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A Mathematical Model of a Zn/Br₂ Cell on Charge

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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.

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.

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 (Br₂⁻). 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 on 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 Br₂⁻ 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.

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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.

Pedlow 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}, 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 \( S_s = S_a \) and \( v_{s,k} = v_{a,k} \).

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 \( (u = D_i/RT) \) 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 Br\textsubscript{3}− 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)

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

Governing equations.—The cell in Fig. 1 is divided into three sections, two electrolyte flow channels of width \( S_a \), and a separator of width \( S_s \). The governing equations for each section, as developed in the PPER 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 \( (c) \) and potential \( (\Phi) \) distributions as functions of the axial \( (x) \) and radial \( (y) \) position.

The electroneutrality condition

\[
\sum z_i c_i = 0 \tag{2}
\]

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

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

where

\[
\text{Ni} = -D_i \nabla c_i - z_i \frac{D_i}{RT} \frac{F c_\Phi}{\nabla \Phi} + v c_i \quad \text{(flow channels)}
\]

and

\[
\text{Ni} = -D_i \nabla c_i - z_i \frac{D_i}{RT} \frac{F c_\Phi}{\nabla \Phi} \quad \text{(separator)}
\]

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

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

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

\[
v_y = 0; \quad v_x = 6u_{avg} \left( \frac{y}{S_A} - \frac{y^2}{S_A^2} \right) \tag{9}\]

The material balance equations given by Eq. [3] can be simplified by assuming that reaction \([4]\) is at equilibrium so that \( R_{Br^-} = R_{Br_3^-} = -R_{Br_3^-}. \) For the species \( Br^- \) and \( Br_3^- \), Eq. [3] for each can be added to get

\[
(-\nabla \cdot N_{Br^-} + R_{Br^-}) + (-\nabla \cdot N_{Br_3^-} + R_{Br_3^-}) = 0 \tag{10}\]

which reduces to a governing equation consisting only of flux terms

\[
\nabla \cdot N_{Br^-} + \nabla \cdot N_{Br_3^-} = 0 \tag{11}\]

Likewise for species \( Br_2^- \) and \( Br_3^- \)

\[
\nabla \cdot N_{Br_2^-} + \nabla \cdot N_{Br_3^-} = 0 \tag{12}\]

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, \( z_i \) 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

\[
\eta = \frac{y}{S} \tag{14}\]

where \( \eta \) is the reaction overpotential defined as

\[
\eta = V_{oc} - \Phi_{oc} - U_{oc} \tag{24}\]

In Eq. [24], \( V_{oc} \) is the electrode potential (either \( V_a \) or \( V_c \)), \( \Phi_{oc} \) is the potential of the solution at the surface of that electrode (either \( \Phi_{oc}^a \) or \( \Phi_{oc}^c \)), and \( U_{oc} \) 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

\[
U_{oc} = U_{j} - U_{oc} = \frac{RT}{n_i F} \sum s_{i} \ln \left( \frac{c_{i,ref}}{d_i} \right) \tag{25}\]

with the subscript \( \text{RE} \) referring to an arbitrary reference electrode. \( V_{oc}, \Phi_{oc}, U_{j}, \) and \( U_{oc} \) are all defined relative to a reference electrode.

The boundary conditions at the separator/electrolyte interface are that the electroneutrality condition holds and that the rate of consumption or production of a species by electrochemical reaction at the electrode is equal to the net normal flux of the species toward or away from the electrode. That is

\[
\text{at } \eta = 0 \quad \text{(anode)} \quad \frac{s_{i,an}}{n_i F} = -N_{si} \tag{21}\]

and

\[
\text{at } \eta = 1 \quad \text{(cathode)} \quad \frac{s_{i,cath}}{n_i F} = N_{si} \tag{22}\]

where \( s_{i,j} \) 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 \( N_{si} \) 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 \( N_{si} \) 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 \( j, s_{i,j} \), is given by the Butler-Volmer equation, as given by White et al. (11)

\[
t_{i,j} = t_{i,ref} \prod_{i} \left( \frac{\mathcal{F} \eta}{RT} \right) \exp \left( \frac{\alpha_i \mathcal{F} \eta}{RT} \right) \tag{23}\]

where \( \mathcal{F} \) is the local dimensionless surface concentration and \( \eta \) is the reaction overpotential, defined as

\[
\eta = V_{oc} - \Phi_{oc} - U_{oc} \tag{24}\]

