

Simulations of Idealized Solid Electrolytes*

Natalie A. W. Holzwarth

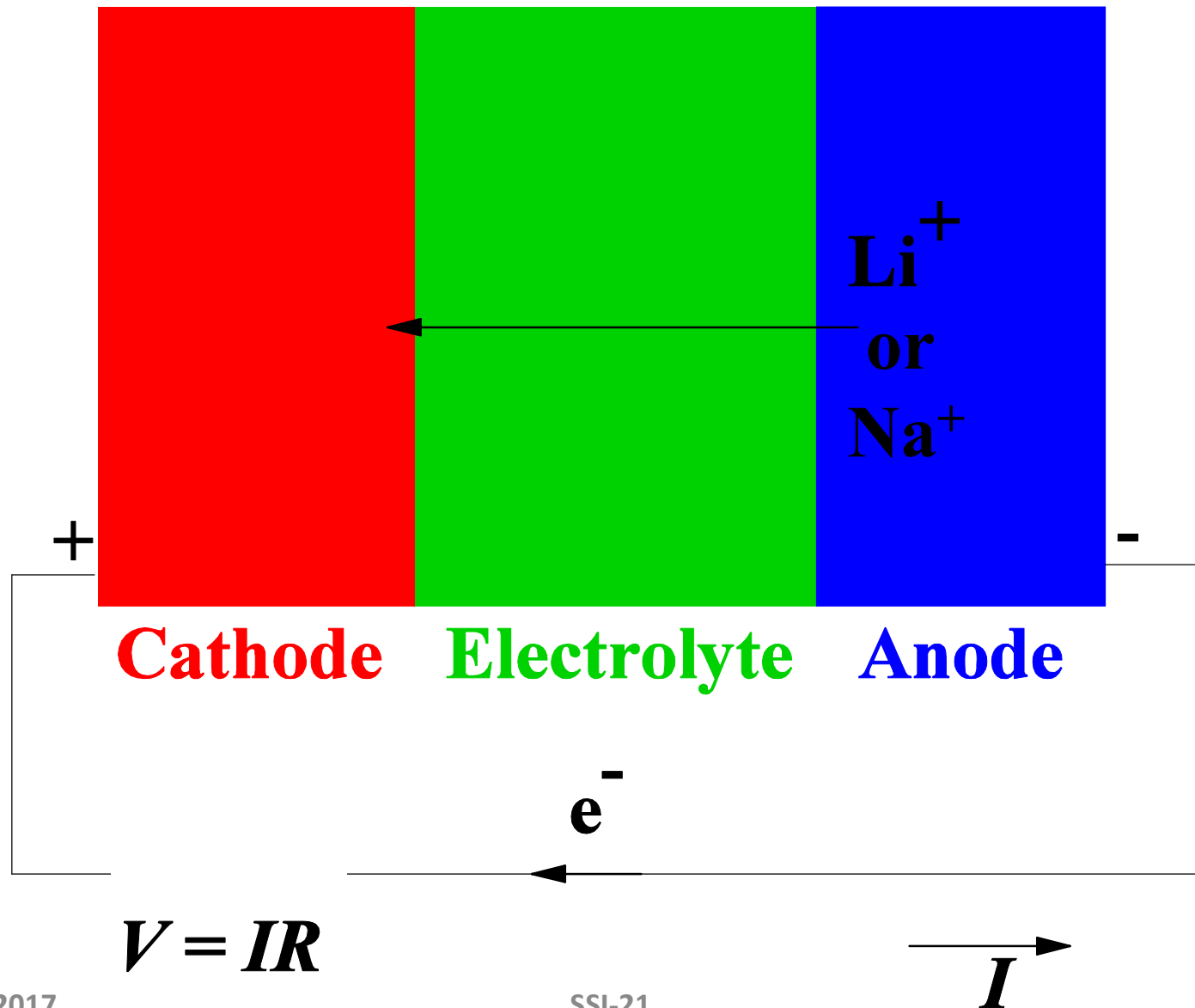
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*Research performed in collaboration with Nicholas Lepley (WFU Ph. D. Dec. 2015), Larry Rush Jr. (WFU MS May 2017), Jason Howard and Ahmad Al-Qawasmeh (WFU graduate students), Yaojun Du (former WFU Postdoc) and in consultation with Zachary Hood from ORNL and Ga Tech. Collaborations with WFU Chemistry Colleagues --Dr. Keerthi Senevirathne (now at Florida A & M U.), Dr. Cynthia Day, Professor Michael Gross, and Professor Abdessadek Lachgar, are also gratefully acknowledged. Research was supported by NSF grant DMR 1507942 and computations were performed on WFU's DEAC cluster.

Outline

- **Motivation – Why solid electrolytes?**
- **Computational tools & reality checks; what can be learned from “first principles” calculations?**
- **Simulations of bulk properties and ion mobility**
 - **Li phosphorus oxynitrides (first developed at Oak Ridge National Laboratory)**
 - **Li thiophosphates**
 - **Related materials including Na electrolytes**
- **Simulations of interfaces with metallic Li and Na**
- **Summary and remaining challenges**

Materials components of a Li or Na ion battery



Development of LiPON electrolyte films at Oak Ridge National Laboratory

Solid State Ionics 53–56 (1992) 655–661
North-Holland



**SOLID
STATE
IONICS**

Sputtering of lithium compounds for preparation of electrolyte thin films

N.J. Dudney, J.B. Bates, R.A. Zuhr and C.F. Luck

Solid State Division, Oak Ridge National Laboratory, P O Box 2008, Oak Ridge, TN 37831-6030, USA

JOURNAL OF SOLID STATE CHEMISTRY **115**, 313–323 (1995)

Synthesis, Crystal Structure, and Ionic Conductivity of a Polycrystalline Lithium Phosphorus Oxynitride with the γ -Li₃PO₄ Structure

B. Wang, B. C. Chakoumakos, B. C. Sales, B. S. Kwak, and J. B. Bates

From Oak Ridge National Laboratory:



Materials Views

www.MaterialsViews.com

Adv. Energy Mater. 2015, 5, 1401408

DOI: 10.1002/aenm.201401408

ADVANCED ENERGY MATERIALS

www.advenergymat.de

Solid Electrolyte: the Key for High-Voltage Lithium Batteries

Juchuan Li,* Cheng Ma, Miaofang Chi, Chengdu Liang, and Nancy J. Dudney*

Advantages

- Compatible and stable with high voltage cathodes and with Li metal anodes

Disadvantages

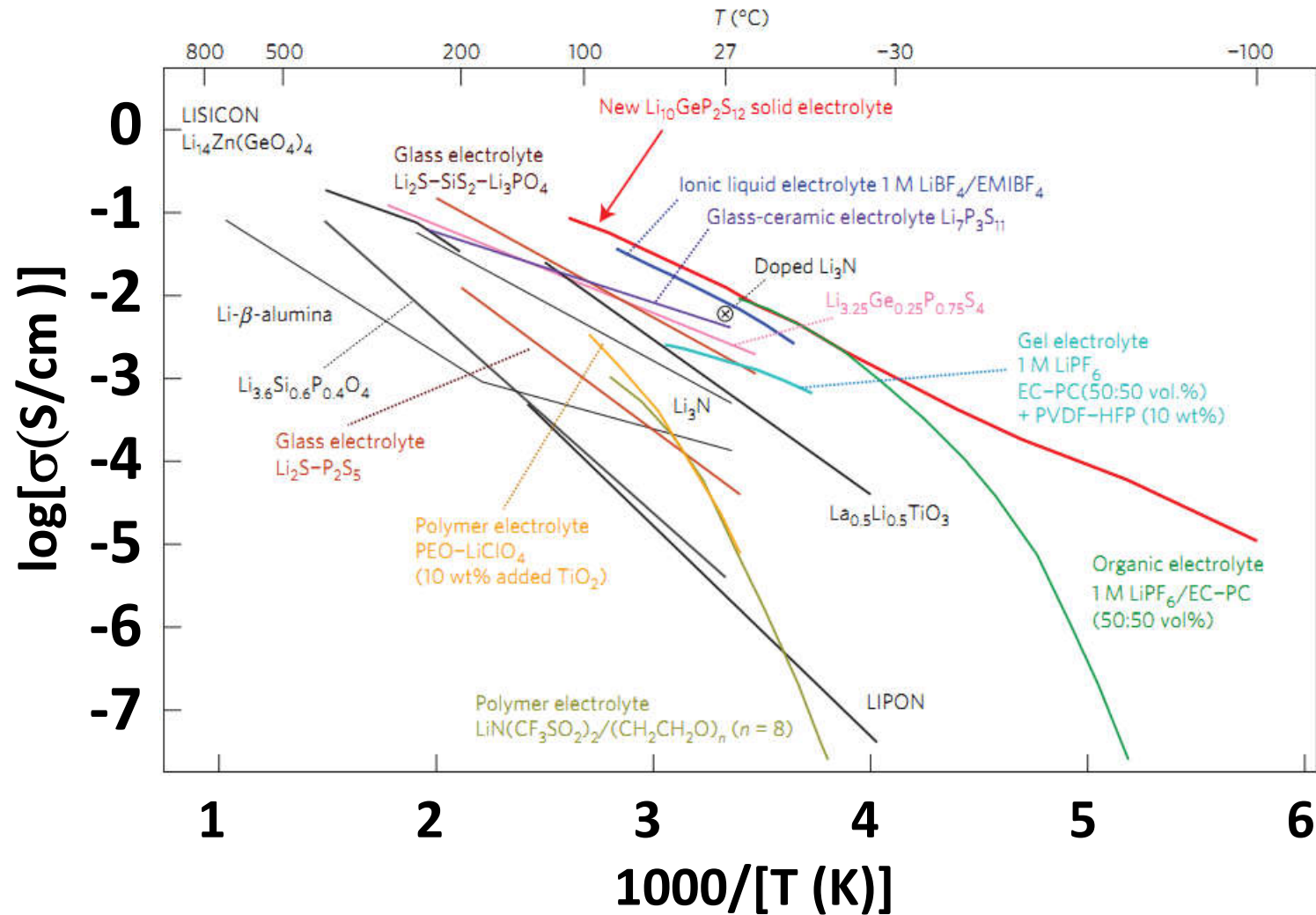
- Relatively low ionic conductivity (Compensated with the use of less electrolyte?)
- Lower total capacity

Demonstrated for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{LiPON}/\text{Li}$

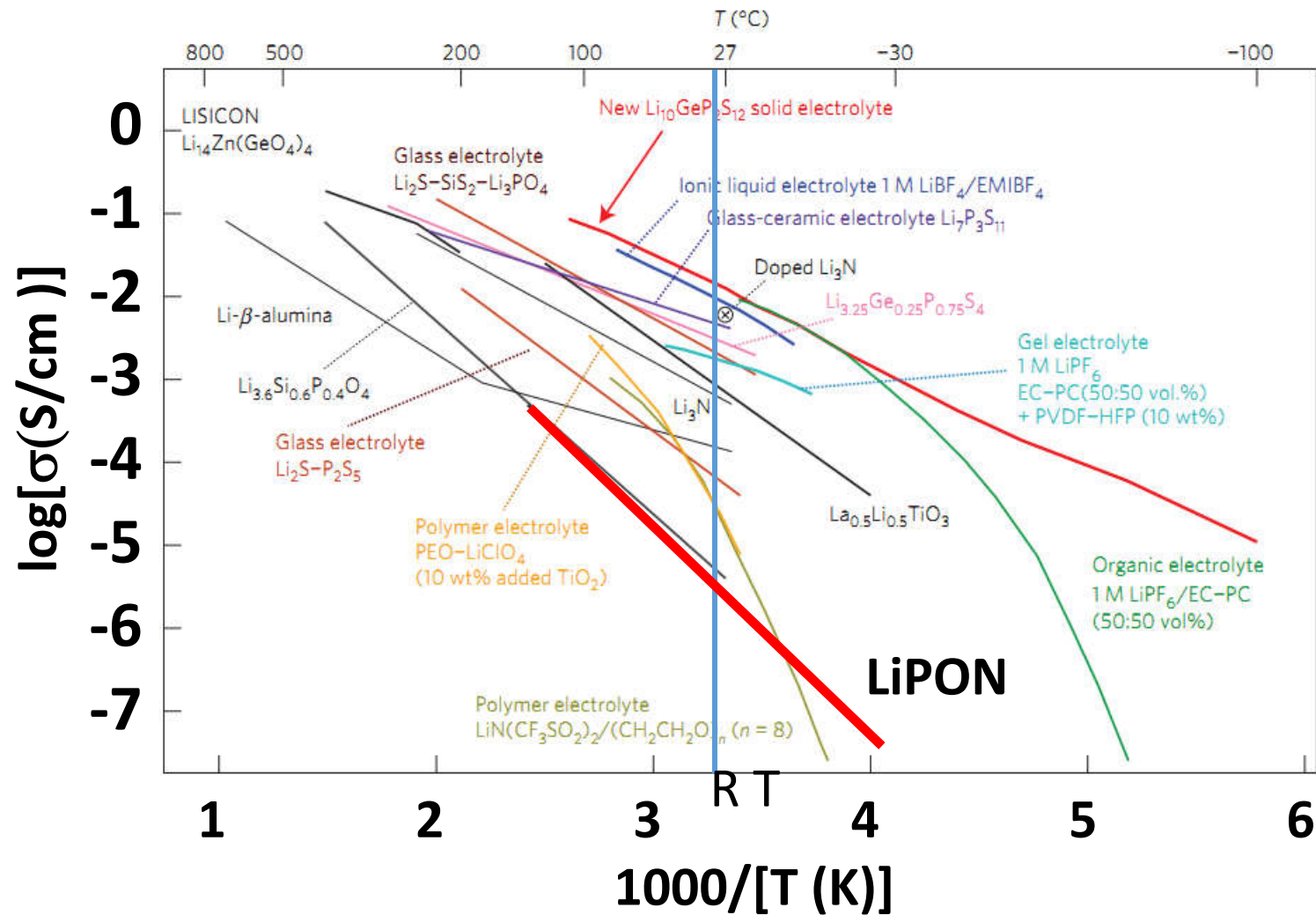
- 10^{-6} m LiPON electrolyte layer achieved adequate conductivity
- 10,000 cycles* with 90% capacity retention

*1 cycle per day for 27 years

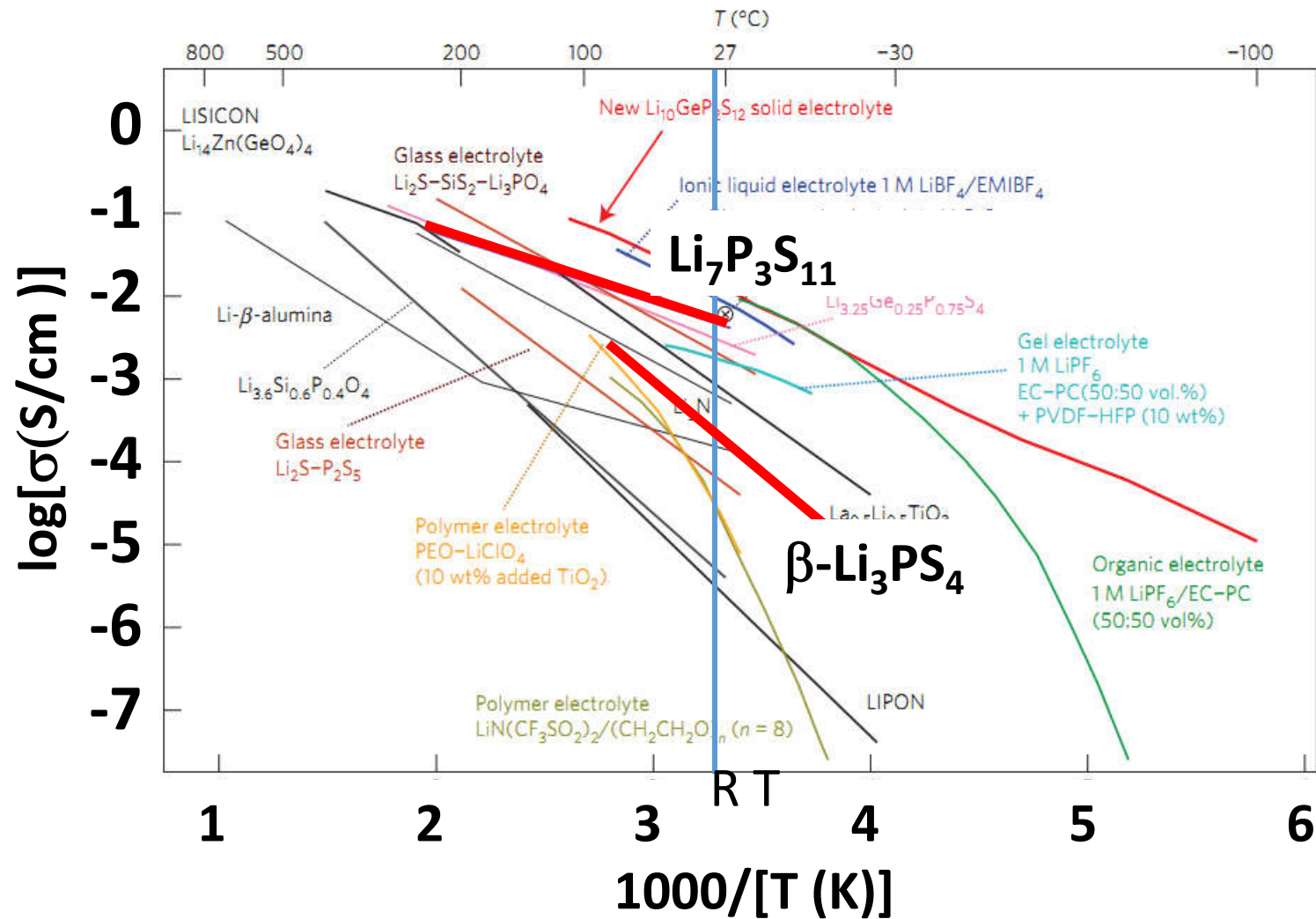
Motivation: Paper by N. Kayama, *et. al* in *Nature Materials* **10**, 682-686 (2011)



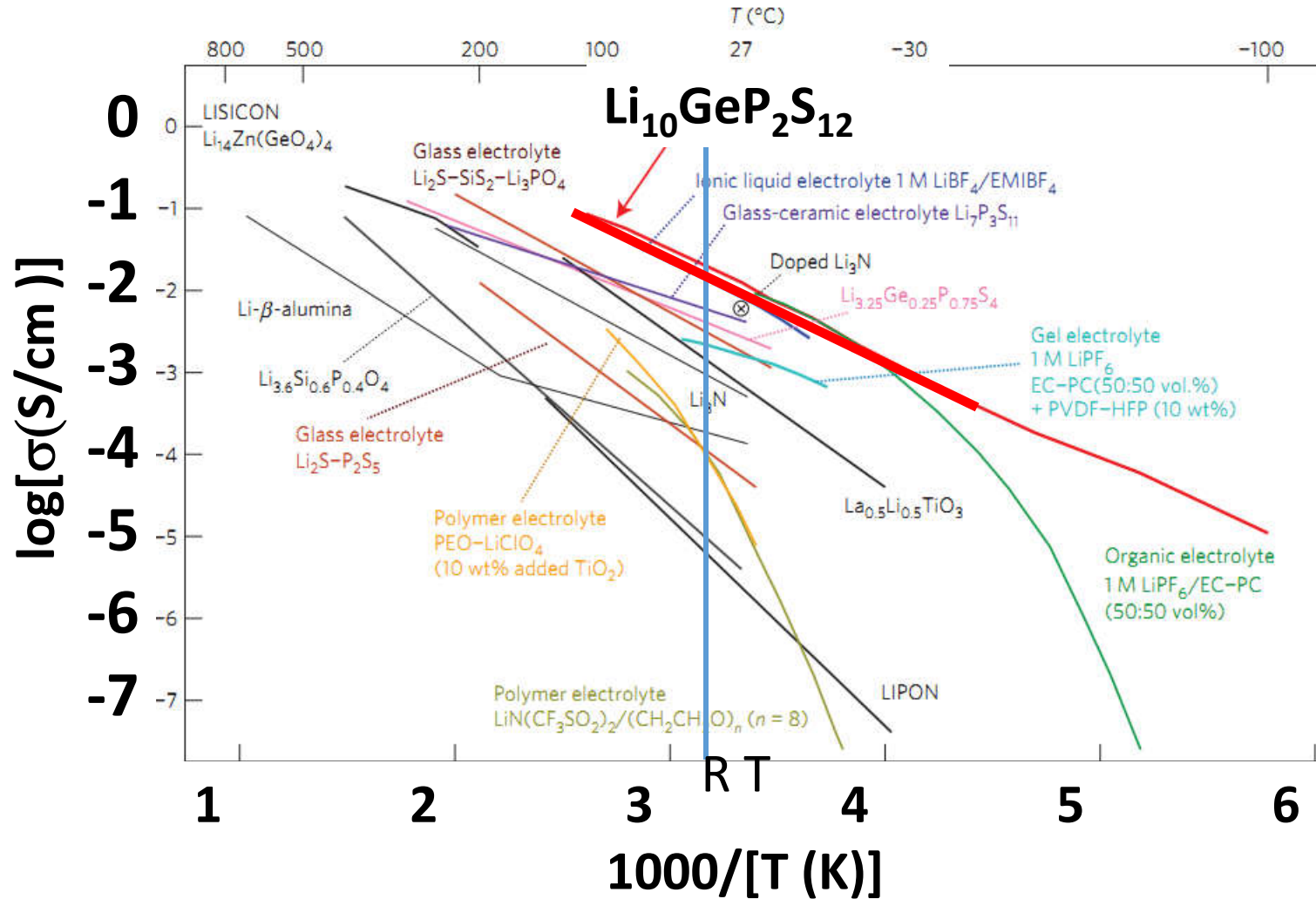
Motivation: Paper by N. Kamaya, *et. al* in *Nature Materials* 10, 682-686 (2011)



