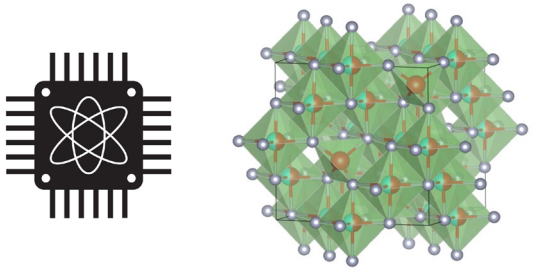
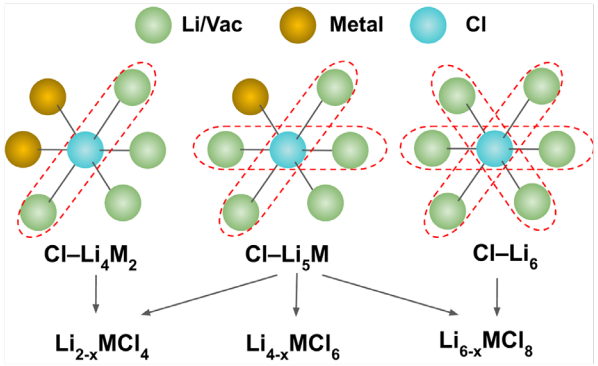




Modeling of Solid-State Conductors

Principal investigator: Gerbrand Ceder
Lawrence Berkeley National Laboratory

2026

Project ID: bat054

Computing support on Kestrel and Swift

Overview

Timeline

- Start date: October 2021
- End date: September 2026
- Percent complete: 90%

Budget

- Total project funding
  - -- FY21 $460,000
  - -- FY22 $460,000
  - -- FY23 $400,000
  - -- FY26 $250,000

Barriers Addressed

- Energy density
- Cycle life
- Cost
- Safety

Partners

- none

Relevance/Objectives

Impact:

- To successfully develop solid-state batteries with high energy density, we need conductors that have **high Li conductivity** and **electrochemical stability** with Li metal anodes
- Superionic conductors tend to be **metastable** – need to understand the thermodynamics and develop rational strategies to stabilize them
- **Halide and oxyhalides** are an emerging class of superionic conductors with good potential to function as catholytes
- **Need** to understand and design better halide Li-ion conductors using less expensive metals

Objectives:

- Understand the fundamental mechanisms by which high Li conductivity can be achieved in solids
- Quantitatively analyze thermodynamic phase stability to rationalize metastability and synthesis procedures
- Uncover new structural classes of halide superionic conductors keeping in mind metals cost and availability
- Create halide conductors with electrochemical activity

Milestones

Date	Milestones	Status
December 2025	Evaluate and compare the Na conductivity of amorphous and crystalline oxyhalides	Completed
March 2026	Evaluate class of inverse spinels as inexpensive Li-ion conductors	Completed
June 2026	Model electrochemical activity of transition metal-doped halides	Completed
September 2026	Synthesize electrochemically active Na/Li halide as catholyte	In progress

Approach

= AI-infused

Combination of **ab-initio calculations, machine learning** and **experiments** to discover and rationalize mechanisms of novel superionic conductors

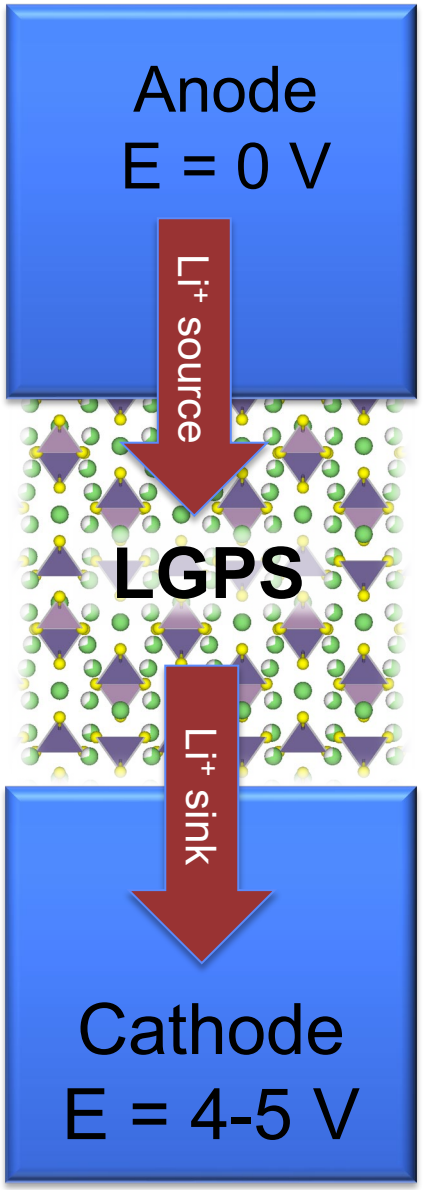
Modeling

- DFT: phase stability and electronic structure at 0 K
  - High-throughput screening to identify low-energy compositions + structures
- High-throughput computational screening
- *Ab initio* molecular dynamics (AIMD) simulations – ion transport kinetics and mechanisms
- Accelerated simulations using machine-learned interatomic potentials (MLIP)

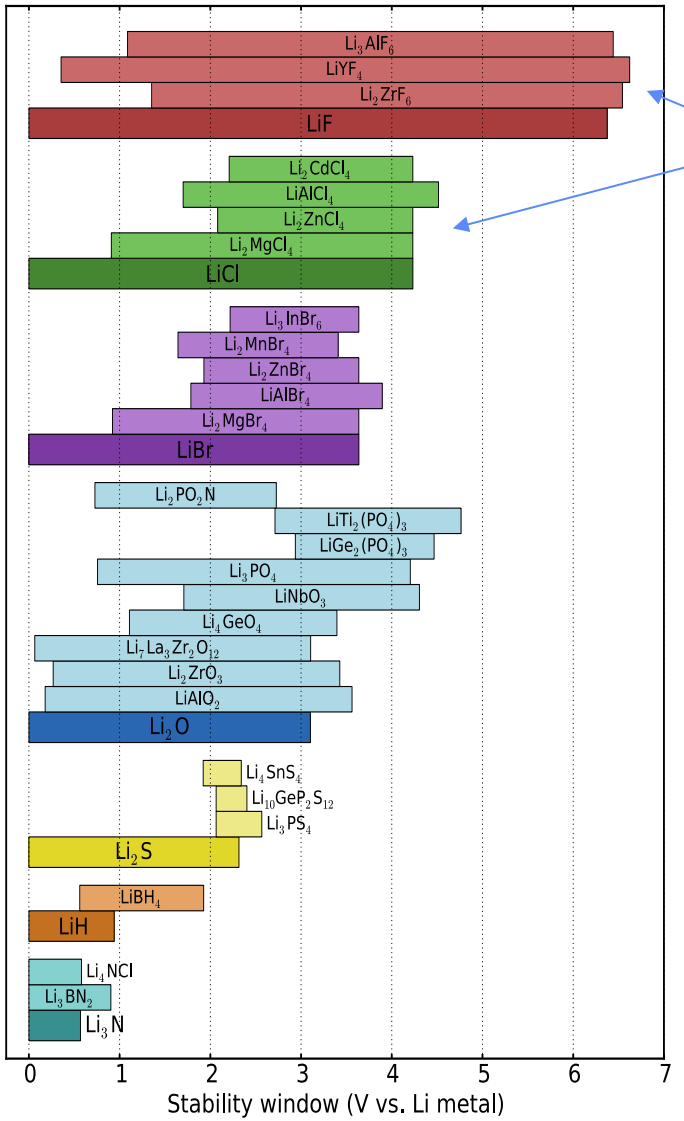
Experiments

- Solid-state synthesis, mechanochemical techniques to stabilize metastable phases
- Electrochemical measurements of Li conductivity, voltage stability window.
- Impedance spectroscopy

