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Analysis of capacity fade in a lithium ion battery

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Abstract

Two parameter estimation methods are presented for online determination of parameter values using a simple charge/discharge model of a Sony 18650 lithium ion battery. Loss of capacity and resistance increase are both included in the model. The first method is a hybrid combination of batch data reconciliation and moving-horizon parameter estimation. A discussion on the selection of tuning parameters for this method based on confidence intervals is included. The second method uses batch data reconciliation followed by application of discrete filtering of the resulting parameters. These methods are demonstrated using cycling data from an experimental cell with over 1600 charge–discharge cycles.

Keywords: Capacity fade; Online parameter estimation; Lithium ion batteries

1. Introduction and motivation

The overall performance of batteries deteriorates over time as the system is cycled repeatedly through multiple iterations of charge and discharge. For high-performance applications it is useful to have accurate knowledge of the present condition of the battery as well as the remaining battery life. The reduction in battery performance can be assumed to manifest in two ways: capacity fade display in the reduction in ability of the battery to store charge and increased area specific impedance (ASI) the resistance to charge transfer which reduces cell potential.

Given the importance of this information for high performance electrochemical systems, significant effort has been devoted to the development of models that describe the discharge behavior of batteries. The majority of these models are empirical or semi-empirical at best [1,2], having limited predictive capability given the strong dependence of cell behavior on factors such as temperature and charge/discharge cycling protocol. However, even models developed using a more mechanistic approach [3], are susceptible to error. These models are typically developed using data that is collected under tightly controlled experimental conditions, which simply do not exist in real-world applications. Nevertheless, these models can be regressed to data and can provide an accurate representation of a battery for a few charging/discharging cycles. As is the case for any model prediction, unknown disturbances and unmodeled phenomena will inevitably influence the system, leading to the divergence of the model prediction from the actual battery performance.

This universal drawback of modeling is typically overcome in real-world applications (e.g. weather forecasting) by periodically updating the parameters of the model to reflect the current state of the system. For a number of dynamic systems, this is not a trivial matter. Often it is difficult to measure these parameter values without disturbing the system, if it is even possible to measure them directly at all. For Li-ion cells, the only method currently available to directly measure the actual capacity is to stop the cycling and physically open the battery in an inert environment. Not only is this counterproductive as the cycling is interrupted, but it is impossible for remote applications such as satellite power systems. Therefore, there is great value in being able to determine updated model pa-

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Nomenclature

a_{ii}	ith element on the diagonal of A
a_n	nth auto-regressive coefficient in a digital filter
A	parameter covariance matrix in parameter estimation
b_n	nth moving-average coefficient in a digital filter
b_i	estimated value of unknown parameter β_i
$d^{(k)}$	arbitrary process disturbance at time/cycle k
$e^{(k)}$	error between measured and model-predicted arbitrary process at time/cycle k; $\hat{y}^{(k)} - y^{(k)}$
i	current drawn from battery during discharge (A)
J	$n \times m$ Jacobian matrix used in parameter estimation for the rates of change of the n measurements with respect to the m undetermined parameters
k	discrete-time increment or alternatively cycle number
ℓ	number of previous cycles considered in hybrid estimation algorithm
m	number of unknown parameters in a general parameter estimation
n	number of experimental measurements used in a general parameter estimation
$P^{(k)}$	parameter set for arbitrary process at time/cycle k
Q	battery capacity (A h)
R	internal battery resistance (Ω)
s^2	measurement covariance found during parameter estimation that approximates true covariance σ^2
t	time (s)
t_{cutoff}	time at which experimental system stops discharging based on a cutoff voltage (s)
$t_{(1-\alpha/2)}$	signifance statistic at $(1-\alpha)$ confidence level found from *Student's t* distribution with ν degrees of freedom
$u^{(k)}$	arbitrary process input at time/cycle k
U	empirical correlation between SOC and open circuit potential of the battery (V)
V	experimentally measured battery potential (V)
$\hat{V}$	model-predicted battery potential (V)
$y^{(k)}$	arbitrary process measurement at time/cycle k
$\hat{y}^{(k)}$	model-predicted value of arbitrary process at time/cycle k
z	unit shift operator

Greek symbols

β_i	general unknown model parameter to be found by estimation
Γ_Q	move-weighting penalty on prior values of Q in hybrid estimation algorithm
Γ_R	move-weighting penalty on prior values of R in hybrid estimation algorithm
θ	state-of-charge (SOC)
θ_{cutoff}	SOC of experimental system when discharging stops based on a cutoff voltage
ν	number of degrees of freedom in a parameter estimation, calculated by $n - m$
σ^2	true process measurement covariance that is approximated by s^2 in parameter estimation
Φ	objective function used in hybrid estimation algorithm
ω_c	cutoff frequency for digital low-pass filter design (Hz)

rameters in a minimally invasive manner, and preferably online.

In the following work, a new estimation algorithm — combining elements of both batch estimation and online moving-horizon estimation [4–7] — is proposed to keep the model parameters updated to the current operating state of the battery on a cycle-to-cycle basis. Based on the most recent discharge curve of a cell, capacity and resistance are calculated through the minimization of an error function that depends on the mismatch between the model and the data from the present cycle as well as a weighted penalty for the deviation of the present parameters from prior values. The addition of the deviation terms smoothes the apparent parameter drift of the system and the weightings are chosen to balance between the smoothness of the parameter drift and the achievement of the smallest possible model/battery data mismatch for a given cycle. The proposed algorithm is demonstrated on 1600+ cycles of data from a Sony 18650 Li-ion cell. The results presented here are presented based on several different tunings of the *parameters of the algorithm* that should not to be confused with the model parameters. As an alternative method, the model parameters are obtained using successive batch estimations for each cycle and then filtered using a discrete, recursive low-pass filter. The results from the filtering analysis are compared to those from the new algorithm, and analogies are drawn between them.

