0013–4686(95)00162–X

THE USE OF MATHEMATICAL MODELING IN THE DESIGN OF LITHIUM/POLYMER BATTERY SYSTEMS

Marc Doyle and John Newman

Energy and Environment Division, Lawrence Berkeley Laboratory and Department of Chemical Engineering, University of California, Berkeley, California 94720, U.S.A.

Abstract—The use of mathematical modeling and computer simulations in the understanding of lithium/polymer battery performance is discussed. A general model of these systems is reviewed, with particular attention to the assumptions involved in the analysis. The parameters required for the model are categorized according to whether they are transport, thermodynamic, or design-adjustable properties, and the experiments necessary to measure these data are described.

The role of mathematical modeling in the design process is also considered. Dimensionless groups and simple correlations useful for characterizing the primary system limitations are given. A general approach to identifying optimum values of system parameters such as electrode thicknesses is reviewed.

Key words: lithium, batteries, polymer electrolytes, modeling

LIST OF SYMBOLS

a specific interfacial area, cm^2/cm^3
c concentration of salt in the solution phase, mol/dm^3
c_t maximum concentration in solid, mol/dm^3
$\hat{C}_p$ average heat capacity per unit mass, $J/g \cdot K$
D diffusion coefficient of lithium salt in the solution, cm^2/s
D_s diffusion coefficient of lithium in the solid electrode particles, cm^2/s
f activity coefficient of the salt
F Faraday's constant, $96\,487\,C/eq$
i_0 exchange current density of the electrode reaction, mA/cm^2
i_1 electronic current density in the solid phase, mA/cm^2
i_2 ionic current density in the solution phase, mA/cm^2
I superficial current density, mA/cm^2
j_n pore wall flux of lithium ions, $mol/cm^3 \cdot s$
L cell thickness, cm
M mass of the cell per unit area, g/cm^2
q capacity density of the positive electrode, C/cm^2
Q specific capacity of the positive electrode, C/g
r radial distance into positive electrode particle, cm
R universal gas constant, $8.3143\,J/mol \cdot K$
R_s average radius of positive electrode particle, cm
t_+^0 transference number of the cation with respect to the solvent velocity
t time, s
t_d discharge time, s
T temperature, K
U open-circuit potential, V
V cell potential, V

V_c cutoff potential, V
x distance from the negative electrode/separator boundary, cm
δ component thickness, cm
ε porosity of electrode
η potential difference at interface of solid and solution phases, V
κ ionic conductivity of electrolyte, S/cm
ρ density, g/cm^3
σ electronic conductivity of solid matrix, S/cm
Φ electrical potential, V

Subscripts
$+$ positive electrode
eff   effective property accounting for porous medium
e electrolyte
s separator or solid phase
t maximum concentration in intercalation material
0   initial condition
1   solid matrix phase
2   solution phase

Superscripts
0   solvent
θ standard cell potential

INTRODUCTION

Several companies have announced their intentions to commercialize rechargeable lithium batteries based on either lithium metal or lithium-ion technology. Most of these cells employ nonaqueous liquid electrolytes; however, some use gelled polymer electrolytes consisting of a nonaqueous liquid suspended in the pores of a polymer. The use of traditional polymer electrolytes is still an important

research area due to advantages in design flexibility and possibly safety.[1, 2] The disadvantages of polymer electrolytes include lower conductivities and lower diffusion coefficients and more difficult positive electrode fabrication processes required to attain good interfacial properties.

At this point in the battery development process, once materials selection and preparation procedures have been optimized, it is essential to proceed with detailed mathematical modeling of the full system if one is to produce the optimum cell design and configuration. Considering the large number of parameters which can be varied, it is prohibitive from both time and cost perspectives to develop the optimum design purely from experimental testing of cells. For these reasons, general models of lithium metal and lithium ion cells have been developed which can be run on a workstation computer[3, 4]. The present work will summarize the assumptions and capabilities of these models and discuss the measurement of experimental data required for the simulations. The use of these simulations for design and optimization purposes is discussed, as well as some simple methods of predicting the primary limitation for a given system.

