First principles modeling of interfaces of lithium (thio) phosphate solid electrolytes and lithium metal anodes*

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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, $Li_4P_2S_6$/Li
  - 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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Communication
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Anomalous High Ionic Conductivity of Nanoporous β-Li_3PS_4

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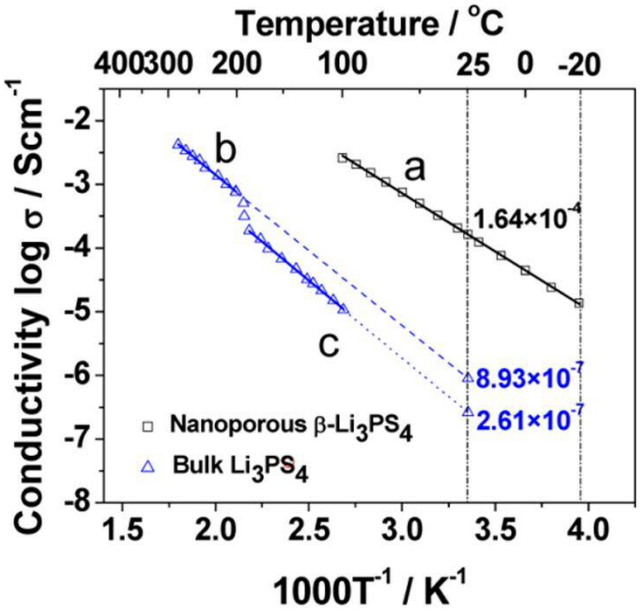


Figure 1. Arrhenius plots for nanoporous β-Li_3PS_4 (line a), bulk β-Li_3PS_4 (line b), and bulk γ-Li_3PS_4 (line c). The conductivity data for bulk Li_3PS_4 are reproduced from the work of Tachez.[10].

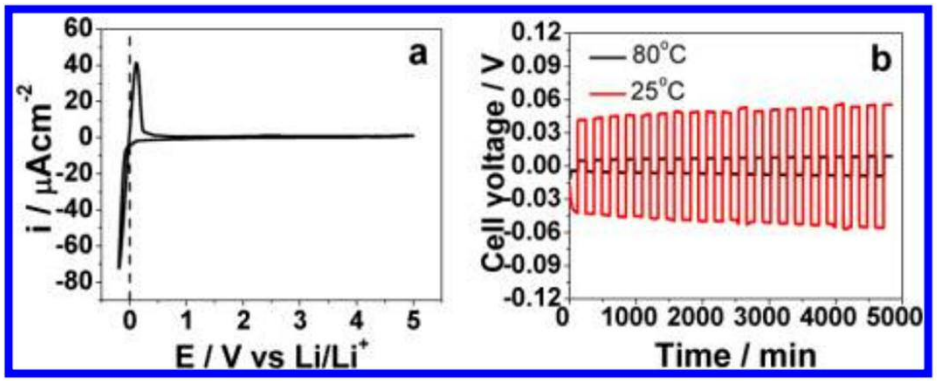


Figure 5. Electrochemical stability of β-Li_3PS_4 and cycling stability with metallic lithium electrodes. (a) CV of a Li/β-Li_3PS_4/Pt cell, where Li and Pt serve as the reference/counter and working electrodes, respectively. (b) Lithium cyclability in a symmetric Li/β-Li_3PS_4/Li cell. The cell was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

Calculational methods:

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)

Exchange-correlation functional:

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

Numerical method:

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

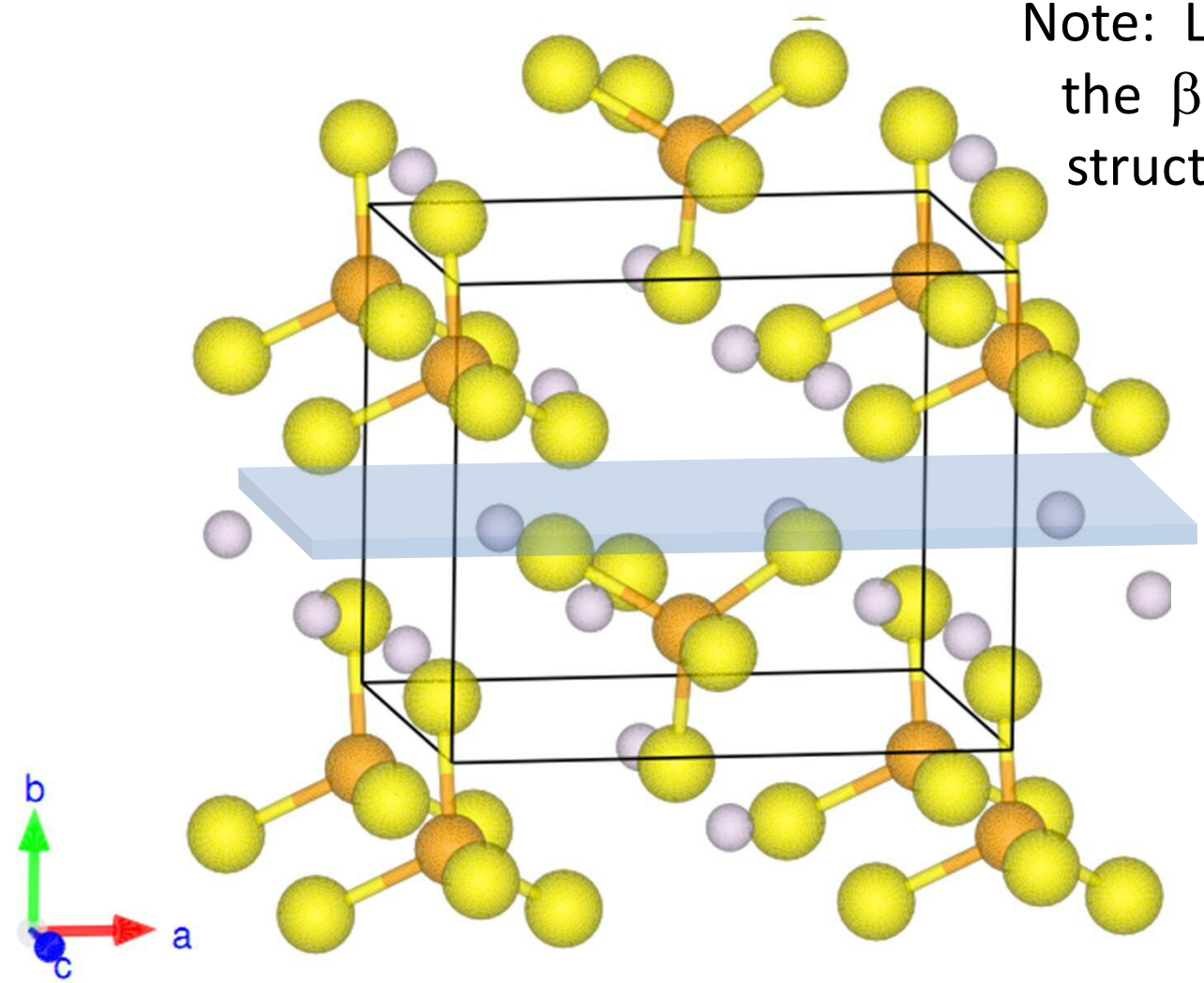
Codes: ATOMPAW ➔ PAW atomic data files (http://pwpaw.wfu.edu)

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)



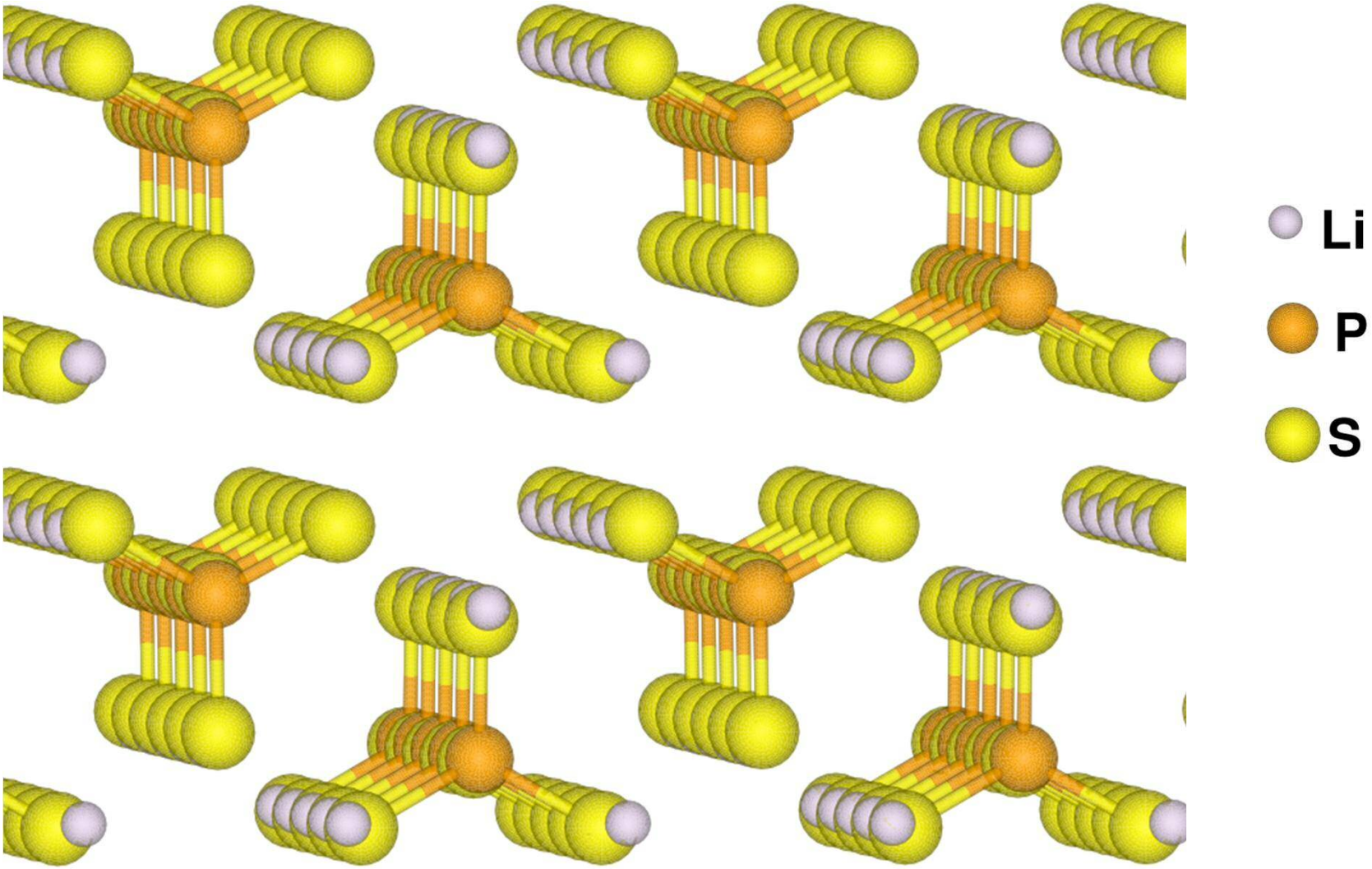
Note: Li_3PS_4 is also found in the β-form with Pmna (#62) structure

