First principles modeling of electrolyte/anode interfaces in an all-solid state battery – γ-Li_3PS_4/Li *

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Outline

- Motivation
  - Why all solid state batteries
  - Why γ-Li_3PS_4/Li
- Calculational methods
- Results
  - γ-Li_3PS_4/Li
  - Other interfaces -- β-Li_3PO_4/Li, *SD*-Li_2PO_2N
  - γ-Li_3PS_4/LiS_2/Li
- Summary and conclusions

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Motivation – why all solid state batteries ?

- Advantages in stability, efficiency, and safety
- Promising new materials with increased conductivity

From ORNL: Experiment on electrolyte Li_3PS_4

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Anomalous High Ionic Conductivity of Nanoporous β-Li_3PS_4

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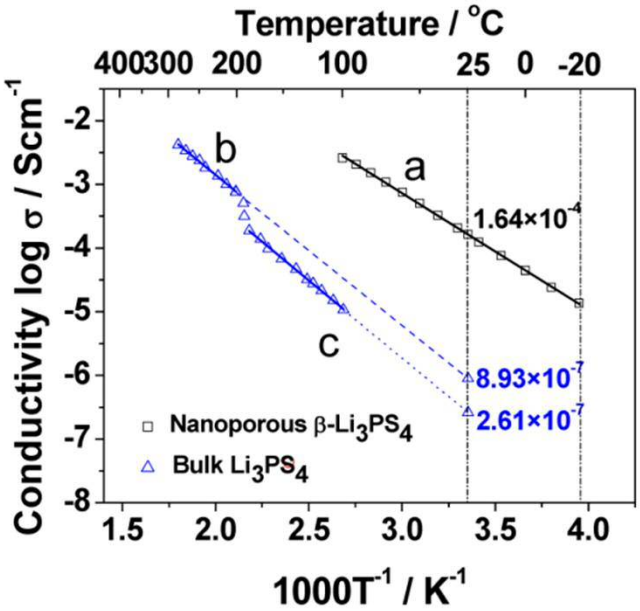

Figure 1. Arrhenius plots for nanoporous β-Li_3PS_4 (line a), bulk β-Li_3PS_4 (line b), and bulk γ-Li_3PS_4 (line c). The conductivity data for bulk Li_3PS_4 are reproduced from the work of Tachez.[10].

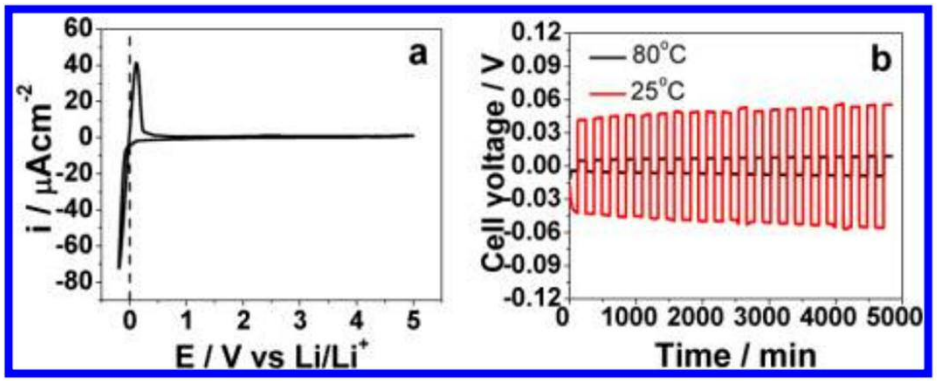

Figure 5. Electrochemical stability of β-Li_3PS_4 and cycling stability with metallic lithium electrodes. (a) CV of a Li/β-Li_3PS_4/Pt cell, where Li and Pt serve as the reference/counter and working electrodes, respectively. (b) Lithium cyclability in a symmetric Li/β-Li_3PS_4/Li cell. The cell was cycled at a current density of 0.1 mA cm^{-2} at room temperature and 80 °C.

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Summary of "first-principles" calculation methods

Exact problem :

Electronic coordinates

Atomic coordinates

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

Born-Oppenheimer approximation

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

Density functional theory

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

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

Approximately equivalent problem :

Electron density

Ground state energy (mean field approximation) : $E_0(\mathbf{r},\rho(\mathbf{r}),\{\mathbf{R}^a\})$

$$H_{eff}(\mathbf{r},\rho(\mathbf{r}),\{\mathbf{R}^a\})\psi_n(\mathbf{r}) = \varepsilon_n\psi_n(\mathbf{r})$$

$$\rho(\mathbf{r}) = \sum_n |\psi_n(\mathbf{r})|^2 \qquad H_{eff}(\mathbf{r},\rho(\mathbf{r}),\{\mathbf{R}^a\}) = \frac{\delta E_0(\mathbf{r},\rho(\mathbf{r}),\{\mathbf{R}^a\})}{\delta\rho(\mathbf{r})}$$

More computational details:

