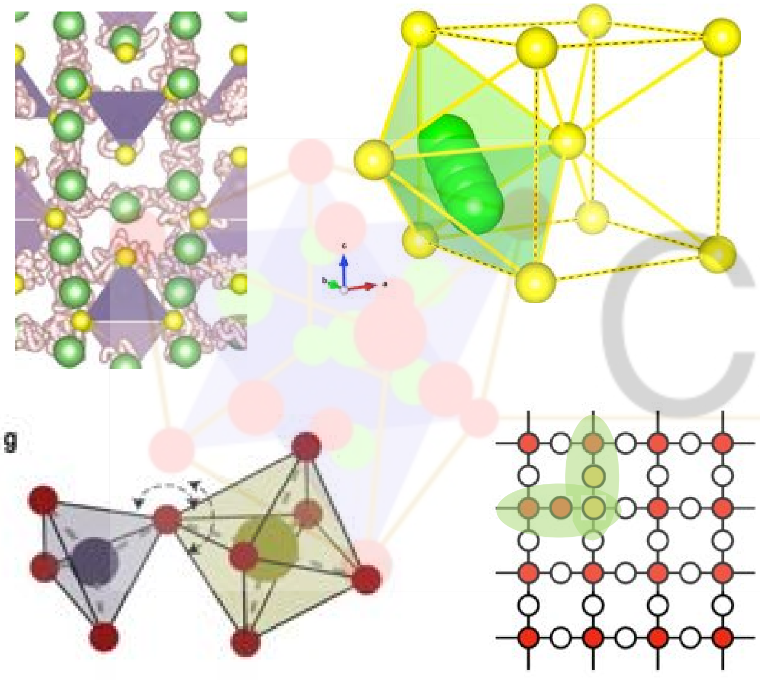
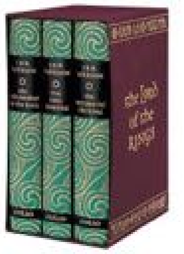
The Complex Mechanisms that Create High Li-ion Mobility in Oxides and Sulfides

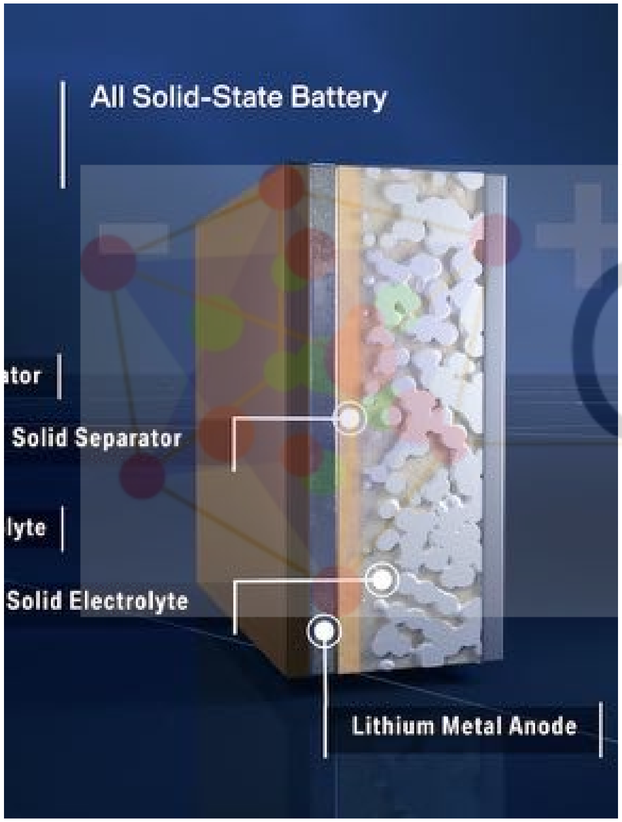


Professor Gerbrand Ceder
University of California at Berkeley
Lawrence Berkeley National Laboratory
ECS Meeting, Atlanta, Oct 10, 2022

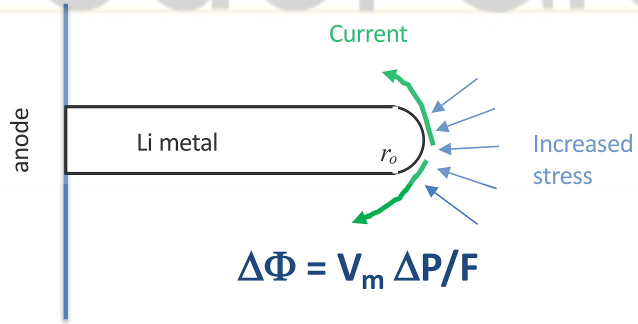
Y. Wang et al. **Design Principles for Solid-State Li-ion Conductors**, Nature Materials, 14 (10), 1026–1031 (2015).
Xiao, Y†., Jun, KJ†, Ceder, G. *et al.* **Lithium Oxide Superionic Conductors Inspired by Garnet and NASICON Structures.** *Adv Energy Mater* (2021)
Jun, KJ†, Sun, Y, Ceder, G. *et al.* **Lithium Superionic Conductors with Corner-sharing Frameworks**, *Nature Materials (2022)*



Importance of High Ionic Conductivity



1. Low resistance of the separator (membrane)
2. Reduce amount of conductor in the composite cathode. Solid electrolyte has high density as compared to liquid electrolyte, therefore want to reduce its amount
3. Limits maximum stress concentration in the solid electrolyte



$$\Delta\Phi = V_m \, \Delta P/F$$

Potential increase at crack tip pushes current away (screening !)