Regardless of the method chosen to analyze the data, it is apparent that the parameters do not obey simple dynamics that can be predicted a priori. Despite being the same type of cells running the same protocol simultaneously under identical conditions, the dynamics of the capacity fade and increased resistance differ significantly between the two individual experiments, further motivating the need for this online, soft-sensing, parameter estimation algorithm.

2. Methodology

The proposed algorithm is devised as a method to observe slow drifts in characteristics of Li-ion batteries. While batch estimations could be performed for each cycle, the values of the parameters obtained in this manner are liable to fluctuate rapidly in a relatively uncorrelated manner. However, it is expected that these model characteristics should vary smoothly and gradually, barring the occurrence of a fault in the system. Therefore, the batch estimations are performed using an objective function that incorporates parameter values from the previous cycle(s) to correlate and smooth the drift of the parameters.

2.1. Experimental system

Two Sony 18650 Li-ion batteries were used to collect data over multiple charge–discharge cycles. These batteries were rated for 1.4 A h. The charging protocol was as follows: constant current was applied at 1 A until the battery reached 4.2 V, then constant voltage was applied at 4.2 V until current dropped to 50 mA. The discharge protocol was as follows: batteries were discharged at a constant 1 C rate (1.4 A) then stopped when the voltage reached 2.8 V. The discharged battery then waited for the charger to become available, typically allowing the cell to rest at open circuit for 5–30 min. While results from both batteries were very similar, only the results from the first battery were included in the final version of this work.

A schematic of the data collection system is provided in Fig. 1. Charging was accomplished using a Hewlett Packard Model 6632B DC Power Supply. An Agilent Technologies electronic load, Model 6060B, was used to draw current from the batteries on discharge. A National Instruments General Purpose Interface Bus (GPIB) was used to control remotely the load and power supply. Data acquisition and control were accomplished using LabVIEW® software version 6.1.

2.2. Dynamic battery discharge model

The MATLAB® and SIMULINK® simulation environments were used to implement this estimation routine. A model of the process is implemented in SIMULINK®. A simple two-parameter model of the battery is defined by the following equations:

$$\frac{\mathrm{d}\theta}{\mathrm{d}t} = -\frac{i(t)}{Q} \tag{1}$$

$$U(\theta) = \sum_{j=0}^{9} a_j \theta^j \tag{2}$$

$$\hat{V}(t) = U(\theta(t)) - Ri(t) \tag{3}$$

where $\theta(t)$ is a quantity called state-of-charge (SOC) that varies between 0 and 1, representing fully discharged and fully charged, respectively. The time-dependent behavior of $\theta(t)$ is given by Eq. (1). Battery capacity Q is assumed to be a constant parameter during the course of a single battery discharge. For the data sets used in this study, $i(t)$, or current load on the battery, was held constant. Thus, $\theta(t)$ decreases linearly over time, but may decease at different rates as the model capacity Q changes. An empirically fit, ninth-order polynomial, $U(\theta)$, maps the SOC to a voltage potential discharge curve being produced by the battery (see Eq. (2)). However, the battery itself has a resistive load, R, so the externally available voltage, $\hat{V}$, is reduced by the quantity $Ri(t)$ as shown in Eq. (3).

The model parameters from Eq. (2) are determined from a normal discharge of the battery system under a variety of assumptions. It is assumed that the initial capacity of the battery is as stated, 1.4 A h. At the 1 C discharge rate (1.4 A) the system never reaches an SOC of 0, since discharge of the system is stopped at a cutoff voltage of 2.8 V. Given a

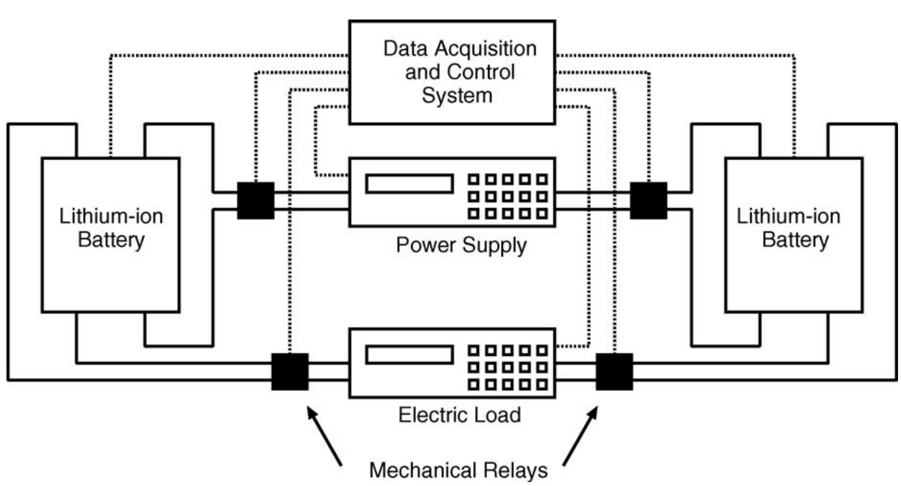

Fig. 1. Schematic layout of battery charge discharge system.

constant discharge rate, i, the SOC at cutoff is given by

$$\theta_{\text{cutoff}} = 1 - \frac{i t_{\text{cutoff}}}{Q} \tag{4}$$

Assuming the initial system resistance R is 0.3 Ω, the resulting voltage profile $\hat{V}(t)$ for a single discharge at a 1 C rate can then be fit to a high-order polynomial. Using the first discharge cycle for the battery, the following relationship is found:

$$U(\theta) = 4 - 251\theta + 266\theta^2 - 1352\theta^3 + 4148\theta^4 - 8.073\theta^5 + 9946\theta^6 - 7472\theta^7 3107\theta^8 - 543\theta^9 \tag{5}$$

Note that this model is not based on the open circuit potential. Also, the polynomial is never updated over the course of the estimation procedure. The values for Q and R will be determined in the estimation procedures.

2.3. Hybrid estimation methodology

The proposed estimation algorithm can be viewed as an extension of traditional online parameter estimation. First, the known input values for the kth cycle, $u^{(k)}$, the current, are used to force the battery to charge and discharge. Unmeasured disturbances, $d^{(k)}$, influence the output of the battery in cycle k. These disturbances could include temperature variation, unmodeled dynamics, or fault occurrences in the battery. Disturbances affect the measured voltage profile for the discharge cycle, $y^{(k)}$, but do not affect the modeled output, $\hat{y}^{(k)}$. The model discharge profile also depends on the current model parameters, $P^{(k)}$, where $P^{(k)} = [Q^{(k)}\ R^{(k)}]^{\mathrm{T}}$. The error between the battery and the model, $e^{(k)}$, is then passed to the optimization routine to determine the best parameter values for the current cycle.

The optimization routine attempts to minimize a weighted combination of the mean-squared error (MSE) for the battery and a penalty based on the squared value of deviations from previous parameter values. For this application, MSE is chosen as the model — data error metric over a simpler form such as sum-squared error (SSE). Since the length of a discharge cycle is not constant, but rather is determined when the system reaches the cutoff voltage, the number of data points in each cycle is variable. Hence, the value of an error metric such as SSE is not directly comparable between cycles of different length. However, the averaging process involved in MSE eliminates the discrepancies between cycles of different length, making it a more appropriate metric for this system.

The minimization of the objective function is accomplished by adjusting the values of $P^{(k)}$. Each cost function evaluation of the optimization returns a new set of values for $P^{(k)}$ to the model, which then recalculates $\hat{y}^{(k)}$ for the cycle. Once the optimization terminates, the final values for $P^{(k)}$are output and also saved for use in subsequent estimation iterations for later cycles. The algorithm increments itself to the next cycle number and repeats the entire process.

2.3.1. Hybrid estimation implementation

The online estimation routine consisted of a nonlinear optimization at each analyzed cycle solved by the unconstrained optimization algorithm *fminsearch* (Nelder-Mead) provided by MATLAB®. The objective function used was:

$$\Phi(Q_i, R_i) = \frac{\int_{t_0}^{t_f} (\hat{V} - V)^2\,\mathrm{d}t}{t_f - t_0} + \Gamma_Q \sum_{j=0}^{\ell} 2^{-j} (Q_i - Q_{i-j})^2 + \Gamma_R \sum_{j=0}^{\ell} 2^{-j} (R_i - R_{i-j})^2 \tag{6}$$

where Q_i and R_i are the model parameters being fit for cycle i, and $\hat{V}$ and V are the battery modeled and experimental voltages, respectively. The initial and final times of the data set are t_0 and t_f. Since the data is sampled at discrete intervals, the data is linearly interpolated and the continuous value of the model — data error is integrated by SIMULINK. Q_{i-j} and R_{i-j} are the values of Q and R from the $(i-j)$th cycle, and Γ_Q and Γ_R are the relative weightings of the move-penalty terms of the objective function. Γ_Q and Γ_R are the magnitudes of the weights for the move penalty for the $(i-1)$th cycle, and the weighting for each cycle prior to that is reduced by a factor of 2. There are two components to this objective function: the integral term measuring the ability of the model to reproduce the data and the terms that penalize large deviations in parameter values between runs. It is necessary to choose the Γ_Q and Γ_R terms carefully so that they do not dominate the model error term in Eq. (6). The ratio between Γ_Q and Γ_R is also important, allowing both parameters to have similar relative impact even though Q and R are of different magnitudes.

In addition to the weighting parameters Γ_Q and Γ_R, another adjustable parameter for tuning algorithm performance is ℓ, the size of the weighting horizon in number of cycles. The case where ℓ equals 0 is a special case, since the move-penalty terms of the objective function become 0, and the objective function simply becomes an unconstrained mean-squared error (MSE) for the present discharge cycle. Due to the geometrically decreasing weights on move penalties at larger values of ℓ, the incremental effects of increasing ℓ to values larger than 4 are essentially negligible.

2.3.2. Parameter confidence intervals from hybrid estimation

In many cases, it is useful to obtain confidence intervals for regressed parameters as a measure of the reliability of the results. A straightforward statistical technique exists for computing these intervals for simple linear least squares, assuming that all errors are normally distributed. A procedure is also available for unconstrained nonlinear least squares (under the same error assumptions), but it is significantly more involved than linear least squares. Given the unconventional objective function used in the hybrid estimation, it would appear difficult to derive such a procedure for this new method.

However, by slightly reformulating the model-data error calculation and considering the parameter drifts as additional measurements, it will be shown that a method exits that can be used to compute confidence intervals.

Constantinides and Mostoufi [8] discuss the calculation of confidence intervals from nonlinear least squares regressions in which more than one type of data is used. In this case, parameters are chosen to minimize a weighted SSE objective function. For the general case with v different types of measurements Y_j, the objective function to be minimized is given by

$$\Phi = \sum_{j=1}^{v} w_j(\hat{Y}_j - Y_j)^{\mathrm{T}}(\hat{Y}_j - Y_j) \tag{7}$$

In the case where the variance for each type of measurement σ_j^2 is known, then the weighting factors w_j can be computed directly and are inversely proportional to σ_j^2. However, it is not uncommon for the variances to be unknown, so one must estimate values.

