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A capacity model based on charging process for state of health estimation of lithium ion batteries

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HIGHLIGHTS

- A capacity model based on charging process is proposed to estimate SOH.
- The accuracy of the model is validated on commercial lithium ion batteries.
- The universality of the model is verified on different batteries and statuses.

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ABSTRACT

The incremental capacity (IC) analysis method is widely used to analyze the aging origins and state of health (SOH) of lithium ion batteries. This paper analyzes the technical difficulties during the application of the IC analysis method at first. A universal capacity model based on charging curve is then proposed, which not only inherits the advantages of IC analysis method but also avoids the tedious data preprocessing procedure, to estimate SOH of lithium ion batteries. The feasibility and accuracy of the model are demonstrated. To verify the accuracy and flexibility of the proposed capacity model, it is applied on different types of lithium ion batteries including $LiFePO_4$, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, and $Li_{4/3}Ti_{5/3}O_4$. Furthermore, the proposed capacity model is applied on the aged cells to validate the model accuracy during the whole life span of lithium ion batteries. The results show that the model error is less than 4% of the nominal capacity for each case.

1. Introduction

Energy crisis and environmental concerns are urgent problems to be solved for world's sustainable development [1–3]. Lithium ion batteries (LIBs) can be used both on static energy storage and transportation energy storage [4,5] thanks to their remarkable advantages such as high specific energy, high efficiency, and long life [6,7]. The two key tasks in battery management system (BMS) are to estimate state of charge (SOC) [8,9] and state of health (SOH) [10–12] to avoid battery abuse and prolong its life span [13]. SOC is the ratio of the remaining capacity to the nominal capacity of the battery [14,15], and SOH reflects the ability of the battery to deliver the peak power and energy compared with the initial state [16]. In recent years, many researchers focused on SOC and SOH estimations. Many robust and accurate estimation techniques to estimate SOC have been studied [17–20]. In contrast, the development of the SOH estimation methods is more challenging due to the complicated electrochemical mechanisms involved in the battery fading [21]. However, the accurate SOH estimation is as crucial as the accurate SOC estimation for the efficient energy management in energy storage systems [12,19].

To analyze SOH of LIBs, a differential transformation is usually executed on the charging curve to generate an incremental capacity (IC) curve [22,23]. The main idea of the IC analysis theory is to transform the voltage plateaus on the voltage curve into clearly identifiable dQ/dV peaks on the IC curve by differentiating the charged capacity (Q) with respect to the terminal voltage (V) [24]. The IC curve is associated with the phenomena of the phase transition during the Li^+ intercalation/deintercalation process of the active material [25]. So SOH could be estimated based on the correlation between the maximum capacity and specific parame-

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ters of IC curve. Dubarry et al. [26] analyzed the cell degradation mechanisms of $LiFePO_4$ (LFP) such as loss of Li inventory and loss of active materials from the intensity, area, and position of IC peaks. Weng et al. [24] established the relationship between SOH and IC peak value through proposing a unified SOC–OCV model to get IC curve. However, the parameters in proposed SOC–OCV model have less relations with the electrochemical phenomena. To make the parameters used to indicate SOH associate with the phenomena of the phase transition, Torai et al. [25] estimated SOH of LFP/graphite by establishing dQ/dV model. The dQ/dV model of the full-cell for the SOH estimation was calculated from the half-cell models by subtracting the anode from the cathode. The differential capacity property of the LFP electrode for a half cell during the oxidation reaction was expressed using a single peak function, and the differential capacity property of the graphite electrode for a half-cell under the reduction reaction was expressed using four peak functions. However, a great quantity of parameters increase the load of parameters identification.

In addition, these models are usually built for a particular type of battery that has specific anode and cathode materials. Therefore, it is extremely difficult to apply the model of one battery with specific electrode materials on another battery with different electrode materials. However, variety of cathode and anode materials are used for their unique merits. Graphite is the most commonly used anode material because of its low charging voltage and wide range of lithium insertion [27]. Lithium titanium oxide (LTO) has been accepted as a novel anode material due to its high power density and long life [28,29]. From the view of cathode materials, $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA), and $LiCoO_2$ (LCO) have high energy density; $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM) and $LiMn_2O_4$ (LMO) are less expensive; $LiFePO_4$ (LFP) is the safest [6]. A universal model for SOH analysis needs to be proposed, which could be easily adapted to all types of batteries comprised of different cathode and anode materials.

