Modeling Solid-Electrolyte-Electrode Interfaces

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Motivation

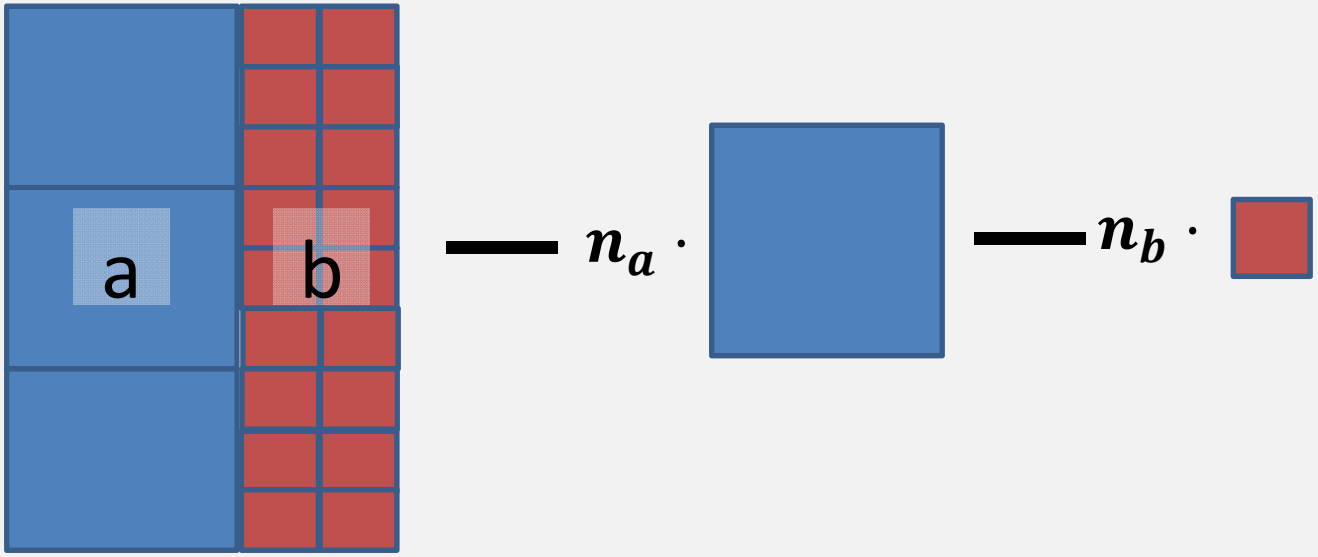
- Solid electrolyte/electrode interfaces more chemically stable
- Enable Li anodes, S cathodes

- Interested in characterizing interface
  - What interface structures are likely?
  - How does variation influence properties?

Formalism

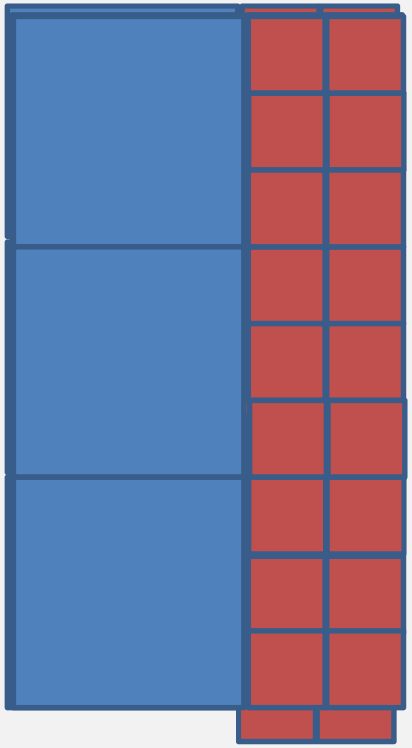
Solid/solid interface energy (γ_{ab}) is given by

$$\gamma_{ab} = \frac{E_{ab} - n_a E_a^{bulk} - n_b E_b^{bulk}}{A}$$



Interface Lattice Mismatch

- 3 different classifications of interfaces depending on lattice alignment
  - Coherent
  - Semi-coherent
  - Incoherent
- Our simulations only consider coherent interfaces