L. Barroso-Luque. Q. Tu, G. Ceder. 2020 *J. Electrochem. Soc.* **167** 020534

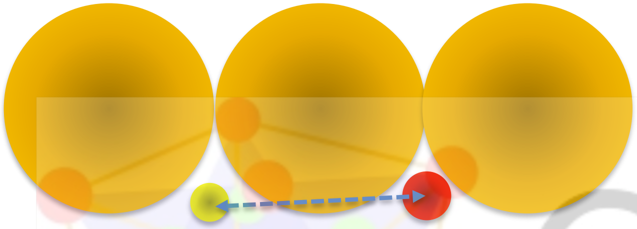
Two principles for creating high ion conductivity

1. Keep energy landscape as flat as possible

2. Increase energy of the carrier

Sulfides and Oxides are Different

S^{2-} 184pm



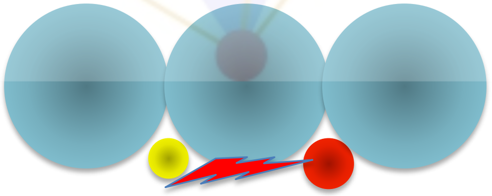
S^{2-} is large and has high screening power

Sulfides: Li+ is myopic

- High screening power of S^{2-}
- Large cation-cation distance
- **anion coordination** sets Li^+ energy

anion coordination is key

O^{2-} 140pm



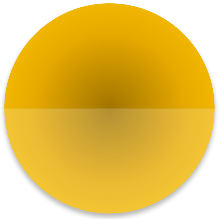
Oxides: cation-cation interaction

- Lower screening by anion
- Shorter cation-cation distances

cation interaction is key

“Flat” energy landscapes: Sulfides

1. Limit coordination changes along the ion migration path
2. Screen the Coulomb interactions between cations by using large anions: sulfides, selenides



S^{2-} is large and has high screening power

Ziqin Rong et al. Chemistry of Materials 27 (17), 6016-6021, DOI: 10.1021/acs.chemmater.5b02342 (2015

Y. Wang et al. Nature Materials, 14 (10), 1026–1031 (2015).

Sulfides: BCC packing of S^{2-} packing provides continuous pathway with low coordination change

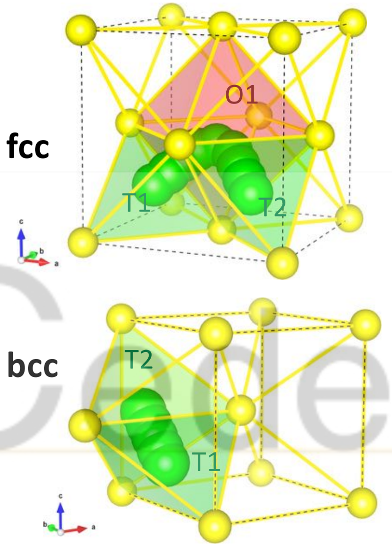
Migration path

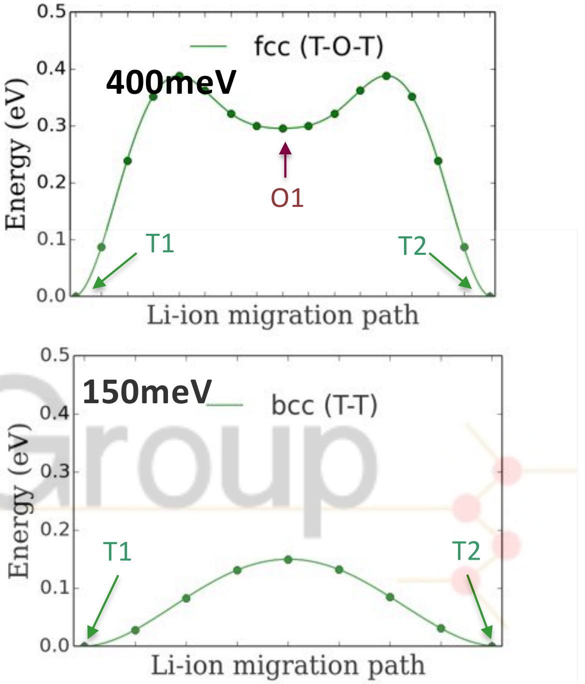
FCC: T-O-T path

4-6-4

BCC: Li ions migrate in a network of tet. sites

4-4-4





Materials	E_a (exp.)	**σ at R.T. (mS/cm)**
$Li_7P_3S_{11}$	0.18	18
$Li_{10}GeP_2S_{12}$	0.21	12
Li_4GeS_4	0.53	2×10^{-4}
Li_2S	0.74	\

