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

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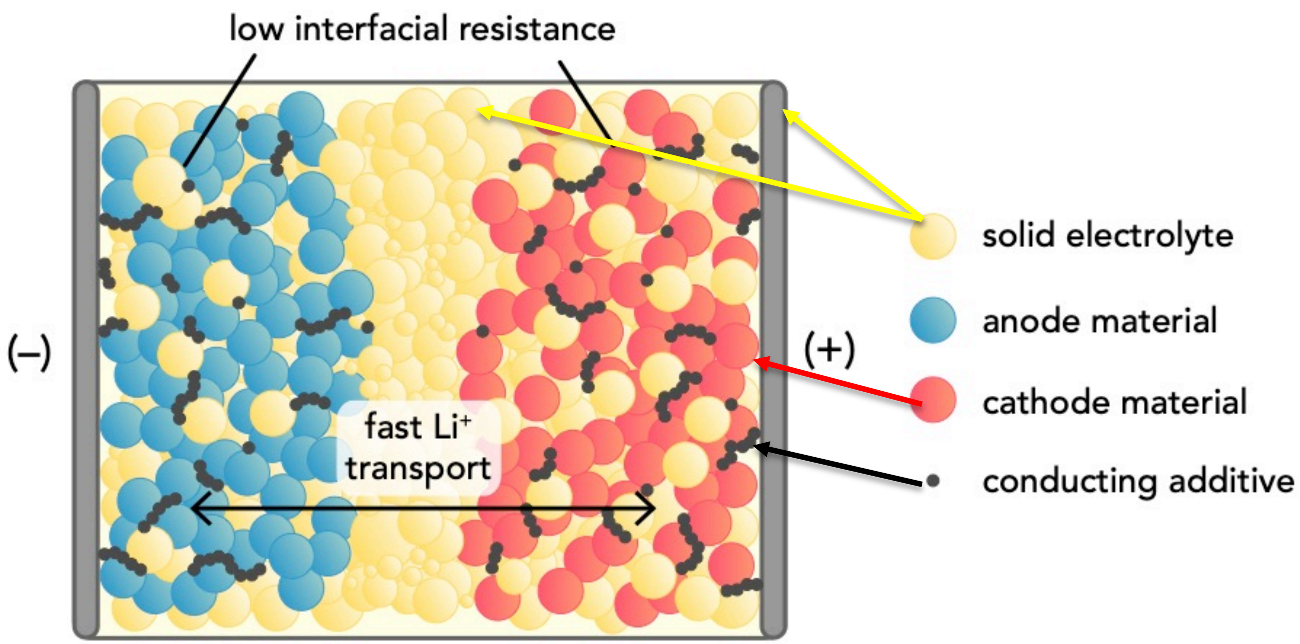
Opportunities and Challenges: All-Solid-State Li-ion Batteries

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 …



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

Challenges :

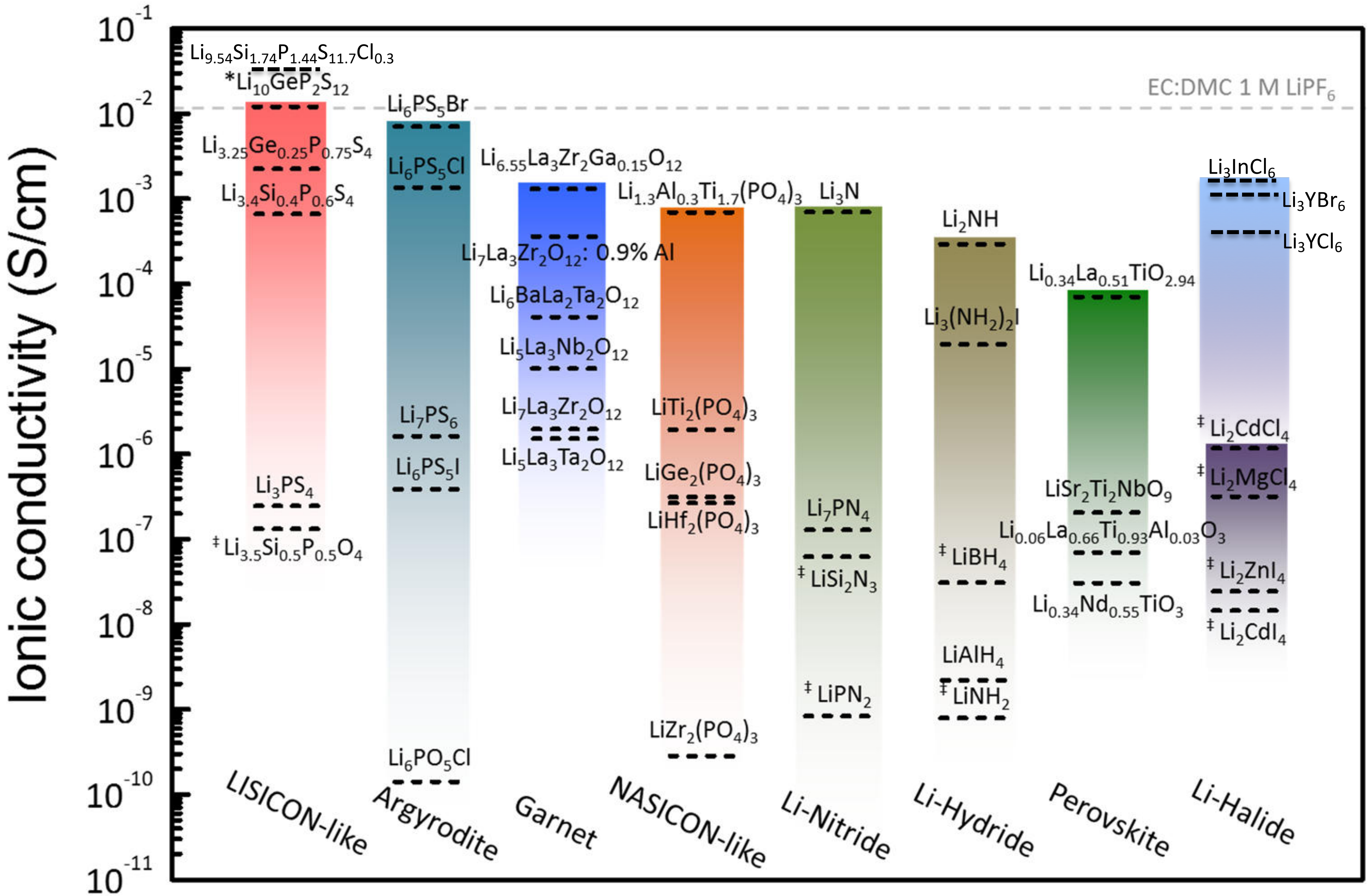
- Li solid electrolyte with high ionic conductivity, good stability, etc.
- Interfaces between electrolyte and electrodes.

Our goal: Use first principles computation to achieve:

- fundamental understanding
- accelerated design

of materials and interfaces.

Solid Electrolyte: super-ionic conductor + other properties



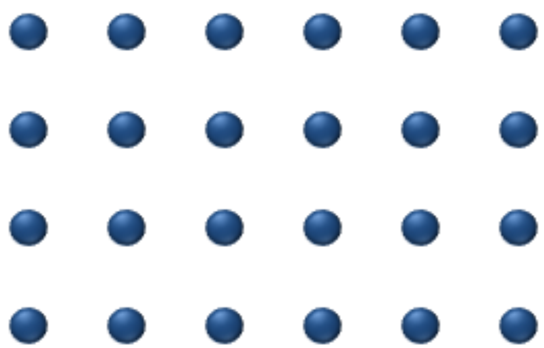
Modified from Shao-horn et al. Chem. Rev. (2016)

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

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



Ionic conductivity

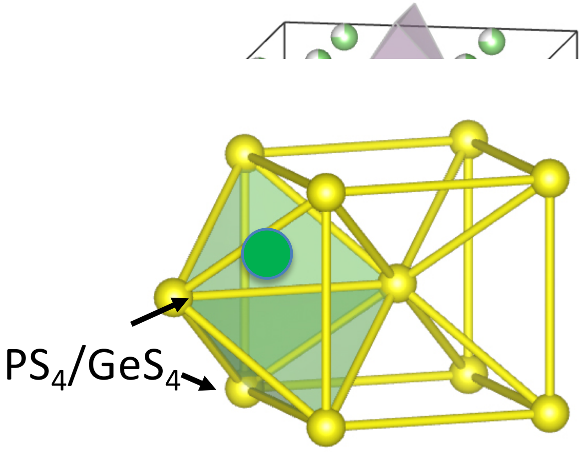
$$\sigma = \frac{q^2}{kT} n D_0 e^{-(\frac{E_a}{kT})}$$

E_a : Activation energy

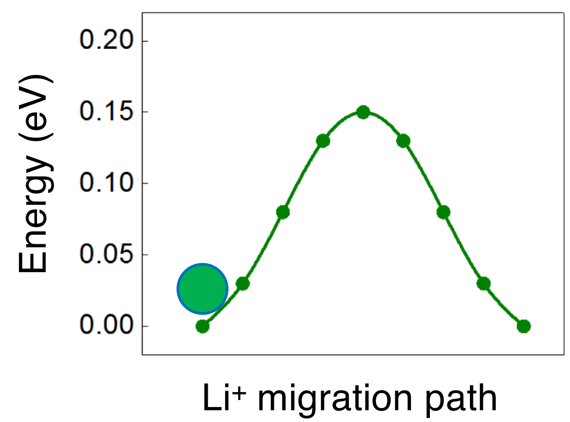
n : mobile carrier concentration

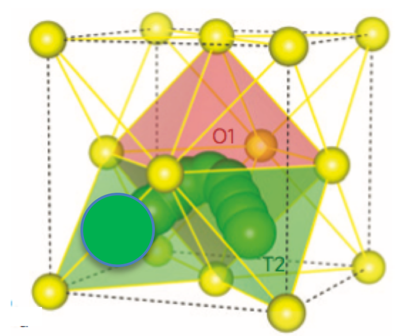
To achieve high ionic conductivity,
low E_a
+
high n

