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Lithium plating in a commercial lithium-ion battery – A low-temperature aging study

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HIGHLIGHTS

- Nondestructive characterization of the degradation effects of lithium plating.
- Capacity retention curves exhibit an inflection point, i.e. maximum aging rate.
- Lithium plating leads to a loss of cyclable lithium which affects the capacity balance.
- Low-temperature plating counteracts its own occurrence during long-term cycling.
- Thickness and area mass of the lithium layer confirm the electrochemical results.

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ABSTRACT

The formation of metallic lithium on the negative graphite electrode in a lithium-ion (Li-ion) battery, also known as lithium plating, leads to severe performance degradation and may also affect the cell safety.

This study is focused on the nondestructive characterization of the aging behavior during long-term cycling at plating conditions, i.e. low temperature and high charge rate. A commercial graphite/$LiFePO_4$ Li-ion battery is investigated in order to elucidate the aging effects of lithium plating for real-world purposes. It is shown that lithium plating can be observed as a loss of cyclable lithium which affects the capacity balance of the electrodes. In this way, lithium plating counteracts its own occurrence during prolonged cycling. The capacity losses due to lithium plating are therefore decreasing at higher cycle numbers and the capacity retention curve exhibits an inflection point. It is further shown that the observed capacity fade is partly reversible. Electrochemical impedance spectroscopy (EIS) reveals a significant increase of the ohmic cell resistance due to electrolyte consumption during surface film formation on the plated lithium. Additional cell opening provides important quantitative information regarding the thickness of the lithium layer and the corresponding mass of the plated lithium.

1. Introduction

The lifetime of Li-ion batteries is crucial concerning their application as energy storage devices in mobile and stationary operation. There are various degradation processes in Li-ion batteries [1–3] which affect performance and durability. It is therefore very important to elucidate the underlying aging mechanisms in order to avoid or mitigate their occurrence. Graphite is the common active material for the negative electrode in Li-ion batteries and it mainly determines the overall aging behavior. The most important degradation mechanisms of the graphite electrode are continuous growth of the solid electrolyte interphase (SEI) and metallic lithium deposition [4].

Lithium plating is different from all other degradation processes in terms of its temperature dependence [5]. It is caused by low-temperature charging with high current and at a high state-of-charge (SOC). However, poor capacity balance can also lead to metallic lithium deposition at higher temperatures. Besides capacity loss and impedance rise lithium plating also presents a serious safety hazard. The metallic lithium can grow dendritically which may cause an internal short circuit of the cell [6–8]. The major aspects of lithium plating in Li-ion batteries are reviewed in Ref. [9], including deposition criteria and different modelling approaches. Intercalation of lithium-ions in the graphite particles and

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lithium plating on the particle surface are competing during low-temperature charging. High charge currents lead to charge transfer limitation at the particle/SEI interface. Lithium plating occurs when the graphite potential is reduced below 0 V vs. Li/Li^+. However, plating might also be due to mass transport limitation. If the lithium-ion diffusion in the graphite particle is too slow, the particle surface becomes saturated with lithium-ions which consequently leads to lithium plating. These polarization effects are both aggravated with decreasing temperature.

There are a lot of aging studies on commercial Li-ion batteries in the literature which mainly address the performance degradation at ambient or high temperatures due to SEI growth and loss of graphite active material [10–13]. However, the occurrence of lithium plating is only shown as a consequence of cycling in a narrow SOC range [14]. Others assume that lithium plating is the reason for fast performance degradation [15].

In this study lithium plating is forced by low-temperature charging in order to investigate the corresponding aging effects. It is important to note that all other degradation processes and side reactions, e.g. SEI growth, are assumed to be negligible at low temperatures according to the Arrhenius equation [5]. Therefore, lithium plating is the only significant aging process at these cycling conditions. However it must be considered that plated lithium metal induces further degradation due to additional surface film formation and electrochemical isolation of active material.

The investigated commercial Li-ion battery contains $LiFePO_4$ (LFP) as active material of the positive electrode. It is known that LFP is highly durable due to negligible degradation processes [16]. Therefore, the observed aging effects are assumed to be entirely caused by lithium plating and its accompanied processes. LFP also exhibits a very flat voltage profile [17] which simplifies the interpretation of full cell voltage profiles. In detail, all voltage plateaus are due to the phase behavior of the graphite electrode. This is crucial for an unambiguous characterization of the aging behavior by nondestructive electrochemical methods [18–20].