In Eq. [24], \( V_{oc} \) is the electrode potential (either \( V_a \) or \( V_c \)), \( \Phi_{oc} \) is the potential of the solution at the surface of that electrode (either \( \Phi_{oc}^a \) or \( \Phi_{oc}^c \)), and \( U_{oc} \) 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

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with the subscript \( \text{RE} \) referring to an arbitrary reference electrode. \( V_{oc}, \Phi_{oc}, U_{j}, \) and \( U_{oc} \) are all defined relative to a reference electrode.

The boundary conditions at the separator/electrolyte interface are that the electroneutrality condition holds (as it
does everywhere in the reactor) and that the normal flux of each species is continuous across the interface. That is, at the anolyte/separato interface

\[ \text{at } y = S_a, \quad \frac{\partial q_i}{\partial y} = \frac{q_i}{N_{na,b}} \]  

[26]

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

\[ \text{at } y = S_a, \quad \frac{\partial q_i}{\partial y} = -\frac{z_i F}{RT} \frac{\partial \Phi}{\partial y} \]

\[ = -\frac{1}{N_{na,b}} \left( \frac{\partial q_i}{\partial y} \right)_{S_a} = \frac{1}{N_{na,b}} \left( \frac{\partial \Phi}{\partial y} \right)_{S_a} \]  

[27]

where \( \partial q_i / \partial y \) and \( \partial \Phi / \partial y \) 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, \( N_{mSs} \), 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 \( i_0 \) is a constant along the length of the reactor and therefore not a function of \( \eta \) as in the previous case. Similarly, \( c_i \) and \( \Phi \) become functions of \( \eta \) 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

\[ \frac{\partial x_i}{\partial x} \approx \frac{x_i - c_{i,ref}}{L} \]  

[28]

In dimensionless coordinates, with \( c_{i,ref} = c_{i,ref} \), Eq. [28] becomes

\[ \frac{\partial \theta_i}{\partial \xi} \approx \frac{\theta_i - 1}{1} \]  

[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/Br₂ 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/Br₂ 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, \( \theta_{i,ref} \), 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 \( \text{Na}^+ \), \( \text{Br}^- \), \( \text{Br}_2^- \), and \( \text{Zn}^{2+} \) at the reference concentrations listed in Table I, and that \( \text{Br}^- \) and \( \text{Br}_2^- \) are uncomplexed. Then, an equilibrium calculation is done using the tri-bromide complexation reaction and \( K_{eq} \) to determine the adjusted concentrations of \( \text{Br}^- \) and \( \text{Br}_2^- \), and the corresponding equilibrium concentration of \( \text{Br}_3^- \). After all other parameters were set, the exchange current densities \( i_{0,ref} \) were picked by trial and error to give current densities similar to that reported by Exxon (13). When compared to values in the literature (19, 20), these \( i_{0,ref} \) were within an order of magnitude.

