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M J. Mader
*Texas A & M University - College Station*

Ralph E. White
*University of South Carolina - Columbia, white@cec.sc.edu*

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A Mathematical Model of a Zn/Br₂ Cell on Charge

M. J. Mader and R. E. White*

Department of Chemical Engineering, Texas A&M University, College Station, Texas 77843

ABSTRACT

A mathematical model of a parallel plate electrochemical cell with a separator and a homogeneous bulk reaction is presented. The model is based on the Zn/Br₂ redox couple and can be used as an aid for the design of an efficient rechargeable storage battery. It is shown that four independent variables exist for the system at a fixed temperature: the effective separator thickness, the residence time, the channel width, and the potential driving force. Performance criteria of interest for the Zn/Br₂ battery are defined. Predictions of performance during the charging process are presented. It is shown that the cell performance improves as the effective thickness of the separator is increased, despite the associated greater cell resistance. It is also shown that a change in the residence time has little effect on cell performance.

Several companies, including Exxon and Energy Research Corporation (ERC), are pursuing the development of a zinc/bromine (Zn/Br₂) battery by building and testing various designs (1). A comprehensive mathematical model which can reasonably predict the performance of a Zn/Br₂ battery could be of great use to these companies as a tool for designing a more efficient system. Such a model would reduce the need to build and test dozens of designs.

A typical Zn/Br₂ flow battery consists of stacks of electrochemical cells in which reversible reactions occur at the electrodes. An aqueous electrolyte solution containing the reacting species is circulated through each cell in a stack and stored in external tanks. To charge the battery, a current or potential is applied to the stack while the fluid is fed to each cell from the external tanks. Energy is stored in the form of Zn and Br₂ when zinc ions (Zn²⁺) in solution are plated as solid Zn on the cathode and bromide ions (Br⁻) react within a porous layer on the anodes to form Br₂, a liquid which is soluble in the aqueous solution. However, any Br₂ that reaches the Zn electrode reacts electrochemically, thereby causing a loss of charge. To help prevent this undesirable reaction, either a separator or a complexing salt which causes an inert, insoluble Br₂-rich phase to be formed, or both, are included. An additional reaction which occurs, in the bulk of the electrolytic solution, is the partial complexation of Br₂ and Br⁻ to tri-bromide ions (Br₃⁻). The battery is discharged by circulating the stored electrolyte through the cell stack with the terminal leads of the cell stack connected to an appropriate load. The reverse of the electrochemical reactions occur at each electrode and energy is released.

In the work presented here, an attempt has been made to include as many of these features as possible into a comprehensive two-dimensional Zn/Br₂ cell model. The goal is to create a cell model from which a greater understanding of the physical phenomena affecting cell performance can be obtained and which gives reasonable performance predictions. The model presented, therefore, is derived to the greatest extent possible from scientific first principles, with a de-emphasis on empirical relationships such as mass transfer coefficients. The scope of this work does not allow all the features of a typical Zn/Br₂ cell design to be included. Only a charge mode for a single cell in the stack is considered. The electrochemical energy storage reactions producing Br₂ and Zn are included, but the Br₂ electrode is modeled without a porous layer. The undesirable Br₂ reaction competing with the Zn-deposition at the cathode is included in the model. A porous separator placed between the two electrodes in the model, but the second, Br₂-rich phase has not been considered. Finally, the complexation of Br₂ and Br⁻ to Br₃⁻ has been included in the model. In addition, a one-dimensional model, called a one-step model, which requires significantly less computation time, yet compares very well to the two-dimensional solution, has been developed.

Analysis of the model provides a set of independently adjustable parameters which are shown to control the performance of the system. To study the effect of physical phenomena on cell performance, performance criteria are defined and the independently adjustable parameters are varied. Results of the variations lead to an understanding of the complex interaction of kinetic, thermodynamic, and transport properties within the cell.

The Zn/Br₂ cell model presented is the first model developed which predicts product conversion, energy efficiency, and other quantities of practical interest to a cell designer, for a separated cell in which multiple electrode reactions occur. White et al. (2) developed a mathematical model of a parallel plate electrochemical reactor (PPER) which can predict similar quantities of interest but does not include a separator. Their work is the most desirable from which to develop a Zn/Br₂ cell model, because they start from first principles and include many of the same features present in a typical Zn/Br₂ cell. Lee and Selman (3, 4) developed a comprehensive model of a Zn/Br₂ cell but their work does not address at all the objectives desired in this work. Van Zee et al. (5) developed a Zn/Br₂ battery model which determines an energy efficiency for the entire battery but cannot predict product conversions. Fedkiw and Watts (6) developed a comprehensive model of the iron/chromium (Fe/Cr) redox battery, which, unfortunately, cannot be used for the Zn/Br₂ battery presented here.

White et al. (2) developed a mathematical model of an electrochemical reactor which, with a few modifications, is useful in developing a model of a Zn/Br₂ cell. The model of White et al. (2) consists of parallel plate electrodes and an electrolyte in laminar flow between them. Their model uses a differential mass balance in two dimensions and can handle multiple electrode reactions, as well as homogeneous reactions in the electrolyte bulk. Additionally, their model can be used to predict current efficiencies and conversions per pass of each species in solution. The model of White et al. (2) is extended here to treat the Zn/Br₂ battery.

Lee and Selman (3, 4) modeled the Zn/Br₂ system with a separator, with the particular interest of studying dendrite growth due to uneven plating of Zn. They consider the Zn/Br₂ cell as a complete unit. However, their model does not address the goals described above for the following reasons. First of all, they consider cell performance only at fixed, typical states of charge and do not vary design parameters, such as electrode length or separator thickness. Second, Lee and Selman propose corrosion of Zn as a possible reaction during charge, while it is felt here that corrosion could not occur on charge due to cathodic protection. Finally, Lee and Selman characterize their separator with parameters such as porosity and a mass-transfer coefficient which are difficult to determine experimentally. Van Zee (7) has shown that the MacMullin number, Nₘ, is an easily determined characteristic of a porous separator which, with the separator thickness, can completely describe its transport properties.

*Electrochemical Society Active Member.
Van Zee et al. (5) developed a simple Zn/Br\textsubscript{2} battery model in which they estimate cell resistances and total energy requirements to run the battery. They have found that by varying the separator thickness the energy efficiency may be increased by at least 1%, which is a considerable energy savings for an often-cycled battery. Their model is limited, however, because it does not include the capability of predicting product conversion. Also, their model does not include the effect of fluid flow rate on cell performance, such as how the flow rate affects the coulombic losses caused by the reduction of bromine at the zinc electrode on charge.

Pendick and Watts (6) have simulated an electrochemical cell which includes a separator and multiple electrode reactions, but they focus on the Fe/Cr redox system which uses porous packed bed electrodes. Their model includes studies at various states of charge, and they follow concentration changes as well as local current densities. Because they study the Fe/Cr system and have done only a small amount of work varying design parameters, their work is not helpful in understanding the Zn/Br\textsubscript{2} system. Also, they have preferred to study power requirements and current flow rather than concentration changes, which are of interest in this work.

