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**TRANSIENT CURRENT DISTRIBUTIONS IN
POROUS ZINC ELECTRODES IN KOH ELECTROLYTE**

by

**Ming-Biann Liu, Y. Yamazaki,
G. M. Cook, and N. P. Yao**

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February 1981

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LIST OF SYMBOLS

a	specific surface area per unit volume for the precipitation of ZnO, cm^2/cm^3
a_0	initial specific surface area per unit volume, cm^2/cm^3
a_m	the specific surface area per unit volume for electrochemical reaction, cm^2/cm^3
C_2°	bulk concentration of zincate ions, mol/cm^3
C_2^{sh}	the threshold concentration of zincate ions for the precipitation of ZnO, mol/cm^3
C_2	concentration of zincate ions in pore electrolyte, mol/cm^3
C_3°	bulk concentration of hydroxide ions, mol/cm^3
C_3	concentration of hydroxide ions in pore electrolyte, mol/cm^3
C_A	concentration of potassium zincate in the pore electrolyte, mol/cm^3
C_B	concentration of potassium hydroxide in the pore electrolyte, mol/cm^3
d	effective reaction penetration depth, cm
D_2	diffusivity of zincate ions, cm^2/sec
D_3	diffusivity of hydroxide ions, cm^2/sec
E	electrode potential, V
E_2^{sh}	dimensionless threshold concentration of zincate ions for precipitation of ZnO ($C_2^{\text{sh}}/C_2^\circ$)
E_2	dimensionless concentration of zincate ions in pore electrolyte (C_2/C_2°)
F	Faraday's constant, 96500 C
g	surface roughness factor of ZnO
i°	exchange current density evaluated at the bulk concentrations of zincate and hydroxide ions, mA/cm^2

Blank

i_e	average current density in pore electrolyte phase, mA/cm ²
i_m	average current density in electrode matrix phase, mA/cm ²
I	overall current density, mA/cm ²
j	dimensionless average current density in electrode matrix phase (i_m/I)
k	effective conductivity of pore electrolyte, mho/cm
k_o	specific conductivity of bulk electrolyte, mho/cm
k_d	mass transfer coefficient of zincate ions from electrochemical reaction site to precipitation site, cm/sec
k_e	specific conductivity of pore electrolyte, mho/cm
k_i	initial effective conductivity of pore electrolyte, mho/cm
k_r	intrinsic precipitation rate constant of ZnO, cm/sec
k_s	overall precipitation rate constant of ZnO, cm/sec
L	total thickness of active segments in the electrode, cm
n	number of electrons transferred in electrode reaction
n_A	maximum surface concentration of compact ZnO, mol/cm ²
N_2	flux of zincate ions, mol/cm ² -sec
N_3	flux of hydroxide ions, mol/cm ² -sec
r_o	initial radius of pores, cm
r_1	inner radius of zinc, cm
r_2	inner radius of ZnO, cm
R	gas constant, J/mol-K
t	time, sec
t_2°	transference number of zincate ions
t_3°	transference number of hydroxide ions
t_e	tortuosity factor of electrode
T	absolute temperature, K

$\bar{V}_{\text{Zn}}$	partial molar volume of Zn, cm ³ /mol
$\bar{V}_{\text{ZnO}}$	partial molar volume of ZnO, cm ³ /mol
x	distance through the electrode, cm
x_1	value of x at the interface between bulk electrolyte and electrode, cm
x_f	value of x at the interface between electrode and backing plate, cm
y	dimensionless distance through the electrode (x/L)
Z_2	charge number of zincate ion
Z_3	charge number of hydroxide ion
α_a	transfer coefficient in anodic direction
α_c	transfer coefficient in cathodic direction
γ	coefficient of the dependence of the specific conductivity of electrolyte on the concentration of zincate ions, mho-cm ² /mol
ϵ	local porosity of electrode
ϵ_0	initial porosity of electrode
ϵ_{Zn}	volume fraction of Zn in electrode
ϵ_{ZnO}	volume fraction of ZnO in electrode
η_2	order of dependence of exchange current density on the concentration of zincate ions
η_3	order of dependence of exchange current density on the concentration of hydroxide ion
θ	surface coverage of compact ZnO divided by n_A
λ	$\Delta\zeta/(\Delta y)^2$
σ	effective conductivity of electrode matrix, mho/cm
σ_0	initial effective conductivity of electrode matrix, mho/cm
σ_m	specific conductivity of electrode matrix, mho/cm

ζ	dimensionless time ($D_3 t/L^2$)
ϕ_m	local potential of electrode matrix phase, V
ϕ_e	local potential of pore electrolyte, V
ϕ_{sh}	threshold overpotential for formation of compact ZnO, V
ψ_e	dimensionless local potential of pore electrolyte ($n_{\phi_e} F/RT$)
ψ_m	dimensionless local potential of electrode matrix ($n_{\phi_m} F/RT$)

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ABSTRACT

We have used a zero-resistance ammeter circuit with a 10-channel operational amplifier to measure the current distribution during a discharge of 10 to 100 mA with simulated zinc porous electrodes in 7.24 M KOH saturated with ZnO. The reaction distribution was found to be highly nonuniform, with 70 to 78% of the charge transfer reaction completed in a depth of 0.01 cm. The high non-uniformity of the initial reaction profile was believed to be due to low conductivity of the electrolyte in the electrode pores. The current distribution changes during passivation of the electrode were experimentally obtained.

A mathematical model based upon a macroscopic averaging technique was used to predict the time dependence of charge transfer reaction profiles. With our mathematical model, we predicted current distributions and overpotentials as a function of time for our segmented zinc electrode discharged at a current of 10 to 100 mA; for these predictions, we used assumed values of both precipitation rate constants for porous ZnO and diffusion coefficients for hydroxide and zincate ions. A gradual decrease in the specific conductivity of the pore electrolyte to 20% of the initial value during discharge yields predictions of current distributions and overpotentials in good agreement with our experimental data. The extent of reduction in the specific conductivity of the pore electrolyte implies a supersaturation of zincate of four times chemical saturation, which has been observed experimentally. At high discharge current (25-100 mA), the passivation behavior of the electrode has been simulated. The results of our experiments and mathematical model show that the effective reaction penetration depth is less than 0.02 cm.

I. INTRODUCTION

The literature contains three basic methods for the experimental determination of current distribution in an electrode. In the first method, the reaction distribution of a discharged electrode is measured by sectioning the electrode and then chemically analyzing each section. This method has been applied to a variety of electrodes: zinc electrodes by Nagy and Bockris¹ and Sunu and Bennion,² the cadmium electrode by Bro and Kang,³ and the copper electrode by Alkire.⁴ The second method is the direct measurement of the current distribution in a presectioned electrode during discharge; this has been done by Szpak and Katan for the Ag/AgCl system,⁵ McBreen for the Ni/Zn

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cell,⁶ Coleman for the MnO_2 electrode,⁷ and Gagnon and Austin⁸ for the $\text{Ag}/\text{Ag}_2\text{O}$ electrode. The third method is the direct measurement of the potential distribution by using numerous reference electrodes along an electrode being discharged; this method has been used by Brodd⁹ in a study of current distribution in a manganese dioxide electrode.

The first method is limited to the case where the electrode reaction causes sufficient solid reaction products during the electrode operation to be measured after sectioning the electrode. The sectioning must be done carefully and quickly since this procedure can result in a net reduction and redistribution of material. The other two direct methods have the advantage of allowing continuous measurements to be made during electrode operation; however, the accuracy of the measurements depends greatly upon the designs of the working electrode and the reference electrodes. The sectioned electrode has been significantly improved by Szpak and Katan, who used thin film technology to fabricate silver electrode segments.⁵ Their electrode consisted of six segments of active material, which were 0.07-cm wide and separated by 0.03 cm; these segments were vapor deposited onto a glass slide and had connecting electrical leads insulated by Teflon tape. To simulate the electrode pore structure, Szpak and Katan placed a glass cover slide above the active segments, which was supported on one end by a Teflon spacer and on the other end by a drop of electrolyte which protruded around the counter electrode. The problem with this simulated porous electrode design is that it is significantly different from that of an actual battery electrode (e.g., the electrolyte is not surrounded by active materials).

In the present study, an improved sectioned electrode that closely simulates an actual porous electrode has been designed and fabricated. The zinc electrode was selected as the first to be investigated since it has been used in the Ni/Zn cells for electric-vehicle propulsion. The purpose of this study was to measure the current distribution in the zinc electrode by using the improved sectioned electrode; based on these data, the reaction penetration depth of the zinc porous electrode in KOH electrolyte was calculated. It is necessary to know the distance that the electrochemical reaction penetrates the electrode because electrodes much thinner than the penetration depth behave like planar electrodes, whereas electrodes much thicker than the penetration depth are not fully utilized. In addition, data obtained on the current distribution and overpotential of our electrode provided a basis for the development of a mathematical model.

II. EXPERIMENTAL

A. Preparation of Segmented Porous Electrodes

The electrodes used in this study consist of segments fabricated by a conventional photolithography technique.¹⁰ Zinc sheet with 0.1-mm thickness and 99.99% purity from United Mineral and Chemical Corp. (New York, NY) was cut into pieces with dimensions of 4 cm by 5.5 cm. Each piece of zinc sheet was coated with Kodak photoresist (KPR) mixed with 10% KPR blue dye. When exposed to ultraviolet radiation through a photographic transparency with a matrix of 100 black dots, the resist polymerizes in the areas struck by the light; these areas then become insoluble. The resist in areas covered by black dots is removed with KPR developer. The resulting sheet is chemically spray etched with 10% nitric acid (by volume) to yield a zinc sheet with

100 holes. The size of the holes was measured by using an optical microscope with a calibrated scale. An electric lead was soldered onto the top of each etched zinc sheet. Zinc sheets were then stacked and glued together until an electrode of desired thickness was formed; the holes were aligned under a Bausch & Lomb microscope to form pores. In addition, a plexiglass backing plate was added to this stack of segmented electrodes. The entire assembly was checked to be certain that no electric short circuits would occur. A typical segmented electrode design is shown in Fig. 1.

Fig. 1. Segmented Porous Electrode

B. Experimental Procedure

A schematic of the apparatus for experimental measurements is shown in Fig. 2. The prepared electrode was mounted on plexiglass plates with "Quick-mount" purchased from Fulton Metallurgical Products Corp. (Saxonburg, PA) and then placed in the cell with the electrolyte solution. The electrolyte was 7.24 M KOH saturated with zinc oxide. The KOH was reagent grade, and the zinc oxide was analytical reagent quality. The electrolyte solutions were prepared with double distilled water and deaerated by passing a stream of purified nitrogen through it. The cell was put in a desiccator and evacuated to eliminate any gas bubbles trapped inside the pores. The counter electrode (CE) was a zinc strip. The Hg/HgO reference electrode (RE) was located at the edge of the plexiglass opening, 0.32 cm from the electrode surface. A Model 173 Potentiostat/Galvanostat equipped with a Model 376 Current Converter (Princeton Applied Research Corp., Princeton, NJ) was used to provide a constant discharge current. The currents passing through each segment were measured with a zero-resistance ammeter circuit¹¹ having a 10-channel operational amplifier (Fairchild Co., Mountain View, CA μ A 759UIC), which provided a virtual ground for each active segment of the electrode. These currents were sequentially

Fig. 2. Apparatus for the Measurements of Current Distributions within Segmented Electrodes

recorded using a 10-channel scanner (Keithley Instruments Inc., Cleveland, OH); the scanning speed was set at 1 sec/channel. With this experimental apparatus, the current distribution in the simulated porous electrode was measured for constant current discharges of 10, 25, and 100 mA as a function of time. Furthermore, the potential was measured with the reference electrode. For these measurements, several segmented zinc electrodes were prepared with the following general characteristics: segment thickness, 0.01 cm; 100 straight pores of 0.0265-cm diameter; negligible resistive film thickness compared with zinc segment thickness; and exposed area of pore matrix, 0.42 cm².

C. Results and Discussion

1. Current Distributions and Overpotentials

In the experiment in which a discharge current of 10 mA was used, the electrode was a stack of one inactive segment (front) followed by five active segments. The inactive segment was necessary because preliminary experiments showed collapse of the resistive film on the front active segment of the electrode when exposed to the bulk electrolyte during discharge, leading to erroneous results. For the other two discharge currents, an additional inactive segment, initially intended for electrode potential monitoring, was placed behind the five active segments and in front of the plexiglass backing plate. Figures 3 and 4 show the current distributions and electrode potentials at discharge currents of 10 and 25 mA, respectively; the active segments are

Fig. 3. Current Distribution and Potential of Segmented Electrode Discharged at 10 mA (23.8 mA/cm^2)

numbered consecutively from one to five (See Fig. 1), starting from the front segment facing the bulk electrolyte. Figure 5 is a plot of the stepwise signals recorded by the scanner. As mentioned earlier, all ten channels of the ammeter circuit were scanned at a rate of one second per channel. Therefore, the five steps appearing every 10 seconds in Fig. 5 represent the current measured in each of the five active segments for that period. In Figs. 3-5, the currents are integrated quantities for each segment.