Li

P

S

γ-Li_3PS_4 [0 1 0] surface



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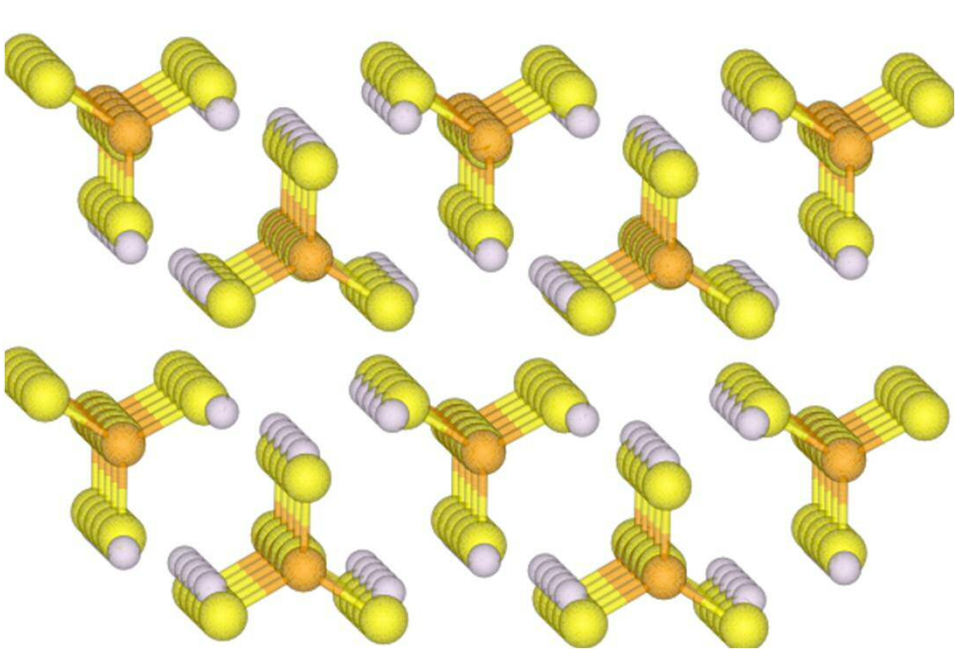
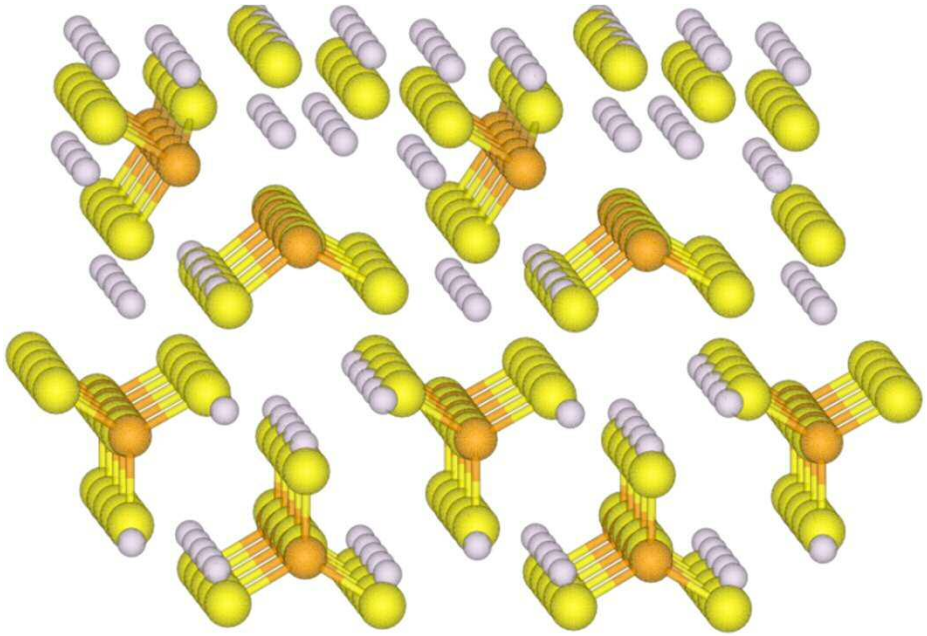
Simulations of ideal γ-Li_3PS_4 [0 1 0] surface in the presence of Li

Li P S

Initial configuration:

Computed optimized structure:

