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Measurements of ageing and thermal conductivity in a secondary NMC-hard carbon Li-ion battery and the impact on internal temperature profiles

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ABSTRACT

The ageing of 75 commercial Li-ion secondary batteries with $LiNiMnCoO_2$| hard carbon chemistry was studied up to 4 years. The nominal capacity was 17.5 Ah. The batteries were cycled at different current rates and between different states of charge. Shelf studies were carried out at different temperatures and at different states of charge. The ageing temperature varied from 18-55 °C. The specific ohmic resistance was obtained as a function of state of health, ageing temperature, and ageing time. We found that the cell tolerated less cycles at higher temperatures. The loss of capacity also increased for storage at higher temperatures, in a predictable manner. We observed that the state of charge at the moment of storage was very important for the loss of discharge capacity. Thermal conductivities of pristine and aged electrodes were measured in the presence and absence of electrolyte solvent and under different compaction pressures. The thermal conductivity was found to range from 0.14–0.41 $WK^{-1}m^{-1}$ for dry electrode active material and from 0.52–0.73 $WK^{-1}m^{-1}$ for electrolyte solvent-soaked electrode active material. The thermal conductivity of the electrode materials did not change significantly with ageing, but a strong correlation was seen between remaining battery capacity and increasing ohmic resistance. To assess the impact of these changes, the measured results were used in a one-dimensional model to compute the battery internal temperature. Temperature profiles were computed as a function of discharging rate (2C - 10C) and ageing time (0 - 4 years). The model showed that the internal temperature can raise by a factor about 2.5 during ageing from the pristine state of health at 100 % to 58 % capacity.

1. Introduction

The need to store energy for transportation make large-sized Li-ion secondary batteries (LIBs) attractive for use in electrical and hybrid electrical vehicles. This is because of their high energy density availability, their zero emission characteristic during operation and their rather low carbon footprint [1,2]. The most important limitation of electrical vehicles compared to gasoline driven vehicles, is their ability to store energy, as measured by the specific battery energy [3]. Materials with higher energy densities are therefore researched. But also more efficient operation of current batteries will be beneficial; *i.e.* charging at higher current densities. To achieve better operating conditions, require fundamental understanding of heat production and heat transfer within the battery, however.

Bandhauer et al. [4] gave a detailed review about thermal issues in Li-ion batteries, especially of thermal effects due to capacity fade, power fade, and self discharge. In addition, they described heat generation mechanisms and demonstrated approaches of thermal modeling [4]. The fact that ageing mechanisms are much faster at elevated temperatures and dependent on the state of charge (SOC), is well reported in literature [5–7]. Broussely et al. [5] showed for a 45 Ah $LiNi_xCo_yAl_xO_2$ | graphite cell, that there is no significant energy fade at 20 °C at 100% SOC for 900 days of storage, while power faded by about 4% for storage at 40 °C at 100% SOC. A power fade of 4% was reached already after storing the battery about 90 days at 60 °C at 100% SOC. Vetter and co-workers [6] explained power fade mainly by impedance rise caused *e.g.* by decomposition of electrolyte and decrease of accessible surface area (growth of the solid electrolyte interface (SEI) on the anode). A

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relation between the thickness of the SEI and the internal resistance was reported by Waldmann et al. [8] for the commercial 18650-cell with a $Ni_{1/3}Mn_{1/3}Co_{1/3}O_2|Li_yMn_2O_4$ blend cathode | graphite chemistry. They observed an increase in the ohmic resistance by a factor of 1.4 from a pristine battery with a graphite electrode thickness of about 83 μm to an aged cell with a thickness of about 91 μm (due to SEI growth). More knowledge of ageing, *e.g.* for different cell chemistries, is therefore of great interest.

The most probable causes of ageing are the side reactions between the electrolyte and the active materials of the electrodes [9]. In addition, reaction products from the positive electrode might interact with the negative electrode or *vice versa* [9]. Since the reactions on the two electrodes are not independent from one another, one should consider an overall capacity degradation. Although ageing may be a more complex phenomenon, an overall degradation rate which fits the Arrhenius equation, has been used by many researchers [5,9–13].

Capacity reduction due to oxidation reactions on the positive and reduction reactions on the negative electrode can be reversible, if the reactions take place at the same time. In this case, the amount of lithium ions lost on the negative is re-inserted on the positive electrode. Such reversible capacity losses are known to be in the range of a few percent per month, depending on temperature, design and cell chemistry [9]. The capacity losses are reversible, because the lithium ions will be available again after the charging of the battery.

