

First Principles Modeling of Electrolyte Materials in All-Solid-State Batteries*

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**With help from: Nicholas Lepley, Ahmad Al-Qawasmeh (graduate students), Cameron Kates (undergraduate student), Yaojun Du (previous physics postdoc) and colleagues from WFU chemistry department – Dr. Keerthi Senevirathne, Dr. Cynthia Day, Professor Michael Gross (visiting from Bucknell U.) and Professor Abdessadek Lachgar.

Outline

- **What is meant by “first principles”?**
 - **Computational methods & validation**
- **Why are we interested in solid electrolytes?**
- **How can “first principles” help?**
 - **Survey of known solid electrolytes**
 - **Prediction of new solid electrolytes**
 - **Study of electrolyte/electrode interfaces**
- **Remaining challenges**

➤ **What is meant by “first principles”?**

A series of well-controlled approximations

Summary of “first-principles” calculation methods

Exact Schrödinger equation:

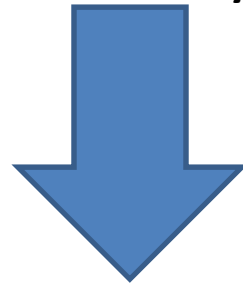
$$\mathcal{H}(\{\mathbf{r}_i\}, \{\mathbf{R}^a\}) \Psi_\alpha(\{\mathbf{r}_i\}, \{\mathbf{R}^a\}) = E_\alpha \Psi_\alpha(\{\mathbf{r}_i\}, \{\mathbf{R}^a\})$$

Electronic coordinates

Atomic coordinates

Born-Oppenheimer approximation

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



Approximate factorization:

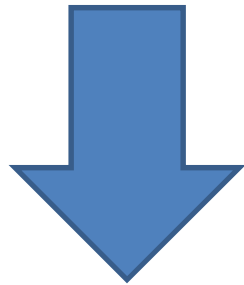
$$\Psi_\alpha(\{\mathbf{r}_i\}, \{\mathbf{R}^a\}) = X_\alpha^{\text{Nuclei}}(\{\mathbf{R}^a\}) \Upsilon_\alpha^{\text{Electrons}}(\{\mathbf{r}_i\}, \{\mathbf{R}^a\})$$

Summary of “first-principles” calculation methods -- continued

Electronic Schrödinger equation:

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

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



Density functional theory

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

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

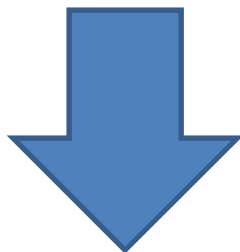
For electronic ground state: $\alpha \Rightarrow 0$

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

Electron
density

$$\mathcal{H}_{\text{KS}}^{\text{Electrons}}(\mathbf{r}, \rho(\mathbf{r}), \{\mathbf{R}^a\}) \psi_n(\mathbf{r}) = \varepsilon_n \psi_n(\mathbf{r}) \quad \rho(\mathbf{r}) = \sum_n |\psi_n(\mathbf{r})|^2$$

Summary of “first-principles” calculation methods -- continued



Nuclear Hamiltonian (usually treated classically)

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

Electron density

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

\Rightarrow Normal modes of vibration

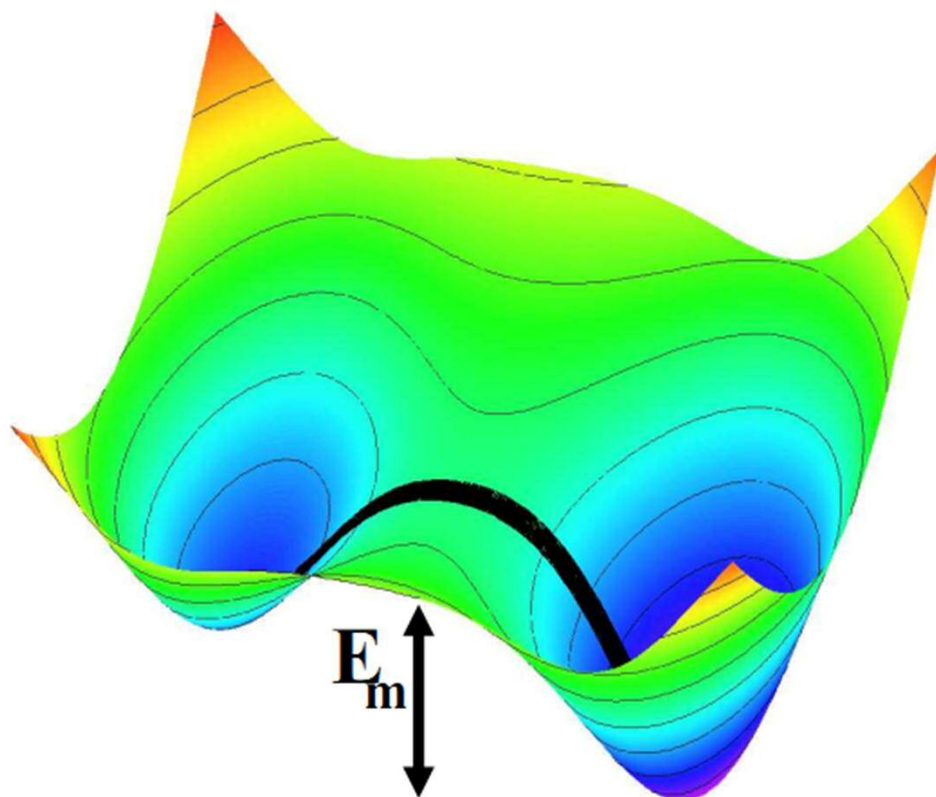
$$\rho(\mathbf{r}) = \sum_n |\psi_n(\mathbf{r})|^2 \Rightarrow \text{Self-consistent electron density}$$

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

Estimate of ionic conductivity assuming activated hopping

Schematic diagram of minimal energy path

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



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

Arrhenius relation

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

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

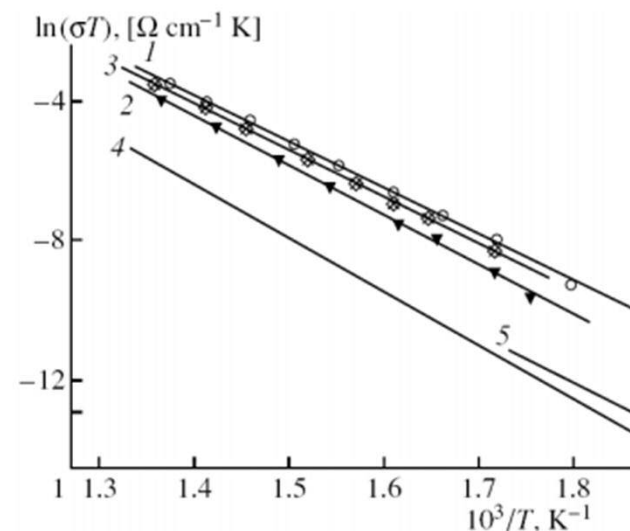


Fig. 2. Temperature dependences of conductivity in $\gamma\text{-Li}_3\text{PO}_4$: (1–3) for single crystals measured along the (1) *a*-axis, (2) *b*-axis, (3) *c*-axis and (4, 5) for a polycrystal (4) according to [4, 5] and (5) according to [7].

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

Public domain codes available for electronic structure calculations



Method	Codes	Comments
LAPW	www.wien2k.at elk.sourceforge.net	Works well for smaller unit cells; variable unit cell optimization not implemented. Need to choose non-overlapping muffin tin radii and avoid “ghost” solutions.
PAW	www.abinit.org www.quantum-espresso.org	Works well for large unit cells (<200 atoms or so); includes variable unit cell optimization.
ATOMPAW	pwpaw.wfu.edu	Generates PAW datasets for <i>abinit</i> and <i>quantum-espresso</i> (and other codes)

Other efforts:

- Gerbrand Ceder’s group at MIT – Materials Project; A Materials Genome Approach -- <http://www.materialsproject.org/>
- Stefano Curtarolo’s group at Duke – Energy Materials Laboratory -- <http://materials.duke.edu/>

ATOMPAW Code for generating atomic datasets for PAW calculations

Holzwarth, Tackett, and Matthews, CPC 135 329 (2001) <http://pwpaw.wfu.edu>

ATOMPAW

INFO

DATASETS

CONTRIBUTERS

CONTACT INFO

NAWH Web

PHYSICS Web

WFU Web

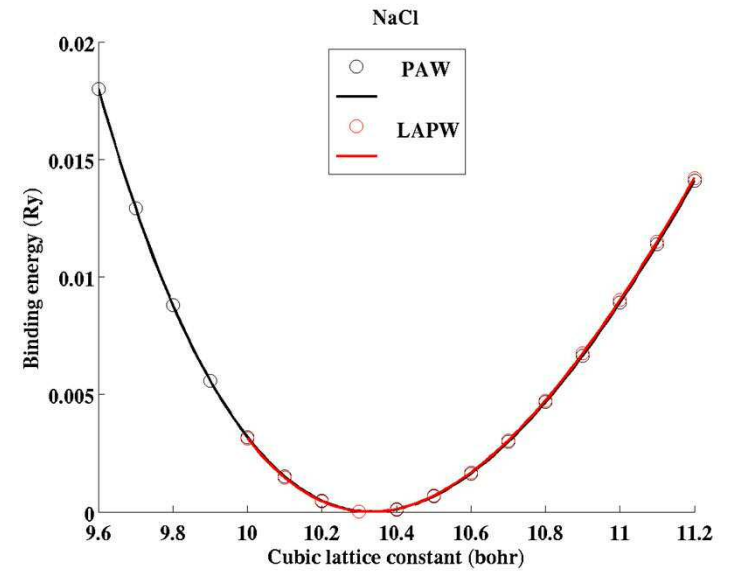
ATOMPAW

Download source code and example files:

- [atompaw-4.0.0.8.tar.gz](#) (5.4mb) [new version](#) atompaw code with solver and coretailpoints bugs corrected; updated version of xml interface (but not completely tested. (01/17/2014).
- [atompaw-3.1.0.3.tar.gz](#) (3.8mb) Updated version of *atompaw* code (01/03/2014 and 09/18/2013 -- Marc Torrent and Francois Jollet introduced improvements to the XML and abinit dataset generation routines; 07/09/2013 -- Marc Torrent introduced small corrections; 06/22/2013 -- Marc Torrent and Francois Jollet added a new option for outputting a file in XML format according to the specifications set up by the [GPAW group](#). The output file format is controled by a menu at the end of the dataset: 2 for standard abinit output, 3 for quantum-espresso (UPF) output, 4 for XML output.) (Older changes: 09/20/2012 -- Yann Pouillon updated the autotools for constructing the tar file; 07/16/2012 -- Geoffrey Pourois corrected GIPAW portion of

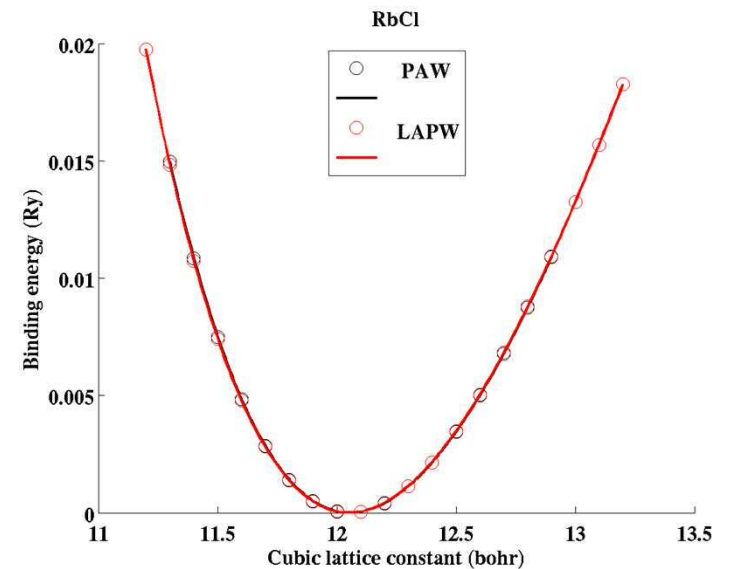
"Small Core" Datasets for PAW Functions

<u>1</u> H																	2 He
<u>3</u> Li	<u>4</u> Be											5 B	6 C	7 N	8 O	9 F	10 Ne
<u>11</u> Na	<u>12</u> Mg											<u>13</u> Al	14 Si	15 P	16 S	17 Cl	18 Ar
<u>19</u> K	<u>20</u> Ca	<u>21</u> Sc	<u>22</u> Ti	<u>23</u> V	<u>24</u> Cr	<u>25</u> Mn	<u>26</u> Fe	<u>27</u> Co	<u>28</u> Ni	<u>29</u> Cu	<u>30</u> Zn	<u>31</u> Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
<u>37</u> Rb	<u>38</u> Sr	<u>39</u> Y	<u>40</u> Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	<u>50</u> Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn



"Large Core" Datasets for PAW Functions

1 H																	2 He
3 Li	4 Be											<u>5</u> B	<u>6</u> C	<u>7</u> N	<u>8</u> O	<u>9</u> F	10 Ne
11 Na	12 Mg											<u>13</u> Al	<u>14</u> Si	<u>15</u> P	<u>16</u> S	<u>17</u> Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	<u>33</u> As	<u>34</u> Se	<u>35</u> Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn








