



Irreversible calendar aging and quantification of the reversible capacity loss caused by anode overhang



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ARTICLE INFO

Keywords:

Calendar aging
Anode overhang
Pressure
Homogeneity of lithium distribution
Reversible capacity fade
Irreversible capacity fade

ABSTRACT

Calendar aging tests are presented quantifying the reversible capacity loss caused by lithium migration from the active part to the overhang of the anode. Based on these tests, capacity loss at five different SOC with respect to the anode is evaluated. The remaining capacity shows a non-linear part in the beginning representing the reversible capacity loss caused by the overhang. The subsequent linear part ending after 100–200 days corresponds to the irreversible capacity loss. By extrapolating the linear part to $t = 0$, the lithium lost to the overhang is measurable for each storage condition. This approach matches well to theoretical values calculated using a simple equation. In later stages of the capacity loss curve, another superposed effect can be observed that decreases capacity fade. The reason is found in an increasing homogeneity of lithium distribution that correlates to the peak height of differential voltage characteristics. In this publication an increasing homogeneity is associated with a higher extractable capacity and vice versa. An especially high increase of homogeneity is observable when a high voltage difference coincides with pressure change due to lithium insertion. Finally, the temperature dependency of the lateral lithium flow is shown for three temperatures at a fixed storage position.

1. Introduction

The knowledge about the origin of capacity fade in lithium-ion batteries is of great importance [1–3] regarding the choice of the most appropriate battery for a product [4] and the best operating strategies for the system. The separation of the irreversible and reversible share of capacity fade [5] plays a key role in describing the root causes of aging. While the irreversible capacity loss is accompanied by capacity fade that is mostly caused by forming SEI (solid-electrolyte-interphase), the reversible loss can be recovered under certain operating strategies like keeping the SOC at a specific value. Thus, it is of particular importance to know under which operation conditions capacity losses occur and under which operation conditions they are recoverable, to avoid performance drops by a too low extractable capacity. Furthermore, understanding the underlying processes of reversible degradation will make it possible to significantly enhance the lifetime of batteries utilized in certain applications.

According to publications by Gyenes et al. [6] and Lewerenz et al.

[7] one of the reversible capacity effects is the lateral flow of active lithium within the electrode from and to the anode overhang. Recently Wilhelm et al. analyzed this effect evaluating Coulombic efficiencies and using x-ray diffraction (XRD) of the anode overhang [8]. The anode overhang is defined by the geometrical anode area, which is not opposed by a cathode (see Section 2.2 and Fig. 3). The anode is oversized in nearly all lithium-ion cells containing a graphite anode. The reason therefore is to prevent lithium plating at the edges of the anode [9]. In some cells the electrodes are coated continuously on both sides to simplify the cell production. In that case additional overhang appears at last winding facing outside and in the first windings. The overhang is considered as passive as it is not directly chargeable or dischargeable, due to comparatively long ionic pathways of mm to cm to the cathode. The time constant is therefore not hours as during a discharge but a few to several 100 days. The extractable capacity can be reversibly increased or decreased depending on the operating conditions in calendar and cyclic aging tests. This phenomenon is called passive electrode effect [7]. A passive electrode arises as well if the lithium-ion transport

Abbreviations: FCE, full cycle equivalents; DVA, differential voltage analysis; PMA, post-mortem-analysis; EC, ethylene carbonate; DMC, dimethylene carbonate; EMC, ethylene-methylene carbonate; DOD, depth-of-discharge; SOC, state-of-charge; HLD, homogeneity of lithium distribution; MinHi, minimum at high SOC

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<https://doi.org/10.1016/j.est.2018.04.029>

Received 27 February 2018; Received in revised form 25 April 2018; Accepted 26 April 2018
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is suppressed e.g. by a dense covering layer on top of the anode facing the separator formed by successively passivated lithium plating [10–12]). The effect describes, in the case of calendar aging, a lateral lithium-ion exchange from the active anode to the passive anode (e.g. overhang) and vice versa. The effect is found to be reversible by changing the SOC back to the previous value [13,14]. The flow direction and the exchange velocity of active lithium within the anode depend on the absolute differences of anode potentials in active and passive area. The maximal shiftable amount of lithium is defined by the percentage share of the anode overhang to the total active area. The SOC dependence of capacity fade has been outlined in various publications such as [13–18]; it was found to be related to the SOC before and during the test.

So far, the passive electrode effect has only been investigated for 229 mAh NMC|Graphite pouch cells [6]; and for 8 Ah [7] and 1.1 Ah [8] LiFePO₄|Graphite cylindrical cells. This publication is the first to quantify the influence of the anode overhang and demonstrate the effect for an automotive 25 Ah prismatic NMC|Graphite cell, so that the impact can be further generalized for another cell design and manufacturer. A simple test with fixed full cell SOC or cell voltage would lead to a shift of anode's SOC, as anode and cathode voltage curves shift relative to each other, if active lithium is lost [18–21]. Therefore, for quantification of the overhang effect the SOC needs to be defined according to the anode SOC, as a simple SOC or voltage approach would gain limited precision. As in this work the SOC is defined relatively to the anode voltage curve, it is referred to as *storage positions*, to avoid misinterpretation with respect to the full cell SOC. The identification of these storage positions is carried out by evaluating the derivative of a low current discharge voltage curve that shows strong characteristics of the graphite electrode of [18–20,22]. This technique is better known as differential voltage analysis (DVA). The determination and adjustment of the corresponding storage position after each check-up is executed after evaluation of the latest measured DVA.