BCC

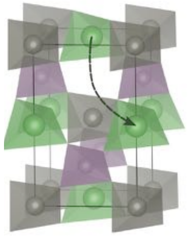
FCC

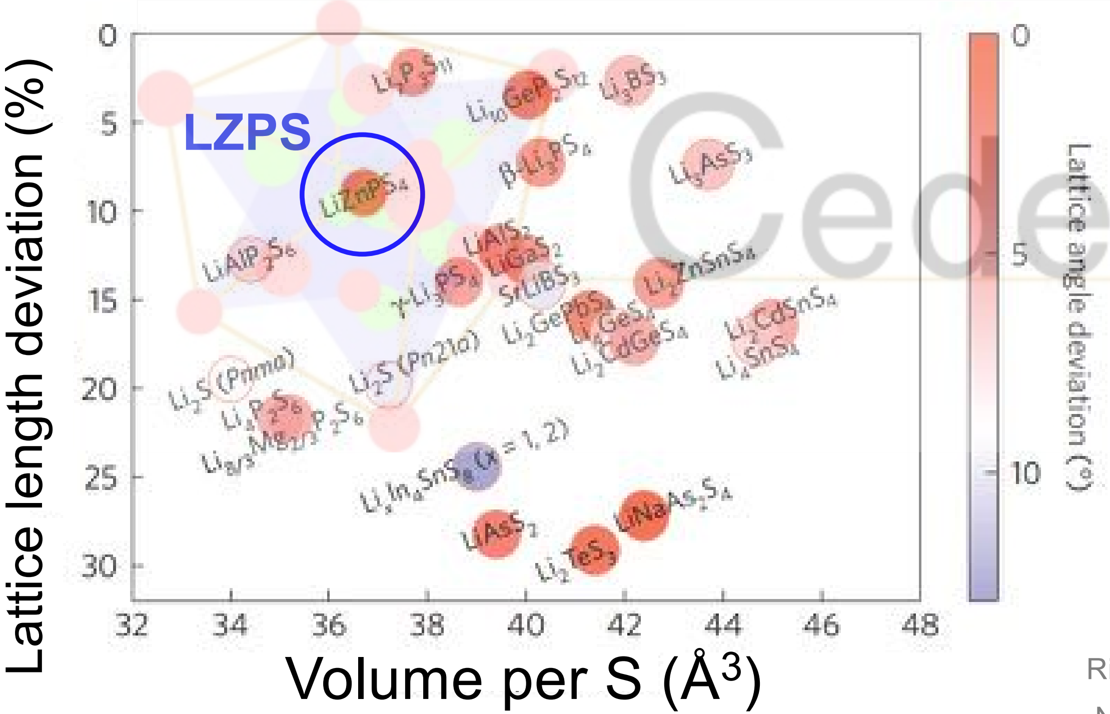
Many known good sulfide-based Li-ion conductors indeed have BCC framework

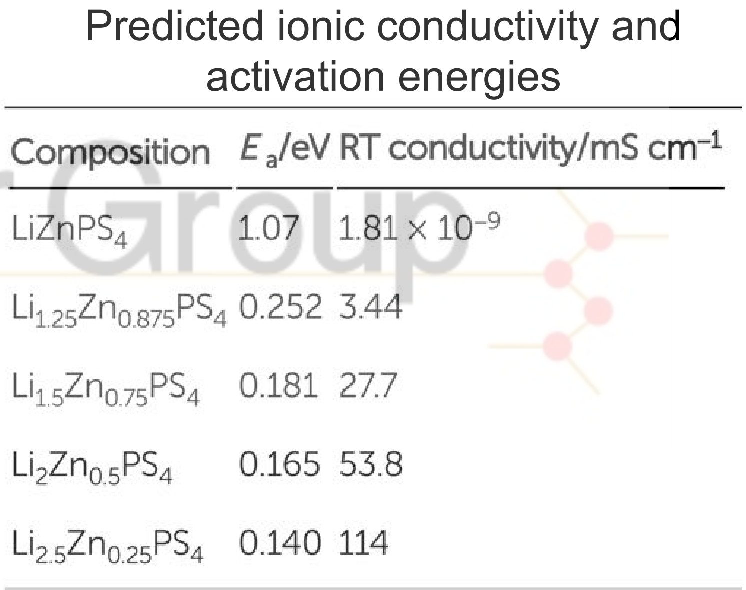
Y. Wang et al. Nature Materials, 14 (10), 1026–1031 (2015).

Find new Sulfide conductors with the BCC feature

The Materials Project







Predicted ionic conductivity and activation energies

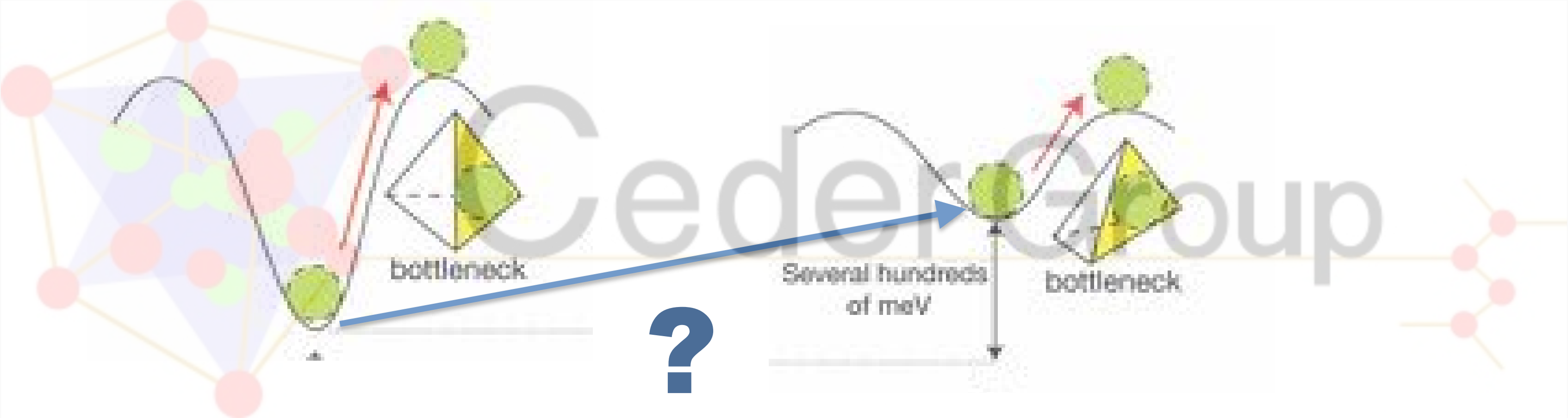
Composition	E_a/eV	RT conductivity/mS cm^{-1}
$LiZnPS_4$	1.07	1.81×10^{-9}
$Li_{1.25}Zn_{0.875}PS_4$	0.252	3.44
$Li_{1.5}Zn_{0.75}PS_4$	0.181	27.7
$Li_2Zn_{0.5}PS_4$	0.165	53.8
$Li_{2.5}Zn_{0.25}PS_4$	0.140	114

