

Crystal Structure of Fast Li-Ion Conductors : Insights from Computation Analysis

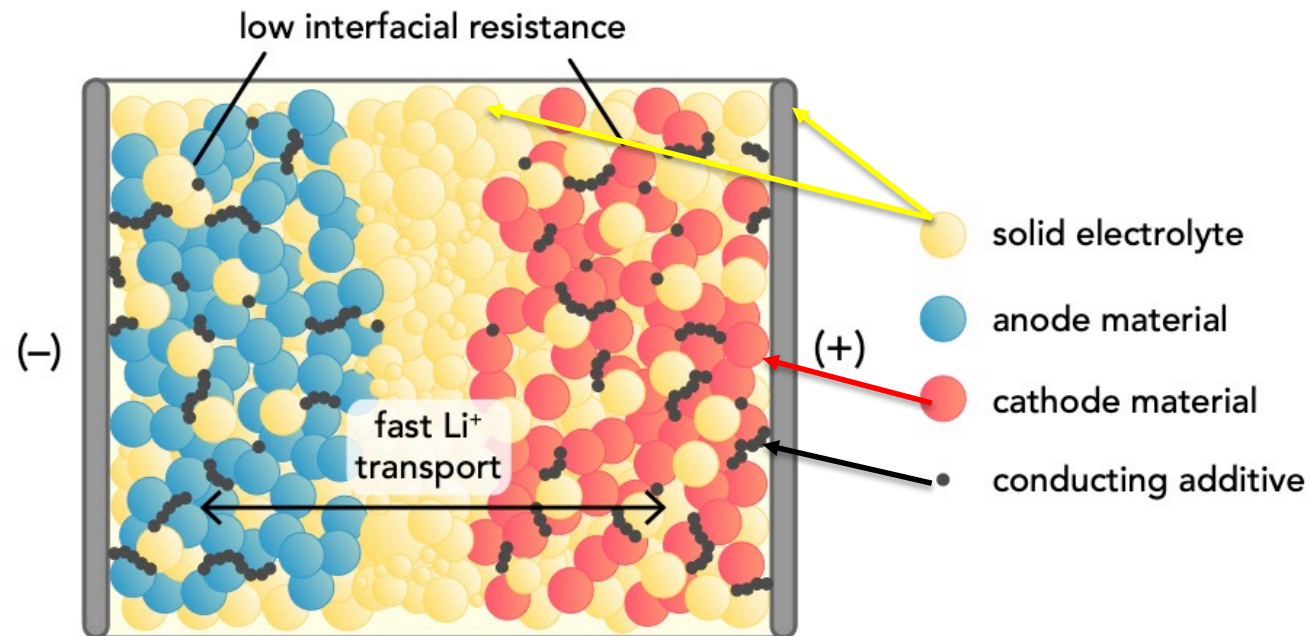
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Opportunities and Challenges: All-Solid-State Li-ion Batteries

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 stability
 - Interface stability
 - Air & moisture stability
- Mechanical property
- Low-cost & scalable synthesis, processing, cell fabrication

Challenges :

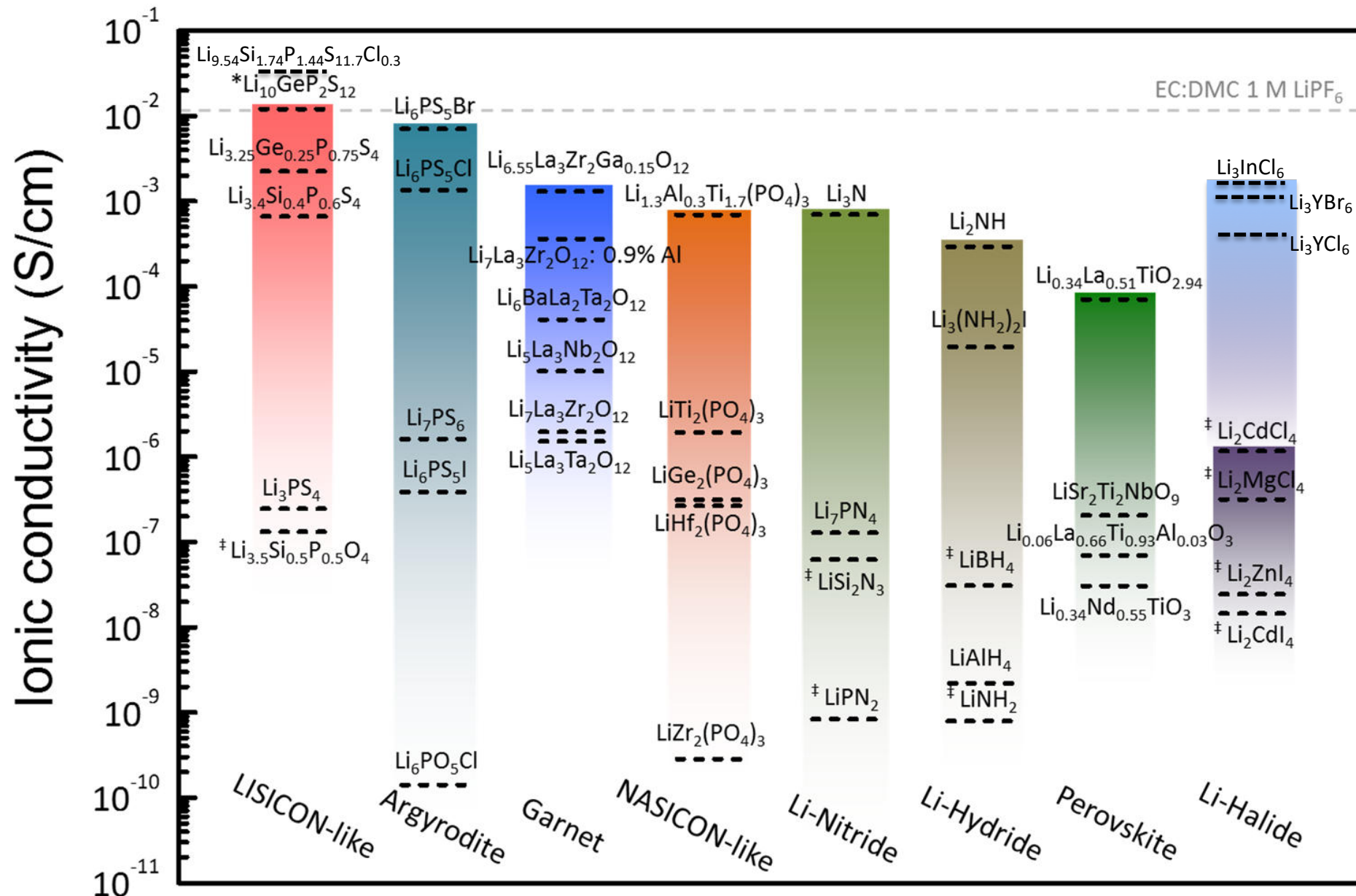
- Li solid electrolyte with high ionic conductivity, good stability, etc.
- Interfaces between electrolyte and electrodes.

Current solid electrolytes do not simultaneously satisfy all desired properties.

Need to develop new systems.

Our goal: Use first principles computation to achieve this

What structures can become super-ionic conductor ?



Why these crystal structures can become super-ionic conductors ?

Can we understand why and then design/predict new ones?

BCC anion framework exhibits lowest barrier energy landscape

Ion migration in solids



Ionic conductivity

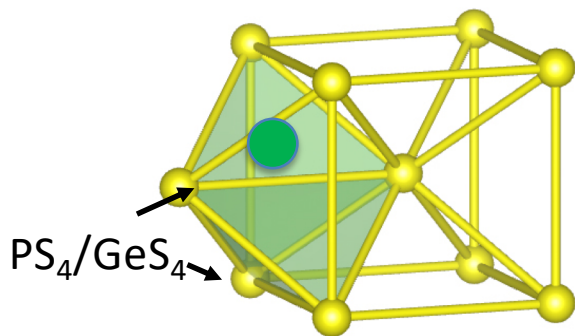
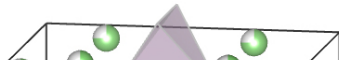
$$\sigma = \frac{q^2}{kT} n D_0 e^{-\left(\frac{E_a}{kT}\right)}$$

E_a : Activation energy

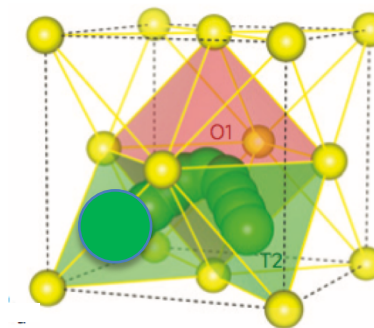
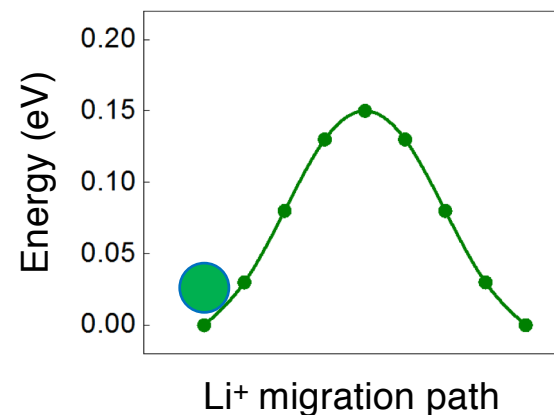
n : mobile carrier concentration

