Modeling the interface of Li metal and Li solid electrolytes from first principles

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Abstract
The ability to form a stable interface with electrode materials is a necessary material property for potential Li battery electrolytes. Simplified theoretical models often fail to agree with experimental observations of the stability of electrode electrolyte interfaces. An example of this disagreement is the thiosulfate electrolyte material Li$_2$PS$_4$, which is predicted by theoretical calculations to be structurally and chemically altered by the presence of lithium. Experimental results on the other hand have demonstrated an electrochemical cell of Li/Li$_2$PS$_4$/Li with excellent cycle life.

Overview
Solid electrolyte materials are of considerable interest for Li-ion battery applications, both for their use as thin films capable of passivating reactive electrode/electrolyte interfaces, and with the discovery of several new high conductivity solids, as bulk electrolyte materials in their own right. This comparative study extends our previous work and examines the stability of electrochemical interface with Li metal for the electrolyte materials Li$_3$PS$_4$ and Li$_2$PO$_4$.

Methods
The computational methods are based on density functional theory using the LDA exchange correlation functional and the Projector Augmented Wave (PAW) formalism. The calculations were performed using the Quantum Espresso and ABINIT software packages.

For studying surfaces and interfaces we define the following energies. The surface energy $\sigma_{\text{surf}}^i$ for a supercell containing n units of a material is given by the formula:

$$\sigma_{\text{surf}}^i = \frac{E_{\text{total supercell}} - n \cdot E_{\text{total bulk}}}{\text{Area}}$$

We can define an analogous interface energy $\sigma_{\text{int}}^i$ for a supercell containing n units of Li and m units of electrolyte with the relation:

$$\sigma_{\text{int}}^i = \frac{E_{\text{total supercell}} - n \cdot E_{\text{total bulk Li}} - m \cdot E_{\text{total bulk electrolyte}}}{\text{Area}}$$

For the vacuum surface calculations slabs of various thickness were examined to make sure that $\sigma_{\text{surf}}^i$ was well converged. For the interface simulations a large number of interface configurations were used to estimate the size of the error due to finite supercell size effects.

Formation Enthalpy:
The formation enthalpy of the electrolyte materials and possible competing phases was computed. In the presence of free Li ($\mu_{\text{Li}}^0$), as such as at Li anode, the formation enthalpy predicts the decomposition of the electrolyte materials according to the following reactions:

Li$_3$PO$_4$ + 8 Li $\rightarrow$ 4 Li$_2$O + Li$_3$P + 6.65 eV

Li$_3$PS$_4$ + 8 Li $\rightarrow$ 4 Li$_2$S + Li$_3$P + 12.30 eV

While the formation enthalpy suggests the electrolytes are unstable, experimental results show that both materials are capable of being cycled hundreds of times with Li electrodes. In our Li$_2$PO$_4$ simulations, Li$_2$O is not observed, while for the Li$_3$PS$_4$ interface there does appear to be a glassy Li$_3$S-like product produced at the interface. For Li$_3$PO$_4$, the experimental stability may be the result of passivation of the interface by Li$_2$S.

Interface Results:
For the Li$_2$PO$_4$ interfaces, the interface energy is positive and on the same order of magnitude as the surface formation energy. The Li$_2$PO$_4$ interface energies on the other hand are negative and an order of magnitude larger than the corresponding surface energies. This reflects the large energy changes associated with the chemical adsorption and disruption of the P-S bonds.

Large kinetic barriers prevent the Li$_2$PO$_4$ interface from decomposing the way the Li$_3$PO$_4$ interface does. An O moved into the Li slab so that the P-O bond is broken results in a configuration 1.2 eV lower in energy than the stable Li$_2$PO$_4$/Li interface. However there is a +2.7 eV barrier associated with this movement. Interestingly, this is comparable to the difference in the P-O and the Li-O bond strengths (2.58 eV).

Partially Density of States
The partial density of states result suggest that the electrolyte stability or instability may be due to the position of the electrolyte valence band relative to the Li Fermi level. Specifically, because the reaction pathway suggested by the formation enthalpy analysis requires that phosphorous change oxidation states from P$^4+$ to P$^3+$ the kinetic barrier that prevents the interface from reacting appears to be the barrier for electron transfer from the Li to the electrolyte. While the Li$_2$PO$_4$ interface is unstable, and has empty conduction state below the Li Fermi level, Li$_3$PO$_4$ does not. Li$_3$PO$_4$ thus appears to be capable of insulating the Li$_3$PS$_4$ by confining the Li electrons in the metal. Our results suggest that this passivation is what enables Li$_3$PO$_4$ to function as an electrolyte material.

Discussion
Our results suggest that the electrochemical interface cannot be adequately described by equilibrium models such as the formation enthalpies. The stability-instability of Li$_2$PO$_4$/Li$_3$PO$_4$ appears to be determined by the presence of a kinetic barrier associated with the reduction of the phosphorus in the electrolyte and the relative position of the Li Fermi level and the P conduction band.

For Li$_2$PO$_4$ and Li$_3$PO$_4$, the interface stability and interface energies do not appear to be qualitatively affected by the phase or cleavage of the electrolyte.

Our simulations suggest that the apparent electrochemical stability of Li$_3$PO$_4$ is due to the formation of passivating Li$_2$S at the interface. This combined formation enthalpy and interface DOS analysis should generalize to other systems.

References: