

Model Reformulation and Design of Lithium-ion Batteries

V.R. Subramanian^{1,*}, V. Boovaragavan¹,
V. Ramadesigan¹, K. Chen² and R.D. Braatz²

¹Department of Chemical Engineering, Tennessee Technological University,
Cookeville, TN 38505

²Department of Chemical & Biomolecular Engineering, University of Illinois,
Urbana-Champaign, Urbana, IL 61801

CONTENTS

Introduction	988
Model Reformulation	991
Reformulation for the Finite Difference Method	991
Reformulation for Polynomial Representation	993
Parameter Estimation for Capacity Fade Prediction.....	997
Optimal Design of Lithium-ion Batteries	1001
Conclusions.....	1003
Acknowledgments	1003
References.....	1004

ABSTRACT Recently, electrochemical power sources have had significant improvements in design, economy, and operating range and are expected to play a vital role in the future in automobiles, power storage, military, mobile-station, and space applications. Lithium-ion chemistry has been identified as a good candidate for high-power/high-energy secondary batteries and commercial batteries of up to 75 Ah have been manufactured. Applications for batteries range from implantable cardiovascular defibrillators (ICDs) operating at 10 μ A current to hybrid vehicles requiring pulses of 100 A. While physics-based models have been widely developed and studied for these systems, these models have not been employed for parameter estimation or dynamic optimization of operating conditions or for designing electrodes for a specific performance objective. This is an unexplored area requiring model reformulation and efficient simulation of coupled partial differential equations. This paper describes model reformulation and its application to (1) parameter estimation and prediction of capacity fade for lithium-ion batteries, and (2) optimal product design.

* To whom all correspondence should be addressed: Vsubramanian@tnstate.edu

KEYWORDS Lithium-ion batteries, product design, Bayesian estimation, Markov Chain Monte Carlo simulation

Introduction

Several issues arise in the operation of lithium-ion batteries—capacity fade, underutilization, abuse caused by overcharging, and thermal runaway caused by operation outside the safe window (Newman et al, 2003). For example, the batteries used in hybrid cars operate at 50% state of charge to enhance life while compromising on utilization (energy efficiency). The capability to accurately predict capacity and internal state variables is highly desired as it can help extend the life of the battery and provide for better operational strategies. Three different approaches have been used in the literature for modeling lithium-ion batteries: (1) empirical models (Plett, 2004), (2) transport phenomena models (Doyle et al, 1993), and (3) stochastic models (Darling and Newman, 1999). Although parameter estimation, design calculations, and dynamic optimization are easiest to apply to empirical models due to their low computational cost, these models fail at many operating conditions and cannot predict the future behavior or current capacity accurately. Several recent studies have tried to understand micro- and nanoscale phenomena in batteries using stochastic methods. These models would need to be coupled with transport phenomena models to predict process behavior of batteries at the system level.

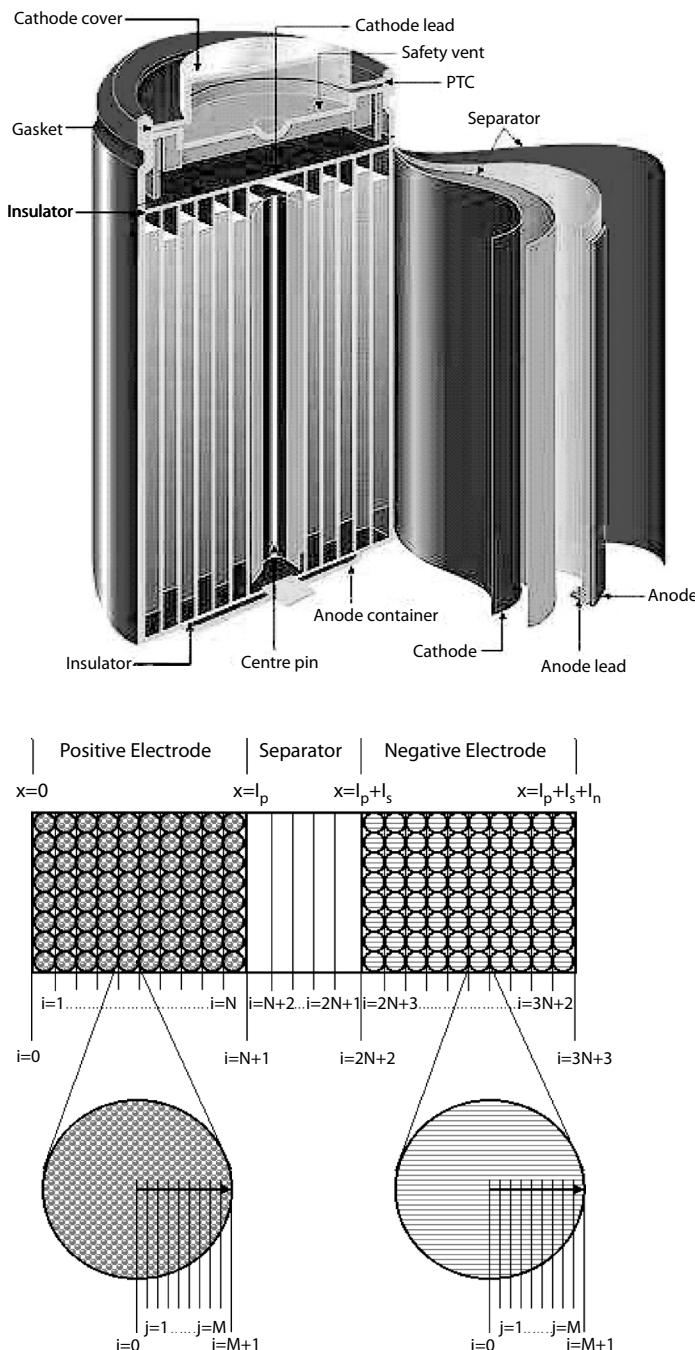
Of the three modeling approaches, transport phenomena models are currently the most promising candidates for use in design because these models can predict both internal and external behavior (system level) with reasonable accuracy. These models are based on porous electrode theory coupled with transport phenomena (Doyle et al, 1993, Botte et al, 2000) and electrochemical reaction engineering. These models are represented by coupled nonlinear partial differential equations (PDEs) in 1 or 2 dimensions and are typically solved numerically, requiring between a few minutes to hours to simulate. As an example of the form of these PDEs, the model equations for the lithium-ion battery cathode are

