Overview of Computer Simulation Methods Used to Study and Design New Materials: Examples from the Study of Solid Electrolytes*

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**With help from: Nicholas Lepley, Ahmad Al-Qawasmeh, Jason Howard, and Larry Rush (physics graduate students), Yaojun Du (previous physics postdoc) and colleagues from WFU chemistry department – Dr. Keerthi Senevirathne, Dr. Cynthia Day, Professor Michael Gross, Professor Abdessadek Lachgar, and Zachary Hood (currently at ORNL)
Outline

- Overview of computational methods
  - What is meant by “first principles”?
  - Evaluation of computational results and comparison with reality
- Why are we interested in solid electrolytes?
- How can computer simulations help?
  - Survey of known solid electrolytes
  - Prediction of new solid electrolytes
  - Study of electrolyte/electrode interfaces
- Remaining challenges
What is meant by “first principles” simulation methods?

A series of well-controlled approximations
Summary of “first-principles” calculation methods

Exact Schrödinger equation:
\[ \mathcal{H}(\{r_i\}, \{R^a\}) \Psi_\alpha(\{r_i\}, \{R^a\}) = E_\alpha \Psi_\alpha(\{r_i\}, \{R^a\}) \]

where
\[ \mathcal{H}(\{r_i\}, \{R^a\}) = \mathcal{H}^{\text{Nuclei}}(\{R^a\}) + \mathcal{H}^{\text{Electrons}}(\{r_i\}, \{R^a\}) \]

Born-Oppenheimer approximation


Approximate factorization:
\[ \Psi_\alpha(\{r_i\}, \{R^a\}) = X_\alpha^{\text{Nuclei}}(\{R^a\}) Y_\alpha^{\text{Electrons}}(\{r_i\}, \{R^a\}) \]
Summary of “first-principles” calculation methods -- continued

Electronic Schrödinger equation:

\[ \mathcal{H}_{\text{Electrons}} (\{r_i\}, \{R^a\}) = \mathcal{H}_{\text{Electrons}} (\{r_i\}, \{R^a\}) = U_{\alpha} (\{R^a\}) + \sum_{i,j} e^2 |r_i - r_j| \]

\[ \mathcal{H}_{\text{Electrons}} (\{r_i\}, \{R^a\}) = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 - \sum_{a,i} \frac{Z_a e^2}{|r_i - R^a|} + \sum_{i<j} \frac{e^2}{|r_i - r_j|} \]

Density functional theory

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

For electronic ground state: \( \alpha \Rightarrow 0 \)

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

\[ \mathcal{H}_{\text{KS}} (r, \rho(r), \{R^a\}) \psi_n (r) = \varepsilon_n \psi_n (r) \]

\[ \rho(r) = \sum_n |\psi_n (r)|^2 \]

Independent electron wavefunction

Electron density

1/16/2015 Seminar at JSNN
Summary of “first-principles” calculation methods -- continued

Nuclear Hamiltonian (usually treated classically)

\[ \mathcal{H}^{\text{Nuclei}} \left( \{ \mathbf{R}^a \} \right) = \sum_a \frac{\mathbf{P}^a_2}{2M^a} + U_0 (\{ \rho(\mathbf{r}) \}, \{ \mathbf{R}^a \}) \]

Electron density
More computational details:

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

Exchange-correlation functionals:

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

Numerical methods:

- “Muffin-tin” construction: Augmented Plane Wave developed by Slater $\rightarrow$ “linearized” version by Andersen:
  - J. C. Slater, Phys. Rev. 51 846 (1937)

Pseudopotential methods:

Outputs of calculations:

Ground state energy:

\[ U_0(\{\rho(r)\}, \{R^a\}) \]

\[ \min_{\{R^a\}} U_0(\{\rho(r)\}, \{R^a\}) \]

⇒ Determine formation energies
⇒ Determine structural parameters
⇒ Stable and meta-stable structures
⇒ Normal modes of vibration

\[ \rho(r) = \sum_n |\psi_n(r)|^2 \]

\[ \{\varepsilon_n\} \]
⇒ Self-consistent electron density
⇒ One-electron energies; densities of states
# Public domain codes available for electronic structure calculations