Now, consider the case of the battery system. In order to use this approach, the error between the battery and model will need to be handled as SSE instead of MSE, despite the previously mentioned advantages of MSE. It also appears that there is only one measurement: the voltage in the battery. However, the move-penalty terms that are included in the original objective function of Eq. (6) can be considered additional measurements. In the case where $\ell = 1$, there end up being three measurements:

$$Y_1 = V, \qquad Y_2 = (Q_i - Q_{i-1}), \qquad Y_3 = (R_i - R_{i-1}) \tag{8}$$

Thus, the objective function becomes

$$\Phi_i = \sum_{k=1}^{n}(\hat{V}_k - V_k) + \Gamma_Q[(\widehat{Q_i - Q_{i-1}}) - (Q_i - Q_{i-1})]^2 + \Gamma_R[(\widehat{R_i - R_{i-1}}) - (R_i - R_{i-1})]^2 \tag{9}$$

where

$$w_1 = 1, \qquad w_2 = \Gamma_Q, \qquad w_3 = \Gamma_R \tag{10}$$

noting that w_1 is assumed to be 1 and the arbitrary weighting parameters Γ_Q and Γ_R are chosen, because nothing is known a priori about the variance of the two "pseudo-measurements" relative to the measurement error. Since no assumptions are made as to how the parameters Q and R drift with time, one hypothesis is to consider that Q and R are Gaussian random variables and that the values of Q_i and R_i found in each cycle are samples from those distributions. In this case, the model of the cycle-to-cycle drift of Q is given by

$$(\widehat{Q_i - Q_{i-1}}) = E[Q_i - Q_{i-1}] = 0 \tag{11}$$

with a similar expression for the R_i term. If this is truly valid, then the objective function further simplifies to

$$\Phi_i = \sum_{k=1}^{n}(\hat{V}_k - V)^2 + \Gamma_Q(Q_i - Q_{i-1})^2 + \Gamma_R(R_i - R_{i-1})^2 \tag{12}$$

which is nearly identical to the objective function proposed in this work for the case where $\ell = 1$. In a future case where a model or proposed model of the time-dependent drift of Q and R is known (such as a square root dependence on time), then that model could alternately be used to find values for $(\widehat{Q_i - Q_{i-1}})$ and $(\widehat{R_i - R_{i-1}})$. Confidence intervals for estimated parameters are given by Constantinides and Mostoufi in the form

$$b_i - t_{(1-\alpha/2)}s\sqrt{a_{ii}} \le \beta_i \le b_i + t_{(1-\alpha/2)}s\sqrt{a_{ii}} \tag{13}$$

where b_i is the value of the parameter β_i obtained by minimizing Φ, $t_{(1-\alpha/2)}$ the significance statistic for a confidence level of $(1-\alpha)$, s the square root of the approximate variance of the error and a_{ii} the ith element of the diagonal of the parameter covariance matrix. Values of $t_{(1-\alpha/2)}$ can either be found by lookup in statistical tables of the *Student's t* distribution or direct computation for a given number of degrees of freedom ν and the desired significance level. ν is given by the number of measurements less the number of parameters being fit. When ν becomes large, this statistic approaches that of the normal distribution. Values for s are obtained from the minimum value of the objective function:

$$\sigma^2 \approx s^2 = \frac{\Phi(b)}{\nu} \tag{14}$$

Finally,

$$A = \left[\sum_{j=1}^{v} w_j J_j^{\mathrm{T}} J_j\right]^{-1} \tag{15}$$

where

$$J_j = \begin{bmatrix} \dfrac{\partial \hat{Y}_{j,1}}{\partial b_1} & \cdots & \dfrac{\partial \hat{Y}_{j,1}}{\partial b_m} \\ \vdots & \ddots & \vdots \\ \dfrac{\partial \hat{Y}_{j,n}}{\partial b_1} & \cdots & \dfrac{\partial \hat{Y}_{j,n}}{\partial b_m} \end{bmatrix} \tag{16}$$

for the case where there are n instances of the jth measurement and m parameters being fit. Now consider the case of battery discharge. The calculation of s is very simple. Using the simplified objective function for the problem, one obtains

$$s^2 = \frac{\Phi_i(Q_i, R_i)}{\nu} = \frac{\Phi_i(Q_i, R_i)}{n+2-2} = \frac{\Phi_i(Q_i, R_i)}{n} \tag{17}$$

where again, n is the number of voltage measurements. Measurements Y_2 and Y_3 have very simple Jacobians to compute:

$$J_2^T J_2 = [1 \quad 0]^T[1 \quad 0] = \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} \tag{18}$$

$$J_3^T J_3 = [0 \quad 1]^T[0 \quad 1] = \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix} \tag{19}$$

The Jacobian for the voltage measurements is somewhat more involved. The voltage model for constant-load discharge is given by Eqs. (1)–(3). Therefore, the Jacobian of the voltage is given by

$$J_1 = \begin{bmatrix} \left.\frac{\partial \hat{V}}{\partial \theta}\right|_{\theta=\theta(t_1)} & \left.\frac{\partial \theta}{\partial Q}\right|_{t=t_1} & \left.\frac{\partial \hat{V}}{\partial R}\right|_{t=t_1} \\ \vdots & & \vdots \\ \left.\frac{\partial \hat{V}}{\partial \theta}\right|_{\theta=\theta(t_n)} & \left.\frac{\partial \theta}{\partial Q}\right|_{t=t_n} & \left.\frac{\partial \hat{V}}{\partial R}\right|_{t=t_n} \end{bmatrix} \tag{20}$$

which simplifies somewhat to

$$J_1 = \begin{bmatrix} \left.\frac{\partial \hat{V}}{\partial \theta}\right|_{\theta=\theta(t_1)} \frac{i\, t_i}{Q^2} & -i \\ \vdots & \vdots \\ \left.\frac{\partial \hat{V}}{\partial \theta}\right|_{\theta=\theta(t_n)} \frac{i\, t_n}{Q^2} & -i \end{bmatrix} \tag{21}$$

