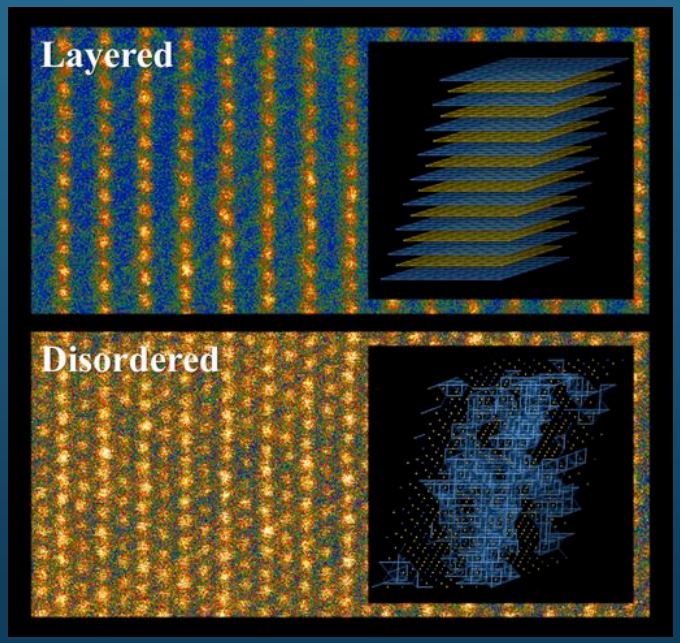
Computational Tools to predict the behavior of solid state conduction



Gerbrand Ceder
Massachusetts Institute of Technology

ARPA-E Workshop Austin Feb 19 2015

U.S. DEPARTMENT OF ENERGY

SAMSUNG ADVANCED INSTITUTE OF TECHNOLOGY

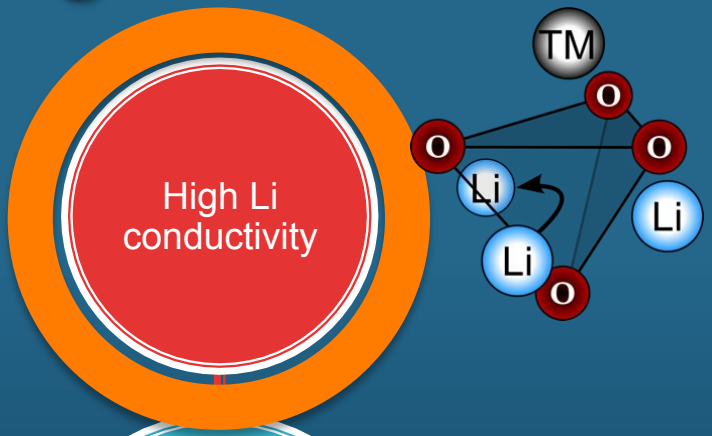
BOSCH Invented for life

umicore materials for a better life

JCESR

What makes a good solid electrolyte?

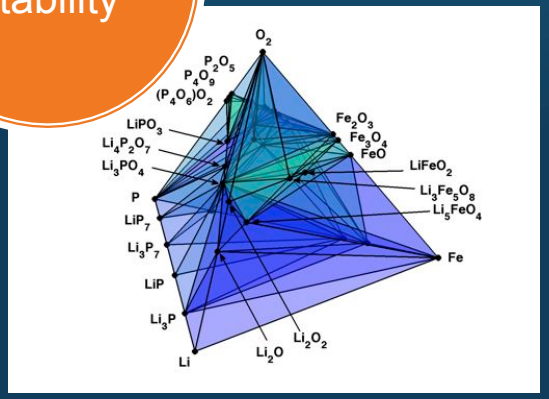
Most of these properties can be computed with high reliability, and in some cases faster and better than experiment

