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Influence of temperature on the aging behavior of 18650-type lithium ion cells: A comprehensive approach combining electrochemical characterization and *post-mortem* analysis

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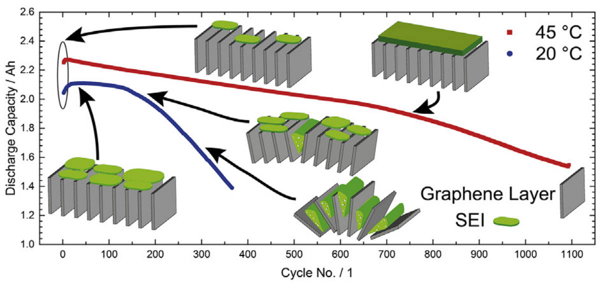
HIGHLIGHTS

- FEC influence on aging and degradation of PC/EC/DMC based electrolyte.
- Complex interaction of electrolyte and electrode in dependency of the temperature.
- Exfoliation of graphite as a result of solvent co-intercalation at 20 °C.
- Exfoliation results into massive electrolyte decomposition and a thick SEI layer.
- Stable and effective SEI at anode enables good electrochemical performance at 45 °C.

GRAPHICAL ABSTRACT



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ABSTRACT

The understanding of the aging behavior of lithium ion batteries in automotive and energy storage applications is essential for the acceptance of the technology. Therefore, aging experiments were conducted on commercial 18650-type state-of-the-art cells to determine the influence of the temperature during electrochemical cycling on the aging behavior of the different cell components. The cells, based on $Li(Ni_{0.5}Co_{0.2}Mn_{0.3})O_2$ (NCM532)/graphite, were aged at 20 °C and 45 °C to different states of health. The electrochemical performance of the investigated cells shows remarkable differences depending on the cycling temperature. At contrast to the expected behavior, the cells cycled at 45 °C show a better electrochemical performance over lifetime than the cells cycled at 20 °C. Comprehensive *post-mortem* analyses revealed the main aging mechanisms, showing a complex interaction between electrodes and electrolyte. The main aging mechanisms of the cells cycled at 45 °C differ strongly at contrast to cells cycled at 20 °C. A strong correlation between the formed SEI, the electrolyte composition and the electrochemical performance over lifetime was observed.

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1. Introduction

Lithium ion batteries (LIBs) offer a high energy density, high power density and high charge/discharge Coulombic and energy efficiencies [1–3]. They are considered as the key technology for portable electronic devices. In the emerging field of automotive applications LIBs are considered as one major energy source to power electric vehicles. The utilization of LIBs in hybrid electric vehicles (HEV), plug-in hybrid electric vehicles (PHEV) and electric vehicles (EVs) is strongly increasing. Furthermore, the upgrade from 12 V to 48 V vehicle electrical systems in internal combustion engine (ICE) powered cars is becoming more popular. Moreover, energy storage systems on a LIB basis are regarded as one possible near-term solution to deal with the fluctuating power generation of renewable energy sources. At contrast to portable electronic devices, for the automotive and energy storage application a much longer-term operation is essential for consumer satisfaction. The goals, as set by the USABC for 2018, are 15 years of calendar life, 1000 cycles for EVs and 5000 cycles for PHEVs before the end-of-life (EOL) of the battery is reached. EOL is defined as a state of health (SOH) of 70–80% in comparison to the discharge capacity of the fresh cell [4,5]. To ensure a sufficient lifetime of the cells for the respective application, it is essential to understand the correlation between the influence of the operation parameters on the electrochemical performance over lifetime and the related aging mechanisms.

Aging of LIBs is a topic of various, very often inter-dependent chemical and physical changes of the cell materials resulting in capacity fading, resistance increase, and thus loss in power and energy densities [6]. Moreover, different aging processes originate from a number of various degradation mechanisms and their interactions. Most studies focus on aging of individual parts of the cell, such as the electrolyte decomposition [7,8], cathode decomposition [9,10], electrolyte and anode interactions [11,12], electrolyte and cathode interactions [13–15], solid electrolyte interphase growth [16,17], graphite aging [18,19], cathode electrolyte interphase growth [20], lithium metal deposition [21,22] and many more [6,23]. Overall, there is still a lack of extensive studies which determine aging of all components and their interactions at different aging conditions (e.g. cycling temperature).

