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Mathematical Modeling of a Primary Zinc/Air Battery

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Zinc is used widely as an anode in many alkaline batteries, such as Zn/Ni and Zn/Air. Optimization of designs of these batteries depend on understanding the zinc chemistry and electrochemistry in alkaline solution and the mass-transport processes in the battery during charge and discharge. While the former has been extensively investigated experimentally, only a few mass-transport models have been presented. Choi, Bennion, and Newman (1) presented a mathematical model for a secondary Zn/Air battery for analysis of the material redistribution in the battery during charge and discharge. Their model includes convective flow caused primarily by osmosis and electro-osmosis forces. It was found that the convective flow is primarily responsible for the nonuniform zinc distribution on the electrode plate. The validity of their conclusion was verified partially by their experiments that showed virtually no zinc redistribution when the convective flow was minimized (2). Sunu and Bennion (3) developed a comprehensive model of a porous zinc electrode to investigate the electrode phenomena in the direction perpendicular to the projected electrode surface. In their model, the mass-transport equations were developed based on concentrated ternary electrolyte theory. Three electrode failure mechanisms (namely, depletion of hydroxide ions, pore plugging by zinc oxide, and surface passivation) were identified by analyzing the model simulations. The validity of their model was verified by good agreement between their model predictions and experimental data of porosity and zinc oxide distributions (4). Their model was used later by Isaacson et al. (5) and Miller et al. (6) to investigate zinc movement in both the vertical and parallel directions to the electrode surface. Good agreement was obtained by Isaacson et al. (5) between their model predictions and experimental chronopotentiometric data.

It should be noted that all previous mathematical models were used to study secondary batteries and that the model verification was conducted using a half cell or a Zn-NiOOH cell. Previous modeling efforts were focused on the zinc electrode; and, consequently, the concentration distributions in the separator were neglected. Although the findings from such research may be useful for design of a primary Zn-Air battery, many aspects of a primary Zn-Air battery are different from a secondary battery. For example, material redistribution is not of as much concern in a primary battery. Instead, the anode material utilization and polarization behavior are more important. In addition, a primary battery is usually built in the “dry” form, namely, with a gelled electrolyte, and the ratio of the amount of zinc to that of KOH is much greater than that in a secondary battery. The model presented here can be used to analyze the performance of a primary Zn-Air battery with respect to design parameters in order to maximize the performance of the battery.

Chemistry and Electrochemistry

Zinc oxide solubility is relatively high in an alkaline solution because dissolved zinc forms various complexes with hydroxide ions. These complex ions include \( \text{Zn(OH)}^2\), \( \text{Zn(OH)}_2^\text{-} \), \( \text{Zn(OH)}_3^\text{-} \), and \( \text{Zn(OH)}^\text{+} \), etc. It is known (7, 8) that only the concentration of \( \text{Zn(OH)}^2\) is appreciable when compared with the other species present in the electrolyte. Therefore, an alkaline zincate solution can be reasonably treated as a ternary electrolyte consisting of K\( \text{OH} \), K\( \text{Zn(OH)}_2^\text{2+} \), and H\( \text{O} \). When ionic species (Zn\( ^{n+} \)) are introduced into the solution by dissolution of Zn, they may remain in the electrolyte as zincate ions or deposit as ZnO (8)

\[
\text{Zn(OH)}^2\text{+} + 2 \text{OH}^- + \text{H}_2\text{O} \rightarrow \text{Zn(OH)}_2\text{2+} + 2 \text{OH}^- + \text{H}_2\text{O} \quad [1]
\]

In addition, \( \text{Zn(OH)}^2\) ions can also precipitate in the form of solid K\( \text{Zn(OH)}_2^\text{2+} \), if the solution is oversaturated with K\( \text{Zn(OH)}_2^\text{2+} \) (9). Although the kinetics of these processes are not clearly understood, a correlation between the alkaline concentration and the solubility of zincate is well established, which is an approximate linear function of hydroxide ion concentration over a certain range (9).

If zinc remains in the solution as Zn\((\text{OH})^2\) and does not precipitate during discharge of a Zn/Air battery, hydroxide ions will be rapidly depleted due to zinc dissolution by OH\( ^- \) ions, which may cause the cell voltage to increase rapidly. On the other hand, if zincate ions decompose into zinc oxide and hydroxide ions when the solution becomes saturated with zincate, the anodic zinc dissolution would continue as long as the electrode is not blocked by the resulting zinc oxide, and as long as hydroxide ions are available. This availability of OH\( ^- \) ions depends on the zincate decomposition rate compared to the discharge rate. Unfortunately, it has been reported that the decomposition of zincate ions is a slow process. Also, the precipitation of solid potassium zincate is undesirable because it will result in a loss of potassium hydroxide.