Example validation of computation methods

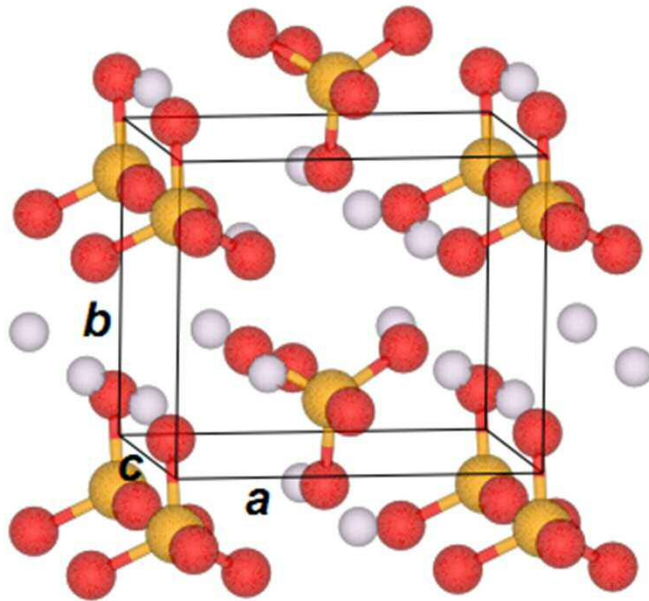
Li₃PO₄ crystals

γ -Li₃PO₄

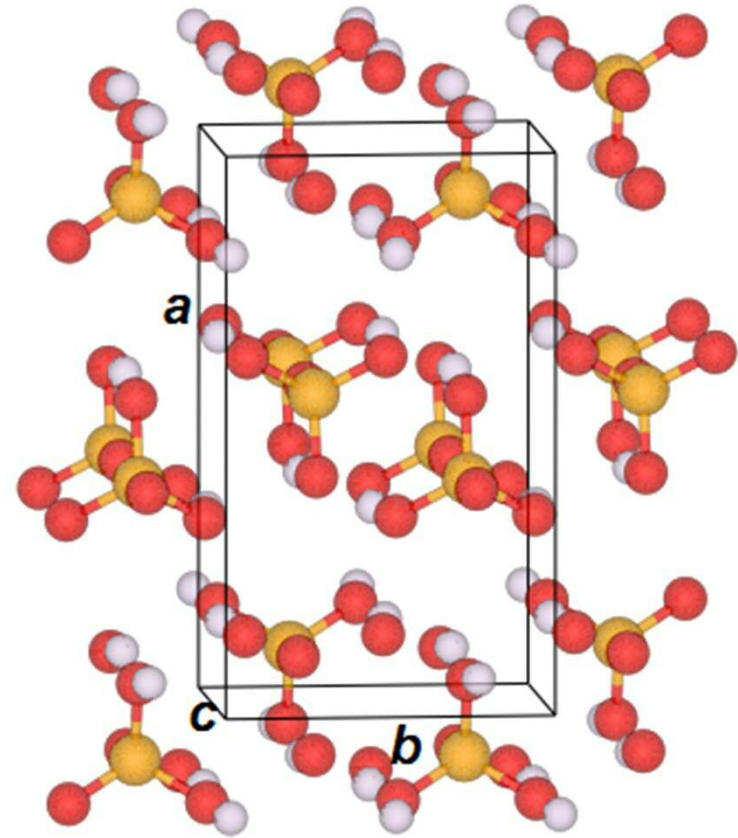
Key

-  Li
-  N
-  O
-  P
-  S

β -Li₃PO₄



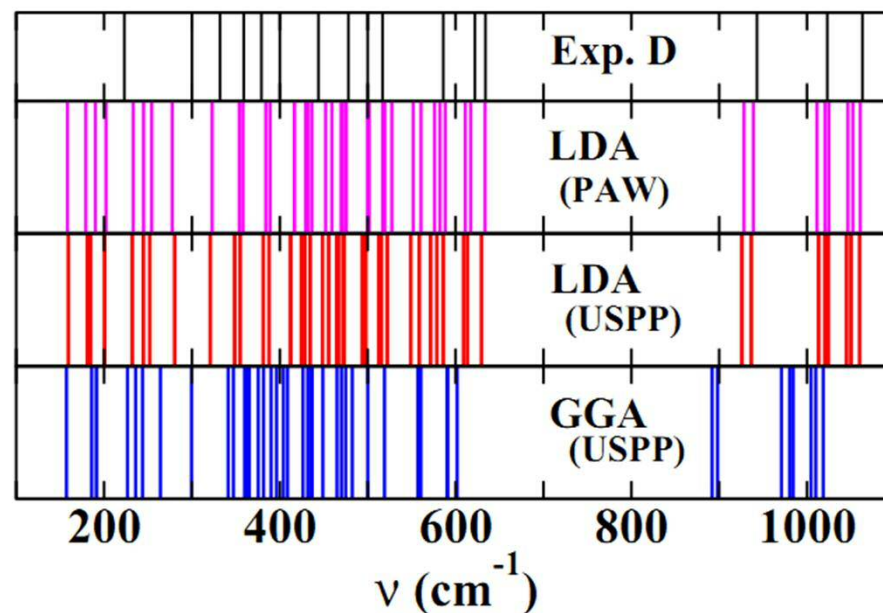
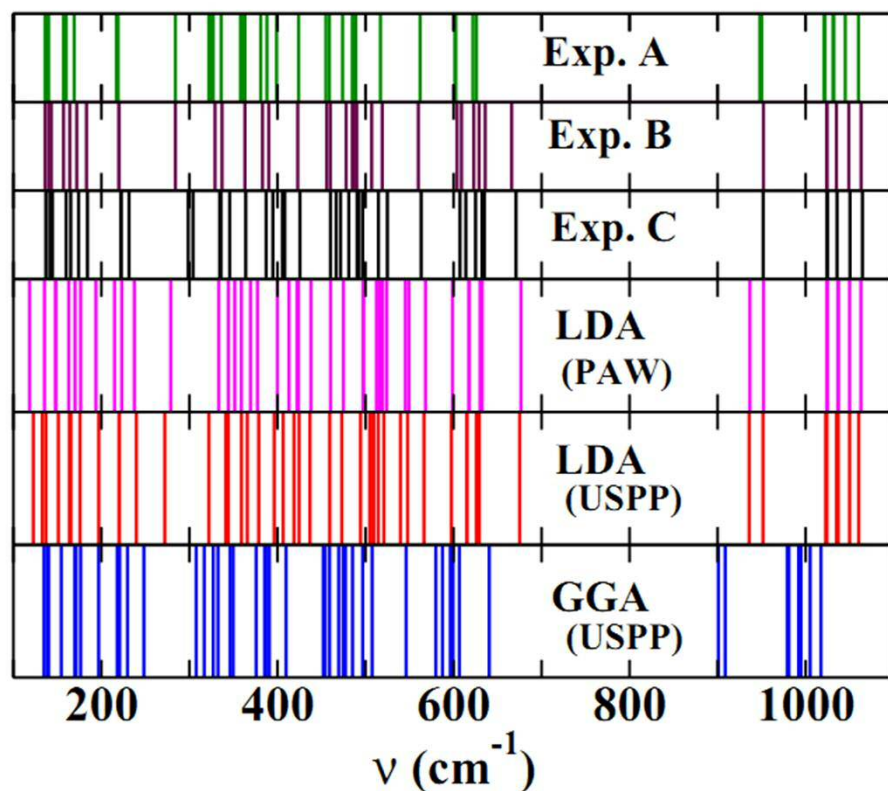
(*Pmn*2₁)



(*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).

➤ What is meant by “first principles”?

A series of well-controlled approximations

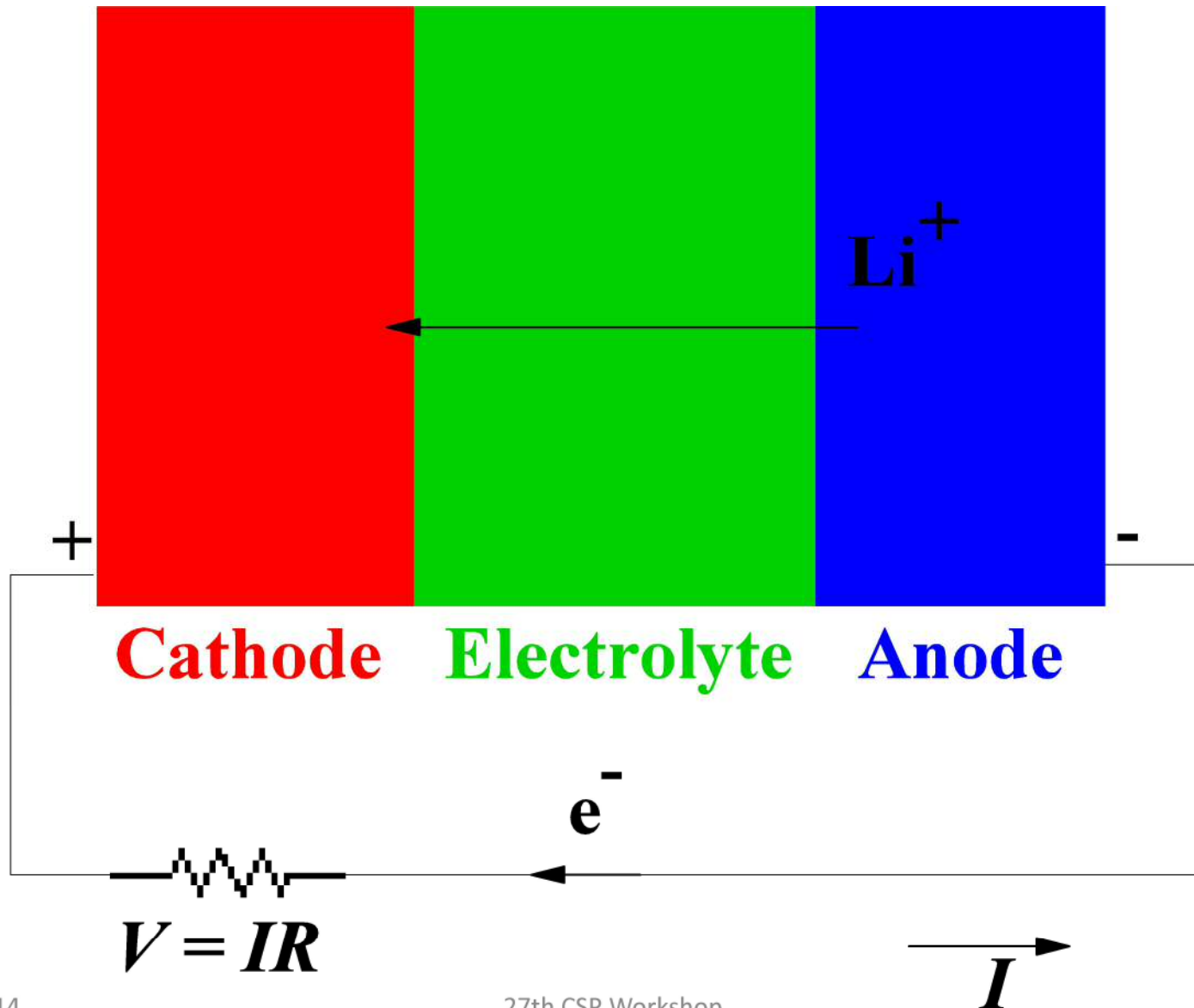
- Born-Oppenheimer Approximation
- Density Functional Approximation
- Local density Approximation (LDA)
- Numerical method: Projector Augmented Wave

Validation

- Lattice vibration modes
- Heats of formation
- Activation energies for lattice migration

➤ What is the interest in solid electrolytes?

Materials components of a Li ion battery



Example: Thin-film battery developed by Nancy Dudney and collaborators at Oak Ridge National Laboratory – **LiPON** (lithium phosphorus oxinitride)

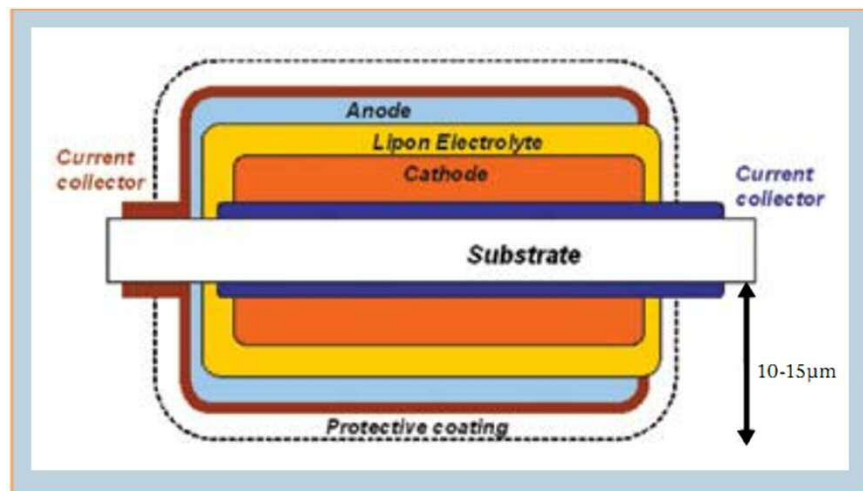


FIG. 1. Schematic cross section of a thin film battery fabricated by vapor deposition onto both sides of a substrate support.

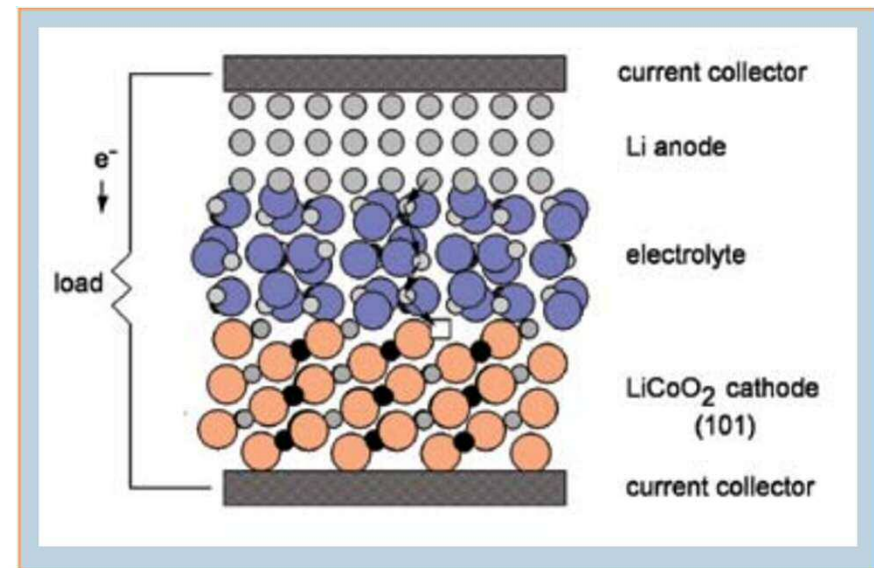


FIG. 2. Schematic illustration of a thin film battery. The arrows indicate the discharge reaction where a Li ion diffuses from the lithium metal anode to fill a vacancy in an intercalation compound that serves as the cathode. The compensating electron is conducted through the device.

From: N. J. Dudney, *Interface* **77**(3) 44 (2008)

Solid vs liquid electrolytes in Li ion batteries

Solid electrolytes

Advantages

1. Excellent chemical and physical stability.
2. Perform well as thin film ($\approx 1\mu$)
3. Li^+ conduction only (excludes electrons).

Disadvantages

1. Reduced contact area for high capacity electrodes.
2. Interface stress due to electrode charging and discharging.
3. Relatively low ionic conductivity.

Liquid electrolytes

Advantages

1. Excellent contact area with high capacity electrodes.
2. Can accommodate size changes of electrodes during charge and discharge cycles.
3. Relatively high ionic conductivity.

Disadvantages

1. Relatively poor physical and chemical stability.
2. Relies on the formation of “solid electrolyte interface” (SEI) layer.
3. May have both Li^+ and electron conduction.

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

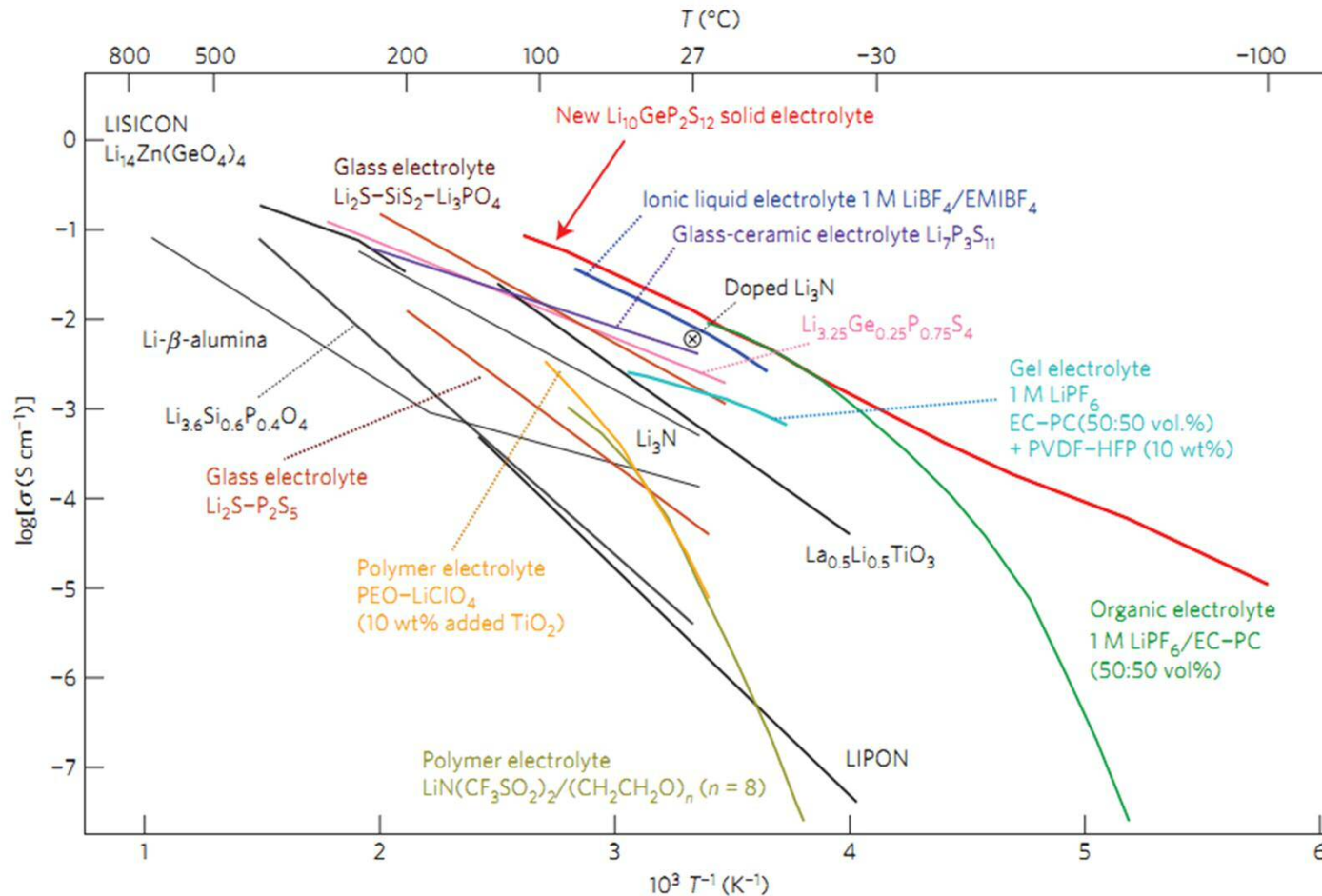


Figure 3 | Thermal evolution of ionic conductivity of the new $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ phase, together with those of other lithium solid electrolytes, organic liquid electrolytes, polymer electrolytes, ionic liquids and gel electrolytes^{3-8,13-16,20,22}. The new $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ exhibits the highest lithium ionic conductivity (12 m S cm⁻¹ at 27 °C) of the solid lithium conducting membranes of inorganic, polymer or composite systems. Because organic electrolytes usually have transport numbers below 0.5, inorganic lithium electrolytes have extremely high conductivities.