In this work, the influence of aging at different temperatures is studied on commercial 18650-type lithium ion cells, based on $Li(Ni_{0.5}Co_{0.2}Mn_{0.3})O_2$/graphite. The cells were cycled at 20 °C and at 45 °C in order to investigate the temperature dependent aging behavior.

To study the electrochemical performance and the thermal impact of the aging effects, the cells were cycled to different state of healths (SOHs). Combined electrochemical and *post-mortem* analysis were performed to investigate the influence of the temperature in detail. The focus of this study is to reveal the major aging mechanisms of the main components, including the anode, cathode and electrolyte. This work provides information about the different stages of aging and the key parameters of the aging mechanisms affecting the cell lifetime. In parallel, a second study will be published by Börner et al. revealing the correlation of aging and the cell behavior under thermal abuse of the presented cells.

2. Experimental

2.1. Cell choice

The cell under investigation is a commercially available 18650-type lithium ion cell. The cell chemistry is based on a $Li(Ni_{0.5}Co_{0.2}Mn_{0.3})O_2$ (NCM) cathode and a graphitic anode. The electrolyte of a fresh cell consists of $LiPF_6$ as electrolyte salt, dimethyl carbonate (DMC), ethylene carbonate (EC) and propylene carbonate (PC) as organic solvents. Fluoroethylene carbonate (FEC), propane-1,3-sultone (PS) and succinonitrile (SN) were used as electrolyte additives to improve the cell performance. The separator consists of a polyethylene (PE) based one layer foil. With a nominal discharge capacity of 2.2 Ah and a maximum discharge current rate of 2C (4.4 A) the cell can be classified as a middle power cell, typically used in applications with the demand of balanced power to capacity ratio, e.g. pedelecs and notebooks. The cell specifications are summarized in Table S1.

2.2. Cell aging and electrochemical analysis

Cycle aging experiments were performed with a Maccor Series 4000 Battery Tester (Maccor, Inc., USA) in a Binder KB 400 climate test chamber (BINDER GmbH, Germany) at constant chamber temperatures of 20 °C and 45 °C. The cycling protocol consists of a constant current/constant voltage (CC/CV) charge followed by a CC discharge. The upper and lower cut-off voltages were set to 4.2 V and 2.75 V respectively in accordance with the MSDS (see supporting information Table S1). The CC step was performed with a C-rate of 1 C (2.2 A) and the CV step until the current falls below C/20 (0.11 A). The end of life was defined as a SOH less than or equal to 90%, 80% and 70%, respectively. In the beginning and after every 50th cycle, the direct current inner resistance (DCIR) was determined with a protocol defined by the VDA (German Association of the Automotive Industry). According to the protocol the discharge resistance is calculated from a 18 s constant current discharge pulse with a high C-rate and the charge resistance is calculated from a charge pulse. The inner resistance in this work was determined at a state of charge (SOC) of 50% with a maximum discharge current of 6 A. The maximum C-rate was defined in a previous test analyzing the behavior of the cells at different C-rates. The voltage response of the cell is shown in Fig. S1. Additional electrochemical impedance spectroscopy (EIS) measurements were performed at 20 °C in potentiostatic mode with a sinusoidal amplitude of 10 mV between 10 kHz and 100 mHz. Electrochemical impedance measurements were performed using a Solartron (AMETEK, Inc., USA) device which consists of a 1287A potentiostat and a 1260A impedance gain phase analyzer. The impedance spectra were recorded at 50% SOC.

2.3. Sample preparation

Before cell opening, an extended discharge step was carried out, composed of a CC/CV protocol (limit $< 0.05C$) to ensure a minimized energy content and reactivity of the cell during disassembly. The discharged cells were subsequently opened in a glove box (M. Braun Inertgas-Systeme GmbH, Germany) under argon atmosphere (O_2, $H_2O < 0.1$ ppm) by slicing the two ends of the metal shell with an cutting tool (build from the workshop), similar to the self-made cutter from Aurbach et al. [24], to prevent short-circuits or any other destructive side-reactions during cell opening. The case was carefully removed to unwind the jelly roll. The individual parts of the cell (outer separator, anode, inner separator, and cathode) were separated. The extracted samples were washed twice with 800 μL dimethyl carbonate (DMC by Sigma-Aldrich, anhydrous, $\geq$ 99%, USA) from both sides to remove residues of the conductive salt and other electrolyte components. Afterwards the samples were dried in the glove box.

2.4. Structure, morphology and composition of electrodes

The electrode morphology was investigated by scanning electron microscopy (SEM). SEM images were obtained using a Carl