

Impact of different aging mechanisms on the thickness change and the quick-charge capability of lithium-ion cells



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ABSTRACT

Different aging mechanisms occur in lithium-ion cells, such as calendar aging during storage, cycle aging while charging and discharging, and aging due to lithium plating caused by excessive charging currents. This work shows that the maximum permissible charging current depends on the aging type and aging degree of the lithium-ion cell and has to be considered accordingly. For this purpose, calendar aged, cycled aged and due to lithium plating aged cells were prepared and measured using the cell thickness method. Our results show that the charging current has to be reduced after calendar aging and aging due to lithium plating. For cycled aged cells it is even possible to increase the charging current. Finally, an in-situ analysis method for determining the aging type is developed, which is based on thickness and voltage change patterns that are typical for each aging type.

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1. Introduction

Lithium-ion batteries are becoming increasingly important for the use in electric cars or plug-in hybrids because of its high energy density. To improve the battery lifetime, it is important to investigate degradation effects in detail. Stress factors that influence the cell's lifetime have to be recognized and should be avoided.

In the literature two aging processes are distinguished. One effect is calendar aging, a worsening of the cell characteristics when the cell is stored especially at high temperatures. Side reactions of the electrodes with the electrolyte are the main reason for the loss of lithium ions [1–4]. Another effect is cycle aging, a worsening of the cell characteristics due to many charging and discharging cycles. The change of the graphite particle size during the cycles causes the particles to lose contact with the current collector. In addition to the mechanical damage, a new solid electrolyte interphase (SEI) is formed on the newly developed surfaces. The rebuilding of the SEI consumes lithium ions during its formation [5,2–4,6]. A further effect is lithium plating caused by excessive charging currents. This effect leads to an irreversible capacity loss. In this case, lithium ions are deposited as lithium metal on the graphite anode surface and can no longer take part in the charge transfer [7,8].

The degree of cell degeneration manifests itself by a change of capacity, inner resistance and the open circuit voltage. Dubarry et al. [9] and Dahn et al. [10] investigated degradation mechanisms by analyzing the cell voltage in detail. In addition the cell thickness change can be measured, which also allows a cell characterization [11].

This work analyzes the voltage and thickness change of lithium-ion cells after degradation by calendar aging, cycling processes and due to lithium plating. With regard to the various aging types, characteristics of the cell thickness change and voltage are presented, which allows the determination of the aging type. Furthermore, the maximum permissible charging current without the occurrence of lithium plating is determined for different aging types and degrees using the cell thickness method (cf. [12]).

2. Experimental

2.1. Measurement setup

For our tests we use one type of lithium-ion pouch cells with a graphite anode and a lithium-nickel-manganese-cobalt-oxide (NMC) cathode. Within the voltage range of 3 V up to 4.15 V the cell capacity is 22 Ah. All investigations are performed using a BaSyTec battery testing system. The cells are mounted on an aluminum ground plate using conductive adhesive for the thermal and mechanical connection. The cell thickness is measured with a dial indicator mounted on a shaft support (cf. Fig. 1). The resolution

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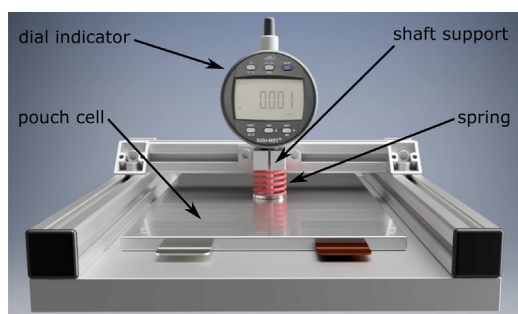


Fig. 1. Setup for the measurement of the cell thickness change similar to Ref. [12,11].

limit of the dial indicator is $1\mu\text{m}$ which is sufficient for our investigations. To prevent the possible influence of gas formation, a spring presses the cell surface around the measurement spot. During the measurement, the entire setup is located in a climate chamber to ensure a constant temperature.

2.2. Cell aging procedure

To carry out tests on aged cells and compare the different aging types, new cells are submitted to calendar aging, cycled aging and lithium plating in steps of 5% capacity loss until the end of life (EOL) criterion (80% remaining cell capacity). For each aging type, we obtain four cells with 95%, 90%, 85% and 80% remaining cell capacity.

For calendar aging the cells are stored at a voltage of 4.15 V and a temperature of 60°C . The calendar aging follows the Arrhenius Law and proceeds faster at high temperature and high state of charge (SOC) [13]. The cell capacity is determined at regular intervals and compared with the initial cell capacity.

