Predictive Engineering of Interfaces and Cathodes for High Performance All Solid-State Lithium-Sulfur Batteries

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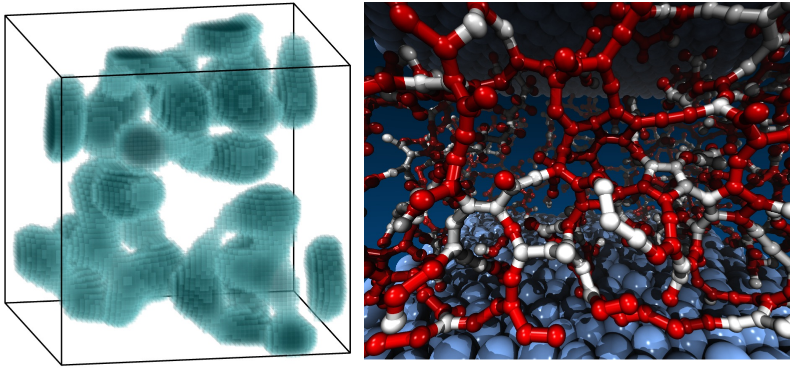
University of Louisville, Kentucky



Project ID: BAT491

June 24, 2021

2021 DOE Vehicle Technologies Office Annual Merit Review

Overview

TIMELINE

- **Start date:** October 1, 2019
- **Project End date:** September 30, 2022
- **Percent complete:** 50%

BARRIERS

High energy density battery chemistry beyond Li-ion (Solid-state lithium-sulfur)

- Need novel solid-state electrolytes with fast ion conduction and stability against lithium
- Interfacial issues at the anode and cathode
- Low cycle life and loss of capacity

BUDGET

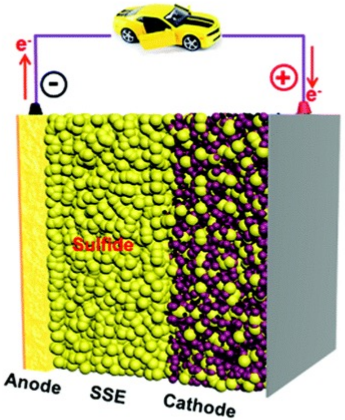
- **Total Project Funding**
  - DOE Share: $1 M / 3years
  - Contractor Share: $0.25 M / 3 years
- **FY 2020 Funding:** $303,137
- **FY 2021 Funding:** $353,703

PARTNERS

- **Interactions/Collaborations**
  - Hui Wang (U. Louisville, Co-PI)
  - Gamini Sumanasekera (U. Louisville, Co-PI)
  - Jacek Jasinski (U. Louisville, Co-PI)
- **Project lead: University of Louisville**

Relevance

All solid-state lithium sulfur batteries (ASLSBs) offer high-energy density, pronounced safety, and suppress polysulfide shuttle; yet they remain far from commercialization



Solid State Li-S battery
Yang *et al*., Chem. Soc. Rev. 49, 2140 (2020)

Main Roadblock

Lack of fundamental understanding of electrochemistry in these systems over atomic scale

Objectives

- Advance atomic-scale understanding of ion-transport, chemical reactions, and material evolution in solid-state Li-S batteries
- Develop novel atomistic interaction models to accurately capture electro-chemical processes over tens of nanometers and tens of nanoseconds
- Computationally-guided design of novel electrolytes, cathode architectures, and interfaces; and realize promising candidates in laboratory

Impact

Electrolyte chemistries, cathode architecture, and interfacial functionalization to deliver solid-state Li/S cells with high S-loading (>6 mg/cm^2) that operate for 1000 cycles at > 600 Wh/kg (@C/3)

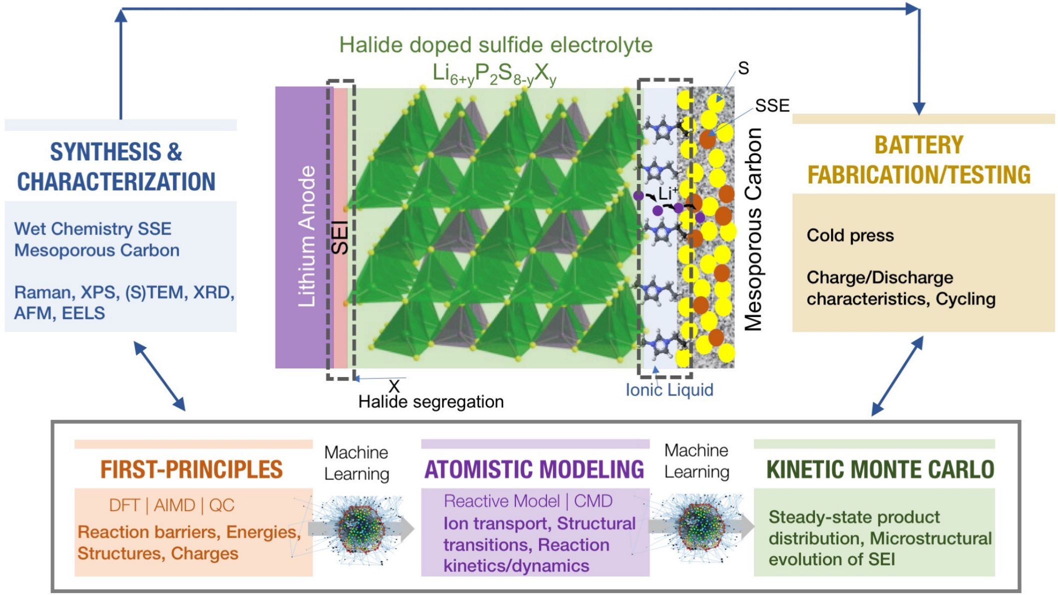
Milestones

	Time	Description of Milestone or Go/no-Go decision	Status
FY 2020	Dec. 2019	Demonstrate scalable electrolyte synthesis with precise composition control	Complete
	Mar. 2020	Optimize electrolyte composition for high Li^+ conductivity and stability against lithium	Complete
	Jun. 2020	Fabricate battery with optimized electrolyte for baseline performance	Complete
	Sep. 2020	Develop interatomic potential models for a representative sulfide electrolyte system	Complete
	Sep. 2020 Go/No-Go)	Optimize electrolyte composition, and interatomic potential models	Complete
FY 2021	Dec. 2020	Extend the interatomic potential model to include cathode, anode, and interfaces	Complete
	Mar. 2021	Optimize ionic liquid functionalization of cathode/electrolyte interfaces and characterization	Complete
	Jun. 2021	Validate interatomic potential model, and coin cell testing with increased S-loading	On schedule
	Sep. 2021 (Go/No-go)	Fundamental understanding of evolution of cathode/electrolyte interfaces and effect of ionic liquid functionalization	On schedule

Approach

Target systems

- Halogen doped sulfide argyrodite **electrolytes** (mixed doping with F) – *LiF is known to stabilize anode-electrolyte interface*
- Mesoporous **cathode** architectures with carbon nanocages
- Functionalization of cathode-electrolyte interface with ionic liquid



SYNTHESIS & CHARACTERIZATION

Wet Chemistry SSE
Mesoporous Carbon

Raman, XPS, (S)TEM, XRD, AFM, EELS

BATTERY FABRICATION/TESTING

Cold press

Charge/Discharge characteristics, Cycling

FIRST-PRINCIPLES

DFT | AIMD | QC
Reaction barriers, Energies, Structures, Charges

ATOMISTIC MODELING

Reactive Model | CMD
Ion transport, Structural transitions, Reaction kinetics/dynamics

