

1999

Material Balance Modification in One-Dimensional Modeling of Porous Electrodes

Mukul Jain

University of South Carolina - Columbia

John W. Weidner

University of South Carolina - Columbia, weidner@engr.sc.edu

Follow this and additional works at: https://scholarcommons.sc.edu/eche_facpub



Part of the [Chemical Engineering Commons](#)

Publication Info

Journal of the Electrochemical Society, 1999, pages 1370-1374.

© The Electrochemical Society, Inc. 1999. All rights reserved. Except as provided under U.S. copyright law, this work may not be reproduced, resold, distributed, or modified without the express permission of The Electrochemical Society (ECS). The archival version of this work was published in the *Journal of the Electrochemical Society*.

<http://www.electrochem.org/>

Publisher's link: <http://dx.doi.org/10.1149/1.1391772>

DOI: 10.1149/1.1391772

This Article is brought to you by the Chemical Engineering, Department of at Scholar Commons. It has been accepted for inclusion in Faculty Publications by an authorized administrator of Scholar Commons. For more information, please contact digres@mailbox.sc.edu.

Material Balance Modification in One-Dimensional Modeling of Porous Electrodes

Mukul Jain* and John W. Weidner**

Center for Electrochemical Engineering, Department of Chemical Engineering, University of South Carolina, Columbia, South Carolina 29208, USA

The material balance used previously in one-dimensional mathematical models of porous electrodes is invalid when there is a non-zero volume change associated with the reaction. It is shown here how the material balance should be modified either to account for a loss in volume, or to account for an inflow of electrolyte from the header into the active pores. A one-dimensional mathematical model is used to illustrate the effect of this correction on the prediction of the delivered capacity and the electrolyte concentration in a lithium/thionyl chloride primary battery.

© 1999 The Electrochemical Society. S0013-4651(98)07-108-0. All rights reserved.

Manuscript submitted July 30, 1998; revised manuscript received November 2, 1998.

Mathematical models are useful in understanding battery operation, in facilitating battery design, and in conjunction with experimental data to aid in accelerated testing. The models, however, are only useful if the assumptions made during the model development are valid for the system under consideration. An assumption that holds for one battery system may not hold for another system with different physical properties. One assumption usually implicit when formulating the material balance for a one-dimensional model of a porous electrode is that the volume is conserved during reaction (see, for example, Ref. 1-3). However, if the volume of the reactants is not equal to that of the products, then a volume change results due to the reaction. The material balance produces erroneous results if this volume change is not accounted for correctly.

To understand how the assumption of volume conservation is often inadvertently incorporated into models, consider a macroscopic model of a porous electrode.^{4,5} In a one-dimensional model, the following differential volume element is used

$$\Delta V = A \cdot \Delta x \quad [1]$$

where the differential thickness, Δx , is large compared to the pore dimensions but small compared to the electrode dimensions. The conservation equations for the dependent variables are usually written such that the cross-sectional area of the volume element, A , is constant, and the material enters or leaves the volume element only in the x direction. However, if volume is not conserved in the reaction, the conservation equations should be modified. Two scenarios are shown in Fig. 1 that result when the reactant volume is greater than the product volume. Figure 1a represents the situation when excess electrolyte, which is present on the top of the porous electrode, fills the porous cathode to make up for the volume reduction. The amount of electrolyte in the header decreases, while the active cross-sectional area in the cathode (shaded portion) remains constant. Figure 1b represents the case when no excess electrolyte is present in the cell. Here, the active cross-sectional area of the porous electrode decreases due to the volume reduction. The lighter shading at the top of the electrode signifies the porous electrode without the electrolyte. This portion of the electrode is no longer electrochemically active since no electrolyte is present.

In a two-dimensional model of the same system, the differential volume element would be constant, and the two cases mentioned above are naturally incorporated into the model either by incorporating the flux from the header into the boundary condition (Fig. 1a), or by using a moving boundary condition (Fig. 1b). In a one-dimensional model, it is easy to overlook these situations because of either the added transport direction (Fig. 1a) or the changing size of the differential volume element (Fig. 1b). It is shown here how the materi-

al balance in a one-dimensional model has to be modified to account for either the inflow of electrolyte from the header or the loss in active volume. A mathematical model of a lithium/thionyl chloride primary battery is used to illustrate the effect of this material balance modification on the prediction of the delivered capacity and the electrolyte concentration. The volume reduction in this battery system is significantly larger than for other batteries.⁶ For example, a one-dimensional model developed for a nickel/cadmium battery¹ will not be significantly affected by incorporating the volume reduction presented in this work. However, the results from existing one-dimensional models of a lithium/thionyl chloride battery can give erroneous results without this correction. Here we show the consequences of neglecting the change in volume during the reaction.