Figures 3 and 4 show that the current distributions in the electrodes were highly nonuniform and that slight variations in electrode potential with respect to the reference electrode occurred throughout the measurements. The nonuniformity in current distributions gradually increased with time until a "steady state" was reached; at steady state, 70% of the charge transfer reaction for the 25-mA discharge (78% for 10 mA) had occurred in the first active segment. These two figures illustrate that the electrode at the 25-mA discharge current attained steady-state current distribution faster than did the electrode at 10 mA.

Figure 5 shows the current distribution changes during the passivation of the segmented zinc electrode. The charge transfer reaction at the first active segment increased to a maximum within 40 sec, followed by a gradual decrease until 130 sec. After 130 sec, the current started to increase

Fig. 4. Current Distribution and Potential of Segmented Electrode Discharged at 25 mA

again as a result of a sharp increase in the electrode potential from -0.8 to $+2.3$ V vs. the Hg/HgO reference electrode. The period of gradual decrease in current at the first active segment is believed to be the result of gradual blockage of the electrode surface by compact type II ZnO, which has been reported by Powers et al.^{12,13} to form at high overpotentials. The increase of current after the sharp increase in the electrode potential is interpreted to be due to zinc dissolution being replaced by oxygen evolution as the electrode reaction. The initial average current density at the first segment was 672 mA/cm^2 ; at this current density, a planar zinc microanode is expected to undergo passivation within 3 sec.¹⁴ However, the segmented electrode underwent passivation at 130 sec. This may imply that (1) local passivation did not occur uniformly and (2) the charge transfer reaction gradually moved from a passivated surface to a non-passivated area with a consequent increase in the electrode potential until the rate of mass transfer of hydroxide ions to the electrode surface was less than that necessary to maintain the discharge current. On the other hand, when the first segment passivated at 130 sec, the inner segments failed to take over the discharge current. This may indicate that the pores were blocked by gaseous bubbles.

Fig. 5. Passivation Behavior of Segmented Electrode Discharged at 100 mA

2. Initial Current Distributions

In each measurement, the simulated porous zinc electrode had been flooded with the electrolyte of 7.24 M KOH saturated with ZnO. Therefore, the concentration of the electrolyte in the pores was the same as that of the bulk electrolyte. A polycrystalline zinc electrode in the KOH electrolyte has a high exchange current density,¹⁵ 0.146 A/cm. This suggests that linear polarization kinetics may be applicable. The problem of current distribution in a porous electrode with constant species concentration and linear polarization kinetics for surface reactions has been solved by Euler and None-maker.^{16,17} In this case, the solution for the current is expressed by the equation,

$$\frac{i_m}{I} = 1 - \frac{k_1}{k_1 + \sigma_1} \left[1 + \frac{\frac{\sigma_1}{k_1} \sinh v(1-y) - \sinh(vy)}{\sinh(v)} \right] \quad (1)$$

where

y = distance through electrode (x) divided by total thickness of active segments in electrode (L)

i_m = average current density in electrode matrix

I = overall current density

k_i = initial effective conductivity of "pore electrolyte"*

σ_i = initial effective conductivity of electrode matrix

Futhermore, in this equation

$$v = L \sqrt{(\alpha_a + \alpha_c) a_o i_o^\circ F (k_i + \sigma_i) / k_i \sigma_i RT}$$

where

α_a = transfer coefficient in anodic direction

α_c = transfer coefficient in cathodic direction

a_o = initial specific interfacial area per unit volume

i_o° = exchange current density evaluated at the bulk concentrations of zincate and hydroxide ions

F = Faraday's constant

R = gas constant

T = absolute temperature

The initial effective conductivities of the pore electrolyte and the electrode matrix can be expressed by

$$k_i = k_o \epsilon_o (1 + t_e)$$

$$\sigma_i = \sigma_m (1 - \epsilon_o)$$

where

k_o = specific conductivity of bulk electrolyte

ϵ_o = initial porosity of electrode

t_e = tortuosity factor of electrode

σ_m = specific conductivity of electrode matrix

*The pore electrolyte is defined as the electrolyte within the pores of the electrode.

Equation 1 was used to obtain the initial theoretical current distribution, i_m/I , as a function of y for our segmented electrodes. The values of k_1 , σ , and ν employed in Eq. 1 were derived by substituting the data given in Appendix A into the above three equations. The results of our calculations of i_m/I vs. y are plotted in Fig. 6 (dashed curve). Also shown in this figure are the experimental data of initial anodic current distributions (i.e., $t = 0$) in the simulated zinc electrode at a discharge current of 10 mA (circles), 25 mA (squares), and 100 mA (triangles). For the case of a discharge current of 10 mA (average current density at the first segment, 59 mA/cm²), there is good agreement between the predicted and experimental data. For the case with discharge currents of 25 mA (average current density at the first segment, 132 mA/cm²) and 100 mA (672 mA/cm²), our experimental data deviated from the calculated results; this deviation increased with increasing discharge current. This discrepancy between the calculated and experimental data is ascribed to the fact that the current densities of the first segment of the electrodes were near to or exceeded the exchange current density, 146 mA/cm².¹⁵ It was concluded that the assumption of linear polarization kinetics is inadequate at high current densities.

Fig. 6. Initial Profile of Integrated Fraction of the Charge Transfer Reaction in Simulated Electrode as Function of Normalized Electrode Depth (dashed curve predicted from Eq. 1)

3. Reaction Penetration Depth

The reaction penetration depth is an important parameter in optimizing the design of a porous electrode. A few studies in the literature^{1,2,18} have reported the reaction penetration depth of zinc porous electrodes in KOH electrolytes. Table 1 presents a summary of the results from these studies as well as this study. The reaction penetration depths given in Table 1 were defined as the depth within which 63.2% of the charge-transfer reaction is completed (analogous to the determination of the time constant of a linear system). In Table 1, the reaction penetration depths range from 6.5×10^{-3} to 3×10^{-1} cm. However, this wide variation of results could be due to the inherent nature of the different electrode designs and different techniques of measurements, which are also listed in Table 1. Nagy *et al.*¹ left the back side of their electrodes open to a large electrolyte reservoir; and consequently, they obtained a more uniform reaction profile throughout their electrode thickness (0.3 cm). Katan *et al.*¹⁹ determined an initial effective depth of reaction of about 0.09 cm on exposed zinc electrode strips by electrochemical reduction with cathodic current until the onset of sharp polarization. Their results could have been easily affected by the masking on the electrode and the location of the ZnO precipitated from the zincate. They indicated that, since the polarization was observed to be several times lower than the predicted value, most of the reaction probably penetrated less than 0.09 cm.

The unique feature of our technique is that we were able to make continuous measurements of current distribution throughout discharge. By this technique, a gradual decrease of reaction penetration depths from initial values to "steady state" during galvanostatic discharges was discovered. However, due to limitations in fabrication technique, the pore sizes of our electrodes, 265 μm , were much larger than those in battery electrodes (microns). Furthermore, in our experiments, electronic currents in the active segments were collected individually through channels of the ammeter circuit (Fig. 2); in an actual battery electrode, ionic currents are changed to electronic currents, which are collected by a conducting plate located at the back of the electrode. Thus, our results are representative of a battery electrode only under the condition that the solid electrode matrix is highly conductive compared with the electrolyte within the electrode pores. If this were not the case, further mathematical treatment would be necessary to account for possible differences in resistive potential between our experimental electrode and a battery electrode. For zinc battery electrodes, the specific conductivity of zinc, 2×10^5 mho/cm, is five orders of magnitude higher than that of the KOH electrolyte, 0.4875 mol/cm. We used about 6 cm of copper wire (gauge no. 28), which imposed a resistance of about 0.01 Ω on each segment, about 3% of the conductivity of the pore electrolyte in that segment.

Sunu *et al.*² used pressed zinc powder electrodes resembling a battery electrode and obtained reaction penetration depths similar to our reported depths. Therefore, our electrodes should be a good tool for simulating the behavior of zinc porous electrodes in alkaline batteries. From the results of Sunu *et al.*² and the present work, we believe that the effective reaction penetration depth of zinc porous electrodes in KOH electrolytes is about 0.01 cm.

Table 1. Reaction Penetration Depths Reported for Zinc Porous Anodes in KOH Electrolytes

Authors	Zinc Porous Electrode Design	Method	Current Density, mA/cm ²	Reaction Penetration Depth, cm
Nagy <u>et al.</u> ¹	Pressed powder electrodes with both sides open to electrolyte.	Sectioning and chemical analysis of Zn and ZnO.	10 to 50	3×10^{-1}
Sunu <u>et al.</u> ²	Pressed powder electrodes backed with current collector plate.	Sectioning and chemical analysis of Zn and ZnO.	20 and 50	6.5×10^{-3} (porosity 0.33) 9.0×10^{-3} (porosity 0.60)
Katan <u>et al.</u> ¹⁹	Single pore electrode casted in plastics.	Microscopic measurement of ZnO front, and electrochemical reduction of ZnO.	714	9.0×10^{-2} (initial)
This Work	Simulated porous electrodes divided into segments.	Continuous measurement of currents through each segment.	23.8 59.5	1.7×10^{-2} (initial) 7.5×10^{-3} ("steady state") 1.45×10^{-2} (initial) 8.5×10^{-3} ("steady state")

III. THEORETICAL

Equation 1 can not be used to explain the current distribution of our experimental data since (1) the concentrations of hydroxide and zincate ions change with time during discharge and (2) the assumption of linear polarization kinetics is inadequate to account for two higher discharge currents. Therefore, a mathematical model is needed to predict the current distributions in the simulated zinc porous electrodes.

A. Mathematical Model

The experimental data provide a basis upon which to use a mathematical model for predicting the behavior of the zinc porous electrode system. As indicated in the review by Newman and Tiedemann,²⁰ several models have been proposed to describe the operation of porous electrodes. Sunu and Bennion² used macroscopic averaging* in conjunction with a ternary electrolyte theory to analyze the behavior of zinc porous electrodes. They found good agreement between their experimental results and theoretical predictions. As a result, we used this model, with some simplifications, to simulate our experimental electrode. The assumptions or simplifications applied to the model of Sunu and Bennion for this report are as follows:

(1) The electrode is one dimensional in the direction perpendicular to the electrode surface (see Fig. 7).

Fig. 7. One-Dimensional Porous Electrode Model

*In the macroscopic averaging treatment, Sunu and Bennion disregarded the actual geometry of the pores and used average values of variables (e.g., current density, pore electrolyte concentration) over a small region of the electrode.

(2) Hydrodynamic (bulk) flow of the electrolyte in the pores is negligible.

(3) The solid matrix is "isopotential;" i.e., the zinc has a much higher conductivity than the electrolyte in the pores and the precipitation of ZnO has minimal effect on the conductivity of the solid electrode matrix.

(4) Diffusion coefficients and activity coefficients of species are constant over the range of concentrations encountered.

(5) The system is isothermal.

(6) Terms in the flux equations describing the interaction of hydroxide ions and zincate ions are neglected.

(7) The insulation film coated on each segment has no effect on the mass transfer in the pore electrolyte.

(8) The nucleation period of ZnO is relatively short so that there is a sufficient number of nuclei for the precipitation of ZnO.

(9) The porosity of the "primary layer" of ZnO has been found to be 0.85;¹⁹ therefore, the mass transfer resistance of hydroxide and zincate ions through the ZnO film is assumed to be relatively small.

Based upon the above assumptions, the following seven relations, which constitute the mathematical model, were obtained.

1. Electrochemical and Chemical Reactions

The process occurring in the zinc electrode containing KOH electrolyte saturated with zinc oxide followed a dissolution-precipitation route.^{12,21} Thus,

In the above reactions, electrochemical discharge of the zinc electrode produces a supersaturated zincate solution from which ZnO is precipitated. At high overpotential, the electrochemical process may be expressed by the reaction

2. Redox Electrochemical Overpotential Expression

The relationship between the local reaction rate at a point on the pore wall and the conditions existing in the electrolyte and the electrode phase at that point can be represented by the following equation:

$$\frac{di_e}{dx} = a_m i_o \left(\frac{C_2}{C_2^o} \right)^{\eta_2} \left(\frac{C_3}{C_3^o} \right)^{\eta_3} \quad (5)$$

$$\left\{ \exp \left[\frac{\alpha_a F}{RT} (\phi_m - \phi_e) \right] - \exp \left[- \frac{\alpha_c F}{RT} (\phi_m - \phi_e) \right] \right\}$$

where

a_m = specific area per unit volume for electrochemical reaction

C_2^o = bulk concentration of zincate ions

C_2 = local concentration of zincate ions

C_3^o = bulk concentration of hydroxide ions

C_3 = local concentration of hydroxide ions

ϕ_m = local potential of electrode matrix phase

η_2, η_3 = orders of dependence of exchange current on the concentrations of zincate and hydroxide ions, respectively

Since the specific conductivity of zinc, 2×10^5 mho/cm, is five orders of magnitude greater than that of electrolyte, the zinc matrix has been assumed to be isopotential and ϕ_m set equal to zero (Assumption (3)).

