



Aging in 18650-type Li-ion cells examined with neutron diffraction, electrochemical analysis and physico-chemical modeling

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ABSTRACT

Aging in NMC/C cells ($\text{NMC-Li}_y(\text{Ni}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33})\text{O}_2$), cycled 1000 times at a 1C rate, has been characterized by *in situ* neutron diffraction and electrochemical analysis. These experimental results have been validated by a physico-chemical aging model, which attributes capacity fade to growth of a continuous SEI film on the anode. Neutron diffraction of the cells indicate a cyclable lithium loss corresponding to a capacity fade of about 23% in both electrodes of the cycled cell. The cycled cell suffers an anode stoichiometry shift from $x = 0.84$ to $x = 0.65$ in Li_xC_6 ($0 \leq x \leq 1$) in its fully charged state and a cathode stoichiometry shift from $y = 0.89$ to $y = 0.81$ in $\text{Li}_y(\text{Ni}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33})\text{O}_2$ ($0 < y \leq 1.05$) in its fully discharged state. Anode ($x = 0$) as well as cathode stoichiometries ($y = 0.54$) remain practically unchanged in the cell's fully discharged and charged states, respectively. These stoichiometry shifts match well with those derived from the model, and both neutron diffraction and model are in good agreement to the electrically determined capacity fade of 21%. In fact, cyclable lithium losses slightly exceed this value. Thus, capacity fade in these cells is mainly due to loss of cyclable lithium into the continuous growth of a SEI film on the anode surface.

1. Introduction

Due to their high energy and power densities, Li-ion batteries are the most favored rechargeable systems in portable electronic devices [1]. Nowadays they are gaining popularity in electric transportation and stationary grid storage systems as well. These large-scale applications demand much longer battery lifespans and thus an understanding of aging mechanisms responsible for reducing lifetime or cycle life is essential [2,3]. The most common cathode material used in commercial portable Li-ion batteries is LiCoO_2 (LCO) due to its high energy density and good cycling performance. However, Co is expensive and considered toxic. For electric vehicles, $\text{Li}_y(\text{Ni}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33})\text{O}_2$ (NMC) seems to be the more preferred cathode materials as their layered structure is more stable, changes in lattice volume are smaller (for $y > 0.5$), and thereby safety and lifetime are enhanced. At the cost of a comparatively lower energy density, LiFePO_4 (LFP) cathodes offer an even better cycling performance and safety, and are usually the optimal choice for stationary grid storage systems.

Several experimental methods are being used to understand Li-ion

batteries during storage as well as during operation [4]. Analytical methods such as electrochemical impedance spectroscopy, microscopy, X-ray and neutron diffraction addressed aging and attributed loss of cyclable lithium and decay of electrode materials as the most important capacity fade mechanisms [5–12]. These occurred due to solid-electrolyte interphase (SEI) layer growth, volume changes in the electrodes during Li-ion intercalation/deintercalation, blockage and structural degradation, Li plating, as well as undesirable phase transformations of active electrode materials. There are several studies which have investigated battery aging by comparing experimental results with simulation models [13–17]. For example, a SEI electron tunneling model, which attributed electron tunneling through the inner SEI layer as the rate determining step, was proposed and simulated to explain capacity fade during storage and cycling by Li et al. [15,16]. This model was validated by experiments on commercial prismatic LFP/C cells. However, no study compared results from aging models to neutron diffraction data. In particular, there is no reported investigation where experimentally observed capacity fading results in 18650-type NMC/C cells using neutron diffraction are compared with a physico-chemical

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model. For non-destructive *in situ* studies of such large format Li-ion cells, neutron diffraction is a suitable and powerful method. Several types of Li-ion cells, such as LCO/C [18,19], NMC/C [20,21] and LFP/C [22–24] have been investigated using neutrons as a probe. These investigations addressed Li plating on the anode [25,26], structural changes within the cathode [21] and spatially resolved inhomogeneities in current densities [27–29] in both prismatic as well as 18650-type cells. However, aging studies in 18650-type cells with neutron diffraction are rare [11,30,12,31,32]. In a recent investigation of aging in commercial 18650-type NMC/C cells with neutrons, capacity fade was attributed to loss of cyclable lithium and cathode material degradation [12]. Our studies investigate the cycling induced aging in similar cell chemistry in more details using additionally physico-chemical modeling and electrochemical analysis.