Richards *et al.*, Energy Environ. Sci. 2016, 9, 3272

N. Suzuki et al. Chem. Mater. 2018, 30, 2236−2244, doi: 10.1021/acs.chemmater.7b03833 (2018)

Oxides: Raise energy of Li-ion to increase its mobility

- Binding energy of Li ≈ 3-4eV.
- But lowering barrier by 50meV raises σ by factor 10



1) Cation-cation interaction
2) Site distortion

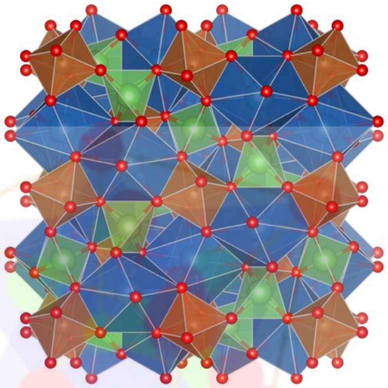
1. Activated Networks (Stuffed): Y. Xiao et al, Adv. Energy Mater. 2101437, DOI: 10.1002/aenm.202101437 (2021)
2. Corner-Sharing Networks: Jun, KJ, Sun, Y, Ceder, G. *et al.*, *Nature Materials (2022)*

Strategy 1: Stuffed Conductors

1. Activated Networks (Stuffed): Y. Xiao et al, Adv. Energy Mater. 2101437, DOI: 10.1002/aenm.202101437 (2021)

Li diffusion network is a network of face-sharing Li sites

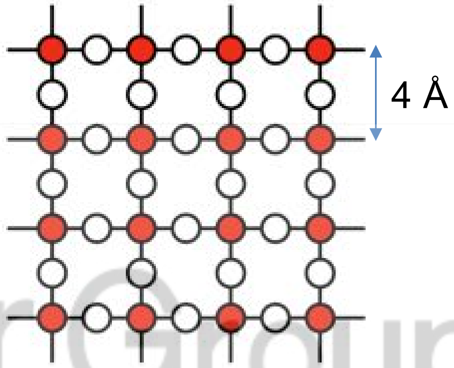
$Li_3La_3Te_2O_{12}$ (Garnet)



$E_a > 1$ eV

Network construction

Network: 2D representation

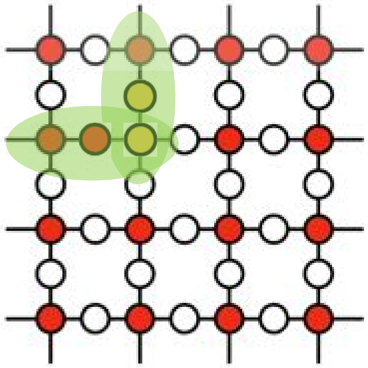


● Occupied Li site

○ Unoccupied Li site

● Stuffed Li

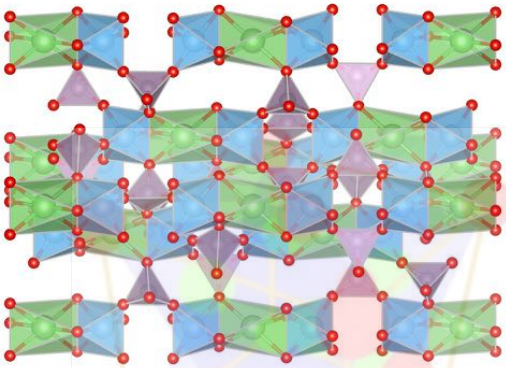
🟩 Activated local env.



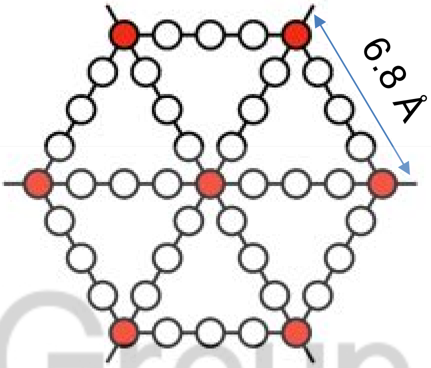
$Li_{3+x}La_3M_2O_{12}$
E_a = 200 meV

Li diffusion network is a network of face-sharing Li sites

$LiTi_2(PO_4)_3$ (NASICON)



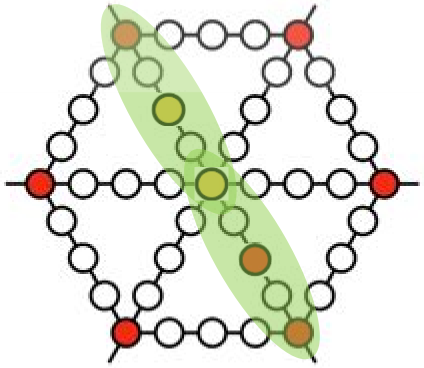
Network construction



● Occupied Li site

○ Unoccupied Li site

$Li_{1+x}Al_xTi_{2-x}(PO_4)_3$

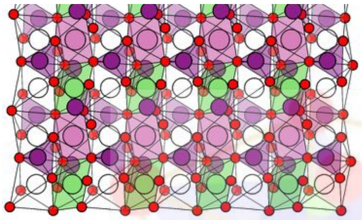


🟡 Stuffed Li

🟢 Activated local env.

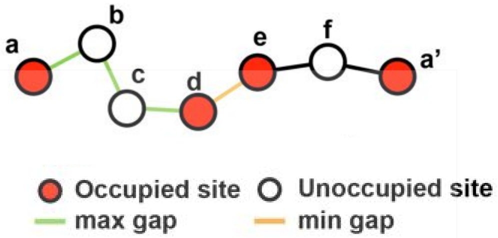
High-throughput search for these features

ICSD compound



Find all possible Li sites using Delaunay tetrahedralization

Analyze the connectivity of occupied and unoccupied sites



Two regimes of interest

Garnet regime:

1. percolation dimensionality = 3
2. max gap size ≤ 4 Å along the transport path in the pristine Li diffusion network.