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

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 :

$$E_0(\mathbf{r}, \rho(\mathbf{r}), \{\mathbf{R}^a\}) \Rightarrow \text{Determine formation energies}$$

$$\min\big|_{\{\mathbf{R}^a\}} \left(E_0(\mathbf{r}, \rho(\mathbf{r}), \{\mathbf{R}^a\})\right) \Rightarrow \text{Determine structural parameters}$$

$$\Rightarrow \text{Stable and meta - stable structures}$$

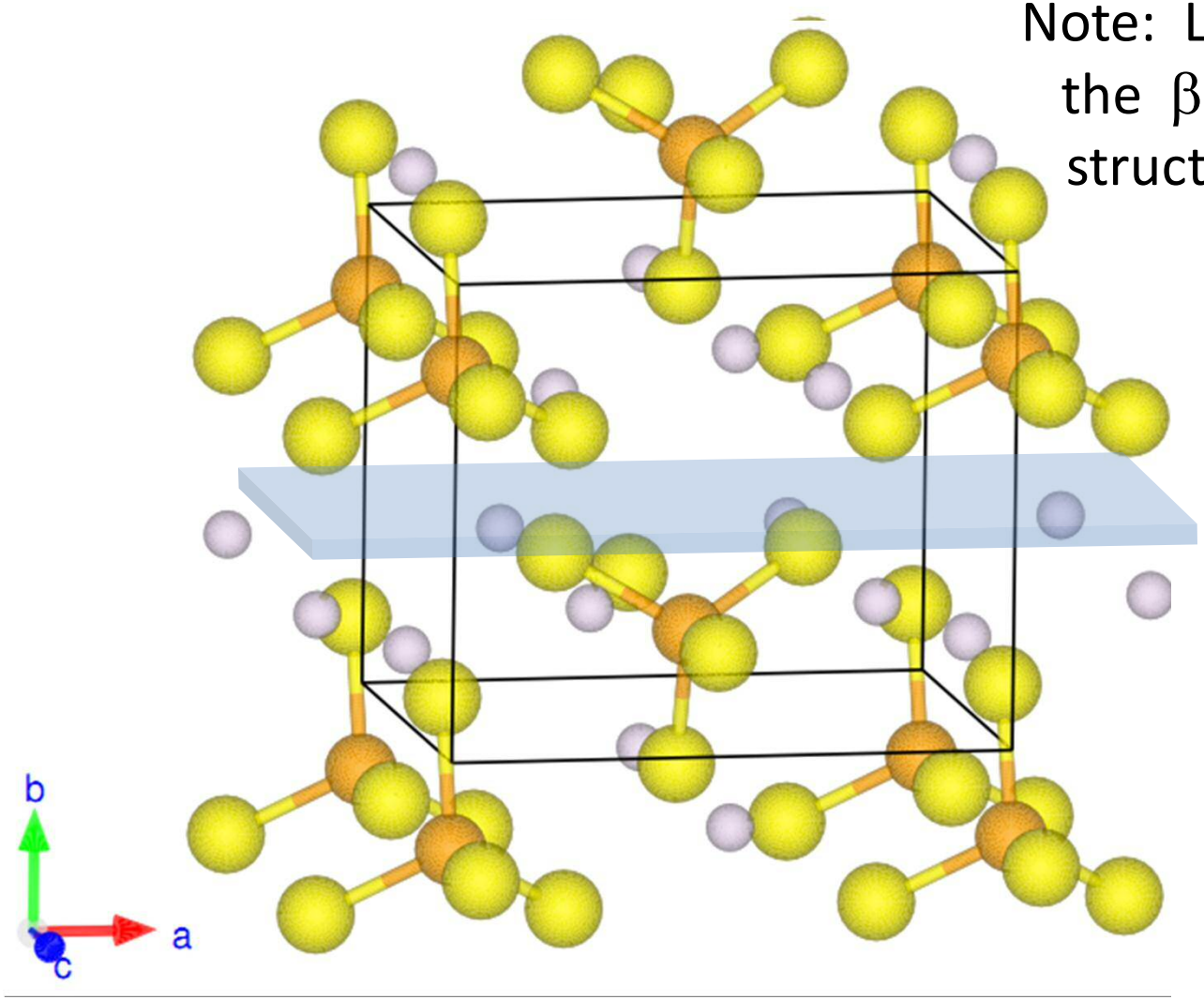
$$\Rightarrow \text{Normal modes of vibration}$$

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

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

Codes: ATOMPAW ➔ PAW atomic data files (http://pwpaw.wfu.edu)
ABINIT ➔ DFT for materials (http://www.abinit.org)
PWSCF ➔ DFT for materials (http://quantum-espresso.org)
VESTA ➔ visualization (http://jp-minerals.org/vesta/en)