**Model Development**

The assumptions needed to develop the model are presented first, followed by the governing equations and boundary conditions.

**Assumptions.**—A schematic of a single cell for the Zn/Br\textsubscript{2} battery is pictured in Fig. 1. It features a parallel plate reactor with a porous separator. Electrolyte is pumped to each side of the cell from separate tanks. The aqueous electrolytic solution consisting of the species Na\textsuperscript{+}, Br\textsuperscript{−}, Br\textsubscript{2}, and Zn\textsuperscript{2+} flows laminarily in the channels on both sides of the separator. It is assumed that species diffuse and migrate through the separator. However, to simplify the analysis, it is assumed that the pressure drop per unit length is identical on both sides of the cell, thereby preventing convective flow through the separator. This assumption is achieved by setting \( S_s = S_c \) and \( \nu_{Vx} = \nu_{Vyl} = \nu_{Vzz} \).

The length \( (L) \) and width \( (W) \) of both electrodes are assumed to be large relative to the gap between the electrodes \( (S) \). Nguyen et al. (8), in an extension of the model of White et al. (2), determined that if the aspect ratio \( (a = S/L) \) is less than 0.2, then the axial diffusion and migration flux terms may be neglected. It is assumed that the mobility of ionic species follows the Nernst-Einstein equation \( (u_i = D_i/RT) \) and that the Butler-Volmer equation can be used to describe the electrochemical reactions. In addition, pseudo-steady-state conditions are assumed to exist. That is, it is assumed that because of a low conversion per pass, the concentration of the feed to the cells, within the external storage tanks, changes very slowly.

On charge, the reactions that are assumed to take place at the electrodes are

\[
\begin{align*}
\text{Br}^{-} & \rightarrow 1/2 \text{Br}_2 + e^- \quad \text{(anode, reaction 1)} \\
1/2 \text{Br}_2 + e^- & \rightarrow \text{Br}^- \quad \text{(cathode, reaction 2)} \\
1/2 \text{Zn}^{2+} + e^- & \rightarrow 1/2 \text{Zn} \quad \text{(cathode, reaction 3)}
\end{align*}
\]

Reaction 1 and 3 are the desired reactions which lead to energy storage. Reaction 2 is an undesired self-discharge reaction which leads to inefficiency and energy losses. Corrosion of Zn by Br\textsubscript{2} during charge according to

\[
\text{Zn} + \text{Br}_2 \rightarrow \text{ZnBr}_2
\]

has been proposed by Lee and Selman (3, 4), but during charge, the zinc is cathodically protected, and thus corrosion is at least negligible and probably nonexistent. Due to the large voltaic driving force, hydrogen evolution at the cathode might be proposed, but this reaction has a small exchange current density on zinc electrodes. In addition, the solution is assumed to have a large enough pH that there is no appreciable concentration of hydrogen ion.

A homogeneous complexation reaction producing \( \text{Br}_3^- \)

\[
\text{Br}_2 + \text{Br}^- \rightarrow \text{Br}_3^- \quad \text{bulk, reaction 4}
\]

occurs in the solution bulk. It is assumed this reaction is fast and, thus, the concentrations of the three species are in equilibrium throughout the cell, according to the equilibrium constant given by Eigen and Kustin (9)

\[
K_{eq} = \frac{c_{\text{Br}_3^-}}{c_{\text{Br}_2}c_{\text{Br}^-}} = 17M^{-1} = 17,000 \text{ (mol/cm}^3\text{)}^{-1}
\]

The governing equations.—The cell in Fig. 1 is divided into three sections, two electrolyte flow channels of width \( S_s \) and a separator of width \( S_c \). The governing equations for each section, as developed in the PFER model of White et al. (2), include the electroneutrality condition and a steady-state material balance equation for each species.

The equations may be used to solve for the concentration \( (c_i) \) and potential \( (\phi_i) \) distributions as functions of the axial \( (x) \) and radial \( (y) \) position.

The electroneutrality condition

\[
\sum \nu_i c_i = 0 \quad \text{(2)}
\]

ensures that there is no buildup of positive or negative charge anywhere in the electrolytic solution. For steady state, the material balance equations for each species are

\[
\begin{align*}
\nabla \cdot \n_i + R_i & = 0 \quad (i = \text{Br}^-, \text{Br}_2, \text{Br}_3^-) \\
\nabla \cdot \n_i & = 0 \quad (i = \text{Na}^+, \text{Zn}^{2+})
\end{align*}
\]

where

\[
\begin{align*}
\n_i & = -D_i \nabla c_i - z_i \frac{D_i}{RT} F \nabla \phi + v_i \\
& \text{(flow channels)}
\end{align*}
\]

and

\[
\begin{align*}
\n_i & = -D_i \nabla c_i - z_i \frac{D_i}{RT} F \nabla \phi \\
& \text{(separator)}
\end{align*}
\]

In the separator, an effective diffusivity, \( D_{i,e} \), is required, given by Van Zee (7) as

\[
D_{i,e} = \frac{D_i}{N_m}
\]

where \( N_m \) is the MacMullin number. The MacMullin number is a characteristic of a porous separator, equivalent to the ratio of the separator's tortuosity to its porosity. However, unlike porosity or tortuosity, it is easily determined and not a property of solution strength, as shown by Van Zee (7). The MacMullin number is given by a resistivity ratio

\[
N_m = \frac{\rho_s}{\rho_o}
\]

where \( \rho_s \) is the resistivity of a solution without a separa-
tor in its midst, and $\rho$ is the resistivity of separator and solution together.

The velocity distribution within the flow channels is assumed to be well-developed laminar flow as given by

$$v_y = 0; \quad v_z = 6v_{avg} \left( \frac{y}{S} - \frac{y^2}{S^2} \right)$$

[9]

The material balance equations given by Eq. [3] can be simplified by assuming that reaction [4] is at equilibrium so that $R_{Br^-} = -R_{Br_2^-}$. For the species $Br^-$ and $Br_2^-$, Eq. [3] for each can be added to get

$$(-\nabla \cdot N_{Br^-} + R_{Br^-}) + (-\nabla \cdot N_{Br_2^-} + R_{Br_2^-}) = 0$$

[10]

which reduces to a governing equation consisting only of flux terms

$$\nabla \cdot N_{Br^-} + \nabla \cdot N_{Br_2^-} = 0$$

[11]

Likewise for species $Br_2$ and $Br_3^-$

$$\nabla \cdot N_{Br_2} + \nabla \cdot N_{Br_3^-} = 0$$

[12]

Since the number of equations has been reduced by one, the equilibrium expression of Eq. [1] is needed to describe the system fully. Therefore, Eq. [1], [2], [4], [11], and [12] comprise the set of governing equations needed to solve the system for the unknown variables, $c_i$ and $\Phi$.