The electrochemistry of zinc anodic dissolution in alkaline solutions has been extensively investigated, as indicated by several review articles on the subject (10-12). However, several reaction mechanisms have been proposed by different researchers, and, unfortunately, agreement about a kinetics expression has not been obtained. It is generally accepted that the anodic zinc dissolution forms zincate ions as follows

\[
\text{Zn} + 4 \text{OH}^- \rightarrow \text{Zn(OH)}_4^{2-} + 2\text{e}^- \quad [2]
\]

Often the reaction orders of zincate and hydroxide ions obtained from the anodic portion of a polarization curve are different from those obtained from the cathodic portion. The reaction order of hydroxide ions varies from 1.0 to 3.6, and that of zincate ions changes from 0.65 to 0.8, and the exchange current density varies from 0.5 to 400 mA/cm\(^2\). For engineering purposes, it may be reasonable to use the Butler-Volmer equation as the overall kinetic expression.

If the anodic current density on a zinc electrode is too high, the electrode will become passivated by the coverage of insulating zinc oxide (ZnO). At room temperature, the minimum current density that will cause the passivation is about 100 to 200 mA/cm\(^2\). For a Zn/Air battery utilizing...
a porous zinc electrode, the actual current density is normally lower than this limiting value. Therefore, electrode passivation may be less important than depletion of hydroxide ions and pore plugging by zinc oxide for the Zn/Air battery.

Both solid zinc oxide (ZnO) and solid potassium zincate (K₂Zn(OH)₄) are electrical insulators and have higher molar volumes than metallic zinc; consequently, their precipitation in a zinc electrode may cause pore blockage in addition to electrode passivation. Their precipitation rates depend on alkaline concentration, initial electrode porosity, and applied current density.

At the air electrode, oxygen gas undergoes several transport steps before being electrochemically reduced at reaction sites. These steps include transfer into the gas fed porous layer by diffusion and convection in the gas phase, dissolution into the electrolyte, and diffusion in the electrolyte phase to the reaction sites. The overall electrochemical reduction is generally expressed as

\[
\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \quad [3]
\]

Oxygen solubility and the electrode kinetics dominate the electrochemical behavior of this electrode. The kinetics of an oxygen electrode have been investigated extensively due to its applications in fuel cells and other important electrochemical industries. The kinetics of this electrode reaction depend on the catalyst used, but are generally very slow compared to that of zinc oxidation at the anode. The oxygen solubility in KOH solution is relatively small, and becomes much smaller in a highly concentrated electrolyte, and consequently, the electrode may suffer a significant voltage loss due to concentration polarization.

Development of the Mathematical Model

Since the validity of the mathematical model for a porous zinc electrode by Sunu and Bennion (3) has been verified by their experiments (4) and by others (5), this work consists of extending their model to include the features of a primary Zn/Air battery and including the separator region and the air electrode. The model consists of mass conservation equations, Ohm’s law in the solution phase and in the solid phase of the zinc electrodes, a volume balance for the solid phase, and kinetic rate expressions for zinc dissolution, oxygen reduction, and zinc oxide and potassium zincate formation. Diffusion and migration are included in the mass-transport equations. The macro homogeneous approach (17, 18) is used to develop the model.

**Porous zinc electrode.**—A general mass balance for species i in the electrolyte phase can be written for one dimension as (17)

\[
\frac{\partial C_i}{\partial t} = - \frac{\partial N_i}{\partial x} + R_i' \quad [4]
\]

where \( N_i \) represents the flux of species i, and \( R_i' \) accounts for the concentration change rate due to electrochemical and chemical reactions. Application of Eq. [4] for each ionic species yields

\[
\frac{\partial C_1}{\partial t} = - \frac{\partial N_1}{\partial x} + \frac{1}{nF} \frac{\partial t_1}{\partial x} + R_1 \quad [5]
\]

\[
\frac{\partial C_2}{\partial t} = - \frac{\partial N_2}{\partial x} + \frac{4}{nF} \frac{\partial t_2}{\partial x} + R_2 \quad [6]
\]

where subscripts, 1 and 2 represent Zn(OH)⁻ and OH⁻, respectively, and \( R_1 \) and \( R_2 \) account for the contribution due to the precipitation of solid zinc oxide and potassium zincate, as presented later.