Oxy-Halide Catholytes: 2016 prediction

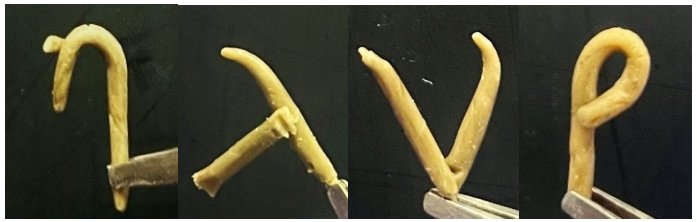


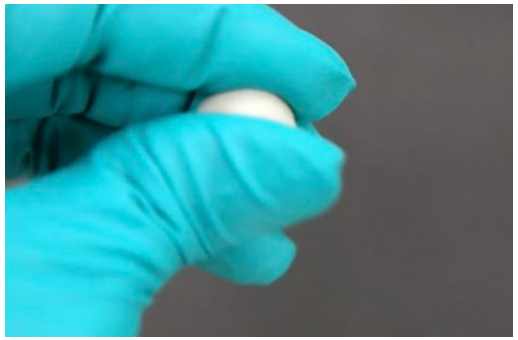
Predicted stability window



Halide SEs have some of the **highest anodic stabilities**

Halide SEs feature wide electrochemical stability window and **mechanical deformability.**





W. Richards, GC et al, Chem. Mater. (2016)

Inverse Spinels (Li_2MCl_4):
Investigate Li-conduction mechanism and produce optimized composition

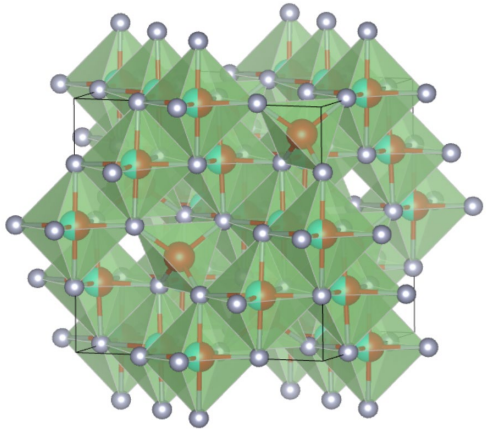
Earth Abundance Problem

Many good Li-ion conducting halides contain very rare and expensive metals

Li_3YCl_6 Li_3InCl_6 $LiMOCl_4$ (M = Ta, Nb)

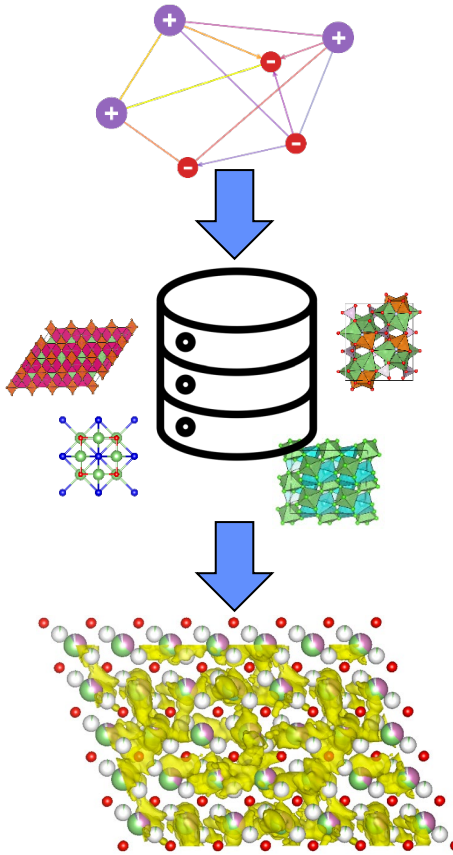
Li_3ErCl_6 Li_3ScCl_6

Reinvestigate inverse-spinel based systems based on Mg



Li_2MgCl_4 inverse spinel

Modeling



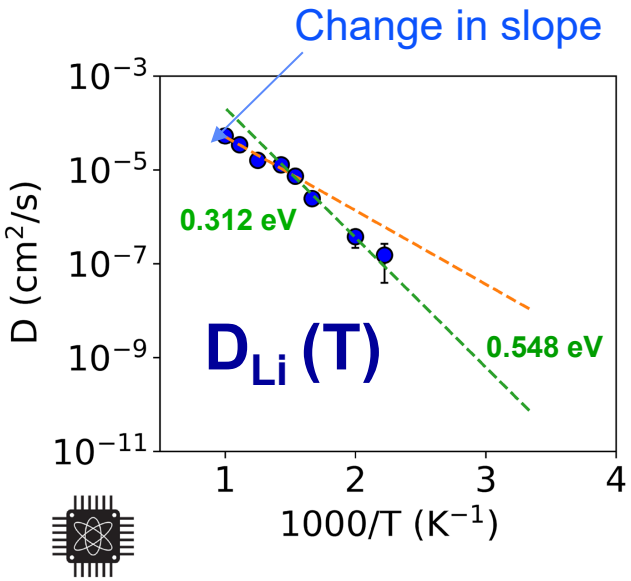
CHGNet

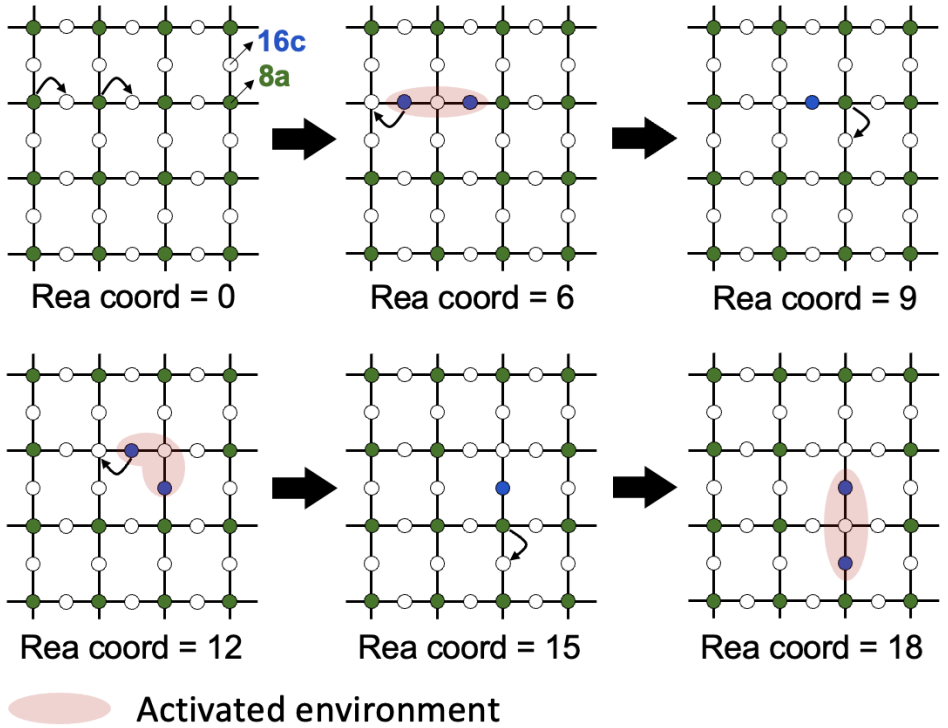
Machine Learning Potential developed for electrochemistry (Deng Ceder et al 2023)

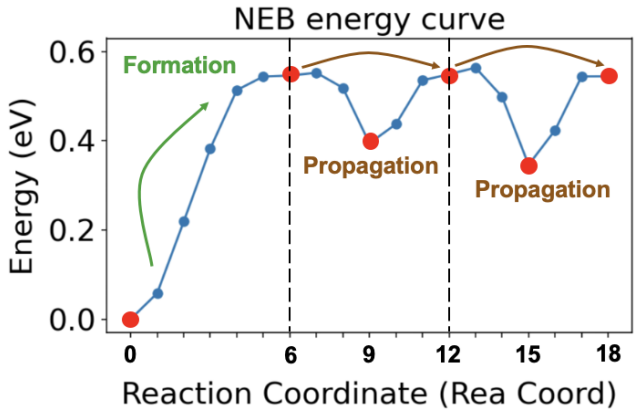
Fine-tune on 25,000 DFT modelled halide structures