A method to measure the homogeneity of lithium distribution (HLD) in a lithium-ion cell with DVA is shown by Lewerenz et al. [23], evaluating the peak height of a characteristic peak at the pure phase of stage 2 of the graphite. The impact of HLD on capacity fade is discussed in this publication exemplarily for large inhomogeneities, which cannot be compensated after a full cycle. In that case the cut-off voltages will terminate the charge or discharge process before all active lithium is exchanged. However to our knowledge, the concept of HLD influencing the extractable capacity and the determination of HDL with DVA is hardly addressed in literature. In this publication a novel theory will be presented that even small differences in HLD can lead to an increase or decrease of extractable capacity. Moreover, the positive influence of a notable change in the pressure gradient on the HLD is discussed.

The temperature dependence keeping the cells at the same SOC has already been presented e.g. by [17] for 25 °C, 40 °C and 60 °C. However, a link to the passive electrode effect and the anode overhang is still missing; with this contribution, we aim at closing this gap.

In this publication the following topics are discussed: First, a method is presented to evaluate the homogeneity of lithium distribution (HLD) for calendar aging tests using DVA (Section 4.1). The impact of pressure change during cycling is then discussed in Section 4.2. The quantification of the overhang is given in Section 4.3. A theory of the impact of the HLD on extractable capacity is described in Section 4.4. The corresponding share of irreversible capacity loss is discussed in Section 4.5. Since the lateral lithium transport within the anode will be a function of temperature, the aging and the impact of the overhang is finally presented for three temperatures in Section 1.1.

2. Experimental

2.1. Aging and check-ups

In this contribution 24 prismatic 25 Ah NMC|Graphite lithium-ion

Table 1

Specifications of the battery used according to datasheet.

Cathode	NMC
Anode	Graphite
Nom. capacity	25 Ah
Charge cut-off voltage	4.1 V
Discharge cut-off voltage	3.0 V

cells are investigated in a calendar aging test. The corresponding shallow cycling tests are currently under review [24]. The information from the datasheet is given in Table 1. More specified results for this cell will be given on the basis of a post-mortem-analysis in Section 2.2. The cells are braced with Al-alloy (AlMg3-5754) plates with a thickness of 20 mm which are tightened with four screws applying a torque of 5 Nm. They are aged at 30 °C and 40 °C for 600–660 d, and at 50 °C for 400 d. The aging tests are interrupted by check-up tests. The check-up temperature is 20 °C. In the course of a check-up, a capacity test at 1C and 0.1C as well as a pulse test are performed.

During check-up, cells are first discharged down to 3.0 V, then charged with 1C (25 A) up to 4.1 V, followed by constant-voltage charging until the current drops below 0.02C (maximum 30 min). Afterwards the cells rest for 10 min before they are discharged again with 1C (25 A) until the voltage of 3.0 V is reached. The latter discharge is used for 1C capacity determination. The determination of the capacity test with 0.1C (2.5 A) is performed analogously.

The pulse test is executed after a 30 min rest period at a SOC of 50% with respect to the current capacity measured at 1C. The pulse test itself consists of a 10 s discharge pulse at 1C with a 60 s rest period and followed by a 10 s charge pulse at 1C with subsequent 60 s rest time. The internal resistance is evaluated at an SOC of 50% after a 10 s discharge.

In this special test the cells are aged according to the characteristics of the anode voltage curve at five different storage positions named Position 1 to Position 5 (shortened to P1-P5). The unit of the storage positions P_x is defined as discharged Ah at 0.1C from a fully charged state. The characteristic storage positions are depicted in Fig. 1. In Fig. 1a the discharge curve measured at 0.1C is shown; in Fig. 1b the corresponding DVA is displayed; and in Fig. 1c the anode curve vs. lithium metal, measured in a coin cell of a harvested electrode, is presented. The half-cell curve is aligned and stretched in x-direction to the characteristic minima of the DVA. The aging test matrix is summarized in Table 2. P2 and P4 are determined by the x-value of the minima of the anode discharge capacity. P3 is defined as the center position of the minima. P1 and P5 are defined relatively to the anode capacity by:

$$P1 = P2 + 3.9Ah \cdot \frac{P4(t) - P2(t)}{P4(t_0) - P2(t_0)} \quad (1)$$

$$P5 = P4 - 2.5Ah \cdot \frac{P4(t) - P2(t)}{P4(t_0) - P2(t_0)} \quad (2)$$

With these definitions of P1 and P5 it is possible to measure the influence of the anode SOC according to well-distributed storage positions. The fraction term on the right corrects the positions in case of loss of anode active material (peak distance).

To identify the influence of anode and cathode on the full cell DVA, the half-cell discharge curves of harvested anode and cathode vs. lithium metal are measured and displayed in Fig. 2a and c. The corresponding dV/dQ curves are shown on the right (Fig. 2b and d). The peaks in the full cell (Fig. 1b) can be assigned solely to the graphite anode. The cathode contributes to the full cell DVA by a rather constant phase from 0 to 8 Ah and an increasing slope from 8 to 25 Ah (Fig. 1b). The half cells are used only partly marked by green dotted lines assigned by full characteristics and full cell voltages.

During aging the anode and cathode voltage curves shift relatively to each other. Therefore, the storage positions are updated after each

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