2. Experimental techniques

2.1. Cell description

Cylindrical 18650-type NMC/C cells, produced under commercial standards, were provided by the battery manufacturer (VW-VM Forschungsgesellschaft mbH and Co. KG, a joint venture between Volkswagen and VARTA Microbattery GmbH). Each cell consisted of a $\text{Li}_{1.05}(\text{Ni}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33})_{0.95}\text{O}_2$ cathode, an organic carbonate based electrolyte (containing 1 M LiPF_6 conducting salt as well as SEI forming and overcharge protecting additives), a monolayer polyolefin-based separator and a graphite anode. The single cathode and anode layers were 63 μm and 47 μm thick, contained about 2 wt.% binder and were coated double-sided on Al-foil and Cu-foil respectively. The cathode contained 3 wt.% highly graphitic carbon as well. The cell balancing was adjusted to obtain an anode/cathode capacity ratio of 1.06. The active material densities of the positive and negative electrodes were 3.28 g cm^{-3} and 1.50 g cm^{-3} , respectively. The cell formation was done by charging and discharging the pristine cells at $C/10$ followed by micro short-circuit detection and cycles for capacity and inner resistance measurement. After cell formation, one cell (labelled as ‘uncycled cell’ in this work) was stored in a 20% state of charge (SOC) at 23 °C, which relates to 20% of the initial cell capacity. The other cell (labelled as ‘cycled cell’ in this work) was cycled for 1000 cycles between 2.5 V and 4.1 V (with a 1C rate at 23 °C) by the battery manufacturer. Simultaneously, two other similar cells were stored and cycled to check the reproducibility of the capacity fade behavior for the cells used in the manuscript. After long term cycling procedure and an additional waiting period of about two years, neutron diffractograms of both uncycled and cycled cells were taken in their fully charged and fully discharged states. Due to the additional waiting period, both cells underwent calendric aging which resulted in a 6% individual capacity fade. For one of the cells, neutron diffractogram was taken at 20% SOC as well, to check the structure at an intermediate state. This particular intermediate SOC was chosen as cells are usually kept in this condition during storage.

2.2. Electrochemical techniques

Long term cycling for 1000 cycles was performed with a CCCV charge (constant current charging to 4.1 V, followed by a constant voltage hold at 4.1 V until a current corresponding to $C/20$ is reached) and a CC discharge (to 2.5 V) with a rate of 1C, using a Maccor battery tester. After about two years, neutron diffraction experiments were performed. Thereafter, charging and discharging experiments at low current (corresponding to a $C/50$ rate), and galvanostatic electrochemical impedance spectroscopy (GEIS) on both cells, were carried out with a Biologic VMP3 potentiostat. Electrical behavior of the cells were always compared in response to the same currents (C rates).

2.3. Neutron diffraction

Neutron diffraction measurements were performed in a Debye–Scherrer geometry under ambient conditions at the high-resolution powder diffractometer SPODI, MLZ Garching [33]. Neutrons having a wavelength of 0.1548 nm were incident on a rectangular cross section of 40 mm \times 30 mm of the cell. The cell edges (about 10 mm) at the top and bottom were not illuminated by the neutron beam, to avoid signals in the diffractograms from the cell holder at the top and the remaining cell plastic cover at the bottom. A neutron detector array consisting of 80 vertical position sensitive detectors collected the neutrons scattered by the cell [34,35]. The cells were continuously rotated during the entire measurement to reduce texture effects and obtain an average signal over cell volume. Five diffractograms were measured for each cell with an acquisition time of 48 min each. Therefore, the total integration time for the averaged diffractograms for each cell was approximately 4 h. Instrumental resolution function was determined with a $\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$ reference material to calculate full widths at half maximum of reflections from the cell. To describe the peak profile shape, a Thompson–Cox–Hastings pseudo-Voigt function was used [36]. A linear interpolation between selected data points was used to fit the background. Multi-phase Rietveld refinements of structural models for the neutron diffraction data were carried out with FullProf software package [37]. For the steel housing and the current collectors, structure independent profile fits had to be used to get a better quality pattern refinement because their crystallites had strong preferred orientations.

3. Experimental results

3.1. Electrical behavior

The aging procedure of cycling the NMC/C cell was initiated after the cell formation protocol was completed. A steady and an approximately linear decrease in the discharge capacity was observed as can be seen in Fig. 1. After completing 1000 cycles, the cycled cell had suffered a capacity loss of 21% relative to the capacity of the uncycled cell. A similar approximately linear trend was seen in the other set of cells which were simultaneously stored and cycled, which supports the reproducibility of this aging study. In general, the value of discharge capacity is strongly dependent on the cycling conditions, e.g. on the C rate and the voltage limits. In this aging study, the upper voltage limit was restricted to 4.1 V and a C rate of 1 C was used. Cycling the cell with a lower C rate and with an upper voltage limit of 4.2 V would have led to a higher value discharge capacity for these cells. In order to compare experimental studies with the model, potential profiles of the cells had to be obtained at a low current. Thus both cells underwent one more cycle, this time with a $C/50$ rate between 2.5 and 4.1 V. The

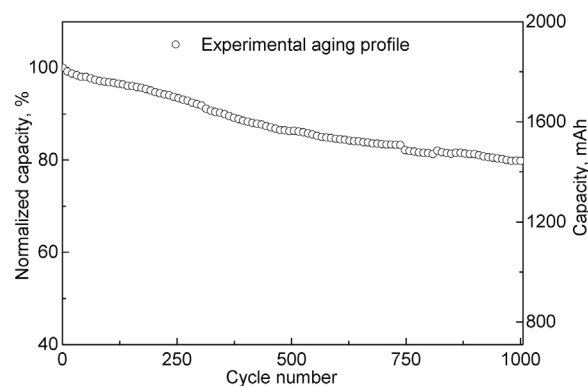


Fig. 1. Experimental aging profile of the NMC/C cell at a 1C rate during the long term cycling procedure. Both normalized capacity as well as discharge capacity of the cell versus the cycle number is shown.

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