NASICON regime:

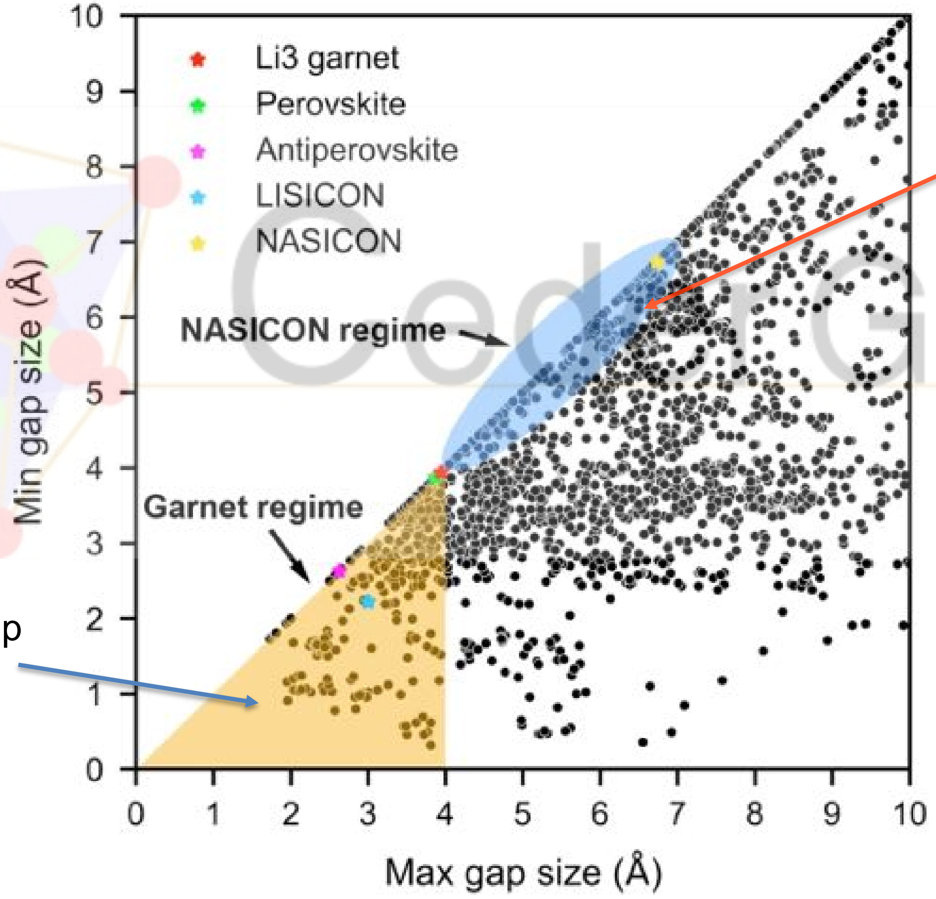
1. percolation dimensionality = 3
2. 4 Å < min gap size = max gap size ≤ 7 Å along the transport path in the pristine Li diffusion network.

- All Li-Li distance < 4 Å: stuffed Li$^+$ will be close enough to occupied Li$^+$ to get energy raising (activation)
- All Li-Li distances are the same: homogenous transport path so activation can propagate without getting trapped.

Y. Xiao et al, Adv. Energy Mater. 2101437, DOI: 10.1002/aenm.202101437 (2021)

Min-Max gap plot and two regimes of interest

Min and max gap sizes for 4,666 compounds



If the max gap size is large, then minimum gap size should remain similar

If the max gap size is small, then minimum gap size is no problem (hop can skip the site)

Five known oxide Li-ion conductors (colored stars) can already be found in these two regimes!

Y. Xiao et al, Adv. Energy Mater. 2101437, DOI: 10.1002/aenm.202101437 (2021)

Multiple candidates from High-throughput search

Regime	Target composition	σ_{RT} (mS/cm)	E_a (meV)	E_{defect} (eV/defect)	E_{above_hull} (meV/atom)
Garnet style	$Li_{2+1/16}Nb_{1/16}Te_{1-1/16}O_4$	**2.7** [0.25, 30]	214 ± 59	0.54	4.8
	$Li_{6+1/8}Sb_{1/8}Te_{1-1/8}O_6$	**0.56** [0.05, 6.1]	262 ± 59	0.58	5.5
	$Li_{6+1/4}Si_{1/4}P_{1-1/4}O_5Br$	**3.2** [0.17, 60]	199 ± 73	0.73	13.9
NASICON style	$LiGa(SeO_3)_2$	**0.21** [0.01, 3.6]	316 ± 70	N/A	0
	$Li_{1+1/4}Mg_{1/4}Sc_{1-1/4}(SeO_3)_2$	**1** [0.05, 22]	245 ± 77	0	0
	$Li_{4+1/2}Mg_{1/2}Ga_{3-1/2}Si_3O_{12}Cl$	**0.72** [0.04, 12]	271 ± 70	0.79	16.8
	$Li_{3+1/8}Mg_{1/8}Sc_{1-1/8}(BO_3)_2$	**0.07** [0.002, 2.2]	326 ± 88	0.72	7.4

Also found by He, X. and Mo, Y., doi:10.1002/aenm.201902078.