To achieve high ionic conductivity,
low E_a
 +
high n

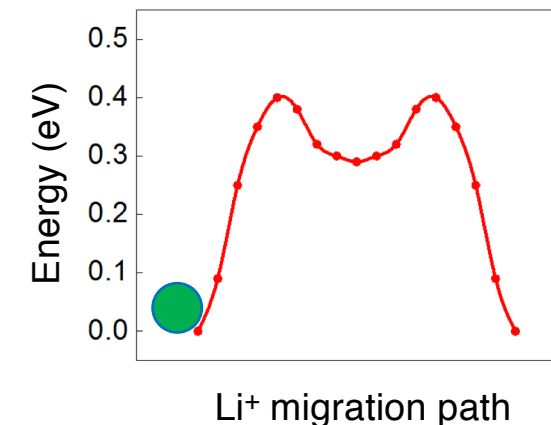
LGPS



In BCC anion lattice
 Face-shared tetrahedra: 0.15 eV

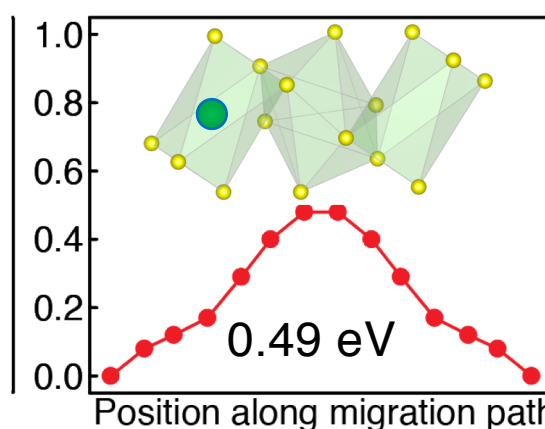
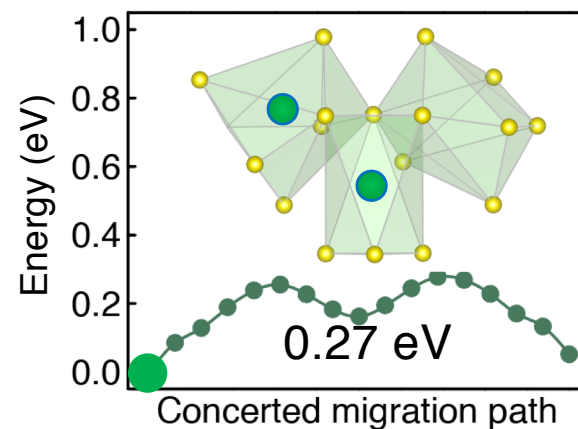
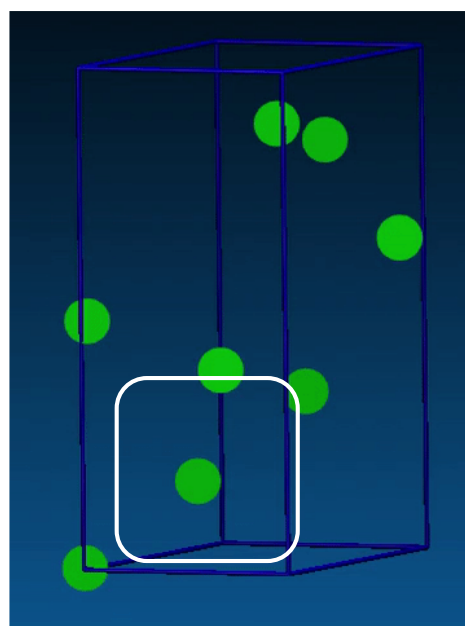
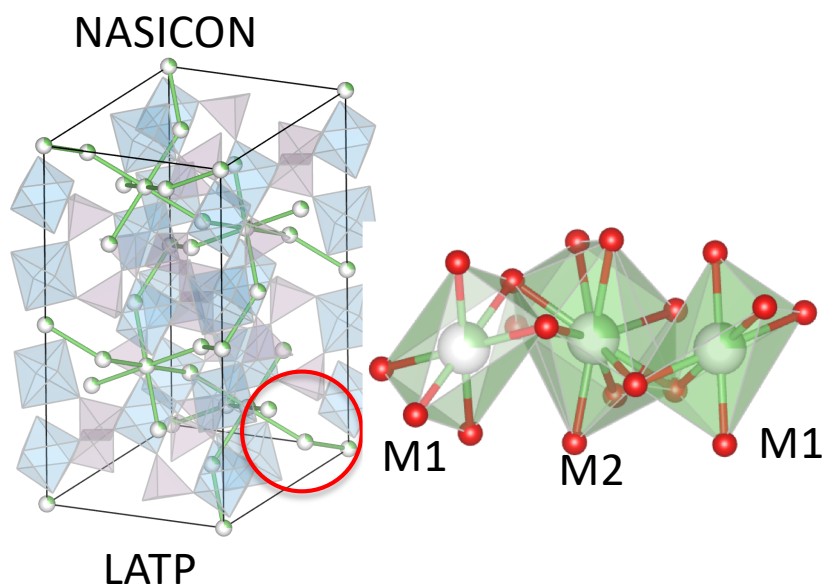
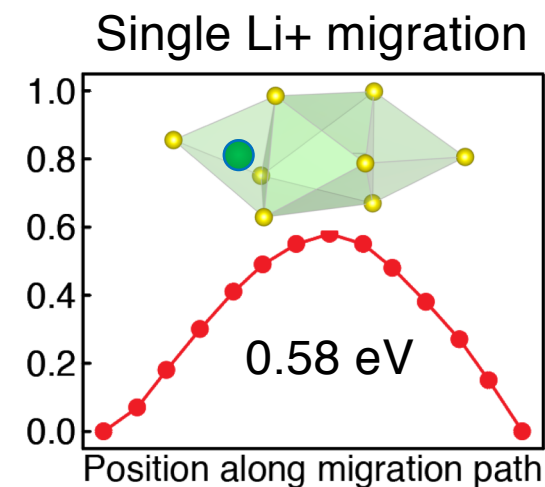
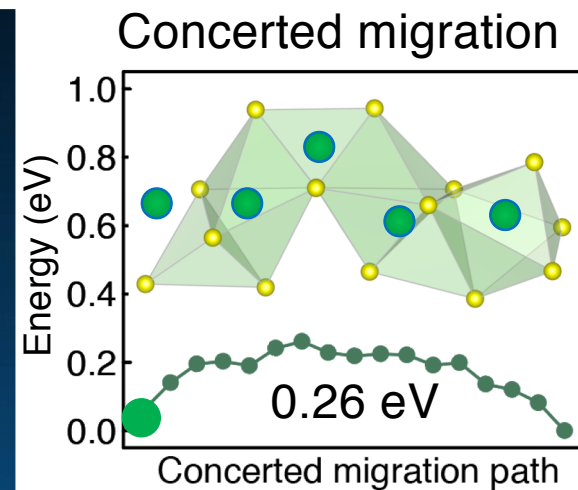
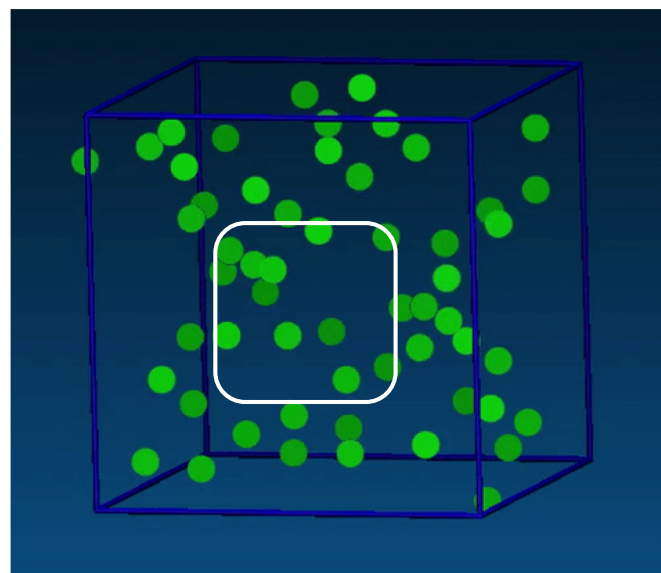
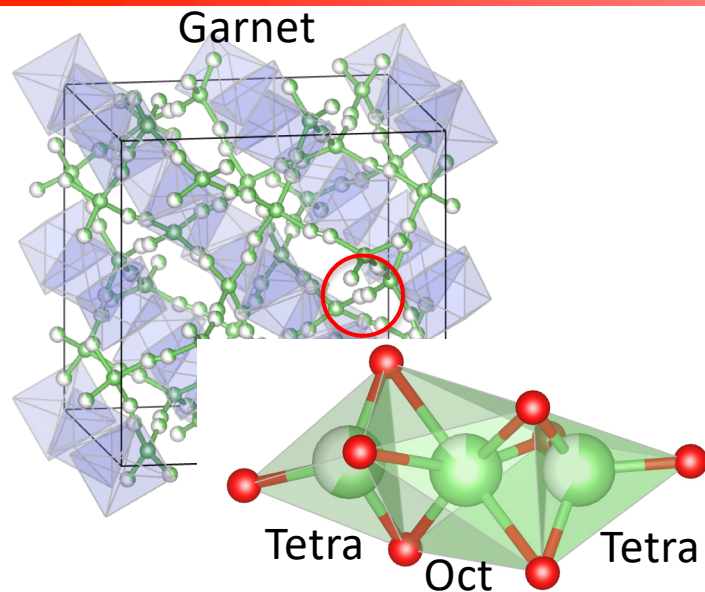