LGPS

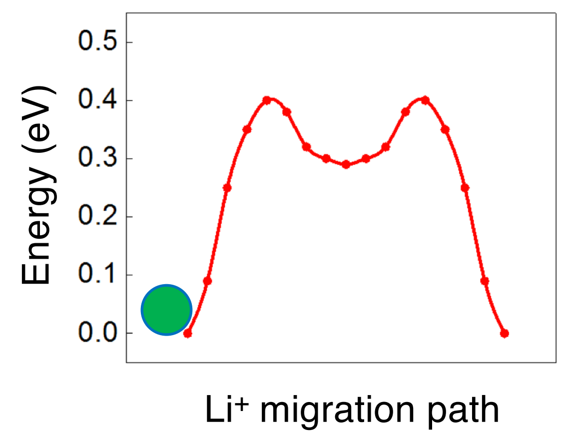


In BCC anion lattice
Face-shared tetrahedra: 0.15 eV





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

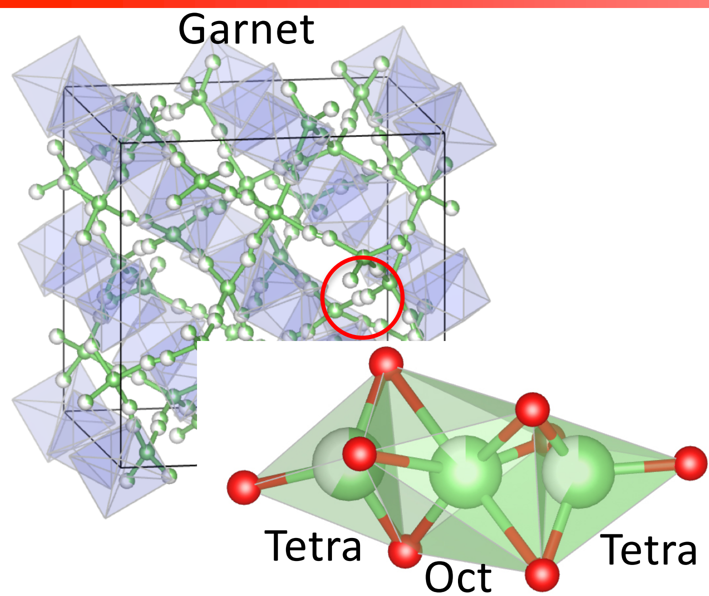


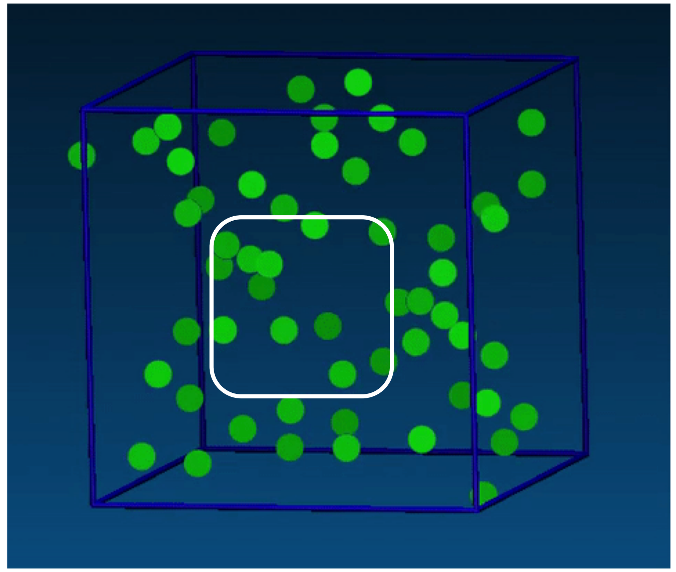
$$\sigma \propto e^{\frac{-E_a}{KT}}$$

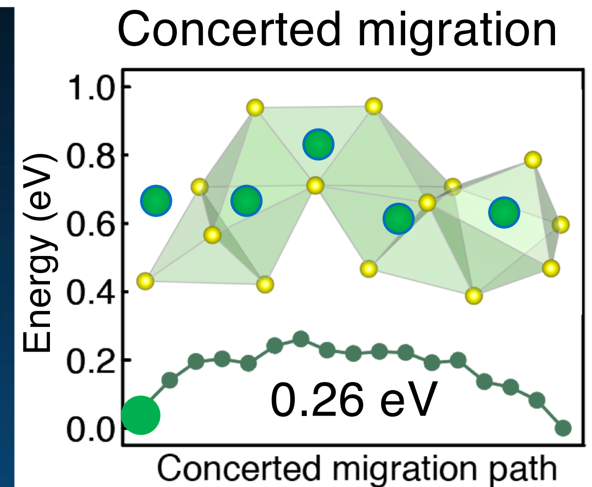
~10^4

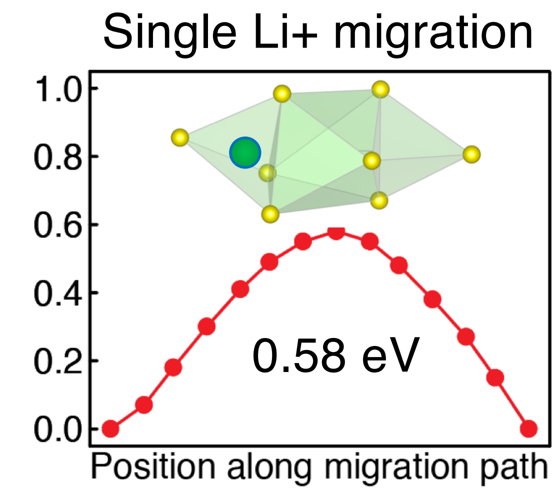
Wang, ... Mo, Ceder, ***Nat. Mater.* 14**: 1026 (2015

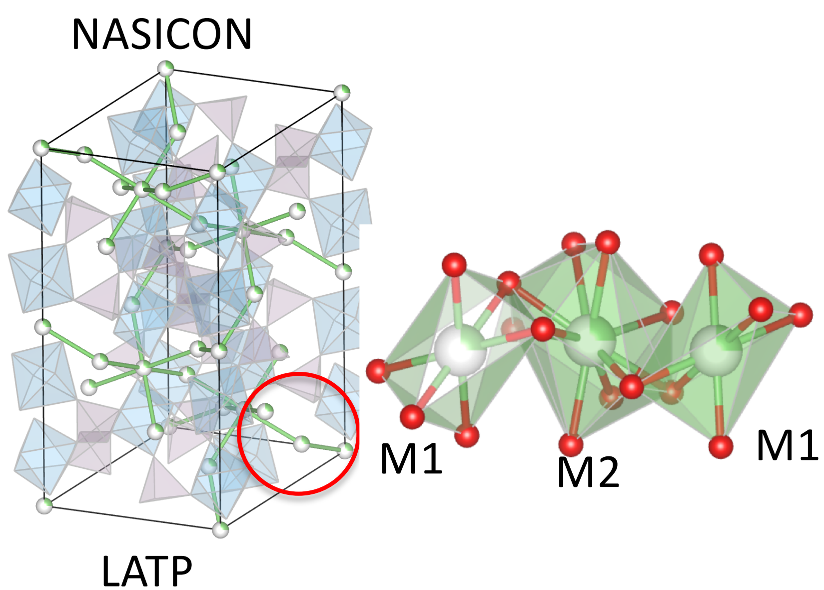
Concerted migration mechanism activates super-ionic conductors

