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A dynamic capacity degradation model and its applications considering varying load for a large format Li-ion battery

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HIGHLIGHTS

- A dynamic capacity degradation model for large format Li-ion battery is proposed.
- The change of the model parameters directly link with the degradation mechanisms.
- The model can simulate the fading behavior of Li-ion battery under varying loads.
- The model can help evaluate the longevity of a battery system under specific load.
- The model can help predict the evolution of cell variations within a battery pack.

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ABSTRACT

The capacity degradation of the lithium ion battery should be well predicted during battery system design. Therefore, high-fidelity capacity degradation models that are suitable for the task of capacity prediction are required. This paper proposes a novel capacity degradation model that can simulate the degradation dynamics under varying working conditions for large-format lithium ion batteries. The degradation model is built based on a mechanistic and prognostic model (MPM) whose parameters are closely linked with the degradation mechanisms of lithium ion batteries. Chemical kinetics was set to drive the parameters of the MPM to change as capacity degradation continues. With the dynamic parameters of the MPM, the capacity predicted by the degradation model decreases as the cycle continues. Accelerated aging tests were conducted on three types of commercial lithium ion batteries to calibrate the capacity degradation model. The good fit with the experimental data indicates that the model can capture the degradation mechanisms well for different types of commercial lithium ion batteries. Furthermore, the calibrated model can be used to (1) evaluate the longevity of a battery system under a specific working load and (2) predict the evolution of cell variations within a battery pack when different cell works at different conditions. Correlated applications are discussed using the calibrated degradation model.

1. Introduction

Lithium ion batteries have been widely used for electrochemical energy storage, e.g., hybrid electric vehicle [1–4], electric vehicle [5–8], submarine [9], airborne system [10], and electrical energy storage for power grid [11] given their high energy density and extended lifecycle. However, degradation is inevitable during practical use, in other words, the state of health (SOH) of a lithium ion battery becomes increasingly worse as the cycle continues [12–15]. Generally, a lithium ion battery degrades with a decrease in capacity and increase in resistance [12,13]. The capacity decrease and resistance increase directly determine the capability of the power output of the lithium ion battery. Therefore, the degradation of lithium ion batteries should be well predicted during design and accurately estimated during cycling. High-fidelity models are needed for a good prediction of degradation, and on-board SOH estimation algorithms are needed for an accurate estimation of SOH.

The prediction of degradation is essential when considering the following problems: (1) How long can a lithium ion battery system functions given a specific working load? (2) How will the capacity of a battery pack evolve when single cells work under different

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conditions [16]? (3) What is the optimal size of a hybrid power system considering the depreciation expense of a lithium ion battery [17]? A high-fidelity capacity degradation model is needed to serve the purpose of prediction. However, such a capacity degradation model for commercial lithium ion batteries is unavailable in the literature to the best knowledge of the authors.

A good degradation model should capture the main degradation mechanisms considering variant aging factors. The main degradation mechanisms of lithium ion batteries include the loss of lithium inventory (LLI), the loss of active material (LAM), and the ohmic resistance increase (ORI) [18–20], as shown in Fig. 1. The most influential factors of the capacity degradation includes the temperature, the depth of discharge (DOD), the accumulated ampere hour, the current rate (C-rate), and the SOC [21–23]. Current degradation models can be categorized into the empirical model and the mechanistic model.

The empirical model has capacity as its unique output [21,24]. However, the empirical model can only predict the cell capacity without considering correlated degradation mechanisms (LAM and LLI), which may significantly influence the prediction results of the model. The mechanistic model, which can capture the degradation mechanism (LAM and LLI) based on the first principle has higher fidelity than the empirical model.

Mechanistic models are developed based the first principle. Physical-based equations are utilized in the mechanistic models to describe the dynamics of the degradation reactions. For example, the growth of the solid electrolyte interface (SEI) film, one of the widely acknowledged causes of LLI and ORI, has been included in the capacity degradation model, which can interpret the degradation trend of a lithium ion battery [25–28]. Furthermore, the SEI growth coupled with particle cracking has been modeled by Liu et al. in [29]. Christensen and Newman [30,31] proposed a mechanistic and prognostic model (MPM) whose parameters directly link with the LAM, LLI and ORI of a lithium ion battery. The dynamics of LAM, LLI and ORI have been described by Arrhenius Equations, but without experimental validation as in [30,31], because the parameters of the MPM cannot be measured directly. However, Han et al. [32] successfully identified the parameters of the MPM. The identified parameters indicate LAM, LLI and ORI, which conform to the general degradation mechanisms of lithium ion batteries. Arrhenius Equations can be used to fit the change of the identified parameters in the MPM, thereby simulating the capacity degradation of lithium ion batteries. However, few previous works have been proposed to fit the parameters with chemical kinetics using Arrhenius Equations. There is still no validated model that can predict the voltage behavior of a lithium ion battery considering all major capacity fading mechanisms (LAM, LLI and ORI) and varying loads (current rate, temperature).

