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A Review of Mathematical Modeling of the Zinc/Bromine Flow Cell and Battery

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ABSTRACT

Mathematical models which have been developed to study various aspects of the zinc/bromine cell and stack of cells are reviewed. Development of these macroscopic models begins with a material balance, a transport equation which includes a migration term for charged species in an electric field, and an electrode kinetic expression. Various types of macroscopic models addressed here and have already been discussed elsewhere (11). Mathematical models which have been developed to study various aspects of the zinc/bromine cell and stack of cells are reviewed. Development of these macroscopic models begins with a material balance, a transport equation which includes a migration term for charged species in an electric field, and an electrode kinetic expression. Ordinary differential equation models that can be used to predict the energy efficiency of the cell as a function of the state of charge. Several models have allowed researchers to better understand the physical phenomena occurring within parallel plate electrochemical flow reactors and have been instrumental in the improvement of the zinc/bromine cell design. Suggestions are made for future modeling work.

The zinc/bromine (Zn/Br₂) flow battery has received much interest as a rechargeable power source because of its good energy density, high cell voltage, high degree of reversibility, and abundant low cost reactants (1-4). Problems with the Zn/Br₂ battery include high cost electrodes, material corrosion, the formation of dendrites during zinc deposition on charge, high self-discharge rates, unsatisfactory energy efficiency, and relatively low cycle life (400-600 cycles) (2, 4, 5). Experimental and modeling efforts have been conducted to alleviate these problems.

Several companies, including Energy Research Corporation (ERC), Gould, and Exxon have developed this battery by building and testing various designs (1). The Exxon design (3, 6-8), which uses a corrosion resistant carbon-plastic composite material for the electrodes, a separator, and a second liquid phase to complex the bromine in the electrolyte to prevent it from participating in the self-discharge reaction, effectively deals with most of the problems mentioned earlier. The main concerns at present are to improve battery efficiency and increase cycle life (1, 2) without sacrificing the attractive low cost of the battery. The experimental approach for obtaining the design variables and operating conditions that yield acceptable high efficiencies and cycle lives can be time consuming and costly. Modeling the system can reduce the experimentation required by pointing out the experimental independent design parameters and how they can be changed to better the cell performance.

Several mathematical models of the Zn/Br₂ cell and a mathematical model of a stack of cells have been presented (4, 9-14). These models have provided researchers with a means to study the various aspects of the Zn/Br₂ cell and gain a greater understanding of the physical phenomena affecting the performance of this battery. The models by Lee and Selman (9), Evans and White (14), and Van Zee et al. (12) provide predictions for many aspects of the Zn/Br₂ cell and battery of interest to designers. These predictions include the current density distributions along the electrode surfaces, the overall battery efficiency, and round trip cell efficiencies. The models reviewed here are all steady-state models and macroscopic in nature. Microscopic models which focus on dendrite initiation and growth during electrodeposition have also been presented (15-17) with one model by Lee (11) which combines a macroscopic model (9) of the Zn/Br₂ flow reactor with a microscopic model describing dendrite growth. These microscopic models, which have contributed much to the understanding of dendrite growth and to the steps which can be taken to reduce their adverse effects, are kept separate from the macroscopic models addressed here and have already been discussed elsewhere (11).

Models of the Zn/Br₂ cell and a stack of cells are based on the recirculation system shown in Fig. 1 and on the parallel plate geometry of an individual cell shown in Fig. 2. Aqueous electrolyte solutions containing reactive species (see Table I for a typical feed composition) are stored in external tanks and circulated through each cell in the stack. Each cell contains two electrodes at which...
reversible electrochemical reactions occur. Sometimes, a porous layer or flow-through porous region is used for the bromine electrode (not shown in Fig. 2). The electrochemical reactions that are assumed to occur (2-4) are, at the bromine electrode

$$2 \text{Br}^- \rightarrow \text{Br}_2 + 2 \text{e}^- \quad [1]$$

and at the zinc electrode

$$\text{Zn}^{2+} + 2 \text{e}^- \rightarrow \text{Zn} \quad [2]$$

To charge the battery, either a constant voltage or a constant current is applied to the stack and energy is stored as Zn and Br2. During charge, the reduction of bromine

$$\text{Br}_2 + 2 \text{e}^- \rightarrow 2 \text{Br}^- \quad [3]$$

at the zinc electrode is an undesired side reaction which competes with zinc deposition and is important to include in the modeling (13). The gap between the positive and negative electrodes, in which electrolyte flows, is usually divided by a porous separator to prevent Br2 from reaching the zinc electrode where it participates in the undesirable reaction [3]. A second liquid phase, organic and known as the “red oil” phase in the Exxon design (3, 6-8), is circulated with the electrolyte to capture bromine and further prevent it from reaching the zinc electrode. The organic phase contains complexing agents like quaternary ammonium salts with which the bromine associates to form an emulsion (2). This emulsion, which is insoluble in water and has a different density than water, travels with the aqueous electrolyte to the storage tank where it is gravitationally separated. Thus, the bromine is effectively stored. In the bulk aqueous electrolyte solution, complexation of Br- and Br2 to form tri-bromide ions (Br3-) occurs (18) according to