Molecular Dynamics Modeling

Inverse Spinels: Results on Li_2MgCl_4





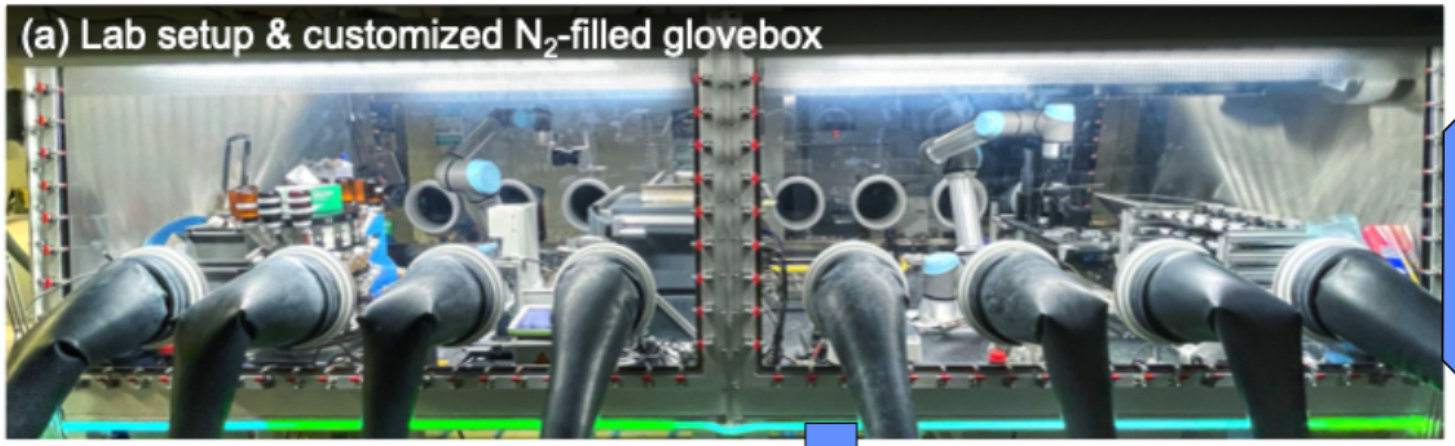


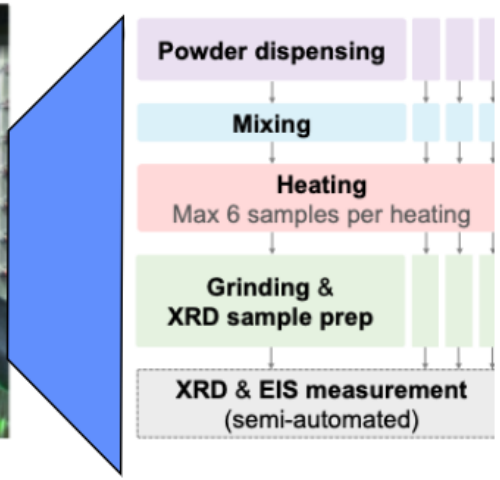
- Modeling shows change of activation energy with T, in agreement with experiment

- The formation of the activated environment is the origin of the low-temperature activation energy.
- The face-sharing configuration imposes a major energetic cost for the low-temperature diffusion.

Need disorder to extrapolate high-T regime to room temperature

Agentic Autonomous Lab Campaign: Increase Conductivity in Inverse Spinels

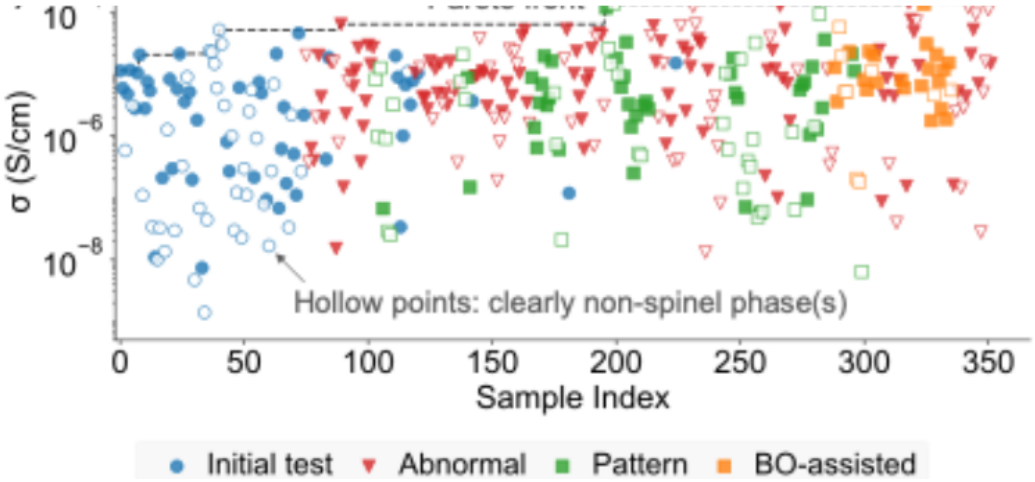




- Agentic AI fully drives the lab
- Multiple competing AI (LLM) systems to generate and very hypothesis
- > 350 autonomous experiments

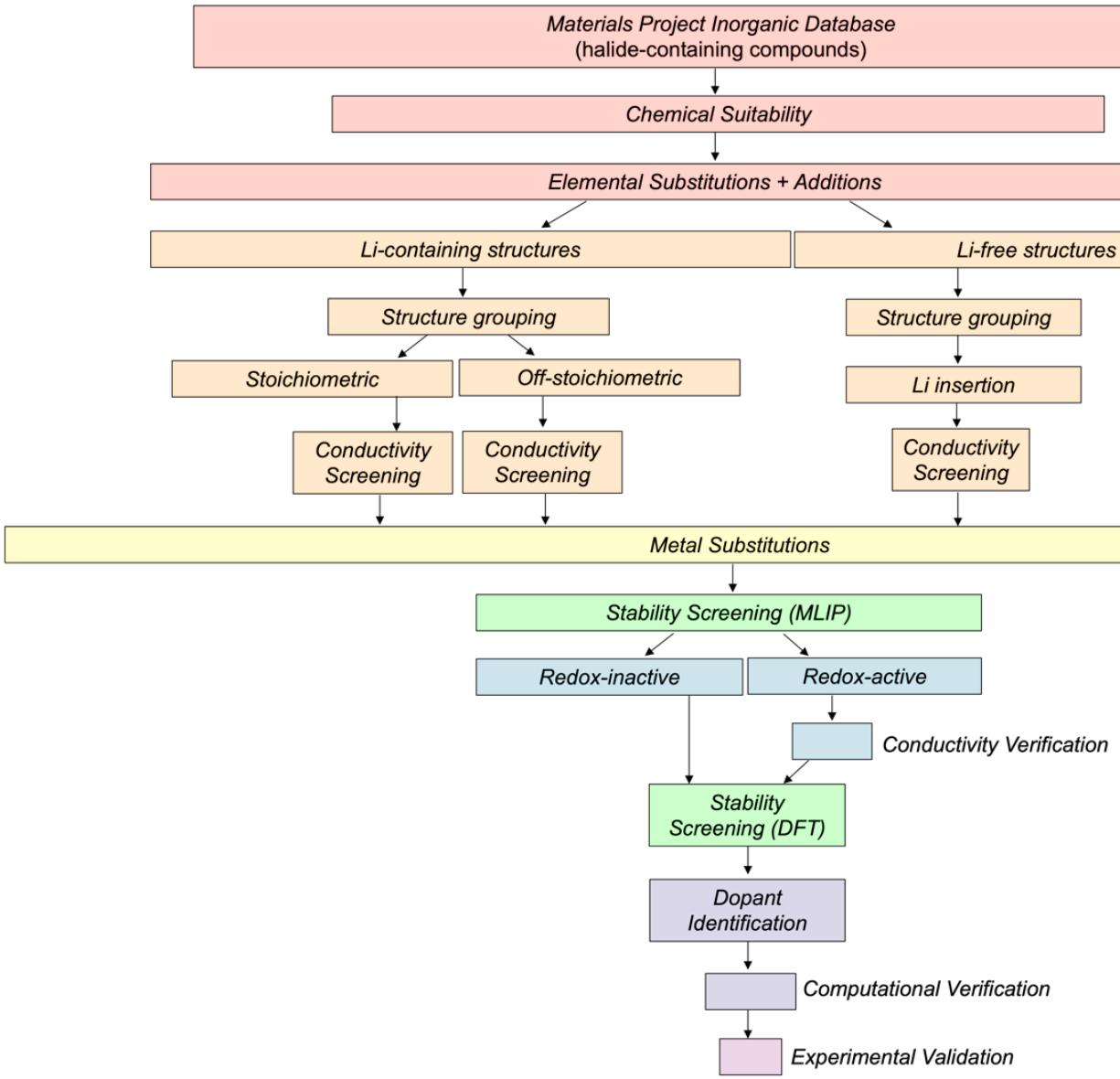
- Fully automated laboratory for the synthesis and testing of Li-halide materials in glovebox
- Agentic campaign using multiple expert LLM systems used to drive optimization in A-lab

