



Evaluation of cyclic aging tests of prismatic automotive LiNiMnCoO₂-Graphite cells considering influence of homogeneity and anode overhang

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ABSTRACT

Cyclic aging tests of 20 compressed prismatic automotive Li(NiMnCo)O₂|Graphite cells are evaluated. The shallow cyclic aging tests are conducted around five average SOCs with respect to the anode. The cells are cycled at two DODs and two C-rates. The irreversible capacity loss is evaluated by the slope of the near-linear part at the end of aging test. The homogeneity of lithium distribution (HLD) is associated with peak height of differential voltage analysis (DVA) and to capacity difference analysis (CDA). The evaluations of DVA, CDA and capacity fade curve are depending mainly on the average SOC and hardly on DOD or C-rate. The trends correlate with the volume expansion originated from the graphite. The highest HLD and the lowest capacity fade are reached around 50% SOC where hardly any additional volume expansion occurs. In the SOC regions with high volume expansion of the graphite the HLD reduces dramatically and the capacity fade rises towards 0% and 100%, respectively. Due to smeared characteristics in DVA, capacity loss cannot be directly separated into shares related to anode overhang, HLD, loss of active material and residual irreversible losses. The combination of cell compression and high gradients of volume expansion during shallow cycling is found to be the root cause for the flattening of DVA curves.

1. Introduction

The understanding of aging mechanisms is one of the most important issues to improve lithium-ion batteries. To understand the aging of lithium-ion batteries, it is necessary to separate the superposed reversible and irreversible aging mechanisms and how they contribute to performance (capacity and resistance) reduction. Moreover, effects from pressure have to be included to assess the optimal compression of the cells. This is all necessary to be able to estimate the lifetime for a certain application and to choose the best operating conditions. At first the findings of the less complex static calendaric aging are presented before the additional effects of cyclic aging are discussed.

In a previous publication [1] the calendaric aging tests of the here presented cells has been subdivided into irreversible capacity losses and reversible losses caused by the anode overhang and losses and gains by the degree of homogeneity of lithium distribution (HLD).

The influence of the geometric anode overhang without opposed cathode was shown for static calendaric aging tests for several

chemistries and cell shapes and sizes [1–4]. It is based on lithium-ion migration within the anode; sometimes called passive electrode effect [2]. The lateral transport can be visualized by color change in post-mortem-analyses [3] or in optical cells [5–9]. The anode overhang acts as a source or a drain for lithium-ions. The exchange velocity is comparable low and depends on the temperature and potential differences between active anode (with opposed cathode) and anode overhang. The maximum shiftable amount of lithium depends on the SOC difference between the anode overhang and the active anode during test and on the percentage of the anode overhang. Thus, in a static test the influence of the overhang can be easily estimated. The anode overhang is especially large for small cells as the active area is comparable low to the winding tolerances. However, there are many efforts made in cell productions to reduce the area of the anode overhang by intermittent coating (double- and single-sided coating) and lower winding tolerances of < 1 mm. For such an optimized 18,650 cell used for TESLA the anode overhang has still an anode overhang of 6.9%.

Another reversible contribution is related to the HLD. In this

Abbreviations: CDA, capacity difference analysis; FCE, full cycle equivalents; DVA, differential voltage analysis; DOD, depth-of-discharge; HLD, homogeneity of lithium distribution; OCV, open circuit voltage; SOC, state-of-charge

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concept, the coherence or simultaneity of the e.g. discharge is considered. The concept is introduced in [10] for the first time. In case all particles are in the same SOC during discharge, most of the lithium-ions can be extracted from the anode before cut-off voltage is reached. In contrast, a low HLD flattens the discharge curve by a low coherence of lithium-ion distribution and the cut-off voltage is reached before all active lithium can be extracted from the anode. The HLD is measurable on behalf of characteristics in the differential voltage analysis (DVA). Sharper peaks are associated with a higher coherence and flatter peaks with a lower coherence of SOC distribution. For the calendaric aging tests, with moderate aging conditions, this was basically only an improvement of HLD leading to a smaller slope of capacity fade [1,2,11,12].

The irreversible losses, by means of calendaric aging, arise from the passivation of lithium-ions at the graphite anode, the so called solid-electrolyte-interphase (SEI) [13,14]. It is discussed in literature that metal dissolution from the cathode followed by deposition on the anode further accelerates this SEI formation [15–17], while for $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ the amount of deposited transition metals on the anode and their impact on the cathode itself is considered to be rather low [18,19]. For cyclic aging at least two further aging mechanisms have to be taken into account: loss of active material [20] and lithium plating [21–23]. The loss of active material of the anode and the cathode is determined by DVA [10,24,25]. For the graphite anode this is measured by reduced distance of the characteristic peaks and for the cathode by increased slope of DVA at high SOC during aging. The loss of active material is mostly associated to cyclic aging, which leads to pressure change by volume work of the anode.

Strong passivated lithium plating (covering layer) is associated with an increase of capacity difference measured at two different C-rates [26]. While at a high C-rate only the direct opposed electrode is active, at a lower C-rate, the lithium-ions behind the covering layer have additional time to migrate to the parts without covering layer. The assumption is that a direct charging and discharging of the anode and the cathode is not possible due to the presence of a covering layer. Thus, the presence of a covering layer increases capacity difference. This method is called capacity difference analysis (CDA). Unfortunately the CDA is not a clear indicator for a covering layer as also very low HLD can lead to a capacity difference increase [10,27]. An example is presented for the case of a covering layer that has formed only on the front side of the double-sided electrode. The μm -thick covering layer on the front side leads to increased pressure on the back side. Applying full cycles the increased pressure on the back side leads to a charge agglomeration at the back side by a pumping effect. A distinct explanation is given in [27]. In this example the cell capacity difference increase is caused by the covering layer and strong cycling-induced inhomogeneities. In a nutshell, a high capacity difference can be caused by strong inhomogeneities and/or by covering layer.

