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Temperature dependency of state of charge inhomogeneities and their equalization in cylindrical lithium-ion cells

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HIGHLIGHTS

- Modification of commercial cylindrical cells for individual access to electrode tabs.
- Measurement of local potentials under various discharge conditions.
- Effect of temperature and current rate on local state of charge distribution.
- Analysis of equalization process of local state of charge inhomogeneities.

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ABSTRACT

The influence of cell temperature on the current density distribution and accompanying inhomogeneities in state of charge (SOC) during cycling is analyzed in this work. To allow for a detailed insight in the electrochemical behavior of the cell, commercially available 26650 cells were modified to allow for measuring local potentials at four different, nearly equidistant positions along the electrodes. As a follow-up to our previous work investigating local potentials within a cell, we apply this method for studying SOC deviations and their sensitivity to cell temperature. The local potential distribution was studied during constant current discharge operations for various current rates and discharge pulses in order to evoke local inhomogeneities for temperatures ranging from 10 °C to 40 °C. Differences in local potentials were considered for estimating local SOC variations within the electrodes. It could be observed that even low currents such as 0.1C can lead to significant inhomogeneities, whereas a higher cell temperature generally results in more pronounced inhomogeneities. A rapid SOC equilibration can be observed if the variation in the SOC distribution corresponds to a considerable potential difference defined by the open circuit voltage of either the positive or negative electrode. With increasing temperature, accelerated equalization effects can be observed.

1. Introduction

The steady increase in energy and power density combined with continuous improvements regarding cycle life and safety extended the application field of lithium-ion batteries (LIB) from consumer electronics towards hybrid and full electric vehicles. To deliver the necessary amount of energy, the packing density in already available cells has been significantly increased [1] and larger cells with advantages regarding energy density have been introduced.

Finding the right operation condition for the usage and charging of the battery is a crucial requirement for a long cycle life and a safe operation [2]. Low temperatures decrease the performance of the cell [3] and improve the risk of lithium deposition on the anode during the charging process [4]. On the contrary, high temperatures foster unwanted side reaction, increasing the thickness of solid electrolyte interphase (SEI) and causing a loss in the capacity and power capability of the cell [5,6]. Variations in the current density distribution in the cell lead to additional heat generation [7–9] and consequently to uneven aging effects throughout the cell [10].

A cell design, which assures uniform utilization of the electrodes, is desirable for any battery. But in terms of cost savings and

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weight reduction, only few tabs are used within considerably long electrode wraps with a length up to meters. This can lead to a restricted representation of the electrodes' behavior at the cell's terminal. To define the optimal operating conditions of the cell, detailed knowledge of the effects leading to state of charge (SOC) and state of health (SOH) inhomogeneities in the cell is necessary.

Studies on the impact of current and temperature on inhomogeneities in the current density during cycling have been performed by Zhang and co-workers using a custom made cell with ten individually accessible positive electrode layers and a single negative electrode. With this approach, they can resolve the current density distribution between several compartments of the cell and measure them directly by additional shunt resistors. Neglecting inhomogeneities arising from the manual production process, this method gives deep insights into the current density distribution within a cell. They studied C-rates ranging from C/5 up to 4C [11], also using different tab patterns [12]. Similar to the setup presented here, a LFP/graphite chemistry is investigated with an electrode thickness of about 65 μm for LFP and about 40 μm for graphite. In sum, their cell exhibits a length of 1.8 m, which is in accordance with our experimental setup (approx. 1.6 m). They reported significant SOC variations during discharge up to 20% at the end of a 2C discharge operation at 21 °C. Further, they highlighted balancing currents occurring during relaxation periods. In their work they refer to a submitted paper for an analysis of the relaxation currents, which we were not able to find. Although the setup presented here is not capable of measuring currents directly, the local potentials can be used as an indicator for a current and SOC distribution. As a subsequent step to previous studies, recent results regarding the SOC variations within a cell due to dynamic current pulses as well as varying ambient temperatures are presented in this work by investigating local potentials in modified commercial cells.

In our previous study, the modification process and the long-term performance of the investigated cell has been presented [13]. In combination with a detailed multi-dimensional physico-chemical model, the inner states such as lithium concentration and heat generation were simulated, matching the experimental results accurately [14]. Furthermore, it has been shown that the current density distribution under alternating current (ac) conditions shows a high temperature dependency accompanied with an observed strong attenuation along the current collectors [15].

