have been reported.⁵ Predicted current densities were calculated for values of iₒ equal to 1, 10 and 100 mA/cm². Figures 5.5 - 5.7 show comparisons of the experimentally-derived current density distributions compared with the predicted
Figure 5.4 Measured current density distribution at 30 mA/cm² discharge current density in 31% KOH.
Figure 5.5 Measured initial current density distribution versus Euler and Nonnemacher predictions at 30 mA/cm² in 31% KOH.
Figure 5.6 Measured initial current density distribution versus Wagner predictions at 30 mA/cm² in 31% KOH.
Figure 5.7 Measured initial current density distribution versus model predictions at 30 mA/cm² in 31% KOH.
current density distributions at various values of $i_0$. The experimental data show good agreement with all three theories at a value of $i_0$ approximately equal to 1 mA/cm$^2$.

Wagner's theory gives the best fit to the experimental data. Wagner models a system closely resembling the model single pore cell used in this study. The value of $i_0$ is low compared to reported values. However, preparations at the electrode surface can influence the measured value of $i_0$. Oxidation of the electrode surface sites prior to experimentation can cause some of the zinc to become inactive initially, thus forcing the reaction further into the pore. This results in a lower observed value of $i_0$. The exchange current density is also a strong function of temperature. Cells were run at a temperature of 17°C which is slightly lower than the temperature at which $i_0$ was measured by previous experimenters.

The theoretical current density distribution predictions point out the strong dependence of current density distribution on $i_0$. As $i_0$ increases, the current density distribution becomes more non-uniform. Non-uniformity of the current density distribution can be an important factor in zinc redistribution and electrode utilization.

5.2.3 PORE CONCENTRATION PROFILE

The cadmium reference electrodes can be used to measure hydroxyl-ion concentration in the pore as a function of time, as described in Chapter 2. Equation (2-38) gives the potential of the cadmium electrode as a function of hydroxyl-ion activity. The difference in hydroxyl-ion activity from one point to another can be determined by measuring the difference between the cadmium potentials at the two points. Neglecting the effect of zincate, the local hydroxyl-ion molality is related to activity by the following expression:

$$a_{\text{OH}} = Y_{\text{KOH}} \cdot m_{\text{OH}}$$

(1)

where $Y_{\text{KOH}}$ is the mean molal activity coefficient of KOH. Substitution
of eq. (1) into eq. (2-38) gives:

$$E_0 - E_i = 0.059 \cdot \log \left( \frac{\gamma_{i,\text{KOH}} \cdot m_{i,\text{OH}^-}}{\gamma_{o,\text{KOH}} \cdot m_{o,\text{OH}^-}} \right)$$

where the subscript $o$ refers to properties at a system reference point and the subscript $i$ refers to properties at a point $i$ in the system. The system reference is located at a point midway between the working and counter electrodes where potential measurements are made. It is assumed that the hydroxyl-ion concentration varies little over time at this point. Because the mean molal activity coefficient at point $i$ is a function of the unknown molality of point $i$, eq. (2) requires an iterative solution. Mean molal activity coefficients of KOH have been measured as a function of hydroxyl-ion molality by several investigators.

The hydroxyl-ion concentration, as determined by the method just described, is given at different pore locations over time in Figure 5.8. Two factors will effect the local hydroxyl-ion concentration: electrode reaction stoichiometry and transport of hydroxyl ions by diffusion, migration and convection. The dissolution reaction consumes hydroxyl ions, resulting in lower $[\text{OH}^-]$. The precipitation reaction releases hydroxyl ions, resulting in higher $[\text{OH}^-]$. Hydroxyl ions will diffuse from areas of high $[\text{OH}^-]$ to low $[\text{OH}^-]$, i.e. towards the mouth of the pore. If ZnO/Zn(OH)$_2$ precipitation occurs towards the mouth of the pore and zinc dissolution occurs towards the root of the pore, hydroxyl ions will migrate towards the root of the pore to satisfy the electroneutrality condition. Finally, density gradients caused by $[\text{OH}^-]$ can cause free convection of hydroxyl ions. In summary, the two reaction steps act in opposite directions, as do migration and diffusion.

Initially, the dissolution reaction causes a reduction of hydroxyl-ion concentration. Reduction of $[\text{OH}^-]$ is most noticeable at the mouth of the pore, where the reaction rate is highest. Similar behavior occurs at the middle of the pore ($y/L \approx 0.60$) later in time and lower in magnitude than at the mouth of the pore. The lack of change in $[\text{OH}^-]$ over time at the root of the pore is further evidence that the electrode reactions are occurring at a very slow rate at the pore root.
Figure 5.8 Hydroxyl-ion concentration as a function of time and distance into pore at 30 mA/cm$^2$ in 31% KOH.
The $[\text{OH}^-]$ reaches a minimum after six minutes, after which it increases rapidly. After fourteen minutes, the $[\text{OH}^-]$ increases above the initial average $[\text{OH}^-]$. Diffusion of hydroxyl ions to the pore mouth can account for some, but not all of the increase. Thus, the precipitation reaction must be occurring. Similarly, precipitation at the middle of the pore appears to start after eleven minutes. The only significant change in concentration at the root of the pore occurs at 33 minutes when the $[\text{OH}^-]$ begins to increase. This may indicate a shift in current towards the root of the pore as a result of non-conducting film formation at the mouth of the pore.

Figure 5.8 gives important qualitative information about $[\text{OH}^-]$ profiles in the pore. However, because of some simplifications, the absolute $[\text{OH}^-]$ values may not be exact. First, internal currents may be generated as a result of concentration gradients, which will introduce an unknown ohmic contribution to the measured open circuit potentials. At regions of high $[\text{OH}^-]$ the dissolution of zinc will occur, while at regions of low $[\text{OH}^-]$ the precipitation of zinc species will occur to relax the concentration gradient. Based on concentration cell experiments, Katan\textsuperscript{7} estimated that internal currents of about 0.2 to 0.4 mA/cm$^2$ could be generated by concentration differences of 0.5 to 0.7 M. It is believed that this phenomenon results in the initial, unexpected upward shift in apparent $[\text{OH}^-]$ at the root of the pore. In addition, the $[\text{OH}^-]$ at the reference point may have decreased slightly because of hydroxyl-ion diffusion to the mouth of the pore.

Secondly, the concentration profile given if Figure 5.8 assumes no concentration gradients perpendicular to the electrode surface. Actually, the results are valid only at a point roughly $18 \times 10^{-4}$ cm above the electrode surface (the reference electrode location). Concentration gradients in a direction perpendicular to the electrode surface will become more significant at higher current densities. Because the dissolution/precipitation reaction occurs in the solution layer very close to the surface, it can be expected that the results in Figure 5.8 tend to underestimate hydroxyl-ion concentration changes. Faraday law calculations of pore hydroxyl-ion concentration tend to support the above argument. These calculations will be discussed later in this section.
One other attempt has been made to measure the $[\text{OH}^-]$ profile in realistically-sized zinc pores. Katan\(^9\) measured the concentration profile in a zinc electrode pore of similar dimensions at a single point in time during a high-rate discharge of 750 mA/cm\(^2\). The $[\text{OH}^-]$ profile was determined by subtracting individual zinc reference electrode potentials from the zinc working electrode potential on open circuit. Unfortunately, the use of the working electrode potential in the calculations, which is averaged over the entire pore length, cannot lead to any meaningful determination of $[\text{OH}^-]$ as a function of distance into the pore. Thus, there is no previous work with which to compare these $[\text{OH}^-]$ determinations. However, the results are consistent with expectations given a knowledge of the reaction mechanism and cell current density.

The concentration gradients shown in Figure 5.8 exhibit a slow relaxation time once the discharge is complete. Measurements made until 15 minutes after a complete discharge showed the existence of a small residual concentration gradient in the pore. This concentration gradient was a small fraction of the gradient observed at the end of the discharge, however.

An approximate $[\text{OH}^-]$ profile can be calculated using Faraday's law with an assumed current density distribution. In order to make this calculation, it is necessary to assume that the initial current density distribution is constant over time. In addition, it is assumed that the pore can be broken up in six small, well-mixed segments between which there is no transport of soluble species. With these assumptions, the rate of zinc dissolution is constant within each segment. Given that zincate precipitation is between two to four times the zincate saturation concentration,\(^{10}\) the time at which precipitation occurs in each segment can be calculated.

Estimated precipitation times for each segment are listed in Table 5.2 for various zincate supersaturation concentrations. Precipitation is observed earlier than predicted because the system is not well-mixed; (as previously mentioned, precipitation originates from a solution layer near the electrode surface which reaches zincate supersaturation quickly).
Table 5.2: Predicted Precipitation Times

<table>
<thead>
<tr>
<th>Pore Segment (y/L)</th>
<th>2X</th>
<th>3X</th>
<th>4X</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.06</td>
<td>10.01</td>
<td>20.03</td>
</tr>
<tr>
<td>2</td>
<td>.22</td>
<td>12.39</td>
<td>24.77</td>
</tr>
<tr>
<td>3</td>
<td>.41</td>
<td>16.08</td>
<td>32.16</td>
</tr>
<tr>
<td>4</td>
<td>.59</td>
<td>20.83</td>
<td>41.67</td>
</tr>
<tr>
<td>5</td>
<td>.78</td>
<td>26.96</td>
<td>53.92</td>
</tr>
<tr>
<td>6</td>
<td>.94</td>
<td>32.16</td>
<td>64.32</td>
</tr>
</tbody>
</table>

* expressed as n times the zincate saturation concentration

The predicted hydroxyl-ion concentrations are shown in Figure 5.9. A comparison between the measured and predicted hydroxyl-ion concentrations is given at a sample time in Figure 5.10. Although the Faraday-Law calculations predict lower-than-observed [OH\(^-\)], the shape of the concentration distribution is similar. There are several reasons why the predictions overestimate [OH\(^-\)]. As discussed before, the system is not well-mixed. In addition, current on the surface will tend to decrease over time with the reduction of electrolyte [OH\(^-\)]. Concentration-gradient-induced currents, in the absence of cell current flow, also result in observed [OH\(^-\)] which are slightly higher than actually present in the pore. Finally, various transport processes, which are neglected in the Faraday-Law calculation, will tend to relax the evolving concentration gradients.

5.2.4 REACTION PENETRATION DEPTH

The initial reaction penetration depth can be calculated from the initial potential distribution as described in Chapter 2. The initial reaction penetration depth is useful in determining the optimal electrode thickness for a specific design application. The initial reaction penetration depth was measured to be 0.11 cm (y/L = 0.72). Substituting appropriate values into equation (2-42) at an exchange current density of 1 mA/cm\(^2\) gives a predicted penetration depth of 0.08 cm, which is close to the measured value.
Figure 5.9 Predicted pore hydroxyl-ion concentration as a function of time at 30 mA/cm$^2$ in 31% KOH.
Figure 5.10  Measured hydroxyl-ion concentration profile versus predicted hydroxyl-ion concentration profile in pore at $t = 5$ minutes at 30 mA/cm$^2$ in 31% KOH.
It has been observed that the reaction will penetrate farther into the pore than the initial penetration depth.\textsuperscript{11} The SEM photographs showing evidence of reaction occurrence at the root of the pore validates this observation.

5.2.5 RATE OF DISCHARGE EFFECTS

The alkaline zinc electrode behavior described in the previous sections was observed to some extent at both the higher and lower rates of discharge. However, there were some observed differences, especially at very high current densities.

5.2.5.1 High Rate of Discharge Results - 1250 mA/cm\textsuperscript{2}

A very high rate of discharge experiment was performed at a current density of 1250 mA/cm\textsuperscript{2}. The experiment was performed, in part, to attempt to reproduce an experiment performed by Katan in a pore of similar geometry and size. Reproduction of Katan's results would both lend credibility to results obtained in experiments described in this paper, and determine applicability of previous results obtained at high current densities to electrode behavior at more realistic current densities.

Optical microscope observations of the discharge behavior are shown in the upper three photographs in Figure 5.11. Initially, a bright-white etch pattern forms over a short period of time as shown in the upper-middle photograph. The etch pattern moved along the surface of the electrode into the pore in a well-defined, observable front. A light-gray colored film, presumably Type I, then covers the electrode surface. Finally, after about twenty seconds a darker film, presumably Type II, began to appear near the mouth of the electrode (upper portion of the upper-right photograph). Cell potential data showed a rapid rise in potential shortly after the appearance of the film. These observations are in agreement with Katan's observations.\textsuperscript{12}
OPTICAL MICROSCOPE and SEM PHOTOGRAPHS

of A ZINC ELECTRODE DISCHARGED AT 1250 mA/cm$^2$ in 31% KOH

Figure 5.11
The SEM photographs of the zinc electrode confirm the in-situ optical observations. The lower-left photograph shows the presence of a dense, compact film at the mouth of the pore. This is in contrast to the porous, flocculent film that is seen in the middle of the pore as shown in the lower-middle photograph. Little activity is observed at the root of the pore (lower-right photograph), as the electrode is similar in appearance to undischarged, polished electrodes. This indicates that the reaction has not proceeded to the root of the pore.

The initial potential distribution at 1250 mA/cm² is different in shape than the initial potential distribution at 30 mA/cm² as shown in Figure 5.12. The initial potential distribution at 1250 mA/cm² is steeper at the mouth of the pore. The initial current density distribution can be calculated from the initial potential distribution with the assumption of Tafel polarization, and is shown in Figure 5.13. The Wagner model prediction, calculated assuming Tafel kinetics, is also shown in Figure 5.13. Unfortunately, agreement with theoretical prediction is not good. The model predicts a steeper-than-observed current density distribution. It may be possible that the differences in boundary conditions between the Wagner model pore and experimental pore are significant at higher current densities.

5.2.5.2 Low Rate of Discharge Results - 7 mA/cm²

A low rate of discharge experiment was performed at a current density of 7 mA/cm². Experimental results were similar to results obtained at 30 mA/cm². Optical-microscope photographs taken at equivalent discharge times were very similar to photographs shown in Figure 5.3. As in the 30 mA/cm² experiment, a zinc etch pattern formed at preferential surface sites. The etch pattern developed more fully over time, and extended gradually into the pore. A milky-white film, covering the surface nearest the mouth of the pore, was observed after 55 minutes. The film extended into the mouth of the pore as the discharge proceeded. No passivating film was observed from either optical micrographs or SEM photographs.
Figure 5.12 Effect of discharge current density on initial potential distribution in pore in 31% KOH.
Figure 5.13 Measured initial current density distribution versus Wagner predictions at 1250 mA/cm² in 31% KOH.
The initial potential distribution is more uniform than the potential distribution obtained for the 30 mA/cm² case. The initial current density distribution is determined from the initial potential distribution, assuming linear polarization. The experimentally-derived current density distribution is compared with theoretical predictions in Figures 5.14 - 5.16. In this case, the best fit is obtained with Euler and Nonnemacher's predictions, although all three theory predictions fit the experimental data closely. In all cases, the best fit is obtained assuming an exchange current density of 1 mA/cm². This observation is consistent with the results obtained at 30 mA/cm², which showed the best curve fit was obtained at an exchange current density of 1 mA/cm².

5.3 ZINC BEHAVIOR IN ALKALINE FLUORIDE ELECTROLYTE - 15% KOH-15% KF

It has been proposed that an alkaline fluoride electrolyte could reduce the problem of zinc redistribution by reducing zinc solubility. Preliminary experiments have shown improvements in cycled-cell performance with an alkaline fluoride electrolyte of composition 15.3% KOH-15% KF. Experiments were performed with the model single pore using the fluoride electrolyte to determine if there were differences in discharge behavior between the two electrolytes. Experiments were performed in pores of diameters identical to those studied in the 31% KOH experiments and at identical current densities to give the best basis for electrolyte comparison.

5.3.1 ELECTROCHEMICAL AND OPTICAL OBSERVATIONS

Optical microscope observations of the discharge behavior are shown in the upper three photographs in Figure 5.17. An etch pattern forms in a manner similar to that observed in 31% KOH, as shown in the upper-middle photograph. However, the upper-right photograph shows the appearance of a blotchy, light-gray film on the electrode surface after six minutes. The film appeared to extend into the pore more rapidly than the film found in 31% KOH.
Figure 5.14 Measured initial current density distribution versus Euler and Nonnemacher predictions at 7 mA/cm² in 31% KOH.
Figure 5.15 Measured initial current density distribution versus Wagner predictions at 7 mA/cm² in 31% KOH.
Figure 5.16 Measured initial current density distribution versus model predictions at 7 mA/cm² in 31% KOH.
OPTICAL MICROSCOPE and SEM PHOTOGRAPHS
of A ZINC ELECTRODE DISCHARGED AT 30 mA/cm² in 31 % KOH

Figure 5.17
Electrode surface morphology varies slightly with position in the pore as evidenced by the SEM photographs in Figure 5.17. The deposit at the mouth of the pore (lower-left photograph) is layered and blotched in appearance. Higher magnification photographs show this film to be porous. The surface morphology at the middle of the pore (lower-middle photograph) is similar in appearance but more porous. The deposit at the root of the pore (lower-right photograph) is nodular in appearance and different from the film present throughout the majority of the pore. This indicates that the reaction has extended to the root of the pore at the completion of the discharge.

