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Parameter Estimation and Capacity Fade Analysis of Lithium-Ion Batteries Using First-Principles-Based Efficient Reformulated Models

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Transport and kinetic parameters of lithium-ion batteries are estimated using a first-principles electrochemical engineering model based on porous electrode theory (1, 2). A full-order model reformulated using advanced mathematical techniques (3, 4) was used for the simulations. Since batteries and other power sources are used in hybrid environments, with devices with time constants less than a second (like a super capacitor or an induction motor), parameter estimation algorithms were developed with high computational efficiency. As a complement to approaches to mathematically model capacity fade that require detailed understanding of each mechanism (5), capacity fade was accurately and efficiently predicted for future cycles by extrapolating the change in effective transport and kinetic parameters with cycle number (N), for a battery under controlled experimental conditions. Parameter estimation using mathematical reformulation (4) was more efficient and robust than full-order models based on the traditional finite difference approach.

Introduction

Electrochemical power sources are expected to play a vital role in future applications in automobiles, power storage, military, mobile, and space. Lithium-ion chemistry has been identified as a preferred candidate for high-power/high-energy secondary batteries. Significant progress has been made towards modeling and understanding of lithium-ion batteries using physics-based first-principles models. These models are based on transport phenomena, electrochemistry, and thermodynamics.

For the analysis and control of lithium-ion batteries in hybrid environments (with a fuel cell, capacitor, or electrical components), methods are needed to simulate state of charge, state of health, and other parameters in near real-time conditions (milliseconds). Full-order physics-based models take up to few seconds to minutes to simulate discharge curves depending on the solver, routines, computers, battery design, and operating conditions, whereas circuit or empirical models (based on the past data) can be simulated in real time. However, the latter models fail at various operating conditions, and use of these models may cause abuse or underutilization of electrochemical power sources. Hence the need arises for a faster model that includes the physics of the system and enables the extraction of transport and kinetic parameters from the model efficiently. This

is made possible by a reformulated model (4) that takes a few milliseconds to predict a discharge curve. The reformulated model is used in parameter estimation algorithms to extract kinetic and transport parameters. Further, the estimated parameters are used to address capacity fade in the battery with cycling.

Reformulated Model

First-principles-based battery models typically solve electrolyte concentration, electrolyte potential, solid-state potential, and solid-state concentration in the porous electrodes and electrolyte concentration and electrolyte potential in the separator. These models are represented by coupled nonlinear PDEs in one or two dimensions, are typically solved numerically, and require a few minutes to hours to simulate. The reformulated model (4) conserves mass, charge, and current in each electrode, unlike traditional finite-difference full-order models. Also, the memory requirement and the computational time and cost are far less compared to finite difference full-order models. These features can be utilized by parameter estimation techniques to extract effective kinetic and transport parameters from experimentally measured voltage discharge curves. Two different nonlinear parameter estimation techniques were used: (i) ordinary least-squares and (ii) Bayesian estimation, which takes into account prior knowledge on the probability distributions for the model parameters. The reformulated model also enabled the application of the Markov Chain Monte Carlo (MCMC) method to quantify the magnitude of uncertainties in the model parameters.

Capacity Fade in Lithium-ion Batteries

The literature is abundant with various possible mechanisms for understanding capacity fade (6). However, mathematical models that include these phenomena are very few (7) and do not include all postulated mechanisms. Such a mathematical model, although highly desirable, has not been forthcoming due to (i) incomplete understanding of all of the capacity fade mechanisms, (ii) a lack of knowledge for the values of the model parameters in these mechanisms, (iii) difficulties in obtaining these values due to cumulative non-separable effects of individual mechanisms occurring simultaneously, and (iv) numerical inability and lack of efficient numerical solvers. Often times in the quest for adding detailed mechanisms, researchers have neglected important electrochemical/transport phenomena typically included in physics-/porous electrode-based battery models by using single-particle models or empirical fits.