In FCC anion lattice
 tetra-oct-tetra: 0.4 eV



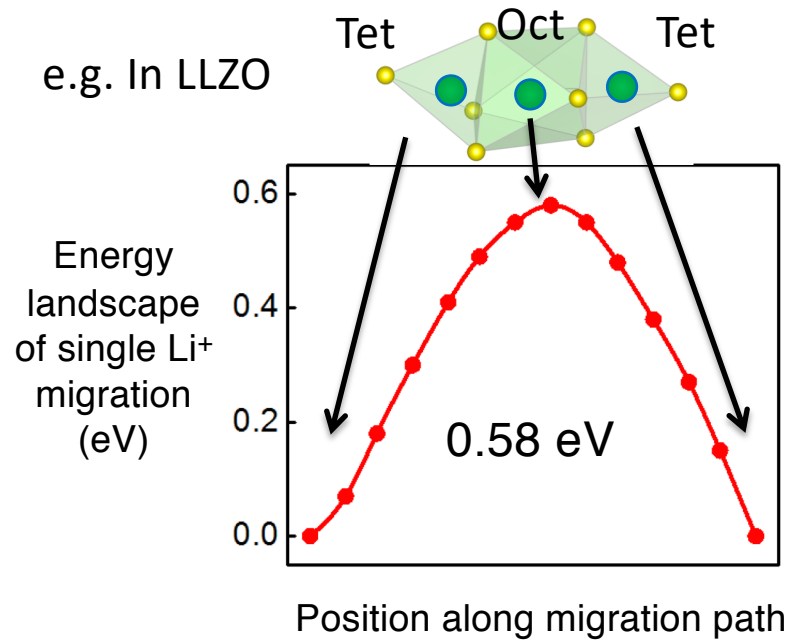
$$\sigma \propto e^{\frac{-E_a}{KT}} \sim 10^4$$

Concerted migration as key diffusion mechanism in super-ionic conductors



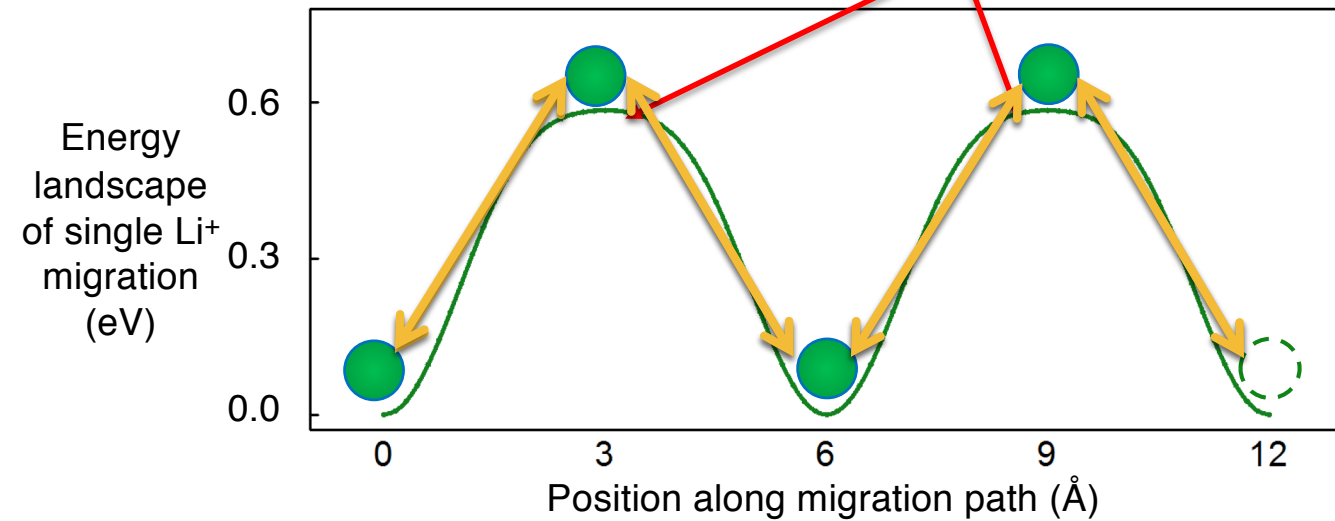
What's the origin of low-barrier concerted migration?

Why concerted migration has lower barrier?

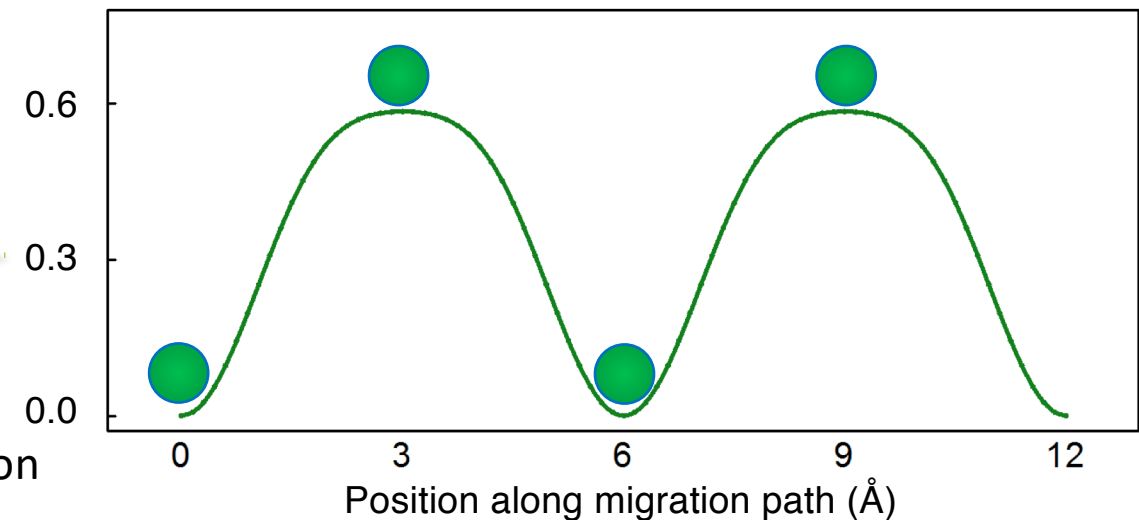
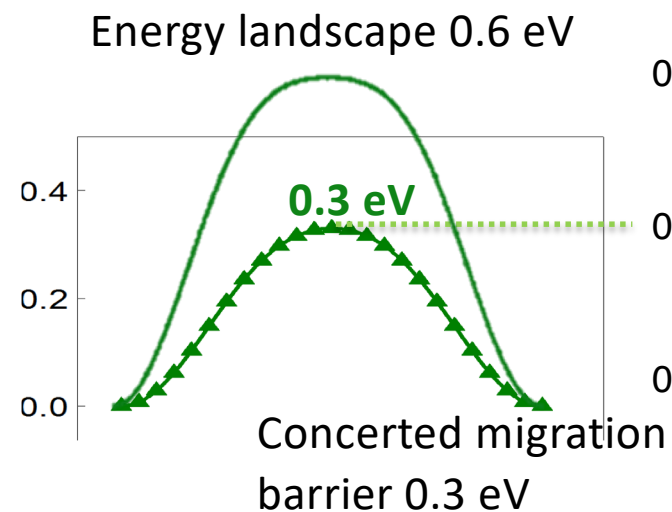


Li-Li Coulomb interaction

High-energy sites occupancy

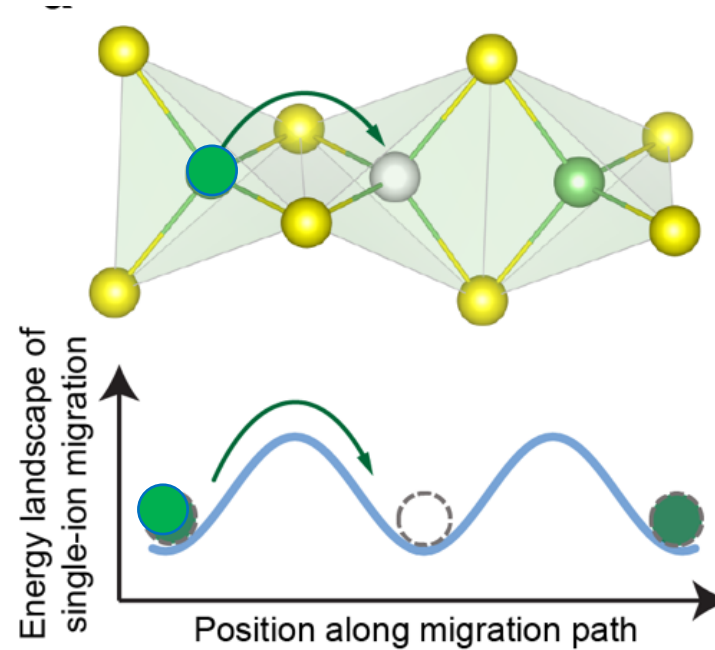
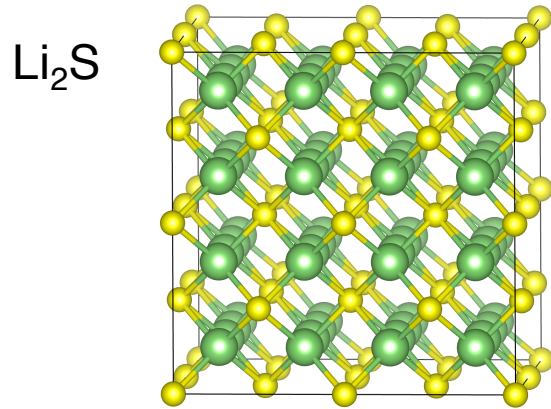


During concerted migration, the down-hill migration of high-energy ions cancels out a part of hill-climbing migration barrier.