3. Ohm's Law in the Solution Phase

Assumption (4) indicates that Ohm's law as given by Sunu² is represented by

$$i_e = -k \left[\frac{d\phi_e}{dx} - \frac{RT(1+t_2^o)}{nF} \frac{d \ln C_A}{dx} + \frac{RT(4-2t_3^o)}{nF} \frac{d \ln C_B}{dx} \right] \quad (6)$$

where

i_e = average current density in pore electrolyte phase

k = effective conductivity of pore electrolyte ($k_e \epsilon^{1+t_e}$)

ϕ_e = potential of pore electrolyte

t_2^o = transference number of zincate ions

t_3^o = transference number of hydroxide ions

n = number of electrons transferred in electrode reaction

C_A = local concentration of potassium zincate

C_B = local concentration of potassium hydroxide

The specific conductivity of the KOH electrolyte, k_e , decreases linearly with increasing concentration of zincate up to chemical saturation;²² no data are available for KOH supersaturated with zincate. In KOH electrolyte containing potassium carbonate, the specific conductivity of 8.3 M KOH was found by Nitabah *et al.*²³ to decrease linearly with the percentage of potassium carbonate up to 100%. By analogy, the specific conductivity of the supersaturated electrolyte was assumed to decrease linearly with increasing zincate concentration; this can be expressed by the equation

$$k_e = k_o - \gamma C_2 \quad (7)$$

where γ is the coefficient of the dependence of the specific electrolyte conductivity on the concentration of zincate ions. For 7.24 M KOH, k_o was measured to be 0.62 mho/cm. The value of γ was then estimated to be 207 mho·cm²/mol from the value for k_o , the specific conductivity of the electrolyte saturated with ZnO (0.4875 mho/cm), and the zincate concentration in the electrolyte (0.64 M).

4. Species Conservation Equations

We can write the conservation equations in the solution phase as

$$\frac{\partial \epsilon C_2}{\partial t} = \frac{-\partial N_2}{\partial x} + \frac{1}{nF} \frac{\partial i_e}{\partial x} - a k_s (C_2 - C_2^{sh}) \quad (8)$$

$$\frac{\partial \epsilon C_3}{\partial t} = \frac{-\partial N_3}{\partial x} - \frac{4}{nF} \frac{\partial i_e}{\partial x} + 2 a k_s (C_2 - C_2^{sh}) \quad (9)$$

where ϵ is the local porosity of the electrode, a is the specific surface area per unit volume for the precipitation of ZnO, k_s is the overall precipitation rate constant of ZnO, C_2^{sh} is the threshold concentration of zincate ions for the precipitation of ZnO, and N_2 and N_3 are the fluxes of zincate and hydroxide ions expressed by

$$N_2 = -D_2 \epsilon \frac{\partial C_2}{\partial x} + \frac{i_e t_2^0}{Z_2 F} \quad (10)$$

$$N_3 = -D_3 \epsilon \frac{\partial C_3}{\partial x} + \frac{i_e t_3^0}{Z_3 F} \quad (11)$$

In Eqs. (10) and (11), D_2 is the diffusion coefficient of zincate ions, and D_3 is the diffusion coefficient of hydroxide ions.

5. Surface Areas and Precipitation Rate Constant (a_m , a , and k_s)

The pore diameter changes with time as discharge current is passed through an electrode due to the precipitation of ZnO. We present a physical model in Fig. 8 for the calculation of the effective specific areas per unit

Fig. 8. Model for Pore Geometry

volume for the electrochemical reaction (a_m) and the precipitation of ZnO (a). In Fig. 8, the boundaries between the ZnO and the electrolyte as well as between the zinc and ZnO are defined by the radii, r_1 and r_2 , respectively; r_0 is the initial pore radius. At low overpotential, the ZnO film (type I) has been observed by various investigators^{18,24} to be highly porous (about 85%). Under this condition, we assumed that the mass transfer resistance of the ZnO film was relatively small (assumption 9). Therefore, the effective specific area per unit volume for the electrochemical reaction is expressed by

$$a_m = a_0 \left(\frac{2\pi r_1 dx}{2\pi r_0 dx} \right)$$

or

$$a_m = a_o \left(\frac{r_1}{r_o} \right) \quad (12)$$

where a_o is the initial specific surface area per unit volume of the pore region in the electrode. The volume fractions of Zn and ZnO and the porosity of the electrode are related as follows:

$$1 - \epsilon_{Zn} - \epsilon_{ZnO} = \epsilon_o \left(\frac{\pi r_2^2 dx}{\pi r_o^2 dx} \right)$$

or

$$1 - \epsilon_{Zn} - \epsilon_{ZnO} = \epsilon_o \left(\frac{r_2}{r_o} \right)^2 \quad (13)$$

and

$$1 - \epsilon_{Zn} = \epsilon_o \left(\frac{\pi r_1^2 dx}{\pi r_o^2 dx} \right)$$

or

$$1 - \epsilon_{Zn} = \epsilon_o \left(\frac{r_1}{r_o} \right)^2 \quad (14)$$

From Eqs. 12 and 14, we derived

$$a_m = a_o \left(\frac{1 - \epsilon_{Zn}}{\epsilon_o} \right)^{1/2} \quad (15)$$

At high overpotential, reaction (4) may occur and a compact ZnO film (type II; porosity, 0.003) forms on the zinc surface.^{12,13,14,24} Therefore, the effective specific surface area per unit volume for the electrochemical reaction was assumed to be gradually reduced by the fraction of "coverage" of this type of ZnO. It was assumed that, when $\phi_m - \phi_e$ is greater than a threshold value, ϕ_{sh} , the formation of compact ZnO is initiated and the surface eventually becomes inactive. The fraction of "coverage" of the ZnO (θ) is, therefore, expressed by the equation,

$$\frac{\partial \theta}{\partial t} = \frac{1}{a_m n_A n F} \frac{\partial i_e}{\partial x} \quad (16)$$

for

$$\phi_m - \phi_e \geq \phi_{sh}$$

where n_A is the maximum surface molar concentration of the compact ZnO, and the effective specific surface area per unit volume for the electrochemical reaction is expressed by the equation

$$a_m = a_o \left(\frac{1 - \epsilon_{Zn}}{\epsilon_o} \right)^{1/2} (1 - \theta) \quad (17)$$

The kinetics of the precipitation of ZnO is not well-known. However, it is believed to undergo the following steps:

- (1) the electrochemical reaction of Zn in the electrolyte produces zincate
- (2) zincate transforms to the ZnO on the electrode surface
- (3) surface decomposition of zincate forms ZnO

Katan et al.¹⁹ proposed that zincate decomposes at the outer boundary of the existing ZnO film. Therefore, the effective specific surface area per unit volume for the precipitation of ZnO was assumed to be

$$a = a_o \left(\frac{r_2}{r_o} \right)^{1/2} \quad (18)$$

Combining Eqs. (13) and (18), we obtained

$$a = a_o \left(\frac{1 - \epsilon_{Zn} - \epsilon_{ZnO}}{\epsilon_o} \right)^{1/2} \quad (19)$$

The precipitation rate of ZnO depends on the rates of steps 2 and 3 above. To a first approximation, the apparent rate constant of the precipitation of ZnO, k_s , is expressed by

$$\frac{1}{k_s} = \frac{1}{k_d} + \frac{1}{gk_r} \quad (20)$$

where k_d is the mass transfer coefficient of zincate (step 2), k_r is the intrinsic precipitation rate constant of ZnO (step 3), and g is a factor to

account for the surface roughness of the ZnO and depends on the discharge current density.²¹ For a diffusion limiting process, the value of k_s is in the range of 10^{-2} to 10^{-3} cm/sec, depending on the length of the diffusion path. For a kinetics limiting process, the value of k_s is equal to gk_r .

6. Conservation Equations of Solid Matrix

These equations are

$$\frac{\partial \epsilon_{Zn}}{\partial t} = \frac{-\bar{V}_{Zn}}{nF} \frac{\partial i_e}{\partial x} \quad (21)$$

$$\frac{\partial \epsilon_{ZnO}}{\partial t} = \bar{V}_{ZnO} a k_s \left(C_2 - C_2^{sh} \right) \quad (22)$$

and

$$\epsilon = 1 - \epsilon_{Zn} - \epsilon_{ZnO} \quad (23)$$

where $\bar{V}_{Zn}$ and $\bar{V}_{ZnO}$ are the partial molar volumes of Zn and ZnO, respectively.

7. Charge Conservation Equation

In a porous electrode, the current is carried out by electronic current in the solid matrix and ionic current in the electrolyte phase. Thus, for a constant current discharge, the total current density at each depth in the electrode is equal to the summation of ionic and electronic current densities at that location; i.e.,

$$i_m + i_e = I \quad (24)$$

B. Computation Procedures for the Model

The two second-order equations, Eqs. 8 and 9, and the two first-order equations, Eqs. 5 and 6, form a set of nonlinear, coupled differential equations. The four unknown variables are i_m , ϕ_e , C_2 , and C_3 , which are all functions of time and position. These equations are solved using the initial and boundary conditions given below:

- (1) At $t = 0$, $C_2 = C_2^\circ$ and $C_3 = C_3^\circ$
- (2) At $x = x_1$, $C_2 = C_2^\circ$ and $C_3 = C_3^\circ$
- (3) For $x_1 \leq x \leq 0$ $i_e = I$ and $L < x \leq x_f$, $i_m = i_e = 0$
- (4) At $x = L$, $i_m = I$

$$(5) \text{ At } x = x_f, \quad dC_2/dx = 0 \text{ and } dC_3/dx = 0$$

$$(6) \quad \phi_m(x) = 0$$

It is convenient to transform the set of differential equations into dimensionless expressions. The following set of definitions is used for this purpose:

$$y = x/L$$

$$j = i_m/I$$

$$E_2 = C_2/C_2^\circ$$

$$E_3 = C_3/C_3^\circ$$

$$\psi_e = \phi_e nF/RT$$

$$\zeta = D_3 t/L^2$$

$$\psi_m = \phi_m nF/RT$$

Furthermore, the following groups are used:

$$P_1 = D_2/D_3$$

$$P_2 = C_3^\circ/C_2^\circ$$

$$P_3 = -4IL/nFD_3C_3^\circ$$

$$P_4 = +ILt_2^\circ/Z_2D_3C_3^\circ F$$

$$P_5 = +ILt_3^\circ/Z_3D_3C_3^\circ F$$

$$P_6 = -nFIL/kRT$$

$$P_7 = ak_s L^2/D_3$$

$$P_8 = a_m i_o^\circ L/I$$

It should be noted that I is negative with respect to the direction of x . Substituting the above definitions and groups into Eqs. 8 and 9, we obtained

$$\frac{\partial(\epsilon E_2)}{\partial \zeta} = P_1 \frac{\partial}{\partial y} \left(\epsilon \frac{\partial E_2}{\partial y} \right) + P_2 \left(\frac{P_3}{4} + P_4 \right) \frac{\partial j}{\partial y} - P_7 (E_2 - E_2^{sh}) \quad (25)$$

and

$$\begin{aligned} \frac{\partial(\epsilon E_3)}{\partial \zeta} = & \frac{\partial}{\partial y} \left(\epsilon \frac{\partial E_3}{\partial y} \right) - (P_3 - P_5) \frac{\partial j}{\partial y} \\ & + 2 (P_7/P_2) (E_2 - E_2^{sh}) \end{aligned} \quad (26)$$

Rearranging Eq. 6 and then substituting the above definitions and groups into this rearranged equation, we derived

$$\begin{aligned} \frac{d\psi_e}{dy} = & P_6 (1 - j) + (1 + t_2^\circ) \frac{d \ln E_2}{dy} \\ & - (4 - 2t_3^\circ) \frac{d \ln E_3}{dy} \end{aligned} \quad (27)$$

Similarly, Eq. 5 can be transformed to

$$\frac{dj}{dy} = P_8 (E_2)^{\eta_2} (E_3)^{\eta_3} \left\{ \exp \left(- \frac{\alpha_a}{n} \psi_e \right) - \exp \left(\frac{\alpha_c}{n} \psi_e \right) \right\} \quad (28)$$

Furthermore, the initial and boundary conditions become:

- (1) At $\zeta = 0$, $E_2 = E_3 = 1$
- (2) At $y = x_1/L$, $E_2 = E_3 = 1$
- (3) At $y = x_1/L \leq y \leq 0$ and $1 < y \leq x_1/L$, $j = 0$
- (4) At $y = 1$, $j = 1.0$
- (5) At $y = x_f/L$, $dE_2/dy = 0$ and $dE_3/dy = 0$