Different mechanisms causing capacity fade include (i) capacity fade during formation cycles, (ii) overcharging, which results in a decrease in capacity in both positive and negative electrodes and the electrolyte, (iii) decomposition of the electrolyte during the reduction process, (iv) self-discharge depending on the purity of materials used in manufacturing, and (v) formation of a passive film on the electrode that grows in thickness as the cycle number increases.

Page limitations preclude the inclusion of a review of electrochemical engineering models and a step-by-step description of what a possible mechanism means in terms of

model formulation and numerical simulation. In part due to the combination of multiple simultaneous mechanisms possible for capacity fade (see Figure 1), the experimental data available (discharge curves at different cycles) may not be sufficiently sensitive to all possible scenarios and mechanisms. To address this, nonlinear parameter estimation and the MCMC method were used to estimate effective model parameters that characterize capacity fade and to quantify uncertainties in the parameters. The use of reformulated models for discharge curves facilitated the application of the latest system theory to quantify and discriminate models and mechanisms using MCMC and polynomial chaos theory.

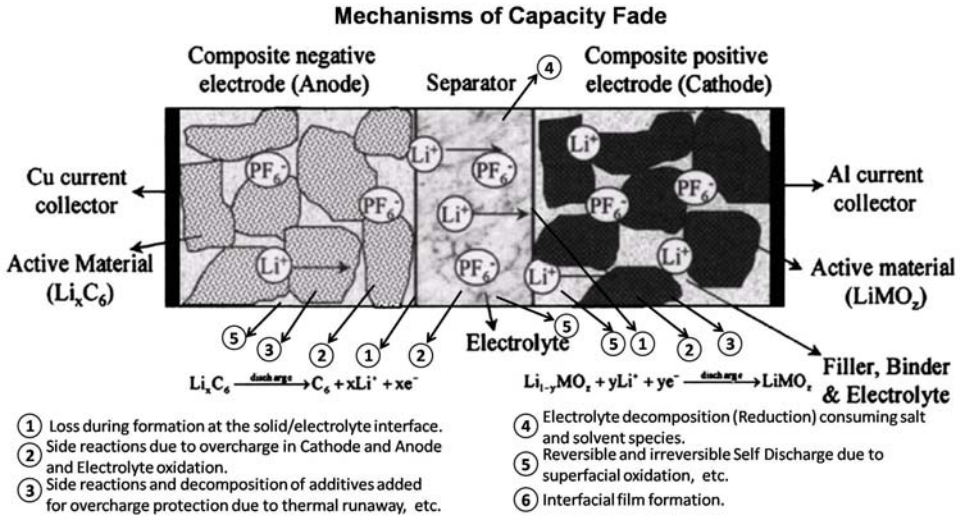

Figure 1: A schematic showing some capacity fade mechanisms postulated in a Li-ion battery.

Parameter Estimation and Uncertainty Analysis Techniques

Nonlinear Parameter Estimation

Many numerical algorithms are available for nonlinear parameter estimation, such as the steepest descent method, the Gauss-Newton method, and the Marquardt method. In this work, the Gauss-Newton method was applied to estimate parameters in the reformulated model. For ordinary least-squares estimation, this Jacobian-based method is an iterative process that reduces the error between the model outputs and the experimental data. The same numerical optimization algorithm was also applied to optimize the objective function for Bayesian estimation, which was formulated in terms of the sum of the least-squares errors and a quadratic term that took prior information on the probability distribution on the model parameters into account (e.g., in the same manner as in equation 5 of Reference (8)).

Uncertainty Quantification

Uncertainties in the model parameter estimates were quantified by three methods: (i) estimation of hyperellipsoidal regions by application of Chi-squared statistics to a Taylor series expansion between the model parameters and the model outputs, (ii) estimation of

nonlinear uncertainty regions by application of F-statistics to the parameter estimation objective function (8, 9), and (iii) estimation of probability distributions by application of Markov Chain Monte Carlo (MCMC) simulation (10, 11). Methods i and ii, which are the most commonly applied, gave highly biased probability distributions for this application, whereas there is no statistical bias in method iii. Other advantages of method iii 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 iii requires many more simulation runs than methods i and ii, which provided further motivation for the use of the reformulated model.