$$\begin{aligned} \varepsilon_p \frac{\partial c}{\partial t} &= \frac{\partial}{\partial x} \left(D_{eff,p} \frac{\partial c}{\partial x} \right) + a_p (1 - t_+) j_p \\ I &= -\sigma_{eff,p} \frac{\partial \Phi_1}{\partial x} - \kappa_{eff,p} \frac{\partial \Phi_2}{\partial x} + \frac{2\kappa_{eff,p} RT}{F} (1 - t_+) \frac{\partial \ln c}{\partial x} \\ \frac{\partial}{\partial x} \left(\sigma_{eff,p} \frac{\partial \Phi_1}{\partial x} \right) &= a_p F j_p, \quad \frac{\partial c_s}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(D_{sp} r^2 \frac{\partial c_s}{\partial r} \right) \end{aligned}$$

Electrochemical modeling of a typical secondary battery involves three regions: positive porous electrode, separator, and negative porous electrode (see Fig. 1). The original model involves 10 PDEs (4 in each electrode + 2 in the separator). If 100 node points are used in the x -direction in each region and 20 node points are used in the r -direction, the original model involves 2×100 (separator) + 3×100 (macroscale in each electrode) + $1 \times 20 \times 100$ (microscale in each electrode) = $200 + 300 \times 2 + 2000 \times 2 = 4800$ differential-algebraic equations (DAEs) in time. This model accounts for diffusion and reaction in the electrolyte phase in the anode/separator/cathode, diffusion (intercalation) in the solid phase in the cathode and anode, ionic and electronic conductivity in the corresponding phases in the porous electrodes (cathode and anode), nonlinear ionic conductivity, and nonlinear kinetics.

While first principles-based models have been discussed in detail in the literature, attempts to rigorously estimate parameters have been minimal. As of today, literature on dynamic optimization or design of lithium-ion batteries based on physics-based models for a specific performance (e.g., minimized capacity fade) is non-existent (the linearized models analyzed in the frequency domain by Smith and Wang (2006) cannot be used for non-constant parameters). For a lithium-ion battery, the process variable could either be current or voltage (e.g., for a given load or current, the battery operates at a voltage that decays with time, or when the battery is operated at a certain voltage, current decays with time). In a hybrid environment, in which batteries operate in series-parallel combination with fuel cells or other devices, energy or power might be specified which is typically delivered by operating the battery at a particular current or voltage profile. To optimize electrochemical power sources, and to produce mini- and micro- batteries and fuel cells for the future, there is an urgent need to develop and implement effective and robust parameter estimation and optimization strategies. While existing models can be used for offline analysis and simulation purposes, these models are unsuitable for parameter estimation, dynamic optimization, or product design. Recently we have begun applying systems engineering methods with the objectives of (1) predicting underutilization and capacity fade, (2) devising optimal operating strategies, and (3) designing new materials for improved performance (e.g., extended life). This paper focuses on the following topics:

1. Development of reformulated efficient models to facilitate parameter estimation, dynamic optimization, and product design.
2. Estimation of transport and kinetic parameters as a function of a battery's cycle life.
3. Design of batteries with higher average utilization over time.

**FIGURE 1**

Lithium-ion battery, cross-sectional view (top) and numerical grid for modeling (bottom).

Model Reformulation

Model reduction is an active area of research for many engineering and science fields (Benner, 2008). There are standard methods available in the literature for reducing a given set of coupled partial differential equations (PDEs) to reduced order models with different levels of accuracy and detail. Proper Orthogonal Discretization (POD) uses the full numerical solution to fit a reduced set of eigenvalues and nodes to get a meaningful solution with a reduced number of equations (Cai and White, 2008). A drawback of POD is that the resulting model needs to be reconstructed when the operating current is doubled, the boundary conditions are changed, or if the parameter values are changed significantly. Orthogonal Collocation (OC) is another widely used technique to reduce the order of the models in a variety of chemical engineering problems. A drawback of the OC technique is its inability to accurately define profiles with sharp gradients and abrupt changes. Certain models might require a large number of collocation points (Wei, 1987). Orthogonal collocation was found to be only as efficient as solving the PDEs using the finite difference method for battery models and resulted in unstable codes for smaller number of points because of the model's DAE nature.

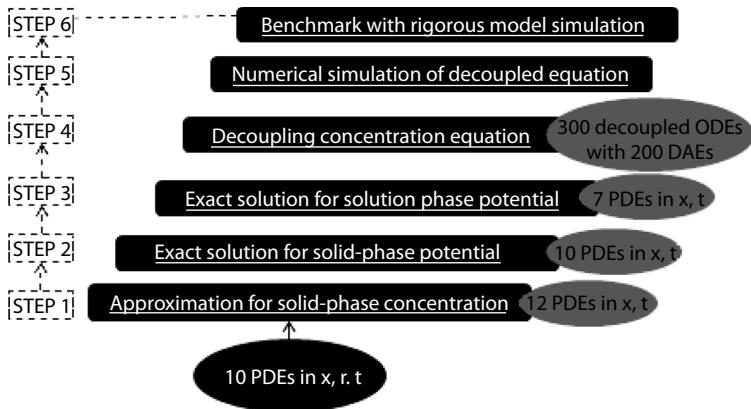
This paper describes a method for mathematical model reformulation that applies various techniques to solve for the dependent variables without losing accuracy. Specific information for the dependent variables in the x direction is provided that was not reported in past papers on the model reformulation (Subramanian et al, 2007; 2009). Volume averaging coupled with polynomial approximation for the solid-phase concentration gives high accuracy at low-to-medium rates of discharge for modeling lithium-ion batteries (Subramanian et al, 2005; Wang et al, 1998). This step converts the model from a pseudo-2D to a 1D model.