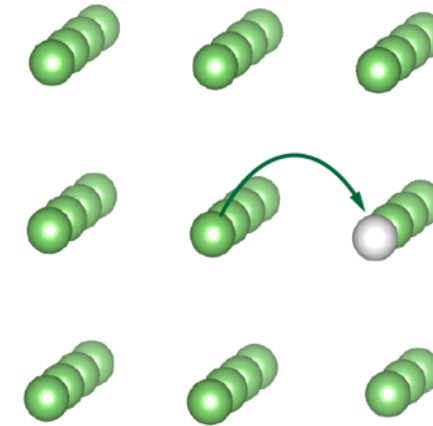


Li⁺ diffusion mechanism : typical solid vs super-ionic conductor

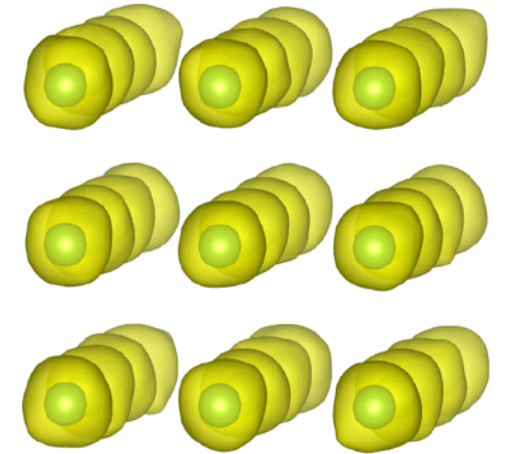
Typical solid



single-ion migration

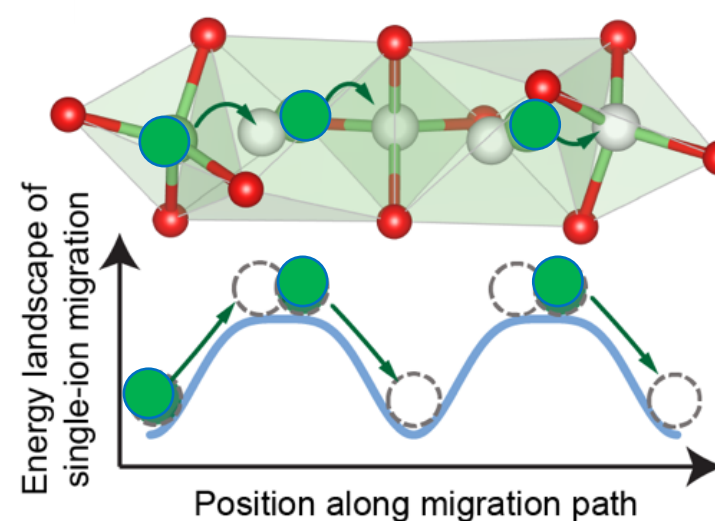
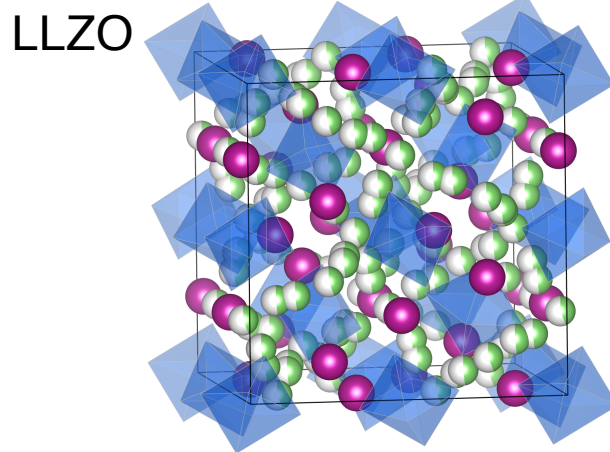