Results and Discussion

The experimental data for the analysis were obtained for the Quallion® BTE cells and chemistry (12). Finite-difference and reformulated models were validated at cycle 0. Using the model parameters at cycle 0 as an initial guess, Figure 2 compares the experimental voltage-discharge curve at cycle 25 with reformulated model output obtained using five model parameters fit by ordinary least-squares to that experimental data set (the five parameters were the effective solid-phase diffusion coefficients and electrochemical reaction rate constants in positive and negative electrodes, and the electrolyte diffusion coefficient). Similar parameter estimations and fits were obtained for various cycle numbers like 50, 100, and 150, etc. Initially 5 different parameters are estimated for each of the cycles as shown in Figure 3a. However, only two parameters, namely the solid-phase diffusion coefficient D_{sn} and the reaction rate constant k_n for the negative electrode, had to significantly change their values to be able to fit the voltage-discharge curves at higher cycle number. Hence the rest of the study was restricted to extracting only these two parameters. Figure 3b shows the variation of these two model parameters for different cycle numbers.

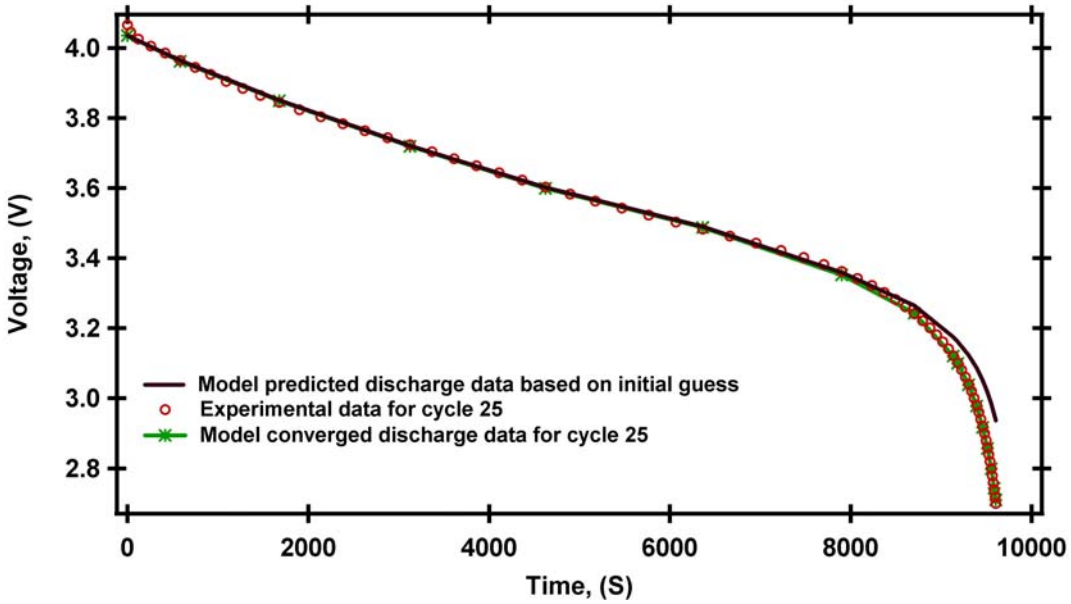

Figure 2: Comparison of model predictions with the experimental data, with five model parameters obtained from ordinary least-squares estimation applied to the experimental data for cycle 25.