As postulated by White et al. (2) and later demonstrated by Nguyen et al. (8), when the aspect ratio ($\alpha = S/L$) is small, then the diffusion and migration terms of the flux expression in the axial, or flow, direction are negligible compared to the radial or normal diffusion and migration terms. Thus, upon converting to the dimensionless variables

$$\eta = y/S$$

[14]

$$\eta' = \begin{cases} \frac{y}{S_{\alpha}} & 0 < y < S_{\alpha} \\ \frac{y - (S_{\alpha} + S_{\beta})}{S_{\beta}} & (S_{\alpha} + S_{\beta}) < y < S \end{cases}$$

[15]

$$\theta_i = c_i/c_{i,ref}$$

[16]

$$P_e = \frac{2S_v_{ave}}{D_{ii}}$$

[17]

the divergence of the flux of species $i$ in Eq. [4], [11], and [12] may be rewritten for the flow channels as

$$\frac{S'}{c_{i,ref} D_{ii}} \left( \nabla \cdot N_i \right) = -\frac{\partial \theta_i}{\partial \eta} R \left[ \frac{\partial \Phi}{\partial \eta} \right] + \frac{\partial \theta_i}{\partial \eta} \frac{\partial \Phi}{\partial \eta} + \frac{D_{ii}}{D_{i}} \Phi \left( \eta' \right) \left( \eta' - \eta \right) \frac{\partial \theta_i}{\partial \eta}$$

[18]

and for the separator as

$$\frac{S'}{c_{i,ref} D_{si}} \left( \nabla \cdot N_i \right) = -\frac{\partial \theta_i}{\partial \eta} \frac{\partial \Phi}{\partial \eta} + \frac{D_{si}}{D_{i}} \Phi \left( \eta' \right) \left( \eta' - \eta \right) \frac{\partial \theta_i}{\partial \eta}$$

[19]

Note that two dimensionless radial variables are used in Eq. [18]. The variable $\eta$ is made dimensionless by the total electrode gap $S$, and is used to define the step size in any section when converting the differential governing equations to finite difference form. The variable $\eta'$ is made dimensionless by the flow channel width $S_{\alpha}$, and is needed to express position within the flow channels, since the local electrolyte velocity depends on the relative position within the channel. Note also that the Peclet number is defined here in terms of $S$ (Eq. [17]) instead of $S_{\alpha}$, which would be more appealing physically; however, since no dimensionless analysis is presented in this paper, the definition of $P_e$ is arbitrary.

**Initial and boundary conditions.** To complete the system of equations, the initial and boundary conditions must be specified. Conditions are specified at the cell entrance, the electrodes, and the electrolyte/separator interface.

The initial conditions at the cell entrance and boundary conditions at the electrodes are the same as specified by White et al. (2). At the cell entrance, the feed concentrations are known, and the electroneutrality condition must hold

$$\eta = 0 \text{ (anode)}$$

[21]

and

$$\eta = 1 \text{ (cathode)}$$

[22]

where $i_{inj}$ is the current density for reaction $j$, $s_i$ is the stoichiometric coefficient for each species in the electrochemical reaction, $n_i$ is the number of electrons transferred in the reaction, and $N_{inj}$ is the net normal flux of species $i$, in which the derivatives are defined to be in the positive $y$ direction. It should be pointed out that the signs used for $N_{inj}$ in Eq. [21] and [22] are consistent with the convention that positive current leaves the anode to enter the electrolytic solution, and negative current from the solution enters the cathode.

The normal component of the current density for reaction $j$, $i_{inj}$, is given by the Butler-Volmer equation, as given by White et al. (11)

$$i_{inj} = i_{inj,ref} \prod_i \left( \frac{\eta_{i,ref}}{\eta} \right)^{\alpha_i} \exp \left( \frac{\eta_{i,ref}}{RT} \eta \right)$$

[23]

where $\alpha_i$ is the dimensionless local surface concentration and $\eta_{i,ref}$ is the reaction overpotential, defined as

$$\eta_{i,ref} = V_{i,ref} - \Phi_{i,ref} - U_{i,ref}$$

[24]

In Eq. [24], $V_i$ is the electrode potential (either $V_a$ or $V_c$), $\Phi_{i,ref}$ is the potential of the solution at the surface of that electrode (either $\Phi_{i,ref}$ or $\Phi_{i,ref}$), and $U_{i,ref}$ is the local open-circuit potential of reaction $j$ at the reference concentrations. The open-circuit potential is a thermodynamic parameter of the solution given by

$$U_{i,ref} = U_{i,ref} - U_{i,ref} - \frac{RT}{n_i F} \sum_i s_i \ln \left( \frac{c_{i,ref}}{d_i} \right)$$

[25]
does everywhere in the reactor) and that the normal flux of each species is continuous across the interface. That is, at the anolyte/separator interface

$$\text{at } y = S_A \quad N_{n,A} = N_{n,S}$$  \[26\]

Expanding with the normal flux terms in Eq. [5] and [6] and converting to dimensionless quantities, this boundary condition becomes

$$\text{at } y = S_A \quad -\frac{\partial \theta}{\partial \eta} \bigg|_A - \frac{zF}{RT} \theta \left( \frac{\partial \Phi}{\partial \eta} \right) \bigg|_A = -\frac{1}{N_n} \left( \frac{\partial \theta}{\partial \eta} \right)_S - \frac{zF}{RT} \theta \left( \frac{\partial \Phi}{\partial \eta} \right)_S \quad \text{[27]}$$

where $\partial \theta / \partial \eta$ and $\partial \Phi / \partial \eta$ are evaluated at the interface, but wholly within the region of their respective subscript. Note that $D_i$ has been canceled from this equation, but the MacMullin number, $N_m$, does not cancel. At the separator/catholyte interface, the boundary condition is similar.

In an effort to cut down on calculation time, a simple model was developed in which only one step was taken in the flow direction (see Mader et al. [12]). This model assumes that $i_o$ is a constant along the length of the reactor and therefore not a function of $y$ as in the previous case. Similarly, $c_i$ and $\Phi$ become functions of $y$ only. In this way, the cell acts much like a CSTR in the flow direction. At a given value of $\eta$, there is only a step change in concentration of a species from its feed value to its exit value, instead of a gradual concentration gradient down the length of the reactor as in the more complicated model. (To distinguish the two models, the simple one will be called the one-step model and the other the continuous model.)

In the one-step model, a finite difference expression over the length of the reactor replaces the axial concentration gradient in the convection term of the continuous model

$$\frac{\partial c_i}{\partial x} \approx \frac{c_i - c_{i,\text{feed}}}{L}$$  \[28\]

In dimensionless coordinates, with $c_i,\text{ref} = c_{i,\text{feed}}$, Eq. [28] becomes

$$\frac{\partial \theta_i}{\partial \zeta} \approx \frac{\theta_i - 1}{1}$$  \[29\]

All other equations from the continuous model remain the same in the one-step model.

Because it essentially becomes a one-dimensional model, the one-step model is a less accurate solution of the electrochemical cell than the two-dimensional continuous model. However, the one-step model does retain the concepts of radial gradients across the cell and the possibility of multiple electrode reactions occurring at each electrode. In addition, the one-step model requires less computer time to solve. The accuracy of the one-step model relative to the continuous model essentially depends on the conversion per pass of the system. The assumption that the concentration in the flow direction is uniform is reasonable for a system only if the conversion per pass is small, as is often the case for a Zn/Br$_2$ cell.

