



Engineer Position in Electron Microscopy at LRCS (Amiens, France)

Study of (dis-)insertion mechanisms within individual cathode crystals (Li / Na-ion battery) by TEM mapping of orientations and crystalline phases using ASTAR system

Laboratory: LRCS (<https://www.lrcs.u-picardie.fr/en/>)

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Duration: One-year position (possibility to extend)

Date: Starts in March/April 2020

Skills for the candidate: PhD in materials science, good knowledge and practice background in TEM and crystallography are required

Prerequisites: strong record and good teamwork skills

Salary: €2.100/month

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Research Project

The inhomogeneity of the (dis-)insertion reactions within the crystals is at the origin of mechanical stresses, fractures and loss of contact that degrade the reversibility of the electrochemical reactions. The lack of uniformity induces significant difficulties in understanding the evolution of the insertion/des-insertion zones and the phase separation mechanisms within the crystalline grains. Up to now, several models have been proposed to account for insertion and phase separation mechanisms such as mobile phase limits [1], intercalation waves [2] and domino cascades [3].

However, recent analyzes question these approaches, such as, for instance, the STXM Operando measurements on LiFePO_4 crystals from W.C. Chueh *et al.* [4]. They showed that lithiation is accompanied by a continuous change in lithium composition within each domain, with several simultaneous processes of solid solution. They also highlighted the presence of Li-rich and Li-poor regions within a single particle that does not lead to mobile phase boundaries. Recently, X. Mu *et al.* [5] (KIT) have shown the possibility of using the TEM ASTAR (NanoMegas) device (crystalline orientation mappings developed from nanobeam electron diffraction) to identify, in individual grains, the LiFePO_4 and FePO_4 phases (with their respective

lattice parameters) and correlate them with the crystalline orientation and the facets of the individual crystals.

In this project, we will focus on 2 positive electrode materials, one for Na-ion batteries $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ (Amam \rightarrow I4/mmm \rightarrow Cmc21) which is a very interesting candidate for high power sodium-ion batteries, and the other for Li-ion batteries $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ (Pnma) which is of interest for its relatively high theoretical energy density.