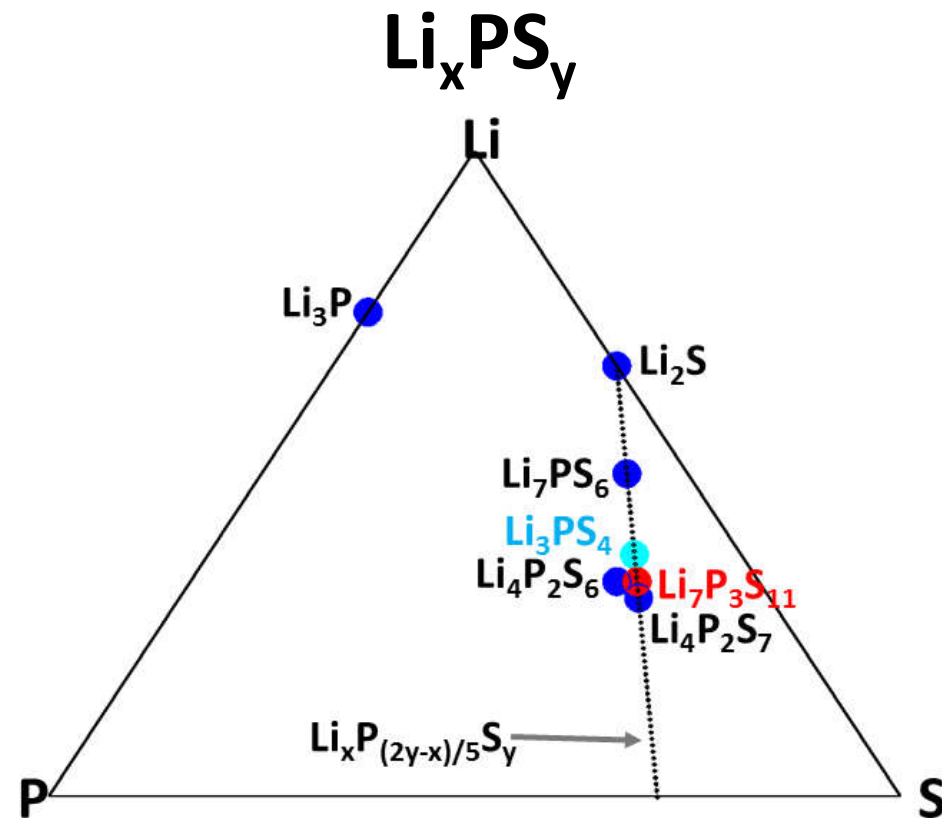
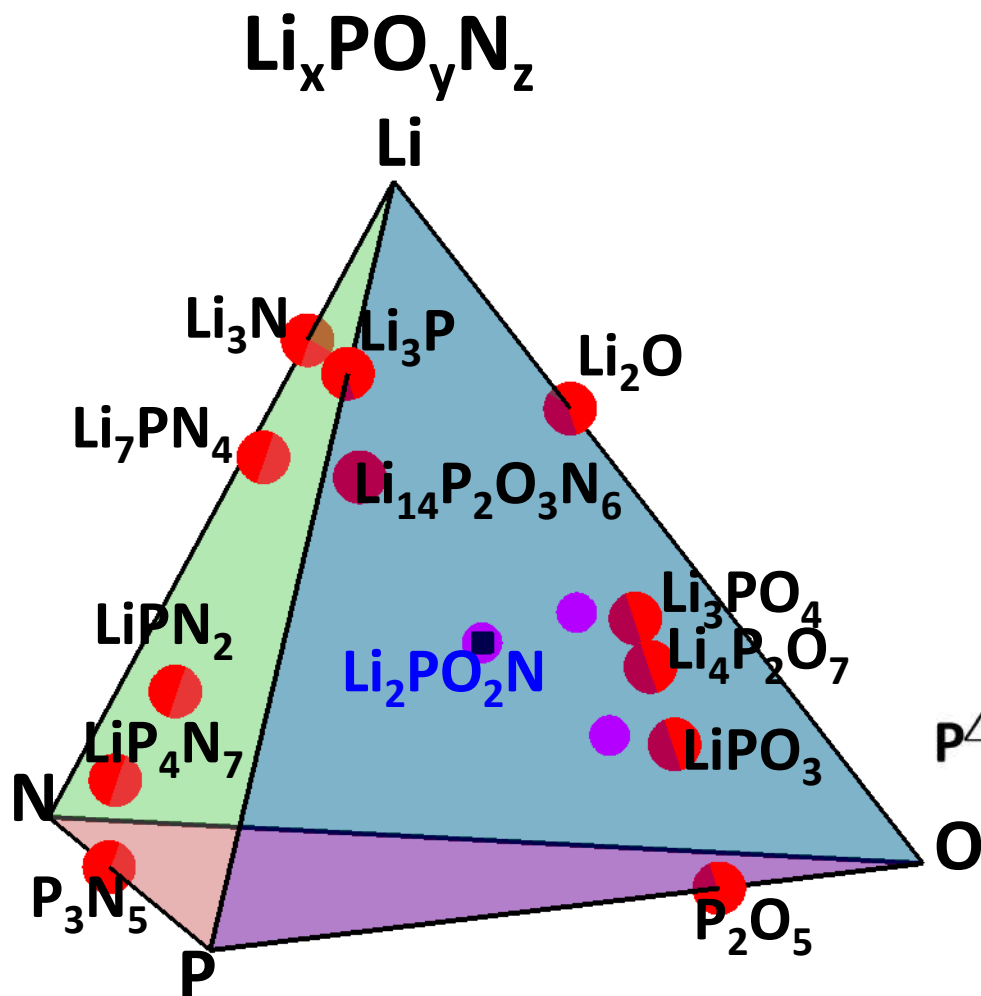
Motivation: Paper by N. Kamaya, *et. al* in *Nature Materials* **10**, 682-686 (2011)



Motivation: Paper by N. Kamaya, *et. al* in *Nature Materials* **10**, 682-686 (2011)



Solid electrolyte families investigated in this study:



+ a few related materials such as Li_4SnS_4 , $\text{Na}_4\text{P}_2\text{S}_6$, Na_3SbS_4

Computational tools

Summary of “first-principles” calculation methods

Exact Schrödinger equation:

$$\mathcal{H}(\{\mathbf{r}_i\}, \{\mathbf{R}^a\}) \Psi_\alpha(\{\mathbf{r}_i\}, \{\mathbf{R}^a\}) = E_\alpha \Psi_\alpha(\{\mathbf{r}_i\}, \{\mathbf{R}^a\})$$

where

$$\mathcal{H}(\{\mathbf{r}_i\}, \{\mathbf{R}^a\}) = \mathcal{H}^{\text{Nuclei}}(\{\mathbf{R}^a\}) + \mathcal{H}^{\text{Electrons}}(\{\mathbf{r}_i\}, \{\mathbf{R}^a\})$$

Born-Oppenheimer approximation

Born & Huang, **Dynamical Theory of Crystal Lattices**, Oxford (1954)



Approximate factorization:

$$\Psi_\alpha(\{\mathbf{r}_i\}, \{\mathbf{R}^a\}) = X_\alpha^{\text{Nuclei}}(\{\mathbf{R}^a\}) Y_\alpha^{\text{Electrons}}(\{\mathbf{r}_i\}, \{\mathbf{R}^a\})$$



Treated with classical mechanics



Treated with density functional theory

Electronic Schrödinger equation:

$$\mathcal{H}^{\text{Electrons}}(\{\mathbf{r}_i\}, \{\mathbf{R}^a\}) \Upsilon_{\alpha}^{\text{Electrons}}(\{\mathbf{r}_i\}, \{\mathbf{R}^a\}) = U_{\alpha}(\{\mathbf{R}^a\}) \Upsilon_{\alpha}^{\text{Electrons}}(\{\mathbf{r}_i\}, \{\mathbf{R}^a\})$$

$$\mathcal{H}^{\text{Electrons}}(\{\mathbf{r}_i\}, \{\mathbf{R}^a\}) = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 - \sum_{a,i} \frac{Z^a e^2}{|\mathbf{r}_i - \mathbf{R}^a|} + \sum_{i < j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

For electronic ground state: $\alpha \Rightarrow 0$



Density functional theory

Hohenberg and Kohn, *Phys. Rev.* **136** B864 (1964)

Kohn and Sham, *Phys. Rev.* **140** A1133 (1965)

Mean field approximation: $U_0(\{\mathbf{R}^a\}) \Rightarrow U_0(\{\rho(\mathbf{r})\}, \{\mathbf{R}^a\})$ Electron density

Kohn-Sham construction: $\rho(\mathbf{r}) \approx \rho_{KS}(\mathbf{r}) = \sum_n |\psi_n(\mathbf{r})|^2$

$$\mathcal{H}_{KS}^{\text{Electrons}}(\mathbf{r}, \rho(\mathbf{r}), \{\mathbf{R}^a\}) \psi_n(\mathbf{r}) = \varepsilon_n \psi_n(\mathbf{r})$$

Independent electron wavefunction

More computational details:

$$\mathcal{H}_{\text{KS}}^{\text{Electrons}}(\mathbf{r}, \rho(\mathbf{r}), \{\mathbf{R}^a\}) = -\frac{\hbar^2 \nabla^2}{2m} + \underbrace{\sum_a \frac{-Z^a e^2}{|\mathbf{r} - \mathbf{R}^a|}}_{\text{electron-nucleus}} + \underbrace{e^2 \int d^3 r' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}}_{\text{electron-electron}} + \underbrace{V_{xc}(\rho(\mathbf{r}))}_{\text{exchange-correlation}}$$

Exchange-correlation functionals:

LDA: J. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992)

GGA: J. Perdew, K. Burke, and M. Ernzerhof, PRL **77**, 3865 (1996)

HSE06: J. Heyd, G. E. Scuseria, and M. Ernzerhof, JCP **118**, 8207 (2003)

Numerical methods:

“Muffin-tin” construction: Augmented Plane Wave developed by Slater → “linearized” version by Andersen:

J. C. Slater, Phys. Rev. **51** 846 (1937)

O. K. Andersen, Phys. Rev. B **12** 3060 (1975) (LAPW)

Pseudopotential methods:

J. C. Phillips and L. Kleinman, Phys. Rev. **116** 287 (1959) -- original idea

P. Blöchl, Phys. Rev. B. **50** 17953 (1994) – Projector Augmented Wave (PAW) method

Outputs of calculations:

Ground state energy:

$$U_0(\{\rho(\mathbf{r})\}, \{\mathbf{R}^a\}) \Rightarrow \text{Determine formation energies}$$

$$\min_{\{\mathbf{R}^a\}} (U_0(\{\rho(\mathbf{r})\}, \{\mathbf{R}^a\})) \Rightarrow \text{Determine structural parameters}$$

\Rightarrow Stable and meta-stable structures

$$\rho_{KS}(\mathbf{r}) = \sum_n |\psi_n(\mathbf{r})|^2 \Rightarrow \text{Self-consistent electron density}$$

$$\{\epsilon_n\} \Rightarrow \text{One-electron energies; densities of states}$$

Nuclear Hamiltonian (usually treated classically)

$$\mathcal{H}^{\text{Nuclei}}(\{\mathbf{R}^a\}) = \sum_a \frac{\mathbf{P}^{a2}}{2M^a} + U_0(\{\rho(\mathbf{r})\}, \{\mathbf{R}^a\}) \rightarrow \text{Normal modes of vibration}$$

Codes used for calculations






Function	Code	Website
Generate atomic datasets	ATOMPAW	http://pwpaw.wfu.edu
DFT; optimize structure	PWscf abinit	http://www.quantum-espresso.org http://www.abinit.org
Structural visualization	XCrySDen VESTA	http://ww.xcrysden.org http://jp-minerals.org/vesta/en/

Validation

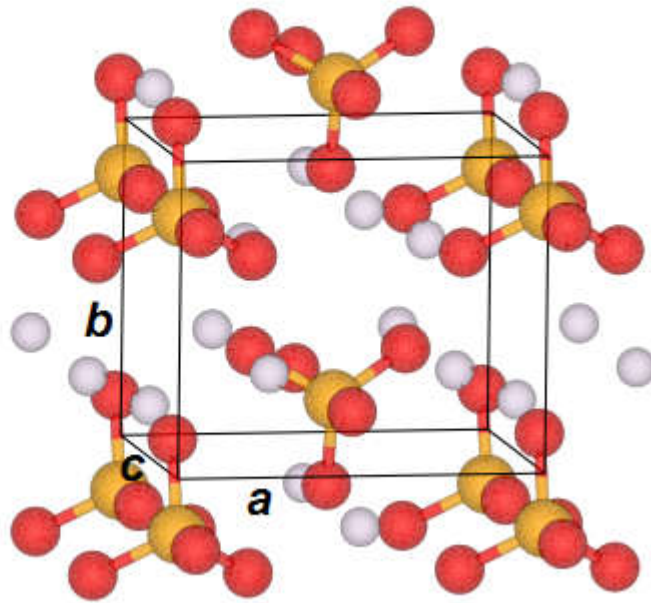
Li₃PO₄ crystals

γ-Li₃PO₄

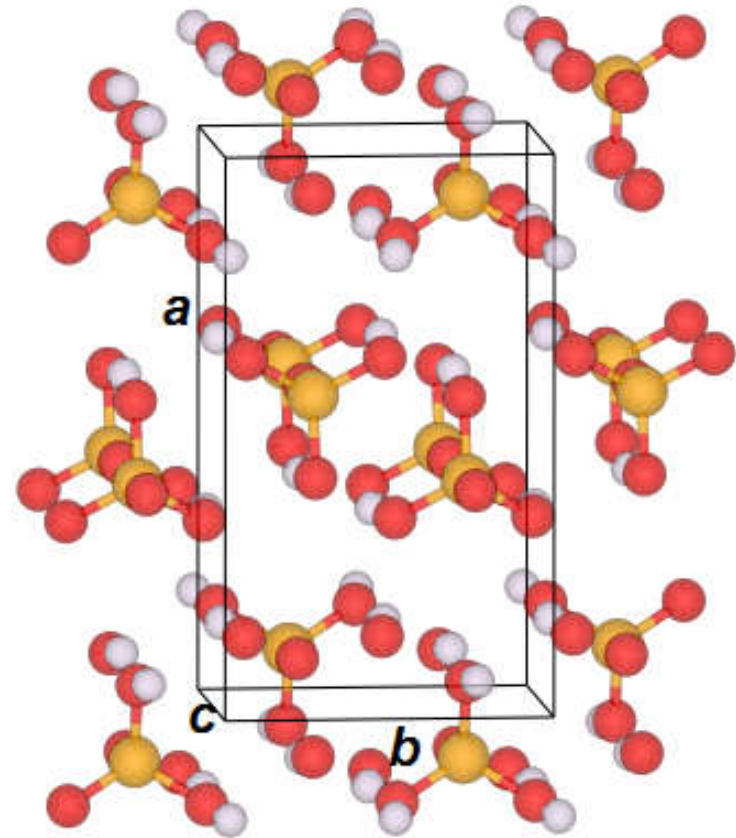
Key

-  Li
-  N
-  O
-  P
-  S

β-Li₃PO₄



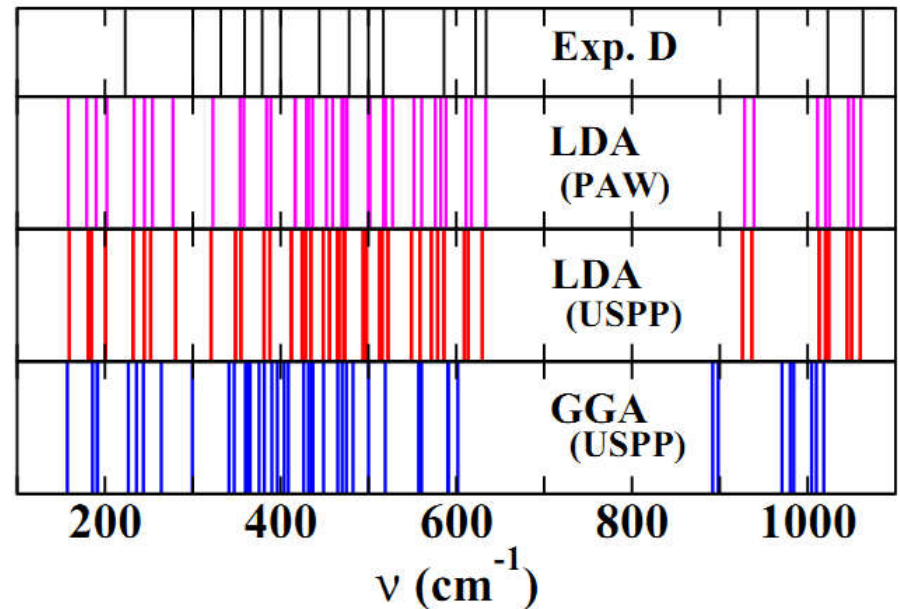
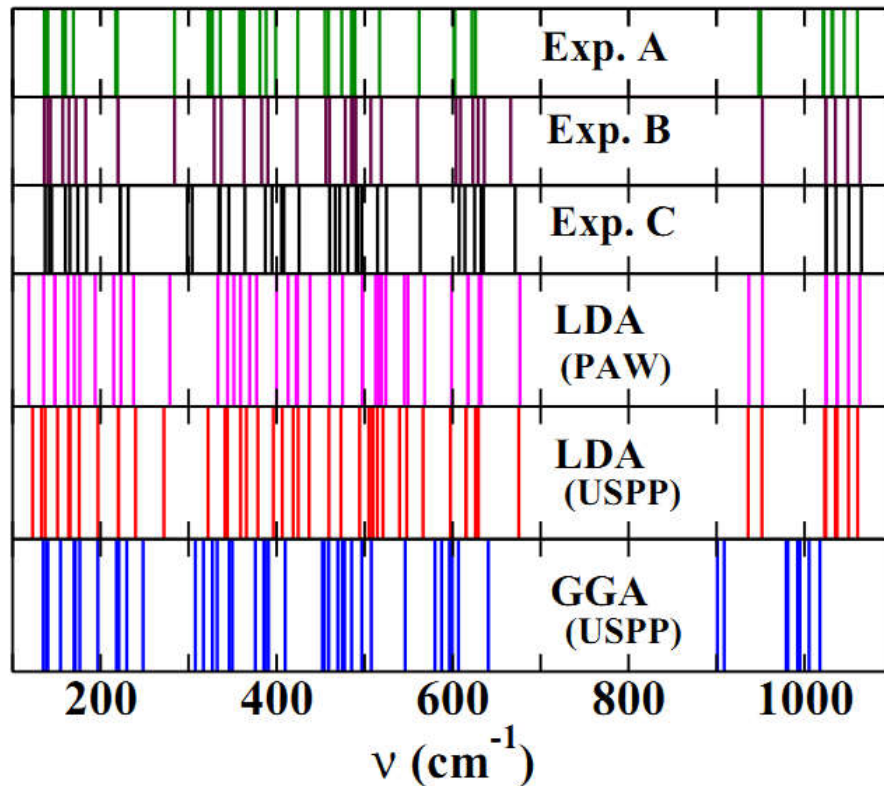
(*Pmn2₁*)



(*Pnma*)

Validation of calculations

Raman spectra – Experiment & Calculation



A: B. N. Mavrin et al, J. Exp. Theor. Phys. **96**,53 (2003); B: F. Harbach and F. Fischer, Phys. Status Solidi B **66**, 237 (1974) – room temp. C: Ref. B at liquid nitrogen temp.; D: L. Popović et al, J. Raman Spectrosc. **34**,77 (2003).