The initial potential distribution observed in 15.3% KOH-15% KF was comparable in shape to the initial potential distribution observed in 31% KOH. The initial potential distribution is steeper near to the mouth of the pore. The reaction penetration depth was determined to be 0.10 cm. The experimentally-derived penetration depth is in reasonable agreement with the theoretical prediction of 0.07 cm (assuming $i_0 = 1$ mA/cm$^2$). Because of cell and reference electrode failures, determinations of potential distribution behavior over time and concentration profile distributions were not made. Alteration of the cell design may be necessary to contain the fluoride electrolyte, which has a very low contact angle with smooth surfaces. This allows the electrolyte to wick out of the cell during discharge.

5.3.2 COMPARISON OF ZINC ELECTRODE BEHAVIOR IN ALTERNATE ELECTROLYTES

As the optical micrographs show, there is a difference in film formation rate between the two electrolytes. The ZnO/Zn(OH)$_2$ film forms more quickly and extends into the pore faster than the film formed in 31% KOH. This is consistent with the expectation that the ZnO film will precipitate at an earlier time because of the reduced solubility of zinc in 15% KOH-15% KF.

The lower conductivity of the fluoride electrolyte results in a slightly more non-uniform initial current density distribution. This is exemplified by the slight reduction in reaction penetration depth.
Finally, surface film morphology is significantly different. Whereas the 31% KOH films are porous and filamentary, the 15% KOH-15% KF films are porous and layered. This may be due in part to the participation of fluoride ions in the precipitation process or possible incorporation of fluoride compounds in surface films.
REFERENCES


CHAPTER 6

CONCLUSIONS

A model zinc electrode single pore cell has been developed to study electrode discharge behavior in alkaline electrolytes. The cell design allows for simultaneous in-situ microscopic optical and electrochemical observation of pores of dimensions approaching those in commercial zinc electrodes. A thin-film cadmium reference microelectrode was designed and fabricated to obtain potential measurements in the cell. The underlying cadmium reference microelectrode is resistant to concentrated alkaline electrolyte, allowing for the stable measurement of transient potential distribution.

Discharge experiments performed in 31% KOH at 30 mA/cm² and 7 mA/cm² discharge rates revealed information about overall reaction mechanism, pore concentration profile and electrode surface morphology. The dissolution-precipitation mechanism for alkaline zinc electrode discharge is consistent with experimental data. Significant hydroxyl ion concentration gradients within the pore of up to 1.5M OH⁻ were found to exist during discharge. Observed concentration gradients are consistent with expectations and can be qualitatively predicted, before the onset of precipitation, by relatively simple theory. The slow relaxation of these gradients may be related to zinc electrode failure modes including zinc redistribution and passivation. Unrelaxed, concentration gradients may become exacerbated as cycle number increases, leading to reduced cell capacity and possible failure.

Surface morphology of zinc electrodes was found to vary with position, rate of discharge and electrolyte composition. At low discharge rates, the surface ZnO/Zn(OH)₂ film changed from a porous, carpet-like structure at the mouth of the pore to a very porous, filamentary structure at the middle of the pore. Whereas at high current densities the surface film changed from a compact, passivating film at the mouth of the pore to a porous, carpet-like film at the root of the pore. There was no optical or electrochemical evidence of passivation at low current densities. However, there is optical and electrochemical evidence of
passivation at very high current densities (1250 mA/cm$^2$ discharge rate).

Initial current density distributions were determined for several discharge rates. Experimentally-derived current distributions showed good agreement with theory at an exchange current density of 1 mA/cm$^2$. Results show a fairly uniform current distribution, showing a four-fold difference in current density from the mouth to the root of the pore. The reaction penetration depth was determined to be about 0.11 cm and is in reasonable agreement with theoretical predictions.

Zinc electrode discharge behavior was studied in 15.3% KOH-15% KF electrolyte. Optical results showed the formation of a surface film sooner than that which occurred in 31% KOH as a result of reduced zinc solubility in the fluoride electrolyte. Earlier film formation would reduce the residence time of zinc species in the electrolyte, which may reduce deleterious zinc redistribution rates. The surface film produced in 15.3% KOH-15% KF was different in morphology than the film produced in 31% KOH, but it still had a porous structure. The reaction penetration depth in 15.3% KOH-15% KF was slightly less than that in 31% KOH, due to the reduced conductivity of the 15.3% KOH-15% KF electrolyte.
ACKNOWLEDGEMENTS

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APPENDIX A

HARDWARE CONFIGURATION

This appendix gives a technical description of the Potentiostat - Reference Electrode Multiplexer (PREM) and the computer interface hardware connections.

A.1 POTENTIOSTAT - REFERENCE ELECTRODE MULTIPLEXER DESCRIPTION

The potentiostat which this instrument is used with maintains the potential of the reference electrode of an experimental cell at a preset level with respect to the working electrode of the cell. This instrument allows the user to choose, under computer control, one out of nine reference electrodes associated with a cell to be the one which has its potential stabilized by the potentiostat. A tenth channel can also be selected and is used to monitor the counter electrode through a BNC connector on the front panel. The gain of each channel can be adjusted from 0.5 - 500 (1 - 1000 for channel 10) by means of front panel trim-pots. A zero adjust for each channel is also available on the front panel. If the reference and working electrodes are not made of the same material, it is necessary to introduce a compensation offset voltage in all the channels (except number 10). There is an on-off switch for this purpose. A front panel trimpot adjusts the offset over a 0 to -3 volt range.

A switch-selectable calibration voltage can be introduced to the inputs of all the channels by inserting the edge connectors, which are on the end of the cable which comes out of the front panel into the card-connector panel.

Note: When setting up the compensation offset, the edge connector must be plugged in and 0 volts calibration voltage selected. Full CCW rotation of the gain trimpots will yield a well-defined gain of 1/2 (1 for channel 10).
TRIG A and TRIG B can be selected under computer control. Writing a ONE to bit a5 of the LSI-11 DRV-11 I/O card generates a negative edge at the TRIG A connector. Writing a ZERO generates a positive edge at the TRIG B connector. The shutter switch can be actuated by writing a ONE to bit a4.

A.1.1 CIRCUIT DESCRIPTION

Op-amps M1 - M10 are wired as non-inverting summing amplifiers. Each channel sum one reference electrode voltage and the adjustable compensation offset voltage. The gain and zero are individually adjustable for each amplifier. In the non-inverting configuration, the summing junction is not held at a virtual ground. This causes the response of the amplifier to a given input to be a function of the input resistances associated with both inputs. This necessitates the application of zero calibration voltage to the reference inputs when setting up the compensation offset, rather than simply disconnecting the reference inputs. Note that since no compensation offset input resistor is tied to M10, it has twice the gain of M1 - M9.

M11 is an analog multiplexer which selects one of the above amplifiers according to the address defined by bits a0 - a3 of the DRV-11. The output of M11 is buffered by voltage follower M12. Note that since the cell's working electrode is connected to ground, it is sufficient to feedback to the potentiostat this voltage, which is simply a function of E(reference), in order to regulate E(reference) - E(working).

M15 and M18 are precision voltage reference integrated circuits and are used to generate the calibration reference and compensation offset voltages, respectively. The 2-volt tap on the divider string for the calibration reference is fed to multiplexer M11 and can be addressed by the DRV-11.

The trailing edge of NEW DATA READY clocks bit a5 from the DRV-11 into D-type flip-flop M17. A ONE yields a negative edge at the TRIG A connector. A ZERO yields a positive edge at the TRIG B connector. Since two sections of M16, which are used as NAND's, are gated by the clock pulse, an edge is generated even if the flip-flop doesn't change state.
A.2 HARDWARE INTERCONNECTIONS

The following three tables document the electrical connections that must exist between the computer, PREM and potentiostat for successful operation of the data-acquisition and experiment-control system.

<table>
<thead>
<tr>
<th>Potentiostat</th>
<th>Color</th>
<th>Channel</th>
<th>A/D Ch.</th>
<th>Cable</th>
</tr>
</thead>
<tbody>
<tr>
<td>External Cell</td>
<td>Black</td>
<td>8A(+-)</td>
<td>56H</td>
<td>A - Black</td>
</tr>
<tr>
<td>S/A Out</td>
<td>Red</td>
<td>8A(+R)</td>
<td>57H</td>
<td>A - Red</td>
</tr>
<tr>
<td></td>
<td>Black</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Electrometer Monitor</td>
<td>Red</td>
<td>8A(R-)</td>
<td>58H</td>
<td>A - Gray</td>
</tr>
<tr>
<td></td>
<td>Black</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>I Output</td>
<td>Red</td>
<td>8B(+-)</td>
<td>59H</td>
<td>B - Red</td>
</tr>
<tr>
<td></td>
<td>Black</td>
<td></td>
<td>59L</td>
<td>B - Black</td>
</tr>
</tbody>
</table>

Note: Table 1 shows connections to Channel 8 of the Buffer Box. Connections should be made in a similar manner to any other channels.

Thus, for the connections listed in Table 1, the following data is available:

<table>
<thead>
<tr>
<th>Data</th>
<th>Channel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Counter - Working Electrode Potential</td>
<td>56</td>
</tr>
<tr>
<td>Counter - Reference Electrode Potential</td>
<td>57</td>
</tr>
<tr>
<td>Reference - Working Electrode Potential</td>
<td>58</td>
</tr>
<tr>
<td>Cell Current</td>
<td>59</td>
</tr>
</tbody>
</table>
Table 2

PREM - Computer DRV-11 Connections

<table>
<thead>
<tr>
<th>LSI-11/23 Burndy Cable</th>
<th>DRV-11 H854 Connector</th>
<th>DRV-11</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>J1-C</td>
<td>OUT 0</td>
</tr>
<tr>
<td>B</td>
<td>J1-K</td>
<td>OUT 1</td>
</tr>
<tr>
<td>C</td>
<td>J1-NN</td>
<td>OUT 2</td>
</tr>
<tr>
<td>D</td>
<td>J1-U</td>
<td>OUT 3</td>
</tr>
<tr>
<td>E</td>
<td>J1-L</td>
<td>OUT 4</td>
</tr>
<tr>
<td>F</td>
<td>J1-N</td>
<td>OUT 5</td>
</tr>
<tr>
<td>G</td>
<td>J1-VV</td>
<td>OUT 6</td>
</tr>
<tr>
<td>H</td>
<td>J1-P</td>
<td>OUT 7</td>
</tr>
<tr>
<td>J</td>
<td>******</td>
<td>******</td>
</tr>
<tr>
<td>K</td>
<td>******</td>
<td>******</td>
</tr>
</tbody>
</table>

Note: Twisted-pair grounds from the ten pin LSI-11/23 Burndy cable are connected to grounds available from DRV-11 board: J1-Y, CC, EE, KK, MM, PP, SS, UU.

Table 3

Potentiostat - PREM Connections

<table>
<thead>
<tr>
<th>Potentiostat</th>
<th>PREM</th>
<th>Cable Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trig. Input (Rising Edge)</td>
<td>Trig B</td>
<td>BNC</td>
</tr>
<tr>
<td>Trig. Input (Descending Edge)</td>
<td>Trig A</td>
<td>BNC</td>
</tr>
</tbody>
</table>
APPENDIX B

SINGLE PORE CELL SOFTWARE

B.1 CELL EXPERIMENT RUN ROUTINE -- POREST

B.1.1 DESCRIPTION

The POREST program controls the course of a single pore cell experiment and data acquisition. The program controls communication between various pieces of hardware and the computer. The program is divided into three sections: initialization section; experiment run section; and completion section. The initialization section allows the program user to set experiment-control parameters and data-acquisition parameters. The experiment run section monitors and directs the course of the experiment by manipulating the PREM and potentiostat/galvanostat. It also controls data acquisition according to the parameters set in the initialization section. The completion section writes and closes the output data file, and restores the hardware to its initial status.

Once these parameters are initialized in the program, POREST reads in each specified reference electrode amplifier value. During this procedure, the cinch-card connector must be plugged into the PREM voltbox. The user inputs the voltbox calibration voltage (set on the face of the PREM), and the computer reads the output voltage for each electrode. The computer then calculates the amplifications which are used in the program. During this time, the reference electrode zero point can be checked by setting the voltbox calibration voltage to zero. If adjustments to the reference electrodes need to be made, the program allows the user to recalibrate the electrodes any number of times.

POREST opens the data file, DL1:PORDAT.FMT, after amplifier calibration is completed. DL1:PORDAT.FMT will contain the differential potential measurements for each electrode along with the time at which they
were taken. The format for data entry is:

<table>
<thead>
<tr>
<th>Field 1</th>
<th>Field 2</th>
<th>Field 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrode #</td>
<td>Potential (volts)</td>
<td>Time (ticks - 1/60th second)</td>
</tr>
</tbody>
</table>

The potential listed will be of the form:

(�reference or counter electrode) - working electrode

Electrode numbers 1 through 7 indicate reference electrode minus working electrode potential measurements taken with current applied to the cell. Electrode number 0 corresponds to counter minus working electrode potential measurements taken with current applied. (Note: counter minus working electrode potentials are fed through amplifier number 10). Electrode numbers 11 through 17 correspond to reference electrode minus working electrode potential measurements taken without current applied to the cell (open circuit). Similarly, electrode number 10 corresponds to counter minus working electrode potential measurements taken without current applied to the cell (open circuit). These electrode codes are used by the data reduction programs, described in the next section, to decipher the data.

Once initialization is completed, control is passed to the experiment run section. The run section contains a main loop which directs the hardware to take complete cell potential measurements at specified times. The time of each measurement, along with the corresponding electrode number and measured potential, is recorded and logged into an array. The time is taken from the internal computer clock through the subroutine GETTIM. A complete cell measurement consists of switching to each reference electrode sequentially, with intermittent pauses, reading the potential, and logging the appropriate time and voltage data. The working minus counter electrode potential is then read.

Once a cell measurement is complete, FOREST updates the open-circuit timer and checks to see if it is time to take an open circuit measurement. If so, the time is reset and the cell current is switched to potentiostat current channel B, which is programmed to be on open circuit. A complete cell measurement is then made, and the Channel A current, which is programmed with the desired charge/discharge current,
is restored to the cell.

POREST then updates the picture time and checks to see if it is time to take a picture. If so, the timer is reset, and the shutter is sequentially opened and closed with a delay of $10/60^{ths}$ of a second between the two operations. Writing a "1" to the fourth bit of the PREM multiplexer will open the shutter and a "0" will close the shutter.

The data arrays contain a maximum of 1000 elements each. Thus, the computer also checks to see if the data arrays are full. If so, the arrays are written to the files.

Finally, POREST checks to see if the experiment is finished. The user signals the end of an experiment by typing any character on the keyboard. The computer checks the keyboard status to determine if any characters have been typed. If so, POREST signals the end of the experiment. Control is passed from the run section to the completion section. If the end-of-experiment has not been detected, POREST delays until it is time to make the next cell measurement and then repeats the above steps.

In the completion section, POREST updates the data file and closes it. Finally, it returns the hardware to its status prior to the experiment.

B.1.2 SOFTWARE CONTROL OF CELL ELECTRONICS

It is necessary for POREST to be able to communicate with the computer and cell hardware in order to control cell progress and data acquisition. A custom I/O driver developed by M. Katz for the DEC LSI-11/23 computer gives programs the ability to communicate with various pieces of I/O hardware in the extended memory environment. Through the I/O driver, programs can easily perform read/write operations with D/A, A/D, and P-I/O interface cards connected to the computer. Through these interface cards, programs can access information from various analog devices and control their operation. The I/O driver was modified to suit the specific needs of this application; modifications are described in section B.5.
Specifically, a single P-I/O card communicates with the PREM to
direct the activities of the PREM, camera and potentiostat/galvanostat.
The P-I/O card passes digital signals, written from the program, to a
16-bit multiplexer. Selecting the desired electrode potentials to read,
taking pictures, and choosing the potentiostat current channel set, can
be accomplished by setting or resetting appropriate bits of the address
word to the multiplexer. The address word is a single byte, assigned to
the following definition:

<table>
<thead>
<tr>
<th>Bit#</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>unused</td>
</tr>
<tr>
<td>6</td>
<td>unused</td>
</tr>
<tr>
<td>5</td>
<td>select current channel</td>
</tr>
<tr>
<td>4</td>
<td>take picture</td>
</tr>
<tr>
<td>3</td>
<td>select electrode</td>
</tr>
<tr>
<td>2</td>
<td>select electrode</td>
</tr>
<tr>
<td>1</td>
<td>select electrode</td>
</tr>
<tr>
<td>0</td>
<td>select electrode</td>
</tr>
</tbody>
</table>

Bits 0 through 3 allow the user to select the proper reference elec­
trode potential to read. For instance, writing a '0' (0000 0000) to the
address word makes the working minus reference electrode 1 potential
signal available to the computer. Writing a '1' (0000 0001) makes the
working minus reference electrode 2 potential signal available. This
continues up to the integer 8 which selects reference electrode 9. Writ­
ing a '9' (0000 1001) makes the working minus counter electrode poten­tial signal available to the computer.