The above equations were solved by the explicit finite difference method²⁵ for the local concentrations of hydroxide and zincate ions, the current in the solid matrix, and the local potential in the electrolyte solution as a function of position in the electrode. The applied constant discharge currents used for these calculations were those given in the experimental section (i.e., 10, 25, and 100 mA). The sufficient condition for convergence of the explicit finite-difference method²⁵ is

$$0 < \lambda \leq 1/2$$

where $\lambda = \Delta\zeta/(\Delta y)^2$. To save computer time and memory, a maximum allowable value of $\lambda = 0.5$ and a reasonably small value of $\Delta y = 0.04$ were used in the calculations. In using the finite difference technique to solve the above equations, we first expanded Eq. 25 to

$$\begin{aligned} \epsilon \left(\frac{\partial E_2}{\partial \zeta} \right) + E_2 \left(\frac{\partial \epsilon}{\partial \zeta} \right) = P_1 \epsilon \left(\frac{\partial^2 E_2}{\partial y^2} \right) + P_1 \left(\frac{\partial \epsilon}{\partial y} \right) \left(\frac{\partial E_2}{\partial y} \right) \\ + P_2 \left(-\frac{3}{4} + P_4 \right) \frac{\partial j}{\partial y} - P_7 (E_2 - E_2^{sh}) \end{aligned} \quad (29)$$

and Eq. 26 to

$$\begin{aligned} \epsilon \left(\frac{\partial \epsilon_3}{\partial \zeta} \right) + E_3 \left(\frac{\partial \epsilon}{\partial \zeta} \right) = \epsilon \left(\frac{\partial^2 E_3}{\partial y^2} \right) + \left(\frac{\partial \epsilon}{\partial y} \right) \left(\frac{\partial E_3}{\partial y} \right) \\ - (P_3 - P_5) \frac{\partial j}{\partial y} + 2(P_7/P_2) (E_2 - E_2^{sh}) \end{aligned} \quad (30)$$

and Eq. 27 to

$$\begin{aligned} \frac{d\psi_e}{dy} = P_6(1 - j) + (1 + t_2^o) \frac{1}{E_2} \frac{dE_2}{dy} \\ - (4 - 2t_3^o) \frac{1}{E_3} \frac{dE_2}{dy} \end{aligned} \quad (31)$$

A network of grid points was then established throughout the region of interest occupied by the independent variables y and ζ . The grid spacings were $\Delta\zeta = 8 \times 10^{-4}$ and $\Delta y = 0.04$, respectively. The time derivatives of variable u were then replaced by the finite difference form

$$\frac{\partial u}{\partial \zeta} = \frac{u_{i,n+1} - u_{i,n}}{\Delta\zeta}$$

Subscripts i and n denote the space-related point having coordinates $i\Delta y$, $n\Delta\zeta$, which is also called the grid-point (i, n) . Similarly, the space derivatives of u were replaced by the central finite-difference forms

$$\frac{\partial u}{\partial y} = \frac{u_{i+1,n} - u_{i-1,n}}{2\Delta y}$$

$$\frac{\partial^2 u}{\partial y^2} = \frac{u_{i-1,n} - 2u_{i,n} + u_{i+1,n}}{(\Delta y)^2}$$

Except at the boundary points, the space derivatives were approximated by the forward finite-difference form

$$\frac{\partial u}{\partial y} = \frac{u_{i+1,n} - u_{i,n}}{\Delta y}$$

or the backward finite-difference form

$$\frac{\partial u}{\partial y} = \frac{u_{i,n} - u_{i-1,n}}{\Delta y}$$

After the derivatives in Eqs. 29 and 30 had been replaced by the finite-difference points, the values of E_2 and E_3 at the $(n+1)$ time step were calculated from the values of the dependent variables E_1 , ϵ , and j calculated at the n th time step. In this calculation scheme, initial and boundary conditions of the hydroxide and zincate concentrations (previously given) as well as the experimental results of initial values ($n=0$) of j were used. By a similar computational method, the values of ϵ , ϵ_{Zn} , and ϵ_{ZnO} at the $(n+1)$ time step were calculated from Eqs. 21-23. These calculated values of E_2 , E_3 , ϵ , ϵ_{Zn} , and ϵ_{ZnO} were then used in Eqs. 28 and 31. Equation 28 was first linearized with the techniques described by Newman.²⁶ Forward and backward finite-difference forms were written for Eqs. 28 and 31, respectively. The combination of these two finite-difference equations yielded a set of difference equations of j , which were solved by double precision algorithms for tridiagonal matrices (subroutine DGTSL).²⁷ The criterion for convergence was set at 10^{-5} , which is defined as the difference between the two successive solutions. The numerical solutions were carried out in double precision on an IBM 370/195 digital computer. Appendix A gives the numerical values used for the dependent variables in the calculations. The computer program derived to obtain the numerical solutions for this model is given in Appendix B.

C. Results and Discussion

As a result of our computations from the mathematical model, we characterized the behavior of a zinc porous electrode in alkaline electrolyte by the dimensionless groups given in Table 2. Each of these dimensionless groups indicates the relative importance of two physiochemical effects. The groups

Table 2. The Dimensionless Groups Characterizing the Behavior of a Zinc Porous Electrode in Alkaline Electrolytes

Dimensionless Group ^a	Physical Meaning	Magnitude ^b	
		Initial State	Steady State
$G_1 = \frac{a_{m o} i_o n F L^2}{k R T}$	$\frac{\text{Electrolyte Resistance}}{\text{Charge-Transfer Resistance}}$	9	48
$G_2 = \frac{4 a_{m o} L^2}{n F D_3 C_3^o \epsilon}$	$\frac{\text{Diffusion Resistance of OH}^- \text{ Ions}}{\text{Charge-Transfer Resistance}}$	4	5
$G_3 = \frac{I L t_2^o}{z_2 F D_2 C_3^o \epsilon}$	$\frac{\text{Diffusion Resistance of Zincate Ions}}{\text{Migration Resistance of Zincate Ions}}$	0.06	0.06
$G_4 = \frac{I L t_3^o}{z_3 F D_3 C_3^o \epsilon}$	$\frac{\text{Diffusion Resistance of OH}^- \text{ Ions}}{\text{Migration Resistance of OH}^- \text{ Ions}}$	0.2	0.2
$G_5 = \frac{a k_s L^2}{D_2 \epsilon}$	$\frac{\text{Diffusion Resistance of Zincate Ions}}{\text{Precipitation Resistance of Zincate Ions}}$	0.6 ^{b, c}	0.6 ^{b, c}
$G_6 = \frac{2 a k_s L^2}{D_3 \epsilon}$	$\frac{\text{Diffusion Resistance of OH}^- \text{ Ions}}{\text{Formation Resistance of OH}^- \text{ Ions through Precipitation of Zincate Ions}}$	0.2 ^{b, c}	0.2 ^{b, c}

^a For G_1 and G_2 , $i_o = i_o^o \left(\frac{C_2}{C_2^o} \right)^{\eta_2} \left(\frac{C_3}{C_3^o} \right)^{\eta_3}$.

^b $I = -23.8 \text{ mA/cm}^2$

^cBased on $k_s = 1 \times 10^{-5} \text{ cm/sec}$

given in this table were derived from the dimensionless groups P_3 through P_8 as follows:

$$G_1 = P_6 \cdot P_8 \cdot (E_2)^{n_2} (E_3)^{n_3}$$

$$G_2 = P_3 \cdot P_8 \cdot (E_2)^{n_2} (E_3)^{n_3} / \epsilon$$

$$G_3 = P_4 / \epsilon$$

$$G_4 = P_5 / \epsilon$$

$$G_5 = P_7 / \epsilon$$

$$G_6 = 2P_7 / P_1 \epsilon$$

For G_2 to G_6 , the porosity is included in the denominator because the effective diffusivity of a species in a porous medium is the product of the diffusivity of the species and the porosity of the medium. In a similar manner, other dimensionless groups may be formed for comparing the relative magnitude of physical parameters. Although the performance of a porous electrode may be controlled by more than two effects, the relative magnitude of the parameters with respect to each other can be employed to estimate which particular effects are the most important ones for a particular electrode design. These parameters are discussed in terms of our simulated porous zinc electrode in the following paragraphs.

1. Electrolyte Conductivity

Our data on initial current distribution of the simulated electrodes, shown in Fig. 6, indicated that the reaction profiles were highly nonuniform and concentrated within the front (*i.e.*, near to bulk electrolyte) 0.02 cm of the first active segment. Newman *et al.*²⁰ have indicated that this kind of reaction profile is a result of a much higher conductivity in the solid electrode matrix than that in the pore electrolyte; this observation is in agreement with assumption 3 given earlier. This finding indicates that G_1 controls the uniformity of the initial reaction within the simulated zinc electrodes. Indeed, we have calculated a large initial G_1 value of 9 from available physiochemical data and the pore geometry of our electrode. As an electrode continues to be discharged, the electrolyte-phase conductivity undergoes further reduction due to the increase of zincate concentration. Consequently, the reaction profile becomes more nonuniform. A concentration of zincate that has three to four times the solubility of ZnO in KOH solution has been usually observed during the discharge of zinc electrodes.²⁸ For a zincate concentration of four times the solubility of ZnO in our electrolyte, according to Eq. 7, the conductivity in the pore electrolyte phase would be reduced by 82%. In order to maintain the initial reaction profile by maintaining a constant G_1 , a decrease of 82% in the exchange current density would be necessary. The dependence of exchange current density on the concentrations of zincate and

hydroxide ions is expressed in Eq. 5, for which the orders of dependence, η_2 and η_3 , are 0 and 0.45, respectively.¹⁵ Accordingly, this equation indicates that a reduction of 98% in the hydroxide ion concentration is required to produce an 82% decrease of exchange current density, but our calculations indicate that this is not likely to occur under the experimental conditions given in Section II. Therefore, a reduction of conductivity in the pore electrolyte phase is probably responsible for the observed time dependence of the reaction profiles shown in Figs. 3-5. A further discussion of the conductivity of the electrolyte with respect to the reaction penetration depth will be given later.

2. Precipitation of ZnO

Reaction (2), the precipitation of ZnO, removes zincate ions from the electrolyte and provides a source for hydroxide ions. The precipitation of ZnO also affects the conductivity of the electrolyte phase, which was assumed to decrease linearly with increasing zincate concentration. As mentioned previously, the precipitation rate of ZnO depends on the rate of transport of zincate to the existing ZnO and the rate of the precipitation reaction. Although the precipitation mechanism of ZnO has been reported elsewhere,²² there does not appear to be a quantitative rate expression for such a process in the literature. Therefore, the mathematical model presented in Section III.A. (Eqs. 28-31) was used to predict the current distribution and overpotential of our segmented zinc electrode at different precipitation rate constants (k_s) and applied currents.*

Figure 9 shows the current distribution (fraction of current in active segments vs. time) predicted for the segmented zinc porous electrode in the KOH electrolyte discharged at a current of 10 mA (23.8 mA/cm²); the rate constants for the precipitation of ZnO were chosen to be 1×10^{-5} cm/sec (series 1) and 1×10^{-4} cm/sec (series 2). The active segments were labeled as A (segment 1 of simulated electrode), B (segment 2), C (segment 3), D (segment 4), and E (segment 5). (This same method of labeling the electrode segments will be used in figures that follow.) Figure 10 shows the overpotential calculated for the simulated electrode at 10-mA discharge current for the two rate constants. The overpotential was defined as the difference between the potential of the electrode solid matrix at $x = L$ and the potential of the electrolyte at the reference electrode, i.e., $\psi_m(L) - \psi_e(RE)$. Our experimental data are also given in these two figures for comparison. As can be deduced from these figures, a rate constant of 1×10^{-5} cm/sec yielded the best prediction of current distribution and overpotential of the segmented electrode. Table 2 give the change of the dimensionless groups from initial values to steady-state values. An examination of the data in Appendix B indicated that the predicted current distribution and overpotentials shown in the figures for $k_s = 1 \times 10^{-5}$ cm/sec were produced by the following alterations occurring in the segmented electrode during discharge: (1) a decrease in the volume fraction of the zinc matrix due to an increase in the average a_m by up to 40% (see Eq. 15); (2) an increase of the zincate concentration

*Numerical values of other variables needed to solve Eqs. 28-31 are given in Appendix A.

Fig. 9. Predicted and Experimental Current Distribution of Segmented Electrode Discharged at 10 mA (precipitation rate constant: series 1, 1×10^{-5} cm/sec; series 2, 1×10^{-4} cm/sec)

to 2.43 M in the pore electrolyte due to a decrease in the specific conductivity of the pore electrolyte by up to 76% (see Eq. 7); and (3) a decrease in the hydroxide concentration by 16% due to a decrease of i_o by 7.5% (see Eq. 5).

Fig. 10. Predicted and Experimental Overpotential of the Segmented Electrode Discharged at 10 mA (series 1 and 2 same as given in Fig. 9)

For the rate constant of 1×10^{-5} cm/sec, we calculated G_5 and G_6 to be about 0.6 and 0.2, respectively. The value of 0.6 for G_5 indicates that the precipitation of ZnO is relatively slow so that zincate ions may diffuse from the location of the charge-transfer reaction; and, consequently, the zincate ions formed are distributed throughout the pores. The value of 0.2 for G_6 implies that the precipitation of ZnO (reaction 3) provides a minor source of hydroxide ions for the charge-transfer reaction.