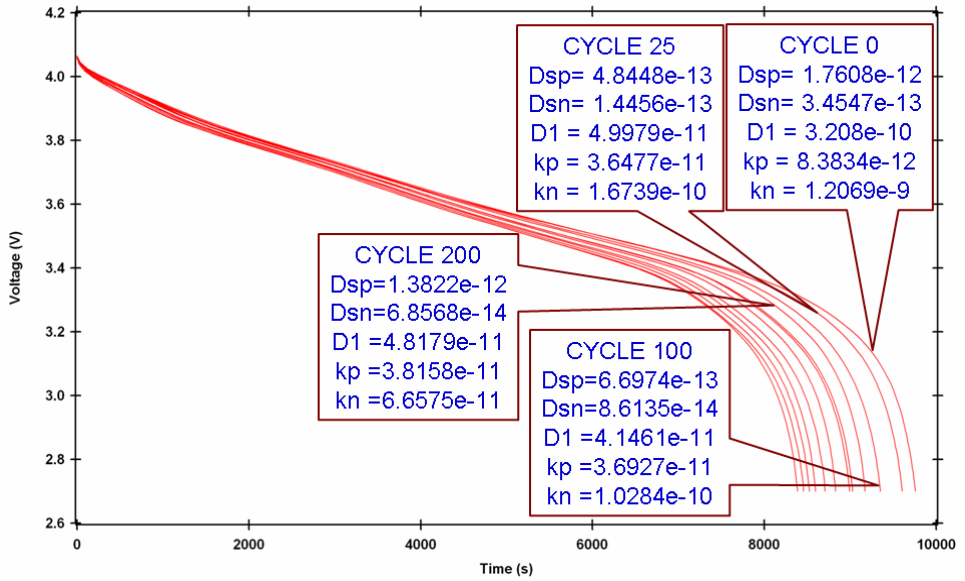

Figure 3a: Five-parameter estimation.

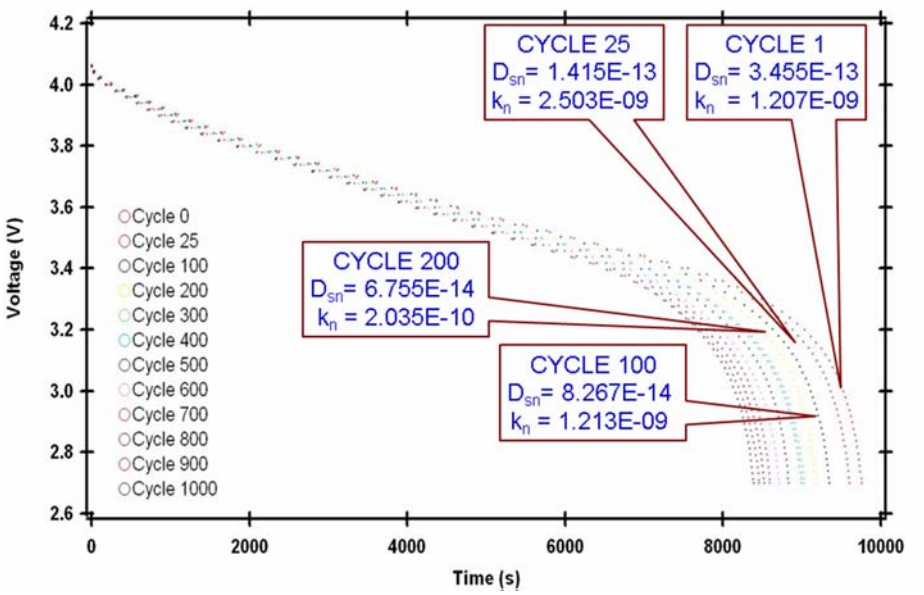

Figure 3b: Two-parameter estimation.

A discrete approach was adopted for the prediction of capacity fade, by keeping track of the change in effective transport and kinetic parameters with cycle number (N). Figure 4 shows the variation of the effective diffusion coefficient and rate constant with cycle number. A power law fit is shown for variations in each parameter as a function of cycle

number. The inset plot in Figure 4 compares the extrapolated model prediction and experimental data at cycle 600 using the power laws for capacity fade fit to parameters predicted only up to cycle 200. The mathematical model provides an accurate prediction of the voltage-discharge curves for higher cycle numbers.