Bit 4 controls the switch to actuate the camera shutter, controlled
by the camera motor drive. Setting bit 4 ('16') opens the camera
shutter. Resetting bit 4 ('0') closes the shutter. A short delay (10
milliseconds or so) is required between setting and resetting bit 4.
Exact timing is not necessary; camera electronics will not allow the
shutter to be closed until the exposure is complete.
Bit 5 allows the user to select the galvanostat current channel used. Typically, one channel is set to the desired charge/discharge current (channel A). The other channel is set to zero current (channel B - open circuit). Setting bit 5 of the address word ('32') selects current channel A of the galvanostat. Resetting bit 5 selects channel B. This capability is useful in placing the cell intermittently on open circuit, to obtain zero-current potential measurements.

To obtain a potential measurement, POREST first selects the reference electrode and then reads the A/D channel which contains the potential reading. To select the reference electrode, the program writes the proper address word to the P-I/O. The program writes to the P-I/O card through the RT-11 system subroutine ISPFNW. The program reads the electrode potential on the A/D card, through the I/O subroutine RDLOGG. One of the subroutine parameters must contain the proper A/D channel to be read. The proper A/D channel depends on the cell hardware connections to the computer buffer box (described in Appendix A). For more information on the I/O driver and subroutines, see M. Katz's documentation.

B.1.3 POREST SAMPLE RUN

Program-generated questions are in capital letters; user responses are in lower case letters and numbers. An explanation of the user-set parameters follows the sample-run listing.

r porest
SINPOR -- VERSION 47
HOW MANY REFERENCE ELECTRODES?
7
TIME BETWEEN EACH MEASUREMENT (MIN,SECS,TICKS)?
0,10,0
TIME BETWEEN MULTIPLEXER SWITCH (TICKS)?
5
TIME TO HOLD CELL ON OPEN CIRCUIT (SECS)?
1
REF.VS. WORKING POTENTIAL CHANNEL (R-)?
58
WORKING VS. COUNTER POTENTIAL CHANNEL (+-)?
56
REF.VS. COUNTER POTENTIAL CHANNEL (R+)?
57
HOW OFTEN DO YOU WANT PICTURES (MIN, SECS)?
2.0
HOW OFTEN DO YOU WANT TO GO TO OPEN CIRCUIT (MIN, SECS)?
1.0
INPUT VOLTAGE FOR REF. ELECTRODE 1
0.0200
OUTPUT VOLTAGE FOR REF. ELECTRODE 1
IS 2.0000
AMPLIFICATION FOR REF. ELECTRODE 1
IS 100.00
INPUT VOLTAGE FOR REF. ELECTRODE 2
0.0200
OUTPUT VOLTAGE FOR REF. ELECTRODE 2
IS 2.0200
AMPLIFICATION FOR REF. ELECTRODE 2
IS 101.00
INPUT VOLTAGE FOR REF. ELECTRODE 3
0.0200
OUTPUT VOLTAGE FOR REF. ELECTRODE 3
IS 2.0100
AMPLIFICATION FOR REF. ELECTRODE 3
IS 100.50
INPUT VOLTAGE FOR REF. ELECTRODE 4
0.0200
OUTPUT VOLTAGE FOR REF. ELECTRODE 4
IS 2.0000
AMPLIFICATION FOR REF. ELECTRODE 4
IS 100.00
INPUT VOLTAGE FOR REF. ELECTRODE 5
0.0200
OUTPUT VOLTAGE FOR REF. ELECTRODE 5
IS 2.0400
AMPLIFICATION FOR REF. ELECTRODE 5
IS 102.00
INPUT VOLTAGE FOR REF. ELECTRODE 6
0.0200
OUTPUT VOLTAGE FOR REF. ELECTRODE 6
IS 2.0000
AMPLIFICATION FOR REF. ELECTRODE 6
IS 100.00
INPUT VOLTAGE FOR REF. ELECTRODE 7
0.0200
OUTPUT VOLTAGE FOR REF. ELECTRODE 7
IS 1.5000
AMPLIFICATION FOR REF. ELECTRODE 7
IS 75.00
INPUT VOLTAGE FOR REF. ELECTRODE 0
0.0200
OUTPUT VOLTAGE FOR REF. ELECTRODE 0
IS .6000
AMPLIFICATION FOR REF. ELECTRODE 0
IS 30.00
DO YOU WISH TO RECALIBRATE ELECTRODES (Y OR N)?
n
TURN ON POTENTIOSTAT, MAKE CONNECTIONS; START CURRENT TYPE Y TO START THE EXPERIMENT
y
TIME = 14.0000
1 AMP. VOLTAGE = 3.0000 ACT VOLTAGE = .030
2 AMP. VOLTAGE = 3.0600 ACT VOLTAGE = .031
3 ........
TIME OF PICTURE 72.0000
ELAPSED TIME = 72.0000
OPEN CIRCUIT MEASUREMENTS
TIME = 157.0000
11 AMP. VOLTAGE = 2.9000 ACT. VOLTAGE = .029
12 AMP. VOLTAGE = 3.0600 ACT. VOLTAGE = .031
13 ........
etc.

The user has specified that seven reference electrodes are being used in the experiment. They have output signal amplifications equal to:

<table>
<thead>
<tr>
<th>reference electrode number</th>
<th>amplification</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100.00</td>
</tr>
<tr>
<td>2</td>
<td>101.00</td>
</tr>
<tr>
<td>3</td>
<td>100.50</td>
</tr>
<tr>
<td>4</td>
<td>100.00</td>
</tr>
<tr>
<td>5</td>
<td>102.00</td>
</tr>
<tr>
<td>6</td>
<td>100.00</td>
</tr>
<tr>
<td>7</td>
<td>75.00</td>
</tr>
<tr>
<td>0</td>
<td>30.00</td>
</tr>
</tbody>
</table>

Complete cell potential measurements will be taken every 10 seconds,
with a delay of 5 ticks (5/60ths of a second) between each individual electrode potential measurement. The cell will be put on open circuit every minute for a period of 1 second, during which a complete cell measurement will be made. Pictures will be taken every two minutes. The hardware electrical connections have been made such that A/D channel 58 handles the working versus reference potential signal, A/D channel 56 handles the working versus counter potential, and A/D channel 57 handles the counter versus reference potential.

B.1.4 POREST FLOWCHART

The main subroutine called by POREST is SINPOR. Following is a complete flowchart detailing SINPOR logic. The next section is listing of POREST and SINPOR.
Obtain electrode amplification

Do Index = 1, Numref + 1

Refout = Refout + 1

Index = Numref + 1

Refout = 0

N

Select electrode channel

Counter electrode

Index = Numref + 1

Buffer(2) = Chann

N

Buf(2) = Index - 1

Send MUX switch to hardware

II ← ISPPWM (Isocode, Chann, Isent, Buf(1), 10)

ERRCHK (III)

Read output voltage

Volout ← RLOGG(Rchann, I, 6, #)

Calculate amplification

Refamp(Index) = Volout/Volin

Index = Index + 1
CRT
Type output voltage, woout; and amplification, Refamp

Y
Index ≤ Numref + 1

N

CRT
Recalibrate (Y/N)?
Read Ans

Y
Ans = Y

N
Open data file
OPEN (unit 9, new file)

Start experiment

Get starting time
GETTIM (Begin)

J
Do J = 1 to Numref + 1
one complete measurement

Open-
Circuit measurement
Occleg = true

Y

N

Ref = working measurement?
I ≤ Numref

Store electrode #
Potdat = I

I ≤ Numref

Potdat = I + 10

Potdat = 0

I > Numref

J ≥ Numref

Potdat = 10

Store electrode channel in buffer
Buf(I) = 1 - 1
Counter (Electrode) → Buf(2) = Cchan

IE ← JSPPWM(Iscode,Chan,Isent,Buf(1),10)

Errchk(II)

Get time of measurement
GETTIM(Potdat)

Save elapsed time
Photo = Potdat

CRT

Type time, Potdat

Read electrode potential
Potdat ← RLOGG(Chan,1,8,0)

Adjust measurements for hardware amplification
Potdat = Potdat/Refamp

CRT

Type

Amplified voltage, Potdat*Refamp
Actual voltage, Potdat

Rest briefly between individual potential measurements
ISLEEP (0,0,0, Multis)

N ← numref + 1

Y

Increment data counter
Count = Count + 1
1. Reset first picture flag
   Segpic = 1.0

2. Open circuit elapsed time
   Ocslap = Photo = Ocsref

3. Open-circuit measurement;
   Ocslap < Ocsim
   Segoc ≠ 0

4. Set Flag
   Ocflag = true

5. Get open circuit time
   GETTIM (Ocref)

6. Ocsref = Ocref - Begin

7. Switch to potentiostat open circuit channel
   Buf(2) = 32

8. II = ISFPWV(Iascode,Mchan,Isent,Buf(1),10)

9. ERRCNP(II)

10. ISLEEP(0,0,1,0)

11. CNT
    Open circuit measurement

12. Restore current to cell
    Buf(2) = 0

13. II = ISFPWV(Iascode,Mchan,Isent,Buf(1),10)
ERRCHK(II)

Knoc = Knoc + 1

Reset flags
Recoc = 0
Ocflag = false

Look for CRT input End of Experiment

II = ITTNR

Character typed?
II > 0

Rest between each complete cell measurement
ISLEEP (0,Matim(1),Matim(2),Matim(3))

Data Buffer full? Kount ≥ 999?

Do I = 1,Kount

FILE
Write Format (1-3)

I = I + 1

Zero Kount Kount = 0

YES

NO
B.1.5 POREST PROGRAM LISTING

To run POREST type
R POREST
which runs:
PROGRAM POREST
CALL SINPOR
STOP
END
When program changes are made, the program must be relinked by
typing
@POREST
which runs:
R LINK
POREST.SAV,POREST=POREST/V/I//
SINPOR, HDCONC/V:1
//
$QBLK
1 SUBROUTINE SINPOR
C VERSION 47 05/16/83
COMMON/HNDLR/MCHAN
C DECLARATIONS
REAL*4 POTDAT(3,1000), REFAMP(10),RTIME,BEGTIM,PHDAT(100)
    REAL*4 PHELAP, PHOTO, PHREF, PHTIM, VOLOUT, VOLIN, PHMIN, PHSEC
    REAL*4 OCTDAT(100), OCMIN, OCSEC, OCTIM, OCELAP, OCREF
    INTEGER BUF(10), DBLK(4), MSTIM(3), RZCHAN, NZCHAN, RNCHAN, PCHAN
    INTEGER TIMLIM(2), CCHAN, REFOUT
LOGICAL OCFLAG
    DATA DBLK/3RHD,0,0,0/
    DATA ISCODE/0207/
    DATA ISCNT/4/
    DATA EOD/-1.0/
    DATA CCHAN/9/
C ZERO COUNTERS, OUTPUT BUFFER
1 DO 5 I=1,10
5 BUF(I)=0
    KNTOC=0
    OCREF=0.0
    BEGOC=0.0
    KNTPH=0
    PHREF=0.0
    KOUNT=0
    BEGPI=0.0
    REFOUT=0

-128-
OCFLAG=.FALSE.

C QUERIES--GET INFO FROM USER
TYPE *, 'SINPOR--VERSION 47'
TYPE *, 'HOW MANY REFERENCE ELECTRODES?'
READ(5,*)NUMREF

TYPE *, 'TIME BETWEEN EACH MEASUREMENT (MIN, SECS, TICKS)?'
READ(5,*)MSTIM(1),MSTIM(2),MSTIM(3)

TYPE *, 'TIME BETWEEN EACH MULTIPLEXER SWITCH (TICKS)?'
READ(5,*)MUXTIM

TYPE *, 'TIME TO HOLD CELL ON OPEN CIRCUIT (SECS)?'
READ(5,*)MOCTIM

TYPE *, 'REF. VS. WORKING POTENTIAL CHANNEL (R-)?'
READ(5,*)RZCHAN

TYPE *, 'WORKING V. COUNTER POTENTIAL CHANNEL (+-)?'
READ(5,*)NZCHAN

TYPE *, 'REF. VS. COUNTER POTENTIAL CHANNEL (R+)?'
READ(5,*)RNCHAN

TYPE *, 'HOW OFTEN DO YOU WANT PICTURES (MIN, SECS)?'
READ(5,*)PHMIN,PHSEC

C CONVERT THIS TO TICKS
PHTIM=(PHSEC*60.0)+(PHMIN*3600.0)

TYPE *, 'HOW OFTEN DO YOU WANT TO GO TO OPEN CIRCUIT (MIN, SEC)?'
READ(5,*)OCMIN,OCSEC

OCTIM=(OSEC*60.0)+(OCMIN*3600.0)

C OPEN COMMUNICATION WITH HD DRIVER -- GET THE CHANNEL
MCHAN=IGETC()
IF(MCHAN.LT.0) GOTO 2000
II=LOOKUP(MCHAN,DBLK)
IF(II.LT.0) GOTO 2010

C OBTAIN REF. ELECTRODE AMPLIFICATION
70 DO 80 IDX=1,NUMREF+1

REFOUT=REFOUT+1
IF(IDX.EQ.NUMREF+1) REFOUT=0

TYPE *, 'INPUT VOLTAGE FOR REF. ELECTRODE ', REFOUT
READ(5,*)VOLIN

C SWITCH TO PROPER CHANNELS 1-10 --> 0-9
C SWITCH FOR REFERENCE-WORKING CHANNELS
BUF(2)=IDX-1
SWITCH FOR COUNTER-WORKING CHANNEL
BUF(2)=IDX-1