Ordered Li sublattice

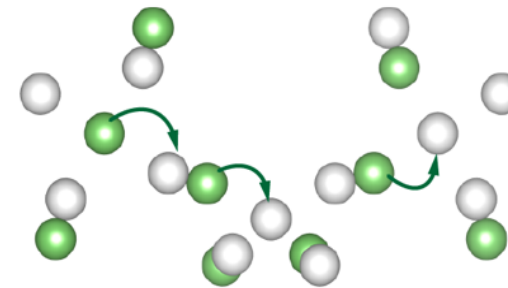


Li⁺ probability density

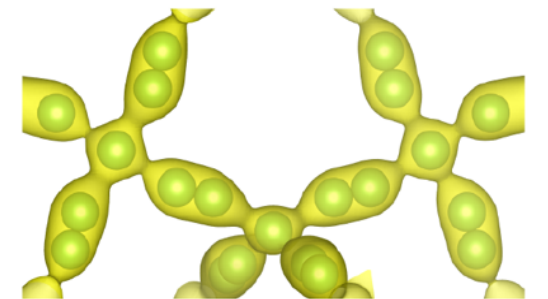
Super-ionic conductor



multi-ion
concerted migration

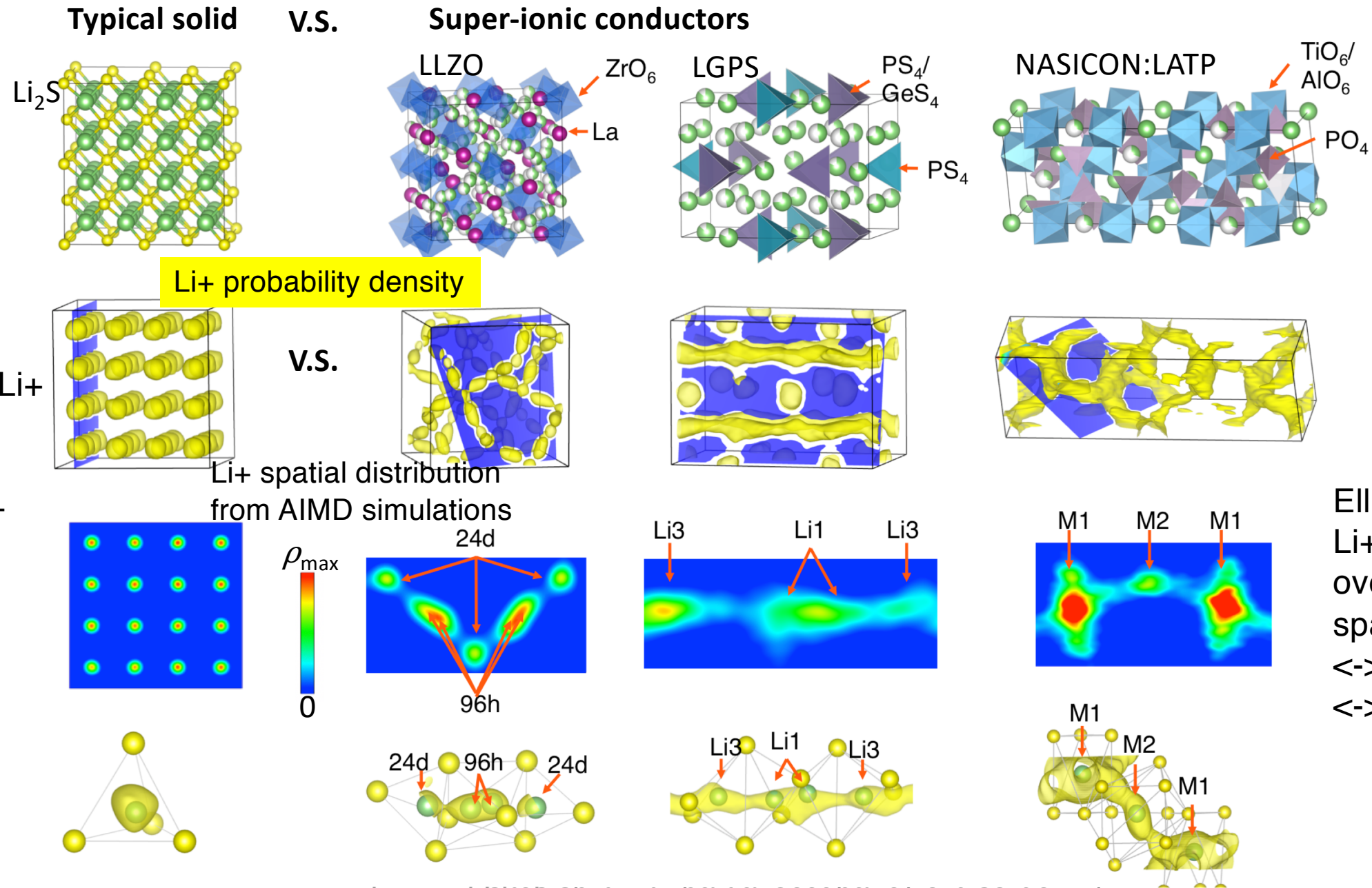


Disordered Li sublattice



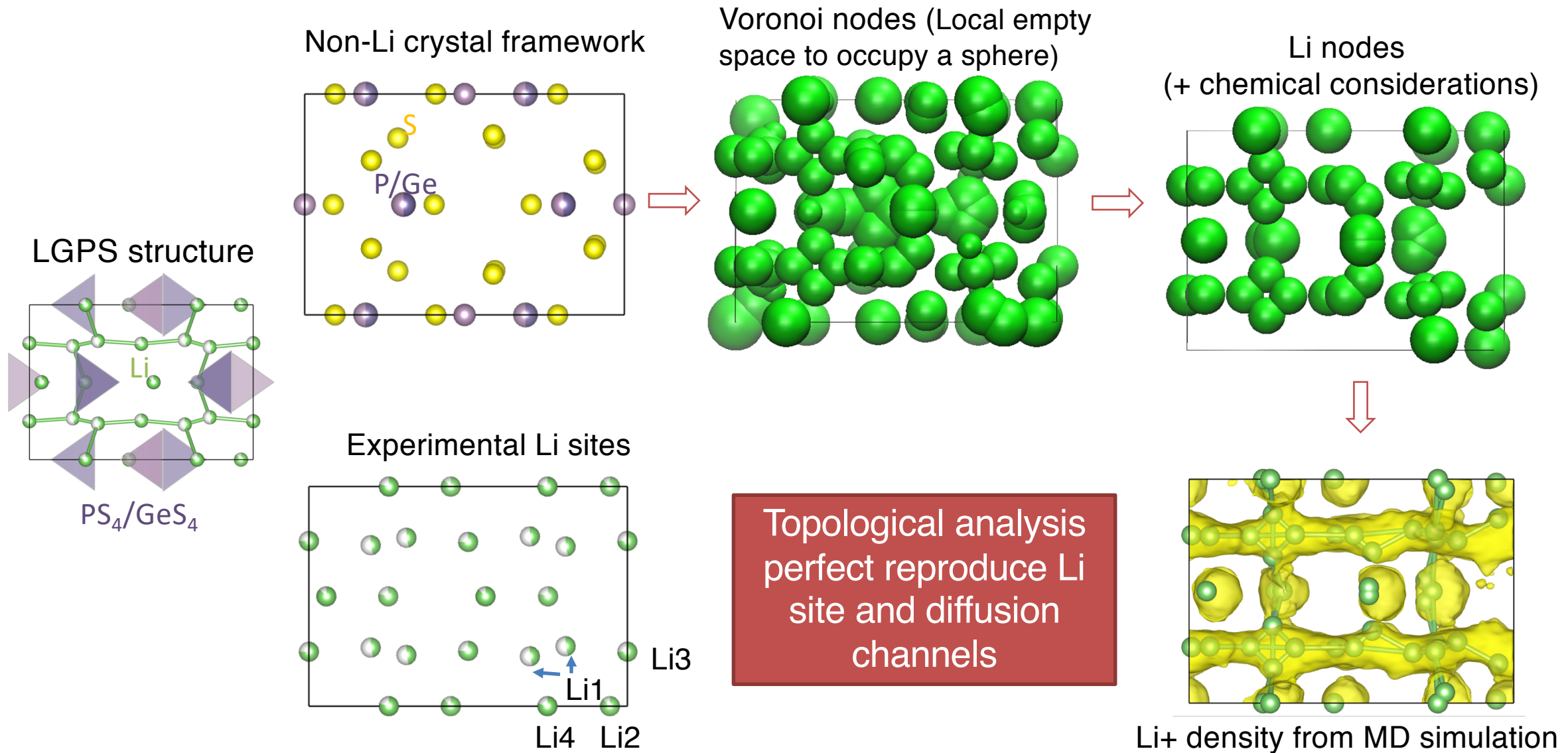
What features of garnet crystal structure make such disordered conductive Li lattice?

Li⁺ site and Li sublattice disordering in crystal structure



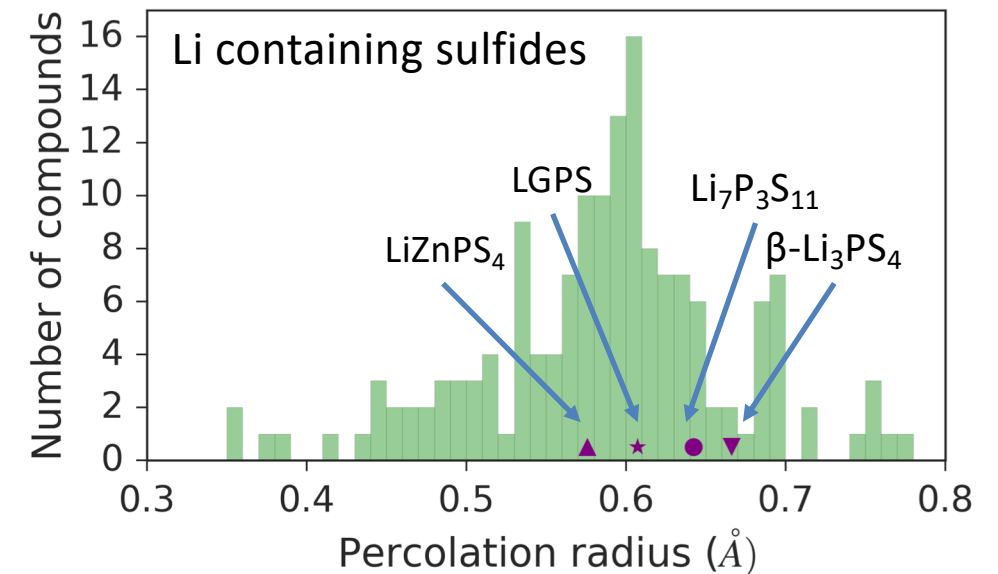
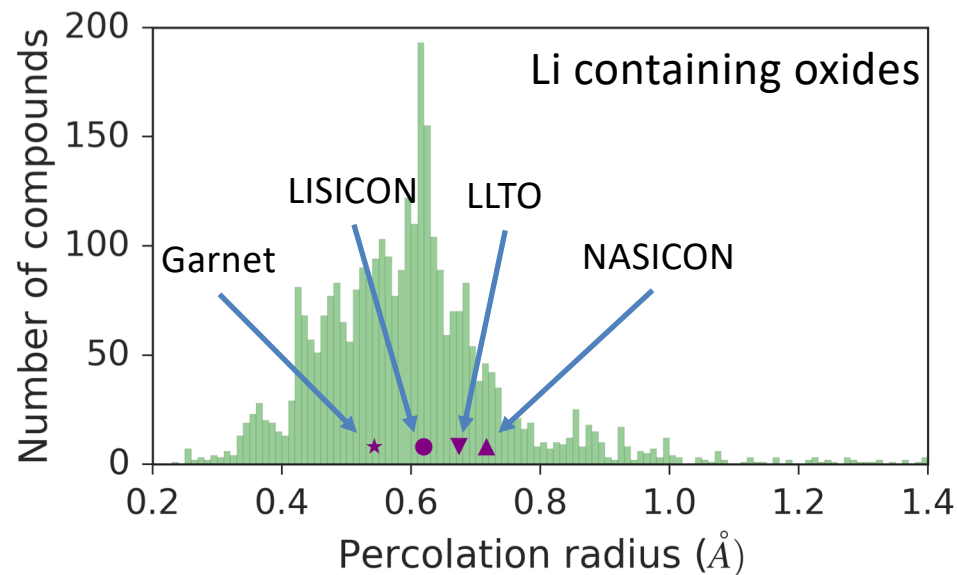
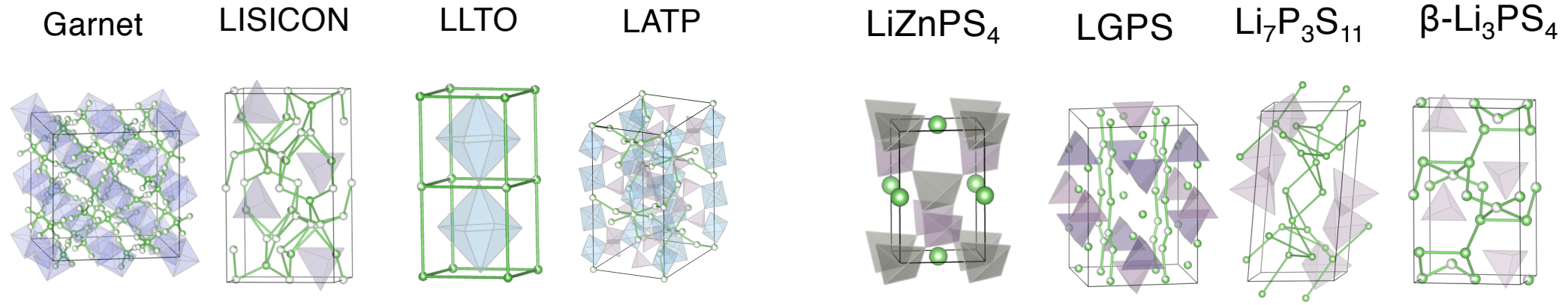
Topological analysis for empty space in crystal structures