Generalized Material Balance

The superficial current density in the solution, i_2 , is due to the movement of charged species, given as

$$i_2 = F \sum_i z_i N_i \quad [2]$$

where N_i is the average flux density of species i in the pores averaged over the cross-sectional area of the electrode. By conservation of charge, the charge leaving the matrix phase must equal the charge entering the solution phase, and this can be expressed as

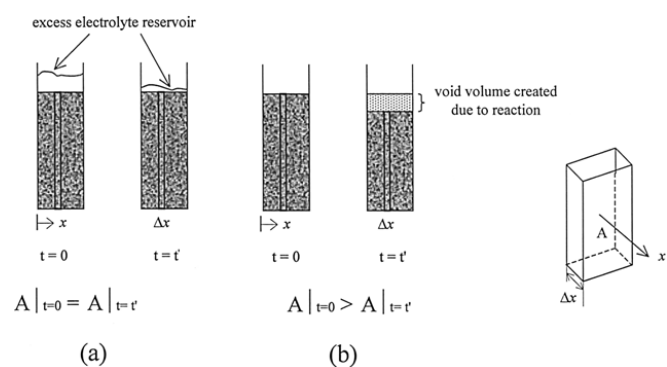


Figure 1. A schematic diagram of the porous electrode depicting the volume change due to the reaction. (a) Excess electrolyte is present at the top (header) of the electrode. The electrolyte in the header moves into the porous electrode as the void space is created by the reaction. Therefore, there is a flux in a direction normal to x . (b) No header is present, and so the electrolyte level in the electrode drops as a result of volume reduction. Therefore, the active cross-sectional area, A , decreases with time.

* Electrochemical Society Student Member.

** Electrochemical Society Active Member.

$$\frac{\partial i_1}{\partial x} + \frac{\partial i_2}{\partial x} = 0 \quad [3]$$

The current transferred from the matrix phase to the solution phase must equal the net rate of the electrochemical reaction per unit volume of the electrode. This can be expressed as

$$j = \frac{\partial i_2}{\partial x} = -\frac{\partial i_1}{\partial x} \quad [4]$$

where j (A/cm³) is the local transfer current density per unit volume of the electrode. The local transfer current is negative for a cathode reaction, and it is related to the local concentration and overpotential through a kinetic expression.⁷ In this work, only one reaction is considered in any region. If there were additional reactions, j would be replaced by a summation over all reactions. In the absence of any nonelectrochemical reactions, the rate of production of species i is given as

$$R_i = -\frac{s_i}{nF} j \quad [5]$$

where s_i is the stoichiometric coefficient of species i (molecular formula M_i) in the electrochemical reaction expressed as



In the porous region, the material balance for species i in the solution phase can be obtained by performing a balance on the differential volume element. If material moves into and out of the volume element only across the plane normal to x , then the accumulation of material in the differential time, Δt , is given by the difference in the flux in the x direction plus the production due to reaction. Mathematically this is expressed as

$$\frac{\Delta(\epsilon c_i A \Delta x)}{\Delta t} = (AN_i)|_x - (AN_i)|_{x+\Delta x} + R_i A \Delta x \quad [7]$$

where c_i is the solution-phase concentration of species i averaged over the pore volume, ϵ is the porosity of the electrode, and A is the cross-sectional area available for material transport.

Similarly, a balance on the matrix-phase volume, when there is a porosity change due to reaction, gives

$$\frac{\Delta[(1 - \epsilon)A \Delta x]}{\Delta t} = A \Delta x \sum_m R_m \hat{V}_m \quad [8]$$

where \hat{V}_m is the specific volume of a solid phase, m , created due to reaction (i.e., precipitation of species m). If the cross-sectional area, A , does not change with time, then Eq. 7 and 8 can be rearranged to give the commonly used governing equations for c_i and ϵ

$$\frac{\partial(\epsilon c_i)}{\partial t} = -\frac{\partial N_i}{\partial x} + R_i \quad [9]$$

$$\frac{\partial \epsilon}{\partial t} = -\sum_m R_m \hat{V}_m \quad [10]$$

Again, two inherent assumptions were made in the derivation of Eq. 9 and 10: (i) the cross-sectional area normal to x does not change with time; and (ii) material only moves into and out of the volume element across the plane normal to x . When a volume reduction occurs due to the reaction, these two assumptions cannot be simultaneously satisfied. Using Eq. 9 and 10 causes a discrepancy in the amount of SOCl_2 in the cell. This leads to the impossible situation that more reactant is consumed than is actually present. Therefore, one of the two assumptions given above must be relaxed.

