



Electrochemical characterization and post-mortem analysis of aged LiMn₂O₄–NMC/graphite lithium ion batteries part II: Calendar aging



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HIGHLIGHTS

- Comprehensive analysis of new and calendar aged cells by numerous methods.
- Application of the DRT to impedance spectra.
- Aged anodes show a reduced overall impedance.
- Dominant aging mechanisms have been clarified.

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ABSTRACT

A detailed post-mortem analysis was carried out for commercial lithium ion batteries stored at 4.2 V and 4.0 V at 60 °C. Complementary electrochemical and physical–analytical investigations revealed that the most significant aging processes for the cells aged at 4.2 V were loss of cycleable lithium, decomposition of the electrolyte and loss of active cathode material (LiMn₂O₄/Li(Ni_{0.5}Mn_{0.3}Co_{0.2})O₂). The cells aged at 4.0 V also exhibited loss of cycleable lithium, but at a smaller extent. In fact, the aged anodes did not show significant changes compared to the new anode.

Electrochemical impedance measurements including symmetric laboratory test cells gained from new and aged cells revealed valuable information about changing charge-transfer processes. The 4.2 V-cathode and both aged anodes surprisingly exhibited a decreased charge-transfer resistance, while the 4.0 V-cathode's charge-transfer resistance increased.

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1. Introduction

High power and energy density of lithium ion batteries made them one of the most attractive energy storage systems. Nowadays they are widely used in portable electronic devices like laptops, cameras and mobile phones. In the past few years lithium ion batteries have drawn much attention for their operation in automotive applications like hybrid vehicles (HEV), plug-in hybrid electric vehicles (PHEV) and full electric vehicles (EV). These applications require long cycle and calendar life, typically up to 15 years, low cost, high power and safe operation.

Although there is a large variety of possible materials combinations for electrodes in lithium ion batteries, combining high cycle

stability and high specific capacity reduces the choices to only a few. Promising candidates for cathodes are layered oxides like Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O₂ which exhibits high specific capacity [1], but discharge at high rates is limited. Improving safety and especially rate capability of the cell, LiMn₂O₄ is added to the cathode because it exhibits the fast kinetics necessary for high power applications [1]. Mn-rich compounds are preferred compared to Ni- or Co-rich materials since they reduce the battery's cost, although their specific capacity is lower and LiMn₂O₄ suffers from rapid degradation especially at elevated temperatures due to manganese dissolution [1,2]. The best anode material considering both specific capacity and cycleability is graphite [2].

It is commonly known that the lifetime of lithium ion batteries is limited by unwanted side reactions [3]. These side reactions may affect all parts of a battery including the electrolyte, the active materials, binder, conducting agents, current collectors and the

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separator, resulting in capacity decrease and/or increase of the overall cell impedance [3–5]. Especially the electrolyte's components are sensitive to exposure at elevated temperatures.

Calendar aging arises independently from other stress like cycling and is permanently present. In daily use lithium ion batteries are often exposed to great stress like high ambient temperature and high storage voltages. This may influence electrochemical processes, kinetics and safety of the cells. Understanding the relevant aging mechanisms in lithium ion batteries is of great importance to face lifetime and safety challenges and to make precise lifetime predictions.

In this work aging phenomena arising from calendar aging are investigated by several physical–analytical methods as well as electrochemical impedance spectroscopy.

2. Experimental

2.1. Cell type

Commercial 18650 lithium ion batteries containing a blend of LiMn_2O_4 and $\text{Li}(\text{Ni}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2})\text{O}_2$ as cathode material and graphite as anode material with an initial capacity of 2 Ah have been used in this work.

2.2. Cell storage

Prior to calendar aging the cells were characterized by a power and capacity test. In order to determine the power and inner resistance 12 A discharge pulses were applied for 10 s at different SOC (between SOC100 and SOC10 in steps of 10% SOC). The voltage and current were taken just prior to the pulse and at the end of the pulse after 10 s to calculate the inner resistance by the following Equation (1).

$$R_{\text{DC}} = \frac{U_{10\text{s}} - U_{0\text{s}}}{I_{10\text{s}} - I_{0\text{s}}} = \frac{\Delta U}{\Delta I} \quad (1)$$

The specific power in W kg^{-1} was calculated by multiplication of voltage and current at the end of the pulse after 10 s divided by the mass of the cell as shown in Equation (2).

$$P = \frac{U_{10\text{s}} \cdot I_{10\text{s}}}{m_{\text{Cell}}} \quad (2)$$

The capacity was determined at a discharge rate of 1C and C/5. The cells were discharged to a voltage of 2.75 V as recommended by the cell supplier.