KINETIC MONTE CARLO

Steady-state product distribution, Microstructural evolution of SEI

Overview of our proposed integrated approach to design high-performance ASLSBs

Key Innovations

- Machine learning based automated framework for developing interatomic potentials
- Development of economical and scalable liquid-based synthesis of electrolyte with good composition control
- Using our patented in situ metal templating method for preparing mesoporous cathode with prescribed architectures

Technical Accomplishments

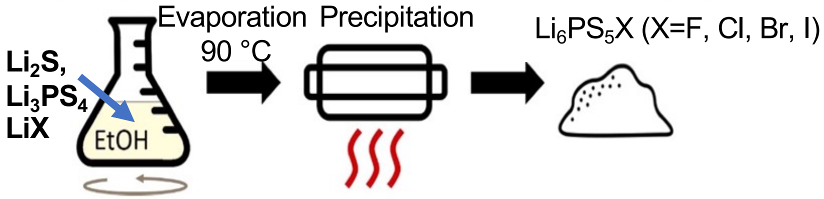
Barriers addressed

- **Scalable synthesis of solid-state electrolyte with precise composition control**
  - Developed a **scalable and economic solvent-based method** to produce solid-state electrolytes (SSE) with excellent composition control; this method enables fluorine doping of sulfide electrolytes
- **Achieving SSEs that offer fast ion conduction and stable interface with lithium**
  - Identified atomic-scale origin of fast ion conduction and high stability in fluorine containing SSE
  - **Optimized composition of SSE** with multiple halogen dopants that provides a) enhanced Li^+ conductivity (~10^{-3} S/cm), and (b) improved stability against Li anode
- **Atomic-scale modeling of solid-state lithium sulfur battery systems**
  - **Developed accurate physics-based interatomic potential models** using machine learning framework to enable classical molecular dynamics simulations of ion transport and material evolution
- **Interfacial impedance at the cathode electrolyte interface**
  - Identified **functionalizing ionic liquids** (IL) that enable **good contact** between Sulfur-carbon cathode and sulfide electrolytes; batteries with IL functionalized cathodes and optimized SSEs show capacity retention of ~550 mAh/g after 100 cycles

Technical Accomplishments

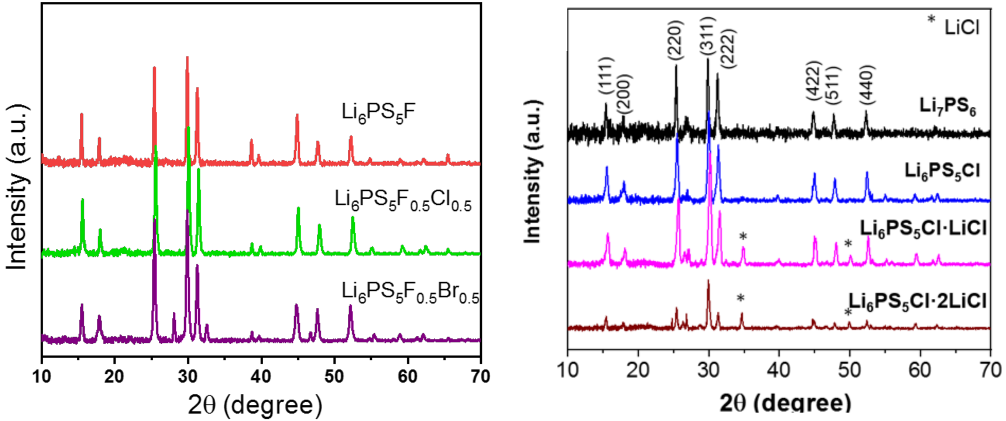
Solvent synthesis of sulfide electrolyte with precise composition control

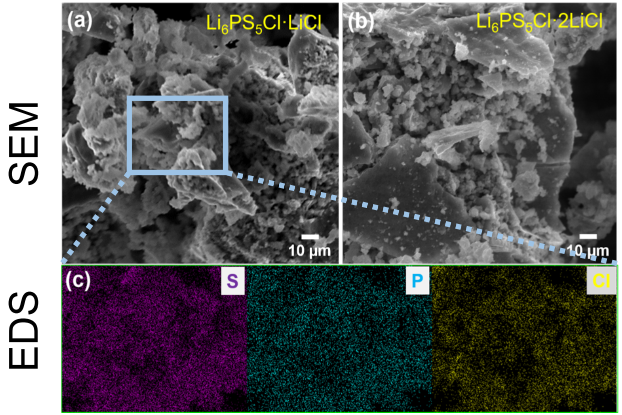
Rapid | Economic | Low temperature | Enables F doping



- Synthesized electrolytes show high phase purity and crystallinity

X-ray diffraction of representative electrolytes synthesized by this method





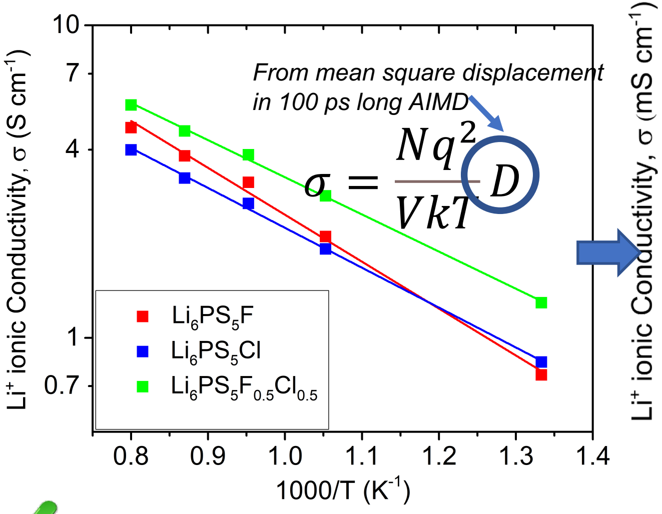
Milestone Q1/Y1: **Demonstrated scalable electrolyte synthesis with precise composition control**

Technical Accomplishments

Design of sulfide electrolytes with mixed halogen doping

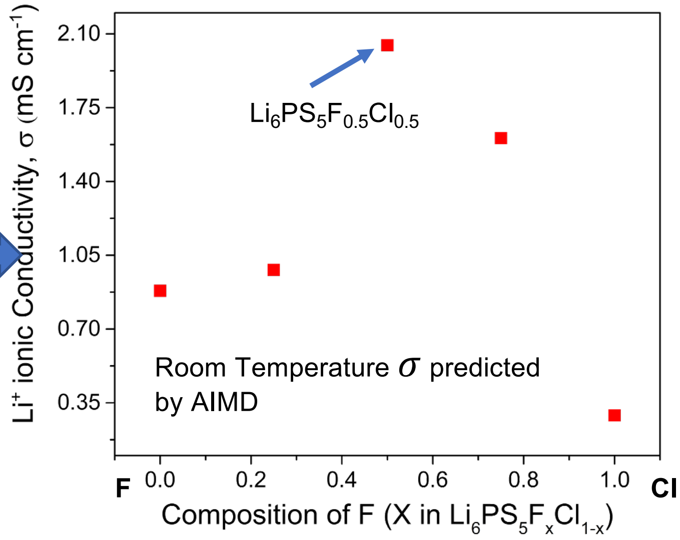
Doping argyrodite electrolytes with two different halogens yields higher Li^+ conductivity as compared to one halogen. AIMD simulations identify $Li_6PS_5F_{0.5}Cl_{0.5}$ as having highest Li^+ conductivity