Formalism

- Want to model interface $\mathbb{I}$ with energy γ_{ab}
- Instead we have interface $\tilde{\mathbb{I}}$ with energy $\tilde{\gamma}_{ab}$

$$\tilde{\gamma}_{ab} = \frac{\tilde{E}_{ab} - n_a E_a^{bulk} - n_b E_b^{bulk}}{A} \approx \gamma_{ab} + \frac{E^{str}}{A}$$

- E^{str} is the energy associated with confining material b to the lattice of material a.
  - Should vary with $\mathrm{n_b}$ ($E^{str} = n_b \sigma_b \cdot A$)

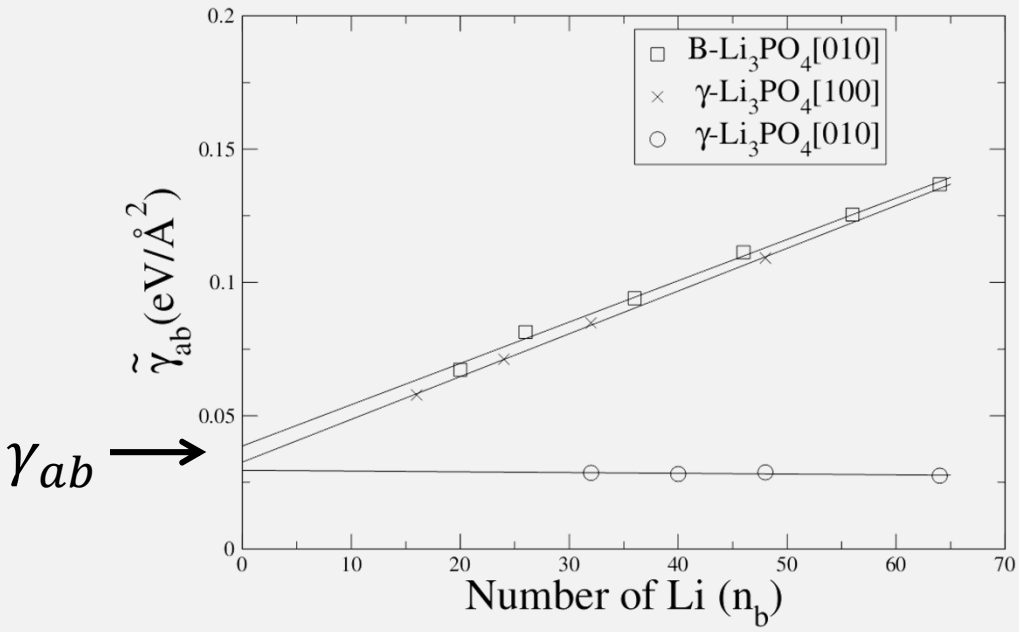
$$\gamma_{ab} = \frac{\tilde{E}_{ab} - n_a E_a^{bulk} - n_b E_b^{bulk} - n_b \sigma_b \cdot A}{A}$$