Figure 11 and 12 show the predicted reaction profiles and overpotentials, respectively, for our segmented electrode discharged at a 25-mA discharge current; three values for k_s were used for these calculations: 1×10^{-4} cm/sec (series 1), 2×10^{-4} cm/sec (series 2), and 5×10^{-4} cm/sec (series 3). For series 2 in Fig. 11, the fractions of current in all five active segments are given; for the other two series, the current fractions are given only for active segments A and B because the current fractions in the other three segments are similar to those of series 2. Examination of the calculated results for the 25-mA discharge current indicated that the specific conductivities of the pore electrolyte were reduced during discharge and that this reduction was affected by the value of k_s . For the values of k_s used for Fig. 11, the specific conductivity of the pore electrolyte was calculated to be reduced during discharge by up to 98% for series 1, 67% for series 2, and 38% for series 3. The predicted electrode behavior at the very end of the curves for series 1 resulted from a great reduction (98%) in the specific conductivity of the pore electrolyte at the first segment.

The values of G_5 and G_6 at these three assumed rate constants were greater than unity. This means that ZnO tends to precipitate at the location of the charge-transfer reaction, and that the precipitation reaction of ZnO (reaction 3) may become an important source of local hydroxide ions.

Fig. 11. Predicted Current Distribution for Three Values of k_s (series 1, 1×10^{-4} cm/sec; series 2, 2×10^{-4} cm/sec; series 3, 5×10^{-4} cm/sec) with Segmented Electrode Discharged at 25 mA

Fig. 12. Predicted Overpotentials for Three Values of k_s (series 1, 1×10^{-4} cm/sec; series 2, 2×10^{-4} cm/sec; series 3, 5×10^{-4} cm/sec) with Segmented Electrode Discharged at 25 mA

Figures 13 and 14 show the predicted and experimental current distributions and overpotentials, respectively, for the zinc electrode discharged at 25 mA with a k_s of 1.5×10^{-4} cm/sec; this value of k_s was chosen because it had given good agreement between the predicted and the experimental results at the 25 mA discharge. (These two figures will be discussed in greater detail later.) As was the case for the electrode discharged at 10 mA, the predicted results were caused by a reduction of the specific conductivity of the pore electrolyte by up to 78%.

Overall, the above results indicated that the current distributions and overpotentials can be accurately predicted from precipitation rate constants of 1×10^{-5} cm/sec for an electrode discharged at 10 mA and 1.5×10^{-4} cm/sec for one discharged at 25 mA. By using these rate constants, we also discovered that the calculated zincate concentrations at both discharge currents were up to approximately four times chemical saturation of ZnO in the pore electrolyte at steady state. These calculated zincate concentrations have been observed experimentally during the discharge of zinc anodes in KOH electrolytes.^{28,29}

There is an explanation for the different precipitation rate constants determined at the two different current densities. The zincate ions formed must transfer from the charge-transfer reaction site (reaction 2) to the precipitation site (reaction 3). The mass transfer coefficient for this process is k_d . The formation of ZnO at the precipitation site (existing

Fig. 13. Predicted and Experimental Current Distributions for Two Exchange Current Densities with Segmented Electrode Discharged at 25 mA

Series 1 and 2: $k_s = 1.5 \times 10^{-4}$ cm/sec

Series 1: $i_o = 146 \text{ mA/cm}^2 (C_2/0.64 \text{ M})^{0.0}(C_3/5.96 \text{ M})^{0.45}$;

$k_e = 0.62 - 0.207(C_2)\text{mho-cm}^{-1}$

Series 2: $i_o = 224 \text{ mA/cm}^2 (C_2/0.64 \text{ M})^{0.67}(C_3/5.96 \text{ M})^{0.14}$;

$k_e = 0.4875 \text{ mho-cm}^{-1}$

Fig. 14. Predicted and Experimental Overpotentials for Two Exchange Current Densities (defined in Fig. 13) with Segmented Electrode Discharged at 25 mA

ZnO) depends on the roughness of the ZnO surface (designated by g) and the intrinsic precipitation rate constant of ZnO, k_r . For diffusion limiting processes, $k_d \ll g \cdot k_r$, and, according to Eq. 20, $k_s = k_d$. For kinetically controlled processes, $k_d \gg g \cdot k_r$, and, again according to Eq. 20, $k_s = g \cdot k_r$. The parameter k_d may be approximated as D/δ_m , where δ_m is the length of the path of zincate ion diffusion from the charger-transfer site to the precipitation site. The diffusion coefficient of zincate ion, D_2 , in the KOH electrolyte³⁰ is 6×10^{-6} cm²/sec. The value of δ_m is likely to be several microns (10^{-4} cm). Thus, the value of k_d is on the order of 10^{-2} to 10^{-3} cm/sec. As a result, the overall k_s for the diffusion-limited precipitation of ZnO would also be 10^{-2} to 10^{-3} cm/sec. Therefore, for the rate constants on the order of 10^{-4} to 10^{-5} cm/sec used in the calculations, the precipitation is probably a kinetically controlled process, and thus $k_s = g \cdot k_r$. We used g as a morphology factor to account for the dependence of the rate constants on the discharge current densities. A small value for g implies that the surface of existing ZnO is smooth, while a large value of g implies that the surface of existing ZnO is more accessible for further precipitation of ZnO. According to Szpak et al.,²¹ during the discharge of zinc electrodes in KOH electrolytes, the precipitates of ZnO are either boulder- or thistle-shaped; scanning electron micrographs showed that boulder-shaped ZnO probably formed at low current density, while ZnO in thistle form appeared at high current densities. The ZnO in thistle form may provide a higher specific surface area per unit area than that for the boulder form; this may account for the increase of rate constants for the precipitation of ZnO with increased discharge current.

3. Exchange Current Density

Figures 13 and 14 show the current distributions and overpotentials, respectively, for two different specific electrolyte conductivities (k_e) and exchange current densities (i_0). For series 1, $k_e = 0.62 \text{ mho/cm} - 0.207(C_2) \text{ mho/cm} \cdot \text{mol}$ and $i_0 = 146 \text{ mA/cm}^2 (C_2/0.64 \text{ M})^{0.0} (C_3/5.96 \text{ M})^{0.45}$; these two values are the same as those used for Figs. 9-12. For series 2, $k_e = 0.4875 \text{ mho/cm}$ and $i_0 = 224 \text{ mA/cm}^2 (C_2/0.64 \text{ M})^{0.67} (C_3/5.96 \text{ M})^{0.14}$; for this series, the values for η_2 and η_3 (Eq. 5) were taken from Dirkse and Hampson.³¹

In these figures, at the steady state, the exchange current density for series 2 is 3.6 times that used for series 1. Consequently, the dimensionless parameters are up to 32 for G_1 and 23 for G_2 . From the physical meaning of G_1 and G_2 , it was concluded that the discharge of the electrode was controlled by the conductivity of the pore electrolyte and the diffusion process. Although the predicted reaction profile of series 2 in Fig. 13 agrees reasonably well with the experimental data, the predicted overpotential of this series in Fig. 14 shows about 25% deviation from the experimental values. Therefore, the increasing nonuniformity in the experimental current distributions with time shown in Figs. 3 and 4 were not brought about by an increase in exchange current density.

4. Mass Transfer

As expressed in Eqs. 10 and 11, the fluxes of zincate and hydroxide ions consisted of contributions from diffusion and migration terms. The relative magnitudes of these contributions can be represented by G_3 and G_4 . For our system, the values of G_3 and G_4 were on the order of 10^{-1} for the electrode discharged at a 10 mA current and about 2 for the electrode discharged at 100 mA. This finding indicates that migration transport relative to diffusion is minor at low discharge current, but is important at discharge currents above 100 mA.

The ratio of G_1/G_2 contains the ratio of D_3/k and, thus, indicates the relative importance of electrolyte resistance and diffusion resistance. In our calculations with $D_3 = 3 \times 10^{-5} \text{ cm}^2/\text{sec}$ and $k_s = 1.5 \times 10^{-4} \text{ cm/sec}$, G_1/G_2 was initially 1.4 but increased to about 7.5 when the supersaturation of zincate reached four times chemical saturation of ZnO in the electrolyte. These results indicate that our system was not limited by charge transfer resistance; this same conclusion was reached from the above examination of exchange current density. Therefore, these G_1/G_2 values suggest that the nonuniformity of the current distribution for our experimental electrode is mainly due to low conductivity in the pore electrolyte. If this is true, then the ratio of G_1/G_2 indicates the relative importance of hydroxide ion diffusion (D_3) to the current-distribution nonuniformity in the simulated electrode. Figure 15 shows the predicted current distributions for three diffusion coefficients of hydroxide ions -- $3 \times 10^{-5} \text{ cm}^2/\text{sec}$ (series 1), $5 \times 10^{-5} \text{ cm}^2/\text{sec}$ (series 2), and $1 \times 10^{-5} \text{ cm}^2/\text{sec}$ (series 3) -- and a k_s of $1.5 \times 10^{-4} \text{ cm/sec}$ during a 25 mA discharge of the segmented electrode. In this figure, the predicted current fractions for segments C, D, and E are similar for all three series and are, therefore, only given for series 1. As shown in Fig. 15, the predicted current distribution of series 2 in the active segments is similar

Fig. 15. Predicted Current Distributions for Three Values of D_3 ($3 \times 10^{-5} \text{ cm}^2/\text{sec}$ for series 1, $5 \times 10^{-5} \text{ cm}^2/\text{sec}$ for series 2, and $1 \times 10^{-5} \text{ cm}^2/\text{sec}$ for series 3) with Segmented Electrode Discharged at 25 mA

to that for series 1. The explanation for this behavior is that the values of G_1/G_2 for both series 1 (1.4 to 7.5) and series 2 (2.3 to 12.5) are greater than unity. However, as also shown in Fig. 15, a decrease of D_3 from $3 \times 10^{-5} \text{ cm}^2/\text{sec}$ (series 1) to $1 \times 10^{-5} \text{ cm}^2/\text{sec}$ (series 3) decreased the fraction of current in segment A; this resulted because the value for G_1/G_2 had been reduced by approximately a factor of three.

The local supersaturation of zincate is determined by diffusion of zincate and the precipitation of ZnO . Therefore, for a given precipitation rate constant of ZnO , the local supersaturation is expected to be reduced by an increase in diffusion and conductivity (see Eq. 7). The increased conductivity would produce a reduction in electrode overpotential for the segmented electrode and less nonuniformity in the current distribution. For the electrode discharged at 25 mA, this effect is illustrated in Fig. 16 for current distribution and Fig. 17 for overpotential ($k_s = 1.5 \times 10^{-4} \text{ cm/sec}$). With an increase in the diffusion coefficient of zincate from $6 \times 10^{-6} \text{ cm}^2/\text{sec}$ (series 1) to $1 \times 10^{-5} \text{ cm}^2/\text{sec}$ (series 2), the local supersaturation of zincate slightly decreases from a maximum of 3.9 to 3.2 times chemical saturation of

Fig. 16. Predicted Current Distributions for Two Values of D_2 ($6 \times 10^{-6} \text{ cm}^2/\text{sec}$ for series 1 and $1 \times 10^{-5} \text{ cm}^2/\text{sec}$ for series 2) with the Segmented Electrode Discharged at 25 mA

Fig. 17. Predicted Overpotentials for Two Values of D_3
 $(6 \times 10^{-6} \text{ cm}^2/\text{sec}$ for series 1 and
 $1 \times 10^{-5} \text{ cm}^2/\text{sec}$ for series 2) with the
 Segmented Electrode Discharged at 25 mA

ZnO, and the local specific conductivity of the pore electrolyte increases from 22% to 40% of the bulk value. As a result, the overpotential decreases by 10 mV (see Fig. 17), and the current decreases by 5% for the first active segment and increases by 5% for the second active segment (see Fig. 16).

5. Passivation

Figure 5 shows the transient behavior of the simulated zinc electrode encountering passivation and then oxygen evolution. In our theoretical calculations, we assumed that a surface blockage by a compact type of ZnO formed on the electrode surface at high overpotential. The mechanism of surface blockage was formulated from our previous results of galvanostatic discharge of zinc microelectrodes in KOH electrolytes.¹⁴ The surface blockage mechanism is expressed mathematically by Eqs. 18 and 19. In our predictions, we assumed that, when the local surface overpotential exceeds a threshold value, the active surface is decreased gradually and becomes totally inactive when it is covered by n_A of compact ZnO. Figures 18 and 19 show the current distributions and overpotential, respectively, predicted for a segmented electrode discharged at 100 mA. For these predictions, the following parameters were used: threshold potential of 42 mV, a maximum coverage of 8.03×10^3 monolayers of compact ZnO, and k_s of $5 \times 10^{-3} \text{ cm/sec}$. In addition, three specific conductivities of the electrolyte at the bulk concentration (k_0) were assumed: 0.6 mho/cm (series 1), 0.4875 mho/cm (series 2), and 0.4 mho/cm (series 3). The five active segments are labeled as before. Among these three series, the predicted current distribution of series 2 is in reasonably good agreement with the experimental data up to 100 sec of discharge, but the prediction of overpotential for this series is significantly below the experimentally determined overpotential. For series 1, the overpotential was not higher than the

Fig. 18. Predicted and Experimental Current Distribution of the Segmented Electrode Discharged at 100 mA (precipitation rate constant of ZnO , 5×10^{-3} cm/sec; specific conductivities at the bulk electrolyte: 0.6 mho/cm for series 1, 0.4875 mho/cm for series 2, and 0.4 mho/cm for series 3)

Fig. 19. Predicted and Experimental Current Overpotential for the Segmented Electrode Discharged at 100 mA (series 1, 2, and 3 defined in Fig. 18)

assumed threshold value, 42 mV, and thus passivation was not encountered. For series 2 and 3, the total passivation of the electrode would occur. In addition, passivation of the first segment for series 3 occurred earlier than that of series 2; this finding resulted because, in series 3, more incremental sections of the first active segment had higher overpotentials than the threshold value.

