PhD Thesis Offer

Li and Mn-rich oxides and oxy-fluorides: new insights into the local order of disordered rock salt materials for battery applications

Keywords: *Li-ion batteries, Oxy-fluorides, Neutron Scattering, Structural Disorder*

Context: Lithium-rich compounds of the general formula $Li_{1+x}(M,M')_{1-x}(O/F)_2$ (where M and M' are transition metals, $x > 0$) exhibiting a disordered rock-salt structure have been of great interest to the battery community for about a decade. When used as positive electrode materials in lithium-ion batteries, these compounds achieve stable specific capacities approaching 175 mAh/g while being free of critical elements such as cobalt and nickel. Lithium diffusion in these compounds is based on a three-dimensional network of interconnected tetrahedral and octahedral sites. These compounds are generally metastable, especially when containing significant amounts of fluorine, and are obtained by unique synthesis methods that "freeze" the cationic and anionic disorder. As a consequence, a simple average rock-salt structure does not capture the true complicated local (dis)order. **This PhD project aims to achieve a more accurate picture of both local and average long-range in these materials, which is key to any detailed understanding of the transport mechanisms and electrochemical performance.**

Project: This PhD project will build upon previous work on the $Li_{1.25}Mn_{0.5+y/2}Nb_{0.25-y/2}O_{2-y}F_y$ (LMNOF) system recently studied at ICMCB[1]. Rock-salt type LMNOF samples were synthesized by high-energy mechanosynthesis, and characterized by electron microscopy, lab X-ray pair distribution function (PDF) analysis and nuclear magnetic resonance (NMR) spectroscopy. It was shown that a combined substitution of oxide with fluorine allows for solid-solutions with a higher Mn^{3+}/Nb^{5+} ratio and improved electrochemical performance. However, significant local-scale structural distortions were observed, contributing to capacity loss in LMNOF-based batteries. **In this context, this new PhD project aims to deepen the understanding of the local structure in disordered rock-salt LMNOF compounds in order to open new strategies for optimized synthesis conditions and improved long-term electrochemical performance. A key focus will be on using neutron scattering methods to gain critical new insights.** The initial phase at the ICMCB will focus on synthesizing LMNOF samples with both natural and isotope-enriched lithium precursors to provide better atomic contrast for neutron scattering. The synthesized compounds will then be characterized using lab X-ray diffraction and PDF analysis to ensure purity, with additional verification through TEM combined with EDS to confirm homogeneity. Following this, lithium battery cells will be prepared using the synthesized compounds as positive electrodes and cycled. Electrode materials will be extracted after cycling for further structural analysis.

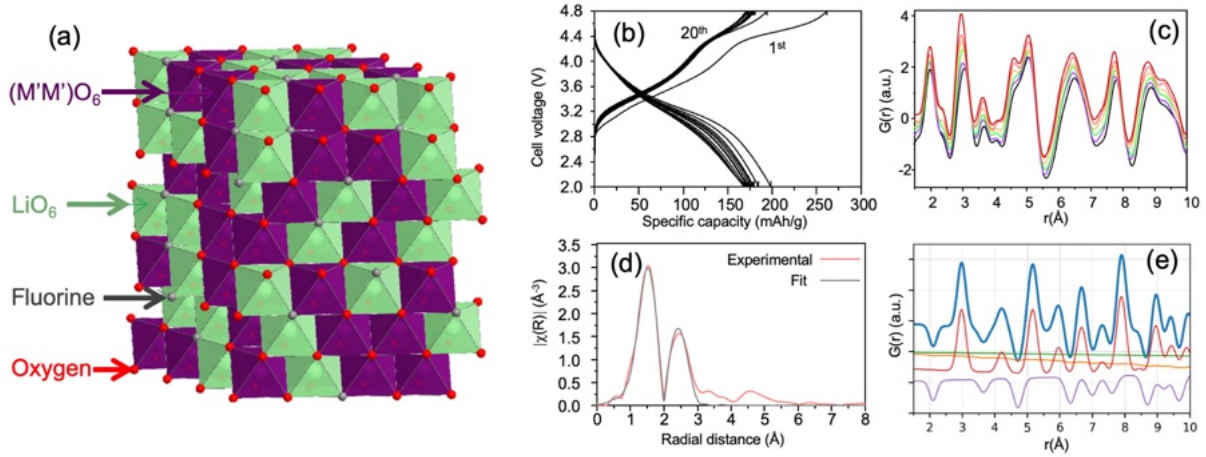

Figure 1: (a) Representation of disordered $Li_{1+x}(M'M'')_{1-x}(O/F)_2$ rock salt structure. (b) Galvanostatic cycling curve for $Li_{1.25}Mn_{0.5}Nb_{0.25}O_2$, showing capacity fade (c) Subtle variation of X-ray PDF for compositions with increasing F content (d) local structural details probed by EXAFS data at Mn K-edge (e) simulated Neutron PDF data illustrating sensitive to Li environments.