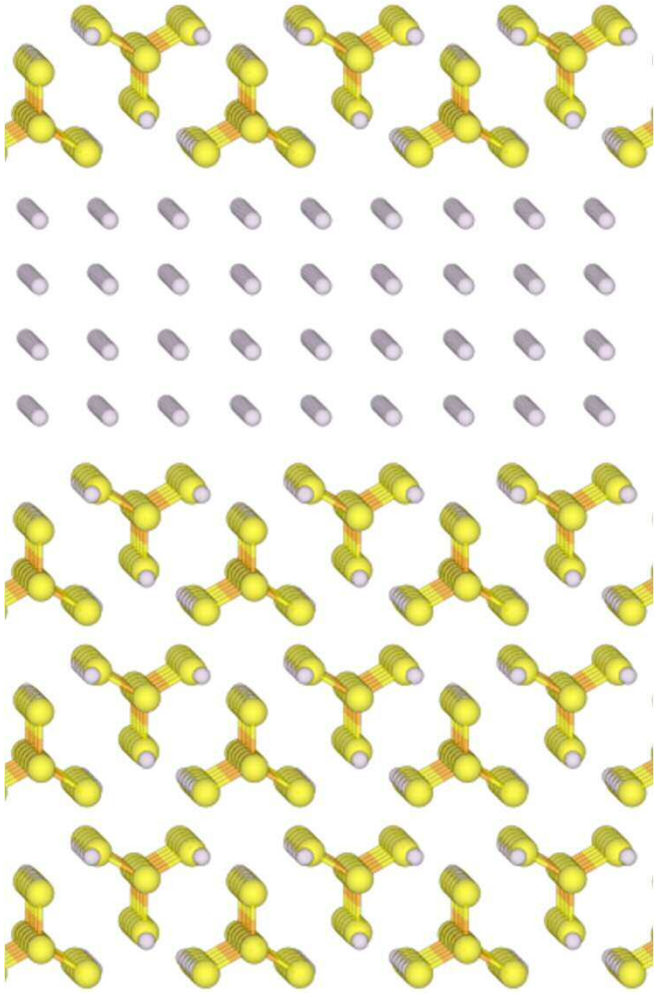




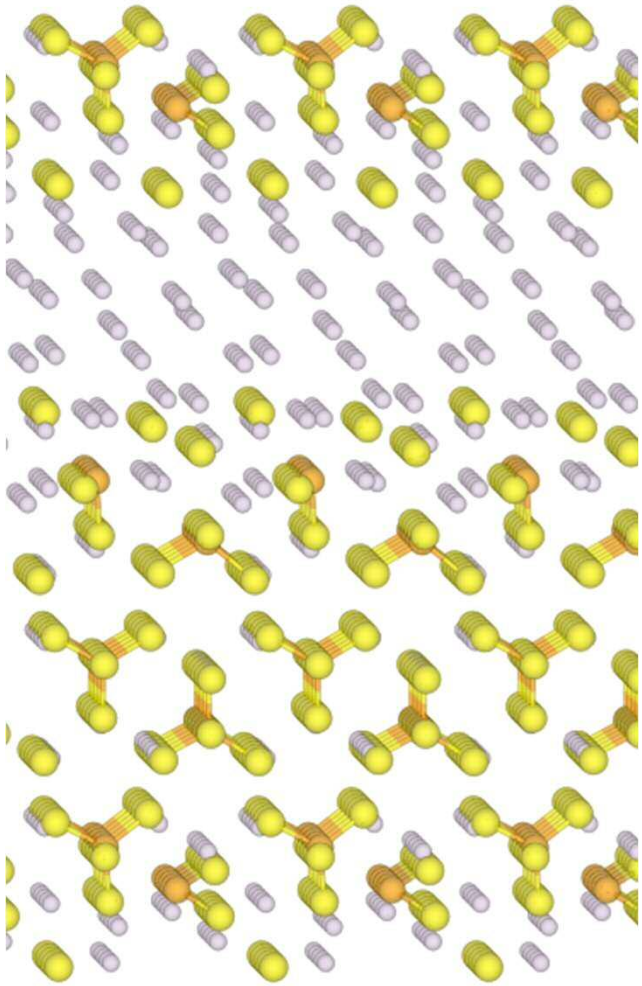
Simulations of ideal γ-Li_3PS_4 [0 1 0] surface in the presence of Li – larger supercell

(calculations performed by Nicholas Lepley)

Initial configuration:



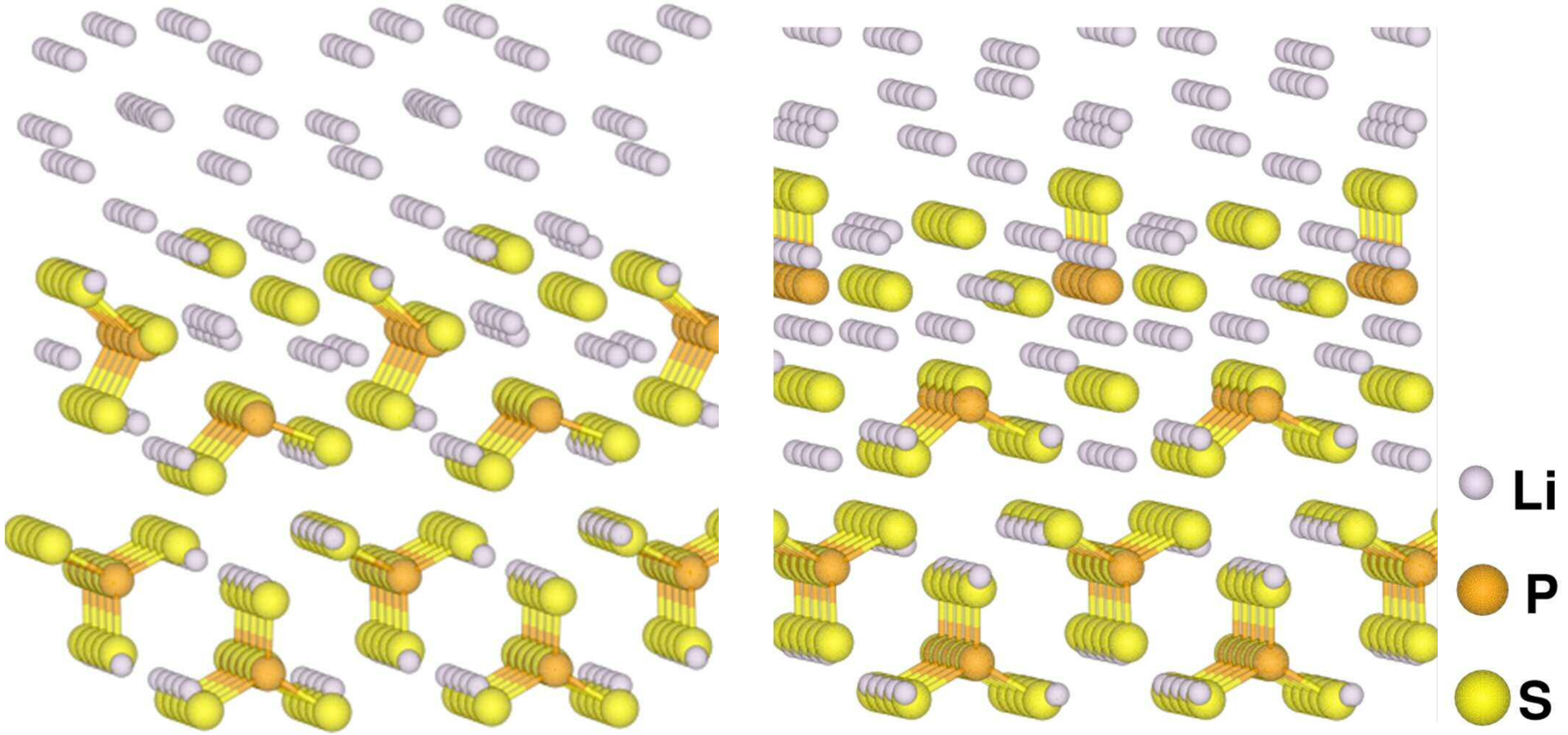
Optimized configuration:



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

(calculations performed by Ahmad Al-Qawasmeh)

