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First Principles Modeling of Electrolyte Materials in All-Solid-State Batteries

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Abstract

This contribution reviews the series of approximations that comprise “first principles” modeling techniques which we have used in recent years to simulate ideal models of solid electrolytes, some of which are of technological interest in the development of all-solid-state battery technologies.

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1. Introduction

The definition of “first principles” calculations varies across various sub-disciplines. First principles calculations of the electronic structure of materials generally implies a series of well-controlled physical, mathematical, and numerical approximations that simulate the properties of actual materials in terms of their constituent electrons and nuclei. One example of the use of these techniques, is in the study of solid electrolyte materials.

The general development of crystalline solids as electrolytes in battery applications has a long history as discussed in several review articles and monographs (Huggins (2009); Takada (2013)). In the present contribution, we describe the use of first-principles calculations for the study of a family of solid electrolyte materials composed of Li phosphates and thiophosphates. The thin film solid electrolyte LiPON developed at Oak Ridge National Laboratory (ORNL) (Dudney (2008); Bates et al. (2000); Yu et al. (1997); Wang et al. (1995a); Bates et al. (1995); Wang et al. (1995b); Bates et al. (1994, 1993, 1992)), is a very widely used solid electrolyte for thin film batteries and a number of other related technologies (Patil et al. (2008)). In addition to studies at ORNL, there has been considerable research (Mascaraque et al. (2013); Kim and Wadley (2009); Hamon et al. (2006); Park et al. (2006)) on the preparation and properties of LiPON materials. One of the outstanding attributes of LiPON electrolytes is its long term stability in contact with a pure lithium anodes (Wang et al. (1996)). LiPON electrolytes have the composition of $\text{Li}_x\text{PO}_y\text{N}_z$ where

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$x = 2y + 3z - 5$; those with the highest ionic conductivities (10^{-6} S/cm) have a glassy structure and a range of values of $0.2 \leq z \leq 0.7$ representing the ideal nitrogen contribution (Dudney (2000, 2008); Mascaraque et al. (2013)). At the present time, we know of no experimental evidence that crystalline members of the LiPON family of materials can approach the conductivities of the LiPON glasses, however, a systematic study of the LiPON family of crystalline materials (Du and Holzwarth (2010b)) has proven useful for developing an understanding of the fundamental structures and properties of LiPON electrolytes. Meanwhile, the structurally and chemically related Li thiophosphate family of materials have recently received attention as promising candidates for solid-state electrolytes (Mizuno et al. (2005b,a, 2006); Yamane et al. (2007); Hayashi (2007); Tatsumisago and Hayashi (2008); Minami et al. (2008); Hayashi et al. (2008, 2009); Trevey et al. (2009); Liu et al. (2013)) where increased ionic conductivities as large as 10^{-3} S/cm have been reported. These materials are characterized by the composition Li_xPS_w . The comparison between the crystalline Li phosphates and corresponding thiophosphates has provided further insight into solid electrolyte development.

In Section 2 we describe “first principles” computational techniques and their validation. In Section 3 we present some results from our studies of lithium phosphate and thiophosphate electrolytes. Section 4 contains a brief summary and discussion.

2. Computational methods

In the context of electronic structure calculations, the term “first-principles” techniques implies a series of well-developed approximations to the exact quantum-mechanical description of a material with N_e electrons and N_N nuclei. Denoting the electron coordinates by $\{\mathbf{r}_i\}$ ($i = 1, 2, \dots, N_e$) and nuclear coordinates by $\{\mathbf{R}_\alpha\}$ ($\alpha = 1, 2, \dots, N_N$), the many-particle Schrödinger equation takes the form

$$\mathcal{H}(\{\mathbf{r}_i\}, \{\mathbf{R}_\alpha\}) \Psi_\alpha(\{\mathbf{r}_i\}, \{\mathbf{R}_\alpha\}) = E_\alpha \Psi_\alpha(\{\mathbf{r}_i\}, \{\mathbf{R}_\alpha\}), \quad (1)$$