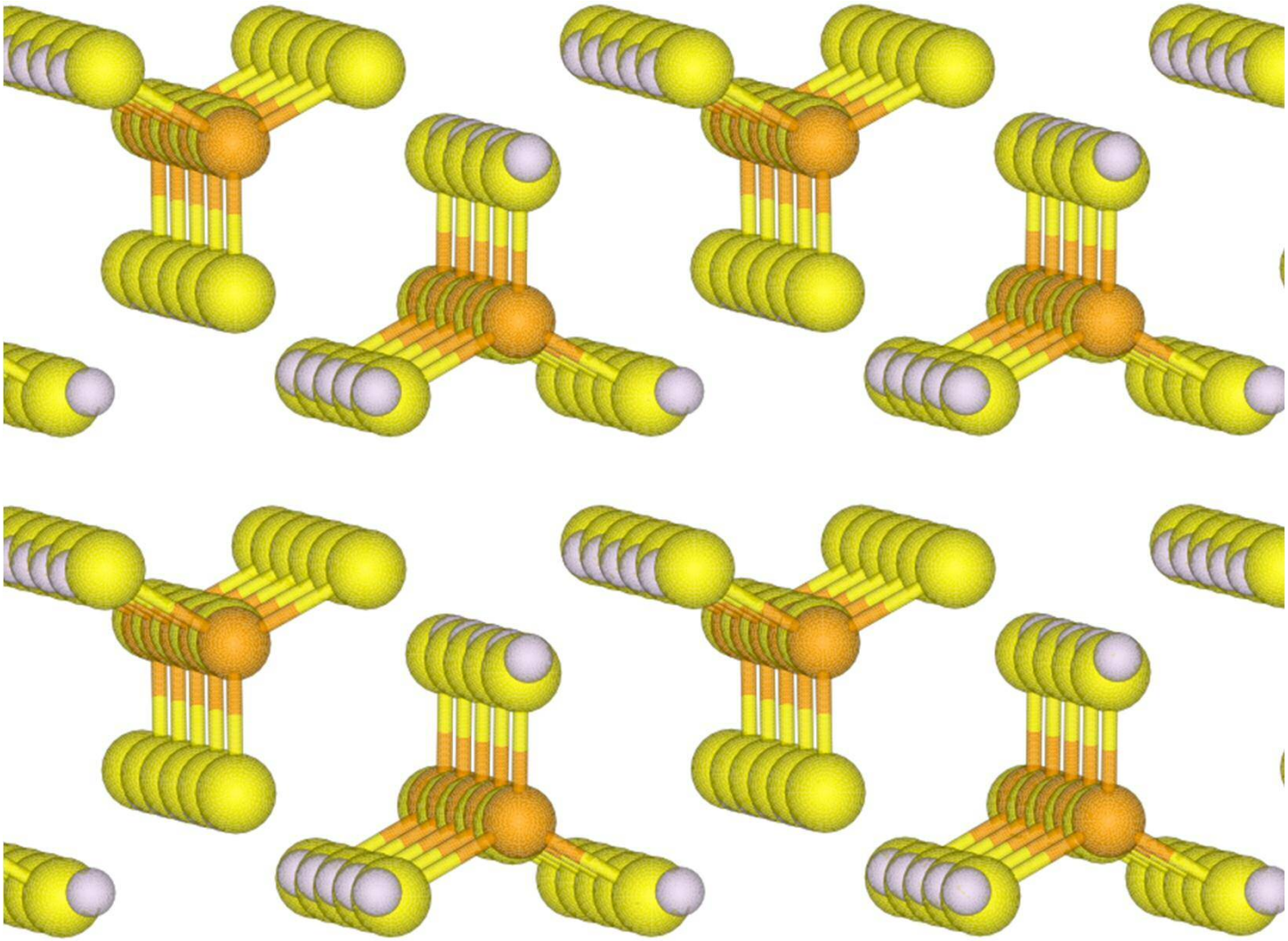
Crystal structure of bulk Li_3PS_4 – γ-form $Pmn2_1$ (#31)



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

Li
N
O
P
S

γ-Li_3PS_4 [0 1 0] surface



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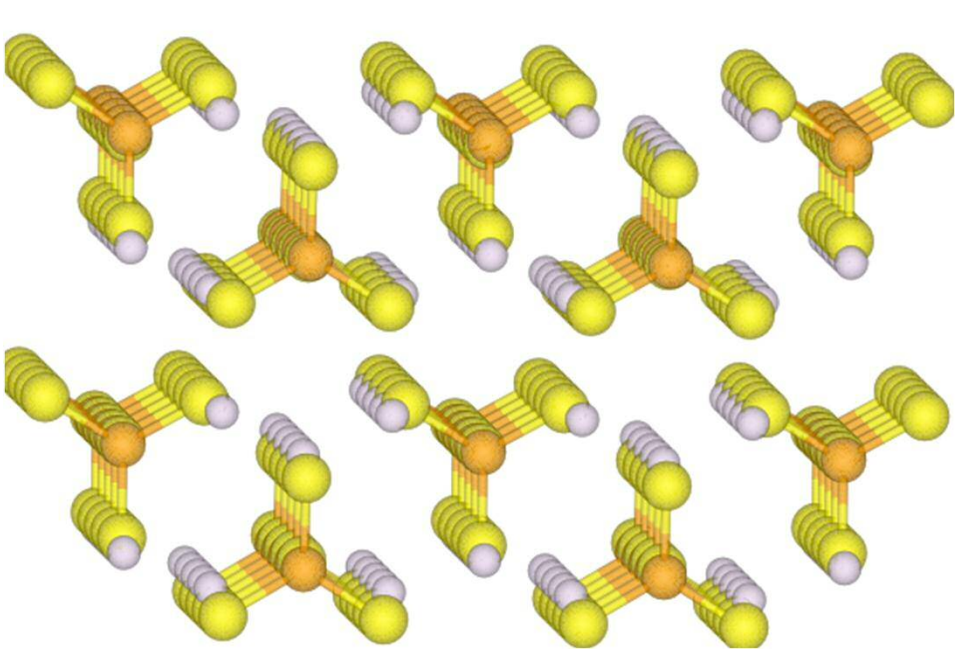
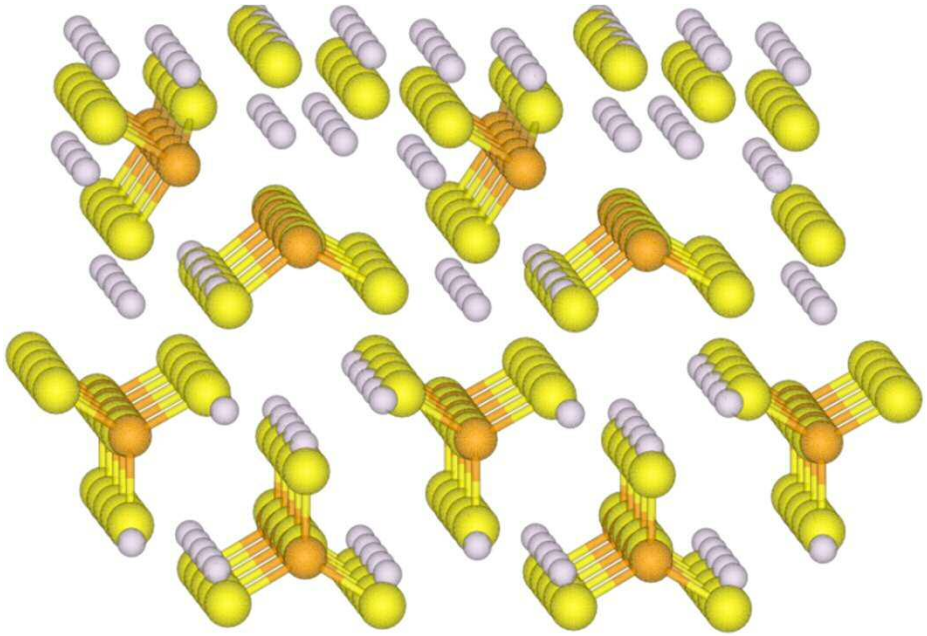
Simulations of ideal γ-Li_3PS_4 [0 1 0] surface in the presence of Li