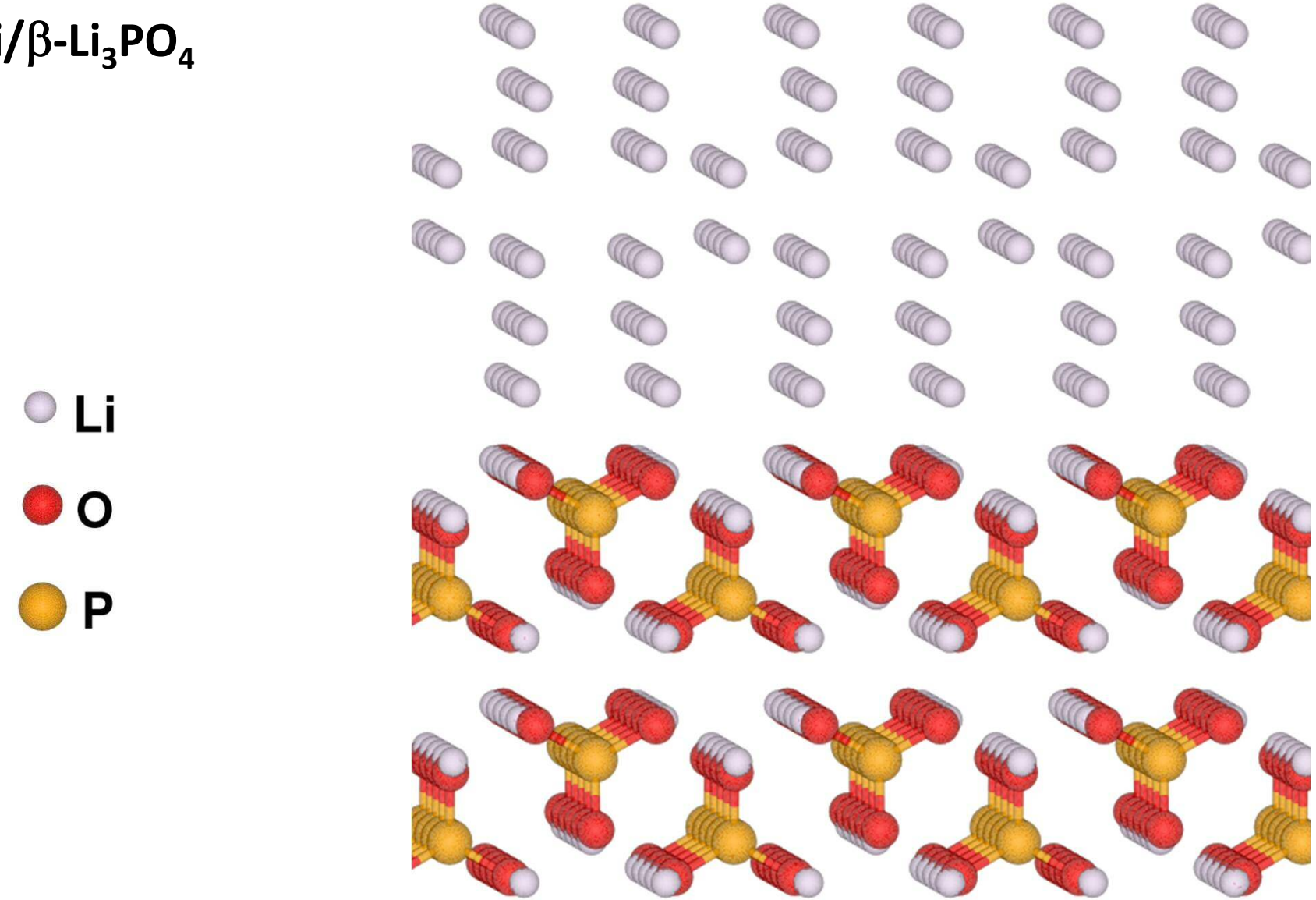
2 electrolyte layers **4 electrolyte layers**



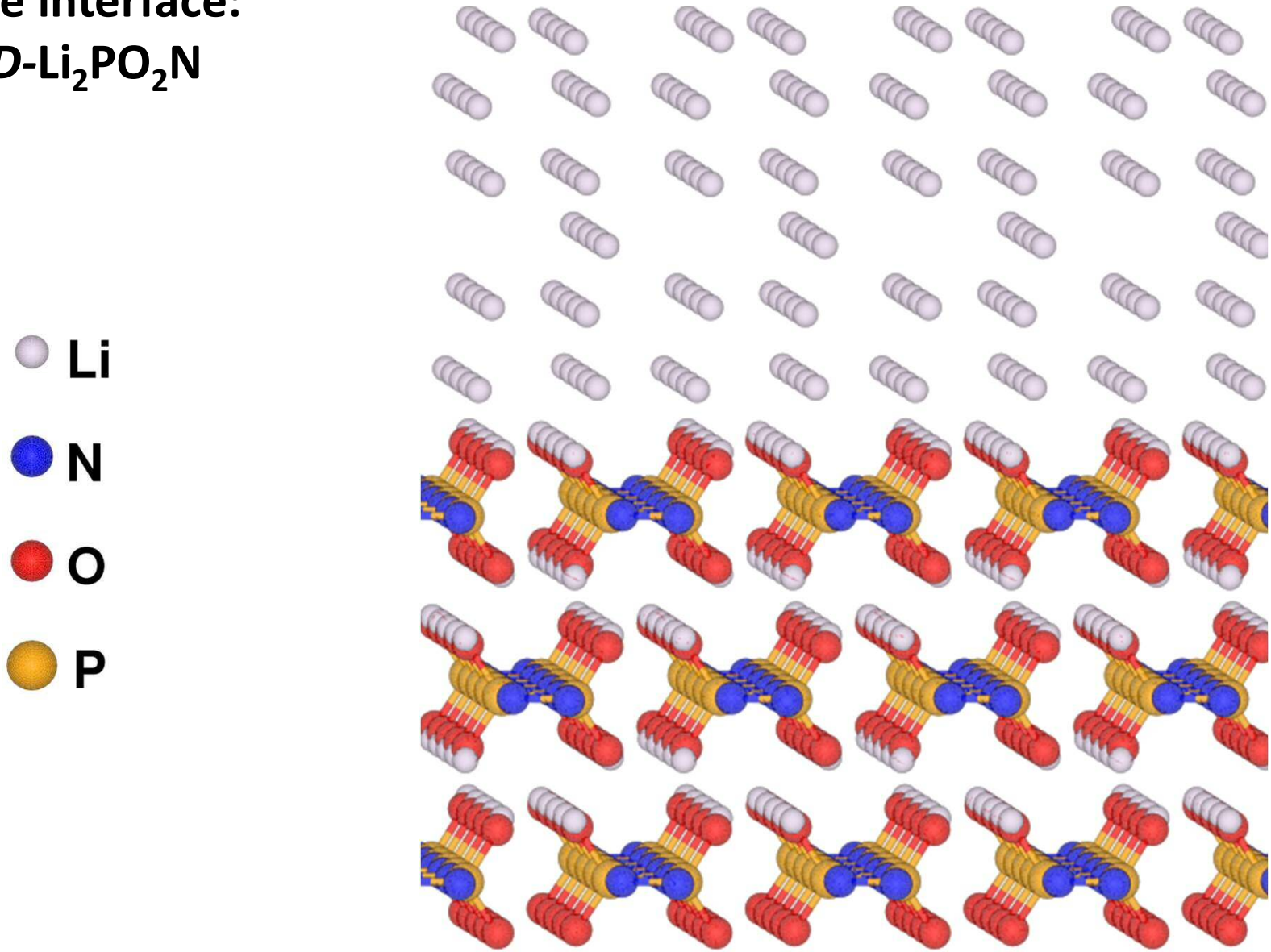
Mystery:

- 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 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



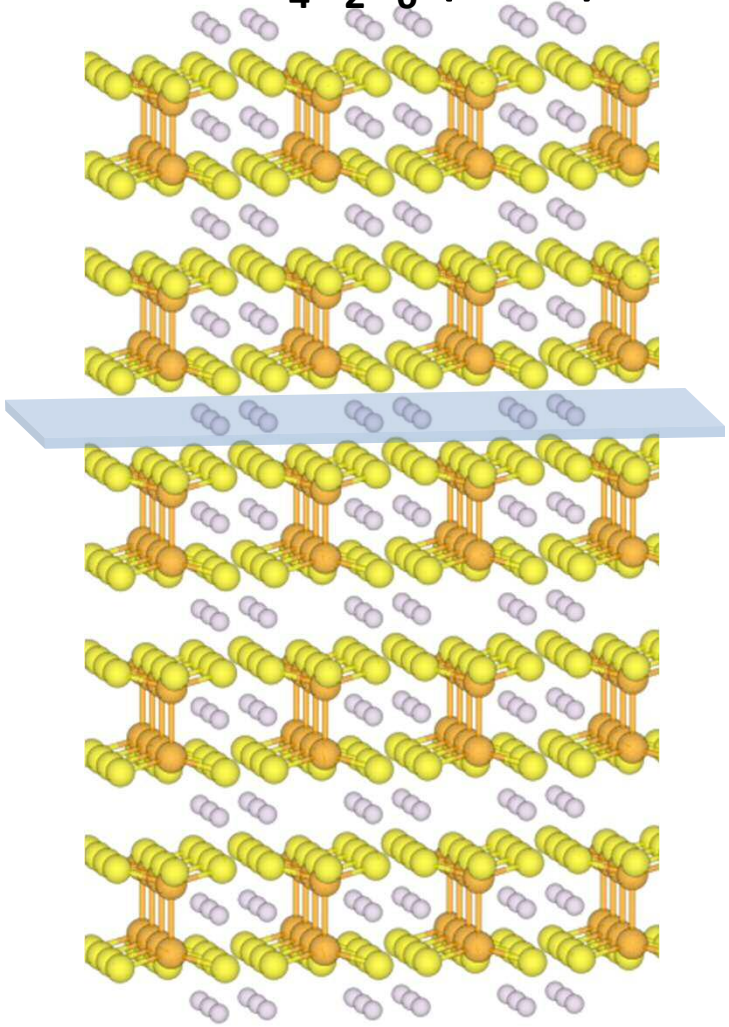
Computational counter example – stable interface: Li/*SD*-Li_2PO_2N



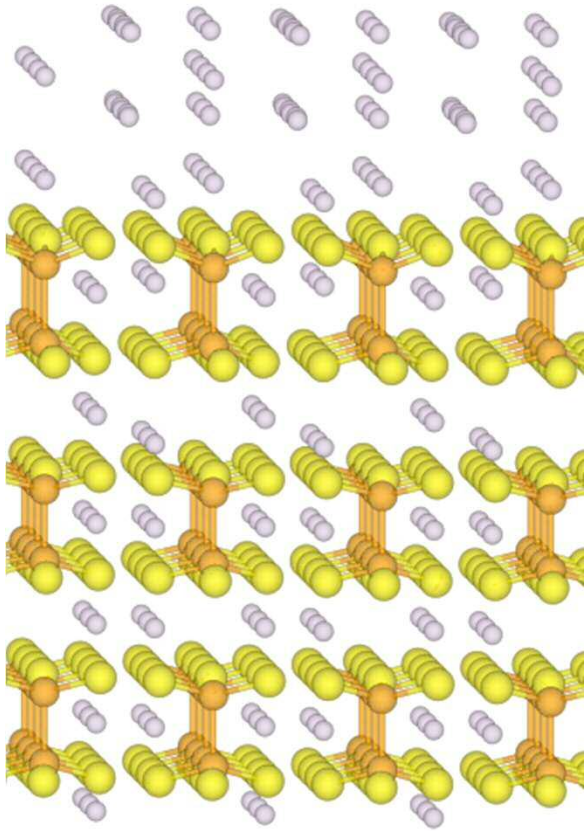
Another example – $Li/Li_4P_2S_6$ -- a more stable thiophosphate?