Formation of hydrogen bubbles during the discharge of a zinc electrode in alkaline media has been reported by Powers,¹³ and this may have occurred in our electrode. Thus, high overpotentials and total passivation may be accurately predicted after a great reduction is made in the gas generated in the electrode pores, which reduces the effective conductivity of the pore electrolyte. A quantitative expression of the formation of hydrogen bubbles is not available. Thus, we did not attempt to incorporate any effect of the formation of hydrogen bubbles in our model.

IV. CONCLUDING REMARKS

The experimental data for the reaction penetration depth of zinc porous electrodes in KOH electrolytes have been summarized in Table 1. (In Table 1, the effective penetration depth was defined as the electrode depth at which

($1 - \frac{1}{e}$) or 63.2% of the discharge reaction has been completed.) Our experimental results show that the effective penetration depth was initially about 0.015 cm, but decreased to 0.008 cm at steady state.

In Fig. 20, we have used the precipitation rate constants given for Fig. 9 and the other physiochemical properties given in Appendix A to calculate the effective penetration depth at steady state and the electrode overpotential as a function of porosity for the electrode discharged at 10 mA. In this figure, the predicted effective reaction penetration depths are normalized with respect to the electrode thickness (0.05 cm), and the overpotential was defined as the difference between the potential of the electrode solid matrix at $x = L$ and that of the pore electrolyte at $x = 0$. Curves 1 (penetration depth) and 1A (overpotential) are predicted for $k_s = 10^{-5}$ cm/sec; curves 2 (penetration depth) and 2A (overpotential) are predicted for $k_s = 10^{-4}$ cm/sec. In Fig. 20,

Fig. 20. Predicted Overpotential and Effective Reaction Penetration Depth ($y_{0.632}$) vs. Porosity for Electrode Discharged at 10 mA

- Series 1. $k_s = 1 \times 10^{-5}$ cm/sec
- Series 2. $k_s = 1 \times 10^{-4}$ cm/sec
- Series 3. $k_e = 0.4875$ mho/cm
- Series 4. $k_e = 0.1$ mho/cm

the penetration depths obtained at the initial state and steady state are represented by a square and a circle; the overpotential at steady state is represented by a triangle. In general, these curves show that, as the porosity is increased, the effective penetration depth is increased slightly, but the overpotential is reduced notably.

The magnitudes of the dimensionless groups of initial and steady-states obtained with $k_s = 10^{-5}$ cm/sec are given in Table 2. At the initial state, since the concentration of species throughout the pores is uniform, there is, consequently, no effect of mass transfer resistance. Therefore the current distribution in our electrode is determined by G_1 . Since the value of G_1 is greater than unity, the nonuniformity of initial current distribution in our electrode is thus due to high electrolyte resistance relative to charge-transfer resistance. At steady state, the value of G_1 increases to 48, which is the highest value as compared with those of other groups. This indicates that the increase of nonuniformity of the current distribution in our electrode from initial state to steady state is due to the increase in electrolyte resistance. According to the expression of G_1 in Table 2, one way to deal with high electrolyte resistance is to reduce the electrode thickness, L . Reduction of electrode thickness also yields decrease of the diffusion resistance of OH^- ions (see G_2 in Table 2). If we reduce the electrode thickness so that G_1 is equal to unity, G_2 thus becomes less than unity. If we define this electrode thickness as the effective reaction penetration depth, d , then by rearranging G_1 , we obtain the expression,

$$d = \sqrt{\frac{kRT}{A_m i_o nF}} \quad (32)$$

In Fig. 20, curves 3 and 4 show predictions of this penetration using Eq. 32. For these predictions, the specific conductivities of the electrolyte (k_e) were assumed to be the previously determined value of 0.4875 mho/cm for curve 3 and 20% of this value, or 0.1 mho/cm, for curve 4 ($k = k_e \epsilon^{1+t_e}$). Other parameters used in these calculations are given in Appendix A. As shown in Fig. 20, curves 1 and 4 are in reasonably good agreement. For both of these curves, the specific conductivities of the pore electrolyte are of the same magnitude (steady state value for curve 1 and assumed value for curve 4), although the calculational methods were different. It was concluded that the reaction profiles within the electrodes were controlled by the conductivity of the pore electrolyte. Curve 3 shows that a great increase of the effective penetration depth will occur with increased porosity if the specific conductivity of the pore electrolyte is unchanged during the discharge. Furthermore, our initial effective penetration depth (square in Fig. 20) is predicted by this curve. Equation 32 implies that the effective penetration depth is proportional to the square root of ϵ^{1+t_e} if other parameters remain fixed. Using the data given by Sunu et al.,² we determined the effective penetration depths to be 6.5×10^{-3} cm and 9.0×10^{-3} cm for porosities of 0.33 and 0.60, respectively; the ratio of these two penetration depths is 0.72. This ratio is only 13% greater than the ratio of 0.64, which was obtained from the ratio of 0.64, which was obtained from the ratio of ϵ^{1+t_e} for $\epsilon = 0.33$ and 0.60,

where t_e is the commonly accepted tortuosity factor of 0.5. Therefore, Eq. 32 may be used to estimate the effective penetration depth of zinc porous electrodes having a solid matrix with a very high conductivity compared with that of the electrolyte. For other cases, the value of k in Eq. 32 is replaced by $k\sigma/k + \sigma$, where σ is equal to $\sigma_m \epsilon_{Zn}$.

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APPENDIX A

Numerical Values Used in Calculations of Current Distributions and Electrode Overpotentials

Variable	Value
L	0.05 cm
C_2°, C_3°	0.64 <u>M</u> , 5.96 <u>M</u>
k_o	0.62 mho/cm
γ	0.207 mho/cm M
σ_m	2×10^5 mho/cm
t_e	0
ϵ_o	0.13
α_a, α_c	1.5, 0.5 ^a
i_o°	146 mA/cm ² ^b
η, ζ	0, 0.45 ^b
a_o	19.8 cm ² /cm ³
t_2°, t_3°	0.05, 0.72 ^c
$\bar{V}_{Zn}, \bar{V}_{ZnO}$	9.15 cm ³ /mol, 14.5 cm ³ /mol
T	298 K
D_2	6×10^{-6} cm ² /sec
D_3	3×10^{-5} cm ² /sec

^aObtained from Ref. 18.^bObtained from Ref. 15.^cObtained from Ref. 2.

APPENDIX B

Computer Programs

For the discharge of the simulated zinc electrode in the KOH electrolyte at 10 mA, Program A was used. Passivation did not occur at this current and the electrode had six segments. For the other two discharge currents, the electrodes had seven segments. For the other two discharge currents, Program B was used and a surface blockage mechanism by compact ZnO was assumed. These two programs were written specifically for $\Delta y = 0.04$ and $\Delta \zeta \leq 8 \times 10^{-4}$.

1. Input Data

DT	dimensionless time increment ($\leq 8 \times 10^{-4}$)
DJ	overall current density (discharge current/ 0.42 A/cm^2)
XL	total thickness of active segments in the electrode ($L = 0.05 \text{ cm}$)
ALPHA	order of dependence of exchange current density on the concentration of hydroxide ions (η_3)
XB	bulk concentration of hydroxide ions ($C_3^0 = 5.96 \times 10^{-3} \text{ mol/cm}^3$)
PSTY	initial porosity of the electrode ($\epsilon = 0.13$)
VZN	partial molar volume of Zn ($\bar{V}_{\text{Zn}} = 9.15 \text{ cm}^3/\text{mol}$)
ALPHZ	order of dependence of exchange current density on the concentration of zincate ions (η_2)
XSZ	bulk concentration of zincate ions ($C_2^0 = 6.4 \times 10^{-4} \text{ mol/cm}^3$)
DOH	diffusivity of hydroxide ions (D_3)
DZN	diffusivity of zincate ions (D_2)
VZND	partial molar volume of ZnO ($\bar{V}_{\text{ZnO}} = 14.51 \text{ cm}^3/\text{mol}$)
AO	initial specific surface area per unit volume ($a_0 = 19.8 \text{ cm}^2/\text{cm}^3$)
EJ	exchange current density evaluated at the bulk concentrations of zincate and hydroxide ions ($i_0^0 = 0.146 \text{ A/cm}^2$)
RKS	overall precipitation rate constant of ZnO (k_s)
CNDI	specific conductivity of bulk electrolyte ($k_i = 0.4875 \text{ mho cm}^{-1}$)
DY	dimensionless increment of the distance through the electrode ($\Delta y = 0.04$)

YPZND	initial volume fraction of ZnO ($\epsilon_{\text{ZnO}}^{\circ} = 0.0$)
EZSH	dimensionless threshold concentration of zincate ions for precipitation of ZnO ($E_2^{\text{sh}} = 1.0$)
THAIF	the reciprocal of maximum surface coverage of ZnO ($1/n_A = 7.5 \times 10^4 \text{ cm}^2/\text{mol}$)
PHISH	dimensionless threshold potential of pore electrolyte for formation of compact ZnO ($\phi_e^{\text{sh}} nF/RT = -3.25$)
NN	total number of mesh points (31 for Program A; 36 for Program B)
M	maximum number of time steps
NMAX	maximum number of iterations
NOUT	number of time steps per each print of the results of calculation
CJ (1,I)	initial current distribution in the electrode (i_m/I) at ith mesh point

2. Computer Output

The execution of the computer programs by the computer will print the input data, and values of the groups defined in the programs. Other output includes the concentration of hydroxide ions (E), the concentration of zincate ions (EZ), volume fraction of Zn (PZN), volume fraction of ZnO (PZNO), porosity (P), current density in the electrode matrix (J), potential in pore electrolyte (SIE), and value of θ (THETA) at each mesh point. Finally, the current densities in the segments are printed.

PROGRAM A

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      C PROGRAM TO CALCULATE CURRENT DISTRIBUTION FOR ZINC ELECTRODE IN KOH
0001      IMPLICIT REAL*8(A-H,O-Z)
0002      DIMENSION E(2,36),E1(2,36),CJ(2,36),CJ1(2,36),CNDE(36)
0003      DIMENSION P(36),PZN(36),PZNO(36),AM(36),A(36)
0004      DIMENSION D(26),XMUF(26),CM(26),DM(26),EM(26),BM(26)
0005      DIMENSION YHUF(26),BT(26)
0006      DATA FN/1.93000E+5/,RT/2.47757E+3/,DR/3.6563664E-2/,NPASS/5/
0007      DATA YCOND/0.1325/,CHECK/1.0D-5/
0008      READ(5,100)DT,DJ,XL,ALPHA,XB,PSTY
0009      READ(5,100)VZN,ALPHZ,XSZ,DOH,DZN,VZNO
0010      READ(5,100)AO,EJ,RKS,CNDI,DY,YPZNO
0011      READ(5,100)E2SH
      C INPUT NO OF MESHES,NO OF TIME STEPS,MAX NO OF ITERATIONS,NO OF STEPS
      C PER PRINT
0012      READ(5,101)NN,M,NMAX,NOUT
0013      WRITE(6,103)NN,M,NMAX,NOUT
0014      NII=NN-NPASS
0015      NL=NM-2
0016      NL1=NL-1
0017      NI=NPASS+1
0018      XL2=XL**2
0019      GA=DJ*XL/FN
0020      GM=GA/(DCH*XB)
0021      GMZ=GA/(DZN*XSZ)
0022      XMU=AO*EJ*FN*XL2/RT
0023      CR=XB/XSZ
0024      WRITE(6,102)DT,GM,XMU,DY,ALPHA,XB,PSTY
0025      WRITE(6,106)GMZ,ALPHZ,XSZ,DOH,DZN,VZN
      C START TO CALCULATE CONSTANTS IN EQNS
0026      F=DZN/DOH
0027      FP=VZN*XB
0028      FPZ=VZN*XSZ
0029      FPOH=VZNO*XB
0030      FPZN=VZNO*XSZ
0031      DTY=DT/DY
0032      YSQ = DY**2
0033      G = DT/YSQ
0034      GZ=F*G
0035      H=DTY*GM
0036      HZ=DTY*GMZ*F
0037      BELTA=DJ*VZN*XL*DTY*0.5/(FN*DOH)
0038      RA=XSZ*XL2*DT/DOH
0039      PHI=RA/XB
0040      Q=FN*DJ*XL/RT
0041      Z2=Q/CNDI
0042      XCOND=YCOND/CNDI
0043      Z3=AO*EJ*XL/DJ
0044      ELTA=VZNO*RA
0045      WRITE(6,120)E2SH
0046      WRITE(6,110)DJ,XL,VZNO,AO,EJ,RKS
0047      WRITE(6,111)F,FP,FPZ,FPOH,FPZN,CR
0048      WRITE(6,112)G,GZ,H,HZ,CNDI,XCOND
0049      WRITE(6,113)BELTA,PHI,ELTA,Z2,Z3,YPZNO
      C INITIAL CONDITIONS
0050      ZPSTY=1.-PSTY-YPZNO