This paper analyzes the technical difficulties during the application of the IC analysis method in the commercial BMS, which include the data distortion during the data preprocessing, the selection of voltage interval, and the fitting error of IC curve. To solve these issues by identifying the IC characteristic parameters from the experimental data directly, a universal capacity model based on charging process is proposed to estimate SOH. The proposed capacity model establishes the correlation between SOH and the phenomena of the phase transition. In addition, compared with Ref. [25], the number of model parameters depending on the number of IC peaks of full cell has been reduced. The versatility and flexibility of the proposed capacity model on different chemistries are validated by different type of LIBs including graphite||LFP, graphite||NCM + LMO, and LTO||LCO cells. Moreover, to illustrate the capability of the proposed capacity model to capture the changes during the whole life span of the battery, the proposed capacity model is also applied on two cells at different aging statuses.

The main contribution of this paper is to propose a universal capacity model based on charging process of LIBs. The proposed universal capacity model is capable to be applied on LIBs with different chemistries due to the flexibility of the model parameter n. Parameters of the proposed model can be used to estimate SOH thanks to their explicit meanings corresponding to the realistic phase transition behavior of the active material. Not only that, but the satisfied accuracy of the proposed universal capacity model during the whole life span of LIBs provides the potential to be applied to estimate SOH accurately. The remainder of this paper is organized as follow. Section 2 illustrates the modeling process. Then, the experiments are introduced in Section 3. The versatility and flexibility of the proposed model are discussed in Section 4. Then the conclusions are summarized in Section 5.

2. Modeling

2.1. Theory

The working mechanism of LIBs is that lithium ions swing between two electrodes after intercalating to or de-intercalating from cathode and anode materials. The average intercalation potential of each electrode can be calculated by Eq. (1) [30],

$$E = -\Delta G/nF \tag{1}$$

where ΔG is the difference of the Gibbs free energy for the intercalation reaction, n is the number of electrons intercalated in each unit cell, and F is the Faraday constant. Therefore, different electrodes have their specific potential ranges and plateaus because the ΔG is unique for different materials.

The open circuit voltage (OCV) of the full cell is the differential voltage between cathode and anode, that is $OCV_{full} = E_{cathode} - E_{anode}$. To meet requirements of different applications, cells with different combinations of cathodes and anodes, such as graphite||LFP cells, graphite||NCM cells,and LTO||NCM cells, are designed and manufactured. As a result, all those cells have distinct OCV curves. In addition, the OCV curve of a cell is changing gradually with the aging of the cell because of different aging origins, such as the active material loss in cathode and anode. In other words, the OCV curve is a reflection of the electrode materials and contains the aging information. As the terminal voltage of LIBs during charging and discharging is determined by the OCV and resistance, the terminal voltage curve inherits the information contained in OCV curve and can be used for SOH diagnostic. To eliminate the influence of resistance, the terminal voltage under 0.05 C charging or discharging is suggested by researchers as a trade-off between test time and accuracy.

The left plot in Fig. 1 shows the terminal voltage curve of cell No. 1 (as shown in Table 2) during 0.05 C charging from SOC = 0% to SOC = 100% before cycling. As shown in Fig. 1, the measured voltage is a monotonous function of the charged capacity. The voltage increases rapidly at the two ends, while the voltage increases tardily at the middle of the curve with several voltage plateaus. The plateau represents the two phase co-existence state of Li-poor phase and Li-rich phase during the charge/discharge process, thus it is the most important characteristic to analyze the performance of the battery. While, as shown in the middle plot of Fig. 1, more than 90% of the capacity is charged from 3.2 V to 3.4 V, which only accounts for less than 20% of whole voltage range. Furthermore, all the voltage plateaus also appear during this voltage range. Thus, it is hard to analyze the statuses and characteristics of cells from the voltage curve directly.

In order to dig out the implicit battery information from the terminal voltage curve, a well known technique – incremental capacity analysis is usually used. The basic theory is: transform the voltage (V) vs. charged capacity (Q) curve into dQ/dV vs. voltage (V) curve. The right plot of Fig. 1 shows the IC transformation results from the terminal curve of cell No. 1 at its fresh status. Several peaks appear in IC curve with each peak corresponding to one voltage plateau in the curve. These peaks in IC curve make the associated phase transition inside the cathode and anode become much more intuitive and sensitive. The area below the IC peak is the capacity between a specific voltage range, and the peak center of IC curve reveals the voltage value of voltage plateau. From the change of peak parameters (those are the peak intensity, width, and center location), the aging origins, such as the loss of active material, the loss of usable lithium-ion, and the increase of the internal resistance, can be analyzed, and then the SOH can be calculated [22].