C SWITCH FOR COUNTER-WORKING CHANNEL
IF (IDEX.EQ.NUMREF+1) BUF(2)=CHAN
C DO MUX SWITCH
II=ISPFNW(ISCODE,MCHAN,ISCNT,BUF(1),10)
CALL ERRCHK(II)
C READ OUTPUT VOLTAGE
VOLOUT=RLOGG(RZCHAN,1,16,0)
C CALCULATE AMPLIFICATION
REFAMP(IDEX)=VOLOUT/VOLIN
TYPE *,'OUTPUT VOLTAGE FOR REF. ELECTRODE ', REFOUT
TYPE *,'IS', VOLOUT
TYPE *,'AMPLIFICATION FOR REF.ELECTRODE', REFOUT
TYPE *,'IS', REFAMP(IDEX)
80 CONTINUE
TYPE *,'DO YOU WISH TO RECALIBRATE ELECTRODES (Y OR N)??'
READ(5,1004) ANS
FORMAT(A1)
IF(ANS.EQ.'Y') GO TO 70
C OPEN DATA FILE
OPEN(UNIT=9,NAME='DL1:PORDAT.FMT',ACCESS='SEQUENTIAL',*
INITIALSIZE=400,TYPE='NEW')
C START EXPERIMENT
TYPE *,'TURN ON POTENTIOSTAT, MAKE CONNECTIONS, START CURRENT'
TYPE *,'TYPE Y TO START THE EXPERIMENT'
READ(5,1003) IDUM
1003 FORMAT(A1)
C GET TIME OF EXPERIMENT START
CALL GETTIM(BEGTIM)
C DATA TAKING ROUTINE
C THIS IS THE MAIN CONTROLLING ROUTINE. THE EXPERIMENT IS
C CONTROLLED FROM HERE AND DATA IS TAKEN AND RECORDED INTO A
C SEQUENTIAL FILE. THE FORM OF THE DATA FILE IS:
C FIELD 1 FIELD 2 FIELD 3
C REF.ELEC.NUM. ELAPSED TIME POTENTIAL
C START MEASUREMENT
C MEASUREMENT CONSISTS OF SENDING A SIGNAL TO THE MULTIPLEXER TO
C SWITCH TO A NEW REF. ELECTRODE. THE A/D LINE IS THEN READ TO
C GET THE MEASURED ZINC-REFERENCE POTENTIAL. BEFORE THE MEASUREMENT
C IS TAKEN, THE ELAPSED TIME IS TAKE.
C AT APPROPRIATE TIMES, A PICTURE CAN BE TAKEN VIA THE PHO
ROUTINE
C
C GET THE CHANNEL
100 DO 999 I=1,NUMREF+1
C PUT ELECTRODE NUMBER OR DISTANCE INTO BUFFER
C IF O.C. MEASUREMENT, BRANCH ACCORDINGLY
IF(OCFLAG) GO TO 105
IF(I.LE.NUMREF.) POTDAT(1,I+KOUNT)
IF(I.LE.NUMREF) POTDAT(1,I+KOUNT)=FLOAT(I)
C SET REF. ELECTRODE NUMBER FOR WORKING - COUNTER ELECTRODE
DATA = 0
IF(I.GT.NUMREF) POTDAT(1,I+KOUNT)=0.0
GO TO 108
C FOR OPEN CIRCUIT DATA ADD 10 TO THE ELEC. NUM. -- CODING
PURPOSE
105 IF(I.LE.NUMREF) POTDAT(1,I+KOUNT)=FLOAT(I)+10.0
IF(I.GT.NUMREF) POTDAT(1,I+KOUNT)=10.0
C GET CORRECT CHANNEL FOR MUX 1-10 --> 0-9
C SWITCH FOR WORKING-REFERENCE CHANNEL
108 BUF(2)=I-1
C IF CALLED FOR, SWITCH FOR WORKING-COUNTER CHANNEL
IF(I.EQ.NUMREF+1) BUF(2)=CCHAN
C DO SWITCH
II=ISPFNW(ISCODE,MCHAN,ISCNT,BUF(1),10)
CALL ERRCHK(II)
C GET TIME
110 CALL GETTIM(POTDAT(2,I+KOUNT))
POTDAT(2,I+KOUNT)=POTDAT(2,I+KOUNT)-BEGTIM
PHOTO=POTDAT(2,I+KOUNT)
TYPE *, 'TIME =', POTDAT(2,I+KOUNT)
C PULSE A/D LINE TO GET POTENTIAL
POTDAT(3,I+KOUNT)=RLOGG(RZCHAN,1,16,0)
C ADJUST VOLTAGE MEASUREMENTS FOR POTENTIOSTAT INTERFACE AMP.
POTDAT(3,I+KOUNT)=POTDAT(3,I+KOUNT)/REFAMP(I)
TYPE *, IFIX(POTDAT(1,I+KOUNT)),'AMP. VOLTAGE = ',
$POTDAT(3,I+KOUNT)*REFAMP(I),' ACT. VOLTAGE = '
C SLEEP UNTIL NEXT MEASUREMENT
CALL ISLEEP(0,0,OMUXTIM
999 CONTINUE
C INCREMENT COUNTER
KOUNT=KOUNT+NUMREF+1
C
C CHECK TO DETERMINE IF WE ARE TAKING AN OPEN CIRCUIT MEASUREMENT, AND
C BRANCH ACCORDINGLY
IF(OCFLAG) GO TO 270
C IS IT TIME TO TAKE A PICTURE
PHELAP=PHOTO-PHREF
IF(PHELAP.LT.PHTIM.AND.BEGPIC.NE.0.0) GO TO 210
C IF YES, CALL PHOTO -- WHICH WILL PULSE MUX BIT 4 TO ON AND
C GENERATE THE PICTURE
C FIRST, RESET THE REFERENCE TIME FOR THE NEXT PICTURE
CALL GETTIM(PHREF)
PHREF=PHREF-BEGTIM
C TAKE PICTURE
BUF(2)=16
II=ISPFNW(ISCODE,MCHAN,ISCNT,BUF(1),10)
CALL ERRCHK(II)
CALL ISLEEP(0,0,0,10)
BUF(2)=0
II=ISPFNW(ISCODE,MCHAN,ISCNT,BUF(1),10)
CALL ERRCHK(II)
INCREMENT THE PHOTO COUNTER AND STORE THE TIME IN PHDAT
KNTPH=KNTPH+1
PHDAT(KNTPH)=PHREF
TYPE*, 'TIME OF PICTURE = ', PHREF
TYPE*, 'ELAPSED TIME = ', PHELAP
C RESET FIRST PICTURE COUNTER
BEGPIC=1.0
C IS IT TIME TO TAKE AN OPEN CIRCUIT MEASUREMENT?
210 OCELAP=PHOTO-OCREF
IF(OCELAP.LT.OCTIM.AND.BEGOC.NE.0.0) GO TO 310
C SET UP FOR OPEN CIRCUIT MEASUREMENT
C PROCEDURE WILL BE TO PUT CELL ON OPEN CIRCUIT, GO BACK TO
C DATA TAKING SECTION -- TAKE MEASUREMENTS, PLACE CURRENT
BACK TO CELL
PUT ON O.C. BY SWITCHING POTENTIOSTAT FROM CHANNEL A TO B
C THIS IS ACCOMPLISHED BY PULSING THE SIXTH MULTIPLEXER BIT
C SET O.C. FLAG
OCFLAG=.TRUE.
C SET REFERENCE TIME FOR NEXT OPEN CIRCUIT MEASUREMENT
CALL GETTIM(OCREF)
OCREF-OCREF-BEGTIM
INITIATE POTENTIOSTAT CHANNEL SWITCHING TO OPEN CIRCUIT

-132-
BUF(2) = 32
II = ISPFNW(ISCODE, MCHAN, ISCNT, BUF(1), 10)
CALL ERRCHK(II)

C WAIT AND TAKE MEASUREMENTS -- THEN RETURN
CALL ISLEEP(0, 0, MOCTIM, 0)
TYPE *,'OPEN CIRCUIT MEASUREMENTS'
GO TO 100

C ON RETURN, RESTORE CURRENT AND UPDATE COUNTERS
270 BUF(2) = 0
II = ISPFNW(ISCODE, MCHAN, ISCNT, BUF(1), 10)
CALL ERRCHK(II)

C INCREMENT O.C. COUNTER AND STORE MOST RECENT O.C. TIME
KNTOC = KNTOC + 1
OCDAT(KNTOC) = OCREF

C RESET FLAGS
BEGOC = 1.0
OCFLAG = .FALSE.

C CHECK TO SEE IF IT IS THE END OF THE EXPERIMENT
C THE USER SIGNALS THE END OF EXPERIMENT BY TYPING ANY CHARACTER
C HAS CHARACTER TO STOP THE EXPT. BEEN PUT IN?
C SET BIT 6 OF JOB STATUS WORD FOR XM BEFORE CHECKING TERMINAL
310 CALL IPOKE("44,"100.OR.IPEEK("44))
II = ITINR()
IF (II.GT.0) GOTO 500
C IF NO CHARACTER, CONTINUE EXPERIMENT
C SLEEP BETWEEN MEASUREMENT
CALL ISLEEP(0, MSTIM(1), MSTIM(2), MSTIM(3))
C IS DATA ARRAY FULL?
IF (KOUNT.LT.990) GOTO 400
C WRITE TO DATA FILE
DO 350 I = 1, KOUNT
WRITE(9,*) POTDAT(1, I), POTDAT(2, I), PODAT(3, I)
350 CONTINUE
C ZERO COUNTER
KOUNT = 0
400 GOTO 100
C
C END OF EXPT. WRITE AND CLOSE DATA FILE
500 DO 550 I = 1, KOUNT
WRITE(9,*) POTDAT(1, I), POTDAT(2, I), POTDAT(3, I)
550 CONTINUE
C WRITE END-OF-DATA MARKER (EOD)
WRITE(9,*), EOD
C WRITE PHOTO TIMES
DO 600 J=1,KNTPH
WRITE(9,*), PHDAT(J)
600 CONTINUE
WRITE(9,*), EOD
CLOSE(UNIT=9,DISPOSE='SAVE')
TYPE *, 'END OF EXPERIMENT, TURN OFF CURRENT'
C SET MULTIPLEXER SWITCH TO 0
BUF(2)=0
II=ISPFNW(ISCODE,MCHAN,ISCNT,BUF(1),10)
CALL ERRCHK(II)
C END
GOTO 9999
C ERROR HANDLING ROUTINE
2000 TYPE *, 'CANNOT ALLOCATE CHANNEL'
GOTO 9999
2010 TYPE *, 'BAD LOOKUP'
GOTO 9999
9999 RETURN
END
C C SUBROUTINE TO GET THE ACTUAL TIME
SUBROUTINE GETTIM(RTIME)
CALL GTIM(JTOP)
CALL JJCVT(JTOP)
N=IAJFLT(JTOP,RTIME)
IF(N.EQ.-2) STOP 'OVERFLOW IN INTEGER*4 - REAL CONVERSION'
RETURN
END
C C SUBROUTINE TO CHECK ERRORS AFTER A CALL TO THE DRIVER WHILE
C SWITCHING MULTIPLEXER OF TAKING PICTURES
SUBROUTINE ERRCHK(II)
C IF ANY OF THE BELOW ARE TRUE, THERE IS AN ERROR
IF(II.EQ.-2) STOP 'NON-EXISTENT FUNCTION CODE, ISCODE'
IF(II.EQ.-1) STOP 'WRONG IWCNT FOR FUNCTION'
IF(II.EQ.2) STOP 'REFERENCE CHANNEL OUT OF RANGE (0-32)'
RETURN
B.2 DATA REDUCTION - PMSGST, MMSGST

The two programs PMSGST and MMSGST reduce potential data for single pore experiments and format the data in a manner suitable for plotting. Both programs are designed to give the user the necessary flexibility to obtain meaningful data from the runs. Program PMSGST prepares potential versus time data for a single reference electrode versus the working electrode. Program MMSGST prepares potential versus time data for single or multiple reference electrodes versus the working electrode. In addition, MMSGST can prepare potential versus distance data at any time during the experiment.

Each program allows the user to omit electronic open circuit and subtract electrode rest potentials from the readings. Electronic open circuit readings can occur if the contact between the reference electrode and computer is physically interrupted by chemical or other means. In addition, open circuit readings occur if the reference electrode signal amplifications are set too high for the range of potentials encountered during the experiment. The output signals will exceed five volts; because the A/D card can read a maximum five volt signal, the signal will be interpreted as five volts. Thus, data are lost. The user should designate the open circuit voltage as equal to five volts divided by the specified reference electrode signal amplification. Signals equal to this value are assumed to reflect meaningless open circuit data.

Reference shorts occur when a reference electrode comes in physical contact with the working electrode. The differential potential from a shorted working and reference electrode pair will be near zero. Thus, signals under the specified reference short voltage will be assumed to be shorted and consequently omitted.

Finally, the user can specify that the electrode rest potential be subtracted from the potential data. Usually, the rest potentials are read just prior to cell current initiation. The user can optionally input the rest potentials by hand. Subtracting rest potentials will result in potential readings which reflect the total overpotential comprised of ohmic (with current applied), concentration, kinetic and
surface effect contributions.

The user can specify the starting and ending experiment times in addition to the time at which data should be plotted. The experiment start time is subtracted from each time measurement to give the elapsed time. Data recorded prior to the requested "start plot" time and after the experiment end time will not be included in the plot. The selected, adjusted potential versus time and potential versus distance data are stored in DL1:PGRAF.FMT.

Both routines can generate plots with only the ohmic-free potentials (indicated in the data file by electrode numbers 10 and above). The resulting formatted data are stored in DL1:POCDAT.FMT. In addition, the interpolated ohmic-free potential readings can be subtracted from the ohmic-contribution-containing readings to obtain an estimate of the ohmic losses. These data are stored in DL1:OGRAP.FMT.

B.2.1 Program PMSGST

B.2.1.1 Description

Program PMSGST generates working electrode minus single reference electrode potential versus time data bases suitable for plotting by program PPLTST (described in the next section). In addition, the program can generate a working minus counter electrode potential data base suitable for plotting by PPLTST. To obtain the latter, the user inputs a '0' for the reference electrode number at the beginning of the program. To obtain a working minus reference electrode plot, the user inputs the actual reference electrode number (1-7).

Additionally, PMSGST will generate a data file containing a list of the picture numbers with the corresponding elapsed time (in minutes). The data are stored in DL1:PORPIC.FMT.
The main subroutine called by PMSGST is PORMSG. Following is a listing of PMSGST and PORMSG.

To run PMSGST type
R PMSGST which runs:
PROGRAM PMSGST
CALL PORMSG
STOP

When program changes are made, the program must be relinked by typing:
@POREST which runs:
R LINK
POREST.SAV,PMSGST=PMSGST/V/I//
PORMSG/V:1

$QBK 1 SUBROUTINE PORMSG C VERSION 28 04/24/82 C

This program massages the data from POREST (SUBROUTINE SINPOR). The data will be handled so that a single reference electrode's voltage-time data is placed into a new file (DL1:PGRAF.PMT). This file can then be graphed on the plotter by PPLTST (SUBROUTINE PLTST) C

DECLARATIONS
REAL*4 TIMDAT(3000),VOLDAT(3000)
REAL*4 TIMDUM(500),VOLDUM(500)
REAL*4 OCTDAT(100),OCVDAT(100)
REAL*4 POSNUM,TIME,VOLTS,REFNUM,BEGTIM,ENDTIM,STTIM,RESTIM
REAL*4 RESPOET(10),VOPEN,SHORTV
REAL*4 PICTIM(100)
REAL*4 OTIME(2),OVLTS(2),NTIME,INTV,NVOLTS C

MAIN ROUTINE
TYPE *, 'PORMSG -- VERSION 28'
TYPE *, 'REF. ELECTRODE POSITION NUMBER TO BE PLOTTED?'
READ(5,*) REFNUM
TYPE *, 'WHAT IS THE OPEN CIRCUIT VOLTAGE FOR THIS RUN?'
READ(5,*) VOPEN
TYPE *, 'DO YOU WANT REFERENCE SHORTS FILTERED?'
READ(5,1001) SHORYN
IF(SHORYN.EQ.'N') GO TO 11
TYPE *, 'INPUT SHORT POTENTIAL (VOLTS)'
READ(5,*) SHORTV
11 TYPE *, 'SHOULD REST POTENTIALS BE SUBTRACTED FROM POTENTIALS?'
READ(5,1001) RESTYN
IF(RESTYN.EQ.'N') GO TO 15
TYPE *, 'DO YOU WANT TO INPUT THE REST POTENTIALS?'
READ(5,1001) RESTIN
IF(RESTIN.EQ.'Y') GO TO 15
TYPE *, 'TIME AT WHICH REST POTENTIALS ARE TO BE READ (SECS)?'
READ(5,*) RESTIM
TYPE *, 'DO YOU WANT TO STORE PICTURE DATA? (Y OR N)?'
READ(5,1001) PICTYN 1001 FORMAT(A1)
TYPE *, 'DO YOU WANT TO STORE OPEN CIRCUIT DATA (Y OR N)?'
READ(5,1001) OCYN
TYPE *, 'DO YOU WANT TO CREATE THE DATA FILE WHICH SUBTRACTS'
TYPE *, 'O.C. DATA FROM THE MEASURED DATA? (Y OR N)?'
READ(5,1001) OFILYN
TYPE *, 'STARTING TIME OF EXPERIMENT (SECONDS)?'
READ(5,*) STTIM
TYPE *, 'ENDING TIME OF EXPERIMENT (SECONDS)?'
READ(5,*) ENDTIM
TYPE *, 'TIME AT WHICH TO START PLOTTING DATA?'
READ(5,*) BEGTIM
TYPE *, 'NUMBER OF REFERENCE ELECTRODES?'
READ(5,*) NUMELE
OPEN(UNIT=9, NAME='DL1: PORDAT.FMT', ACCESS='SEQUENTIAL',
*TYPE='OLD')
NUMPT=O
NUMPIC=2
KOUNT=O
NUMOC=O
DO 25 I=1,10
RESPOT(I)=0.0
25 CONTINUE
C C READ AND FILTER DATA
C C GET REST POTENTIALS IF DESIRED
IF(RESTYN.EQ.'N') GO TO 45
IF(RESTIN.EQ.'Y') GO TO 37
DO 35 MIND=1,10000
READ(9,*) POSUM, TIME, VOLTS
IF(TIME/60.0.LT.RESTIM) GO TO 35
IF(POSNUM.NE.1.0) STOP 'INCORRECT REST TIME'
RESPOT(1)=VOLTS
DO 30 J=1,NUMELE
READ(9,*) POSNUM, TIME, VOLTS
RESPOT(J+1)=VOLTS
30 CONTINUE
C C PROCESSING
REWIND 9
GO TO 45
C C REWIND DATA FILE FOR PROCESSING
GO TO 45
C READ REST POTENTIALS
DO 40 J=1,8
TYPE *, 'INPUT REST POTENTIAL FOR ELECTRODE', J
READ(5,*) RESPOT(J)
40 CONTINUE
C C IF REFNUM EQUALS ZERO THEN WE WANT TO FILTER WORKING MINUS C COUNTER ELECTRODE