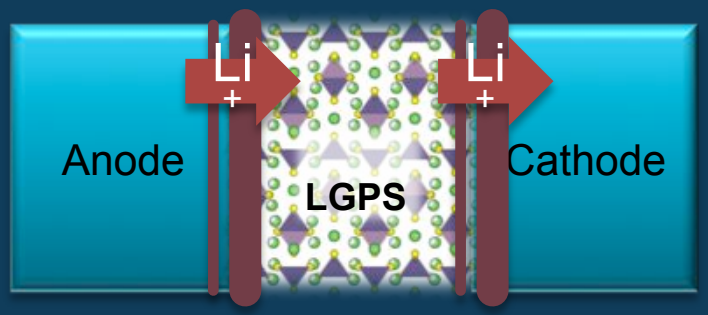


Low electronic conductivity

Li-ion conductor

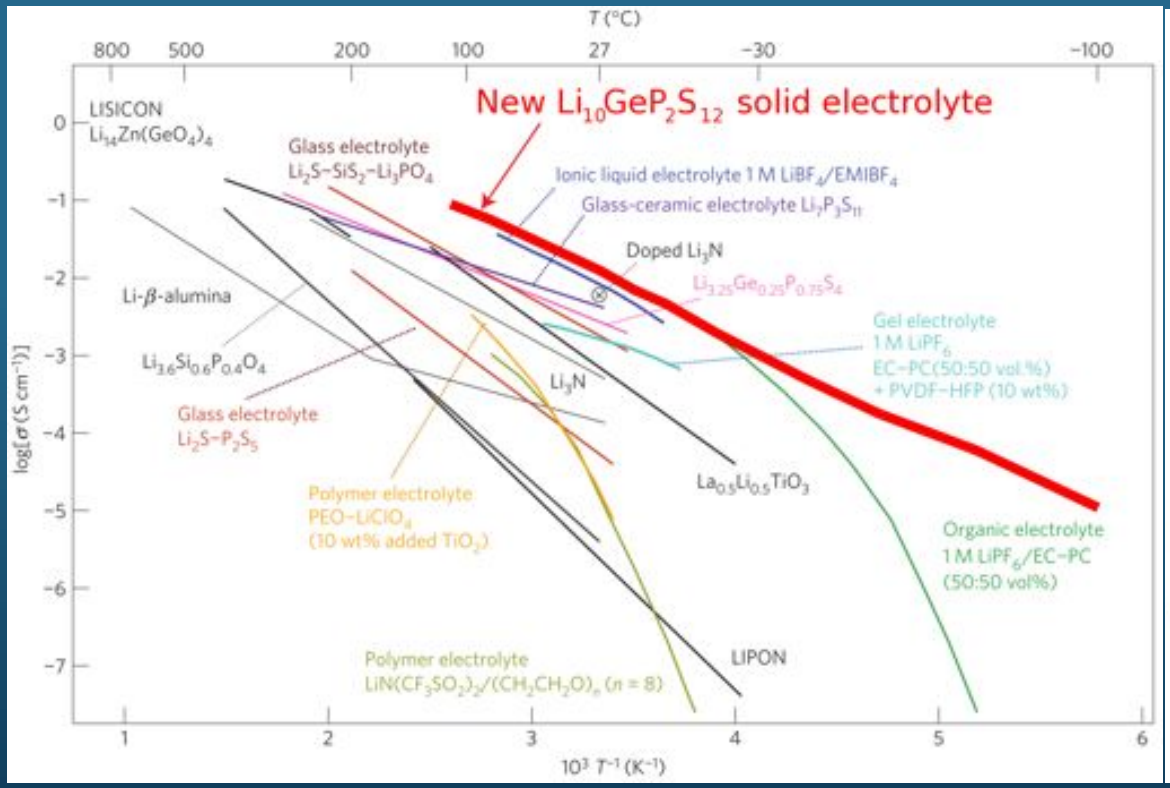
Phase stability

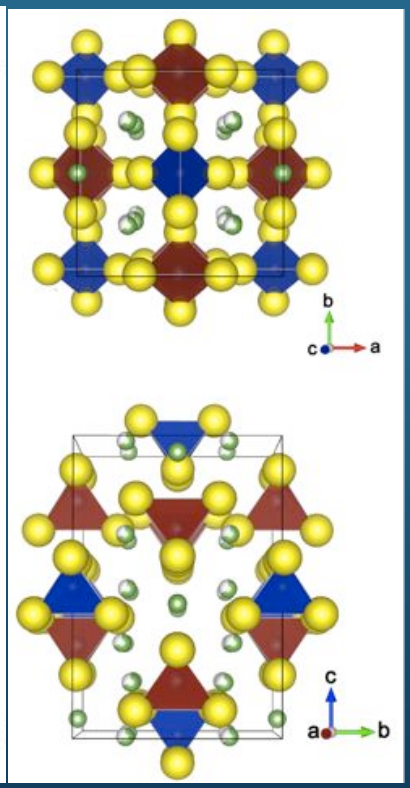




Electro-chemical stability

$Li_{10}GeP_2S_{12}$: a new superionic conductor





CLAIMS MADE ABOUT NEW MATERIAL

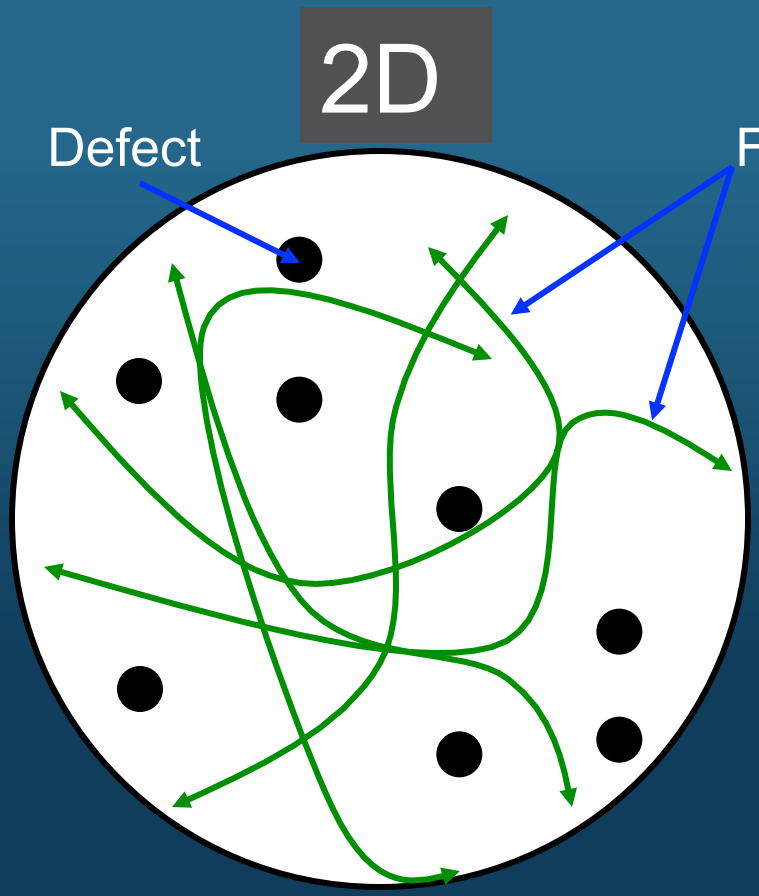
- conductivity: 12 mS/cm @ 25 °C $E_a \approx 240$ meV
- 1D conductor
- electrochemical window: > 5V

OTHER ISSUES

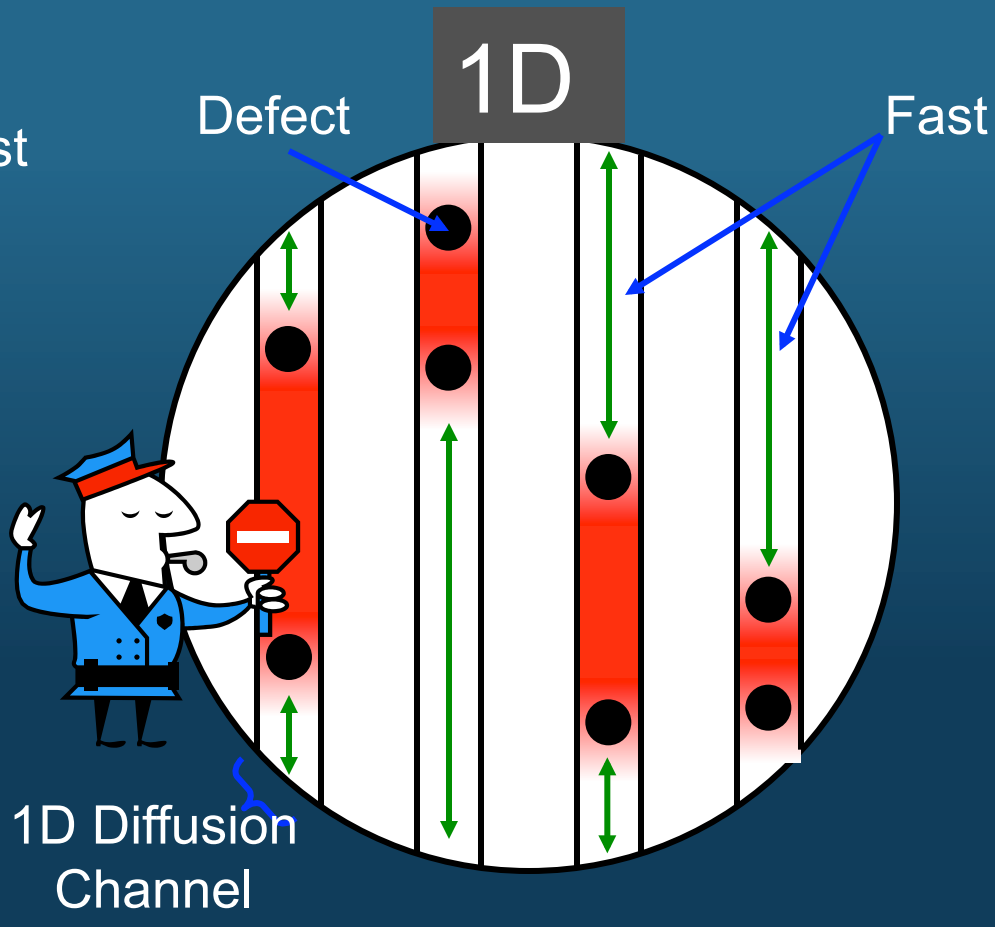
- Cost of Ge
- Moisture sensitivity of sulfides

N. Kamaya et al., A lithium superionic conductor. Nat. Mater. **10**, 682-686 (2011)

1D Diffusion is pathological and does not scale to larger lengths



Presence of defects does not impede diffusion

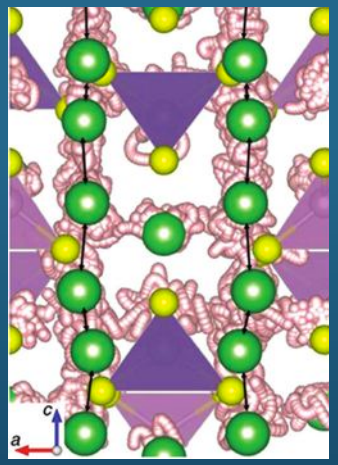


Diffusion can not get around defects

R. Malik,et al. Nano Letters, 10 (10), 4123-4127 (2010).

*M*ethods to compute ionic mobility and diffusion

ab initio molecular dynamics



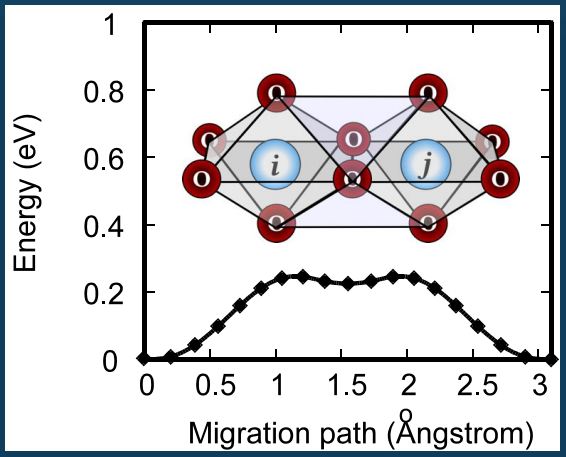
- Calculate trajectories of atoms using Newtonian Dynamics but quantum mechanical forces