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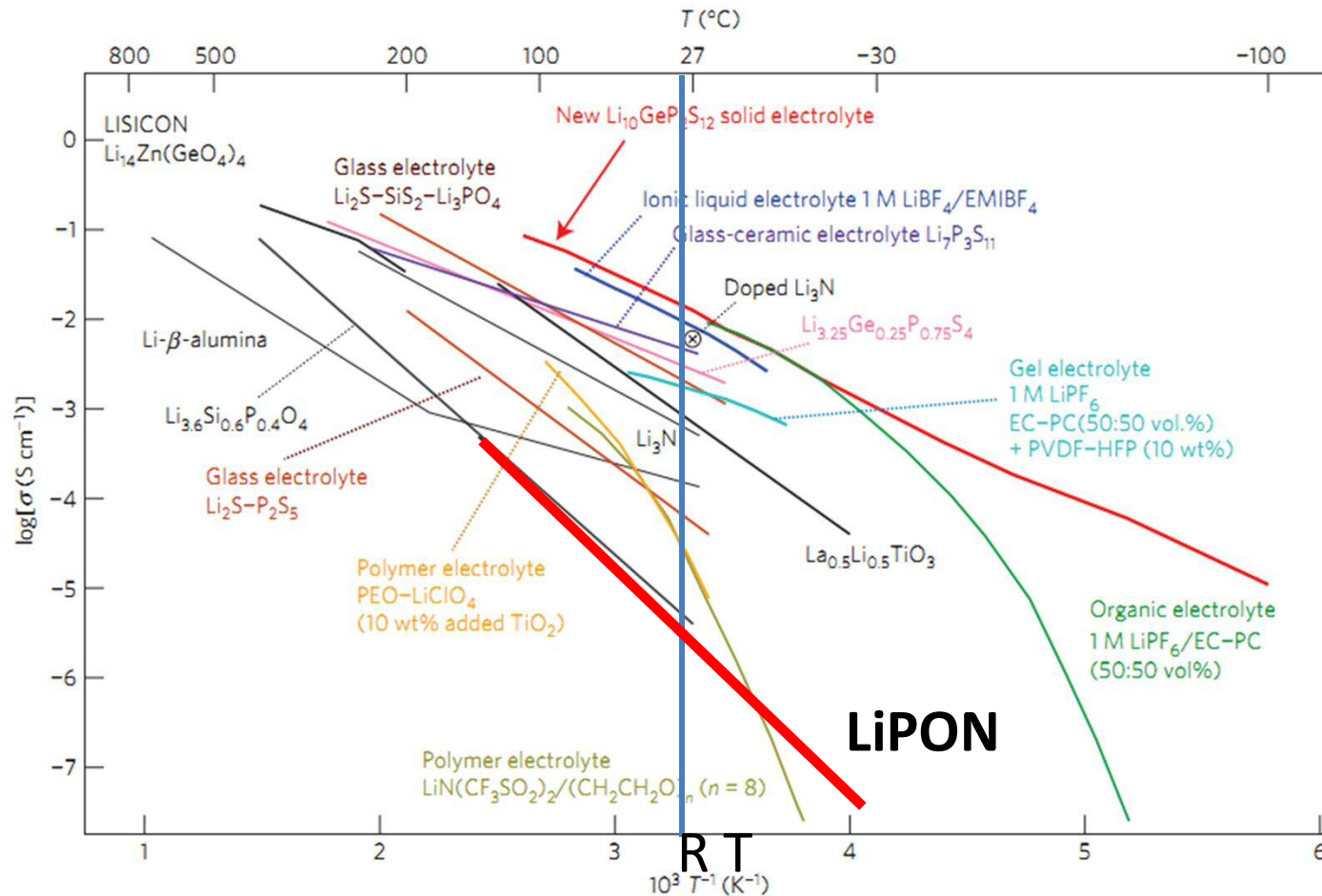


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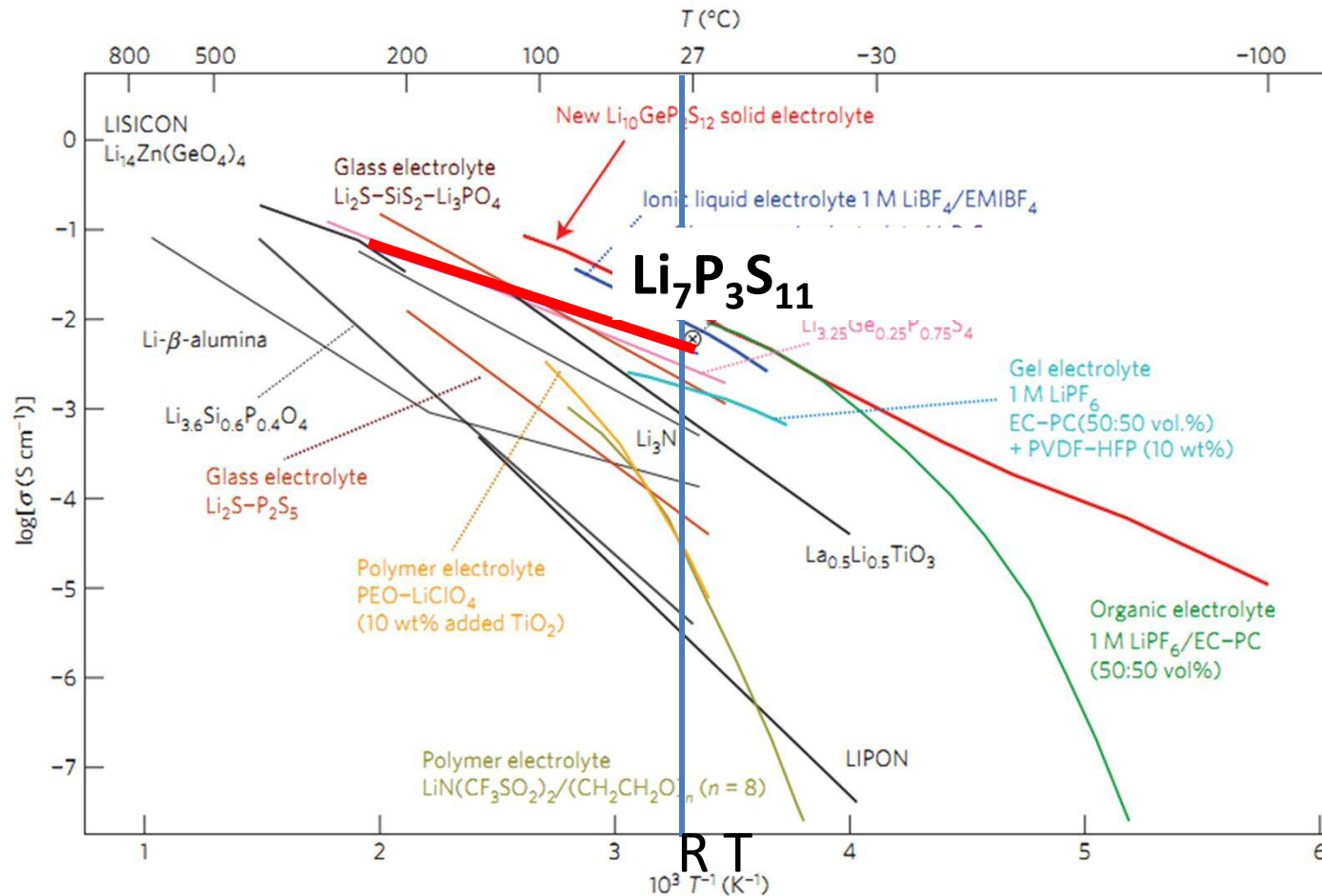


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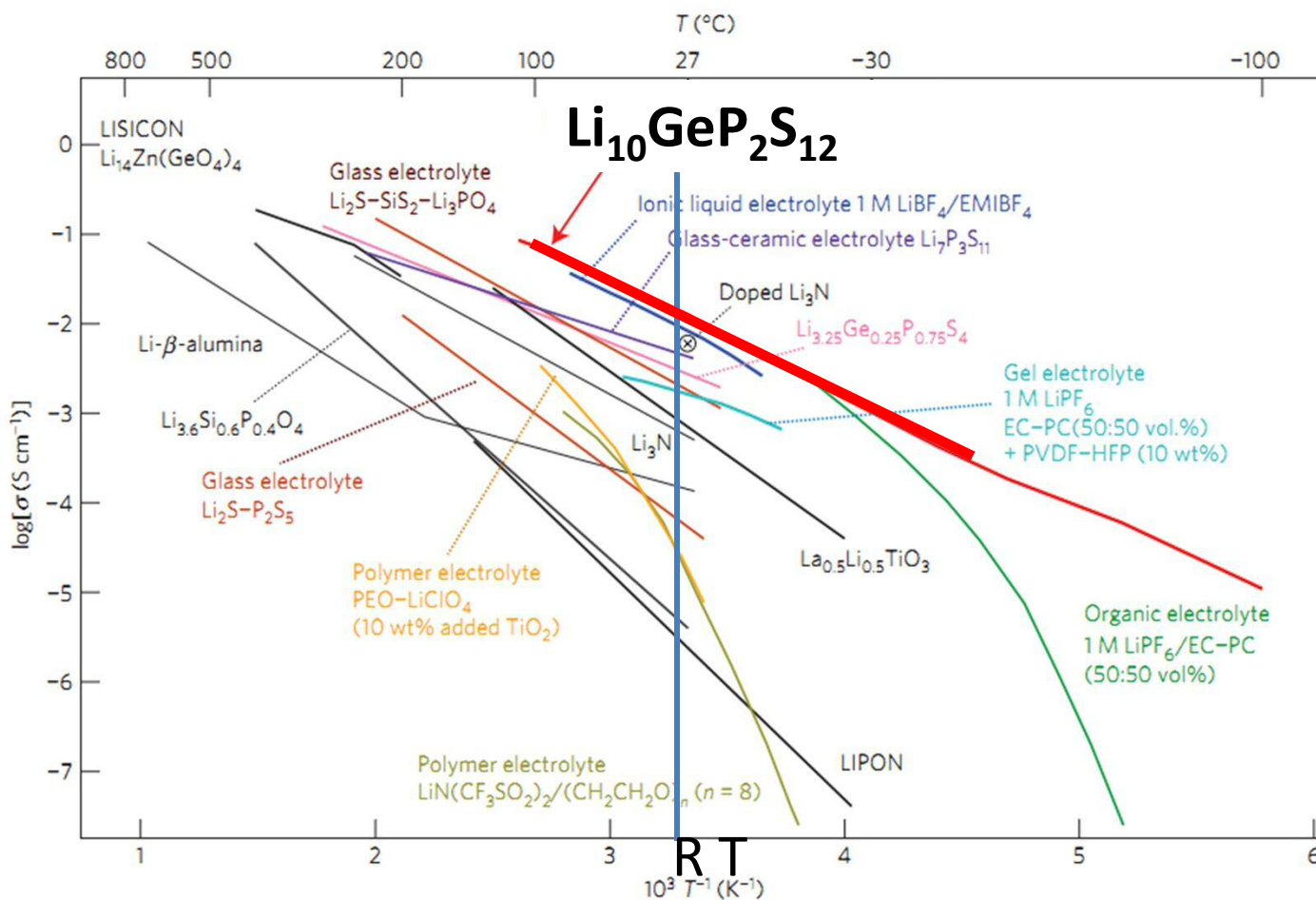


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How can computer simulations contribute to the development of materials?

- Examine known materials and predict new materials
 - Structural forms
 - Relative stabilities
 - Analyze vibrational modes and other experimentally accessible properties
- Model ion migration mechanisms
 - Vacancy migration
 - Interstitial migration
 - Vacancy-interstitial formation energies

The $\text{Li}_2\text{PO}_2\text{N}$ story

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))

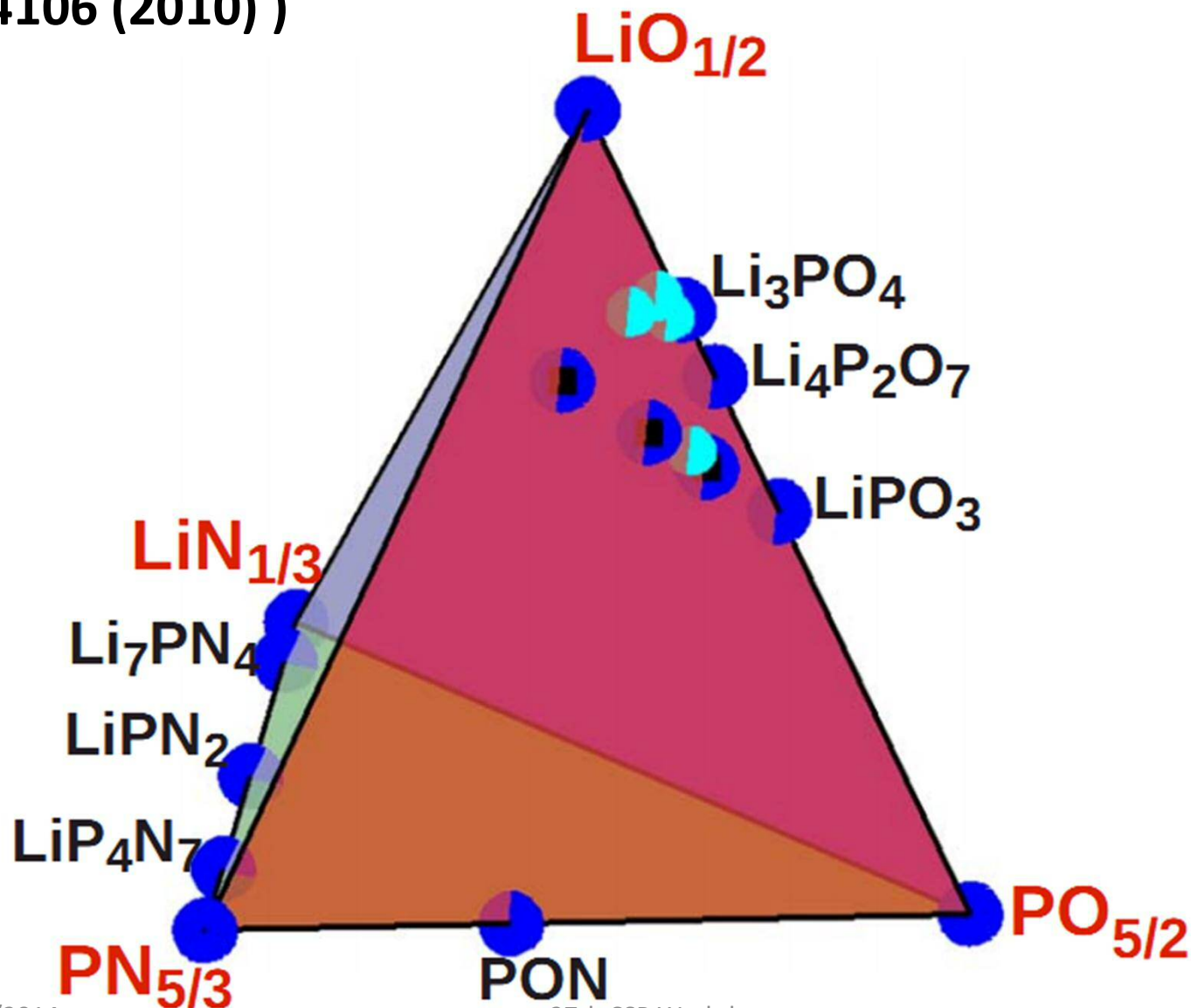


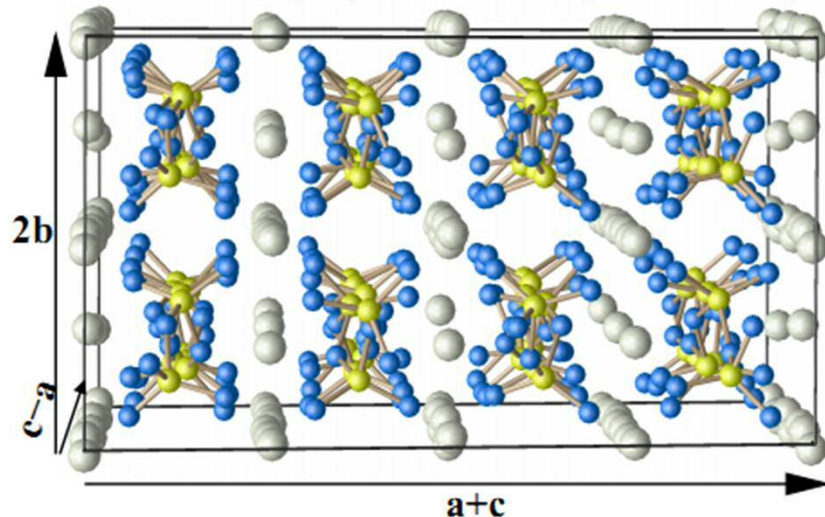
Table 1. Calculated heats of formation for Li phosphates, phospho-nitrides, and thiophosphates and related materials. The structural designation uses the the notation defined in the International Table of Crystallography⁸⁵ based on structural information reported in the International Crystal Structure 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>P</i> 6 ₃ / <i>m</i> <i>m</i> <i>c</i> (#194)	- 0.94 (- 0.45*)
γ -Li ₃ PO ₄	<i>Pnma</i> (#62)	-21.20 (-21.72*)	P ₃ N ₅	<i>C</i> 2/ <i>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>R</i> 3 <i>c</i> (#161)	-15.45 (-15.53*)
β -Li ₃ PS ₄	<i>Pnma</i> (#62)	- 8.28	<i>o</i> -P ₂ O ₅	<i>F</i> dd2 (#43)	-15.78
Li ₄ P ₂ O ₆	<i>P</i> $\bar{3}$ 1 <i>m</i> (#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>P</i> 6/ <i>m</i> <i>m</i> <i>m</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>P</i> 6 ₃ / <i>m</i> <i>m</i> <i>c</i> (#194)	- 6.35 (- 6.57*)
Li ₇ P ₃ S ₁₁	<i>P</i> $\bar{1}$ (#2)	-20.01	Li ₃ P	<i>P</i> 6 ₃ / <i>m</i> <i>m</i> <i>c</i> (#194)	- 3.47
LiPO ₃	<i>P</i> 2/ <i>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>P</i> 6 ₃ / <i>m</i> <i>m</i> <i>c</i> (#194)	- 4.09
<i>s</i> 1-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>P</i> 2 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			