$$\text{Br}_3^- + \text{Br}^- \rightarrow \text{Br}_3^- \quad [4]$$

In addition, zinc ions can react with bromide in the electrolyte to form several different zinc-bromine complexes (19-21)

$$\text{Br}_3^- + 2 \text{Br}^- \rightarrow \text{Br}_3^- \quad [5]$$

$$\text{Zn}^{2+} + 2 \text{Br}^- \rightarrow \text{ZnBr}_2 \quad [6]$$

$$\text{Zn}^{2+} + 3 \text{Br}^- \rightarrow \text{ZnBr}_3^- \quad [7]$$

$$\text{Zn}^{2+} + 4 \text{Br}^- \rightarrow \text{ZnBr}_4^- \quad [8]$$

Other species, in addition to those listed in Table I and which appear in reactions [5]-[8], probably exist as postulated by Hsie et al. (19, 20). The extent to which these species are present and influence cell performance is assumed negligible in all of the models (4, 9-14) presented so far. Discharge occurs when the battery is connected to a load and the backward directions of reactions [1] and [2] take place at the positive and negative electrodes, respectively.

**Discussion**

The models of the Zn/Br2 electrochemical reactor (4, 9-14) have been developed to understand the physical phenomena occurring and to determine how cell performance can be improved. These models have been used to investigate the relative importance of the species transport, electrophoresis, cell geometry, operating conditions, secondary electrode reactions, and chemical reactions in the electrolyte bulk on cell performance. Key design considerations such as the thickness of the separator, the initial electrolyte concentration, the electrolyte flow rate, the applied cell potential or current, and the thickness of the porous bromine electrode have been addressed by the various models. Models have shown which quantities and groups of quantities are the independent adjustable parameters of the cell and model predictions have shown how these parameters can be adjusted to improve cell performance. The model by Putt (4) was developed to provide a rational approach for optimizing the Gould design and for later scale-up. A similar model, developed by Lee and Selman (9), is used to examine the effects of certain design parameters on the current density distribution along the electrode surfaces. Lee (11) extended Lee and Selman's model (9) to obtain the approximate time dependent behavior of the current density distribution. He went on to link his macroscopic model with a microscopic model, describing the growth of zinc dendrites, to determine how to reduce dendrite growth rates for which these zinc species are postulated. Recent developments include the models of Van Zee et al. (12) who have simplified the original macroscopic model of the entire Zn/Br2 battery to determine how overall efficiency can be increased by changing certain design conditions. The models by Mader and White (13) and Evans and White (14) are similar to the models of Putt (4) and Lee and Selman (9) but make different simplifying assumptions. Their models attempt to include as many of the cell features in the model as is possible because of the belief that a detailed model will yield the most realistic and useful predictions for use by cell designers. As the Zn/Br2 battery technology has progressed, the need to model different aspects of this battery has arisen. For example, the dendrite problem has been one of the major obstacles in the development of a viable Zn/Br2 system, therefore prompting the work of Putt (4) and Lee (11). These models (4, 9-14), with their different predictive capabilities, have been developed to meet the changing needs in the development of the Zn/Br2 system and to...
providing a sound theoretical basis for future development of this battery.

The following equations form the basis for the models to be discussed. The material balance equation for species i is

\[ \frac{\partial c_i}{\partial t} = -\nabla \cdot N_i + R_i \]  \hspace{1cm} \text{(9)}

Since all of the models discussed here are steady-state models, the accumulation term \( \frac{\partial c_i}{\partial t} \) is set equal to zero. Using dilute solution theory (22), the flux of species i \( (N_i) \) may be written as

\[ N_i = v_c - D_i \nabla c_i - \frac{D_{ij}}{R_T} \nabla \Phi \]  \hspace{1cm} \text{(10)}

where the three terms on the right-hand side of Eq. (10) represent convection, diffusion, and migration, respectively. The term \( R_i \) in Eq. [9], represents production of species i due to chemical reaction and is used, for example, to account for the complexing of the bromine, reaction \( [4] \). The production of species i due to electrochemical reactions that occur at the flat electrodes is incorporated into the boundary conditions of the models. These electrochemical reactions are usually assumed to follow a Butler-Volmer type rate expression (23)

\[ i_j = i_{o,j} \exp \left( \frac{\alpha_j F}{R_T} \eta_i \right) \left( \frac{1 + \eta_i}{\eta_i + \eta_{j,ref}} \right) \]  \hspace{1cm} \text{(11)}

where \( i_j \) is the faradaic direct current density due to electrochemical reaction \( j \), \( \eta_i \) is the dimensionless local surface concentration of species i, and \( \eta_{j,ref} \) is the local overpotential (i.e., the potential driving force for the electrochemical reaction \( j \)).