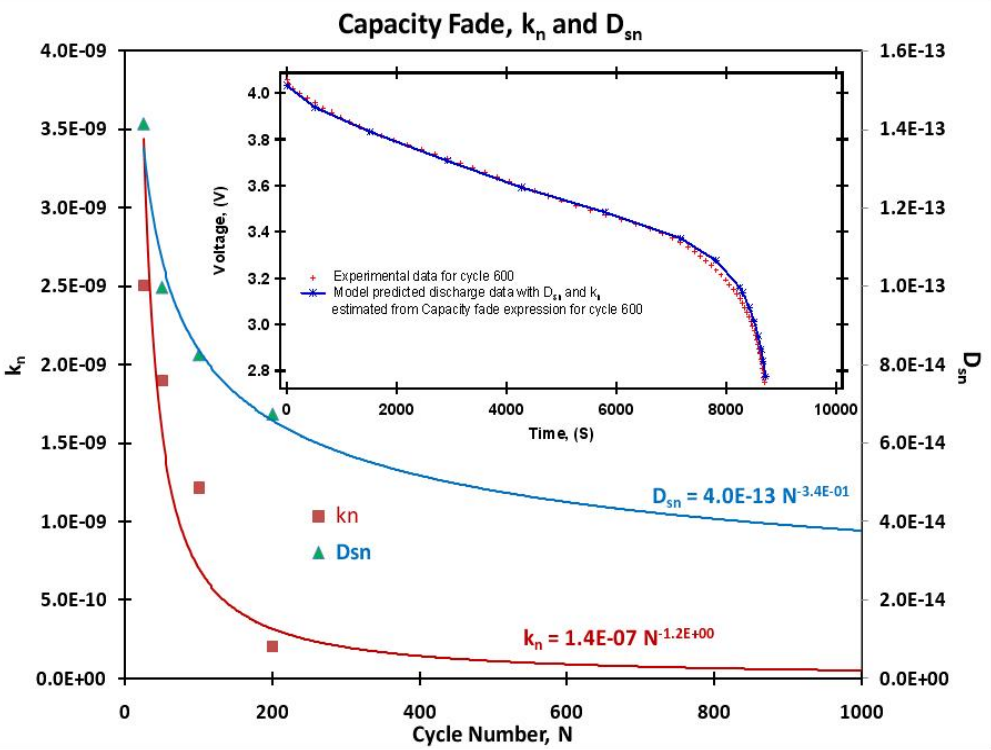

Figure 4: Variation in the effective solid-phase diffusion coefficient at the negative electrode.

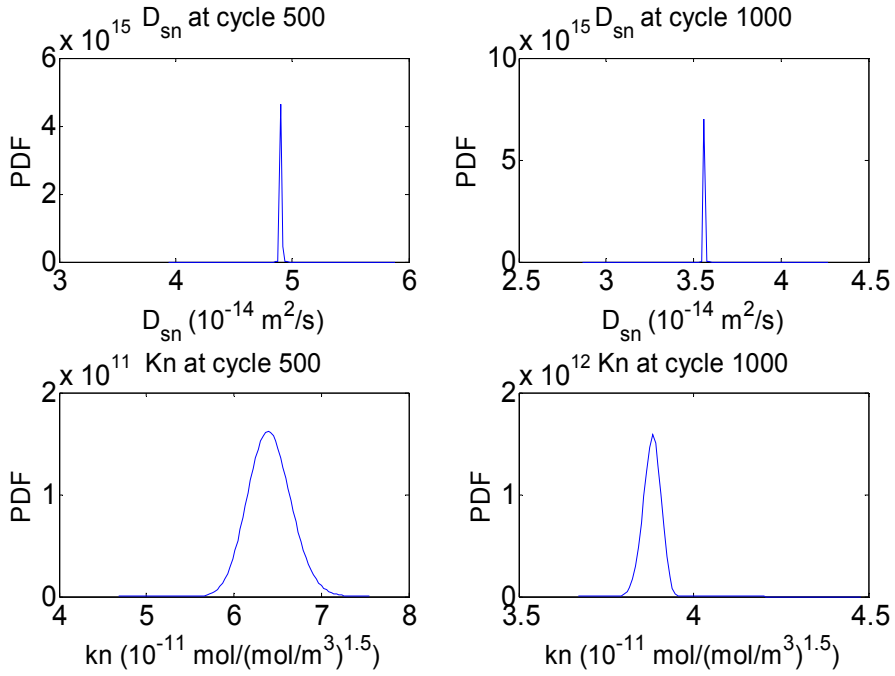

Figure 5: Uncertainty quantification for the effective solid-phase diffusion coefficient D_{sn} and the reaction rate constant k_n for the negative electrode at cycle 500 and 1000 (13).

