

In Situ Electron Diffraction using Liquid-Electrochemical TEM for Monitoring Structural Transformation in Single Crystals Of Cathode Materials for Li-Ion Batteries

Olesia M. Karakulina³, Walid Dachraoui^{1,2}, Artem M. Abakumov⁴, Joke Hadermann³,
Arnaud Demortière^{1,2*}

¹. Laboratoire de Réactivité et Chimie des Solides (LRCS), Amiens, France.

². Réseau sur le Stockage Electrochimique de l'Energie (RS2E), Amiens, France

³. EMAT, University of Antwerp, Antwerp, Belgium

⁴. Skoltech Center for Electrochemical Energy Storage, Moscow, Russian Federation

* Corresponding author: arnaud.demortiere@energie-rs2e.com

The development of efficient Li-ion batteries is vital for transforming our energy-greedy society to one that is more sustainable, where renewable energy will be efficiently stored and widely used. Ideally, for rechargeable and long-lasting batteries, the electrode materials should be able to reversibly (de)intercalate Li ions. This process can result in significant transformations of the cathode's structure while trying to accommodate the changing conditions. It is crucial to know which structural changes occur at the unit cell level to understand the evolution of the electrochemical performance and degradation routes of the different cathode materials.

During the past decade, new in situ/operando analytical tools have been developed to monitor structural and chemical transformations, resulting in important advances in knowledge on electro-chemical energy storage. Liquid cell electron microscopy is a developing technique that allows us to apply the powerful capabilities of the electron microscope to image and analyze materials immersed in liquid. The liquid/bias cell (Protochips) [2] consists of silicon nitride on silicon support called E-chip, which separate the liquid from the microscope vacuum and confine it into a layer that is thin enough for TEM imaging. The importance of liquid cell microscopy in electrochemistry is that liquid cell experiments enable direct imaging of key phenomena during battery operation and relate the structural and compositional changes to the electrochemical behaviors [3, 4].

Electron diffraction tomography (EDT) was developed by Kolb *et al.* [5] to decrease the multiple scattering effects in electron diffraction experiments and enable the quantitative use of the measured reflection intensities within the kinematical approximation, as is preferable for structure solution. EDT is based on the acquisition of a series of off-zone electron diffraction patterns by tilting a crystal around a single axis.

In this work, we have demonstrated that electron diffraction tomography data can be successfully collected in the in situ regime in an electrochemical cell with liquid electrolyte, mimicking the Li-ion battery. The quality of the diffraction data is sufficient to detect the structural changes occurring in the positive electrode (cathode) material upon charge, including variations in the unit cell parameters and changes in the occupancy of the Li positions and interatomic distances. This opens numerous possibilities for the structure solution and refinement of a wide range of nanosized particles from in situ transmission electron microscopy experiments, ranging from battery materials to electrocatalysts, as well as any nanosized particles that undergo changes or crystallization in a liquid environment.

Combining precession electron diffraction with in situ EDT experiments will further improve the quality of crystallographic information as it will allow taking into account dynamical diffraction contribution intrinsic in electron diffraction. However, performing such experiments will require an electrochemical holder to be present next to the precession electron diffraction attachment in the same microscope, a rare experimental setup. However, in the case of lithium-ion battery cathodes comprising 3d transition metals as the “heaviest” elements, the dynamical effects are not very severe and kinematic refinement (as used in the current paper) is sufficient to retrieve reliable information. Furthermore, the use of very sensitive cameras and direct electron detectors with high dynamic ranges can further increase the signal-to-noise ratio, allowing shorter exposure times while collecting more reflections, thus further improving the quality of the refinement while decreasing the beam damage effects.

