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Short communication

Spatially resolved in operando neutron scattering studies on Li-ion batteries

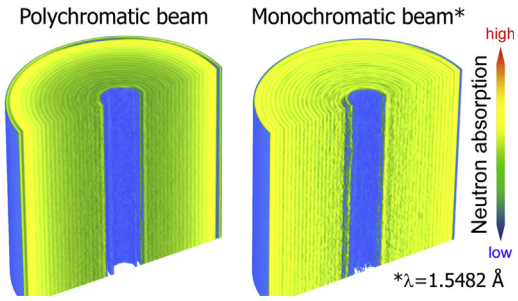
A. Senyshyn [a,*], M.J. Mühlbauer [a,b], O. Dolotko [a,b], M. Hofmann [a], T. Pirling [c], H. Ehrenberg [d]

[a] Forschungs-Neutronenquelle Heinz Maier-Leibnitz FRM II, Technische Universität München, Lichtenbergstraße 1, D-85748 Garching b. München, Germany
[b] Material Science, Technische Universität Darmstadt, Petersenstrasse 23, D-64287 Darmstadt, Germany
[c] Institut Laue-Langevin, 6 rue Jules Horowitz, Grenoble Cedex 9 BP 156-38042, France
[d] Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM-ESS), Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany

HIGHLIGHTS

- In operando spatially resolved neutron powder diffraction.
- Probe of spatial lithium distribution in both cathode and anode.
- Both fresh and degraded cells studied have spatially uniform lithium distribution.
- Details of Li-ion battery design deduced using neutron radiography and tomography.
- Advantages of using monochromatic neutron beam for studies of lithium distribution.

GRAPHICAL ABSTRACT



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ABSTRACT

Spatially-resolved neutron diffraction has been applied to probe the lithium distribution in radial direction of a commercial Li-ion cell of 18650-type. The spatial evolution of selected Bragg reflections for $LiCoO_2$ (positive electrode, "cathode") and graphite and lithium intercalated graphite (negative electrode, "anode") was observed and evaluated by taking beam attenuation and cell geometry effects into account. No evidences for lithium inhomogeneities have been found for the investigated set of cells. Computed neutron tomography using a monochromatic neutron beam confirmed the homogeneous lithium distribution. The relevance of the monochromatic beam to neutron imaging studies of Li-ion cells is discussed.

Li-ion batteries are considered as the major energy storage technology in the field of portable electronics and electric vehicles. Applications in electromobility demand for rechargeable batteries with higher energy density, improved output power, lower weight and lower costs. These performance parameters are determined by numerous degrees of freedom, from chemical and structural details of the used materials up to the cell design and processing. An optimization of such complicated electrochemical devices requires "live" information about processes occurring inside the cell. This

* Corresponding author.
E-mail addresses: anatoliy.senyshyn@gmail.com, anatoliy.senyshyn@frm2.tum.de (A. Senyshyn).

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calls for new dedicated experimental techniques, which are non-destructive and capable to study complete operational cells without a need to disassemble them. Hereby, the risks of material oxidation, electrolyte evaporation or uncontrolled changes of the state of charge are minimized. Furthermore, 3D information on cell components on different length scales is of high relevance. Neutron scattering is already a well established tool for the characterization of complex Li-ion batteries [1]. The major advantageous features are: (1) the high penetration depths of thermal neutrons, which suits perfectly for non-destructive studies on complete devices, (2) the capability to localize light elements, e.g. hydrogen, lithium, (3) the excellent phase contrast depending on specific isotopes and complementary to the X-ray absorption contrast, (4) the interaction with nuclei, so that the neutron scattering lengths are not dependent on $\sin(\theta)/\lambda$, and accurate structure factors can be measured over a broad range of diffraction angles. Such data sets provide precise bond-lengths and allow Debye–Waller factor analysis along with the direct determination of lithium diffusion pathways by probability density function analysis. Therefore, numerous neutron scattering studies of Li-ion cells have been performed. The evolution of polycrystalline electrode materials was revealed *in situ* by neutron powder diffraction [2–10]. The solid-electrolyte formation processes have been investigated by small angle neutron scattering [11] and neutron reflectometry [12]. Neutron imaging (especially computed neutron tomography) has been established as an excellent method for "live" studies (in operando) of the full cell design and the electrochemical behavior of Li-ion cells. These results are displayed by a 3D visualization of the local neutron attenuation contrast with a spatial resolution down to the range of several μm [13–16].

