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Capacity-loss diagnostic and life-time prediction in lithium-ion batteries: Part 1. Development of a capacity-loss diagnostic method based on open-circuit voltage analysis

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HIGHLIGHTS

- Develop a multi-mechanistic and non-destructive capacity-loss diagnostic technique.
- The open-circuit voltage of a cell is taken as the diagnostic indicator.
- Establish a simultaneous coordinate system for capacity-loss mechanisms.
- Present a straightforward capacity-loss diagnostic flowchart.

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ABSTRACT

Effective capacity-loss diagnosis and life-time prediction are the foundations of battery second-use technology and will play an important role in the development of the new energy industry. Of the two, the capacity-loss diagnostic, as a precondition of the life-time prediction, needs to be studied first. Performing a capacity-loss diagnosis for an aging cell consists of finding the decisive degradation mechanisms for the cell's capacity degradation. Because a cell's capacity just equals the span of the open-circuit voltage (OCV), when suspect degradation mechanisms affect a cell's capacity, they will leave corresponding and particular clues in the OCV curve. Taking a cell's OCV as the diagnostic indicator, a multi-mechanistic and non-destructive diagnostic method is developed in this paper. To establish an unambiguous relationship between OCV changes and the combinations of the decisive mechanisms, all the possible OCV changes under various aging situations are systematically analyzed based on a novel simultaneous coordinate system, in which the effects of each suspect capacity-loss mechanism on the OCV curve can be clearly represented. As a summary of the analysis results, a straightforward diagnostic flowchart is presented. By following the flowchart, an aging cell can be diagnosed within three steps by observation of the OCV changes.

1. Introduction

The use of a lithium-ion battery as a storage system is currently the best choice for mobile applications such as electric vehicles and portable electronics, based on comprehensive considerations of its energy and power density and cycle-life [1]. The battery capacity, as a figure of merit, indicates the battery's maximum energy consumption capability, but unfortunately, the capacity fades gradually during the aging progress [2]. Effective capacity-loss diagnosis and life-time prediction are not only the foundations of battery second-use technology but also a precondition for the development of new energy industry. To estimate and predict the capacity state throughout a battery's lifetime, two basic problems need to be solved: (1) identifying the battery capacity-loss mechanisms and (2) modeling the progression of capacity-loss within the corresponding mechanisms. This paper focuses on the realization of an effective technique for the capacity-loss diagnosis of aging cells.

The capacity degradation of a lithium-ion battery is mainly attributed to two categories of battery degradation mechanisms: the loss of lithium inventory (LLI) and the loss of active material

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(LAM) [3–9]. Furthermore, the LAM can be further subdivided into four specific subclasses: the loss of active material in the lithiated positive electrode (LAM$_{\text{liPE}}$), in the delithiated positive electrode (LAM$_{\text{dePE}}$), in the lithiated negative electrode (LAM$_{\text{liNE}}$), and in the delithiated negative electrode (LAM$_{\text{deNE}}$) [3]. All five mechanisms can be collectively referred to as the suspect capacity-loss mechanisms. Performing a capacity-loss diagnosis for an aging cell consists of finding the mechanisms that determine the cell's capacity degradation from these suspect degradation mechanisms [3].

The most definitive method for capacity-loss diagnosis is to make direct comparisons between the active electrode materials of cells at various aging states in terms of their morphology, structure, and composition using specialized instruments and means such as XANES, SEM, and EELS [10–13]. However, in this approach, the cells will be dismantled to collect the experimental samples. These unrecoverable damages mean that this method can only be applied once during the lifetime of a cell and that it is only suitable for laboratory research.

As a non-destructive method, electrochemical impedance spectroscopy (EIS) technology is used in this field [14–16]. The EIS results provide abundant impedance information at various aging states, and the mechanism of LLI caused by the growth of a solid electrolyte interphase (SEI) can be clearly confirmed by the observation of an impedance increase in a certain frequency range. However, for the other suspect mechanisms that may lead to capacity degradation, the EIS method still would not provide sufficient evidence.

To diagnose each suspect capacity-loss mechanism, a novel and powerful mechanistic model is presented in Ref. [3], which can simulate specific potential behaviors within various degradation mechanisms by adjustments of the loading ratio between the two electrodes and the extent of degradation in the two electrodes. Based on this model, suspect mechanisms can be identified by incremental capacity analysis (ICA) and differential voltage analysis (DVA) of a cell's voltage.