No excess electrolyte present—If there is no excess electrolyte, A is not constant and Eq. 7 and 8 must be rearranged to give the following expressions

$$\frac{\partial(\epsilon c_i)}{\partial t} = -\frac{\partial N_i}{\partial x} + R_i - \frac{\epsilon c_i}{A} \frac{\partial A}{\partial t} \quad [11]$$

$$\frac{\partial \epsilon}{\partial t} = -\sum_m R_m \hat{V}_m + \frac{\epsilon}{A} \frac{\partial A}{\partial t} \quad [12]$$

The rate of change of the area can be related to the stoichiometry and the molar volume of the reactants and products as

$$\frac{\partial A}{\partial t} = -\frac{A}{nF} j \sum_k s_k \hat{V}_k \quad [13]$$

where \hat{V}_k is the specific molar volume of species k . Equation 13 can be substituted into Eq. 11 and 12 to yield the following material balances for the case when the cross-sectional area changes as a result of the volume reduction in the electrode

$$\frac{\partial(\epsilon c_i)}{\partial t} = -\frac{\partial N_i}{\partial x} + R_i + \frac{\epsilon c_i}{nF} j \sum_k s_k \hat{V}_k \quad [14]$$

$$\frac{\partial \epsilon}{\partial t} = -\sum_m R_m \hat{V}_m - \frac{\epsilon}{nF} j \sum_k s_k \hat{V}_k \quad [15]$$

The cross-sectional area, the electrolyte concentration, and the porosity must be tracked throughout the discharge, and therefore Eq. 13 through 15 must be solved simultaneously to obtain A , c_i , and ϵ .

Excess electrolyte in header.—If excess electrolyte is present in the header space, then the differential volume created by the volume reduction is filled with electrolyte from the header. Although the cross-sectional area of the differential volume is constant with time, the material balance given by Eq. 9 does not hold, since the flux from the header is across a plane that is not normal to x . The flux from the header can be incorporated by adding a term to Eq. 9 that corresponds to this flux. If the concentration of species i in the header is the initial concentration, then the additional flux term is given as $(-c_i^0 R_i \Delta \hat{V}_i)$, which is the rate at which species i enters from the header per unit volume of the porous electrode. Therefore, the material balance becomes

$$\frac{\partial(\epsilon c_i)}{\partial t} = -\frac{\partial N_i}{\partial x} + R_i + \frac{c_i^0}{nF} j \sum_k s_k \hat{V}_k \quad [16]$$

Equations 10 and 16 are solved simultaneously to obtain c_i and ϵ .

Material Balance for Lithium/Thionyl Chloride Battery

The equations developed in the previous section are applied to a lithium/thionyl chloride battery. Figure 2 is a schematic diagram of the cross section of a spirally wound Li/SOCl₂ cell as modeled in this work. The four regions in the diagram are the lithium foil anode, the lithium chloride (LiCl) film that forms on the anode surface, the separator, and the porous carbon cathode. The components are rolled together, and then the cell roll is inserted in a cylindrical can (commercial D size). The electrolyte, which consists of lithium tetrachloroaluminate (LiAlCl₄) in thionyl chloride (SOCl₂), is poured into the can, filling the porous regions of the roll. Henceforth, SOCl₂ is referred to as the solvent, while LiAlCl₄ is referred to as the salt. Excess electrolyte resides at the top of the electrode/separator assembly. The anode surface and the cathode current collector are the boundaries of the model region.