The model input variable parameters are the length of the electrode (\( L \)), the average velocity of the electrolyte (\( \bar{v} \)), the flow channel width (\( S_a \)), the thickness of the separator (\( S_s \)), the MacMullin number (\( N_{mSs} \)), and the applied cell potential (\( E_{cell} = V_s - V_r \)). Note that the total electrode gap (\( S \)) is a linear combination of the flow channel widths 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, \( L/\bar{v} \), the flow channel width, \( S_a \) (which appears alone as the denominator in the definition of \( \eta \)), the effective separator thickness, \( N_{mS} \) (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, \( E_{cell} \) (since \( V_s \) 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/Br₂ cell, the model indicates that \( N_{mS}S \) is also an independent variable for flow by a separator.
In this study, each of the individual parameters, $L$, $v_{ave}$, $S_a$, $S_b$, $N_{M}$, 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, within 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 $S_b$ is varied to alter $N_{M}S_b$, with $N_{M}$ varying between 1.5 and 10.0, and $S_b$ between 0.02 and 0.12 cm. For $E_{cell}$, $V_c$ is set equal to 0 V for convenience, and $V_a$ 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 the test for consistency can be found by referring to Mader (21).

Performance criteria.—To develop a meaningful set of performance criteria for the Zn/Br$_2$ cell to charge, 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 anode material. Second, it is important that a rechargeable battery system should be capable of charging at a 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, $P_{cell}LW$. So, in general, the energy consumption per mole of product stored can be defined as

$$a_1 = \frac{(E_{cell})(LW)_{avg}}{P_{cell}LW}$$

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

$$a_{Br_2} = \frac{(E_{cell})(LW)_{avg}}{S_b} \frac{i_{ave}}{\Delta C_{Br_2}}$$

where $\Delta C_{Br_2} = (C_{Br_2,feed,A} + C_{Br_2,feed,S})$ - $\Delta C_{Br_2} = (C_{Br_2,feed,A} + C_{Br_2,feed,S})$. The energy consumption per mole of Zn stored is defined by using Eq. [33] for $P_{Zn}$, giving

$$a_{Zn} = \frac{(n_F)(E_{cell})}{S_{l,Zn,ave}} \frac{i_{ave}}{i_{l,Zn,ave}}$$

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

$$\eta_T = \eta_{coul} \eta_V$$
The coulombic efficiency is a measure of the fraction of current passed which gives the desired reaction. At the anode, the Br₂ 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

\[ \eta_c = \frac{1}{1 + \frac{[\text{cell}]}{[\text{volts}]} } \]  

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

\[ \eta_v = \frac{U_{\text{cell}} - U_{\text{ref}}}{E_{\text{cell}}} \]  

The applied cell potential, \( E_{\text{cell}} \), includes the two causes of voltaic inefficiency, the overpotentials, \( \eta_p \), 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

\[ \text{IR drop} = \Phi_a - \Phi_e \]  

where \( \Phi_a \) and \( \Phi_e \) are the potentials of the electrolytic solution at the Br₂ 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

\[ \eta_t = \frac{\eta_c \eta_v}{\left( \frac{\text{IR drop}}{E_{\text{cell}}} \right)} \]  

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

\[ \eta_{\text{Zn}} = \frac{\eta_c \eta_v}{\left( \frac{\text{IR drop}}{E_{\text{cell}}} \right)} \]  

which indicates that the energy consumption per mole of Zn is a function of only \( \eta_c \) and fixed system parameters. Note particularly that \( \eta_{\text{Zn}} \) 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 Br₂ yields the same value of minimum energy consumption of 344.1 kJ/mol Br₂, since at 100% efficiency 1 mol of Zn is produced for every mole of Br₂ 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/Br₂ cell as predicted by the one-step and by the continuous models is presented in Table III. The continuous model for the Zn/Br₂ 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 \( \eta_c \) and \( \Phi \). To achieve this accuracy, step sizes on the order of \( \Delta \chi = 10^{-2} \) are required at the entrance due to the large driving force instantaneously applied, while in the last 60% of the reactor length, step sizes of \( \Delta \chi \approx 0.01 \) 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 \( \eta_t \), at 5.6% in the case shown. The agreement is very good for the Zn/Br₂ cell because the fractional conversion of reactant is small, about 1.3% for Br₂⁻ and 0.8% for Zn₂⁺ when \( S_s = 0.065 \) cm. As the channel width, \( S_s \), gets smaller, the conversion increases due to a smaller reactor volume. Consequently, the agreement between models worsens, to about 10% for \( \eta_t \) when \( S_s = 0.02 \) cm, at which the conversion for Br₂⁻ is about 4.1% and for Zn₂⁺ 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/Br₂ cell model can be used to predict cell efficiency. 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 Br₂ yields the same value of minimum energy consumption of 344.1 kJ/mol Br₂, since at 100% efficiency 1 mol of Zn is produced for every mole of Br₂ stored.