$$D = 2dt\left\langle [\vec{r}(t)]^2 \right\rangle$$

$$\sigma(T) = Ne^2 D / Vk_B T$$

- Only possible for good conductors and elevated temperature

Nudged Elastic Band

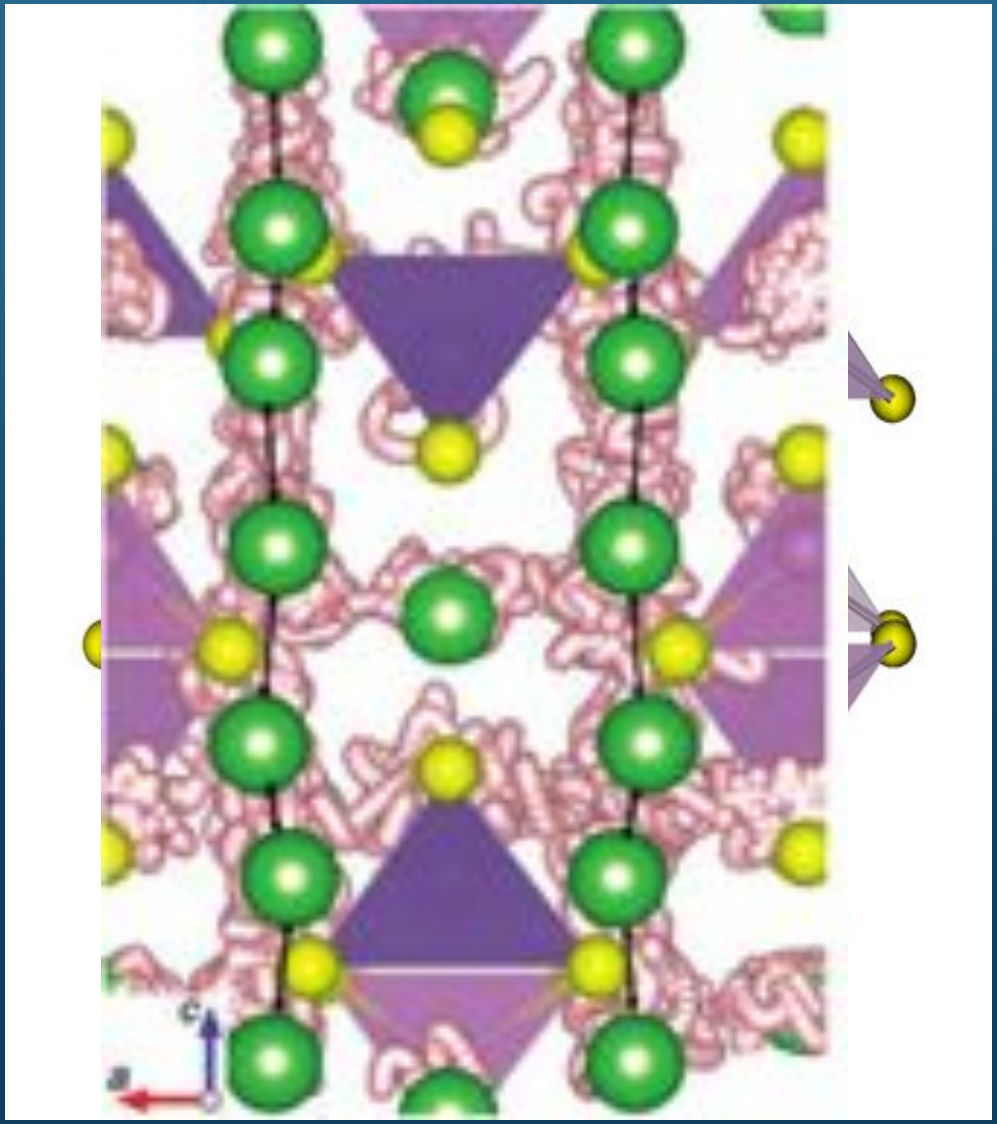


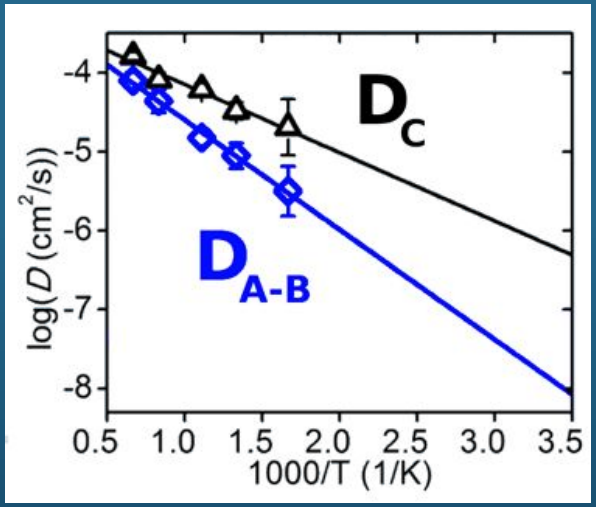
- Calculate activated state energy for ion migration
- Obtain approximation for D from diffusion model

$$\Gamma = v^* \exp(\frac{-\Delta E_b}{kT})$$

$$D = \frac{\Gamma r_j^2 f}{2d}$$

LGPS: Ab initio method confirms high Li conductivity, but predicts 3D conduction pathway





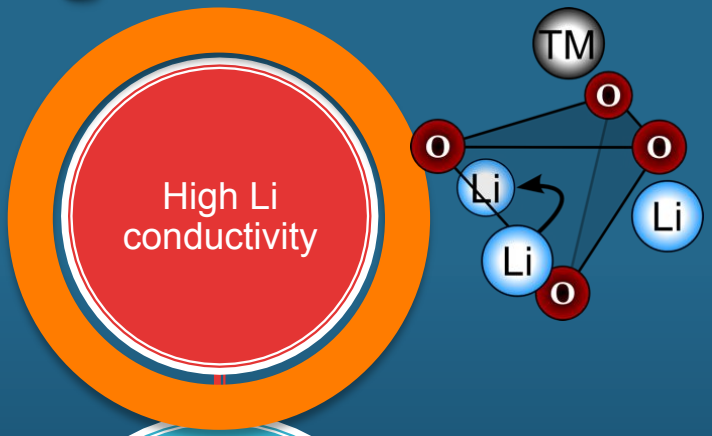
	computation[1]	exp
activation energy (meV)	210	240
conductivity @ 300 K (mS/cm)	13	12

3D conductivity confirmed experimentally by A Kuhn et al, PCCP 2013, May 30 2013

Y. Mo, S. P. Ong, G. Ceder, First principles study of the $Li_{10}GeP_2S_{12}$ lithium super ionic conductor material. Chem. Mater. **24** 15-17 (2012)

What makes a good solid electrolyte?