Evolution of conductivity over an AI-driven experimental campaign, spanning 56 days and 350 samples



VTO computing support on Kestrel and Swift
Collaboration with ESRA on building of autonomous system

Technical Accomplishment: Developed High-Throughput Modeling Pipeline for Finding Novel Li-halide conductors



❑ Pool of Candidates

❑ Conductivity screening
- Framework-based
- Enabled with MLIP

❑ Metal substitutions
- Which metals can the framework host?

❑ Stability screening
- CHGNet → DFT GGA
- E_{hull} and E_{elem}

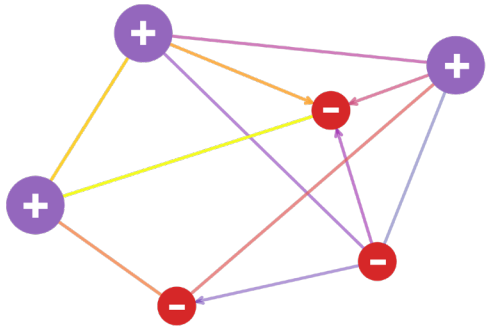
❑ Experimental validation in progress with A-lab

Collaboration with KyuJungJun and Bowen Deng (MIT)

Early identification of high-conducting halide prototypes

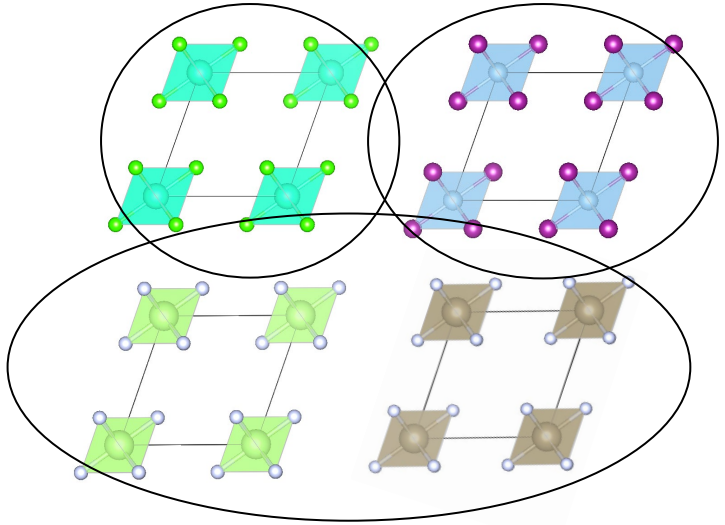
Fine-tuning CHGNet for Halides

25k DFT-D3 snapshots



CHGNet-halide	
Energy MAE	11 meV/atom
Force MAE	97 meV/Å
Stress MAE	0.184 GPa

Framework grouping



3,837 Li-containing groups
6,073 Li-free groups

CHGNet MD Screening

- Add Li to Li-free structures
- Consider Li-deficient and Li-excess

Conductivity Screening
(CHGNet MD)

900K 100ps
(> 300 mS/cm)

600K 100ps
(> 100 mS/cm)

Metal substitutions

Refining search to find compounds that are likely to be synthesized

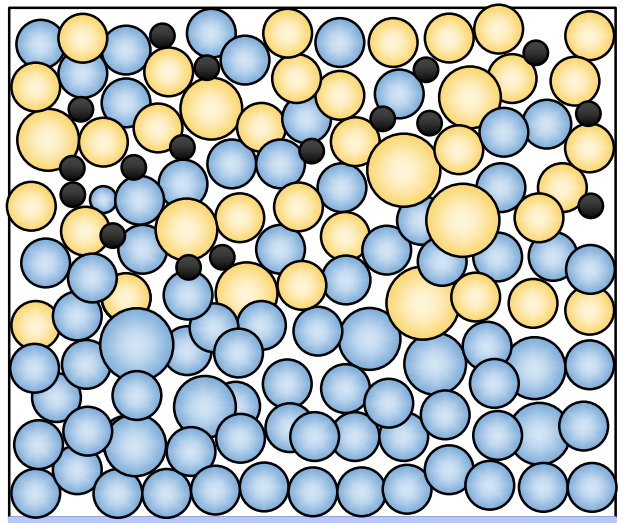
VTO computing support on Kestrel and Swift

Collaboration with KyuJungJun and Bowen Deng (MIT)

Technical Accomplishment: Novel Search for Electrochemically Redox-Active Li-ion Conductors as Catholytes (eREAL)

Problem

Solid state composite cathodes have a large volume fraction of inactive materials (> 40%)



Li metal anode

Solution

Can we make the solid-state catholyte electrochemically active while preserving good ionic conductivity?

