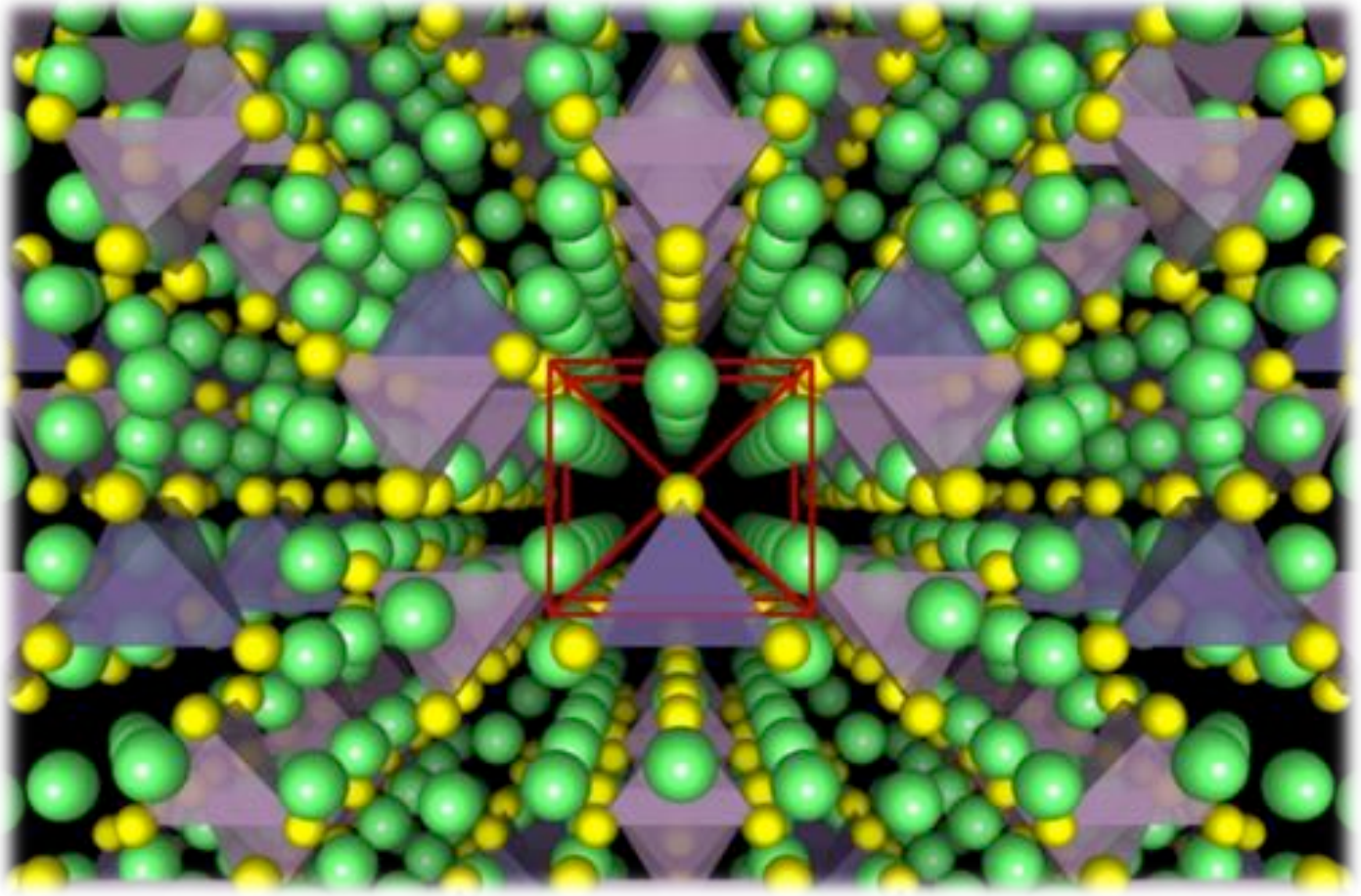
Predicting the Interfacial reactions between electrodes and solid state electrolytes

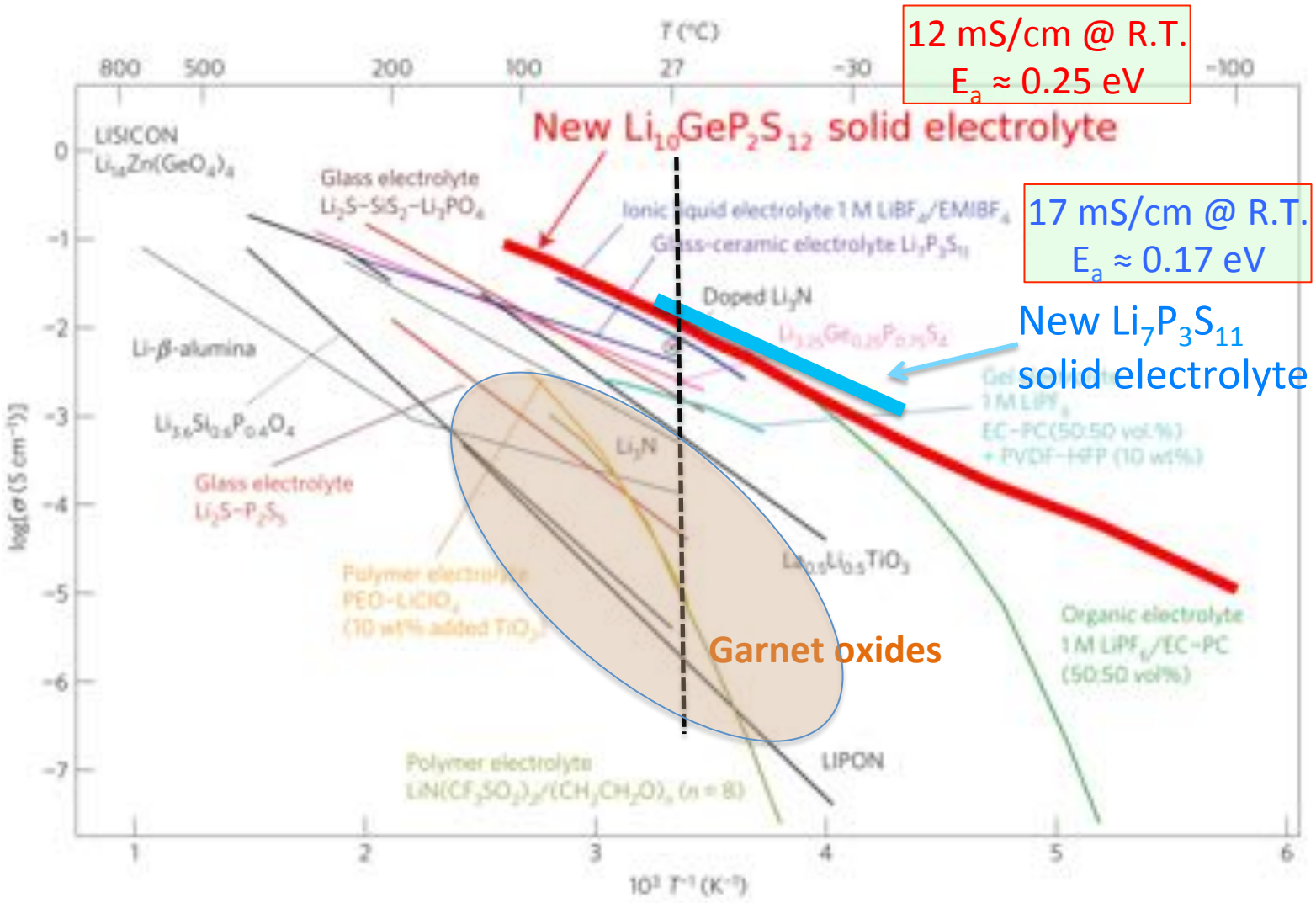


Slides will be posted at ceder.berkeley.edu

SAMSUNG ADVANCED INSTITUTE OF TECHNOLOGY

Gerbrand Ceder
UC Berkeley
ECS Meeting, Honolulu Oct 6 2016

Recent advances in solid-state lithium conductors

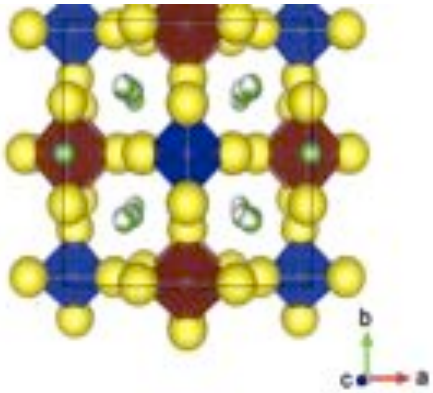


N. Kamaya et al., *Nat. Mater.* **10**, 682-686 (2011)
Y. Seino et al., *Energy Environ. Sci.*, **7**, 627 (2014)

Good understanding of what creates high Li-conductivity

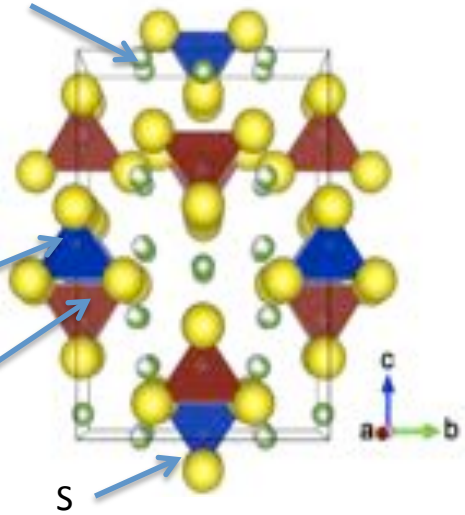
$Li_{10}GeP_2S_{12}$
Crystal structure[1]

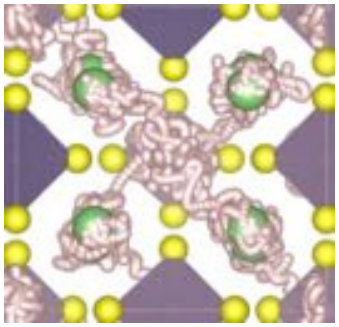
Top view



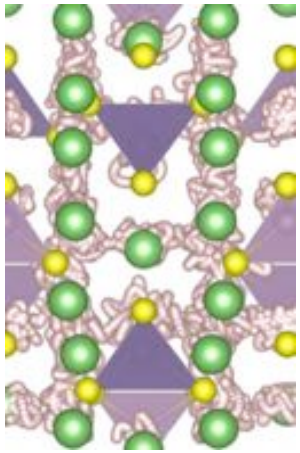
Li/Vacancy

Side view



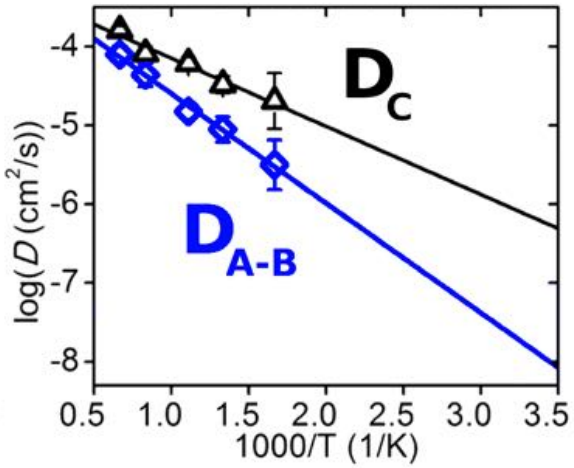


A-B plane



C axis

Li^+ diffusion in $Li_{10}GeP_2S_{12}$ from ab-initio molecular dynamics simulation[2]



	Activation energy (eV)	Conductivity at R.T. (mS/cm)
Exp.[1]	0.25	12
Comp.[2]	0.21	13

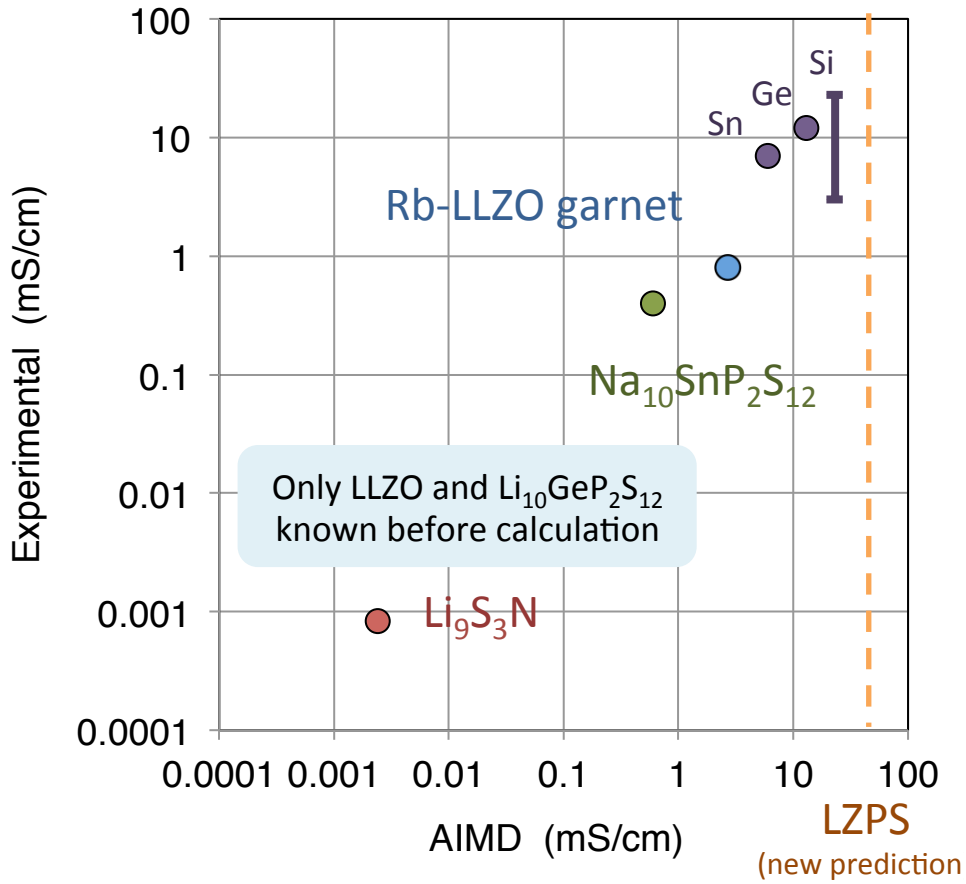
[1] N. Kamaya *et al.*, Nat. Mater. **10**, 682-686 (2011)
[2] Y. Mo, S. P. Ong, G. Ceder, Chem. Mater. **24** 15-17 (2012)

Excellent DFT predictions on conductivity

DFT vs. Experiment

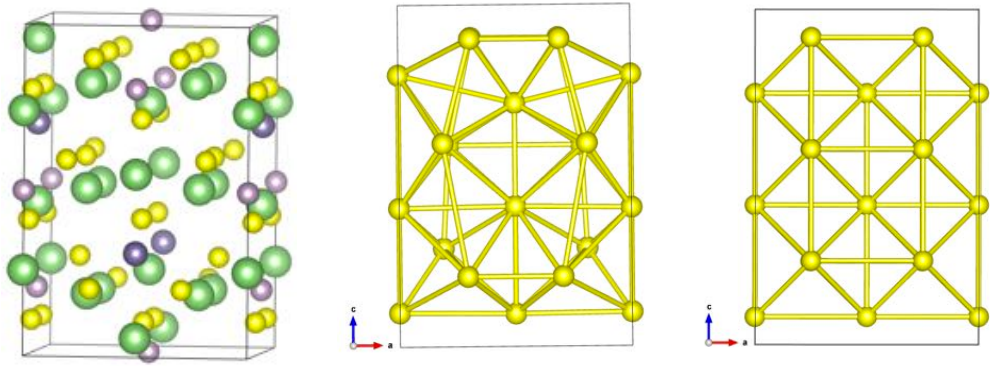
	E_a (eV)	σ_{RT} (mS / cm)
Li_9S_3N (DFT)	0.53	2.40E-03
Li_9S_3N (Exp)	0.52	8.30E-04
$Li_{10}SiP_2S_{12}$ (DFT)	0.2	23
$Li_{10}SiP_2S_{12}$ (Exp)	0.196	2.3
$Li_{11}Si_2PS_{12}$ (Exp)	0.19	
$Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$ (Exp)		25
$Li_{10}GeP_2S_{12}$ (DFT)	0.21	13
$Li_{10}GeP_2S_{12}$ (Exp)	0.25	12
$Li_{10}SnP_2S_{12}$ (DFT)	0.24	6
$Li_{10}SnP_2S_{12}$ (Exp)	0.27	4
$Na_{10}SnP_2S_{12}$ (DFT)	0.317	0.6
$Na_{10}SnP_2S_{12}$ (Exp) (*)	0.356	0.4
$Li_{7.08}La_{2.96}Rb_{0.04}Zr_2O_{12}$ (DFT)	0.21	2.74
$Li_{7.25}La_{2.875}Rb_{0.125}Zr_2O_{12}$ (Exp)	0.29	0.8

Predictions



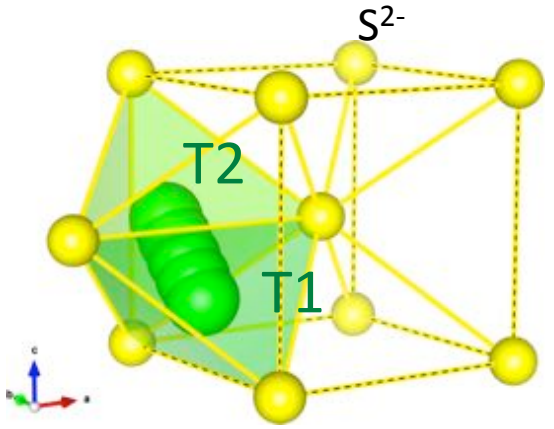
(*)Richards et al, Nature Communications 7, 11009 (2016)

The anatomy of superionic conductors - insight from LGPS and other conductors



- In $Li_{10}GeP_2S_{12}$ and $Li_7P_3S_{11}$ the sulfur anion arrangements are very close to bccc
- Some other sulfides have anion sublattice matched to close-packed frameworks (fcc/hcp)

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



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

Novel conductor predicted

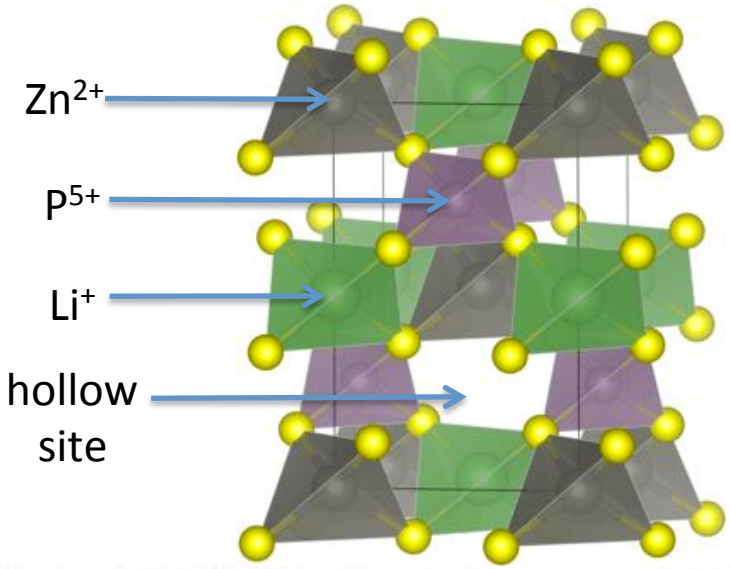


Table 1 Calculated activation energy (E_a) and extrapolated room temperature (RT) conductivity for $Li_{1+2x}Zn_{1-x}PS_4$ from MD simulations

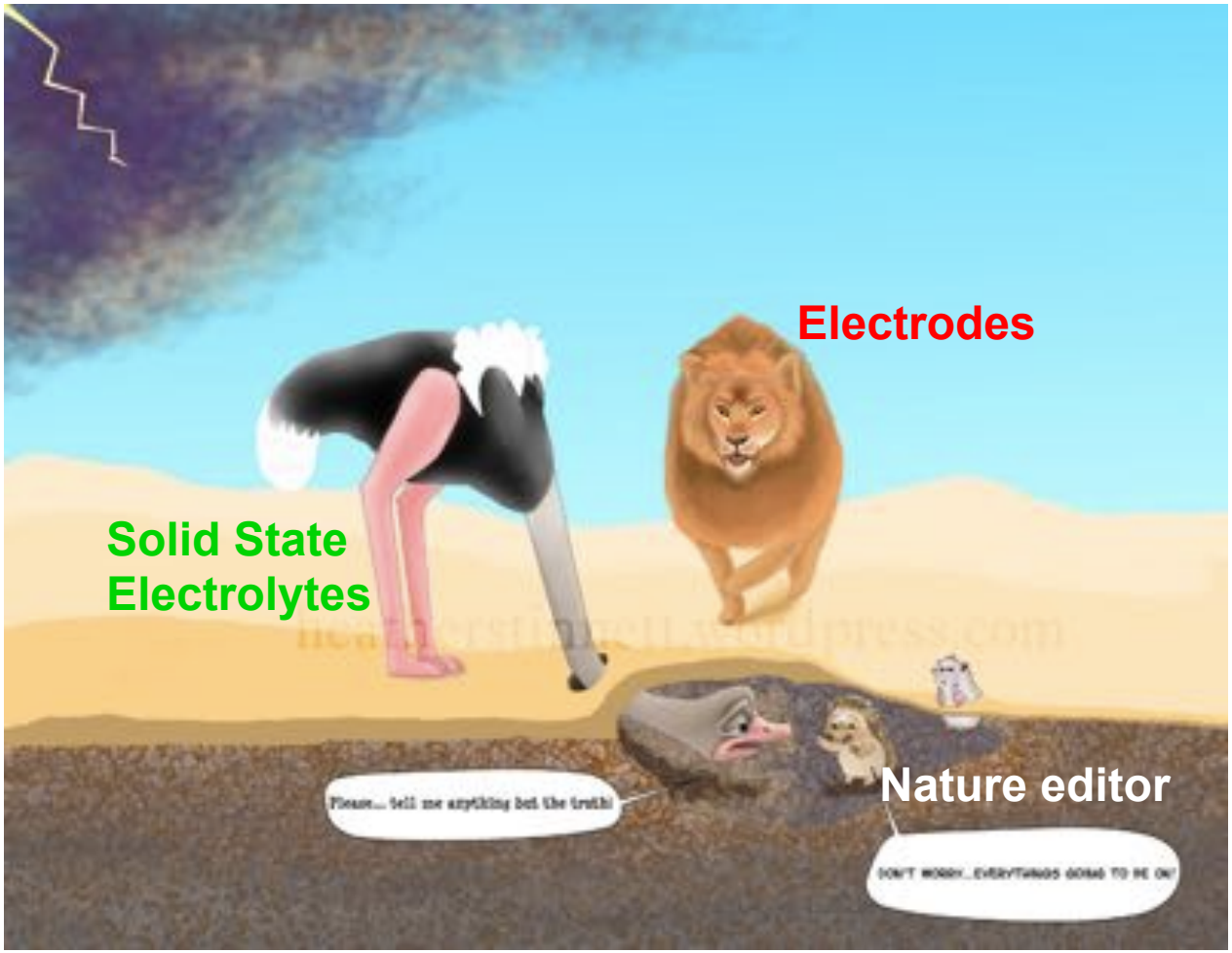
Composition	E_a/eV	RT conductivity/mS cm^{-1}
$LiZnPS_4$	1.07	1.81×10^{-9}
$Li_{1.25}Zn_{0.875}PS_4$	0.252	3.44
$Li_{1.5}Zn_{0.75}PS_4$	0.181	27.7
$Li_2Zn_{0.5}PS_4$	0.165	53.8
$Li_{2.5}Zn_{0.25}PS_4$	0.140	114

W. Richards, Energy and Env. Sc. 10.1039/C6EE02094A 2016

Some requirements for good solid state electrolytes

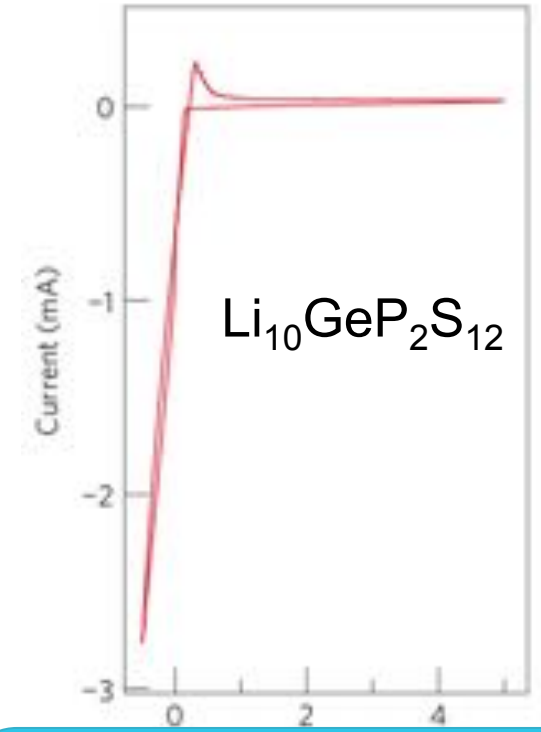
- High Li^+ conductivity
- No electron conductivity
- Processability
- No interfacial reactions with electrodes (or passivation)

Electrochemical Stability



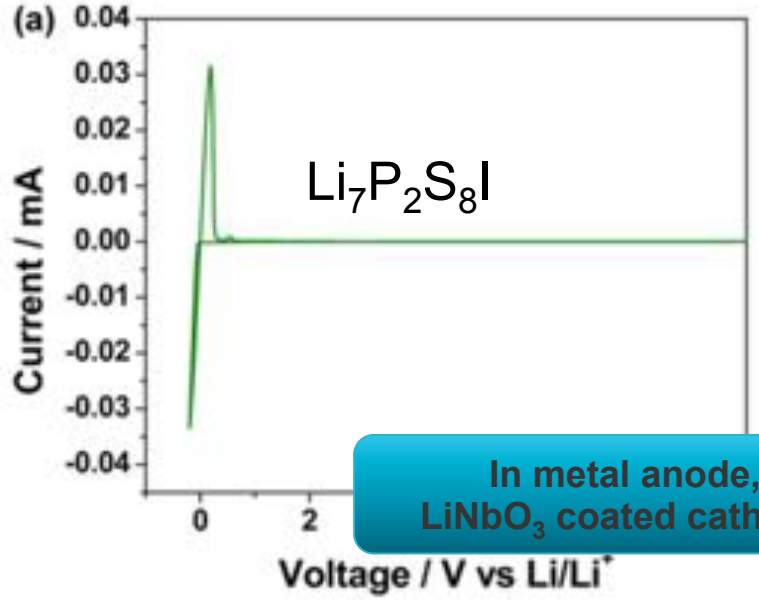
W.D. Richards et al., *Interface Stability in Solid-State Batteries,* Chem. Mat, 28 (1), 266-273 (2016).

Remarkable stability claims have been made



BUT,
in all reported cells electrode coatings are required!

N. Kamaya *et al.,* Nature Materials, 2011, 10 (9), pp 682-686.



In metal anode, $LiNbO_3$ coated cathode

Rangasamy *el al.,* J. Am. Chem. Soc., 2015, 137 (4), pp 1384–1387

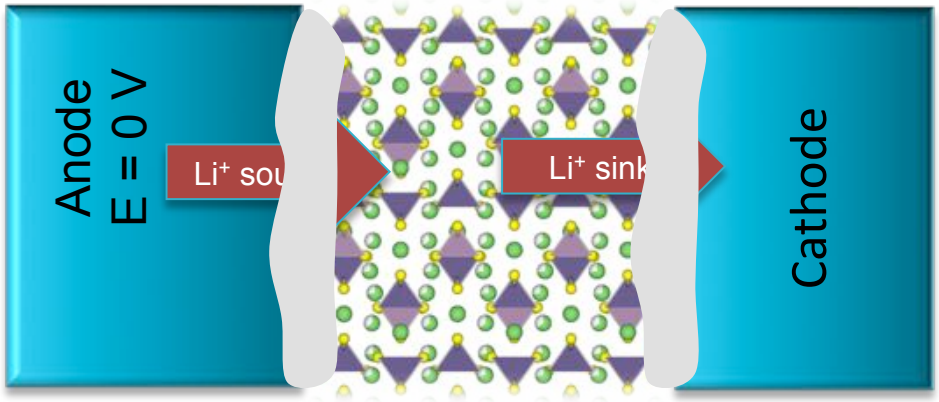
In metal anode, Li_2SiO_3 coated cathode

Lots of stability claims made for contact with Li metal

LiPON,
$Li_3P_3S_{11}$
$Li_{10}GeP_2S_{12}$

1. Electrochemical Stability

No chemical reaction with electrodes

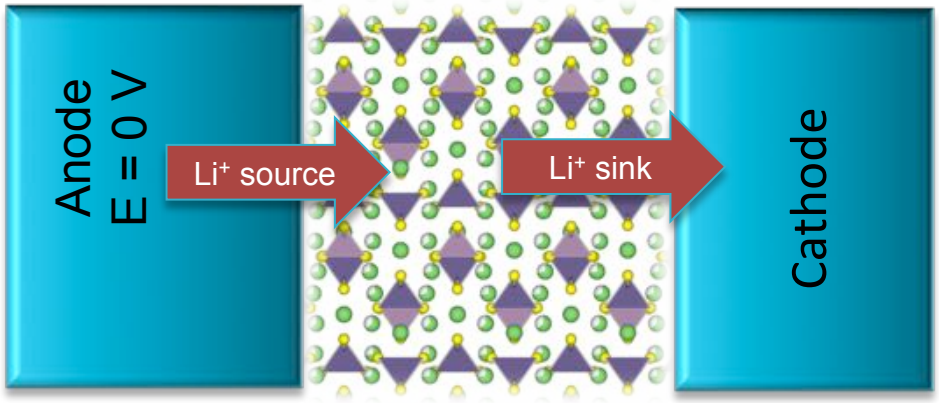


2. Chemical + Electrochemical Stability

Including chemical reaction with electrodes

1. Electrochemical Stability

No chemical reaction with electrodes



Li+ can always be removed or inserted as it is a fast-ion conductor

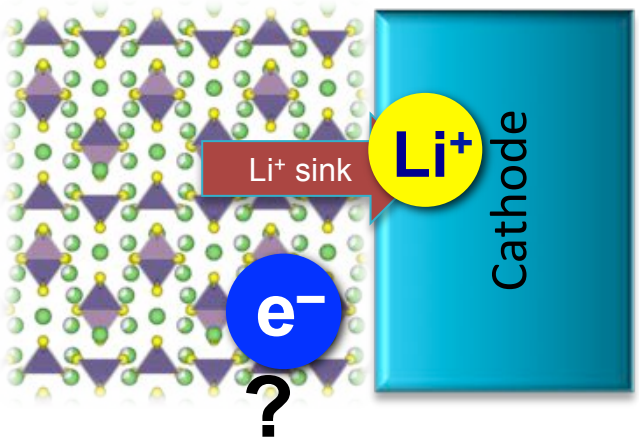
e− requires oxidation/reduction

These are fast processes, kinetics cannot help you

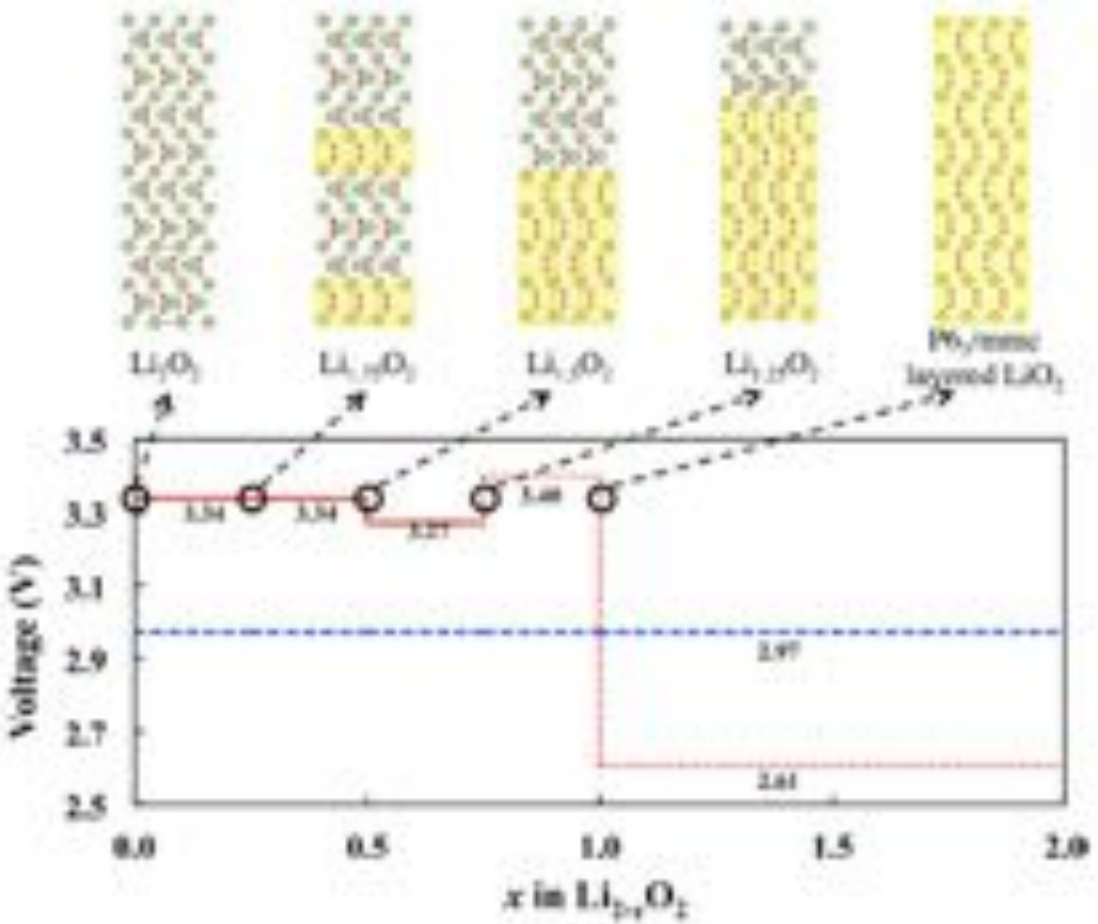
How stable can an oxide conductor be ?

Require voltage stability up to 4.5 or 5V

Li-oxides/peroxides: Metastable oxidation of the oxygen anion starts at about 3.3V



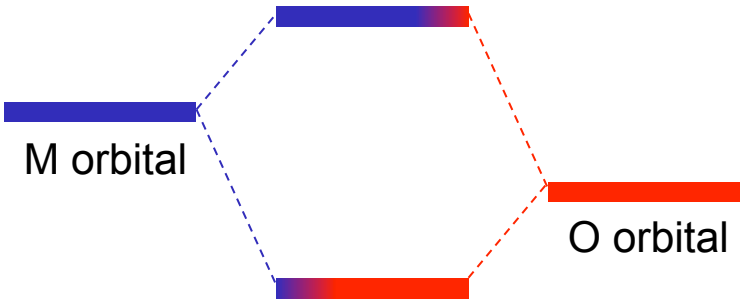
At what potential are electrons extracted from oxides ?



SY Kang and GC, dx.doi.org/10.1021/cm401720n | Chem. Mater. 2013, 25, 3328−3336

When a transition metal is present, oxidation voltage moves up

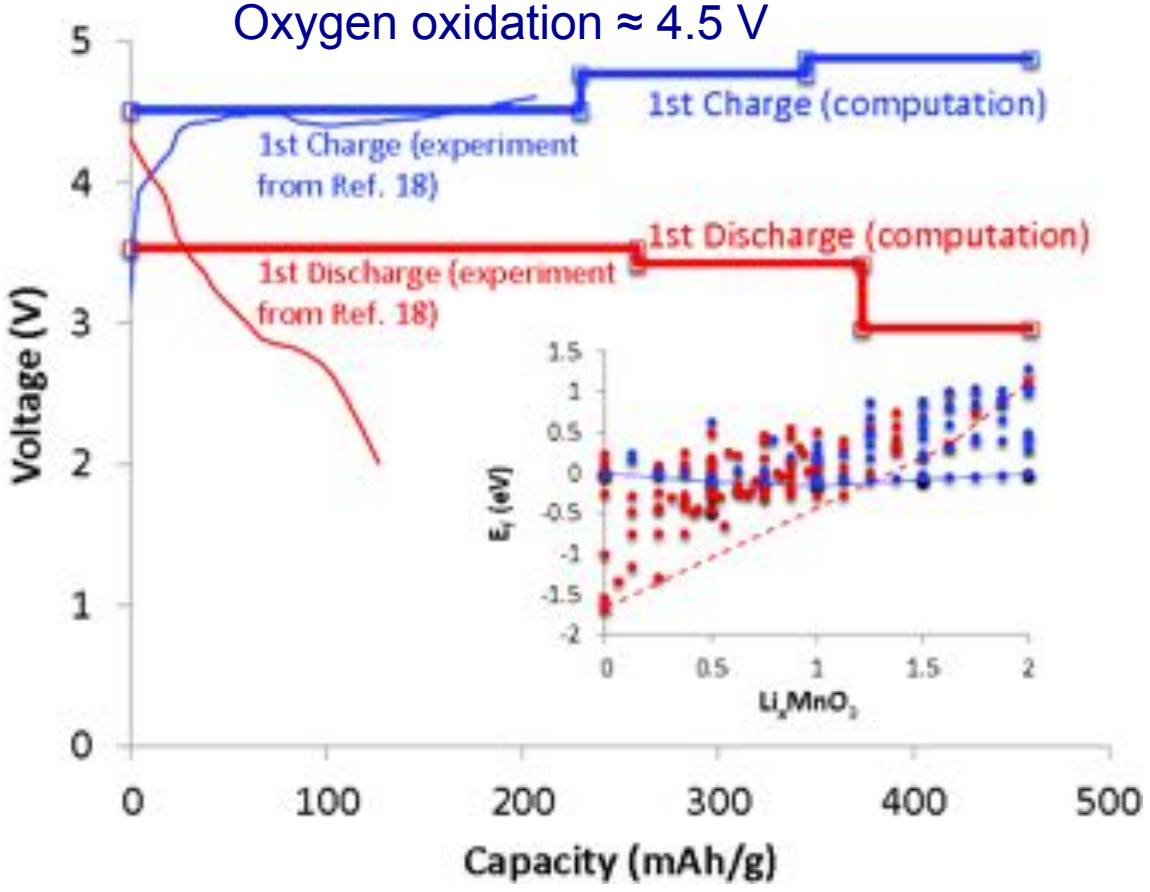
Hybridization with a metal increase the voltage for oxygen oxidation



MK Aydinol and GC, Phys Rev B, 57 (3) 1354 1997

Li_2MnO_3

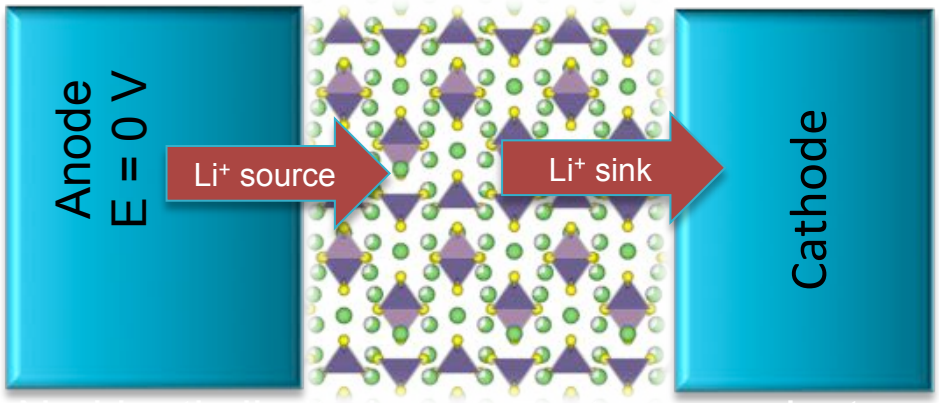
Oxygen oxidation ≈ 4.5 V



Lee, E., Persson, K. A. (2014). Adv. Energy Mater., 4: 1400498. doi: 10.1002/aenm.201400498

Given strong stabilization of oxygen by Mn in Li_2MnO_3 difficult to imagine solid oxide electrolytes to have much higher anodic stability than 4.5V

How to calculate Electrochemical Stability



Thermodynamics is well defined

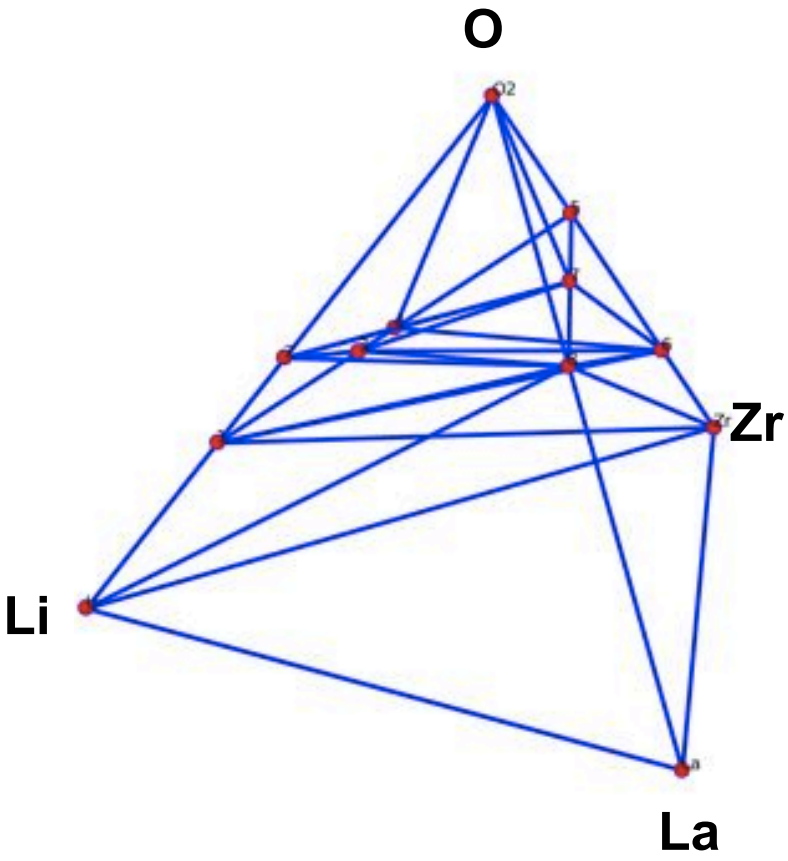
Equilibrium under high and low Li chemical potential:

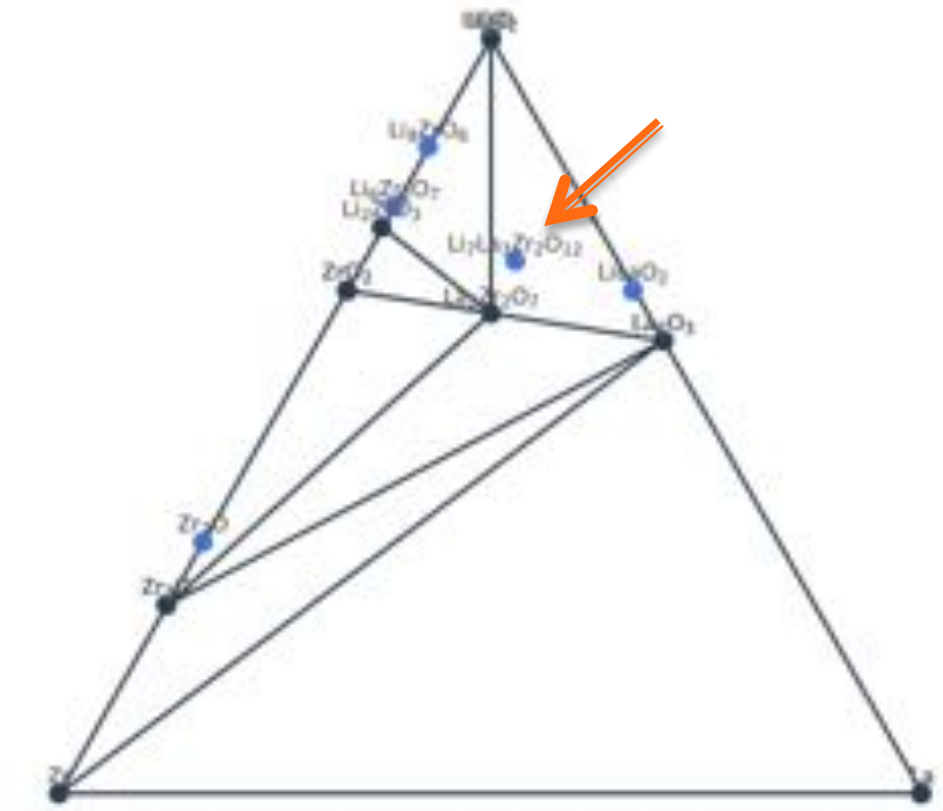
$$\Phi = G - \mu_{Li} x_{Li}$$

Y. Mo, S. P. Ong, G. Ceder, Chem. Mater. **24** 15-17 (2012)

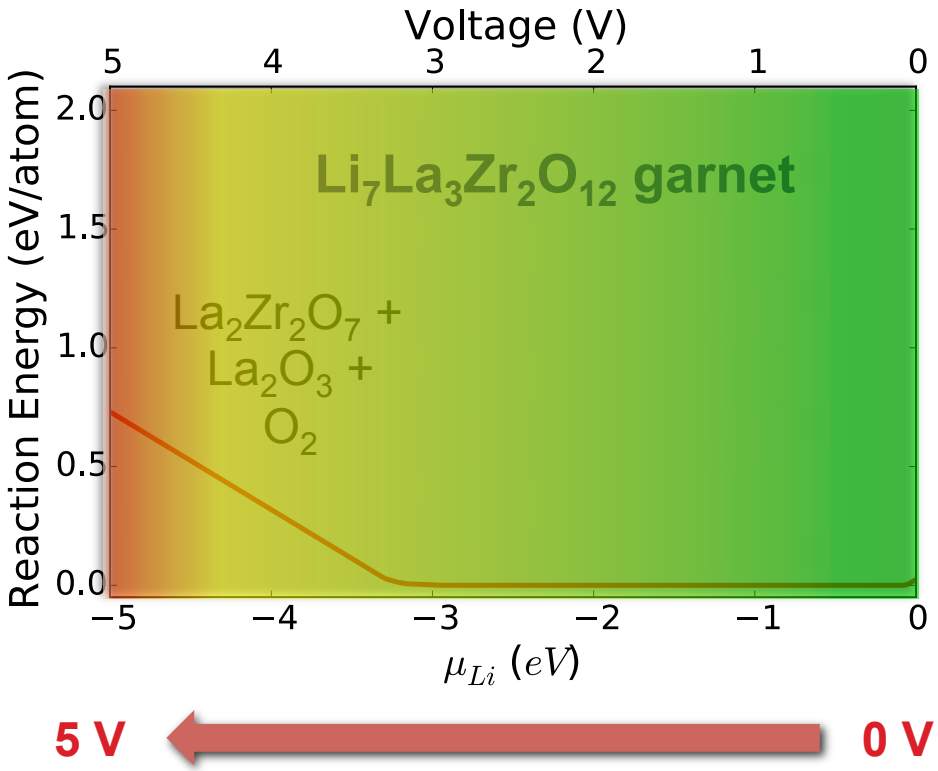
Need energy of all phases in the chemical space

Project at some Li chemical potential





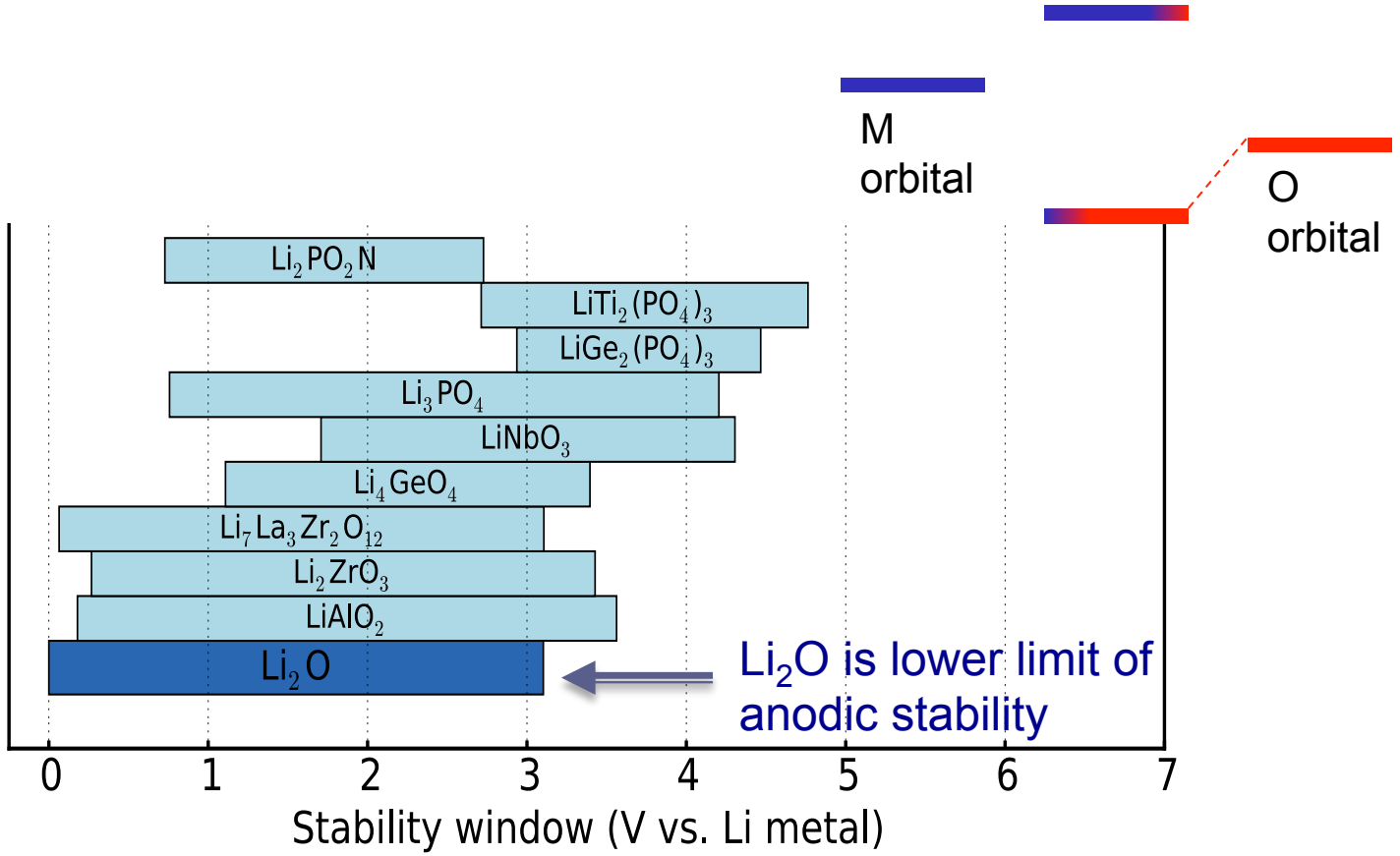
Stability range for oxide garnet is much larger



Decomposition to:
$Zr(O_2)$ + La_2O_3 + Li_8ZrO_6

W.D. Richards et al., *Interface Stability in Solid-State Batteries,* Chem. Mat, 28 (1), 266-273 (2016).

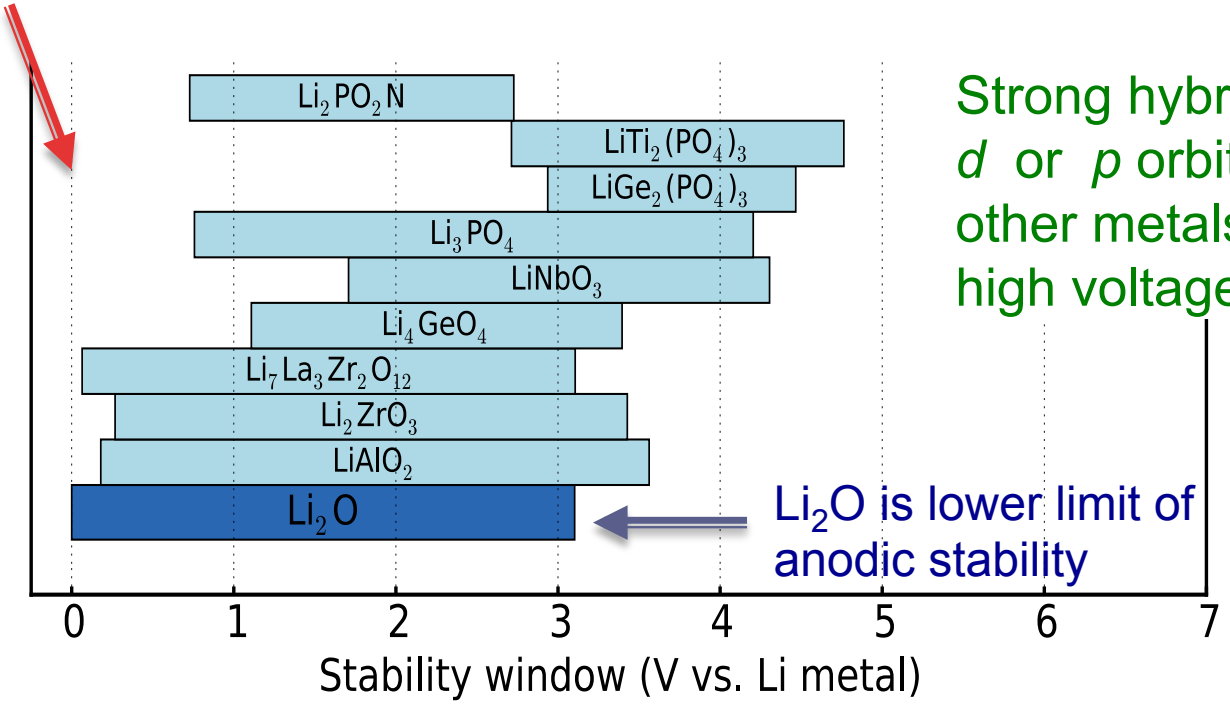
More oxides



All reaction decomposition products can be found in the Supplementary Information in W.D. Richards et al., Chem. Mat, 28 (1), 266-273 (2016).

More oxides

BUT … Possibility of reduction of metal will decrease stability against Li anode

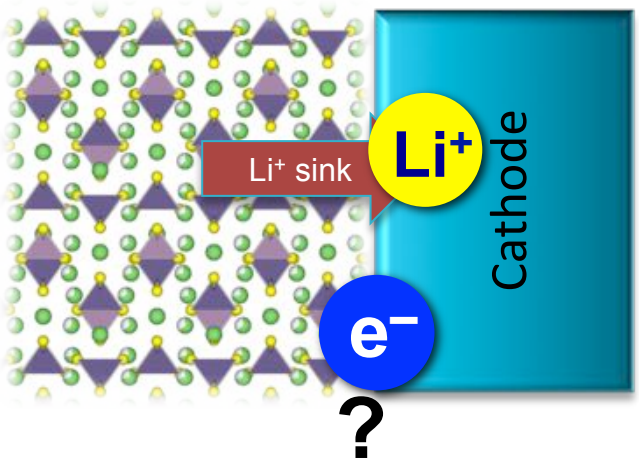


Strong hybridization with *d* or *p* orbitals from other metals will increase high voltage stability

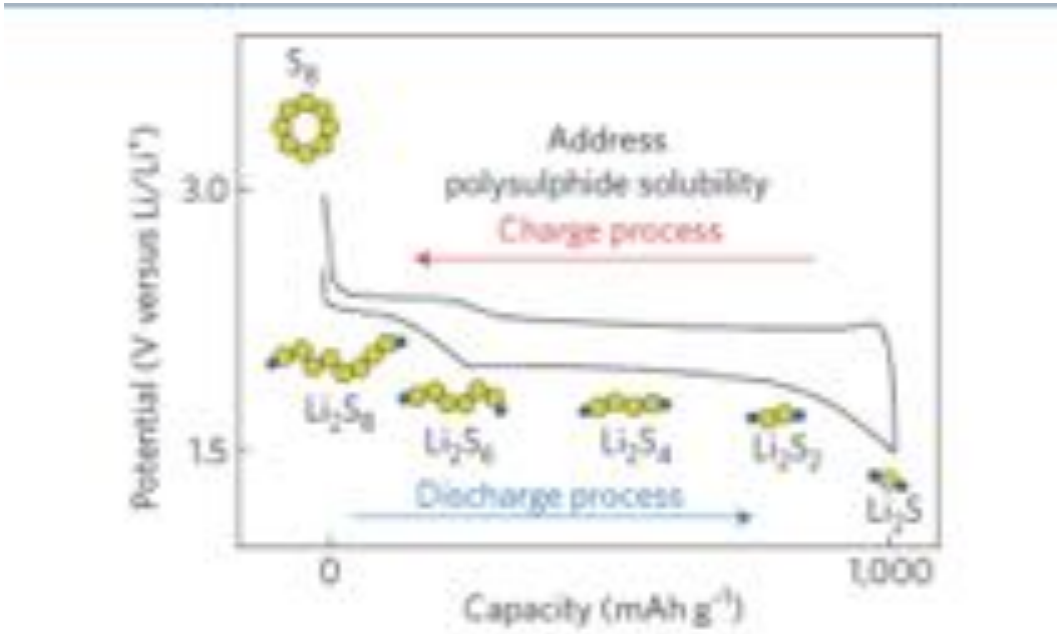
Li_2O is lower limit of anodic stability

All reaction decomposition products can be found in the Supplementary Information in W.D. Richards et al., Chem. Mat, 28 (1), 266-273 (2016).

Oxidation of Sulfide Conductor

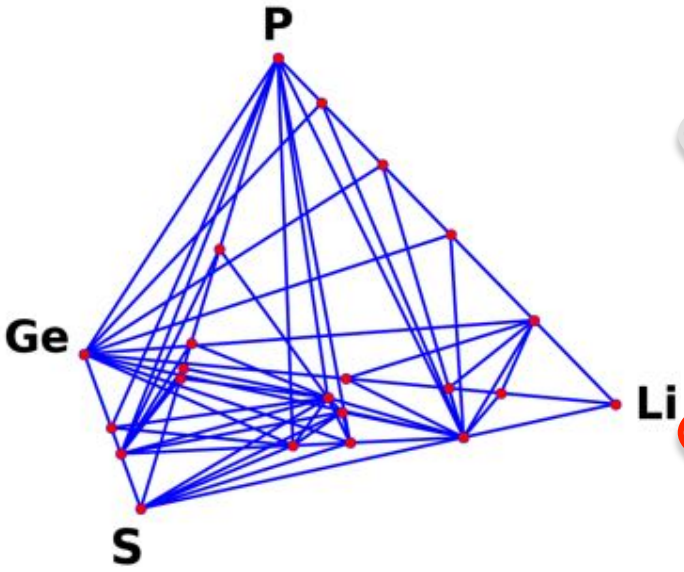


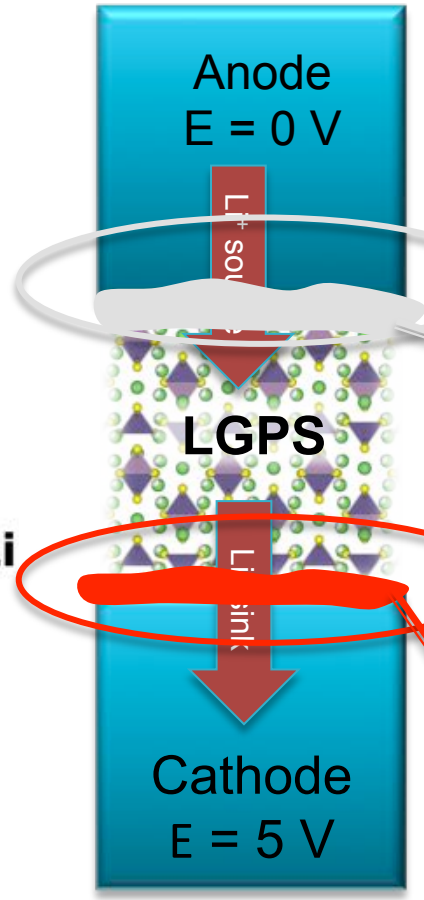
Li-S battery charges at about 2.3 – 2.4V:

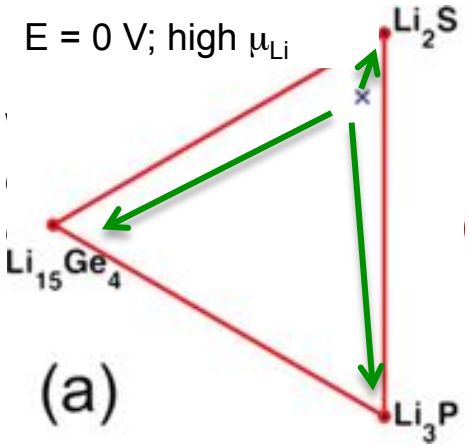


Difficult to imagine Sulfides have much higher redox potential than ≈ 2.5V

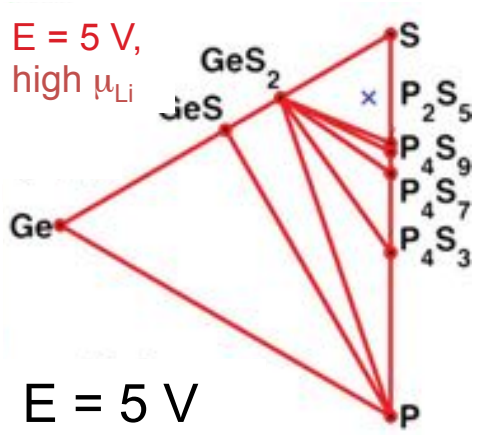
Electrochemical Stability is embedded in the quaternary phase diagrams







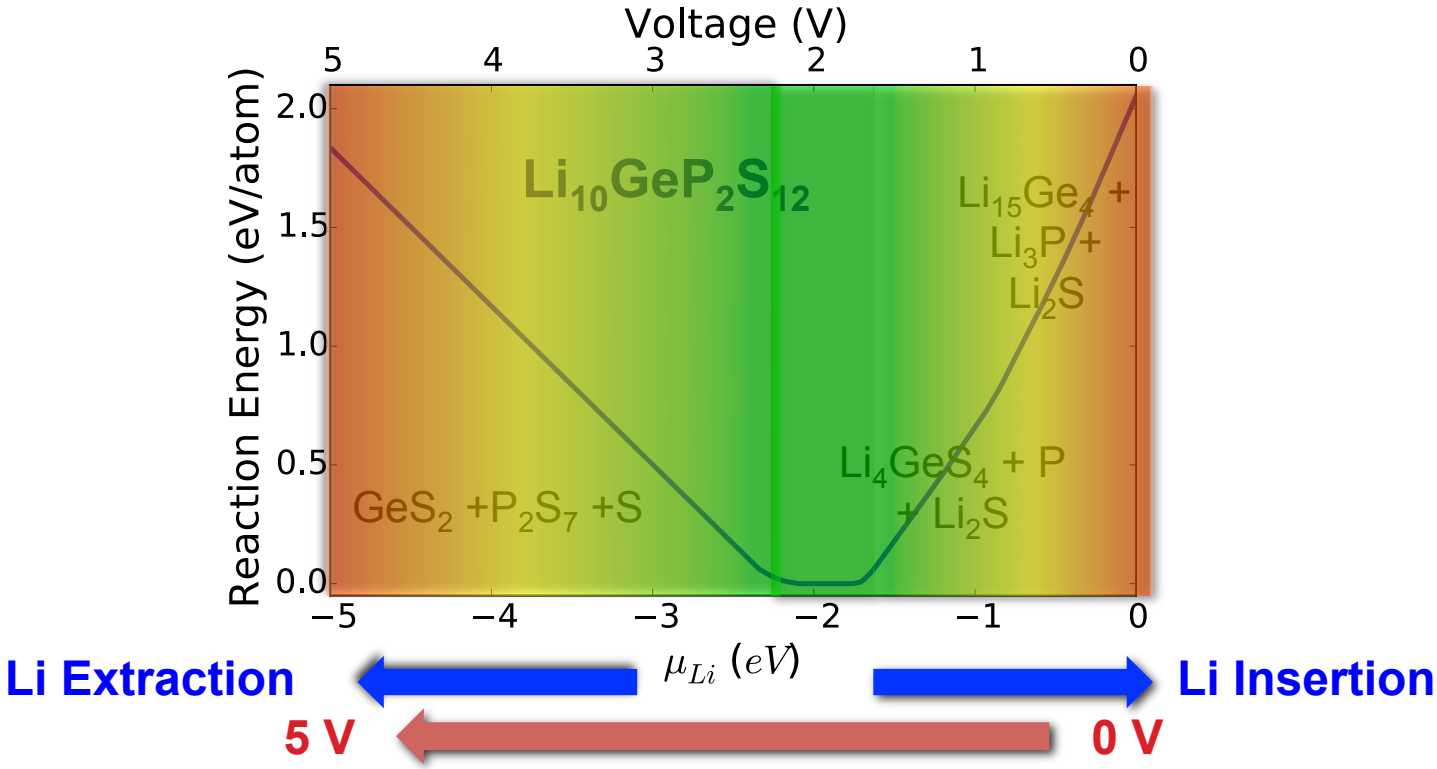
Decomposition into Li_2S, Li_3P, $Li_{15}Ge_4$



Decomposition into S, GeS_2, P_2S_5

The Materials Project

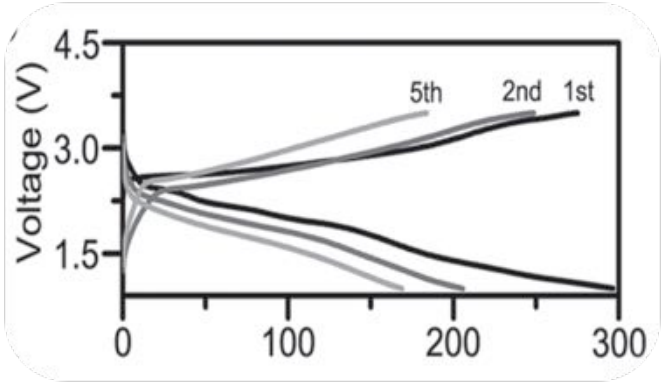
Stability range for LGPS is actually quite narrow.



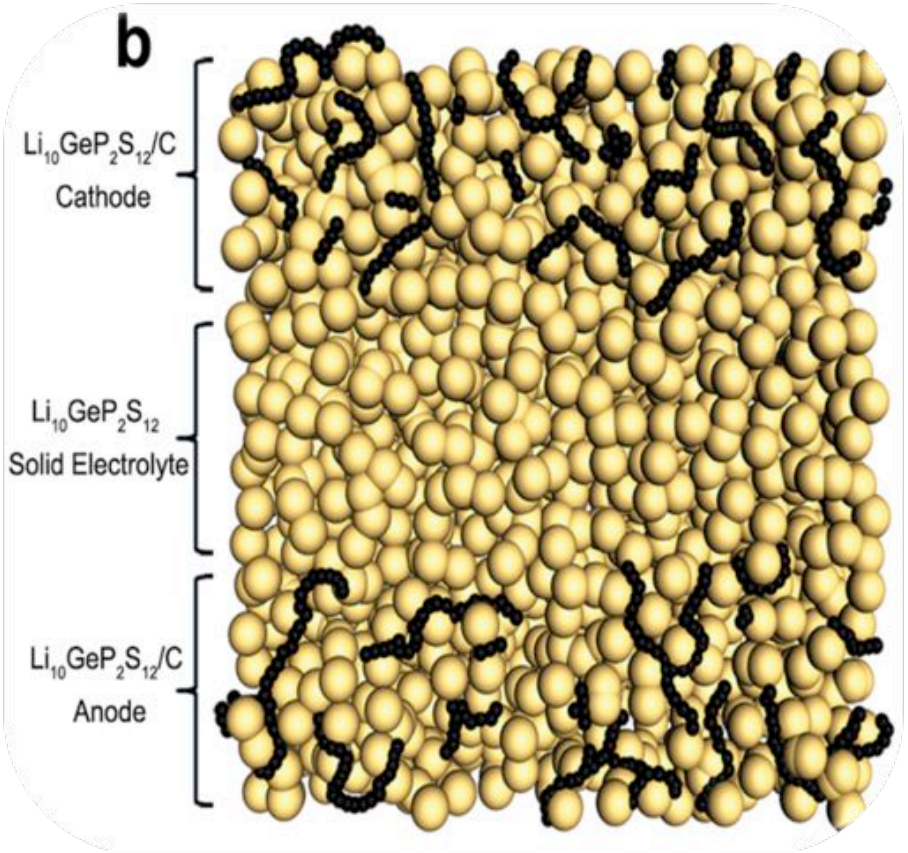
An electrolyte only battery …

Decomposition products actually become electrochemically active

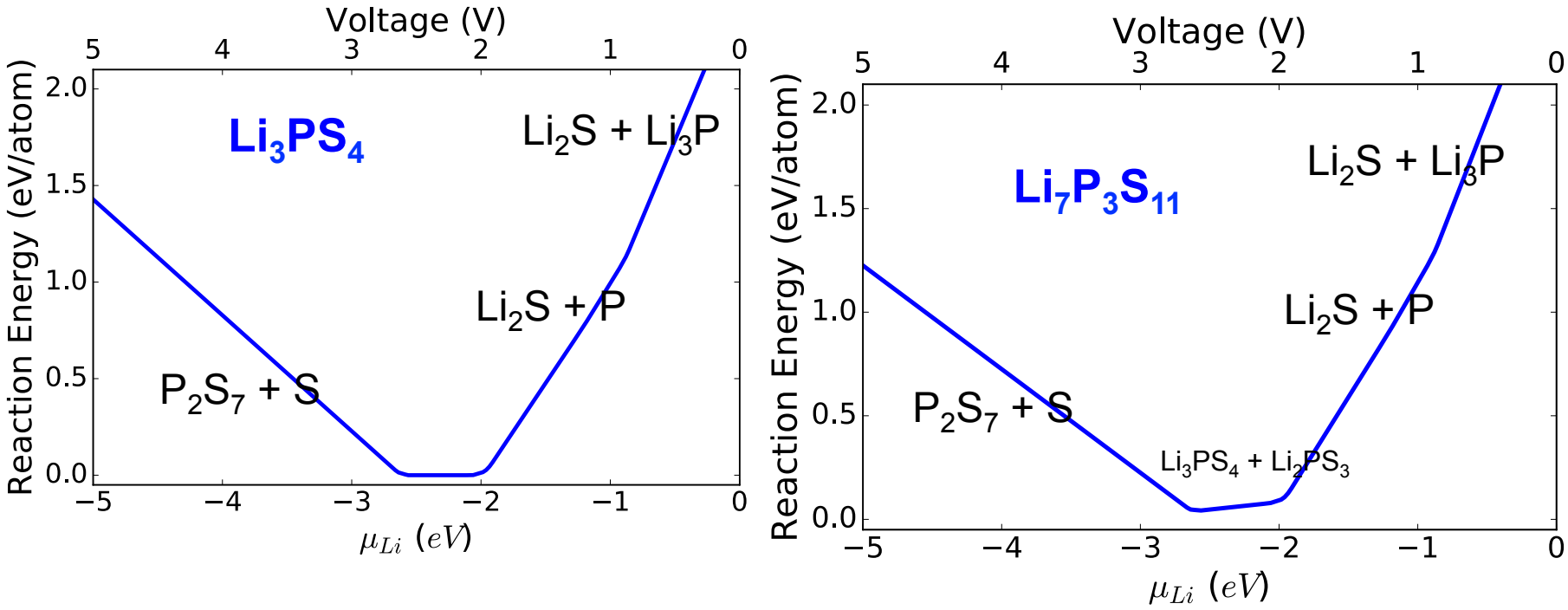
Han et al. Adv. Mater. 2015



LGPS as anode, cathode, and electrolyte



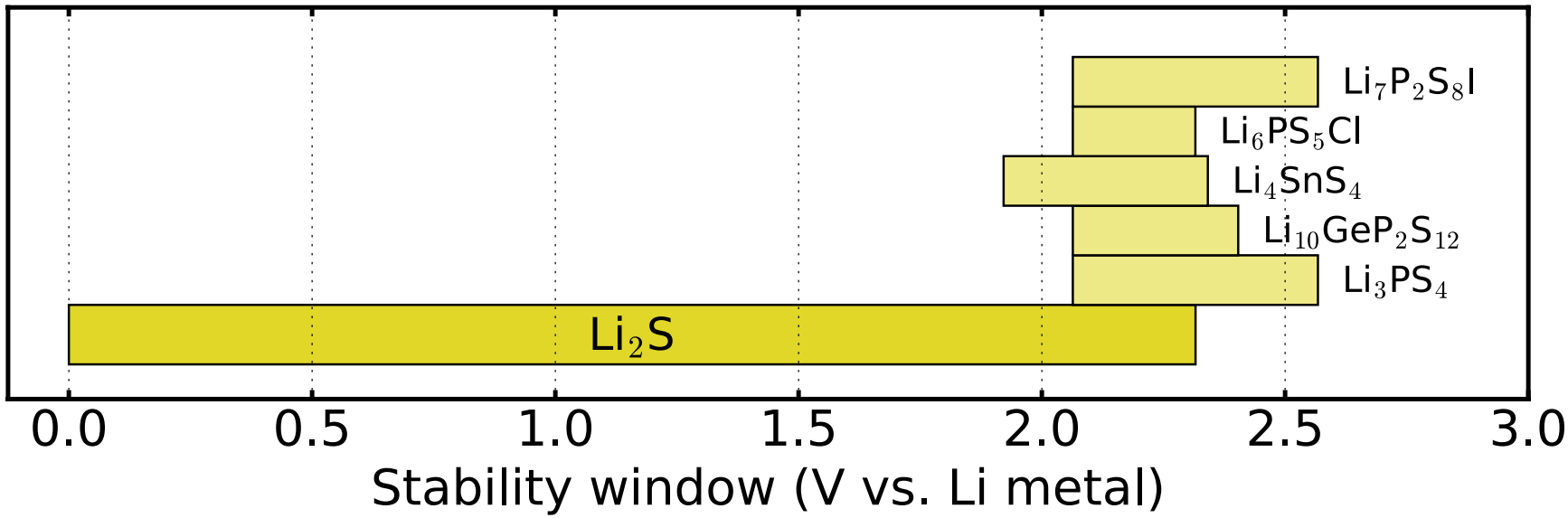
Same for Li_3PS_4 and $Li_7P_3S_{11}$



W.D. Richards et al., *Interface Stability in Solid-State Batteries,* Chem. Mat, 28 (1), 266-273 (2016).

