

Sujet de Thèse
THESE EN COTUTELLE
POUR LA RENTREE 2025
FINANCEMENT : BOURSE

PROJET DE THESE

L'ingénierie de l'entropie pour ajuster la mobilité ionique dans les électrolytes solides au sodium et au lithium pour une application dans les batteries tout-solides.

1. Le sujet de recherche choisi et son contexte scientifique

Addressing the environmental and societal challenges posed by conventional energy sources requires a shift toward renewables like solar and wind power. However, the unpredictable nature of these sources demands advanced energy storage solutions to ensure a stable and reliable supply. Among these, batteries stand out as a transformative technology [1,2]. They not only drive the transition to electric and hybrid vehicles but also enable the seamless integration of solar and wind energy into smart grids, shaping the future of sustainable energy. As the demand for advanced electrochemical energy storage solutions continues to rise, all-solid-state batteries (SSBs) have gained attention as a promising technology. Their appeal lies in their high practical energy and power densities, along with enhanced safety (no flammable liquid electrolyte). The development of this technology relies on solid electrolyte (SE) materials with superionic conductivity ($\sigma_i > 10^{-3} \text{ S.cm}^{-1}$) and negligible electronic conductivity ($\sigma_e < 10^{-9} \text{ S.cm}^{-1}$) at room temperature, excellent (electro)chemical stability, and ease of processing (mechanical softness), etc. [3,4]. Indeed, driven by the relentless search for superior solid electrolytes, researchers have uncovered *ceramic materials*—both *crystalline and amorphous*—boasting conductivities that exceed those of traditional liquid (organic) electrolytes, redefining the landscape of energy storage, and the majority of them are sulphide based. These solid electrolytes offer both benefits and challenges. While their relative softness [5,6] enables good contact with electrode components, their narrow (electro)chemical stability window presents a challenge [7,8]. To enable the reversible operation of solid-state batteries, engineered interfaces are often required to shield them from direct interaction with the cathode and/or anode. Classical strategies to achieve high ionic conductivities involve iso- or aliovalent substitution in the host lattice and thus leading to increased site disorder, increased Li^+/Na^+ vacancies, etc. Taking as an example the reference Na_3PS_4 (SE), ionic conductivities σ_{Na} around 1 mS cm^{-1} was measured upon (i) isovalent-ion substitution of Sb^{5+} for P^{5+} or Se^{2-} for S^{2-} in Na_3PS_4 [9-12] and (ii) aliovalent-ion substitution of Sn^{4+} for P^{5+} or halide doping Cl^- on the S^{2-} site in Na_3PS_4 [13-16].

Breaking away from conventional approaches, *multielement-substituted (high-entropy)* solid electrolytes (SEs) have recently garnered significant interest for their potential to enhance both conductivity and (electro)chemical stability. The term “*high entropy*” typically describes materials with configurational entropy of $\Delta S_{\text{conf}} \geq 1.5R$, where R is the gas constant. This value is determined by the distribution of elements across similar crystallographic sites. However, systematic control over ΔS_{conf} through compositional tuning—known as entropy engineering—remains largely unexplored. To date, only a handful of materials have been explored, including garnet, perovskite, Na Super Ionic CONductor (NASICON), argyrodite $\text{Li}_6\text{PS}_5\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), and $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS)-type compounds. In this regards, the high-entropy versions of LGPS-type ($\text{Li}_{9.54}[\text{Si}_{0.6}\text{Ge}_{0.4}]_{1.74}\text{P}_{1.44}\text{S}_{11.1}\text{Br}_{0.3}\text{O}_{0.6}$) and lithium argyrodite materials (e.g., $\text{Li}_{6.5}[\text{P}_{0.25}\text{Si}_{0.25}\text{Sb}_{0.25}\text{Ge}_{0.25}]\text{S}_5\text{I}$ and $\text{Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{0.8}\text{Br}_{0.7}$) have opened new frontiers. These

advanced compounds have demonstrated remarkable ionic conductivities exceeding 10 mS cm^{-1} at room temperature, positioning them as frontrunners for the next generation of high-performance solid-state batteries. Moreover, increased dopant/substituent solubility in such materials can enhance charge-carrier concentration, potentially unlocking optimized performance and novel properties.