The models of Putt (4) and Lee and Selman (9) have been used to investigate methods of smoothing the current density distribution along the negative (zinc) electrode. During charge and under certain operating conditions such as a high charging rate, the deposited metal may exhibit areas of roughness as well as protrusions. The worst case of such nonuniform deposition is the formation and growth of long needle-like metallic protrusions called dendrites. Due to spherical diffusion to the dendrite tip, among other factors, dendrites can rapidly propagate, reaching deeper into the electrolyte, and may even span the gap between the elec-

### Thin diffusion layer models

The models by Putt (4), Lee and Selman (9, 10), and Lee (11) are sometimes referred to as thin diffusion layer models (24). They include the assumption that the concentrations of the species in the flow channels remain constant, over the channel gaps and entire reactor length, except within thin diffusion layers adjacent to the electrode surfaces. This simplifying assumption was first introduced in a model of a parallel plate electrochemical reactor by Parrish and Newman (25) and seems reasonable for low conversions per pass. However, White et al. (24) have pointed out the shortcomings of this assumption, especially the fact that models which include this assumption cannot predict the conversion per pass of a reactant. Hence, many cell performance criteria important to cell designers such as cell efficiencies, as defined by Mader and White (13), cannot be determined with the thin diffusion layer models.

For these models, Eqs. [9] and [10] are simplified for the electrolyte bulk and diffusion layers as follows. For the electrolyte bulk, Eqs. [9] and [10] reduce to the two-dimensional Laplace equation

\[ \nabla \Phi(x, y) = 0 \]  \hspace{1cm} \text{(13)}

since uniform composition is assumed. For the thin diffusion layers, the migration of species is assumed negligible, relative to convection and diffusion. This assumption is based on Levich’s (26) work which showed that the migration term can be neglected when excess supporting electrolyte is present. This assumption and the assumption that no homogeneous reactions occur are used to reduce Eqs. [9] and [10] to the well known convective diffusion equation (22)

\[ v_x \frac{\partial c_i}{\partial x} = D_i \frac{\partial^2 c_i}{\partial y^2} \]  \hspace{1cm} \text{(14)}

To calculate \( \Phi \) within the thin diffusion layers, Eq. (13) must then be used. As White et al. (24) have pointed out, this use of Eq. (13) may have little effect on the predicted potential in the diffusion layers but because the overall effect may be significant, the electrochemical reaction rate depends exponentially on the solution potential.

The models of Putt (4) and Lee and Selman (9) have been used to investigate methods of smoothing the current density distribution along the negative (zinc) electrode surface. During charge, and under certain operating conditions such as a high charging rate, the deposited metal may exhibit areas of roughness as well as protrusions. The worst case of such nonuniform deposition is the formation and growth of long needle-like metallic protrusions called dendrites. Due to spherical diffusion to the dendrite tip, among other factors, dendrites can rapidly propagate, reaching deeper into the electrolyte, and may even span the gap between the elec-

### Table II. A comparison of the macroscopic models of the Zn/Br2 flow system

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Features not yet included in a model:
1. Zinc complexation reactions in the bulk electrolyte.
2. A bromine-rich second phase circulated with the electrolyte.
3. Time dependence (i.e., the dynamic problem).

*a* Calculation is separate from model.
troduces and short the cell. Also dendrites may cause separator damage and may result in decreased cell capacity due to loss of active material (17). It has been reported that the dendrite problem is more severe at higher current densities (4). Hence, it is desirable to have a uniform current density distribution so that there are no localized areas having current densities substantially higher than the average. The models by Putt (4) and Lee and Selman (9) can be used to provide the design criteria for achieving the optimum current density distribution.

Putt's model, which is limited to the charge half cycle, can be used to predict the current and potential distributions along the electrodes given the total current to the cell, electrode concentrations, electrolyte conductivity, and the electrode kinetic parameters. The model consists of a set of algebraic, integral, and partial differential equations which are solved iteratively. The cell geometry considered is the same as that shown in Fig. 2. Putt used this geometry even though his positive electrode was a flow-through porous electrode (4).