Phosphate chain materials: LiPO_3 plus N

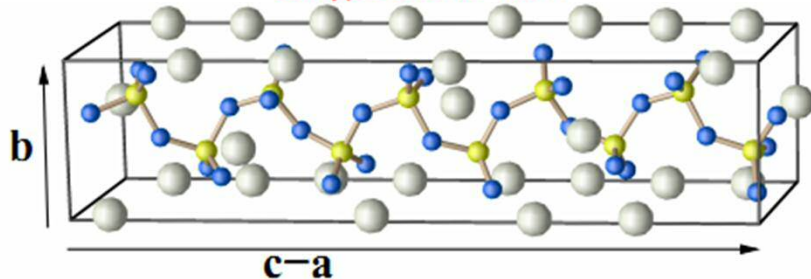
LiPO_3 in $P2/c$ structure; 100 atom unit cell

Chain direction perpendicular to plane of diagram



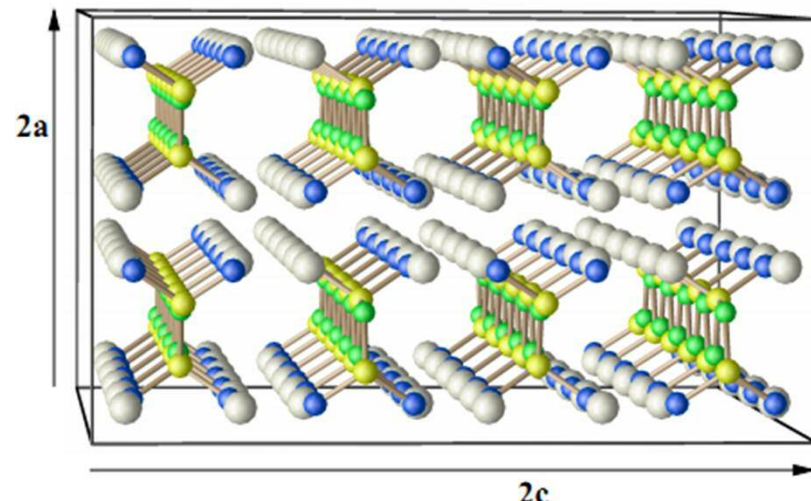
Ball colors: \bullet = Li, \bullet = P, \bullet = O.

Single chain view



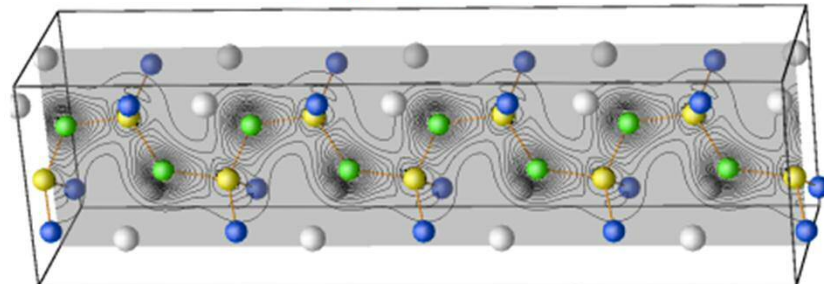
$s_1\text{-Li}_2\text{PO}_2\text{N}$ in $Pbcm$ structure; 24 atom unit cell

Chain direction perpendicular to plane of diagram

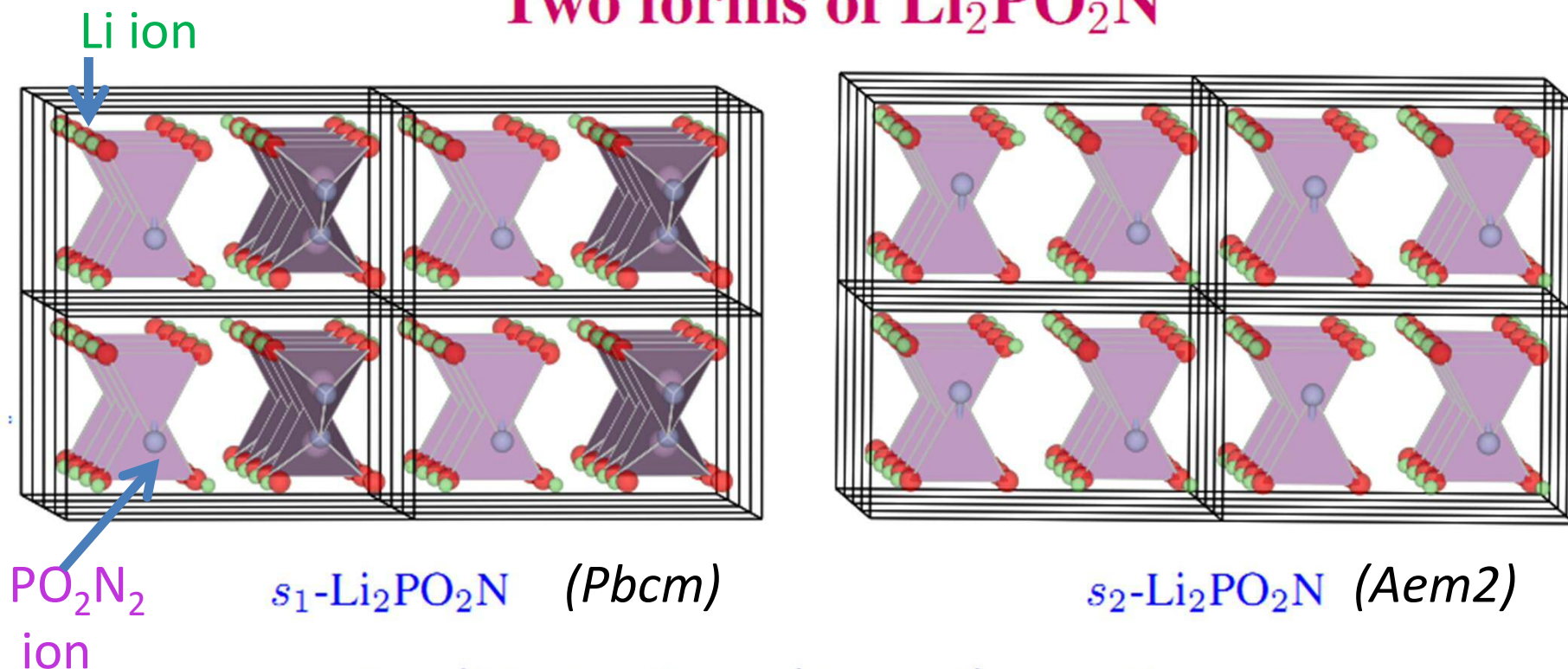


Ball colors: \bullet = Li, \bullet = P, \bullet = O, \bullet = N.

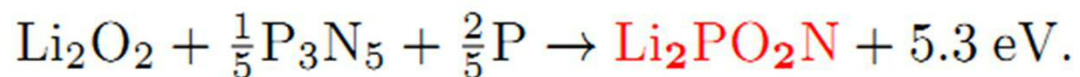
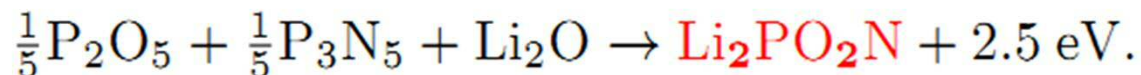
Single chain view



Two forms of $\text{Li}_2\text{PO}_2\text{N}$



Possible exothermic reaction pathways:



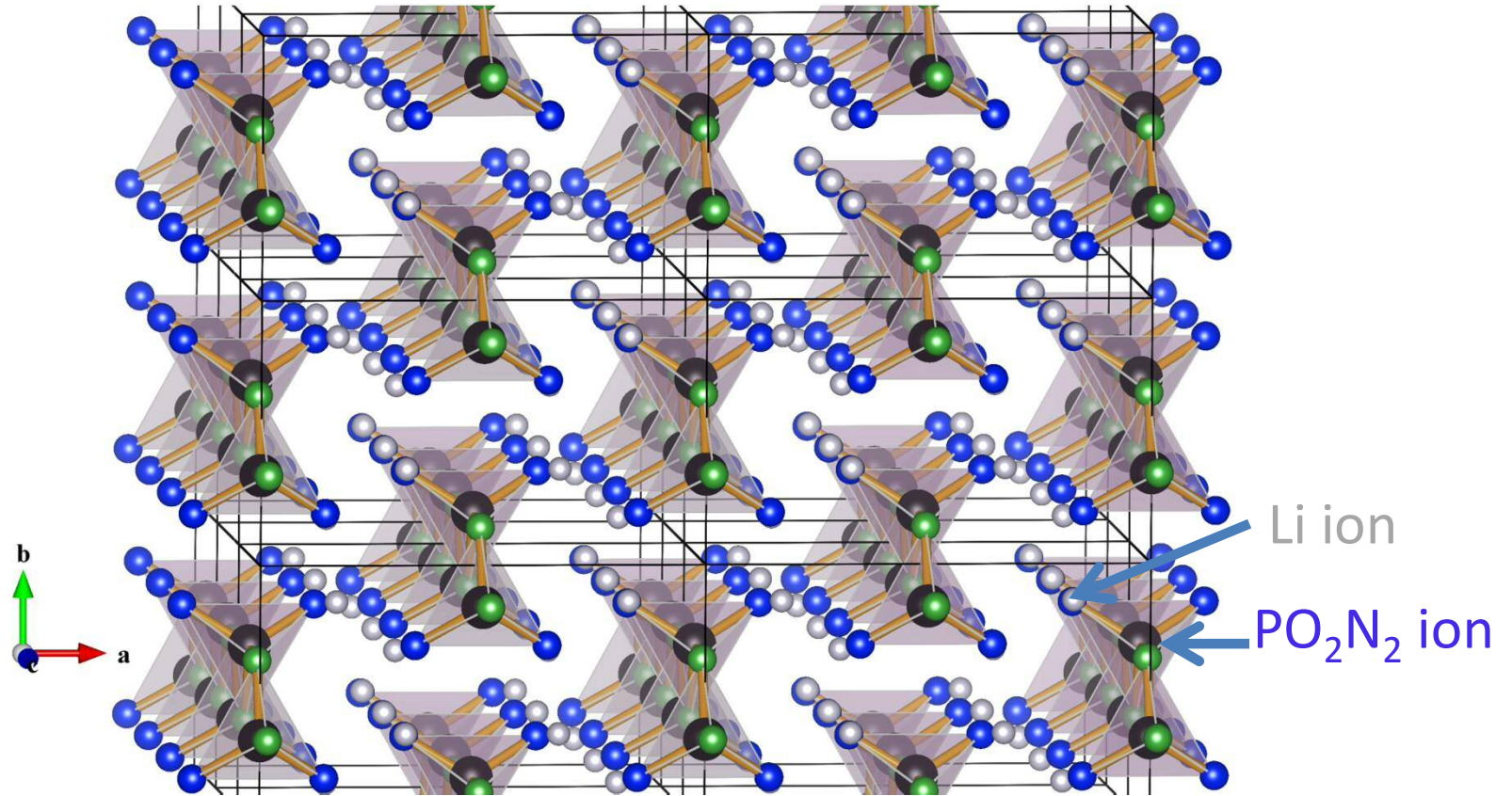
Synthesis of $\text{Li}_2\text{PO}_2\text{N}$ by Keerthi Senevirathne, Cynthia Day, Michael Gross, and Abdessadek Lachgar

Method: High temperature solid state synthesis based on reaction

$$\text{Li}_2\text{O} + \frac{1}{5}\text{P}_2\text{O}_5 + \frac{1}{5}\text{P}_3\text{N}_5 \rightarrow \text{Li}_2\text{PO}_2\text{N}$$

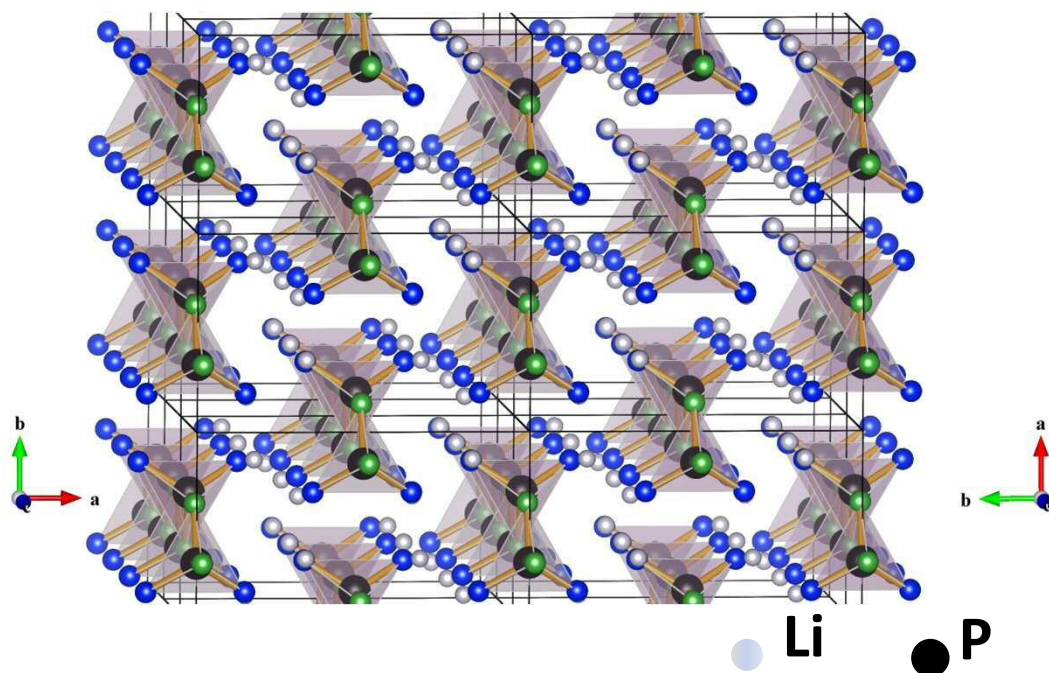
Structure from X-ray refinement: $\text{Cmc}2_1$