DESCRIPTION OF THE MODELS

The one-dimensional, macroscopic model of the lithium metal cell (shown in Fig. 1) uses concentrated solution theory to describe transport in the solution phase and porous electrode theory to treat the composite positive electrode[5, 6]. The electrolyte is assumed to consist of a binary salt in a single solvent; however, mixtures of several nonaqueous liquids or high and low molecular weight polymers can be treated as a single solvent without significant loss of rigor. The composite positive electrode can consist of a solution phase, a solid active-material phase, and any conductive filler or binding additives, all of known volume fraction. In porous-electrode theory, the various phases are assumed to be superimposed continua so that there is perfect connectivity between all points of the electrode in each

lithium foil   composite
negative electrode   positive electrode

polymer
electrolyte

δ_s δ_+

$x = 0$

Fig. 1. Lithium/polymer cell sandwich, consisting of lithium foil negative electrode, solid polymer electrolyte, and composite positive electrode.

phase. The active insertion material is treated as spherical particles with a constant, known diameter; additional assumptions include that lithium has a constant diffusion coefficient in the solid phase and that no volume changes occur upon insertion or deinsertion of the lithium.

Under the above assumptions, one can show that the concentration of electrolyte obeys the equation

$$\varepsilon \frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D_{\text{eff}} \frac{\partial c}{\partial x}\right) + aj_n(1 - t_+^0), \qquad (1)$$

where $\varepsilon = 1$ and $j_n = 0$ in the separator phase ($0 < x < \delta_s$) and the effective transport properties are assumed to follow the Bruggeman relation[7]. The potential in the solution phase is measured with a lithium reference electrode,

$$\frac{\partial \Phi_2}{\partial x} = -\frac{i_2}{\kappa_{\text{eff}}}$$
$$+ \frac{RT}{F}(1 - t_+^0)\left(1 + \frac{\partial \ln f_A}{\partial \ln c}\right)\frac{\partial \ln c}{\partial x}, \qquad (2)$$

where here also we must use an effective conductivity given by $\kappa_{\text{eff}} = \varepsilon^{3/2}\kappa$. These two equations are sufficient to describe the separator region of the cell; the unknowns are c and Φ_2, and we take $i_2 = I$.

In the positive electrode we must apply Ohm's law in the solid phase:

$$I - i_2 = -\sigma \frac{\partial \Phi_1}{\partial x}. \qquad (3)$$

The distribution of the insertion process in the porous electrode is determined by a Butler-Volmer kinetics expression,

$$j_n = \frac{i_0}{F}\left(\exp\left(\frac{\alpha_a F}{RT}(\eta - U)\right) - \exp\left(-\frac{\alpha_c F}{RT}(\eta - U)\right)\right), \qquad (4)$$

where $\eta = \Phi_1 - \Phi_2$ and for insertion processes $U = U(c_s)$. The concentration of lithium in the solid phase is determined by the local rate of insertion and Fick's second law

$$\frac{\partial c_s}{\partial t} = D_s\left(\frac{\partial^2 c_s}{\partial r^2} + \frac{2}{r}\frac{\partial c_s}{\partial r}\right), \qquad (5)$$

with boundary conditions,

$$j_n = -D_s \frac{\partial c_s}{\partial r} \quad \text{at} \quad r = R_s, \qquad (6)$$

$$\frac{\partial c_s}{\partial r} = 0 \quad \text{at} \quad r = 0, \qquad (7)$$

and $c_s(t = 0, r) = c_{s,0}$. $\qquad (8)$

The last equation needed to complete the description of the porous electrode is

$$aFj_n = \frac{\partial i_2}{\partial x}, \qquad (9)$$

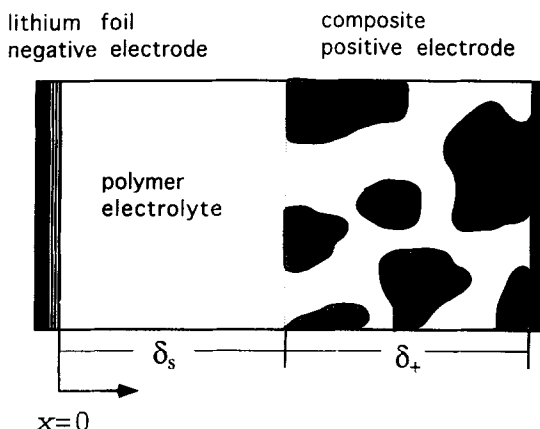which is the definition of the pore-wall flux of lithium out of the solid phase into the solution phase.