The reactions included in the model are the oxidation of lithium at the anode



and the reduction of SOCl₂ followed by precipitation of LiCl at the cathode

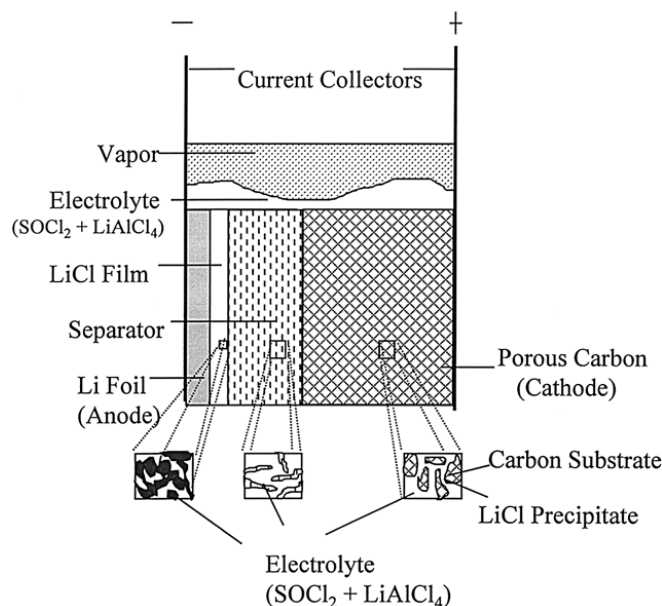


Figure 2. Schematic diagram of a lithium/thionyl chloride cell. The anode, separator, and the porous cathode are stacked together, and the assembly is spirally wound and inserted into a D size cell.



Reaction 2 is the net result of SOCl_2 reduction and the subsequent precipitation of the insoluble LiCl salt. Since the focus of the present work is on the material-balance discrepancy due to reaction, only the material balances in the porous cathode are discussed in this paper. The entire model is presented and discussed elsewhere.⁷

As evident from reaction 2, for every mole of SOCl_2 (solvent) reduced, two moles of LiCl are deposited in the cathode. Therefore, the total volume lost as a result of the reduction of a mole of SOCl_2 is $(\hat{V}_{\text{SOCl}_2} - 2\hat{V}_{\text{LiCl}})$, and the solid volume created is $2\hat{V}_{\text{LiCl}}$. The three scenarios mentioned earlier are discussed in context of a Li/SOCl_2 cell model: (i) no excess electrolyte is present, and therefore the cross-sectional area changes with time; (ii) excess electrolyte is present in the header; and (iii) no accounting is made in the material balance to incorporate the volume reduction. The first two cases represent real events, while the third case results from an omission during the model development.

No excess electrolyte present.—When no reservoir of excess electrolyte is present, the volume reduction leads to a decrease in the active cross-sectional area of the porous electrode. This effect can be incorporated into the material balance in a manner described while developing Eq. 14 where the loss in area is related to the stoichiometry of the reaction, and is given as

$$\frac{\partial(\epsilon c_i)}{\partial t} = -\frac{\partial N_i}{\partial x} + R_i + (2\hat{V}_{\text{LiCl}} - \hat{V}_o)R_o \epsilon c_i \quad (i = +, -, o) \quad [17]$$

where the subscripts $+$, $-$, and o refer to Li^+ , AlCl_4^- , and SOCl_2 , respectively.

Since the solvent is consumed in this system, the salt concentration increases as discharge proceeds. Concentrated solution theory⁵ is used to develop the equations describing the species transport. The species flux, N_i , is obtained by inversion of the multicomponent diffusion equation.⁵ The resulting flux expression for a binary electrolyte salt and the solvent is given as

$$N_i = -D_e \frac{\partial c_i}{\partial x} + \frac{i_2 t_i^*}{F} + c_i v^* \quad (i = +, -, o) \quad [18]$$

where v^* is the volume average velocity. By definition, the transference number of the solvent is zero (i.e., $t_o^* = 0$), and the effective diffusion coefficient of the salt through the solvent, D_e , is defined as

$$D_e = D\epsilon^{1.5} \quad [19]$$

where the exponent accounts for the tortuosity of the electrode.⁵

Equations 17 and 18 are combined to obtain the material balance for the salt

$$\epsilon \frac{\partial c}{\partial t} + c \frac{\partial \epsilon}{\partial t} = -\frac{\partial}{\partial x} \left(-D_e \frac{\partial c}{\partial x} + \frac{i_e t^*}{F} + c_i v^* \right) + \frac{j}{F} \left[1 - \frac{\epsilon c}{2} (\hat{V}_o - 2\hat{V}_{\text{LiCl}}) \right] \quad [20]$$

