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Low temperature aging mechanism identification and lithium deposition in a large format lithium iron phosphate battery for different charge profiles

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HIGHLIGHTS

- A turning point is found for the current rate and cut-off voltage limits for degradation when charging at low temperature.
- The process of lithium deposition is investigated by incremental capacity analysis.
- The aging mechanism is quantitatively identified through a mechanic model using the PSO algorithm.

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ABSTRACT

Charging procedures at low temperatures severely shorten the cycle life of lithium ion batteries due to lithium deposition on the negative electrode. In this paper, cycle life tests are conducted to reveal the influence of the charging current rate and the cut-off voltage limit on the aging mechanisms of a large format $LiFePO_4$ battery at a low temperature (−10 °C). The capacity degradation rates accelerate rapidly after the charging current reaches 0.25 C or the cut-off voltage reaches 3.55 V. Therefore the scheduled current and voltage during low-temperature charging should be reconsidered to avoid capacity degradation. Lithium deposition contributes to low-temperature aging mechanisms, as something needle-like which might be deposited lithium is observed on the surface of the negative electrode after disassembling the aged battery cell. To confirm our explanation, incremental capacity analysis (ICA) is performed to identify the characteristics of the lithium deposition induced battery aging mechanisms. Furthermore, the aging mechanism is quantified using a mechanistic model, whose parameters are estimated with the particle swarm optimization algorithm (PSO). The loss of reversible lithium originating from secondary SEI formation and dead lithium is confirmed as the cause of the aging.

1. Introduction

Lithium ion batteries have become popular in the automobile industry due to their high energy and power density; however, capacity degradation in practical use restricts their broader application. Capacity degradation can be caused by multiple factors, including material properties, manufacturing techniques and practical operating conditions. The pervasively acknowledged aging mechanisms of lithium batteries are the loss of lithium ion (LLI), the loss of electrode active material (LAM), and an increase in resistance (IIR) [1,2]. LLI occurs mainly on the surface of the anode due to SEI decomposition and regeneration. In terms of LAM, the loss of positive electrode material is largely responsible, although structural damage to the negative electrode of graphite induced by lithium intercalation and deintercalation in Ref. [3], is a second explanation for LAM. The increasing thickness of the SEI film causes IIR [4–6]. In previous studies, a tank model is proposed that illustrates the issue graphically and vividly [1].

Previous studies provide several enlightened approaches to analyzing the capacity degradation of lithium ion batteries. Some ex situ post-mortem technologies are widely utilized to investigate the fading of individual electrodes, such as X-ray diffraction (XRD)

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and scanning electron microscopes (SEM) [7,8]. An in situ non-invasive method, impedance spectroscopy (IS), has also been recommended [9–11]. Additionally, for the semi-quantitative analysis of battery aging mechanisms, ICA and differential voltage analysis (DVA) have been used, as in Refs. [1,12–20]. To quantify the LLI and LAM, a prognostic/mechanistic model is introduced in Refs. [1,2,17–23]. By means of identifying the parameters of the model, the aging mechanism is directly clarified [1].

Batteries age far more at low temperatures than at room temperature [5,24]. It is reported that low-temperature degradation mainly occurs during the charging process due to lithium deposition, the potential for which is more likely to be achieved in the anode due to its elevated resistance at low temperatures [24,25]. S.S Zhang et al. [26] reported that even at a low current rate, the electrode potential at the anode is below 0 V vs. Li/Li^+ over a half period of charging. The low potential at the anode leads to lithium deposition, which definitely damages the battery. Jiang Fan et al. studied the effects of different low-temperature voltage profiles on lithium ion batteries and suggested that lithium plating will occur at high-rate charging [25].

Low temperatures are unavoidable in practical use, however, although they are known to damage the battery. Therefore, the charging protocol should adapt to the low temperature environment to avoid possible capacity degradation. For instance, pulse heating can efficiently heat the battery to mitigate the effects of low temperatures [27]. Nevertheless, the polarization on the anode surface will be stronger with a higher rate of charge, which results in increased lithium deposition [25]. In addition, a high current rate can bring about cell capacity decay and impedance increase, whether through a pulse charge or a conventional charge [25]. Furthermore, battery degradation is aggravated by a higher charge cut-off voltage [28–30]. Hence, the low temperature charging must to be modified.

Lithium ion batteries with a $LiFePO_4$ cathode are ideal for low temperature capacity fading research because $LiFePO_4$ is more stable than the other cathode materials [31,32]. We employ $LiFePO_4$ as the battery cathode to avoid the degradation inherent in other cathodes and help us focus on studying the capacity degradation caused by lithium deposition at the anode.