Irreversible capacity losses are mostly allocated to an irreversible, lithium-consuming reaction on the negative electrode. The ageing of carbonaceous negative electrodes as well as metal oxide positive electrodes has been described in detail by Vetter et al. [6]: The ageing of the negative electrode is mainly ascribed to changes of the electrode/electrolyte interface - the formation and growth of a solid electrolyte interface. Several processes occur at the positive side during ageing, for example degradation or changes of binder and conducting agents, corrosion of the current collector, and surface film formation due to oxidation of electrolyte. Ageing products from the positive electrode might interact with the negative electrode as well [6].

During fast charging, the key concerns for manufacturers are large temperature gradients, spatial non-uniformity of current [14], and Li-plating. Battery design can influence the current distribution, state of charge (SOC), temperature and voltage distribution [15]. This will influence the local degradation in different ways, because degradation is temperature-dependent. Therefore performance and cycle life do also depend on battery design [16,17]. As a result, knowledge of internal heat production and internal temperature profiles does not only give the ability to adjust a proper and possibly needed cooling system outside the battery. It will also improve the understanding of interplay of phenomena that lead to ageing. To control this interplay, can help enhance lifetime. Internal temperature profiles have thus been modeled and measured *in-situ* [18–21].

Large temperature gradients can be a result of reduced surface-volume ratio, the local heat generation rate in the battery, as well as of the low cross-plane thermal conductivity. Thus, for an exact description of internal temperature profiles, heat sources have to be determined as well as thermal conductivities of all battery components. Ohmic resistances are reported to change during ageing [22]. The thermal conductivity of the graphite electrode is also reported to change for different states of charge [23,24]. There are some reports on thermal conductivities of Li-ion secondary battery components [25], but they have not been thoroughly investigated [4] and included in a thermal model for battery heat productions. There is, to the best of our knowledge, no reports on the experimental determination of the cross-plane thermal conductivity of an electrolyte soaked separator. However, Vishwakarma and Jain found an in-plane thermal conductivity of $0.5 \pm 0.03\,WK^{-1}m^{-1}$ [26], using a transient DC heating method.

It is therefore the aim of this paper to report changes in ohmic resistances and thermal conductivities during ageing for a series of pristine and used battery components. We shall report ageing effects in terms of changes in internal ohmic resistance and loss of capacity. This will be done for battery calendar life and for battery cycle life at various temperatures. For calender life, we measure ageing from a particular state of charge when the battery is at a specific temperature. For cycle life, we measure ageing after the battery was exposed to discharge/charge cycles. We define the state of health (SOH) as the fraction of the available 1C-discharge capacity at a certain state of age for the pristine battery. The overall aim of the work is to give the impact of ageing on a one-dimensional temperature profile model of a pouch cell perpendicular to the plane of the electrodes for typical operating conditions of the battery.

2. Procedure

The battery was a commercial Li-ion pouch cell with a $LiNiMnCoO_2$ (NMC) - hard carbon chemistry. 100 % SOC was defined at 4.1 V and 0 % SOC was defined at 2.5 V. Hence, the upper voltage limit was chosen to be 0.1 V lower than the limit which is usually used for this chemistry. At these voltage limits, the nominal capacity of the battery was 17 Ah. (The rated battery capacity was 17.5Ah, but we operated it with a capacity range of 17Ah.) The pouch cell consisted of 24 alternating cathode and anode stackings. The entire battery had a lenght, width, and thickness close to 23, 15, and 0.5 cm, respectively, neglecting the battery housing.

2.1. Apparatus - ageing studies

The batteries were cycled with a PEC SBT-0550 battery tester. This tester has 24 channels for simultaneous cell testing and can test battery cells in the range of 0-5 V and 0-50 A. While being tested and characterized, the cells were placed in a vertical upright position in a custom-made battery cell rack. No mechanical pressure was applied to the pouch cells. The cells' fixture is reported in the appendix. This set-up ensured a similar temperature distribution around the battery cells. All life tests were performed in temperature rooms where the temperature was controlled within 0.1 °C. The cycle life tests were performed in temperature chambers from Termaks. These chambers were again placed inside a fire-protected and air-conditioned room ($\sim 6\,m^3$) within the battery test laboratory.

2.2. Experimental - ageing studies

In total 75 cells were chosen and ageing studies were carried out within an operating temperature range of 18 °C - 55 °C. The nominal rated currents were 17.5 A (1C-rate, 35.93 A/m^2) at discharge and charge. A constant current - and a current step-down charge was used. All cells were taken from the same production batch.

The cell life study encompassed a cycle life study and a calendar (shelf) life study at test conditions as described in subsections 2.2.1 and 2.2.2. All cells were characterised with a 2-cycle characterisation test at 25 ±1 °C. This characterisation test included measuring the 1C discharge capacity (Ah) for all cells at 25 °C. In addition a high power pulse test was performed to obtain the ohmic resistance and the overvoltage in the cell as function of state of charge. The characterisation routine was performed with a frequency of every 100–200 cycle or 30–90 days of storage time.