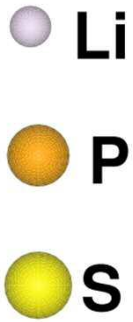
(preliminary results from Cameron Kates)

Bulk $Li_4P_2S_6$ ($P\bar{3}1m$)



[0 0 1] surface of $Li_4P_2S_6$ plus Li





Back to mystery:

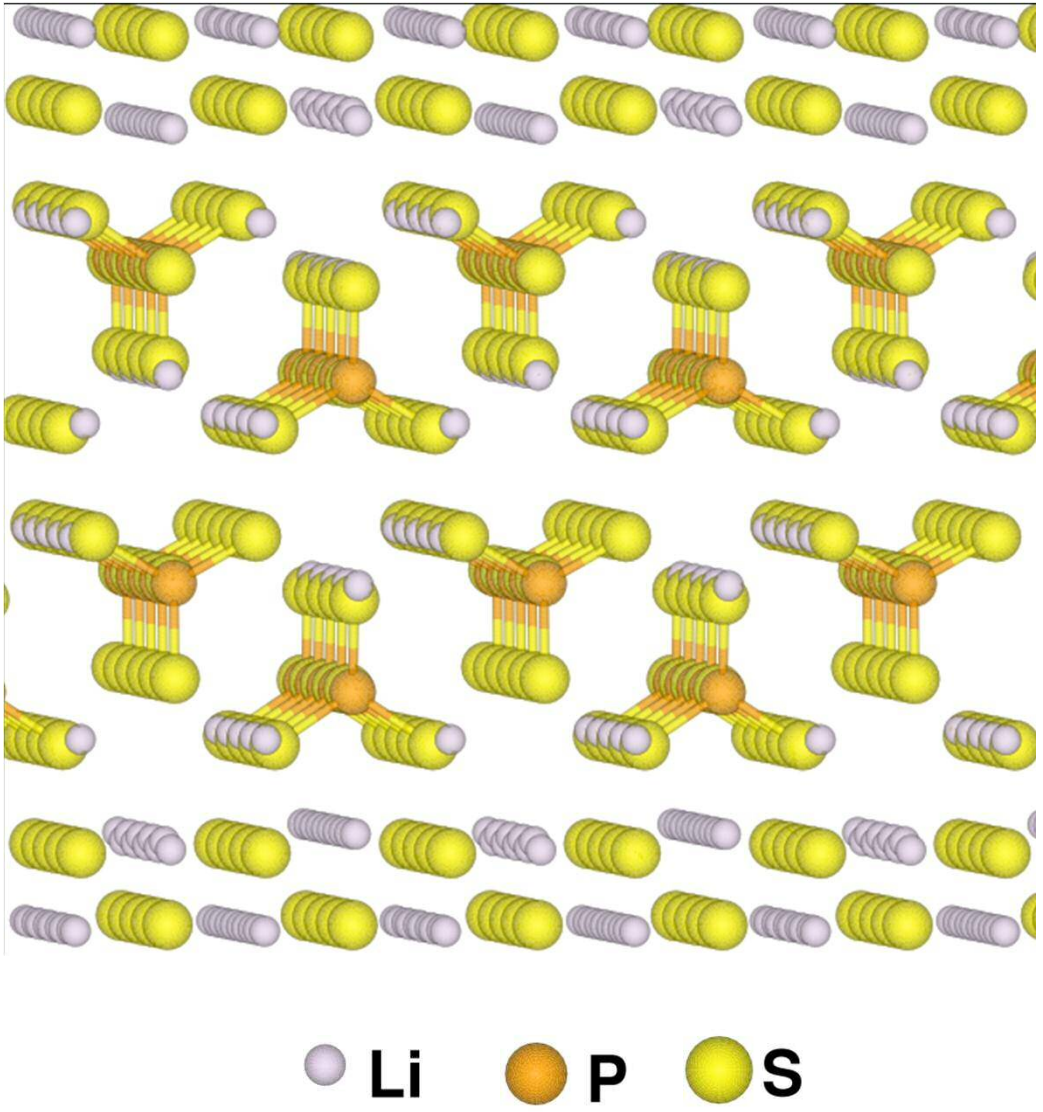
- **Models of ideal Li_3PS_4 surfaces are computational found to be structurally (and chemically) altered by the presence of Li metal. (Also found for β-Li_3PS_4 and for various initial configurations of Li metal.)**
- **Experimentally, the ORNL group has found that solid Li_3PS_4 electrolyte samples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

Possible solution:

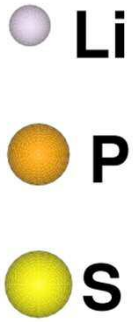
- **Thin protective buffer layer at Li_3PS_4 surface can stabilize electrolyte – for example $Li_2S/Li_3PS_4/Li_2S$**