Finally, based on electron diffraction pattern obtained using liquid-electrolyte cell, we demonstrated that dark field (DF) imaging can be used to follow delithiation process in a single crystal of LFP cathode material. The DF contrast inside the crystal changes strongly with electrochemical delithiation process and exhibits initial LiFePO_4 phase and FePO_4 delithiated phase. This turn out to be a new approach to directly monitor the lithiation/delithiation mechanism in an individual cycled crystal, which enables to address several key questions around Li diffusion pathway and mechanism inside a single particle.

References:

- [1] Deng, D. et al., *Energy Sci. Eng.* **3(5)** (2015), p. 385.
- [2] <http://www.protochips.com/products/poseidon-select/>
- [3] Lutz, L. et al., *Nano Lett.* **18** (2018), p. 1280.
- [4] Dachraoui, W. et al., *Microsc. Microanal.* **22** (2016), p. 24.
- [5] Kolb, U. et al., *Ultramicroscopy*, **107(6–7)** (2007), p. 507.

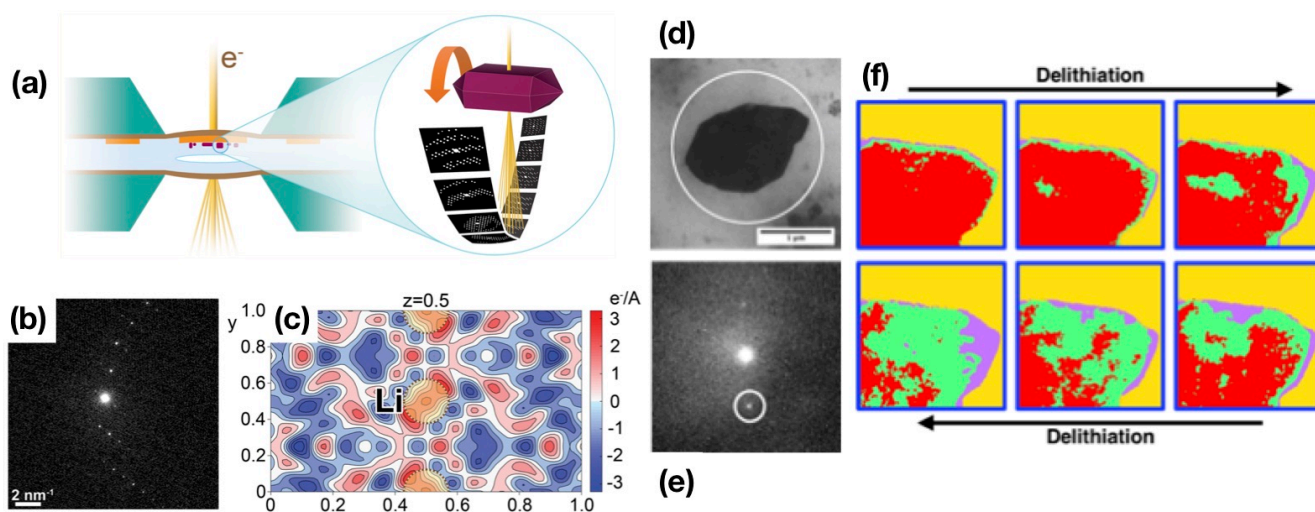


Figure 1. (a) Schematic of electron diffraction tomography during electrochemical cycling of a single LFP cathode crystal inside conventional liquid electrolyte (b) In situ electron diffraction in liquid electrolyte (1.0 M LiPF_6 EC/DMC (1:1) (LP30)) obtained using a CMOS camera (Oneview Gatan). (c) Difference Fourier maps of scattering density for LiFePO_4 before inclusion of any Li atoms to the structure refinement. A pronounced peak of scattering density indicates the presence and location of Li in LiFePO_4 (position indicated with a yellow disk). (d-e) TEM image of LFP single crystals in liquid electrolyte LP30 and electron diffraction pattern with spot selected for the dark field imaging. (f) Dark field images of single LFP crystal during the delithiation process, which is treated by machine learning (Weka) for the segmentation step to visualize Li_xFePO_4 phases.