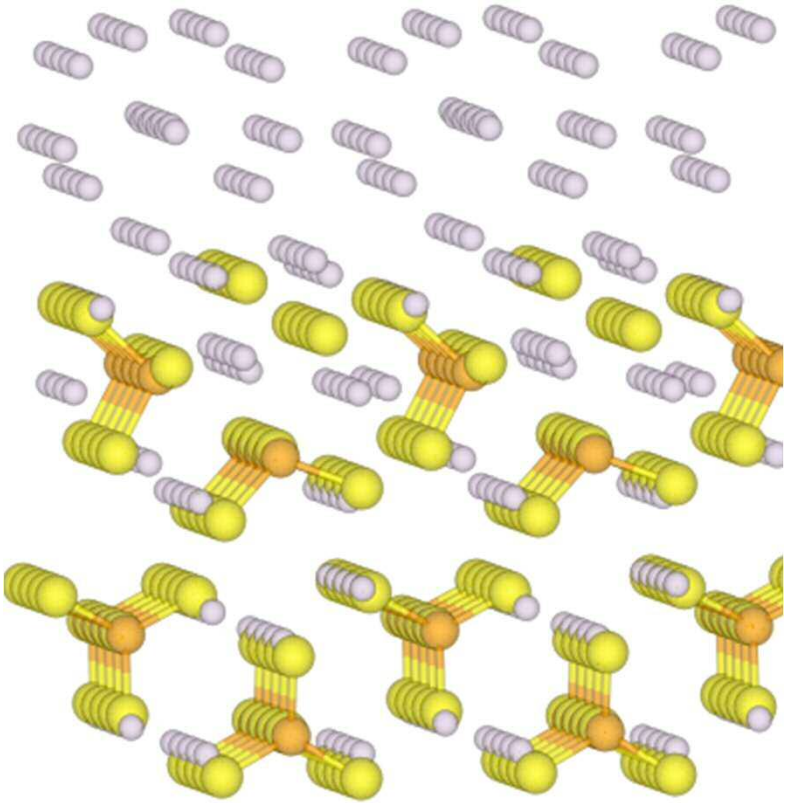
Initial configuration:

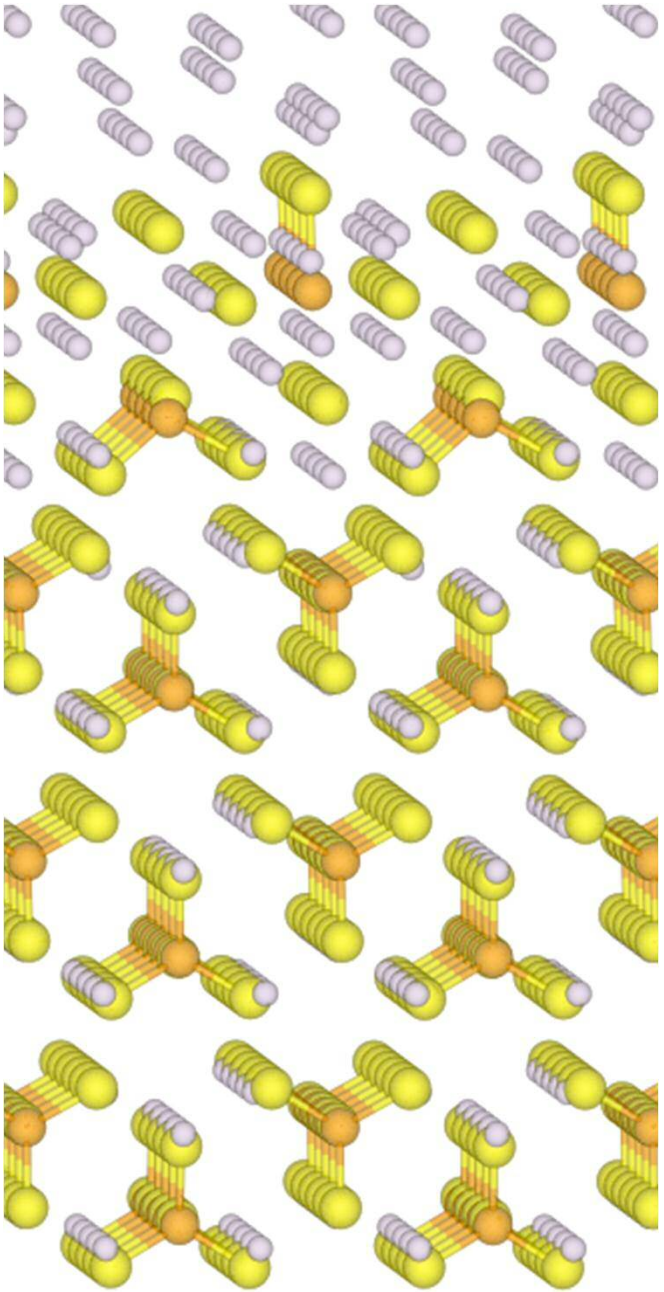
Computed optimized structure:





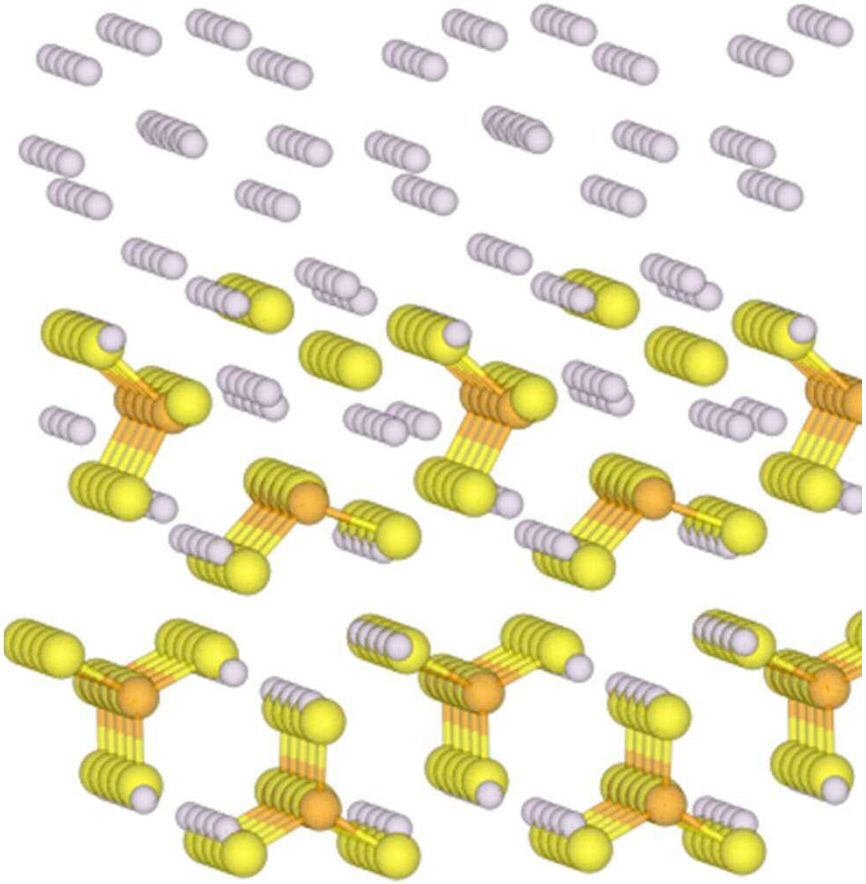
More simulations of ideal γ-Li_3PS_4 [0 1 0] surface in the presence of Li – supercells containing 12 Li atoms and 2 or 4 electrolyte layers



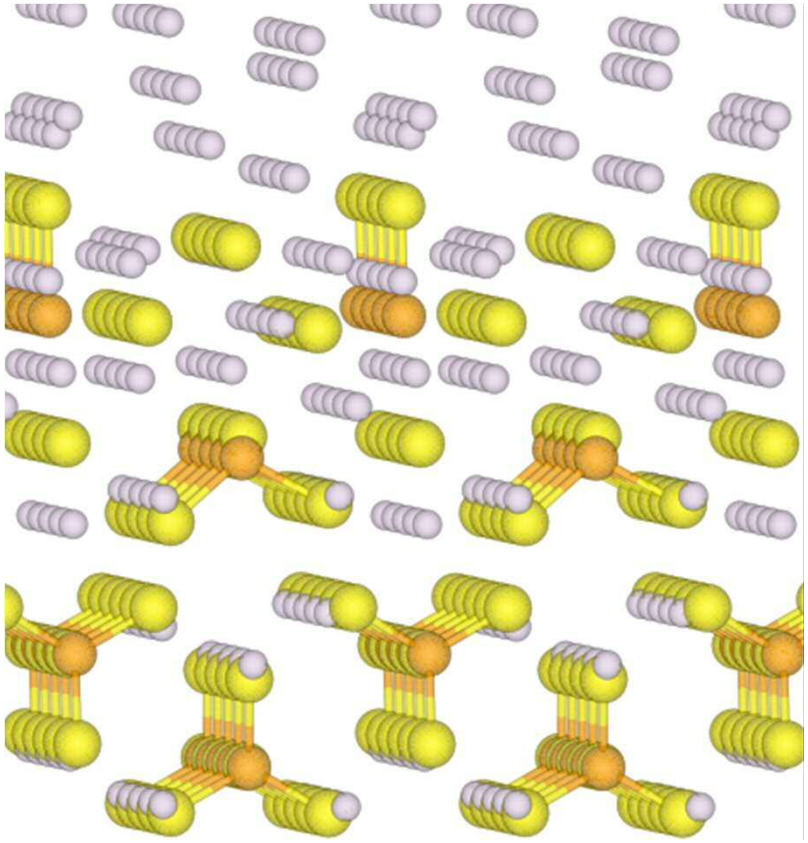


γ-Li_3PS_4 [0 1 0] surface in the presence of Li – supercells containing 12 Li atoms and 2 or 4 electrolyte layers (greater detail)