Since the electrolyte is immobilized by an added gelling agent in a primary Zn/Air battery, the solution convection is probably insignificant and, consequently, is not included here. Also, the effect of the interaction between potassium hydroxide and zincates on the transport process is not included, which probably does not introduce an appreciable error to the model predictions, as indicated by the model simulations presented by Sunu and Bennion (3) and Isaacson et al. (5). Therefore, based on the derivations by Sunu and Bennion (3), the fluxes, \( N_1 \) and \( N_2 \) can be expressed as

\[
N_1 = -D_{CA} \frac{\partial C_A}{\partial x} + \frac{t_1}{z_1v_{IA}}t_2 \quad [7]
\]

\[
N_2 = -D_{CB} \frac{\partial C_B}{\partial x} + \frac{t_2}{z_2v_{IB}}t_2 \quad [8]
\]

where subscripts 1, 2, A, and B represent Zn(OH)⁻, OH⁻ ions, potassium zincate (K₂Zn(OH)₄), and potassium hydroxide, respectively, \( t_i \) is the charge number of species i, and \( i_2 \) is the current density in the solution phase, and \( r \) is a tortuosity factor. The diffusion coefficients \( D_i \) (i = A and B) and the transference numbers \( t_i \) (i = 1, 2) are defined with respect to the volume average velocity \( v \). The symbol \( v_j \) represents the number of ionic species per molecule for species j.

The current density in the solution phase, \( i_2 \), can be calculated using a modified Ohm’s law for the ternary electrolyte solution as given by Sunu and Bennion (3)

\[
i_2 = -\frac{\partial \phi}{\partial x} \frac{1}{nF} \left( \frac{1}{v_{IA}} \frac{\partial v_{IA}}{\partial x} + \frac{1}{v_{IB}} \frac{\partial v_{IB}}{\partial x} \right) \quad [9]
\]

where \( \phi \) is the potential in the electrolyte relative to a reference electrode of the same kind as the zinc electrode, \( s_i \) is the stoichiometric coefficient of species i in reaction [2], \( \kappa \) is the electrolyte conductivity, and \( \mu_i \) is the chemical potential of species i, which can be related to the concentrations of ionic species as follows (19)

\[
\mu_A = \mu_0^A + RT \ln \left( \frac{[C_1] + [C_2]}{[C_1]} \right) \quad [10]
\]

\[
\mu_B = \mu_0^B + RT \ln \left( \frac{[C_1] + [C_2]}{[C_1]} \right) \quad [11]
\]

where \( \gamma_A \) and \( \gamma_B \) are the mean activity coefficients of A and B which are assumed to be independent of the electrolyte concentration in this work.

The porosity of the zinc electrode increases as zinc dissolves and decreases as ZnO and K₂Zn(OH)₄ precipitate. The rate of change of the porosity is a function of time which can be expressed in terms of the partial molar volumes of zinc, zinc oxide, and potassium zincate and the precipitation reaction rates

\[
\frac{\partial \rho}{\partial t} = \frac{1}{2F} \left( V_{Zn} \frac{\partial \rho_{Zn}}{\partial x} - V_{ZnO} \rho_{ZnO} - V_{Zn} \rho_{Zn} \right) \quad [12]
\]

where \( V_i \) is the partial molar volume of species i (i = Zn, ZnO, and K₂Zn(OH)₄) and \( \rho_{Zn} \) and \( \rho_{ZnO} \) are the precipitation rates of solid ZnO and K₂Zn(OH)₄, respectively.

The potential in the solid phase of the electrode changes according to Ohm’s law

\[
i_s = I - i_2 = -\sigma(1 - \epsilon) \frac{\partial \phi}{\partial x} \quad [13]
\]

where \( I \) is the applied current density, \( \phi_0 \) is the potential in the solid phase, \( i_s \) is the current density in the solid phase, and \( \sigma(1 - \epsilon) \) represents the effective electrode conductivity with \( \epsilon \) representing the porosity related only to metallic zinc. A charge balance for the currents (\( i_s \) and \( i_2 \)) and the electrochemical reaction (reaction [2]) yields the equation

\[
\frac{\partial \phi}{\partial x} = \frac{\partial i_1}{\partial x} = \frac{i_1}{j_s} \quad [14]
\]
where $j_b$ is the transfer current per unit volume of the electrode due to reaction [2], which can be expressed by a Butler-Volmer equation (15, 16)

$$j_b = \alpha \beta \frac{F}{C_{\text{ref}}} \left( \frac{C_2}{C_{\text{ref}}} \right)^p \exp \left[ \frac{2 \alpha \beta F}{R T} (\epsilon - \epsilon_{\text{ref}}) \right]$$

- $$\alpha = a_o \left[ 1 - \epsilon_1 \left( \frac{1 - \epsilon}{1 - \epsilon_1} \right)^\gamma \right]$$

where $\alpha_o$ is the surface area of metallic zinc per unit volume of the electrode which is assumed here to be proportional to $(1 - \epsilon)$.