In this paper, cycle life tests are conducted to reveal the influence of the charging rate and the cut-off voltage limit on the aging mechanisms of a large format $LiFePO_4$ battery at a low temperature (−10 °C). An experiment matrix was created to conduct a low-temperature cycling test. Lithium deposition was observed using SEM after disassembling the battery post-aging. ICA is used to investigate the low temperature aging mechanism. A mechanistic/prognostic model is employed to quantitatively reveal the LLI, LAM and IIR that occurred during low-temperature charging. Parameter changes in the mechanistic model help to quantify the degradation mechanisms, and we confirm that the main reason for low temperature aging is LLI due to lithium deposition at the anode. Based on the test results, when charging a $LiFePO_4$ battery in a low temperature environment, here −10 °C, the charge current rate should be restricted to less than 0.25 C and the cut-off voltage to less than 3.55 V.

2. Experiment

2.1. Commercial lithium-ion battery and test equipment

This paper utilizes a commercial large format $LiFePO_4$/graphite lithium ion battery with a nominal capacity of 11.5 Ah. Isothermal experiments were performed on the batteries in an environmental chamber (DONGGUAN BELL) using a multichannel bench testing system (Neware CT-4008).

2.2. Reference performance test

A reference performance test (RPT), which comprises a capacity test, micro rate test (close to equilibrium) and hybrid pulse power characterization (HPPC) test, is developed to assess the battery's basic performance. The actual capacity is measured by two charge and discharge cycles, both at a rate of 1/3C with 1 h rest between each cycle. The low current profile of a 1/20 C charge and discharge rate is used to calculate the incremental capacity (IC) curves. The objective of the HPPC test is to measure the resistance of the charge and discharge at different states of charge (SOC) [33]. In consideration of the daily conditions of an electric vehicle, the time increment for discharge and regeneration is 30 s and 10 s, respectively. Derived from the manufacturer's maximum allowable discharge and charge current for 30 s and 10 s, the relative rates are 2 C and 1.5 C, respectively. An entire HPPC test consists of 10 cycles of this profile separated by 10% depth of discharge (DOD) CC 1/3C rate segments, followed by 1 h rest [33]. An entire RPT is shown in Fig. 1. Through such a test, the capacity, equilibrium characteristics and internal resistance can be evaluated.

2.3. Cycle life test at low temperature

A cycle life test was performed at −10 °C on 13 proposed cells under different conditions such as varied charge current rates, charge cut-off voltages and charge cut-off currents to analyze the aging mechanism when charging a lithium battery at a low temperature, as presented in Table 1. The discharge regime is consistent at 1/3 C current rate and 2.0 V cut-off voltage.

The cycle life test consists of a total of 50 cycles for each cell using the constant current – constant voltage (CC–CV) charge protocol as illustrated in Table 1. Prior to the cycling tests, a primary characterization test was conducted to measure the cells' basic features. The cycle life test was separated by the RPT at an ambient temperature to record the cells' feature at 10 cycle intervals. The cycle life test and RPT were repeated after a rest period of 10 h to ensure the experimental temperature. It should be noted that before the final RPT was conducted, the cells remained at the ambient temperature over 10 days due to a breakdown in the environmental chamber.

2.4. Battery disassembling and half battery assembling

Cell disassembly aimed at investigating the electrode dynamism through half cells and analysis by means of SEM. Before opening, cells were utterly discharged by CC discharge at a rate of 1/3 C and then by CV discharge to a cut-off voltage of 1/20 C at 2.0 V to reduce

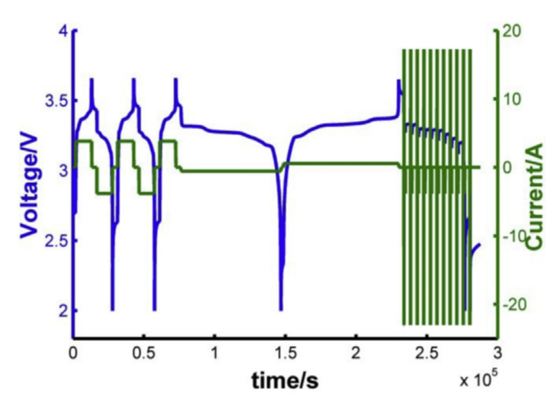

Fig. 1. Reference performance test protocol at room temperature.