Short-term effects of lithium plating are already known [21,22] and allow for an indirect detection and quantification of this aging process [23]. The operating conditions for lithium plating in the investigated battery were also identified in our previous study [23]. These conditions are applied here in order to characterize the long-term effects of lithium plating on the battery performance. Furthermore, the reversibility of the plating losses is investigated by recovery cycling at higher temperatures. In addition to the electrochemical results, aged cells are opened in different aging states for quantitative information about the plating process. This includes determination of the lithium layer thickness and the mass of the plated lithium metal.

2. Experimental

2.1. Commercial Li-ion battery and electrochemical test equipment

The investigated commercial Li-ion battery is a cylindrical 26650-type cell with 2.5 Ah rated capacity. Like mentioned before, the cell chemistry is based on a graphite (negative electrode) and LFP (positive electrode). This determines the voltage range of 2.0 V–3.6 V, i.e. discharge and charge cutoff voltage. The battery is allowed to be operated down to −30 °C, according to the data sheet.

Electrochemical measurements are performed on a BaSyTec CTS battery test system which is combined with a Gamry G750 card for electrochemical impedance spectroscopy (EIS). All cells are cycled and characterized in an ESPEC climate chamber in order to assure constant and controlled temperature conditions. Temperature equilibration is assumed to be completed after a 10 h rest period.

2.2. Electrochemical aging tests

The aging tests consist of constant current – constant voltage (CCCV) low-temperature cycling at −22 °C. This cyclic aging is interrupted after every 20th cycle for the characterization tests at 25 °C. In detail, CC charging is performed with currents of 1C (2.5 A, corresponding to 1.25 mA cm^{-2}) or C/2 which is followed by a CV phase until the current relaxes below C/20. This determines the full capacity (1.0 SOC). Another SOC value (0.8 SOC) is investigated in order to elucidate the effects of SOC on the aging behavior. 0.8 SOC is performed similar to the full capacity. However, the charging step is stopped at 80% of the full capacity. After charging to the aforementioned SOC values, the cells are completely discharged with C/2. This cycling procedure is repeated after a rest period of 1 h.

The characterization test includes a CCCV capacity measurement with 1C charge/discharge current and C/20 CV phases. Afterwards, an EIS measurement is performed at 0.5 SOC with a frequency range of 10 kHz–10 mHz and an AC-amplitude of C/50. This is followed by a detailed investigation of the voltage profile, i.e. a capacity test with smaller charge/discharge current (C/10). The reversibility of the capacity losses is checked by continued cycling at 25 °C after the low-temperature aging tests.

Two cells are tested for each aging conditions in order to confirm reproducibility. MATLAB is used for data evaluation and signal processing.

2.3. Cell opening and quantitative investigations

Additional cells are cycled at −22 °C with 1C in the full capacity range (1.0 SOC) for the quantitative investigations after cell opening. All cells are completely discharged (multiple discharge steps to 2.0 V with decreasing current) before opening in order to reduce the safety hazard due to metallic lithium. The cells are opened at different aging states in a glove-box under argon atmosphere. Afterwards, pictures of the negative electrode's surface are taken in order to investigate the optical changes due to lithium plating. Separation of the negative electrode layer from the positive electrode and separator layer allows for determination of the graphite electrode thickness by a digital thickness gauge from Mitutoyo. The thickness of the copper current collector (10 μm) can be determined after water exposure which leads to delamination of the active material layers. It must be noted that the current collector is coated on both sides. An unaged cell (0 cycles) without lithium plating serves as a reference, i.e. thickness of the unplated electrode. Thus it is possible to derive the thickness of the lithium layer from measuring the thickness of the complete electrode layer. Thicknesses are measured immediately after taking the pictures in order to avoid significant effects of air exposure. The thickness of each electrode is measured at five different points on the surface for averaging.

Masses of the plated lithium are determined by punching out the negative electrode layer to get circular pieces with an area of 20 cm^2 (both sides). This mass per unit area can be easily translated for the complete cell by knowledge of the total electrode area. It is assumed that the metallic lithium is completely transferred to lithium carbonate by prolonged air exposure. Subsequent oven drying leads to loss of the residual electrolyte. In this way, the mass of the plated lithium can be determined from the differences of the dried area mass compared to the unplated reference cell. Details of the calculation are shown later (Section 3.5.3.). The masses of metallic lithium are determined for the inner and outer part of the jelly roll in order to investigate the distribution of lithium metal in the cell.