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

Other efforts:

ATOMPAW Code for generating atomic datasets for PAW calculations

ATOMPAW

Download source code and example files:

- atompaw-4.0.0.12.tar.gz (5.4mb) 12/23/2014: Slight update of new version of atompaw code. In addition to previous updates, added PBESOL output for Quantum Espresso interface and added interface for SOCORRO.
- 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 controlled by a menu at
"Small Core" Datasets for PAW Functions

"Large Core" Datasets for PAW Functions
What do computer simulations have to do with reality?

Example comparison of computational results with experimental measurements --
Li₃PO₄ crystals

Key

- Li
- N
- O
- P
- S

\( \beta\text{-Li}_3\text{PO}_4 \)

\( \gamma\text{-Li}_3\text{PO}_4 \)

\((Pmn2_1)\)

\((Pnma)\)
Validation of calculations
Raman spectra – Experiment & Calculation

\[
\text{\(\gamma\)-Li}_3\text{PO}_4
\]


\[
\text{\(\beta\)-Li}_3\text{PO}_4
\]
Estimate of ionic conductivity assuming activated hopping

Schematic diagram of minimal energy path
Approximated using NEB algorithm\textsuperscript{a}  
- “Nudged Elastic Band”

Arrhenius relation
\[ \sigma \cdot T = Ke^{-E_A/kT} \]

From: Ivanov-Shitz and co-workers,  

\[ \begin{align*}
\ln(\sigma T), [\text{Ω cm}^{-1} \text{ K}] \\
\text{10}^2/T, [\text{K}^{-1}] \\
\end{align*} \]

Fig. 2. Temperature dependences of conductivity in $\gamma$-Li$_3$PO$_4$: (1–5) 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].

\[ E_A = 1.14, 1.23, 1.14, 1.31, 1.24 \text{ eV for } 1,2,3,4,5, \text{ respectively.} \]

\textsuperscript{a}Henkelman and Jónsson, _JCP_ **113**, 9978 (2000)
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

Cathode  Electrolyte  Anode

\[ V = IR \]
Example: Thin-film battery developed by Nancy Dudney and collaborators at Oak Ridge National Laboratory – LiPON (lithium phosphorus oxinitride)

**Solid vs liquid electrolytes in Li ion batteries**

### Solid electrolytes

**Advantages**
1. Excellent chemical and physical stability.
2. Perform well as thin film (≈1μ).
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.
Arthur Robinson and Jürgen Janek

“All-solid-state batteries are an emerging option for next-generation technologies”

Figure from Toyota Motor Co.

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**Figure 3** Thermal evolution of ionic conductivity of the new Li$_{10}$GeP$_2$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 Li$_{10}$GeP$_2$S$_{12}$ exhibits the highest lithium ionic conductivity (12 mS 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.

![Diagram of LiPON](image)

**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 mS 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.

![Graph showing thermal evolution of ionic conductivity](image)

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How can computer simulations contribute to the development of materials?

- Computationally examine known materials and predict new materials and their properties
  - Structural forms
  - Relative stabilities
  - Direct comparisons of simulations and experiment
  - Investigate properties that are difficult to realize experimentally

Of particular interest in battery materials --

- Model ion migration mechanisms
  - Vacancy migration
  - Interstitial migration
  - Vacancy-interstitial formation energies
The Li$_2$PO$_2$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 Crystallography\textsuperscript{85} based on structural information reported in the International Crystal Structure Database.\textsuperscript{86} The heats of formation $\Delta H$ (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.