**Parameters.**—The parameters used in the model consist of the fixed parameters of the cell and the independently adjustable parameters. The fixed parameter values used in the Zn/Br$_2$ cell model are given in Table I. The system was set up to simulate as closely as possible the design of Exxon (5, 13, 14) from which the most design parameters were available. The feed composition at initial conditions, $\theta_{\text{feed}}$, is assumed to be the same in both channels, for convenience. To determine the concentration of each species in the feed, it is first assumed that the solution is composed of Na$^+$, Br$^-$, Br$_2$, and Zn$^{2+}$ at the reference concentrations listed in Table I, and that Br$^-$ and Br$_2$ are uncomplexed. Then, an equilibrium calculation is done using the tri-bromide complexation reaction and $K_{	ext{eq}_{\text{Br}^3-}}$ to determine the adjusted concentrations of Br$^-$ and Br$_2$, and the corresponding equilibrium concentration of Br$_3^-$.

The literature contains a variety of parameter values and methods for determining these parameters. The adjusted parameter values for the Zn/Br$_2$ cell were chosen to duplicate current densities reported in Ref. (13). When compared to values in the literature (19, 20), these $i_{o,\text{ref}}$ were within an order of magnitude. The model input variable parameters are the length of the electrode ($L$), the average velocity of the electrolyte ($v_{\text{ave}}$), the flow channel width ($S$), the thickness of the separator ($S_s$), the MacMullin number ($N_m$), and the applied cell potential ($E_{\text{cell}} = V_e - V_r$). Note that the total electrode gap ($S$) is a linear combination of the flow channel width ($S$) and the separator thickness, and is therefore not an input variable, since it is completely specified by the other widths. Upon reviewing the governing equations and boundary conditions and analyzing the model results, it is found that only four independently adjustable parameters exist in the model, although six input variables may be specified. A meaningful set of independent parameters consists of the residence time of the electrolyte in the cell, $L/v_{\text{ave}}$ (which appears as a ratio in the term $\text{Pec}$), the flow channel width, $S$ (which appears alone as the denominator in the definition of $\eta$), the effective separator thickness, $N_mS_s$ (which appears as a product in the denominator of the finite difference form of Eq. [27], as shown in Ref. [21]), and the cell potential, $E_{\text{cell}}$ (since $V_e$ and $V_r$ are relative to the same reference potential). Van Zee (7) showed in a separator flow-through experiment that the product $N_mS_s$ is important as a group, and not $N_m$ or $S_s$, separately. In the case of the Zn/Br$_2$ cell, the model indicates that $N_mS_s$ is also an independent variable for flow by a separator.

Table I. Fixed parameter values for the Zn/Br$_2$ cell

<table>
<thead>
<tr>
<th>Reaction (j)</th>
<th>$i_{o,\text{ref}}$ (A/cm$^2$)</th>
<th>$P_{\text{ref}}$</th>
<th>$q_{\text{ref}}$</th>
<th>$\theta_{\text{ref}}$</th>
<th>$U_j^{\text{ref}}$ (V)</th>
<th>$U_j^{\text{ref}}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0331</td>
<td>0.5</td>
<td>0.5</td>
<td>1</td>
<td>1.087</td>
<td>1.783</td>
</tr>
<tr>
<td>2</td>
<td>0.0331</td>
<td>0.5</td>
<td>0.5</td>
<td>1</td>
<td>1.087</td>
<td>1.783</td>
</tr>
<tr>
<td>3</td>
<td>1.000</td>
<td>0.5</td>
<td>0.5</td>
<td>1</td>
<td>-0.763</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Reactions (Homogeneous, bulk) $K_{	ext{eq}_{\text{Br}^3-}} = 17000$ (mol/cm$^3$)$^{-1}$

Stoichiometry and electrochemical reaction orders

<table>
<thead>
<tr>
<th>Species (i)</th>
<th>$x_i$</th>
<th>$D_{\text{ref}}$ ($\text{cm}^2$/s)</th>
<th>$c_{i,\text{ref}}$ (mol/cm$^3$)</th>
<th>$\theta_{\text{ref}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$</td>
<td>0</td>
<td>1.334</td>
<td>1.00</td>
<td>1.000</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>1</td>
<td>2.084</td>
<td>3.00</td>
<td>0.983</td>
</tr>
<tr>
<td>Br$_2$</td>
<td>0</td>
<td>1.310</td>
<td>0.65</td>
<td>0.0203</td>
</tr>
<tr>
<td>Br$_3^-$</td>
<td>2</td>
<td>0.754</td>
<td>1.00</td>
<td>1.000</td>
</tr>
<tr>
<td>Br$_4^-$</td>
<td>1</td>
<td>1.310</td>
<td>0.10</td>
<td>0.510</td>
</tr>
</tbody>
</table>

* Chosen to duplicate current densities reported in Ref. (13).
* See Ref. (15).
* The reference electrode is reaction [3] at the reference conditions.
* See Ref. (9).
* Limiting reactant at Br$^-$ electrode.
* Limiting reactant at Zn electrode.
* See Ref. (16-18); $D_{\text{ref}}$ assumed equal to $D_{\text{ave}}$.
* At initial charging conditions, the feed to each channel is assumed to be the same, for convenience.
In this study, each of the individual parameters, $L$, $v_{ave}$, $S_a$, $S_o$, $N_m$, and $E_{cell}$ are set at values to be expected in a typical Zn/Br$_2$ battery. The parameter $L/v_{ave}$ is varied by changing either $L$ or $v_{ave}$, or both, during runs. The length, $L$, is varied between 20 and 30 cm in this study, while $v_{ave}$ is varied between 2.0 and 1.5 cm/s. The channel flow width ($S_a$) is assigned values between 0.005 and 0.10 cm. Either $N_m$ or $S_o$ is varied to alter $N_mS_o$ with $N_m$ varying between 1.5 and 10.0, and $S_o$ between 0.02 and 0.12 cm. For $E_{cell}$, $V_a$ is set equal to 0 V for convenience, and $V_s$ is varied between 1.85 and 2.025 V.

**Solution Technique and Material Balance Closure**

Having set the fixed and variable parameters, the system equations can be solved for the concentration and potential distributions by using an implicit stepping technique in the axial direction (for the two-dimensional model) and Newman’s technique (16) in the radial direction. This solution procedure is discussed by White et al. (2) and Mader et al. (12). To ensure that the average current densities predicted by the model are consistent with the predicted average exit concentrations of each species, a material balance closure is done on each species. At steady state, the molar (or mass) rate of consumption or production of a species by electrochemical and homogeneous reaction within the cell must equal the net molar (or mass) flow rate of that species through the reactor from entrance to exit. A quantitative evaluation of the material balance closure statement was done for each case studied and the model predictions were found to be consistent each time. Further information on this test for consistency can be found by referring to Mader (21).