Putt's model is based on Eq. (9) and (10) and on conservation of charge. The separator is treated as a region of electrolyte whose dimensions are such that its ionic resistivity is that of the separator (i.e., the concept of an "effective separator thickness" is used). The terminal connections are located on the electrodes at the electrolyte exits (i.e., trailing ends). The kinetics of the zinc electrode and the porous bromine electrode are assumed to obey the linear form of the Butler-Volmer equation for flat plate electrodes

$$i = \beta n F v $$

The iterative solution procedure begins by using guesses of the faradaic current densities \(i_1(x)\) and \(i_2(x)\), where \(i_1(x)\) is the current density in the electrolyte adjacent to the negative electrode and \(i_2(x)\) is the current density in the electrolyte adjacent to the positive electrode. Conservation of charge is applied at the negative and positive electrodes to obtain the current density in the electrolyte. Equations (11) and (12) are developed from Eq. (9) and (10). Transport of species is accounted for by using the current balance, Eq. (16), and Ohm's law for the separator. The one-dimensional (x) reactant and terminal resistances on these distributions. The current density in the separator as a function of position along the positive and negative electrodes as well as the concentration in the separator is a function of the dimensionless axial (x-direction) distance are calculated given the cell dimensions, operating conditions, kinetic parameters, and physical constants. The model consists of integral and algebraic equations which are solved using orthogonal collocation.

The governing equations for Lee and Selman’s model are developed from Eq. (9) and (10). Transport of species in the separator is assumed to occur by diffusion rather than by flow. An analytical solution to Eq. (14) is used to obtain the concentration of the zinc ions at the electrode surface and this concentration is then used to calculate the concentration of the zinc ions. Eq. (15) is used to obtain new estimates of the faradaic current density distributions, \(i_1(x)\) and \(i_2(x)\). The calculation process is repeated until successive estimates of \(i_1(x)\) and \(i_2(x)\) differ by less than some prescribed tolerance.

Putt used his model to determine the important design criteria for smoothing the current density distributions. A current density of 40 mA/cm² and an electrode length of 30.48 cm were input into the model to obtain the results reported. Minimums in the current density distributions were detected at distances approximately 13% from the leading edge (where the electrolyte enters) to the trailing edge (where the electrolyte exits) of the electrode. It is at this position where the combined effects of concentration polarization and electrode resistance seem to have the most influence.

Some simplifying assumptions made in the development of Putt’s model should be questioned. The linear form of the Butler-Volmer equation used by Putt applies only at small values of the overpotential. This assumption becomes invalid when overpotentials are necessary large. Therefore, the porous bromine electrode should not be treated as a flat plate electrode because the electrokinetics and mass transport in both cases will be substantially different. Evans and White (14), for example, have shown that it is important to include the electrokinetics and mass-transfer effects within the porous layer in the modeling. Concerning the solution technique, Putt notes that his iterative scheme becomes erratic at times and thus convergence to the solution may be difficult for some cases. To handle this convergence problem, Putt used a weighted average of the previous iterate, \(i_2(x)_{k-1}\), and the current iterate, \(i_2(x)_k\), to obtain a new guess for \(i_2(x)_k\)

$$i_2(x)_k = (0.98)i_2(x)_{k-1} + (0.02)i_2(x)_k$$

Thus, only small changes in successive iterates result and it is reasonable to assume that the convergence is quite slow in some instances.

Similar to Putt’s model, Lee and Selman’s (9) model was developed to predict current density distributions and, in particular, to determine the effects of the separator and terminal resistances on these distributions. The geometry considered is the parallel plate design shown in Fig. 2. The current density distributions on the positive and negative electrodes as well as the current density in the separator is obtained using the current balance, Eq. (16), and Ohm’s law for the separator. The model is then used to calculate the concentration of the zinc ions at the electrode surface and this concentration is then used to calculate the concentration of the zinc ions. Eq. (15) is used to obtain new estimates of the faradaic current density distributions, \(i_1(x)\) and \(i_2(x)\). The calculation process is repeated until successive estimates of \(i_1(x)\) and \(i_2(x)\) differ by less than some prescribed tolerance.

Using boundary conditions consistent with the common assumptions of thin diffusion layer models, analytical solutions have been obtained for Eq. (15), (14), and (18). Lee and Selman used these analytical solutions, which are integral equations involving the current density, in the model to calculate the two-dimensional (x, y) electrolyte potential profile, the one-dimensional (x) reactant concentration profile, and the one-dimensional (x) electrode potential profile. Ohm’s law for the separator is used to relate the solution potential on either border of the separator to the current density in the separator.

$$\frac{d\phi_{sep}(x) - \phi_{sep}(x)}{dx} = \frac{S_i}{k_{sep}}i_{sep}(x)$$

Equation (11) is used to calculate electrochemical reaction rates at the electrode surfaces. A concentration overpotential term is included in Eq. (12) as in Putt’s work.
Lee and Selman’s (9) model has been extended by Lee (11) to obtain estimates of the time dependent behavior of the Zn/Br₂ cell. Such predictions are useful because it is important to know how the cell performance changes over time. For example, it is desirable to keep the energy efficiency of the system near its optimum value throughout the discharge, and have it drop off only at the very end of the discharge. Lee (11) considered an entire half-cell system, either the positive flow channel and its corresponding anolyte storage tank or the negative flow channel and its corresponding catholyte storage tank. Time propagation is simulated by running consecutive steady-state cases, as was done by Lee et al. (30) in earlier work.