**Table II. Demonstration that the effective separator thickness is an independent parameter**

<table>
<thead>
<tr>
<th>( N_{\text{m}} )</th>
<th>( S_s ) (cm)</th>
<th>( N_{\text{m}}S_s ) (cm)</th>
<th>( S = S_s + S_s ) (cm)</th>
<th>( \eta_t ) (mA/cm²)</th>
<th>( t_{\text{calc}} ) (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>0.06</td>
<td>0.12</td>
<td>0.19</td>
<td>0.6322</td>
<td>20.54</td>
</tr>
<tr>
<td>3.0</td>
<td>0.04</td>
<td>0.12</td>
<td>0.17</td>
<td>0.6322</td>
<td>20.54</td>
</tr>
<tr>
<td>6.0</td>
<td>0.02</td>
<td>0.12</td>
<td>0.15</td>
<td>0.6322</td>
<td>20.54</td>
</tr>
</tbody>
</table>

**Table III. Comparison of the one step to the continuous model for the Zn/Br₂ cell**

<table>
<thead>
<tr>
<th>Input parameters: ( L/v_{\text{avg}} = 15s ), ( E_{\text{cell}} = 1.9V ), ( S_s = 0.065 ) cm</th>
<th>% Difference (from continuous)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( t_{\text{calc}} ) (mA/cm²)</td>
<td>19.69</td>
</tr>
<tr>
<td>( \text{IR drop} ) (mV)</td>
<td>15.146</td>
</tr>
<tr>
<td>( E_{\text{ref}} ) (mV)</td>
<td>10.507</td>
</tr>
<tr>
<td>( E_{\text{ref}} ) (mole/cm²) ( \times 10^9 )</td>
<td>6.724</td>
</tr>
<tr>
<td>( \Phi_a ) (mole/cm²) ( \times 10^9 )</td>
<td>0.619</td>
</tr>
<tr>
<td>( \Phi_e ) (mole/cm²) ( \times 10^9 )</td>
<td>0.619</td>
</tr>
</tbody>
</table>
performance at a specific state of charge as a function of any of the independent parameters. Figures 2-5 show some of the performance predictions that can be made at the initial state of charge corresponding to the feed concentrations listed in Table I.

For instance, the predicted effect of $E_{cell}$ on $P_{Br_2}$ and $P_{zn}$, at initial charging conditions, is shown in Fig. 2. Note that the rate at which $Br_2$ is stored is significantly different from the rate at which Zn is stored. It is important that $P_{Br_2}$ is not greater than $P_{zn}$ throughout all states of charge, since the amount of product ($Br_2$ and Zn) and of reactant ($Br^-$ and $Zn^{2+}$) would become greatly mismatched quickly, causing battery failure. This problem is resolved when considering performance under charging conditions. Figure 2 also suggests that the battery can be
charged about as rapidly as desired, by increasing the applied cell potential. However, since the amount of current passed will also increase with \( E_{\text{cell}} \), the maximum allowable value of current density to avoid dendrite growth must be carefully considered.

In Fig. 3, the predicted effect of \( S_r \) on the energy consumption per mole of \( Br_2 \) is illustrated at initial charging conditions. The dashed line indicates the theoretical minimum value of \( \omega_{\text{mex}} \) for \( Br_2 \). At values of \( S_r \) less than 0.02 cm, the energy consumption per mole of \( Br_2 \) stored rises unacceptably high, while for values of \( S_r \) greater than 0.05 cm, \( \omega_{\text{mex}} \) levels out to about 368 kJ/mol of \( Br_2 \). Figure 3 shows that, at the initial state of charge, the energy consumption per mole of \( Br_2 \) is dramatically and adversely affected by narrow flow channels. It suggests that designing a cell with channel widths of less than 0.02 cm is not advisable.