The cycle aging is performed at a temperature of 25°C . At this temperature high charging and discharging currents are permitted and there is little calendar aging. The charging currents are 15 A ($\approx 3/4C$) to prevent lithium plating and the discharging currents are 25 A ($\approx 5/4C$). Between charging and discharging there is a relaxation time of 30 min. The remaining cell capacity is checked at regular intervals.

For the aging due to lithium plating, the cells are charged at a temperature of 0°C applying a high current so that the required aging is achieved in a few cycles. Through this treatment, lithium plating is uniform on the anode surface according to Uhlmann et al. [8] who reports a homogeneous morphology of lithium plating.

2.3. Measurement plan

At a temperature of 25°C the aged cells are charged and discharged with a current of 0.5 A ($\approx C/40$) in the voltage range of 3 V up to 4.15 V. For each cell, the voltage and thickness curves are monitored depending on the aging type and aging degree. The voltage and thickness curves without aging are shown in Fig. 2. It is similar for all cells used at their begin of life. Since the cathode potential is stepless and almost linear [14], the kinks in the voltage curve can be assigned to the graphite anode. The same is true for the thickness curve. Its behavior can be attributed to the anode which exhibits certain changes in the graphite intercalation compound as a function of the state of charge [15–18,11]. The NMC cathode is volumetrically stable up to 4.15 V vs. Li/Li⁺ and its thickness variation is thus negligible [19].

On the basis of the derivatives, the position of the kinks can be determined more accurately, for instance the voltage bend as

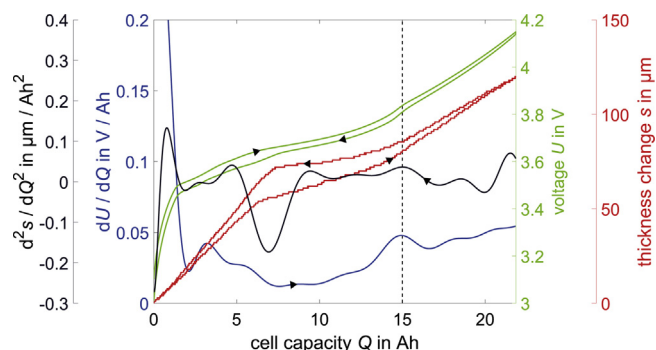


Fig. 2. Voltage and thickness change of a cell without aging while charging and discharging with a current of 0.5 A ($\approx C/40$) and their respective derivatives.

described in Ref. [15,20] at 50% anode SOC. For our cell this corresponds to 15 Ah. The derivative of the thickness change shows a local maximum at this state of charge, too.

In another experiment the maximum permissible charging current is determined for all aged cells at a temperature of 0°C . For this purpose, a constant charging current of 0.5 A up to 4.15 V without a constant voltage phase is used and the charging current is increased by 0.5 A with each additional cycle, until the maximum permissible charging current without lithium plating is found. To detect the first occurrence of lithium plating, we use the cell thickness method described by Bitzer et al. [12] applied in our previous work [21]. This method takes advantage of the fact that the lithium ions, which are deposited as lithium metal on the graphite anode, require more volume than ions intercalated into the graphite anode. The additional thickness increase is detectable with the measurement setup.

3. Results and discussion

3.1. Cell voltage

The voltage graphs and their derivatives are shown in Fig. 3 after calendar aging (a), cycle aging (b) and aging due to lithium plating (c) normalized to the remaining cell capacity. For the reference we use a fresh cell.

In Fig. 3a the derivative of the voltage hardly changes during calendar aging except for the cell with 80% remaining cell capacity which shows deviations in the derivative of the voltage. The voltage kink at 50% anode SOC is visible for all cells at the same position with exception of the 80% aged cell. Because of the normalized presentation this means that the loss of lithium ions and the degradation of the cathode is similar to the loss of active anode material. For the 80% aged cell, the local maximum at 70% shifts to the right which implies a greater loss of active cathode material than active anode material (cf. Ref. [9]). Compared to the other curves, the peaks are smeared out which is a sign of greater inhomogeneity in the anode.

The derivative of the voltage curve for cycle aging shows smoother curves as aging proceeds. At a remaining cell capacity of approx. 80% the peaks of the derivative have almost vanished. This may result from the mechanical load during cycle aging, which has caused the anode material to fracture. The fractured anode material may lead to areas with slightly different SOC's even for low currents that result in a mixed potential. For aged cells it is difficult to determine the exact positions of the minima and maxima in the derivative. However, a minimum at approx. 35% cell SOC is achieved by all aging degrees. This implies that the loss of active anode material is almost equal to the loss of active cathode material.

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