

Multimodal study of dis-sodiation mechanisms within individual $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ cathode crystals using 4D-STEM-ASTAR and STXM-XANES

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Further development of the rechargeable and long-lasting ion-batteries requires a comprehensive study of plenty of processes undergoing on micro- and nano-scale in cathode active material during battery charge/discharge cycle. The discharge process results in significant transformations of the cathode's structure while trying to accommodate the changing conditions, such as migration of transition metals, loss of oxygen, or rearrangements of the metal–oxygen polyhedra. Thus, a piece of experimental information about structural changes occurring at the unit cell level becomes crucial for the evolution of the electrochemical performance and degradation routes of a cathode active material.

In situ liquid electrochemical TEM [1] is one the most powerful analytical tools allowing to follow structural and chemical transformations in battery active materials at nanoscale with high spatial resolution in liquid high-vapor conventional electrolytes. For instance, very recently, the changes in the unit cell structure of lithium battery cathode materials (LFP) during electrochemical cycling in liquid electrolyte were determined for nano-particles using in situ electron diffraction tomography [2]. The same compound was earlier comprehensively studied by means of 4D-STEM (ASTAR system from NanoMegas) [3] and other techniques as electron ptychography [ref].

This work demonstrated that the use of ASTAR system allowed to identify the LiFePO_4 and FePO_4 phases in individual grains and correlate them with the crystalline orientation and the facets of the individual crystals. ASTAR system is phase and crystalline orientation mappings developed from nanobeam electron diffraction. Precession of electron beam (to reduce dynamical effects) and relatively low acquisition/total scan time (to preserve the sensitivity to electron beam samples) are some of the most valuable advantages of this system, particularly in in-situ electrochemical liquid TEM studies.

The growing demand of the modern industry to store an increasing amount of renewable energy in a sustainable way on the one hand and concerns about future Li availability on the other hand rekindled interest for sodium-ion battery technology, owing to the natural abundance of sodium. Sodium vanadium (III) fluorophosphate, $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ (NVPF), attracting great interest as a potential positive electrode for Na-ion batteries due to its exceptional rate and electrochemical cycling capabilities was chosen as an object of our study. During the charging process, the leaving of two Na^+ ions leads to the change of vanadium oxidation state ($\text{VIII} \rightarrow \text{VIII/IV} \rightarrow \text{VIV}$) and corresponding structural transformations ($\text{Amam} \rightarrow \text{I4/mmm} \rightarrow \text{Cmc21}$) which can be registered with help of ASTAR system. Our research is aimed to couple liquid electrochemical TEM studies with ASTAR system and, thus, to observe the evolution of the insertion/de-insertion zones of Na^+ ions in individual positive electrode crystals and to correlate them with structural inhomogeneities, orientations and crystalline facets. The obtained in situ observations should resolve a dispute on the models

proposed to account for insertion and phase separation mechanisms: mobile phase limits, intercalation waves [4] and domino cascades [5].

Here, we would like to present the first results of our TEM studies of NVPF. In our work we employed Poseidon in situ electrochemical liquid cell TEM holder (Protochips) and TEM equipped with Oneview camera (GATAN) and 4D STEM ASTAR system. Thanks to 4D-STEM system we succeeded to follow the structural and, thus, phase transformations of NVPF grains during charge/discharge process in coin-cell battery. The results of obtained phase mapping are in good agreement with corresponding galvanostatic curves and available X-ray diffraction synchrotron data.

More recently, we mapped by STXM-XANES (SOLEIL, beamline HERMES) (energies of V and O) then by STEM-EELS (energies of Na) the same individual grains of NVPF de-sodiated ex-situ at different charge states [6]. Added to 4D-STEM phase and orientation mappings on these same grains, the analysis of these results will provide some answers concerning the (dis)-sodiation mechanisms in the NVPF material. Based on this multimodal study, we correlated structural and chemical behaviors in high-resolution maps to improve reliability and draw evidence of Na diffusion pathway inside single grains.

Acknowledgments:

We acknowledge RS2E and ANR for the funding of the present project.

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