Air electrode.—The mass transport in the gas phase is relatively fast compared to that in the liquid phase and, consequently, the mass transport in the gas phase can be treated as if it were a steady-state case. It can be estimated that the mass-transport resistance in the gas phase is negligible compared to that in the electrolyte phase (21). Additionally, the cathode is relatively thin compared to the anode, and the reaction zone is even thinner. Therefore, the cathode can be considered as a flat-plate electrode with a large specific surface area, and its electrochemical behavior can be expressed by the equation

$$I = - \alpha \beta \frac{F}{C_{\text{ref}}} \left( \frac{C_2}{C_{\text{ref}}} \right)^p \exp \left[ \frac{2 \alpha \beta F}{R T} (\epsilon - \epsilon_{\text{ref}}) \right]$$

where $I_1$ represents the limiting current density due to the diffusion of dissolved oxygen in the electrolyte. IUPAC solubility data (22) show that the oxygen solubility and electrolyte concentration has the following relation

$$C_{\text{O}_2} = C_{\text{O}_2}^\infty \exp (-k C_{\text{O}_2})$$

where $k$ is a constant with units of cm$^3$/mol, $C_{\text{O}_2}^\infty$ is the oxygen solubility in pure water, $C_{\text{O}_2}$ represents the total concentration of the electrolyte. Therefore, the limiting cathodic current density can be further expressed as

$$I_1 = I_{\text{ref}} \exp (-k C_{\text{O}_2} - C_{\text{O}_2})$$

where $I_{\text{ref}}$ represents the limiting current density at the reference total concentration, $C_{\text{ref}}$. Consequently, Eq. [23] can be rewritten as

$$I = - \alpha \beta \frac{F}{C_{\text{ref}}} \left( \frac{C_2}{C_{\text{ref}}} \right)^p \exp \left[ \frac{2 \alpha \beta F}{R T} (\epsilon - \epsilon_{\text{ref}}) \right]$$

Summary of the modeling equations.—Equations [5], [6], [9], [12]-[14], [19], and [26] present a complete set of the equations which describe the concentrations of Zn(OH)$_2^+$ and OH$^-$; the potentials $\phi_b$ and $\phi_t$, the porosities $\epsilon$ and $\epsilon_1$, and current density $i_b$ as functions of time and position. With proper boundary conditions and initial conditions, the solution of these equations can be obtained by using a numerical method.

Boundary conditions.—Figure 1 shows a schematic view of the model cell, which consists of three boundaries and two regions. At the current collector, namely, the back side of the zinc electrode ($x = 0$), the current density in the solid phase is equal to the applied discharge current density; the current density in the electrolyte phase equals zero, and the flux of each species is zero. At the Zn electrode/separator interface ($x = x_s$), continuity of the fluxes of all species is specified. The current density in the solid phase becomes zero, and the current density in the electrolyte then equals the applied discharge current density. At the cathode ($x = x_d$), it is assumed that the concentrations of all species within the electrode are uniform, and a mass balance for species i must be used to derive the boundary conditions

$$\delta (\epsilon - \epsilon_1^t + \epsilon_1^c) \frac{\partial C_i}{\partial t} = N_{i_{\text{in}}} \frac{\delta x}{\delta t}$$

where $\epsilon_1$ and $\epsilon_1^c$ are initial porosities of the cathode reaction zone and the separator, respectively. The term $\epsilon_1$ -
Table I. Input parameters

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_0$</td>
<td>$1.0 \times 10^3 \text{cm}^2/\text{cm}^2$</td>
<td>†</td>
</tr>
<tr>
<td>$a_1$</td>
<td>$1.0 \times 10^3 \text{cm}^2/\text{cm}^2$</td>
<td>†</td>
</tr>
<tr>
<td>$b_0$</td>
<td>$1.0 \times 10^{-7} \text{cm}$</td>
<td>†</td>
</tr>
<tr>
<td>$\varepsilon_e'$</td>
<td>0.731</td>
<td></td>
</tr>
<tr>
<td>$b_1$</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>$x_1$</td>
<td>0.4 cm</td>
<td></td>
</tr>
<tr>
<td>$x_2$</td>
<td>0.42 cm</td>
<td></td>
</tr>
<tr>
<td>$\sigma$</td>
<td>$10^2 \text{S/cm}$</td>
<td>†</td>
</tr>
</tbody>
</table>

