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Short communication

Effect of fatigue/ageing on the lithium distribution in cylinder-type Li-ion batteries

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HIGHLIGHTS

- Spatially-resolved neutron diffraction study on charged LiCoO2.|C cell of 18650 type.
- 2D lithium distribution in the graphite anode in charged state was probed *in operando*.
- Experimental data on “fresh” and “fatigued” (1000 cycles, CCCV, 1C) are compared.
- Extended cell cycling leads to a reduction of mean lithiation of the graphite anode.
- Uniformity of lithium distribution in the cell is affected by a cell fatigue.

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ABSTRACT

The lithium concentration in the graphite anode of fatigued (cycled 1000 times at 25 °C) Li-ion cell of 18650-type has been probed non-destructively by spatially resolved neutron diffraction. The amount x of Li in Li_xC_6 has been determined in a central plane of a cylinder-type Li-ion cell. A radial mesh with a gauge volume of $2 \times 2 \times 20$ mm^3 was used. Besides the evidently lower lithiation grade, caused by a lack of free movable lithium and a loss of electrolyte, a development of fatigue-driven spatial lithium inhomogeneities has been observed in radial direction. Observed changes have been discussed in light of their correlations to an increase of the internal cell resistance and to a change of the electrolyte concentration.

Due to their excellent characteristics lithium-ion batteries are nowadays dominating the segment of energy storage applications for portable electronics and electric vehicles. Despite their relatively simple principle of operation, modern industrial Li-ion cells are complicated electrochemical devices, whose performance is highly affected by numerous factors either of external or internal origin [1]. Understanding of processes supplementing the operation and performance of Li-ion cell and their prediction are the major challenges of the electrochemical energy storage. There, among various key factors, the fatigue of Li-ion cells is one of the most relevant parameters defining the cell parameters over long time and determining its reliability and safety.

Fatigue processes in Li-ion batteries are usually studied by microscopy, electrochemical measurements, impedance spectroscopy and investigations using these techniques in combination [2], whilst detailed and systematic structural studies are rather limited. It has been shown that a variation of the material composition can improve cycling stability, e.g. using different additives to the electrolyte [3,4] or specially chosen cathode materials blends [5,6]. This indicates that various factors are involved in the aging behavior of Li-ion cells. Different origins for cell degradation are reported in literature: lithium plating/dendrite growth [7]; cation disorder and microcrack formation of the $LiCoO_2$ particles in the cathode [8]; increase in thickness of the solid-electrolyte interphase on the

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anode and/or reduction of the electrolyte [9,10] etc. Based on electrochemical measurements and cell life modeling Santhanagopalan et al. [11], proposed a loss of free transport lithium and a loss of active carbon (anode) as possible reasons for capacity fade. In-situ neutron diffraction experiments on systematically aged cylindrical 18650-type cells in charged and discharged states [12] revealed no measurable loss of active carbon. However a loss of free movable lithium (well-correlated to the capacity fade) was reflected in a decrease of the Rietveld refined lithium concentrations at both cathode and anode sides. Electrochemically this effect can be explained as an electrode slippage [13] between negative and positive electrode leading to a deposition of movable lithium on the graphite anode surface along with other products arising from electrolyte decomposition.

The major contribution to fatigue is caused by processes on the anode side [14], whilst the cathode performance remains nearly unaffected [15]. Being by far not trivial, the problem of cell fatigue further gains in complexity when homogeneity issues over larger cell volumes are additionally taken into account. Requests for higher volumetric and gravimetric energy densities or increased power output lead to differences concerning the optimum arrangements of electrode stacks or rolls. This in turn results in non-uniform electrolyte wetting, current and/or lithium distribution, which cause inhomogeneities of the lithium distribution occurring on different length scales [16] and depending on various factors. For example in Ref. [17] the lithium concentration inside the graphite anode of cylindrical 18650-type cells has been recently found correlated to the electric connection scheme of current leads to current collectors. For an active cell cycling an inhomogeneous deterioration of the anode and the cathode at the edges of a pouch-back cell has been already observed in Ref. [18]. In the current article we report how ageing affects the lithium distribution inside the graphite anode based on the comparison of a “fatigued” and a “fresh” cylinder-type Li-ion cell. This work is a continuation of our neutron scattering studies on cylinder-type Li-ion batteries *vs.* various factors, e.g. charge/discharge [19], fatigue [12], low temperature [20], lithium intercalation into graphite [21], cation mixing [22] and spatial homogeneity [17,23].

