

**Ph.D in Chemistry and Materials Science****Tailoring halospinel for redox-active catholytes in  
Li-ion solid-state batteries**

**Laboratory:** Institut Charles Gerhardt de Montpellier (ICGM)

Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB)

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**Starting date:** 1<sup>st</sup> October, 2026

**Funding:** RS2E, employer CNRS, ca. 1800€/month net salary

**Scientific context:** Li-ion solid-state batteries (Li-SSBs) have recently emerged as safe and high energy density storage systems compared to conventional lithium-ion batteries (LIBs). Currently, chloride-based SSEs ( $\text{Li}_3\text{InCl}_6$ ,  $\text{Li}_3\text{YCl}_6$ ) have been widely investigated to couple with high-voltage positive electrode materials in Li-SSBs. Generally, the positive electrode in Li-SSBs is a composite matrix containing electrode material, solid-state electrolyte (catholyte), and electronic additive. Depending on the fabrication conditions, the positive electrode material often represents 45 – 70 wt.% of the electrode composite and the rest is occupied by non-electroactive materials (catholyte and electronic additive). Redox-innocent catholytes are generally used in the cathode composite to ensure a fast  $\text{Li}^+$  diffusion process inside the matrix. If the redox-innocent catholyte is replaced by a redox-active one, the catholyte can participate in both  $\text{Li}^+$  diffusion and reversible electrode reactions, which can significantly improve the electrode's areal capacity.

In this project, new materials adopting the halospinel structure, possessing both  $\text{Li}^+$  mobility and redox activity, will be explored. The local and average structure of the materials will be investigated through a combination of different techniques: X-ray/neutron diffraction, X-ray absorption spectroscopy, Raman spectroscopy, and  $^{67}\text{Li}$  solid-state nuclear magnetic resonance spectroscopy. Finally, the ionic/electronic conductivity as well as the electrochemical performance of these compositions will be evaluated in Li-ion solid-state cells.

**Working environment:** This Ph.D thesis will take place in the “Batteries” group of ICGM (Montpellier) and in close collaboration with the “Energie: Matériaux et Batteries” research group at ICMCB (Bordeaux). The material syntheses, structural characterizations, and electrochemical cycling will be taken place at ICGM. Several stays at ICMCB will be planned during the Ph.D thesis to perform  $^{67}\text{Li}$  ss-NMR measurement to further investigate  $\text{Li}^+$  local environment. Possibility to be trained in DFT calculations to interpret the  $^{67}\text{Li}$  ss-NMR data. The activity on DFT calculations can be carried out at ICMCB or from distance at ICGM.

**Ph.D profile and skill acquirement:** Through this project, the student will acquire strong skills in material synthesis, structural characterizations, and electrochemistry. The candidate should have a Master degree in Chemistry, Materials science or associated fields. The candidate should be highly motivated and willing to work between two different research groups. Previous experience in solid-state chemistry and electrochemistry is a plus.

**Application/Contact:** Interested candidates are requested to send their CV, motivation letter, and the names of two references (including their contact details) to Long Nguyen ([long-hoang-bao.nguyen@umontpellier.fr](mailto:long-hoang-bao.nguyen@umontpellier.fr)) and Dany Carlier ([dany.carlier@icmcb.cnrs.fr](mailto:dany.carlier@icmcb.cnrs.fr)).