Based on Ref. [3], this paper develops a non-destructive and multi-mechanistic diagnostic method with a novel technique for systematic classification of suspect capacity-loss mechanisms. In this method, a cell's open-circuit voltage (OCV) is selected as the diagnostic indicator. Because a cell's capacity just equals the span of the OCV [4,5,12,13], as the suspect degradation mechanisms affect the cell's capacity, they will leave corresponding and particular clues in the OCV curve. Thus, this paper seeks to diagnose aging cells by establishing an unambiguous relationship between OCV changes and the combinations of the decisive capacity-loss mechanisms.

In line with this purpose, this study proceeds gradually, and the remaining sections are arranged as follows. In Section 2, a novel simultaneous coordinate system (SCS) is established. Based on this SCS, the effects of each capacity-loss mechanism on the OCV curve can be independently represented, and changes to each of the OCV's characteristic components can be clearly analyzed. In Section 3, all possible combinations of suspect capacity-loss mechanisms as well as the decisive mechanisms are listed, and the changes in OCV for each combination are systematically discussed. Based on the results, a capacity-loss diagnostic flowchart is proposed, and a specific example of a LiFePO$_4$/graphite cell is taken to demonstrate the analysis and diagnosis process in Section 4. Finally, the conclusions are presented in Section 5.

2. Simultaneous coordinate system for a lithium-ion battery

Battery capacity degradation is the joint result of the five suspect capacity-loss mechanisms (i.e., LLI, LAM$_{\text{liPE}}$, LAM$_{\text{dePE}}$, LAM$_{\text{liNE}}$, and LAM$_{\text{deNE}}$) [3]. To independently represent the effect of each capacity-loss mechanism and to systematically discuss OCV changes under all possible aging situations, a simultaneous coordinate system for lithium-ion batteries is first established in this paper, which is developed from an improvement on the approach in Ref. [3].

2.1. Simultaneous coordinate system development

The new simultaneous coordinate system (SCS) is established with two significant features:

First, as shown in Fig. 1, the SCS is composed of four coordinate axes. In this system, the axis [PE] indicates the amount of lithium in the positive electrode (PE) and is chosen as a reference coordinate axis of this system; the axis [NE] indicates the amount of lithium in the negative electrode (NE); the axis [APE] indicates the amount of lithium in the available PE; and the axis [ANE] indicates the amount of lithium in available NE. Herein, to prevent lithium plating on the NE, the axis [NE] is generally wider than the axis [PE] for a general commercial lithium-ion cell.

Second, in this SCS, the axes [APE] and [ANE] are always covered by complete potential profiles of PE and NE, respectively, according to the corresponding relationship between the electrode potential and the lithium content in the available electrode materials [17–20]. As shown in Fig. 1, taking a LiFePO$_4$/graphite cell as an example, a flat and wide potential plateau (approximately 3.43 V vs. Li) is shown on axis [APE], which corresponds to a two-phase reaction with LiFePO$_4$ and FePO$_4$ as end members [21], and, attributed to five different two-phase transition processes in graphite, five stages can be observed on axis [ANE], where Stage ❶ and Stage ❷ of approximately 85 mV and 120 mV vs. lithium, respectively, are relatively notable [20].

2.2. Capacity-loss mechanism represented in the SCS

In Ref. [3], the effects of the five suspect capacity-loss mechanisms on corresponding electrode potentials and cell voltage are elaborated: LAM$_{\text{liPE}}$ and LAM$_{\text{deNE}}$ will cause the potential profile of corresponding electrode to shrink towards the low SOC endpoints; LAM$_{\text{dePE}}$ and LAM$_{\text{liNE}}$ will cause the potential profile of corresponding electrode to shrink towards the high SOC endpoints; and LLI will cause the NE's potential profile to make a relative shift to the PE's.

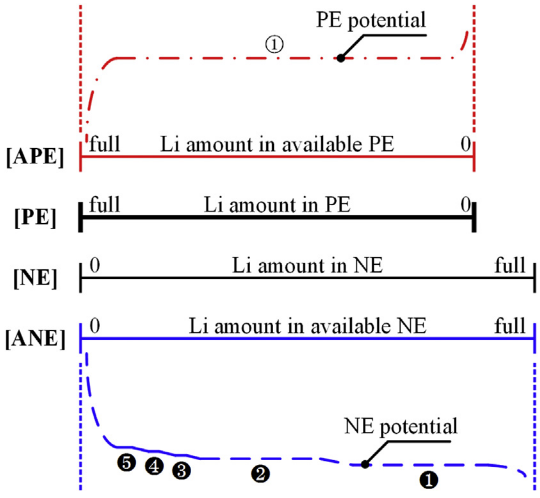

Fig. 1. Simultaneous coordinate system for a lithium-ion battery, where the mark '0' indicates the completely delithiated state and the mark 'full' indicates the fully lithiated state.