All Sulfides

DFT calculated stability windows

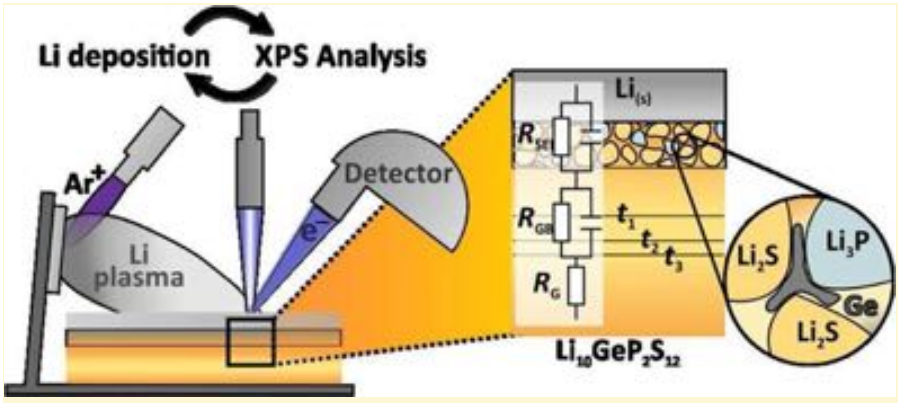


Recent XPS experiments show thiophosphate electrolyte reduction by Li-metal

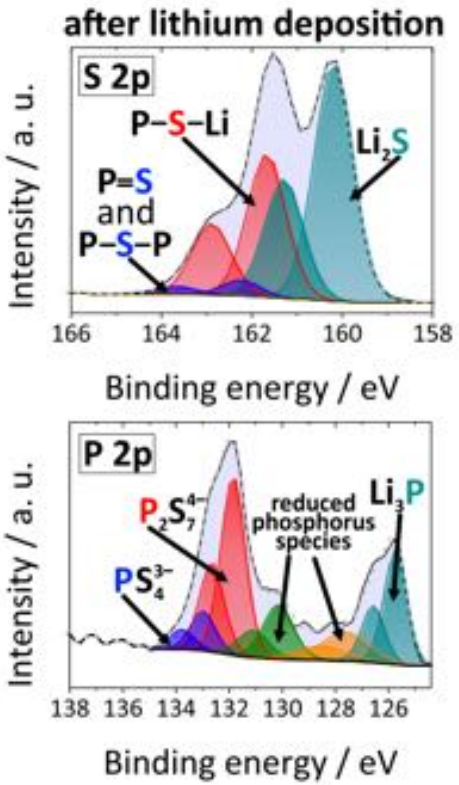
DFT predictions at Li-metal interface:

$Li_7P_3S_{11}$ - > Li_2S + Li_3P

$Li_{10}GeP_2S_{12}$ - > Li_2S + Li_3P + $Li_{15}Ge_4$

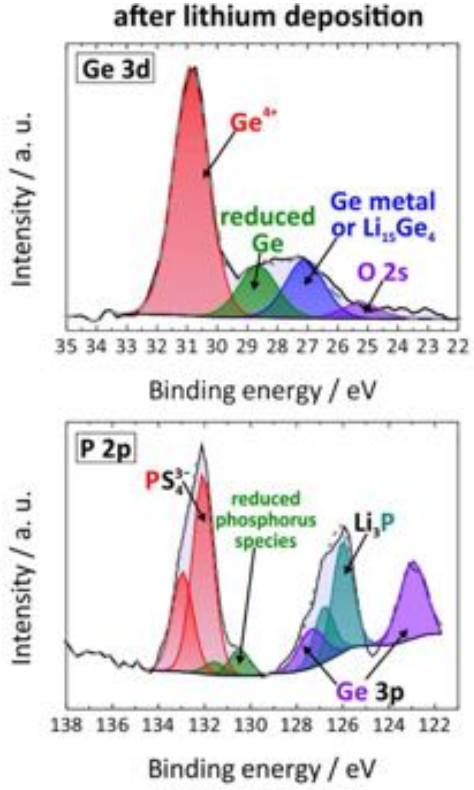


$Li_7P_3S_{11}$



S. Wenzel *et al.*, Solid State Ionics 286 24–33 (2016)

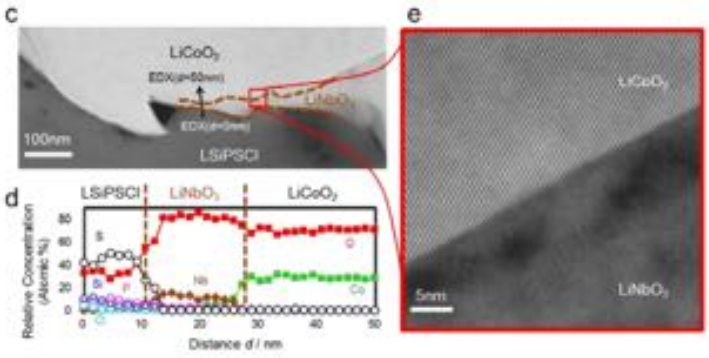
$Li_{10}GeP_2S_{12}$



S. Wenzel *et al.*, Chem. Mater. (2016)

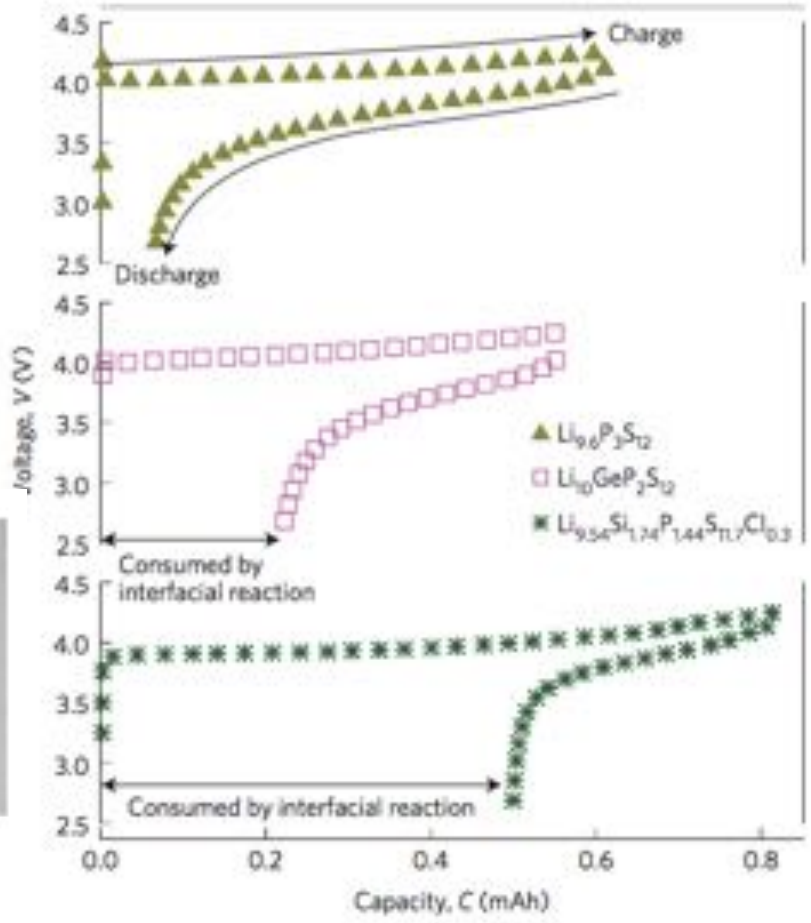
Very recent experiment confirmed theoretical predictions: **Thiophosphates unstable against high voltage cathode and Li metal**

- The consumed capacity during the first charge–discharge process indicates the occurrence of side reactions leading to the generation of the surface layer.
- Coating layer ($LiNbO_3$) of the cathode is required
- Stable cycling only achieved using the $Li_4Ti_5O_{12}$ anode.



Electrochemical stability of the LGPS family

Characterized by $LiCoO_2$/solid electrolyte/Li cell



Kato and Kanno *et al.*, Nature Energy (2016)

Summary on Sulfides

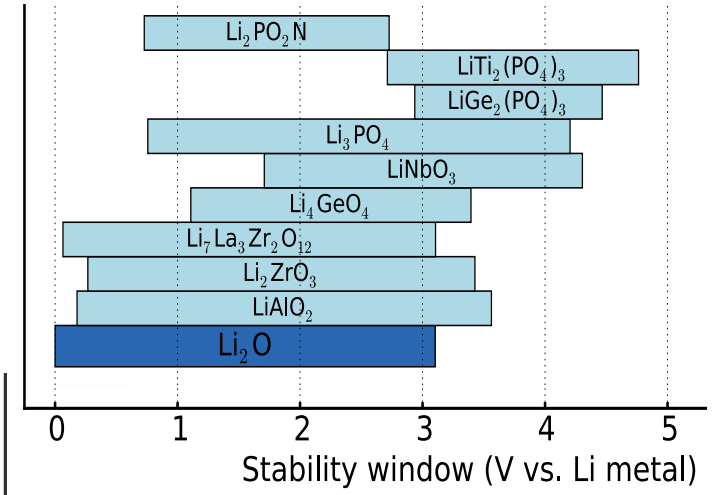
- Sulfides will decompose against Li metal into Li_2S and Li_3P (or other phosphides).
- If a metal cation is present, such as Ge, it will be reduced to the metal, and potential alloy with Li
- On all systems investigated in detail experimental evidence is in agreement with computational predictions
- Li_2S and Li_3P are insulating and as such may be able to lead to a passivation SEI

W.D. Richards et al., *Interface Stability in Solid-State Batteries,* Chem. Mat, 28 (1), 266-273 (2016).

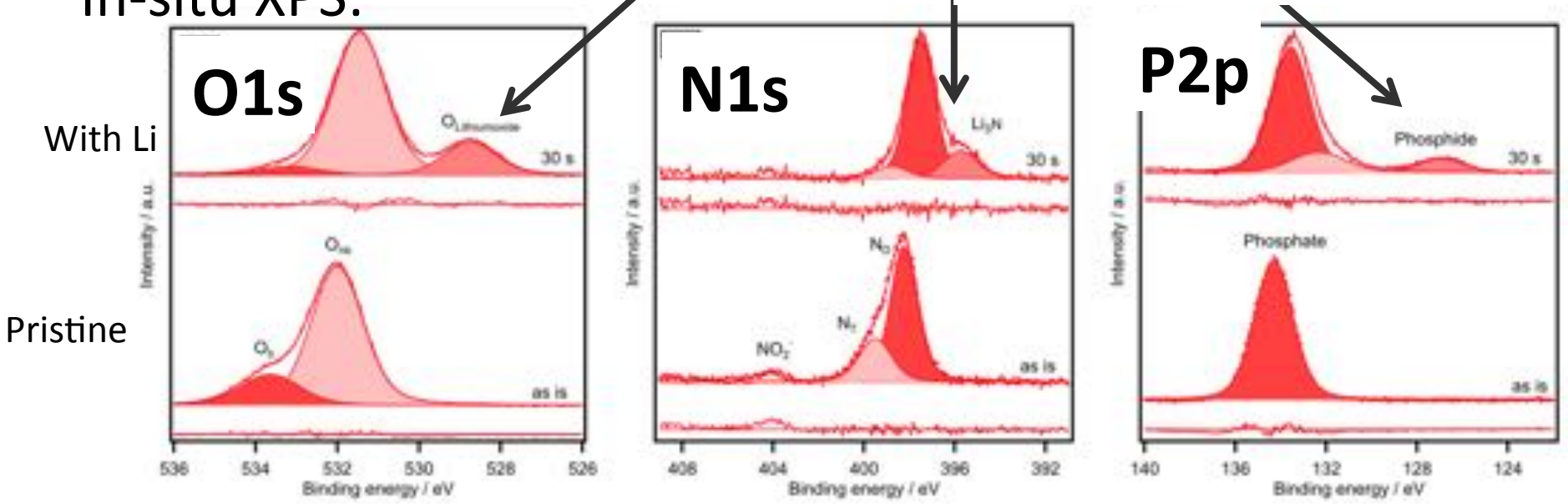
Similar results recently seen in LiPON

Our prediction:

LiPON + Li -> $Li_2O + Li_3N + Li_3P$



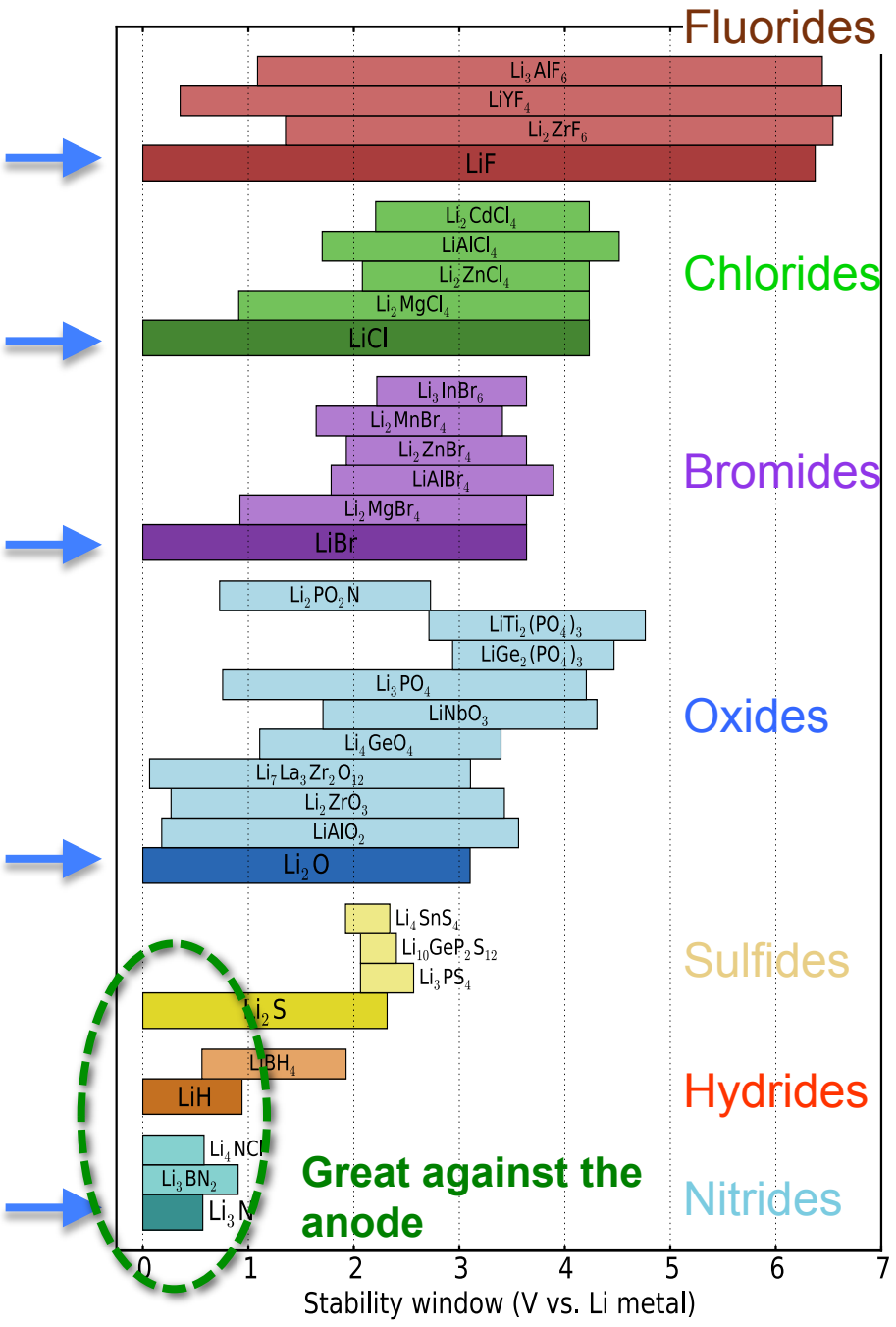
In-situ XPS:



A. Schwöbel et al. Solid State Ionics 273 (2015) 51–54

Thermo analysis easily applied to wide range of systems

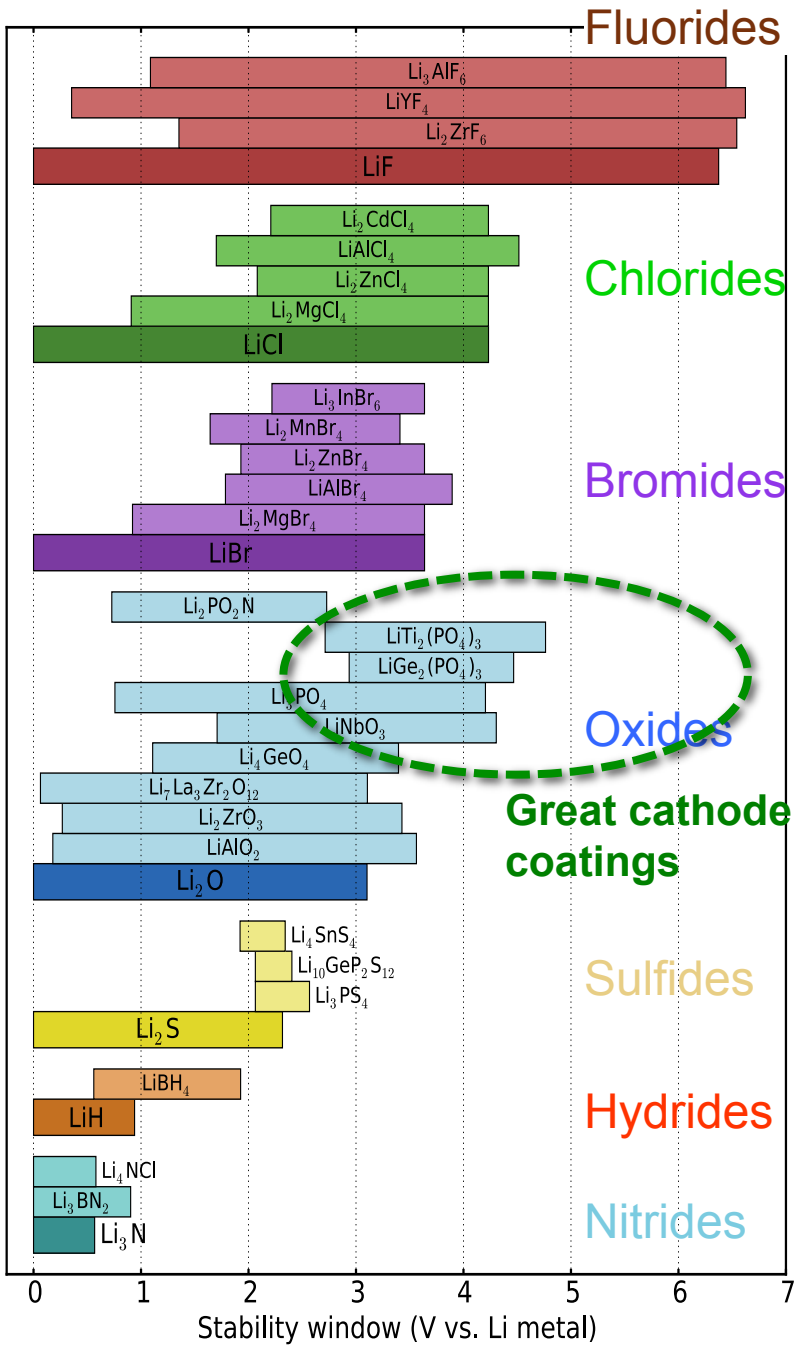
- Simple binaries Li-anion set the best possible stability against Li-metal
- Adding other components reduces stability against Li metal



W.D. Richards, et al. Chemistry of Materials, 28 (1), 266-273 (2016)

Limit at high voltage is modified by other cations

- Cations that move up anion oxidation potential (e.g. through inductive effect) raise the anodic high voltage stability
- Explains good performance of barrier layers ($LiNbO_3$, $LiAlO_2$, Li_2ZrO_3)



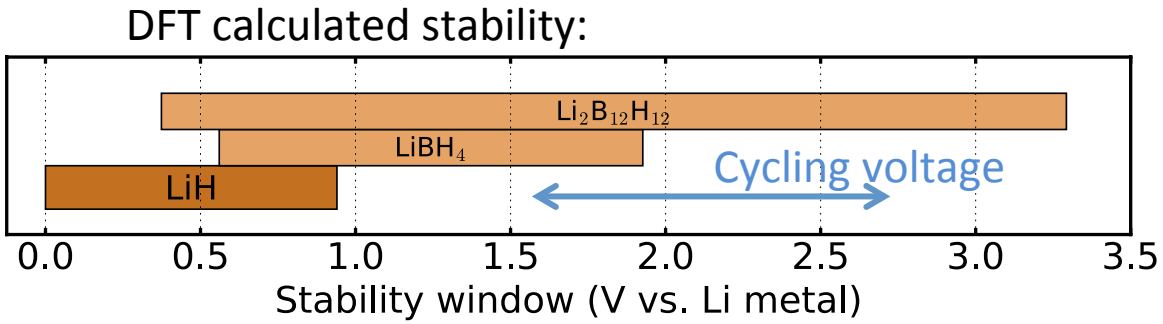
W.D. Richards, et al. Chemistry of Materials, 28 (1), 266-273 (2016)

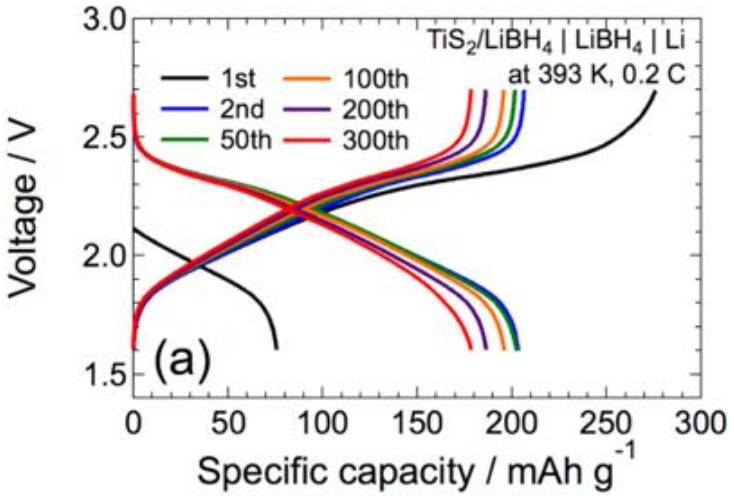
But passivation may help.
Need to investigate the passivation products

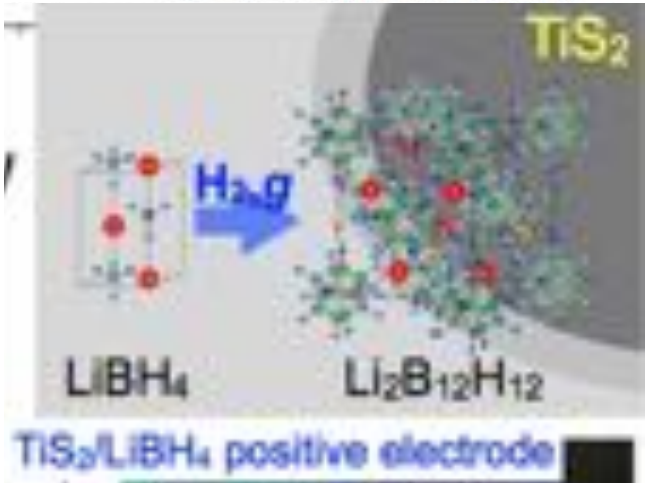
W.D. Richards, et al. Chemistry of Materials, 28 (1), 266-273 (2016)

Passivating interface between $LiBH_4$ and TiS_2

- DFT predicts limited stability window of $LiBH_4$
  - Forms layer of $Li_2B_{12}H_{12}$ at high voltage (>2 V)
- Experimental cell has good stability and shows the expected decomposition products





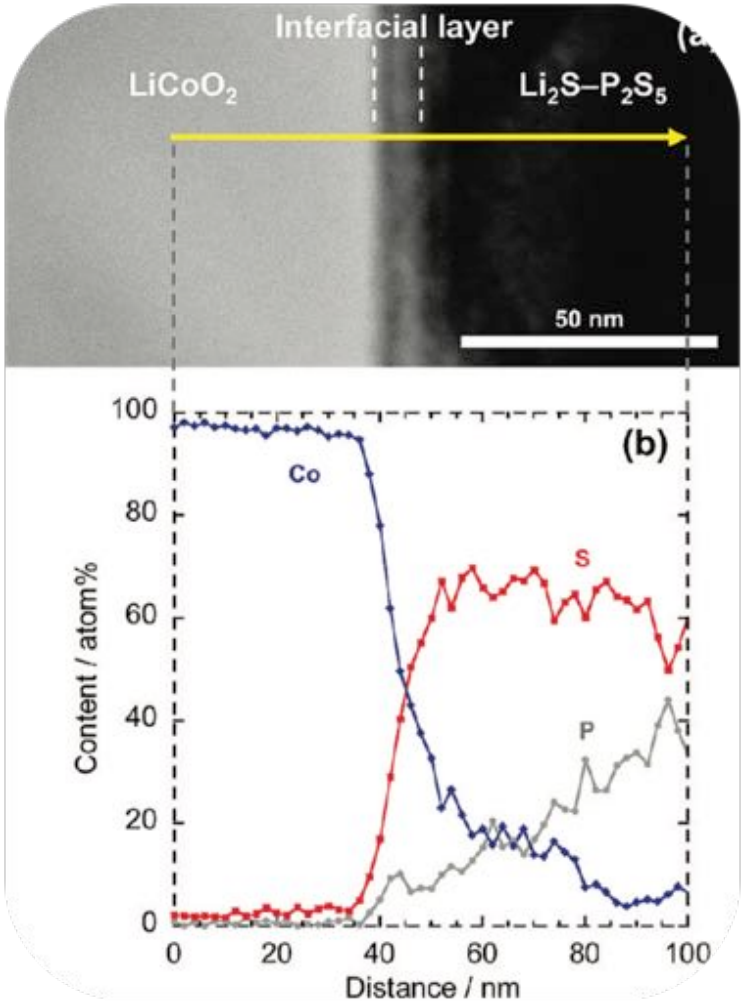


Unemoto et al. Chem. Mater. **2015** 10.1021/acs.chemmater.5b02110

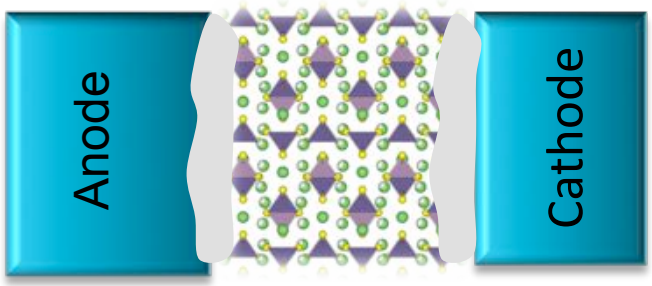
Electrochemical + Chemical Reactivity with the Cathode

W.D. Richards, et al. Chemistry of Materials, 28 (1), 266-273 (2016)

Electrochemical + chemical reactivity with cathode

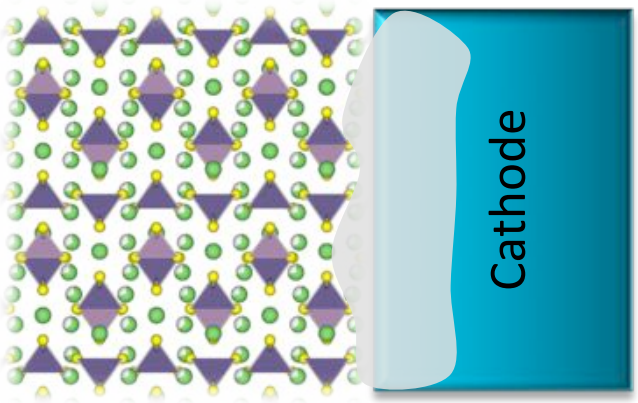


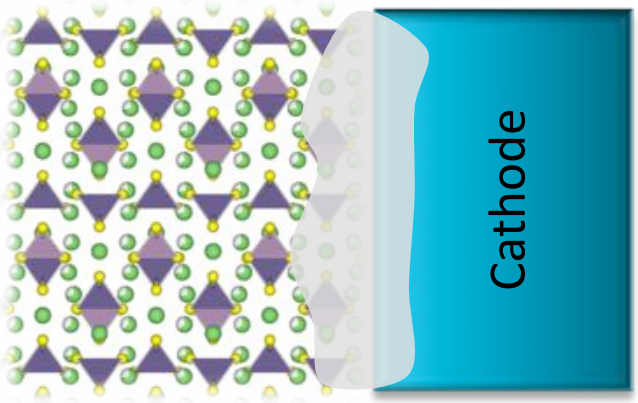
Sakuda et al. Chem. Mater. 2009

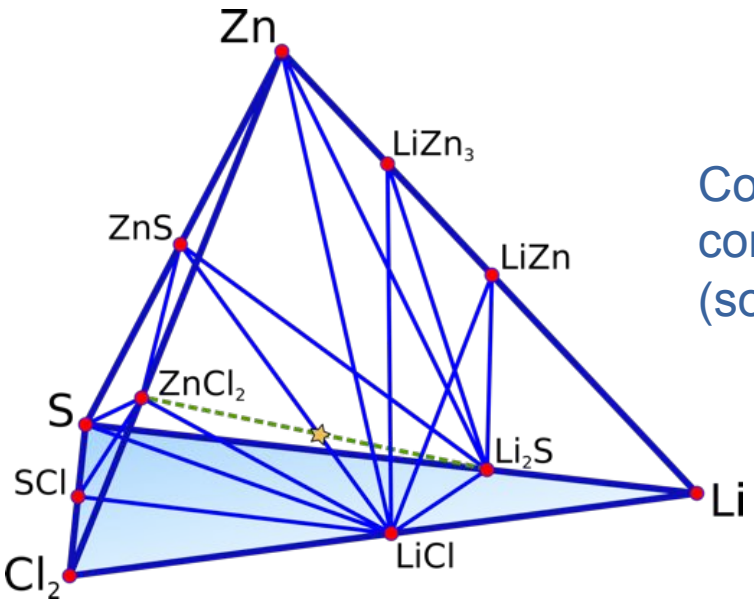


Why this is complicated

Cathode and electrolyte react in undefined ratio

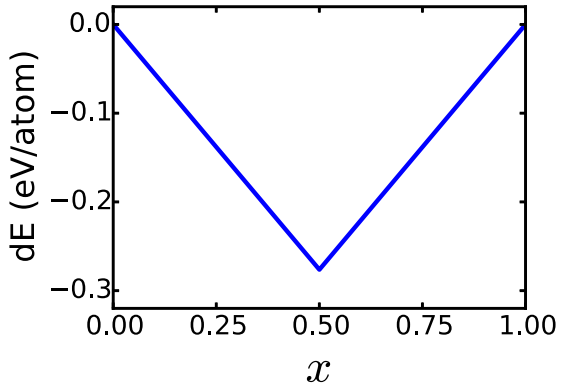






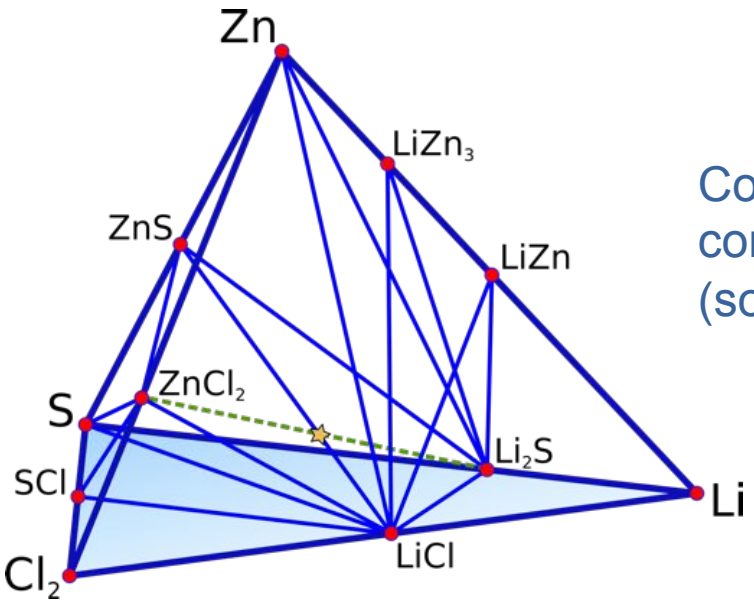
Construct the phase diagram made up of combined elements of cathode and electrolyte (sometimes as many as 7-8 elements)