Lee modified the steady-state model (9) to include conditions which govern the changes occurring over successive time intervals. Two overall material balances, one on the channel cell and one on the corresponding storage tank, are combined to yield the following expression for the concentration change with time

\[ c_{b,c} = c_{b,c} + \frac{LW}{V_{cell}} \left( t_2 - t_1 \right) \left[ \langle i \rangle - \langle i \rangle_{t_1} + \langle N_{sep} \rangle_{t_2} - \langle N_{sep} \rangle_{t_1} \right] \]

In Eq. [20], \( \langle i \rangle \) is the average current density calculated from the current density distribution obtained from the steady-state model (9) at the conditions of time \( t_2 \), \( \langle N_{sep} \rangle \) is the flux of the species entering the channel from the separator. This quantity is estimated using the average transference number of the species and the separator current density obtained from the steady-state model (9) at time \( t_1 \). For the catholyte channel, Lee also accounted for the charging thickness of the zinc deposit as time progresses, its influence on the electrolyte velocity in the channel, and its subsequent effect on the concentration profile in the thin diffusion layer.

Lee (11) used his model to show several time dependent effects of the design criteria on cell performance. He showed that the average cell current will degrade faster when the cell is operated at higher applied voltages. Near the end of charge, as reactant concentrations diminish and polarization becomes severe, increasing flow velocity was shown to prolong cell life (i.e., by sustaining the average current density at a fairly high level) because it improves the mass transfer of the reactants. Also, the unevenness of the zinc deposit was found to become quite considerable (e.g., 40 µm differences) after long periods of charging (e.g., 6h).

A thin diffusion layer model for predicting corrosion rates in compartmented flow cells, as shown in Fig. 2, has also been presented by Lee and Selman (10). The model is used to study the corrosion rate of the zinc during charge by the reaction product of the positive electrode, brome. The model consists of a set of algebraic and partial differential equations which are solved analytically to yield a set of integral equations. Equations [9] and [10] are used to determine the concentration distribution of the corrosive species (Br₂ in the Zn/Br₂ flow cell), thus the corrosion rate. Concentration changes are assumed to vary linearly in the separator from the anolyte bulk concentration to the catholyte bulk concentration. In the separator, transport is assumed to occur by diffusion only. The governing equations in the flow channels are simply

\[ C_{b,A} = \text{a constant (specified)} \]

\[ C_{b,C} = \text{a constant (calculated)} \]

where C represents the concentration of the corrosive species and subscripts b, A, and C indicate the bulk, anolyte, and catholyte, respectively. In the separator, the flux of the corrosive species is

\[ N_{sep} = D_{sep} \frac{C_{b,A} - C_{b,C}}{S_i} \]

Equation [14] applies in the thin diffusion layer adjacent to the zinc electrode surface. The kinetics for the corro-

Lee and Selman’s model (9) is more complete than Putt’s model in the sense that fewer simplifying assumptions are made. For example, the terminal tabs are not assumed to be located at the cell exit ends, the separator is considered a separate cell region and not as an “effective” span of electrolyte, and Eq. [11] as opposed to Eq. [15] is used. However, in Lee and Selman’s model, the assumption that transport occurs by migration only in the separator may lead to large errors when significant concentration differences exist between the anolyte and catholyte, giving rise to a large diffusion contribution to the flux there. The models of Putt (4) and Lee and Selman (9) may be used to test the assumption of constant current density along the electrode surfaces made in the development of other parallel plate electrochemical reactor models (10-14, 27-29).
losses in the battery due to pumping the electrolyte and concentration profile of the corrosive species proposed by Lee may exist regions of differing potential, perhaps below the zinc electrode and the adjacent solution (V \approx r) is due to the protective energy required to reduce shunt.

Lee and Selman (10) found that two dimensionless parameters, K_1 and K_2, govern the corrosion rate and its distribution along the cathode in their model. K_1 represents the ratio of mass-transfer resistance in the catholyte channel to kinetic resistance of the corrosion process at the zinc electrode. K_2 represents the ratio of diffusion resistance in the separator to kinetic resistance of the corrosion process at the zinc electrode. The concentration of the corrosive species is plotted as a known quantity and the steady-state concentration profile is a quantity to be calculated.