| Structure parameters |

| Reaction kinetic parameters |

| $i_{\text{a,ref}}$ | $3.0 \times 10^{-3} \text{A/cm}^2$ | † |
| $a_0$  | 0.5 | |
| $\phi_{\text{a,ref}}$ | -1.353 V | 27 |
| $p$    | 1.0 | † |
| $q$    | 1.0 | † |
| $i_{\text{c,ref}}$ | $1.5 \times 10^{-18} \text{A/cm}^2$ | † |
| $b_1$  | 1.0 | |
| $b_2$  | 1.0 | † |
| $\phi_{\text{c,ref}}$ | 0.301 V | |
| $n_{\text{a}}$ | 0.5 A/cm$^2$ | † |
| $k_{\text{r}}$ | $1.85 \times 10^{-5} \text{s}^{-1}$ | † |
| $\xi$  | 1 | |
| $\alpha_0$ | $K C_i \left( \frac{C_i}{C_{i,r}} \right)^{\frac{1}{2}} / (C_{i,p}^{3})$ | † |
| $a_0$  | 0.2 | † |
| $K$    | $3.0 \times 10^{-7} \text{mol/cm}^3$ | † |
| $b_0$  | $0.175 \times 10^{-7} \text{cm}^2/\text{mol}$ | 22 |
| $k_0$  | $1.8 \times 10^{-17} \text{s}^{-1}$ | † |
| $\xi_1$ | 3 | † |
| $s_1$  | 4 | |
| $s_0$  | 0 | † |
| $a_{i,2}$ | 0 | |
| $a_{i,2}$ | 4 | |
| $z_1$  | -2 | |
| $z_2$  | -1 | Montgomery (23).

Although the initial electrode potentials ($\phi_a$, $\phi_c$, and $\phi_r$) in both the solid phases in the anode and the cathode and in the electrolyte phase are not needed, initial guesses for these three variables are required for the iteration method. It was found that their values are critical for obtaining a converged solution for the first time step. To obtain values close to the solution, the initial guess values were obtained as follows. The electrode potential in the solid phase at the cathode ($\phi_c$) was set to a given value ($\phi_{c,\text{ref}}$); then the potential in the solution at the cathode was estimated by solving Eq. [26]}

\[ \phi(x_s) = \phi_c - \phi_{c,\text{ref}} + \frac{RT}{\rho} \ln C_x \]  

where

\[ C_x = I + \sqrt{I^2 + 4YZ} \frac{2Y}{2Y} \]  

\[ Y = a_0 \delta_{i,\text{ref}} \left( \frac{C_i}{C_{i,r}} \right)^{\beta} \]  

\[ Z = a_0 \delta_{i,\text{ref}} \left[ \exp \left\{ -k_0 \left( C_i - C_{i,r} \right) - \frac{I}{I_{\text{ref}}} \right\} \right]^{\alpha} \]  

The potential in the separator can be assumed to be linearly distributed, and, consequently, the potential in the solid phase at the anode can be estimated by solving the equation

\[ I = x_0 a_{i,\text{ref}} \left\{ \left( \frac{C_i}{C_{i,r}} \right)^{\frac{1}{3}} \exp \left\{ \frac{2a_0 F}{RT} \phi_{a}(x_s) - \phi(x_s) - \phi_{a,\text{ref}} \right\} \right\} \]  

As shown in Fig. 1, the adjustable design parameters are the electrode thickness ($x_s$), the initial zinc loading (related to $\varepsilon_i$), initial zincate concentration ($C_{i,1}$), initial KOH concentrations ($C_{i,2}$), gelling agent content (upon which the diffusion coefficient of each species and electrolyte conductivity depend), and the separator thickness ($x_s - x_1$). An
exploration for the optimum values of these parameters has been conducted by varying these parameters as described below in the Results and Discussion section. All fixed input parameters for the program are listed in Table I.

Since the solution of the model equations yields the concentrations, porosity, and the potentials as a function of position and time, other dependent variables such as the cell voltage, each component of the cell voltage loss, and the anode material utilization can be calculated as follows. The cell voltage is the potential difference at the current collector (x = 0) and at the cathode (x = x2): E = Φa - Φc. Cell voltage loss is due to the overpotential at the anode (ηa), ohmic loss across the separator (ηb), and the overpotential at the cathode (ηc). The anode material utilization for a given cutoff cell voltage can be calculated from the time to the cutoff cell voltage and the applied current density

$$\frac{V_{zo}}{2F} \frac{I_t}{(1 - e^x)x_t} \times 100\% \quad [33]$$

or from the electrode porosity change at the cutoff cell voltage

$$\frac{(1 - e^x)x_0 - \int_{x_0}^{x_2} (1 - e^x)dx}{(1 - e^x)x_s} \times 100\% \quad [34]$$