eREAL concept:
electrochemically **Re**dox-**A**ctive **H**alides

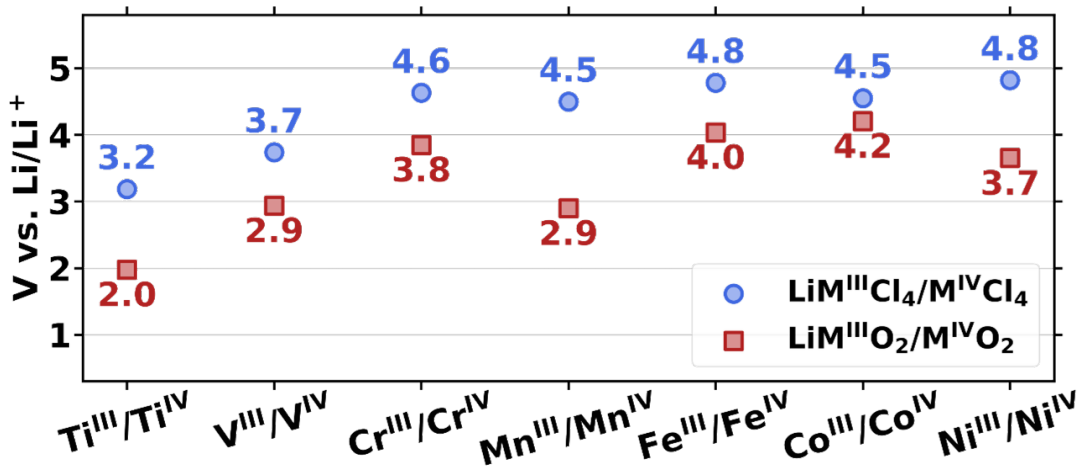
Challenges

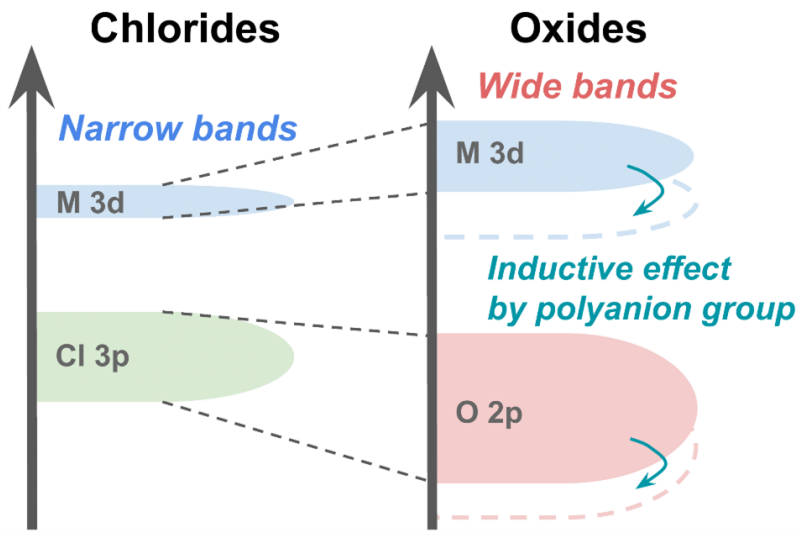
- Voltage matching of of eREAL and cathode
- Interfacial Stability with cathode
- Electrochemical stability over cathode voltage range
- eREAL needs to provide electronic and ionic conductivity over its Li-intercalation range

Initiated Modeling Study to Understand Challenges with eREAL concept

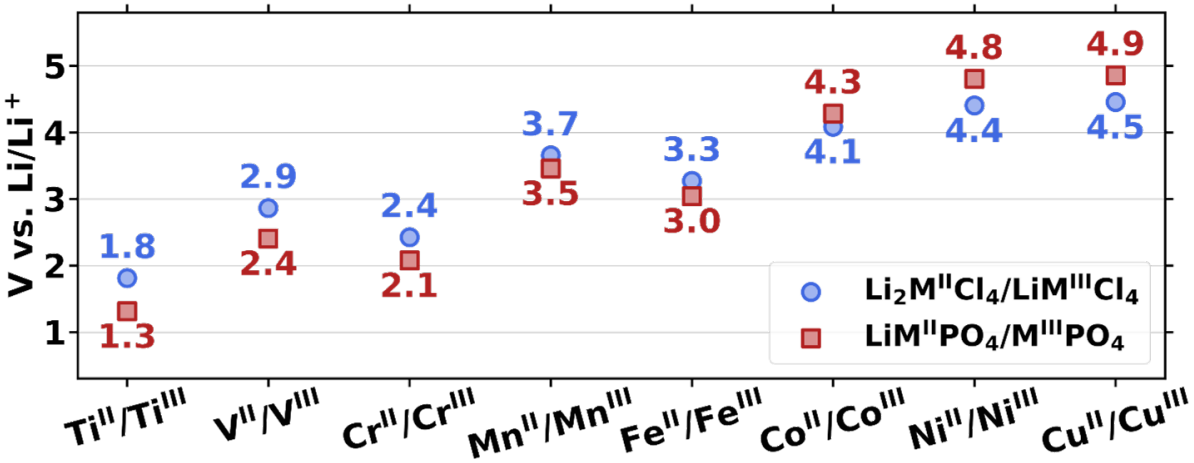
Technical Accomplishment: Determined redox voltages in chlorides

Chlorides vs. layered oxides, M^{3+}/M^{4+} voltages





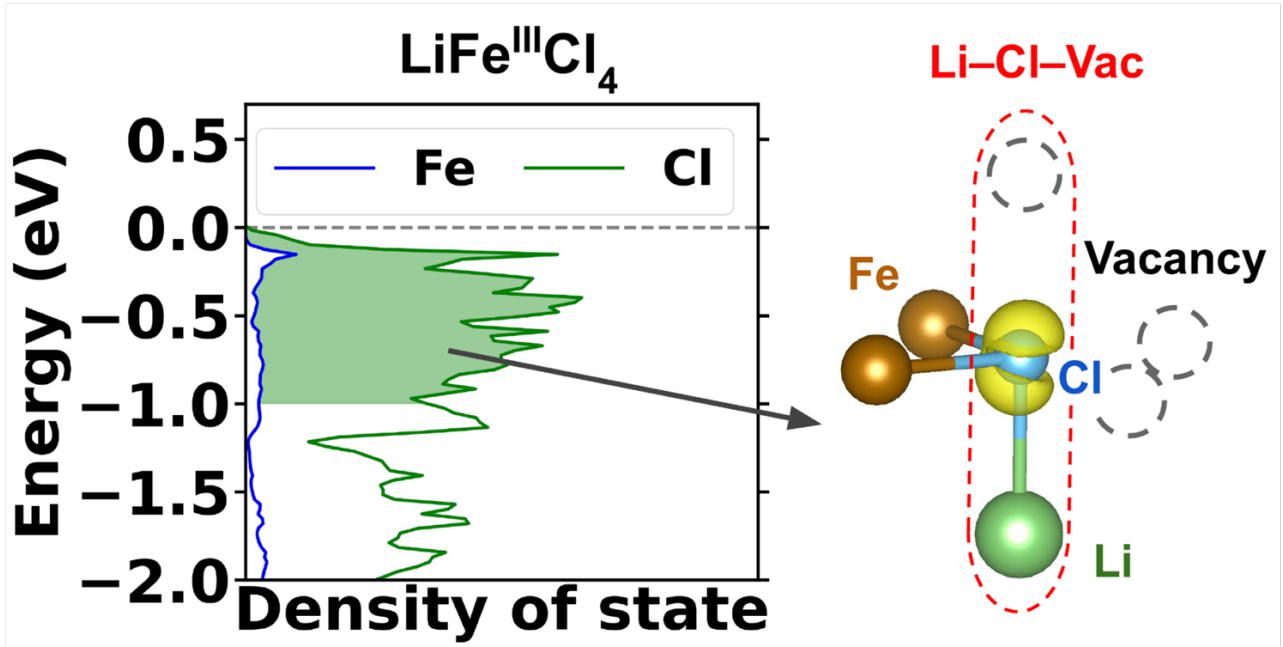
Chlorides vs. olivine, M^{2+}/M^{3+} voltages

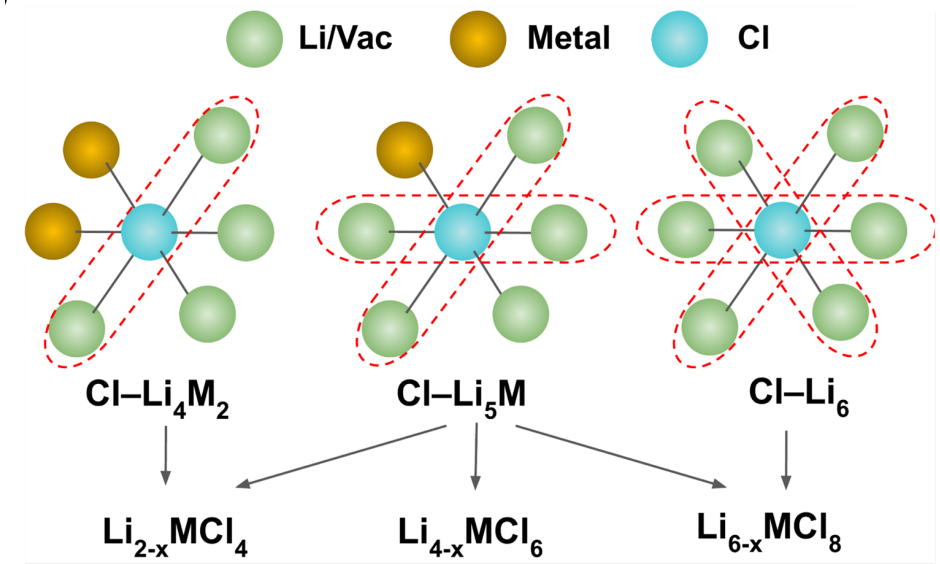


- Redox voltages in chlorides are considerably higher than in layered oxides and similar or higher than those in phosphates
- M–Cl bonds are more ionic than M–O bonds, leading to less metal d–anion p orbital hybridization.
- High redox voltage of transition metals will interfere with Cl oxidation potential (next slide)