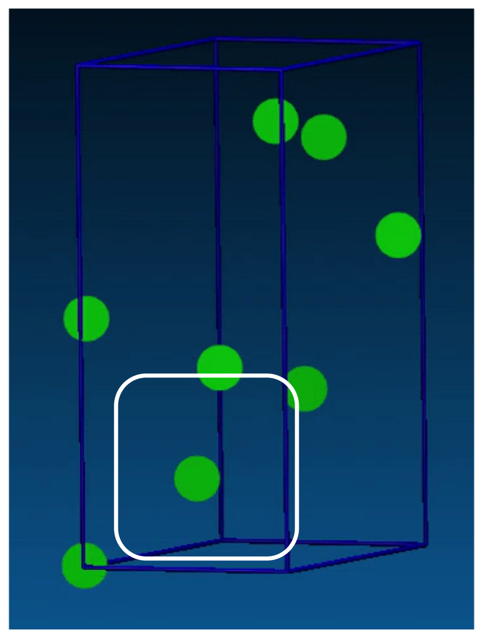


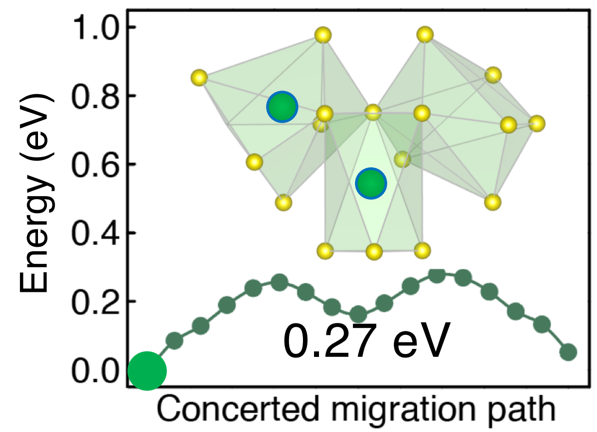


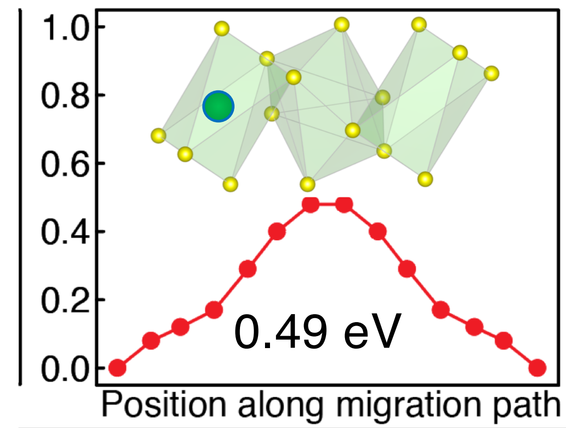










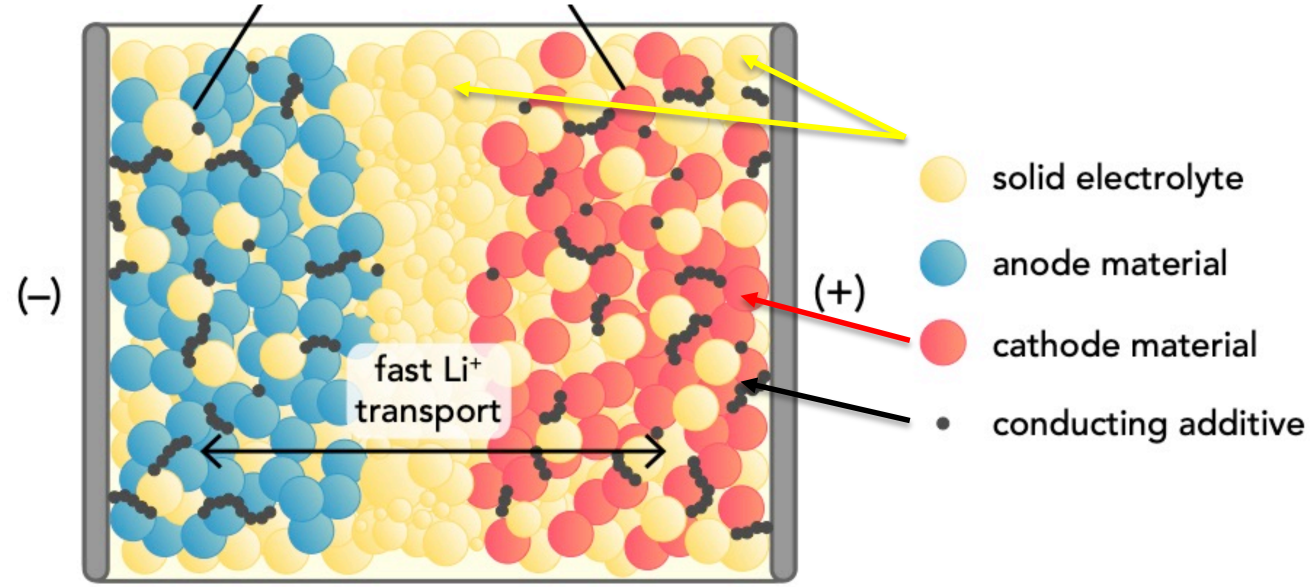


Challenge: Complex crystal structure and unique Li-ion sublattice are required to achieve concerted migration

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:

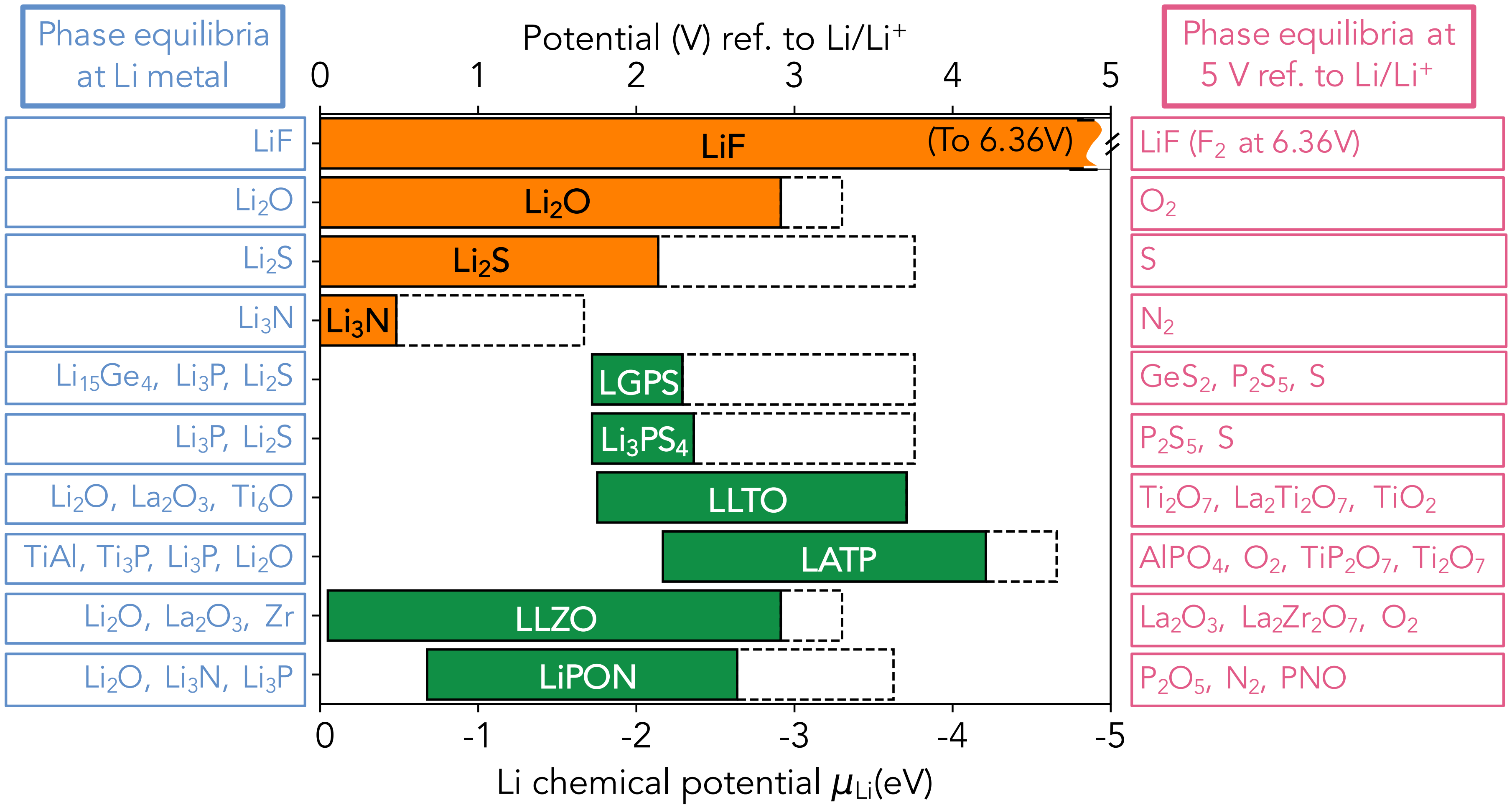
1. The <u>reduction</u> / <u>oxidation</u> of the solid electrolyte materials at applied voltage.
2. <u>Chemical reaction</u> between solid electrolyte and electrodes.
3. <u>Electrochemical reaction</u> (during cycling voltage) between solid electrolyte and electrodes.

Zhu, He, Mo, ***J. Mater. Chem. A***, 2016,4, 3253-3266
Nolen, Zhu, He, Bai, Mo, ***Joule*** 2018, 2, 2016-2046
Park, Bai, …, Mo, Jung, ***Adv. Energy Mater.*** 2018, 1800035

Thermodynamic Intrinsic Electrochemical Window of Solid Electrolyte

Li binary stable against Li metal

Cation reduction at low potential



S oxidation in sulfide at > ~2.3V

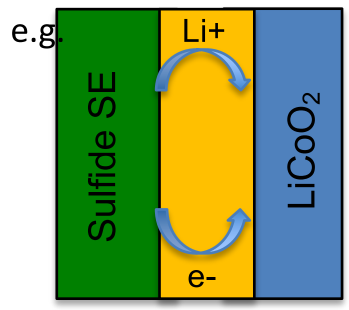
Oxidation in oxides may be kinetically limited.

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

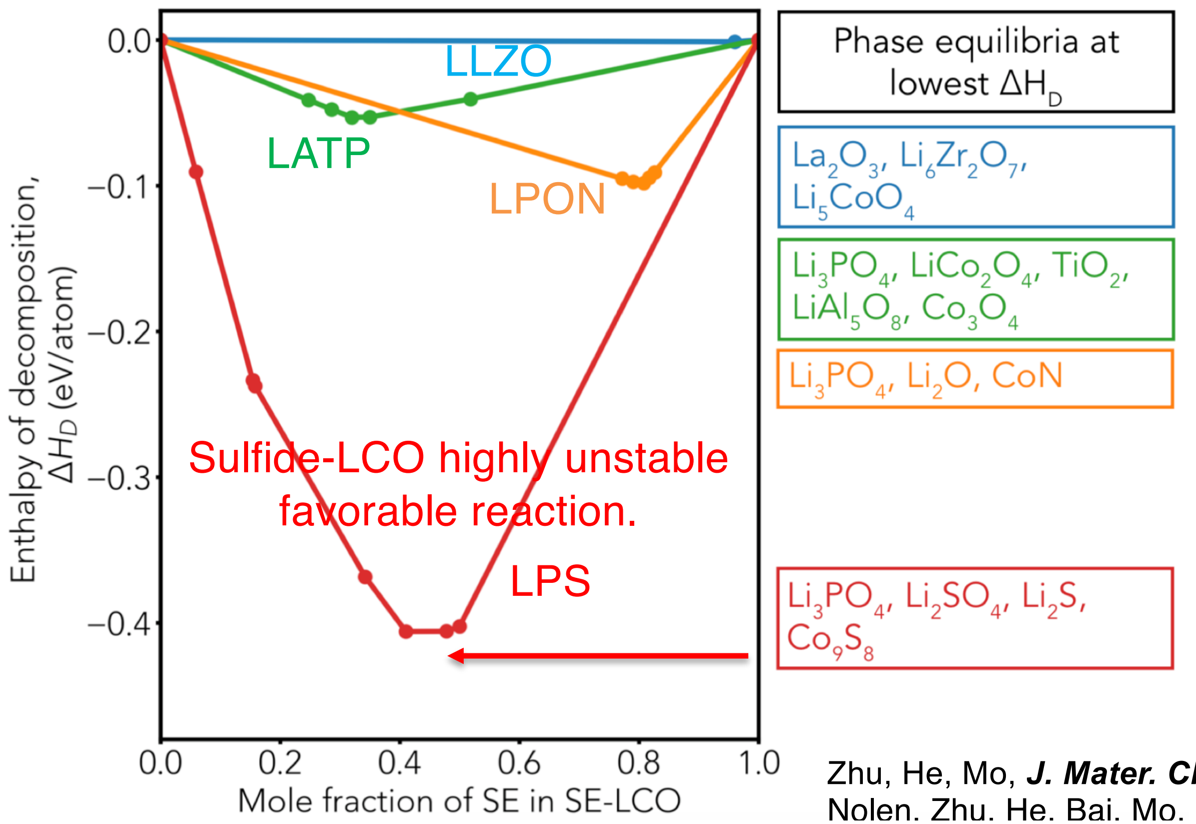
Nolan, Zhu, He, Bai, Mo, ***Joule***, 2018, 2, 2016-2046