This work will focus on the impact of different operating temperatures on the cell's electrical and electrochemical performance and their effect on local SOC inhomogeneities during static and dynamic load profiles. Both the development of SOC inhomogeneities and the accompanied equilibration processes after switching off the current are investigated by the means of local potential measurements.

2. Experimental work

The cell used in this work is a commercial 26650 cylindrical $LiFePO_4$/graphite cell with a nominal capacity of 2.5Ah. In its original state, the cell exhibits four negative and four positive internal current tabs, which are spot welded to the respective cell terminal. Opening the cell as exemplarily illustrated in Fig. 1 a) and b) for the cathode side allowed the separation of these tabs during the modification process and made each current tab accessible individually. The modification process and cell parameters have been published in our previous work in more detail [13]. It has been demonstrated, that the modification process has negligible impact on the electrochemical performance of the cell during measurement in both time [13] and frequency domain [15]. The almost equidistant position of the current tabs as shown in Fig. 1 c) allows for a symmetric operation of the cell. A current terminal T_{mn} with the respective terminal voltage U_{Tmn} is defined by one current tab of the anode (A_m) and one of the cathode (C_n) with $m,n \in \{1;4\}$. As cylindrical cells are used, the two outermost current tabs C_1 and A_1 are defined as terminal T_{11} and the two innermost tabs C_4 and A_4 are defined as terminal T_{44}, as illustrated schematically in Fig. 1 c).

In the first set of experiments, the focus is laid on the variation of current density distribution for 0.1, 0.5, 1, and 2C discharge rates and the impact of different ambient temperatures (10, 20, 30, and 40 °C) prevailing during operation. The cell temperature was controlled by a Memmert IPP200 incubator. To monitor the heat generation during cycling, an external as well as an internal T-type thermocouple was attached to and placed inside the cell center, respectively. Table 1 gives an overview of the applied measurement sequence. Prior to the measurement, the climate chamber temperature was adjusted and the cell was placed inside for 2 h to equilibrate. A BaSyTec CTS system was used for cycling. For charging the cell between each discharge step, the tab configuration was switched to $A_2\&A_4$ and $C_1\&C_3$ and a constant current constant voltage (CCCV) charging protocol with $I_{charge} = 0.2C$ and $U_{cutoff} = 3.6V$ was applied. The asymmetrical tab combination, accessing two cathode and two anode tabs together with the applied CV phase was regarded to guarantee a homogeneous SOC distribution after the charging step; a crucial prerequisite for the subsequent measurements. The charging step was followed by a relaxation phase of 30 min to allow for the equilibration of possible temperature and concentration gradients across the electrodes. To discharge the cell, only terminal T_{11} (A_1-C_1) was used and currents of 0.1, 0.5, 1, and 2C were applied to this terminal configuration. In addition to the BaSyTec battery tester, an Agilent 34972 with a 20 channel multiplexer was used for supplementary voltage measurements at the terminals T_{22}, T_{33}, and T_{44} during the discharge process. It is worth mentioning that all charge processes have not been performed at the same temperature. Instead, the charge temperature was the same as the discharge temperature. Despite the different temperatures, the high power capability of the cell as well as the slow charging current resulted in only negligibly small capacity differences during the charge processes at 10 and 40 °C.

In the second set of experiments, the equilibration processes along the electrode and their temperature dependency are investigated. The applied measurement sequence is described in Table 2. The cell was again fully charged following the same CCCV protocol and tab configuration as described followed by a consecutive stepwise discharge by means of and intermittent 1C current rate, applied at terminal T_{11}. The discharge pulses of 1C for 3 min resulted in a SOC change of approximately 5% and, hence, 20 discharge-relaxation steps were conducted until the cell was fully discharged. Between each discharge step, a relaxation period of 150 min was included to examine the transient voltage evolution at the four different positions along the electrodes. At the end of the 40 h measurement sequence, the temperature was adjusted and the cell was recharged. In accordance with the continuous discharge current measurements (sequence #1) the intermittent discharge current measurements (sequence #2) were carried out for 10, 20, 30, and 40 °C.

3. Results and discussion

3.1. Current density distribution

As described in the previous section, the cell was discharged by applying current to terminal T_{11} (A_1-C_1) only. The voltage was measured at the current-carrying terminal and at three additional equidistant positions along the electrode. Fig. 2 exemplarily shows the discharge voltage of the cell for 0.1C at 10 °C and 40 °C. To accentuate the four different potential curves, the discharge profile