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New method evaluating currents keeping the voltage constant for fast and highly resolved measurement of Arrhenius relation and capacity fade

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HIGHLIGHTS

- Floating currents correlate to capacity loss rate.
- Enables fast and high resolution Arrhenius plot.
- Different dominating aging mechanism <45 °C and >50 °C.
- Resistance and reversible effects are separable from capacity fade.

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ABSTRACT

The evaluation of floating currents is a powerful method to characterize capacity fade induced by calendaric aging and enables a highly resolved representation of the Arrhenius relation. The test arrangement is simple and could constitute a cheap alternative to state-of-the-art calendaric aging tests including check-up tests. Therefore the currents to maintain a constant voltage are evaluated. This method is validated by analyzing nine cylindrical 8 Ah $LiFePO_4$|Graphite battery cells during calendaric aging at 25 °C, 40 °C and 60 °C at 3.6 V (100% SOC). The 3.6 V are kept by applying constant voltage while the floating currents are logged. The floating currents correlate with the rate of capacity loss measured during capacity tests. The floating currents reveal to be rather constant at 25 °C, linearly increasing at 40 °C and decreasing from a higher level at 60 °C. Additional tests with three test cells, with the temperature rising from 40 to 60 °C in steps of 5 K, exhibit non-constant currents starting from 50 °C on with high variations amongst the tested cells. Once stored above 50 °C, the cells exhibit increased floating currents compared to the measurement at the same temperature before exceeding 50 °C.

1. Introduction

Lithium-ion batteries are usually examined by means of cyclic aging or calendaric aging tests. The boundary conditions for calendaric aging are defined by the state-of-charge (SOC) or by the voltage of the cell and the ambient temperature [1,2]. Generally these factors are kept constant to be able to clearly determine if aging is caused by the SOC or by cell voltage and temperature.

The question whether the aging is path-invariant or not is hardly addressed in literature, where test conditions such as SOC and temperature are interchanged [2,3]. The answer to this question is quite useful to know, as the modeling of path-invariant aging can be implemented in a rate-based way. This is by far easier than if there is a path dependency with respect to temperature or SOC, where the aging rates depend on the cells' prehistory.

Abbreviations: FCE, full cycle equivalents; EC, ethylene carbonate; DMC, dimethylene carbonate; EMC, ethylene-methylene carbonate; DEC, diethylene carbonate; LFP, lithium iron phosphate; SEI, solid electrolyte interphase; DOD, depth-of-discharge; SOC, state-of-charge.

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Furthermore there are two strategies to keep the SOC or voltage constant. Mostly the cells are just charged or discharged to a certain voltage level or SOC and then stored at a specific temperature (storage test) [4]. Sometimes they are floated, which means that the voltage is kept by a charger at a constant voltage level (float test) [1,5]. Float tests maintain a constant SOC recharging the battery and compensating self-discharge effects and side reactions [6]. During storage tests the cell voltage may decrease because of these processes, wherefore the aging tests will take place with a successively lower lithiated anode. The influence of floating the cell vs. open circuit storage tests is not clearly discussed in literature. Käbitz et al. [2] report that keeping the cell at constant voltage compared to open circuit voltage leads to a measureable difference only at 100% SOC as the aging rates at lower SOC do hardly differ. Nevertheless the floating current to keep the voltage is not or scarcely measured or evaluated. One example is the work of Zeng et al. [7], where the floating currents are evaluated at extremely high potentials of 4.5 V for a $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ cathode to measure the parasitic reactions at 30 °C ambient temperature.

The calendaric aging for lithium-ion batteries is described in literature to be strongly depending on the active material of the cathode and the anode, the coating quality, the electrolyte solvent, conductive salts, additives and any impurities as reported by Vetter et al. [8]. Thus calendaric aging tests on isolated components like the electrolyte are hardly sufficient to understand a complete cell arrangement and its aging. Commonly the calendaric aging of battery cells is characterized by capacity loss according to loss of active lithium and increase of internal resistance due to increasing solid-electrolyte-interphase (SEI) [9]. However, performing periodic check-ups including e.g. capacity and pulse tests converts any calendaric aging test to some extent into a cycle test. Therefore the check-up frequency has to be a compromise between time resolution and minimizing the checkup influence by extending the time in between the check-ups. Also a moderate temperature and a sufficiently low C-rate should be chosen for these tests to ensure that check-ups will most probably not contribute to aging.

It is challenging to compare calendaric aging tests from different publications if they are executed under different check-up conditions. Check-up tests can be influenced by reversible capacity effects like self-discharge [8] or compensation currents [6] that might be influenced by check-up frequency, C-rate and temperature. These reversible capacity effects are not easily separable by standard capacity tests.