Unstable SE-Cathode Interface : Interface Coating is Needed

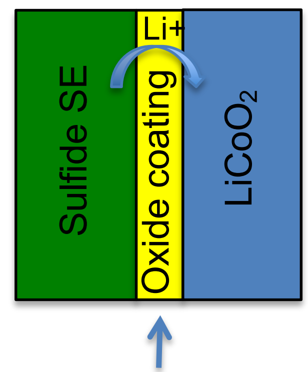
Incompatible interface
Sulfide SE-LCO



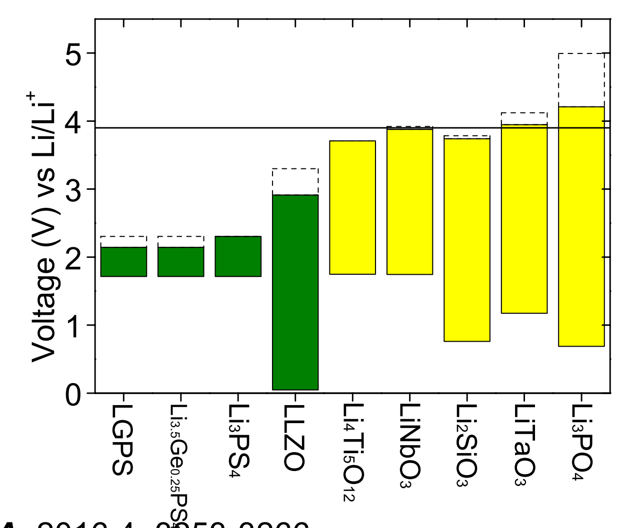
Mixed conducting interphaselayer formed
-> Sustained decomposition.
-> Thick interphase layer.
-> High interfacial resistance.



Mitigation strategy:
Converting to Type 3
by **coating**

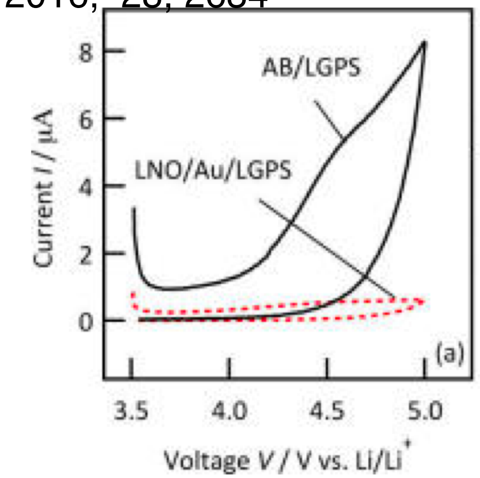


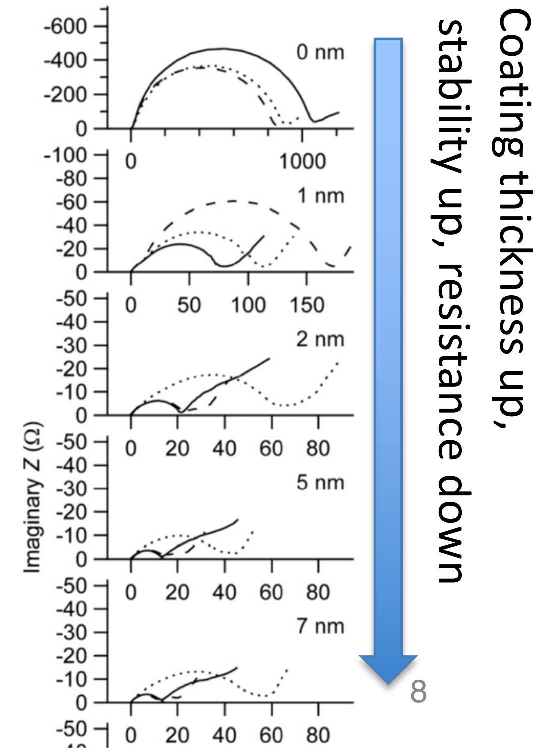
Oxide coating layer,
(e.g. $LiNbO_3$, Li_3PO_4, etc.)
serves as artificial SEI



Zhu, He, Mo, ***J. Mater. Chem. A***, 2016,4, 3253-3266
Nolen, Zhu, He, Bai, Mo, ***Joule*** 2018, 2, 2016-2046

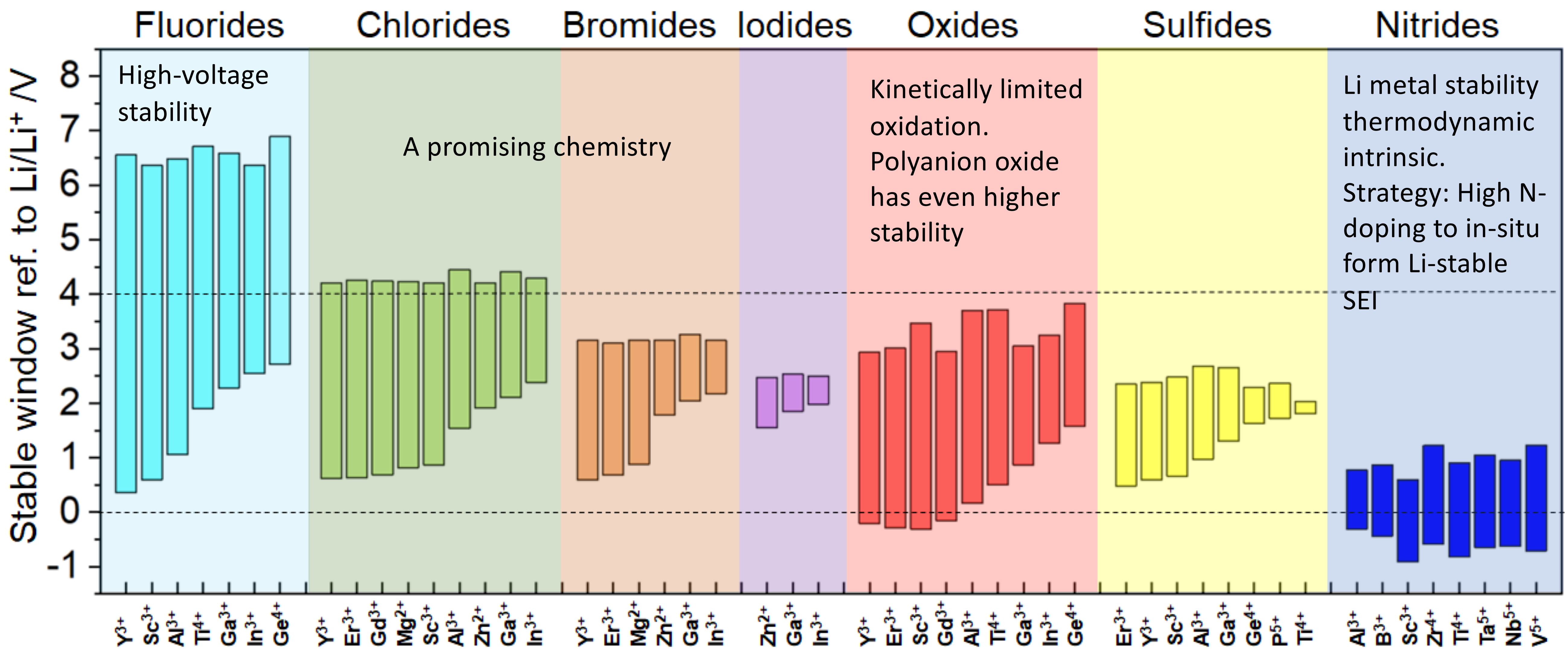
Kanno et al. Chem. Mater. 2016, 28, 2634





Electrochemical window for different anion chemistry

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



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

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

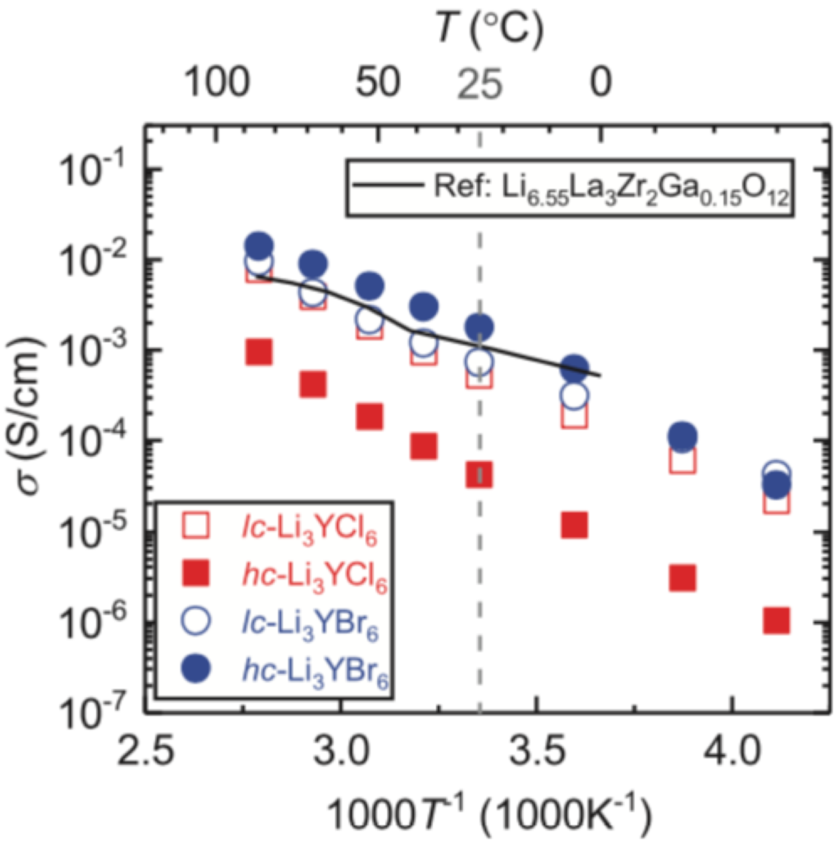
New Halide Solid Electrolyte by Panasonic