Heats of formation – Experiment & Calculation



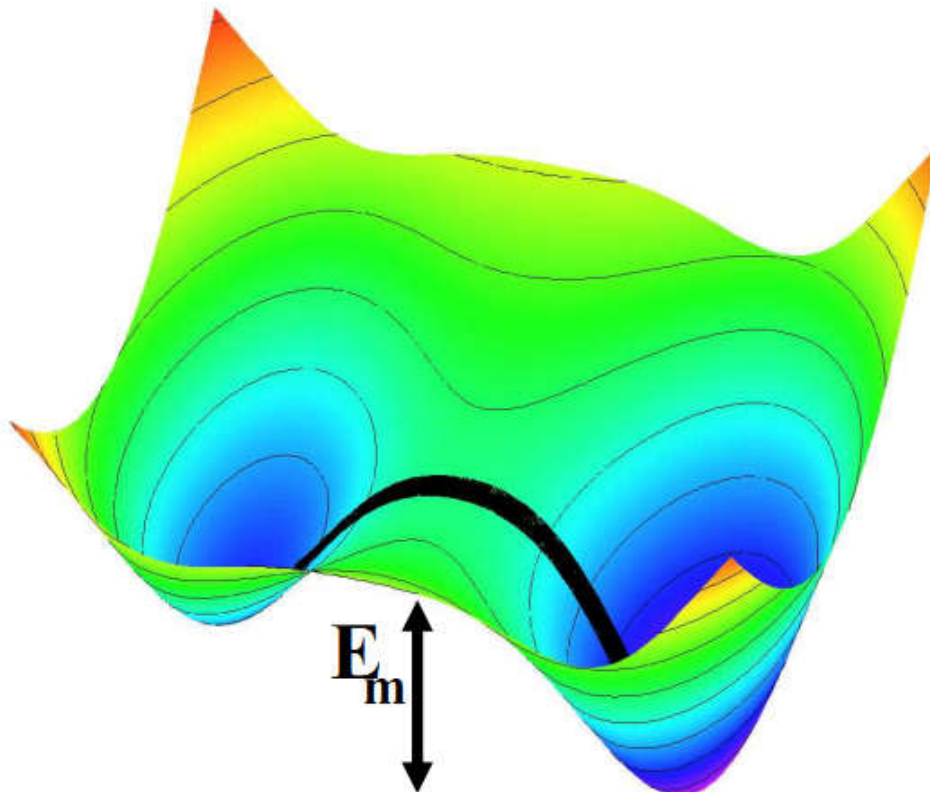
Table 1. Calculated heats of formation for Li phosphates, phospho-nitrides, and thiophosphates and related materials. The structural designation uses the notation defined in the International Table of Crystallography⁸⁵ based on structural information reported in the International Crystal Structure Database.⁸⁶ The heats of formation ΔH (eV/FU) are given in units of eV per formula unit. When available from Ref. [31] and [32] experiment values are indicated in parentheses. Those indicated with “*” were used fitting the O and N reference energies as explained in the text.

Material	Structure	ΔH (eV/FU)	Material	Structure	ΔH (eV/FU)
β -Li ₃ PO ₄	<i>Pmn</i> 2 ₁ (#31)	-21.23	N ₂ O ₅	<i>P6</i> ₃ / <i>mmc</i> (#194)	- 0.94 (- 0.45*)
γ -Li ₃ PO ₄	<i>Pnma</i> (#62)	-21.20 (-21.72*)	P ₃ N ₅	<i>C2/c</i> (#15)	- 3.02 (- 3.32*)
γ -Li ₃ PS ₄	<i>Pmn</i> 2 ₁ (#31)	- 8.37	<i>h</i> -P ₂ O ₅	<i>R3c</i> (#161)	-15.45 (-15.53*)
β -Li ₃ PS ₄	<i>Pnma</i> (#62)	- 8.28	α -P ₂ O ₅	<i>Fdd</i> 2 (#43)	-15.78
Li ₄ P ₂ O ₆	<i>P</i> $\bar{3}1m (#162)$	-29.72	P ₂ S ₅	<i>P</i> $\bar{1}$ (#2)	- 1.93
Li ₄ P ₂ O ₇	<i>P</i> $\bar{1}$ (#2)	-33.97	P ₄ S ₃	<i>Pnma</i> (#62)	- 2.45 (- 2.33)
Li ₅ P ₂ O ₆ N	<i>P</i> $\bar{1}$ (#2)	-33.18	SO ₃	<i>Pna</i> 2 ₁ (#33)	- 4.84 (- 4.71*)
Li ₄ P ₂ S ₆	<i>P</i> $\bar{3}$ 1 <i>m</i> (#162)	-12.42	Li ₃ N	<i>P6/mmm</i> (#191)	- 1.60 (- 1.71*)
Li ₄ P ₂ S ₇	<i>P</i> $\bar{1}$ (#2)	-11.59	Li ₂ O	<i>Fm</i> $\bar{3}$ <i>m</i> (#225)	- 6.10 (- 6.20*)
Li ₇ P ₃ O ₁₁	<i>P</i> $\bar{1}$ (#2)	-54.84	Li ₂ O ₂	<i>P6</i> ₃ / <i>mmc</i> (#194)	- 6.35 (- 6.57*)
Li ₇ P ₃ S ₁₁	<i>P</i> $\bar{1}$ (#2)	-20.01	Li ₃ P	<i>P6</i> ₃ / <i>mmc</i> (#194)	- 3.47
LiPO ₃	<i>P2/c</i> (#13)	-12.75	Li ₂ S	<i>Fm</i> $\bar{3}$ <i>m</i> (#225)	- 4.30 (- 4.57)
LiPN ₂	<i>I</i> $\bar{4}$ 2 <i>d</i> (#122)	- 3.65	Li ₂ S ₂	<i>P6</i> ₃ / <i>mmc</i> (#194)	- 4.09
<i>s1</i> -Li ₂ PO ₂ N	<i>Pbcm</i> (#57)	-12.35	LiNO ₃	<i>R</i> $\bar{3}$ <i>c</i> (#167)	- 5.37 (- 5.01*)
<i>SD</i> -Li ₂ PO ₂ N	<i>Cmc</i> 2 ₁ (#36)	-12.47	Li ₂ SO ₄	<i>P2</i> ₁ / <i>c</i> (#14)	-14.63 (-14.89*)
<i>SD</i> -Li ₂ PS ₂ N	<i>Cmc</i> 2 ₁ (#36)	- 5.80			

Estimate of ionic conductivity assuming activated hopping

Schematic diagram of minimal energy path

Approximated using NEB algorithm^a
 – “Nudged Elastic Band”



Arrhenius relation

$$\sigma \cdot T = K e^{-E_A/kT}$$

From: Ivanov-Shitz and co-workers,
Cryst. Reports **46**, 864 (2001):

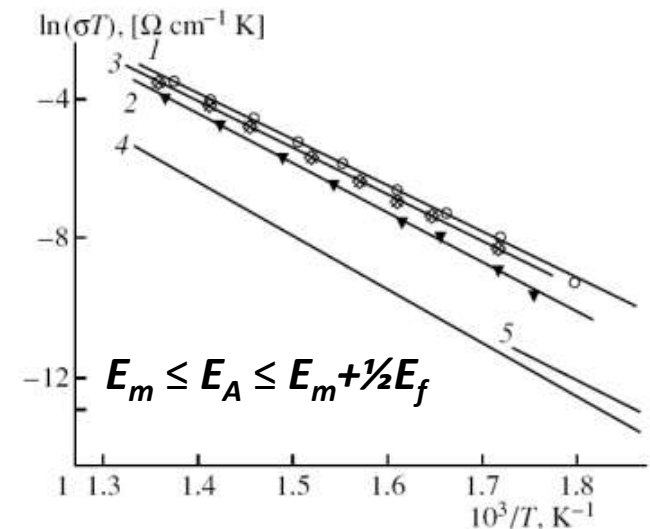


Fig. 2. Temperature dependences of conductivity in $\gamma\text{-Li}_3\text{PO}_4$: (1-3) for single crystals measured along the (1) *a*-axis, (2) *b*-axis, (3) *c*-axis and (4, 5) for a polycrystal (4) according to [4, 5] and (5) according to [7].

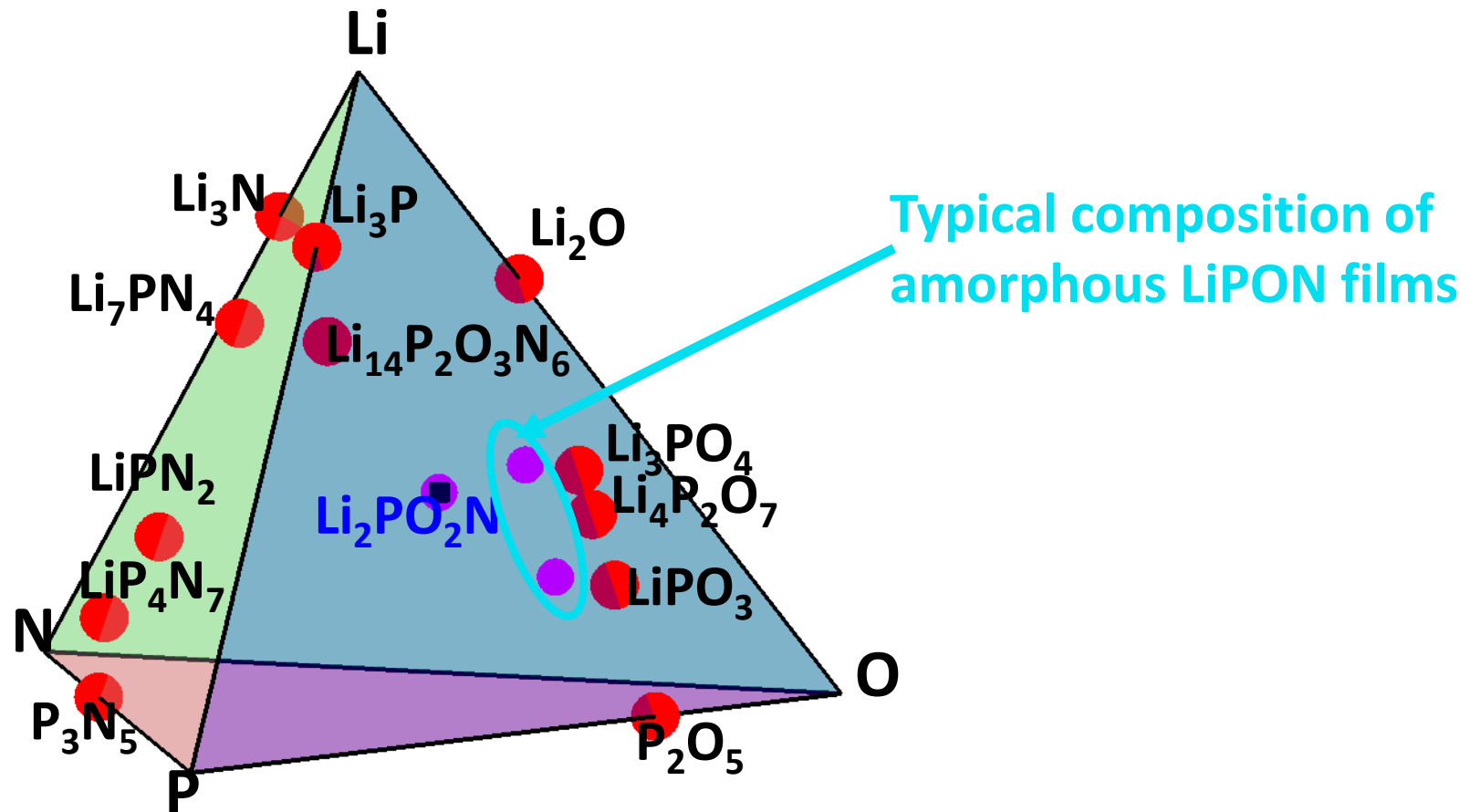
$E_A = 1.14, 1.23, 1.14, 1.31, 1.24$ eV for 1,2,3,4,5, respectively.

^aHenkelman and Jónsson, *JCP* **113**, 9978 (2000)

Arrhenius activation energies – simulation and experiment

Material	Simulation			Experiment	
	E_m (eV)	E_f (eV)	E_A (eV)	E_A (eV)	Ref.
LiPON				≈0.6	Amorphous
γ-Li₃PO₄	0.3	1.7	1.1	1.13	Single crystal
SD-Li₂PO₂N	0.4	2.0	0.4-1.4	0.6	Poly. crystal
Li₁₄P₂O₃N₆	0.3	0.3	0.3-0.4		
Li₇PN₄+O	0.5	-	0.5	0.48	Poly. crystal
β-Li₃PS₄	0.2	0.0	0.2	0.4	Poly. crystal
Li₇P₂S₁₁	0.2	0.0	0.2	0.1	Poly. crystal

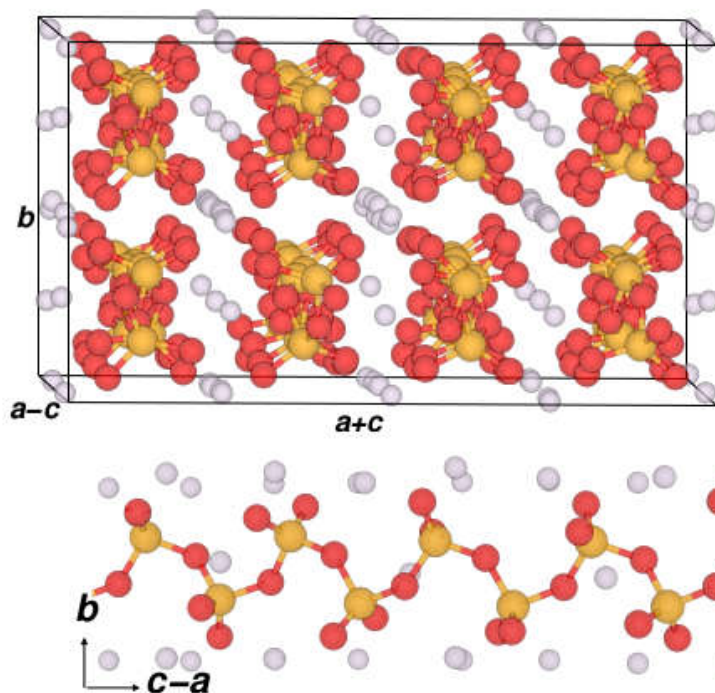
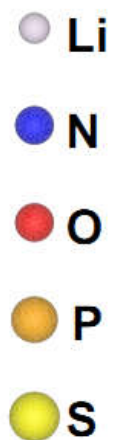
**Systematic study of LiPON materials – $\text{Li}_x\text{PO}_y\text{N}_z$ –
(Yaojun A. Du and N. A. W. Holzwarth, Phys. Rev. B 81, 184106 (2010))**



Experimentally known structure



Key



Computationally predicted structure

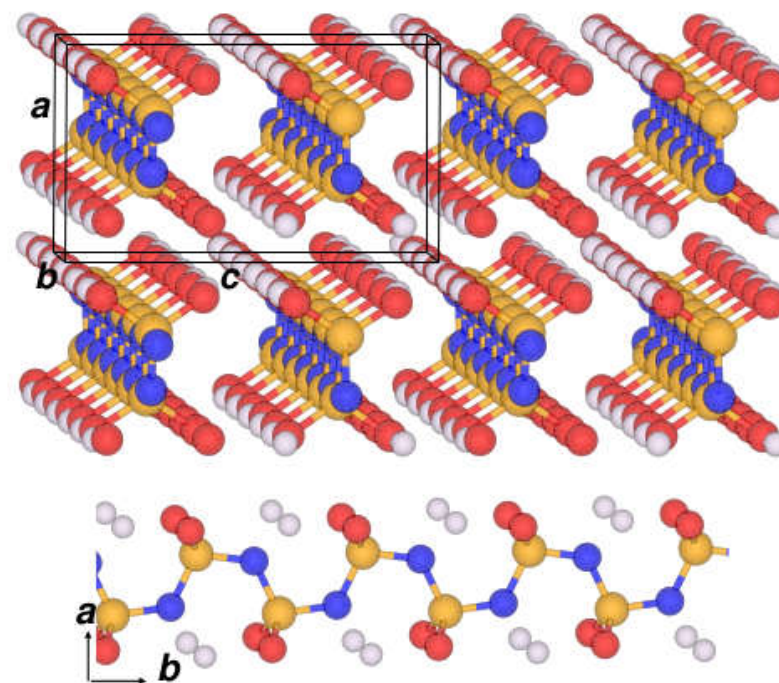


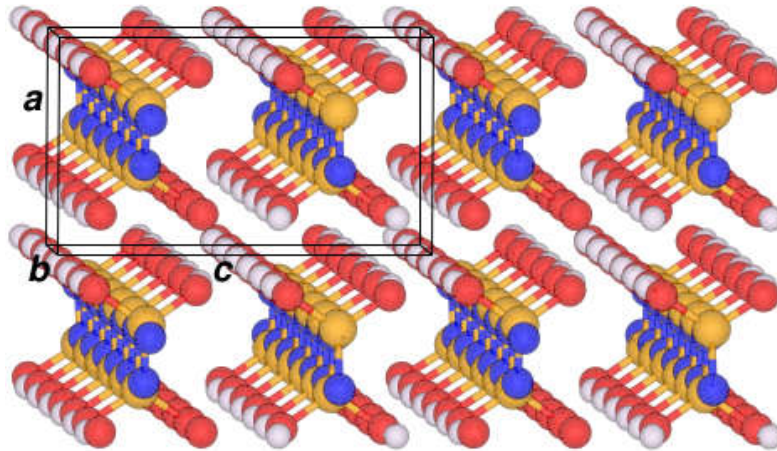
Fig. 7. Ball and stick diagrams for LiPO_3 in the $P2/c$ structure (20 formula units per unit cell) and $s_1\text{-Li}_2\text{PO}_2\text{N}$ in the $Pbcm$ structure (4 formula units per unit cell) from the calculated results. For each crystal diagram, a view of a horizontal chain axis is also provided for a single phosphate or phospho-nitride chain.

Computationally predicted structure

Key

- Li
- N
- O
- P
- S

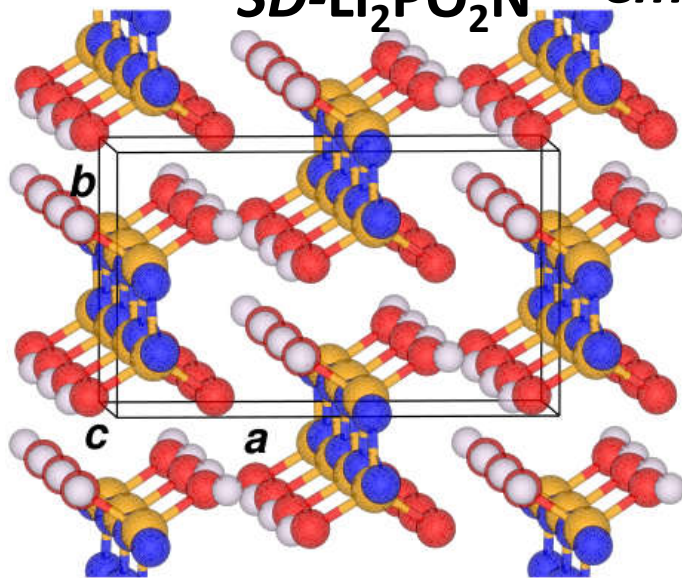
s_1 -Li₂PO₂N *Pbcm*



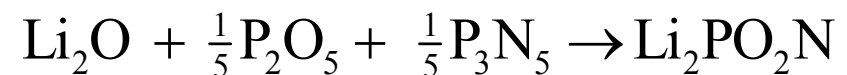
Calculations have now verified that the *SD* structure is more stable than the s_1 structure by 0.1 eV/FU.