Boundary conditions at the positive electrode/current collector boundary $(x = \delta_+)$ include

$$\frac{\partial c}{\partial x} = 0 \quad \text{and} \quad i_2 = 0. \tag{10}$$

At the internal boundary $(x = \delta_s)$, we require continuity of the concentration and flux of electrolyte.

At the lithium electrode $(x = 0)$, we can arbitrarily set $\Phi_2 = 0$, and we apply a Butler-Volmer kinetic expression, similar to equation 4, which determines the potential drop of the interface. For a galvanostatic discharge we have

$$\frac{\partial c}{\partial x}(x = 0) = -\frac{I(1 - t_+^0)}{FD}. \tag{11}$$

Also, an initial condition applies in the solution phase throughout the cell,

$$c(t = 0, x) = c_0. \tag{12}$$

Thus, in the positive electrode we have six equations and six unknowns $(c, \Phi_2, c_s, i_2, j_n, \text{and} \Phi_1)$. An energy balance of the form[8]

$$M\hat{C}_p \frac{dT}{dt} = I\left(U_0 - V - T_0 \frac{dU}{dT}\right), \tag{13}$$

is also incorporated in the model[9]. This expression provides the temperature as a function of time in the cell due to internal heat generation from both reversible and irreversible phenomena.

PARAMETERS REQUIRED FOR THE MODEL

As mentioned previously, a model with this level of sophistication requires a large number of experimental parameters to be known in order to carry out simulations. Also, as the saying goes, a model is only as good as the parameters that go into it. Thus experimental characterization of the inherent properties of the materials being used is an integral part of the modeling effort. These can be classified as either transport, thermodynamic, or design-adjustable parameters. In this section we will run through all of the parameters that are needed and make some comments about methods of obtaining these data experimentally.

Transport properties

We will start with the transport properties of the solution phase, which includes κ, D, and t_+^0. These three transport properties are sufficient to describe the binary, concentrated electrolyte if each is known as a function of both salt concentration and temperature. The ionic conductivity is best measured with ac impedance[10] from the high-frequency intercept of the real axis on a complex plane plot. The method of restricted diffusion can be used to measure the salt diffusion coefficient accurately in both liquid and solid polymer electrolyte solutions[11–13]. This method involves monitoring the relaxation of a concentration gradient using either optical methods or the *emf* of a symmetric cell. The lithium ion transference number is best obtained

using either the moving boundary method[14] (in liquid solvents) or some variation of the Hittorf method[13, 15] (for solid polymers). All of the above methods have the advantage of obtaining differential values of the transport properties, *ie* the properties apply at particular values of the salt concentration, which is very important in solid polymer electrolytes where the transport properties may depend strongly on salt concentration. In addition, the transference-number measurements make no unwarranted assumptions about either solution ideality or interfacial equilibrium.

The required transport properties in the solid phase include σ and D_s. The electronic conductivity of the solid matrix can be estimated from the Bruggeman relation

$$\sigma_{eff} = (1 - \varepsilon)^{3/2}\sigma$$

once the bulk, or free-stream, value is known. This can be measured from dc four-point probe techniques on a nonporous sample, and may need to be measured as a function of % conductive filler and also as a function of state of charge (c_s). One will also need to consider that σ_{eff} may vary if different methods are used to disperse the electrode components together. The lithium diffusion coefficient in the solid phase can effectively be measured using current- or potential-step techniques[16]. This is best carried out on a nonporous sample, and a knowledge of the working area of the sample is required. The measurement should also be carried out as a function of state of charge; however, because the model requires a constant value of D_s, one may want to use its average value in the simulations.