Since the electrolyte contains a binary salt, the cation and anion concentrations are equal to the total salt concentration (i.e., $c_+ = c_- = c$). In addition, c and c_o are related to each other by the fact that the partial volumes of the salt and the solvent sum to unity in each region (i.e., the electrolyte contains only salt and solvent). This is expressed mathematically as

$$c\hat{V} + c_o\hat{V}_o = 1 \quad [21]$$

The porosity in the cathode changes with time as a result of the precipitation of LiCl and a change in the area, as explained while developing Eq. 15. Therefore, the rate of change of cathode porosity can be expressed as

$$\frac{\partial \epsilon}{\partial t} = j \left[\frac{\hat{V}_{\text{LiCl}}}{F} + \frac{(1 - \epsilon)}{2F} (\hat{V}_o - 2\hat{V}_{\text{LiCl}}) \right] \quad [22]$$

where the first term is due to the precipitation of LiCl , and the second term is due to the change in electrode area. For this system, Eq. 13 can be written as

$$\frac{\partial A}{\partial t} = \frac{A}{2F} j (\hat{V}_o - 2\hat{V}_{\text{LiCl}}) \quad [23]$$

A material balance similar to Eq. 20 can be written for the solvent. The solvent balance, salt balance, solid-phase (LiCl) balance, and Eq. 21 can be combined to yield an overall material balance, that allows one to solve explicitly for the volume average velocity, given as Eq. 24

$$v^* = \frac{i_e \hat{V}_o}{F} \quad [24]$$

In summary, Eq. 20, 22, 23, and 24 are used to solve for the four unknowns A , c , ϵ , and v^* .

Excess electrolyte in header.—When a reservoir of excess electrolyte is present at the top of the assembly, it is assumed that the void space created by the volume differential is filled with this electrolyte. This excess electrolyte remains at its initial concentration. This effect is accounted for by combining Eq. 16 and 18 to yield the material balance for the salt as

$$\epsilon \frac{\partial c}{\partial t} + c \frac{\partial \epsilon}{\partial t} = -\frac{\partial}{\partial x} \left(-D_e \frac{\partial c}{\partial x} + \frac{i_e t^*}{F} + c v^* \right) + \frac{j}{F} \left[1 - \frac{c_o}{2} (\hat{V}_o - 2\hat{V}_{\text{LiCl}}) \right] \quad [25]$$

The porosity in the cathode changes as a result of LiCl precipitation, but no area change is involved. Therefore, Eq. 22 reduces to

$$\frac{\partial \epsilon}{\partial t} = j \frac{\hat{V}_{\text{LiCl}}}{F} \quad [26]$$

The salt material balance (Eq. 25), a similar balance for the solvent, the solid-phase balance (Eq. 26), and Eq. 21 are combined to yield the overall material balance, which is same as that given by Eq. 25. Here the three unknowns, c , ϵ , and v^* are obtained by solving Eq. 24, 25, and 26.

No material-balance correction.—Equations 9 and 18 combined to yield

$$\epsilon \frac{\partial c}{\partial t} + c \frac{\partial \epsilon}{\partial t} = -\frac{\partial}{\partial x} \left(-D_e \frac{\partial c}{\partial x} + \frac{i_e t_+}{F} + c v^* \right) + \frac{j}{F} \quad [27]$$

Again, the overall material balance is obtained in a manner similar to the previous two cases, and the volume average velocity is given as

$$v^* = \frac{i_e}{2F} [2\hat{V}t_+ + (\hat{V}_o - \hat{V}_{\text{LiCl}})] \quad [28]$$

Equations 26, 27, and 28 can be solved for the three unknowns c , ϵ , and v^* .

Maximum theoretical capacity.—It is helpful to examine the three cases detailed above by comparing the maximum theoretical capacity a cell can deliver. The end of discharge for a cathode-limited cell design can occur by one of two mechanisms: (i) plugging of all the pores in the cathode or (ii) consumption of all the solvent (i.e., reactant) in the cell. The latter mode of cell failure can be avoided by adding excess electrolyte in the header above the cell.

When no excess electrolyte is present, either of the two failure modes mentioned above is possible. In order to achieve the maximum theoretical capacity due to pore plugging, the reaction must be uniform throughout the cathode. Under this assumption, the transfer current density, j , can be expressed as $(-I_{\text{app}}/d_{\text{pe}}A)$. When no excess electrolyte is present, the area, A , changes with time, and therefore j changes with time. Equation 13 is integrated to yield a time dependent j which is substituted into Eq. 22, and then Eq. 22 is integrated from $\epsilon = \epsilon^o$ to $\epsilon = 0$ to give

$$Q_{\text{max}} = \frac{2\epsilon^o F A^o d_{\text{pe}}}{\hat{V}_o} \quad [29]$$

If the solvent is consumed before the pores are plugged, the maximum theoretical capacity is obtained by multiplying the total moles of SOCl_2 in the cell by $2F$ to give

$$Q_{\text{max}} = 2A^o c_o^o F (\epsilon^o d_{\text{pe}} + \epsilon_s d_s) \quad [30]$$

Therefore, the maximum theoretical capacity when no excess electrolyte is present is the smaller of Eq. 29 and 30.