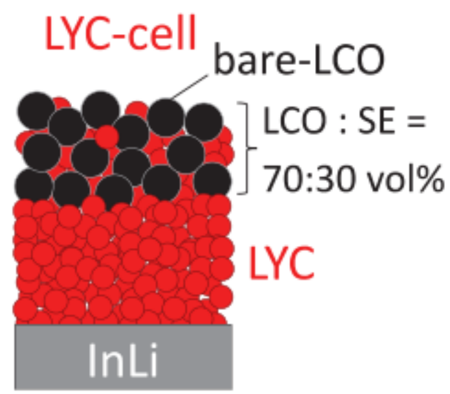
Asano et al., Adv. Mater. 2018, 30, 1803075

- Li_3YCl_6 – hcp Cl 0.51 mS/cm@300K
- Li_3YBr_6 – fcc Br 1.7 mS/cm@300K

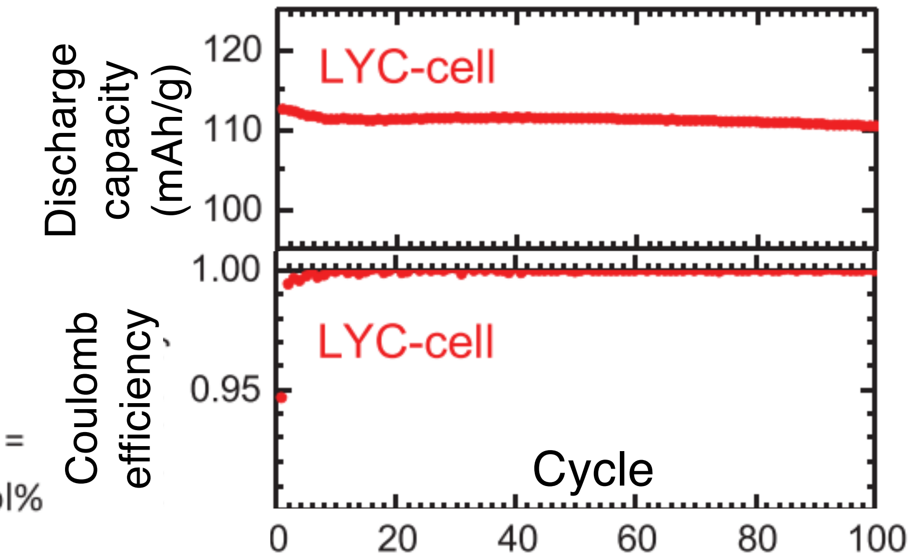
Advantages:

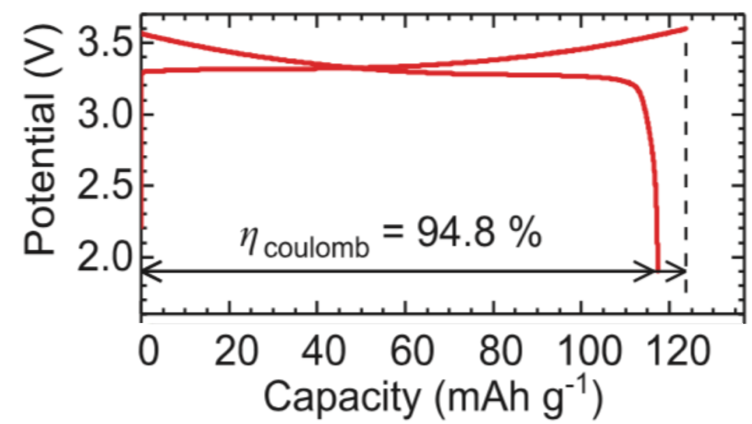
✧ High ionic conductivity (10^4 -10^3 mS/cm at RT)
✧ Electrochemical stability
✧ Interface compatibility
✧ Air stability, Mechanical deformability, etc.





