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Ageing of lithium-ion battery modules with dissipative balancing compared with single-cell ageing

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ABSTRACT

In contrast to numerous published lithium-ion cell ageing investigations, reports regarding the ageing behaviour of entire modules are scarce. This study compares the ageing behaviour of lithium-ion battery modules with the one of single cells. A capacity-based cell matching procedure is performed to minimise the capacity spread among the blocks of constructed modules. So, the newly introduced state of inhomogeneity (regarding capacity and resistance) is reduced up to 10%, but, however, also observed to increase rather linearly over the modules' lifetime. The balancing behaviour of the battery management system stays unaffected of this increased inhomogeneity.

To gain a deeper insight into the ageing behaviour of multi-cell batteries, the modules are disassembled and analysed in terms of local temperature distribution and cell-to-cell variation. After 1200 equivalent full cycles, the modules show an overall module capacity loss which is about 12%. Thereby, the module ageing study reveals a capacity fade which is even approximately 2% lower compared with the one of single cells. The state of inhomogeneity for capacity of high quality lithium-ion cells after 1200 equivalent full cycles is still smaller than 1%.

1. Introduction

Till today, lithium-ion batteries are mainly deployed in mobile devices such as cell phones and laptops [1]. However, recent and future areas of application, such as electromobility and stationary energy storage, will increase their demand [2]. Regarding the avoidance of greenhouse gases, a global market introduction of battery electric vehicles (BEV) in combination with an increased share of regenerative energies in the grid is considered to be inevitable. However, less than 2% of the newly registered cars in Germany in 2013 were pure or hybrid electric [3]. One of the reasons for the low percentage of product acceptance is the high cost of BEV, which is mainly because of the expenses associated with the battery storage system. In general, a substantial investment in BEV, grid storage projects and other large-scale applications must be ascribed to battery packs over their life-time. As the costs are depreciated over multiple years, long-term costs and return projections are needed to evaluate the profitability of the used battery packs. Therefore, an uncertainty exists owing to the ageing behaviour of lithium-ion battery packs, which complicates the economic evaluation. Consequently, a profound understanding of the ageing behaviour of lithium-ion cells, modules and packs is mandatory.

Numerous studies on the ageing behaviour of lithium-ion batteries at the cell level have been presented in past and recent publications [4–16], in contrast to investigations at the battery pack or at the module level. The consequences of ageing generally result in a loss of capacity and increase of impedance, with the latter resulting in a loss of power capability [17]. The main reasons for ageing can generally be subdivided into three main groups, which include the loss of active lithium, the degradation of electrode materials and deteriorated ionic kinetics [4]. Among the numerous ageing mechanisms of lithium-ion cells, the formation and evolution of passive layers at the interfaces of electrodes and the electrolyte take on a key role. The layer at the anode is usually referred to as the solid electrolyte interphase (SEI), and the one at the cathode as the solid permeable interphase (SPI) [18]. The name of the SPI is derived from its only partly passivating nature, in contrast to the SEI, which ideally inhibits any decomposition of the electrolyte after formation [19–21]. In both cases, the passive layers grow in thickness over their life-time, especially at a high state of charge (SOC) and high temperatures [22–24]. As the formation and evolution of these layers results in reduced capacity because of the consumption of active lithium accompanied by an increase of impedance, long operation periods at high SOC and

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temperatures should generally be avoided for lithium-ion cells [23,25–28]. For a more comprehensive description of the various ageing mechanisms of lithium-ion cells, such as lithium plating or the effects of volumetric changes of active materials, the reader is referred to [16,22,25,29,30].

Apart from the works describing the ageing behaviour or mechanisms of lithium-ion cells, statistical investigations conclude that variations in the initial lithium-ion cell-to-cell parameters (e.g. capacity and impedance parts) will increase with the progress of ageing, even for cells cycled in the laboratory under controlled ambient conditions [31–35]. Cell-to-cell (or lot-to-lot) variations in the new state must be ascribed to the production process, wherein variations in the manufacturing process parameters may occur [36,37]. Manufacturing costs are reported to rise excessively with a comparably low improvement of cell performance when trying to reduce process parameter tolerances such as the mixing or thickness tolerance compared with common rejection criteria [36]. In contrast to these intrinsic causes of cell parameter variations, mainly extrinsic causes are assumed to be responsible for an increase in the parameter spread with the progress of ageing in multi-cell battery units (e.g. parallel blocks, modules and packs). Such extrinsic causes include temperature gradients in the battery pack or deviations in the conductor resistances, cell contact resistances and also their type of interconnection [38,39]. Cells that are connected in series are loaded with the same current but can be operated within different voltage swings because the weakest cell always determines the performance of the entire string [40]. In contrast, differences in the cell resistances in parallel connected cells cause an uneven current distribution, which in turn results in SOC drifts [41]. As the SOC influences the open-circuit voltage (OCV), these drifts automatically equalise at pause periods. In summary, during ageing, lithium-ion cell-to-cell parameter variations increase in the field because of the aforementioned extrinsic reasons, whereby a link to initial cell-to-cell variations in the new state because of production tolerances should additionally be assumed [35].