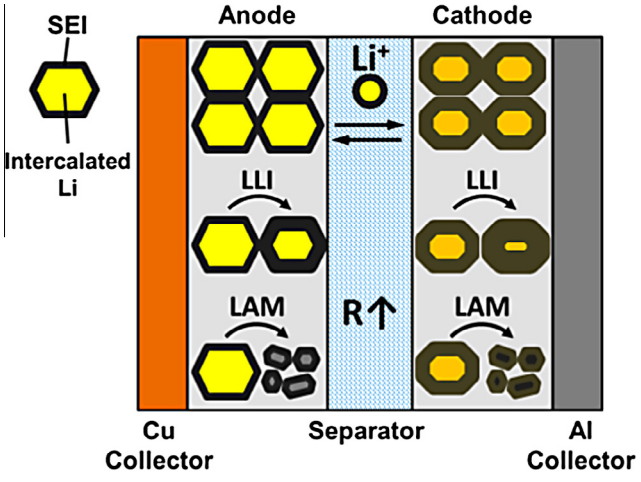

Fig. 1. Typical degradation mechanisms of Li-ion battery.

On-board SOH estimation is an active research topic, upon which researchers have provided plenty of effective approaches [12,13]. Useful on-board SOH estimation includes extended Kalman filtering [33–35], support vector regression [36,37], probability density function [38], and Delphi method [39] etc. A good on-board SOH estimation algorithm can help improve the estimation accuracy of the battery's state of charge (SOC) and state of function (SOF) [40], thereby benefiting the optimization strategies of the power management for a hybrid electric system [41]. Current on-board estimation algorithms for SOC, SOH or SOF, require a proper update of the open circuit voltage (OCV). A high-fidelity capacity degradation model can serve the purpose of updating the OCV throughout the lifecycle of a lithium ion battery, thereby improving the accuracy of on-board estimation algorithms. However, there are few validated degradation models that can predict the voltage of a lithium ion battery considering capacity fading, to the best knowledge of the authors.

This paper builds a novel capacity degradation model with chemical kinetics considering varying loads for different types of commercial large-format lithium ion batteries. The predicted capacity degradation can fit well with the experimental data. With good prediction of battery voltage considering degradation throughout the whole battery lifecycle, the model can be used to update the OCV, which is the critical information for a successful on-board estimation of SOC, SOH, and SOF. Moreover, the model can be used to (1) determine the optimal size of a battery in a hybrid power system; (2) evaluate the longevity of a battery system design under a specific working load; (3) predict the capacity evolution of cell inconsistency within a battery pack when different cells work at different conditions.

2. Experimental settings

2.1. Battery

Degradation tests were conducted upon three types of commercial lithium ion batteries, of which the specifications are listed in Table 1. The batteries are assigned with capital characters A, B, and C for the convenience of further discussion. Two of the batteries have cathodes with $LiFePO_4$ (LFP), whereas the other has a mixed cathode material with $LiMn_2O_4$ (LMO) and $LiNi_xCo_yMn_zO_2$ (NCM). All batteries have anodes with graphite, marked as "G" in Table 1.

2.2. Degradation test

Fig. 2 shows the design of the degradation test. All batteries were fully charged at 1/3C, and fully discharged at 1.5C within one cycle using a Digatron tester inside a thermal chamber. The environmental temperature inside the thermal chamber switches from 45 °C (5 °C) to 5 °C (45 °C) after every 90 cycles, as shown in Fig. 2. The reason for selecting this test profile is to simulate the practical working condition of a pure electric vehicle. A temperature of 45 °C (5 °C) indicates the average working temperature

Table 1
Specifications of commercial batteries.

Battery	Cathode	Anode	Rated capacity (Ah)	Voltage range (V)
A	LFP	G	11	2.5–3.6
B	LFP	G	60	2.5–3.6
C	LMO + NCM	G	10	3.0–4.2