After the power and capacity test, the standard charging procedure recommended by the manufacturer was applied. Cells were charged at a constant current rate of 2 A from 2.75 V to 4.2 V and subsequently the voltage was held constantly at 4.2 V until the total charging time exceeded 3 h.

Eight identical cells are stored at 60 °C, five cells at a voltage of 4.2 V (SOC100) and three at 4.0 V. The batteries are stored at open circuit potential, thus no trickle charge is applied and the cell is allowed to change its voltage by self-discharge between two characterization segments. During storage specific power, 1C and C/5 capacity are monitored every 20 days. The characterization was carried out with a Battery Cycler (BaSyTec GmbH, Germany) at room temperature.

2.3. Laboratory test cells

For post-mortem analysis and further inspection of the new and aged cells, the batteries were opened in an argon-filled glovebox. Electrode disks with a diameter of 18 mm were punched out for use

in laboratory test cells (EL-Cells, EL-Cell GmbH, Germany) [6]. Before using the electrode sheets the coating had to be removed on one side of the current collector in order to get electrical contact in the EL-Cells. Particularly with aged electrodes the coating easily flakes off or sticks to the separator, making it a challenge to gain fully coated electrode sheets. After removing the coating the sheet was washed in dimethyl carbonate to remove any residuals from the electrolyte and dried afterward at room temperature. The preparation procedure, together with the fact that the coating of the aged electrodes easily flakes off makes it nearly impossible to investigate surface layers or contact resistances between the active material and the current collector.

For all laboratory test cells a glass fiber separator (EL-Cell GmbH, Germany) with a diameter of 18 mm and a thickness of 1.55 mm served as the electrolyte reservoir. 1 M LiPF_6 in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) at a ratio of 1:1 (v/v%) was used as the electrolyte in the laboratory test cells.

In total three types of laboratory test cells were prepared.

- *Half cells* having anode or cathode as working electrode and metallic lithium as counter and reference electrode (e.g. data shown in Fig. 10).
- *Full cells* with cathode and anode plus metallic lithium as reference electrode to monitor the potentials of anode and cathode during cycling (e.g. data shown in Figs. 11 and 12)
- *Symmetric cells* with two cathodes or two anodes [7], set to the same potential (e.g. data shown in Figs. 16 and 17)

2.4. Electrochemical investigation

A slow constant current discharge at C/50 was conducted at the aged electrode to distinguish between capacity fade from loss of active material and from increase of the inner resistance.

Slow-scan cyclic voltammetry was carried out at anode and cathode half cells at a scanning rate of $5 \mu\text{V s}^{-1}$ to investigate the redox voltages and peak heights of new and aged electrodes.

Furthermore half cells were subjected to rate tests with C-rates at C/10 and 1C to check the rate capability of new and aged electrodes.

Full cells with reference electrodes were assembled to measure the potentials of the anode and cathode during cycling of new and aged cells. In these experiments the potentials of anode and cathode were monitored against the Li-reference electrode while cycling the cell between 4.2 V and 2.75 V.

Electrochemical impedance spectroscopy (EIS) was carried out using a Gamry Instruments Potentiostat PCI4G300-51021 (Series-G300). Full batteries were discharged to SOC10 at a rate of C/5 and kept at OCV for four hours before the measurement started. The impedance of batteries was measured in pseudo-potentiostatic mode every 20 days during calendar aging in the frequency range between 10^5 Hz and 2 mHz with a perturbation voltage of 1 mV at temperatures of 23 °C, 0 °C and –10 °C. Laboratory test cells were directly investigated with EIS after assembly in a frequency range between $3 \cdot 10^5$ Hz and 2 mHz at the same perturbation voltage and at temperatures of 23 °C, 10 °C and 0 °C. Before the measurement the battery was kept for three hours at the desired temperature to be equilibrated. Temperature control was achieved in a climate chamber.

For the analysis and interpretation of the impedance spectra the DRT (distribution of relaxation times) method was applied. This method was introduced more than 10 years ago for the evaluation of impedance spectra measured from solid oxide fuel cells and is presented in-depth in Refs. [8–10]. As shown recently [11,12] it is also suitable to derive adequate equivalent circuit models for lithium-ion batteries.

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