Using the definitions for $J_{1\ldots3}$, the value for A is obtained:

$$A = \left[J_1^T J_1 + \Gamma_Q J_2^T J_2 + \Gamma_R J_3^T J_3\right]^{-1}$$
$$= \left[\begin{bmatrix} \sum_{k=1}^{n} \left(\frac{\partial \hat{V}_i}{\partial Q}\right)^2 & \sum_{k=1}^{n} \frac{\partial \hat{V}_i}{\partial Q}\frac{\partial \hat{V}_i}{\partial R} \\ \sum_{k=1}^{n} \frac{\partial \hat{V}_i}{\partial Q}\frac{\partial \hat{V}_i}{\partial R} & \sum_{k=1}^{n} \left(\frac{\partial \hat{V}_i}{\partial R}\right)^2 \end{bmatrix} + \begin{bmatrix} \Gamma_Q & 0 \\ 0 & \Gamma_R \end{bmatrix}\right]^{-1} \tag{22}$$

Using these equations, it is now possible to compute the confidence intervals. Note that Γ_Q and Γ_R both influence the confidence intervals by their inclusion in A. Since Γ_Q and Γ_R are not based on actual variances, it must be emphasized that excessively large values of these parameters will yield narrower confidence intervals than what may actually be valid. In practice, this procedure calculates confidence intervals very similar to those that would be obtained if the move-penalty terms were not incorporated. As seen in Fig. 4, the confidence range begins decreasing with increasing Γ_Q and Γ_R. Since larger values of Γ_Q and Γ_R correspond to smaller variances or expected drifts in Q and R, it is expected that one would have a higher degree of confidence in parameters that are known to drift less. Nevertheless, values of Γ_Q and Γ_R should be chosen judiciously.

2.4. Digital filtering

A second analysis method is proposed where the model parameters are calculated at each cycle using simple batch estimation techniques. Then a discrete, low-pass filter is applied to the values to remove the high-frequency variations. Due to its simplicity, a second-order Butterworth filter (IIR) was constructed using the MATLAB® Signal Processing Toolbox. When developing a low-pass filter, a crossover frequency must be supplied. For a discrete (digital) filter, it is generally sufficient to specify the ratio between the cutoff frequency and the sampling rate. The battery system is not truly a discrete-time system, since the data points, i.e. estimated parameter values, do not correspond to sequential, evenly spaced samples. Instead, each estimate corresponds to an entire discharge cycle, which does not have a fixed duration. However, for the purposes of this analysis, the cycle-to-cycle frequency is arbitrarily assumed to be 1 Hz. Therefore, a filter designed with a cutoff frequency of 0.01 Hz will reject dynamics of parameter changes that occur over fewer than 100 cycles. In other words, the filtered values for capacity and resistance should only exhibit dynamics that occur over at least 100 cycles.

3. Results

Several different studies were performed to gauge the performance of the proposed hybrid estimation algorithm. One of the main assumptions in this problem is that the parameters drift slowly enough that they can be held constant for the duration of a single cycle. If this assumption is valid, it is improbable that the actual parameter value will have changed significantly from one cycle to the next. Therefore, it is desirable to tune the algorithm to produce parameter profiles with reduced high-frequency “chatter” in the signal, much like a low-pass filter. However, if the move-penalty weights are too high, the parameter values will lag and the error in the resulting model could be unacceptable. The studies discussed herein consider the effects of changing move-penalty weights and varying the length of the move-penalty horizon. These results are compared to results obtained by digital filtering. From these studies, recommendations are made for appropriate magnitudes of algorithm tuning parameters and filter specifications.

3.1. Effects of hybrid estimation algorithm tuning parameters

One experiment was performed where the move-penalty weights Γ_Q and Γ_R were varied while the move horizon length ℓ was fixed at 2. The results of this experiment are presented in Fig. 2. As was expected, the smallest weights ($\Gamma_Q = 2$ and $\Gamma_R = 4$) produced results that were extremely similar to the unweighted case. The estimated values of Q and R exhibit a very high variation over an underlying steady

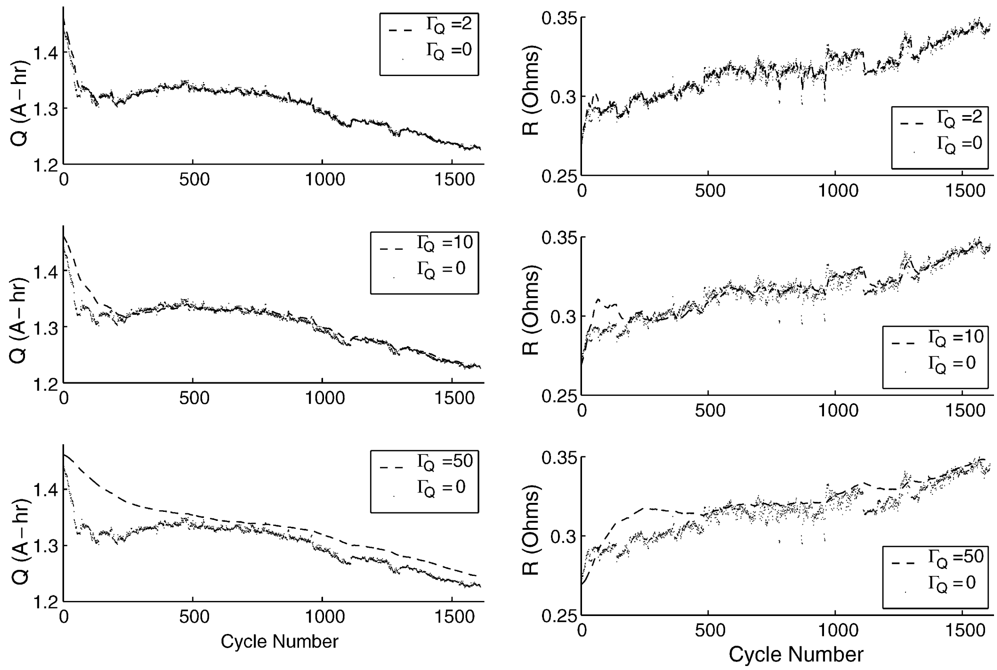

Fig. 2. Capacity fade and resistance change with various values of Γ_Q and Γ_R. Note that $\Gamma_R = 2\Gamma_Q$. The move horizon length parameter ℓ was fixed at 2.

decrease and increase, respectively. It is doubtful that the actual condition of the battery changes as rapidly as predicted. Alternately, the case with the largest weights ($\Gamma_Q = 50$ and $\Gamma_R = 100$) yields parameter trends that are very smooth and gradual, but appear to lag significantly behind the unweighted results. This too is unacceptable. Finally, a reasonable compromise weighting appears to be about ($\Gamma_Q = 10$ and $\Gamma_R = 20$). In this case, the highest frequency noise components are not present, but the estimated values still converge to the long-term trends of the unweighted case rapidly.