Lee and Selman (10) found that two dimensionless parameters, K_i and K, govern the corrosion rate and its distribution along the cathode in their model. K_1 represents the ratio of mass-transfer resistance in the catholyte channel to kinetic resistance of the corrosion process at the zinc electrode. K_2 represents the ratio of diffusion resistance in the separator to kinetic resistance of the corrosion process at the zinc electrode. The concentration of the corrosive species is plotted as a known quantity and the steady-state concentration profile is a quantity to be calculated.

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The authors believe that these regions do not contribute significantly to the overall kinetics and that the foregoing arguments hold true. However, it should be pointed out that this matter is still under investigation (32, 33).

Finally, significant disagreement between the concentration profile of the corrosive species proposed by Lee and Selman (10) in Fig. 2 of their paper and the concentration profile of Br_2 in Fig. 8 of Evans and White (14) suggests that the bulk electrolyte concentration should not be treated as a constant. This suggestion applies to the thin diffusion layer models. Also, the anolyte bulk concentration is a set quantity in Lee and Selman’s model (10). The feed concentration is more appropriately used as a known quantity and the steady-state concentration profile is a quantity to be calculated.

An algebraic Zn/Br_2 battery model.—Van Zee et al. (12) presented a simple algebraic model of Exxon’s design (3, 6-9) of the Zn/Br_2 battery which can be used to predict the energy efficiency of the battery for various electrolyte resistivities and cell dimensions. This model is used to help select design parameters to minimize the energy losses in the battery due to pumping the electrolyte and due to the protective energy required to reduce shunt currents. This model includes the recirculation system, as shown schematically in Fig. 1, and is based on the cell geometry shown in Fig. 2.

Van Zee et al. (12) calculate the energy efficiency of the Zn/Br_2 battery as

$$E_{in} = E_c - (E_D + E_{pc})$$

where $E_c$ is the energy capacity of the battery. $E_c$ is the input energy to the battery, $E_D$ and $E_{pc}$ are the protective energies required to minimize shunt current losses during discharge and charge, respectively. $E_D$ and $E_{pc}$ are the pumping energies during discharge and charge, respectively. Ohm’s law is used to calculate $E_c$ and $E_c$, given the appropriate current densities and estimated cell resistance. The cell resistance is calculated by multiplying the electrolyte resistance by the sum of the effective electrolyte thicknesses of the anolyte channel, separator and catholyte channel. This “effective thickness” concept was used earlier by Putt (4) to account for the higher resistance offered by the separator relative to the surrounding electrolyte. Van Zee et al. (12) used effective thicknesses for three regions of the cell to account for the “tortuosity” and “porosity” of each region. The equations for $E_D$ and $E_{pc}$ are derived for the system using Kirchoff’s loop and node rules and are given by Grimes et al. (7). $E_D$ and $E_{pc}$ are determined based on calculated pressure drops and an assumed pump efficiency. The algebraic set of equations which result from the analysis are solved in sequence given the cell dimensions, physical properties, and operating conditions.

Van Zee et al. (12) used their model to show that the energy efficiency of the Zn/Br_2 battery is a complicated function of the electrolyte resistivity and electrolyte channel width when all other geometric parameters and physical properties are specified. They showed that a maximum energy efficiency (79.6%) exists at a certain electrolyte resistivity (5.5 Ω-cm) for a given channel width (0.062 in.). Also, the model is used to show that an optimal separator thickness exists for a given set of design criteria.

The model presented by Van Zee et al. (12) is useful for obtaining rough estimates of energy efficiencies for an entire Zn/Br_2 battery, but it is of limited utility for the design of an individual Zn/Br_2 flow cell. The model is based on the assumption of constant electrolyte resistivity throughout charge and discharge, whereas this property would change as the concentration of the species change. The transport taking place inside the cell is treated in an approximate manner, for example, the tortuosity and porosity are arbitrarily specified. The kinetics of the electrochemical reactions are not included in the model.

Other Zn/Br_2 cell models.—Mader and White (13) and Evans and White (14) present mathematical models for
the Zn/Br2 flow cell which predict the performance of the cell as a function of the cell dimensions and operating conditions. The model by Evans and White (14) is an extension of the model by Mader and White (13). Both models follow the modeling approach outlined by White et al. (24). Performance criteria of interest to cell designers, such as conversions per pass and total cell efficiency, are defined by Mader and White and are calculated based on predicted concentration and potential distributions. Like the previously discussed models, these two models were developed to aid in understanding the physical phenomena occurring within the Zn/Br2 cell and to determine ways of improving cell efficiency. The models attempt to account for as many of the cell feed characteristics as possible because of the belief that “detailed” models offer the most realistic and, hence, useful predictions for battery development. Also such models can be used to study the many aspects of the system and how they interact to affect overall performance.