Experimentally realized structure

SD-Li₂PO₂N *Cmc2₁*

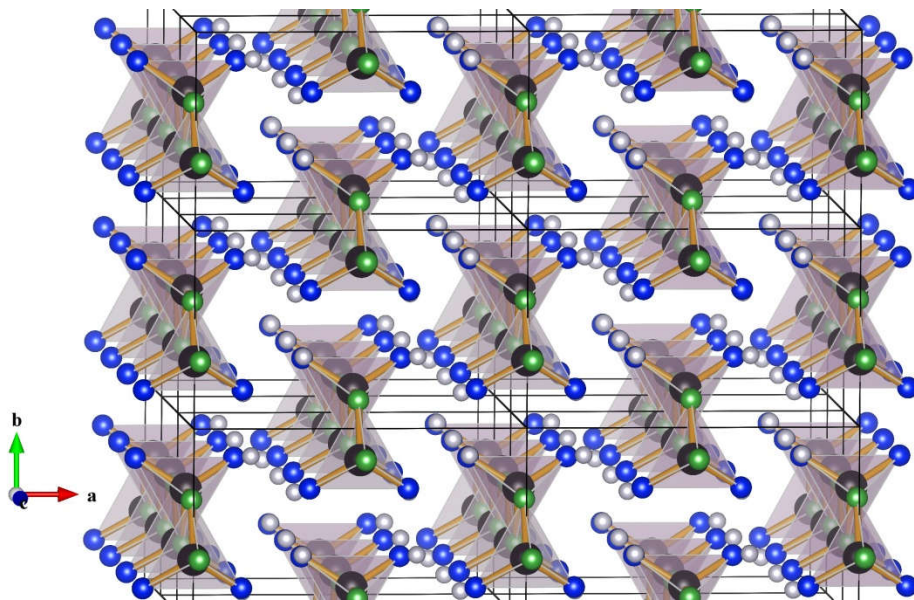


Synthesis of Li₂PO₂N by Keerthi Senevirathne, Cynthia Day, Michael Gross, and Abdessadek Lachgar (SSI 233, 95-101 (2013))
High temperature solid state synthesis using reaction:



Comparison of synthesized $\text{Li}_2\text{PO}_2\text{N}$ with Li_2SiO_3

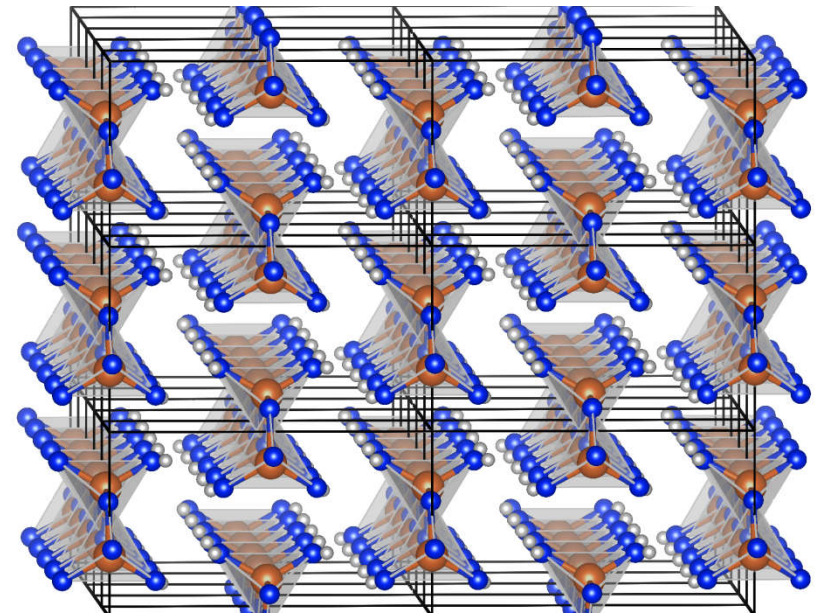
$\text{SD-Li}_2\text{PO}_2\text{N}$ ($Cmc2_1$)



$a=9.07 \text{ \AA}$, $b=5.40 \text{ \AA}$, $c=4.60 \text{ \AA}$

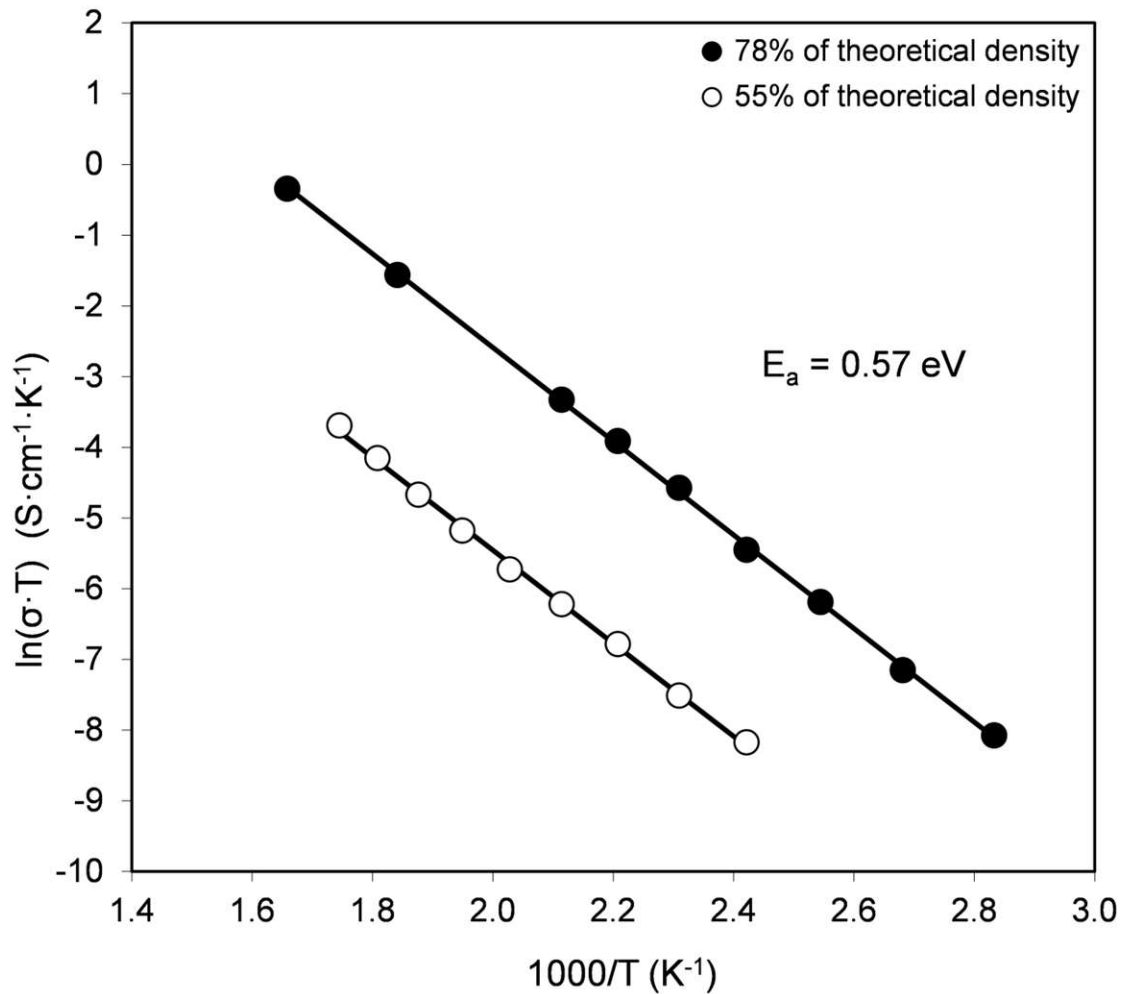


Li_2SiO_3 ($Cmc2_1$)



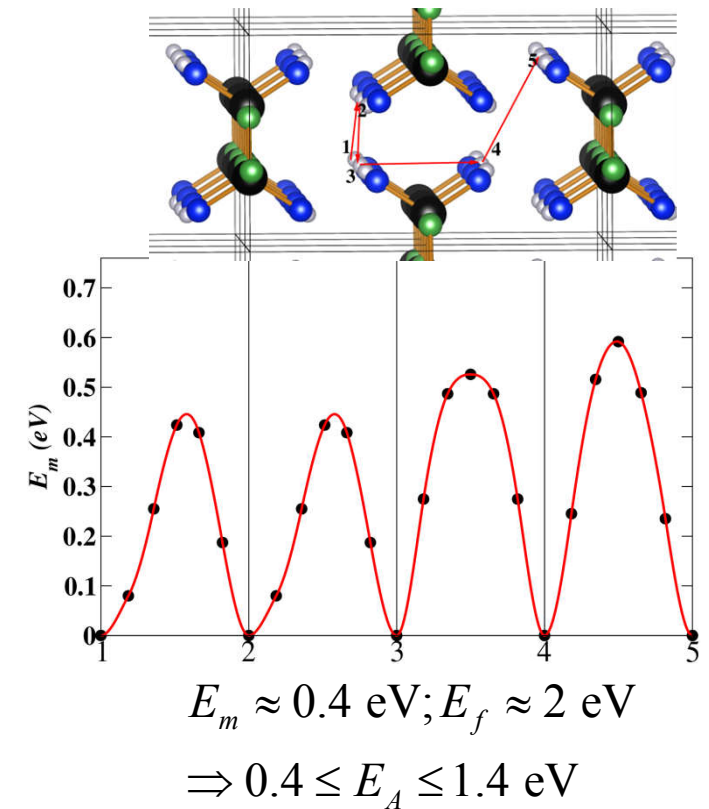
$a=9.39 \text{ \AA}$, $b=5.40 \text{ \AA}$, $c=4.66 \text{ \AA}$
K.-F. Hesse, Acta Cryst. B33, 901 (1977)

Ionic conductivity of $SD\text{-Li}_2\text{PO}_2\text{N}$



$\sigma \approx 10^{-6} \text{ S/cm}$ at 80° C

NEB analysis of E_m (vacancy mechanism)



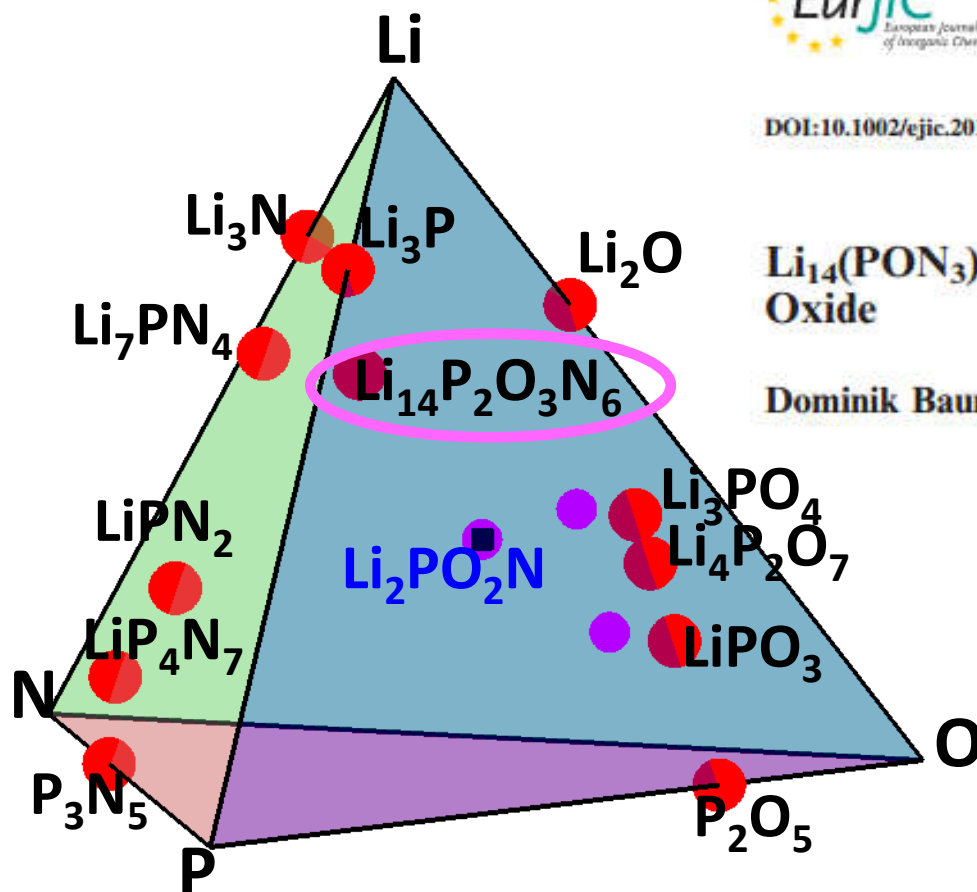
➔ Sample has appreciable population of vacancies

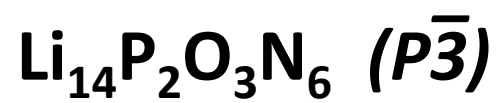
DOI:10.1002/ejic.201403125

Li₁₄(PON₃)₂O – A Non-Condensed Oxonitridophosphate Oxide

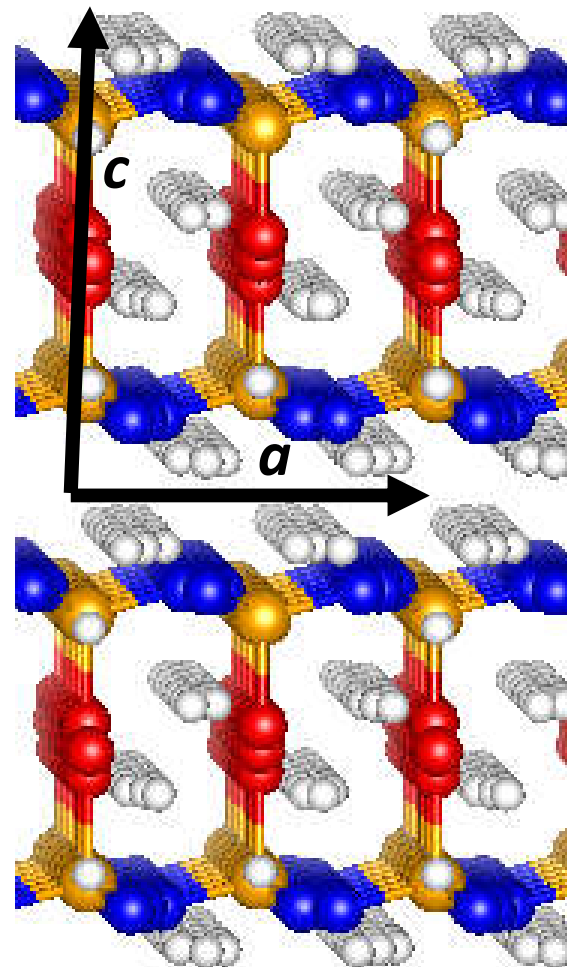
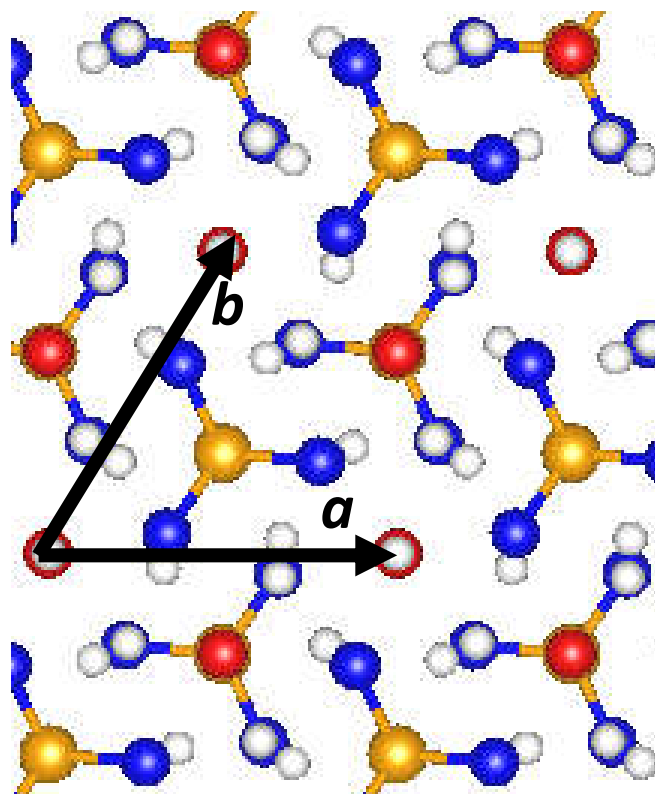
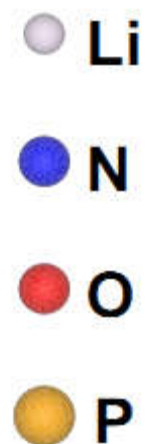
Dominik Baumann^[a] and Wolfgang Schnick^{*[a]}

European Journal of Inorganic Chemistry 2015, 617-621 (2015)

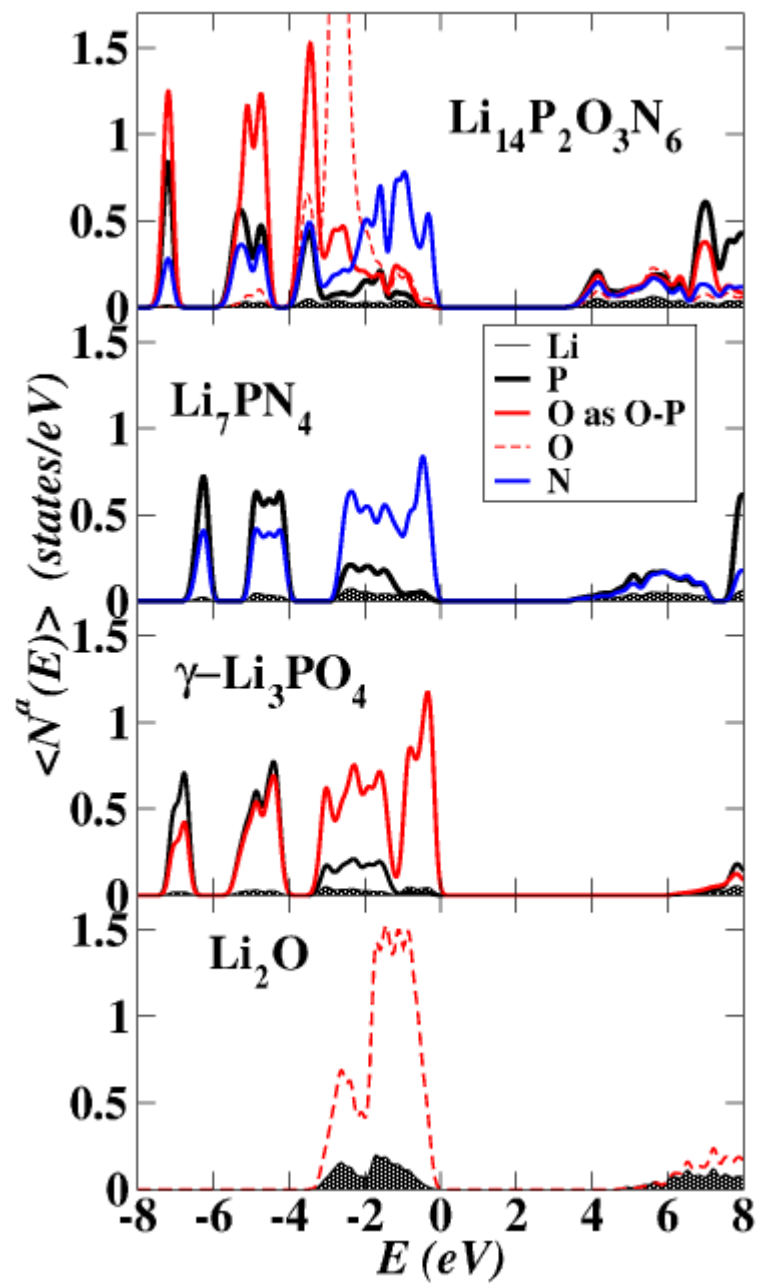


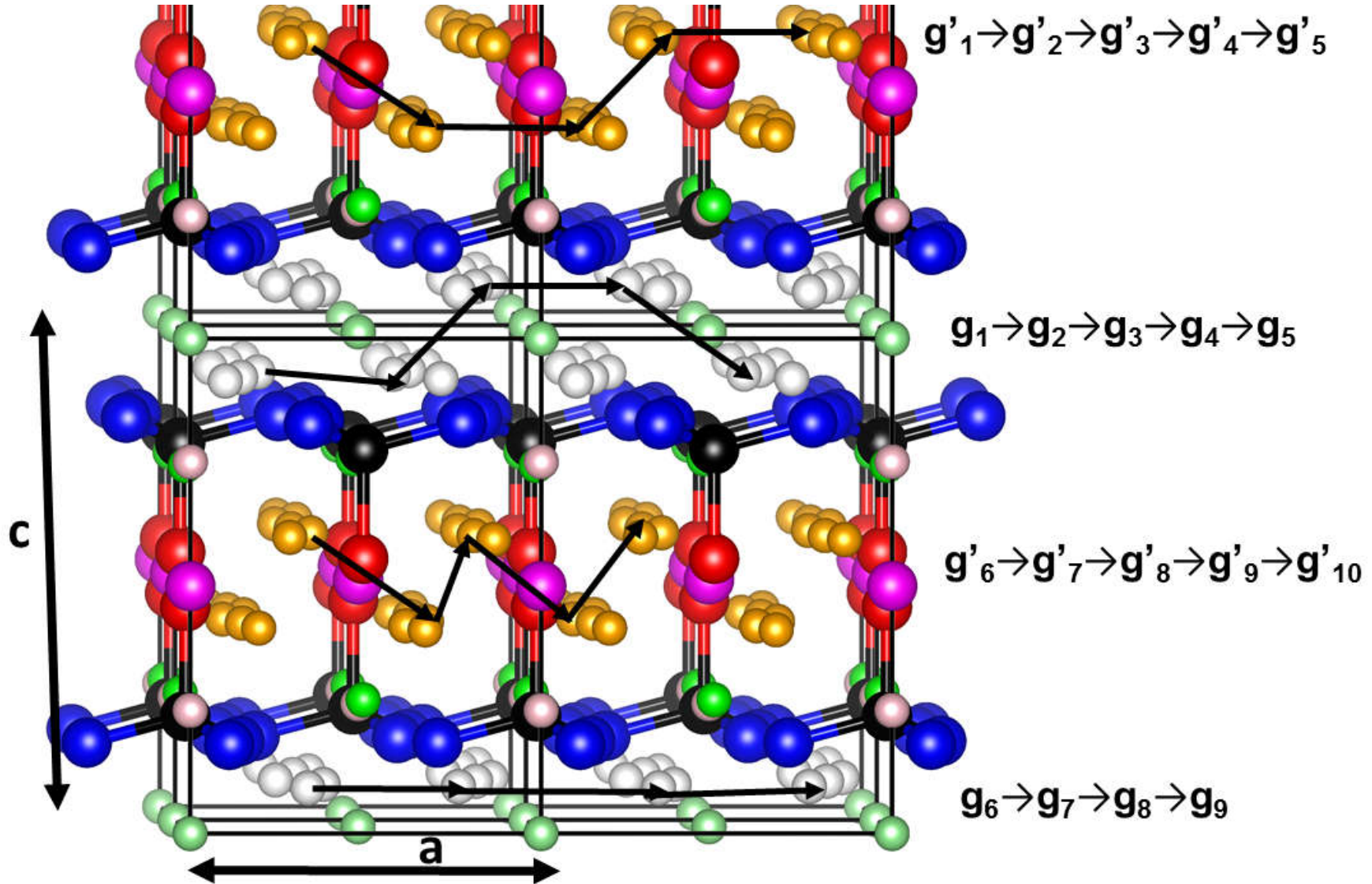


Key



Comparison of partial densities of states of various $\text{Li}_x\text{PO}_y\text{N}_z$ materials





Al-Qawasmeh & Holzwarth, manuscript submitted.