VTO computing support on Kestrel and Swift

Technical Accomplishment: Controlling Cl- oxidation will be challenging





- Electronic density of state shows that the top of valence band corresponds to orphaned Cl 3p orbitals along the linear Li–Cl–Vacancy motifs.
- **The Cl orbitals along these Li/Vac–Cl–Li/Vac linear motifs have little protection from hybridization**.
- At typical oxide cathode voltages (e.g NMC) Cl^- oxidation may occur)

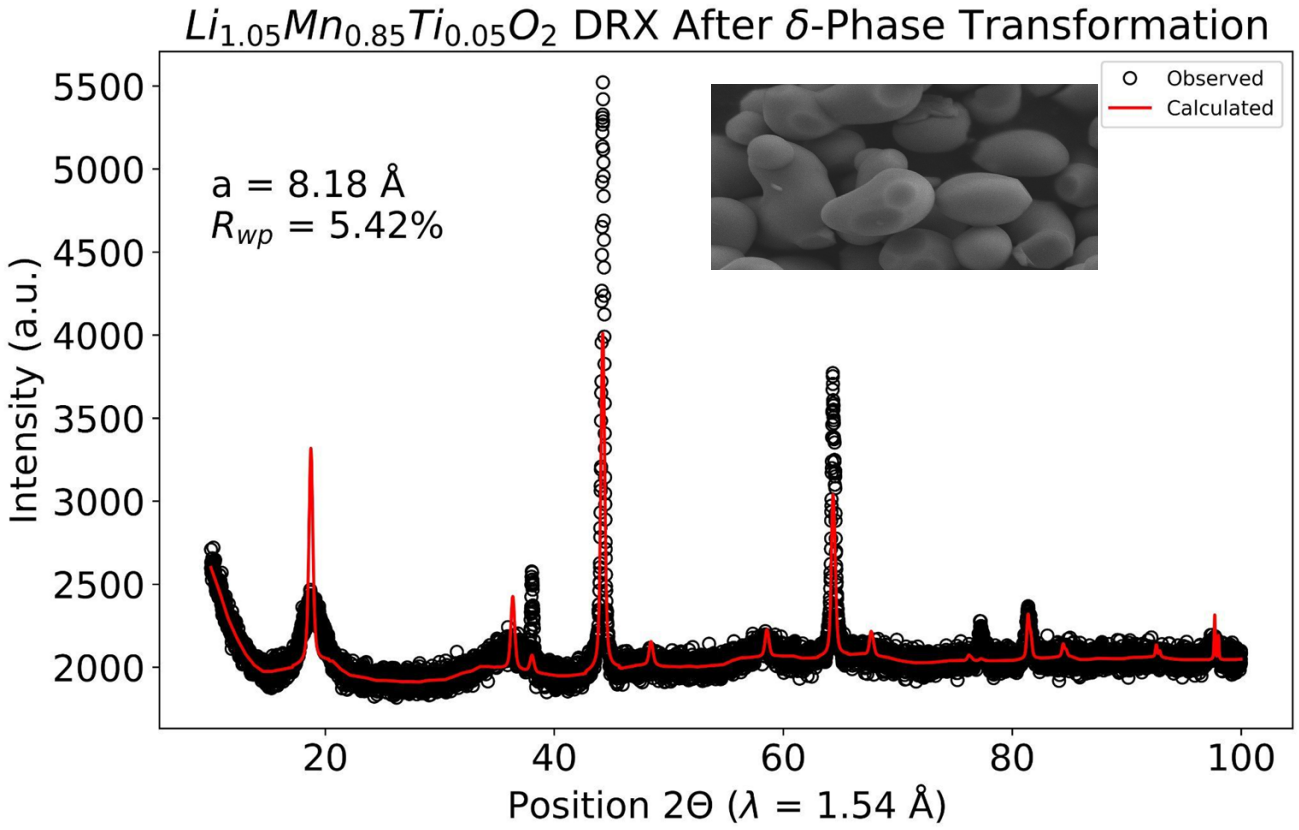
VTO computing support on Kestrel and Swift

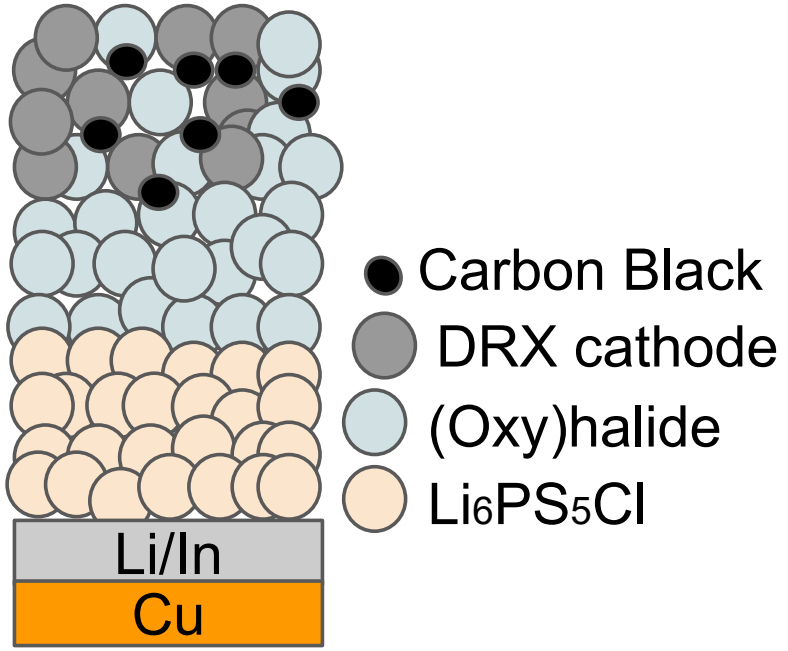
Technical Accomplishment: Integrated DRX cathode with solid-state halide electrolyte (collaboration with DRX consortium)

δ- DRX
- Molten-salt synthesis at 1100C
- Partially ordered spinel domain (**δ** phase)