-- well reproduce Li sites and Li diffusion channels



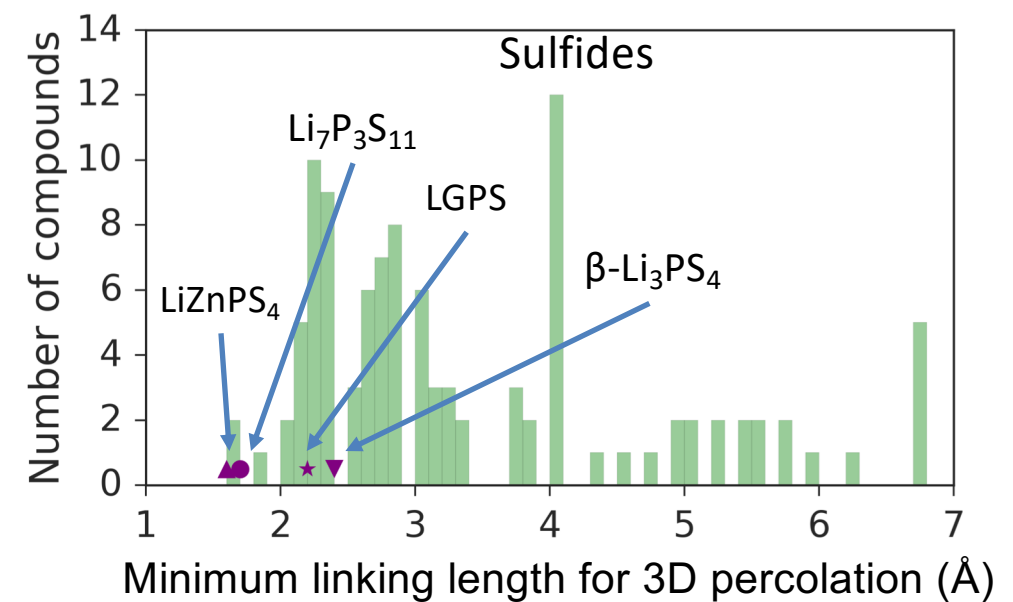
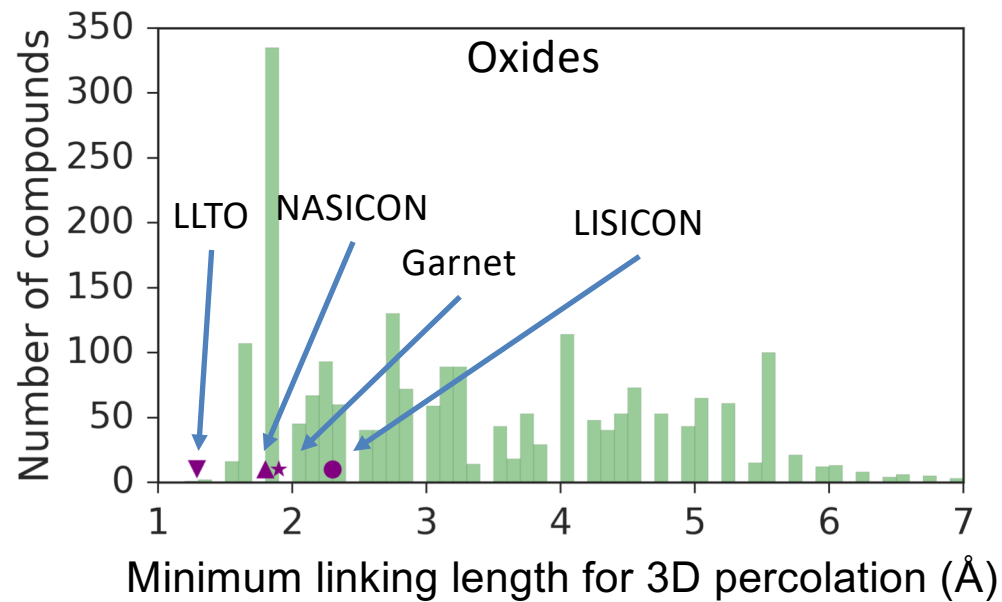
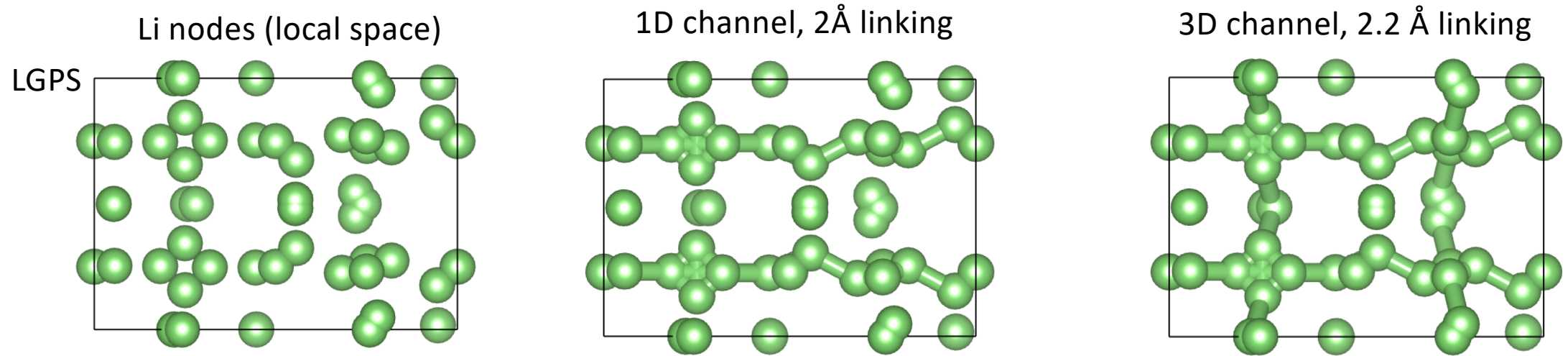
Li+ percolation radius should be appropriate: Not too big Not too small