When excess electrolyte is present, A is constant and Eq. 26 can be integrated to give

$$Q_{\text{max}} = \frac{\epsilon^o F A^o d_{\text{pe}}}{\hat{V}_{\text{LiCl}}} \quad [31]$$

Since the electrolyte is in excess, the cell will not run out of electrolyte and Eq. 31 is the maximum theoretical capacity.

For the parameters given in Table I, $\hat{V}_o/2$ is greater than \hat{V}_{LiCl} , and the capacity predicted by Eq. 29 is lower than that predicted by Eq. 31. The reduced capacity without excess electrolyte is a result of a decrease in the electrolyte level in the electrode due to the volume reduction, which results in less volume for the LiCl precipitate to occupy. In the event of no volume reduction, $\hat{V}_o/2$ is equal to \hat{V}_{LiCl} , and Eq. 29 and 31 are equivalent.

Results and Discussion

The focus of the present work is to account for the volume reduction in the material balance in the porous cathode. The key param-

eters that determine whether or not a change in volume due to reaction is significant are the specific molar volumes and the properties of the cathode. The parameters for a lithium/thionyl chloride cell are listed in Table I. A complete list of model parameters can be found elsewhere.⁷ Using the parameters given in Table I and with no excess electrolyte present, the theoretical capacities given by Eq. 29 and 30 are approximately 9.43 and 11.25 Ah, respectively. Therefore, no more than 9.43 Ah of capacity can be removed from the cell. This limit corresponds to the point at which the active pores are uniformly plugged with LiCl , though a small amount of reactant (i.e., solvent) remains in the cell. Adding a reservoir of excess electrolyte increases the maximum theoretical capacity of the cell from 9.43 to 16.7 Ah, where the latter value is obtained from Eq. 31. Increasing the cell capacity by adding excess electrolyte seems counterintuitive since the mode of failure is pore plugging not electrolyte consumption. However, adding excess electrolyte also prevents a portion of the cell from drying out (see Fig. 1). Therefore, the entire cathode remains active throughout the discharge, and more capacity can be realized before all the pores become plugged.

Figure 3 shows the simulated discharge curves (i.e., cell voltage vs. charge removed) obtained from the Li/SOCl_2 model⁷ at a low discharge rate (250 Ω load) with different material-balance equations. The dashed line represents the discharge curve when no excess electrolyte is present (Eq. 20, 22, 23, and 24). The capacity is approximately 9.26 Ah, which corresponds to 98% of the theoretical maximum given by Eq. 29. The solid line represents the case when excess electrolyte is in the header (Eq. 24, 25, and 26). The capacity is approximately 16.2 Ah, which corresponds to approximately 97% of the theoretical maximum given by Eq. 31. The dotted line represents the case when no accounting is made for the volume reduction in the material balance (Eq. 26, 27, and 28). Using these equations, 15.4 Ah of capacity are removed from the cell. However, removing this much capacity is impossible since there is only 11.25 Ah of capacity available in the electrolyte according to Eq. 29. This physically impossible situation arises because the governing equations do not account for the volume reduction as a result of the reaction. The unintended consequence, in effect, is the spontaneous creation of SOCl_2 . In other words, using Eq. 25 instead of 27, and substituting c^o by c will also result in the dotted line in Fig. 3.