For cells which are interconnected in multi-cell battery units, it is questionable whether this increasing spread of cell characteristics accelerates the ageing behaviour compared with that of single cells. For example, a 20% mismatch in the ohmic resistance of two $LiFePO_4$ (LFP)-based cells connected in parallel led to a lifetime reduction by 40% when compared with an optimally matched compound [41]. However, the ageing behaviour of these parallel compounds was not compared with that of single cells. In addition, most of the ageing experiments in the laboratory are only performed with single lithium-ion cells because multi-cell battery unit investigations result in a higher complexity and higher measurement equipment requirements.

Therefore, this publication aims to compare the ageing behaviour of modules with that of single cells and evaluates present challenges in a module ageing study. So, temperature influences, influences of contact resistances and the resulting impact on cell balancing are examined. For this purpose, two modules consisting of 112 lithium-ion cells each were constructed. The ageing behaviour of the modules during more than one year of cycling is compared with the results of an ageing study at the cell level. Both studies use similar load profiles (i.e. for an electromobility application) and ageing diagnosis methods to provide a good comparability of the results.

2. Experimental

2.1. Methods used for ageing diagnosis

A check-up routine was used to track the degradation of the lithium-ion battery cells and modules. This routine consisted of capacity and resistance measurements. At the module level, the spread among cell blocks (group of 14 cells in parallel) was also evaluated by a newly introduced parameter which is the state of inhomogeneity (SOI).

2.1.1. Capacity measurement

The check-up routine measured capacities under similar conditions. At 25 °C, the cells were completely charged with a constant current of 0.7 A (approximately 0.25 C) and a constant voltage of 4.2 V, until the current dropped below 0.1 A (constant current, constant voltage (CCCV) charging). After that, the cells were discharged with a constant current of 3 A (approximately 1 C) to 2.5 V, followed by a constant voltage period with a cut-off current of 0.1 A (CCCV discharging). An additional constant voltage discharge period was used to reduce the impacts of the cell impedance and the cell temperature on the measurement of the actual capacity. For the measurements obtained at the module level, the voltage limits were multiplied by the amount of cells connected in series. The charge and discharge currents were multiplied by the amount of cells connected in parallel.

2.1.2. Resistance measurement

After the capacity measurement, the check-up routine charged the cells and modules to 50% of their measured capacity. At this SOC, the internal resistance $R_{ac,1\ kHz}$ was determined to monitor the changes in cell impedance. This value represents the real part of the cell impedance at 1 kHz and is determined by an excitation of the cells or modules with a sinusoidal current. For the battery modules, the resistance was measured with an impedance measurement device (HIOKI BT3562), which directly measured the resistance at 1 kHz. For single cells, an electrochemical impedance spectroscopy (EIS) measurement from 10 kHz to 10 mHz was performed and the $R_{ac,1\ kHz}$ value was extracted from the resulting data. A Gamry G750 potentiostat was used to obtain EIS measurement. Unless otherwise defined, the definition of "resistance" in this study always refers to the value of $R_{ac,1\ kHz}$.

2.1.3. State of inhomogeneity

To identify the increasing inhomogeneity between the cells within each module during the progress of ageing, a new state referred to as SOI was defined. The SOI reveals the spread between the maximum and minimum value of a battery parameter in percent:

$$SOI_X = \frac{X_{max} - X_{min}}{X_{max}}, \quad (1)$$

where X can refer to the capacity, ohmic resistance or temperature. The concept of the SOI can also be transferred to other parameters and used both for single cells and modules.

2.2. Introduction of examined cells

To obtain representative results for battery ageing in BEVs, lithium-ion cells with typical characteristics for electromobility were required for this ageing study. As the range of electric vehicles is substantially determined by the energy content of the traction battery, these batteries usually comprise high-energy lithium-ion cells. Moreover, the traction battery has to provide sufficient peak power for accelerating the vehicle. To meet these requirements, Panasonic NCR18650PD nickel–cobalt–aluminium (NCA) cells with a nominal capacity of 2.8 Ah were used in the study. They feature a high specific energy of 214 w h kg^{-1}, a high energy density of 577 w h l^{-1} and a low internal resistance of approximately 20 mΩ [42]. The operating voltage range of these cells ranges from 2.5 V to 4.2 V. To compare battery ageing at the