Formalism

- We calculate $\tilde{\gamma}_{ab}$
- For a given geometry we have

$$\tilde{\gamma}_{ab} \approx \gamma_{ab} + n_b \sigma_b$$

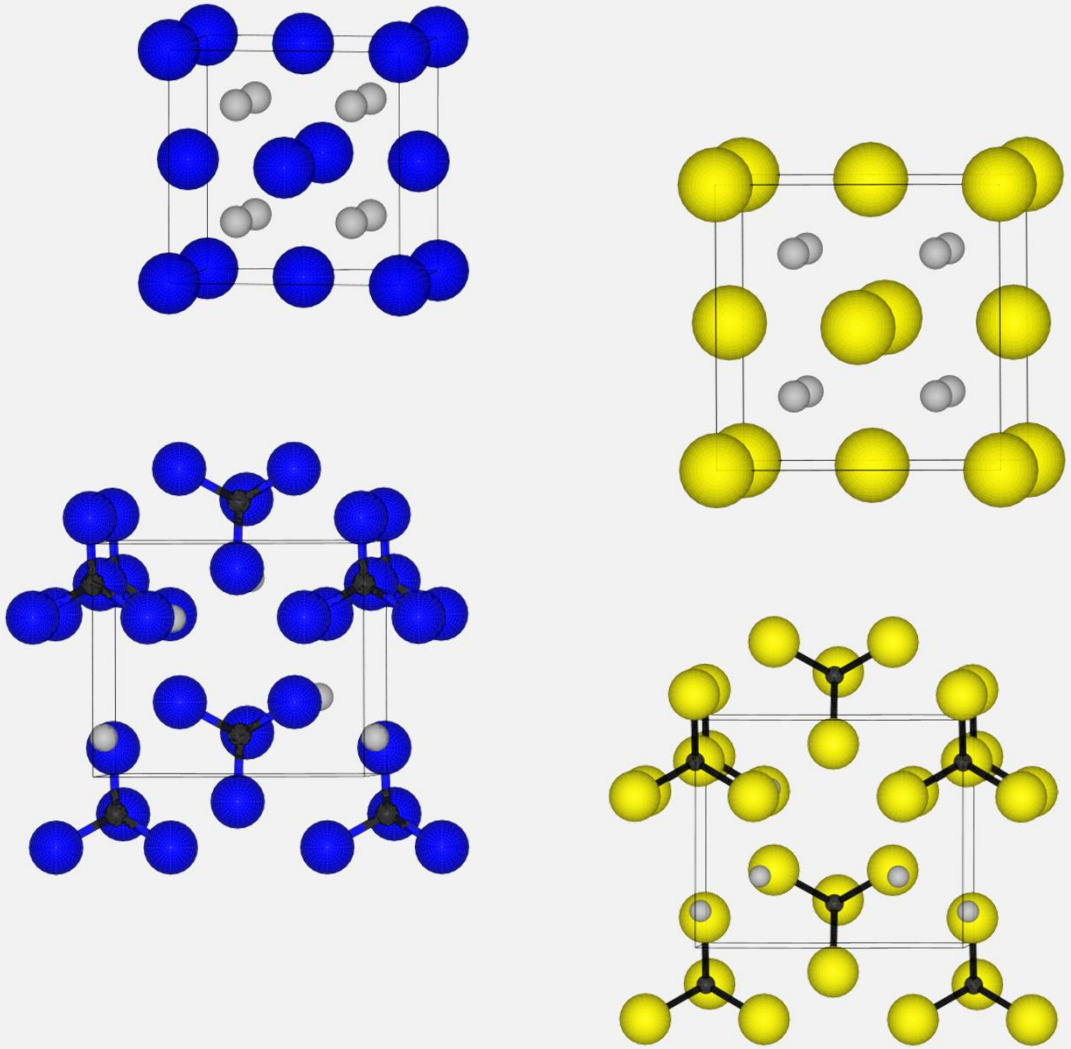
- Equation for a line with γ_{ab} as the y-intercept