**Results and Discussion**

Once the consistency of the solution technique is verified, the concentration and potential distributions can be used to analyze the Zn/Br$_2$ cell model. First, performance criteria of specific interest to this cell are derived. Then, $N_mS_o$ is verified as an independent parameter. Next, the two-dimensional model and one-step model predictions are compared. Examples of performance predictions that can be obtained from the Zn/Br$_2$ model at initial charging conditions are then presented. Finally, the performance of the cell as a function of the state of charge of the system is considered for three values of the effective separator thickness, $N_mS_o$, and three values of the residence time.

**Performance criteria**—To develop a meaningful set of performance criteria for the Zn/Br$_2$ cell, the desirable characteristics of a rechargeable battery system should be considered. First, it is important to keep the cell current at a relatively low level to prevent dendritic growth of zinc during charging. Second, it is important that a rechargeable battery can be charged quickly. A third desirable characteristic, during the charging process, is a low rate of energy consumption relative to the rate of storage of the product. The rate of energy consumption is the product of the applied voltage and the total cell current. The charging rate is equivalent to the rate of production, $P_{cell}$. So, in general, the energy consumption per mole of product stored can be defined as

$$w_i = \frac{I_{cell}(L/W)E_{cell}}{P_{cell}}$$

[34]

Note that the electrode area cancels out. Substituting Eq. [31] for the production rate of Br$_2$, into Eq. [34] and rearranging yields

$$w_{br_2} = \frac{(E_{cell})(L/W)i_{ave}}{S_o} \Delta C_{br_2}$$

[35]

where $\Delta C_{br_2} = (C_{br_2,feed,o} + C_{br_2,feed,a}) - (C_{br_2,feed,o} + C_{br_2,feed,a})$. The energy consumption per mole of Br$_2$ stored is defined by using Eq. [33] for $P_{br_2}$, giving

$$w_{br_2} = \frac{n_{br_2}E_{cell}(i_{ave})}{S_o}$$

[36]

A final characteristic desirable in a rechargeable battery is a high energy efficiency, a quantity related to the energy consumption term. The energy efficiency is defined as the product of the coulombic efficiency and the voltaic efficiency

$$\eta_T = \eta_c\eta_V$$

[37]
The coulombic efficiency is a measure of the fraction of current passed which gives the desired reaction. At the anode, the \( \text{Br}_2 \) reaction runs uncontested so that the coulombic efficiency is unity. The coulombic efficiency of more interest is the current efficiency at the cathode, which is defined as

\[
\varepsilon_c = \frac{|i_{\text{avg}}|}{i_{\text{cell}}} \tag{38}
\]

The voltaic efficiency on charge is defined as the ratio of the theoretical voltage required for charging, to the actual applied voltage. The theoretical required voltage is given by the open-circuit potential of the cell based on the reference conditions. That is, it is the difference of the half-cell potentials for the desired reactions. Therefore, the voltaic efficiency on charge is given by

\[
\varepsilon_e = \frac{U_{\text{cell}} - U_{\text{ref}}}{E_{\text{cell}}} \tag{39}
\]

The applied cell potential, \( E_{\text{cell}} \), includes the two causes of voltaic inefficiency, the overpotentials, \( \eta \), defined earlier in conjunction with the Butler-Volmer equation, and the potential drop across the cell due to ohmic resistance of the separator and the electrolyte. The potential drop across the cell, or IR drop, is defined as

\[
\text{IR drop} = \Phi_{\text{an}} - \Phi_{\text{c}} \tag{40}
\]

where \( \Phi_{\text{an}} \) and \( \Phi_{\text{c}} \) are the potentials of the electrolytic solution at the \( \text{Br}_2 \) electrode and Zn electrode, respectively.

Substituting the definitions of coulombic and voltaic efficiencies into Eq. [37], the total energy efficiency of the cell on charge may be rewritten as

\[
\varepsilon_r = \frac{|i_{\text{avg}}|}{i_{\text{cell}}} \frac{(U_{\text{cell}} - U_{\text{ref}} - \Delta \text{ir})}{(i_{\text{cell}})E_{\text{cell}}} \tag{41}
\]

which is the fraction of energy applied to the cell that leads to useful storage of energy. Note that this definition of total energy efficiency does not take into account energy losses external to the charging process, such as the energy required to pump the electrolyte or the heat losses caused by friction. A procedure for estimating such additional losses is given by Van Zee et al. (5).

The energy efficiency as defined in Eq. [41] may be used to redefine the energy consumption per mole of Zn. Solving Eq. [41] for \( E_{\text{cell}} \), substituting into Eq. [38] and rearranging gives

\[
o_{\text{ir}} = \frac{(U_{\text{cell}} - U_{\text{ref}} - \Delta \text{ir})|\eta_0|\Phi_{Zn,\text{ref},1} \epsilon_{i}}{\epsilon_{r}} \tag{42}
\]

which indicates that the energy consumption per mole of Zn is a function of only \( \epsilon_{r} \) and fixed system parameters. Note particularly that \( o_{\text{ir}} \) is a minimum when the energy efficiency is 100%. Using the values in Table I for the constants in Eq. [42] and assuming 100% efficiency, the minimum possible energy consumption per mole of Zn produced is 344.1 kJ/mol Zn. A similar calculation for \( \text{Br}_2 \) yields the same value of minimum energy consumption of 344.1 kJ/mol \( \text{Br}_2 \), since at 100% efficiency 1 mol of \( \text{Br}_2 \) is produced for every mole of \( \text{Br}_2 \) stored.

**Effective separator thickness**—A simple verification that the product \( N_{\text{m}}S_s \) is an independent parameter in a cell with a separator, and not \( N_{\text{m}} \) or \( S_s \) separately, is given in Table II. While keeping \( L/V_{\text{avg}} \), \( E_{\text{cell}} \), and \( S_s \) constant, the reactor performance is the same when \( N_{\text{m}} \) and \( S_s \) are adjusted, as long as the effective separator thickness, \( N_{\text{m}}S_s \), is held constant. Note that Table II also shows that the total cell gap, \( S \), may be adjusted without affecting the reactor performance, thus verifying that \( S \) is not an independent parameter for a separated cell.

**Comparison of the one-step and the continuous models**.—A comparison of performance criteria for the Zn/\( \text{Br}_2 \) cell as predicted by the one-step and by the continuous models is presented in Table III. The continuous model for the Zn/\( \text{Br}_2 \) cell employs a variety of axial step sizes in order to step down the reactor as quickly as possible and still retain accuracy to three digits in solving for \( c_0 \) and \( \Phi \). To achieve this accuracy, step sizes on the order of 6% of the reactor length, step sizes of \( h = 0.01 \) are acceptable. The agreement between the one-step and continuous models is as good as 1.3%, for IR drop in the case shown. The worst agreement between the two techniques is for \( \epsilon_{r} \), at 5.6% in the case shown. The agreement is very good for the Zn/\( \text{Br}_2 \) cell because the fractional conversion of reactant is small, about 1.3% for \( \text{Br}^{-} \) and 0.8% for \( \text{Zn}^{2+} \) when \( S_s = 0.065 \text{cm} \). As the channel width, \( S_s \), gets smaller, the conversion increases due to a smaller reactor volume. Accordingly, the agreement between models worsens, to about 10% for \( \epsilon_{r} \), when \( S_s = 0.02 \text{cm} \), at which the conversion for \( \text{Br}^{-} \) is about 4.1% and for \( \text{Zn}^{2+} \) is about 2.6%. Because the agreement is good and the difference in computation time is so great (up to 100 times faster for the one step), the one-step model is used in all subsequent work to predict the performance of the cell.