Optimization of electrolyte composition using AIMD simulations



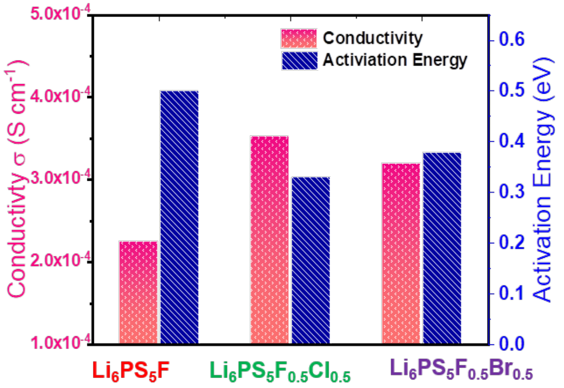
From mean square displacement in 100 ps long AIMD

$$\sigma = \frac{Nq^2}{VkT}D$$



Room Temperature σ predicted by AIMD

Our AIMD predictions are consistent with experiments

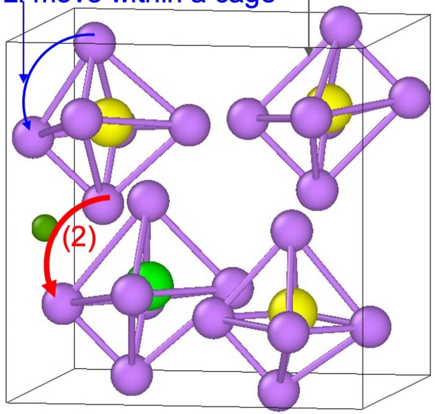


Room Temperature σ measured by experiment

Milestone Q2/Y1: Optimized electrolyte composition for high Li^+ conductivity

Technical Accomplishments

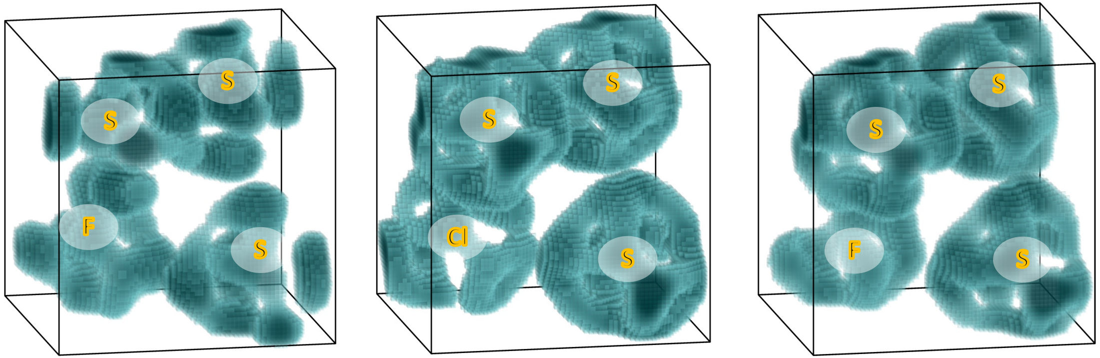
Atomistic origin of fast Li-ion conduction



Li cages made up of 24g / *48h* sites surrounding central S / X

(1) Li move within a cage

(2) Inter-cage Li hop (contributes to macroscopic Li diffusion) – assisted by halogen at face center (4a)



σ_{Li} at RT

Li_6PS_5F (0.32 mS/cm)

Li_6PS_5Cl (0.9 mS/cm)

$Li_6PS_5F_{0.5}Cl_{0.5}$ (2.2 mS/cm)

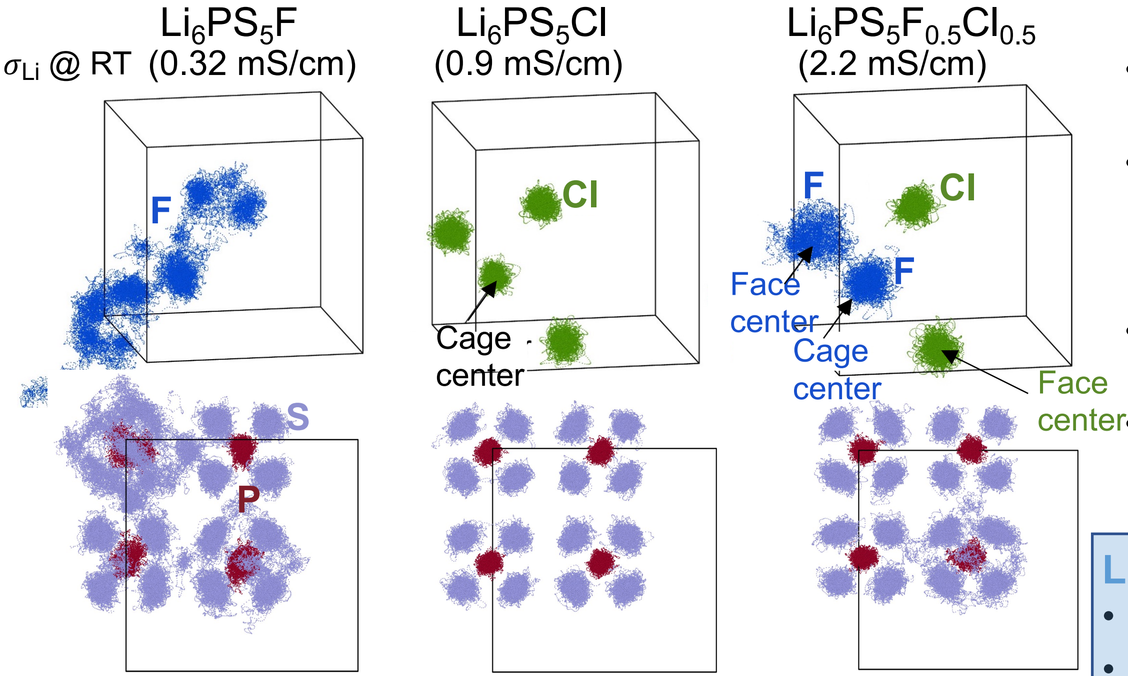
Lithium probability distribution map over entire AIMD trajectory at 750 K (100 ps)

Jump Frequency at 750 K (10^{10} s^{-1})	Li_6PS_5F	Li_6PS_5Cl	$Li_6PS_5F_{0.5}Cl_{0.5}$
Inter-cage	2.29	3.04	**3.83**
Intra-cage	35.4	48.1	**48.6**

✓ **Milestone Q2/Y1: Optimized electrolyte composition for high Li⁺ conductivity**

Technical Accomplishments

Disorder in F suppresses both intra- and inter-cage hops


Li_6PS_5F σ_{Li} @ RT (0.32 mS/cm)

Li_6PS_5Cl (0.9 mS/cm)

$Li_6PS_5F_{0.5}Cl_{0.5}$ (2.2 mS/cm)

Temporal trajectory of halogens (top) and PS_4 tetrahedra (bottom) over 100 ps long AIMD trajectory at 750 K

Intracage hops

- Li coordination around cage centers F (~4), S (~6), Cl (~5) → fastest hopping around F
- **Pronounced motion of F** enhances vibration in PS_4 → **suppresses hopping**

Inter-cage hops

- Hops mediated by face center Cl are ~2 times faster than F (stronger Li-F bond)
- In Li_6PS_5F, disorder in F further slows down hops due to association with multiple F atoms (~3x slower than 1 F mediated hops)