A second study was conducted varying the move horizon length, ℓ, while maintaining the move-penalty weights at the values determined previously to be most reasonable ($\Gamma_Q = 10$ and $\Gamma_R = 20$). As seen in Fig. 3, the effect of the increasing horizon length was to smooth out the predicted value curve at the expense of convergence rate, similar to

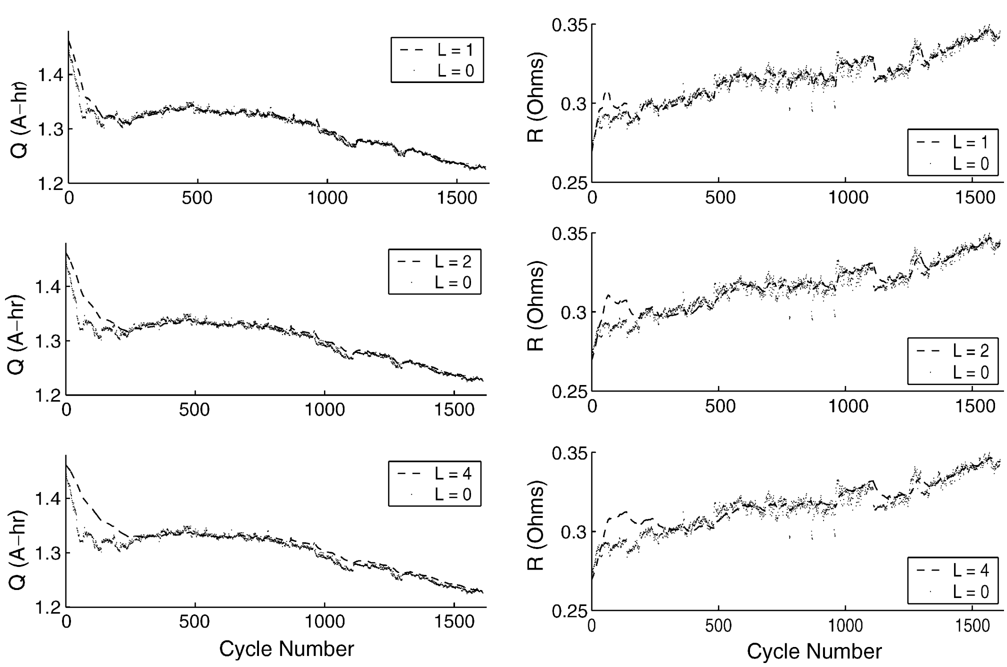

Fig. 3. Capacity fade and resistance change using various values of ℓ in the estimation. The move-penalty weighting parameters were fixed at $\Gamma_Q = 10$ and $\Gamma_R = 20$.

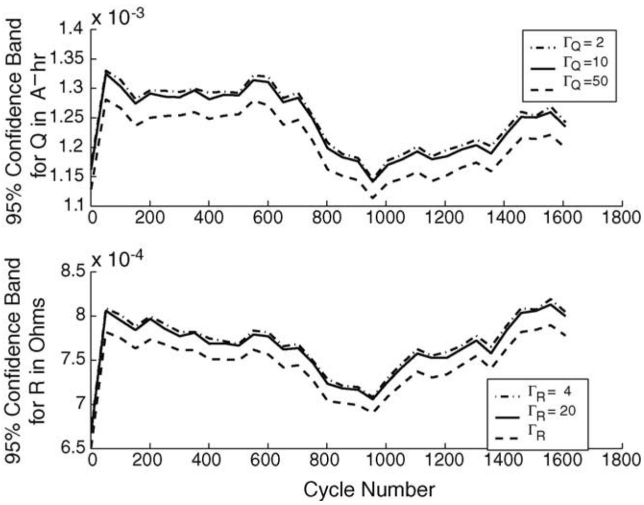

Fig. 4. 95% Confidence intervals for Q and R over 1600 charge–discharge cycles.

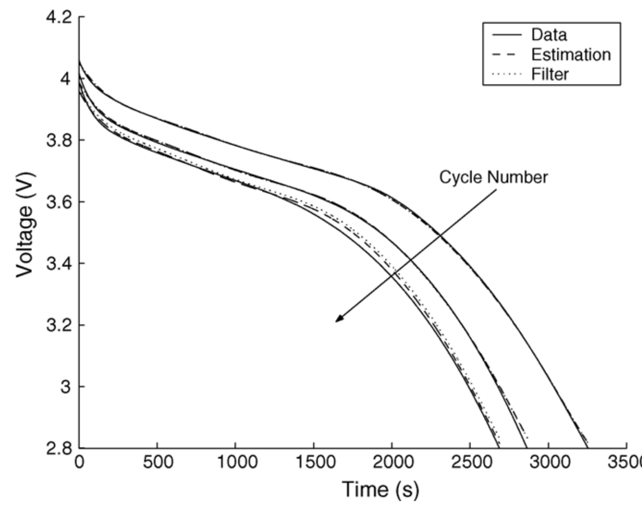

Fig. 5. Model fidelity for the battery for three cycles {1, 800, 1425} using parameters obtained through hybrid estimation and low-pass filtering.

increasing the weighting factors Γ_Q and Γ_R. Fig. 3 also illustrates that the differential effect between $\ell = 4$ and $\ell = 2$ is approximately equivalent to that between $\ell = 2$ and $\ell = 1$. With the weighting scheme currently implemented, the effects of setting ℓ larger than 4 are essentially negligible. For the particular values of the weighting parameters used in this study, a value of $\ell = 2$ yields the best blend of smoothing the profiles without adding excess lag and unduly reducing the accuracy of the model.