[1] Deville et al. *Inorg. Chem.* (2024) https://doi.org/10.1021/acs.inorgchem.3c03863

Subsequently the project focus will switch towards advanced local structure analysis using PDF techniques. Studies will be undertaken at the ILL before and after cycling for both natural and enriched lithium containing samples to calculate the PDF G(r) function which can provide details on short range Li environments. It is also planned to perform synchrotron X-ray PDF and EXAFS analyses using natural lithium samples to probe operando or ex situ electrodes in various states of charge. This phase aims to provide comprehensive insights into the structural changes that occur during battery operation. Finally, a detailed analysis of all these data with be required, focusing on structural modeling using Reverse Monte Carlo (RMC) techniques. For example, the RMCProfile software package can be employed to model the structure of various LMNOF samples, integrating neutron diffraction, neutron and X-ray PDF, and EXAFS data for accurate modeling of both short- and long-range structure details. The project will culminate with a new and accurate description of the local and average structural models, offering a deeper understanding of the structural rearrangements during battery operation. **The ultimate goal of this PhD project is to achieve a comprehensive understanding of the structural changes in rock salt-type materials during battery operation.** By integrating experimental data from neutron and X-ray PDF analyses with advanced modeling techniques, we anticipate that valuable insights will be discovered, which can enhance the performance and sustainability of next generation battery materials.

Environment: This PhD is based both at the ICMCB in Bordeaux and the Institut Laue–Langevin (ILL) in Grenoble. The ICMCB is a research laboratory with extensive resources for materials synthesis, shaping, processing and characterization. It is jointed managed by the CNRS, Bordeaux INP, and the Université de Bordeaux. The project will utilize the X-ray diffraction platform of the ICMCB, which is well equipped with multiple diffractometers for advanced structural and operando studies. At the ILL, in a highly multidisciplinary campus located at the heart of the French Alps, the student will benefit from cutting-edge large scale neutron scattering instruments, and unique interactions with skilled scientific experts. The ILL offers one of the most intense continuous neutron flux sources in the world; which affords unique possibilities for both operando (beamline D20) studies and insight into locally disordered materials (beamline D4). It is anticipated the project will include scientific missions to other large scale user facilities for (e.g. operando PDF, EXAFS), as well as opportunities to present results in national and international congresses.

Candidate: The desired profile is a young scientist holding or about to obtain a Master's degree (or equivalent) with a focus on materials and/or solid-state chemistry, highly motivated by exploratory synthesis and with a strong interest in fundamental understanding of structure-property relationships in new materials. Expected and required skills include, experience in solid state chemistry, materials science, and basic crystallography, with a working knowledge of common tools for materials characterization and data handling. Additional skills in electrochemistry and X-ray or neutron scattering methods are appreciated but not essential.

Calendar: Applications are currently being accepted and considered. **This PhD contract starts in the fall of 2025, for a duration of 3 years, with an anticipated dissertation defense in late 2028.** The exact start date may vary depending on the circumstances of the successful candidate. The project is co-financed by the ILL and the Bordeaux INP engineering school, and the PhD student will spend approximately half of his/her time at the ILL and the other half at the ICMCB. The number, dates and duration of the visits may vary according to the progress of the project. The student will be enrolled at Université de Bordeaux, the institution which will award the PhD diploma.

Application: Your application package (curriculum vitae, diploma transcripts, letter of motivation) should be sent to the PhD supervisors listed below. Interviews with both ICMCB and ILL staff will be organized for shortlisted candidates.

PhD Supervision: The PhD student will be accompanied by 4 co-supervisors: Dr. Marie GUIGNARD (ICMCB) and Prof. Dany CARLIER (ICMCB) are specialists in materials for batteries (from synthesis to electrochemical cycling, including the study of their structure before, during and after cycling). Dr. Matthew SUCHOMEL (ICMCB) is an expert in laboratory X-ray scattering, PDF and diffraction experiments. Dr. Gabriel CUELLO (ILL) is an instrument scientist at the ILL, responsible for beamline D4, and is a specialist in neutron scattering, particularly concerning neutron PDF methods.