$Li_6PS_5F_{0.5}Cl_{0.5}$ provides best combination

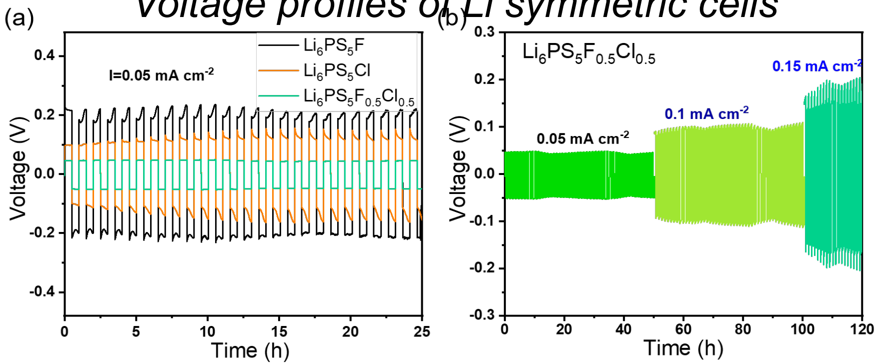
- F in cage center
- Low motion (disorder) of face center F
- High fraction of Cl mediated inter-cage jumps (~1.5 that by F)

✓ **Milestone Q2/Y1: Optimized electrolyte composition for high Li^+ conductivity**

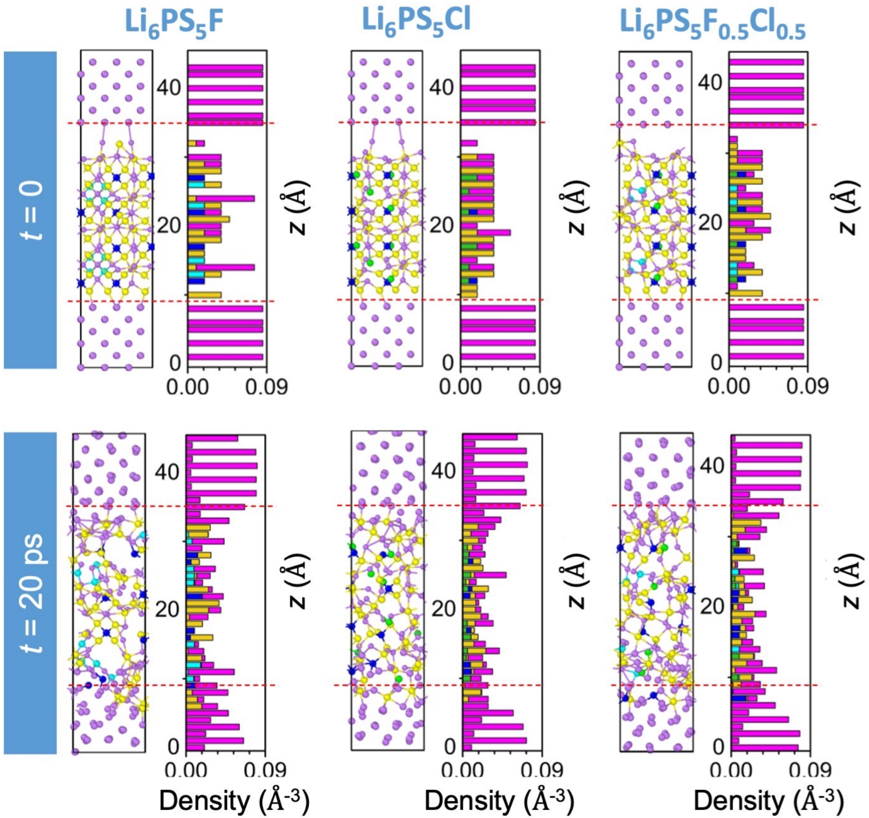
Technical Accomplishments

Doping with multiple halogen also enhances stability against Li-anode

Voltage profiles of Li symmetric cells



- $Li_6PS_5F_{0.5}Cl_{0.5}$SE can cycle at high current density of 0.15 mA/cm^2, while the other cells failed at lower curren densities
- AIMD shows that all electrolytes undergo reductive decomposition of PS_4 – 13% of Li from anode moves in electrolyte forming new Li-P, and Li-S bonds. Li-X bonds form at interface



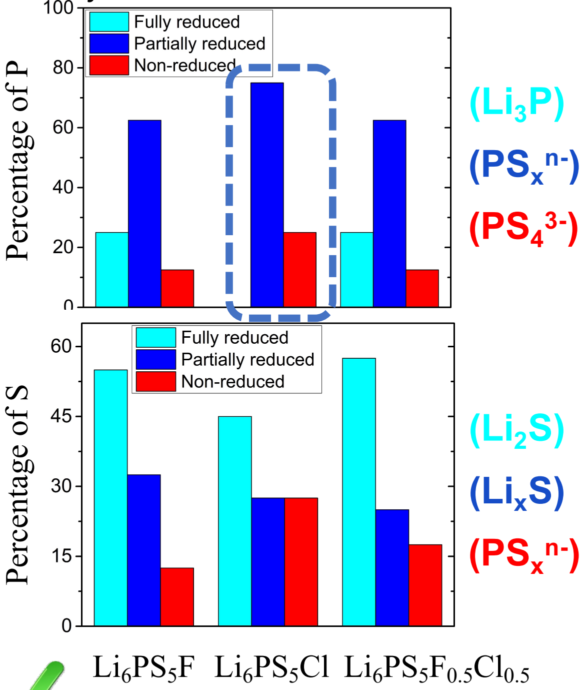
Density distribution of different atoms across interface obtained from AIMD simulations at 300 K

Milestone Q2/Y1: Optimized electrolyte composition for high Li$^+$ conductivity and stability against Li

Technical Accomplishments

Composition of SEI from AIMD simulations and XPS characterization

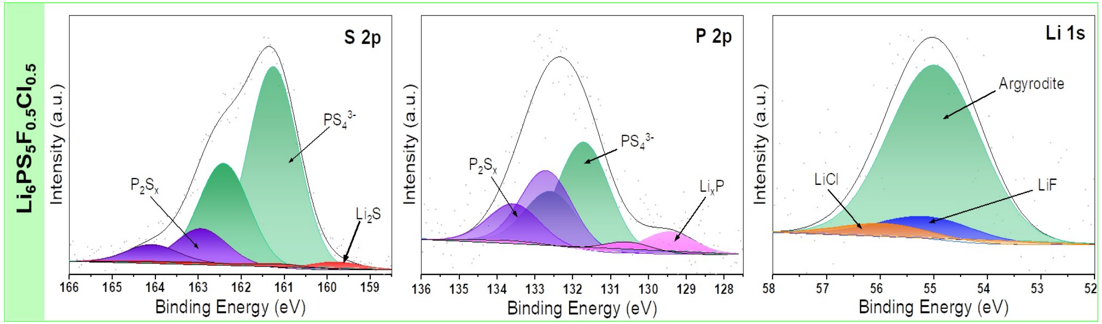
Reduction levels classified using Bader analysis of interfacial structure from AIMD



- **Li | Li_6PS_5Cl** : Li_xS + PS_x^{n-} (mostly PS_2) + PS_4 + LiCl **(No Li_3P)**
- **Li | $Li_6PS_5F_{0.5}Cl_{0.5}$** : Li_xS + PS_x^{n-} (mostly PS_3) + PS_4 + **Li_3P** + LiF + LiCl
- **Li | Li_6PS_5F** : Li_xS + PS_x^{n-} (mostly PS_3) + PS_4 + **Li_3P** + LiCl + LiF

Ionic conductivity of Li_3P ~10 mS/cm → SEI for F containing electrolytes show lower impedance.