Li_3PO_4/Li interface for different phases and cleaves of Li_3PO_4

Materials Considered

- Li_2O/Li
- Li_2S/Li
- Li_3PO_4/Li
- Li_3PS_4/Li
- Li_3PS_4/Li_2S



Oxygen

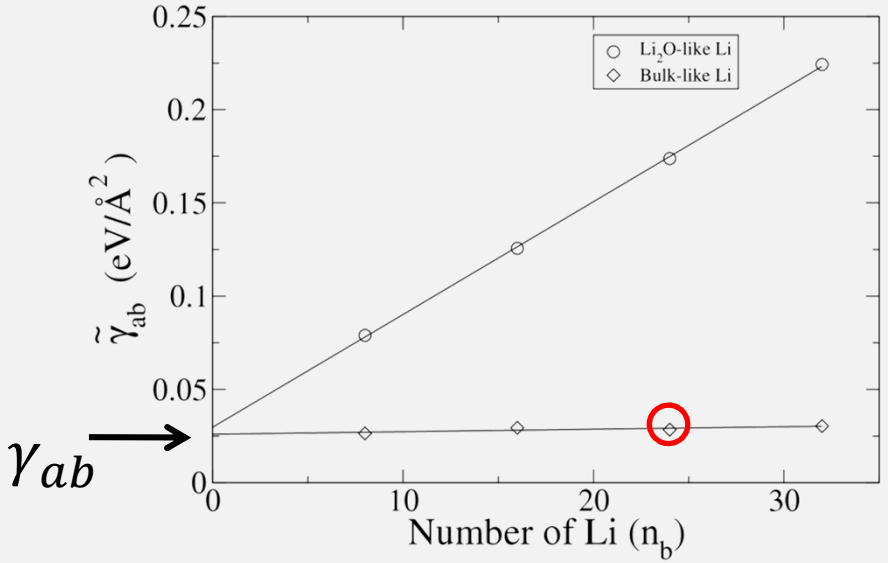
Sulfur

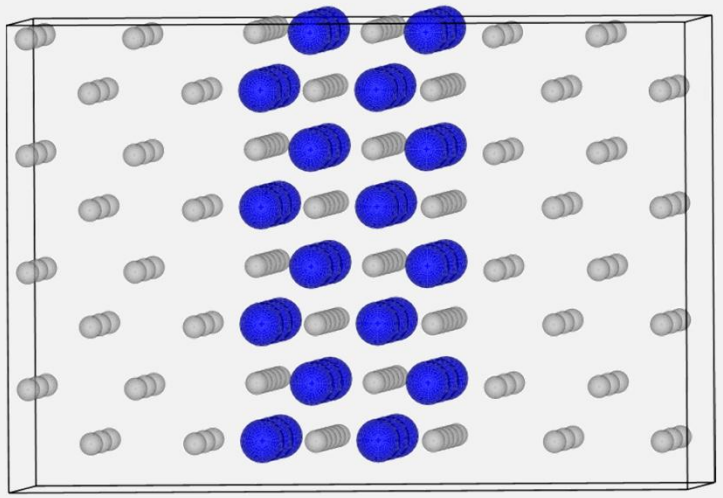
Lithium

Phosphorous

Li_2O/Li

- Good test system
- Stable against Li at equilibrium
- Multiple Li and interface geometries considered