Results and Discussion

A comparison of the discharge curves between the model prediction and the experimental data provided by MATSI, Inc. (24) is presented in Fig. 2 for the battery specifications given in Table I. There are some discrepancies between the two sets of experimental data, probably because some uncertain experimental conditions may be involved. Although no attempt was made to fit the model prediction to the experimental data by using a parameter estimation technique, the model prediction curve was adjusted to be close to the experimental data by manually changing three parameters: the exchange current density for the zinc electrode reaction (iex,ref), and the two reaction rate constants for the precipitation of solid zinc oxide and solid potassium zincate (kz and kzn). The exchange current density for the zinc electrode reaction was chosen within the range of those reported in the literature, while the other two parameters (kz and kzn) were chosen arbitrarily. It can be seen from Fig. 2 that there is good agreement between the model predictions and the experimental data. The model predictions indicate that there is a rapid drop in cell voltage during the initial state of discharge, which is the expected behavior of a Zn/Air battery (25, 26). Depletion of hydroxide ions is responsible for this cell voltage drop. Following the initial drop is a plateau which extends almost to the end of discharge. Further interpretation of the discharge behavior is presented next by analyzing each component of the cell voltage loss and the distributions of the potential in the solution, the transfer current per unit volume, and the concentrations.

The cell voltage loss is attributed to the overpotentials at both the anode and cathode and the ohmic drop across the separator. Figure 3 shows the model predictions for each component of the cell voltage loss as a function of time. The overpotential at the anode is defined by the difference between the potential in the solid phase and that in the electrolyte adjacent to the electrode surface at x = x2

$$\eta_a = \phi_a(x_s) - \phi_a(x_2) - \phi_{a,ref} \quad [35]$$

The ohmic drop across the separator is defined by the potential difference in the electrolyte at the cathode and at the anode near the separator/electrode interfaces

$$\eta_b = \phi_c(x_2) - \phi_c(x_a) \quad [36]$$

and the overpotential at the cathode is defined similarly to that at the anode

$$\eta_c = \phi_a(x_2) - \phi_a(x_c,ref) \quad [37]$$

Although the cathode is a major source for cell voltage loss because of the slow kinetics for oxygen reduction, the overpotential at the cathode decreases slightly during discharge because the oxygen solubility increases as the electrolyte concentration decreases during discharge. The voltage loss across the separator increases continuously during discharge because both the porosity and the electrolyte concentration decrease, and consequently, the effective electrolyte conductivity is decreased. However, the voltage loss across the separator is negligible compared to those at the anode and the cathode. The overpotential at the anode increases rapidly at the beginning of discharge, reaches a near-plateau region, and finally increases sharply.
that at the back side. At the end of discharge, a sharp peak
trode. This is because the reactant (OH⁻) is more available
the anodic reaction preferentially occurs in the front
transfer current per unit volume as a function of the posi-
tion. The reaction rate is sensitive to the reactant concentration
behavior determines the battery performance.

Evidently, the zinc electrode be-
the negative direction, which causes a rise in the driving
potential in the electrolyte and a rapid change in the
OH⁻ concentration as shown in Fig. 5 and Fig. 8.

Since the kinetics of the zinc electrode reaction are fast,
the reaction rate is sensitive to the reactant concentration
and the electrode potential. Figure 4 shows the predicted
transfer current per unit volume as a function of the posi-
tion. The anodic reaction preferentially occurs in the front
side of the electrode, as if the transfer current were limited
within a very narrow region. This reaction zone does not
expand significantly, but gradually moves into the electrode.
This is because the reactant (OH⁻) is more available
and because the driving force for the reaction (potential
difference) in the front side of the electrode is higher than
that at the back side. At the end of discharge, a sharp peak
forms in the middle of the electrode due to a sharp shift in the
potential in the electrolyte and a rapid change in the OH⁻
concentration as shown in Fig. 5 and Fig. 8.

Figure 5 shows the predicted potential in the electrolyte
as a function of position. The potential shifts gradually in
the negative direction, which causes a rise in the driving
force for the reaction at the anode as the discharge pro-
ceeds. At the end of discharge, the potential shifts signifi-
cantly in the positive direction in the region toward the
back side of the electrode. Since the discharge is carried
out at a constant current, the anode reaction is forced to
occur at a constant rate; consequently, the electrode po-

tential in the solid phase is drawn to a very positive value
with time at an early state of discharge and decreases at
later states of discharge because the precipitation of zinc
oxide is a slow process, which results in a buildup in the
zincate concentration. On the other hand, the concentra-
tion of hydroxide ions decreases continuously, causing a
rapid rise in the zincate saturation level, and, conse-

Fig. 4. The predicted transfer current per unit volume as a function of
position at different states of discharge. The input parameters are the
same as those for Fig. 2.

Fig. 5. The potential in the electrolyte phase as a function of position
at different states of discharge. The input parameters are the same as
those for Fig. 2.