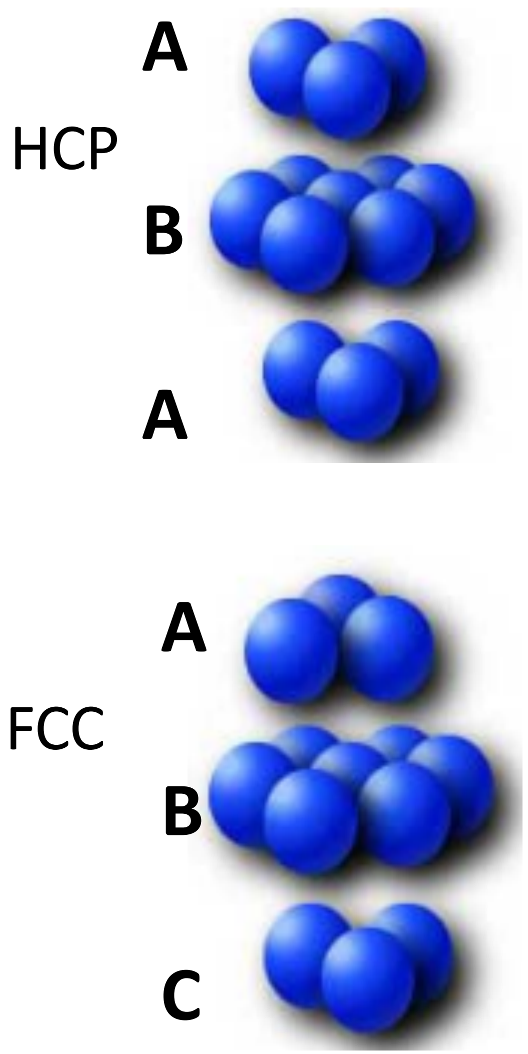
T = 25 °C, 0.1 C



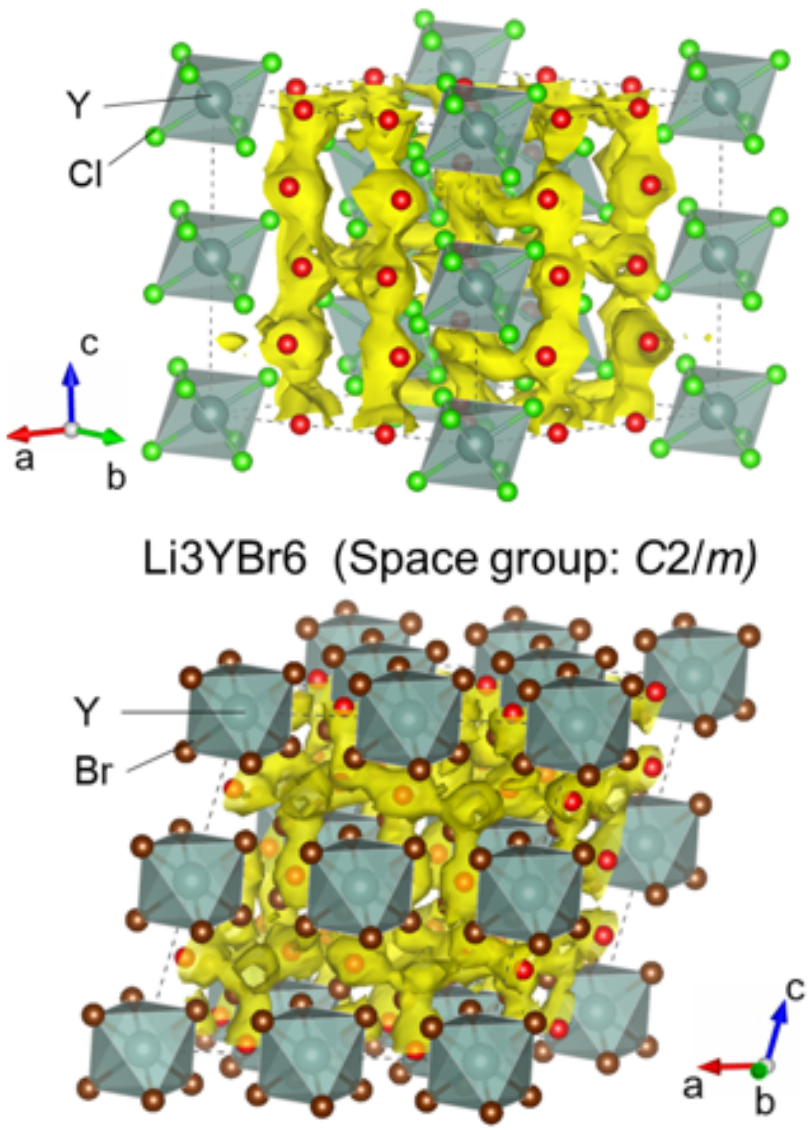


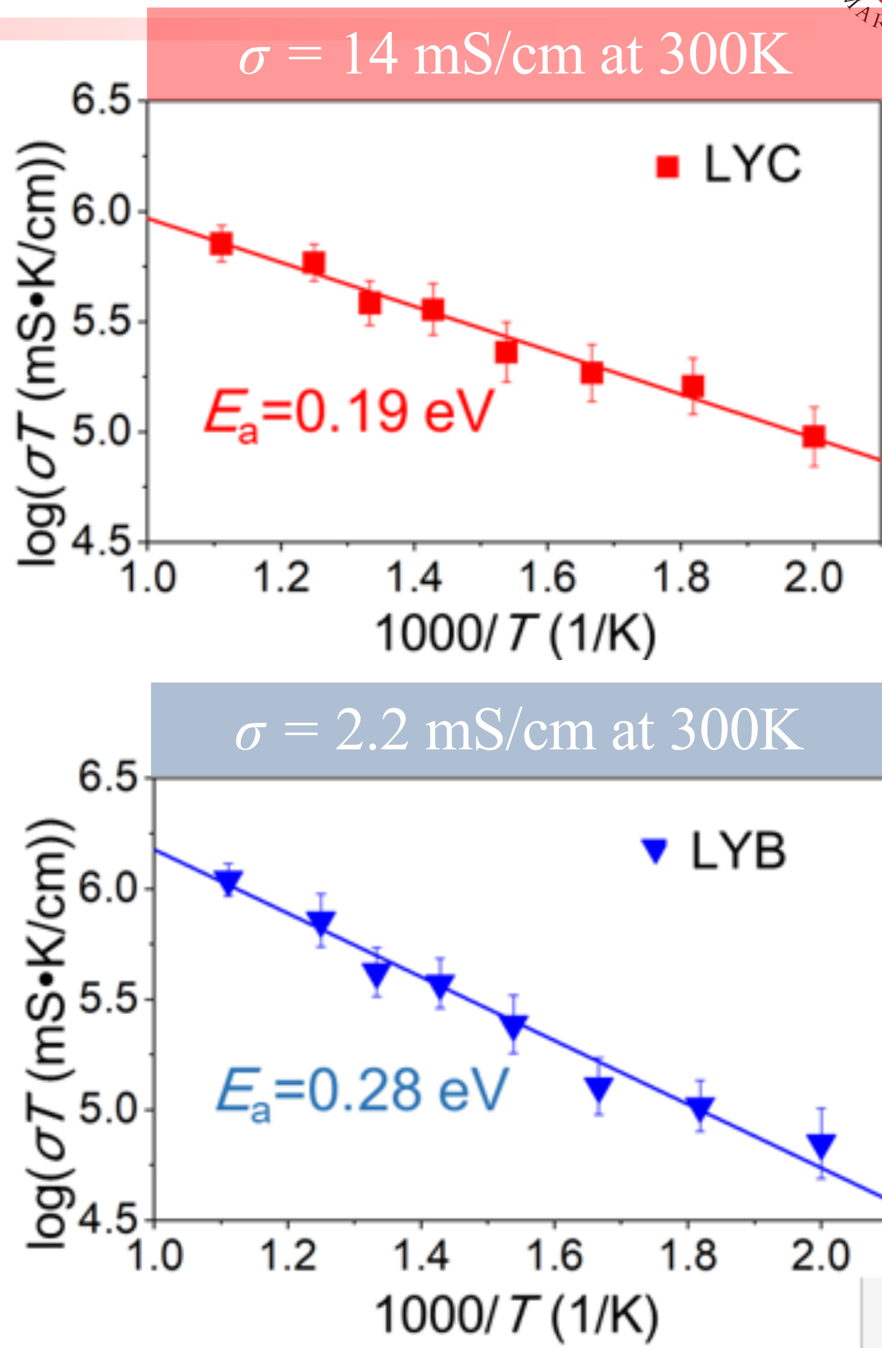
High Li+ conductivity confirmed in Ab initio molecular dynamics simulation

Close-packing Cl/Br anion sublattice



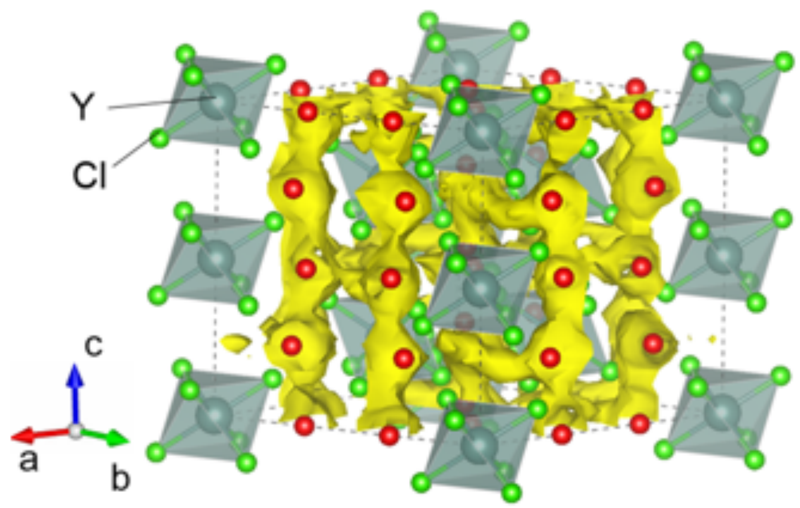
Li ion diffusion trajectories



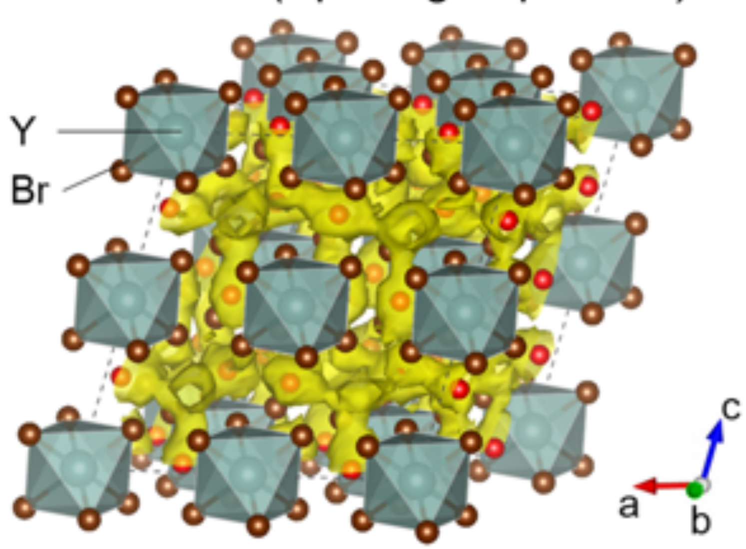


Intrinsic low migration barrier in close-packed Cl/Br sublattice

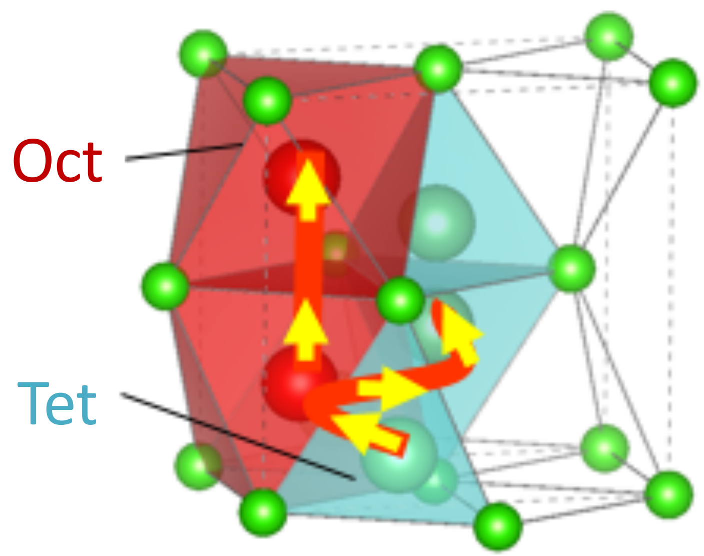
Li3YCl6 (Space group: $P\bar{3}m1$)

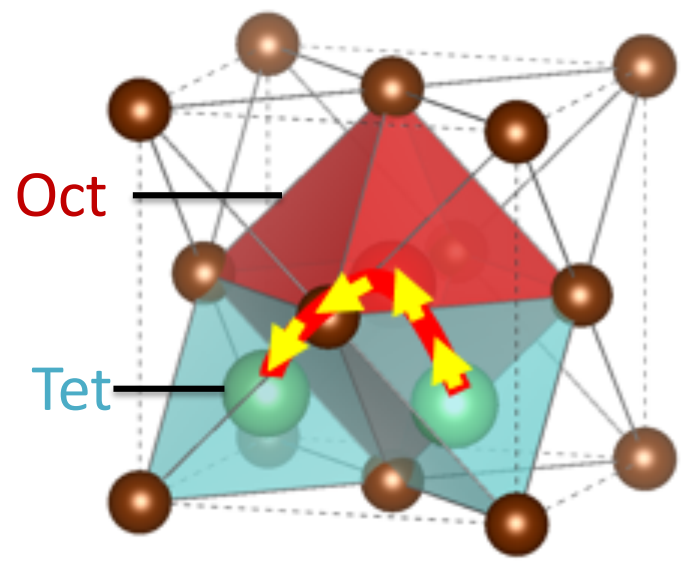


Li3YBr6 (Space group: $C2/m$)