Topological
analysis of
all inorganic
structures
in ICSD



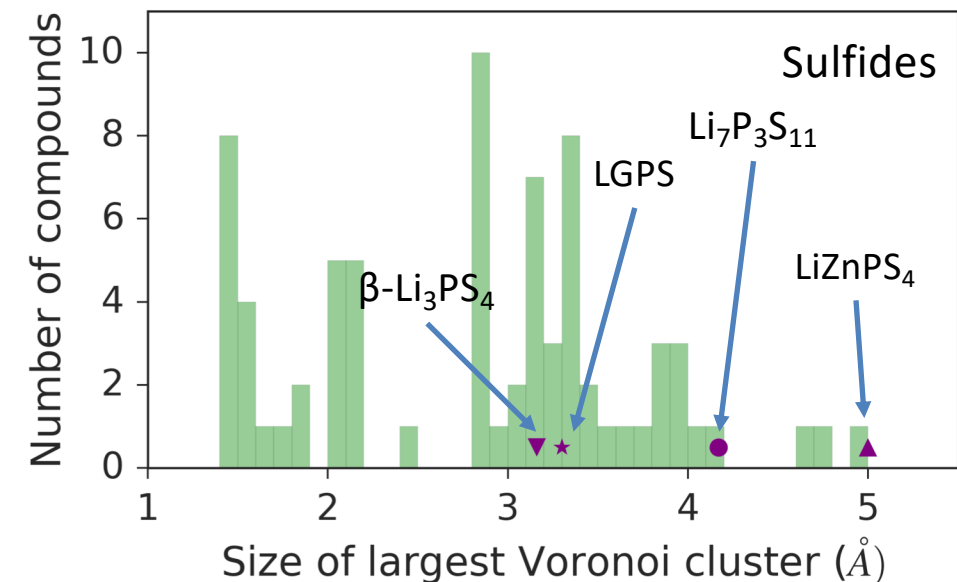
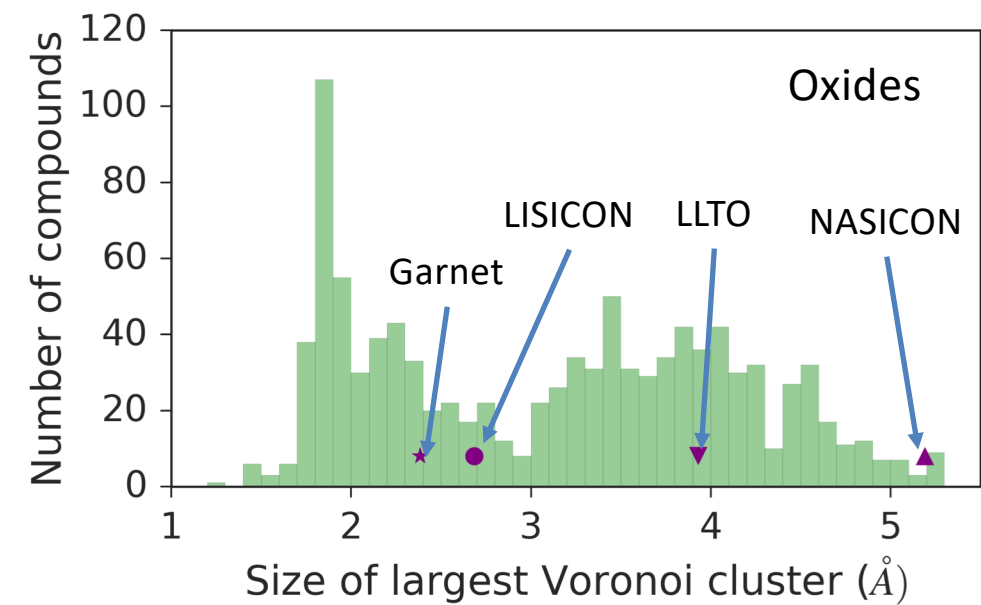
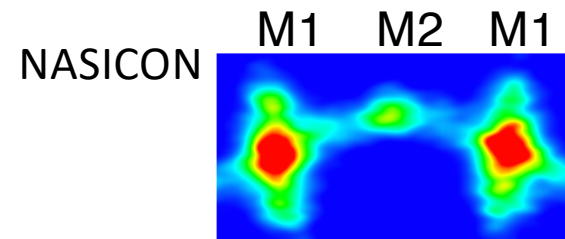
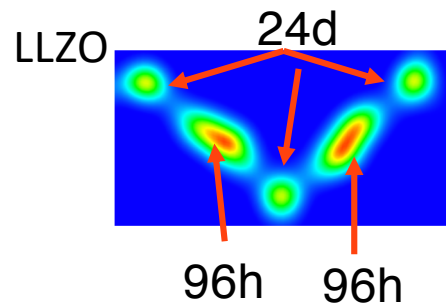
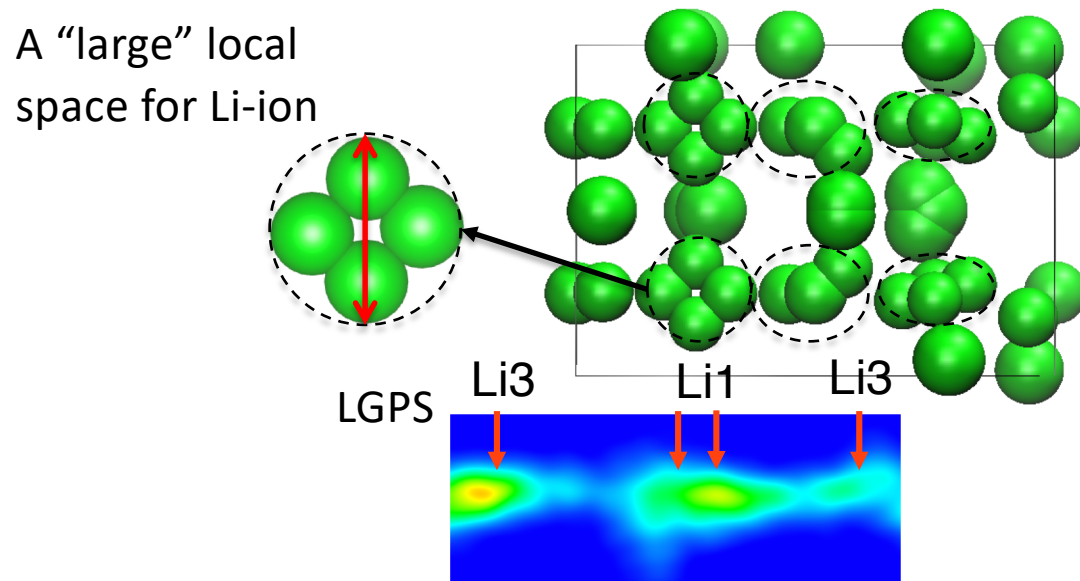
- Li-ion percolation radius are within 0.54 - 0.72 $\text{\AA}$ in fast Li-ion conductors
- The diffusion channel size should not be too small or too large

3D Network for Li⁺ Diffusion : Well-Connected Li Local Space



Known Li-ion conductors form connected 3D percolation network by <2.5Å pathways

Enlarged Li site : a key feature in Super-ionic conductors



- Topological analysis confirmed large local space in the structure correspond to the disordered sites.
- Enlarged Li sites promote the disordering of Li sublattice.

High-Throughput Screening of New Structures for Li-Ion Conductors



Crystal Structure requirement for fast-ion conductors

- Decent size of ion channel
- Well-connected diffusion pathways
- Enlarged site to promote Li⁺ sublattice disordering

Inorganic Crystal Structure Database (ICSD)

Li oxides
5537

Li sulfides
510

1 Basic materials check
2866 157

2 Percolation radius
2212 114

3 3D diffusion network
983 59

4 Enlarged Li site
704 40

5 Practical considerations
229 36

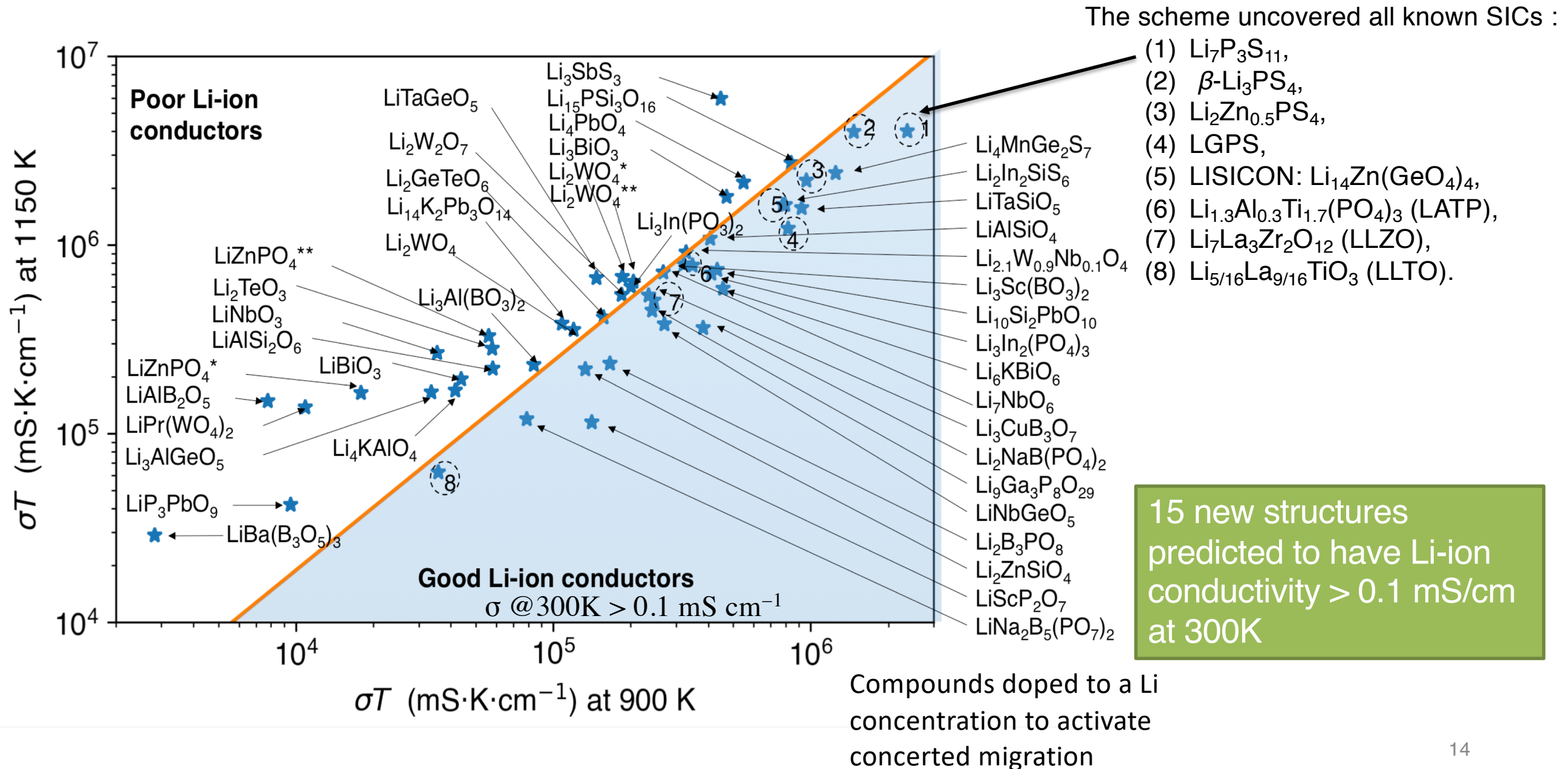
6 Unique structural framework
76 13

76 oxides and 13 sulfides

High-throughput Screening
performed on all Li-containing
oxides and sulfides in ICSD.