Below is a description of the step-by-step procedure to reduce the ten coupled nonlinear PDEs (in x , r , t) in the battery model to a small number of DAEs (< 50). The approach considers each dependent variable separately and finds a suitable mathematical method to minimize the computational cost associated with that particular variable. The dependency of a chosen variable with other dependent/independent variables is kept intact.

We have attempted and arrived at various possible ways of simulating this model including the finite element method (FEM), finite difference method solved using BANDJ (Newman, 1968) or DASSL (Brenan et al, 1989), and orthogonal collocation. This paper only describes the most efficient approaches we have found for solving this system of equations.

Reformulation for the Finite Difference Method

This section describes model reformulation used with finite difference method (see Fig. 2 for a flowchart of the procedure).

**FIGURE 2**

Schematic of steps involved in reformulation using the finite difference method.

The governing equation for the solid-phase potential is derived from Ohm's law for the positive and negative electrodes. If j_p was a constant, the governing equation can be solved to obtain a closed-form solution. However, j_p is a nonlinear function of the dependent variables. If finite difference method is applied in the x -direction, the solid-phase potential equation is given by

$$\sigma_{\text{eff},p} \frac{\Phi_{1,i+1} - 2\Phi_{1,i} + \Phi_{1,i-1}}{h_1^2} = a_p F j_p, \quad i = 1, \dots, N, \quad (1)$$

where N is the number of interior node points. Eq. (1) can be written in matrix form as

$$A\Phi_1 = j_p + b. \quad (2)$$

The dependent variable Φ_1 can be eliminated (expressed in terms of j_p) by inverting the coefficient matrix in Eq. (2). Typically 50 node points might be needed to obtain a converged solution. Matrix methods can be used to derive and store the inverse matrix and solution *a priori* in the computer to eliminate the need for keeping Φ_1 in the model equations. A general expression can be obtained for the eigenvalues and eigenvectors as a function of N , the number of node points, so that there is no loss of accuracy. For the original equation with the boundary conditions, the exact solution for each eigenvalue is

$$\lambda_i = 2 \left(1 - \cos \frac{\pi(2i-1)}{(2N+1)} \right), \quad i = 1, \dots, N. \quad (3)$$

Although similar equations can be derived for eigenvectors as a function of N , a numerical approach can be more efficient. Similar steps can be performed (although the equations are more complicated for other variables) as shown in Fig. 2 and discussed elsewhere (Subramanian, et al, 2007; 2009).

After reformulation, even if 50 node points are used in each region, the resulting 150 decoupled equations for c coupled with 100 decoupled algebraic equations (AEs) for $c_{s,surf}$ or $j_{p/n}$ and 100 decoupled ordinary differential equations (ODEs) for $c_{s,ave,p/n}$ (which occurs only in the electrode) can be solved very efficiently. After this step, the reformulated models can be run in <100 ms, which is required in a hybrid environment that may have supercapacitors with time constants <1 s.

The reformulated models have been compared with models from the literature. Both external/system (voltage-time curve, process variable) and internal variables match exactly for rates less than 2C. The computational cost is much higher for finite difference/volume/element methods that need to perform matrix algebra as a function of N , the number of node points. We could not derive any analytical expressions reported in the literature for banded matrices in mixed domains (cathode/separator/anode) with varying diffusion coefficients in each region. While it is possible that there exists an analytical solution, numerical analysis can be performed to obtain them empirically as a function of N . Our computational experience suggested that the finite difference method was not the best possible approach for the reformulation. The next section presents a more efficient method that implements model reformulation using a polynomial representation.

Reformulation for Polynomial Representation

A more efficient option than finite differences is to write j_p as a sum of polynomials or other pre-specified functions:

$$j_p = \sum_{i=0}^N \alpha_{pi} f_i(x). \quad (4)$$

The governing equation for the solid-phase potential can be integrated with respect to x to obtain

$$\Phi_1 = c_1 + c_2 x + \frac{a_p F}{\sigma_{eff,p}} \sum_{i=0}^N \alpha_{pi} \int \left(\int f_i(x) dx \right) dx. \quad (5)$$

In the literature, various kinds of polynomials such as Chebyshev polynomials (Varma and Morbidelli, 1999) have been used for model reformulation. If the pre-specified functions have exact double integrals, the solution is analytical with numerical error approaching zero as long as the functions form a complete basis and enough terms are chosen in Eq. (4). If simple polynomials are chosen, then

$$j_p = \sum_{i=0}^N \alpha_{pi} x^i \quad (6)$$

and

$$\Phi_1 = c_1 + c_2 x + \frac{a_p F}{\sigma_{eff,p}} \sum_{i=0}^N \alpha_{pi} \frac{x^{i+2}}{(i+1)(i+2)}. \quad (7)$$

The above integration constants are solved from the boundary conditions. Using a polynomial for j_p is more advantageous than using the finite difference, finite element, or finite volume methods for reformulating Φ_1 as double integration to get Φ_1 is less computationally expensive than inverting matrices. Using one of the above reformulation approaches, an analytical solution can be derived for the solid-phase potential distribution in each porous electrode. This reformulation enables a closed-form solution for the solid-phase potential distribution in each electrode as a function of other dependent variables without compromising on accuracy and without losing any physics of the battery system. Moreover, this reformulation technique reduces one PDE for the solid-phase potential to one algebraic equation. At this stage, the original model for the solid-phase potential is reduced to

$$\Phi_1(x) = 4.2 + \frac{a_p F}{\sigma_{eff,p}} \sum_{i=0}^N \frac{\alpha_{pi}}{i+1} \left(\frac{x^{i+2}}{i+2} - l_p^{i+1} \right). \quad (8)$$