Arrhenius activation energies – simulation and experiment

Material	Simulation			Experiment	
	E_m (eV)	E_f (eV)	E_A (eV)	E_A (eV)	Ref.
LiPON				≈0.6	Amorphous
γ-Li₃PO₄	0.3	1.7	1.1	1.13	Single crystal
SD-Li₂PO₂N	0.4	2.0	0.4-1.4	0.6	Poly. crystal
Li₁₄P₂O₃N₆	0.3	0.3	0.3-0.4		
Li₇PN₄+O	0.5	-	0.5	0.48	Poly. crystal
β-Li₃PS₄	0.2	0.0	0.2	0.4	Poly. crystal
Li₇P₂S₁₁	0.2	0.0	0.2	0.1	Poly. crystal

Other electrolyte materials -- thiophosphate

LiPON and $\text{LiS}_2\text{-P}_2\text{S}_5$ conductivities

X. Yu, J. B. Bates, G. E. Jellison, Jr., and F. X. Hart, J. Electrochem. Soc. **144** 524-532 (1997):

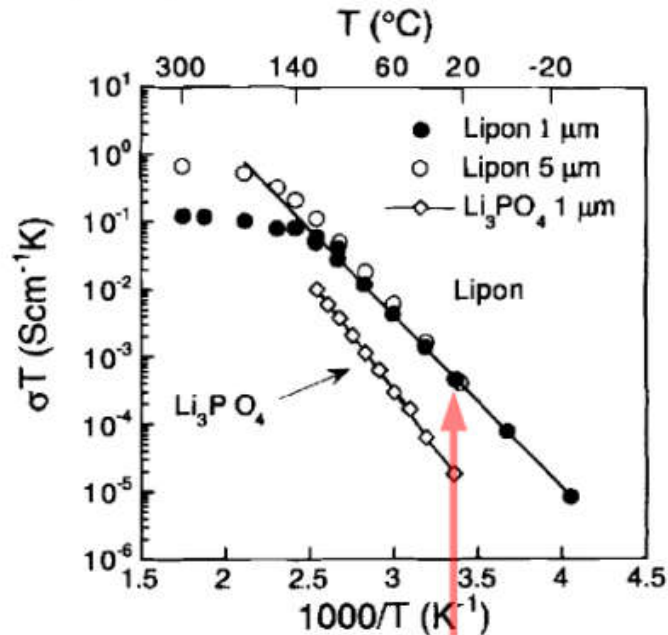


Fig. 3. Arrhenius plot of ionic conductivity of Lipon and Li_3PO_4 vs. temperature.

$$\sigma = 2 \times 10^{-6} \text{ S/cm}$$

$$E_a = 0.5 \text{ eV}$$

M. Tatsumisago and A. Hayashi, J. Non-Cryst. Solids **354** 1411-1417 (2008):

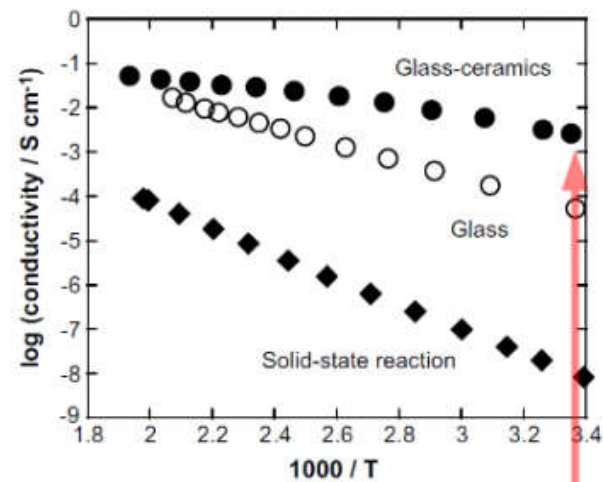
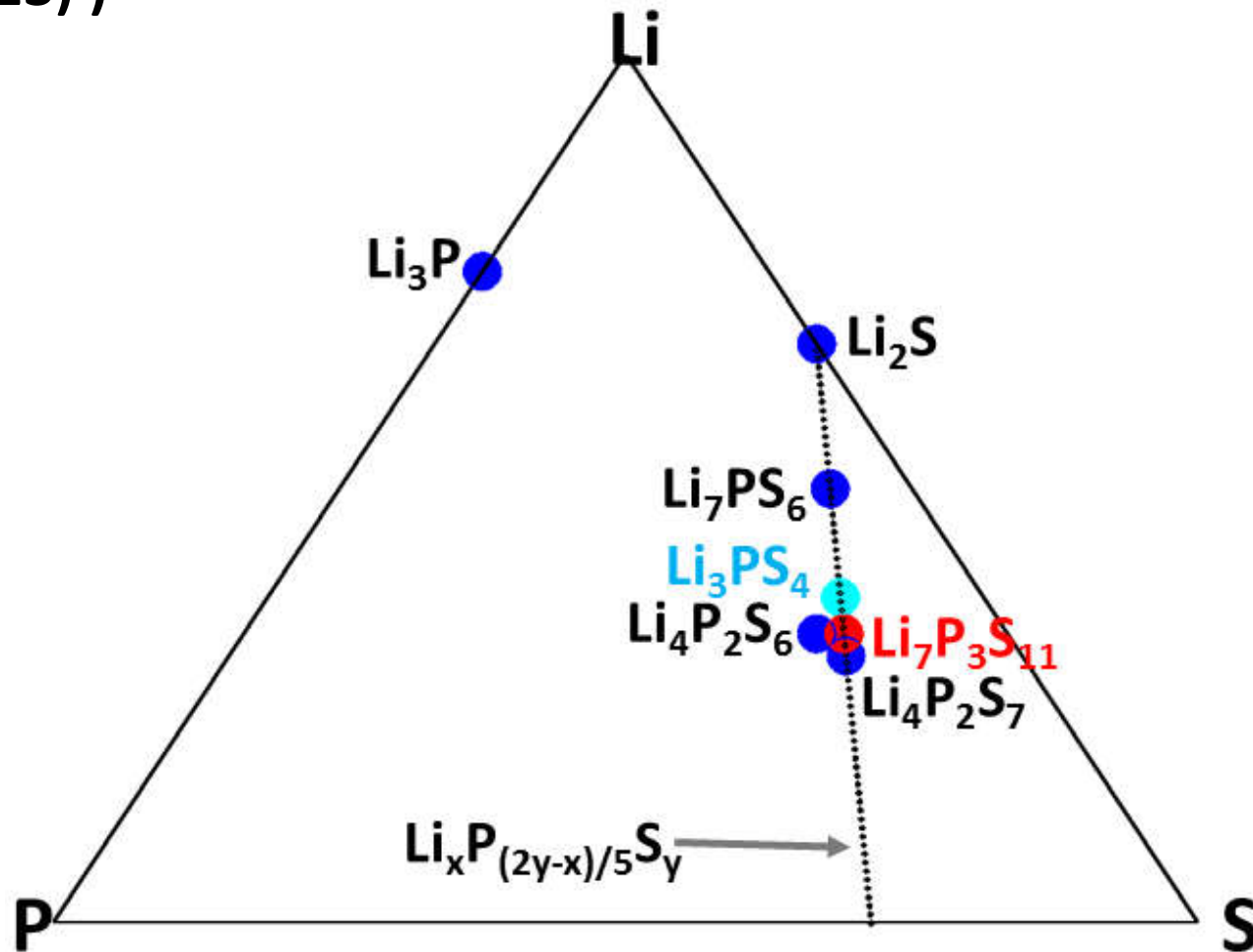


Fig. 5. Temperature dependences of the conductivities for the $70\text{Li}_2\text{S} \cdot 30\text{P}_2\text{S}_5$ glass and glass-ceramics. The conductivity data for the sample prepared by solid-state reaction are also shown.

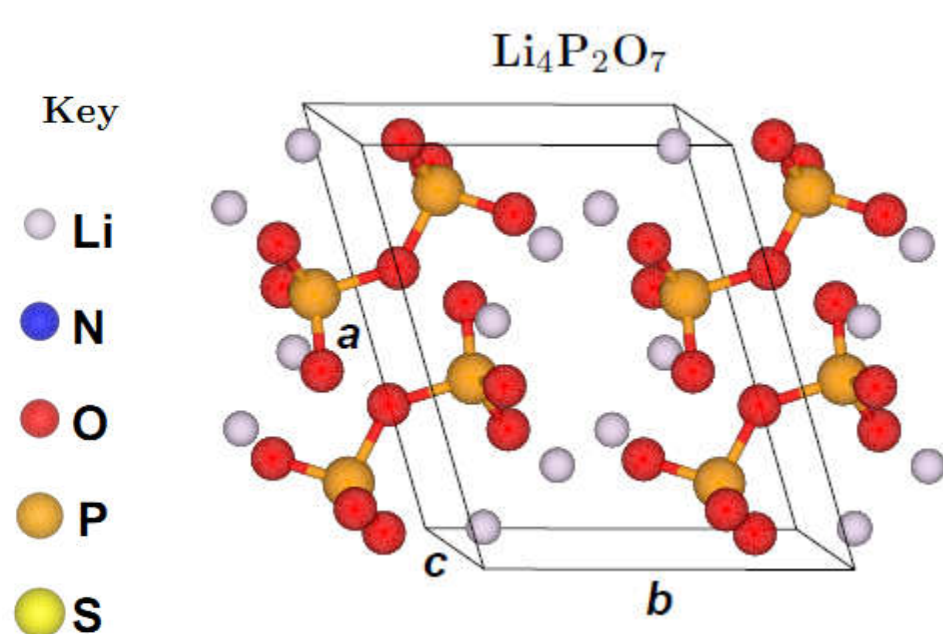
$$\sigma = 3 \times 10^{-3} \text{ S/cm}$$

$$E_a = 0.1 \text{ eV}$$

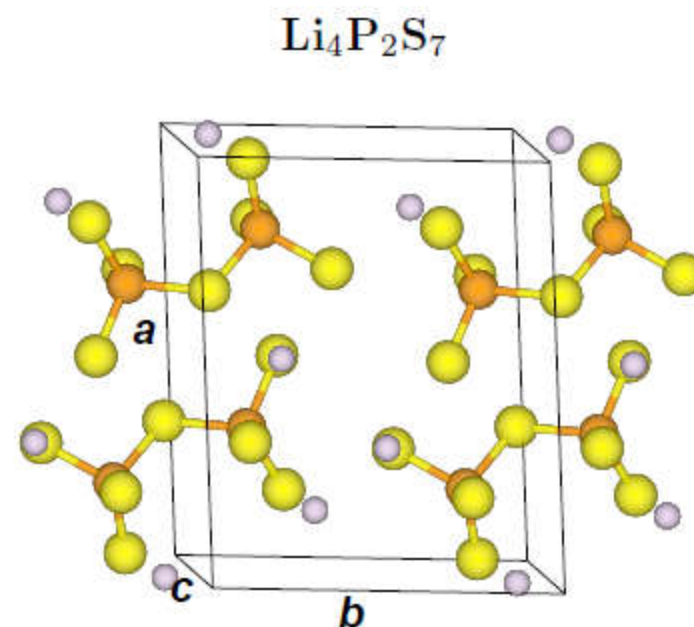
Systematic study of Li_xPS_y materials – (N. D. Lepley and N. A. W. Holzwarth, J. Electrochem. Soc. 159, A538 (2012), Phys. Rev. B 88, 104103 (2013))



Comparison of some lithium phosphates and thiophosphates

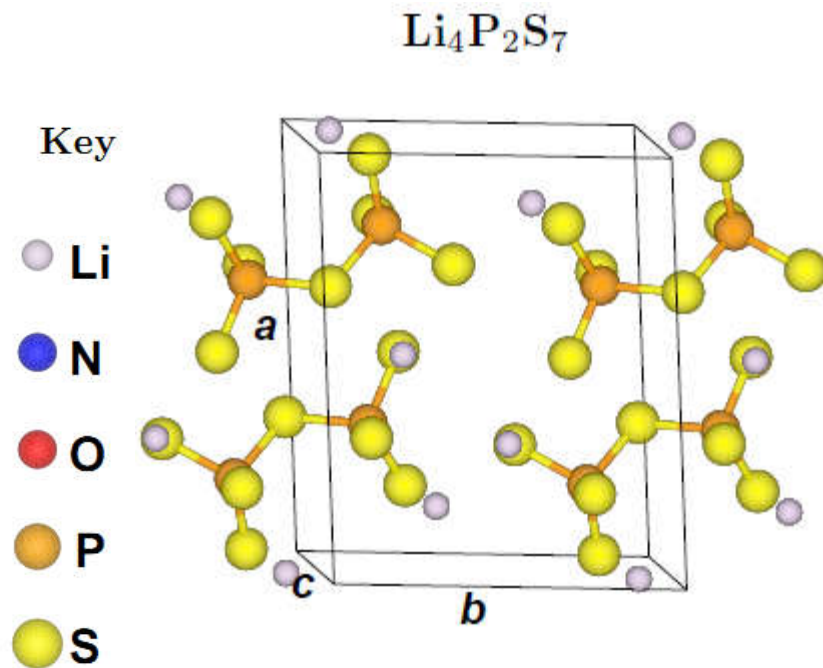


Crystallizes (experimentally and computationally) into $P\bar{1}$ structure

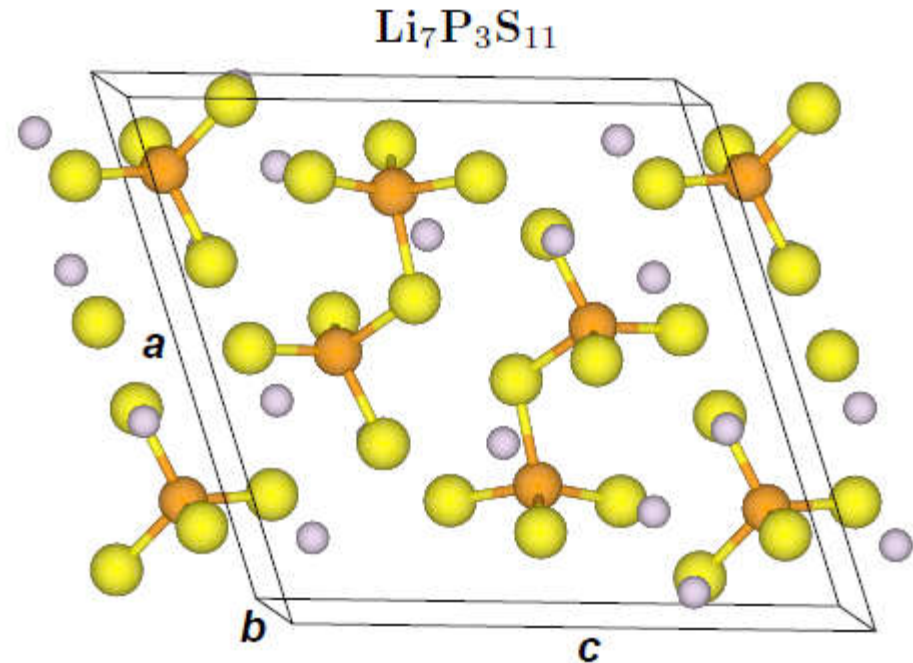


Experimentally amorphous; computationally metastable in $P\bar{1}$ structure

Some lithium thiophosphate crystal structures



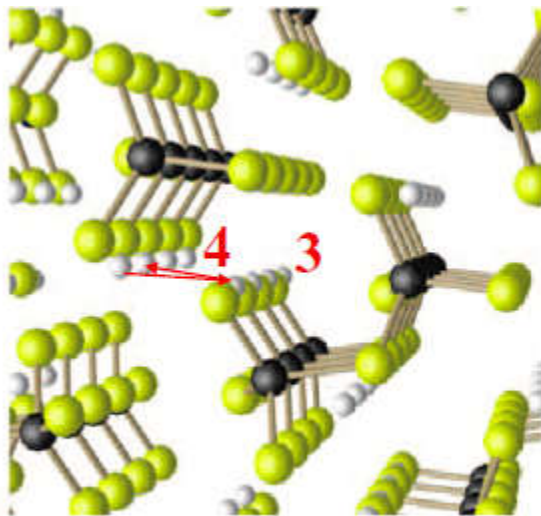
Experimentally amorphous;
computationally metastable
in $P\bar{1}$ structure



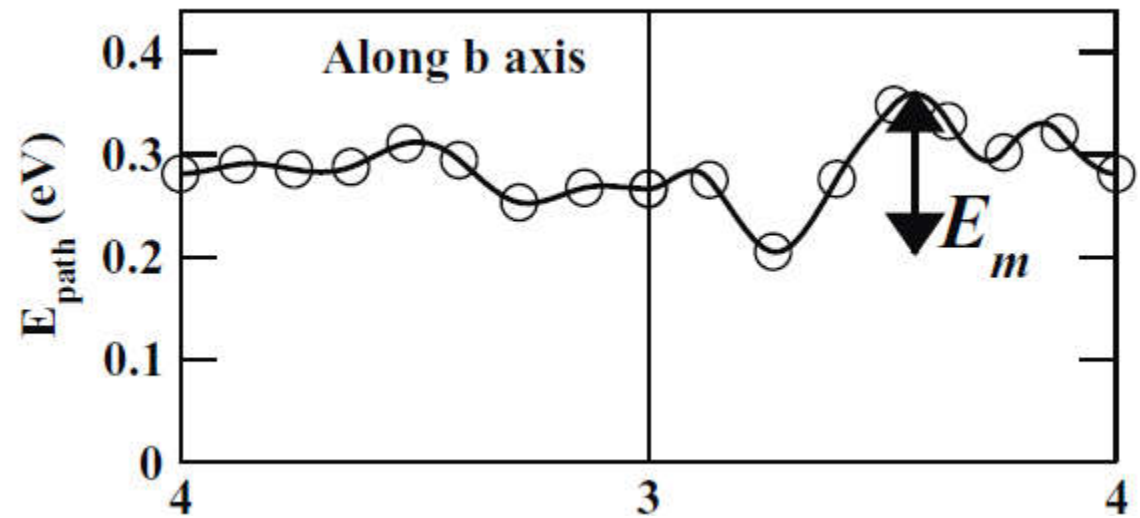
Experimentally and computationally
metastable in $P\bar{1}$ structure

Vacancy migration analysis from NEB results

for $\text{Li}_7\text{P}_3\text{S}_{11}$: Lepley & Holzwarth, *JECs* **159**, A538-A547 (2012)



● Li ● P ● S



$$E_m \approx 0.15 \text{ eV}; E_f \approx 0 \text{ eV}$$

$$\Rightarrow E_A = E_m + \frac{1}{2}E_f \approx 0.15 \text{ eV}$$

Experiment -- A Hayashi *et al.*, *J. Solid State Electrochem.* **14**, 1761 (2010):

$$\sigma \approx 2 - 3 \times 10^{-3} \text{ S/cm}$$

$$E_A \approx 0.12 - 0.18 \text{ eV}$$

Anomalous High Ionic Conductivity of Nanoporous $\beta\text{-Li}_3\text{PS}_4$

Zengcai Liu,[†] Wujun Fu,[†] E. Andrew Payzant,^{†,‡} Xiang Yu,[†] Zili Wu,^{†,§} Nancy J. Dudney,[‡] Jim Kiggans,[‡] Kunlun Hong,[†] Adam J. Rondinone,[†] and Chengdu Liang^{*,†}