(Oxy)halide
- $LiTaOCl_4$
- Li_3InCl_6

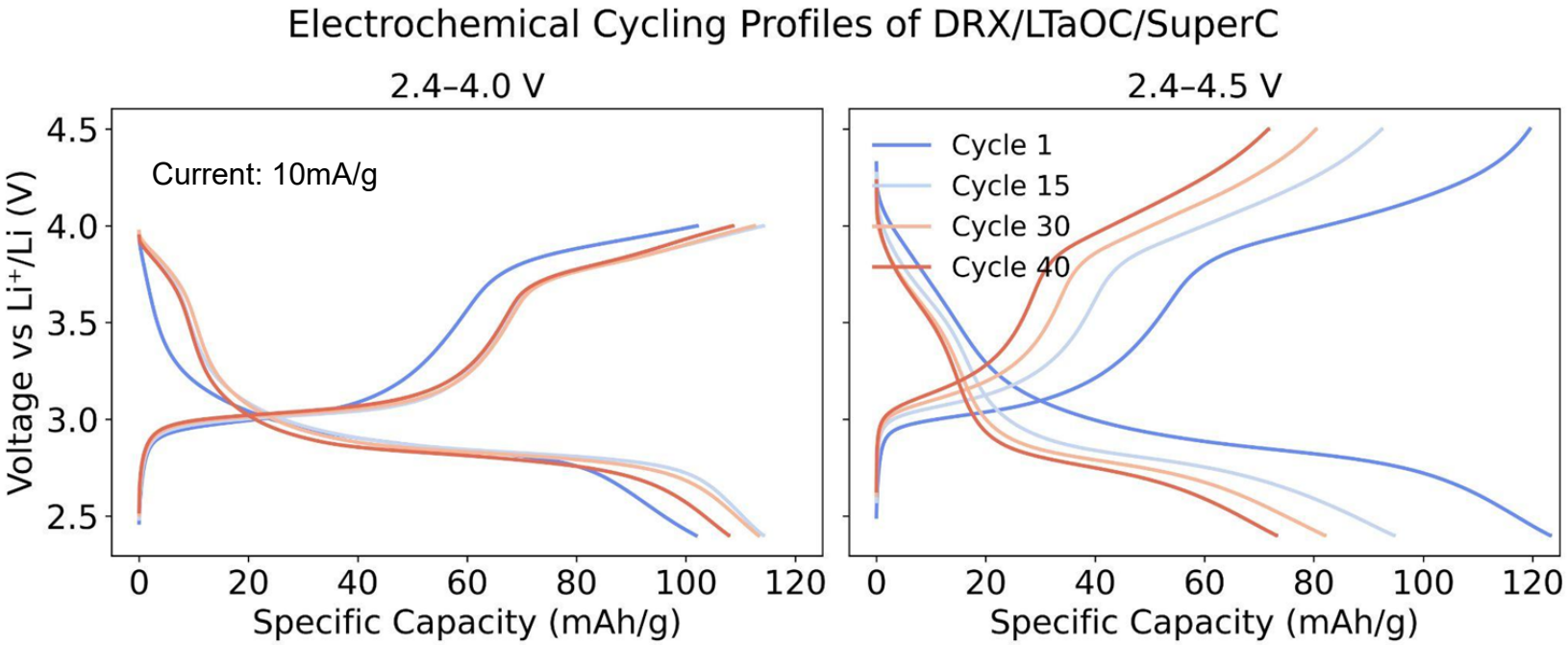
ASSB Design with a Bilayer Structure
- Catholyte (DRX+ (oxy)halide + C)
- (oxy)halide
- Li6PS5Cl argyrodite

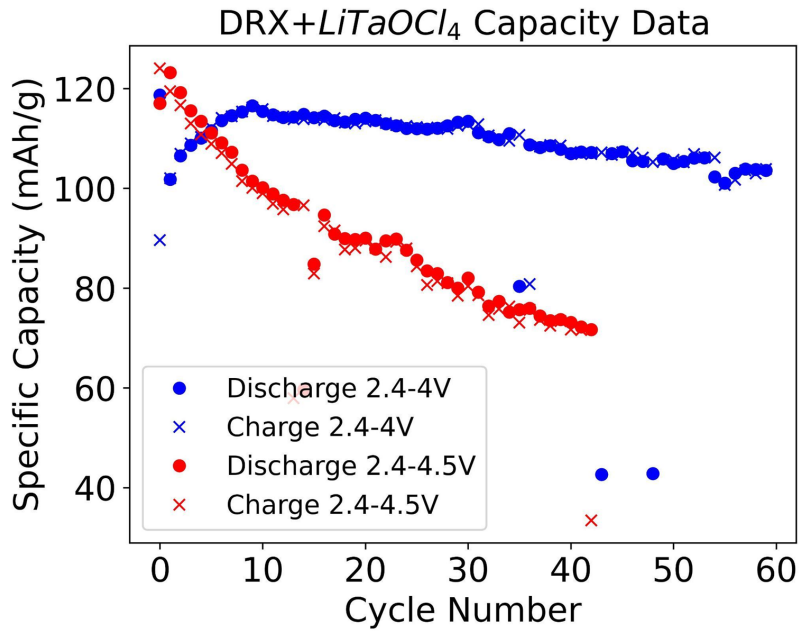




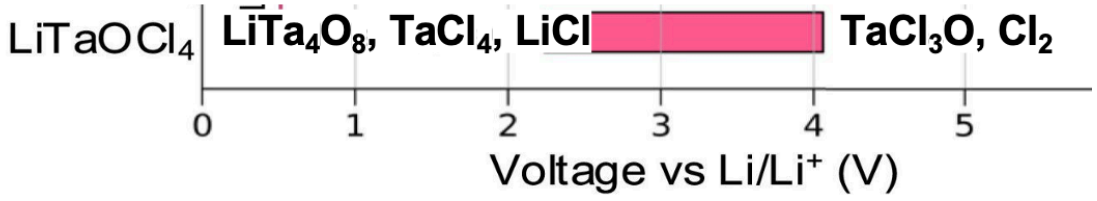
Collaboration with DRX consortium

Technical Accomplishment: Integrated DRX cathode with solid-state halide electrolyte (collaboration with DRX consortium)





Computed Electrochemical Stability



- DRX cycles well with $LiTaOCl_4$ as catholyte when voltage is limited to 4.4V
- Rapid capacity fade is observed when cycling to 4.5V, consistent with the predicted oxidation limit

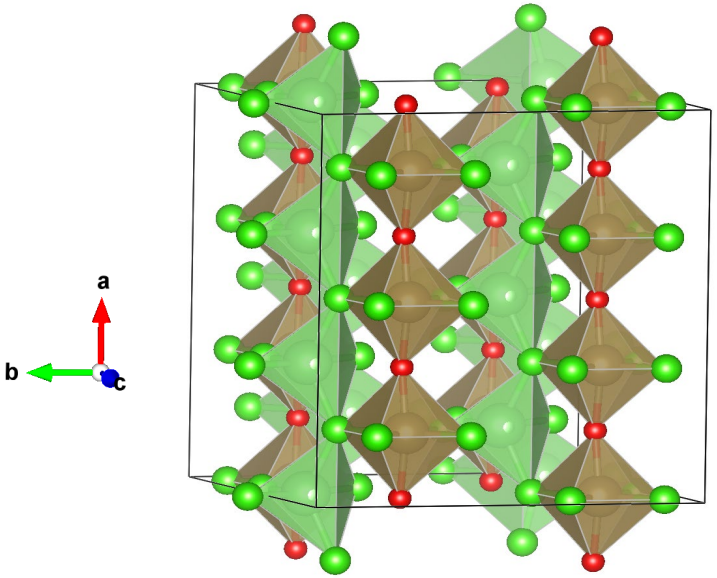
*Jun, K., Wei, G., Yang, X., Chen, Y. & Ceder, G. Matter **8**, 102001 (2025).*

Collaboration with DRX consortium

Technical accomplishment: Computational exploration of crystalline and amorphous oxyhalide SEs

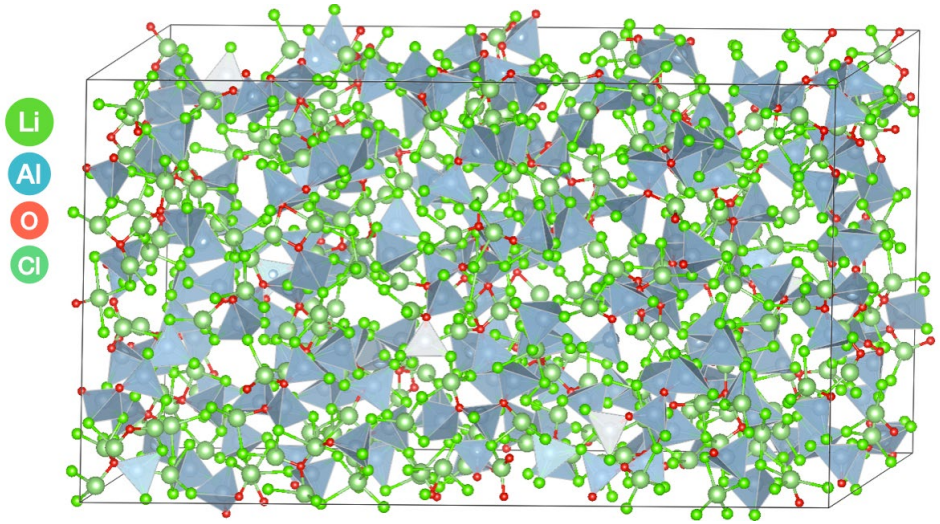
Crystalline *non-close-packed conductor*