Fig. 6. The predicted porosity as a function of position at different states of discharge. The input parameters are the same as those for Fig. 2.

other hand, the porosity in the separator decreases contin-
uously because the precipitated zinc oxide and potassium
zincate accumulate continuously in this region. Therefore,
it may be inferred that pore blockage is unlikely to occur
in the zinc electrode; however, it may occur in the sepa-

Figures 7 and 8 show the predicted concentration profiles of zincate and hydroxide ions at different states of dis-
charge. The concentration of zincate ions increases rapidly
with time at an early state of discharge and decreases at
later states of discharge because the precipitation of zinc
oxide is a slow process, which results in a buildup in the
zincate concentration. On the other hand, the concentra-
tion of hydroxide ions decreases continuously, causing a
rapid rise in the zincate saturation level, and, conse-

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sium zincate. As described earlier, zinc oxidation occurs within a narrow zone, and this zone moves into the electrode. Correspondingly, the highest zincate concentration appears near the reaction zone, and this concentration peak becomes broader and gradually moves into the electrode as shown in Fig. 7. The concentration of the hydroxide ions decreases with discharge, but is larger near the cathode as expected (Fig. 8).

Figures 9 and 10 show the solid zinc oxide and solid potassium zincate as a function of position at different states of discharge. As expected, the amount of zinc oxide increases with discharge time, and its distribution is similar to that of potassium zincate. As shown in Fig. 10, the amount of solid potassium zincate increases near the end of discharge. This process will result in a rapid decrease in the concentration of hydroxide ions, and, consequently, will lead to electrode failure. It should be noted that the predicted amount of solid potassium zincate is small compared to that of ZnO.

Figure 11 shows the predicted discharge curves at different discharge rates. The predicted cell voltage increases, and the plateau region becomes flatter as the discharge rate decreases. Furthermore, the anode material utilization decreases with increasing discharge rate as indicated by the cell voltage reading 0.9 V at a lower state of discharge. The predicted discharge curves shown in Fig. 11 are qualitatively consistent with experimental data reported in the literature. However, at the high discharge rate, it appears that the predicted anode material utilization is
higher than that normally observed experimentally. One possible explanation for this is that the passivation of the zinc electrode due to zinc oxide precipitation may be an important factor in the electrode failure at a high discharge rate; this factor has not been included in the model.

The material loading is an important parameter in designing a zinc electrode. The optimum material loading is affected by many factors such as the electrolyte concentration, electrode thickness, and discharge rates. Figure 12 shows the predicted cell voltage as a function of state of discharge for electrodes loaded with different amounts of zinc. The electrode with a theoretical capacity of 630 mAh/cm² has an initial porosity of 0.731, the capacities of the other two electrodes are increased by 20% and 40% from this base case, respectively, giving the electrode porosities of 0.677 and 0.623. It is generally expected that the material utilization may decrease, but the delivered capacity may increase or at least be the same as the material loading level is increased. However, Fig. 12 indicates that both the material utilization and the delivered capacity decrease as the material loading is increased. This may be due to less electrolyte being available for a higher material loading.

Figure 13 shows the predicted discharge curves for different electrode thicknesses. By increasing the electrode thickness, the electrode capacity can be increased if the material utilization is the same. Figure 13 indicates that such a means is effective in increasing electrode capacity. Experimental data (24) also show that the material utilization is almost the same for the electrode thicknesses of 0.4 and 0.5 cm at the discharge current density of 20 mA/cm². Therefore, the model predictions are consistent qualitatively with the experimental data.
The predicted cell voltage as a function of state of discharge at different gelling content in the electrolyte. The other input parameters are the same as those for Fig. 2.

It is generally thought that to reduce the internal resistance of a Zn/Air battery the separator thickness should be reduced to a minimum. Figure 14 shows the predicted cell voltage as a function of discharge state for different separator thicknesses. As expected, the cell voltage decreases when the separator thickness is increased; however, the anode material utilization increases with separator thickness. This beneficial effect of a thicker separator may be a special case for the Zn/Air battery because material utilization depends strongly on the ratio of the amount of hydroxide ions to that of zinc. This is true because the separator serves as an electrolyte reservoir; and, consequently, the anode material utilization increases with the separator thickness. In selection of separator materials, it is therefore recommended that a relatively thick separator be used.

The viscosity of the electrolyte increases exponentially with the content of a gelling agent. A small amount of the gelling agent, for example, 0.5 weight percent (w/o), causes the viscosity to rise by three orders of magnitude. If transport parameters such as the electrolyte conductivity and diffusion coefficient of each species vary inversely with viscosity, the performance of the battery would be significantly affected by the content of the gelling agent. Simulations with the modified parameters based on the viscosity indicated that the cell voltage drops rapidly to the cut-off voltage with a small utilization of the active material (<5%). Such a utilization is unrealistic compared to those observed in experiments. The measured conductivity of the 31 w/o KOH and 2 w/o ZnO electrolyte with various Carbopol (gelling agent) decreases by about 2% per 0.5% Carbopol (21). A possible explanation is that the gelling agent becomes a solid porous absorber for the electrolyte. Within the pores of this structure the ions of the electrolyte may pass relatively freely despite the apparently high viscosity of the phase. Therefore, the effect of gelling agent content on the transport parameters is treated in the same way as that used for a porous medium. That is, the electrolyte conductivity and diffusion coefficient of each ionic species are modified by multiplying by a correction factor according to the amount of gelling agent. Figure 15 shows the predicted effect of gelling content on the discharge curves. As can be seen, the effect of gelling agent is insignificant, the anode material utilization does not change, and the cell voltage decreases only slightly when the gelling agent changes from 0.2 to 2.2%. Therefore, the amount of gelling agent needed can be determined based simply on ease of electrolyte handling.