Thermodynamic parameters

Thermodynamic data for the overall cell reaction include an exchange current density and two transfer coefficients for each half reaction, as well as open-circuit potential data. The former of these are extracted from a micropolarization experiment on a flat, nonporous sample[17]. Microelectrodes have been used for these measurements on the lithium surface.[18] Kinetic parameters for the insertion reaction have not been studied to much of an extent due to complications with mass-transfer limitations in both the solution and solid phases[19]. However, these complications are certainly possible to surmount in theory. Exchange current densities for insertion processes are often extracted from *ac*-impedance measurements by ascribing a particular semicircle to the interfacial resistance; this is not recommended except as a last resort due to difficulties in interpretation of the impedance spectra.

The mean molar activity coefficient of the solid polymer electrolyte can be determined from concentration-cell data if the transference number is known[14]. This parameter is, of course, a function of the salt concentration and temperature. The open-circuit potential as it depends on state of charge is usually measured by a coulometric titration, which amounts to a very-low-rate discharge that effectively eliminates cell polarizations. The model also requires the maximum solid-phase lithium concentration.

This can be calculated from the maximum coulombic capacity of the electrode, if this is known:

$$c_t - c_{s,0} = \frac{Q\rho}{F},$$

with Q being the capacity in units of C/g. Otherwise, it can be estimated from the density and molecular weight of the insertion material, along with a knowledge of the final stoichiometry of the insertion reaction (eg, $Li_{0.8}CoO_2$). Some other thermodynamic parameters that are needed include all of the component densities and the maximum salt concentration in the polymer solvent.

Design-adjustable parameters

Finally, there are several geometric parameters that are design adjustable and may often be fixed by practical considerations. First, the volume fraction (or mass fraction) of each component of the porous electrode must be determined. The average particle size for the insertion material particles is required and can either be estimated by filtering the powder through a fine mesh or measured from light-scattering experiments. Also, the specific surface area per unit volume must be known. This can be measured through various means, or could also be estimated from

$$a = \frac{3(1 - \varepsilon)}{R_s},$$

which assumes that the particles are spherical. Other parameters in this category include component thicknesses, initial states of charge in either electrode, initial solution-phase salt concentration, initial cell temperature, discharge rate, and cutoff potential or desired discharge time.

Generalization to the lithium-ion cell

The above model is easily modified to treat the lithium ion cell[4], which replaces the lithium metal negative electrode with a second insertion compound. We simply replace the boundary condition at $x = 0$ with an identical set of the six equations used to model the positive electrode. The equations and boundary conditions are symmetric about the separator and all of the parameters discussed above for the positive electrode must be known for both electrodes.

Summary of simulation results

The computer programs that have been developed are able to provide transient profiles across the cell of each of the six independent variables. In addition, cell potential, state of charge, and temperature as a function of time are all provided. Several choices of charge and discharge modes are provided to the user, including galvanostatic, potentiostatic, constant power, and certain combinations of these (eg, potentiostatic taper charge). The program also has the option of calculating the cell's specific energy, average specific power, and peak specific power at any desired depth of discharge. Several different lithium metal and lithium-ion systems have been simulated in previous work. Positive electrodes treated have included manganese dioxide, titanium disulfide, and cobalt dioxide; these have been combined with negative electrodes such as lithium metal and lithium carbon.

METHODS OF EVALUATING SYSTEM LIMITATIONS

The two main limitations to the high-rate discharge of polymer based lithium systems are predicted by simulations to be solution-phase ohmic and diffusion limitations. Thus, much attention has been given to the use of dimensionless parameters to determine when one of these limitations is dominant. Also, the simplified cases of complete diffusion control or ohmic control of the discharge have been treated, and analytic expressions for the energy-power and capacity-rate behavior of these systems have been developed for use in design purposes.