2 electrolyte layers



4 electrolyte layers



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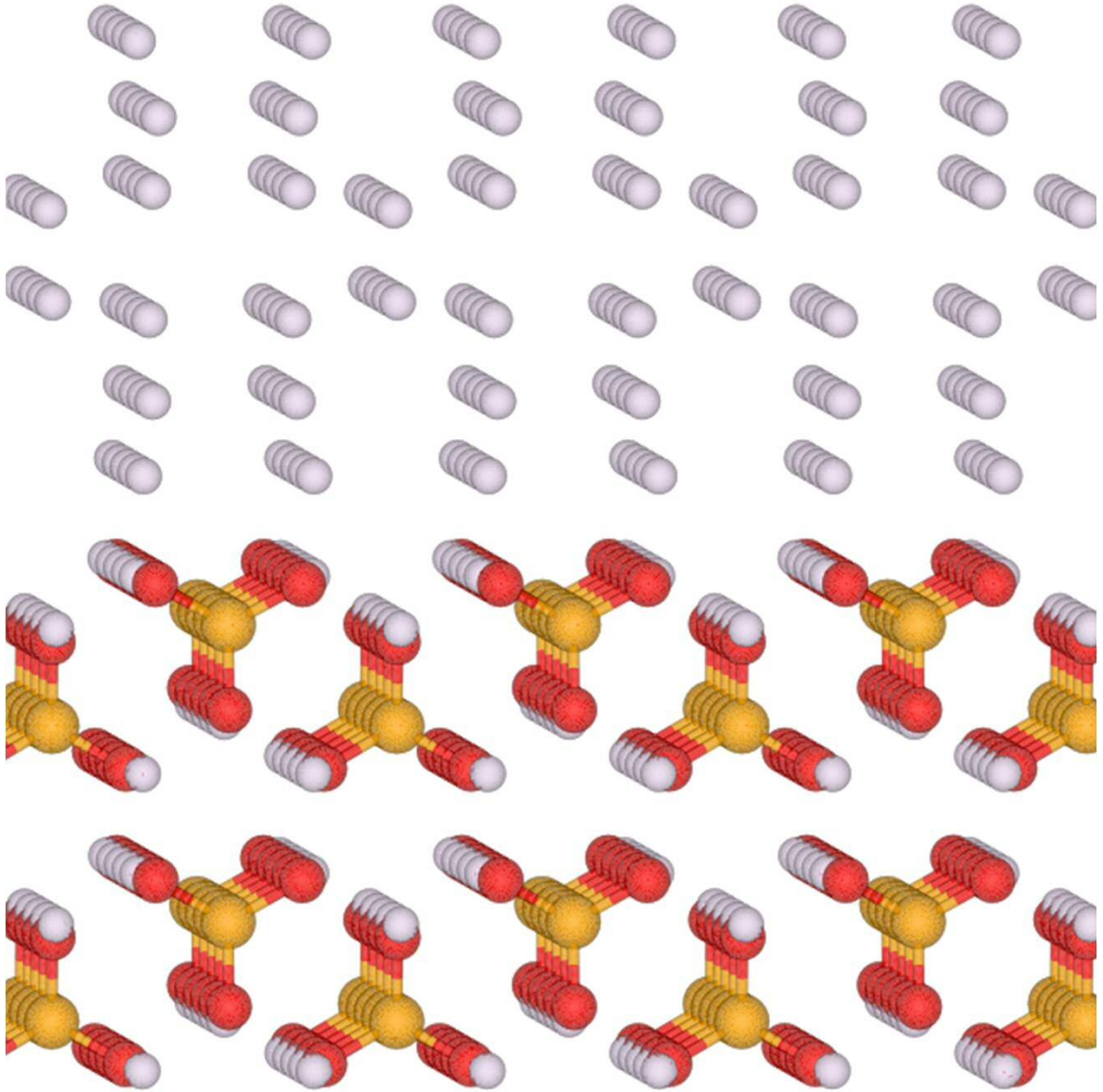
Mystery:

- **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 β-Li_3PS_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: Li/β-Li_3PO_4