Conclusions
A mathematical model of a primary Zn/Air battery is presented and used to predict cell performance for particular cell designs and operating conditions. The model agrees well with experimental data and could be used to determine the optimum design parameters for other operating conditions of a primary Zn/Air battery.

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LIST OF SYMBOLS
- \( a_s \): initial specific surface area of the zinc electrode, \( \text{cm}^2/\text{cm}^2 \)
- \( a_c \): effective specific surface area of the cathode, \( \text{cm}^2/\text{cm}^2 \)
- \( a_p \): initial value of solid zinc oxide, mol/cm\(^3\)
- \( a_r \): specific surface area of the zinc substrate, \( \text{cm}^2/\text{cm}^2 \)
- \( C_{1,\text{eq}} \): concentration of potassium zincate, mol/cm\(^3\)
- \( C_{1,\text{sol}} \): equilibrium concentration of potassium zincate with oxide in potassium hydroxide solution, mol/cm\(^3\)
- \( C_{r,\text{eq}} \): equilibrium concentration of potassium zincate with solid potassium zincate in potassium hydroxide solution, mol/cm\(^3\)
- \( C_{r,\text{ref}} \): reference concentration of potassium zincate, mol/cm\(^3\)
- \( C_{2,\text{eq}} \): concentration of potassium hydroxide, mol/cm\(^3\)
- \( C_{2,\text{ref}} \): reference concentration of potassium hydroxide, mol/cm\(^3\)
- \( C_{\text{O}_{2},\text{sol}} \): concentration of dissolved oxygen at the interface between gas phase and electrolyte, mol/cm\(^3\)
- \( C_{\text{O}_{2},\text{ref}} \): reference concentration of dissolved oxygen, mol/cm\(^3\)
- \( C_t \): total electrolyte concentration, mol/cm\(^3\)
- \( C_{\text{t,ref}} \): total electrolyte concentration at a reference state, mol/cm\(^3\)
- \( D_A \): diffusion coefficient of potassium zincate, cm\(^3\)/s
- \( D_B \): diffusion coefficient of potassium hydroxide, cm\(^2\)/s
- \( F \): Faraday constant, 96,487 C/mol
- \( I \): applied discharge current density, A/cm\(^2\)
- \( i_1 \): limiting current density of the air electrode due to diffusion of dissolved oxygen, A/cm\(^2\)
- \( i_{\text{ref}} \): limiting current density of the air electrode due to diffusion of dissolved oxygen evaluated at reference alkaline concentration, A/cm\(^2\)
- \( i_s \): current density in the solid phase of the zinc electrode, A/cm\(^2\)
- \( i_2 \): current density in the electrolyte phase, A/cm\(^2\)
- \( i_{\text{ex}} \): exchange current density for zinc oxidation evaluated at a reference state, A/cm\(^2\)
- \( i_{\text{ox}} \): exchange current density for oxygen reduction evaluated at a reference state, A/cm\(^2\)
- \( j_s \): transfer current per unit volume in the zinc electrode, A/cm\(^3\)
- \( K \): equilibrium constant for ZnO precipitation reaction, mol/cm\(^3\)
- \( k_c \): constant in the expression for the solubility of oxygen in KOH, cm\(^3\)/mol
- \( k_0 \): a proportionality in the kinetic expression for ZnO precipitation, mol/cm\(^3\)
- \( k_r \): reaction rate constant for precipitation of zinc oxide, s\(^{-1}\)
- \( k_n \): reaction rate constant for precipitation of zincate solid, s\(^{-1}\)
- \( N_i \): number of species i, mol/cm\(^3\)/s
- \( n \): number of electrons involved in the anode reaction
- \( n_e \): number of electrons transferred in the oxygen reduction reaction
- \( p \): reaction order with respect to hydroxide ion concentration for the cathodic reaction at the cathode reaction order with respect to the concentration of dissolved oxygen for the cathodic reaction at the air electrode
- \( q \): reaction order with respect to hydroxide ion concentration for the cathodic reaction at the air electrode
- \( R \): universal gas constant, 8.314 J/mol-K
REFERENCES