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(contd)

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0051      DO 10 I=1,NN
0052      E(1,I)=1.0
0053      E(2,I)=1.0
0054      PZN(I)=ZPSTY
0055      PZNO(I)=YPZNO
0056      P(I)=PSTY
0057      CJ1(1,I)=0.
0058      CJ1(2,I)=0.
0059      CJ(2,I)=0.
0060      10  CONTINUE
0061      READ(5,100)(CJ(1,I),I=1,NN)
0062      WRITE(6,104)
0063      WRITE(6,118)(E(1,I),E(2,I),PZN(I),PZNO(I),P(I),CJ(1,I),CJ(2,I),
1I=1,NN)
0064      DO 15 K=1,M
0065      T=FLOAT(K)*DT
C CALCULATE NEW POROSITY
0066      DO 50 I=1,NN
0067      RR=(1.-PZN(I)-PZNO(I))/PSTY
0068      A(I)=AO*DSQRT(RR)
0069      SC=E(2,I)-E2SH
0070      IF(SC.LE.0.)GO TO 55
0071      PZNO(I)=PZNO(I)+ELTA*A(I)*SC*RKS
0072      55  IF(I.EQ.6)GO TO 51
0073      IF(I.EQ.NN)GO TO 52
0074      IF(I.LE.5)GO TO 53
0075      PZN(I)=PZN(I)-BELTA*(CJ(1,I+1)-CJ(1,I-1))
0076      GO TO 53
0077      51  PZN(I)=PZN(I)-2.*BELTA*(CJ(1,I+1)-CJ(1,I))
0078      GO TO 53
0079      52  PZN(I)=PZN(I)-2.*BELTA*(CJ(1,I)-CJ(1,I-1))
0080      53  P(I)=1.-PZNO(I)-PZN(I)
0081      50  CONTINUE
C SET BOUNDARY CONDITIONS
0082      E1(1,1)=1.0
0083      E1(2,1)=1.0
0084      CJ(1,NN)=1.0
0085      CJ1(1,NN)=1.0
C CALCULATE NEW VALUES OF CONCENTRATIONS
0086      D5=Z2*DY
0087      DO 16 I=1,NN
0088      IJ=I
0089      RR=(1.-PZN(I))/PSTY
0090      AM(I)=DSQRT(RR)
0091      IF(I.EQ.1)GO TO 703
0092      IF(I.EQ.NN) GO TO 18
0093      XE1=0.25*G*(P(I+1)-P(I-1))/P(I)
0094      XEZ1=XE1*F
0095      XE=(G-XE1)*E(1,I-1)+(1.-2.0*G)*E(1,I)+(G+XE1)*E(1,I+1)
0096      XEZ=(GZ-XEZ1)*E(2,I-1)+(1.0-2.0*GZ)*E(2,I)+(GZ+XEZ1)*E(2,I+1)
0097      CEP=2.56+FP*E(1,I)
0098      CEPZ=1.05-FPZ*E(2,I)
0099      SC=E(2,I)-E2SH
0100      IF(SC.LE.0.)GO TO 56
0101      DEZ=A(I)*PHI*RKS*SC

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0102      GO TO 91
0103      56  DEZ=0.
0104      91  IF(I.LE.5)GO TO 301
0105          YJ=0.5*(CJ(1,I+1)-CJ(1,I-1))
0106          GO TO 302
0107      301  YJ=0.
0108      302  DE=(2.+FPOH*E(1,I))*DEZ/P(I)
0109          DEO= CR*(1.-FPZN*E(2,I))*DEZ/P(I)
0110          E1(1,I)=XE+DE-YJ*H*CEP/P(I)
0111          IF(E1(1,I).LE.0.)GO TO 41
0112          E1(2,I)=XEZ-DEO+YJ*HZ*CEPZ/P(I)
0113          GO TO 703
0114      18  E1(1,I)=E1(1,NN-1)
0115          E1(2,I)=E1(2,NN-1)
0116      703  CNDE(I)=D5/(P(I)*(1.-XCOND*(E(2,I)-1.0)))
0117      16  CONTINUE
0118          DO 800 I=1,NM
0119              J=NPASS+I
0120              D1=1.05*(E1(2,J+1)-E1(2,J))/E1(2,J)
0121              D2=2.56*(E1(1,J+1)-E1(1,J))/E1(1,J)
0122              D(I)=D1-D2
0123              YMUFI=Z3*DY*AM(J)*(E1(1,J)**ALPHA)*(E1(2,J)**ALPHZ)
0124      800  CONTINUE
0125          IF(K.GT.1)GO TO 956
0126          CJ(2,NN)=0.0
0127          DO 801 I=2,NM
0128              J=NN-I+1
0129              CJ(2,J)=CJ(2,J+1)-D(NM-I+1)-CNDE(J)*(1.-CJ(1,J))
0130      801  CONTINUE
0131      956  JCONT=0
0132      951  JCONT=JCONT+1
0133          IF(JCONT.GT.NMAX)GO TO 31
0134          DO 802 I=1,NM
0135              J=NPASS+I
0136              D1=-0.75*CJ(2,J)
0137              D2=0.25*CJ(2,J)
0138              D3=DEXP(D1)
0139              D4=DEXP(D2)
0140              XMUFI=1./((YMUFI)*(0.75*D3+0.25*D4))
0141              D5=(1.-D1)*D3-(1.-D2)*D4
0142              BT(I)=YMUFI*D5
0143      802  CONTINUE
0144              DM(1)=XMUFI(2)+XMUFI(3)+CNDE(7)
0145              EM(1)=-XMUFI(3)
0146              BM(1)=CNDE(7)+D(2)+BT(2)*XMUFI(2)-BT(3)*XMUFI(3)
0147              DO 803 I=2,NL1
0148                  NL2=I+1
0149                  NL3=I+2
0150                  J=NPASS+I+1
0151                  CM(I)=-XMUFI(NL2)
0152                  EM(I)=-XMUFI(NL3)
0153                  DM(I)=XMUFI(NL2)+XMUFI(NL3)+CNDE(J)
0154                  BM(I)=CNDE(J)+D(NL2)+BT(NL2)*XMUFI(NL2)-BT(NL3)*XMUFI(NL3)
0155      803  CONTINUE
0156          N1=NN-1

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0157      NL2=NL+1
0158      NL3=NL+2
0159      J=NPASS+NL2
0160      CM(NL)=-XMUF(NL2)
0161      DM(NL)=XMUF(NL2)+XMUF(NL3)+CNDE(N1)
0162      BM(NL)=CNDE(N1)+D(NL2)+BT(NL2)*XMUF(NL2)+(1.-BT(NL3))*XMUF(NL3)
0163      CALL DGTSL(NL,CM,DM,EM,BM,INFO)
0164      IF(INFO.NE.0)GO TO 31
0165      DO 804 I=1,NL
0166      J=NPASS+I+1
0167      804 CJ1(1,J)=BM(I)
0168      DO 805 I=2,NN
0169      J=NPASS+I
0170      CJ1(2,J)=(-CJ1(1,J)+CJ1(1,J-1)+BT(I))*XMUF(I)
0171      805 CONTINUE
0172      CJ1(2,6)=CJ1(2,7)-D(1)-CNDE(6)
0173      DO 810 I=1,2
0174      DO 810 J=NI,NN
0175      IF(DABS(CJ1(I,J)).LE.1.0D-6)GO TO 810
0176      IF(DABS(CJ1(I,J)-CJ1(I,J)).GT.CHECK)GO TO 806
0177      810 CONTINUE
0178      J=K/NOU
0179      J=J*NOU
0180      IF(J.NE.K)GO TO 402
0181      DO 601 I=1,NPASS
0182      J=NPASS+1-I
0183      D1=1.05*(E1(2,J+1)-E1(2,J))/E1(2,J)
0184      D2=2.56*(E1(1,J+1)-E1(1,J))/E1(1,J)
0185      CJ1(2,J)=CJ1(2,J+1)-D1+D2-CNDE(J)
0186      601 CONTINUE
0187      41 WRITE(6,108)T
0188      WRITE(6,104)
0189      WRITE(6,117)(E(1,I),E(2,I),PZN(I),PZNO(I),P(I),CJ1(1,I),CJ1(2,I),
1CNDE(I),I=1,NN)
0190      DO 815 I=1,5
0191      J=I*5+1
0192      815 CM(I)=CJ1(1,J+5)-CJ1(1,J)
0193      WRITE(6,117)(CM(I),I=1,5)
0194      IF(IJ.LT.NN)GO TO 40
0195      402 DO 955 I=1,2
0196      DO 955 J=1,NN
0197      955 E(I,J)=E1(I,J)
0198      GO TO 15
0199      806 DO 401 J=NI,NN
0200      CJ(1,J)=CJ1(1,J)
0201      401 CJ(2,J)=0.5*(CJ(2,J)+CJ1(2,J))
0202      GO TO 951
0203      15 CONTINUE
0204      GO TO 40
0205      31 WRITE(6,109)
0206      100 FORMAT(6E12.5)
0207      101 FORMAT(4I8)
0208      102 FORMAT(5H0DT =,E12.5/5H GM =,E12.5/5H XMU=,E12.5/5H DY =,E12.5/
17H ALPHA=,E12.5/5H C0 =,E12.5/11H POROSITY =,E12.5)
0209      103 FORMAT(5H0 NN=,I5/5H M =,I8/' NMAX=',I5/' NOU=',I5)

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0210          104  FORMAT(7X,1HE,13X,2HEZ,13X,3HPZN,12X,4H ZNO,12X,1HP,14X,1HJ,11X,
                1'SIE',12X,'CNDE')
0211          106  FORMAT(5H GHZ=,E12.5,8H ALPHZ =,E12.5,6H COZ =,E12.5/5H DOH=,E12.5
                1,5H DZN=,E12.5,5H VZN=,E12.5)
0212          108  FORMAT(5H0 T =, E12.5)
0213          109  FORMAT(' NOT CONVERGENT')
0214          110  FORMAT(' DJ,XL,VZNO,AD,EJ,RKS',6E12.5)
0215          111  FORMAT(' F,FP,FPZ,FPOH,FPZN,CR',6E12.5)
0216          112  FORMAT(' G,GZ,H,HZ,CNDI,XCOND',6E12.5)
0217          113  FORMAT(' BELTA,PHI,ELTA,Z2,Z3,YPZNO',6E12.5)
0218          117  FORMAT(1X,8E14.5)
0219          118  FORMAT(1X,7E15.5)
0220          120  FORMAT(' E2SH',E12.5)
0221          40   STOP
0222          END