The governing equation for the liquid-phase potential is given by the modified Ohm's law. If $\kappa_{eff,p}$ is a constant, the governing equation for electrolyte potential can be solved analytically as

$$\begin{aligned} \Phi_2(x) &= k_1 - I \int_{\kappa_{eff,p}} \frac{1}{dx} - \sigma_{eff,p} \int \frac{1}{\kappa_{eff,p}} \frac{\partial \Phi_1}{\partial x} dx \\ &\quad + \frac{2RT}{F} (1 - t_+) \ln c. \end{aligned} \quad (9)$$

$\kappa_{eff,p}$ is a nonlinear function of the dependent variable (electrolyte concentration) for various chemistries. If the function governing the variation of $1/\kappa_{eff,p}$ with respect to the other dependent variables has an exact integral, then this equation has an analytical solution. If not, simple polynomials are chosen as $\frac{1}{\kappa_{eff,p}} = \sum_{i=0}^N \zeta_{pi} x^i$. Then

$$\Phi_2(x) = k_1 - I \sum_{i=0}^N \zeta_{pi} \frac{x^{i+1}}{i+1} - \sigma_{eff,p} \Upsilon + \frac{2RT}{F} (1 - t_+) \ln c \quad (10)$$

where Υ is a product of two summations resulting from integration.

The Galerkin-collocation (GC) type weighted-average method is used to solve for the constants. For example, each constant ζ_{pi} is obtained by minimizing the residue of the governing equation with a weighting function given by the coefficient of the particular constant as

$$\begin{aligned} & \frac{1}{l_p} \int_{x=0}^{l_p} w_1 Ge(\Phi_2) \Big|_{cathode} dx + \frac{1}{l_s} \int_{l_p}^{l_p+l_s} w_2 Ge(\Phi_2) \Big|_{separator} dx \\ & + \frac{1}{l_n} \int_{l_p+l_s}^L w_3 Ge(\Phi_2) \Big|_{anode} dx = 0, \end{aligned} \quad (11)$$

where w_1 , w_2 , and w_3 are the weight functions and $Ge(\Phi_2)$ denotes governing equation for Φ_2 . Six of the constants in the polynomials are obtained from the boundary conditions at $x = 0$, $x = l_p$, $x = l_p + l_s$, and $x = L$. At the electrode/separator interfaces, both the electrolyte potential and its fluxes are continuous. Similarly, polynomial representations are used for the other dependent variables arising from the solid-phase concentration equations and pore-wall flux expression. The GC technique is more stable and provides accurate solutions with lesser number of terms in the polynomial representation compared to the OC technique.

The dependent variable for the electrolyte in each region is approximated with polynomial expressions and substituted in the governing equation for electrolyte concentration to get separate equations in each region and the constants are found using the weighted residual:

$$\begin{aligned} & \frac{1}{l_p} \int_{x=0}^{l_p} w_1 Ge(c) \Big|_{cathode} dx + \frac{1}{l_s} \int_{l_p}^{l_p+l_s} w_2 Ge(c) \Big|_{separator} dx \\ & + \frac{1}{l_n} \int_{l_p+l_s}^L w_3 Ge(c) \Big|_{anode} dx = 0. \end{aligned} \quad (12)$$

Both for the electrolyte potential and concentration, six of the constants in the polynomials are found from boundary conditions. In addition, volume averaging is performed to the original set of PDEs. The electrolyte concentration can be volume-averaged over the respective region as:

$$\begin{aligned} & \varepsilon_p \int_{x=0}^{l_p} \frac{\partial c}{\partial t} dx + \varepsilon_s \int_{x=l_p}^{l_p+l_s} \frac{\partial c}{\partial t} dx + \varepsilon_n \int_{x=l_p+l_s}^L \frac{\partial c}{\partial t} dx \\ & = D_{\text{eff},p} \left(\frac{\partial c}{\partial x} \Big|_{x=l_p} - \frac{\partial c}{\partial x} \Big|_{x=0} \right) + a_p (1 - t_+) \int_{x=0}^{l_p} j_p dx \\ & + D_{\text{eff},s} \left(\frac{\partial c}{\partial x} \Big|_{x=l_p+l_s} - \frac{\partial c}{\partial x} \Big|_{x=l_p} \right) + \\ & + D_{\text{eff},n} \left(\frac{\partial c}{\partial x} \Big|_{x=L} - \frac{\partial c}{\partial x} \Big|_{x=l_p+l_s} \right) + a_n (1 - t_+) \int_{x=l_p+l_s}^L j_n dx. \end{aligned} \quad (13)$$