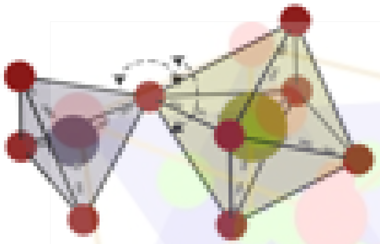
Y. Xiao et al, Adv. Energy Mater. 2101437, DOI: 10.1002/aenm.202101437 (2021)

Strategy 2: Corner-sharing frameworks

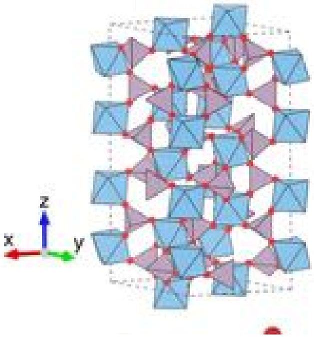
Jun, KJ†, Sun, Y, Ceder, G. *et al.* **Lithium Superionic Conductors with Corner-sharing Frameworks**, *Nature Materials (2022)*

Corner-sharing frameworks

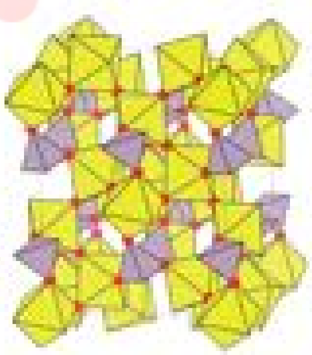
Framework with only corner-sharing connectivity



$Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ (NASICON-type)

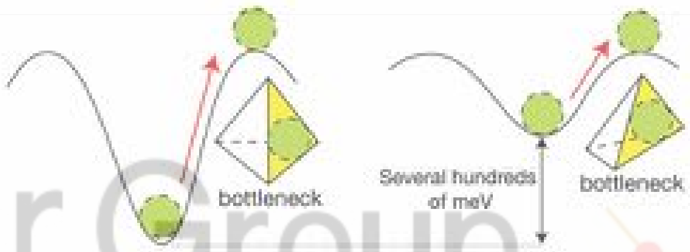


$LiTa_2PO_8$

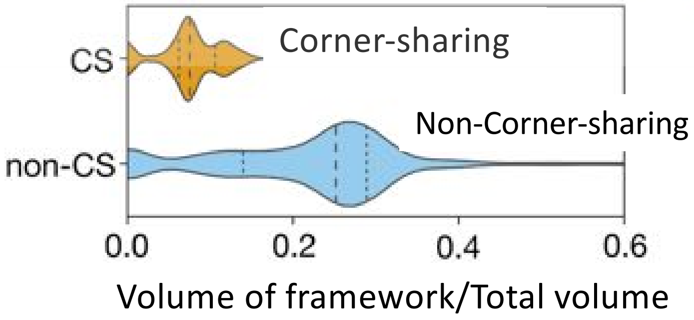


Two Benefits

1. More distorted lithium environment



2. Lower density of non-Li cations



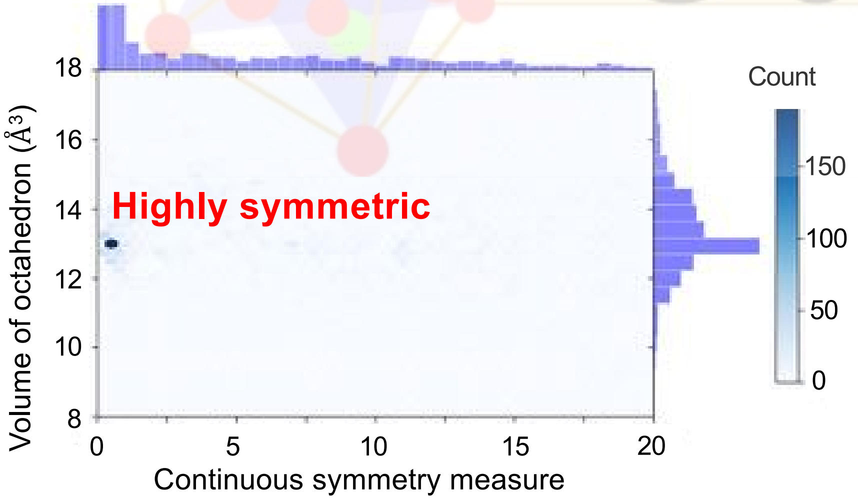
Corner-sharing frameworks have more distorted sites

Continuous symmetry measure (CSM)

