State of health estimation in composite electrode lithium-ion cells

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HIGHLIGHTS

- An electrochemical model for a composite LMO-NMC half cell is outlined.
- An extended Kalman filter is used to estimate each composite active material.
- Estimates are validated with half cells, aged under constant current cycling.
- Active material estimates correctly predict the observed capacity fade.
- A differential capacity analysis confirms that active materials are lost at a similar rate.

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ABSTRACT

Electrochemical models of lithium-ion batteries have been increasingly considered for online state of health estimation. These models can more accurately predict cell performance than traditional circuit models and can better relate physical degradation mechanisms to changes in model parameters. However, examples of state of health estimation algorithms that are validated with experimental data are scarce in the literature, particularly for cells with a composite electrode. The individual electrode active materials in a composite electrode may degrade at different rates and according to different physical mechanisms, and online estimation of this degradation facilitates more robust knowledge of how battery performance changes over its life. In this paper we use a reduced-order electrochemical model for a composite $LiMn_2O_4$-$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (LMO-NMC) electrode cell for online estimation of active material loss. Experimental data collected from composite electrode half cells that were aged under constant current cycling are used in an extended Kalman filter to estimate model parameters associated with loss of each active material. The capacity loss predicted by the online estimates agrees well with the measured capacity loss. Additionally, a differential capacity analysis demonstrates that active materials lose capacity at a similar rate, the same conclusion obtained from the online estimation algorithm.

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1. Introduction

Hybrid and electric vehicles using Lithium-ion (Li-ion) battery packs are gaining popularity among consumers, as performance and cost continue to improve. State of health (SOH) is one important metric that must be estimated by the vehicle's battery management system (BMS), typically defined by the degradation of capacity and available power over the life of the battery. Accurate knowledge of SOH not only gives the driver an accurate miles-to-empty metric, but it also helps maintain an accurate battery

model within the BMS by accounting for changes in model parameters throughout the battery's life. An accurate battery model is critical for estimating cell state of charge (SOC) and available power, in order to keep the battery pack operating safely and efficiently [1].

Increased attention has been given to electrochemical-based models for SOC and SOH estimation over traditional circuit models, due to their ability to capture the internal physics of the battery and incorporate model parameters that are directly associated with degradation mechanisms [1–3]. However the governing equations of electrochemical models are complex and rely on partial differential equations (PDEs) that describe the spatial variation of Li concentration and potential throughout the cell [1,4], making them more difficult to use in traditional state estimation algorithms. Therefore, approximations and model-order reduction

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techniques can be used to reduce the set of PDEs to ordinary differential equations (ODEs) more suitable for online estimation and control. One such approximation is known as the single particle model (SPM), which approximates the three-dimensional electrode as a single, spherical particle, with an averaged current density applied at the particle surface [5–7]. In the SPM, diffusion of Li throughout the spherical particle is still governed by a PDE, and although it is possible to design a SOC/SOH observer using a model with PDEs [8–10], these methods require significant computational effort and may not be practical in an onboard BMS. Therefore, model-order reduction methods that eliminate the reliance on PDEs are an important step towards designing practical electrochemical model-based state estimators. Various model-order reduction techniques have been applied for SOC estimation, including discretization of the PDE [11], a polynomial approximation [8,12,13], eigenvalue selection [2], and the Pade approximation [14].

Electrochemical-based models can be used for SOH estimation by estimating the model parameters that change as the battery ages. In many common battery chemistries, the dominant aging mechanisms include loss of cyclable Li and internal resistance growth due to a side reaction at the solid—electrolyte interface (SEI) [15,16] and loss of active material either through dissolution in the electrolyte [15,16] or through electrical isolation induced by cracking of the electrode conductive matrix [16,17]. There have been several investigations into using electrochemical-based models for online SOH estimation, using various methods. An unscented Kalman filter was used to estimate the active material fractions of each electrode [13], though the results were not validated experimentally. Least squares techniques were used to estimate model parameters associated with aging [10,12,18,19]; however the computational effort required by these approaches may limit their applicability to onboard estimation. In general, electrochemical model-based SOH estimation algorithms that are validated with experimental aging data are scarce in the literature, particularly for cells with composite electrodes. Composite electrodes complicate the problem due to differences in the utilization and dominant aging mechanisms between each composite material [20,21]. Previous work attempted to estimate capacity loss in a composite LiMn$_2$O$_4$-LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ (LMO-NMC) cell, where loss of cyclable Li was the dominant aging mechanism [22]; however this work did not consider loss of active material as an additional mechanism that could be accelerated at later stages of life or at high temperatures [23,24].

In this paper, a reduced-order electrochemical model for a composite LMO-NMC cell is used in an extended Kalman filter to estimate loss of active material. The estimation is validated experimentally using data from composite electrode half cells that were aged over the course of 20 constant current cycles. The estimation results are then analyzed using differential capacity curves in order to distinguish between a process affecting only one active material, or simultaneous degradation of both active materials.

2. Model development

The model used in this paper has been described in previous work [14,22,20], and is based on the traditional single particle model, with some modifications to accommodate the composite electrode. The PDE governing Li concentration in the electrode particles is ill-suited for traditional control and estimation; instead, the relationship between Li concentration and current input is approximated by a low order ODE using the Pade approximation [7,25]. Since the kinetic and concentration overpotentials of a cell under load are dependent on the Li concentration at the electrode/electrolyte interface, the Pade approximation is performed at the particle surface. The result is a linear transfer function that relates the Li surface concentration to the current input. As is typical of model-order reduction methods, a tradeoff can be made between the order of the approximated linear transfer function and accuracy of the approximation. In this work, a 3rd order approximation was used for the solid diffusion PDE, since it has been shown to have good agreement in the frequency range that is typical for automotive drive cycles [7]. The resulting state dynamics, voltage output equation, and state definitions are shown in equations (1)–(3).

In the context of the SPM, estimating loss of active material translates to estimating the model parameters ε_{LMO} and ε_{NMC}, which represent the total active material volume fractions of each material. These two parameters are treated as additional states in the model. Therefore, the complete state vector consists of 3 states that combine to give the surface and bulk concentration of the LMO particle ($c_{s,LMO}$ and $\bar{c}_{LMO}$), 3 states that combine to give the surface and bulk concentration of the NMC particle ($c_{s,NMC}$ and $\bar{c}_{NMC}$), and 2 states representing the active material volume fractions of LMO and NMC (ε_{LMO} and ε_{NMC}). The parameters a_i and b_i are a result of the Pade approximation, and are functions of the particle radius and diffusion coefficient [7,25]. There are no state dynamics assumed for the two volume fraction states, since they change slowly over time. The input, u, is current and the output potential for the LMO or NMC particle, Φ_i, is a nonlinear function of the open circuit voltage (OCV) evaluated at the surface concentration, U_i, the kinetic overpotential, η_i, and an ohmic loss.

$$\dot{x}(t) = \begin{cases} x_2(t) \\ x_3(t) \\ -\dfrac{1}{b_{3,LMO}}x_2(t) - \dfrac{b_{2,LMO}}{b_{3,LMO}}x_3(t) + \dfrac{R_{p,LMO}}{3b_{3,LMO}FAL x_7(t)}\beta_{LMO}(t)u(t) \\ x_5(t) \\ x_6(t) \\ -\dfrac{1}{b_{3,NMC}}x_5(t) - \dfrac{b_{2,NMC}}{b_{3,NMC}}x_6(t) + \dfrac{R_{p,NMC}}{3b_{3,NMC}FAL x_8(t)}\beta_{NMC}(t)u(t) \\ 0 \\ 0 \end{cases} \tag{1}$$