**Performance predictions at the initial state of charge**.—The Zn/\( \text{Br}_2 \) cell model can be used to predict cell

![Table III. Comparison of the one-step to the continuous model for the Zn/\( \text{Br}_2 \) cell](image)
Fig. 2. The effect of applied cell potential on the production rate per area of electrode, of Br₂ and Zn, at initial charging conditions.

Fig. 3. The effect of channel width on the energy consumption per mole of Br₂ stored, at initial charging conditions.

Fig. 4. The effect of effective separator thickness on the average current density and potential drop across the cell, at initial charging conditions.

Fig. 5. The effect of effective separator thickness on the total energy efficiency, at initial charging conditions (\(\varepsilon_0 = 0.9384\)).
the amount of Zn$^{2+}$ which has been consumed and deposited for following the state of charge of a Zn$\text{Br}_2$ battery is quoted as Zn. The percentage of Zn$^{2+}$ plated as solid Zn, the concentration and potential distributions in the cell charge—Figures of Exxon (13) has determined that a convenient parameter is SA for three values of $\frac{L}{v_{avg}}$ as charging continues, as discussed below.

Performance predictions at various states of charge.—Figures 6–11, in which the state of charge is followed for three values of $N_{e,SA}$ (Fig. 6–8) and three values of $L/v_{avg}$ (Fig. 9–11), resolve the problems found of mismatched production rates and poorer performance as the effective separator thickness is increased at the thicker separator.

Although pseudo-steady state is assumed in the model, the concentration and potential distributions in the cell do change over long periods of time, and therefore the state of charge and cell performance also change. Bellows of Exxon (13) has determined that a convenient parameter for following the state of charge of a Zn$\text{Br}_2$ battery is the amount of Zn$^{2+}$ which has been consumed and deposited as Zn. The percentage of Zn$^{2+}$ plated as solid Zn, then, can be defined as the difference between the original amount of Zn$^{2+}$ introduced as feed to the system and the amount of Zn$^{2+}$ currently entering the cell. The initial feed concentration of Zn$^{2+}$ introduced to both channels of the cell is $c_{\text{Zn}^{2+},\text{feed},A}$ while the amount currently entering the system is $c_{\text{Zn}^{2+},\text{feed},C}$ in the anolyte and $c_{\text{Zn}^{2+},\text{feed},C}$ in the catholyte. Therefore, the percentage of Zn$^{2+}$ plated relative to the start-up concentration of Zn$^{2+}$ is:

$$\% \text{Zn}^{2+} \text{plated} = 100% \times \left[ 1 - \frac{S_A(c_{\text{Zn}^{2+},\text{feed},A} - c_{\text{Zn}^{2+},\text{feed},C})}{S_A(c_{\text{Zn}^{2+},\text{feed},A} - c_{\text{Zn}^{2+},\text{feed},C}) + S_C(c_{\text{Zn}^{2+},\text{feed},C} - c_{\text{Zn}^{2+},\text{feed},C})} \right]$$  \hspace{1cm} [43]

or, when $S_A = S_C$:

$$\% \text{Zn}^{2+} \text{plated} = 100% \times \left[ 1 - 0.5(\theta_{\text{Zn}^{2+},\text{feed},A} + \theta_{\text{Zn}^{2+},\text{feed},C}) \right]$$  \hspace{1cm} [44]

Bellows (13) claims that when approximately 70% of the Zn$^{2+}$ ions are plated, the system is fully charged. Because of the large amount of computer time required to follow the state of charge, studies were limited to approximately 25% of Zn$^{2+}$ plated.

In order to follow the concentration distribution as a function of the state of charge, it is necessary to assume that the exit average concentration of each species in each channel, at a known state of charge, will be the feed concentration of each species for that particular channel at some later state of charge. That is, it is reasonable to assume that since the composition of anolyte and catholyte is assumed to change slowly under pseudo-steady-state conditions, then the composition leaving the cell at any state of charge will eventually be duplicated in the storage tanks and thus in the feed to the anolyte and catholyte channels. Also, it is assumed that the anolyte is...
stored in a tank separate from the catholyte tank, so that the feed composition of each channel changes independently. Although the assumptions that the process is under pseudo-steady-state conditions and that the exit composition at one state of charge is the feed composition at a future state of charge are valid only for very low conversion, these assumptions at least present a rough estimate of the performance possible as a function of the state of charge.

Cases studied under charging conditions include three effective thicknesses of the separator and three settings of residence time, under otherwise fixed conditions. For all cases, the start-up composition of the electrolyte is the same as that used to study initial charging conditions. The applied cell potential and channel are also fixed, with \( E_{\text{cell}} = 1.9 \) V and \( S_a = 0.065 \) cm. For the cases in which the effective separator thickness is varied, \( L/v_{\text{avg}} \) is fixed at 15s and the three values of \( N_{eS_a} \) studied are 0.06, 0.12, and 0.18 cm. For the cases in which the residence time is varied, \( N_{eS_a} = 0.18 \) cm and the three values of \( L/v_{\text{avg}} \) studied are 10, 15, and 20s. These cases were chosen as representative of typical cell designs. The performance of the cells with different separators under charging conditions is shown in Figs. 6-8 and the performance of the cells at different residence times is shown in Figs. 9-11.

The predicted effect of \( N_{eS_a} \) on \( \varepsilon_t \) under charging conditions is demonstrated in Fig. 6. For each of the three cases shown, \( \varepsilon_t \) improves through the initial charging process, levels off at a maximum efficiency, and then drops at 15s and the three values of \( N_{eS_a} \) studied are 0.06, 0.12, and 0.18 cm. For the cases in which the residence time is varied, \( N_{eS_a} = 0.18 \) cm and the three values of \( L/v_{\text{avg}} \) studied are 10, 15, and 20s. These cases were chosen as representative of typical cell designs. The performance of the cells with different separators under charging conditions is shown in Figs. 6-8 and the performance of the cells at different residence times is shown in Figs. 9-11.

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Likewise, the thickest separator, at 0.18 cm, has the slowest production rate at initial charging conditions, but shows the best performance at the highest states of charge. At initial charging conditions, \( P_{\text{zn}} \) is significantly less than \( P_{\text{br}} \), but as the state of charge increases to the moderate to high range, \( \text{zn} \) is deposited faster than \( \text{br} \), is stored, for each of the cells considered. This behavior is important to the success of the \( \text{zn}/\text{br} \) battery. Because the battery is a closed system, it is necessary that in a complete cycle of charge and discharge, \( \text{br} \) is not produced in excess of the amount of \( \text{zn} \) deposited, and vice versa. Figure 7 shows that although \( \text{br} \) is initially produced faster than \( \text{zn} \), fortunately the relative rates reverse so that through a full charging process, the amounts of each stored species will be approximately equivalent. Integration of \( P_{\text{zn}} \) and \( P_{\text{br}} \) over the length of charge will indicate whether \( \text{br} \) or \( \text{zn} \) is lost in each cycle, allowing prediction of the number of cycles until the concentrations are badly mismatched.

