



PhD Thesis in Materials Science

**RS2E funding:
French Electrochemical Energy Storage Network**

Study of local structural properties in primary & secondary particles of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ by advanced TEM

Skills / Prerequisites for the candidate: Master in Materials Science or Chemistry-Physics, good knowledge in characterization techniques. An experiment in electron microscopy and/or Li-ion batteries would be an asset.

Date and duration: the beginning of October 2019, 3 years.

Laboratories/Network: [LRCS](#) (Amiens) and [ICMCB](#) (Bordeaux), [RS2E](#) network

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Lab 1: LRCS (Amiens, main location)

Supervisor : [Arnaud Demortière](#)

Email : arnaud.demortiere@energie-rs2e.com

Co-supervisor : Nadir Recham

Lab 2: ICMCB (Bordeaux)

Supervisor : [Laurence Croguennec](#)

Email : laurence.croguennec@icmcb.cnrs.fr

Co-supervisor : Jacob Olchowka

Scientific Project:

The intensive development around Li-ion batteries for electric vehicles leads to wonder about the reduction of their environmental impacts while continues to improve their performance. $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ spinel material (LMNO) and its variants are turned out to be highly promising as new cathode materials. This material indeed does not contain cobalt and can exchange 0.5 Li per transition metal via a two-electron redox reaction involving nickel ions ($\text{Ni}^{2+} \rightarrow \text{Ni}^{4+} + 2e^-$) at a potential close to 4.7 V (vs. Li^+/Li). It therefore delivers an energy density of 700 Wh/kg, with a theoretical capacity of 147 mAh/g and the Li-ion diffusion occurs in three dimensions in the cubic structures.

Depending on the distribution of the Ni and Mn atoms in the crystal lattice, $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ adopts 2 different crystallographic structures: **(i)** the ordered structure ($P4_332$) in which Ni and Mn occupy the octahedral sites 4a and 12d, respectively and **(ii)** the disordered structure ($Fd-3m$) in which the Ni and Mn atoms are randomly distributed in the octahedral sites 16d and which, exhibits a slight oxygen non-stoichiometry compensated by the reduction of a small amount of Mn^{4+} ions to Mn^{3+} . The transition between the ordered and disordered phases (and the creation of Mn^{3+}) is closely related to the formation of impurities of the $\text{Li}_x\text{Ni}_{1-x}\text{O}$ type that can be removed by post-synthesis annealing in air at about 700°C [1].

In order to optimize the performance and stability of this positive electrode material, many studies have focused on the correlation between their electrochemical performance and their physicochemical properties, including crystal structure, Mn^{3+} content, particle size and morphology.

Better properties of electronic conductivity and ion diffusion have been reported for the disordered structure and it has been shown that the Mn^{3+} ion content plays a critical role in the performance of the LMNO. However, the difficulties associated with identifying these phases (for example, impossible in XRD) made it difficult to assess their specific roles and interdependencies on the performance and stability of materials, and thus hindered the process. optimization of this material. It is therefore necessary to find new characterization tools to: **(i)** accurately analyze the distribution of ordered and disordered phases as well as the $Li_xNi_{1-x}O$ impurity in the initial materials, at the particle scale and **(ii)** to establish correlations with the mode of synthesis and battery performance (e.g. cyclability, power handling, thermal stability).