Spatially-resolved neutron powder diffraction studies were performed on $LiCoO_2|C$ cells of 18650-type. One of them was previously cycled 1000 times (CCCV, 1C, 3.0–4.2 V) at 25° C [12]. The lithium distribution inside the cell was non-destructively probed at the engineering diffractometer STRESS-SPEC (Heinz Maier-Lebnitz Zentrum, Garching b. München, Germany) [24]. The spatial evolution of two peaks related to lithiated graphite stages, namely 001 LiC_6 and 002 LiC_{12}, was studied using a monochromatic neutron diffraction setup. The gauge volume was defined by horizontal slits with an opening of 2 mm for the primary beam and a radial oscillating collimator limiting the acceptance of the diffracted beam to a width of 2 mm at the centre of the sample stage. The methodology of the experiment and its setup is described elsewhere [17,23]. Prior to neutron experiment the “fatigued” cell was cycled 3 times in the voltage window 3.0 V-4.2 V using a CCCV protocol with 0.4 A charging current and then mounted on the goniometer in fully charged state. The gauge volume scheme is shown in Fig. 1a for the horizontal slice. Each radial scan contains 8 points. Scans were performed along bisects $\omega = 0°, 45° \ldots 315°$. An exposure time of 300 s per point was chosen.

Obtained diffraction data were analysed in terms of the mean lithium concentration x in Li_xC_6 rather than diffraction intensities of the charged anode. This enables a direct comparison of Li-ion cells of various kinds or at different state-of-health. The lithium concentrations in the “fatigued” $LiCoO_2|C$ cell of 18650-type were evaluated for the predefined mesh (Fig. 1a). The results are shown by points and interpolated values in Fig. 1b and c as surface and contour plots, respectively. Spatially-resolved neutron diffraction data for a “fresh” cell have been taken from Ref. [17] and are depicted in Fig. 1e–g using a consistent presentation\color scheme.

Both cells, “fresh” and “fatigued”, display lower lithium concentrations close to the centre pin and the current leads, where coating of the counter electrode is missing\interrupted (Fig. 1). However the differences between lithiated and non-lithiated regions seem to be less pronounced for the “fatigued” cell when compared to the “fresh” one, which can be associated with a generally lower lithiation grade. For the fully charged cell a mean lithium concentration of $<x> = 0.61(5)$ has been found in the graphite anode of the “fatigued” cell. In comparison the “fresh” cell reached an average lilthium concentration of $<x> = 0.85(4)$. The amount of lost active lithium has been found well correlated to the reduction of the cell capacity, i.e. a mean lithium concentration of $<x> = 0.85(4)$ corresponding to a capacity of 2600 mAh for the “fresh” cell compares well to a lithium amount of $<x> = 0.61(5)$ in the “fatigued” cell with ca. 2000 mAh residual capacity.

Not only the magnitude, but also the shape of the lithium distribution inside the graphite anode has been found affected by an extended cell cycling. This is best illustrated by the deviation from the plateau-like behavior, established for the “fresh” cell previously [17]. The lithium concentration plateau has been defined at $x_P = 0.88(1)$, whilst for fatigued cell the x_P had been set at 0.61. Surface plots $x\text{-}x_p$ for both „fresh“ and „fatigued“ cells adopting consistent color/isoline scheme are shown in Fig. 2a–b. Besides regions close to the centre pin and current lid the deviations from the plateau-like behavior $|x\text{-}x_p|$ do not exceed 0.05 for the “fresh” cell. In the “fatigued” cell, possessing essentially lower lithiation grade, the deviations from the plateau-like behavior became more pronounced, i.e. at the outer part of the cell a broad range with $|x\text{-}x_p|$~0.15 has been observed.

Any deviations from constant lithium concentrations could indicate regions of increased/faster or reduced/slower fatigue/aging. This might be relevant for the stable cell operation and persistence of its properties. Here, especially the presence of an “island” with anomalously high lithium concentration on the outer part of the “fatigued” cell is very important. The lithium distribution in the graphite anode can be linked to the current distribution during charge or discharge, which, in turn, is defined by the resistive paths for the current within a cell. Assuming a similar resistivity per length unit for both positive and negative current collector one may expect a linear increase of the total resistance of a current path within the current collector *vs.* the distance from the tab position. For the cell design explored in the current study both positive and negative electrode stripes are electrically connected at their opposite ends (see Fig. 2e–f). This configuration leads to a total resistance of the current path from the positive to the negative tab independent of the position *l*, i.e. a homogeneous current density *i* versus *l* (Fig. 2c).

The internal resistance is supposed to be independent on *l*, but it is known to be strongly affected by various factors, like state-of-health, state-of-charge, temperature etc [20]. Upon cell aging the internal resistance typically increases: in the current case the internal resistance for “fresh” and “fatigued” cells was estimated from the initial drop of open cell voltage upon current application as large as 0.127(2) Ω and 0.191(1) Ω in charged state.

Both “fresh” and “fatigued” cells have been chosen from the same batch possessing the same design, chemistry and scheme of electric connection of electrode stripes. Higher deviations from the plateau-like behavior on the outer part of the “fatigued” cell can be attributed to a nonlinear current distribution along the position *l* (see Fig. 2d) and, thus, might involve a nonlinear behavior of resistance along electrode stripe. The combination of electrolyte resistance from anode, cathode and separator, as well as the contact