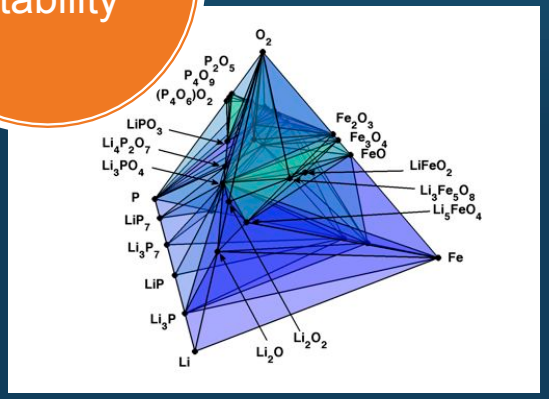
All of these properties can be computed with high reliability, and in some cases faster and better than experiment

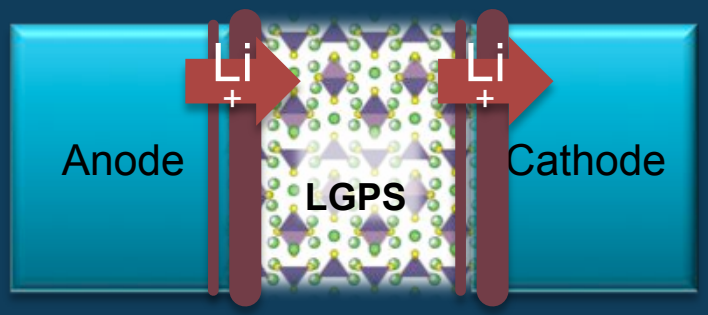


Low electronic conductivity

Li-ion conductor

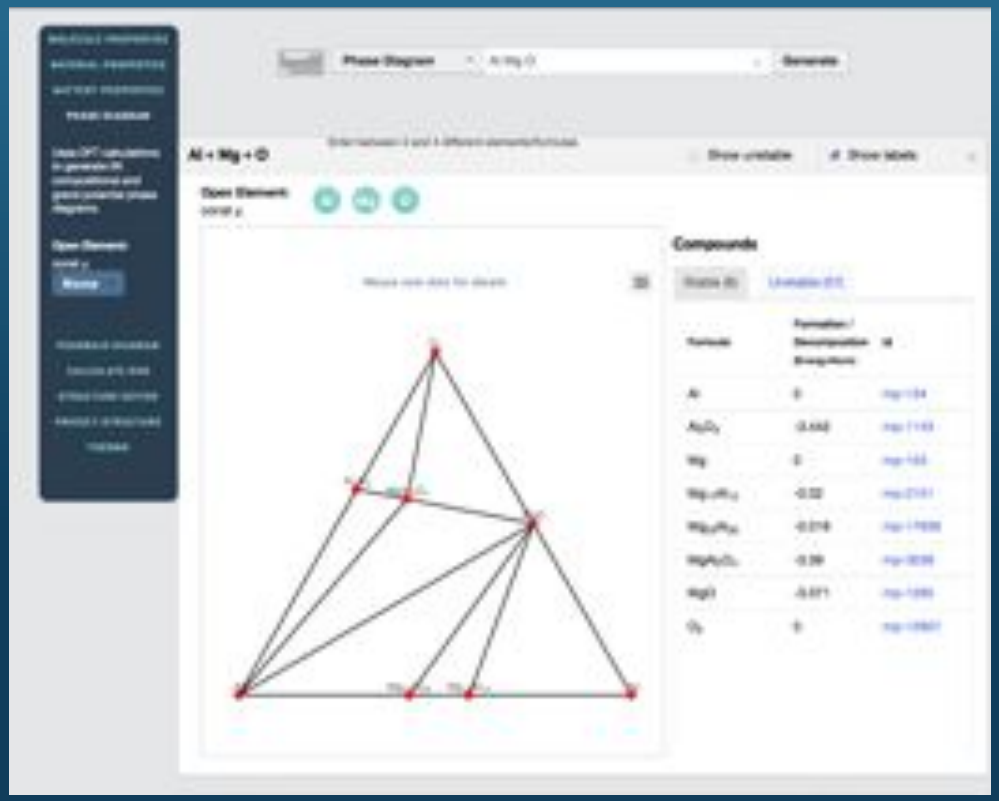
Phase stability





Electro-chemical stability

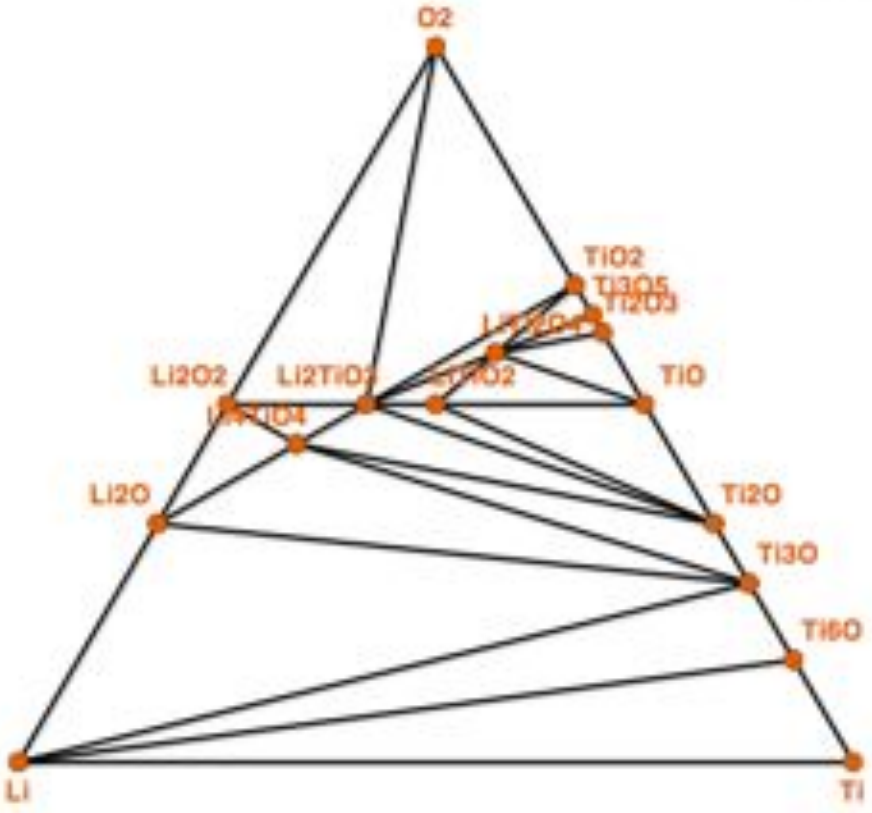
Materials Project: Tens of Thousands of Phase Diagrams available



- Over 60,000 inorganic compounds
- Growing monthly
- > 1Milion property values
- Multiple tools

www.materialsproject.org

Stability of a compound need to be evaluated against all possible compounds in the relevant chemical space



www.materialsproject.org

Name	Form. E/Atom	Decomp. E/Atom	Id
Li_2O_2	-1.770	0.000	841
Li_2TiO_3	-2.997	0.000	2931
Li_4TiO_4	-2.721	0.000	9172
$LiTi_2O_4$	-3.263	0.000	5670
$LiTiO_2$	-2.973	0.000	25417
O_2	0.000	0.000	--
Ti	0.000	0.000	72
Ti_2O	-2.045	-0.000	1215
Ti_2O_3	-3.321	0.000	458
Ti_3O	-1.577	0.000	2591
Ti_3O_5	-3.401	0.000	1147
Ti_6O	-0.908	0.000	882
TiO	-2.880	0.000	1203
TiO_2	-3.515	0.000	390

25 Unstable Compounds

Name	Form. E/Atom	Decomp. E/Atom	Id
Li	0.001	0.001	10173
Li	0.003	0.003	51
Li_2O_2	-1.770	0.000	27756
$LiTiO_2$	-2.967	0.006	6944
Ti	0.114	0.114	73
Ti	0.063	0.063	6985
Ti	0.007	0.007	46
Ti_3O_5	-3.393	0.009	8057
Ti_4O_5	-3.105	0.020	10734
Ti_4O_7	-3.428	0.004	12205
Ti_5O_9	-3.444	0.006	748
Ti_6O_{11}	-3.454	0.007	30524
Ti_9O_{17}	-3.468	0.012	27273
TiO	-2.651	0.228	2664

Are there materials related to $Li_{10}GeP_2S_{12}$?