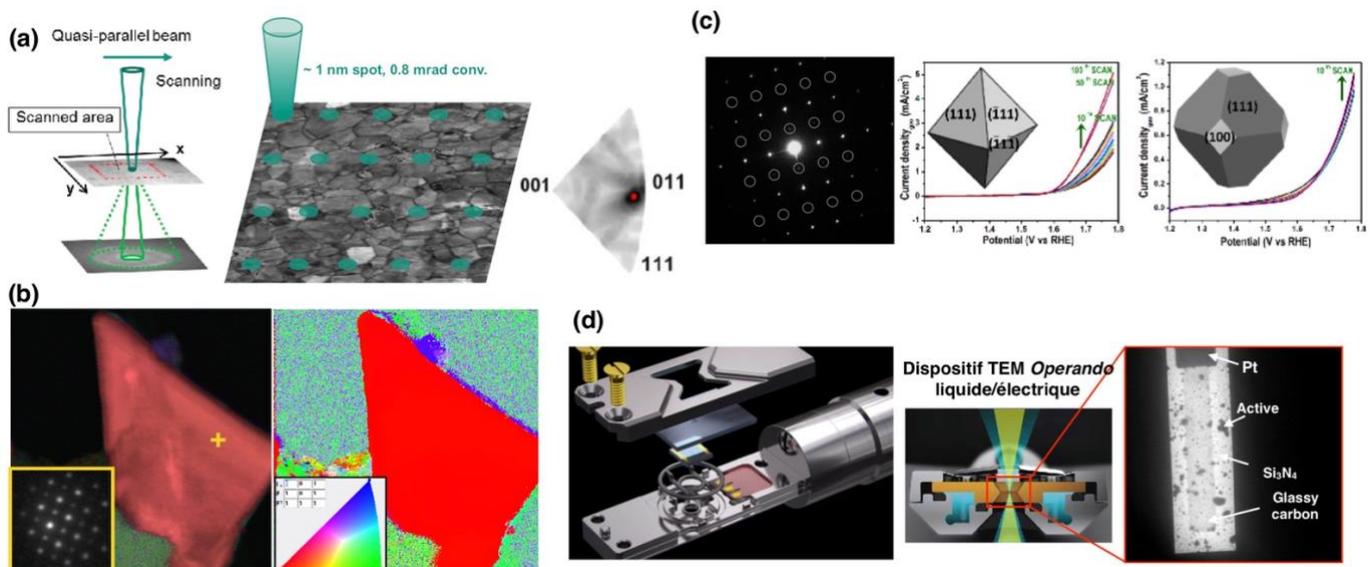


Figure 1. (a) schema showing the principle of orientation and phase mapping (ASTAR) with scanning of a nanoscale parallel beam. Each diffraction pattern being associated with a position on the image, a 4D image is obtained containing the structural information for each scanned point. A "pattern matching" treatment is then applied from the prior known crystal structure to identify the orientation of the crystal with respect to the incident beam. This same process can be done to map different phases (b) ASTAR phase and orientation mapping preliminary results of a LNMO crystal, diffraction pattern corresponding to the yellow dot (c) Electronic diffraction pattern of the LMNO on which we can distinguish the superstructure peaks associated with the ordered phase ($P4_332$). Evolution of current density versus potential for two different secondary particle morphologies [4]. (d) Schema of the in situ TEM cell consisting of two e-chips compressed. The two thin Si_3N_4 windows allow transmission of the electron beam. The liquid is introduced into the cell by the microfluidic device and the electrode material studied is placed on the working electrode. TEM image of the cell filled with liquid electrolyte in which the glassy carbon electrode coated with active material crystals is visualized.

And the other hand, the morphology of the primary particles is decisive on the performances. For example, Ohzuku *et al.* [4] demonstrated that primary particles of octahedral and faceted LNMO [111] exhibited better performance in terms of stability, polarization, and cycling than primary particles smaller in size and with mixed faceting. The detailed study of the role of the crystalline facets in Li transport and in the reactivity of the positive electrode material with the electrolyte has not yet been realized and could provide an improvement in the understanding of these phenomena.

Finally, it has been demonstrated that the LMNO materials having micrometer-sized secondary particles overcome that having nanoscale sizes, in terms of capacity retention during cycling and fast-speed performance, essentially due to the limitation of reactivity with the electrolyte. Within the secondary particles (Figure 1c) many phenomena may occur during cycling such as the evolution of grain boundaries, the appearance of cracks, the migration of species on the surface and the modification of crystalline phases. These developments impact the performance of the electrodes and must be better understood in order to improve the synthesis and manufacturing processes.

Recently, Kubel *et al.* (KIT) [5] have shown the possibility of using the device ASTAR in TEM, a device for mapping crystalline phases developed from electron diffraction with a nanometric beam, to identify precisely within the crystals the lithiated zones ($LiFePO_4$) and delithiated ($FePO_4$). The figure 1b exhibits the first results using ASTAR system on an individual crystal in which we clearly distinguish the orientation and the phase of disordered LMNO.

We propose in this project to use the ASTAR device (Figure 1a) installed in our TEM, to study the local crystalline structure (ordered vs. disordered phases and impurities of $Li_xNi_{1-x}O$) of primary particles (impact of morphology and faceting) and secondary particles (grain boundaries) of $LiMn_{1.5}Ni_{0.5}O_4$ spinel material. The treatment of experimental

electron diffraction patterns will be done automatically, compared with the simulated pictures for the intermediate phases formed during cycling. From the phase and orientation mappings, it will also be possible to characterize the phase joints and the grain boundaries, respectively. The correlation of all of this structural information with the electrochemical data will allow us to better understand the evolution of LNMO electrode material performance. Furthermore, several TEM analyses will be made at different state of charge such as HRTEM, EELS, EDX and STEM-HAADF at high resolution.

The synthesis of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ materials of different structures, stoichiometries and morphologies will be realized at the ICMCB. Different precursors (oxides, hydroxides) and different methods of synthesis will be considered, in order to control the growth of particles in different sizes and crystallographic orientations [8-10] and to modulate their reactivity [10-12]. These different materials will be cycled in batteries, they will then be characterized ex situ in the charged state and in the discharged state of the battery, after a growing number of cycles performed at different speeds.

In a second step, the ASTAR system can be coupled to our liquid-electrochemical TEM cell in order to carry out Operando measurements and analyze the evolution of the crystalline phases according to the state of charge and discharge [6,7]. Finally, this study will be completed using X-ray synchrotron analysis such as PDF, EXAFS and NanoDiffractionCT.

This study may be extended to other materials of interest, including the study of $\text{Na}_3(\text{V}_{1-x}\text{M}_x)_2(\text{PO}_4)_2\text{F}_{3-y}\text{O}_y$ and $\text{Na}_x[\text{Fe}_{0.5}\text{Mn}_{0.5}]\text{O}_2$ systems as positive electrode materials for Na-ion batteries.

Methodology and Work Organization:

The different steps of the thesis: **(1)** Synthesis of a series of materials $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ having different structures and morphologies. Characterization of their structural (XRD, TEM) and electrochemical properties. **(2)** Preparation of a series of materials which will be recovered in the charged state and in the discharged state of the battery, after an increasing number of cycles performed at different regimes. They will be characterized ex situ. **(3)** Elaboration of phase mappings (ordinate / disordered and $\text{Li}_x\text{Ni}_{1-x}\text{O}$ impurities) and phase boundaries of the primary particles in their initial state and in different states of charge and discharge. Development of grain boundary maps within secondary particles at different states of charge and discharge. **(4)** Coupling of the liquid-electrochemical TEM cell to the ASTAR system to analyze the evolution of the crystalline phases as a function of the state of charge. **(5)** EELS/EDX spectroscopic measurements of primary and secondary particles in the initial state and at different states of charge and discharge. **(6)** X-ray synchrotron radiation measurements will be carried out using different techniques such as PDF, EXAFS and NanoDiffractionCT.

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