The governing equations are the mass balance for each species, Eq. [9], in two dimensions and the electroneutrality condition

$$\sum_{i} c_{i} z_{i} = 0 \quad [27]$$

Equation [10] is used to describe the flux of each species in the flow channels. In the separator, the convection term in Eq. [10] is neglected and effective diffusivities are used. In the channels, the species mass balances are simplified by deleting certain partial derivative terms because they can be shown to be small relative to the other terms in the equation. Specifically, when the aspect ratio ($\alpha = S/L$) is small, the diffusion and migration terms of the flux expression in the $x$ (axial) direction are negligible relative to the diffusion and migration terms in the $y$ (radial) direction as demonstrated by Nguyen et al. (27). Equation [11] is used to describe the electrode kinetics. The homogeneous, chemical reaction [4] is included in both models and is assumed to be at equilibrium according to the equilibrium constant given by Eigen and Kustin (19)

$$K_{eq} = \frac{c_{Br^{2-}}}{c_{Br^{-}} c_{Br_{2}}} = 17M^{-1} \quad [28]$$

The parasitic reduction of bromine at the zinc electrode, reaction [3], is also accounted for in both models. The resulting dimensionless equations are solved by using the finite difference technique and Newman’s BAND(J) subroutine (22, 34). The solution technique is an iterative finite difference technique and Newman’s BAND(J) subroutine (22, 34). The solution technique is an iterative

The governing equations of this model include those used in the work of Mader and White and the equations used to describe the porous bromine electrode. The material balance equation for species i in the porous layer is

$$E_{eq} = \frac{c_{Br^{2-}} - c_{Br^{-}}}{c_{Br^{-}}} = 17M^{-1} \quad [28]$$

In Eq. [30], $a$ is the specific electroactive surface area of the porous material and $i_{s}$ is the current density, due to electrochemical reaction $j$ based on the electroactive surface area within the porous electrode. $i_{s}$ is calculated using Eq. [11]. Since convective transport is assumed to be negligible in the porous region, Eq. [10] without the convection term is used to calculate the flux of each species within the porous layer.

![Fig. 4. Schematic of the Zn/Br2 cell modeled by Evans and White (14).](https://example.com/image-url)
Evans and White used their model to determine the effects of the mass transfer and electrokinetics in the porous bromine electrode on the round trip performance of the cell. They found that increasing the porous bromine electrode thickness increased the cell efficiency. The model revealed that, for the kinetic parameters investigated, the reaction controlled conditions existed where diffusion of reactive species into and out of the porous electrode was virtually uninhibited. The independent adjustable parameters in Evans and White’s model were determined to be the residence time of electrolyte in the cell ($L/v_{avg}$), the flow channel width ($S_A$), the MacMullin number of the porous electrode ($N_{PE}$), the thickness of the separator ($S_{sep}$), the thickness of the porous electrode ($S_{por}$), the MacMullin number of the porous electrode material ($a$), and, either the applied cell potential ($E_{cell}$) or the applied current density ($J$). For the porous electrode thicknesses investigated, the predictions showed the greater round trip energy efficiencies result for thicker porous electrodes. Evans and White show that round trip energy efficiencies of about 70% should be possible for the Zn/Br$_2$ cell.

Evans and White’s model is perhaps the most complete of all the cell models discussed in that it accounts for many features of the cell and does not require many of the simplifying assumptions made in the development of the other models (4, 9-12). For example, the assumptions of constant bulk concentrations, no homogeneous chemical reactions, and no diffusion contribution to the flux in the separator. The model can be used to determine the effects of the design criteria on cell performance for a full charge/discharge cycle. The kinetic parameters used, as mentioned earlier, were taken from the work of Mader and White (13) and are listed in Table II of that paper. Other kinetic parameters may produce a diffusion limited condition, which may also be of interest. Given experimental results from a working cell, the model should provide an excellent means of determining certain system parameters such as diffusivities, $D_i$, and electrokinetic constants, $k_{i,ref}$, $a_{np}$, and $a_{a}$. The model would have to be expanded within a parameter estimation scheme such as ZXSSQ in the IMSL software library (36), so that model predictions could be fitted to the experimental data by finding the “best” values for these system parameters. Unfortunately, very little experimental data for the Zn/Br$_2$ system is currently available.

Summary and Recommendations
Models of the Zn/Br$_2$ flow cell have been used to show the important design criteria for improving cell performance. The models of Pütz (4), Lee and Selman (9, 10), and Lee (11) have provided important information for improving current density distributions. The model by Van Zee et al. (12) has been used to show how certain design parameters can be changed to achieve an optimum overall performance for the entire Zn/Br$_2$ battery system. Mader and White (13) and Evans and White (14) have established many of the independent design parameters for an individual cell and have shown how to improve cell efficiency, via changes in these design criteria.

Future modeling work of the Zn/Br$_2$ battery should include features not yet accounted for by existing models. For example, the model by Evans and White (14) should be extended to include zinc complexing (reactions [5]-[8]), a second bromine-rich phase, time dependence (i.e., the dynamic problem), and a self-contained recirculation system consisting of a cell, the two electrolyte storage tanks, and the connecting piping.