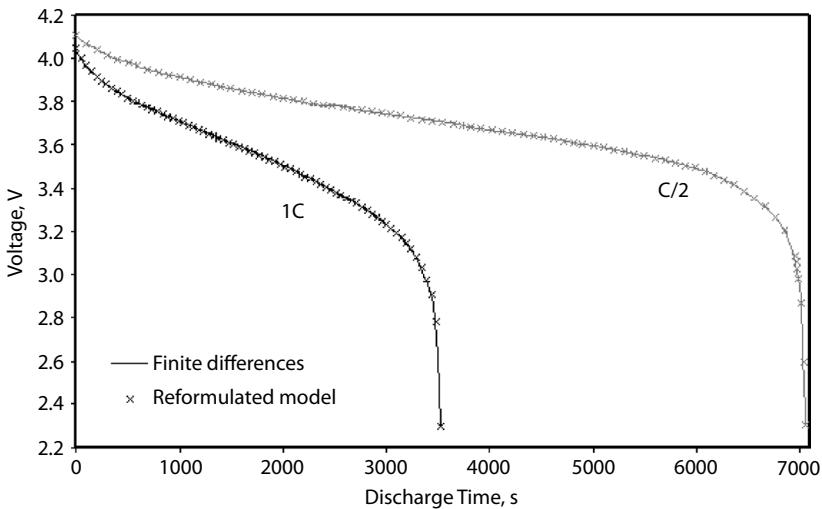


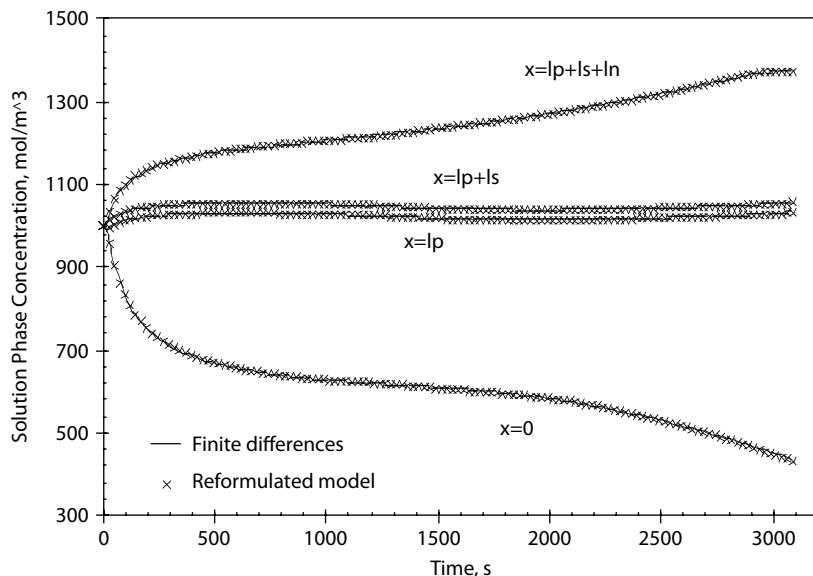
FIGURE 3
Discharge curves for 1C and 0.5C rate.

This equation can be simplified and integrated to obtain

$$C_{ave}^{Total} = \frac{\varepsilon_p C_{ave}^{Cathode} + \varepsilon_s C_{ave}^{Separator} + \varepsilon_n C_{ave}^{Anode}}{\varepsilon_p l_p + \varepsilon_s l_s + \varepsilon_n l_n} = 1000. \quad (14)$$

This equation is true for any chemistry and can also be derived from the overall mass balance of the cell. This facilitates a quicker convergence of the concentration profiles in terms of polynomials. If this condition is not used, more number of terms may be needed in the polynomial representation to maintain numerical stability.

The discharge potential is the measured variable (see Fig. 3). The discharge curves are shown for 1C (30 A/m^2) and 0.5C rates of galvanostatic discharge. It can be seen that, for these rates of discharge, the reformulated model compares very well with the original numerical model. The merit of this approach is evident when comparing the number of governing equations that are solved. The reformulated model specifies 47 DAEs as opposed to 4800 DAEs for the original model. The reformulated model uses a maximum of 47 specified equations for a converged solution that compares very well even with the original finite difference code. The reformulated model predicts the intrinsic non-measurable (state) variables accurately as shown in Fig. 4, with the CPU time reduced by two orders of magnitude. The reformulated model takes only 15–50 ms to predict a discharge curve in FORTRAN environment whereas the original model can take up to a few seconds to minutes depending on the solver, environment, and the computer.

**FIGURE 4**

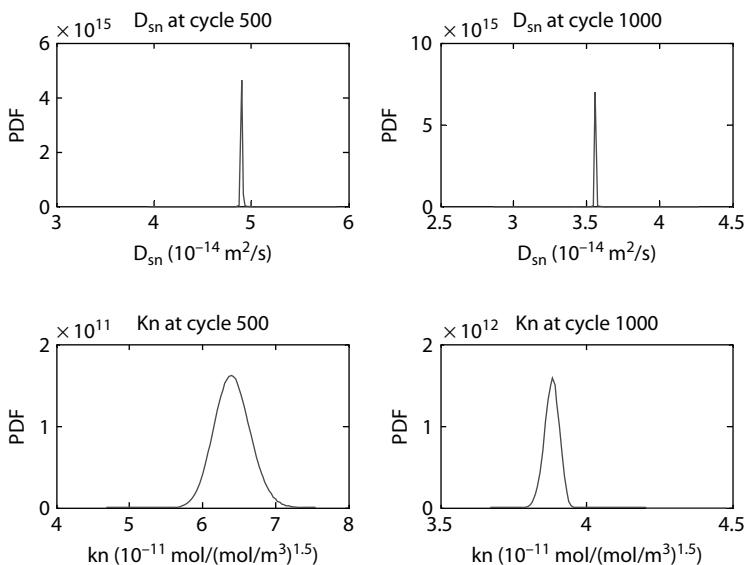
Solution phase concentration at different times for 1C rate at different interfaces.

Parameter Estimation for Capacity Fade Prediction

The protocol that is commonly used in cycling a lithium-ion battery consists of first charging at constant current then charging at constant potential until the potential reaches a uniform value across the intercalating particles, then the protocol follows discharging the battery at constant current or potential. The battery loses its capacity to hold and deliver the energy when the number of cycle increases. These losses are mainly due to the variations in the transport and kinetic parameters caused by the reduced pore volume in the porous electrodes.

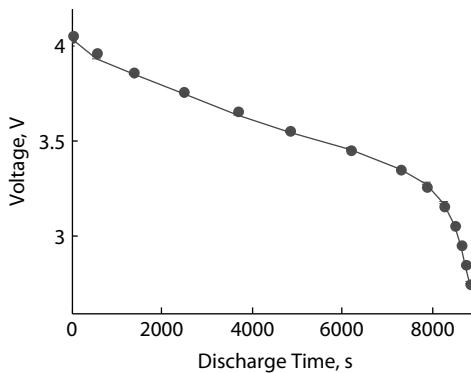
In addition, researchers have observed a major loss in the discharge time period over which one can utilize the battery (Ramadass et al, 2004). This loss is an especially important prediction for batteries installed in remote applications like satellites, but is also important when using battery models to optimize operations. To enable such a level of model sophistication, a model that updates transport and kinetic parameters as a function of cycle number is developed. This information can be used to provide guidance to the development of first-principles models for capacity fade that introduce additional reactions (Ramadass et al, 2004), models for SEI layer growth, etc.