In Fig. 8, the energy consumption based on both \( \text{br} \) and \( \text{zn} \) is illustrated as charging progresses, for the three values of \( N_{eS_a} \). As the cell is charged, \( \omega_{\text{br}} \) increases quite dramatically and is particularly sensitive to the thickness of the separator. At an initial state of charge, the value of \( \omega_{\text{br}} \) is identical for every value of \( N_{eS_a} \), but as the state of charge progresses past 20% of the \( \text{zn} \) ions deposited, the energy required to produce and store a mole of \( \text{br} \) when \( N_{eS_a} = 0.06 \) cm is more than double that required when \( N_{eS_a} = 0.18 \) cm. The value of \( \omega_{\text{zn}} \) is likewise sensitive to the effective thickness of the separator.

As with the production rates, it is important that the energy consumed to produce and store each of \( \text{br} \) and \( \text{zn} \) be equivalent for a full cycle of the battery. Figure 8 demonstrates that over a large amount of charging, the energy consumption per mole of \( \text{zn} \) is about the same as the consumption per mole of \( \text{br} \).
Consideration of Fig. 6-8 as a whole shows that the value of the three separators considered, the thickest one, with \( N_s S_s = 0.18 \) cm, is by far the best. This thickness gives the highest efficiency and production rates of \( \text{Br}_2 \) and \( \text{Zn}^{2+} \) per area of electrode, over the range of charge considered, and provides a dramatically lower energy consumption per mole of both \( \text{Br}_2 \) and \( \text{Zn}^{2+} \). In addition, when \( N_s S_s \) has a value of 0.18 cm, Fig. 6-8 suggests that to achieve the best battery, charging should be begun approximately when the status of the battery is at a state of charge of 3% \( \text{Zn}^{2+} \)-plated, rather than at a fully discharged state, and that the battery should be charged up only to a 20% deposit of \( \text{Zn}^{2+} \). Within this range of charge, \( \epsilon, \Phi_{an}, \Phi_{cat}, \) and \( \omega_{an}, \omega_{cat} \), all reach optimum values and \( P_{an} \) and \( \omega_{an} \) deteriorate, but at acceptable rates. On the other hand, at states of charge lower than a 5% deposit of \( \text{Zn}^{2+} \) ions, performance criteria begin to deviate from their optimum values rapidly.

In Fig. 9-11, a change in residence time on cell performance under charging conditions is shown to have little effect. Figure 9 shows that varying the residence time between values of 10, 15, and 20s has only a slight effect on \( \epsilon_t \), and the divergence that occurs is most pronounced at initial charging states or when the battery is charged for extended periods of time.

In Fig. 10, again there is very little variance in production rates of either \( \text{Br}_2 \) or \( \text{Zn}^{2+} \) as the residence time is changed. Perhaps most remarkable is that at the highest states of charge illustrated (above 15% deposition of \( \text{Zn}^{2+} \)), the production rate of \( \text{Br}_2 \) per surface area of anode is equivalent for all three residence times. Note that \( P_{an} \) starts out at an initial state of charge very low relative to the rate of storage of \( \text{Br}_2 \).\( P_{an} \) rises slightly and then drops off slower than \( P_{an} \) with \( \text{Zn}^{2+} \) eventually being produced at a rate higher than \( \text{Br}_2 \) is stored. Such behavior again is desired, because over a cycle of charge and discharge, it is important that neither \( \text{Br}_2 \) nor \( \text{Zn}^{2+} \) be produced.

In Fig. 11, through all states of charge, \( \omega_{an} \) diverges very little due to different values of \( L/v \). On the other hand, \( \omega_{an} \) is shown to be unaffected by \( L/v \) only when the energy consumption is at its most optimum, between states of 5% and 10% deposition of \( \text{Zn}^{2+} \). A residence time of 20s provides the minimum value of \( \omega_{an} \) for all states of charge.

Consideration of Fig. 9-11 shows that a change of residence time has little effect on overall cell performance, whether efficiency, production rate, or energy consumption. This is especially true relative to the change in performance undergone, as charging progresses, when \( N_s S_s \) is varied. The optimum value of \( L/v \) among the three values considered, is the largest time, 20s. The trends shown suggest that lengthening the residence time beyond 20s will further enhance the predicted performance. If the charging process is restricted between 5 and 20% of \( \text{Zn}^{2+} \)-plated as discussed earlier, however, then Fig. 9-11 indicate that the value of \( L/v \) used has virtually no effect on \( \epsilon_t, P_t, \) or \( \omega_{an} \).

Conclusions
The \( \text{Zn}/\text{Br}_2 \) cell model presented is a useful tool to aid in the design of a complete battery system. Its ability to predict accurately the performance of cells within batteries currently under development by Exxon, ERC, and others is untested because data are very limited for proprietary reasons. However, it is a versatile model which can be extended easily or modified to fit assumptions not used here. In addition, the model can be used in conjunction with a parameter estimation technique and experimental results from a working cell to determine unknown system constants such as diffusivities, \( D_i \) exchange current densities, \( i_{ex,an} \) and \( i_{ex,cat} \), and reaction transfer coefficients, \( \alpha_{anj} \) and \( \alpha_{catj} \).

