Solid Electrolyte Chemistry with Fast Ion Conduction and Good Electrochemical Stability: Insights from First Principles Computation

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Opportunities and Challenges: All-Solid-State Li-ion Batteries

Opportunities and potentials:
- Improved safety: non-flammable ceramic electrolyte
- High energy density: Li metal anode and/or high-voltage cathode
- High power, long cycle life, wide temperature range...

Challenges:
- Li solid electrolyte with high ionic conductivity, good stability, etc.
- Interfaces between electrolyte and electrodes.

Solid electrolyte needs to satisfy:
- High ionic conductivity
- Stability:
  - Electrochemical (under voltage)
  - Interfaces (with electrode)
  - Air & moisture
- Mechanical property
- Low-cost & scalable synthesis, processing, cell fabrication

Our goal: Use first principles computation to achieve:
- fundamental understanding
- accelerated design of materials and interfaces.
Solid Electrolyte: super-ionic conductor + other properties

Solid electrolyte needs to satisfy:
- High ionic conductivity
- Stability:
  - Electrochemical (under voltage)
  - Interfaces (with electrode)
  - Air & moisture
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Current solid electrolytes do not simultaneously satisfy all desired properties. Need to develop new systems.

BCC anion framework exhibits lowest barrier energy landscape

Ion migration in solids

In BCC anion lattice
Face-shared tetrahedra: 0.15 eV

In FCC anion lattice
tetra-oct-tetra: 0.4 eV

\[ \sigma = \frac{q^2}{kT} n D_0 e^{-\frac{E_a}{kT}} \]

\( E_a \): Activation energy
\( n \): mobile carrier concentration

To achieve high ionic conductivity, low \( E_a \) + high \( n \)

Wang, ... Mo, Ceder, Nat. Mater. 14: 1026 (2015)
Concerted migration mechanism activates super-ionic conductors

Challenge: Complex crystal structure and unique Li-ion sublattice are required to achieve concerted migration.
Interface Stability in All-Solid-State Li-ion Batteries

Significant amount of solid-solid interfaces in solid-state batteries:

- Interface compatibility & stability. (coulombic efficiency, cycle life)
- Interfacial ionic transport. (Rate performance)
- Formation of interphase layer?

Thermodynamics indicate that the interface may degrade and an interphase layer may form due to:
1. The reduction / oxidation of the solid electrolyte materials at applied voltage.
2. Chemical reaction between solid electrolyte and electrodes.
3. Electrochemical reaction (during cycling voltage) between solid electrolyte and electrodes.

Nolen, Zhu, He, Bai, Mo, Joule 2018, 2, 2016-2046
Thermodynamic Intrinsic Electrochemical Window of Solid Electrolyte

Li binary stable against Li metal

Cation reduction at low potential

Phase equilibria at Li metal

LiF
Li₂O
Li₂S
Li₃N
Li₁₅Ge₄, Li₃P, Li₂S
Li₃P, Li₂S
Li₂O, La₂O₃, Ti₄O
Ti₃Al, Ti₃P, Li₃P, Li₂O
Li₂O, La₂O₃, Zr
Li₂O, Li₃N, Li₃P

Phase equilibria at 5 V ref. to Li/Li⁺

LiF (F₂ at 6.36V)
O₂
S
N₂
GeS₂, P₂S₅, S
P₂S₅, S
Ti₂O₄, La₂Ti₂O₇, TiO₂
AlPO₄, O₂, TiPO₂₇, Ti₂O₇
La₂O₃, La₂Zr₂O₇, O₂
P₂O₅, N₂, PNO

S oxidation in sulfide at > ~2.3V

Oxidation in oxides may be kinetically limited.

Zhu, He, Mo, *ACS Appl. Mater. Interfaces*, 2015, 7 (42), 23685
Unstable SE-Cathode Interface: Interface Coating is Needed

Incompatible interface
Sulfide SE-LCO

Mitigation strategy:
Converting to Type 3 by coating

Oxide coating layer,
(e.g. LiNbO₃, Li₃PO₄, etc.)
serves as artificial SEI

Mixed conducting
interphaselayer formed
-> Sustained decomposition.
-> Thick interphase layer.
-> High interfacial resistance.

Sulfide-LCO highly unstable favorable reaction.


Coating thickness up, stability up, resistance down

Nolen, Zhu, He, Bai, Mo, Joule 2018, 2, 2016-2046
Electrochemical window for different anion chemistry

Ternary compound Li-M-X (M=cation, X=F, Cl, Br, I, O, S, N)

- Fluorides: High-voltage stability
- Chlorides: A promising chemistry
- Bromides: Kinetically limited oxidation. Polyanion oxide has even higher stability
- Iodides: A promising chemistry
- Oxides: A promising chemistry
- Sulfides: Li metal stability thermodynamic intrinsic. Strategy: High N-doping to in-situ form Li-stable SEI
- Nitrides:

Wang, ... Mo, *Angew. Chem. Int Ed.* 2019, 58, 8039
New Halide Solid Electrolyte by Panasonic

Asano et al., Adv. Mater. 2018, 30, 1803075

- \( \text{Li}_3 \text{YCl}_6 \) – hcp Cl \( 0.51 \text{ mS/cm@300K} \)
- \( \text{Li}_3 \text{YBr}_6 \) – fcc Br \( 1.7 \text{ mS/cm@300K} \)

Advantages:
- High ionic conductivity (\( 10^4 \) - \( 10^3 \) mS/cm at RT)
- Electrochemical stability
- Interface compatibility
- Air stability, Mechanical deformability, etc.

