Synthesis and characterization of plastic crystals as novel ionic conductors for next generation all-solid-state batteries

This topic is subject to funding through the 397 Doctoral School competition. Contact Arnaud Perez if you are interested (arnaud.perez@sorbonne-universite.fr).

https://ed397.sorbonne-universite.fr/fr/future-doctorate-candidate/ed397-competition.html

Key-words: Solid-state chemistry, Ionic Conductors, Oxysulphides, Synthesis, Electrochemistry

Summary of the PhD project

Among the next-generation energy storage technologies, all-solid-state batteries (ASSBs) are very close to commercialization and attracting intense research effort from researchers and companies. By replacing the liquid electrolyte and carbon anode used in Li/Na-ion batteries with a solid electrolyte and a lithium/sodium metal anode, this technology has the potential to achieve 70% higher energy densities than Li/Na-ion batteries, as well as a higher power density that means faster charge and discharge cycles.[1]

The main limitation to the development of this technology is to identify new inorganic materials with atomic structures that allow the rapid diffusion of lithium/sodium ions at room temperature, with conductivities reaching 10^{-2} S/cm and above.

The quest to synthesize better ionic conductors is ongoing, with several structural families standing out for their remarkable properties. In recent years, the scientific community has become increasingly interested in a family of materials with remarkable ionic conductivity properties.[2–6] Plastic crystals are materials with properties intermediate between a solid and a liquid (Figure 1a).[7] They have dynamic crystalline structures with molecular anions undergoing rapid rotational motions that are correlated with rapid cation migration (Figure 1bc). Typically, these materials are stabilized at high temperatures, when they have sufficient energy to allow the reorientation of the anions. To use these materials in next-generation batteries, there is a clear challenge to develop room-temperature plastic crystals with high ionic conductivity.[8,9]

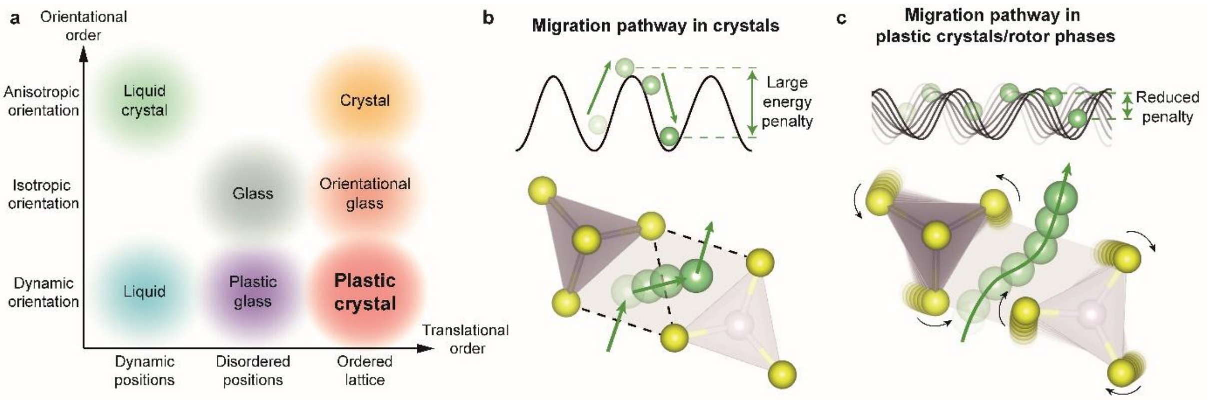

Figure 1: (a) Plastic crystals, or rotor phases, are one of the intermediate states of matter between solid and liquids, with orientational freedom of molecular species at fixed lattice points. (b) The migration of cations in ordered crystals is hindered by the passage through structural “bottlenecks” which results in large energy penalties for migration. (c) In plastic crystals, the rotational properties of molecular anions flatten the energy landscape for cation migration.