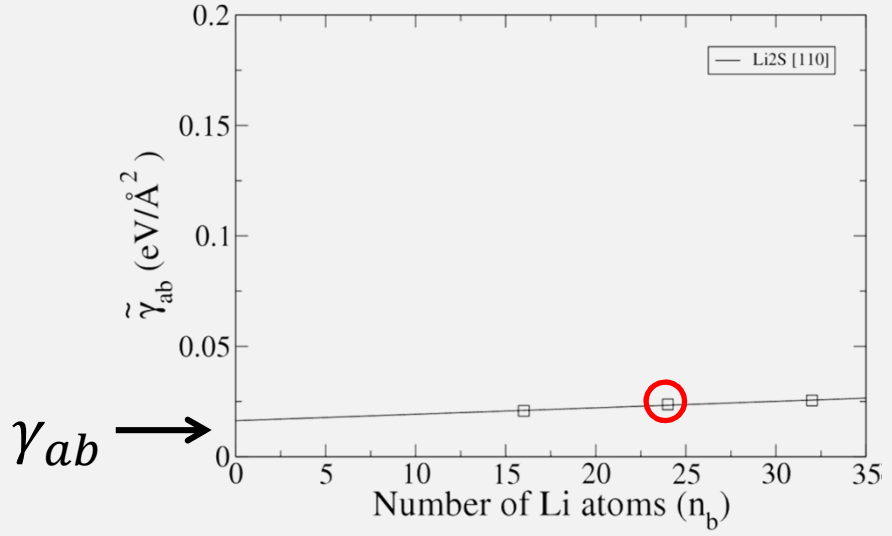


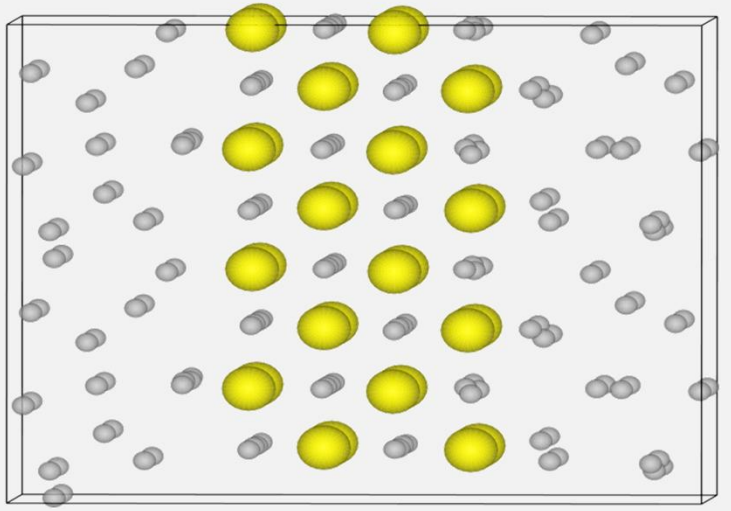
Oxygen

Lithium

Li_2S/Li

- Relevant for Li_3PS_4 and glassy electrolytes
- Stable against Li at equilibrium



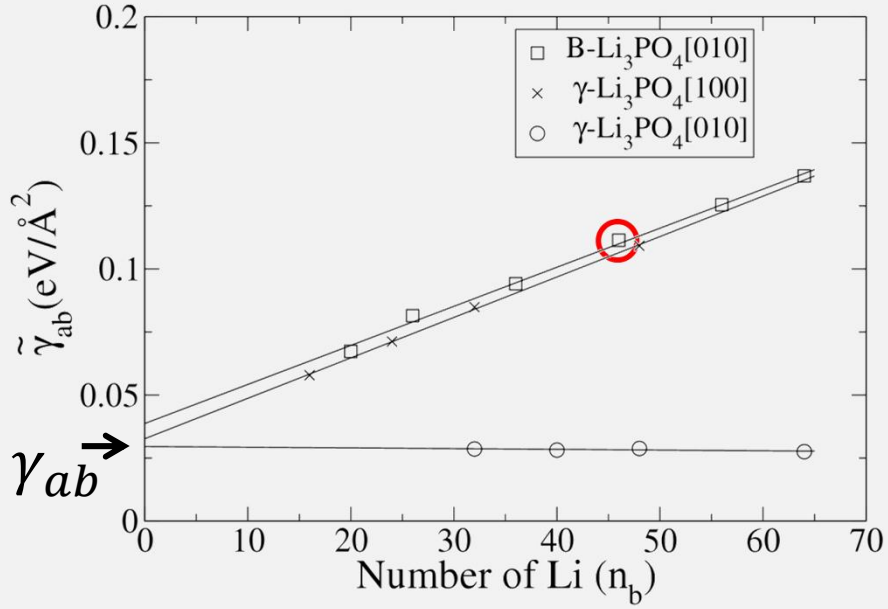


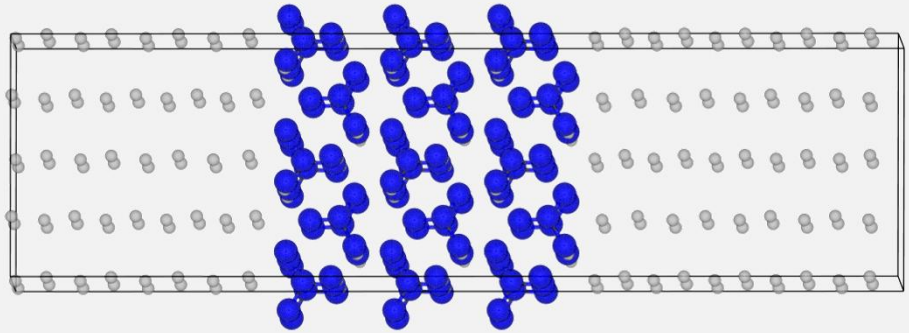
Sulfur

Lithium

Li_3PO_4/Li

- Similar to LiPON electrolyte
- Unstable against Li at equilibrium
- Interface is observed to be stable