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LIST OF SYMBOLS
\begin{itemize}
  \item $c$, specific electroactive surface area of the porous electrode, $\text{cm}^{-1}$
  \item $c_i$, concentration of species $i$, $\text{mol/cm}^3$
  \item $c_{i,ref}$, reference concentration of species $i$, $\text{mol/cm}^3$
  \item $c_{b,a}$, concentration of corrosive species in the anolyte bulk, $\text{kmol/m}^3$
  \item $c_{b,c}$, concentration of corrosive species in the catholyte bulk, $\text{kmol/m}^3$
  \item $c_{s}$, concentration of corrosive species at the electrode surface, $\text{kmol/m}^3$
  \item $D_i$, diffusion coefficient of species $i$, $\text{cm}^2/s$
  \item $D_{sep}$, effective diffusivity of the corrosive species in the separator, $\text{m}^2/s$
  \item $E_{cell}$, energy required for pumping electrolyte on charge, $J$
  \item $E_{cell}$, energy required for pumping electrolyte on discharge, $J$
  \item $E_{SC}$, energy required for shunt current protection on charge, $J$
  \item $E_{SD}$, energy required for shunt current protection on discharge, $J$
  \item $F$, Faraday’s constant, 96,487 $\text{C/mol}$
  \item $I$, total cell current, $A$
  \item $i_i$, current density, $A/m^2$
  \item $i_{i,pot}$, current density vector, $A/m^2$
  \item $i_{i,sep}$, current density in separator, $A/m^2$
  \item $i_j$, current density due to electrochemical reaction $j$, $A/m^2$
  \item $I_n$, total current density at zinc electrode ($=I_LW$), $A/cm^2$
  \item $i_{i,ref}$, exchange current density of electrochemical reaction $j$, $A/cm^2$
  \item $i_1$, electronic current density in negative electrode, $A/cm^2$
  \item $i_2$, electronic current density in positive electrode, $A/cm^2$
  \item $i_3$, faradaic current density at the surface of the negative electrode, $A/cm^2$
  \item $i_4$, faradaic current density at the surface of the positive electrode, $A/cm^2$
  \item $i_5$, average current density, $A/cm^2$
  \item $i_6$, average dimensionless current density
  \item $i_{1,ref}$, first-order electrochemical reaction rate constant, $m/s$
  \item $K_{eq}$, equilibrium constant for tri-bromide reaction, $\text{cm}^3/mol$
  \item $L$, electrode length, $\text{cm}$
  \item $L/v_{avg}$, residence time of the reactor, $s$
  \item $N_{i}$, flux vector of species $i$, $\text{mol (cm}^2 \times s)$
  \item $N_{i,sep}$, flux of corrosive species through separator, $\text{mol/(m}^2\text{s})$
  \item $<N_{i,sep}>$, flux of species entering the channel from the separator, $\text{mol/(m}^2\text{s})$
  \item $N_{i,ref}$, MacMullin number in the separator
  \item $N_{i,PE}$, MacMullin number in the porous electrode
  \item $N_{i,SE}$, effective separator thickness, $\text{cm}$
  \item $P_i$, anodic reaction order of species $i$ in reaction $j$
  \item $Q_i$, cathodic reaction order of species $i$ in reaction $j$
  \item $R$, gas law constant, 8.314 $\text{J/(mol} \times K)$
  \item $R_i$, production rate of species $i$ due to reaction, $\text{mol/(cm}^2 \times s)$
  \item $R_{i,ref}$, production rate of species $i$ due to homogeneous reaction, $\text{mol/(cm}^2 \times s)$
  \item $R_i$, production rate of species $i$ due to electrochemical reaction, $\text{mol/(cm}^2 \times s)$
  \item $S_A$, electrode gap, $\text{cm}$
  \item $S_A$, anolyte channel width, $\text{cm}$
  \item $S_B$, thickness of the electrode, $\text{cm}$
  \item $S_{c,neg}$, thickness of the negative electrode, $\text{cm}$
  \item $S_{c,pos}$, thickness of the porous electrode, $\text{cm}$
  \item $S_t$, thickness of the separator, $\text{cm}$
  \item $T$, temperature, $K$
  \item $U_{i,ref}$, open-circuit potential of reaction $j$ based on the reference concentrations, $V$
  \item $v$, velocity vector, $\text{cm/s}$
  \item $v_{ave}$, average velocity of the electrolyte, $\text{cm/s}$
  \item $V$, flow velocity, $\text{cm/s}$
  \item $V$, electrode potential, $\text{V}$
  \item $V_a$, anode potential, $\text{V}$
\end{itemize}
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