Unknown parameters that were estimated are the solid-phase diffusion coefficient D_{sn} and the reaction rate constant k_n in the negative electrode.

**FIGURE 5**

Bayesian estimation for the solid-phase diffusion coefficient D_{sn} and the reaction rate constant k_n for the negative electrode at cycle 500 and 1000.

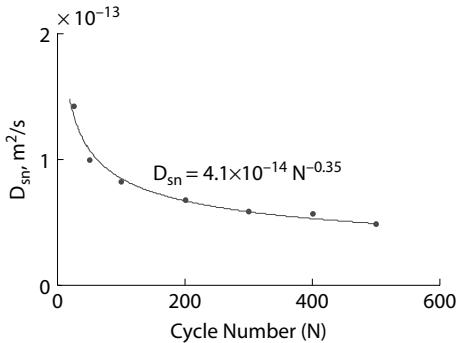
Bayesian estimation was used to estimate the model parameters from experimental data obtained using lithium-ion batteries from Quallion® LLC. Uncertainties in the model parameter estimates were quantified by three methods: (1) estimation of hyperellipsoidal regions using linearized statistics, (2) estimation of nonlinear uncertainty regions using F-statistics, and (3) estimation of probability distributions by application of Markov Chain Monte Carlo (MCMC) simulation (Hermanto et al., 2008; Tierney, 1994). Methods 1 and 2, which are the most commonly applied, gave highly biased probability distributions in this application, whereas there is no statistical bias in method 3. Other advantages of method 3 include its explicit consideration of constraints and arbitrary non-Gaussian distributions for prior knowledge on the parameters, and that it exactly handles the full nonlinearity in the model equations. Method 3 requires many more simulation runs than methods 1 and 2, which provides further motivation for the derivation of the low-order reformulated model. Figure 5 shows the probability density functions of two model parameters obtained by MCMC simulation, with statistically significant reductions in both the solid-phase diffusion coefficient D_{sn} and the reaction rate constant k_n for the negative electrode. These model parameters reduced monotonically with cycle number, which is consistent with a monotonic decrease in the pore volume in the negative electrode.

**FIGURE 6**

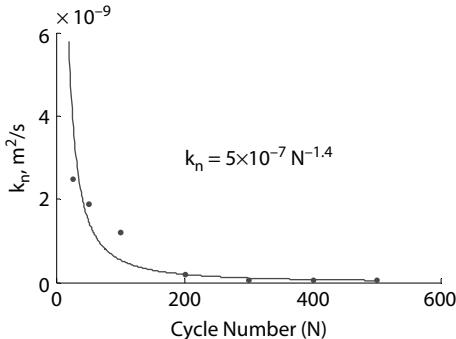
Comparison of the experimental voltage-discharge curve with the model prediction with estimated parameters for cycle 500. Each red dot is a data point, the blue line is the model prediction, and the 95% predictive intervals were computed based on the parametric uncertainties reported in Fig. 5. Similar quality fits and prediction intervals occurred for the other cycles.

The effect of the parameter uncertainties on the accuracy of the predictions of the lithium-ion battery model was then quantified by polynomial chaos expansions (Wiener, 1938). This approach avoids the high computational cost associated with applying the Monte Carlo method or parameter gridding to the simulation code by first computing a series expansion for the simulation model, followed by application of robustness analysis to the series expansion. The very low computational cost of the series expansion enables the application of the Monte Carlo method, gridding the parameter space, or the application of norm-based analytical methods (Ma and Braatz, 2001; Nagy and Braatz, 2004; 2007). 95% prediction intervals computed for each cycle provided confidence that the model can be used for predictions and design (see Fig. 6).

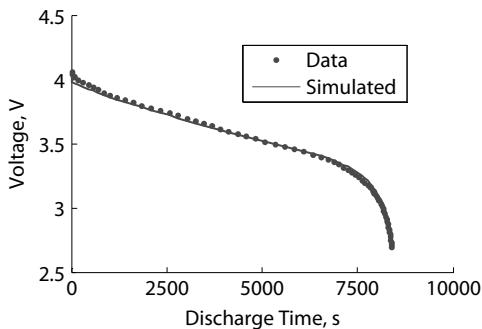
A battery is no longer useful once its capacity becomes too low. Even for the same manufacturing line, the lifetime varies widely from battery to battery. It would be useful for a microprocessor to provide an estimate of the number of useful cycles remaining in the battery. We explored the use of the model to predict the remaining battery life based on voltage-discharge curves measured in past cycles. To characterize the degradation in the model parameters, a power law was fit to the estimated parameter values from cycles 25 to 500 (see Figs. 7 and 8). Implicitly assuming that the changes in the parameter values are the result of the same mechanism in later cycles, the parameter values for the subsequent cycles were predicted using the power law expressions. The voltage-discharge curve predicted by this model was in very good agreement with the experimental data at cycle 1000 (see Fig. 9), indicating that the model was suitable for prediction of capacity fade.

**FIGURE 7**

Power law fit for the solid-phase diffusion coefficient in the negative electrode based on the estimated parameter value from the first 500 cycles.

**FIGURE 8**

Power law fit for the reaction rate constant for the negative electrode based on the estimated parameter value from the first 500 cycles.

**FIGURE 9**

Comparison of the experimental voltage-discharge curve with the model prediction using parameter values calculated from the power law fits in Figs. 7 and 8.