where \mathcal{H} denotes the quantum mechanical Hamiltonian, and E_α and $\Psi_\alpha(\{\mathbf{r}_i\}, \{\mathbf{R}_\alpha\})$ denote the energy eigenvalue and the corresponding eigenfunction, respectively. The solution of Eq. (1) with $N_N N_e$ coupled variables, is intractable for all but the smallest systems. The analysis of Born and Oppenheimer (Born and Huang (1954)) noting that the electron mass is 10^{-3} times smaller than the nuclear mass, leads to an approximate separation of the nuclear and electronic motions. Operationally, the nuclei are treated as classical particles with interaction energies consistently determined by expectation values of the electronic Hamiltonian. The electronic Hamiltonian and the corresponding Schrödinger equation should be solved for each set of nuclear positions $\{\mathbf{R}_\alpha\}$. The solution of the Born-Oppenheimer electronic Schrödinger equation is further approximated with the use of density functional theory developed by Kohn, Hohenberg, and Sham (Hohenberg and Kohn (1964); Kohn and Sham (1965)), representing the effects of the N_e electrons in terms of their density and the corresponding a self-consistent mean-field. The reliability of density functional theory in the representation of real materials depends on the development of the exchange-correlation functional form. While this remains an active area of research, the local density approximation (LDA) (Perdew and Wang (1992)) and the generalized gradient approximation (GGA) (Perdew et al. (1996)) often work well, particularly for modeling the ground state properties of solid electrolytes. Within density functional theory, the electronic energy of a system of N_e electrons can be expressed as a sum of contributions:

$$E(\rho, \{\mathbf{R}_\alpha\}) = E_K + E_{ee} + E_{xc} + E_{eN} + E_{NN}, \quad (2)$$

representing the electronic kinetic energy, the coulombic electron-electron repulsion, the exchange-correlation energy, the electron-nuclear interaction energy, and the nuclear-nuclear interaction energies respectively. The electron density $\rho(\mathbf{r})$ is self-consistently determined from Kohn-Sham single particle wavefunctions for each state n :

$$H^{KS} \psi_n = \epsilon_n \psi_n \quad \text{where} \quad \rho(\mathbf{r}) = \sum_{n=1}^{N_e} |\psi_n(\mathbf{r})|^2 \quad \text{and} \quad H^{KS} = \frac{\partial E(\rho, \{\mathbf{R}_\alpha\})}{\partial \rho(\mathbf{r})} \quad (3)$$

at self-consistency. Here, H^{KS} denotes the Kohn-Sham Hamiltonian.

In addition to well-controlled mathematical and physical approximations, numerical approximations are needed to solve the density functional equations. There are many successful numerical schemes, most of which grew from the frozen-core approximation (von Barth and Gelatt (1980)) and from the refinement of the pseudopotential formalism

(Phillips and Kleinman (1959)) with the development of first-principles pseudopotentials (Hamann et al. (1979); Kerker (1980)). A significant boost to the field was contributed by Car and Parrinello (Car and Parrinello (1985)) who showed that within the Born-Oppenheimer approximation, the self-consistent electronic structure algorithm could be efficiently coupled to the adjustment of the nuclear coordinates for structural and molecular dynamics studies. In addition to the adjustment of the nuclear coordinates, techniques were developed to allow for variable simulation cells in order to simulate the effects of pressure, stress, or phase transitions. (Andersen (1980); Parrinello and Rahman (1981); Wentzcovitch (1991)) Response function methods and density-functional perturbation theory methods were developed by Gonze, (Gonze (1997); Gonze and Lee (1997)) allowing for the exploration of materials properties in the vicinity of equilibrium including the dynamical matrix and phonon modes. The efficiency and accuracy of the pseudopotential approach was significantly improved with the introduction of so-called ultra-soft pseudopotentials (USPP) by Vanderbilt (Vanderbilt (1990)) and the projector augmented plane wave (PAW) method by Blöchl. (Blöchl (1994))

An invaluable contribution to the success of computational studies of materials, particularly those discussed in this contribution, has been the development of several open source software projects such as ABINIT (Gonze et al. (2009)) and QUANTUM ESPRESSO. (Giannozzi et al. (2009)) These codes make use of many of the state-of-the-art formalism developments including those listed above. These projects promote scientific productivity by reducing the duplication of coding efforts and by allow developers and users to share in the implementation and debugging of a common code system. The pseudopotential data files were generated using the ATOMPAW package (Holzwarth et al. (2001)) and the USPP package (Vanderbilt (1990)) Also important is the development of visualization tools. In the present work, OpenDx (OpenDX (1999)), XCrySDen (Kokalj (1999, 2003)), and VESTA (Momma and Izumi (2011)) were used.

