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# Probing chemical heterogeneity of Li-ion batteries by *in operando* high energy X-ray diffraction radiography

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## HIGHLIGHTS

- X-ray diffraction radiography used to probe the SOC distribution in flat Li-ion cell.
- Spatial distribution of lithium (averaged over cell thickness) reported at SOC = 100%.
- Local SOC heterogeneities occurred at both cathode and anode.

## ABSTRACT

Uniformity of the crystal structure of battery electrodes inside a commercial prismatic Li-ion battery ($LiCoO_2|C$) with a nominal capacity of 1200 mAh were examined by diffraction of a monochromatic photon beam (60 keV). Selected structural parameters related to lithium concentrations in the positive and negative electrodes were determined averaging over cell thickness on a $1 \times 1$ $mm^2$ grid, thus resembling an experimental radiography technique with a pixel size of 1 $mm^2$, where the diffraction signal is used instead of attenuation of the photon beam. Non-uniformities in a prismatic Li-ion battery were unambiguously revealed by remarkable differences of the diffraction signals and systematic deviations of structural properties at different scan positions. Observed lithium heterogeneities at nominal state-of-charge (SOC) = 100% state are attributed to SOC deviations caused by the current distribution inside the examined prismatic cell.

Performance, stability and safety of Li-ion batteries are seriously influenced by the cell homogeneity on both macro- and microscopic scales. It is intrinsic to Li-ion batteries to be electrically isolated systems, so that quantification of the uniformity of their properties (chemical, current, charge and/or temperature) is often non-trivial. Taking the cell apart and harvesting of the materials for further *ex situ/post mortem* characterisations is a popular task, which, however, might not necessarily reflect the initial/original state. There are just few methodologies capable to probe the cell homogeneity under real operating conditions, *i.e. in operando*, and only a limited number of reports on real cells.

In the field of theoretical battery simulations a large number of models was exploring Bruggeman's assumptions [1] about the ideal microstructure, isotropy of transport and uniform distributions. Next generation battery models [2,3] are based on porous electrodes and concentration solution theories describing charge/discharge processes and transport kinetics in both bulk and electrolyte phases of the battery in form of 1D distributions. 3D simulations of Li-ion batteries and battery packs got a strong boost after implementation of the Newman model in Finite Element Analysis Software, e.g. Ansys, Comsol or Matlab Simulink [4–6].

Simulations of different phenomena and properties of Li-ion cells on cell level or battery packs were reported: thermal management [7], heat transfer [8] and cooling performance [9], impact of electrode manufacturing [10], short-circuit detection [11] and nail penetration [12], graphite particle cracking [13], cyclic behaviour [14], capacity fading [15], mechanical integrity [16] *etc*.

Modeling techniques [17] unambiguously reveal non-uniformities in the concentration distribution, electrochemical potential, and exchange current density of the battery in various cell parts are affected by temperature, state-of-charge, state-of-health *etc*. In Ref. [18] the non-homogeneous degradation of a large-format $LiMn_2O_4$ (LMO)/Graphite cell (more pronounced at the cell edges) was studied using a combination of simulation and experiment. Also, authors [19] reported a spatially resolved model of a possible cell inhomogeneity and compared current, voltage and SOC distribution for 8 Ah and 75 Ah cells in fresh state and at end of life. Recently, a report [20] on a simulation of a local potential distribution on the example of a commercial LFP/

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graphite 26650-type cell and its comparison to the experimental data collected via a Multi-Tab Cell Approach [21] was reported, that is when a cell is upgraded with several additional current tabs at different positions. Strong deviations from uniform behaviour were noticed, *i.e.* heterogeneity up to 40% at 2C discharge, which was also reflected by a strong temperature gradient in radial direction.

It has been shown that the proposed Multi-Tab Cell Approach can be potentially adapted to different cell geometries and may give a necessary experimental evidence for optimisation of electrode/tab configuration and cooling strategy. Despite no evidence for a change of the cell state was reported [20,22], the Multi-Tab Cell Approach requires an opening of the Li-ion cell, which can cause possible material oxidation, surface passivation or electrolyte evaporation. Furthermore, without a direct comparison to Finite Element Modeling, the OCV profile changes (reflecting integral value of the battery) can hardly be attributed to the desired material properties. This calls for a dedicated alternative technique capable to quantify heterogeneity in Li-ion cells under *in operando* conditions.

Among numerous experimental techniques addressing the problem of heterogeneity in Li-ion batteries microscopy (either X-ray microscopy, electron microscopy, scanning probe microscopy *etc.*) is the most straightforward [23]. Most remarkable examples are: colorimetry studies of lithiated graphite anodes [24], formation of lithium dendrites [25], details of the lithiation of CuO particles using sub-30 nm resolution [26] and recent visualisation of spinel oxide lithiation via *in situ* transmission electron microscopy [27].

Computed radiography and/or tomography (CT) using either magnetoresonance, X-ray or neutron-based sources are considered as more sophisticated imaging techniques in battery research when compared to microscopy. Depending on the research problem the imaging experiments are performed at different scales defined by the desired field of view and resolution. Nanotomography (*i.e.* nanometer-resolved imaging experiment) is often used for probing of microstructure and morphology of agglomerates and particles in battery electrodes [28], micrometer-sized radiography and tomography is applied for a non-destructive view into small format (coin-type, 18650-type *etc.*) Li-ion cell upon operation [29], degradation [30,31] or misuse conditions [32,33]. X-ray based techniques are dominating the high-resolution domain (e.g. nanotomography), whilst at voxel sizes above 30 μm neutron based radiography and tomography start to complement X-ray CT [34–36]. A significant gain in elemental sensitivity can be obtained by the application of energy-resolved CT [37,38].