Fig. 4

Finally, there is no utility in adjusting the algorithm parameters Γ_Q, Γ_R, and ℓ to obtain smooth parameter trends if it produces unacceptable error between the model and the battery voltage. Therefore, the hybrid estimation was performed using the ideal parameter values determined from the previous two experiments. Three discharge cycles were selected from early, mid, and late in the data: cycles 1, 800, and 1425, respectively. The comparison between the data and the model using the estimated parameters is presented in Fig. 5. Clearly, the agreement is quite good, particularly for cycles 1 and 800. Although the results for cycle 1425 were not quite as accurate, they are still encouraging, considering the simplistic empirical nature of the underlying model.

3.2. Digital filtering

Filtering has been suggested as an alternate means of utilizing noisy parameter estimates for individual cycles and producing smooth trajectories for parameter values over time. In practice, it has proved to be a very simple and effective method for accomplishing this task. Using readily available tools such as MATLAB® Signal Processing Toolbox and SIMULINK®, a number of Butterworth low-pass digital filters were synthesized with various crossover frequencies and used to process model parameter values obtained from estimations on single cycles. The general form of the second-order recursive digital filter (IIR) is given by

$$\hat{y}(k) = -a_1\hat{y}(k-1) - a_2\hat{y}(k-2) + b_0 y(k) + b_1 y(k-1) + b_2 y(k-2) \quad (23)$$

where $\hat{y}$ is the filtered value of the quantity y and k is the discrete-time unit. The signs on the coefficients are defined in this manner, because the digital filter can also be equivalently represented in the following discrete-time transfer function:

$$\hat{y}(z) = \frac{b_0 + b_1 z^{-1} + b_2 z^{-2}}{1 + a_1 z^{-1} + a_2 z^{-2}} y(z) \quad (24)$$

where z is the unit shift operator. The results are shown in Fig. 6.

In Fig. 6, the cutoff frequencies used for the various filters were {0.001, 0.01, 0.1} Hz for the capacities, Q, and {0.0005, 0.005, 0.05} Hz for the resistances, R. The filter coefficients for the Q values are listed in Table 1, while those for R are listed in Table 2. Based on the behavior of these filters, cutoff frequencies of approximately 10^{-2} Hz are appropriate for this system.

To ensure that parameter values obtained by the filters were still valid for the system, these filtered parameter values were used to generate model output for cycles 1, 800, and 1425, as was done for the hybrid estimation results. The model output was compared to the experimental output in

Table 1
Filter coefficients (as defined in Eq. (23)) used for filtering Q

Coefficient	$\omega_c = 0.001$	$\omega_c = 0.01$	$\omega_c = 0.1$
a_1	$-1.991e+00$	$-1.911e+00$	$-1.143e+00$
a_2	$9.912e-01$	$9.150e-01$	$4.128e-01$
b_0	$9.826e-06$	$9.447e-04$	$6.745e-02$
b_1	$1.965e-05$	$1.889e-03$	$1.349e-01$
b_2	$9.826e-06$	$9.447e-04$	$6.745e-02$

ω_c is design cutoff frequency in Hz. Values are obtained using the Butterworth filter tool in the MATLAB Signal Processing Toolbox.

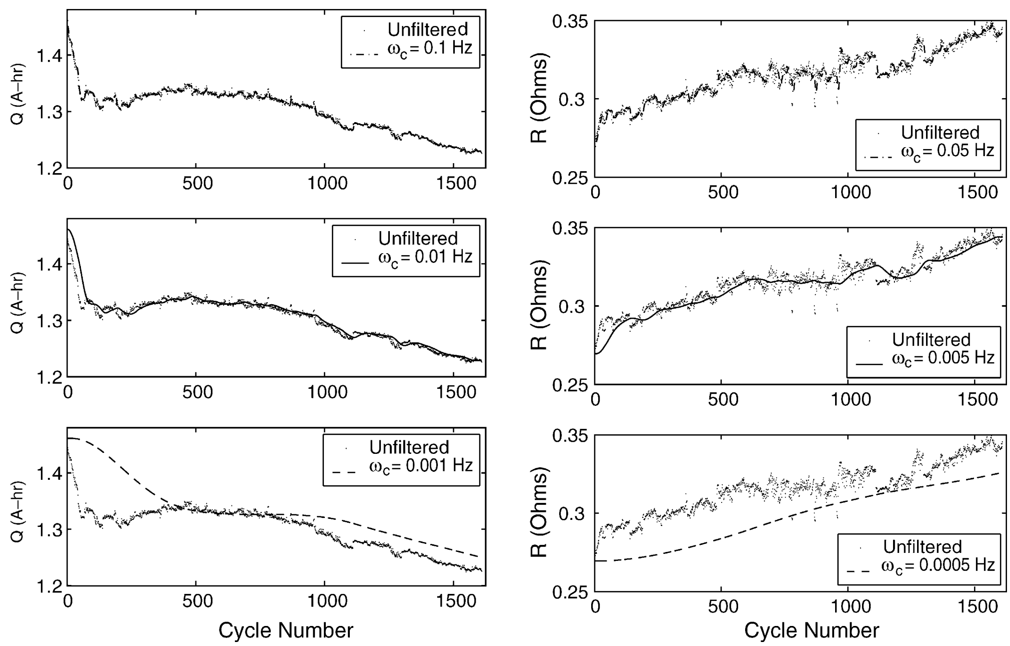

Fig. 6. Capacity fade and resistance change in the battery smoothed by three digital Butterworth filters.