Figure 4 illustrates the predicted effect of \( N_{\text{mex}}/S_r \) on the IR drop and on \( I_{\text{avg}} \), at initial charging conditions. Figure 4 shows that the potential drop increases as \( N_{\text{mex}}/S_r \) increases, as expected, since the separator contributes to the overall cell ohmic resistance. Figure 4 also shows that the average current density drops with increasing \( N_{\text{mex}}/S_r \) since the cell mass-transfer resistance is increased by the thicker separator.

Figure 5 demonstrates the predicted effect of \( N_{\text{mex}}/S_r \) on the total energy efficiency at initial charging conditions. Because \( E_{\text{cell}} \) is fixed at 1.9V, the voltaic efficiency is fixed at \( 1.783/1.9 = 0.9384 \). Thus, Fig. 5 is actually a measure of the change of coulombic efficiency with effective separator thickness. At initial charging conditions, the relationship between \( E_r \) and \( N_{\text{mex}}/S_r \) is nearly linear, with the efficiency surprisingly dropping as the separator resistance increases. This performance suggests that, at least at the state of charge considered, the increased mass transfer and ohmic resistance of the separator unfortunately influences the cell performance more strongly than does the beneficial aspect of preventing \( Br_2 \) diffusion from the anode to the cathode. This trend is reversed 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 \( N_{\text{mex}}/S_r \) (Fig. 6-8) and three values of \( L/v_{\text{avg}} \) (Fig. 9-11), resolve the problems found of mismatched production rates and poorer performance as the effective separator thickness is increased at the initial state of charge.

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 \( Zn/Br_2 \) 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 \( C_{zn^{2+},\text{feed,a}} \) while the amount currently entering the system is \( C_{zn^{2+},\text{ref,a}} \) in the anolyte and \( C_{zn^{2+},\text{ref,c}} \) in the catholyte. Therefore, the percentage of \( Zn^{2+} \) plated relative to the start-up concentration of \( Zn^{2+} \) is

\[
%Zn^{2+} \text{ plated} = 100% \times \left[ \frac{S_r(S_{zn^{2+},\text{ref,c}} - S_{zn^{2+},\text{ref,a}}) + S_r(S_{zn^{2+},\text{ref,c}} - S_{zn^{2+},\text{ref,a}})}{S_r(S_{zn^{2+},\text{ref,c}} + S_{zn^{2+},\text{ref,a}})} \right]
\]

or, when \( S_r = S_c \):

\[
%Zn^{2+} \text{ plated} = 100% \times \left[ 1.0 - 0.5(\theta_{zn^{2+},\text{feed,a}} + \theta_{zn^{2+},\text{feed,c}}) \right]
\]

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 \( E_{\text{on}} = 1.9V \) and \( S_A = 0.065 \) cm. For the cases in which the effective separator thickness is varied, \( /v_{\text{avg}} = 10 \), 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 Fig. 6-8 and the performance of the cells at different residence times is shown in Fig. 9-11.