Discharge capacity (mAh/g) vs. Coulomb efficiency vs. Cycle

\( T = 25 ^\circ \text{C}, 0.1 \text{ C} \)
High Li+ conductivity confirmed in Ab initio molecular dynamics simulation

Close-packing Cl/Br anion sublattice

Li ion diffusion trajectories

$\sigma = 14 \text{ mS/cm at 300K}$

$E_a = 0.19 \text{ eV}$

$\sigma = 2.2 \text{ mS/cm at 300K}$

$E_a = 0.28 \text{ eV}$
Intrinsic low migration barrier in close-packed Cl/Br sublattice

Li$_3$YCl$_6$ (Space group: $P\bar{3}m1$)

Li$_3$YBr$_6$ (Space group: C2/m)

Li$^+$ migration pathway

Diffusion Energy Barrier

Oct
Tet
Oct
Tet
Fast ion conduction in Cl/Br lattice is general (not cation specific)

**Table: Conductivity and Activation Energy**

<table>
<thead>
<tr>
<th>Composition</th>
<th>$\sigma$ at 300K (mS/cm)</th>
<th>$E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_3$YCl$_6$</td>
<td>AIMD: 14 Expt.: 0.5</td>
<td>AIMD: 0.19 ± 0.03 Expt.: 0.40</td>
</tr>
<tr>
<td>Li$_3$YBr$_6$</td>
<td>AIMD: 2.2 Expt.: 1.7</td>
<td>AIMD: 0.28 ± 0.02 Expt.: 0.37</td>
</tr>
<tr>
<td>Li$_{10}$GeP$<em>2$S$</em>{12}$</td>
<td>AIMD: 14$^{[1]}$ Expt.: 12$^{[2]}$</td>
<td>AIMD: 0.21 ± 0.01$^{[1]}$ Expt.: 0.23$^{[2]}$</td>
</tr>
<tr>
<td>Li$_7$La$_3$Zr$<em>2$O$</em>{12}$</td>
<td>AIMD: 1.1$^{[1]}$ Expt.: 0.5$^{[3]}$</td>
<td>AIMD: 0.26 ± 0.02$^{[1]}$ Expt.: 0.30$^{[3]}$</td>
</tr>
<tr>
<td>Li$_3$ScCl$_6$</td>
<td>AIMD: 29 Expt.: --</td>
<td>AIMD: 0.18 ± 0.04 Expt.: --</td>
</tr>
<tr>
<td>Li$_3$HoCl$_6$</td>
<td>AIMD: 21 Expt.: --</td>
<td>AIMD: 0.19 ± 0.03 Expt.: --</td>
</tr>
<tr>
<td>Li$_3$ScBr$_6$</td>
<td>AIMD: 1.4 Expt.: --</td>
<td>AIMD: 0.30 ± 0.04 Expt.: --</td>
</tr>
<tr>
<td>Li$_3$HoBr$_6$</td>
<td>AIMD: 3.8 Expt.: --</td>
<td>AIMD: 0.26 ± 0.04 Expt.: --</td>
</tr>
</tbody>
</table>
Halide solid electrolytes exhibit wide electrochemical window

**Asano et al.** Adv. Mater. 2018, 1803075

Calculated thermodynamic electrochemical window

**Wang, ... Mo, Angew. Chem. Int Ed.** 2019, 58, 8039
Chloride/Bromide SE Exhibit Good SE-Cathode Interface Stability

- Interface stability with cathode among the best among SSEs, comparable to oxides.
- Stability remains at charged states.

Thermodynamic calculations

Wang, ... Mo, *Angew. Chem. Int Ed.* 2019, 58, 8039
Conclusion

• Achieving both high ion conductivity and electrochemical stability are required for SEs but challenging in Oxides and Sulfides.

• Chlorides and Bromides exhibit low Li+ migration barrier in close-packed FCC/HCP anion lattice bypassing previous design principles (BCC, concerted migration, etc.).

• Chlorides exhibit decent electrochemical window and good interface stability with cathode.

• Chlorides and Bromides are promising chemistry as solid electrolytes to simultaneously achieve fast ion conduction and good stability.


He, Zhu, Mo, *Nature Commun.* 2017, 8, 15893

Zhu, He, Mo, *ACS Appl. Mater. Inter.* 2015, 7 (42), 23685


Zhu, He, Mo, *Advanced Science* 2017, 1600517