The research in the proposed PhD project will focus on the development of high-entropy Li^+/Na^+ ceramic materials (crystalline or amorphous) that are sulphide based. To achieve this, a comprehensive screening of a broad range of compositions will be conducted. In this context, we will focus on multielement-substituted combinations of Li^+/Na^+ halides (Cl, Br, and I) with chalcogenide materials such as GeS_2 , Ga_2S_3 , In_2S_3 , Bi_2S_3 , SnS_2 , and others.

2. *L'état du sujet dans le laboratoire et l'équipe d'accueil*

The recruited PhD student will join the functional materials group at the LPCA Laboratory and profit from recent research and skills available in the fields of materials science and more precisely in the domain of ionic conductors. The group is specialised in the synthesis of glass and glass-ceramic materials for both environmental and energy applications. Considering that the performance of Solid electrolyte is closely linked to the composition, structure, and properties of the materials, such as ionic and/or electronic transport properties, our team has developed expertise in the synthesis and characterization of amorphous materials, enabling them to establish the connections between these characteristics and properties. The full cycle of research, including the synthesis of new high-entropy material (melt-quenching method in evacuated silica tubes and the mechanical milling technique using Planetary Micro Mill Pulverisette 7 premium line), analysis of macroscopic and transport properties, and structural characterization of materials using advanced experimental and theoretical methods, is carried out in-house to develop ionic conductors contains sodium and lithium ions. Since 2018 (see the publication list), two theses have been defended on the development of sodium-ion conducting materials (T. BOUNAZEF and A. SAMMOURY). A project has been launched on the lithium-ion solid electrolyte LLZO (Y. DABAKI). In this context, the LPCA proposes a thesis project focused on the study of new high-entropy Li^+/Na^+ ceramic materials (crystalline or amorphous) that are sulphide-based.

3. *Le programme et l'échéancier de travail*

The work to be carried out within the framework of this research project involves the synthesis of new sulphide based high-entropy materials (HEM), the characterization of their physico-chemical properties, and evaluating the potential of these HEM to be used as a solid electrolytes in all-solid-state batteries. The Tasks are:

- Synthesis of HEM materials using the melt-quenching method in silica tube under vacuum
- Structural verification using laboratory X-ray diffraction (XRD)
- Macroscopic properties measurements such as density and DSC measurements.
- The study of the transport properties in using a combination of different analytical techniques such as complex impedance spectroscopy, the Wagner method, and the radioactive tracer diffusion method.
- The Structural analysis using (1) high energy X-ray diffraction and neutron scattering techniques. They make it possible to clearly establish certain short- and medium-distance correlations in the materials and to formulate hypotheses on the conduction mechanisms that are likely to operate and (2) Raman studies of both amorphous materials and their crystalline counterparts that are employed to obtain information on the local structure of materials.
- DFT modelling of Raman data using the local calculation means of ULCO University (Platform Calculco). To this end, the Gaussian 16 software associated with its GaussView graphical user interface is employed. DFT calculations allow the identification of characteristic vibrational signatures and the most stable specific bond configurations in glasses and crystals

- Electrochemical characterization of the promising SEs obtained via half-cell configuration (coin-cell, swagelocks)

Durée de thèse = 36 mois	
0-3 mois	Bibliographical work, training on synthesis techniques
2-24 mois	Materials synthesis and macroscopic characterization: XRD, density, DSC, SEM, conductivity and radioactive tracer diffusion measurements
6-24 mois	Structural characterization: HEXRD, ND, Raman, etc. DFT modeling of Raman structural data
18-30 mois	Solid electrolyte characterization
30-36 mois	PhD writing

4. Les retombées scientifiques et économiques attendues

On the fundamental level, this study aims to develop new high-entropy solid electrolyte materials with high ionic conductivity, while exploring their structural properties and ion transport mechanisms. This research is pivotal, with far-reaching implications in solid-state physics and energy storage.

The research also has industrial significance, as all-inorganic solid-state batteries (SSBs) are considered a promising route to enhance the energy and power density of rechargeable lithium and sodium batteries. Moreover, the successful development of a novel solid electrolyte could potentially lead to a patent filing.

The outcomes of this research will be disseminated through at least one publication in a peer-reviewed international scientific journal, along with an oral presentation or poster at an international conference.

Références

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