The predicted effect of \( N_{s}S_\) on \( \epsilon_f \) under charging conditions is demonstrated in Fig. 6. For each of the three cases shown, \( \epsilon_f \) improves through the initial charging process, levels off at a maximum efficiency, and then drops steadily as the cell is charged further. At initial charging conditions, up to about 2% of \( \text{Zn}^{2+} \) storage, the efficiency is best for the cell with the thinnest separator (0.06 cm) and worst for the cell using the thickest separator (0.18 cm). This behavior is due to the differences in cell mass transfer and ohmic resistance for the three separators. As the charging process continues, however, \( \epsilon_f \) becomes optimum for the cell with the thickest separator and the lowest for the cell with the thinnest separator considered, as shown in Fig. 6. In addition, the discrepancy between cell designs becomes more pronounced as the amount of charge progresses. Figure 6 shows, therefore, that the separator overcomes the disadvantage of an increased cell resistance when the effective thickness of the separator is increased, by minimizing the amount of \( \text{Br}_2 \) which diffuses from the anolyte to the catholyte. Therefore, a thicker separator is necessary to improve the cell energy efficiency, especially when the cell is to be driven to a high state of charge. For instance, if it is desired to keep \( \epsilon_f \) above 0.5 through a state of charge of 30% \( \text{Zn}^{2+} \) plated, then \( N_{s}S_\) must be greater than 0.18 cm.

The response of \( P_{\text{zn}} \) and \( P_{\text{br}} \) to the three cells of various effective separator thickness, as charging progresses, is shown in Fig. 7. Again, for the lowest states of charge, the cell with the separator of width 0.06 cm shows the best performance, having the highest production rate for either \( \text{Br}_2 \) or \( \text{Zn} \), but as charging continues, the production rate drops to the lowest of the three cases considered.

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 \( \text{Br}_2 \) is stored, for each of the cells considered. This behavior is important to the success of the \( \text{Zn}/\text{Br}_2 \) battery. Because the battery is a closed system, it is necessary that in a complete cycle of charge and discharge, \( \text{Br}_2 \) is not produced in excess of the amount of \( \text{Zn} \) deposited, and vice versa. Figure 7 shows that although \( \text{Br}_2 \) 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 \( P_{\text{br}} \) and \( P_{\text{zn}} \) over the length of charge will indicate whether \( \text{Br}_2 \) or \( \text{Zn}^{2+} \) 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 \( \text{Br}_2 \) and \( \text{Zn} \) is illustrated as charging progresses, for the three values of \( N_{s}S_\). As the cell is charged, \( \omega_{\text{sp}} \) increases quite dramatically and is particularly sensitive to the thickness of the separator. At an initial state of charge, the value of \( \omega_{\text{sp}} \) is identical for every value of \( N_{s}S_\), but as the state of charge progresses past 20% of the \( \text{Zn}^{2+} \) ions deposited, the energy required to produce and store a mole of \( \text{Br}_2 \) when \( N_{s}S_ = 0.06 \) cm is more than double that required when \( N_{s}S_ = 0.18 \) cm. The value of \( \omega_{\text{sp}} \) 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 \( \text{Br}_2 \) 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 \( \text{Br}_2 \).
Consideration of Fig. 6-8 as a whole shows that the value of the three separators considered, the thickest one, with $N_a S_a = 0.18$ cm, is by far the best. This thickness gives the highest efficiency and production rates of $\text{Br}_2$ and $\text{Zn}$ 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 $\text{Zn}$. In addition, when $N_a S_a$ has a value of 0.18 cm, Fig. 6-8 suggest that to achieve the best battery, charging should be begun approximately when the status of the battery is at a state of charge of 5% $\text{Zn}^{2+}$ 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, $\xi$, $P_{\text{en}}$, and $\omega_{\text{en}}$, all reach optimum values and $P_{\text{en}}$ and $\omega_{\text{en}}$ deteriorate, but at acceptable rates. On the other hand, at states of charge lower than 5% $\text{Zn}^{2+}$ plated, $\xi$, $P_{\text{en}}$, and $\omega_{\text{en}}$ exist at decidedly nondesirable values, while at states of charge higher than a 20% 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 20 s has only a slight effect on $\xi$, 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 $\text{Zn}$ 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 $P_{\text{en}}$ starts out at an initial state of charge very low relative to the rate of storage of $\text{Br}_2$. $P_{\text{en}}$ rises slightly and then drops off slower than $P_{\text{en}}$ with $\text{Zn}$ 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 excess $\text{Br}_2$ nor excess $\text{Zn}$ be produced.