For solid electrolytes which are electronically insulating and which operate in their ground electronic states, the calculation of the electronic energy $E(\rho, \{\mathbf{R}_a\})$ using density functional theory (Eq. (2)) works quite well. By using constrained optimization of the energy $E(\rho, \{\mathbf{R}_a\})$ over the nuclear coordinates $\{\mathbf{R}_a\}$, it is possible to study structural parameters of stable and meta-stable structures. A reasonable estimate of the heat of formation ΔH of each compound material can be computed from the ground state energies at zero temperature and these are useful in quantifying the expected stability of the materials in various structures and compositions.

It is always important to question the reliability of computer simulations for describing real materials. Typically, it has been reported Du and Holzwarth (2007) that results obtained using the LDA exchange-correlation functional (Perdew and Wang (1992)) tend to underestimate the lattice parameters by 2% while results obtained using the GGA exchange-correlation functional (Perdew et al. (1996)) tend to overestimate the lattice parameters by 1%. On the other hand, for most materials, the fractional coordinates computed for the non-trivial site positions are nearly identical (within 0.1%) for LDA and GGA calculations in comparison with experiment. Similar findings have been reported in the literature for a wide variety of computational studies of insulating, non-transition metal materials.

One quantitative indication of the accuracy of the calculations is the comparison of computed and measured normal modes of vibrations. Fortunately, there have been several reports of experimental measurements of Raman and infrared absorption spectra of crystalline Li_3PO_4 (Tarte (1967); Harbach and Fischer (1974); Riedener et al. (2000); Smith et al. (2002); Mavrin et al. (2003); Popović et al. (2003)); therefore our simulations of the zone center phonon modes serve as a validity check the calculations. Figure 1 shows two similar but distinct crystal structures of Li_3PO_4 for which the normal modes have been studied.

Figure 2 shows the spectra of Raman active modes calculated using the LDA and GGA exchange-correlation functions and USPP (Vanderbilt (1990)) and PAW (Holzwarth et al. (2001)) pseudopotential datasets compared with various experimental measurements for the γ and β structures. There is variation among the various experimental measurements for γ - Li_3PO_4 , some of which can be attributed to temperature and some attributed to resolution. In terms of comparing experiment to the calculations, it is striking that for frequencies $\nu > 600 \text{ cm}^{-1}$, the results calculated using the LDA functional are in good agreement with experiment, while the agreement deteriorates at lower frequencies. These high frequency modes are mainly due to internal vibrations of the PO_4 tetrahedra. The lack of agreement for the lower frequency modes is likely to be due to numerical error which is also reflected in the differences between the two LDA calculations using USPP and PAW datasets. The good agreement between the simulations and experiment for the higher frequency vibrational modes of these materials motivated the choice of the LDA functional for most of our simulation studies on the Li phosphates and thiophosphates (Du and Holzwarth (2007, 2008a,b); Holzwarth et al.

