

# Importance of the constant voltage charging step during lithium-ion cell formation



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## ABSTRACT

The formation process is the final step in lithium-ion cell manufacturing and has a major impact on the performance, the cycle life and the safety of the cells. To support the formation of a highly permeable and stable solid electrolyte interphase (SEI), the formation procedure must be well defined. The purpose of this paper is to outline the importance of the constant voltage (CV) charging step during the formation process of lithium-ion cells. Therefore,  $\text{Li}(\text{Ni}_{1/3} \text{Co}_{1/3} \text{Mn}_{1/3})\text{O}_2/\text{graphite}$  based lithium-ion cells are charged with and without CV charging step during the formation process and their aging behavior is compared. For a deeper understanding of the aging mechanism, a differential voltage analysis (DVA) as well as several post-mortem analyses, e.g. SEM/EDS analysis and areal capacity determination by half-cell measurements, are performed. A strong correlation of the CV charging step during the formation process and the aging behavior of the cells is concluded. It is concluded that the omission of the CV charging step provokes the formation of an inhomogeneous and porous SEI, leading to accelerated loss of cycleable lithium and graphite anode degradation.

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## 1. Introduction

Due to their high power and energy density, lithium-ion (Li-ion) battery cells have become more and more important for the operation in electrical vehicles and as stationary energy storage [1–4]. Certainly, these applications require long-lasting, high quality Li-ion battery cells. One of the key influence factors for a high performance and long-lasting Li-ion cell is the formation of the solid electrolyte interphase (SEI) through electrolyte decomposition on the negative electrode. This reaction causes irreversible charge loss (ICL) within the first charge/discharge cycle of the formation process [5–8]. Peled [9] first introduced and described the characteristics of the SEI. The most important functionality includes the protection of the graphite anode against further electrolyte decomposition and graphite exfoliation while being highly permeable for Li-ions [6,10–14]. Even though the SEI is mainly formed during the first cycles of the formation process, it is continuously growing over the cycle life due to further electrolyte composition [15,16], leading to further ICL and possible graphite exfoliation. Furthermore, volume changes of graphite anode during lithiation and delithiation (approx. 10–10.7%) can induce active material loss and accelerates SEI restructuring due to

electrode and particle cracking [14–21]. Hence, the cell aging behavior is mainly influenced by the initial SEI formation and the growth over lifetime [14,16,22]. The stability of the formed SEI is affected by the electrolyte composition, the structure of the electrodes and the formation protocol. The total electrolyte volume as well as the composition of the non-aqueous solvents and the additives mainly contribute to the SEI growth and cell performance [11,13,21–23]. Furthermore, the crystalline structure as well as cracks and defects in the carbon material of the anode influence the SEI formation [6,8,14,24].

To guarantee a homogeneous SEI growth, the state-of-the-art formation process starts with pre-charging using a small charging current, followed by several aging intervals at elevated temperatures. Subsequently, in the conditioning phase, the cells are fully charged with a constant current, constant voltage (CC-CV) charging protocol and run through certain aging sequences for self-discharge characterization. Finally, the cells are charged several times CC-CV and discharged in order to check the capacity and determine the internal resistance. These values are often used as quality criteria.

In addition to the huge influence on cell quality, the formation process is also the most expensive process step in cell production with a share of 18–32 % [5,25–27]. Therefore, many efforts have been made to reduce the process cost and shorten the process time. For example, An et al. proposed a formation protocol which is up to

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six times faster compared to a reference process [28]. Others reduced the process time by limiting the Li intercalation into graphite, using a maximum charging voltage of 3.7 V [29]. In order to reduce process costs, we prior introduced serial formation methods and showed the major influence on the charging profile of the cells. The difficult implementation of the CV charging step was derived as one of the outcomes of these investigations [30]. Therefore, in this paper the importance of the CV charging step during the formation process is investigated with the aim of process time optimization and cost reduction. In order to determine the influence of the CV charging step on the cell quality and the aging behavior, Li-ion battery cells are charged with and without CV charging step during the formation process. Afterwards, cyclic aging tests were carried out. For detailed investigation of the ongoing aging mechanisms, the differential voltage analysis (DVA) is performed and the aged electrode material is examined by a scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM/EDS). Post-mortem capacity determination is conducted by half-cell measurements in order to verify the DVA results.

## 2. Experimental

### 2.1. Test cells

To investigate the influence of the CV charging step on the SEI formation quality and aging behavior of the cells, six stack-type pouch cells with a nominal capacity of 2 Ah were manufactured.

The cells contain an NMC111 cathode consisting of 3.5 wt% polyvinylidene fluoride binder (PVdF, Solvay S.A.), 2.0 wt% carbon black, 2.0 wt% graphite (both Timcal Ltd.) as conductive additives and 92.5 wt%  $\text{Li}(\text{Ni}_{1/3} \text{Co}_{1/3} \text{Mn}_{1/3})\text{O}_2$  particles (NMC, BASF SE), a graphite based anode composed of 94.5 wt% graphite (Hitachi) active material, 1.5 wt% carboxymethyl cellulose (CMC, Inabata & Co., Ltd.), 2.3 wt% styrene-butadiene rubber (SBR, Zeon) as binder and 1.7 wt% carbon black (Timcal Ltd.), a polyolefine separator and a  $\text{LiPF}_6$  based electrolyte (1 M  $\text{LiPF}_6$  in EC:EMC 3:7 (wt:wt) with 2 wt% vinylene carbonate and 2 wt% biphenyl).