As mentioned earlier, the mode of failure for the two physically realizable cases is pore plugging. This is evident from Fig. 4, which shows the porosity profile at the end of discharge for all three cases. The porosity at the front end of the cathode is very close to zero for all three cases, indicating that the plugging of the pores resulted in the end of discharge. The porosity throughout the electrode is low

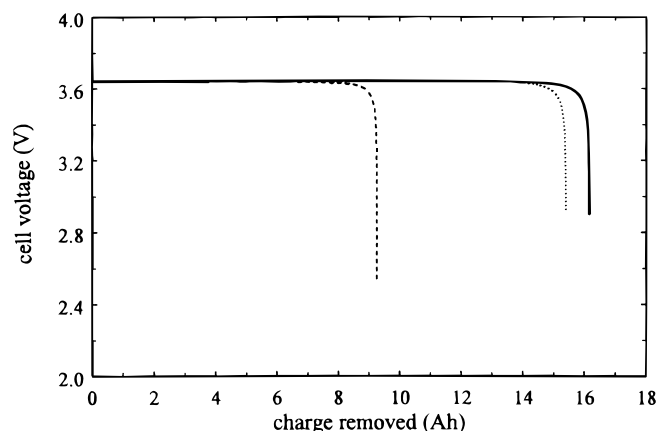


Figure 3. Discharge voltage vs. charge removed for the two scenarios shown schematically in Fig. 1 [i.e., (a) excess electrolyte (—); and (b) area decreasing with time (---)]. Also included is the discharge curve that results if no accounting is made of the volume reduction due to the reaction (·····). In all three cases, the lithium/thionyl chloride cell is discharged across a constant load of 250 Ω at 25°C.

Table I. A list of key parameters used in the model. A complete list of model parameters can be found elsewhere.⁷ SNL signifies parameters used in D size cells at Sandia National Laboratories.

Parameter	Value	Ref.	Parameter	Value	Ref.
\hat{V} (cm^3/mol)	77.97	8	ϵ_s	0.95	SNL
\hat{V}_{LiCl} (cm^3/mol)	20.5	9	ϵ^o	0.835	SNL
\hat{V}_o (cm^3/mol)	72.63	10	d_s (cm)	0.023	SNL
c^o (mol/cm^3)	0.001	SNL	d_{pe} (cm)	0.085	SNL

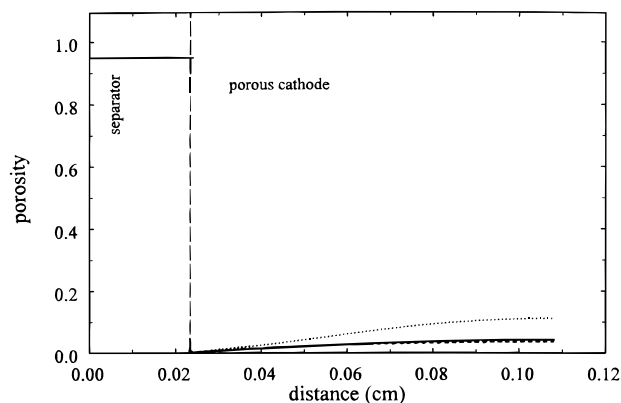


Figure 4. The porosity profile at the end of discharge for the two scenarios shown schematically in Fig. 1 [i.e., (a) excess electrolyte (—); and (b) area decreasing with time (---)]. Also included is the discharge curve that results if no accounting is made of the volume reduction due to the reaction (·····). In all three cases, the lithium/thionyl chloride cell is discharged across a constant load of 250 Ω at 25°C.

for the two cases where proper accounting of the volume reduction is made, either by changing electrode area or through the influx of excess electrolyte from the header. Although the porosity profiles for these two cases are very similar, the capacities seen in Fig. 3 are significantly different. In the case when the electrode area changes with time (i.e., no excess electrolyte), the profile seen in Fig. 4 is for the remaining active volume. The porosity of the inactive volume does not go to zero. If no accounting is made of the volume reduction due to the reaction, some pore volume remains, but the mode of failure is still the plugging of the front end of the porous cathode.

The solvent (i.e., SOCl_2) concentration profile in the cell at the end of discharge is shown in Fig. 5. Some solvent remains for all three cases, although the concentration profiles are different. If no accounting is made of the volume reduction due to the reaction, the solvent concentration in the cathode is lower than that in the separator, as opposed to the other two cases where the concentration in the cathode is higher. Also, the solvent is not consumed as early as predicted by Faraday's law (see Eq. 30). As stated earlier, only 11.25 Ah of SOCl_2 are added to the cell when no excess electrolyte is present, yet Fig. 3 indicates that 15.4 Ah of capacity is removed. Using the governing equations (Eq. 26, 27, and 28) for the case when no accounting is made of the volume reduction causes a discrepancy in the amount of SOCl_2 present in the cell.