Within this publication, a tool to measure floating currents is presented that in a steady state will solely return the pure loss of charge that is strongly correlated to loss of capacity or loss of active lithium respectively. Thus the capacity loss, the internal resistance and any reversible capacity effect can be separated. The reversible capacity effects can be observed in the transient effect at the beginning of the floating test before a steady state is reached. This part gives information about reversible capacity effects like the passive electrode effect presented in our previous publication [10]. Finally the floating currents are a good measurand to check the Arrhenius behavior as will be shown later.

2. Experimental

In the calendaric aging tests cylindrical 8 Ah cells with lithium iron phosphate (LFP) on the cathode side, graphite on the anode side and (EC-DMC-DEC-EMC)-$LiPF_6$ electrolyte were employed. They belong to a larger test set published before [10].

The cells are stored at three temperatures 25 °C, 40 °C and 60 °C and at a cell potential of 3.6 V, which corresponds to about 100% SOC. For each test condition, three cells are included. The accuracy of the temperature over time of the 110 l Memmert oven is ± 0.2 K for all tests, measured with a temperature sensor positioned on the case of each cell.

The voltage is kept at 3.6 V ± 2.5 mV by constant voltage charging utilizing a self-constructed battery floater that enables temperature measurement on the cell case (sensor type: DS18B20; precision: ±0.5 K), measurement and adjustment of the applied cell voltage, and a charging current source including high-precision measurement. This device will be referred to as 'floater' or 'floater unit' in the following. A picture of the floater device is shown in Fig. 1 a. One box includes two independent floater units and is able to connect two temperature sensors to capture the surface temperature of the battery. The costs for such a prototype are in the order of 100 € including two floater units.

Fig. 1 b shows the principle schematic of the floater hardware. The battery is contacted with a four point connection to the floater. A high precision amplifier (AD8220) is used to measure the battery voltage. To keep the battery voltage constant at 3.6 V, a PI control loop with a large time constant is used. First of all, the measured battery voltage is stored in our logging system, so it is available for evaluation (not depict). Secondly, this voltage is the negative input of the battery sourcing amplifier (OPA551); the positive input is connected to a high-precision reference voltage, which is adjustable by a precision potentiometer. This is used to control both the battery voltage and the float voltage. The battery current or floating current is captured by means of a high-accuracy battery fuel gauge (DS2756). The resolution of the measured current value amounts to 15 bit (one direction) and is averaged over 4096 values over 2.8 s. The maximum offset value is denoted as ± 7.8125 $\mu V \cdot \Omega^{-1}$ and the current gain error as 1% of the actual value. The current is captured by a shunt resistor with a value of 1 Ω and an accuracy of 1%. The shunt resistor's temperature dependency is neglected. All in all, after an offset calibration, the floater unit is capable to measure float currents with a precision of 2% for currents greater than 100 μA and with a maximum deviation of 1 μA for currents smaller than 100 μA.

To validate the precision of the floater, a reference measurement was accomplished. By this, instead of a battery, the currents over three simple resistors (18 kΩ, 39 kΩ and 220 kΩ) are measured with the floater unit and compared with the results of an Agilent 34401A 6.5 digits' multimeter with a specified precision of 2 μA. Table 1 depicts the measured currents for a representative floater $I_{(Floater)}$ and a reference multimeter $I_{(Agilent)}$.

With the stated resolution of the test setup, Table 1 shows a good accordance with the stated floater's precision. The floating currents' offset is corrected by measuring the current value in the unplugged state during the check-ups.

The floating currents necessary to maintain 3.6 V during aging are measured for each cell. Due to data logger problems no data between about day 300 and day 700 of the storage tests at 25 °C and 40 °C were recorded. However, as the trend of the floating currents follows a linear-like behavior, these tests may be simply interpolated, which will be described later in this publication.

The floating is interrupted for check-up tests after initially 14 days, and the period is reduced for slow aging conditions during testing time. At each check-up, a capacity test at 1 C and 0.25 C and a pulse test were performed.

The capacity test is executed in a temperature chamber (Binder MK53) at 25 °C with a variation of ± 2 K using a Digatron MCFT 20-05-50ME test station with a precision of 0.1% of the current measurement. During the capacity test the discharged cells are charged with 1 C (8 A) up to 3.65 V, followed by constant-voltage charging down to I < 0.05 C (maximum 2 h). Afterwards the cells rest for 30 min before they are discharged with 1 C (8 A) until the cut-off voltage of 2.0 V is reached. The determination of the capacity test with 0.25 C (2 A) is performed analogously.