In Fig. 11, through all states of charge, $\omega_{\text{en}}$ diverges very little due to different values of $L/v_{\text{sys}}$. On the other hand, $\omega_{\text{en}}$ is shown to be unaffected by $L/v_{\text{sys}}$ only when the energy consumption is at its most optimum, between a 5% and 10% deposition of $\text{Zn}^{2+}$. A residence time of 20 s provides the minimum value of $\omega_{\text{en}}$ 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 $N_a S_a$ is varied. The optimum value of $L/v_{\text{sys}}$ among the three values considered, is the largest time, 20 s. The trends shown suggest that lengthening the residence time beyond 20 s will further enhance the predicted performance. If the charging process is restricted between 5 and 20% deposition of $\text{Zn}^{2+}$ as discussed earlier, however, then Fig. 9-11 indicate that the value of $L/v_{\text{sys}}$ used has virtually no effect on $\xi$, $P_{\text{en}}$, or $\omega_{\text{en}}$.

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 needed 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, $i_{\text{en}}$, and reaction transfer coefficients, $a_{\text{en}}$, and $a_{\text{en}}$.

Acknowledgment

This work was supported in part by the Center for Energy and Minerals Research at Texas A&M University.

LIST OF SYMBOLS

- $c_i$: concentration of species $i$, mol/cm$^3$
- $c_{\text{ave}, i}$: average concentration of species $i$ in the anolyte channel, mol/cm$^3$
- $c_{\text{feed}, i}$: feed concentration of species $i$, mol/cm$^3$
- $c_{\text{ref}, i}$: reference concentration of species $i$, mol/cm$^3$
- $D_i$: diffusion coefficient of species $i$, cm$^2$/s
- $D_{\text{ex}}, j$: effective diffusion coefficient of species $i$ in the separator, cm$^2$/s
- $d$: density of pure solvent, kg/cm$^3$
- $D_{\text{diff}}$: diffusion coefficient of limiting reactant, cm$^2$/s
- $e_{\text{cell}}$: applied cell potential ($= V_0 - V_e$), V
- $I$: Faraday's constant, 96,487 C/mol
- $E_{\text{cell}}$: total cell current, mA
- $i_{\text{ave}}$: average current density at an electrode ($= I/LW$), mA/cm$^2$
- $i_{\text{n}}$: normal component of current density due to reaction $j$, mA/cm$^2$
- $i_{\text{n}, \text{ave}}$: normal average current density due to reaction $j$, mA/cm$^2$
- $i_{\text{ex}}, j$: exchange current density of reaction $j$, mA/cm$^2$
- $IR$ drop: potential drop across the cell ($= \Phi_{\text{ref}} - \Phi_e$), V
- $K_{\text{eq}}$: equilibrium constant for tri-bromide reaction, mol/cm$^3$
- $L$: electrode length, cm
- $L/v_{\text{sys}}$: residence time of the reactor, s
- $N_i$: flux vector of species $i$, mol/cm$^2$-s
- $N_{\text{cell}}$: number of electrons passed in reaction $j$
- $N_m$: MacMullin number in the separator
- $N_{\text{sep}}$: effective separator thickness, cm
- $N_{\text{sid}}$: normal component of the flux (y- or η-direction) of species $i$, mol/cm$^2$-s
- $P_i$: production rate of species $i$ per electrode area, mol/cm$^2$-s
- $P_{\text{br}}$: anodic reaction order of species $i$ in reaction $j$
- $P_{\text{e}}$: Peclot number ($= 2S\sqrt{\nu_{\text{sys}}/D_i}$)
- $P_{\text{ cath}}$: cathodic reaction order of species $i$ in reaction $j$
- $R$: gas law constant, 8.314 J/mol·K
- $S_i$: homogeneous reaction rate, mol/cm$^2$-s
- $S_{\text{an}}$: total electrode gap, cm
- $S_{\text{c}}$: electrolyte channel width, cm
- $S_{\text{ch}}$: catholyte channel width, cm
- $S_{\text{c}}$: stoichiometric coefficient of species $i$ in reaction $j$
- $S_{\text{r}}$: width of the separator, cm
- $T$: temperature, K
- $U_{\text{cell}}$: standard half-cell potential, V
- $U_{\text{cell}}, j$: open-circuit potential of reaction $j$ based on the reference concentrations, $V$
- $V_{\text{br}}$: electrolyte velocity vector, cm/s
- $V_{\text{an}}$: anode potential, V
- $V_{\text{sys}}$: average velocity of the electrolyte, cm/s
- $V_{\text{c}}$: cathode potential, V
- $V_{\text{v}}$: velocity component of the electrolyte in the x-direction, cm/s
- $W$: breadth of electrode, cm
- $x$: axial coordinate, cm
- $y$: normal coordinate, cm
- $z_i$: charge number of species $i$