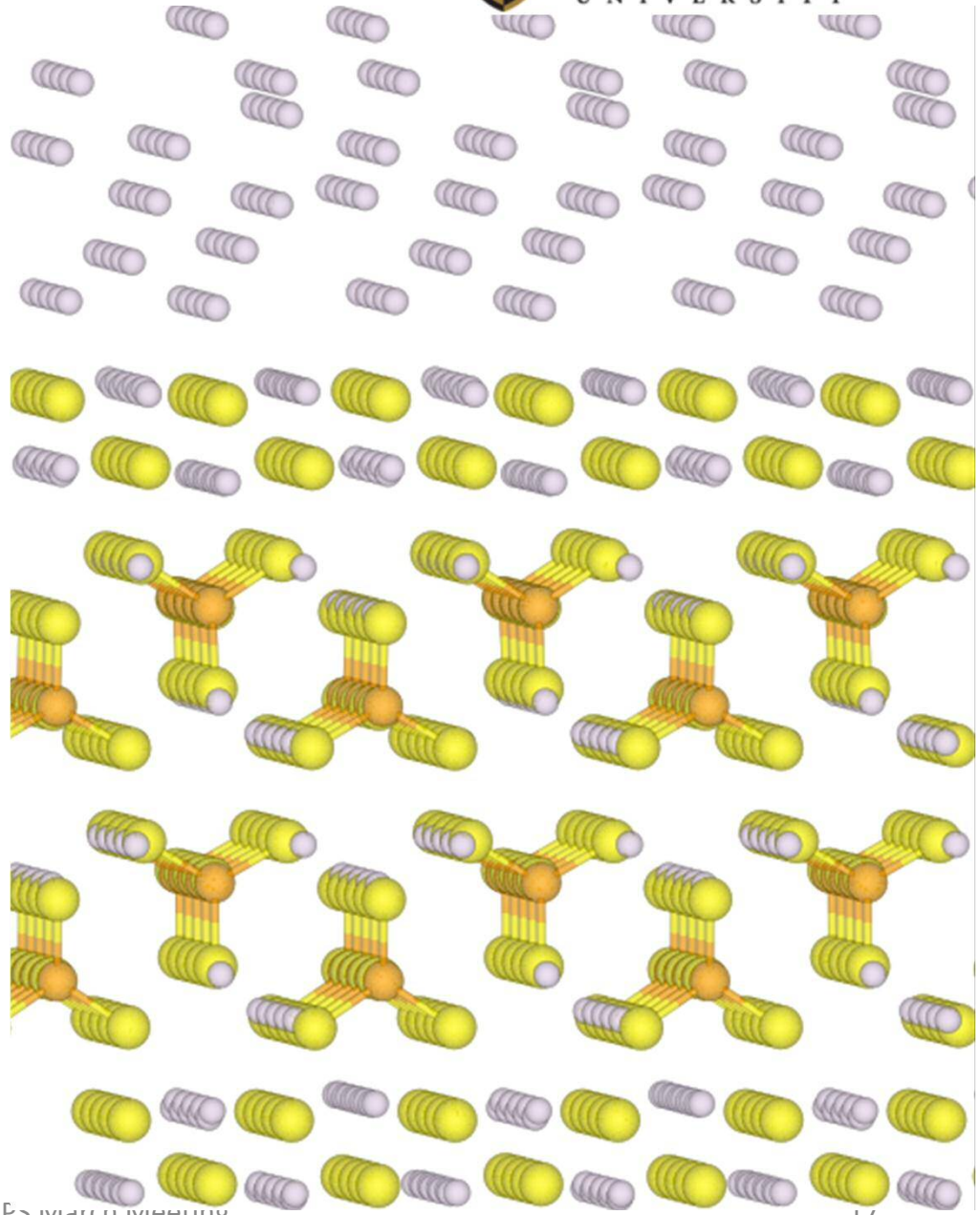
Idealized $Li_2S/Li_3PS_4/Li_2S$ system

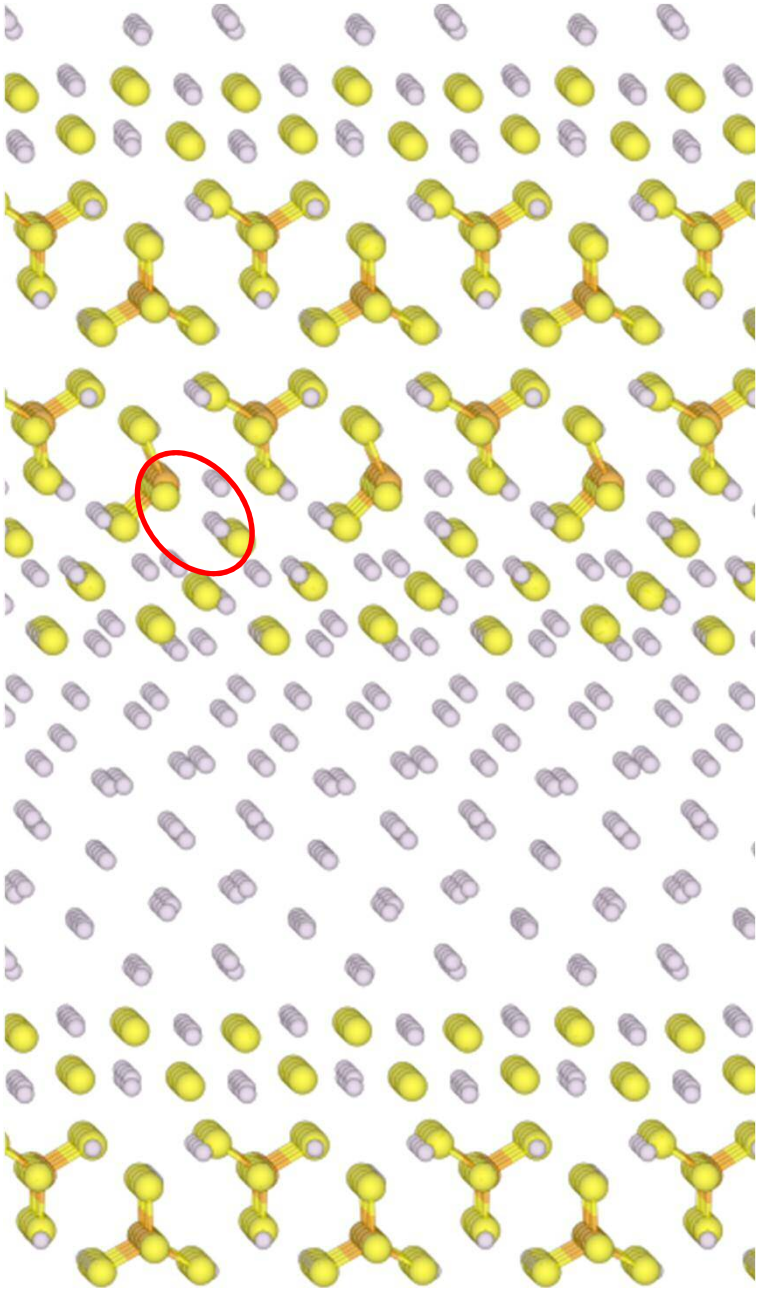
Details:
Thin film of cubic Li_2S oriented in its non-polar [1 1 0] direction, optimized on [0 1 0] surface of γ-Li_3PS_4. While the Li_2S film was slightly strained, the binding energy of the composite was found to be stable with a binding energy of -0.9 eV.



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







Another idealized $Li_2S/Li_3PS_4/Li_2S$ system optimized in presence of Li

Li

P

S

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Summary and conclusions:

- **Models of ideal Li_3PO_4 and Li_2PO_2N 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.**
- **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 provide some stability with respect to Li metal.**
- **Computation results consistent with the conclusion that the ORNL samples of Li/ Li_3PS_4/Li cells may form thin buffer layer in first few cycles and making them stable to further cycling.**

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