Oxygen

Lithium

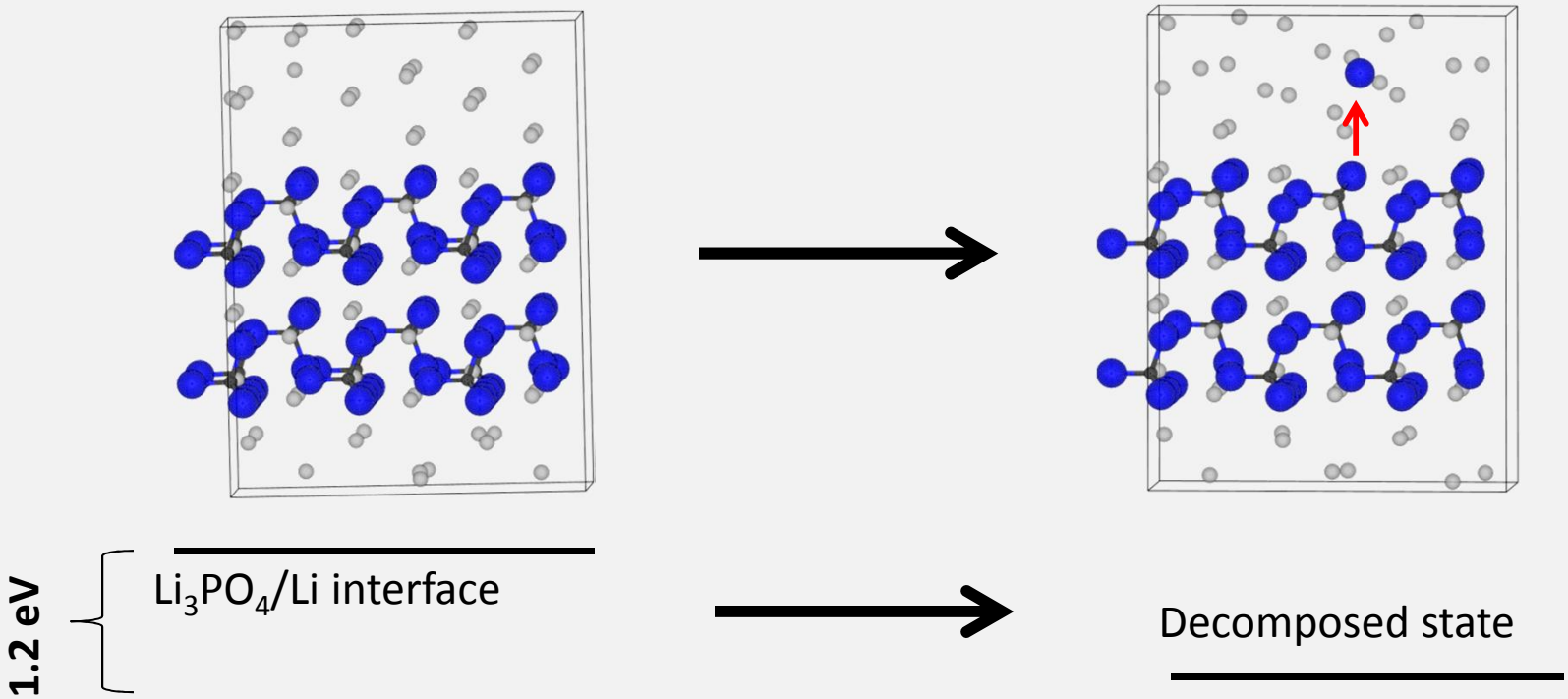
Phosphorous

Li_3PO_4/Li cont'd

- Unstable against Li at equilibrium:

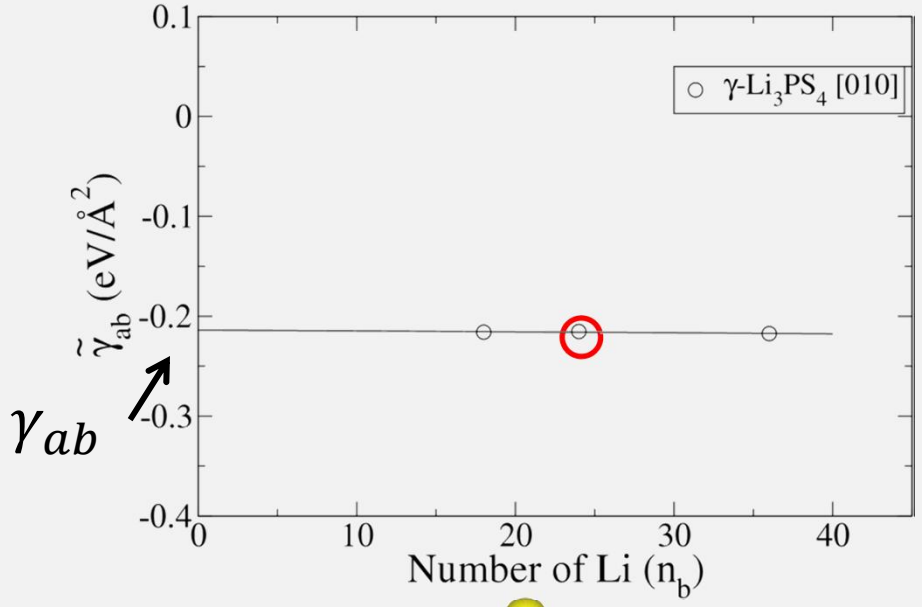
$$\mathbf{Li_3PO_4 + 8\,Li \xrightarrow{yields} Li_3P + 4Li_2O + 6.64\,eV}$$

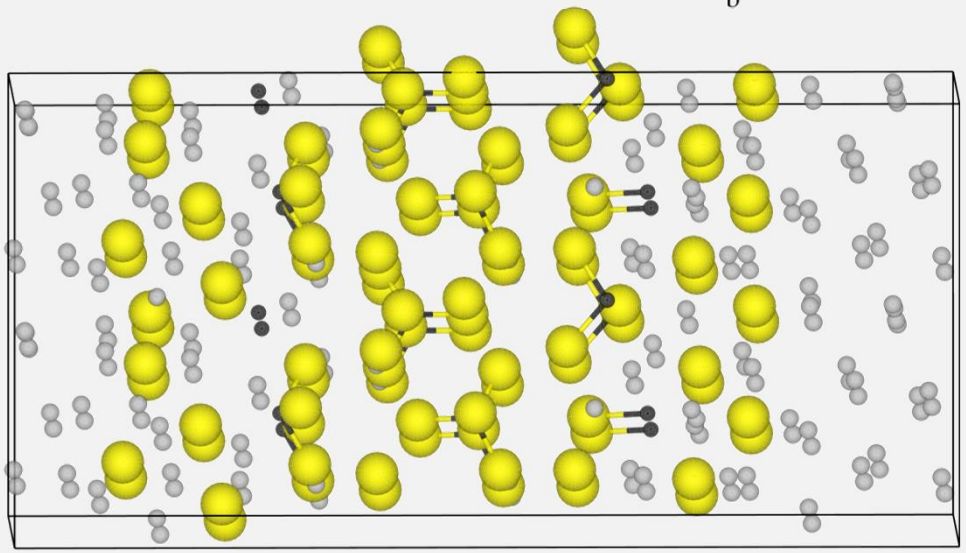
- Investigated Li_3PO_4 decomposition



Li_3PS_4/Li

- Focus of several recent experimental works
- Unstable against Li at equilibrium
- Reactions occur at interface