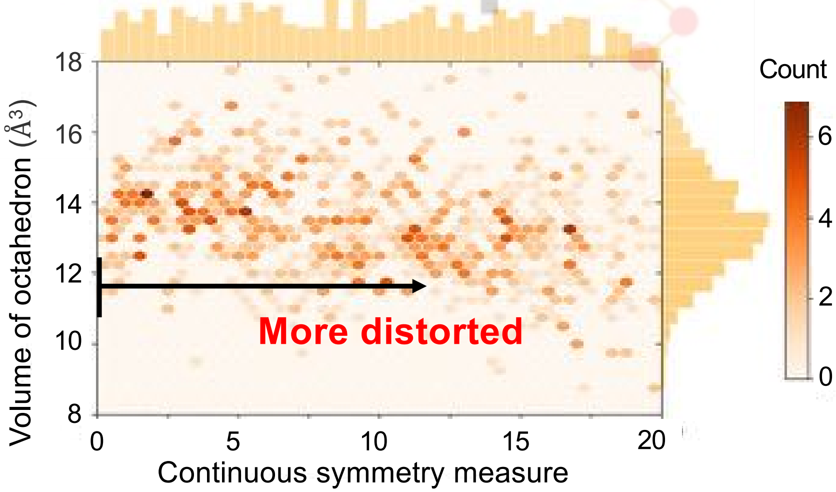
- An index of distortion

0 Perfectly symmetric ↔ CSM ↔ 100 Completely distorted

Non-Corner Sharing



Corner Sharing



Discovery of > 10 novel superionic conductors

+ rediscovery of 12 known fast Li-ion conductors

Target composition	$\sigma_{300\ K}$ (mS/cm)	E_a (eV)	Target E_{hull} (eV/atom)	E_d (eV/defect)
$LiIn(IO_3)_4$	**18.0** (3.57, 90.9)	0.155 ± 0.040	0.0	N/A
$LiScAs_2O_7$	**23.3** (4.26, 128)	0.177 ± 0.042	0.021	0.64
$Li_5B(SO_4)_4$	0.330 (0.0368, 4.90)	0.330 ± 0.061	0.023	1.56
$Li_3B(PO_4)_2$	0.166 (0.00721, 3.83)	0.326 ± 0.078	0.028	1.63
$Li_2B_3PO_8$	0.251 (0.00744, 8.44)	0.269 ± 0.087	0.015	1.67
$LiZnBO_3$	0.605 (0.0104, 35.3)	0.220 ± 0.101	0.009	0.12
$Li_3In(BO_3)_2$	0.121 (0.0027, 5.33)	0.300 ± 0.094	0.009	0.50
$LiGa(SeO_3)_2$	0.212 (0.013, 3.57)	0.320 ± 0.070	0.0	N/A
$LiTiPO_5$	**1.70** (0.098, 29.7)	0.212 ± 0.071	0.019	0.79
$Li_2Mg_2(SO_4)_3$	**2.74** (0.145, 52.0)	0.232 ± 0.073	0.011	0.81

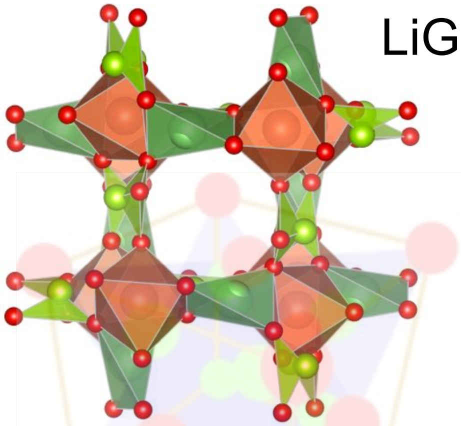
Only an initial screening…

More superionic conductors out there!

Jun, KJ†, Sun, Y†, Ceder, G. *et al.*, ***Nature Materials*** *(2022)*

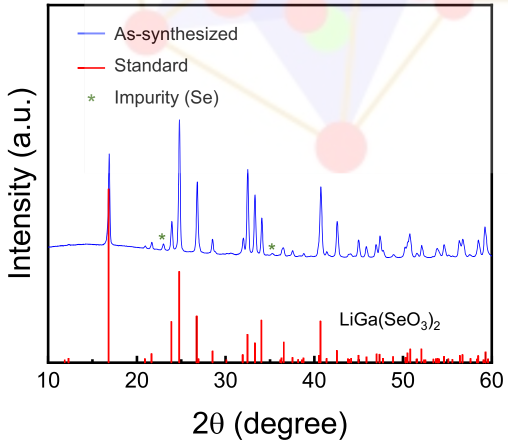
Experimental verification

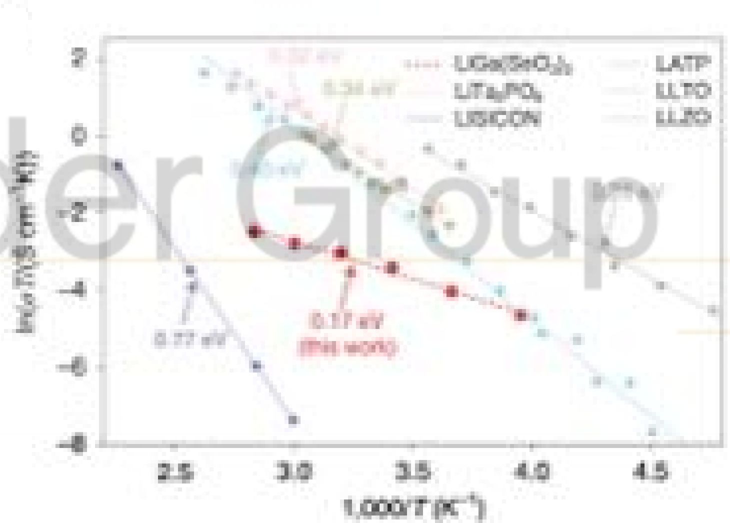
Notoriously difficult with new materials due to challenges sintering dense pellets, minimizing boundary resistance, etc.



$LiGa(SeO_3)_2$ – A superionic conductor predicted by both features!

- Synthesized by solid-state method
- Spark-plasma sintering at 300℃ (160 Mpa) to 76% relative density





$\sigma_{Li,bulk}$ **: 0.11 mS/cm** at 300 K

E_a : **0.17 eV**

Lowest measured activation energy among any oxide solid electrolytes

Jun, KJ†, Sun, Y†, Ceder, G. *et al.*, ***Nature Materials*** *(2022)*

Other concepts put forward in literature

cooperative motion

concerted motion

correlated motion

When anion polyhedral are present:

Cogwheel effect

Paddle-wheel effect

Revolving door mechanism

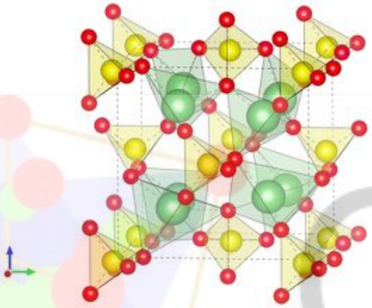
Investigation of a possible paddlewheel effect

- Investigated β-LPS and agyrodite-like $Li_5PS_4(BH_4)_2$
- Ab initio molecular dynamics simulations
- Carefully track when Li hops and when polyanion group rotates and investigate time and spatial correlation

Is there a paddle-wheel effect ?