Besides conventional absorption-based imaging, there are several extended techniques promising to give benefit to the area, namely

- scattering tomography (either diffraction [39] or pair distribution function [40]), capable to visualise long- and short-range order phases inside the material;
- 3D X-ray diffraction [41], capable to distinguish individual grains within the agglomerated particle and probe their structure;
- coherent diffraction imaging (or lensless microscopy) [42] – a technique potentially suitable for mapping the morphology of single particles in battery materials.

Recently, two successful examples of X-ray diffraction tomography [43] and coherent diffraction imaging [44] applications were reported along with synchrotron X-ray tomographic microscopy and scanning X-ray diffraction [45], indicating a clear trend towards “imaging meets diffraction” [46]. In neutron scattering this can be seen by the rapid development of Bragg edge imaging (having certain advantages for pulsed sources), which was recently applied for studies of a 18650-type cell [47].

Due to its unique features (low energy of thermal neutrons, localisation capability for light atoms, separation of contributions from transition metals, accurate Debye-Waller factors *etc.*) neutron diffraction (either monochromatic or time-of-flight) is well suited for studies of battery-related materials. The high penetration depth of thermal neutrons enables neutron powder diffraction studies of 18650-type cells in medium and high-resolution. Different cell properties are reported, *i.e. in situ* evolution of crystal structures of electrode materials at different chemical composition [48], state-of-charge [49,50], state-of-health [51,52], storage [53] or temperature [54]. The majority of performed studies on 18650-type cells are limited to commercial battery materials. For neutron diffraction studies of new generation battery materials there is a number of lab-based electrochemical cells developed, resembling either the design of coin [55], pouch bag [56,57], prismatic [58] or cylinder-type rollover cells [59–61].

Besides neutron scattering a variety of X-ray based analytical techniques successfully contributes to battery research [62]. X-ray diffraction (either lab- or synchrotron-based) is widely explored for the studies of crystal structures of new materials and their evolution upon lithium insertion/extraction in different kinds of *in situ* cells. For example, fast charge/discharge of $LiFePO_4$-based 18650-type cells was studied using time-resolved high energy synchrotron X-Ray diffraction [63]. In Ref. [64] the authors showed that the cell design can be directly related to the strong reaction non-uniformities during *in operando* X-ray diffraction studies. Energy-dispersive X-ray diffraction seems to be dominating in the field of spatially-resolved studies of Li-ion batteries (either coin-type [65], 18650 [66], high-capacity pouch [67] or grid scale [68] cells), but several studies using monoenergetic synchrotron radiation appeared recently. Lin et al. [69] published an *in operando* X-ray diffraction study on a 18650-type cell using monochromatic high-energy (115 keV) synchrotron radiation. Yu et al. [70] reported diffraction data (105.7 keV, integrated over the cell thickness) collected at 1785 locations (2 mm grid) of a commercial 4.7 Ah pouch cell with dimensions 140 × 102 × 14 mm using a photon beam of 0.3 mm in diameter. Diffraction signals from the cell constituents were successfully used for non-contact determination of local SOC, local temperature, and local mechanical strain.

In this study fixed energy (monochromatic) X-ray diffraction was applied to analyze a commercial prismatic Li-ion cell. The prismatic cell based on a $LiCoO_2$ cathode and a graphite anode[1] was chosen based on several criteria: “simple” cell chemistry, comparably small thickness (5 mm), a rigid (aluminium) cell housing and a straightforward cell design. The cell layout was studied non-destructively by X-ray computed tomography using a v|tome|x s 240® tomography scanner from GE. The experimental setup, strategy of data collection, reconstruction and visualisation was similar to that reported in Ref. [71].

X-ray diffraction using fixed high energy (60 keV) photons was performed at the synchrotron beamline P02.1 at PETRA III at DESY (Hamburg, Germany) [72]. The prismatic cell was mounted on a sample stage enabling sample translations in two dimensions perpendicular to the beam. The cell alignment was performed using a goniometer head (Model 1003) from HUBER Diffraktionstechnik and was controlled by a laser and a transmission X-ray signal measured by a silicon diode. 2D diffraction data were collected in transmission geometry using a Perkin Elmer XRD1621 detector with a detector-to-sample distance of 2.691 m.

Prior to the experiment, the cell was cycled three times (CCCV, 3.0–4.2 V, 400 mAh current, 0.01C cuttoff) using a VMP3 potentiostat from BioLogic. Typical charge/discharge profiles of cell voltage, capacity, dQ/dE and dE/dQ are shown in Fig. S1. Structural studies were conducted on the cell in fully charged state. Scans were carried out on a 47 mm × 38 mm grid with 1 × 1 $mm^2$ “pixel” size (consistent with the dimension of the beam size) and diffraction data was collected at every point on the grid (Fig. 1). The 2D diffraction data for each point (out of 1867 collected) were obtained by averaging with subsequent darkfield correction of ten diffraction pictures with exposure of 1 s each, which were subsequently corrected for geometrical aberrations and detector non-linearities using the program Fit2D [73].

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[1] Determined *ex situ* by EDX analysis of extracted electrode material.