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PROGRAM B

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      C PROGRAM TO CALCULATE CURRENT DISTRIBUTION FOR ZINC ELECTRODE IN KOH
0001      IMPLICIT REAL*8(A-H,O-Z)
0002      DIMENSION E(2,36),E1(2,36),CJ(2,36),CJ1(2,36),CNDE(36)
0003      DIMENSION P(36),PZN(36),PZNO(36),AM(36),A(36),THETA(36)
0004      DIMENSION D(26),XMUF(26),CM(26),DM(26),EM(26),BM(26)
0005      DIMENSION YMUF(26),BT(26)
0006      DATA FN/1.93000E+5/,RT/2.47757E+3/,DR/3.6563664E-2/
0007      DATA YCOND/0.1325/,CHECK/1.00-5/
0008      READ(5,100)DT,DJ,XL,ALPHA,XB,PSTY
0009      READ(5,100)VZN,ALPHZ,XSZ,DOH,DZN,VZNO
0010      READ(5,100)AO,EJ,RKS,CNDI,DY,YFZNO
0011      READ(5,100)E2SH,THAIF,PHISH
      C INPUT NO OF MESHES,NO OF TIME STEPS,MAX NO OF ITERATIONS,NO OF STEPS
      C PER PRINT
0012      READ(5,101)NN,M,NMAX,NCUT
0013      WRITE(6,103)NN,M,NMAX,NCUT
0014      NPASS=5
0015      NM=NN-2*NPASS
0016      NL=NN-1
0017      NL1=NL-1
0018      NI=NPASS+1
0019      N=NPASS+NM
0020      XL2=XL**2
0021      GA=DJ*XL/FN
0022      GM=GA/(DOH*XB)
0023      GMZ=GA/(DZN*XSZ)
0024      XMU=AO*EJ*FN*XL2/RT
0025      CR=XB/XSZ
0026      WRITE(6,102)DT,CM,XMU,DY,ALPHA,XB,PSTY
0027      WRITE(6,106)GMZ,ALPHZ,XSZ,DOH,DZN,VZN
      C START TO CALCULATE CONSTANTS IN EQNS
0028      F=DZN/DOH
0029      FP=VZN*XB
0030      FPZ=VZN*XSZ
0031      FPOH=VZNO*XB
0032      FPZN=VZNO*XSZ
0033      DTY=DT/DY
0034      YSQ = DY**2
0035      G = DT/YSQ
0036      GZ=F*G
0037      H=DTY*GM
0038      HZ=DTY*GMZ*F
0039      BELTA=DJ*VZN*XL*DTY*0.5/(FN*DOH)
0040      RA=XSZ*XL2*DT/DOH
0041      PHI=RA/XB
0042      Q=FN*DJ*XL/RT
0043      Z2=Q/CNDI
0044      XCOND=YCOND/CNDI
0045      Z3=AO*EJ*XL/DJ
0046      ELTA=VZNO*RA
0047      THAI=GA*DTY*THAIF/(AO*DOH)
0048      WRITE(6,120)E2SH,THAIF,THAI,PHISH
0049      WRITE(6,110)DJ,XL,VZNO,AO,EJ,RKS
0050      WRITE(6,111)F,FP,FPZ,FPOH,FPZN,CR
0051      WRITE(6,112)G,GZ,H,HZ,CNDI,XCOND

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0052      WRITE(6,113)BELTA,PHI,ELTA,Z2,Z3,YPZNO
          C INITIAL CONDITIONS
0053      ZPSTY=1.-PSTY-YPZNO
0054      DO 10 I=1,NN
0055          E(1,I)=1.0
0056          E(2,I)=1.0
0057          PZN(I)=ZPSTY
0058          PZNO(I)=YPZNO
0059          P(I)=PSTY
0060          CJ1(1,I)=0.
0061          CJ1(2,I)=0.
0062          CJ(2,I)=0.
0063          AM(I)=1.0
0064          THETA(I)=0.0
0065      10  CONTINUE
0066      READ(5,100)(CJ(1,I),I=1,NN)
0067      WRITE(6,104)
0068      WRITE(6,118)(E(1,I),E(2,I),PZN(I),PZNO(I),P(I),CJ(1,I),CJ(2,I),
          1I=1,NN)
0069      DO 15 K=1,M
0070          T=FLOAT(K)*DT
          C CALCULATE NEW POROSITY
0071      DO 50 I=1,NN
0072          RR=(1.-PZN(I)-PZNO(I))/PSTY
0073          A(I)=AO*DSQRT(RR)
0074          SC=E(2,I)-E2SH
0075          IF(SC.LE.0.)GO TO 55
0076          PZNO(I)=PZNO(I)+ELTA*A(I)*SC*RKS
0077      55  IF(I.EQ.6)GO TO 51
0078          IF(I.EQ.N)GO TO 52
0079          IF(I.LE.5.OR.I.GT.N)GO TO 53
0080          YJ=CJ(1,I+1)-CJ(1,I-1)
0081          GO TO 890
0082      51  YJ=2.*(CJ(1,I+1)-CJ(1,I))
0083          GO TO 890
0084      52  YJ=2.*(CJ(1,I)-CJ(1,I-1))
0085      890  IF(CJ(2,I).GT.PHISH)GO TO 53
0086          THETA(I)=THETA(I)+0.5*THAI*YJ
0087          IF(THETA(I).LE.1.0)GO TO 53
0088          THETA(I)=1.0
0089      53  PZN(I)=PZN(I)-BELTA*YJ
0090          P(I)=1.-PZN(I)-PZNO(I)
0091      50  CONTINUE
          C SET BOUNDARY CONDITIONS
0092      E1(1,1)=1.0
0093      E1(2,1)=1.0
0094      CJ(1,N)=1.0
0095      CJ1(1,N)=1.0
          C CALCULATE NEW VALUES OF CONCENTRATIONS
0096      D5=Z2*DY
0097      DO 16 I=1,NN
0098          IJ=I
0099          RR=(1.-PZN(I))/PSTY
0100          AM(I)=DSQRT(RR)
0101          IF(I.EQ.1)GO TO 703

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0102      IF(I.EQ.NN) GO TO 18
0103      XE1=0.25*G*(P(I+1)-P(I-1))/P(I)
0104      XEZ1=XE1*F
0105      XE=(G-XE1)*E(1,I-1)+(1.-2.0*G)*E(1,I)+(G+XE1)*E(1,I+1)
0106      XEZ=(GZ-XEZ1)*E(2,I-1)+(1.0-2.0*GZ)*E(2,I)+(GZ+XEZ1)*E(2,I+1)
0107      CEP=2.56+FP*E(1,I)
0108      CEPZ=1.05-FPZ*E(2,I)
0109      SC=E(2,I)-E2SH
0110      IF(SC.LE.0.)GO TO 56
0111      DEZ=A(I)*PHI*PKS*SC
0112      GO TO 91
0113      56 DEZ=0.
0114      91 IF(I.EQ.N)GO TO 300
0115      IF(I.LE.5.OR.I.GT.N)GO TO 301
0116      YJ=0.5*(CJ(1,I+1)-CJ(1,I-1))
0117      GO TO 302
0118      300 YJ=0.5*(CJ(1,I)-CJ(1,I-2))
0119      GO TO 302
0120      301 YJ=0.
0121      302 DE=(2.+FPOH*E(1,I))*DEZ/P(I)
0122      DEO= CR*(1.-FPZN*E(2,I))*DEZ/P(I)
0123      E1(1,I)=XE+DE-YJ*H*CEP/P(I)
0124      IF(E1(1,I).LE.0.)GO TO 41
0125      E1(2,I)=XEZ-DEO+YJ*HZ*CEPZ/P(I)
0126      GO TO 703
0127      18 E1(1,I)=E1(1,NN-1)
0128      E1(2,I)=E1(2,NN-1)
0129      703 CNDE(I)=D5/(P(I)*(1.-XCOND*(E(2,I)-1.0)))
0130      16 CONTINUE
0131      DO 800 I=1,NM
0132      J=NPASS+I
0133      D1=1.05*(E1(2,J+1)-E1(2,J))/E1(2,J)
0134      D2=2.56*(E1(1,J+1)-E1(1,J))/E1(1,J)
0135      D(I)=D1-D2
0136      YMUFI(I)=Z3*DY*AM(J)*(E1(1,J)**ALPHA)*(E1(2,J)**ALPHZ)
0137      YMUFI(I)=YMUFI(I)*(1.-THETA(J))
0138      IF(YMUFI(I).GE.1.0E-11)GO TO 800
0139      YMUFI(I)=1.E-11
0140      800 CONTINUE
0141      IF(K.GT.1)GO TO 956
0142      CJ(2,N)=0.
0143      DO 801 I=2,NM
0144      J=N-I+1
0145      CJ(2,J)=CJ(2,J+1)-D(NM-I+1)-CNDE(J)*(1.-CJ(1,J))
0146      801 CONTINUE
0147      956 JCONT=0
0148      951 JCONT=JCONT+1
0149      IF(JCONT.GT.NMAX)GO TO 31
0150      DO 802 I=1,NM
0151      J=NPASS+I
0152      D1=-0.75*CJ(2,J)
0153      D2=0.25*CJ(2,J)
0154      D3=DEXP(D1)
0155      D4=DEXP(D2)
0156      XMUFI(I)=1./(YMUFI(I)*(0.75*D3+0.25*D4))

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0157      D5=(1.-D1)*D3-(1.-D2)*D4
0158      BT(I)= YMUF(I)*D5
0159      802  CONTINUE
0160      DM(1)=XMUF(2)+XMUF(3)+CNDE(7)
0161      EM(1)=-XMUF(3)
0162      BM(1)=CNDE(7)+D(2)+BT(2)*XMUF(2)-BT(3)*XMUF(3)
0163      DO 803 I=2,NL1
0164      NL2=I+1
0165      NL3=I+2
0166      J=NPASS+I+1
0167      CM(I)=-XMUF(NL2)
0168      EM(I)=-XMUF(NL3)
0169      DM(I)=XMUF(NL2)+XMUF(NL3)+CNDE(J)
0170      BN(I)=CNDE(J)+D(NL2)+BT(NL2)*XMUF(NL2)-BT(NL3)*XMUF(NL3)
0171      803  CONTINUE
0172      N1=N-1
0173      NL2=NL+1
0174      NL3=NL+2
0175      J=NPASS+NL2
0176      CM(NL)=-XMUF(NL2)
0177      DM(NL)=XMUF(NL2)+XMUF(NL3)+CNDE(N1)
0178      BM(NL)=CNDE(N-1)+D(NL2)+BT(NL2)*XMUF(NL2)+(1.-BT(NL3))*XMUF(NL3)
0179      CALL DGTSL(NL,CM,DM,EM,BM,INFO)
0180      IF(INFO.NE.0)GO TO 31
0181      DO 804 I=1,NL
0182      J=NPASS+I+1
0183      804  CJ1(1,J)=BM(I)
0184      DO 805 I=2,NM
0185      J=NPASS+I
0186      CJ1(2,J)=(-CJ1(1,J)+CJ1(1,J-1)+BT(I))*XMUF(I)
0187      805  CONTINUE
0188      CJ1(2,6)=CJ1(2,7)-D(1)-CNDE(6)
0189      DO 810 I=1,2
0190      DO 810 J=NI,N
0191      IF(DABS(CJ1(I,J)).LE.1.0D-6)GO TO 810
0192      IF(DABS(CJ(I,J)-CJ1(I,J)).GT.CHECK)GO TO 806
0193      810  CONTINUE
0194      J=K/NOOUT
0195      J=J*NOOUT
0196      IF(J.NE.K)GO TO 402
0197      DO 601 I=1,NPASS
0198      J=NPASS+1-I
0199      D1=1.05*(E1(2,J+1)-E1(2,J))/E1(2,J)
0200      D2=2.56*(E1(1,J+1)-E1(1,J))/E1(1,J)
0201      CJ1(2,J)=CJ1(2,J+1)-D1+D2-CNDE(J)
0202      601  CONTINUE
0203      41  WRITE(6,108)T
0204      WRITE(6,104)
0205      WRITE(6,117)((E(1,I),E(2,I),PZN(I),PZNO(I),P(I),CJ1(1,I),CJ1(2,I),
1THETA(I),I=1,NN)
0206      DO 815 I=1,5
0207      J=I*5+1
0208      815  CM(I)=CJ1(1,J+5)-CJ1(1,J)
0209      WRITE(6,117)(CM(I),I=1,5)
0210      IF(IJ.LT.NN)GO TO 40

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0211      402 DO 955 I=1,2
0212          DO 955 J=1,NN
0213      955 E(I,J)=E1(I,J)
0214          GO TO 15
0215      806 DO 401 J=NI,N
0216          CJ(1,J)=CJ1(1,J)
0217      401 CJ(2,J)=0.5*(CJ(2,J)+CJ1(2,J))
0218          GO TO 951
0219      15 CONTINUE
0220          GO TO 40
0221      31 WRITE(6,109)
0222      100 FORMAT(6E12.5)
0223      101 FORMAT(4I8)
0224      102 FORMAT(5HODT =,E12.5/5H GM =,E12.5/5H XMU=,E12.5/5H DY =,E12.5/
17H ALPHA=,E12.5/5H CO =,E12.5/11H POROSITY =,E12.5)
0225      103 FORMAT(5H0 NN=,I5/5H M =,I8/' NMAX=',I5/' NOUT=',I5)
0226      104 FORMAT(7X,1HE,13X,2HEZ,13X,3HPZN,12X,4H ZNO,12X,1HP,14X,1HJ,11X,
1'SIE',12X,'THETA')
0227      106 FORMAT(5H GHZ=,E12.5,8H ALPHZ =,E12.5,6H COZ =,E12.5/5H DOH=,E12.5
1,5H DZN=,E12.5,5H VZN=,E12.5)
0228      108 FORMAT(5H0 T =, E12.5)
0229      109 FORMAT(' NOT CONVERGENT')
0230      110 FORMAT(' DJ,XL,VZNO,AO,EJ,RKS',6E12.5)
0231      111 FORMAT(' F,FP,FPZ,FPOH,FPZN,CR',6E12.5)
0232      112 FORMAT(' G,GZ,H,HZ,CNDI,XCOND',6E12.5)
0233      113 FORMAT(' BELTA,PHI,ELTA,Z2,Z3,YPZNO',6E12.5)
0234      117 FORMAT(1X,8E14.5)
0235      118 FORMAT(1X,7E15.5)
0236      120 FORMAT(' E2SH,THAIF,THAI,PHISH',4E12.5)
0237      40 STOP
0238      END

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