$LiMOCl_4$, M = $(Nb/Ta)^{5+}$



σ_{RT}= 12.4 mS/cm (M = Ta)
E_a= 0.23 eV

Investigated many amorphous compositions with modeling (over 1000 atoms for 5 ns)



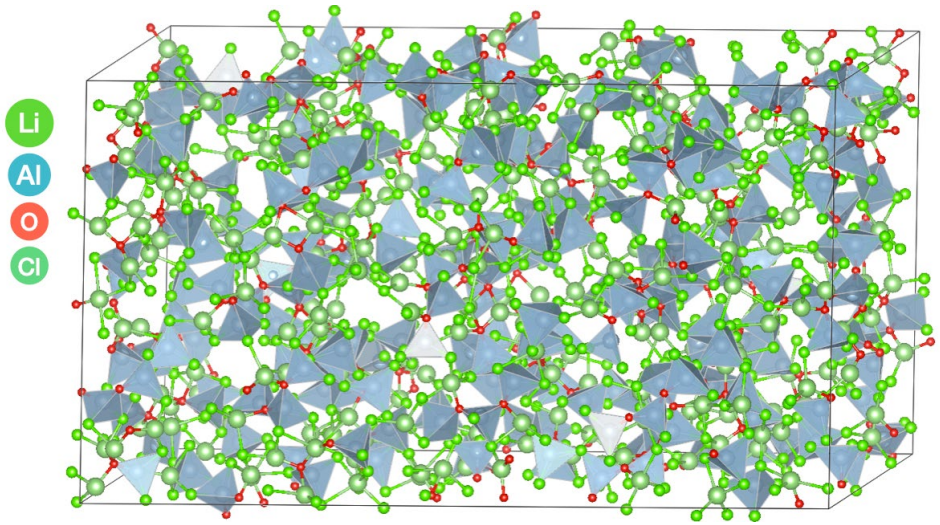
Amorphous $AMX_{2.5}O_{0.75}$ compounds were simulated for long timescales using a combination of active learning and neural network machine-learning potentials

Y. Tanaka et al., Angewante Chemie, 2023.

VTO computing support on Kestrel and Swift

Technical accomplishment: Computational exploration of crystalline and amorphous oxyhalide SEs

Investigated many amorphous compositions with modeling (over 1000 atoms for 5 ns)



Amorphous $AMX_{2.5}O_{0.75}$ compounds were simulated for long timescales using a combination of active learning and neural network machine-learning potentials

Computed conductivity in amorphous oxychlorides

Agreement with experiment is good

Material	σ(300K) (mS/cm)	Error (mS/cm)
$LiAlCl_{2.5}O_{0.75}$	0.93 (exp: 1.5-0.79)	0.25
$NaAlCl_{2.5}O_{0.75}$	1.26 (exp: 1.33-0.14)	0.21
$KAlCl_{2.5}O_{0.75}$	1.17	0.29
$LiGaCl_{2.5}O_{0.75}$	0.81	0.21
$LiInCl_{2.5}O_{0.75}$	1.01	0.29
$LiAlBr_{2.5}O_{0.75}$	1.63	0.43
$LiAlI_{2.5}O_{0.75}$	1.54	0.36

- Regardless of chemistry, all amorphous systems demonstrate a consistent conductivity of ~ 1 mS/cm.
- Metal seems mostly important in determining amorphous structure

Responses to Previous Year Reviewers' Comments

- Reviewers gave overall positive comments about the project, describing it as well design with a good approach. Some comments were made about the Overview slide missing, and regarding the challenge of experimental validation of novel materials and the testing of catholyte in an actual composite cathode

- We have added the Overview slide back
- In response to the comments we have initiated evaluation of several chloride catholyte materials with DRX cathodes (in collaboration with the DRX consortium). Initial results are added in this presentation
- We are also initiating a collaboration with Dr Chen at LBNL for testing in full solid-state cells
- We are aware of the challenge in synthesizing and testing novel materials. This is a broad and ongoing challenge for the field. We are planning to address this with a more fundamental focus on the synthesizability of halides

Collaborators

- **Massachusetts Institute of Technology**: Dr. KyuJung Jun, Dr. Bowen Deng
- **Lawrence Berkeley National Laboratory**: Dr. Yu Chen, Dr. Livia Puggens Matte, Dr. Tara Mishra, Professor Kristin Persson, Dr. Anubhav Jain, Dr. Guoying Chen
- **University of California, Berkeley**: Dr. Shuoyan Xiong
- **National Center for Electron Microscopy** –LBNL: Jiana Zhen, John Turner, Rohan Dhall
- **University of Utah**: Professor Huiwen Ji
- **University of Sydney**: Professor Maxim Avdeev
- **DRX consortium** (DOE)
- **Umicore Specialty Materials**:

Publications

Jun, K., Wei, G., Yang, X., Chen, Y. & Ceder, G. Exploring the soft cradle effect and ionic transport mechanisms in the $LiMXCl_4$ superionic conductor family. Matter 8, 102001 (2025).

Wei G.; Binci L.; Ceder G.; Microscopic Mechanisms of Superionic Na-ion Conductivity in Crystalline and Amorphous $NaMOCl_4$ (M = Nb, Ta) Solid Electrolytes. *ACS Energy Lett.* **2026**, 11 (2), 1861–1870

Presentations

G. Ceder. Ionic Conduction Mechanisms in Halides and Oxy-Halides, Pacific Chem Meeting, Dec 17 2025

G. Ceder. From Modeling to Viable Materials, ENSM Award Lecture (virtual) – Oct 2025.

G. Ceder. Ionic Conduction Mechanisms in Halides and Oxy-Halides, ICMAT, July 1, Singapore

G. Ceder. Modeling of Solid State Conductors, AMR meeting, June 1, Washington DC

Remaining Challenges and Barriers

- Synthesis of novel predicted materials can be challenging. There is no exact criterion for determining whether a modelled material can be synthesized.
- We need scalable approaches to introduce disorder at low T in inverse spinel materials such as Li_2MgCl_4
- While Electrochemically Redox Active Halides are an exciting novel concept, their voltage and chemical compatibility with typical oxide cathodes still needs to be verified.

Proposed Future Directions

We plan to more extensively focus on three areas:

1) Establish better guidelines for which novel halides can be **synthesized**, thereby making the computational discovery process more efficient. This will be done by making extensive use of **A-lab-GPSS** which is the **autonomous synthesis and testing lab** completely enclosed in a glove box.

2) Continue **to investigate computationally the properties of electrochemically active halide conductors** and evaluate their compatibility with oxide cathodes, through both modeling and experiments. If successful, this concept can increase cathode energy density by 20-40%.

3) Continue to use modeling to **understand the mechanism of Li transport** in known ionic conductors in order to suggest improvements and more optimized materials.

Summary

- We are pursuing multiple **pathways to increase energy density** in solid-state system, through an approach that emphasizes **fundamental insights** and **computational** and **AI-guided** research, combined with **experimental verification and autonomous laboratories**
- We consider **earth abundance** and lower cost elements as an important design guideline for new materials.
- We identified the relevant and critical Li conduction mechanism in **inverse halide spinels**
- We demonstrated the use of **agentic-AI and an autonomous laboratory** in a campaign to synthesize and optimize novel Li-conducting halide spinels.
- We computationally evaluated the voltage of different transition metals in potentially **electrochemically active halide conductors**. We find that the voltages are higher than for the same redox couple in oxides. The high voltage may compete with Cl^- oxidation, which could present challenges for stability of the materials when high voltage cathodes are used.
- We demonstrated the **integration of a DRX cathode with a halide catholyte** into a composite cathode