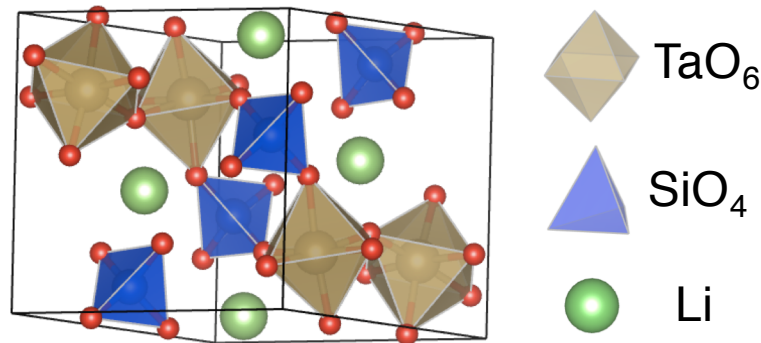
- Simple criteria can uncover all known super-ionic conductors (LGPS, LPS, LISICON, Garnet, NASICON, etc.)
- Discovered a large number of new crystal systems for fast Li-ion conduction.

New Li-ion Conductors confirmed by AIMD simulations

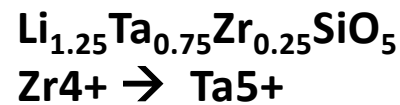
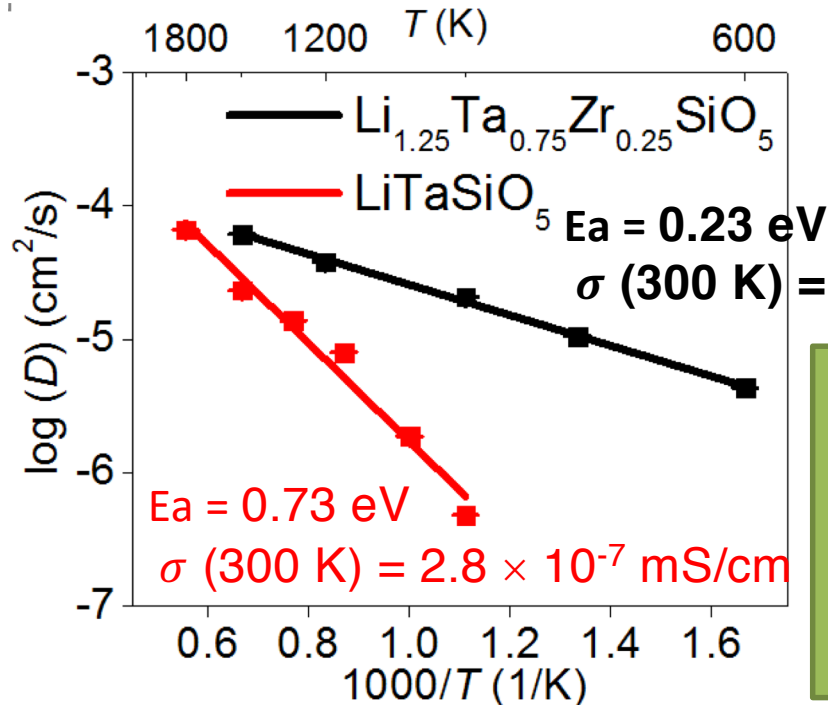


Experimental confirmation of $\text{Li}_{1+x}\text{Ta}_{1-x}\text{Zr}_x\text{SiO}_5$

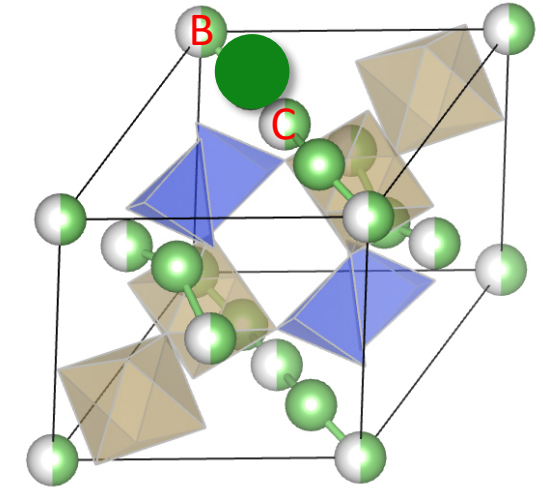
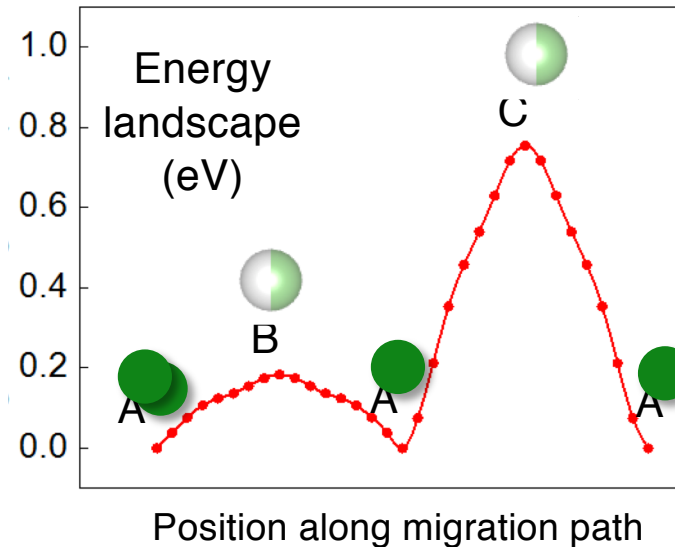
LiTaSiO_5 Not been studied for Li diffusion.



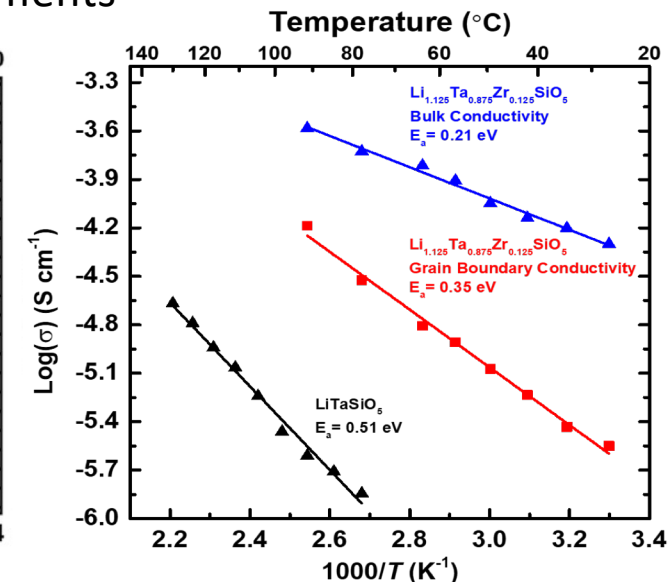
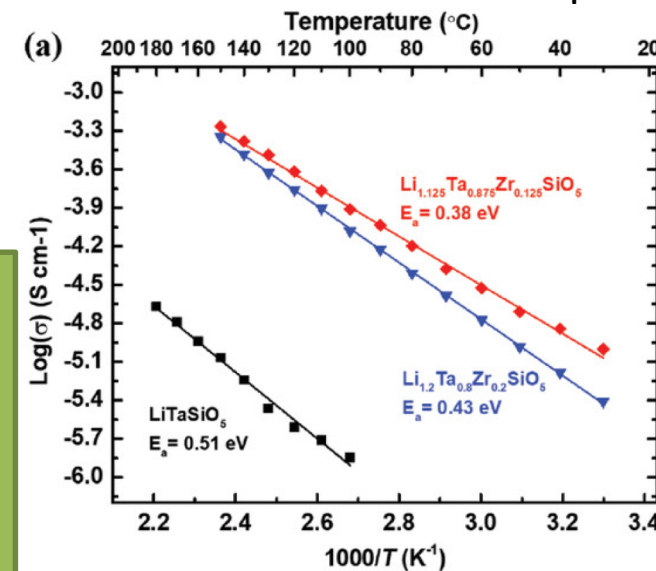
Computation: AIMD



Demonstrated our design strategy in discover and design new super-ionic conductors



Experiments



Conclusions



- Topological analysis with basic chemical considerations well reproduce Li sites and diffusion channels in ionic conductors.
- Large data analysis performed on all Li-containing oxides and sulfides, and identified the key features of fast Li-ion conductors.
 - Diffusional channel size should be in a narrow range
 - Connected 3D Li⁺ diffusion network has short-distance connectivity
 - Enlarged Li sites given by large local space in the crystal structures promote the disordering of Li⁺ sublattice.
- High-throughput screening combined with ab initio molecular dynamics simulation identified all known fast Li-ion conductors and predicted 15 new structures.

He, Bai, Liu, Nolan, Ling, Mo ***Adv. Energy Mater.*** (online)

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

He, Zhu, Epstein, Mo, ***NPJ Comp Mater*** 2018, 4, 18

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