Li

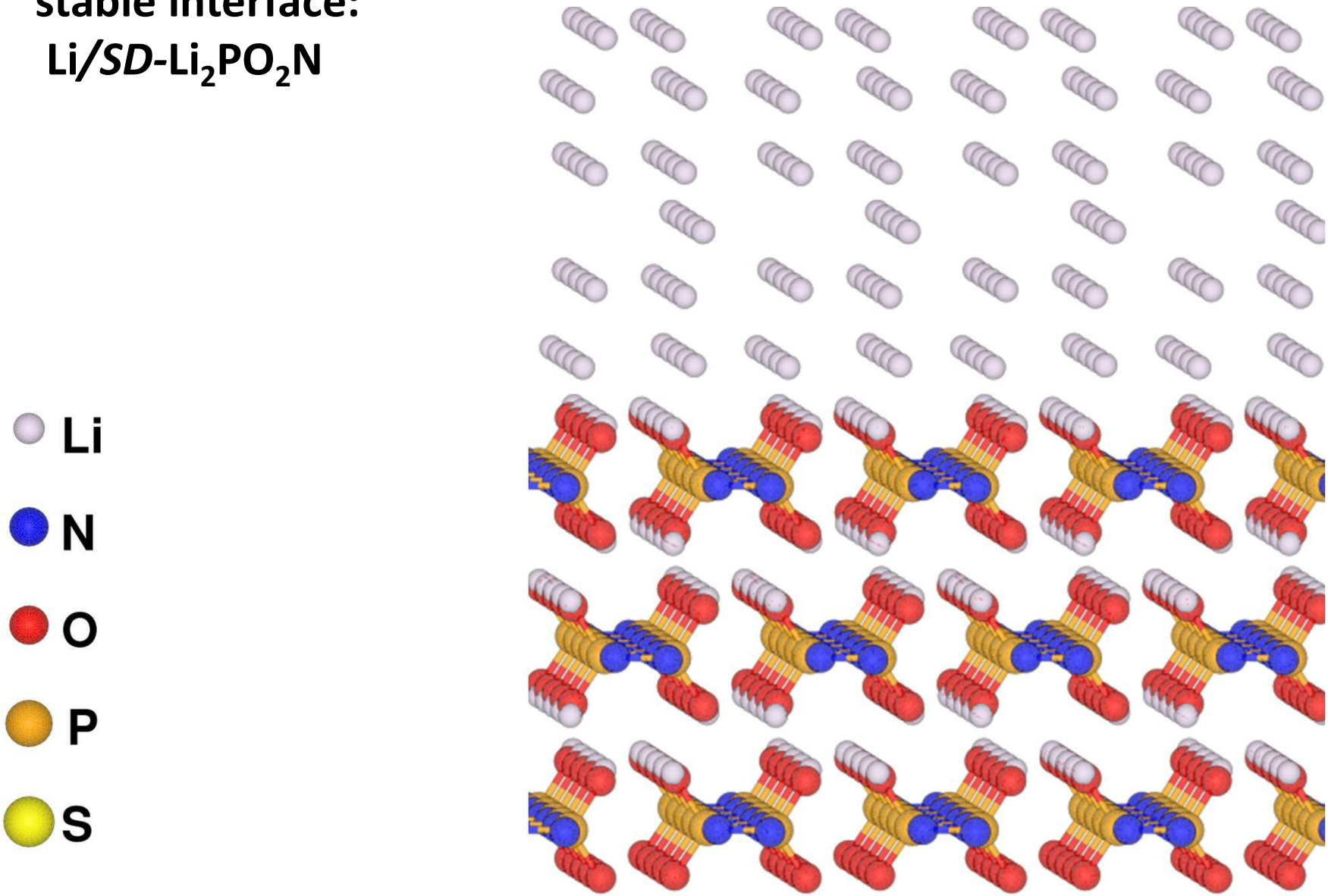
N

O

P

S

Computational counter example – stable interface: Li/*SD*-Li_2PO_2N



Back to mystery:

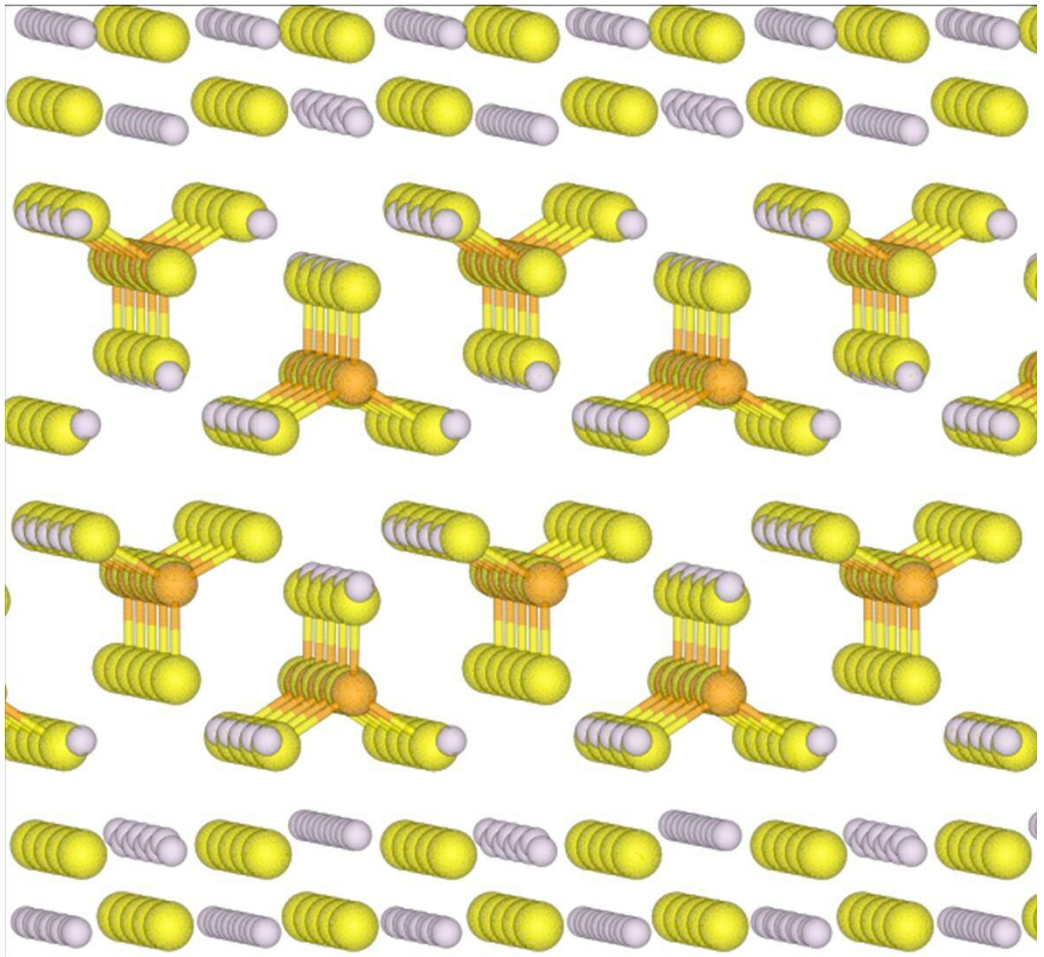
- **Models of ideal Li_3PS_4 surfaces are computational found to be structurally (and chemically) altered by the presence of Li metal. (Also found for β-Li_3PS_4 and for various initial configurations of Li metal.)**
- **Experimentally, the ORNL group has found that solid Li_3PS_4 electrolyte samples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