Our AIMD findings are consistent with our XPS characterization

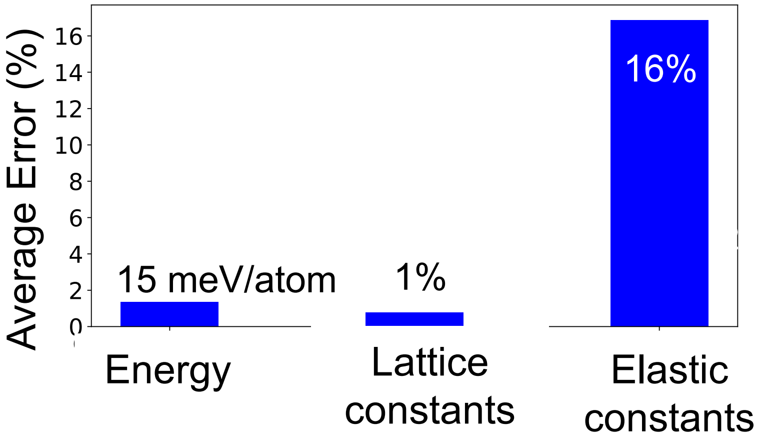


Go/No-Go/Y1: Optimized electrolyte composition for high Li^+ conductivity and stability against Li – $Li_6PS_5F_{0.5}Cl_{0.5}$ provides good combination of conductivity and stability

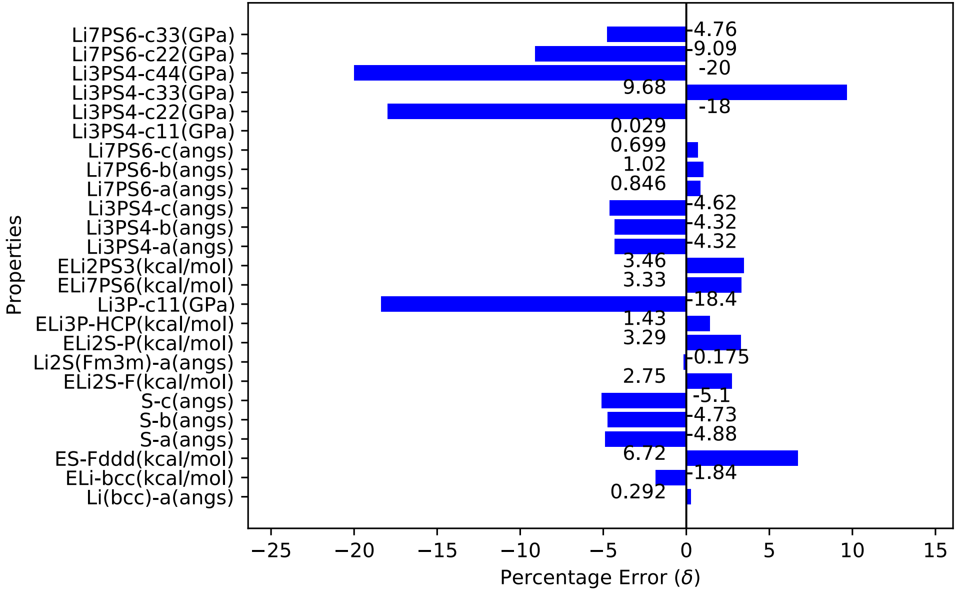
Technical Accomplishments

Developed a reactive force field for Li-P-S ternary system with good predictive power

ReaxFF prediction error relative to DFT



Errors in ReaxFF predictions for selected phases

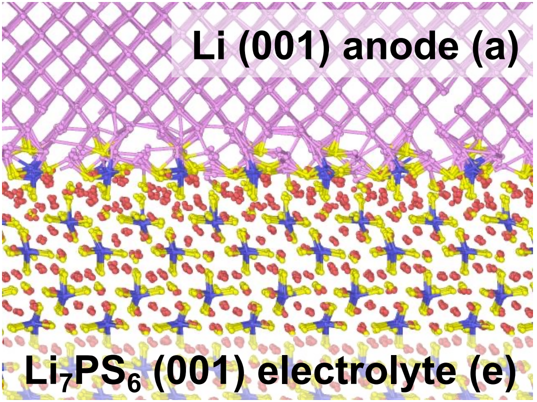


✓ Q4/Y1 and Go/No-Go/Y1: **Developed interatomic potential for electrolyte**

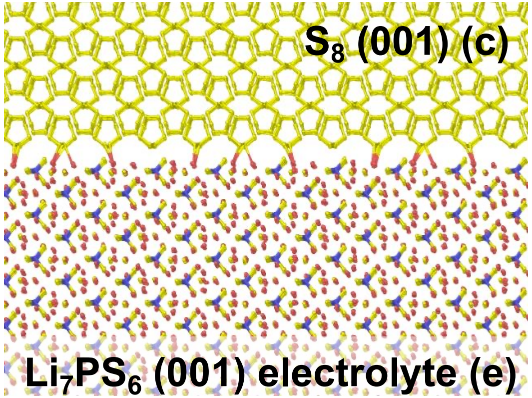
Technical Accomplishments: Material evolution at interfaces predicted by ReaxFF agree with previous first principles calculations