In attempting to characterize a system, the first question one can answer is whether the desired discharge rate is high enough to drive the salt concentration to zero during the discharge. For nonporous electrodes, it is straightforward to estimate the limiting current; however, for porous electrodes, the limiting current is reduced by some factor that depends in a complicated way on the geometric parameters of the electrode as well as the reaction rate distribution in the porous electrode. For systems having a nearly uniform current distribution, which is expected from insertion compounds having a very sloped open-circuit potential, it has been shown that the limiting current is given by[20]

$$i_{lim} = \frac{FDc_0}{(1 - t_+^0)L_s f(r, \varepsilon)}, \quad (14)$$

where

$$f(r, \varepsilon) = \frac{1}{2(1 + \varepsilon r)} + \frac{1}{r\varepsilon^{3/2}}\left(\frac{(1 + r)^2}{2}\right)$$
$$+ \frac{1}{r\varepsilon^{3/2}(1 + \varepsilon r)}\left(\frac{\varepsilon}{3} + \frac{\varepsilon r}{2} - r - \frac{1}{2} - \frac{\varepsilon(1 + r)^3}{3}\right).$$

(15)

Here we define r as the ratio of positive electrode thickness to separator thickness. This is really a worst-case scenario because there may not be sufficient time during the discharge to reach a steady-state situation. The ratio of the time of discharge to the time constant for solution-phase diffusion is then a key parameter:

$$S_e = \frac{L^2 I}{FD(1 - \varepsilon)(c_t - c_{s,0})\delta_+}. \quad (16)$$

If $S_e < 1$ then there will be sufficient time during the discharge to reach a pseudo-steady-state with respect to solution-phase transport. This means that the concentration difference in the solution can be estimated from the value required to produce zero net

anion flux:

$$\Delta c = \frac{I(1 - t_+^0)L}{FD}. \tag{17}$$

This expression must be used with caution because the diffusion coefficient will be different in the porous electrode from that in the separator region of the cell. Equation 17 is most reliably used to estimate the concentration drop across the separator by taking the characteristic length to be $L = \delta_s$.

An analogous parameter for diffusion inside of the solid electrode particles can be used to assure that this will not be an important concern

$$S_+ = \frac{R_s^2 I}{FD_s(1 - \varepsilon)(c_t - c_{s,0})\delta_+}. \tag{18}$$

If $S_+ < 1$, then diffusion limitations inside of the solid electrode particles may be neglected. If diffusion limitations in the solution and solid phases are not important, then it is likely that the system is ohmically limited. Because of the relatively facile charge-transfer kinetics of the lithium and insertion electrode surfaces, ohmic resistances in the poorly conducting polymer phase will generally dominate kinetic resistances at the surfaces.

Optimization of system parameters

A procedure developed to identify optimum values for the design-adjustable parameters uses an application-specific approach. It is assumed *a priori* that the system must be optimized for a specific discharge time; this fact then provides a constraint on the equations involved. Additional constraints include that the cell potential cannot fall below some cutoff potential ($V > V_c$) and that the capacity of the cell be completely exhausted at the end of discharge[21]. Also, we assume that the separator thickness, transport and thermodynamic parameters, and the temperature of operation are all fixed by material constraints. Under this approach, the system can be optimized to obtain either a maximum specific energy or maximum specific capacity. This procedure is somewhat tedious to perform numerically; thus, some effort has been expended to develop analytical expressions for the energy and capacity that can be used in the limiting cases mentioned previously[20, 21]. When the expressions apply, the optimization procedure can be performed on a spreadsheet.

The results of these calculations generally follow one's intuition: thicker, less porous electrodes are desired for long-discharge-time applications and thinner, more porous electrodes are better for short discharge times. Simplified cases[21] have allowed a dimensionless discharge time to be defined that can be useful for a comparison of whether a given system falls into the long- or short-discharge-time category

$$T = \frac{U\kappa_s t_d}{q_+ L_s^2}. \tag{19}$$

This parameter is also useful for comparisons between different battery systems.

SUMMARY

Detailed mathematical models are essential to the design and understanding of complex systems such as rechargeable lithium batteries. One such model is reviewed here, with emphasis given to the parameters required for the simulations and how these parameters may be obtained experimentally. Rather than trial-and-error battery design, we emphasize here a systematic approach involving characterization of the thermodynamic and transport properties of the materials being used, followed by simulation of the full system and optimization of the design-adjustable parameters for a given application.