<table>
<thead>
<tr>
<th>Material</th>
<th>Structure</th>
<th>$\Delta H$ (eV/FU)</th>
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<tbody>
<tr>
<td>$\beta$-Li$_3$PO$_4$</td>
<td>$Pmn2_1$ (#31)</td>
<td>-21.23</td>
</tr>
<tr>
<td>$\gamma$-Li$_3$PO$_4$</td>
<td>$Pnma$ (#62)</td>
<td>-21.20 (-21.72*)</td>
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<td>$\gamma$-Li$_3$PS$_4$</td>
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<td>Li$_5$P$_2$O$_6$N</td>
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<td>LiPO$_3$</td>
<td>$P2_1/c$ (#13)</td>
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<td>s1-Li$_2$PO$_2$N</td>
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<td>SD-Li$_2$PO$_2$N</td>
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<td>$Cmc2_1$ (#36)</td>
<td>-5.80</td>
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<th>Material</th>
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<th>$\Delta H$ (eV/FU)</th>
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<td>N$_2$O$_5$</td>
<td>$P6_3/mmc$ (#194)</td>
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<td>P$_3$N$_5$</td>
<td>$C2/c$ (#15)</td>
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<td>$h$-P$_2$O$_5$</td>
<td>$R3c$ (#161)</td>
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<td>-6.35 (-6.57*)</td>
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<td>Li$_2$S</td>
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<td>LiNO$_3$</td>
<td>$R3c$ (#167)</td>
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<td>Li$_2$SO$_4$</td>
<td>$P2_1/c$ (#14)</td>
<td>-14.63 (-14.89*)</td>
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Phosphate chain materials: LiPO$_3$ plus N

LiPO$_3$ in $P2_1/c$ structure; 100 atom unit cell
Chain direction perpendicular to plane of diagram

$s_1$-Li$_2$PO$_2$N in $Pbcm$ structure; 24 atom unit cell
Chain direction perpendicular to plane of diagram

Ball colors:  ⋄ = Li, ☢ = P, ◆ = O.

Single chain view

Ball colors:  ⋄ = Li, ☢ = P, ◆ = O, Ⓕ = N.

Single chain view
Two forms of Li$_2$PO$_2$N

Possible exothermic reaction pathways:

\[ \frac{1}{5} \text{P}_2\text{O}_5 + \frac{1}{5} \text{P}_3\text{N}_5 + \text{Li}_2\text{O} \rightarrow \text{Li}_2\text{PO}_2\text{N} + 2.5 \text{ eV}. \]

\[ \text{Li}_2\text{O}_2 + \frac{1}{5} \text{P}_3\text{N}_5 + \frac{2}{5} \text{P} \rightarrow \text{Li}_2\text{PO}_2\text{N} + 5.3 \text{ eV}. \]

\[ \text{LiNO}_3 + \text{Li} + \text{P} \rightarrow \text{Li}_2\text{PO}_2\text{N} + \frac{1}{2} \text{O}_2 + 7.0 \text{ eV}. \]
Synthesis of Li$_2$PO$_2$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: Cmc2$_1$
Comparison of synthesized and predicted structures of Li$_2$PO$_2$N:

**Synthesized**

**Predicted**

$SD$-$Li_2PO_2N\ (Cmca)$

$s_2$-$Li_2PO_2N\ (Aem2)$

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 $\text{Li}_2\text{SiO}_3$

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

$\text{Li}_2\text{SiO}_3 \ (Cmc2_1)$

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

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

Electronic band structure of \( SD-Li_2PO_2N \)
More details of \( SD-Li_2PO_2N \) structure

**Ball and stick model**

Isosurfaces (maroon) of charge density of states at top of valence band, primarily \( \pi \) states on N.
Vibrational spectrum of $SD$-$Li_2PO_2N$
Stability of $SD$-$Li_2PO_2N$ in air

Thermogravimetric analysis curve in air

Note: no structural changes were observed while heating in vacuum up to 1050$^\circ$ C.
Ionic conductivity of SD-Li$_2$PO$_2$N

NEB analysis of $E_m$ (vacancy mechanism)
Summary of measured and calculated conductivity parameters in Li$_x$PO$_y$N$_z$ materials

Measured activation energies $E_A^{\text{exp}}$ compared with calculated migration energies for vacancy ($E_m^{\text{cal}}$ (vac.)) and interstitial ($E_m^{\text{cal}}$ (int.)) mechanisms and vacancy-interstitial formation energies ($E_f^{\text{cal}}$). All energies are given in eV.