In this project, we will study the factors controlling the phase transition temperature to the plastic crystal phase, in order to understand how this phase can be stabilized at room temperature. We will use original oxysulfide anions developed in our team, with different symmetry properties to systematically modify the rotational properties of the anion. The synthesis of these materials has already been explored in our team, using low-temperature synthesis methods in aqueous media. We will use these materials, as well as other compositions to be identified, and study their rotational properties as a function of temperature using different characterization techniques.

A better understanding of the structure-property relationships in plastic crystals will guide us to propose new compositions and test them in solid-state batteries.

Supervision arrangements

The doctoral student will be supervised by Arnaud Perez (CNRS Research Fellow, 2 supervised theses, 1 defended, including 1 funding from ED397). The thesis supervision will be provided by Christel Laberty-Robert (Professor Sorbonne University, HDR). The doctoral student will benefit from the environment of the RMES (Reactive Material for Energy deviceS) team within the Laboratoire de Chimie de la Matière Condensée de Paris (LCMCP) as well as the training and missions offered by ED397 of Sorbonne University. Regular meetings with the supervisors will allow close monitoring of the progress of the research.

Thematic

Energy storage/Solid-state Batteries/Synthesis of new ionic conductors/Plastic crystals

Domain

Materials for electrochemical energy storage

Objectives

Synthesis and characterization of new materials.

Understanding structure-property relationship in plastic crystals.

Context

This project will be carried out at the Laboratoire de Chimie de la Matière Condensée de Paris, part of Sorbonne Université, within the Reactive Material for Energy deviceS (RMES) team (https://lcmcp.upmc.fr/site/rmes-2/). The group has a broad range of expertise covering organic/inorganic/hybrid materials, synthesis, processing and sintering of ceramics and electrochemical characterization methods that place it in an ideal position to develop innovative ideas at the crossroads of material science disciplines, a scientific culture largely developed at the LCMCP.

The RMES team is part of the French Network on Electrochemical Energy Storage (https://www.energie-rs2e.com/fr) which nurtures strong scientific connections between research labs to accelerate the development of energy storage. The team therefore benefits from dynamic collaborations together with the development and mutualization of advanced in situ/operando characterization techniques, including at synchrotron facilities.

Methods

This project will involve the use of soft chemistry synthesis methods (low temperature, water/solvent). Structural (X-ray/neutron diffraction, PDF, NMR) and spectroscopic (XAS, electrochemical impedance) characterizations will be combined to develop a comprehensive model of the discovered materials. Particular attention will be paid to techniques that provide access to information on the local structure and dynamic properties.

In situ and operando techniques will be used to fully understand the temperature-dependent properties of the prepared materials.

Expected results

This project will improve our understanding of the dynamic properties of ionic conductors. We hope that this new knowledge will help us discover new materials suitable for the development of next-generation solid-state batteries.

Conditions of the research project

Funding via a doctoral scholarship from ED397. The doctoral student will benefit from the equipment of the LCMCP and the characterization platforms of Sorbonne University.

International reach

This project is part of international materials research, with the main competing teams in the United States, Japan, England, Germany. This project is open to international collaborations and participation in conferences abroad.

Opportunities of collaboration

The team is part of the RS2E collaborative network, giving access to a broad spectrum of expertise and characterization tools dedicated to energy storage materials, including at synchrotron facilities.

Objectives for promoting the doctoral student's research work: dissemination, publication and confidentiality, IP rights.

Participation in national and international conferences. Publication of results in peer-reviewed journals. Possible patent filing on pertinent results.

Profile and skills required

The PhD candidate should have a strong interest for experimental research and teamwork. Previous research experience in synthetic chemistry of inorganic materials, crystallography and/or electrochemistry is ideal, but any other experience in material science that might seem valuable to this project should be put forward during the application.

This project will involve multiple characterization techniques, calling for good communication within the team and with collaborators to understand and master the techniques used. A good English level is required, both written and oral, as publications of results in scientific journals and participations to international conferences is expected.