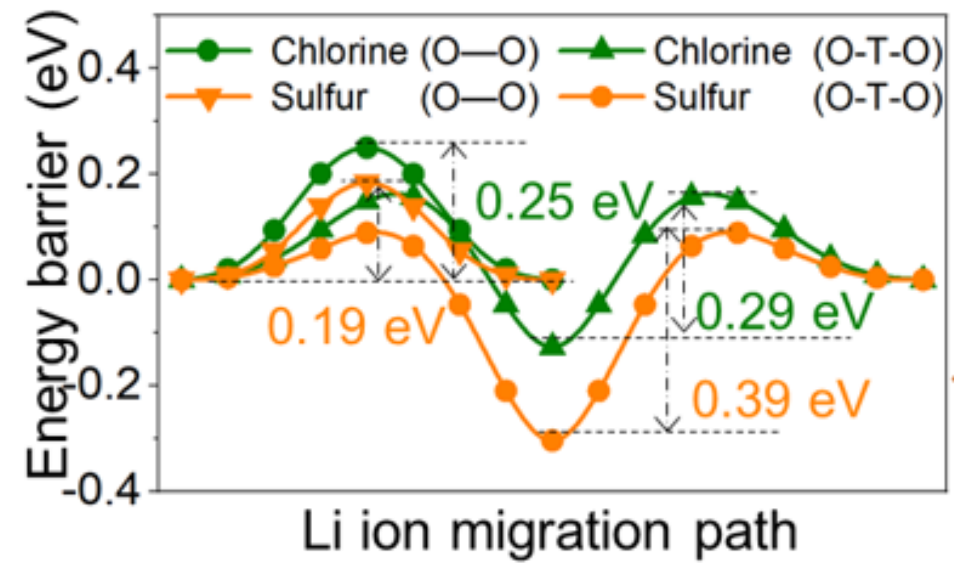


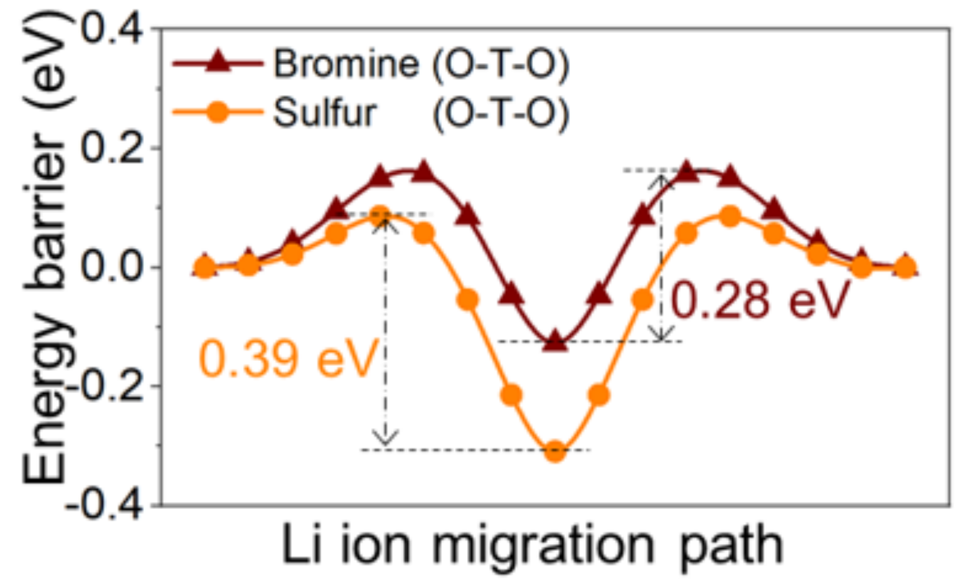
Li+ migration pathway



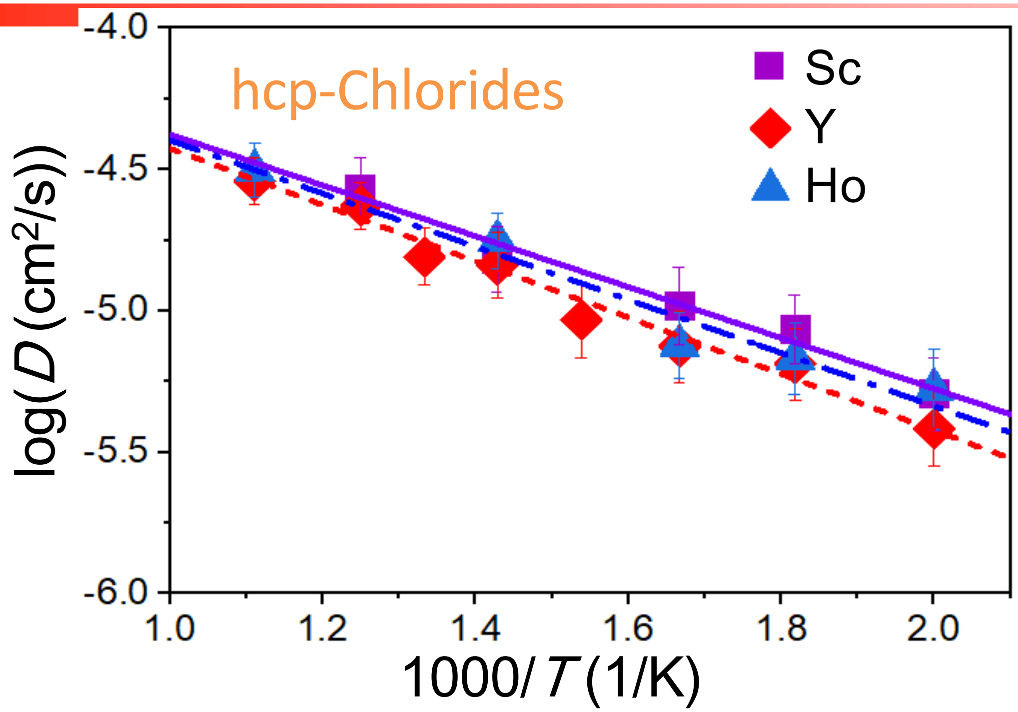


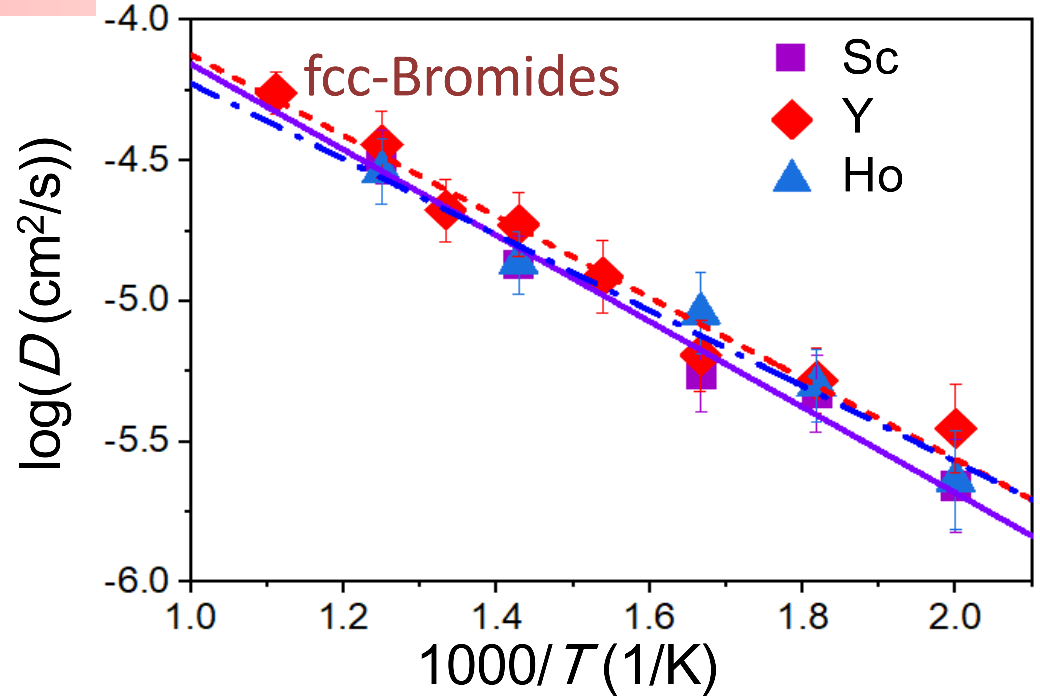
Diffusion Energy Barrier





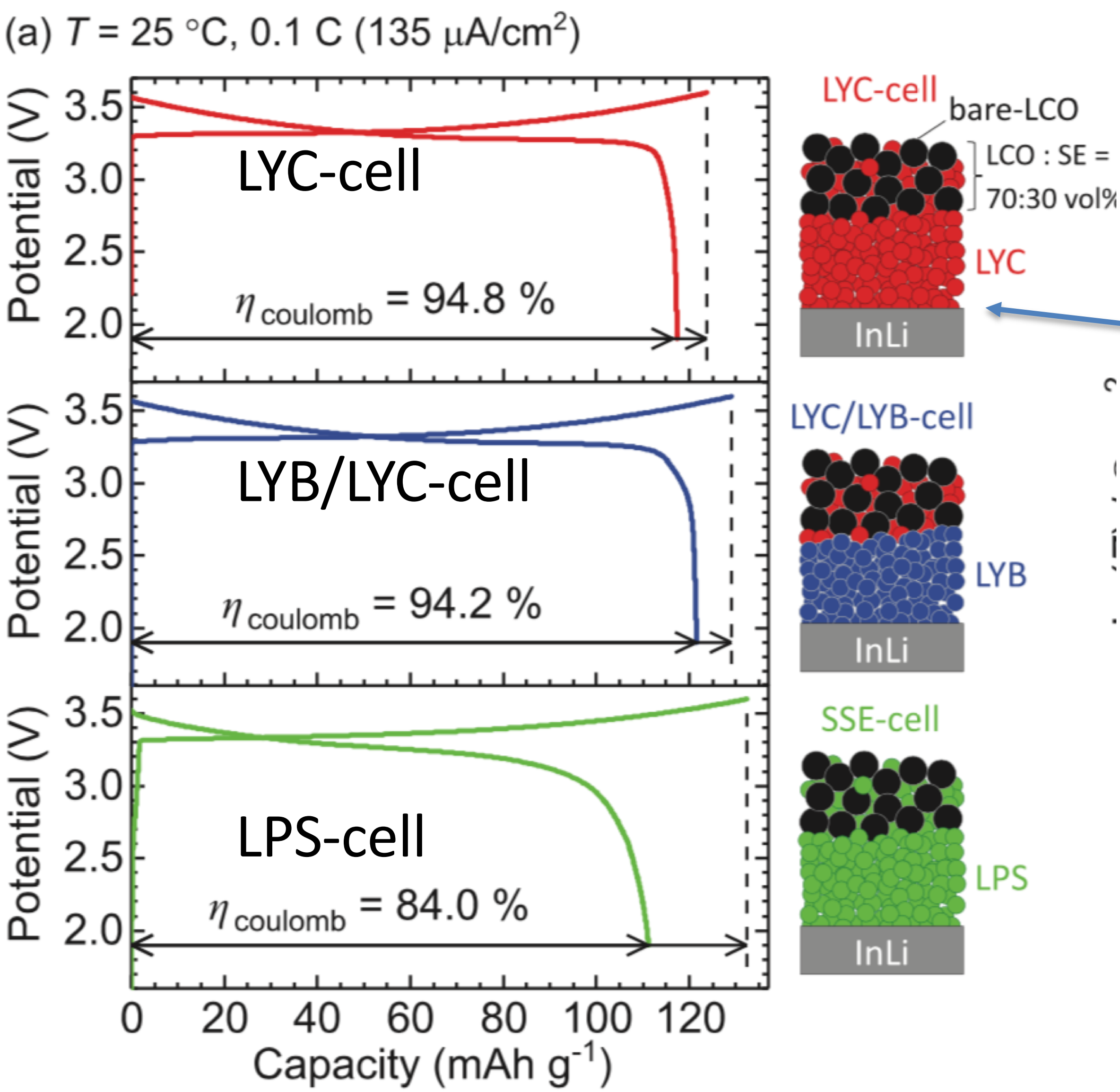
Fast ion conduction in Cl/Br lattice is general (not cation specific)