<table>
<thead>
<tr>
<th>Material</th>
<th>Form</th>
<th>$E_A^{\text{exp}}$</th>
<th>$E_m^{\text{cal}}$ (vac.)</th>
<th>$E_m^{\text{cal}}$ (int.)</th>
<th>$E_f^{\text{cal}}$</th>
<th>$E_A^{\text{cal}}$</th>
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<tbody>
<tr>
<td>$\gamma$-Li$_3$PO$_4$</td>
<td>single crystal$^a$</td>
<td>1.23, 1.14</td>
<td>0.7, 0.7</td>
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Summary of the Li$_2$PO$_2$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
From ORNL: Experiment on electrolyte Li$_3$PS$_4$

Anomalous High Ionic Conductivity of Nanoporous β-Li$_3$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 β-Li$_3$PS$_4$ (line a), bulk β-Li$_3$PS$_4$ (line b), and bulk γ-Li$_3$PS$_4$ (line c). The conductivity data for bulk Li$_3$PS$_4$ are reproduced from the work of Tachez.$^{10}$

Figure 5. Electrochemical stability of β-Li$_3$PS$_4$ and cycling stability with metallic lithium electrodes. (a) CV of a Li/β-Li$_3$PS$_4$/Pt cell, where Li and Pt serve as the reference/counter and working electrodes, respectively. (b) Lithium cyclability in a symmetric Li/β-Li$_3$PS$_4$/Li cell. The cell was cycled at a current density of 0.1 mA cm$^{-2}$ at room temperature and 80 °C.
Crystal structure of bulk Li$_3$PS$_4$ – γ-form
Pmn$_2_1$ (#31)

Note: Li$_3$PS$_4$ is also found in the β-form with Pnma (#62) structure
γ-Li$_3$PS$_4$ [0 1 0] surface
Simulations of ideal $\gamma$-Li$_3$PS$_4$ [0 1 0] surface in the presence of Li

Initial configuration:

Computed optimized structure:
More simulations of ideal $\gamma$-Li$_3$PS$_4$ [0 1 0] surface in the presence of Li–supercells containing 12 Li atoms and 2 or 4 electrolyte layers
\( \gamma \)-Li₃PS₄ [0 1 0] surface in the presence of Li – supercells containing 12 Li atoms and 2 or 4 electrolyte layers (greater detail)
Mystery:

- Models of ideal Li$_3$PS$_4$ surfaces are computational found to be structurally (and chemically) altered by the presence of Li metal. (Also found for $\beta$-Li$_3$PS$_4$ and for various initial configurations of Li metal.)

- Experimentally, the ORNL group has found that solid Li$_3$PS$_4$ electrolyte samples can be prepared in Li/ Li$_3$PS$_4$/Li cells and cycled many times.
Computational counter example – stable interface:
Li/β-Li$_3$PO$_4$
Computational counter example – stable interface: Li/SD-Li$_2$PO$_2$N
Back to mystery:

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

Possible solution:

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

Details:
Thin film of cubic \( \text{Li}_2\text{S} \) 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 \( \text{Li}_2\text{S} \) film was slightly strained, the binding energy of the composite was found to be stable with a binding energy of -0.9 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$_3$PO$_4$ and Li$_2$PO$_2$N surfaces are computational found to structurally stable in the presence of Li metal.
- Models of ideal Li$_3$PS$_4$ surfaces are computational found to be structurally (and chemically) altered by the presence of Li metal. (Also found for $\beta$-Li$_3$PS$_4$ and for various initial configurations of Li metal.)
- Thin protective buffer layer of Li$_2$S at Li$_3$PS$_4$ surface can stabilize electrolyte; Li$_2$S/Li$_3$PS$_4$/Li$_2$S is found to be stable in the presence of Li metal.
- Experimentally, the ORNL samples of solid Li$_3$PS$_4$ electrolyte, prepared in Li/ Li$_3$PS$_4$/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

- 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.