Recently reported computed neutron tomography studies on commercial Li-ion cells of the 18650-type [3] revealed a pronounced contrast between the electrode layers (rolled around a center pin) in the discharged state, which vanishes during cell charge. This effect is attributed to the inhomogeneous lithium distribution in the discharged state, when the major amount of lithium is situated inside the positive electrode ($LiCoO_2$) and the negative electrode (graphite) is nearly Li-free. The lithium intercalation into the negative electrode results in a more uniform lithium distribution between the electrodes (ideally, in the fully charged state LiC_6/LiC_{12} and $Li_{0.5}CoO_2$) reducing the contrast. In addition to this coherent interlayer contrast depending on the state of charge, a neutron attenuation gradient in radial direction has been observed which is affected neither by fatigue nor by the state-of-charge. It has also been attributed to the distribution of lithium inside the cell, corresponding to a scenario when more lithium is concentrated in the outer part of the cell. However, from the electrochemical point of view this situation with a non-uniform Li concentration is inconsistent with the homogeneous capacity expected from the equipotentials along the metal foil current collectors in commercial cells. This calls for an alternative technique capable to quantify the lithium distribution inside the Li-ion cell in operando. Spatially-resolved neutron diffraction is the method of choice for this task, but to our knowledge its application to energy storage systems with complicated geometries is limited so far to Fe/NaCl based batteries [17]. Just recently an *in situ* neutron diffraction study of the inhomogeneous degradation in a $Li_xMn_2O_4$/graphite-based commercial pouch-cell battery has been reported [18].

Nevertheless, in addition to the quantification of lithium uniformity of the following conceptual questions still have to be answered:

- Is it possible to obtain and evaluate the spatially-resolved diffraction signal from a highly neutron-absorbing commercial cylindrical cell of the 18650-type?
- What is the influence of discrete electrode layers on the diffraction signal, and which gauge volume is eligible? Or in other words: up to which extent can the rolled electrode layers be modeled as an isotropic medium?

A spatially-resolved neutron powder diffraction experiment can be performed at nearly any kind of engineering diffractometer equipped with translation and rotation stages for sample positioning and a suitable collimation. A sketch of such a setup is displayed in Fig. 1a. The shape of the gauge volume is defined by the collimation of the incident and scattered neutron beam and the

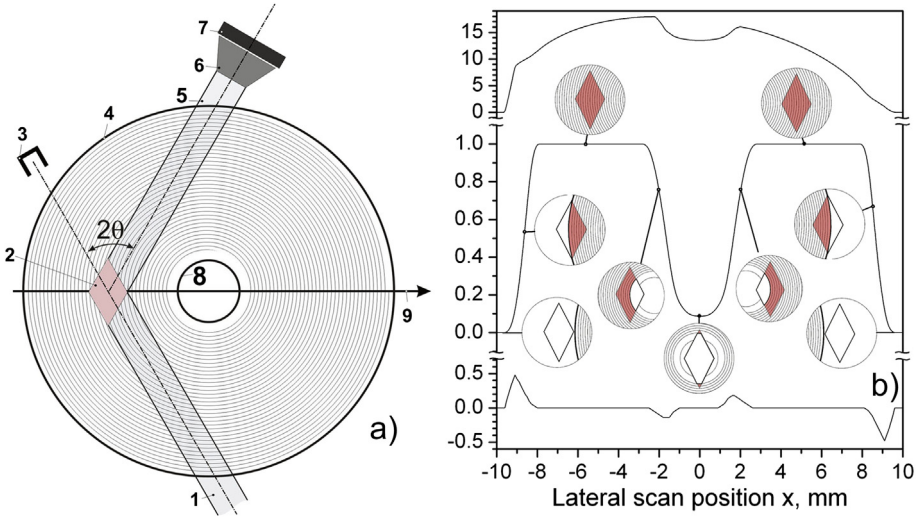

Fig. 1. (a) Sketch of spatially resolved neutron diffraction experiment on a cylindrical Li-ion cell, where 1 and 5 correspond to the incident and elastically scattered neutron beam, 2 is the gauge volume, 3 is the direct beam catcher, 4 and 8 are the cell housing and center pin, 6 is the oscillating radial collimator, 7 is the 2D neutron detector and 9 indicates the scanning direction *x*. The effective gauge volume, containing the actually scattering material, is marked by red color. (b) Typical dependencies of the neutron path length through the cylindrical cell (top, in mm), the fraction of the gauge volume filled with material (middle, relative units) and the resulting shift for the center of mass of the effective gauge volume (bottom, mm). The insets show the gauge volume for different positions of the lateral scan. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)