REFERENCES

1. M. B. Armand, in *Polymer Electrolyte Reviews—1* (Edited by J. R. MacCallum and C. A. Vincent), Elsevier Applied Science, London (1987).
2. F. M. Gray, *Solid Polymer Electrolytes* VCH, New York, (1991).
3. M. Doyle, T. F. Fuller and J. Newman, *Modeling of Galvanostatic Charge and Discharge of the Lithium/Polymer/Insertion Cell*, J. electrochem. Soc. **140**, 1526 (1993).
4. T. F. Fuller, M. Doyle and J. Newman, *Simulation and Optimization of the Dual Lithium Ion Insertion Cell*, J. electrochem. Soc. **141**, 1 (1994).
5. J. Newman, *Electrochmical Systems* Prentice-Hall, Englewood Cliffs, NJ (1991).
6. J. Newman and W. Tiedemann, *Porous-Electrode Theory with Battery Applications*, AIChE J. **21**, 25 (1975).
7. D. A. G. Bruggeman, *Annalen der Physik* **24**, 636 (1935).
8. D. Bernardi, E. Pawlikowski and J. Newman, *A General Energy Balance for Battery Systems*, J. electrochem. Soc. **132**, 5 (1985).
9. C. R. Pals, M. Doyle, T. F. Fuller and J. Newman, *Modeling of Adiabatic and Isothermal Galvanostatic Discharge Behavior of the Lithium/Polymer/Insertion Cell*, in *Douglas N. Bennion Memorial Symposium Proceedings* (Edited by R. W. White and J. Newman) The Electrochemical Society Proceedings Series, Pennington, NJ (1994).
10. C. D. Robitaille and D. Fauteux, *Phase Diagram and Conductivity Characterization of Some PEO-LiX Electrolytes*, J. electrochem. Soc. **133**, 315 (1986).
11. J. Newman and T. W. Chapman, *Restricted Diffusion in Binary Solutions*, AIChE J. **19**, 343 (1973).
12. S. D. Thompson and J. Newman, *Differential Diffusion Coefficients of Sodium Polysulfide Melts*, J. electrochem. Soc. **136**, 3362 (1989).
13. Y. Ma, M. Doyle, T. F. Fuller, L. C. De Jonghe and J. Newman, *The Measurement of a Complete Set of Transport Properties for a Concentrated Solid Polymer Electrolyte Solution*, J. electrochem. Soc. accepted.
14. R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, Butterworths, London, 2nd, Ed. (1959).
15. P. G. Bruce, M. T. Hardgrave and C. A. Vincent, *The Determination of Transference Numbers in Solid Polymer Electrolytes Using the Hittorf Method*, S. S. Ionics **53-56**, 1087 (1992).

16. D. Guyomard and J. M. Tarascon, *Li Metal-Free Rechargeable LiMn₂O₄/Carbon Cells: Their Understanding and Optimization*, J. electrochem Soc. **139**, 937 (1992).

17. C. A. C. Sequeira and A. Hopper, *S. S. Ionics* **9&10**, 1131 (1983).

18. M. W. Verbrugge and B. J. Koch, *Microelectrode Investigation of Ultrahigh-Rate Lithium Deposition and Stripping* General Motors Research Publication, GMR-7876 (1993).

19. A. J. Vaccaro, T. Palanisamy, R. L. Kerr and J. T. Malay, *Electrochemical Investigations of Alkali-Metal Intercalation Reactions in TiS_2 : Chronoamperometric*

Determination of Mass and Charge Transport Properties of Liquid Electrolyte Systems, J. electrochem. Soc. **129**, 682 (1982).

20. M. Doyle and J. Newman, *Modeling the Performance of Rechargeable Lithium-based Cells: Design Correlations for Limiting Cases*, J. Power Sources, Proceedings of the 7th International Meeting on Lithium Batteries, May 1994.

21. J. Newman, *Optimization of Porosity and Electrode Thickness with a Reaction-Zone Model*, in *Douglas N. Bennion Memorial Symposium Proceedings* (Edited by R. E. White and J. Newman) The Electrochemcial Society Proceedings Series, Pennington, NJ (1994). *J. Electrochem. Soc.*, **142**, 97 (1995).