ReaxFF MD
300 K, 0.2 ns

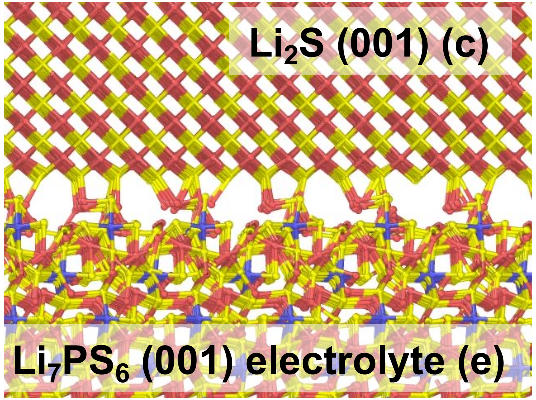
Anode



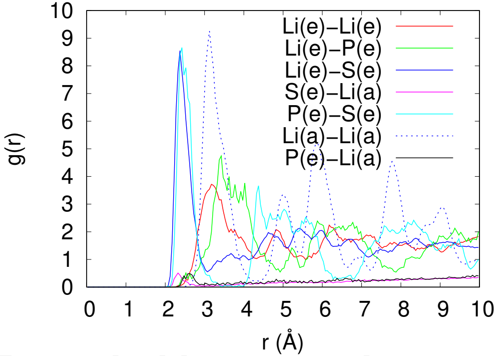
Fully charged state

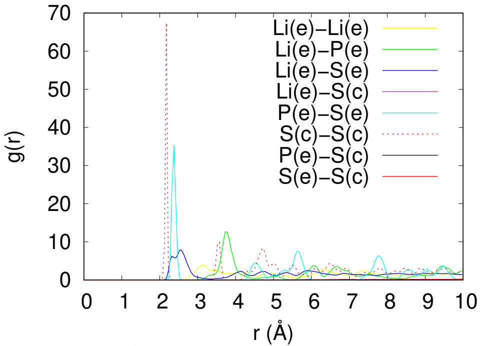


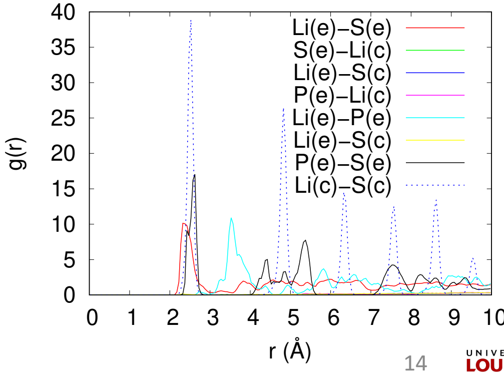
Fully discharged state



RDF for
various pairs
at the
interface



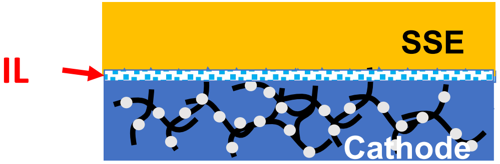




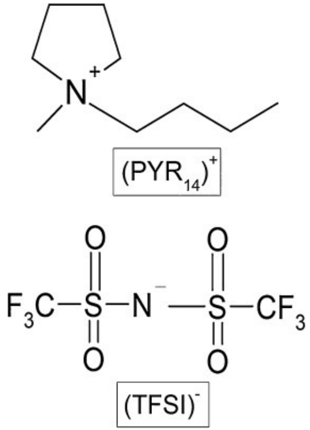
✓ **Q1/Y2: Extended interatomic potential to interfaces**

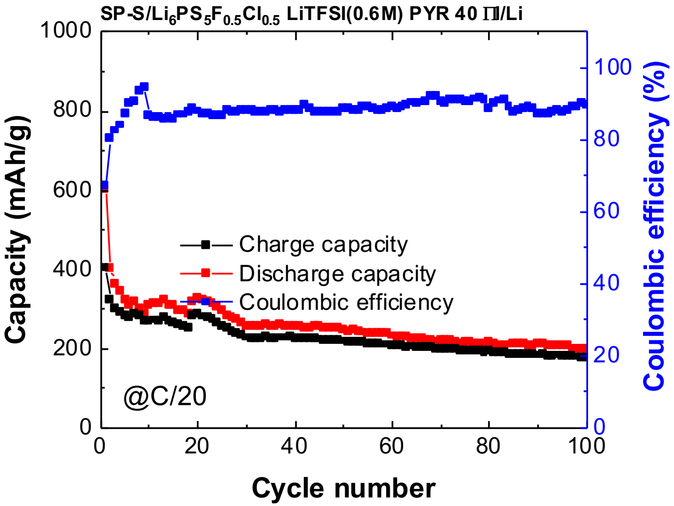
Technical Accomplishments

Fabrication of battery using optimized electrolyte | C-S cathode: Super P-S (3:2) - 88 wt%, AB binder – 2 wt%, CMC - 5 wt%, SBR – 5 wt%; dr blade coating - 350 µm (1.3 – 1.5 mg/cm^2) / $Li_6PS_5F_{0.5}Cl_{0.5}$ SSE / Li anode



Ionic liquid (IL) functionalization



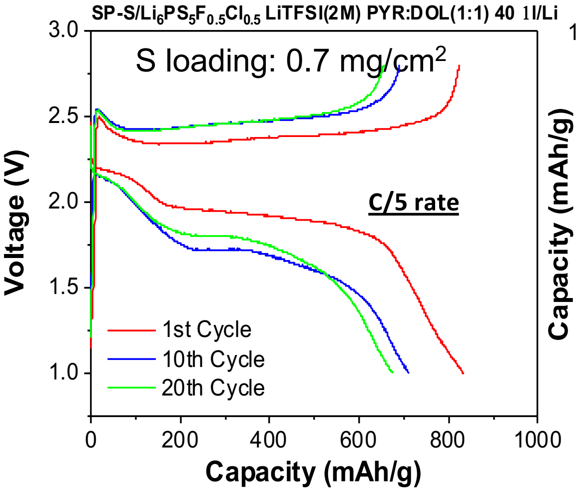


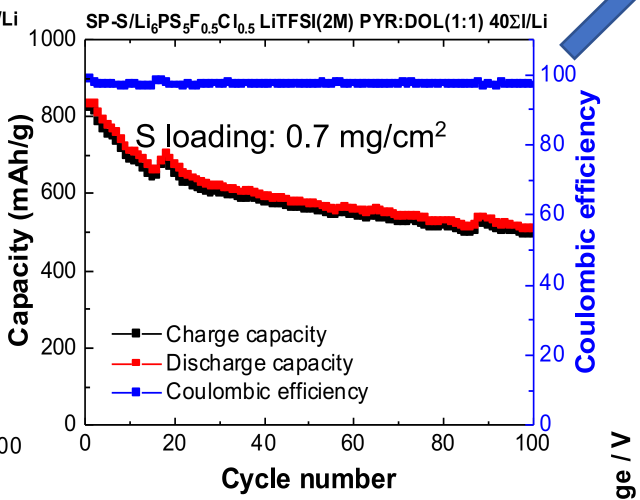
- Batteries with fully solid cathode/electrolyte interface suffers from poor contact. They show poor discharge capacity (~50 mAh/g) and fail to charge after first cycle
- Functionalizing cathode with IL (e.g., 40 µL of 0.6 M LiTFSI in PYR-IL) shows good promise with capacity retention of 200 mAh/g after 100 cycles

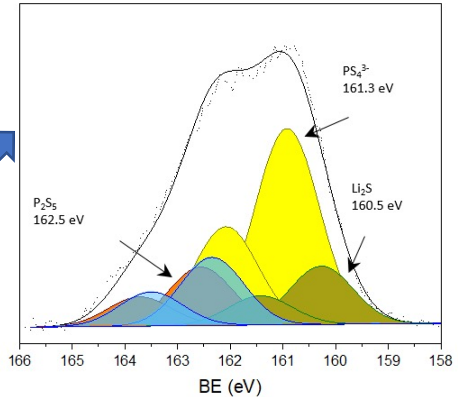
Milestone Q3/Y1: Fabricate battery with optimized electrolyte for baseline performance

Technical Accomplishments

Fabrication of battery using optimized electrolyte

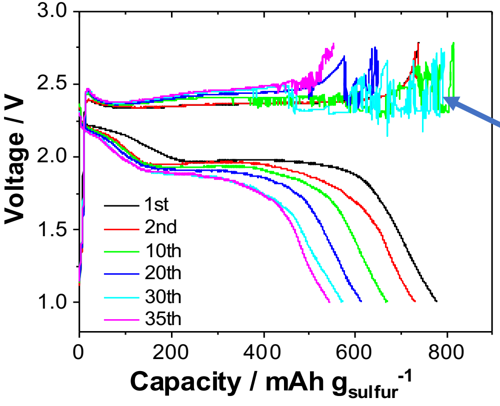






XPS of cathode/electrolyte interface shows formation of bridging S-S bonds (P_2S_x)

Sulfur loading – 1.5 mg/cm^2



Poor electrical conduction in cathode

- Diluting IL with DOL improves performance. Optimum battery performances for low sulfur loading (0.7 mg/cm^2) was achieved with 40 μL of 2M LiTFSI in PYR:DOL=1:1.
- Porosity of the cathode needs to be engineered to reach higher S-loading

✓ **Milestone Q2/Y2: Optimize ionic liquid functionalization of cathode/electrolyte interfaces and characterization**

Response to Previous Year Reviewers' Comments

This project started in FY 2020. It was not evaluated last year

Collaboration and Coordination with other institutions

Team: The project is a **collaboration** between four faculty-led groups who are all co-located at University of Louisville.