Bibliography

(1) Schnell, J.; Günther, T.; Knoche, T.; Vieider, C.; Köhler, L.; Just, A.; Keller, M.; Passerini, S.; Reinhart, G. All-Solid-State Lithium-Ion and Lithium Metal Batteries – Paving the Way to Large-Scale Production. *Journal of Power Sources* **2018**, *382*, 160–175. https://doi.org/10.1016/j.jpowsour.2018.02.062.

(2) Hanghofer, I.; Gadermaier, B.; Wilkening, H. M. R. Fast Rotational Dynamics in Argyrodite-Type Li_6PS_5X (X: Cl, Br, I) as Seen by ^{31}P Nuclear Magnetic Relaxation—On Cation–Anion Coupled Transport in Thiophosphates. *Chem. Mater.* **2019**, *31* (12), 4591–4597. https://doi.org/10.1021/acs.chemmater.9b01435.

(3) Famprikis, T.; Dawson, J. A.; Fauth, F.; Clemens, O.; Suard, E.; Fleutot, B.; Courty, M.; Chotard, J.-N.; Islam, M. S.; Masquelier, C. A New Superionic Plastic Polymorph of the Na^+ Conductor Na_3PS_4. *ACS Materials Lett.* **2019**, *1* (6), 641–646. https://doi.org/10.1021/acsmaterialslett.9b00322.

(4) Skripov, A. V.; Skoryunov, R. V.; Soloninin, A. V.; Babanova, O. A.; Tang, W. S.; Stavila, V.; Udovic, T. J. Anion Reorientations and Cation Diffusion in $LiCB_{11}H_{12}$ and $NaCB_{11}H_{12}$: ^{1}H, ^{7}Li, and ^{23}Na NMR Studies. *J. Phys. Chem. C* **2015**, *119* (48), 26912–26918. https://doi.org/10.1021/acs.jpcc.5b10055.

(5) Tang, W. S.; Yoshida, K.; Soloninin, A. V.; Skoryunov, R. V.; Babanova, O. A.; Skripov, A. V.; Dimitrievska, M.; Stavila, V.; Orimo, S.; Udovic, T. J. Stabilizing Superionic-Conducting Structures via Mixed-Anion Solid Solutions of Monocarba-Closo-Borate Salts. *ACS Energy Lett.* **2016**, *1* (4), 659–664. https://doi.org/10.1021/acsenergylett.6b00310.

(6) Sun, Y.; Wang, Y.; Liang, X.; Xia, Y.; Peng, L.; Jia, H.; Li, H.; Bai, L.; Feng, J.; Jiang, H.; Xie, J. Rotational Cluster Anion Enabling Superionic Conductivity in Sodium-Rich Antiperovskite Na_3OBH_4. *J. Am. Chem. Soc.* **2019**, *141* (14), 5640–5644. https://doi.org/10.1021/jacs.9b01746.

(7) Ding, J.; Gupta, M. K.; Rosenbach, C.; Lin, H.-M.; Osti, N. C.; Abernathy, D. L.; Zeier, W. G.; Delaire, O. Liquid-like Dynamics in a Solid-State Lithium Electrolyte. *Nat. Phys.* **2025**, 1–8. https://doi.org/10.1038/s41567-024-02707-6.

(8) Zhang, Z.; Li, H.; Kaup, K.; Zhou, L.; Roy, P.-N.; Nazar, L. F. Targeting Superionic Conductivity by Turning on Anion Rotation at Room Temperature in Fast Ion Conductors. *Matter* **2020**, *2* (6), 1667–1684. https://doi.org/10.1016/j.matt.2020.04.027.

(9) Zhang, Z.; Roy, P.-N.; Li, H.; Avdeev, M.; Nazar, L. F. Coupled Cation–Anion Dynamics Enhances Cation Mobility in Room-Temperature Superionic Solid-State Electrolytes. *J. Am. Chem. Soc.* **2019**, *141* (49), 19360–19372. https://doi.org/10.1021/jacs.9b09343.