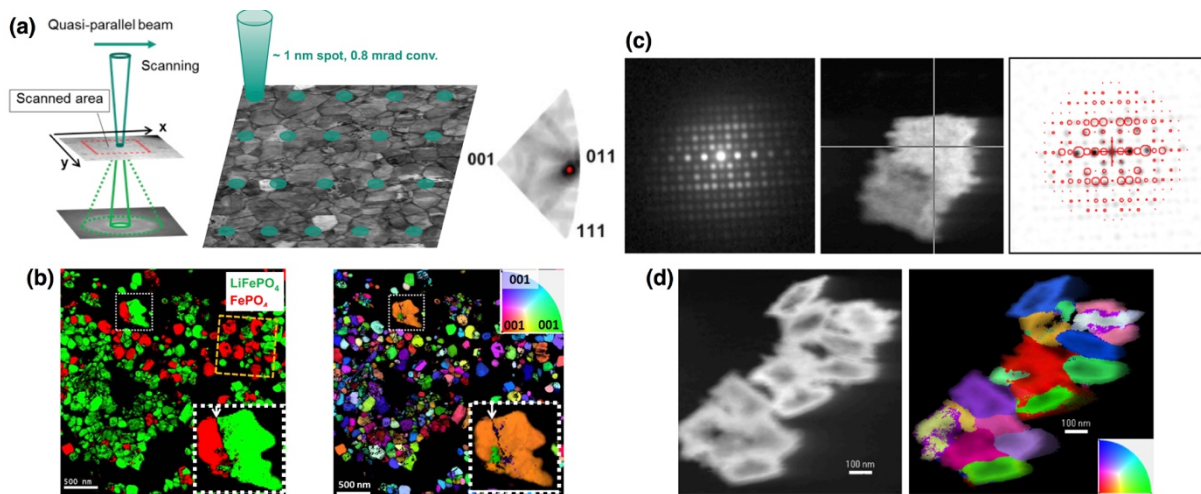


Figure 1 - (a) Schematic showing the principle of orientation and phase mapping (ASTAR) with the scanning of a parallel beam of nanometric size. Each diffraction pattern being associated with a position on the image, a 4D image is obtained containing the structural information for each scanned point. A "pattern matching" treatment is then applied from the crystal structure a priori known to identify the orientation of the crystal with respect to the incident beam. This same process can be carried out to map different phases (b) Example of mapping on LiFePO_4 particles partially delithiated with the associated orientation map [5]. (c) Electron diffraction pattern associated with the measurement of a 1 nm zone defined by growth on the crystal. Illustration of the pattern matching process from the $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ Pnma structure. (d) Orientation mapping of $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ particles with different orientations.

We propose here to focus on the methodological development based on the use of our *in situ* TEM electrochemical device (Select Poseidon Holder from Protochips) and on the ASTAR system (NanoMegs) for crystalline orientation mapping, in order to observe and analyze, in real time and with a nano-metric resolution, the Na^+ and Li^+ ion (dis-)insertion mechanisms within individual positive electrode crystals. The main goal is to observe the evolution of the insertion or des-insertion zones (zones more or less rich in Na^+ or Li^+) and to correlate them with structural in-homogeneities, orientations and crystalline facets. These *operando* observations will allow us to get a better insight into phase separation mechanisms and their dynamics within crystals, for which many questions remain unresolved, in particular for Na-ion materials (NVPF), which did not intensively investigate so far. The research project will be in collaboration with scientists who are specialists in battery materials, *operando* electrochemical TEM and ASTAR system.

Furthermore, we will also compare two different approaches that are coupled to precession technique: (a) phase and orientation mapping using ASTAR system and (b) dark field imaging for which we recently got very interesting results in terms of reaction monitoring. Optimization steps will be needed to find diffraction and



imaging conditions in an organic liquid medium while minimizing the effects of the electron beam. It will therefore be for each associated analytical technique to determine a specific methodology for monitoring in real time the insertion process. Sample preparation and assembly of e-chips, choice of electrolyte, electrochemical cycling conditions will be key parameters to optimize for a high-quality characterization. In addition, the recent acquisition of a new speed camera (30 to 300 fps, Oneview Gatan) has significantly improved our ability to observe process kinetics and study their impact on structural changes.

Stages of the study: **(1)** Structural characterizations of $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ and $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ individual crystals using ASTAR system at different state of charge (ex situ condition), **(2)** Optimization of Operando TEM conditions to both electrochemical cycle individual crystals in conventional electrolyte and acquire SAED patterns. **(3)** Monitor in real-time the lithiation or sodiation process in individual crystals using ASTAR system in orientation / crystalline phase ASTRA system and monitoring in dark field. **(4)** Comparison with dark field image and EELS techniques in terms of ability to follow electrochemical reaction inside individual cathode crystals.

Publications: [1] A. K. Padhi, K. S. Nanjundaswamy, J. B. Goodenough, *J. Electrochem. Soc.* 144, 1188–1194 (1997). [2] G. K. Singh, G. Ceder, M. Z. Bazant, *Electrochim. Acta* 53, 7599–7613 (2008). [3] C. Delmas, M. Maccario, L. Croguennec, F. Le Cras, F. Weill, *Nat. Mater.* 7, 665–671 (2008). [4] W.C. Chueh, et al. *Science* 353.6299 (2016): 566-571. [5] Mu, X., Kobler, A., Wang, D., Chakravadhanula, V. S. K., Schlabach, S., Szabó, D. V., Kübel, C. (2016). Comprehensive analysis of TEM methods for $\text{LiFePO}_4/\text{FePO}_4$ phase mapping: spectroscopic techniques (EFTEM, STEM-EELS) and STEM diffraction techniques (ACOM-TEM). *Ultramicroscopy*, 170, 10-18.