The cyclic aging for shallow DOD at distributed average SOC's are shown only in a few publications known to the authors. In a contribution by Ecker et al. [28] a V-shape over the average SOC is obtained for a 18,650 cell with $\text{Li}(\text{MnNiCo})\text{O}_2$ vs. graphite. In that case the aging at low and high SOC is highest, which correlates to SOC regions with high pressure gradients. The expansion has not been directly measured but was correlated from the combination of dilatometric measurements of another cell [29] and anode characteristics in the DVA. However, in other publications no V-shape can be observed. For example Takei et al. [30] showed for cylindrical 18,650 cells with LiCoO_2 /hard carbon that for a DOD of about 20% no change in aging is observed below an average SOC of about 50%. From 50% SOC on, the capacity fade increases with increasing average SOC. Keil et al. [31] tested a 18,650 cylindrical cell with the active materials $\text{Li}(\text{NiCoAl})\text{O}_2$ vs. graphite. In Fig. 7 of this publication capacity fade of 20% DOD tests are shown for average SOC of about 35%, 55% and 75%. Assuming that the slope of the last part correlates to the irreversible capacity fade the losses at 75% are highest and decrease with lower average SOC. Käßitz

et al. [32] tested a $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ vs. graphite in a pouch cell design. The cells were cycled with 10% DOD around 5%, 50% and 95% SOC. According to the slope at the end of test, the losses are higher for higher average SOC. Moreover, 10% and 20% DOD tests on 25 Ah pouch cells based on NMC (4.4:2) vs. graphite from EIG are presented in [33,34]. They exhibit that the aging increases with average SOC. Especially the aging at 80% average SOC is significantly higher. This cell was tested in an uncompressed state. For all these cells used in the three publications data of a pressure evolution over a full cycle is missing.

In this publication the cyclic aging is investigated for shallow DOD in dependence of DOD, C-rate and SOC at room temperature for a compressed prismatic automotive cell. The results from capacity, internal resistance, CDA and DVA measurements are presented in Section 3. The impact of the anode overhang and HLD is discussed in Section 4.1. A distinct discussion of the DVA and the aging for the test conditions is given in the Sections 4.2–4.5. Finally, the irreversible capacity loss is presented in Section 4.6.

2. Experimental

In this contribution 20 prismatic 25 Ah NMC/Graphite lithium-ion cells are investigated in a cyclic aging test. The corresponding calendaric aging tests are already published in a previous publication [1]. There, detailed information with respect to the cell, volume work and results of post-mortem-analysis are given. Therefore, the cell is introduced only briefly, here.

The investigated cell has $\text{Li}(\text{Ni}_x\text{Mn}_y\text{Co}_{1-x-y})\text{O}_2$ (NMC) as positive electrode with an stoichiometry 1:1:1 and on the negative electrode graphite as active material. The graphite anode facing the separator is coated with spherical Al_2O_3 particles with a diameter of about 30 nm. The nominal capacity is 25 Ah. The cells can be cycled according to data sheet between 3.0 V and 4.1 V. They are compressed with Al-alloy plates with a thickness of 20 mm, which are tightened with four screws applying a torque of 5 N m.

The cells are aged at room temperature (20 °C) at current rates of 1C and 3C and a depth-of discharge (DOD) of 6% and 12% respectively. In this special test the cells are cycled around average SOC that are not defined according to full cell constraints like cell voltage or SOC but according to the degree of lithiation of the anode. The average SOC are calculated regarding the characteristic peaks of the DVA (Fig. 1) associated to the graphite anode [11,24,25,35]. The unit of the average SOC P_x is defined as discharged Ah at 0.1C from a fully charged state. In this publication, the cells are cycled around five different average SOC, named Position 1 to Position 5 (shortened to P1–P5). 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 $P3 = (P2 + P4) / 2$. P1 is defined relatively to the anode capacity by $P1 = P2 + 3.9 \text{ Ah} \cdot \frac{P4(t) - P2(t)}{P4(t_0) - P2(t_0)}$ and P5 by $P5 = P4 - 2.5 \text{ Ah} \cdot \frac{P4(t) - P2(t)}{P4(t_0) - P2(t_0)}$. With these definitions of P1 and P5 it is possible to measure the influence of the anode SOC according to well-distributed average SOC with minimal overlap of the test conditions. The aging test matrix is summarized in Table 1 and the average SOC and the different DODs are shown in Fig. 1a. For each position only one cell is tested so that reproducibility of the cell is not measured directly. However, the reproducibility considering calendaric aging is very high [1].

As the anode and cathode voltage curves shift relatively to each other during aging, the average SOC is updated after each check-up, evaluating the DVA of the 0.1C discharge curve. Therefore, the aging is performed at varying SOC or voltage of the full cell.

After the cells are fully charged, the corresponding storage condition is adjusted voltage-based using the same discharge current rate of 0.1C as for the DVA until the dedicated voltage is reached. After a 60 min rest the OCV U_{rest} is measured. To avoid a drift due to small asymmetries in charge and discharge during cycling, the test is

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