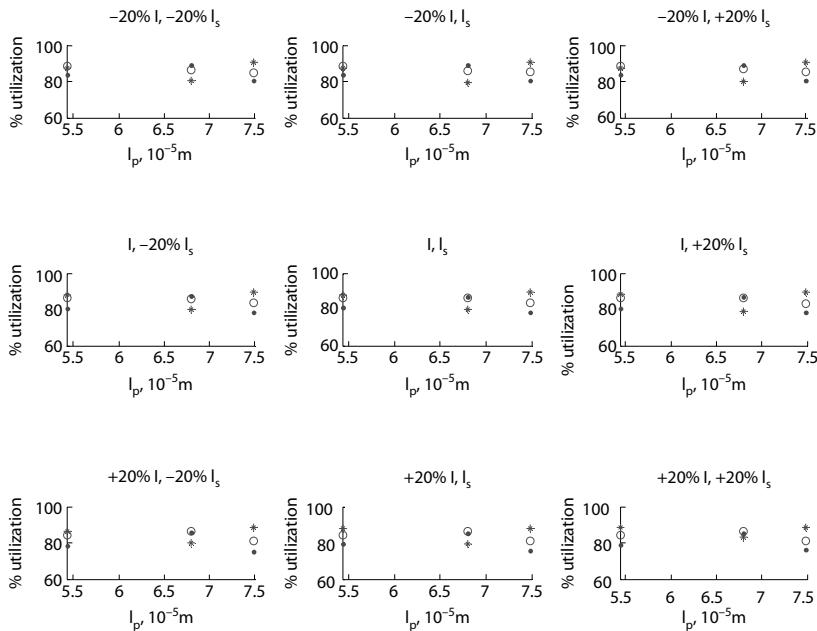
The computation time required for parameter estimation using the reformulated model was between 100 and 300 ms. Compare this to the minutes to hours required for the standard finite difference method directly applied to the battery model.

Optimal Design of Lithium-ion Batteries

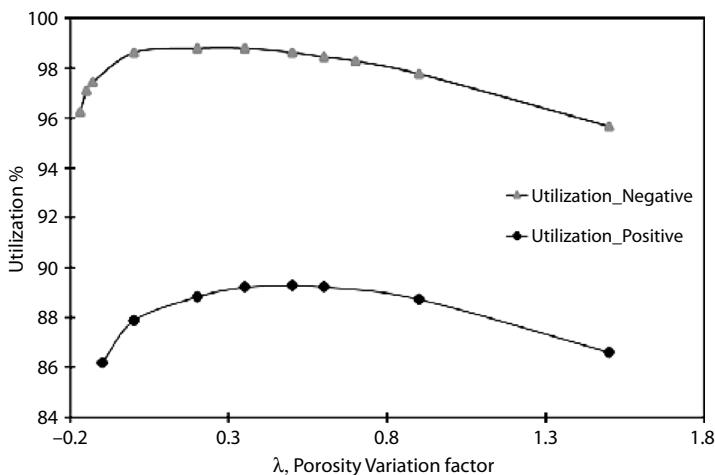
Prof. Newman and his group have applied macroscopic models to optimize the electrode thickness or porosity (Srinivasan and Newman, 2004). These studies have been performed by comparing the Ragone plots for different design parameters. A single curve in a Ragone plot may involve hundreds of simulations wherein the applied current is varied over a wide range of magnitude. Ragone plots for different configurations are obtained by changing the design parameters (e.g., thickness) one at a time, and by keeping the other parameters constant. This process of generating a Ragone plot is quite tedious and typically Ragone curves reported in the literature are not smooth because of computational constraints.

To our knowledge, the literature does not report the application of such first-principles models to the global optimization of multiple battery design parameters. Also, batteries are typically designed only to optimize the performance at cycle one of the battery, whereas in practice most of the battery's operation occurs under significantly degraded conditions. The reformulated model is sufficiently computationally efficient to enable the simultaneous optimal design of multiple parameters over any number of cycles by including the model for capacity fade (Figs. 7 and 8). Further, the model can be used to quantify the effects of model uncertainties and variations in the design parameters on the battery performance. As an example of such robustness analysis, the utilization averaged over 1000 cycles are reported in Fig. 10 for the battery design obtained by (1) simultaneous optimization of the applied current density (I) and thicknesses of the separator and the two electrodes (l_s, l_n, l_p) for cycle 1, and (2) variations in these four design parameters. The battery design optimized for cycle 1 does not maximize the cycle-averaged utilization.

We are also investigating the optimal design of *distributions* of properties, which cannot be reasonably handled by one-at-a-time optimization. In particular, we are optimizing porosity distributions and particle size distributions across the electrode, in addition to the standard design parameters considered in Fig. 10. Figure 11 shows some sample results in which the linear porosity distribution is optimized across the cathode thickness to maximize the utilization of the electrodes. More than 3% improvement in utilization occurred by using spatially-varying porosity within the positive electrode. The oral presentation will include additional product design results.

**FIGURE 10**

Utilization averaged over cycle 25, 500, and 1000 for a 3-level 4-factor factorial design. The title of each plot indicates the deviation in the design variables I and l_s from their values optimized for cycle 1. Circles, stars, and dots are for the l_n value optimized for cycle 1 and $\pm 20\%$ of that value, respectively.

**FIGURE 11**

Utilization of positive and negative electrodes with linearly varying porosity as $\varepsilon_p = \varepsilon_{p0}(1 + 2\lambda(x/l_p))/(1 + \lambda)$.

Conclusions

This paper employs a systems engineering approach for the modeling and design of lithium-ion batteries. An efficient approach is presented to simulate the discharge behavior of lithium-ion battery models for galvanostatic boundary conditions with improved computational efficiency using a polynomial representation. The approach is similar to Galerkin-collocation based on weighted residuals coupled with analytic solution of the algebraic equations and volume averaging for the variables of interest. The DAE nature and structure of the model is exploited to solve for some of the dependent variables analytically. The model reformulation method is demonstrated at low-to-moderate rates of discharge. The method should be valid and applicable to other engineering models with a DAE nature such as fuel cells and monolith reactors. Also, for the use of dynamic model in feedback control algorithms with microchips, computer memory (RAM) is likely to be a concern. The proposed reduction in the number of DAEs and states would also enable the implementation of more advanced robust controller algorithms.