● Li ● P ● O ● N



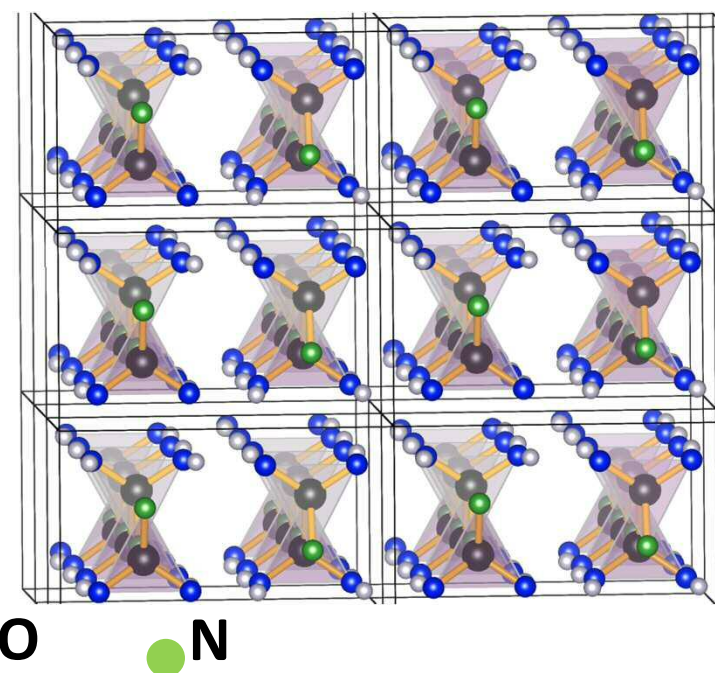
Comparison of synthesized and predicted structures of $\text{Li}_2\text{PO}_2\text{N}$:

Synthesized



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

Predicted

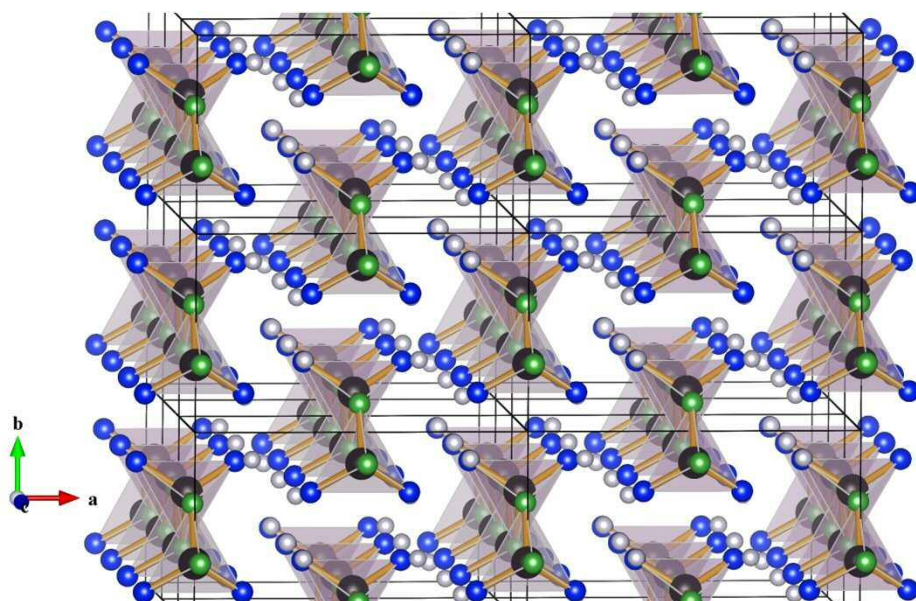


$s_2\text{-Li}_2\text{PO}_2\text{N}$ ($Aem2$)

Calculations have now verified that the SD structure is more stable than the s_2 structure by 0.1 eV/FU.

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

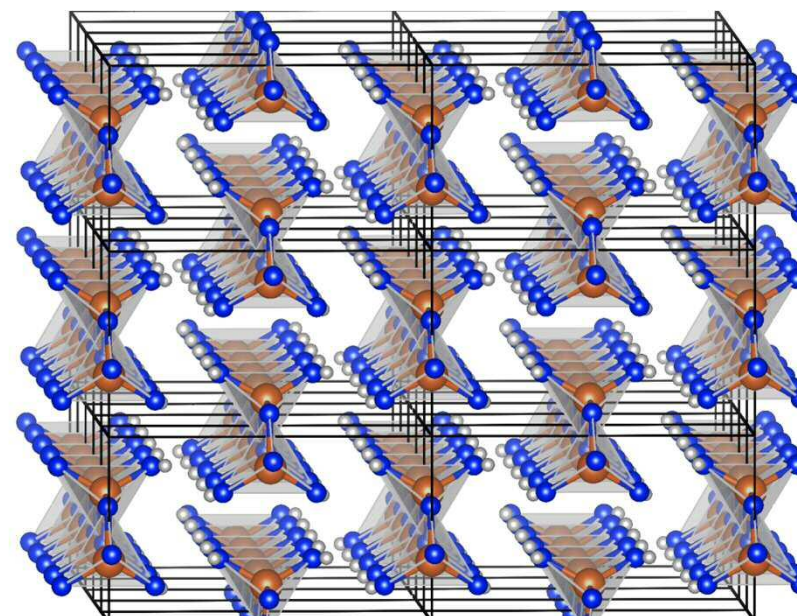
$\text{SD-Li}_2\text{PO}_2\text{N}$ ($Cmc2_1$)



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



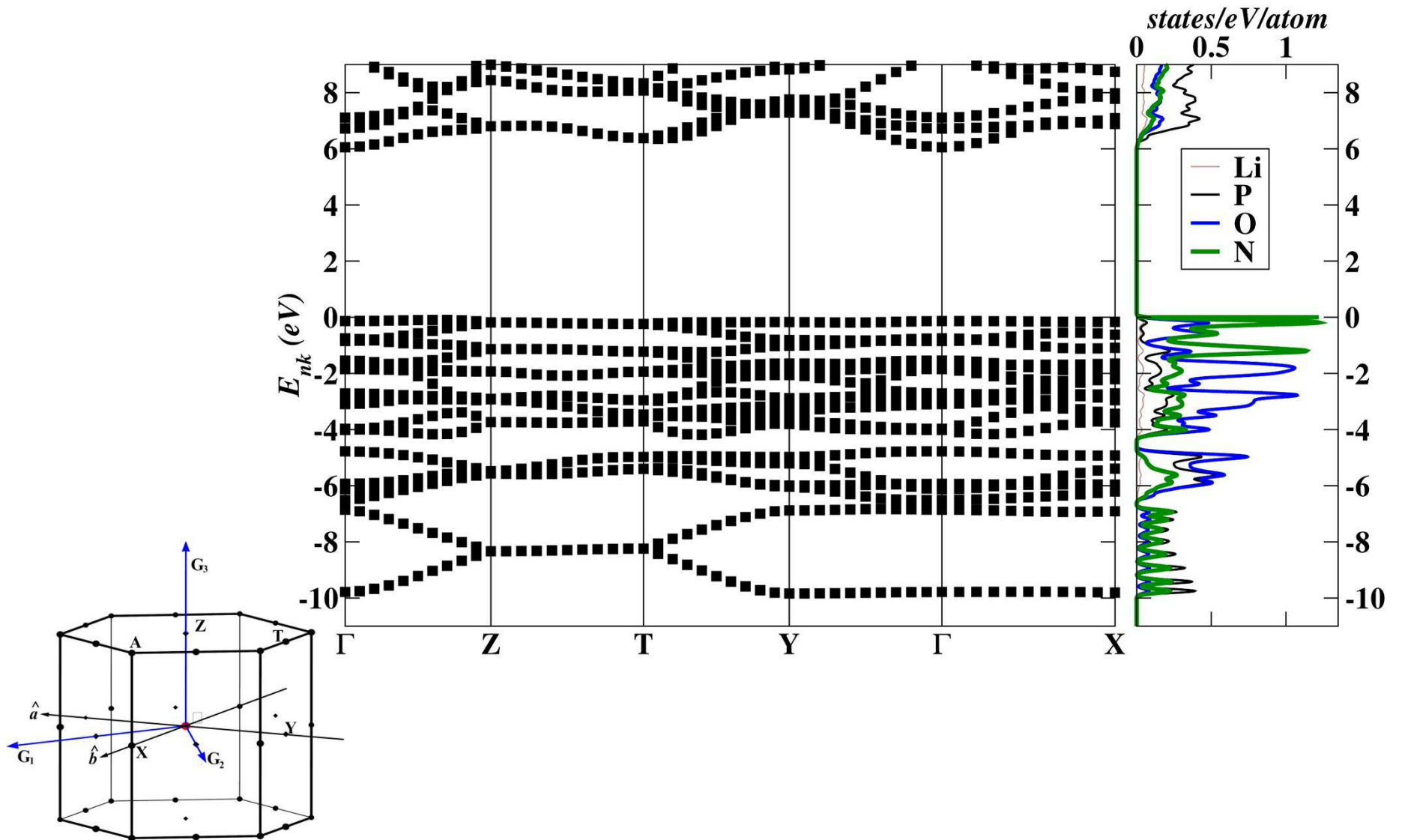
Li_2SiO_3 ($Cmc2_1$)



$a=9.39 \text{ \AA}$, $b=5.40 \text{ \AA}$, $c=4.66 \text{ \AA}$

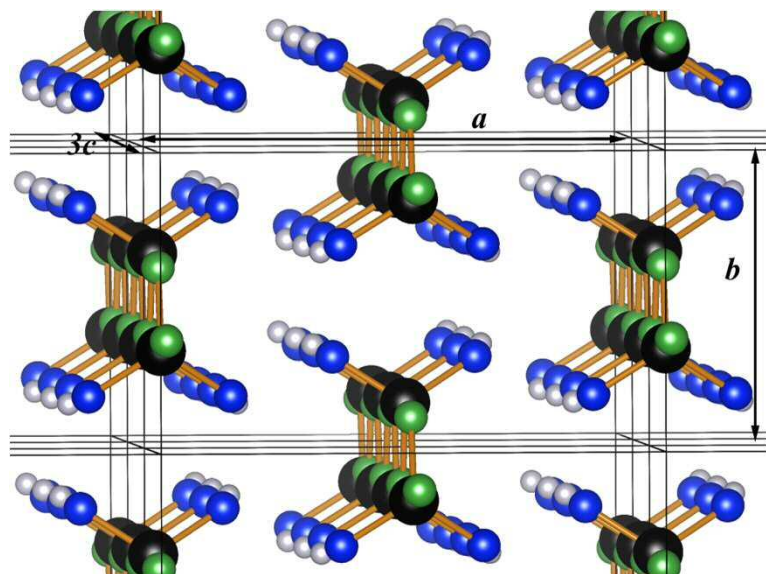
K.-F. Hesse, Acta Cryst. B33, 901 (1977)

Electronic band structure of $SD\text{-Li}_2\text{PO}_2\text{N}$

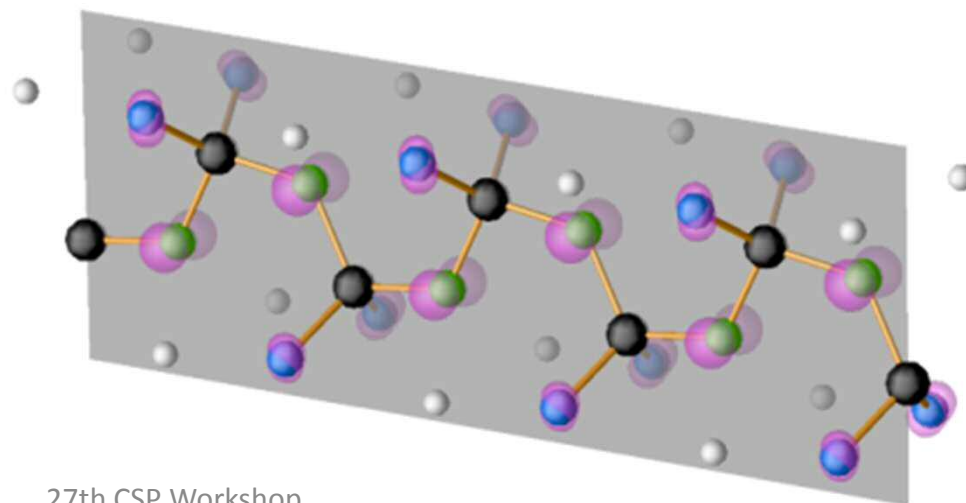
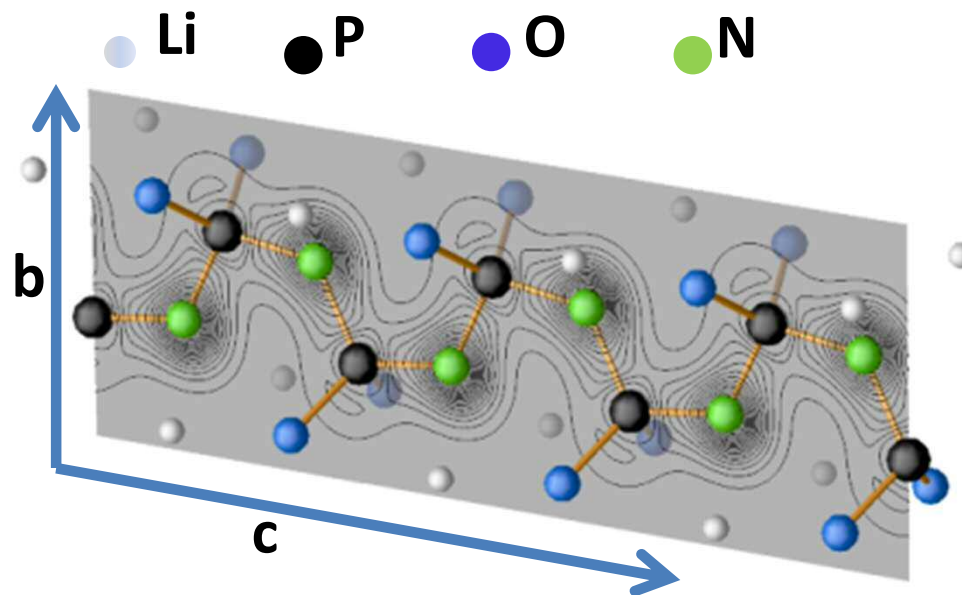