- DFT is chemistry agnostic
  - Easily replace chemical species

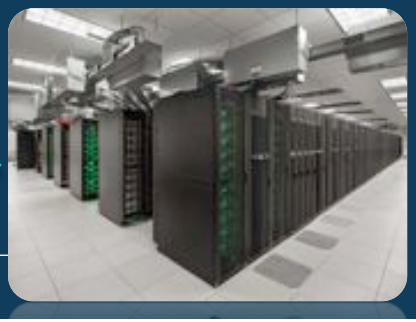
Substitutions

Anion: Air/moisture sensitivity

S → Se, O

Cation: Price, reduction potential

Ge → Si, Sn



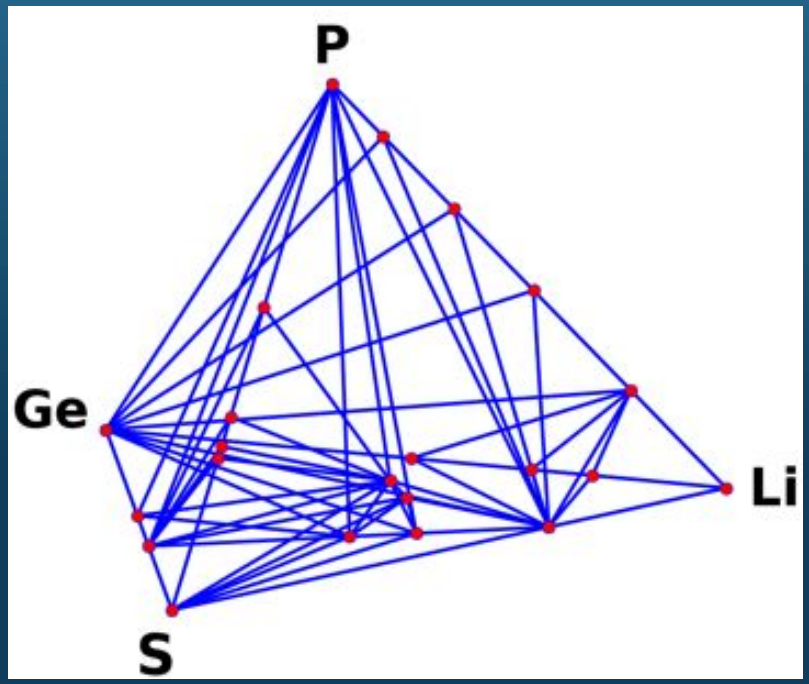
Can this compound be made with other anions and cations ?

$E_{above\ hull}$ of $Li_{10}MP_2X_{12}$ (meV/atom)

	Si	Ge	Sn
O	92	70	97
S	17	15	13
Se	16	16	19

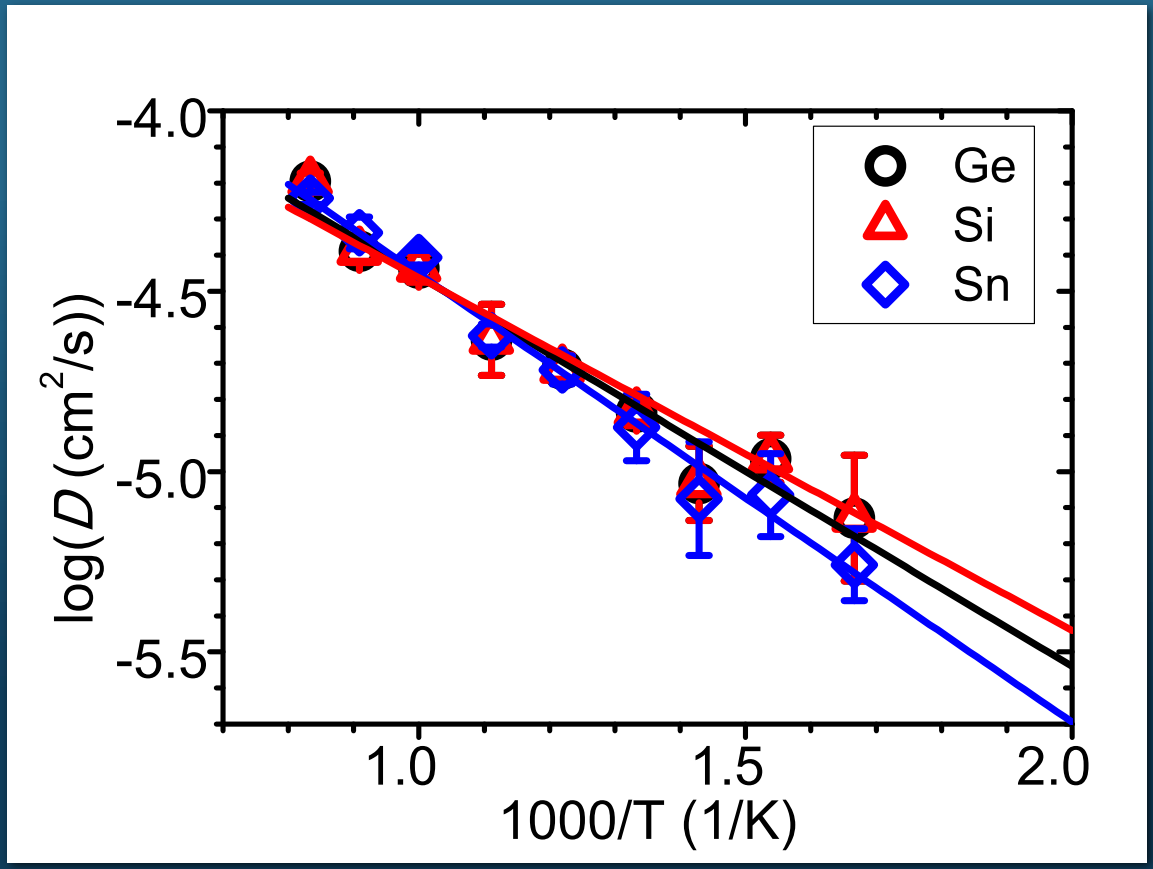
< 20 meV, potentially entropically stabilized

$Li_{10}SiP_2S_{12}$ and $Li_{10}SnP_2S_{12}$ are good candidates for Li-ion conductors



S. P. Ong, Y. Mo, W. D. Richards, L. Miara, H. S. Lee, G. Ceder. Energy Environ. Sci. (2012) doi: 10.1039/C2EE23355J

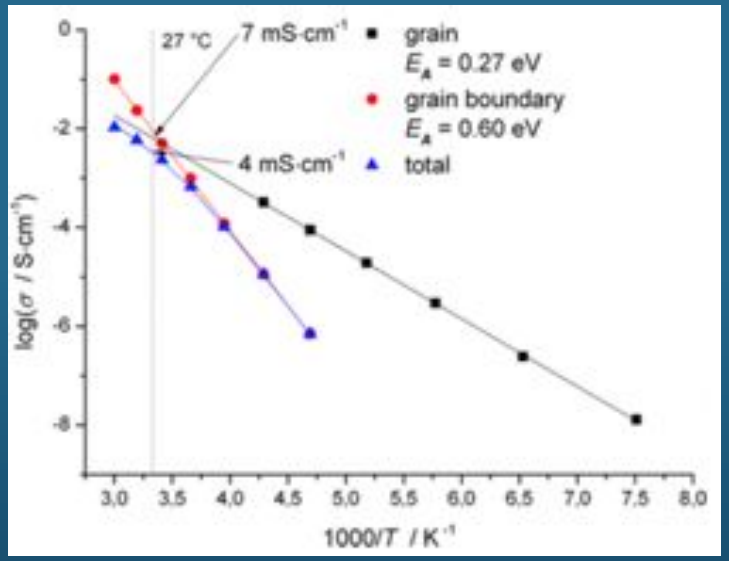
Prediction that the Sn and Si versions will exist and have high ion conductivity



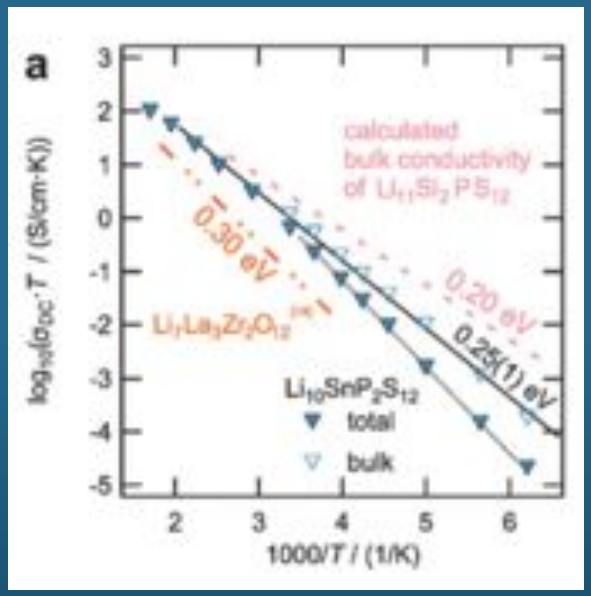
Prediction of Sn and Si -based “LGPS with high Li-ion conductivity