Greek

- $\alpha$: aspect ratio, $S/L$
- $\alpha_{\text{br}}$: anodic transfer coefficient for reaction $j$
- $\alpha_{\text{cath}}$: cathodic transfer coefficient for reaction $j$
- $\Delta \Phi$: difference in average concentration of bromine-carrying species (Br$^+$ and Br$^-$) from entrance to exit, mol/cm$^3$
- $\epsilon$: coulombic efficiency
- $\eta$: total cell energy efficiency
- $\gamma$: voltaic efficiency
- $\xi$: dimensionless axial coordinate ($x/L$)
- $\eta_{\text{norm}}$: dimensionless normal coordinate ($y/S$)
- $\phi_{\text{soe}}$ or $U_{\text{in}}, j$: overpotential at electrode surface ($V_{\text{c}} - \Phi_{\text{soe}} - U_{\text{in}}, j$), V
- $\eta'$: dimensionless normal coordinate, specific to a flow channel
- $\theta_i$: dimensionless concentration of species $i$ ($c_i/c_{\text{ref}}$)
- $\theta_{\text{feed}, i}$: dimensionless feed concentration of species $i$
- $\theta_{\text{en}, i}$: dimensionless concentration of species $i$ at the electrode surface
- $\rho$: resistivity of separator and its surrounding electrolyte solution, $\Omega$-cm
- $\rho_{\text{en}}$: resistivity of the pure electrolyte solution, $\Omega$-cm
A MATHEMATICAL MODEL

The Lithium Surface Film in the Li/SO₂ Cell

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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 Li₂SO₃, Li₂SO₄, Li₂SO₅, 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, electrochemical degradation (1, 3), anodic polarization (2), self-discharge rates (3), rechargeability (4), and safety (1, 5).

One of the most extensively studied interphases between the Li anode and a liquid electrolyte is the LiCl film in the Li/SOCl₂ 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 LF across it, behaves as an electronic insulator preventing the formation of Li₃SO₄. No assignment was given to the peak at 166 eV. Experiments of the sulfide. The sulfur 2P1/2 2P3/2 doublet separation, 1.3 eV separates the 163.2 eV peak from the Li₂S main peak, 168.8, 166, and probably 163.2 eV. Considering that only 1.3 eV separates the 163.2 eV peak from the Li₂S main peak at 161.9 eV, the former could be the 2P1/2 transition of the sulfide. The sulfur 2P1/2 - 2P3/2 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 found on the anodes of partially discharged and stored LiSO₂ cells. Infrared (IR) spectral and XPS analyses of the film indicated the presence of several Li sulfur-oxy compounds including Li₂SO₄ and Li₂SO₅. Lately, we have examined by SEM, IR, and XPS, the Li surfaces of a large number of Li/SO₂ cells after they have undergone 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 LiSO₂ cell comprises a complex mixture of several Li sulfur-oxy compounds and Li₂S. Our results are reported in this paper.

Experimental

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

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