POTENTIALS -- SO ACT ACCORDINGLY

IF(REFNUM.EQ.0.0) GO TO 115

INDRES=INT(REFNUM)

DO 100 I=1,15000

READ(9,*) POSNUM,TIME,VOLTS C

FILTER DATA

IF(TIME/60.LT.BEGTIM) GO TO 80

IF(TIME/60.GE.ENDTIM) GO TO 80

IF(POSNUM.NE.REFNUM) GO TO 50 C

READINGS

CHECK FOR BAD CONNECTION

IF(VOLTS.LE.-VOPEN.OR.VOLTS.GE.VOPEN) GO TO 80 C

REF. ELECTRODE SHORTS

IF(ABS(VOLTS).LE.SHORTV.AND.SHORYN.EQ.'Y') GO TO 80 C

DATA IN ARRAY -- CONVERT TICKS TO MINUTES

NUMPT=NUMPT+1

TIMDAT(NUMPT)=(TIME/3600.0)-(STTIM/60.0)

VOLDAT(NUMPT)=VOLTS+RESPOT(INDRES) C

CHECK FOR OPEN CIRCUIT DATA

OPEN CIRCUIT DATA IS IDENTIFIED BY THE FACT THAT 10 IS ADDED C

to each of the ref. elec. numbers, i.e. ref. elec. 11 indicates C

that the time and volt data is open circuit data for ref. elec. 1 C

50

IF(POSNUM.NE.REFNUM+10.0.OR.OCYN.NE.'Y') GO TO 80 C

CHECK FOR BAD CONNECTION DATA

IF(VOLTS.LE.-VOPEN.OR.VOLTS.GE.VOPEN) GO TO 80 C

REF. ELECTRODE SHORTS

IF(ABS(VOLTS).LE.SHORTV.AND.SHORYN.EQ.'Y') GO TO 80 C

MEMENT COUNTER

NUMOC=NUMOC+1 C

STORE DATA

OCTDAT(NUMOC)=(TIME/3600.0)-(STTIM/60.0)

OCVDAT(NUMOC)=VOLTS+RESPOT(INDRES) C

CHECK FOR END OF FILE

80 IF(POSNUM.EQ.-1.0) GO TO 140

CONTINUE C

FILTER WORKING MINUS COUNTER ELECTRODE DATA

115 INDRES=8

DO 130 I=1,15000

READ(9,*) POSNUM,TIME,VOLTS C

FILTER DATA

IF(TIME/60.LT.BEGTIM) GO TO 120

IF(TIME/60.GT.ENDTIM) GO TO 120

IF(POSNUM.NE.REFNUM) GO TO 117 C

CHECK FOR BAD CONNECTION DATA

IF(VOLTS.LE.-VOPEN.OR.VOLTS.GE.VOPEN) GO TO 120 C

STORE DATA

IN ARRAY

NUMPT=NUMPT+1

TIMDAT(NUMPT)=(TIME/3600.0)-(STTIM/60.0)

VOLDAT(NUMPT)=VOLTS+RESPOT(INDRES) C

CHECK FOR OPEN CIRCUIT DATA

117 IF(POSNUM.NE.REFNUM+10.0.OR.OCYN.NE.'Y') GO TO 120 C

CHECK FOR BAD CONNECTION DATA

IF(VOLTS.LE.-VOPEN.OR.VOLTS.GE.VOPEN) GO TO 120 C

INCREMENT COUNTER AND STORE DATA
NUMOC=NUMOC+1
OCTDAT(NUMOC)=TIME/3600.0-(STTIM/60.0)
OCVDAT(NUMOC)=-VOLTS+RESPOT(INDRES) C CHECK FOR END OF FILE
120 IF(POSNUM.EQ.-1.0) GO TO 140 130 CONTINUE C FINALLY, IF
DESIRED GENERATE A PICTURE TIME FILE 140 IF(NUMPT.LE.500) GO TO 149 C
REDUCE DATA TO 500 POINTS OR LESS FOR PLOTTING PURPOSES
149 IRES=(NUMPT/500)+1 C SPOOL EVERY IRES POINT INTO DUMMY

BUFFER
DO 145 I=1,NUMPT IF(REMAINDER IS ZERO, STORE POINT
IF(MOD(I,IRES).NE.0) GO TO 145
145 KOUNT=KOUNT+1
TIMDUM(KOUNT)=TIMDAT(I)
VOLDUM(KOUNT)=VOLDAT(I) 145 CONTINUE C REFILL DATA BUFFER
NUMPT=KOUNT
DO 147 I=1,NUMPT
TIMDAT(I)=TIMDUM(I)
VOLDAT(I)=VOLDUM(I) 147 CONTINUE C
149 IF(PICTYN.EQ.'N') GO TO 200 C VARIABLE TIME AND VOLTS CONTAIN THE FIRST TWO PICTURES
PICTIM(1)=(TIME/3600.0)-(STTIM/60.0)
PICTIM(2)=(VOLTS/3600.0)-(STTIM/60.0)
DO 150 I=1,100
READ(9,*) TIME C CHECK FOR END OF FILE
IF(TIME.EQ.-1.0) GO TO 200 C INCREMENT PICTURE COUNTER
150 NUMPIC=NUMPIC+1 C CONVERT TO MINUTES
PICTIM(NUMPIC)=(TIME/3600.0)-(STTIM/60.0) 150 CONTINUE C
CLOSE OLD FILE 200 CLOSE(UNIT=9) C C WRITE DATA TO GRAPHING FILE
C OPEN NEW FILE
TYPE *, 'WRITING TO PGRAPH'
OPEN(UNIT=9,NAME='DL1:PGRAPH.FMT',ACCESS='SEQUENTIAL',
*INITIALSIZE=200,TYPE='NEW') C WRITE TO FILE
WRITE(9,*) NUMPT
DO 300 I=1,NUMPT
WRITE(9,*) TIMDAT(I),VOLDAT(I)
300 CONTINUE C CLOSE FILE
WRITE TO PICTURE FILE IF DESIRED
IF(PICTYN.EQ.'N') GO TO 500
TYPE *, 'WRITING TO PORPIC'
OPEN(UNIT=9,NAME='DL1:PORPIC.FMT',ACCESS='SEQUENTIAL',
*INITIALSIZE=100,TYPE='NEW') C WRITE PICTURE NUMBER AND TIME
TO FILE
DO 400 I=1,NUMPIC
WRITE(9,*) I,PICTIM(I) 400 CONTINUE C CLOSE FILE
CLOSE(UNIT=9) C WRITE TO OPEN CIRCUIT DATA FILE IF DESIRED
500 IF(OCYN.EQ.'N') GO TO 999
TYPE *, 'WRITING TO POCDAT'
OPEN(UNIT=9,NAME='DL1:POCDAT.FMT',ACCESS='SEQUENTIAL', *INITIALSIZE=100,TYPE='NEW') C WRITE NUMBER OF DATA POINTS TO FILE
WRITE(9,*) NUMOC C WRITE DATA
DO 600 I=1,NUMOC
WRITE(9,*) OCTDAT(I),OCVDAT(I) 600 CONTINUE C CLOSE FILE
CLOSE(UNIT=9) 999 IF(OFILYN.EQ.'N') GO TO 999 C OBTAIN IR CONTRIBUTION FROM MEASURED POTENTIAL READINGS C BY SUBTRACTING THE CURRENT READINGS FROM O.C. READINGS IN C POCDAT.FMT FROM MEASURED DATA IN PGRAPH.FMT C RESULTS ARE STORED IN OGRAPH.FMT C LINEAR INTERPOLATION IS USED TO GET PROPER O.C. READINGS C
KNTOC=2
NUMDAT=0 C OPEN FILES
OPEN(UNIT=9,NAME='DL1:PGRAPH.FMT',ACCESS='SEQUENTIAL', $TYPE='OLD')
OPEN(UNIT=8,NAME='DL1:POCDAT.FMT',ACCESS='SEQUENTIAL', $TYPE='OLD') CREWIND FILES
REWIND 8
REWIND 9 C C GET NUMBER OF POINTS
READ(8,*) NUMOC
READ(9,*) NUMPT C READ FIRST TWO O.C. POINTS
READ(8,*) OTIME(1),OVOLTS(1)
READ(8,*) OTIME(2),OVOLTS(2) C READ AND INTERPOLATE
DO 2000 I=1,NUMPT
READ MEASURED VOLTAGE
READ(9,*) TIME,VOLTS
CHECK IF INSIDE INTERPOLATION RANGE
IF(TIME.LT.OTIME(1)) GO TO 2000
IF(TIME.LT.OTIME(2)) GO TO 1550 C READ NEXT O.C. VOLTAGE
IF(KNTOC+1.GT.NUMOC) GO TO 3000
KNTOC=KNTOC+1
OTIME(1)=OTIME(2)
OVOLTS(1)=OVOLTS(2)
READ(8,*) OTIME(2),OVOLTS(2) C DO LINEAR INTERPOLATION 1550
IF(TIME.EQ.OTIME(1)) GO TO 1650
NTIME=(OTIME(2)-OTIME(1))/(TIME-OTIME(1))
INTV=OVOLTS(1)+((OVOLTS(2)-OVOLTS(1))/NTIME)
GO TO 1700 1650 INTV=OVOLTS(1) 1700 NVOLTS=VOLTS-INTV C STORE IN BUFFER
NUMDAT=NUMDAT+1
TIMDAT(NUMDAT)=TIME
VOLDAT(NUMDAT)=NVOLTS 2000 CONTINUE C C CLOSE AND WRITE TO FILE 3000 C CLOSE(UNIT=8)
CLOSE(UNIT=9)
OPEN(UNIT=9,NAME='DL1:OGRAPH.FMT',ACCESS='SEQUENTIAL',
B.2.2 Program MMSGST

B.2.2.1 Description

Program MMSGST generates working electrode minus single or multiple reference electrode potential versus time data bases suitable for plotting by program MPLTST (described in the next section). The user can specify any combination of reference electrode to plot. In addition, the user can request a potential versus distance into pore plot at a specified time during the experiment. All rest potential, open circuit, experiment starting times, etc. will be utilized for both plot types.

To specify a potential versus distance plot, the user responds to the "potential versus time" query with 'N'. The user must specify the reference electrode numbers to be included in the plot along with the corresponding pore locations of the reference electrodes (expressed in millimeters into the pore).

B.2.2.2 MMSGST Program Listing

The main subroutine called by MMSGST is MULMSC. Following is a listing of MMSGST and MULMSG.

To run MMSGST type

which will run:

PROGRAM MMSGST
CALL MULMSG
STOP
END

When program changes are made, the program must be relinked by typing @MMSGST
which runs:

```c
R LINK
MMSGST.SAV,MMSGST=MMSGST/V/I//
MULMSG/V:1
//
$QBLK
1
SUBROUTINE MULMSG
C
VERSION 21 05/01/82
C
THIS PROGRAM MASSAGES THE DATA FROM POREST (SUBROUTINE SINPOR).
C
THE DATA WILL BE HANDLED SO THAT A ONE OR MORE ELECTRODE'S
C
VOLTAGE-TIME DATA IS PLACED INTO A NEW FILE
(DL1:PGRAPH.FMT)
C
THIS FILE CAN THEN BE GRAPHED ON THE PLOTTER BY MPLTST
C
(SUBROUTINE PORPLT)
C
C
DECLARATIONS
C
REAL*4 TIMDAT(7,500),VOLDAT(7,500)
REAL*4 OCTDAT(7,100),OCVDAT(7,100)
REAL*4 POSNUM,TIME,VOLLTS<REFNUM(10),BEGTIM(10),ENDTIM(10)
REAL*4 STTIM(10),VOPEN(10),SHORTV
REAL*4 OTIME(2),OVOLTS(2),NTIME,INTV,NVOLTS,RESTIM,PORDIS
REAL*4 RESPOT(10),REFDIS(10),CURTIM(10)
INTEGER NUMPT(10),NUMOC(10),NUMDAT(10)
DATA EOD/-1.0/
DATA PORDIS/1.5748
C
C
MAIN ROUTINE
C
TYPE *, 'MULMSG -- VERSION 21'
TYPE *, 'PLOT OF POTENTIAL VS. TIME?'
READ(5,1001) REGYN
TYPE *, 'NUMBER OF CURVES TO PLOT?'
READ(5,* ) NUMELE
TYPE *, 'DO YOU WANT REFERENCE SHORTS FILTERED?'
READ(5,1001) SHORYN
IF(SHORYN.EQ.'N') GO TO 11
TYPE *, 'INPUT SHORT POTENTIAL'
READ(5,* ) SHORTV
11 TYPE *, 'SHOULD REST POTENTIALS BE SUBTRACTED FROM POTENTIAL DATA?'
READ(5,1001) RESTYN
IF(RESTYN.EQ.'N') GO TO 15
TYPE *, 'DO YOU WANT TO INPUT REST POTENTIALS?'
READ(5,1001) RESTIN
```
IF(RESTIN.EQ.'Y') GO TO 15
TYPE *, 'TIME AT WHICH REST POTENTIALS SHOULD BE TAKEN (SEC)'
READ(5,*) RESTIM
15 IF(REGYN.EQ.'N') GO TO 35
DO 30 I=1,NUMELE
TYPE *, 'REF. ELECTRODE POSITION NUMBER TO BE PLOTTED?'
READ(5,*) REFNUM(I)
TYPE *, 'WHAT IS THE OPEN CIRCUIT VOLTAGE FOR THIS ELECTRODE?'
READ(5,*) VOPEN(I)
TYPE *, 'STARTING TIME OF EXPERIMENT (SECONDS) FOR REF. ELEC. '
$REFNUM(I)
READ(5,*) STTIM(I)
TYPE *, 'ENDING TIME OF EXPERIMENT (SECONDS) FOR REF. ELEC. '
$REFNUM(I)
READ(5,*) ENDTIM(I)
TYPE *, 'TIME AT WHICH TO START PLOTTING DATA?'
READ(5,*) BEGTIM(I)
30 CONTINUE
GO TO 39
35 NUMCUR=NUMELE
TYPE *, 'NUMBER OF REFERENCE ELECTRODES TO PLOT?'
READ(5,*) NUMELE
TYPE *, 'STARTING TIME OF EXPERIMENT (SECONDS)?'
READ(5,*) EXPST
DO 36 I=1,NUMCUR
TYPE *, 'TIME (SECS) AT WHICH TO START CURVE',I,' PLOTTING?'
READ(5,*) CURTIM(I)
36 CONTINUE
DO 37 I=1,NUMELE
TYPE *, 'REFERENCE ELECTRODE POSITION NUMBER TO BE PLOTTED?'
READ(5,*) REFNUM(I)
C
GET DISTANCES
TYPE *, 'DISTANCE INTO PORE (MM) FOR REF. ELEC.', I , 'REFNUM(I)
READ(5,*) REFNUM(I)
C
GET DISTANCES
TYPE *, 'DISTANCE INTO PORE (MM) FOR REF. ELEC.', REFNUM(I)
READ(5,*) REFDIS(REFNUM(I))
37 CONTINUE
39 TYPE *, 'DO YOU WANT TO STORE OPEN CIRCUIT DATA (Y OR N),'
READ(5,1001) OCYN
FORMAT(A1)

1001 TYPE *, 'DO YOU WANT TO CREATE THE DATA FILE WHICH SUB-
TRACTS'

1002 TYPE *, 'O.C. DATA FROM MEASURED DATA? (Y OR N)'
READ(5,1001) OFILYN
OPEN(UNIT=9,NAME='DL1:POPDAT.FMT',ACCESS='SEQUENTIAL',
*TYPE='OLD')
DO 40 I=1,NUMELE
NUMDAT(I)=0
NUMOC(I)=0
NUMPT(I)=0
RESPOT(I)=0.0
40 CONTINUE
C
C GET REST POTENTIALS IF DESIRED
IF(RESTYN.EQ.'N') GO TO 60
IF(RESTIN.EQ.'Y') GO TO 46
DO 45 MIND=1,10000
READ(9,*), POSNUM, TIME, VOLTS
C SEARCH
IF(TIME/60.0.LT.RESTIM) GO TO 45
IF(POSNUM.NE.1.0) STOP 'INCORRECT REST TIME'
RESPOT(1)=VOLTS
READ NEXT SERIES OF POTENTIALS
DO 43 J=1,7
READ(9,*), POSNUM, TIME, VOLTS
RESPOT(J+1)=VOLTS
43 CONTINUE
C
C REWIND DATA FILE
REWIND 9
GO TO 60
45 CONTINUE
C
C READ REST POTENTIALS
46 DO 47 L=1,7
TYPE *, 'INPUT REST POTENTIAL FOR ELECTRODE',L
READ(5,*), RESPOT(L)
47 CONTINUE
C
C IF(REGIN.EQ.'N') GO TO 6000
C
READ AND FILTER DATA
DO 100 I=1,15000
READ(9,*), POSNUM, TIME, VOLTS