More details of *SD*-Li₂PO₂N structure

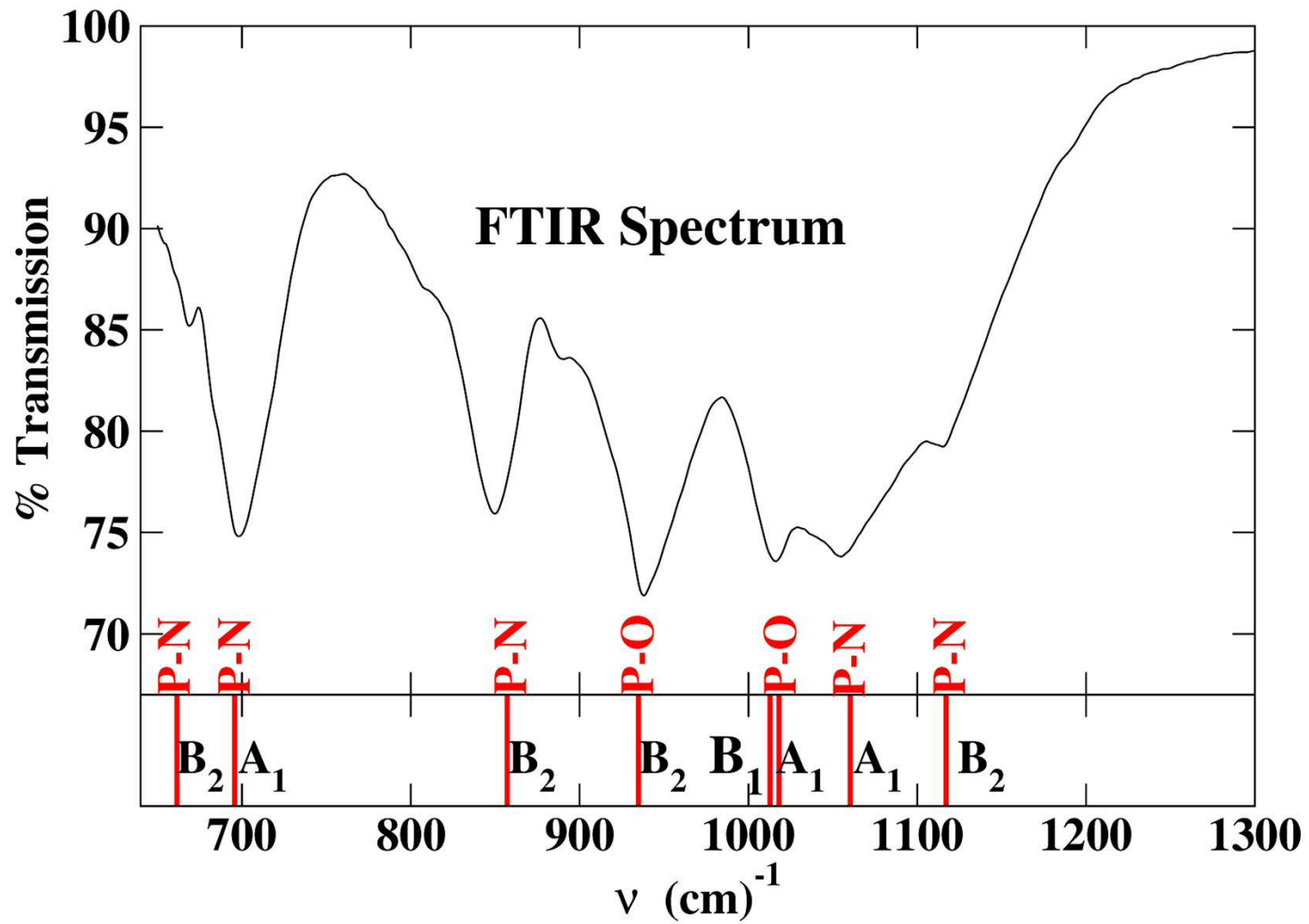
Ball and stick model



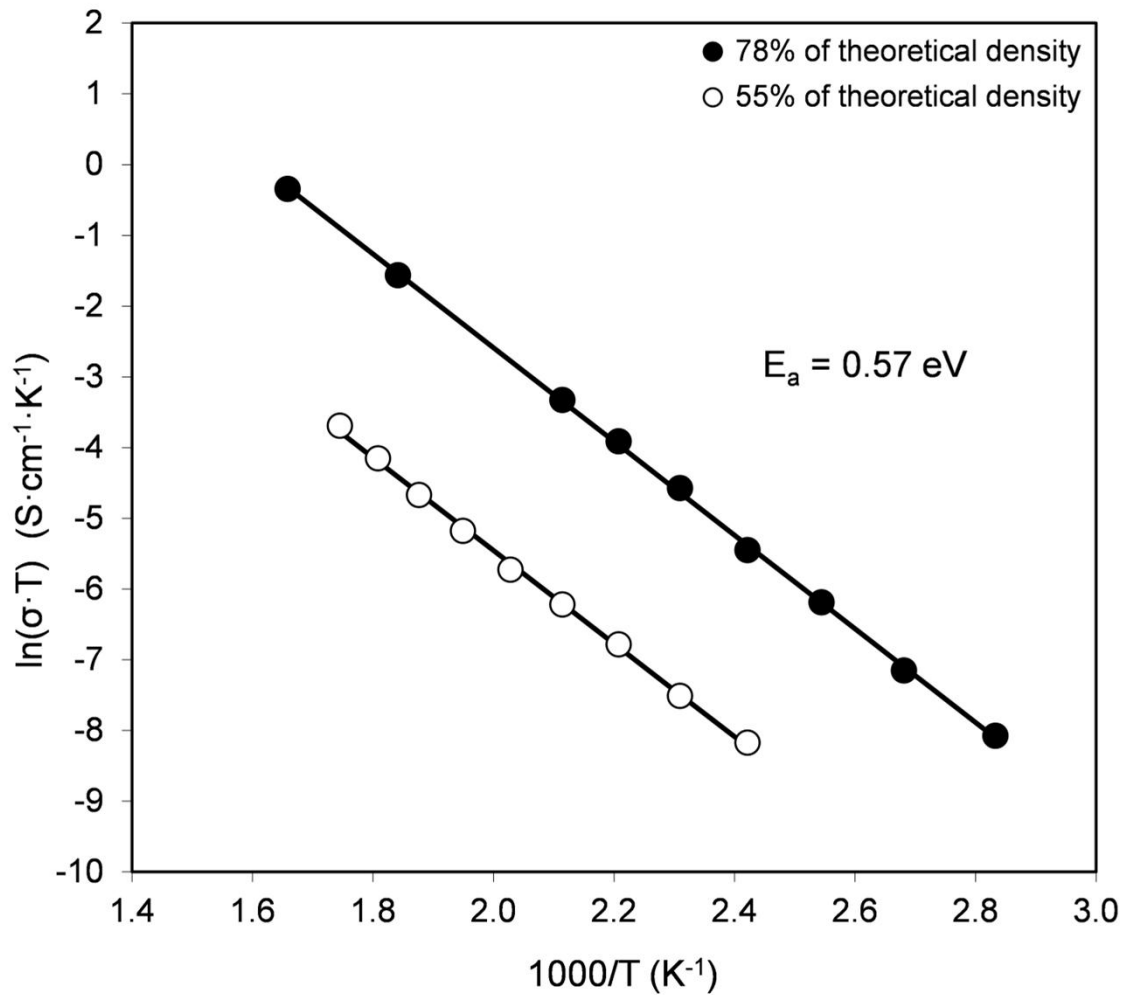
Isosurfaces (maroon) of charge density of states at top of valence band, primarily π states on N.



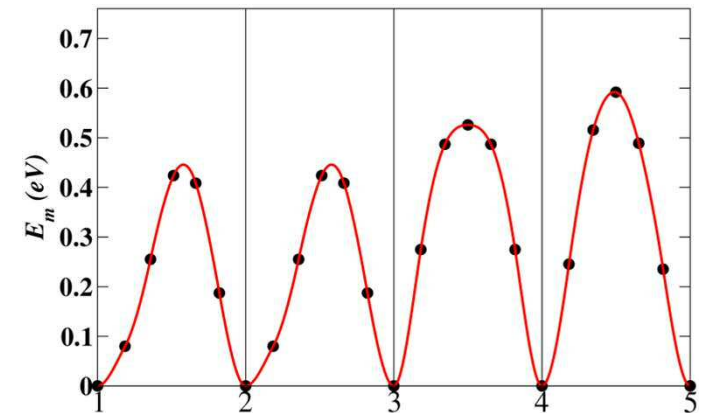
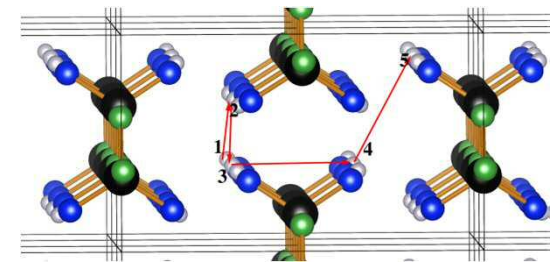
Vibrational spectrum of $SD\text{-Li}_2\text{PO}_2\text{N}$



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



NEB analysis of E_m (vacancy mechanism)



Summary of the $\text{Li}_2\text{PO}_2\text{N}$ story

- ❑ Predicted on the basis of first principles theory
- ❑ Subsequently, experimentally realized by Keerthi Seneviranthe and colleagues; generally good agreement between experiment and theory
- ❑ Ion conductivity properties not (yet) competitive

Simulations of other solid electrolytes and electrolyte/electrode interfaces

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^{*,†}

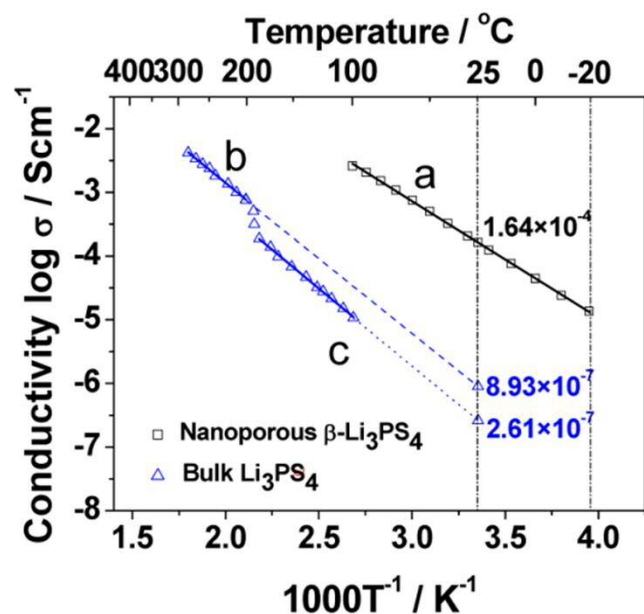


Figure 1. Arrhenius plots for nanoporous $\beta\text{-Li}_3\text{PS}_4$ (line a), bulk $\beta\text{-Li}_3\text{PS}_4$ (line b), and bulk $\gamma\text{-Li}_3\text{PS}_4$ (line c). The conductivity data for bulk Li_3PS_4 are reproduced from the work of Tachez.¹⁰

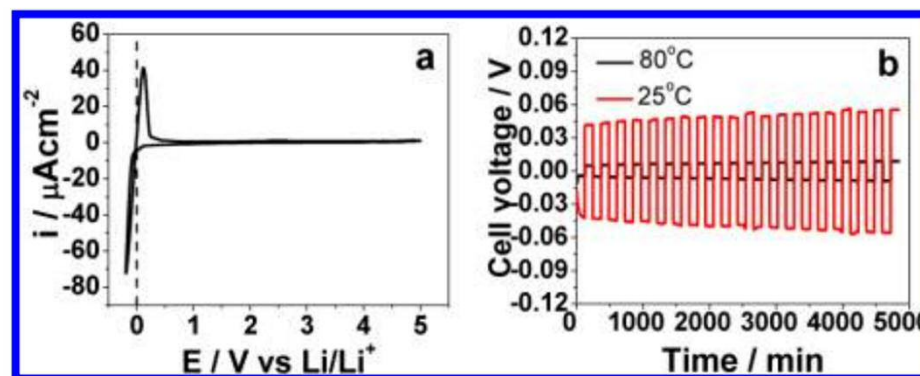
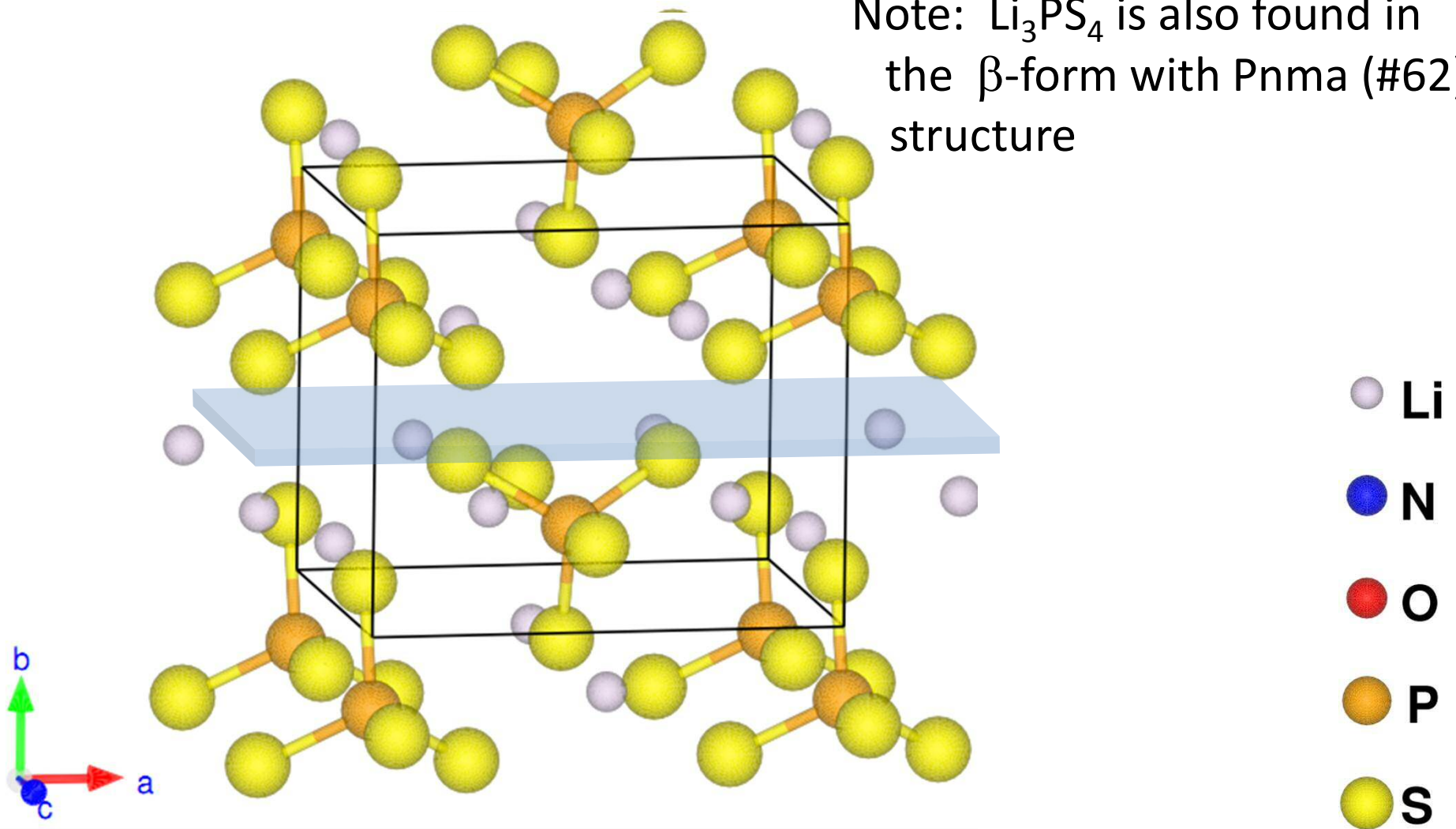


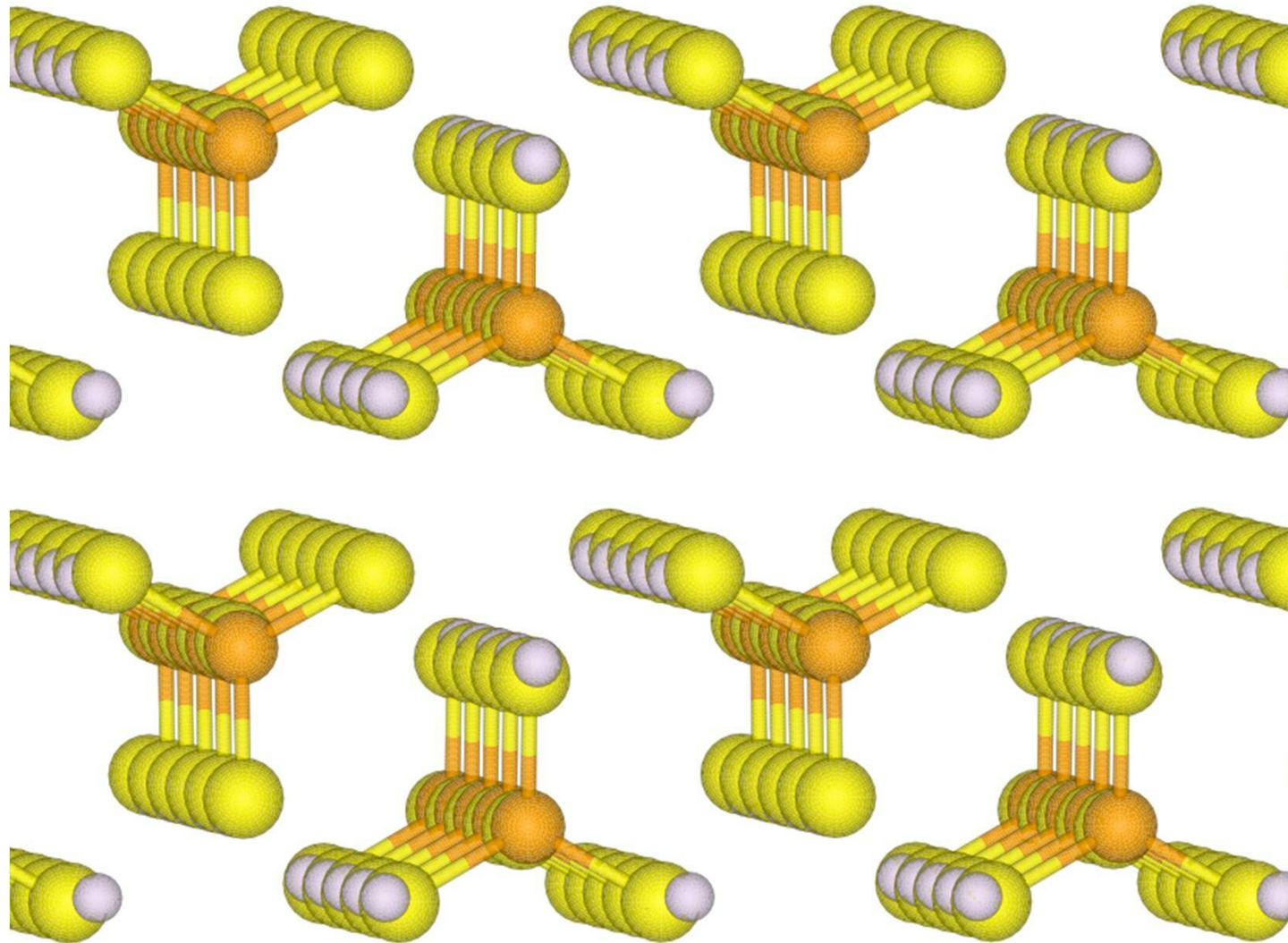
Figure 5. Electrochemical stability of $\beta\text{-Li}_3\text{PS}_4$ and cycling stability with metallic lithium electrodes. (a) CV of a $\text{Li}/\beta\text{-Li}_3\text{PS}_4/\text{Pt}$ cell, where Li and Pt serve as the reference/counter and working electrodes, respectively. (b) Lithium cyclability 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 $80 \text{ }^\circ\text{C}$.