S. P. Ong, Y. Mo, W. D. Richards, L. Miara, H. S. Lee, G. Ceder. Energy Environ. Sci. (2012) doi: 10.1039/C2EE23355J

$Li_{10}SnP_2S_{12}$



Bron *et al.*, J. Am. Chem. Soc., 135 (42), pp 15694–15697 (2013)



A. Kuhn *el al.*, Phys. Chem. Chem. Phys., 16, 14669-14674 (2014)

NANOMYTE® SSE-10
Jan, 2015

NEI Announces Ready-to-Cast Solid Electrolyte Slurry for Lithium Ion Batteries

Posted on January 21, 2015 by Krista Martin

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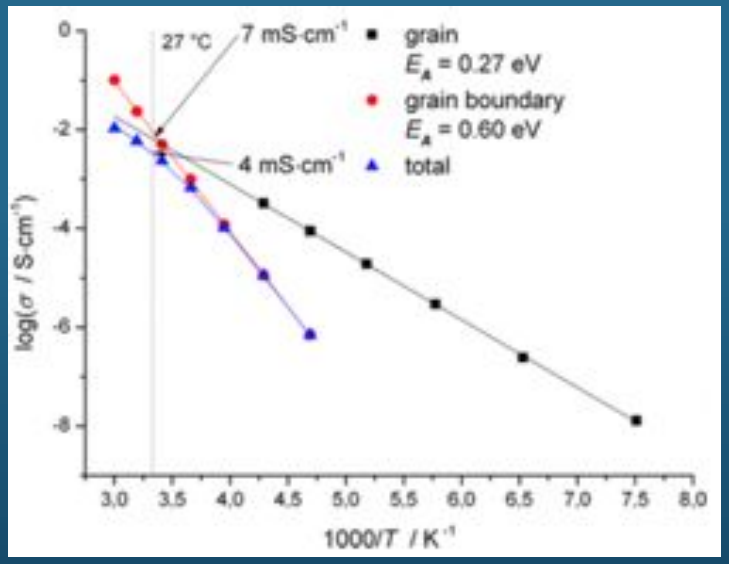
January 21, 2015

Somerset, New Jersey (USA) – NEI Corporation, a leading developer and manufacturer of specialty cathode, anode, and electrolyte materials for Lithium-ion batteries, announced today that they are expanding their offering of patent-pending, solid electrolyte materials. Over the past year, NEI has supplied multi-kilogram quantities of their newly developed solid electrolyte powder, NANOMYTE® SSE-10 ($Li_{10}SnP_2S_{12}$ or LSPS). SSE-10, which has now been used by a multitude of scientists and engineers for developing and prototyping "all solid" Lithium batteries, is now being made available in the form of a slurry or dispersion that can be cast into flexible tapes. NANOMYTE® SSE-10D is composed of surface-modified LSPS particles dispersed in organic solvent, which can be removed after the tape or film is formed.

$Li_{10}SnP_2S_{12}$ prediction now confirmed



Bron *et al.*, J. Am. Chem. Soc., 135 (42), pp 15694–15697 (2013)

Experimental confirmation of $Li_{10}SnP_2S_{12}$:

E_a: 270 meV
σ_{300K}: 7 mS/cm

Calculated properties:
E_a: 240 meV
σ_{300K}: 6 mS/cm

NEI Announces Ready-to-Cast Solid Electrolyte Slurry for Lithium Ion Batteries

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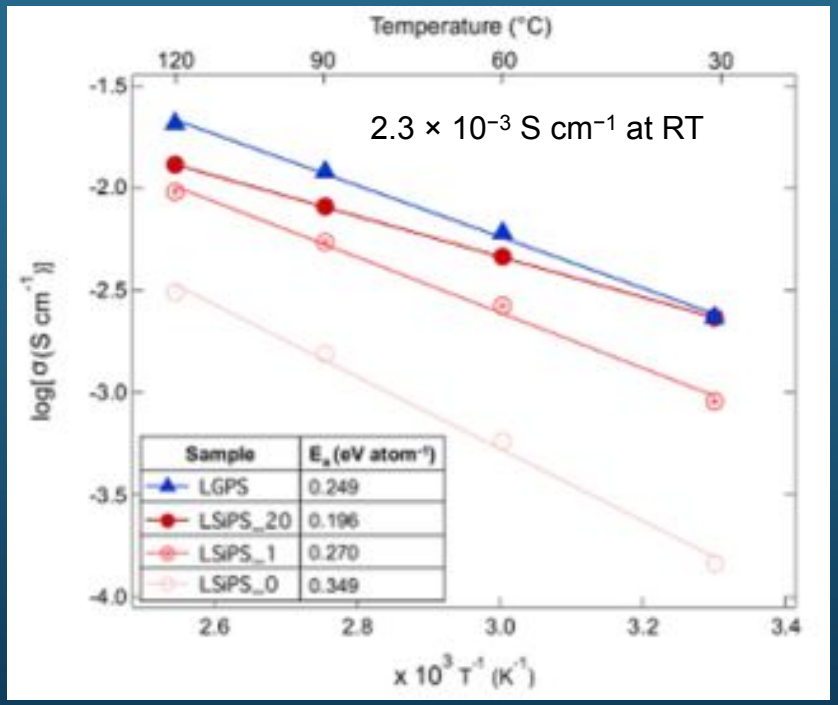
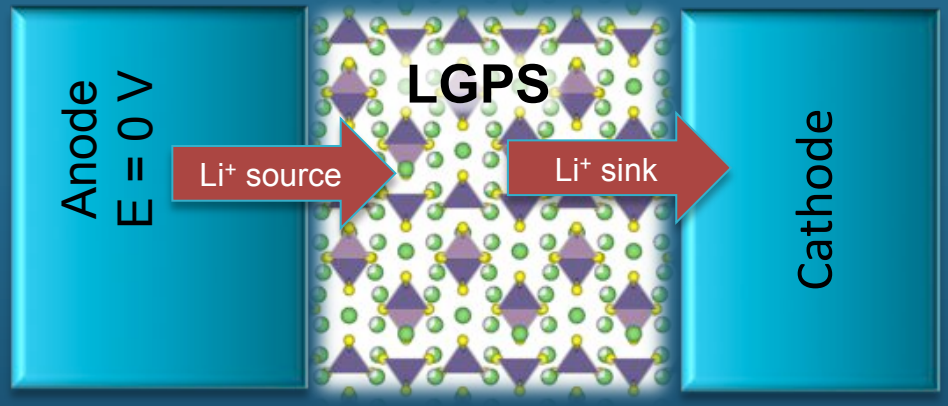


J.M. Whiteley, *el al.*, J. Electrochem. Soc., 161 (12), A1812-A1817 (2014)

Electrochemical Stability



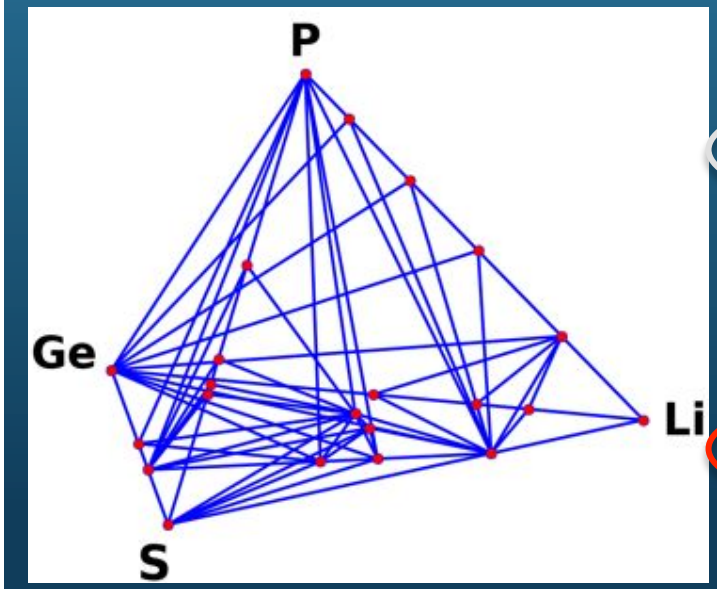
- Anode is a potential Li source with very high chemical potential for Li