Approach



Predicted to decompose to ZnS and LiCl

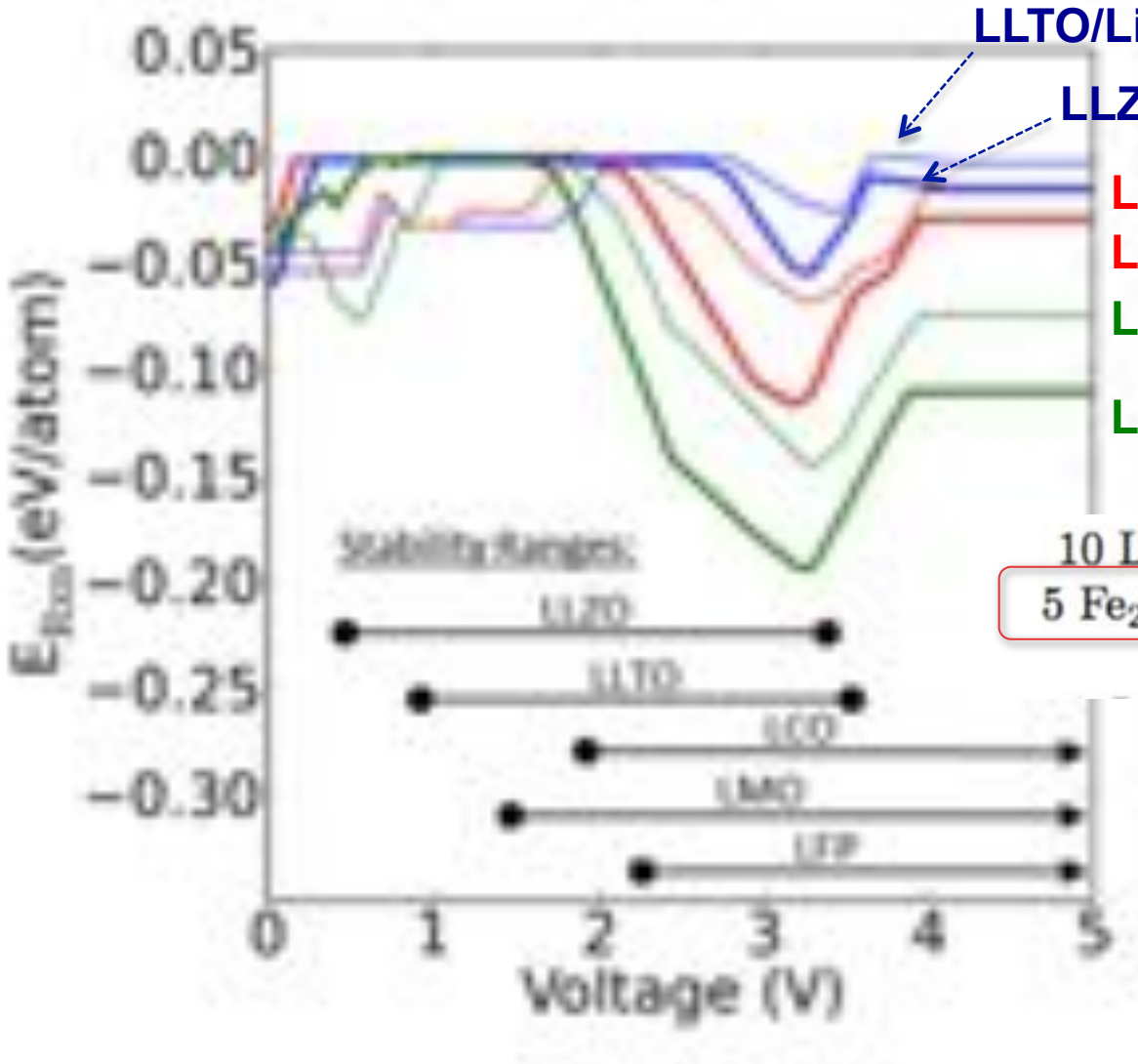
$$\Delta E[C_a, C_b] = \min_x \{E_{pd}[xC_a + (1-x)C_b] - xE[C_a] - (1-x)E[C_b]\}$$



Construct the phase diagram made up of combined elements of cathode and electrolyte (sometimes as many as 7-8 elements)

W.D. Richards, et al. Chemistry of Materials, 28 (1), 266-273 (2016)

Example: LLZO and LLTO against common cathodes

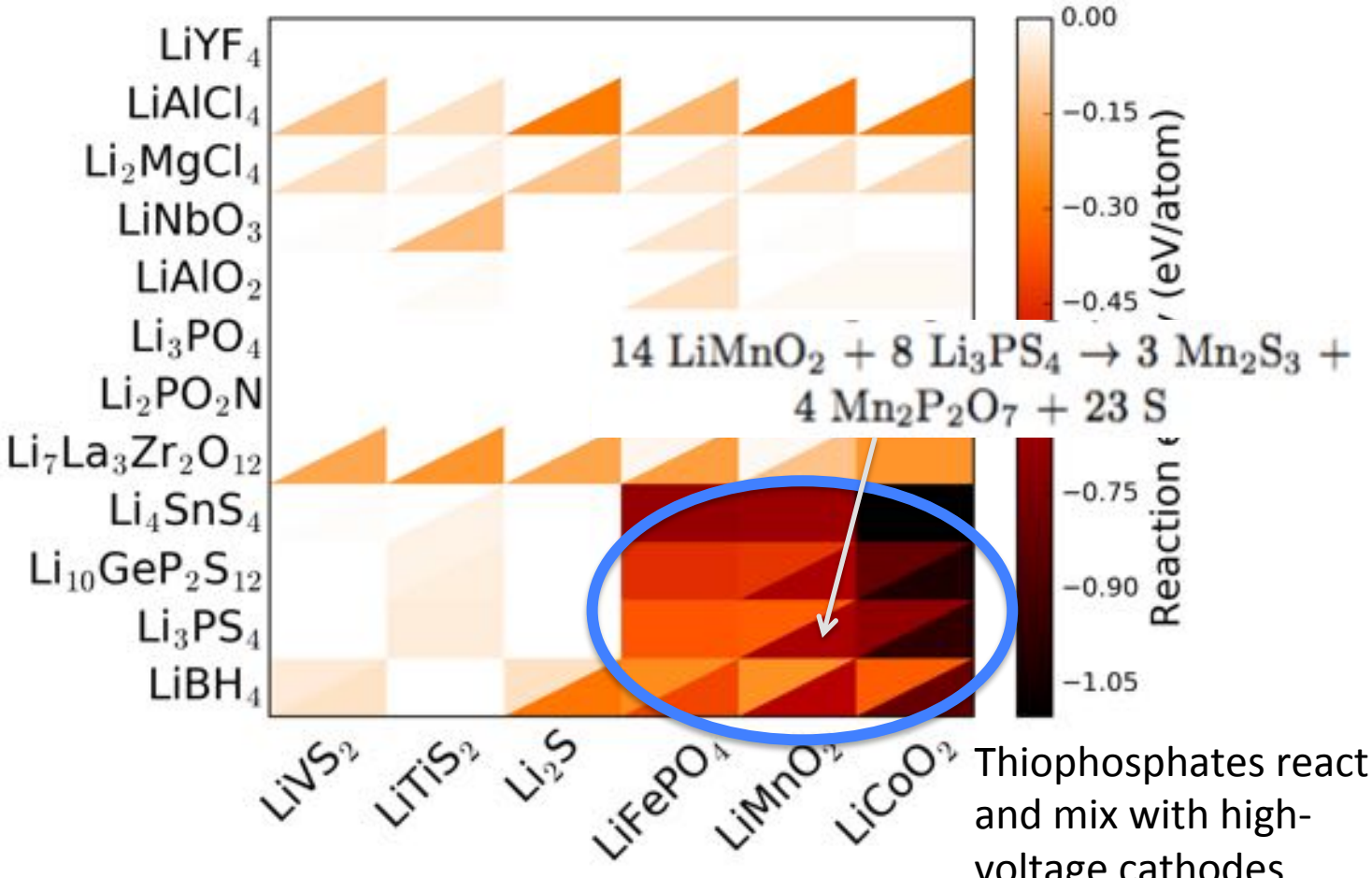


$$10\ LiFePO_4 + 3\ Li_7La_3Zr_2O_{12} \rightarrow 5\ Fe_2O_3 + 7\ Li_3PO_4 + 3\ LaPO_4 + 3\ La_2Zr_2O_7$$

W.D. Richards, et al. Chemistry of Materials, 28 (1), 266-273 (2016)

L. Miara et al. Chem. Mater., 27 (11), 4040–4047 (2015

Selecting an electrolyte/cathode combination

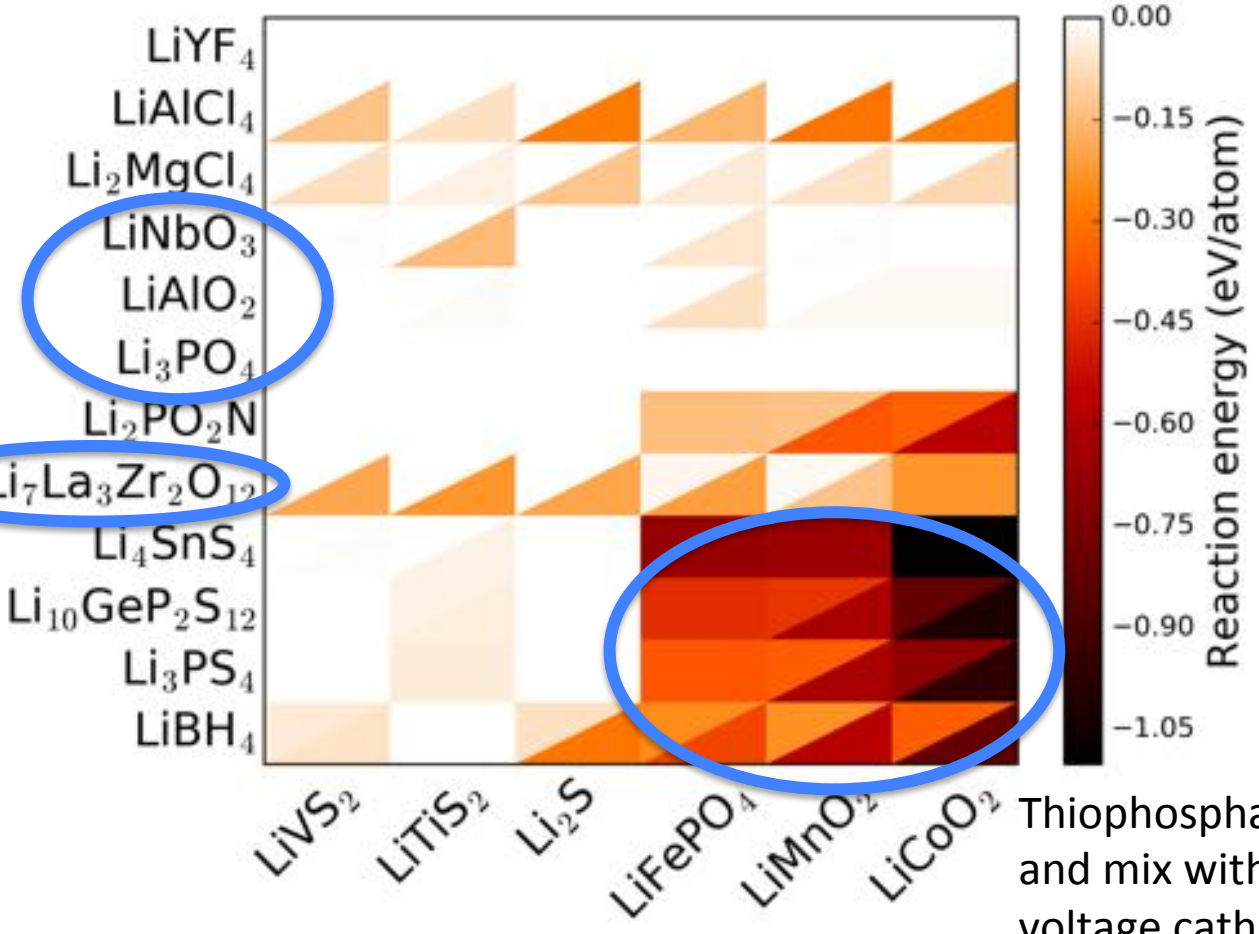


Thiophosphates react and mix with high-voltage cathodes

Reaction energy at cathode chemical potential

Reaction energy with mixing

Selecting an electrolyte/cathode combination



Good coatings

Good voltage stability, but mixing may be a concern

Thiophosphates react and mix with high-voltage cathodes

Reaction energy at cathode chemical potential

Reaction energy with mixing

Summary

- Ab-initio methods predict Li conductivity extremely well.
- Electrochemical stability can be computed and seems to be in very good agreement with detailed experimental studies
- Sulfides have poorer electrochemcial stability than oxides. React to Li_2S and Li_3P against Li metal. Undergo oxidation at the cathode
- Adding metals to the conductor may raise the anodic limit but almost always comes at the expensive of cathodic stability
- Chemical reactivity with cathodes lowers electrochemical voltage limit
- Barrier layers will be required for most (if not all) sulfides, and possibly many oxides