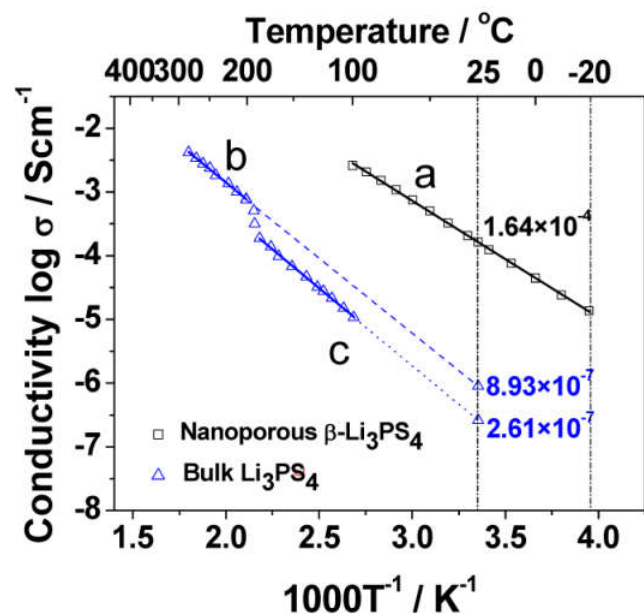


Figure 1. Arrhenius plots for nanoporous $\beta\text{-Li}_3\text{PS}_4$ (line a), bulk $\beta\text{-Li}_3\text{PS}_4$ (line b), and bulk $\gamma\text{-Li}_3\text{PS}_4$ (line c). The conductivity data for bulk Li_3PS_4 are reproduced from the work of Tachez.¹⁰

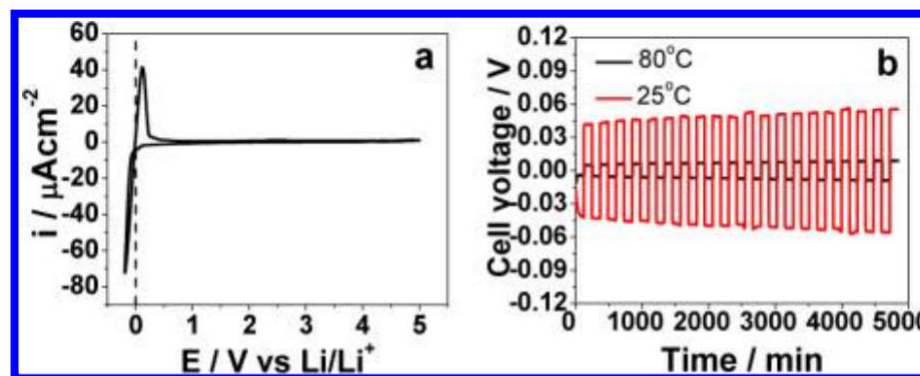
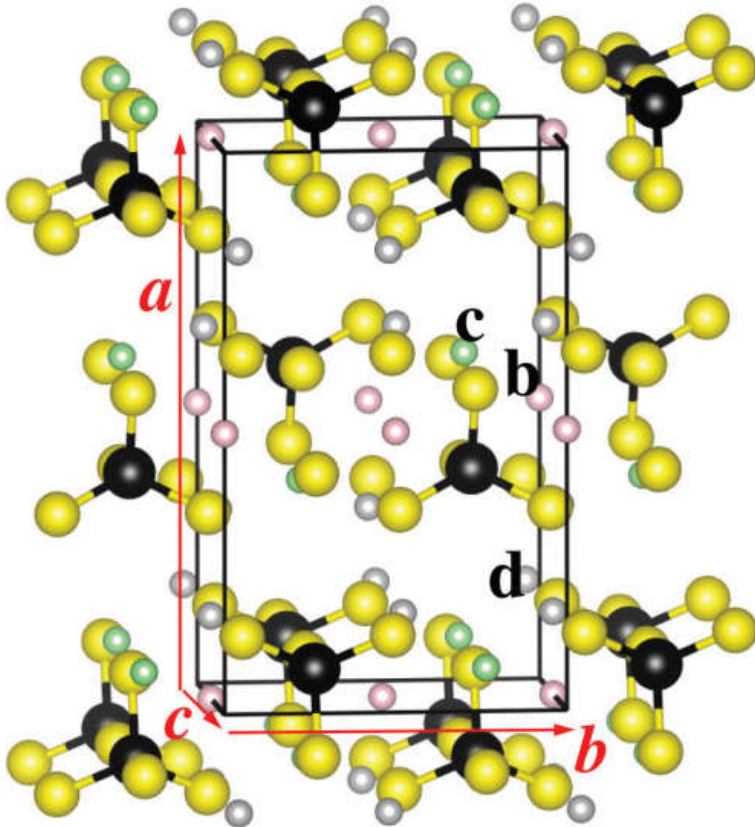


Figure 5. Electrochemical stability of $\beta\text{-Li}_3\text{PS}_4$ and cycling stability with metallic lithium electrodes. (a) CV of a $\text{Li}/\beta\text{-Li}_3\text{PS}_4/\text{Pt}$ cell, where Li and Pt serve as the reference/counter and working electrodes, respectively. (b) Lithium cyclability in a symmetric $\text{Li}/\beta\text{-Li}_3\text{PS}_4/\text{Li}$ cell. The cell was cycled at a current density of 0.1 mA cm^{-2} at room temperature and 80 °C.

β -Li₃PS₄

● Li ● P ● S

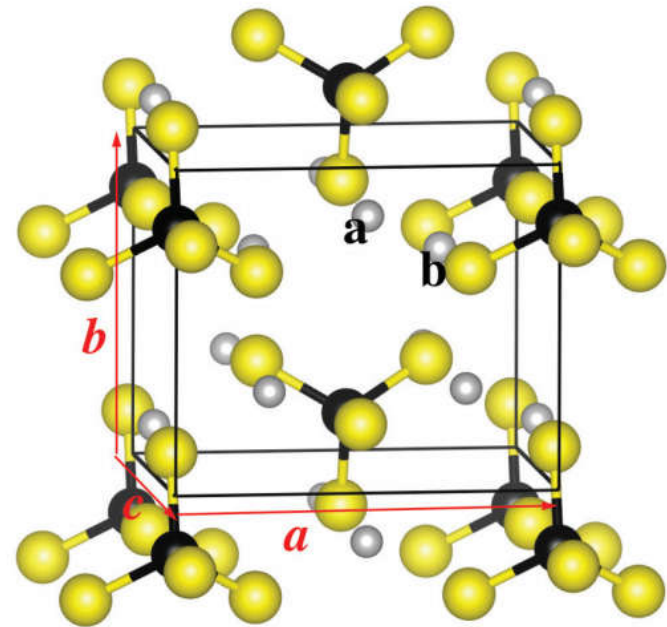


$$E_m \approx 0.2 \text{ eV}; E_f \approx 0.0 \text{ eV}$$

$$E_A = E_m + \frac{1}{2}E_f \approx 0.2 \text{ eV}$$

$$E_{exp} = 0.4 - 0.5 \text{ eV}$$

γ -Li₃PS₄



$$E_m \approx 0.3 \text{ eV}; E_f \approx 0.8 \text{ eV}$$

$$E_A = E_m + \frac{1}{2}E_f \approx 0.7 \text{ eV}$$

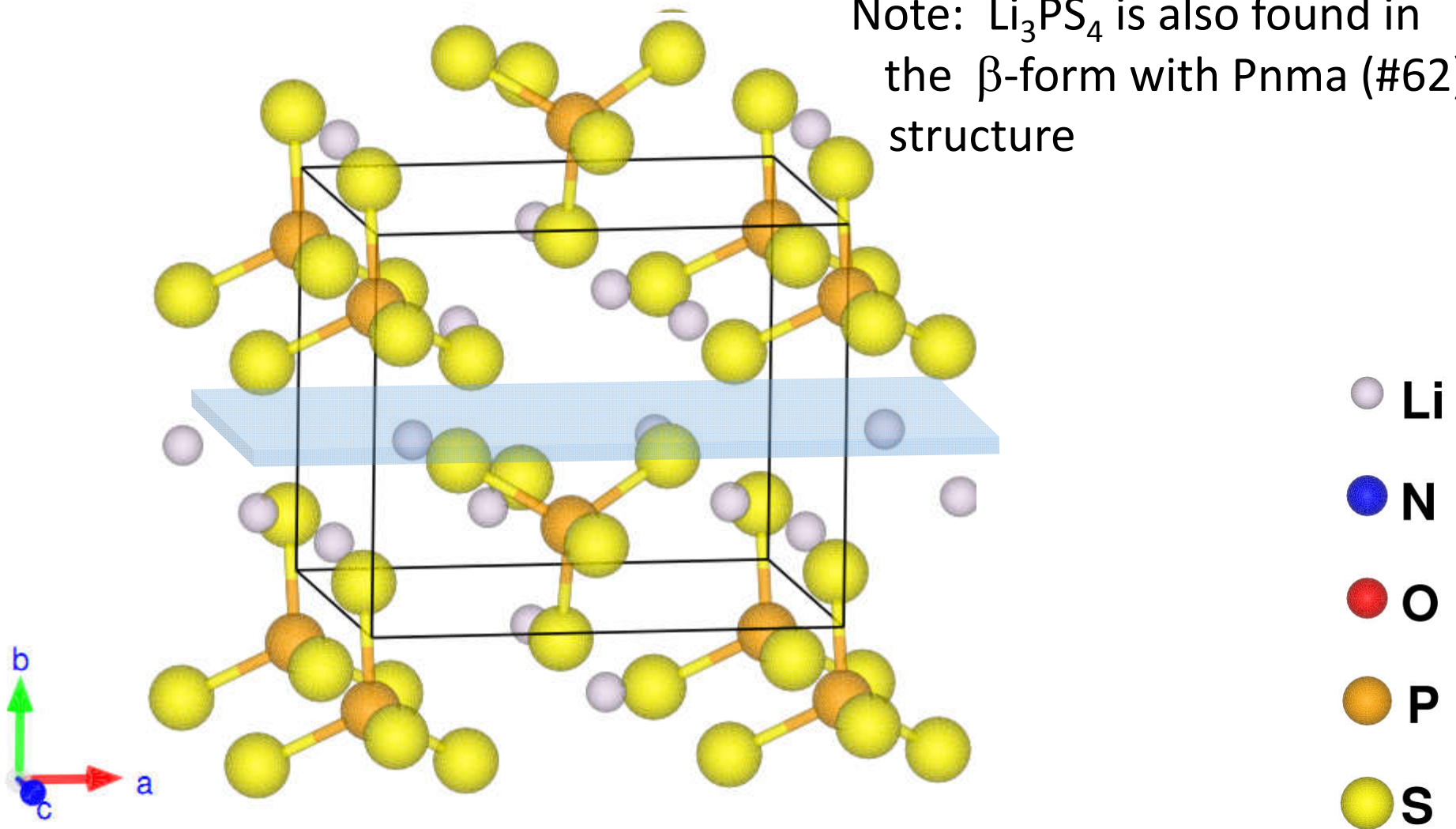
$$E_{exp} = 0.5 \text{ eV}$$

Lepley, Du, and Holzwarth, *PRB* **88**, 104103 (2013)

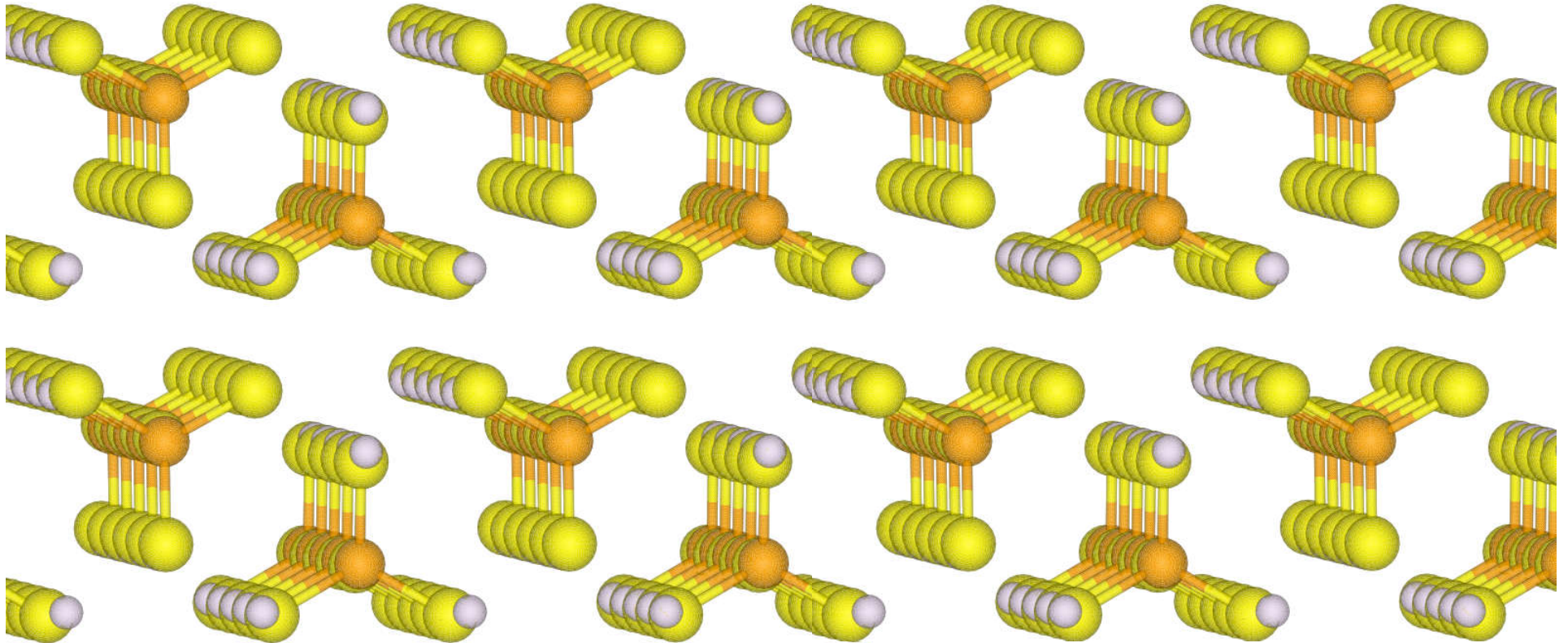
Models of Idealized Interfaces

Crystal structure of bulk Li_3PS_4 – γ -form $\text{Pmn}2_1$ (#31)

Note: Li_3PS_4 is also found in the β -form with Pnma (#62) structure



γ -Li₃PS₄ [0 1 0] surface

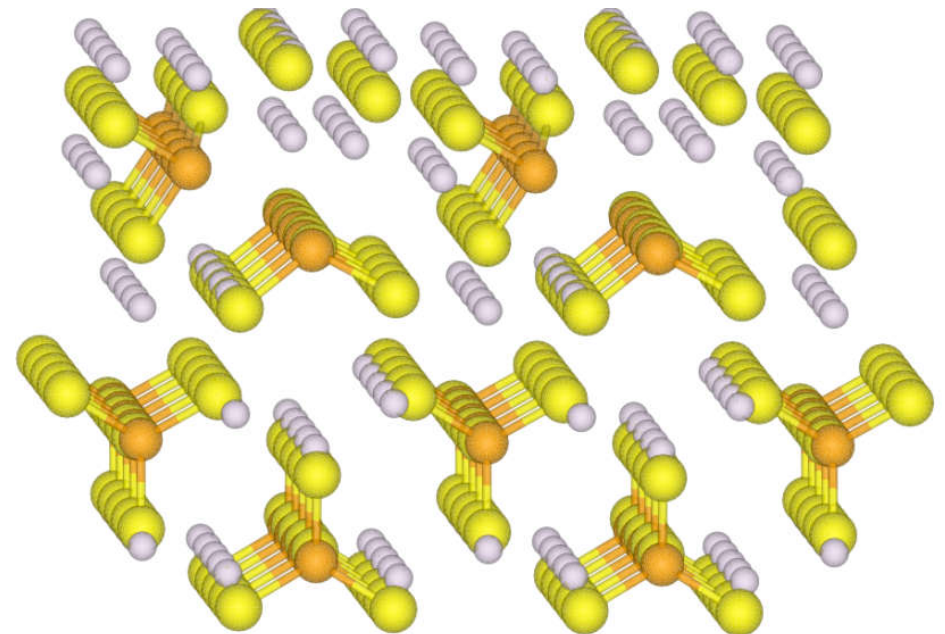
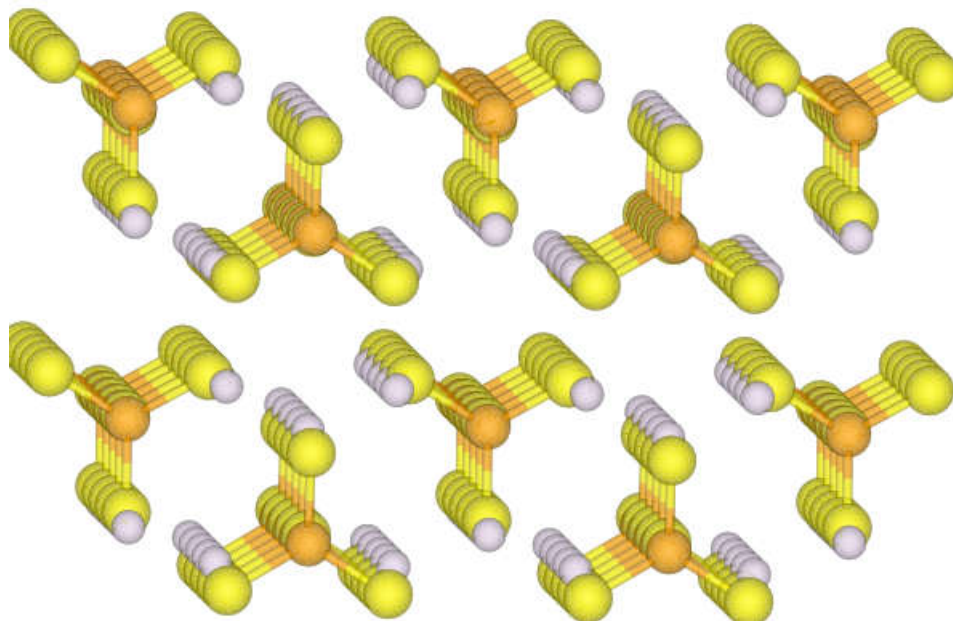


Simulations of ideal γ -Li₃PS₄ [0 1 0] surface in the presence of Li

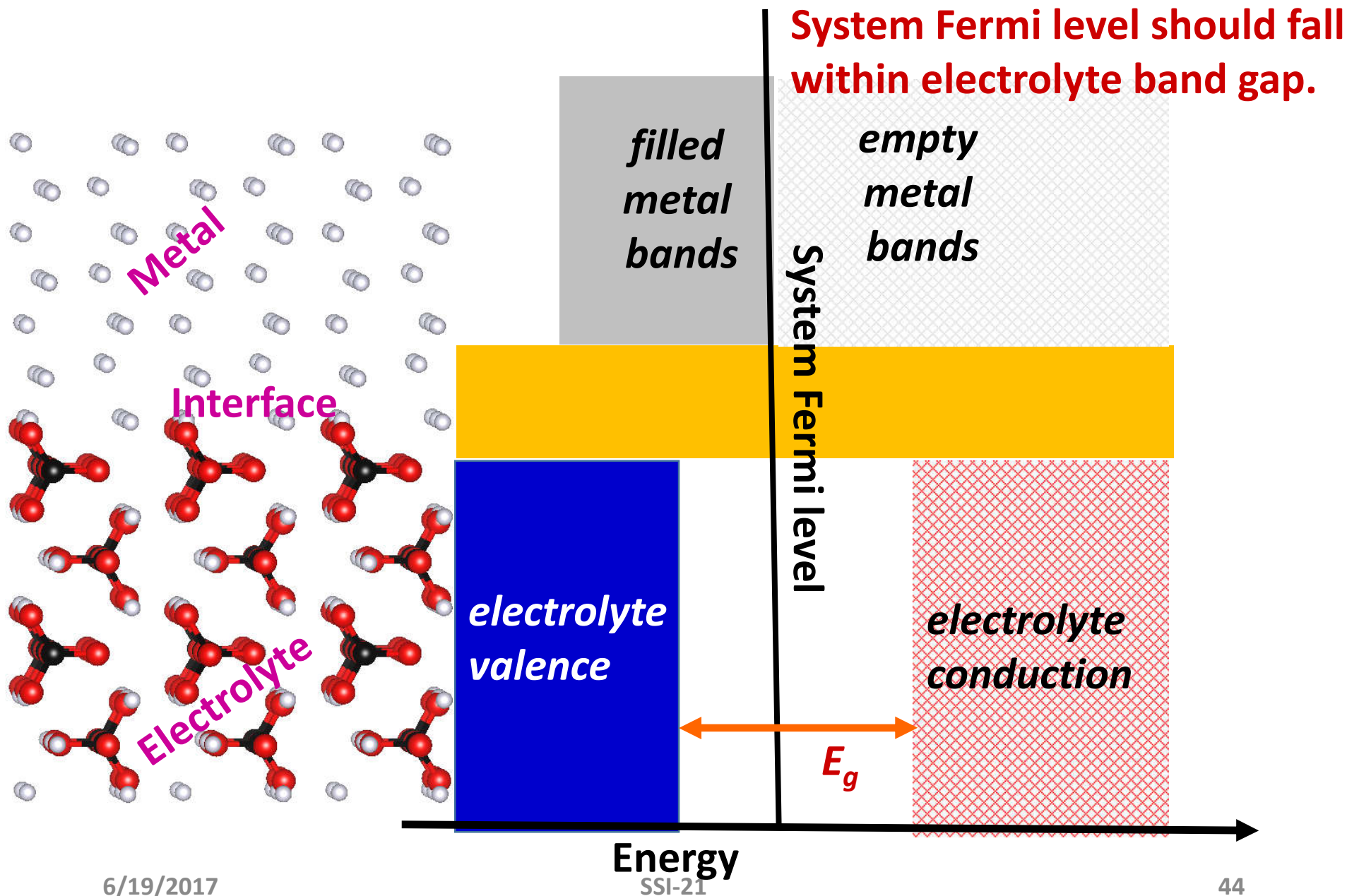
Initial configuration:



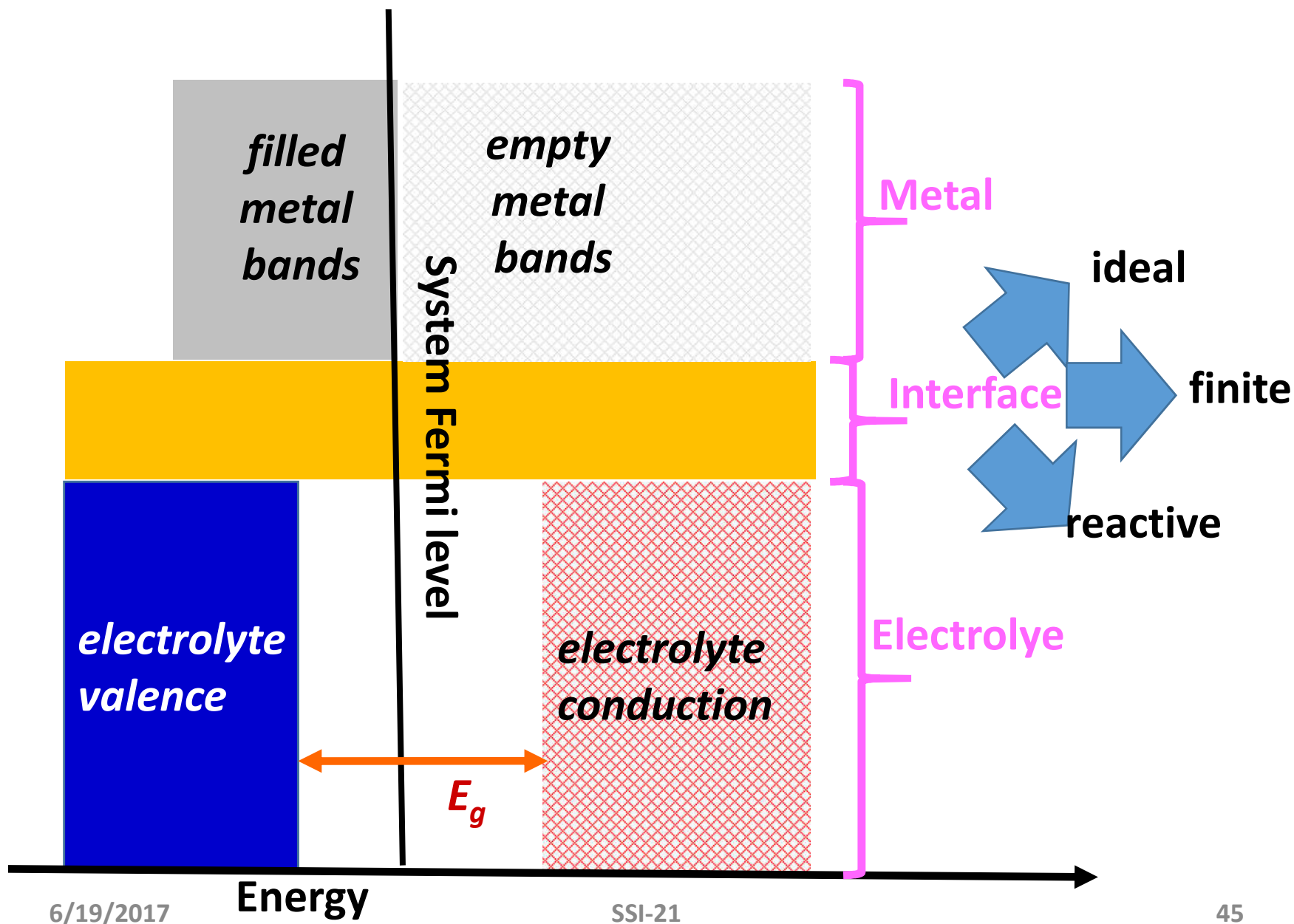
Computed optimized
structure:



Energy diagram for ideal electrolyte/metal interface

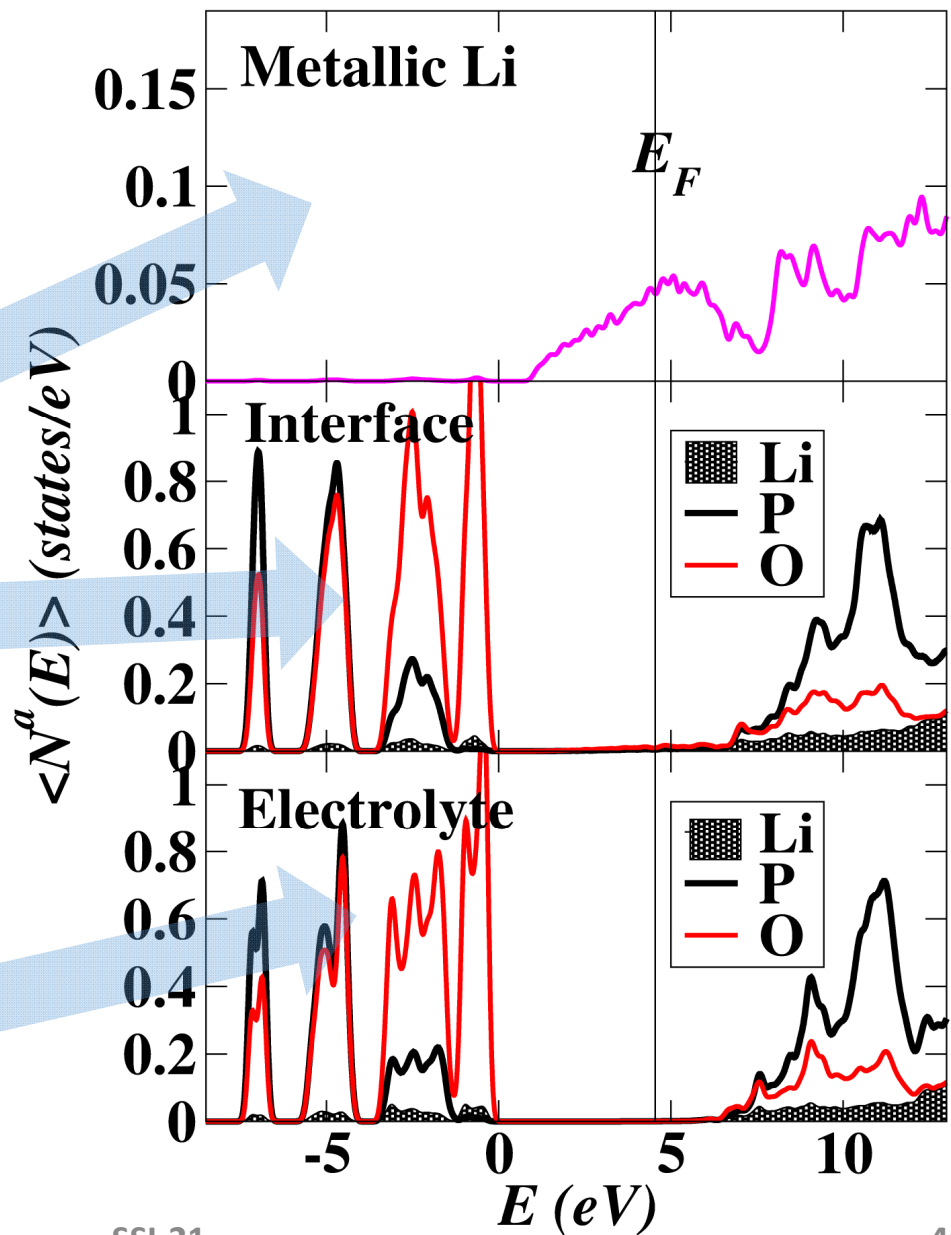
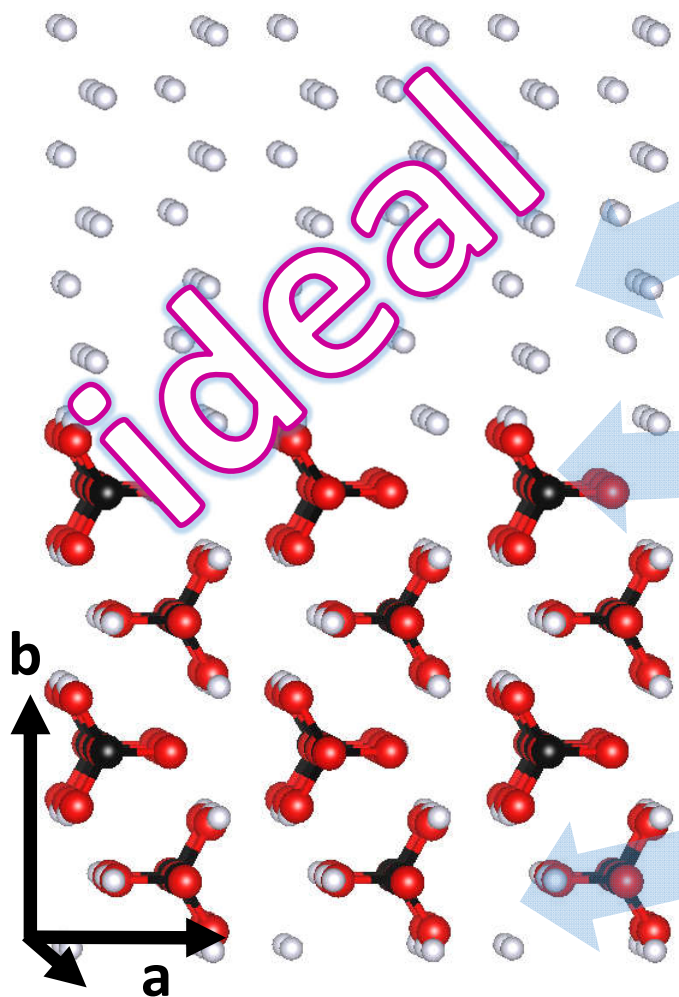


Possible interface configurations

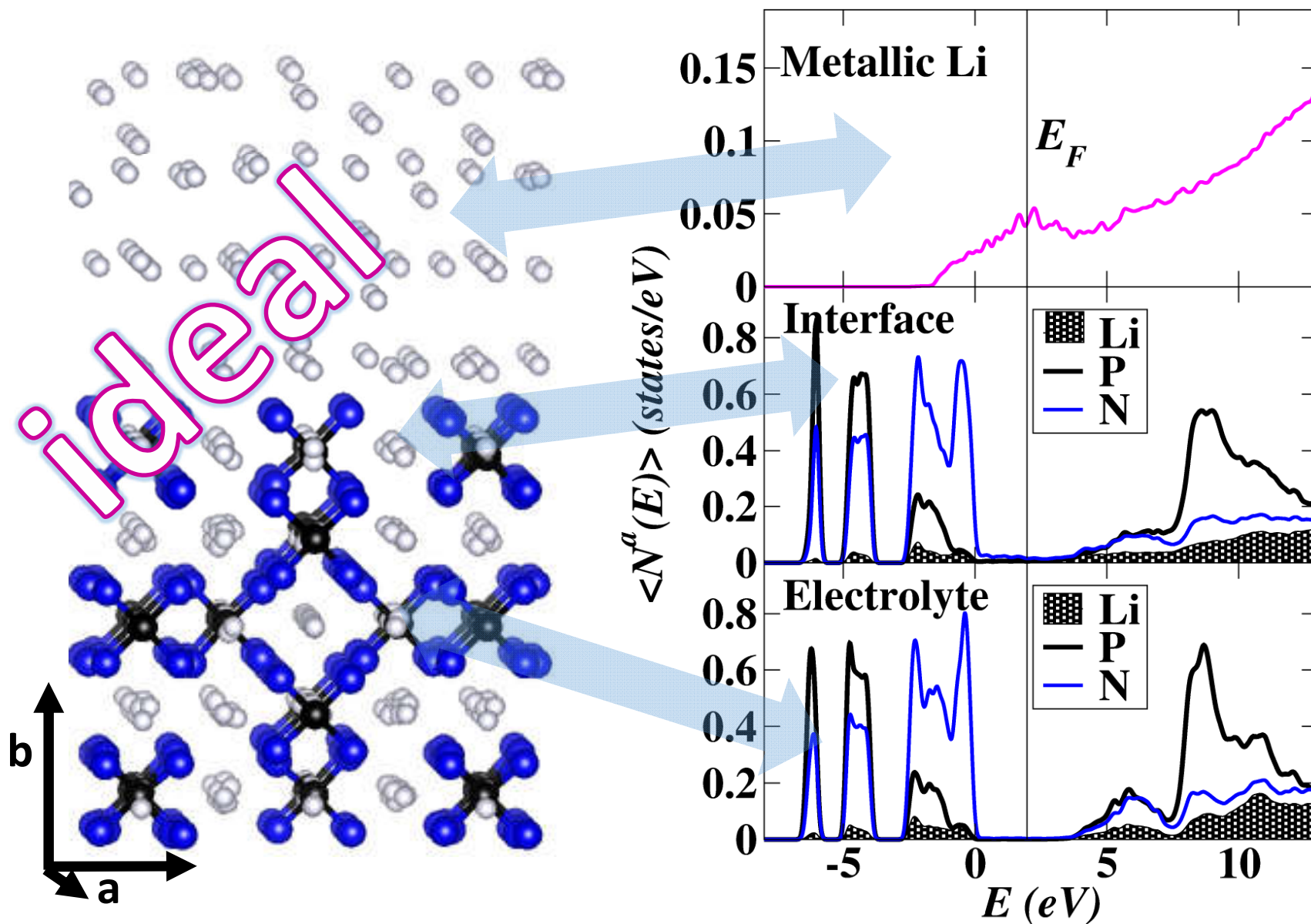


γ -Li₃PO₄/Li system

Li P O
 ● ● ●

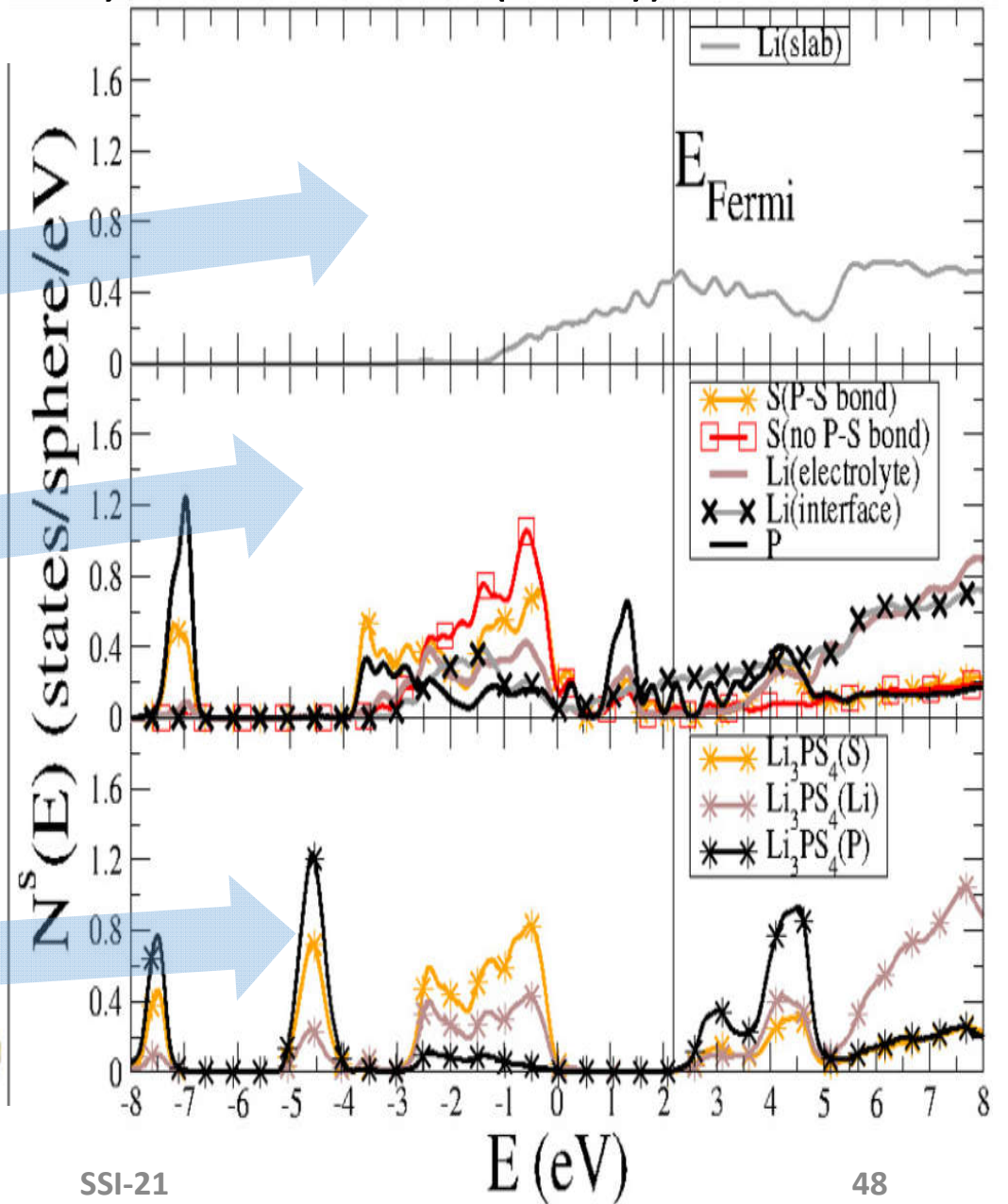
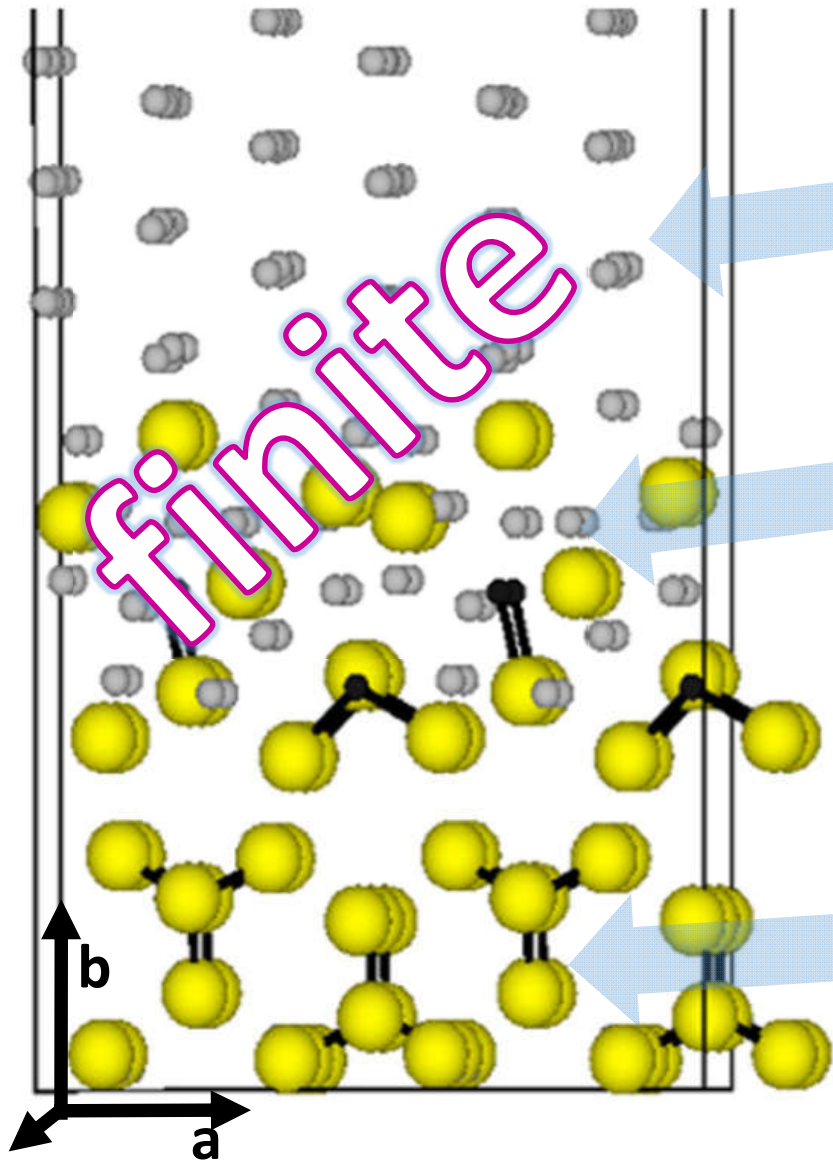