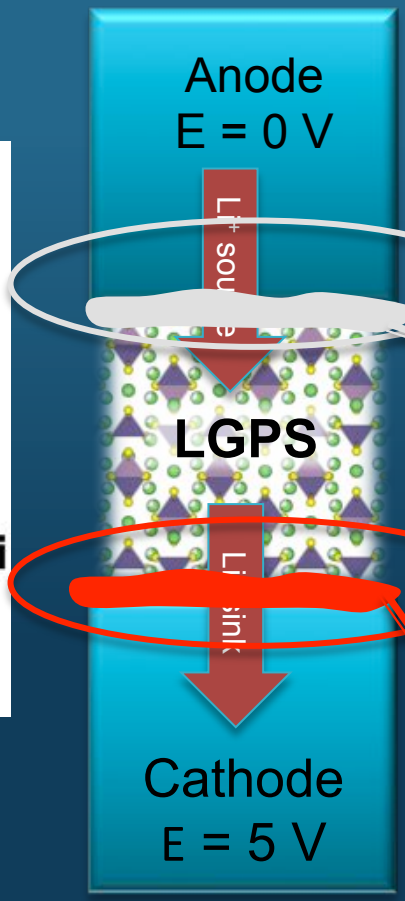
- Cathode is a potential Li sink with very low chemical potential for Li
- No kinetic limitations ! Fast ion conductor allows Li extraction and anion can be oxidized

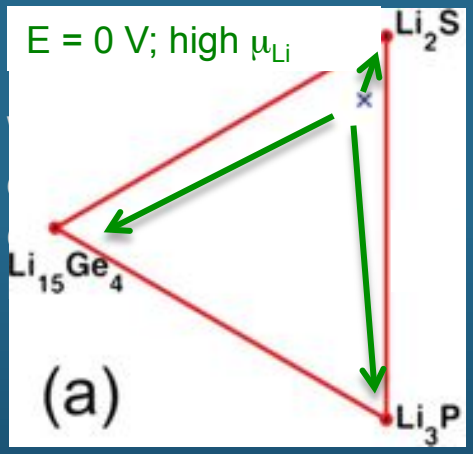
Problem is thermodynamically well defined

Equilibrium under high and low Li chemical potential: $\Phi = G - \mu_{Li}\, x_{Li}$

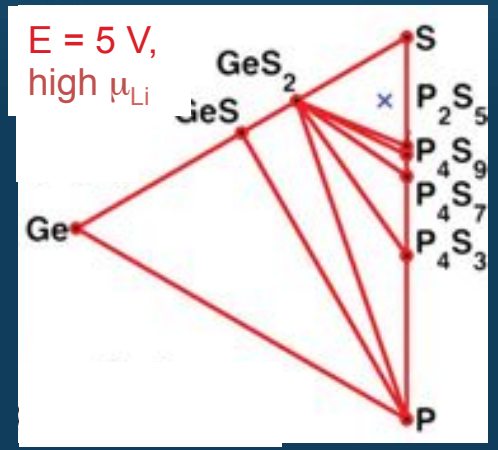
Electrochemical Stability is embedded in the quaternary phase diagrams





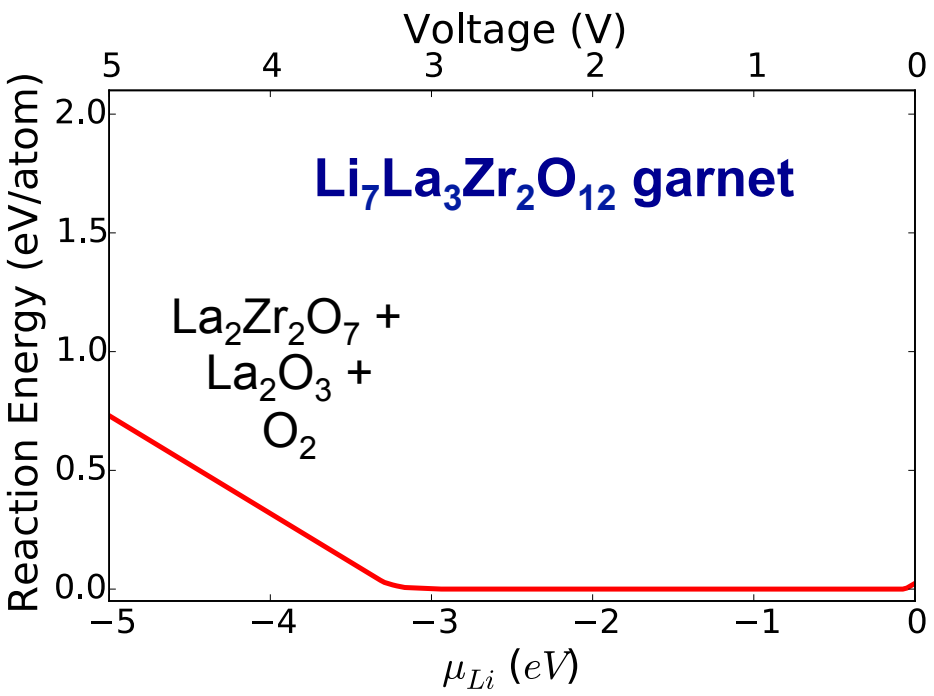


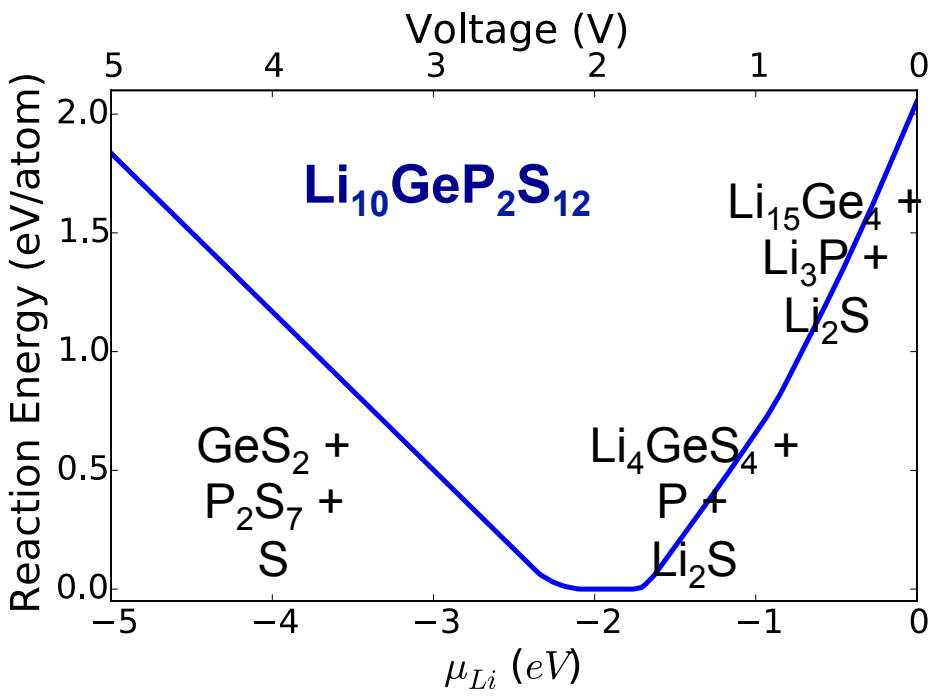
Decomposition into Li_2S, Li_3P, $Li_{15}Ge_4$