Possible solution:

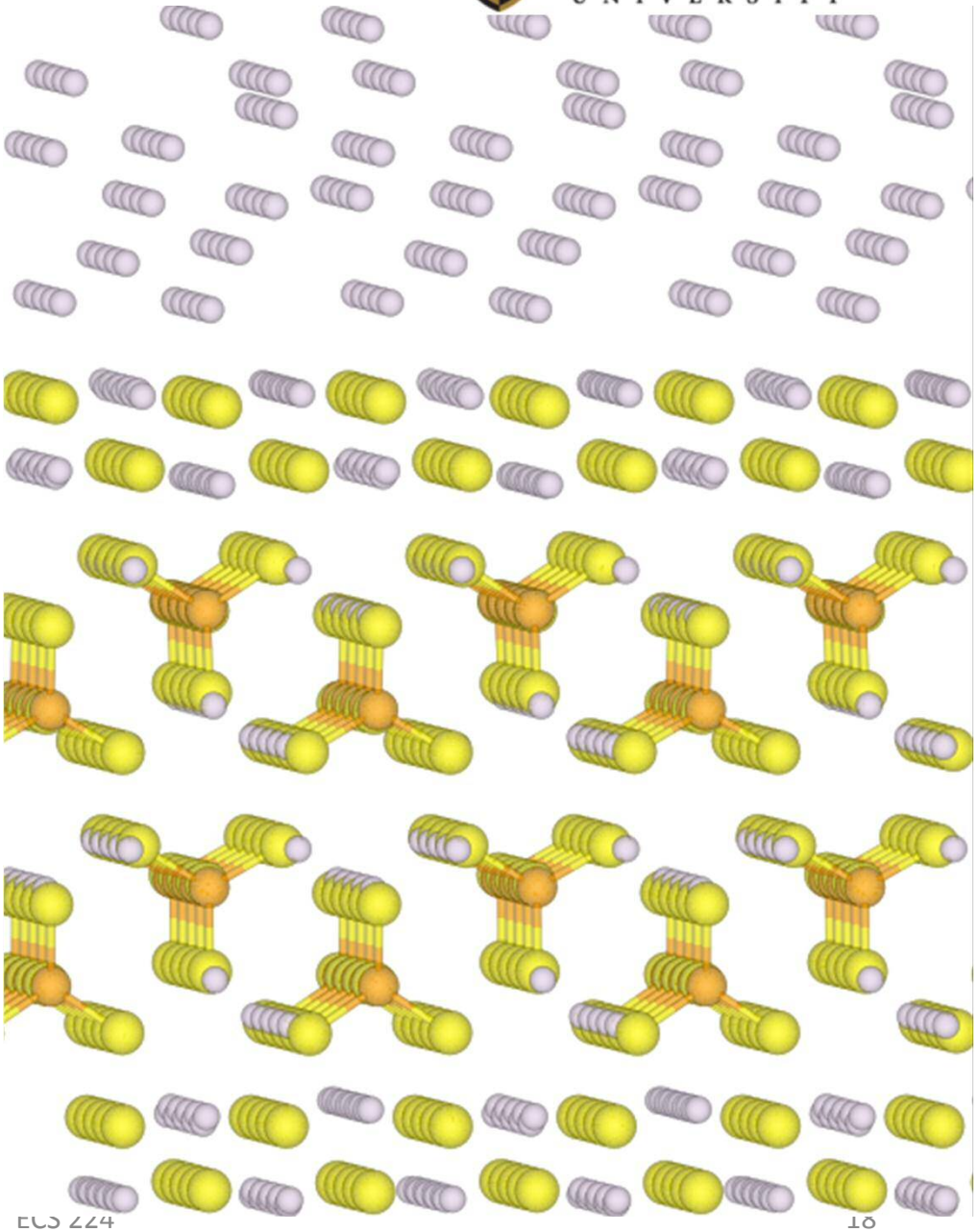
- **Thin protective buffer layer at Li_3PS_4 surface can stabilize electrolyte – for example $Li_2S/Li_3PS_4/Li_2S$**

Idealized $Li_2S/Li_3PS_4/Li_2S$ system

Details:
Thin film of cubic Li_2S oriented in its non-polar [1 1 0] direction, optimized on [0 1 0] surface of γ-Li_3PS_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 eV.



Idealized $Li_2S/Li_3PS_4/Li_2S$ system optimized in presence of Li



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Summary and conclusions:

- **Models of ideal Li_3PO_4 and Li_2PO_2N surfaces are computational found to 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 β-Li_3PS_4 and for various initial configurations of Li metal.)**
- **Thin protective buffer layer of Li_2S at Li_3PS_4 surface can stabilize electrolyte; $Li_2S/Li_3PS_4/Li_2S$ is found to be stable in the presence of Li metal.**
- **Experimentally, the ORNL samples of solid Li_3PS_4 electrolyte, prepared in Li/ Li_3PS_4/Li cells and cycled many times, may form thin buffer layer in first few cycles.**