-145-
DO 80 J=1,NUMELE
C FILTER DATA
IF(TIME/60.GE.ENDTIM(J)) GO TO 80
IF(TIME/60.GE.ENDTIM(J)) GO TO 80
IF(POSNUM.NE.REFNUM(J)) GO TO 50
C CHECK FOR BAD CONNECTION READINGS
IF(VOLTS.LE.-VOPEN(J).OR.VOLTS.GE.VOPEN(J)) GO TO 80
C CHECK FOR REF. ELECTRODE SHORTS
IF(ABS(VOLTS).LE.SHORTV.AND.SHORYN.EQ.'Y') GO TO 80
C STORE DATA IN ARRAY --CONVERT TICKS TO MINUTES
NUMPT(J)=NUMPT(J)+1
TIMDAT(J,NUMPT(J))=(TIME/3600.0)-(STTIM(J)/60.0)
VOLDAT(J,NUMPT(J))=VOLTS+RESPOT(REFNUM(J))
C CHECK FOR END OF REF. ELEC. DATA
C CHECK FOR OPEN CIRCUIT READINGS, IF DESIRED
TO THE
C REF. ELEC. NUM., I.E. REF. ELEC. 11 MEANS THAT THE
FOLLOWING DATA
C IS OPEN CIRCUIT DATA FOR REF. ELEC. 1
C
50 IF(POSNUM.NE.REFNUM(J)+10.0.OR.OCCYN.NE.'Y') GO TO 80
C CHECK FOR BAD CONNECTION READINGS
IF(VOLTS.LE.-VOPEN(J).OR.VOLTS.GE.VOPEN(J)) GO TO 80
C CHECK FOR REF. ELECTRODE SHORTS
IF(ABS(VOLTS).LE.SHORTV.AND.SHORYN.EQ.'Y') GO TO 80
C INCREMENT COUNTER
NUMOC(J)=NUMOC(J)+1
C STORE DATA IN ARRAY
OCTDAT(J,NUMOC(J))=TIME/3600.0)-STTIM(J)/60.0)
OCVDAT(J,NUMOC(J))=VOLTS+RESPOT(REFNUM(J))
80 CONTINUE
IF(POSNUM.EQ.-1.0) GO TO 200
100 CONTINUE
IF(POSNUM.EQ.-1.0) GO TO 200
100 CONTINUE
C CLOSE OLD FILE
200 CLOSE(UNIT=9)
C
C WRITE DATA TO GRAPHING FILE
C OPEN NEW FILE
TYPE *, 'WRITING TO PGRAPH'
OPEN(UNIT=9, NAME='DL1: PGRAPH.FMT', ACCESS='SEQUENTIAL',
*INITIALSIZE=200,TYPE='NEW')
SUM # OF DATA POINTS -- TOTAL
DO 250 I=1,NUMELE
KOUNT=KOUNT+NUMPT(I)
KNTOC=KNTOC+NUMOC(I)
250 CONTINUE
C WRITE TO FILE
WRITE(9,*) TIMDAT(J,I),VOLDAT(J,I)
300 CONTINUE
C WRITE END-OF-DATA MARK
WRITE(9,*) EOD,EOD
400 CONTINUE
C CLOSE FILE
CLOSE(UNIT=9)
C
WRITE TO OPEN CIRCUIT DATA FILE IF DESIRED
IF(OCYN.EQ.'N') GO TO 999
TYPE *, 'WRITING TO POCDAT'
OPEN(UNIT=9,NAME='DL1:POCDAT.FMT',ACCESS='SEQUENTIAL',
*INITIALSIZE=100,TYPE='NEW'
C WRITE NUMBER OF DATA POINTS TO FILE
WRITE(9,*) KNTOC
C WRITE DATA
DO 600 J=1,NUMELE
DO 500 I=1,NUMOC(J)
WRITE(9,*) OCCTDAT(J,I),OCVDAT(J,I)
500 CONTINUE
C WRITE END-OF-DATA MARK
WRITE(9,*) EOD,EOD
600 CONTINUE
C CLOSE FILE
CLOSE(UNIT=9)
C
999 IF(OFILYN.EQ.'N') GO TO 999
C OBTAIN IR CONTRIBUTION FROM MEASURED POTENTIAL READINGS
C BY SUBTRACTING THE CURRENT READINGS FROM O.C. READINGS IN
C POCDAT.FMT FROM MEASURED DATA IN PGRAPH.FMT
C RESULTS ARE STORED IN OGRAPH.FMT
C LINEAR INTERPOLATION IS USED TO GET PROPER O.C. READINGS
C
KNTELE=1
KNTOC=2
KNTDAT=0
C OPEN FILES
OPEN(UNIT=9,NAME='DL1:PGRAPH.FMT',ACCESS='SEQUENTIAL',
*INITIALSIZE=100,TYPE='NEW')
$\text{TYPE='OLD'}$

\text{OPEN(UNIT=8,NAME='DL1:POCDAT.FMT',ACCESS='SEQUENTIAL',}$

\text{$\text{TYPE='OLD'}$)

\text{REWIND 8}

\text{REWIND 9}

\text{C}

\text{C GET NUMBER OF POINTS}

\text{READ(8,*)) KOCTOT}

\text{READ(9,*)) KOUNT}

\text{C READ FIRST TWO O.C. POINTS}

\text{READ(8,*)) OTIME(1),OVOLTS(1)}

\text{READ(8,*)) OTIME(2),OVOLTS(2)}

\text{C READ AND INTERPOLATE}

\text{DO 2000 I=1,KOUNT+NUMELE}

\text{C READ MEASURED VOLTAGE}

\text{READ(9,*)) TIME VOLTS}

\text{C CHECK FOR END-OF-DATA MARKER}

\text{IF(TIME.NE.EOD) GO TO 1400}

\text{C READ FIRST TWO O.C. POINTS FOR THE NEXT REFERENCE ELECTRODE}

\text{C CHECK IF WE ARE POINTING AT EOD MARKER}

\text{IF(OTIME(2).EQ.EOD) GO TO 1375}

\text{C READ EOD MARKER}

\text{1350 READ(8,*)) OTIME(1),OVOLTS(1)}

\text{KNTOC=KNTOC+1}

\text{C CHECK TO SEE IF INDEED WE ARE AT EOD MARKER}

\text{IF(OTIME(1).EQ.EOD) GO TO 1375}

\text{KNTOC=KNTOC+1}

\text{GO TO 1350}

\text{1375 IF(KNTOC+1.GT.KOCTOT+NUMELE) GO TO 3000}

\text{READ(8,*)) OTIME(1),OVOLTS(1)}

\text{READ(8,*)) OTIME(2),OVOLTS(2)}

\text{KNTOC=KNTOC+2}

\text{KNTOE=KNTOE+1}

\text{GO TO 2000}

\text{1400 IF(TIME.LT.OTIME(1)) GO TO 2000}

\text{IF(TIME.LT.OTIME(2)) GO TO 1550}

\text{C READ NEXT O.C. VOLTAGE}

\text{IF(KNTOC+1.GT.KOCTOT+NUMELE) GO TO 3000}

\text{KNTOC=KNTOC+1}

\text{OTIME(1)=OTIME(2)}

\text{OVOLTS(1)=OVOLTS(2)}

\text{READ(8,*)) OTIME(2),OVOLTS(2)}

\text{IF(OTIME(2).EQ.EOD) GO TO 2000}

\text{C DO LINEAR INTERPOLATION}
IF(TIME.EQ.OTIME(1)) GO TO 1650
NTIME=(OTIME(2)-OTIME(1))/(TIME-OTIME(1))
INTV=OVOLTS(1)+((OVOLTS(2)-OVOLTS(1))/NTIME)
GO TO 1700
1650 INTV=OVOLTS(1)
1700 NVOLTS=VOLTS-INTV
C STORE IN BUFFER
KNTDAT=KNTDAT+1
NUMDAT(KNTELE)=NUMDAT(KNTELE)+1
TIMDAT(KNTELE,NUMDAT(KNTELE))=TIME
VOLDAT(KNTELE,NUMDAT(KNTELE))=NVOLTS
2000 CONTINUE
C
C CLOSE AND WRITE TO FILE
3000 CLOSE(UNIT=8)
CLOSE(UNIT=9)
KOUNT=0
DO 3500 I=1,NUMELE
KOUNT=KOUNT+NUMDAT(I)
3500 CONTINUE
OPEN(UNIT=9,NAME='DL1:OGRAPH.FMT',ACCESS='SEQUENTIAL',
$INITIALSIZE=200,TYPE='NEW'
C WRITE NUMBER OF DATA POINTS
WRITE(9,*),KOUNT
DO 4000 J=1,NUMELE
DO 4000 I=1,NUMDAT(J)
WRITE(9,*),TIMDAT(J,I),VOLDAT(J,I)
4000 CONTINUE
C WRITE END-OF-DATA MARK
WRITE(9,*),EOD,EOD
5000 CONTINUE
C CLOSE FILE
CLOSE(UNIT=9)
GO TO 9999
C
6000 DO 7000 I=1,NUMCUR
DO 6500 J=1,10000
C SEARCH FOR CORRECT TIME
READ(9,*),POSNUM,TIME,VOLTS
IF(TIME/60.0.LT.CURTIM(I)) GO TO 6500
C AT PROPER POSITION?
6100 IF(POSNUM.NE.REFNUM(NUMPT(I)+1).AND.POSNUM.NE.REFNUM(NUMPT(I)
$+1)+10) GO TO 6200
IF(POSNUM.GT.10.) POSNUM=POSNUM-10
NUMPT(I)=NUMPT(I)+1
TIMDAT(I,NUMPT(I))=REFDIS(POSNUM)/PORDIS
VOLDAT(I,NUMPT(I))=-VOLTS+RESPOT(POSNUM)

6200 READ(9,* ) POSNUM,TIME,VOLTS
IF(NUMPT(I).LT.NUMELE) GO TO 6100
GO TO 7000

6500 CONTINUE
7000 CONTINUE
C
C CLOSE AND WRITE TO FILE
CLOSE(UNIT=9)
DO 7500 I=1,NUMCUR
KOUNT=KOUNT+NUMPT(I)
7500 CONTINUE
OPEN(UNIT=9,NAME='DL1 :PGRAPH.FMT',ACCESS='SEQUENTIAL',
$INITIALSIZE=200,TYPE='NEW')
TYPE *,'WRITING TO PGRAPH'
C
WRITE NUMBER OF DATA POINTS
WRITE(9,* )KOUNT
DO 8000 J=1,NUMCUR
DO 7700 I=1,NUMPT(J)
WRITE(9,* ) TIMDAT(J,I),VOLDAT(J,I)
7700 CONTINUE
WRITE(9,* ) EOD,EOD
TIMNET=(CURTIM(J)-EXPST)/60.0
TYPE *,'CURVE',J,'PLOTTED AT',TIMNET,'MINUTES'
8000 CONTINUE
C
9999 STOP
END

B.3 DATA PLOTTING PROGRAM - PPLTST,MPLTST

Programs PPLTST and MPLTST use formatted data produced by PMSGST and
MMMSGST, respectively, to produce potential versus time and potential
versus distance plots on a Tektronix 4200 plotter. The plotting pro-
grams use plotter subroutines constructed from basic plotter commands
(Plot10) to produce high-resolution graphs. The plotter subroutines
were written in FORTRAN by J. Nichols and are stored in GRAFIL.OBJ. Both programs give the user the option to set the X and Y axis scales or
to have the computer set the X and Y axis scales. The computer will set the axis scales such that the plotted curves will fill the space allowed for the graph.

Data must be stored in DL1:PGRAPH.FMT. Thus, if ohmic-free potential data or ohmic contribution data are to be plotted, the appropriate data file (DL1:POCDAT.FMT or DL1:OGRAPH.FMT) should be copied into DL1:PGRAPH.FMT.

B.3.1 Program PPLTST

B.3.1.1 Description

Program PPLTST plots potential versus time data produced by PMSGST. The plotter should be properly setup before running the program. Program operation is simple; the user need only decide whether to manually set the X and Y axis scales, and input the appropriate plot title. The user can also specify the plot symbol type (circles, triangle, points, etc.) used to plot points on the curve.

B.3.1.2 PPLTST Program Listing

The main subroutine called by PPLTST is PORPLT. Following is a listing of PPLTST and its main subroutine PORPLT.

To run PPLTST type

R PPLTST
which runs:

PROGRAM PPLTST
CALL PORPLT
STOP
END

When program changes are made, the program must be relinked by typing

@PPLTST
which runs:

R LINK
PPLTST.SAV=PPLTST/P:250./V/I; /
PORPLT, GRAFIL, PLOT62, ADEOUT/V:1
//
$QBLK
SUBROUTINE PORPLT
C VERSION 6 05/04/83
TYPE *, 'PORPLT -- VERSION 6'
LOGICAL ERR
LOGICAL*1 ANS
DIMENSION ITIT(40)
DIMENSION VEL(501),X(501)
XAMAX=-1.E06
YAMAX=-.E06
XAMIN=1.E06
YAMIN=1.E06
TYPE *, 'NOTE: SYMBOL TYPES ARE AS FOLLOWS:'
TYPE *, '-1 = LINE, 0 = POINT, 1 = CIRCLE, 2 = PLUS'
TYPE *, '3 = BOX, 4 = TRIANGLE, 5 = HEXAGON, 6 = ASTERISK'
TYPE *, ''
TYPE *, 'WHICH SYMBOL TYPE DO YOU WANT?'
READ(5,*) ICHAR
OPEN(UNIT=11,NAME='DL1:PGRAPH.FMT', TYPE='OLD', *ACCESS='SEQUENTIAL', ERR=5
NUNIT=11
READ(11,*) NPOINT
GOTO 7
WRITE(7,*)'FAILED ON FILE OPEN'
STOP
CONTINUE
TYPE *, NPOINT
DO 10 I=1,NPOINT
READ(11,*) XXX,VV
C THIS NEXT LINE IS A PATCH TO GET PLOTTER MARKINGS CORRECT
VV=1000.*VV
VEL(I)=VV
X(I)=XXX
XAMAX=AMAX1(YAMAX,VV)
XAMIN=AMIN1(XAMIN,XXX)
YAMIN=AMIN1(YAMIN,VV)
10 CONTINUE
TYPE *, 'DO YOU WISH TO SET THE X AND Y SCALE (Y OR N) ?'
READ(5,1111) ANS
IF(ANS.EQ.'Y') GO TO 80
14 CONTINUE
WRITE(7,*)'READY?'
READ(5,1111) ANS
1111 FORMAT(A4)
IBAUD=40
IU=2
IPL=1
57 CONTINUE
CALL AXIS(YAMAX,YAMIN,XINCRE,NYTICK,YMAX,YMIN,.TRUE.)
CALL AXIS(XAMAX,XMIN,XINCRE,NXTRICK,XMAX,XMIN,.TRUE.)
CALL INITT(IBAUD)
CALL TERM(IU,4096)
CALL WINDEF(LXMIN,LXMAX,LYMIN,LYMAX)
CALL PLINIT(IPL)
CALL PLON
CALL IGRAF
IF(YINCRE.LT.1.0.AND.XINCRE.LT.1.0)
$CALL MODLBL(.FALSE.,.FALSE.,.FALSE.,.FALSE.)
IF(YINCRE.LT.1.0.AND.XINCRE.GE.1.0)
$CALL MODLBL(.TRUE.,.FALSE.,.FALSE.,.FALSE.)
IF(YINCRE.GE.1.0.AND.XINCRE.LT.1.0)
$CALL MODLBL(.FALSE.,.TRUE.,.FALSE.,.FALSE.)
IF(YINCRE.GE.1.0.AND.XINCRE.GE.1.0)
$CALL MODLBL(.TRUE.,.TRUE.,.FALSE.,.FALSE.)
CALL TWINDO(LXMIN,LYMAX,LYMAX)
CALL GRAPH(XMIN,XMAX,XINCRE,NXTRICK,YMIN,YMAX,YINCRE,NYTRICK)
CALL XLABLE(13,'time(Minutes)',ERR)
CALL YLABLE(21,'potential(millivolts)',ERR)
CALL DATPLT(X,VEL,NPOINT,O,ICHAR)
WRITE(7,*),'TYPE IN THE DESCRIPTION OF THE EXPERIMENT'
READ(5,1001) ITIT
1001 FORMAT(40A2)
CALL TITLE(72,ITIT,ERR)
WRITE(7,*),'TYPE XMIN and XMAX'
READ(5,*) XAMIN,XAMAX
WRITE(7,*),'TYPE YMIN AND YMAX'
READ(5,*) YAMIN,YAMAX
GOTO 14
CLOSE(UNIT=NUNIT)
END
3.2.2 Program MPLTST

3.2.2.1 Description

Program MPLTST plots either potential versus time or potential versus distance data produced by MMSGST. The program operates in a similar manner as PPLTST. The user can manually or automatically set the X and Y axis scales and input the plot title. Also, the user can specify the plot symbol type used to plot points on separate curves.