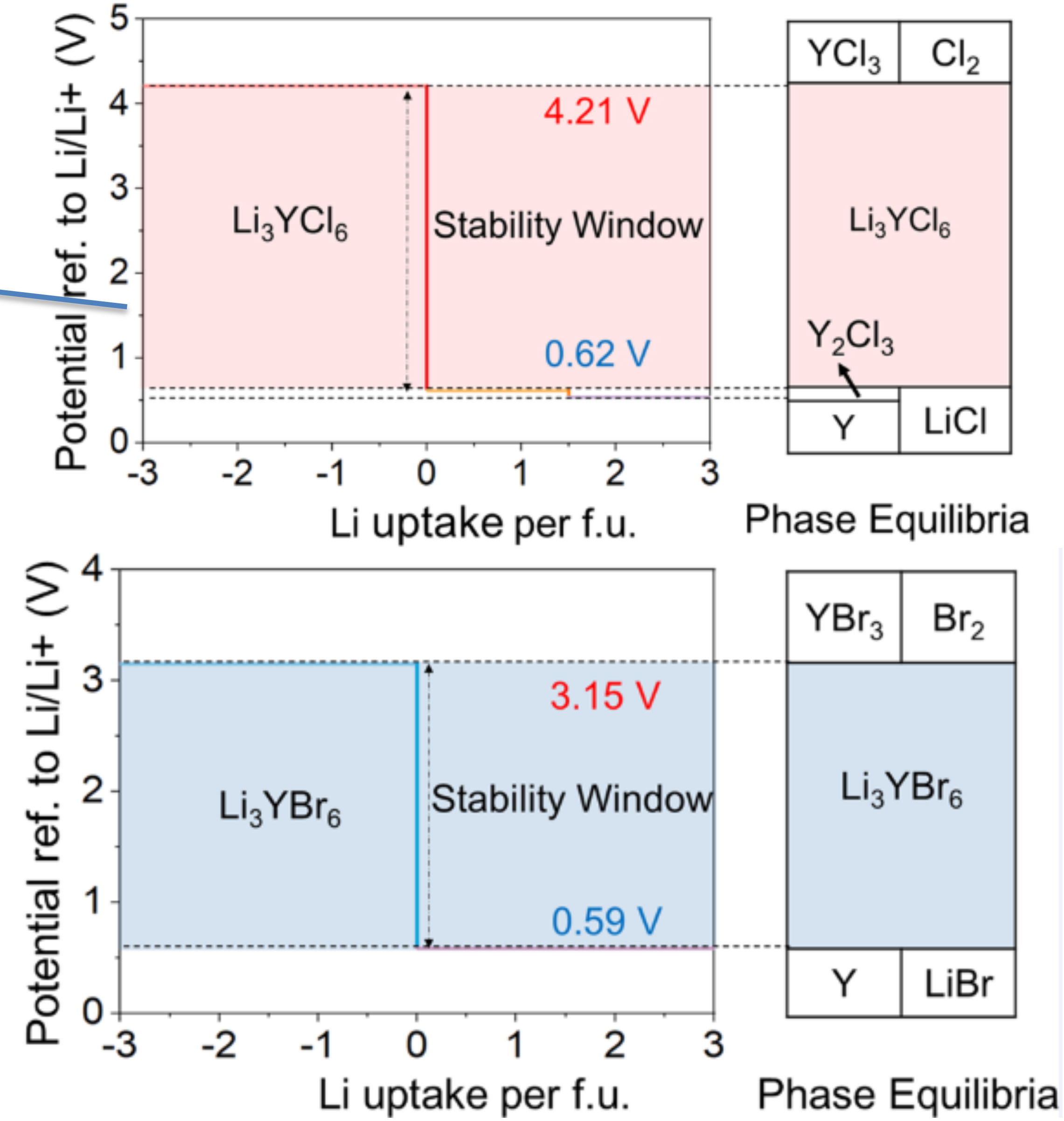
	σ at 300K (mS/cm)		E_a (eV)	
Composition	AIMD	Expt.	AIMD	Expt.
Li_3YCl_6	14	0.5	0.19 ± 0.03	0.40
Li_3YBr_6	2.2	1.7	0.28 ± 0.02	0.37
$Li_{10}GeP_2S_{12}$	14[1]	12[2]	0.21 ± 0.01[1]	0.23[2]
$Li_7La_3Zr_2O_{12}$	1.1[1]	0.5[3]	0.26 ± 0.02[1]	0.30[3]
Li_3ScCl_6	29	--	0.18 ± 0.04	--
Li_3HoCl_6	21	--	0.19 ± 0.03	--
Li_3ScBr_6	1.4	--	0.30 ± 0.04	--
Li_3HoBr_6	3.8	--	0.26 ± 0.04	--

Halide solid electrolytes exhibits wide electrochemical window



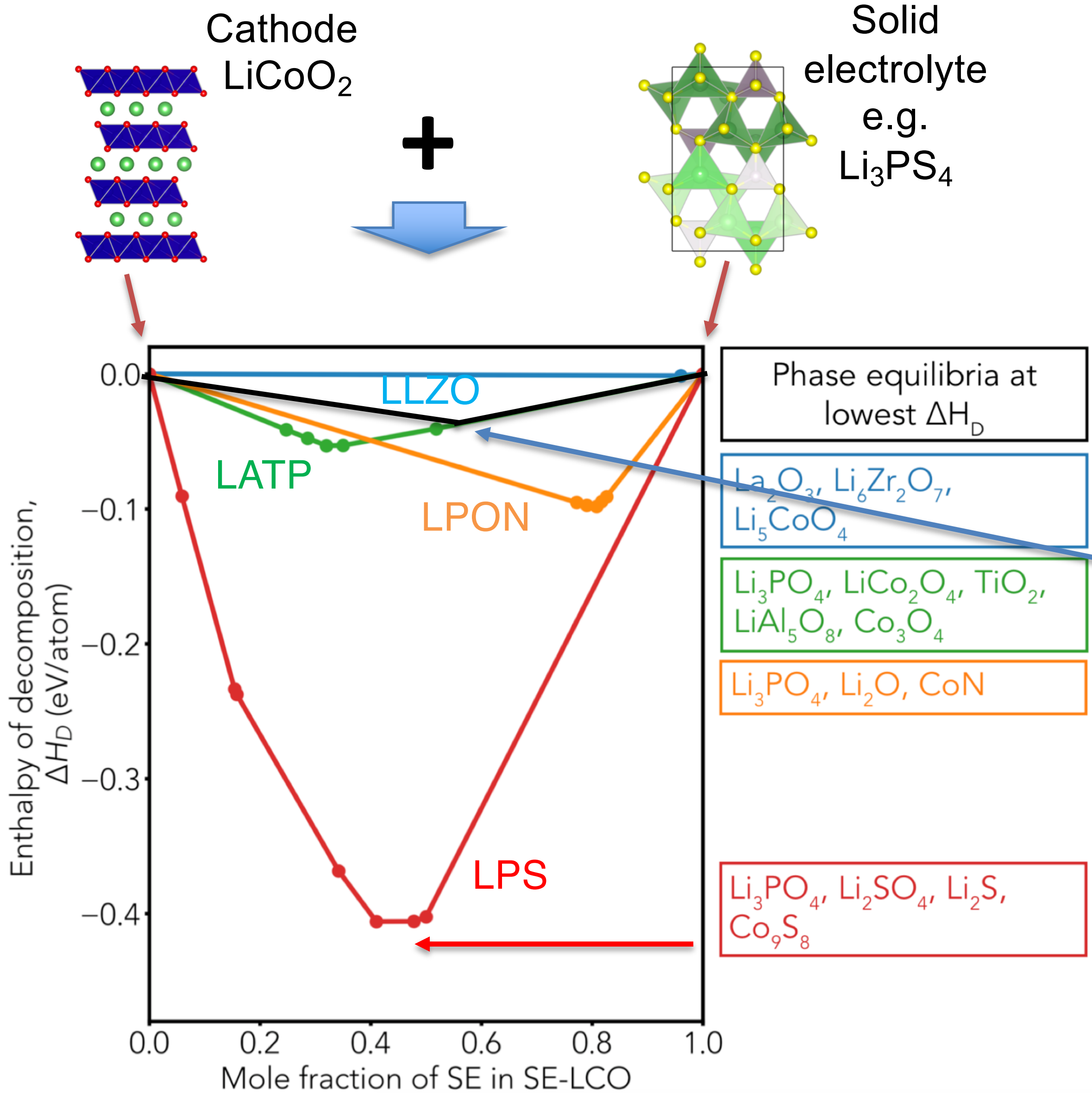
Asano et al. ***Adv. Mater.*** 2018, 1803075

Calculated thermodynamic electrochemical window



Wang, ... Mo, ***Angew. Chem. Int Ed.*** 2019, 58, 803

Chloride/Bromide SE Exhibit Good SE-Cathode Interface Stability



Thermodynamic calculations

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

C_{SE}	$C_{electrode}$	x_m	$\Delta E_{D,min,mutual}$ (meV/atom)
LYC	$LiCoO_2$	0.56	-37
LYC	$Li_{0.5}CoO_2$	0.42	-24
LYB	$LiCoO_2$	0.63	-44
LYB	$Li_{0.5}CoO_2$	0.66	-58
LYC	$LiFePO_4$	0.42	-29
LYC	$FePO_4$	0.62	-20
LYB	$LiFePO_4$	0.32	-14
LYB	$FePO_4$	0.36	-46

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.

Wang, Bai, Nolan, Liu, Gong, Sun, Mo, ***Angew. Chem. Int Ed.*** 2019, 58, 8039

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

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

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Nolen, Zhu, He, Bai, Mo, ***Joule*** 2018, 2, 2016-2046

Zhu, He, Mo, ***J. Mater. Chem. A*** 2016,4, 3253-3266

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