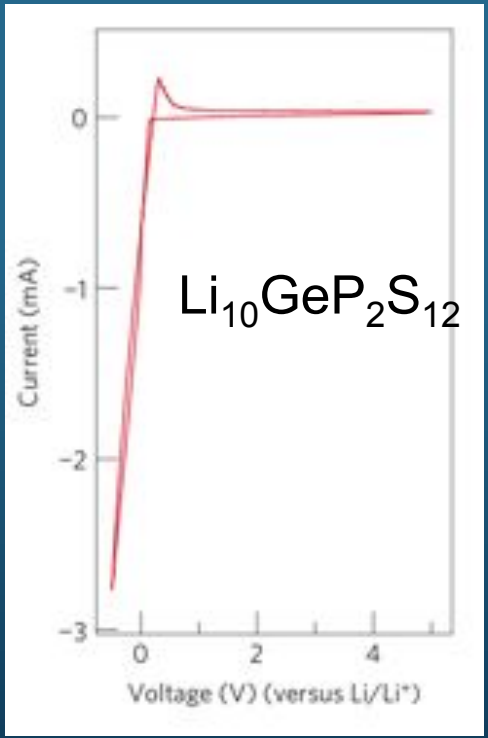
Decomposition into S, GeS_2, P_2S_5

Stability range for LGPS is actually quite narrow. Larger for oxide garnet



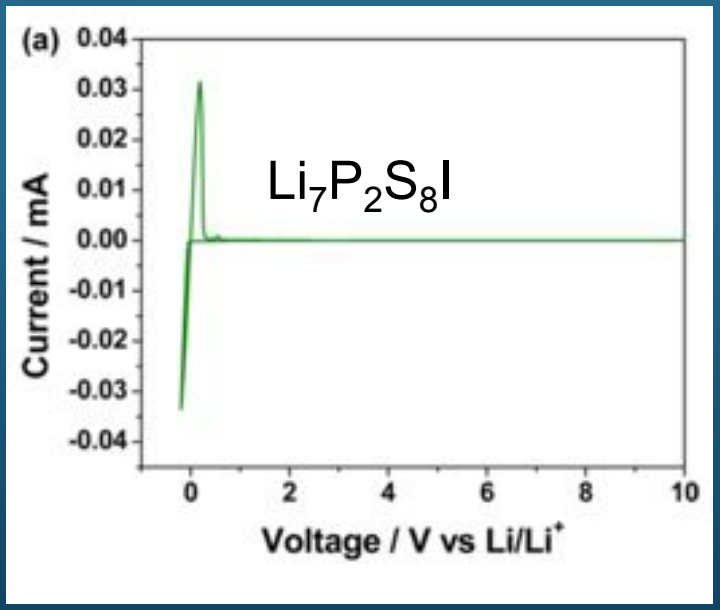


C-V scans can not show decomposition on a relevant scale



Current–voltage curve of Li/ $Li_{10}GeP_2S_{12}$/Au cell. The decomposition potential of the new $Li_{10}GeP_2S_{12}$ phase exceeds 5 V.

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



Cyclic voltammogram for a Li/$Li_7P_2S_8I$/Pt cell at a scan rate of 1 mV/s, demonstrating that the new electrolyte phase is stable up to 10 V vs Li/Li^+.

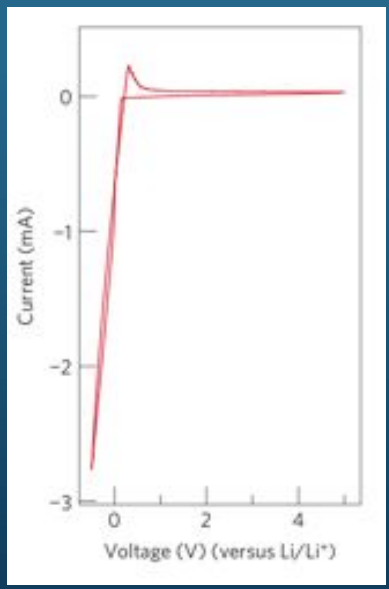
Rangasamy *el al.,* J. Am. Chem. Soc., 2015, 137 (4), pp 1384–1387

Current generated when the (LGPS) interface near the cathode decomposes

Assume material decomposes with all Li extraction

1nm interface: 9×10^{-5} mAh

Scan rate 1mV/s: 0.3μA



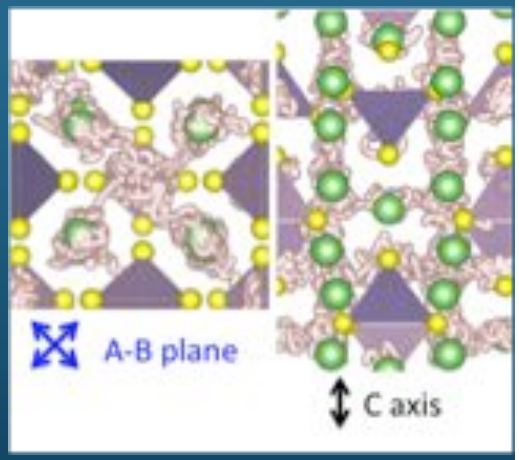
Current for decomposition of interface is not observable in typical C-V tests

Electrochemical Stability

- We need better and more rigorous approaches to evaluate electrochemical stability.
- These should involve interfacial characterization after testing.
- Praying for “kinetic protection” is unlikely to be successful
- Barrier layers will be required for most (if not all) sulfides

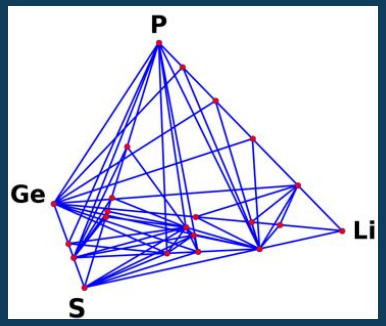
The trajectory towards novel $Li_{10\pm1}MP_2X_{12}$ ionic conductors

- Within one year of experimental findings of LGPS, ab-initio computing
  - **confirms** high Li conductivity
  - **corrects** dimensionality of diffusion
  - **corrects** claimed electrochemical stability
  - **proposes** different, less expensive variants in $Li_{10}SiP_2S_{12}$ and $Li_{10}SnP_2S_{12}$
- All predictions confirmed within one year



Infrastructure that was needed

- High-throughput computing environment to iterate rapidly
- Pre-computed multi-component phases diagrams
- Rapid ab-initio MD



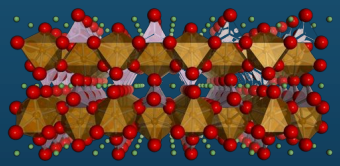
A really hard problem …

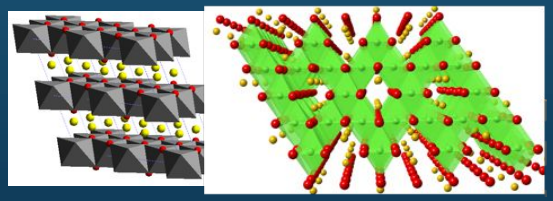
Can we diffuse multi-valent ions at room temperature ?

Why Modeling: Lessons from Lithium Cathodes

Li-intercalation

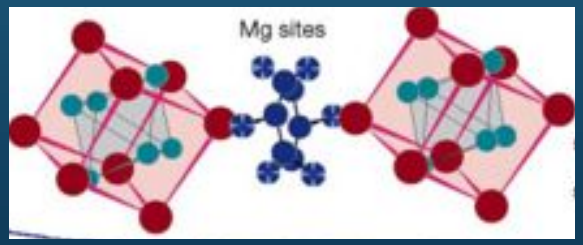
- After more than 40 years of research only a handful of functioning high energy density Li cathode materials – even less commercially available





MV-intercalation

- More difficult than Li-ion. Since 2000 only one well functioning cathode (Mo_6S_8)



Need computational machinery to pre-screen and direct towards promising design directions

Materials Project: Voltage + stability screening