Table 2
Filter coefficients (as defined in Eq. (23)) used for filtering R

Coefficient	$\omega_c = 0.0005$	$\omega_c = 0.005$	$\omega_c = 0.05$
a_1	$-1.996e+00$	$-1.956e+00$	$-1.561e+00$
a_2	$9.956e-01$	$9.565e-01$	$6.413e-01$
b_0	$2.462e-06$	$2.414e-04$	$2.008e-02$
b_1	$4.924e-06$	$4.827e-04$	$4.016e-02$
b_2	$2.462e-06$	$2.414e-04$	$2.008e-02$

ω_c is design cutoff frequency in Hz. Values are obtained using the Butterworth filter tool in the MATLAB Signal Processing Toolbox.

Fig. 5. There appears to be good agreement between the model using filtered parameters and experiment over all cycles. Moreover, the parameters obtained using this method appear to offer comparable performance to those obtained using the hybrid estimation technique.

4. Discussion

It is well known that capacity of electrochemical cells decreases with time [1,3]. A battery that has been recharged 100 times cannot store as much power as a brand new battery. Consequently, it was expected that the estimation algorithm would show the capacity parameter in the model studied decreasing as the cycle number increased. Additionally, due to irreversible reactions, the internal resistance of a battery will increase with the number of cycles. Both of these experimentally observed trends were captured by the tested hybrid estimation algorithm and discrete filtering of batch estimation results.

The new algorithm was designed as a hybrid between two more traditional types of estimation: offline batch estimation and online recursive estimation. Each estimation solution found is a result of the solution of a batch estimation problem. However, knowledge gained from solutions of the problem at earlier cycles is used to weight the objective function used in the current estimation, thereby increasing the confidence in the parameter estimates, more akin to recursive estimation. This approach assumes that the dynamics of the parameters being estimated are slow with respect to the length of each data cycle. Hence, they are assumed constant for the duration of a single cycle, but can vary from cycle-to-cycle. See [9] for a discussion of categories of adjustable parameters. The hybridization of batch and recursive estimation is a novel approach to data reconciliation.

One typical downfall of batch estimation for use in online applications is that the algorithms used are typically not fast enough to achieve a solution within one time interval. This technique mitigates this issue, since a solution is computed once per cycle and not once per sample period. The battery system used to generate data for this study has a sample time of 1 s, but a complete cycle is about 50 min long. The solution times of the estimations are approximately 15 s, making it impossible to solve this type of problem at each time step, but very practical on a cycle-to-cycle basis. This technique should be applicable to a number of batch processes. Any process that operates in repeated, discrete cycles on the order of several minutes or higher may be able to benefit.

The theoretical mathematical properties of this algorithm have not yet been analyzed. Investigation of the stability, convergence, robustness in the presence of plant/measurement uncertainty, or any other desirable property would be a nontrivial exercise at best. It is certainly an area open for future research. This algorithm has provided excellent performance in the application problem studied, despite the absence of rigorous proofs of stability or convergence. The absence of such proofs surrounding an algorithm should not be the sole criterion for its dismissal; Allgöwer et al. [7] state that the extended Kalman filter (EKF) does not have a lot of strong theory supporting its use, but has nevertheless proved useful in a number of applications. The EKF has also been used previously for online estimation of battery capacity fade [10–12]. However, it will not work for the battery model used in this discussion, since this model is not *observable* in the traditional dynamical systems context, a strict requirement of the Kalman filter and EKF. *Observability* for linear systems is discussed in both [13,14] (among others), with a significant discussion of the Kalman filter included in [13]. The concept of observability is extended for nonlinear systems in [15]. In addition to observability, the extended Kalman filter requires linearization of the nonlinear dynamic model and estimates of the state and measurement noise characteristics. Depending on the system, these requirements can prove unwieldy. Additionally, the EKF and other online recursive estimation techniques compute updates at each sample point. For a system such as the battery studied here, sampling occurs frequently (on the order of seconds), whereas the parameter dynamics of interest occur on a much longer time scale (on the order of days, weeks, or months). Consequently, even if it were possible to use an EKF, it would require substantially more computational effort for very little added benefit. Thus, the hybrid estimation method proposed here is useful and advantageous in this circumstance since it offers the “fading memory” effects of recursive estimation at a more reasonable intermediate time scale.

Digital filtering also appears to be a viable approach for developing smooth parameter estimates in this electrochemical system. Filter tunings are readily obtained and simple to implement. Using the filters, it is possible to obtain parameter profiles that are relatively smooth without exhibiting excessive lag. Therefore, model fidelity remains high. Additionally, the filtering work provides insight on methods to further improve the hybrid estimation algorithm. Since it is assumed that the process and/or measurement are subject to significant noise, the recursive low-pass filters place a low weight on the present measured value relative to prior filtered estimates. This weighting scheme suggests that the current scheme employed for the weighting parameters through the move horizon may not be an appropriate one.

Nevertheless, both methods demonstrate promising means to monitor unmeasurable parameters of electrochemical systems online without relying on semi-empirical correlations developed under highly controlled laboratory conditions.

5. Conclusions

Two methods have been presented for analyzing capacity fade in Li-ion batteries. Both the hybrid estimation and the digital filtering techniques offer the user the ability to monitor the long-term condition of the battery while minimizing the noise attributable to cycle-to-cycle variation. More traditional approaches for online parameter tracking, particularly the extended Kalman filter, are impractical for this type of application given the orders of magnitude difference between sampling interval and the time scales of parameter drift. Additionally, the EKF is precluded for this particular application since the dynamic battery model used is not observable. Finally, results from the hybrid estimation method can be used under certain conditions to compute confidence intervals for the unknown parameters Q and R, if a quantitative measure of reliability is desired.

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