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

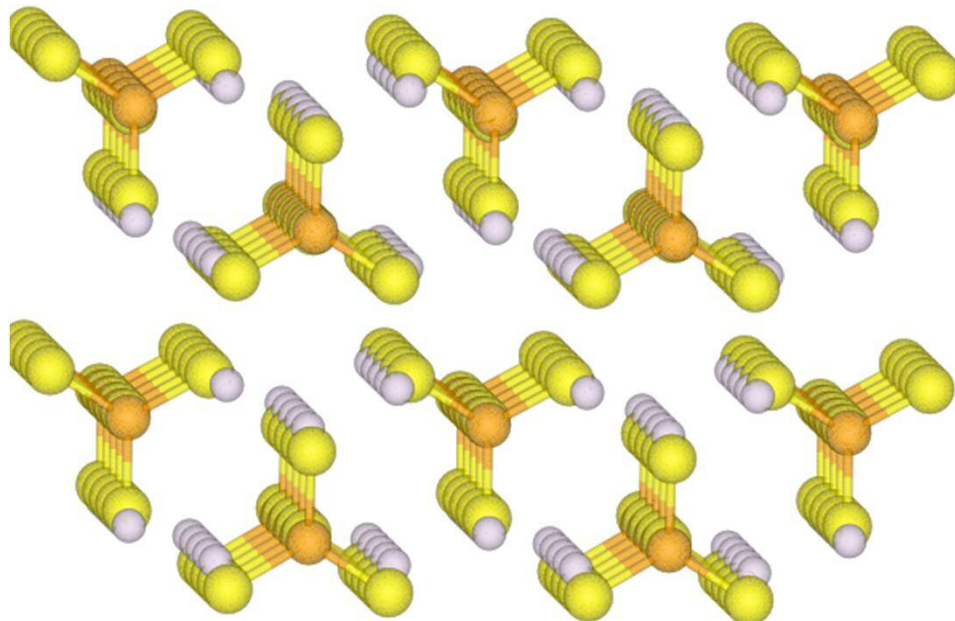


γ -Li₃PS₄ [0 1 0] surface

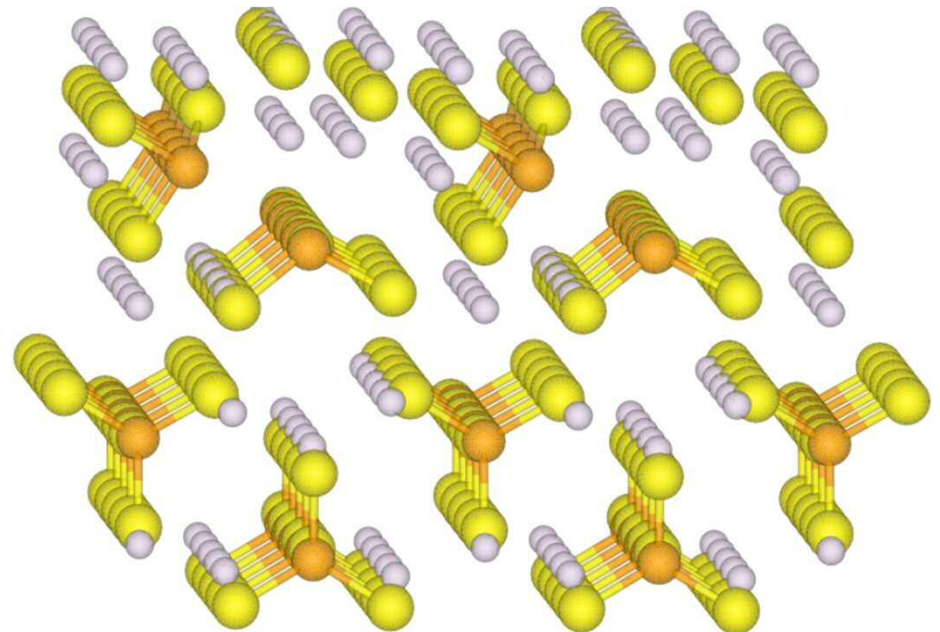


Simulations of ideal γ -Li₃PS₄ [0 1 0] surface in the presence of Li

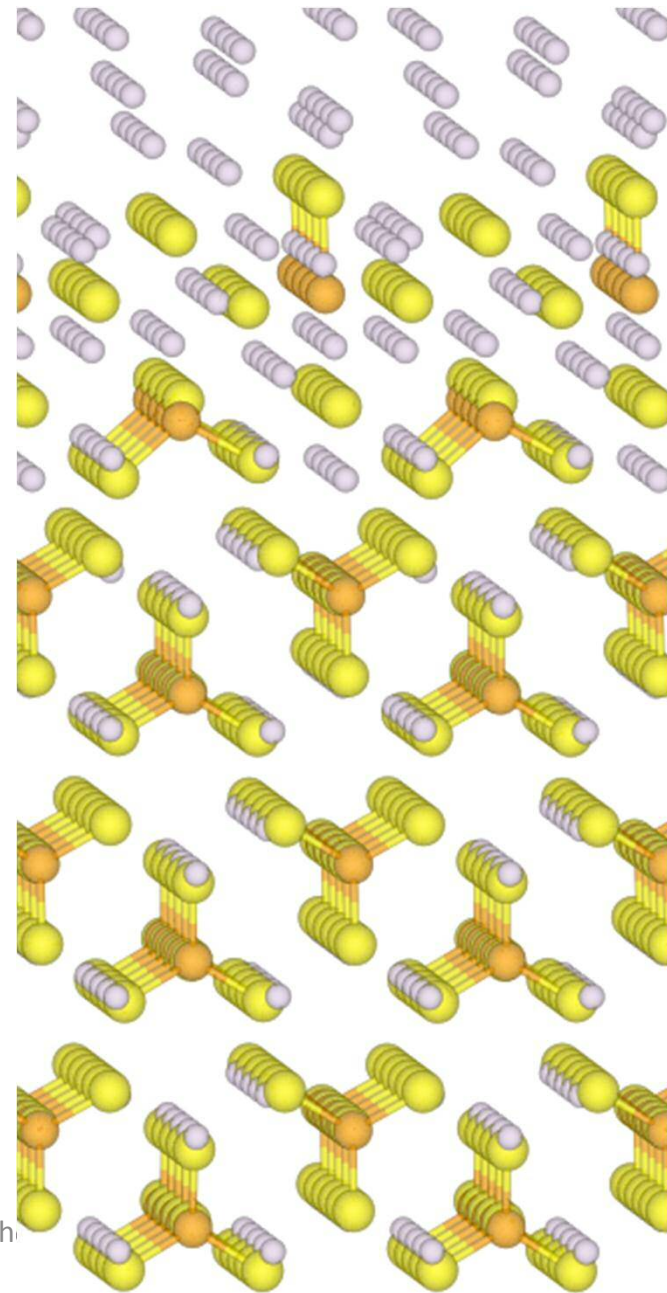
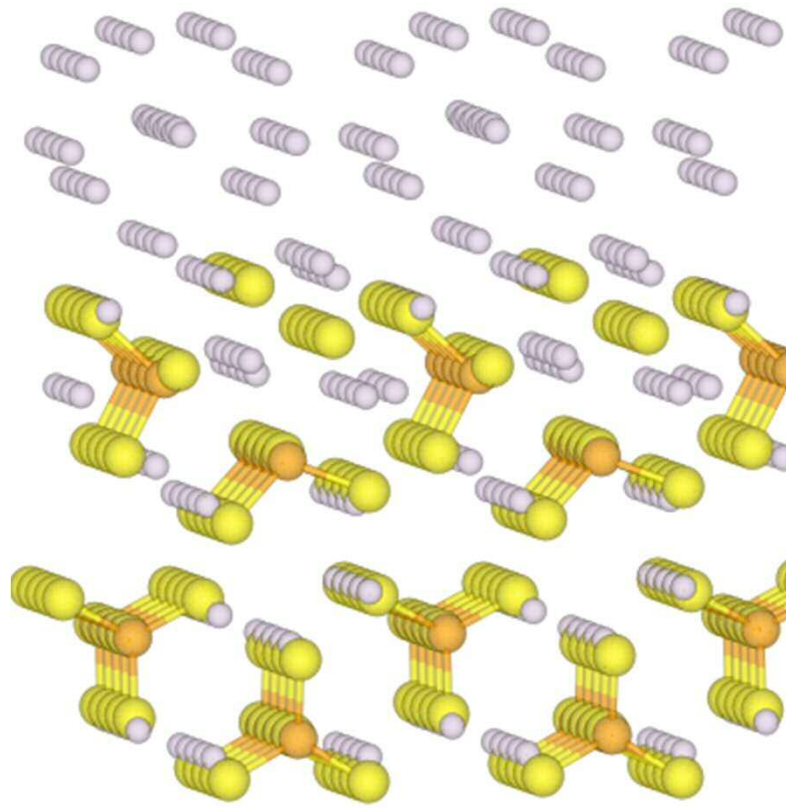
Initial configuration:



Computed optimized
structure:

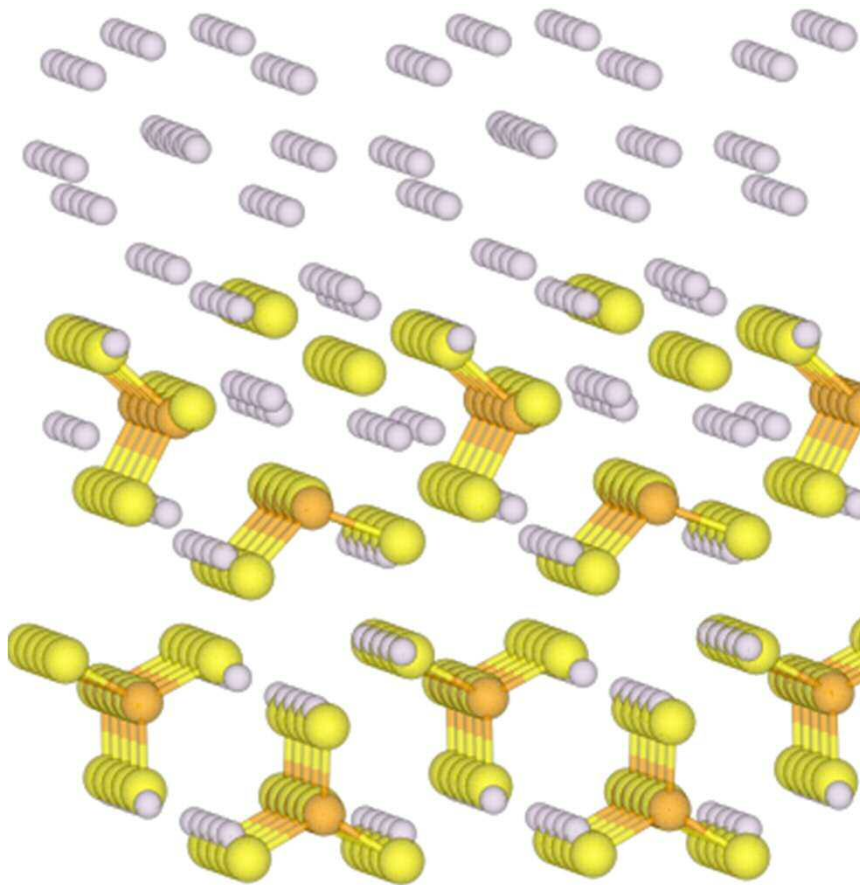


**More simulations of ideal
 γ -Li₃PS₄ [0 1 0] surface
in the presence of Li –
supercells containing
12 Li atoms and
2 or 4 electrolyte layers**

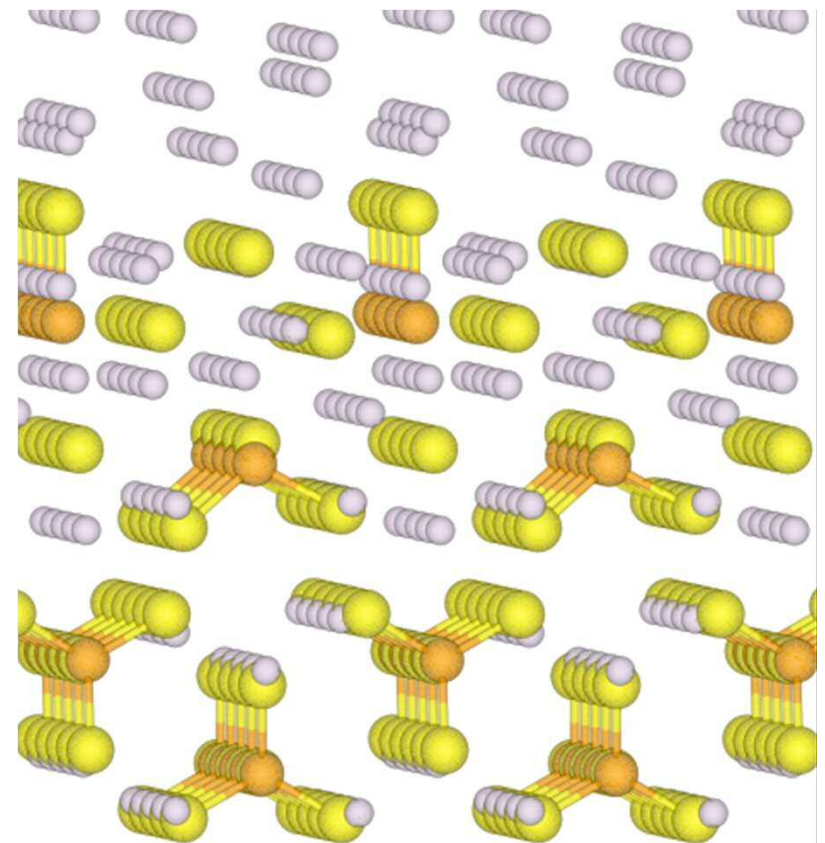


γ -Li₃PS₄ [0 1 0] surface in the presence of Li –
supercells containing 12 Li atoms and 2 or 4 electrolyte layers
(greater detail)