The cells comprise a stack of 10 cathode layers and 11 anode layers. Every electrode is coated in both sides with active-material and the anode overhang amounts to 2 mm at all edges. An image of the used pouch cell is shown in Fig. 1.

The theoretic areal capacity of the uncycled anode material within the cell is  $2.8 \text{ mAhcm}^{-2}$  and for the cathode  $2.3 \text{ mAhcm}^{-2}$ . After a calendering step the porosity amounts to 30% and the one-side coating thickness to  $56 \mu\text{m}$  for both electrodes. The loading level of the anode and cathode material as well as important cell characteristics can be found in Table 1. Further coating process and

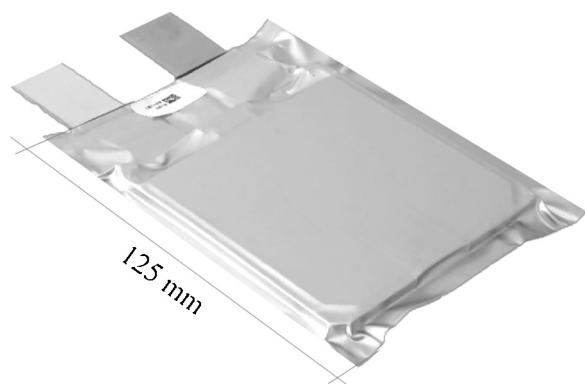


Fig. 1. 2 Ah stack-type pouch cell used for the formation and aging experiments.

Table 1

Specifications of the 2 Ah stack-type pouch cells used for the formation and aging experiments.

Description	Value
Nominal Capacity	2 Ah
Voltage window	2.7–4.2 V
Cathode area per sheet	$50.3 \text{ cm}^2$
Anode area per sheet	$56.2 \text{ cm}^2$
Stack geometry	$7.5 \times 7.5 \text{ cm}^2$
Anode active material mass loading	$8.0 \text{ mgcm}^{-2}$
Cathode active material mass loading	$14.7 \text{ mgcm}^{-2}$

chemistry data are published in [31]. The cells were assembled in a dry room with a dew point below  $-40^\circ\text{C}$ .

### 2.2. Cell formation process

The cells were filled with 8 g electrolyte and sealed under vacuum. After a total soaking time of 3 h the cells were pre-charged with a current of 0.2 A for 3.5 h in a climate chamber at  $23^\circ\text{C}$  ( $\pm 3^\circ\text{C}$ ), using a BaSyTec XCTS cell tester. For homogeneous electrolyte wetting, the cells rested alternately at  $23^\circ\text{C}$  and  $45^\circ\text{C}$  for 3 days. The successive conditioning phase includes the first charge/discharge cycle (2.7–4.2 V) of the cells. Subsequently, all cells were charged to a defined SOC and stored for 7 days for self-discharge determination. Finally, a cell characterization was performed including two full charge/discharge regimes at 0.5C and a pulse-power test for the determination of the internal resistance in charge and discharge direction, using a current of 2 A. To investigate the influence of the CV charging step during the formation process, three cells were processed with the standard protocol which includes a CV charging step (CC-CV charged cells) during the charge cycle. Another three cells were cycled without CV charging step (CC charged cells). Both formation protocols can be seen in Table 2. The process includes a conditioning phase where the cells are first fully charged to 4.2 V and discharged to 2.7 V with 0.5C. During the formation process and the testing, the pouch cells were compressed with a mechanical pressure of 0.5 MPa by using a jig. This compression prevents layer delamination and optimizes the cell performance.

The ICL during the first cycle is calculated based on the charge capacity during pre-charging and conditioning  $C_C$  and the discharge capacity  $C_D$  of the cells (see Eq. (2.1)).

$$ICL = \frac{C_C - C_D}{C_C} \quad (2.1)$$

The internal resistance is determined by a current pulse test during the cell characterization. Therefore, a discharge pulse with 1C at a defined cell potential of 3.7016 V after a rest-time of 2 h is applied. To calculate the internal resistance  $R_i$ , the open circuit voltage prior to the pulse  $U_{0s}$  as well as the voltage after 10 s of the pulse  $U_{10s}$  together with the absolute value of the pulse current  $I_p$  were used (see Eq. (2.2)).

$$R_i = \frac{U_{10s} - U_{0s}}{|I_p|} \quad (2.2)$$

### 2.3. Cyclic aging

To evaluate the cell quality, the test cells were aged during 500 cycles with 2C between 2.7 V and 4.2 V including a CV charging step to C/20. After every 50th cycle a pulse power test with 1C in charge and discharge direction for internal resistance determination at a defined cell potential (CC-CV charging to 3.7 V) was performed. To compare the aging behavior of the test cells, the

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