- *Narayanan (PI)* – First-principles atomic-scale modeling, interatomic potential development
- *Wang (co-I)* -- Synthesis of sulfide electrolytes
- *Sumanasekera (co-I)* – Synthesis of cathode architectures and battery fabrication
- *Jasinski (co-I)* – Electrochemical Characterization

Argonne National Laboratory

Anh T. Ngo, Larry Curtiss, Subramanian Sankaranarayanan

- First-principles data for interatomic potential development
- Machine learning strategies and frameworks

Oak Ridge National Laboratory

Yan Chen, Jagjit Nanda, Niina Jalarvo

- Initiated discussion for neutron-diffraction studies of electrolytes to gain insights into structure (site disordering) sulfide electrolytes synthesized by liquid phase synthesis

Remaining Challenges and Barriers

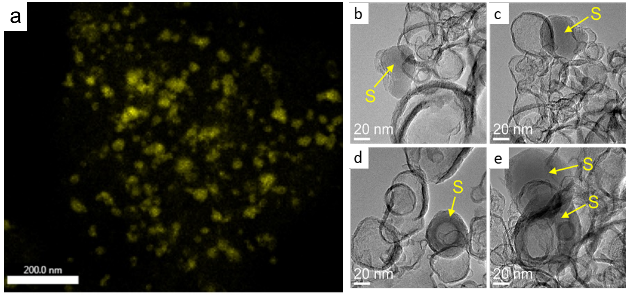
- Identify effect of **crystallinity, and extended defects** (e.g., grain boundary) **on Li-ion conduction** in sulfide electrolyte
- Fundamental understanding of **long-time nanoscale dynamics** of evolution of electrified interfaces: *reactions, rates, composition of SEI/CEI, ion-transport across interfaces, effect of electric field*
- Identify **reasons for failure of cathode architectures at high sulfur loading**, and successes of ionic liquid functionalization
- Synthesis of **mesoporous composite cathodes** co-infiltrated with solid electrolyte and sulfur (**high loading > 6 mg/cm^2**) while maintaining good electronic and ionic conductivity: *Currently used cathode formulation fails beyond S-loading of 3 mg/cm^2*
- **Minimize** the amount of **liquid** functionalizing agents (i.e., ionic liquids)

Future Work

Rest of FY 2021

- Rigorous validation of ReaxFF predictions of dynamic properties (ion transport) and interface evolution against first-principles calculations, and experiments
- ReaxFF-MD to understand effect of crystallinity and extended defects on ion conduction in sulfide electrolytes
- Advanced characterization and first principles modeling to understand role of IL at cathode/electrolyte interface
- Develop coin cell batteries with cathodes at S-loading > 5 mg/cm^2 without compromising on capacity retention at ~100 cycles. Adding CNT and SSE in cathode; and use 3D current collectors to optimize ionic/electronic conduction

Our preliminary work on CNC composite cathode shows good promise for achieving S-loading > 6 mg/cm^2



FY 2022

- MD simulations to understand nanosecond atomic-scale dynamics of interfacial evolution: identify reactions, rates, and ion transport across SEI, electric field effects. kMC models informed by MD can access higher length/time scale
- MD simulations to gain insights into the connections between ion-conduction, sulfur reduction, and strain in composite cathodes made of network of carbon nanocages (CNCs)
- Produce CNC based composite cathodes with prescribed architectures guided by computation, to achieve S-loading > 6 mg/cm^2 that can retain capacity of 600 Wh/kg over at least 500 cycles.

Any proposed future work is subject to change based on funding levels

Summary

Relevance: Enable electrolyte chemistries, cathode architecture, and interfacial functionalization to deliver solid-state Li/S cells with high S-loading (>6 mg/cm^2) that operate for 1000 cycles at > 600 Wh/kg (@C/3)

Approach: Our integrated approach involves 1) liquid phase synthesis, 2) first-principles and atomic-scale modeling, 3) machine-learning to develop physics-based reactive models, 4) battery fabrication, and 5) advanced electrochemical characterization.

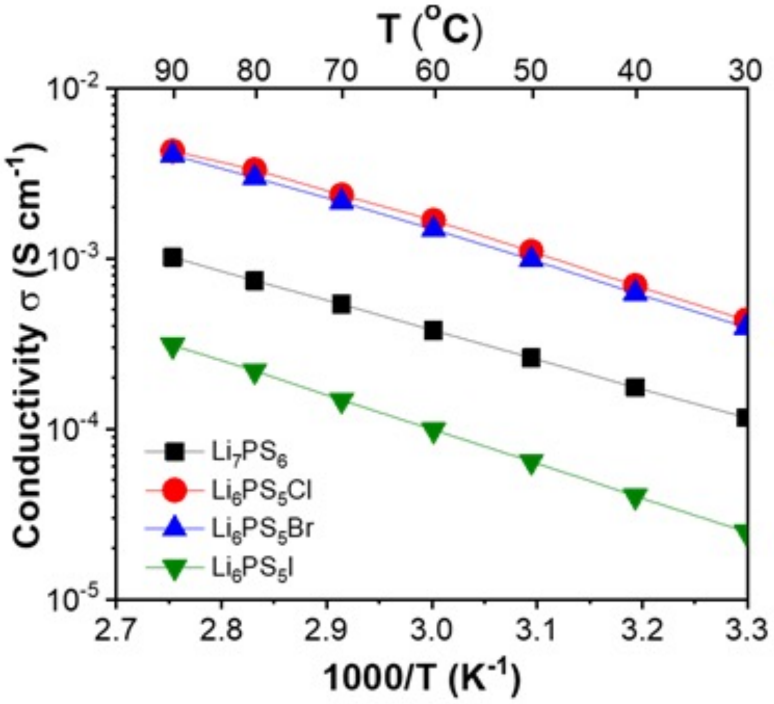
Technical Accomplishments: Developed an economical, scalable, and rapid solution-based synthesis method for sulfide electrolytes with excellent control over composition and phase purity; identified electrolyte composition to simultaneously achieve fast Li ion conduction and form stable SEI at Li anode; identified the reactions between sulfide electrolyte and anode; developed a new reactive interatomic potential model for Li-P-S ternary system; identified IL functionalizing agents that improve contact at the cathode/electrolyte interface

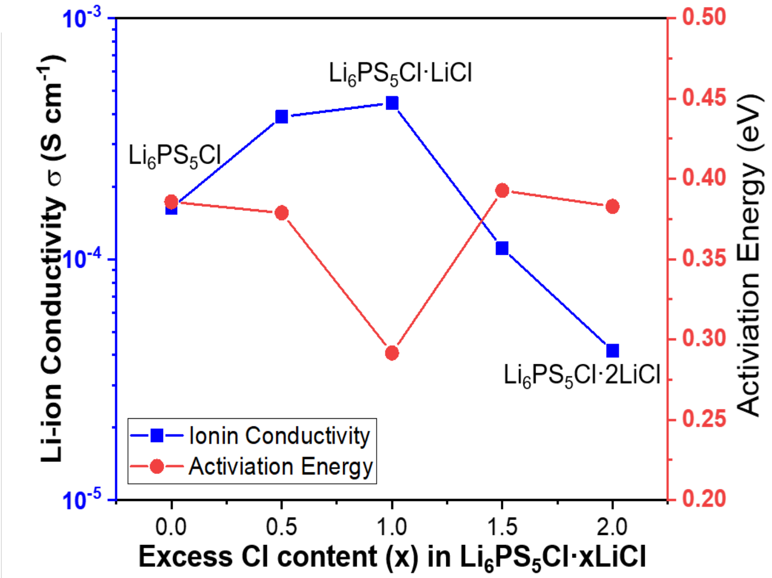
Collaborations: 3 co-PIs at U. Louisville with expertise in synthesis, characterization and battery fabrication; first-principles data and machine learning strategies for model development (ANL); initiated discussion for neutron scattering experiments on sulfide electrolytes (ORNL)