Li₇PN₄/Li system



γ -Li₃PS₄/Li system

(Lepley *et al.*) PRB 92 21401 (2015)



Anomalous High Ionic Conductivity of Nanoporous $\beta\text{-Li}_3\text{PS}_4$

Zengcai Liu,[†] Wujun Fu,[†] E. Andrew Payzant,^{†,‡} Xiang Yu,[†] Zili Wu,^{†,§} Nancy J. Dudney,[‡] Jim Kiggans,[‡] Kunlun Hong,[†] Adam J. Rondinone,[†] and Chengdu Liang^{*,†}

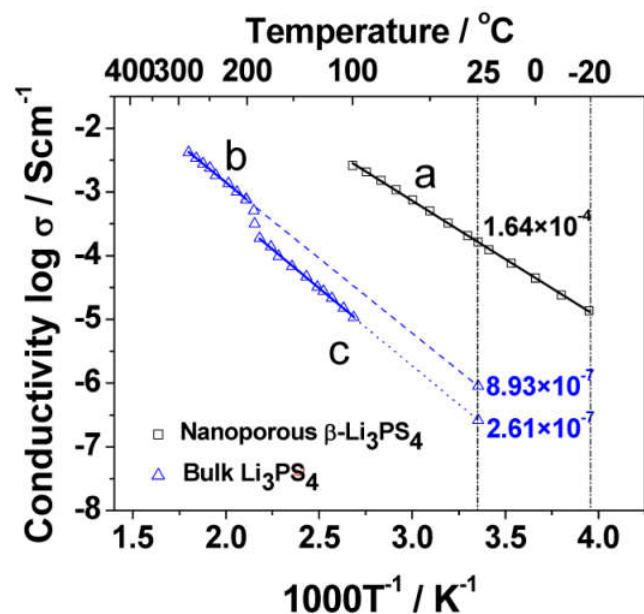


Figure 1. Arrhenius plots for nanoporous $\beta\text{-Li}_3\text{PS}_4$ (line a), bulk $\beta\text{-Li}_3\text{PS}_4$ (line b), and bulk $\gamma\text{-Li}_3\text{PS}_4$ (line c). The conductivity data for bulk Li_3PS_4 are reproduced from the work of Tachez.¹⁰

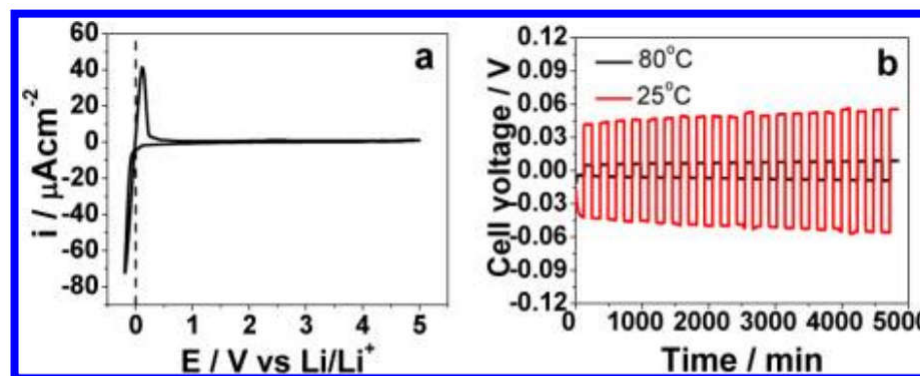
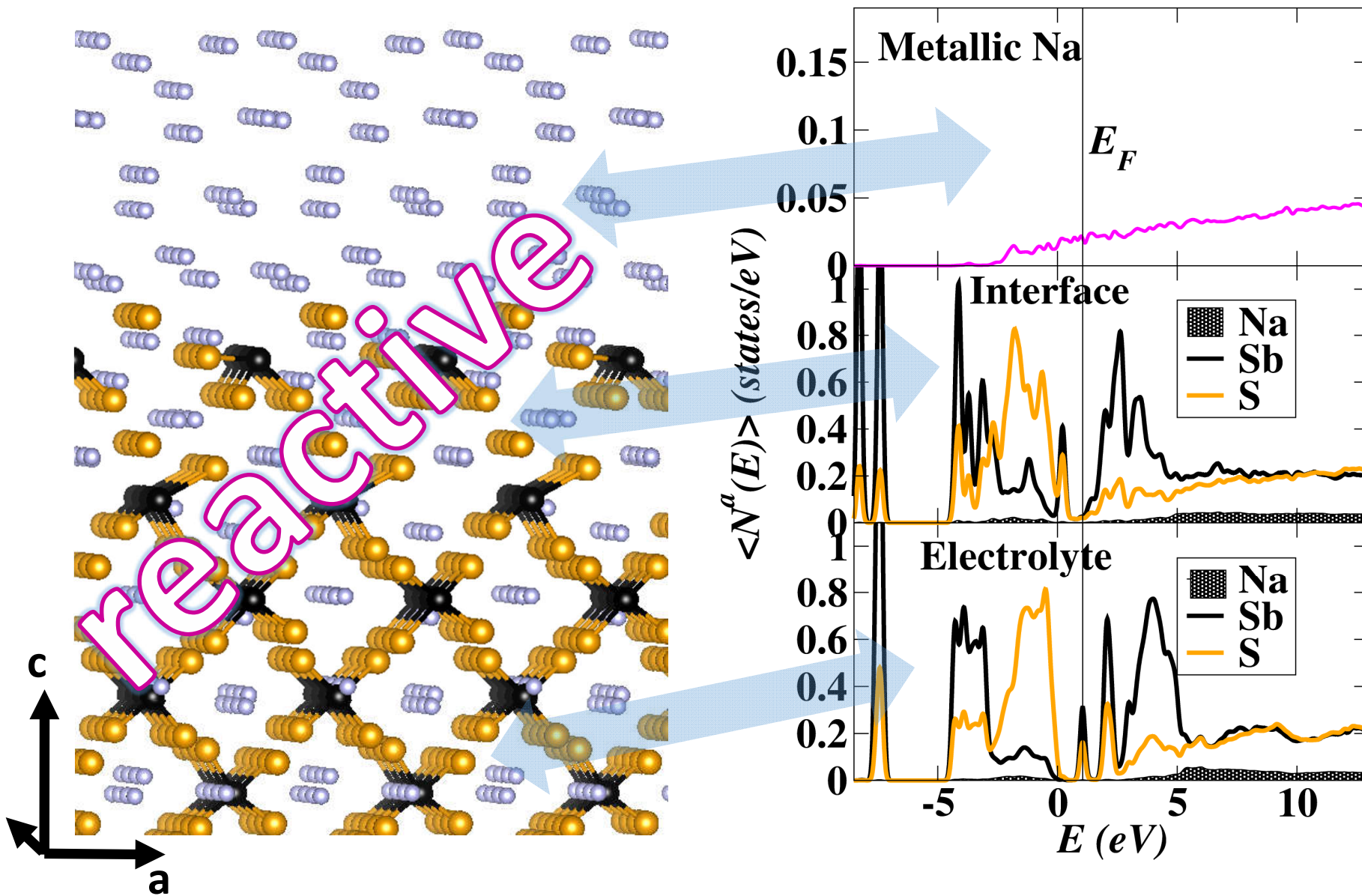


Figure 5. Electrochemical stability of $\beta\text{-Li}_3\text{PS}_4$ and cycling stability with metallic lithium electrodes. (a) CV of a $\text{Li}/\beta\text{-Li}_3\text{PS}_4/\text{Pt}$ cell, where Li and Pt serve as the reference/counter and working electrodes, respectively. (b) Lithium cyclability in a symmetric $\text{Li}/\beta\text{-Li}_3\text{PS}_4/\text{Li}$ cell. The cell was cycled at a current density of 0.1 mA cm^{-2} at room temperature and $80 \text{ }^\circ\text{C}$.

Na₃SbS₄/Na system (from MS thesis of L. Rush, Jr.)



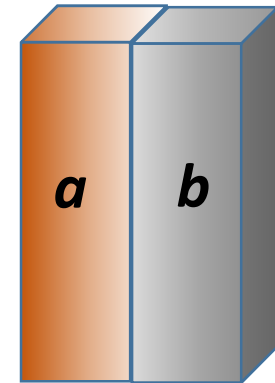
Quantitative study of interfaces –
 (Lepley & Holzwarth, *PRB* **92** 214201 (2015))

Within any given periodic simulation cell with n_a units of material a and with n_b units of material b , we can define an interface energy:

$$\tilde{\gamma}_{ab}(\tilde{\Omega}, n_a, n_b) = \frac{\tilde{E}_{ab}(\tilde{\Omega}, A, n_a, n_b) - n_a E_a - n_b E_b}{A}$$

area of interface
within supercell

bulk energies

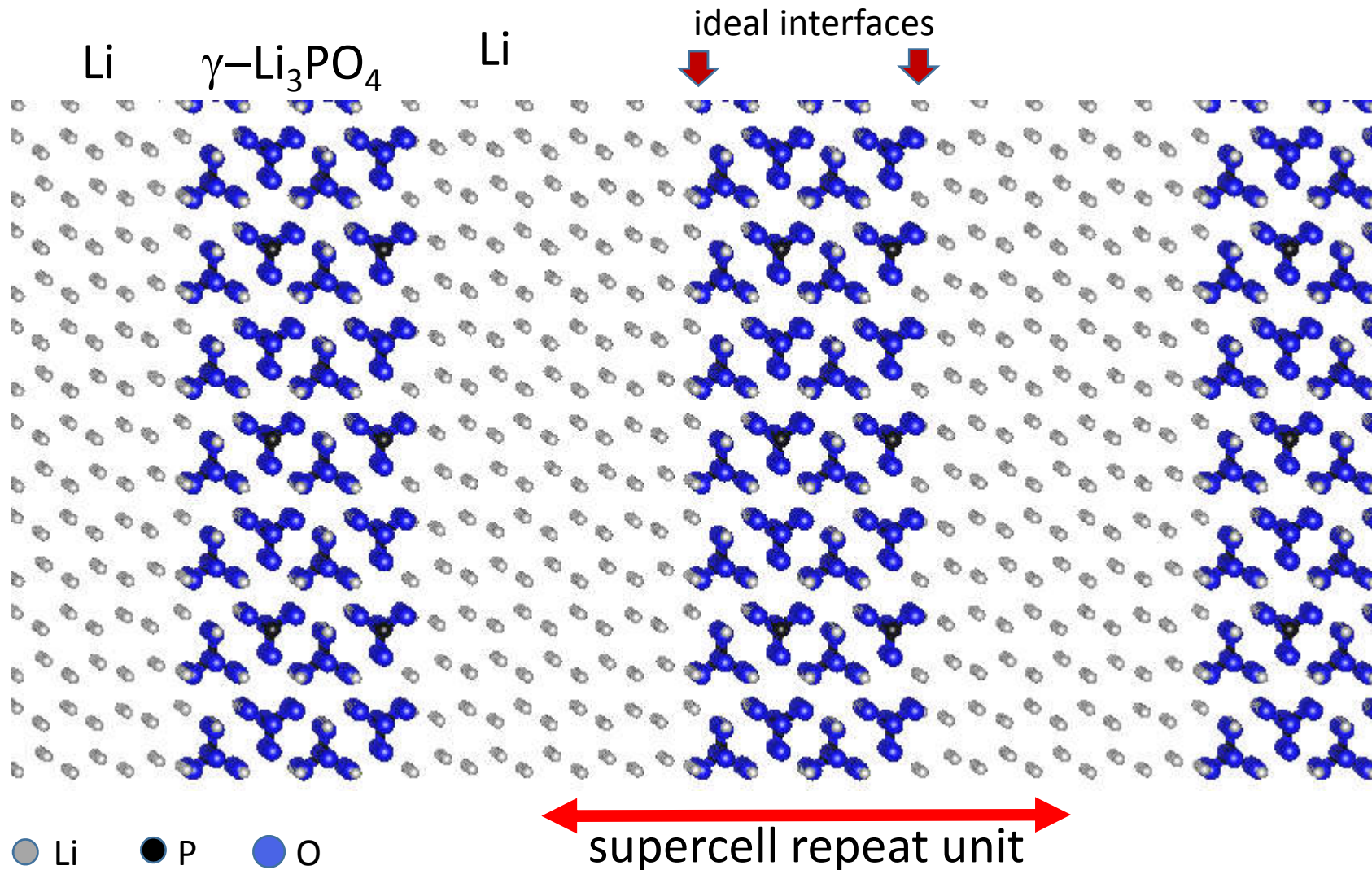


In order approximately remove the effects of lattice strain:

- Design the supercell to be commensurate with lattice a
- Now the strain will scale with the amount of material b

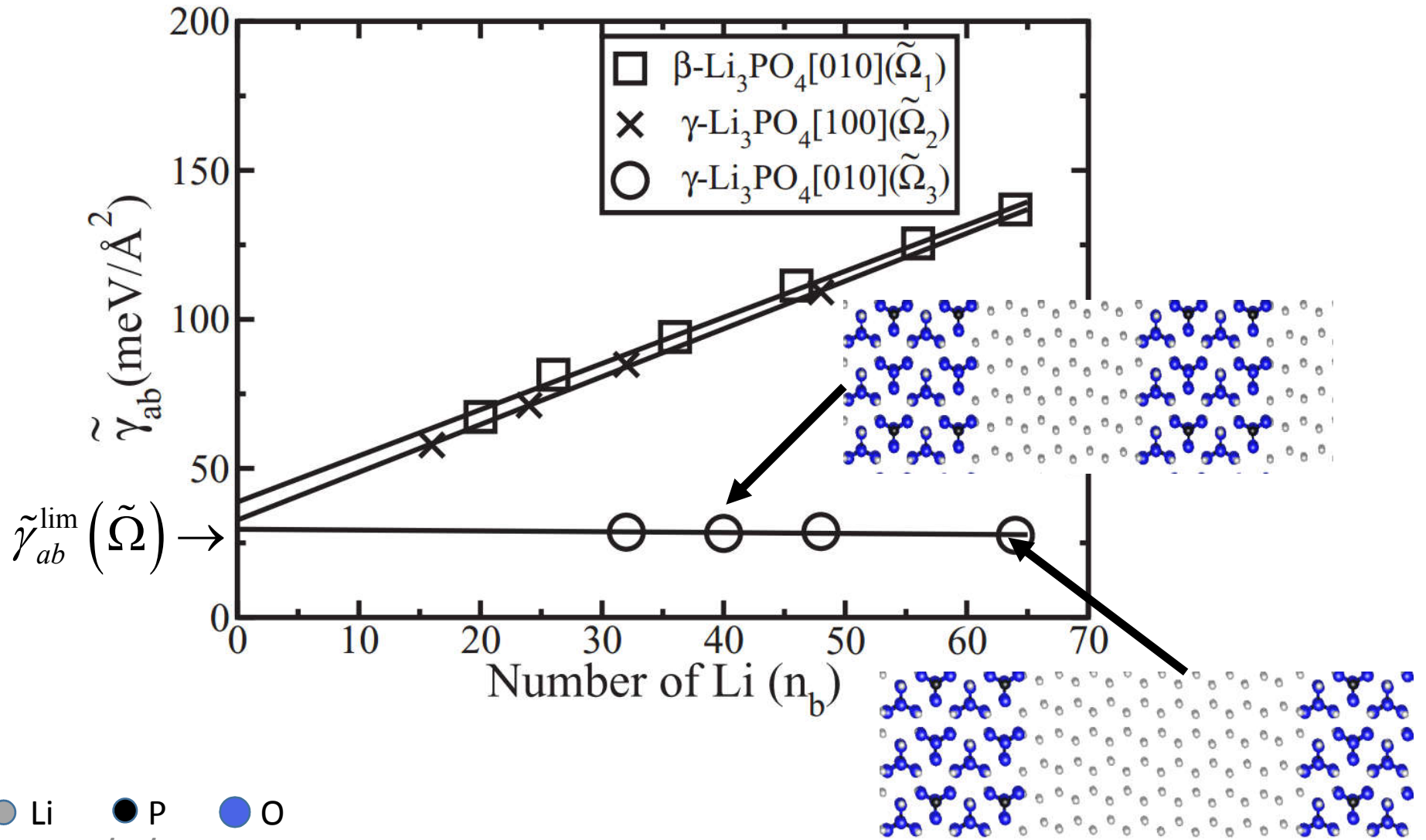
$$\Rightarrow \tilde{\gamma}_{ab}(\tilde{\Omega}, n_a, n_b) = \tilde{\gamma}_{ab}^{\text{lim}}(\tilde{\Omega}) + n_b \sigma$$

It is convenient to model the interface between a solid electrolyte and solid electrode in the slab geometry using a periodic simulation cell:



Lepley's linear equation for the interface

energy: $\tilde{\gamma}_{ab}(\tilde{\Omega}, n_a, n_b) = \tilde{\gamma}_{ab}^{\text{lim}}(\tilde{\Omega}) + n_b \sigma$



● Li ● P ● O

6/19/2017

SSI-21

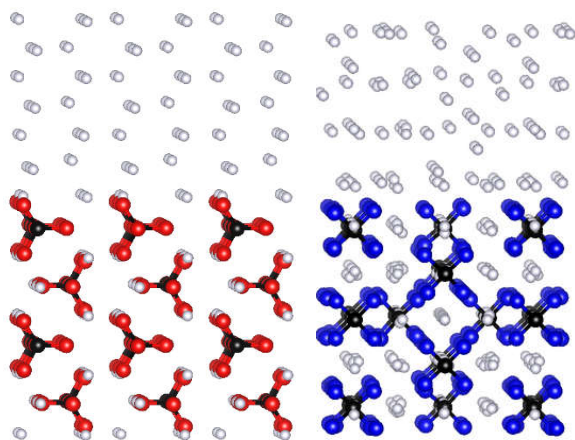
53

Some simulated interface energies

System	$\tilde{\gamma}_{ab}^{\text{lim}}(\tilde{\Omega})$ (eV/Å²)
$\beta\text{-Li}_3\text{PO}_4/\text{Li}$	0.04
$\gamma\text{-Li}_3\text{PO}_4/\text{Li}$	0.03
$\text{Li}_{14}\text{P}_2\text{O}_3\text{N}_6/\text{Li}$	0.05
$\text{Li}_7\text{PN}_4/\text{Li}$	0.04
$\text{Li}_2\text{O}/\text{Li}$	0.03
$\text{Li}_2\text{S}/\text{Li}$	0.02

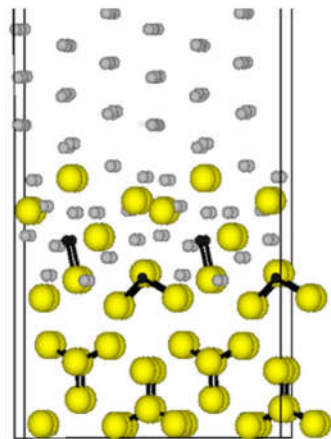
Summary of interface results

ideal



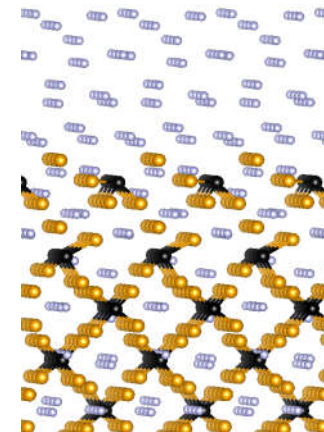
$\gamma\text{-Li}_3\text{PO}_4/\text{Li}$ $\text{Li}_7\text{PN}_4/\text{Li}$

finite



$\gamma\text{-Li}_3\text{PS}_4/\text{Li}$

reactive



$\text{Na}_3\text{SbS}_4/\text{Na}$

Thoughts on the role of simulations in developing battery technology

- Ideal research effort in materials includes close collaboration of both simulations and experimental measurements.
- For battery technology, there remain many opportunities for new materials development.