Predicting Crystal Structures and Ionic Conductivity in Mixed-Halide Solid Electrolytes Using Machine Learning Potentials

Aurélie CHAMPAGNE[1,2]
[1]CNRS-ICMCB, Bordeaux France
[2]Lawrence Berkeley National Lab, Berkeley, USA

aurelie.champagne@icmcb.cnrs.fr
achampagne@lbl.gov

Machine learning interatomic potentials (MLPs) have revolutionized computational materials modeling by enabling accurate simulations at length and time scales far exceeding the reach of traditional *ab initio* methods [1-2]. Coupled with advances in computational resources, this progress allows for the investigation of more realistic and complex systems, such as components in next-generation batteries.

The growing demand for safer and higher-performance lithium-ion (Li-ion) batteries has driven the search for solid-state alternatives to flammable liquid electrolytes. Among these, Li-containing ternary halides, particularly Li_3MX_6 (M = trivalent metal, X = Cl, Br), have attracted significant attention due to their high room-temperature ionic conductivities and robust oxidative stability, which makes them compatible with oxide-based cathode materials [3]. These materials exhibit diverse crystal structures - typically trigonal, orthorhombic, and monoclinic - with their stability and ionic conductivity strongly influenced by the specific elemental composition and crystal symmetry [4-5].

I will present new insights into the composition-structure-property relationships in halide solid electrolytes (SEs) for all-solid-state Li-ion batteries. I will demonstrate how variations in cation and anion chemistry affect the stability of crystal structures, offering strategies to enhance ionic conductivity. A key challenge arises from the partial occupations of specific Wyckoff sites within the structures (random vacancy distribution and solid solutions), leading to over 50,000 symmetry-inequivalent atomic arrangements for some compositions. To address this complexity, I employ MLP-based simulations [6-7] to efficiently estimate formation energies, rank inequivalent configurations, and subsequently conduct molecular dynamics simulations to probe ionic transport properties.

These findings provide valuable guidance for the rational design of high conductivity halide SEs, leveraging compositional and structural tuning to optimize performance.

References

1. V. L. Derringer, M. A. Caro, G. Csanyi, *Adv. Mater.* **31** (2019) 1902765.
2. T. Mueller, A. Hernandez, C. Wang, *J. Chem. Phys.* **153** (2020) 050902.
3. T. Asano, A. Sakai, S. Ouchi, M. Sakaida, A. Miyasaki, S. Hasegawa, *Adv. Mater.* **30** (2018) 1803075.
4. E. Van der Maas, W. Zhao, Z. Cheng, T. Famprikis, M. Thijs, S. R. Parnell, S. Ganapathy, M. Wagemaker, *J. Phys. Chem. C* **127** (2023) 125-132.
5. X. Li, J. T. Kim, J. Luo, C. Zhao, Y. Xu, T. Mei, R. Li, J. Liang, X. Sun, *Nature Comm.* **15** (2024) 53.
6. C. Chen, S. P. Ong, *Nature Comput. Sci.* **2** (2022) 718-728.
7. B. Deng, P. Zhong, K. Jun, J. Riebesell, K. Han, C. J. Bartel, G. Ceder, *Nature Machine Intell.* **5** (2023) 1031-1041.