The reformulated model was applied with robust Bayesian estimation to predict future capacity fade in lithium-ion batteries. Predictions were demonstrated for the first 1000 cycles of a Quallion® LLC 250 mAh cell. The nonlinear nature of the models motivated the use of the MCMC approach to quantify the uncertainties in the parameter estimates. The reformulated model facilitates such a rigorous approach, as the MCMC approach requires many simulation runs to construct accurate distributions for the parameter estimates. The reformulated model should facilitate dynamic optimization for better operational strategies for improved energy efficiency and design for better electrode materials for improved performance.

Acknowledgments

The authors are thankful for the partial financial support of this work by the National Science Foundation (CBET – 0828002 and 0828123), the U.S. Army Communications-Electronics Research, Development, and Engineering Center (CERDEC) under contract number W909MY-06-C-0040, and the Oronzio de Nora Industrial Electro-chemistry Postdoctoral Fellowship of The Electrochemical Society.

References

- Beck, J. V., Arnold, K. J. (1977). *Parameter Estimation in Engineering and Science*. Wiley, New York.
- Benner, P. <http://www.math.tu-berlin.de/~baur/D1.html> (referred on December 31, 2008).
- Botte, G. G., Subramanian, V. R., White, R. E. (2000). Mathematical Modeling of Secondary Lithium Batteries. *Electrochim. Acta*, 45, 2595.
- Braatz, R. D., Alkire, R. C., Seebauer, E. G., Rusli, E., Gunawan, R., Drews, T. O., He, Y. (2006). Perspectives on the Design and Control of Multiscale Systems. *J. of Process Control*, 16, 193.
- Brenan, K. E., Campbell, S. L., Petzold, L. R. (1989). *Numerical Solution of Initial-value Problems in Differential-Algebraic Equations*. North-Holland, New York.
- Cai, L., White, R. E. (2008). Reduction of Model Order Based on Proper Orthogonal Decomposition for Lithium Ion Battery Simulations. *J. Electrochem. Soc.*, article in press.
- Darling, R., Newman, J. (1999). Dynamic Monte Carlo Simulations of Diffusion in $\text{Li}_y\text{Mn}_2\text{O}_4$. *J. Electrochem. Soc.*, 146, 3765.
- Doyle, M., Fuller, T. F., Newman, J. (1993). Modeling the Galvanostatic Charge and Discharge of the Lithium/Polymer/Insertion Cell. *J. Electrochem. Soc.*, 140, 1526.
- Hermanto, M. W., Kee, N. C., Tan, R. B. H., Chiu, M.-S., Braatz, R. D. (2008). Robust Bayesian Estimation of Kinetics for the Polymorphic Transformation of L-glutamic Acid Crystals, *AIChE J.*, 54, 3248.
- Ma, D. L., Braatz, R. D. (2001). Worst-case Analysis of Finite-time Control Policies. *IEEE Trans. on Control Syst. Tech.*, 9, 766.
- Nagy, Z. K., Braatz, R. D. (2004). Open-loop and Closed-loop Robust Optimal Control of Batch Processes using Distributional and Worst-case Analysis. *J. of Process Control*, 14, 411.
- Nagy, Z. K., Braatz, R. D. (2007). Distributional Uncertainty Analysis Using Power Series and Polynomial Chaos Expansions. *J. Process Control*, 17, 229.
- Newman, J. (1968). Numerical Solution of Coupled, Ordinary Differential Equations. *Ind. Eng. Chem. Fund.*, 7, 514.
- Newman, J., Thomas, K. E., Hafezi, H., Wheeler, D. R. (2003). Modeling of Lithium-ion Batteries. *J. Electrochem. Soc.*, 150, A176.
- Osaka, T., Nakade, S., Rajamäki, M., Momma, T. (2003). Influence of Capacity Fading on Commercial Lithium-ion Battery Impedance. *J. Power Sources*, 119–121, 929.
- Plett, G. L. (2004). Extended Kalman Filtering for Battery Management Systems of LiPB-based HEV Battery Packs, Part 1. Background. *J. Power Sources*, 134, 252.
- Ramadass, P., Gomadam, P. M., White, R. E., Popov, B. N. (2004). Development of First Principles Capacity Fade Model for Li-ion Cells. *J. Electrochem. Soc.*, 151, A196.
- Smith, K., Wang, C. Y. (2006). Solid State Diffusion Limitations on Pulse Operation of a Lithium Ion Cell for Hybrid Electric Vehicles. *J. Power Sources*, 161, 628.
- Subramanian, V. R., Boovaragavan, V., Ramadesigan, V., Arabandi, M. (2009). Mathematical Model Reformulation for Lithium-ion Battery Simulations—Galvanostatic Boundary Conditions. *J. Electrochem. Soc.*, 156, A260.

- Subramanian, V. R., Diwakar, V. D., Tapriyal, D. (2005). Efficient Macro-Micro Scale Coupled Modeling of Batteries. *J. Electrochem. Soc.*, 152, A2002.
- Subramanian, V. R., Boovaragavan, V., Diwakar, V. D. (2007). Towards Real-time (Milliseconds) Simulation of Physics Based Lithium-ion Battery Models. *Electrochem. Solid-State Lett.*, 10, A225.
- Tierney, L. (1994). Markov Chains for Exploring Posterior Distributions. *Ann. Stat.*, 22, 1701.
- Varma, A., Morbidelli, M. (1999). *Mathematical Methods in Chemical Engineering*. Oxford University Press, London.
- Srinivasan, V, Newman, J, (2004). Design and Optimization of a Natural Graphite Iron Phosphate Lithium-Ion Cell. *J. Electrochem. Soc.*, 151, A1530.
- Wang, C. Y., Gu, W. B., Liaw, B. Y. (1998). Micro-macroscopic Coupled Modeling of Batteries and Fuel Cells. Part I: Model Development. *J. Electrochem. Soc.*, 145, 3407.
- Wei, J., (1987). *Advances in Chemical Engineering*, Vol. 13, Academic Press.
- Wiener, N. (1938). The Homogeneous Chaos. *Am. J. Math.*, 60, 897.