2 electrolyte layers



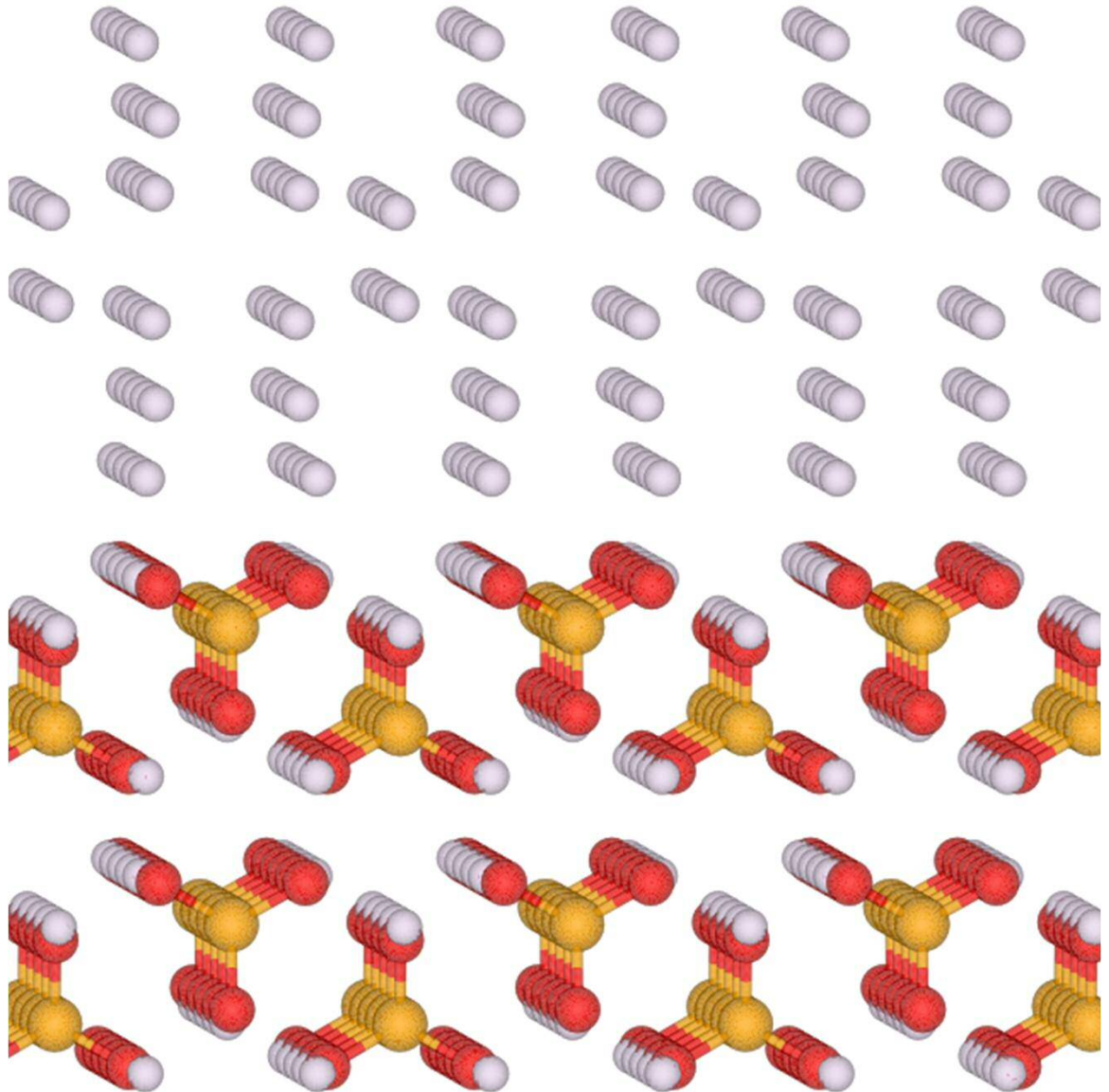
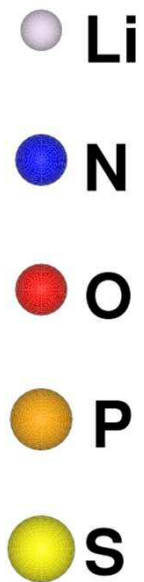
4 electrolyte layers



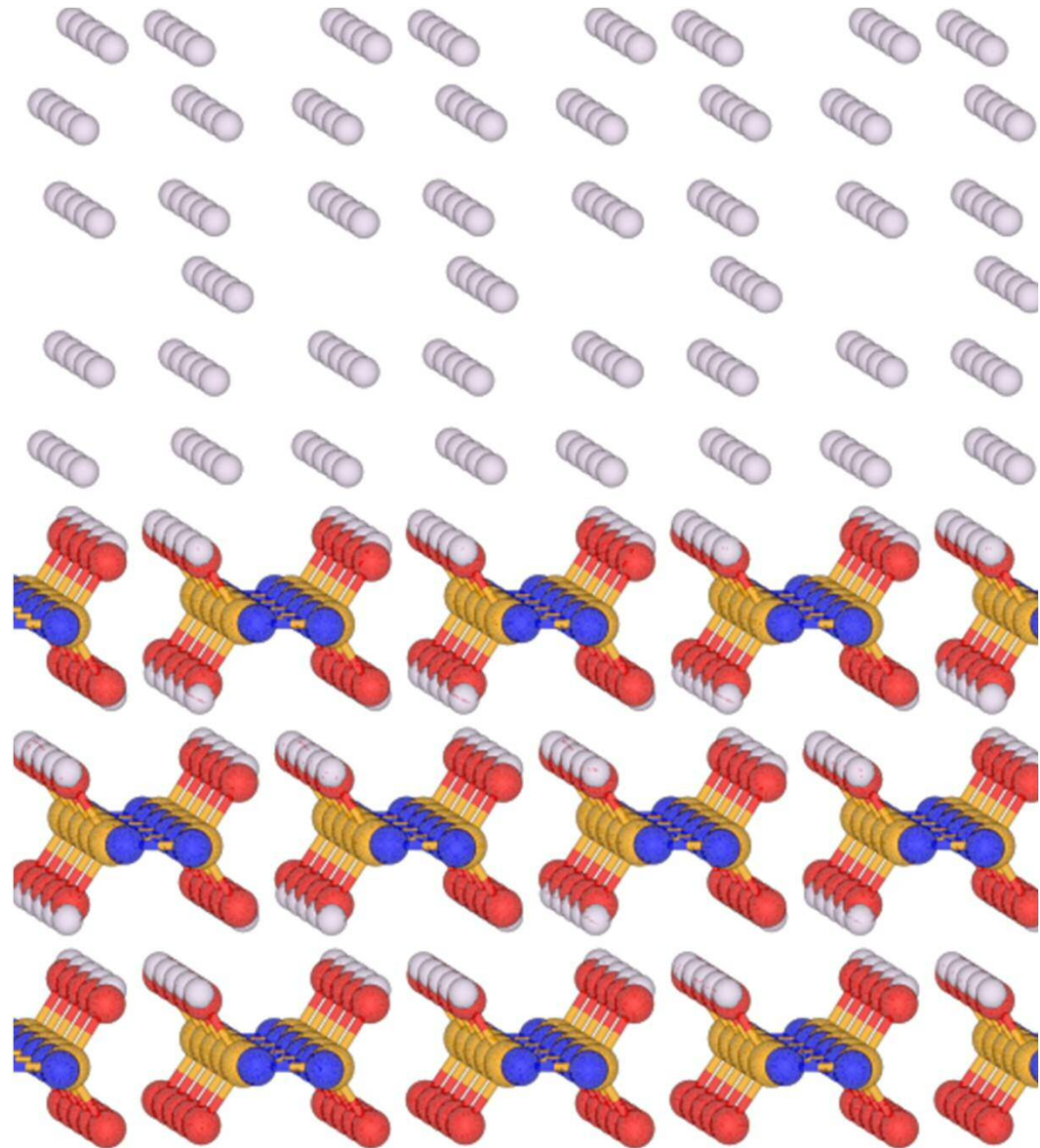
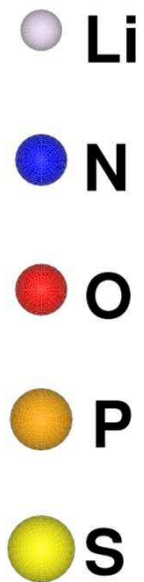
Mystery:

- **Models of ideal Li_3PS_4 surfaces are computational found to be structurally (and chemically) altered by the presence of Li metal. (Also found for $\beta\text{-Li}_3\text{PS}_4$ and for various initial configurations of Li metal.)**
- **Experimentally, the ORNL group has found that solid Li_3PS_4 electrolyte samples can be prepared in Li/ Li_3PS_4 /Li cells and cycled many times**

Computational counter example – stable interface: $\text{Li}/\beta\text{-Li}_3\text{PO}_4$



Computational counter example – stable interface: $\text{Li}/\text{SD-Li}_2\text{PO}_2\text{N}$



Back to mystery:

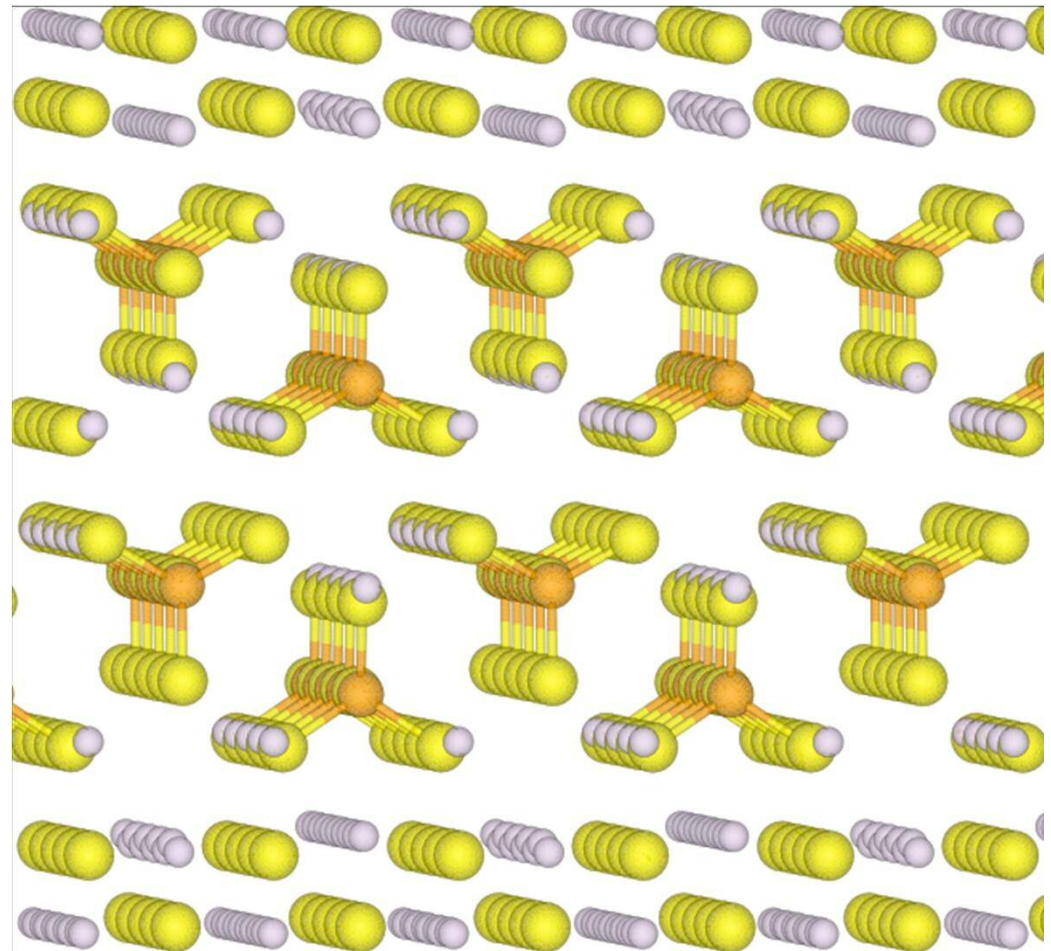
- **Models of ideal Li_3PS_4 surfaces are computational found to be structurally (and chemically) altered by the presence of Li metal. (Also found for $\beta\text{-Li}_3\text{PS}_4$ and for various initial configurations of Li metal.)**
- **Experimentally, the ORNL group has found that solid Li_3PS_4 electrolyte samples can be prepared in Li/ Li_3PS_4 /Li cells and cycled many times.**

Possible solution:

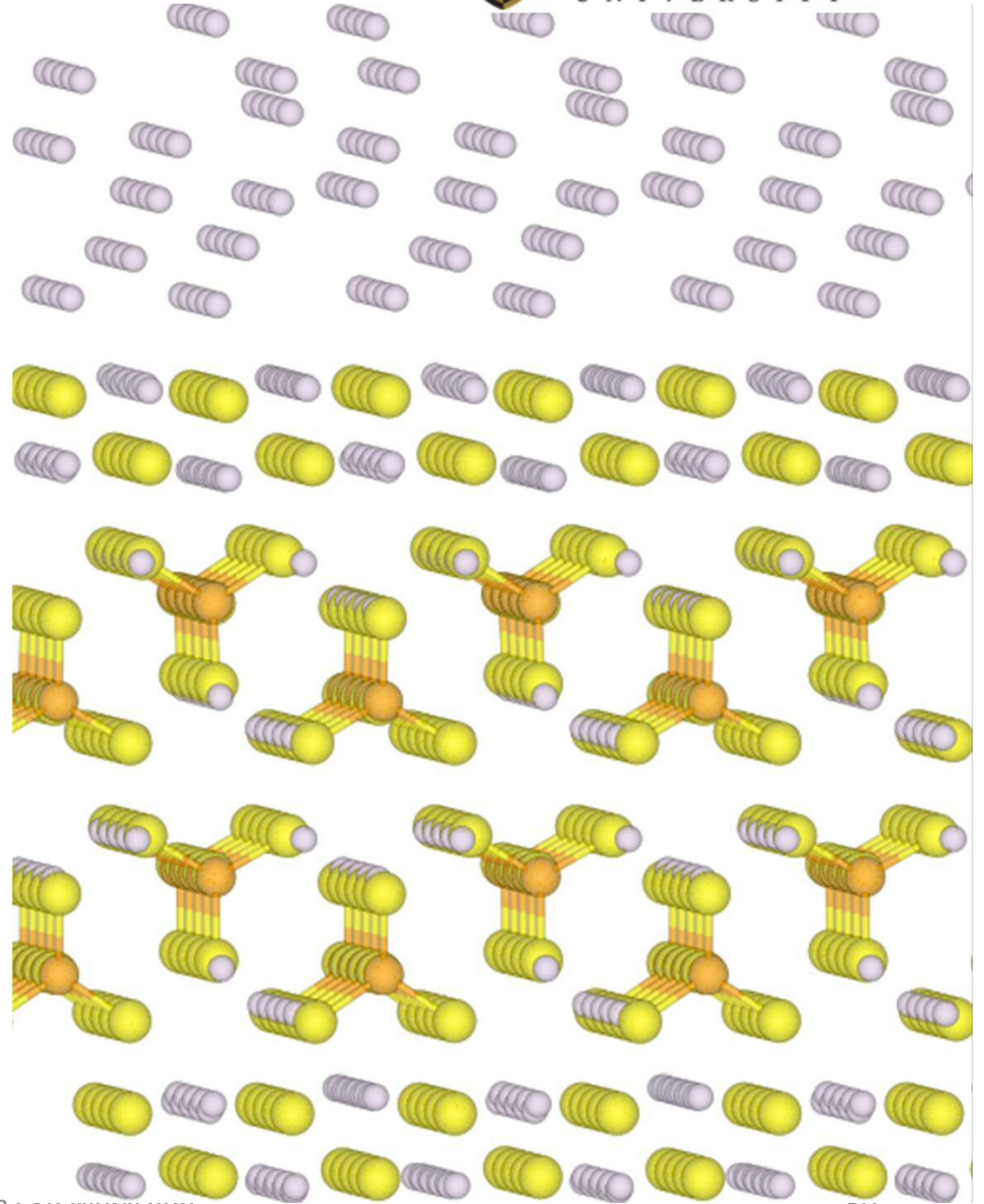
- **Thin protective buffer layer at Li_3PS_4 surface can stabilize electrolyte – for example $\text{Li}_2\text{S}/\text{Li}_3\text{PS}_4/\text{Li}_2\text{S}$**

Idealized $\text{Li}_2\text{S}/\text{Li}_3\text{PS}_4/\text{Li}_2\text{S}$ system

Details:
Thin film of cubic Li_2S oriented in its non-polar $[1\ 1\ 0]$ direction, optimized on $[0\ 1\ 0]$ surface of $\gamma\text{-Li}_3\text{PS}_4$. While the Li_2S film was slightly strained, the binding energy of the composite was found to be stable with a binding energy of $-0.9\ \text{eV}$.



Idealized $\text{Li}_2\text{S}/\text{Li}_3\text{PS}_4/\text{Li}_2\text{S}$
system optimized
in presence of Li



Summary of the interface simulations:

- Models of ideal Li_3PO_4 and $\text{Li}_2\text{PO}_2\text{N}$ surfaces are computational found to be structurally stable in the presence of Li metal.
- Models of ideal Li_3PS_4 surfaces are computational found to be structurally (and chemically) altered by the presence of Li metal. (Also found for $\beta\text{-Li}_3\text{PS}_4$ and for various initial configurations of Li metal.)
- Thin protective buffer layer of Li_2S at Li_3PS_4 surface can stabilize electrolyte; $\text{Li}_2\text{S}/\text{Li}_3\text{PS}_4/\text{Li}_2\text{S}$ is found to be stable in the presence of Li metal.
- Experimentally, the ORNL samples of solid Li_3PS_4 electrolyte, prepared in $\text{Li}/\text{Li}_3\text{PS}_4/\text{Li}$ cells and cycled many times, may form thin buffer layer in first few cycles.

Additional thoughts

- **Limitations of first principles modeling**
 - Small simulation cells**
 - Zero temperature**
- **Possible extensions**
 - Develop approximation schemes for treatment of larger supercells**
 - Use molecular dynamics and/or Monte Carlo techniques**