The user must inform the program which type of plot is desired. If a potential versus time plot is desired, the user responds will signal a potential versus distance plot. In either case, the program will automatically label the X and Y axes appropriately.

In the case of multiple electrode potentials versus time plots, the computer pauses between each curve plot to give the user time to change plot pens (to a different color or texture). The user types 'Y' to direct the program to continue to the next curve.

B.3.2.2 MPLTST Program Listing

The main subroutine called by MPLTST is MULPLT. Following is a listing of MPLTST and MULPLT.

To run MPLTST type

```
R MPLTST
which runs:
PROGRAM MPLTST
CALL MULPLT
STOP
END
```

When program changes are made, the program must be relinked by typing:

```
@MPLTST
which runs:
R LINK
MPLTST.SAV=MPLTST/P:250.//V/I/ //
MULPLT,GRAFIL,PLOT62, ADEOUT/V:1
//
$QBLK
```

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SUBROUTINE MULPLT
C VERSION 8 05/03/83
TYPE *, 'MULPLT--VERSION 8'
LOGICAL ERR
LOGICAL*1 ANS
DIMENSION ITIT(40)
DIMENSION XPLLOT(501), YPLLOT(501), KOUNT(10), ICHAR(10)
XAMAX=1.E06
YAMAX=1.E06
XAMIN=1.E06
YAMIN=1.E06
DO 2 I=1,10
ICHAR(I)=-1
KOUNT(I)=0
2 CONTINUE
3 OPEN(UNIT=11, NAME='DL1: PGRAPH.FMT', TYPE='OLD',
*ACCESS='SEQUENTIAL', ERR=5)
NUNIT=11
C GET NUMBER OF DATA POINTS
READ(11,*) NPOINT
GOTO 7
5 WRITE(7,*) 'FAILED ON FILE OPEN'
STOP
7 CONTINUE
TYPE *, 'PLOT OF POTENTIAL VS. TIME?'
READ(5,1101) REGYN
1101 FORMAT(A1)
TYPE *, 'HOW MANY CURVES TO PLOT?'
READ(5,*) NUMREF
TYPE *, 'NOTE: SYMBOL TYPES ARE AS FOLLOWS:'
TYPE *, '-1 LINE, 0 POINT, 1 CIRCLE, 2 PLUS'
TYPE *, '3 BOX, 4 TRIANGLE, 5 HEXAGON, 6 ASTERISK'
TYPE *, '
TYPE *, 'DEFAULT SYMBOL IS -1'
TYPE *, 'DO YOU WANT DEFAULT VALUES?'
READ(5,1101) SYMDEF
IF(SYMDEF.EQ.'Y') GO TO 9
DO 8 I=1, NUMREF
TYPE *, 'SYMBOL TYPE FOR CURVE', I
READ(5,*) ICHAR(I)
8 CONTINUE
9 TYPE *, NPOINT
IF(REGYN.EQ.'N') GO TO 15
DO 12 J=1, NUMREF
READ(11,*) XXX,VV  
IF(XXX.EQ.-1.0) GO TO 12  
C THIS NEXT LINE IS A PATCH TO GET PLOTTER MARKINGS CORRECT  
VV=1000.*VV  
KOUNT(J)=KOUNT(J)+1  
YAMAX=AMAX1(YAMAX,VV)  
XAMAX=AMAX1(XAMAX,XXX)  
XAMIN=AMIN1(XAMIN,XXX)  
YAMIN=AMIN1(YAMIN,VV)  
GO TO 10  
12 CONTINUE  
GO TO 18  
C THIS NEXT SECTION SETS THE PLOTTER MARKINGS FOR POT.VS. DIST.  
DO 17 J=1,NUMREF  
READ(11,*) XXX,VV  
IF(XXX.EQ.-1.0) GO TO 17  
VV=1000.*VV  
KOUNT(J)=KOUNT(J)+1  
YAMAX=AMAX1(YAMAX,VV)  
XAMAX=AMAX1(XAMAX,XXX)  
XAMIN=AMIN1(XAMIN,XXX)  
YAMIN=AMIN1(YAMIN,VV)  
GO TO 16  
17 CONTINUE  
18 TYPE *, 'DO YOU WISH TO SET THE X & Y SCALE (Y OR N).DOM  
READ(5,1111) ANS  
IF(ANS.NE.'Y') GO TO 20  
TYPE *, 'TYPE XMIN,XMAX'  
READ(5,*) XAMIN,XAMAX  
TYPE *, 'TYPE YMIN,YMAX'  
READ(5,*) YAMIN,YAMAX  
20 WRITE(7,*),'READY?'  
READ(5,1111) ANS  
1111 FORMAT(A4)  
57 IBAUD=40  
IU=2  
IPL=1  
CALL AXIS(YAMAX,YAMIN,YINCRE,NYTICK,YMAX,YMIN,.TRUE.)  
CALL AXIS(XAMAX,XAMIN,XINCRE,NXTICK,XMAX,XMIN,.TRUE.)  
CALL INITT(IBAUD)  
CALL TERM(IU,4096)  
CALL WINDEF(LXMIN,LXMAX,LYMIN,LYMAX)  
CALL PLINIT(IPL)
CALL PLON
CALL IGRAF
IF(YINCRE.LT.1.0.AND.XINCRE.LT.1.)
$CALL MODLBL(.FALSE.,.FALSE.,.FALSE.,.FALSE.)
IF(YINCRE.GE.1.0.AND.XINCRE.GE.1.)
$CALL MODLBL(.TRUE.,.FALSE.,.FALSE.,.FALSE.)
CALL TWINDO(LXMIN,LXMAX,LYMIN,LYMAX)
CALL GRAPH(XMIN,XMAX,XINCRE,NXTICK,YMIN,YMAX,YINCRE,NYTICK)
IF(REGYN.EQ.'Y') CALL XLABLE(10,'Time (min)',ERR)
IF(REGYN.EQ. 'N')
$CALL XLABLE(38,'Dimensionless Distance Into Pore (x/L)',ERR)
CALL XLABLE(14,'Potential (mV)',ERR)
C PLOT DATA
C REWIND DATA FILE
REWIND 11
C FIRST READ DUMMY RECORD
READ(11,*) DUMMY
IF(REGYN.EQ. 'N') GO TO 100
DO 70 I=1,NUMREF
C LOAD UP DATA BUFFER
DO 60 J=1,KOUNT(I)
READ(11,*),X Plot(J),Y Plot(J)
C ADJUST VOLT DATA TO MILLIVOLT DATA
Y Plot(J)=Y Plot(J)*1000.0
60 CONTINUE
C READ END OF DATA MARKER
READ(11,*) DUMMY,DUMMY
ITY=ICHAR(I)
C PLOT LINE
IPOINT=KOUNT(I)
CALL DATPLT(X Plot,Y Plot,I POINT,0,ITY)
TYPE *, ' WHEN READY FOR NEXT LINE, TYPE Y'
READ(5,1111) ANS
70 CONTINUE
C THIS NEXT SECTION PLOTS POTENTIAL VS. DISTANCE DATA
DO 170 I=1,NUMREF
C LOAD UP DATA BUFFER
DO 160 J=1,KOUNT(I)
READ(11,*),X Plot(J),Y Plot(J)
C ADJUST DATA TO GET PLOTTER MARKINGS CORRECT
Y Plot(J)=Y Plot(J)*1000.0
170 CONTINUE
DATA PATCH PROGRAM -- PFIXST

B.4.1 Description

PFIXST is a data patch program which gives the user the ability to patch data in the event that run conditions necessitate a change in electrode amplifications during an experiment. Typically, the amplification may be set too high for the range of potentials encountered during the experiment. In this case, the output voltage will exceed five volts. However, because the A/D card can read up to a maximum of five volts, the signal will be interpreted as five volts and data will be lost. If this condition is spotted during monitoring, then it can be remedied by adjusting the electrode amplification until the output signal lowers to below five volts. This procedure necessitates a method to patch the data since the FOREST routine assumes constant signal amplification.

Data to be patched must be stored in DL1:PORDAT.FMT. Patched data will be stored in DL1:FIXDAT.FMT, thus, saving the original data. The program simply asks for the programmed and actual amplifications for each reference electrode, and the time period over which to adjust the data. If no change in a particular electrode is required, then the programmed amplification should be equal to the actual amplification.
Once the desired changes are input, PORFIX patches the data. The potential data to be patched are found and then multiplied by the programmed amplification divided by the actual amplification. Once changes are completed, the entire file is written to DL1:FIXDAT.FMT.

B.4.2 PFIXST Program Listing

The main subroutine called by PFIXST is PORFIX. Following is a listing of PFIXST and PORFIX.

To run PFIXST, type

```
R PFIXST
```

which runs:
```
PROGRAM PFIXST
CALL PORFIX
STOP
END
```

When program changes are made, the program must be relinked by typing

```
@PFIXST
```

which runs:
```
R LINK
PFIXST.SAV,PFIXST=PFIXST/V/I/
PORFIX/V:1
```

📜 $QBLK

1 SUBROUTINE PORFIX
C VERSION 5 03/20/83
C THIS PROGRAM IS USED TO "FIX" DATA THAT HAS BEEN COLLECTED
C FROM SINGLE PORE EXPERIMENTS. THIS MAY BE REQUIRED, WHEN
C DURING A RUN, THE AMPLIFIED VOLTAGE EXCEEDS 5 VOLTS AND
C A REDUCTION IN AMPLIFICATION IS CALLED FOR
C THE USER INPUTS THE PROGRAMMED AMPLIFICATION, THE REVISED
C AMPLIFICATION, AND THE TIME PERIOD DURING WHICH THE ADJUSTMENTS
C SHOULD BE MADE. THE DATA SHOULD BE STORED IN
C CONTINUE
C
C READ FILE, ADJUST DATA, AND WRITE FILE
DO 100 I=1,15000
  DO 90 J=1,NUMELE+1
    READ(9,* ) POSNUM,TIME,VOLTS
C CHECK PARAMETERS
IF(POSNUM.EQ.EOD) GO TO 200
IF(TIME/60.0.LT.BEGTIM(J)) GO TO 80
IF(TIME/60.0.GE.ENDTIM(J)) GO TO 80
C ADJUST DATA
VOLTS=VOLTS*(PRGAMP(J)/ACTAMP(J))
C WRITE DATA
80 WRITE(8,*) POSNUM,TIME,VOLTS
90 CONTINUE
100 CONTINUE
C CLOSE DATA FILES AND RETURN
C
C WRITE REST OF FILE,VERBATIM
200 WRITE(8,*) EOD
   WRITE(8,*) TIME
   WRITE(8,*) VOLTS
   DO 300 I=1,1000
       READ(9,*) TIME
       IF(TIME.EQ.EOD) GO TO 400
       WRITE(8,*) TIME
   300 CONTINUE
400 WRITE(8,*) EOD
   CLOSE(UNIT=9)
   CLOSE(UNIT=8)
   STOP
END

B.5 I/O DRIVER MODIFICATIONS - HD

Previous sections have described and referenced program calls to the I/O driver to initiate various input/output functions. The I/O driver and I/O subroutines were written in FORTRAN by M. Katz to allow users to conduct I/O operations while in the extended memory monitor of the RT-11 operating system of the DEC LSI-11/23 computer. The I/O driver has been slightly modified to increase the I/O capability for this operation. Specifically, a small section of code has been added to allow POREST to communicate to an additional P-I/O board connected to the PREM. Only the Preamble, Initialization, and Talk sections have been altered. The following changes to the program documented by M. Katz (pp.131-134) are listed below.
Preamble Section
add POT$FN=207 ;potentiostat code
after CLK$FN=206 ;Clock code, non existent function
add POTOUT=167752 ;output register of 3rd P-I/O
after EXTOUT=167762 ;output register of 2nd P-I/O

Initialization Section
add BNEF8 ;continue search
after F7: CMP R3,#CLK$FN ;general clock access?
delete BNE SPFNER ;if no, wrong code
add F8: CMP R#,#POT$FN ;potentiostat-ref. elode function
BNE SPFNER ;if no, wrong code
JMP POT ;if yes, branch to it
after ;JMP CLK ;if yes, branch

Talk Section
add BR TTLK ;go
POT: MOV #POTOUT,R3 ;put out address of 3rd P-I/O
JMP SELREF ;go
after EXT; MOV #EXTOUT,R3 ;put out address of 2nd P-I/O
add SELREF:BIT #177766,2(R5) ;is elode # >= 0 or <=9?
BEQ POTWRT ;o.k. write
MOV #2,(R5) ;error code is 2
JMP HDERR

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POTWRT: MOV 2(R5),R2 ;move output word to R2
COM R2 ;take compliment of #
MOV R2,@R3 ;write ref.elode # to P-I/O
JMP HDDONE
REFERENCES


APPENDIX C

1  SUBROUTINE MULMSG
C  VERSION 21  05/01/82
C  THIS PROGRAM MASSAGES THE DATA FROM POREST (SUBROUTINE SINPOR).
C  THE DATA WILL BE HANDLED SO THAT A ONE OR MORE ELECTRODE'S
C  VOLTAGE-TIME DATA IS PLACED INTO A NEW FILE (DL1:PGRAPH.FMT)
C  THIS FILE CAN THEN BE GRAPHED ON THE PLOTTER BY PPLTST
C (SUBROUTINE PORPLT)
C
C DECLARATIONS
C REAL*4 TIMDAT(7,500),VOLDAT(7,500)
C REAL*4 OCTDAT(7,100),OCVDAT(7,100)
C REAL*4 POSNUM,TIME,VOLTS,REFNUM(10),BEGTIM(10),ENDTIM(10)
C REAL*4 STTIM(10),VOPEN(10),SHORTV
C REAL*4 OTIME(2),OVOLTS(2),NTIME,INTV,NVOLTS,RESTIM,PORDIS
C REAL*4 RESPOT(10),REFDIS(10),CURTIM(10)
C INTEGER NUMPT(10),NUMOC(10),NUMDAT(10)
C DATA EOD/-1.0/
C DATA PORDIS/1.5748/
C
C MAIN ROUTINE
C TYPE *,'MULMSG -- VERSION 21'
C TYPE *,'PLOT OF POTENTIAL VS. TIME?'
READ(5,1001) REGYN
C TYPE *,'NUMBER OF CURVES TO PLOT?'
READ(5,*) NUMELE
C TYPE *,'DO YOU WANT REFERENCE SHORTS FILTERED?'
READ(5,1001) SHORYN
IF(SHORYN.EQ.'N') GO TO 11
C TYPE *,'INPUT SHORT POTENTIAL'
READ(5,*) SHORTV
11 TYPE *,'SHOULD REST POTENTIALS BE SUBTRACTED FROM POTENTIAL
DATA?'
READ(5,1001) RESTYN
IF(RESTYN.EQ.'N') GO TO 15
C TYPE *,'DO YOU WANT TO INPUT REST POTENTIALS?'
READ(5,1001) RESTIN
IF(RESTIN.EQ.'Y') GO TO 15
C TYPE *,'TIME AT WHICH REST POTENTIALS SHOULD BE TAKEN (SECS)?'
READ(5,*) RESTIM
15 IF(REGYN.EQ.'N') GO TO 35
DO 30 I=1,NUMELE