Sulfur

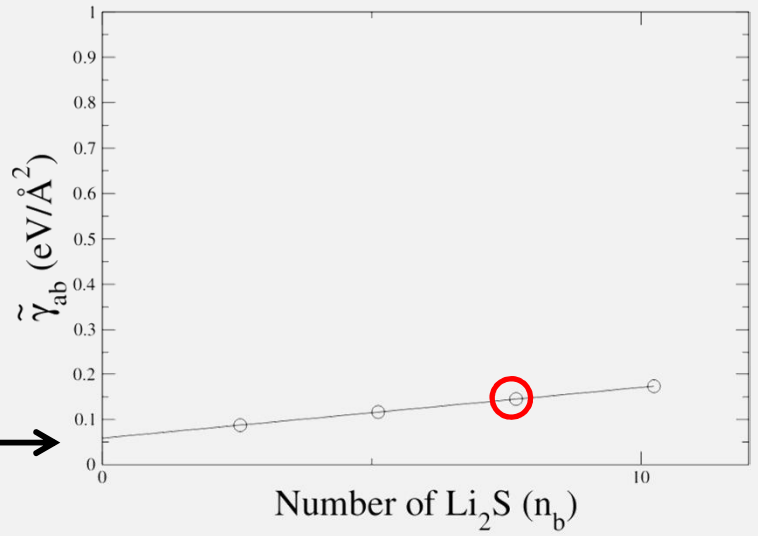
Lithium

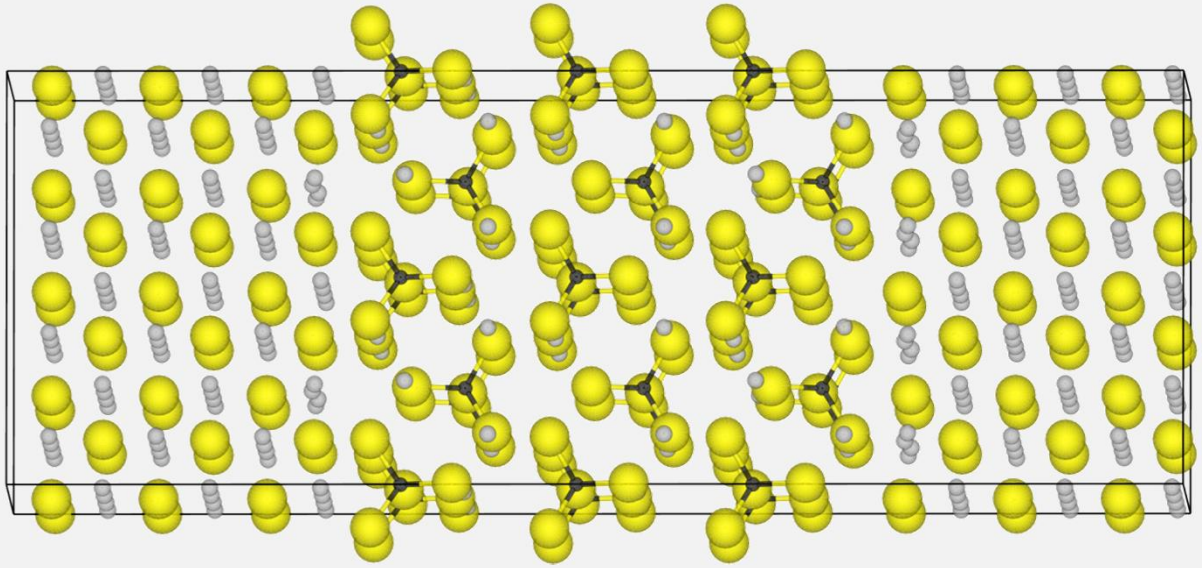
Phosphorous

Li_3PS_4/Li_2S

- We also looked at the stability of the Li_3PS_4/Li_2S interface

γ_{ab} →





Sulfur

Lithium

Phosphorous

γ_{ab} Table

Interface	Description	γ_{ab} (eV/Å^2)
Li2O/Li	Li2O[110]/Bulk Like Li	0.0260
Li2O/Li	Li2O[110]/Li2O-like Li	0.0300
Li2S/Li	Li2S[110]/Bulk Like Li	0.0163
Li_3PO_4/Li	β-Li_3PO_4 [010]	0.0387
Li_3PO_4/Li	γ-Li_3PO_4 [100]	0.0326
Li_3PO_4/Li	γ-Li_3PO_4 [010]	0.0313
Li_3PS_4/Li	γ-Li_3PS_4 [010]	-0.2160
Li_3PS_4/Li_2S	γ-Li_3PS_4 [010]/Li_2S[110]	0.0160

Conclusions

- Developed a new method for removing strain effects from the energetics of model interfaces
- Investigated several electrolyte materials
  - Li_3PO_4/Li interface is (meta)stable
  - Li_3PS_4/Li interface appears to be passivated by Li_2S-like layer
- Negative interface energy associated with reactivity at the interface