Conclusions

The consequences of disregarding the volume changes due to reaction in a porous electrode were presented. It was shown how the material balance should be modified for systems where the specific volume of the reactants is not the same as that of the products. The modified governing equations were implemented, and the effect was illustrated by simulating the discharge behavior for a lithium/thionyl chloride (Li/SOCl_2) primary battery.⁷ Two different situations were shown, each representing a different battery design. In one case, the governing equations were developed to treat change in active electrode volume when no excess electrolyte is present. In the other case, the governing equations describe the influx of electrolyte from the cell header. If no accounting is done for the volume reduction, the battery is predicted to consume approximately 37% more reactant (solvent) than is actually present in the cell.

The University of South Carolina assisted in meeting the publication costs of this article.

List of Symbols

A	active cross-sectional area of the electrode, cm^2
c	electrolyte concentration, mol/cm^3
c_i	concentration of species i , mol/cm^3

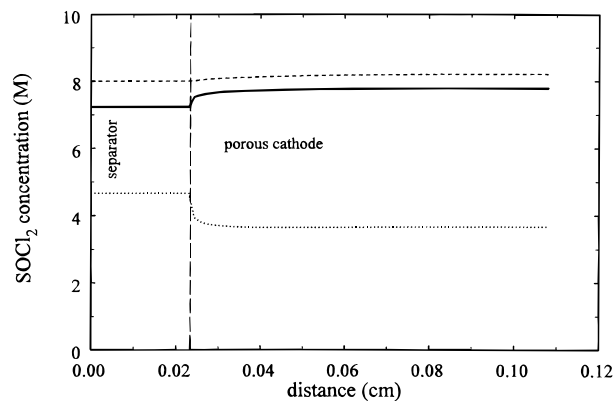


Figure 5. The solvent concentration profile at the end of discharge for the two scenarios shown schematically in Fig. 1 [i.e., (a) excess electrolyte (—); and (b) area decreasing with time (---)]. Also included is the discharge curve that results if no accounting is made of the volume reduction due to the reaction (·····). In all three cases, the lithium/thionyl chloride cell is discharged across a constant load of 250 Ω at 25°C.

D	diffusion coefficient of the binary electrolyte, cm^2/s
D_e	effective diffusion coefficient of the binary electrolyte, cm^2/s
d_{pe}	cathode thickness, cm
d_s	separator thickness, cm
F	Faraday's constant, 96,487 C/equiv
I_{app}	total cell current, A
i_1	superficial current density in the matrix phase, A/cm^2
i_2	superficial current density in the solution phase, A/cm^2
j	transfer current density, A/cm^3
n	number of electrons transferred in the electrochemical reaction, equiv/mol
Q_{max}	maximum capacity, C
R	universal gas constant, 8,314 J/mol K
R_i	rate of production of species i due to reaction, $\text{mol}/\text{cm}^3 \text{ s}$
s_i	stoichiometric coefficient of species i
t	time, s
t_i	transference number of species i relative to v^*
v^*	superficial volume average velocity, cm/s
\hat{V}_i	partial molar volume of species i , cm^3/mol
x	distance along axis normal to the electrode/electrolyte interface, cm

Greek

ϵ	porosity of the porous electrode
------------	----------------------------------

Subscripts

e	electrolyte
i	species index
k	species index
m	solid species index
o	solvent
p	porous electrode
$+$	cation
$-$	anion

Superscripts

o	initial value
-----	---------------

References

1. R. E. White and D. Fan, *J. Electrochem. Soc.*, **138**, 17 (1991).
2. T. I. Evans, T. V. Nguyen, and R. E. White, *J. Electrochem. Soc.*, **136**, 328 (1989).
3. K. Tsaur and R. Pollard, *J. Electrochem. Soc.*, **131**, 975 (1984).
4. J. Newman and W. Tiedemann, *AIChE J.*, **21**, 25 (1975).
5. J. Newman, *Electrochemical Systems*, Prentice Hall, Inc., Englewood Cliffs, NJ (1973).
6. N. Marincic, *J. Appl. Electrochem.*, **5**, 313 (1975).
7. M. Jain, G. Nagasubramanian, R. G. Jungst, and J. W. Weidner, *J. Electrochem. Soc.*, Submitted.
8. W. K. Behl, J. A. Christopoulos, M. Ramirez, and S. Gilman, *J. Electrochem. Soc.*, **120**, 1619 (1973).
9. R. H. Perry and D. Green, *Chemical Engineers' Handbook*, 6th ed., McGraw-Hill, New York (1984).
10. S. Szpak and H. V. Venkatesetty, *J. Electrochem. Soc.*, **131**, 961 (1984).