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TYPE *, 'REF. ELECTRODE POSITION NUMBER TO BE PLOTTED?'
READ(5,*) REFNUM(I)
TYPE *, 'WHAT IS THE OPEN CIRCUIT VOLTAGE FOR THIS ELECTRODE?'
READ(5,*) VOPEN(I)
TYPE *, 'STARTING TIME OF EXPERIMENT (SECONDS) FOR REF. ELEC.', $REFNUM(I)
READ(5,*) STTIM(I)
TYPE *, 'ENDING TIME OF EXPERIMENT (SECONDS) FOR REF. ELEC.', $REFNUM(I)
READ(5,*) ENDTIM(I)
TYPE *, 'TIME AT WHICH TO START PLOTTING DATA?'
READ(5,*) BEGTIM(I)
30 CONTINUE
GO TO 39
35 NUMCUR=NUMELE
TYPE *, 'NUMBER OF REFERENCE ELECTRODES TO PLOT?'
READ(5,*) NUMELE
TYPE *, 'STARTING TIME OF EXPERIMENT (SECONDS)?'
READ(5,*) EXPST
DO 36 I=1,NUMCUR
TYPE *, 'TIME (SECS) AT WHICH TO START CURVE', I, 'PLOTTING?'
READ(5,*) CURTIM(I)
36 CONTINUE
DO 37 I=1,NUMELE
TYPE *, 'REFERENCE ELECTRODE POSITION NUMBER TO BE PLOTTED?'
READ(5,*) REFNUM(I)
GET DISTANCES
TYPE *, 'DISTANCE INTO PORE (MM) FOR REF. ELEC.', REFNUM(I)
READ(5,*) REFDIS(REFNUM(I))
37 CONTINUE
39 TYPE *, 'DO YOU WANT TO STORE OPEN CIRCUIT DATA (Y OR N)?'
READ(5,1001) OCYN
1001 FORMAT(A1)
TYPE *, 'DO YOU WANT TO CREATE THE DATA FILE WHICH SUBTRACTS' O.C. DATA FROM MEASURED DATA? (Y OR N)'
READ(5,1001) OFILYN
OPEN(UNIT=9, NAME='DL1: PORDAT.FMT', ACCESS='SEQUENTIAL',
*TYPE='OLD')
DO 40 I=1,NUMELE
NUMDAT(I)=0
NUMOC(I)=0
NUMPT(I)=0
RESPOT(I)=0.0
40 CONTINUE
C KNOXC=0
C KOUNT=0
C GET REST POTENTIALS IF DESIRED
IF(RESTYN.EQ.'N') GO TO 60
IF(RESTIN.EQ.'Y') GO TO 46
DO 45 MIND=1,10000
READ(9,*) POSNUM,TIME,VOLTS
C SEARCH
IF(TIME/60.0.LT.RESTIM) GO TO 45
IF(POSNUM.NE.1.0) STOP 'INCORRECT REST TIME'
RESPOT(1)=VOLTS
C READ NEXT SERIES OF POTENTIALS
DO 43 J=1,7
READ(9,*) POSNUM,TIME,VOLTS
RESPOT(J+1)=VOLTS
CONTINUE
C REWIND DATA FILE
REWIND 9
GO TO 60
CONTINUE
GO TO 60
C READ REST POTENTIALS
DO 47 L=1,7
TYPE *, 'INPUT REST POTENTIAL FOR ELECTRODE', L
READ(5,*)) RESPOT(L)
CONTINUE
C 60 IF(RENYN.EQ.'N') GO TO 6000
C READ AND FILTER DATA
DO 100 I=1,15000
READ(9,*)) POSNUM,TIME,VOLTS
DO 80 J=1,NUMELE
C FILTER DATA
IF(TIME/60.LT.BEGTIM(J)) GO TO 80
IF(TIME/60.GE.ENDTIM(J)) GO TO 80
IF(POSNUM.NE.REFNUM(J)) GO TO 50
C CHECK FOR BAD CONNECTION READINGS
IF(VOLTS.LE.-VOPEN(J).OR.VOLTS.GE.VOPEN(J)) GO TO 80
C CHECK FOR REF. ELECTRODE SHORTS
IF(ABS(VOLTS).LE.SHORTV.AND.SHORYN.EQ.'Y') GO TO 80
C STORE DATA IN ARRAY -- CONVERT TICKS TO MINUTES
NUMPT(J)=NUMPT(J)+1
TIMDAT(J,NUMPT(J))=(TIME/3600.0)-(STTIM(J)/60.0)
VOLDAT(J, NUMPT(J)) = -VOLTS + RESPOT(REFNUM(J))

C CHECK FOR END OF REF. ELEC. DATA
C CHECK FOR OPEN CIRCUIT READINGS, IF DESIRED
C OPEN CIRCUIT READINGS ARE IDENTIFIED BY ADDITION OF 10 TO THE
C REF. ELEC. NUM., I.E. REF. ELEC. 11 MEANS THAT THE FOLLOWING
C DATA IS OPEN CIRCUIT DATA FOR REF. ELEC. 1
C
IF(POSNUM.NE.REFNUM(J)+10.0.OR.OCYN.NE.'Y') GO TO 80
C CHECK FOR BAD CONNECTION READINGS
IF(VOLTS.LE.-VOPEN(J).OR.VOLTS.GE.VOPEN(J)) GO TO 80
C CHECK FOR REF. ELECTRODE SHORTS
IF(ABS(VOLTS).LE.SHORTV.AND.SHORYN.EQ.'Y') GO TO 80
C INCREMENT COUNTER
NUMOC(J)=NUMOC(J)+1
C STORE DATA IN ARRAY
OCTDAT(J, NUMOC(J))=(TIME/3600.0)-(STTIM(J)/60.0)
OCVDAT(J, NUMOC(J))=-VOLTS+RESPOT(REFNUM(J))

80 CONTINUE
IF(POSNUM.EQ.-1.0) GO TO 200
100 CONTINUE
C CLOSE OLD FILE
200 CLOSE(UNIT=9)
C
C WRITE DATA TO GRAPHING FILE
C OPEN NEW FILE
TYPE *
'WRITING TO PGRAPH'
OPEN(UNIT=9, NAME='DL1: PGRAPH.FMT', ACCESS='SEQUENTIAL',
*INITIALSIZE=200, TYPE='NEW')
C SUM # OF DATA POINTS -- TOTAL
DO 250 I=1, NUMELE
KOUNT=KOUNT+NUMPT(I)
KTOC=KTOC+NUMOC(I)
250 CONTINUE
C WRITE TO FILE
WRITE(9, *) KOUNT
DO 400 J=1, NUMELE
DO 300 I=1, NUMPT(J)
WRITE(9, *) TIMDAT(J, I), VOLDAT(J, I)
300 CONTINUE
C WRITE END-OF-DATA MARK
WRITE(9, *) EOD, EOD
400 CONTINUE
C CLOSE FILE
CLOSE(UNIT=9)

C WRITE TO OPEN CIRCUIT DATA FILE IF DESIRED
IF(OCYN.EQ.'N') GO TO 999
TYPE *, 'WRITING TO POCDAT'
OPEN(UNIT=9, NAME='DL1:POCDAT.FMT', ACCESS='SEQUENTIAL',
*INITIALSIZE=100, TYPE='NEW')
C WRITE NUMBER OF DATA POINTS TO FILE
WRITE(9,*) KNTOC
C WRITE DATA
DO 600 J=1, NUMELE
DO 500 I=1, NUMOC(J)
WRITE(9,*) OCTDAT(J,I), OCVDAT(J,I)
500 CONTINUE
C WRITE END-OF-DATA MARK
WRITE(9,*) EOD, EOD
600 CONTINUE
C CLOSE FILE
CLOSE(UNIT=9)

C
999 IF(OFILYN.EQ.'N') GO TO 9999
C OBTAIN IR CONTRIBUTION FROM MEASURED POTENTIAL READINGS
C BY SUBTRACTING THE CURRENT READINGS FROM O.C. READINGS IN
C POCDAT.FMT FROM MEASURED DATA IN PGRAPH.FMT
C RESULTS ARE STORED IN OGRAPH.FMT
C LINEAR INTERPOLATION IS USED TO GET PROPER O.C. READINGS
C
KENTELE=1
KNTOC=2
KNTDAT=0
C OPEN FILES
OPEN(UNIT=9, NAME='DL1:PGRAPH.FMT', ACCESS='SEQUENTIAL',
$TYPE='OLD')
OPEN(UNIT=8, NAME='DL1:POCDAT.FMT', ACCESS='SEQUENTIAL',
$TYPE='OLD')
REWIND 8
REWIND 9
C
C GET NUMBER OF POINTS
READ(8,*) KOCTOT
READ(9,*) KOUNT
C READ FIRST TWO O.C. POINTS
READ(8,*) OTIME(1), OVOLTS(1)
READ(8,*) OTIME(2), OVOLTS(2)
C READ AND INTERPOLATE
DO 2000 I=1,KOUNT+NUMELE
C READ MEASURED VOLTAGE
READ(9,*) TIME,VOLTS
C CHECK FOR END-OF-DATA MARKER
IF(TIME.NE.EOD) GO TO 1400
C READ FIRST TWO O.C. POINTS FOR THE NEXT REFERENCE ELECTRODE
C CHECK IF WE ARE POINTING AT EOD MARKER
IF(OTIME(2).EQ.EOD) GO TO 1375
C READ EOD MARKER
1350 READ(8,*) OTIME(1),OVOLTS(1)
KNTOC=KNTOC+1
C CHECK TO SEE IF INDEED WE ARE AT EOD MARKER
IF(OTIME(1).EQ.EOD) GO TO 1375
GO TO 1350
1375 IF(KNTOC+1.GT.KOCTOT+NUMELE) GO TO 3000
READ(8,*) OTIME(1),OVOLTS(1)
READ(8,*) OTIME(2),OVOLTS(2)
KNTOC=KNTOC+2
KNTELE=KNTELE+1
GO TO 2000
1400 IF(TIME.LT.OTIME(1)) GO TO 2000
IF(TIME.LT.OTIME(2)) GO TO 1550
C READ NEXT O.C. VOLTAGE
IF(KNTOC+1.GT.KOCTOT+NUMELE) GO TO 3000
KNTOC=KNTOC+1
OTIME(1)=OTIME(2)
OVOLTS(1)=OVOLTS(2)
READ(8,*) OTIME(2),OVOLTS(2)
IF(OTIME(2).EQ.EOD) GO TO 2000
C DO LINEAR INTERPOLATION
1550 IF(TIME.EQ.OTIME(1)) GO TO 1650
NTIME=(OTIME(2)-OTIME(1))/(TIME-OTIME(1))
INTV=OVOLTS(1)+((OVOLTS(2)-OVOLTS(1))/NTIME)
GO TO 1700
1650 INTV=OVOLTS(1)
1700 NVOLTS=VOLTS-INTV
C STORE IN BUFFER
KNTDAT=KNTDAT+1
NUMDAT(KNTELE)=NUMDAT(KNTELE)+1
TIMDAT(KNTELE,NUMDAT(KNTELE))=TIME
VOLDAT(KNTELE,NUMDAT(KNTELE))=NVOLTS
2000 CONTINUE
C
C   CLOSE AND WRITE TO FILE
3000   CLOSE(UNIT=8)
       CLOSE(UNIT=9)
KOUNT=0
DO 3500 I=1,NUMELE
KOUNT=KOUNT+NUMDAT(I)
3500 CONTINUE
OPEN(UNIT=9,NAME='DL1:OGRAPH.FMT',ACCESS='SEQUENTIAL',
$INITIALSIZE=200,TYPE='NEW')
TYPE *, 'WRITING TO OGRAPH'
C   WRITE NUMBER OF DATA POINTS
WRITE(9,*) KOUNT
DO 5000 J=1,NUMELE
DO 4000 I=1,NUMDAT(J)
WRITE(9,*) TIMDAT(J,I),VOLDAT(J,I)
4000 CONTINUE
C   WRITE END-OF-DATA MARK
WRITE(9,*), EOD,EOD
5000 CONTINUE
C   CLOSE FILE
CLOSE(UNIT=9)
GO TO 9999
C
6000   DO 7000 I=1,NUMCUR
       DO 6500 J=1,10000
C   SEARCH FOR CORRECT TIME
READ(9,*), POSNUM,TIME,VOLTS
IF(TIME/60.0.LT.CURTIM(I)) GO TO 6500
C   AT PROPER POSITION?
6100 IF(POSNUM.NE.REFNUM(NUMPT(I)+1).AND.POSNUM.NE.REFNUM(NUMPT(I)+1)+10) GO TO 6200
IF(POSNUM.GT.10.) POSNUM=POSNUM-10
NUMPT(I)=NUMPT(I)+1
TIMDAT(I,NUMPT(I))=REFDIS(POSNUM)/PORDIS
VOLDAT(I,NUMPT(I))=-VOLTS+RESPOT(POSNUM)
6500 CONTINUE
7000 CONTINUE
C
C   CLOSE AND WRITE TO FILE
CLOSE(UNIT=9)
DO 7500 I=1,NUMCUR
KOUNT=KOUNT+NUMPT(I)
7500 CONTINUE
OPEN(UNIT=9,NAME='DL1:PGRAF.FMT',ACCESS='SEQUENTIAL',
$INITIALSIZE=200,TYPE='NEW')
TYPE *, 'WRITING TO PGRAPH'
WRITE NUMBER OF DATA POINTS
WRITE(9,*) KOUNT
DO 8000 J=1,NUMCUR
DO 7700 I=1,NUMPT(J)
WRITE(9,*) TIMDAT(J,I),VOLDAT(J,I)
7700 CONTINUE
WRITE(9,*) EOD,EOD
TIMNET=(CURTIM(J)-EXPST)/60.0
TYPE *, 'CURVE', J, 'PLOTTED AT', TIMNET, 'MINUTES'
8000 CONTINUE
CLOSE(UNIT=9)
C
9999 STOP
END
APPENDIX D

1 SUBROUTINE PORFIX
C VERSION 5 03/20/83
C THIS PROGRAM IS USED TO "FIX" DATA THAT HAS BEEN COLLECTED
C FROM SINGLE PORE EXPERIMENTS. THIS MAY BE REQUIRED, WHEN
C DURING A RUN, THE AMPLIFIED VOLTAGE EXCEEDS 5 VOLTS AND
C A REDUCTION IN AMPLIFICATION IS CALLED FOR
C THE USER INPUTS THE PROGRAMMED AMPLIFICATION, THE REVISED
C AMPLIFICATION, AND THE TIME PERIOD DURING WHICH THE ADJUSTMENTS
C SHOULD BE MADE. THE DATA SHOULD BE STORED IN DL1:PORDAT.FMT.
C THE ADJUSTED DATA WILL BE STORED IN DL1:FIXDAT.FMT
C
C DECLARATIONS
REAL*4 POSNUM,BEGTIM(10),ENDTIM(10)
REAL*4 TIME,VOLTS,PRGAMP(10),ACTAMP(10)
DATA EOD/-1.0/

C OPEN INPUT AND OUTPUT FILES
OPEN(UNIT=9,NAME='DL1:PORDAT.FMT',ACCESS='SEQUENTIAL',
$TYPE='OLD')
OPEN(UNIT=8,NAME='DL1:FIXDAT.FMT',ACCESS='SEQUENTIAL',
$INITIALSIZE=400,TYPE='NEW')

C MAIN ROUTINE
TYPE *, 'PORFIX -- VERSION 5'
TYPE *, 'NUMBER OF REFERENCE ELECTRODES?'
READ(5,*) NUMELE
DO 30 I=1,NUMELE+1
  TYPE *, 'PROGRAMMED AMPLIFICATION FOR REF. ELECTRODE ',I,' ?'
  READ(5,*) PRGAMP(I)
  TYPE *, 'ACTUAL AMPLIFICATION FOR REF. ELECTRODE ',I,' ?'
  READ(5,*) ACTAMP(I)
  TYPE *, 'BEGINNING TIME TO START DATA ADJUSTMENT (SECS)?'
  READ(5,*) BEGTIM(I)
  TYPE *, 'ENDING TIME TO COMPLETE DATA ADJUSTMENT (SECS)?'
  READ(5,*) ENDTIM(I)
30 CONTINUE

C READ FILE, ADJUST DATA, AND WRITE FILE
DO 100 I=1,15000
  DO 90 J=1,NUMELE+1
    READ(9,*) POSNUM,TIME,VOLTS
    CHECK PARAMETERS
    IF(POSNUM.EQ.EOD) GO TO 200
    IF(TIME/60.0.LT.BEGTIM(J)) GO TO 80
    IF(TIME/60.0.GE.ENDTIM(J)) GO TO 80
    ADJUST DATA
    VOLTS=VOLTS*(PRGAMP(J)/ACTAMP(J))
    WRITE DATA
  80 WRITE(8,*) POSNUM,TIME,VOLTS
  90 CONTINUE
100 CONTINUE

C CLOSE DATA FILES AND RETURN
WRITE REST OF FILE, VERBATIM

WRITE(8,*) EOD
WRITE(8,*) TIME
WRITE(8,*) VOLTS
DO 300 I=1,1000
READ(9,*) TIME
IF(TIME.EQ.EOD) GO TO 400
WRITE(8,*) TIME
CONTINUE
300
400 WRITE(8,*) EOD
CLOSE(UNIT=9)
CLOSE(UNIT=8)
STOP
END
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