Future Work: Gain insights into ion-conduction, material evolution, and reactions at electrified interfaces; computationally guided design of composite cathodes; development of coin cells that operate at S-loading (> 6 mg/cm^2)

TECHNICAL BACK-UP SLIDES

Li ion conductivity of electrolytes synthesized by our solvent-based method are on par with that obtained from state-of-the-art ball milling methods

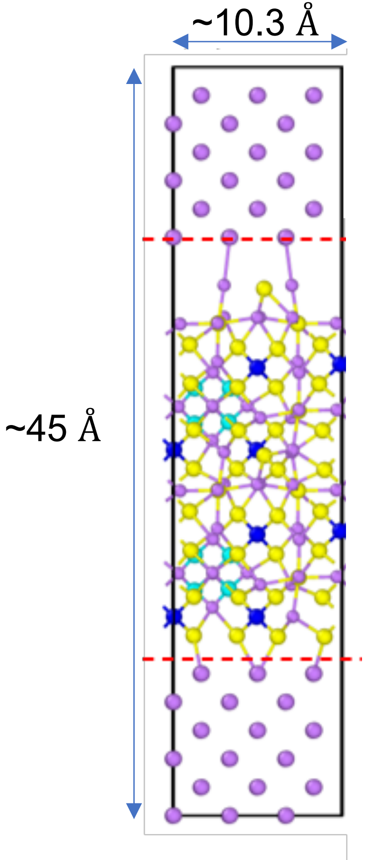




Arnold et al. *J. Power Sources* 464, 228158 (2020)

AIMD simulations of anode/electrolyte interfaces

3 × 3 Li (001) || 1 × 1 Li_6PS_5X (001) for 20 ps at 300 K



- 6 layers of Li on each side of the electrolyte
- Epitaxial strain at the interface < 1 %
- (001) facets are known to be the most stable surface for Li and Li_6PS_5X

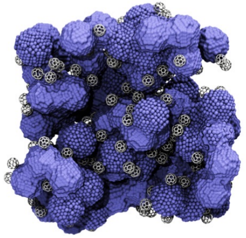
- AIMD calculations are performed using VASP
- 300 K, 20 ps
- Perdew-Burke-Ernzerhof functional **(GGA-PBE)**
- Plane-Wave Energy cut off: 500 eV
- K point sampled at Γ-point only

Automated machine learning workflow to develop interatomic potentials

Large datasets obtained from first-principles calculations are employed

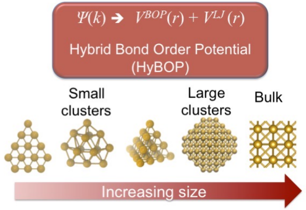
Co/C (Tersoff)

Porous metal-organics



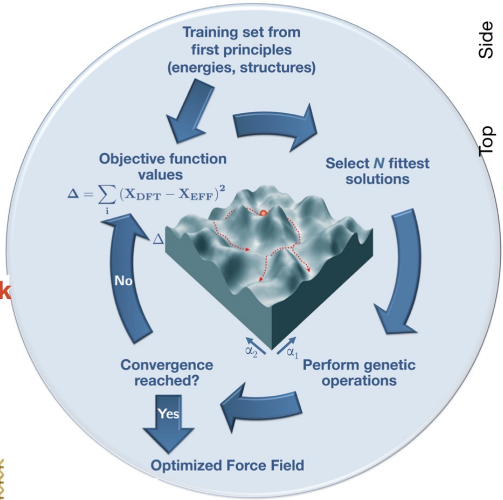
Gold: Nanoclusters to bulk

Catalysis



$\Psi(k) \rightarrow V^{BOP}(r) + V^{LJ}(r)$

Hybrid Bond Order Potential (HyBOP)



Training set from first principles (energies, structures)

Select N fittest solutions

Perform genetic operations

Convergence reached?

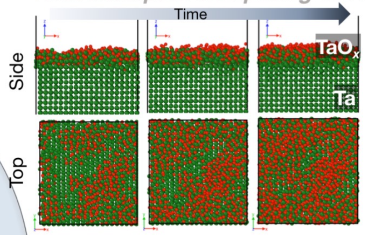
Objective function values

$\Delta = \sum_i (X_{DFT} - X_{EFF})^2$

Optimized Force Field

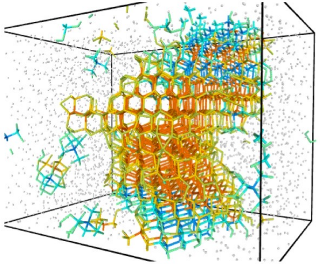
Ta/O (CTIP)

Neuromorphic computing devices



Water (Coarse-grained BOP)

Nucleation/grain growth



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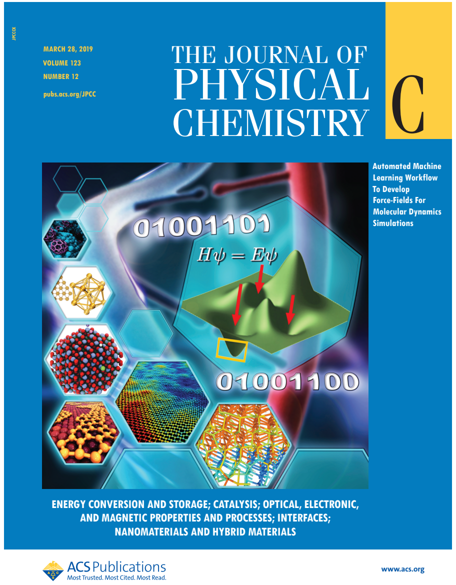

JPCCCK

MARCH 28, 2019
VOLUME 123
NUMBER 12
pubs.acs.org/JPCC

THE JOURNAL OF
PHYSICAL
CHEMISTRY
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Automated Machine Learning Workflow To Develop Force-Fields For Molecular Dynamics Simulations

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H. Chan*, **B. Narayanan***, Sankaranarayanan et al.,
J. Phys Chem. C (2019) **(*Equal contribution)**

Large training set from quantum calculations

Li-P-S ternary system

UNARY

Li

bcc
hcp
fcc
trigonal
hexagonal
cubic

S

P2/c
Pnnm
Fddd
$P2_1$
$Pca2_1$
C2/c
P1

P

P1
Cmce
Pmna
P2/c
$Pca2_1$
R-3m
Immm

TERNARY

Li-P-S

Li_7PS_6
Li_3PS_4
$Li_7P_3S_{11}$
Li_2PS_3

BINARY

Li-S

fcc
hcp
ortho
tetra
Li_2S

Li-P

Li_3P
Li_3P_7
LiP
LiP_5
LiP_3

P-S

P_4S_3
P_4S_5
P_4S_7
P_4S_9
$Pca2_1$
P_2S_5

- Equation of state
- Elastic constants
- Structure, energies, and charges from AIMD snapshots

~2000 structures/energy
~40 condensed phases (lattice parameters)
~100 elastic constants

Battery cycling with S loading of 1.5 mg/cm^2

C-S cathode: Super P-S (3:2) - 88 wt%, AB binder – 2 wt%, CMC - 5 wt%, SBR – 5 wt%; dr blade coating - 350 µm (1.3 – 1.5 mg/cm^2) / **$Li_6PS_5F_{0.5}Cl_{0.5}$ SSE** / **Li anode**

Cathode functionalization: 40 µL of 2M LiTFSI in PYR:DOL=1:1.