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LIST OF SYMBOLS

- \( c_i \): concentration of species \( i \), mol/cm\(^3\)
- \( \overline{c}_{av,an} \): average concentration of species \( i \) in the anolyte channel, mol/cm\(^3\)
- \( \overline{c}_{ref} \): reference concentration of species \( i \), mol/cm\(^3\)
- \( D_i \): diffusion coefficient of species \( i \), cm\(^2\)/s
- \( E_{j} \): effective diffusion coefficient of species \( i \) in the separator, cm\(^2\)/s
- \( d_i \): density of pure solvent, kg/cm\(^3\)
- \( D_{li} \): diffusion coefficient of limiting reactant, cm\(^2\)/s
- \( E_{cell} \): applied cell potential (= \( V_s - V_o \), V)
- \( I \): Faraday's constant, 86,487 C/mol
- \( I_{total} \): total cell current, mA
- \( i_{ave} \): average current density at an electrode (= \( I/LW \)), mA/cm\(^2\)
- \( i_{j} \): normal component of current density due to reaction \( j \), mA/cm\(^2\)
- \( \overline{i}_{av,an} \): normal average current density due to reaction \( j \), mA/cm\(^2\)
- \( i_{ex,an} \): exchange current density of reaction \( j \), mA/cm\(^2\)
- \( I_{RD} \): potential drop across the cell (= \( \Phi_{an} - \Phi_{cat} \), V)
- \( K_{eq} \): equilibrium constant for tri-bromide reaction, mol/cm\(^3\)
- \( L \): electrode length, cm
- \( L/\nu \): residence time of the reactor, s
- \( N_i \): flux vector of species \( i \), mol/cm\(^2\)-s
- \( N_{nl} \): number of electrons passed in reaction \( j \)
- \( N_m \): MacMullin number in the separator
- \( N_{w} \): effective separator thickness, cm
- \( N_{w} \): normal component of the flux (\( y \)- or \( \eta \)-direction) of species \( i \), mol/cm\(^2\)-s
- \( P_i \): production rate of species \( i \) per electrode area, mol/cm\(^2\)-s
- \( P_{an} \): anodic reaction order of species \( i \) in reaction \( j \)
- \( P_{cat} \): cathodic reaction order of species \( i \) in reaction \( j \)
- \( R \): gas law constant, 8.314 J/mol-K
- \( R_{i} \): homogeneous reaction rate, mol/cm\(^2\)-s
- \( S_i \): total electrode gap, cm
- \( S_{an} \): catholyte channel length, cm
- \( S_{cat} \): anode channel width, cm
- \( s_j \): stoichiometric coefficient of species \( i \) in reaction \( j \)
- \( S_{an} \): anolyte channel width, cm
- \( S_{cat} \): catholyte channel width, cm
- \( S_{an} \): width of the separator, cm
- \( S_{cat} \): electrode gap, cm
- \( \Phi_{an} \): anode potential, V
- \( \Phi_{cat} \): cathode potential, V
- \( \Phi_{cell} \): potential of electrode, V
- \( \Phi_{electrolyte} \): electrolyte potential, V
- \( V_s \): average potential of the electrolyte, V
- \( V_e \): velocity component of the electrolyte in the x-direction, cm/s
- \( v \): velocity of the electrode, V
- \( w \): breadth of the electrode, cm
- \( x \): axial coordinate, cm
- \( y \): normal coordinate, cm
- \( z_i \): charge number of species \( i \)

Greek
- \( \alpha \): aspect ratio, \( S/L \)
- \( \alpha_{an} \): anodic transfer coefficient for reaction \( j \)
- \( \alpha_{cat} \): cathodic transfer coefficient for reaction \( j \)
- \( \Delta \sigma \): average difference in concentration of bromine-carrying species (\( \text{Br}_2 \) and \( \text{Br}^- \)) from entry to exit, mol/cm\(^2\)
- \( \epsilon \): coulombic efficiency
- \( \epsilon_\alpha \): total cell energy efficiency
- \( \epsilon_\gamma \): voltaic efficiency
- \( \xi \): dimensionless axial coordinate (x/L)
- \( \eta \): dimensionless normal coordinate (y/S)
- \( \eta \): potential at electrode surface (\( V_e - \Phi_{cell} \))
- \( \gamma \): dimensionless normal coordinate, specific to a flow channel
- \( \eta_i \): dimensionless concentration of species \( i \) (\( c_i/c_i^{ref} \))
- \( \eta_{ref} \): dimensionless feed concentration of species \( i \)
- \( \Delta \xi \): dimensionless concentration of species \( i \) at the electrode surface
- \( \rho \): resistivity of separator and its surrounding electrolytic solution, ohm-cm
- \( \rho_0 \): resistivity of the pure electrolytic solution, ohm-cm

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The Lithium Surface Film in the Li/SO₂ Cell

K. M. Abraham* and S. M. Chaudhri

EIC Laboratories, Incorporated, Norwood, Massachusetts 02062

ABSTRACT

Evidence is presented which suggests that the Li surface film in the LiSO₂ cell comprises a complex mixture of products which include Li₂S and several Li sulfur-oxy compounds. Elemental analysis, IR spectral, and XPS data indicate that the Li sulfur-oxy compounds may be Li₂SO₄, Li₂SO₃, Li₂SO₂, and Li₂SO₆.

Lithium batteries, particularly those containing liquid electrolytes, owe their stability to protective films on the Li anode surface. These films, formed by spontaneous reaction of Li with the electrolyte solution, have been identified to affect such battery properties as voltage decay, between the Li anode and a liquid electrolyte is the LiC₁₀₄ Li anode surface. These films, formed by spontaneous reaction of Li with the electrolyte solution, have been identified to affect such battery properties as voltage decay, self-discharge and serves as a barrier to further reactions across it, behaves as an electronic insulator preventing rechargeability (4), and safety (1, 5).

The Lithium Cell

One of the most extensively studied interphases between the Li anode and a liquid electrolyte is the LiCl film in the Li/ClO₄ cell (1, 3). Studies of the morphological and electrical properties of this film have led to the recognition of it as a solid electrolyte interphase (SEI). Such an interphase, while allowing the migration of Li across it, behaves as an electronic insulator preventing self-discharge and serves as a barrier to further reactions between the Li anode and the electrolyte. It is now accepted that a SEI or a conceptually similar film exists in all liquid electrolyte Li batteries and the film is formed instantaneously upon contact of the Li anode with the electrolyte. This compact SEI is believed to be the “protective” film. The latter is often covered by a coarse porous film whose thickness is determined by, among other factors, the length of exposure of the Li electrode to the electrolyte. The chemical composition and physical properties of Li surface films have also been studied in PCl/ClO₂ (6), THF/LiAsF₆ (7), and Li,S, (8).

It has been believed all along that the Li surface film in the LiSO₄ cell solely comprised Li₂SO₄ (1). However, recent studies have begun to indicate a more complex composition for the film. Auger spectroscopic results of Nebesny et al. (9) of fresh Li surfaces after exposure to low levels of SO₄ indicate the presence of Li,S and Li₂O. X-ray photoelectron spectroscopic (XPS) studies of similar Li surfaces by Hoenigman and Keil (10) showed the presence of Li sulfur-oxy compounds in addition to Li₂O and Li,S. The latter authors also found only Li₂O and Li,S at low levels of SO₄ exposure. With longer SO₄ exposure, however, they observed the evolution of XPS peaks at 168.8, 166, and probably 163.2 eV. Considering that only 1.3 eV separates the 163.2 eV peak from the Li,S main peak at 161.9 eV, the former could be the 2P⁵/₂ transition of the sulfide. The sulfur 2P⁷/₂ - 3/₂ doublet separation, evaluated from the spectra of a number of Li sulfur-oxy compounds, is ~1 eV. The peak at 168.8 eV was assigned to Li₂SO₄. No assignment was given to the peak at 166 eV. Recently we reported (11) on the composition of the Li surface film in the LiSO₄ cell comprised a complex mixture of several Li sulfur-oxy compounds including Li₂S, and Li₂SO₄. Lately, we have examined by SEM, IR, and XPS, the Li surfaces of a large number of LiSO₄ cells after they have been subjected to various regimes of discharge, such as partial and full discharge at low to moderate rates, high current pulse discharge, and forced overdischarge. The results of these studies have led us to conclude that the Li surface film in the LiSO₄ cell comprises a complex mixture of products including several Li sulfur-oxy compounds and Li,S. Our results are reported in this paper.

Experimental

All the experiments involving manipulation of air sensitive materials were carried out inside a Vacuum Atmo-