Bayesian estimation was also used to estimate the model parameters from experimental data obtained using lithium-ion batteries from Quallion® LLC. Figure 5 shows the resulting probability density functions for two model parameters obtained by the MCMC method; with statistically significant reductions in both the effective 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.

The effect of the parameter uncertainties on the accuracy of the predictions of the lithium-ion battery model was quantified by polynomial chaos expansions (14). 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 (15-17). 95% prediction intervals computed for each cycle provided confidence that the model can be used for predictions and design (Figure 6).

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 similar to what was done for ordinary least-squares estimation. 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 (Figure 7), indicating that the model was suitable for prediction of capacity fade.

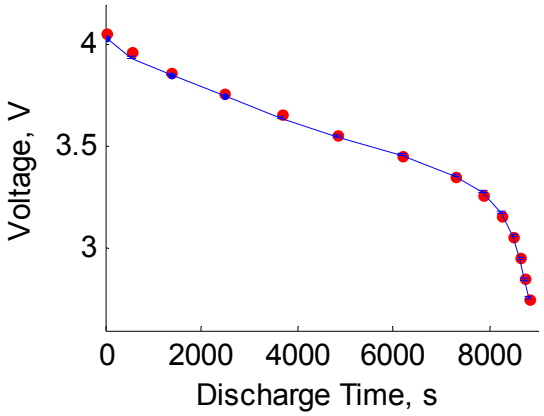

Figure 6. Comparison of the experimental voltage-discharge curve with the model prediction for cycle 500. Each red dot is a data point, the blue line is the model prediction, and the 95% predictive intervals were computed based on the parametric uncertainties

reported in Figure 5. Similar quality fits and prediction intervals occurred for the other cycles (13).

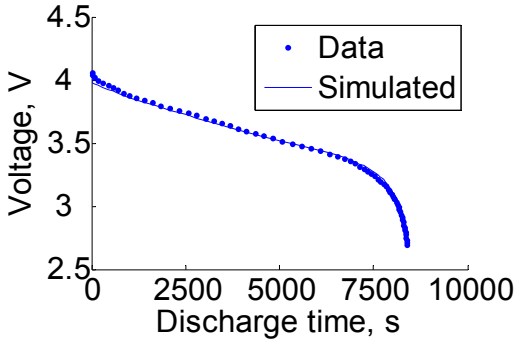

Figure 7. Comparison of the experimental voltage-discharge curve with the model prediction using parameter values calculated from the power law fits (13).

In summary, the effective solid-phase diffusion coefficients and electrochemical reaction rate constants in positive and negative electrodes, and the electrolyte diffusion coefficient were estimated and tracked as a function of N. Uncertainties in parameter estimates were quantified by the MCMC method, which indicated that (i) nearly all of the variation in voltage-discharge curves could be explained by changes in only two model parameters, and (ii) the changes in the estimated parameter values due to capacity fade were due to actual changes in the model parameters rather than uncertainties in the parameter estimation due to limited parameter identifiability and limited data. After characterizing uncertainties in the parameters, the effects of the parameter uncertainties on the outputs of the system were quantified using polynomial chaos theory. Small prediction intervals provided, as well as comparisons of model predictions with experimental data, provided confidence in the ability of the model to predict capacity fade.

Future Directions

As a next step, mechanisms will be added to the existing battery model and predictions and confidence intervals will be compared. Future work also includes uncertainty analysis for design calculations and capacity fade predictions with multiscale models.

Acknowledgments

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