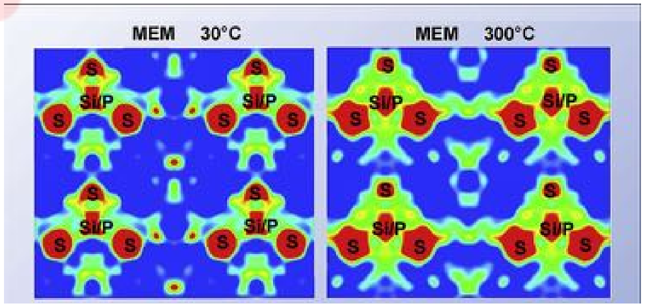
Claim is that polyhedron rotation facilitates faster Li-ion diffusion

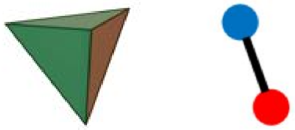
But never precisely defined in the literature



HT-Li_2SO_4 phase

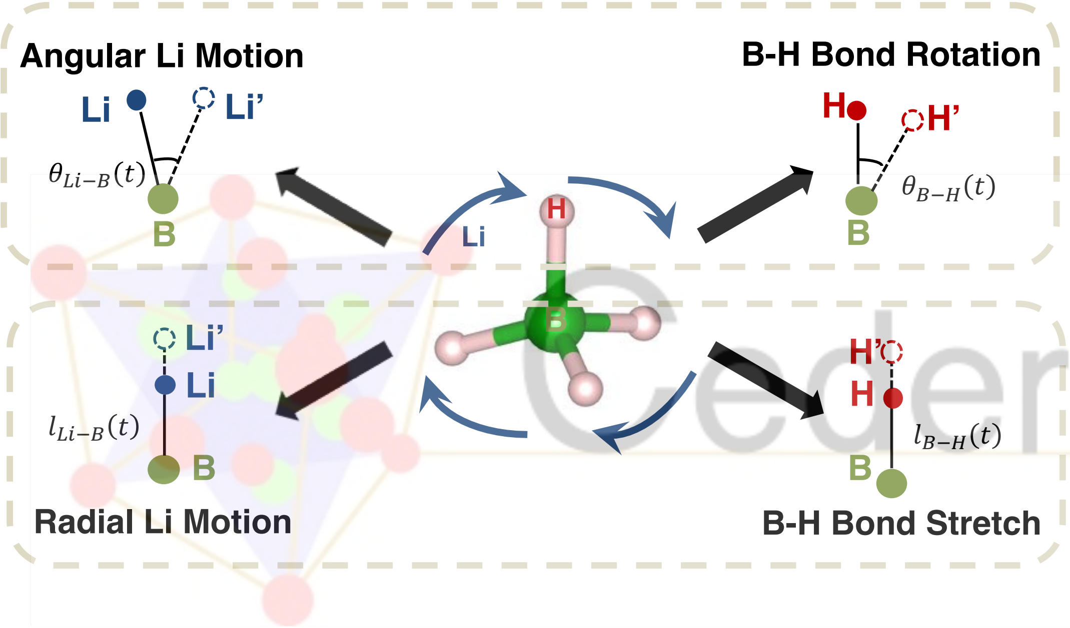
Experimental and theoretical evidence is vague and of a “correlative nature” : e.g. quasi-elastic neutron scattering (QENS), NMR showing fast polyhedral reorientation at high temperature

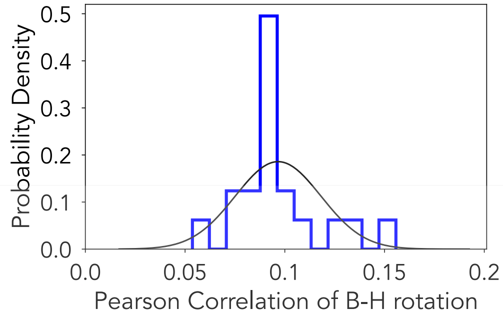


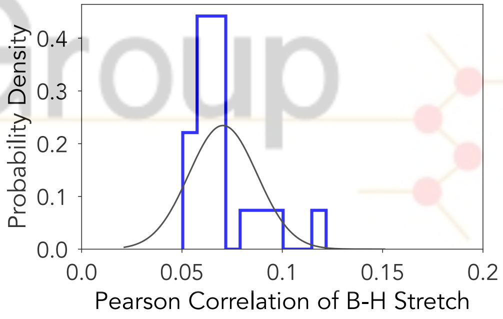


Zhang, Z. *et al.* Targeting Superionic Conductivity by Turning on Anion Rotation at Room Temperature in Fast Ion Conductors. *Matter* **2**, 1667–1684 (2020).

$Li_5PS_4(BH_4)_2$: No Correlation between Li diffusion and BH_4 motion







For either rotation mode or stretch mode, the maximum correlation coefficient observed is less than 0.2, and most of the coefficients are smaller than 0.1, which means Li diffusion is **not correlated** to BH_4 rotation/stretch. Therefore, **the enhanced conductivity in this material is not related to any "paddle-wheel" mechanism**.

Y. Sun, GC et al. Matter (2022), DOI: 10.1016/j.matt.2022.08.029 (2022)

Summary

- **High ion conductivity** is achieved by keeping the energy landscape flat through control of coordination changes along the path, or by raising the energy of the moving ion.
- **Sulfides**: Because of the large size and high screening power of S^{2-} Li+ is short-sighted in sulfides. Low energy path is mostly about optimizing **coordination** changes. E.g. BCC principles
- **Oxides**: **cation-cation interaction** is more important and leads to more complex relations between structure and ionic conductivity. **Activated Diffusion Networks** and **Corner-sharing frameworks** are two criteria by which to search for high ionic conductivity structures (but there may be others)
- There are many Li-ion conductors out there !
- No theoretical evidence so far for a **paddle-wheel** effect