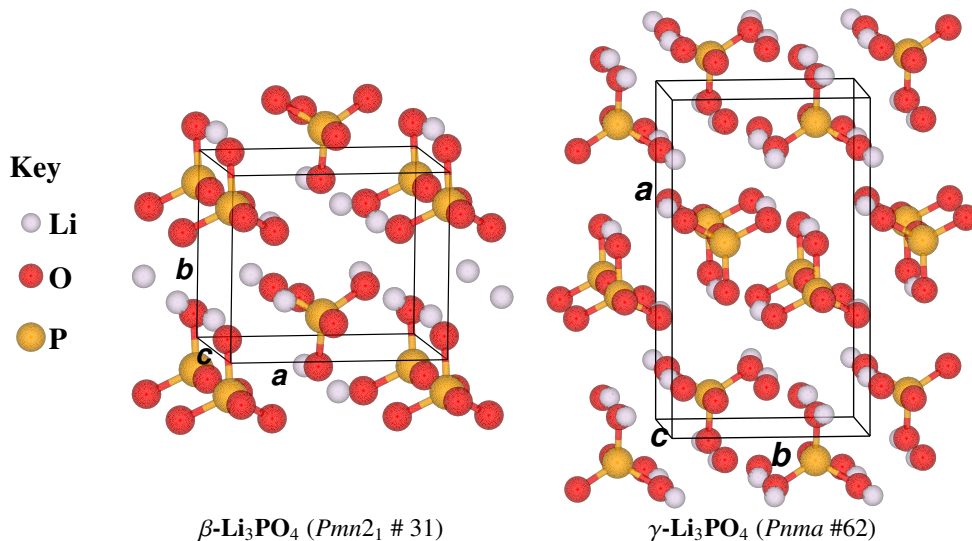


Fig. 1. Ball and stick diagrams for the structures of $\beta\text{-Li}_3\text{PO}_4$ and $\gamma\text{-Li}_3\text{PO}_4$, each with the indicated space group name and number as listed in the *International Table of Crystallography*. Hahn (2002) The orthorhombic unit cells and the corresponding lattice parameters a , b , and c are also indicated. The key shown at the left indicates the ball conventions.

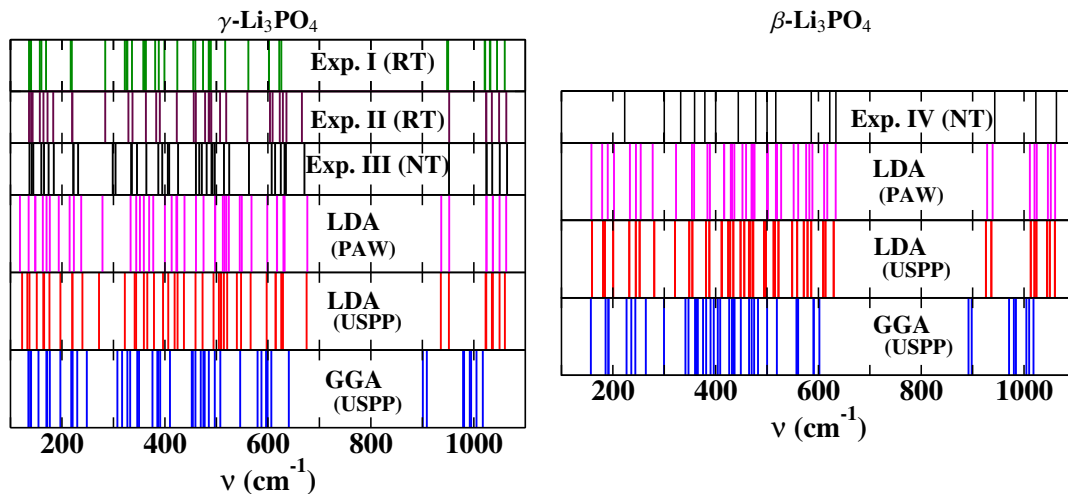


Fig. 2. Comparison of experimental and calculated Raman spectra for $\gamma\text{-Li}_3\text{PO}_4$ (left) and $\beta\text{-Li}_3\text{PO}_4$ (right). The experimental measurements were performed at room temperature (RT) and at liquid nitrogen temperature (NT). Exp. I was taken from Ref. [Mavrin et al. (2003)] and Exp. II and III were taken from Ref. [Harbach and Fischer (1974)], and Exp. IV was taken from Ref. [Popović et al. (2003)]. These are compared with calculated results using PAW and USPP formalisms and LDA and GGA exchange-correlation functionals.

(2011); Du and Holzwarth (2010a,b); Lepley and Holzwarth (2011, 2012); Senevirathne et al. (2013); Lepley et al. (2013)).

3. Some results for solid electrolytes based on lithium phosphates and thiophosphates

In the course of a systematic study of the family of crystalline compounds of $\text{Li}_x\text{PO}_y\text{N}_z$ compounds, the possibility of substituting N for O in natural LiPO_3 was studied computationally. Du and Holzwarth (2010b) Starting from the $P2/c$ structure of natural LiPO_3 , the 20 bridging oxygens were replaced by nitrogens and 20 additional Li atoms were

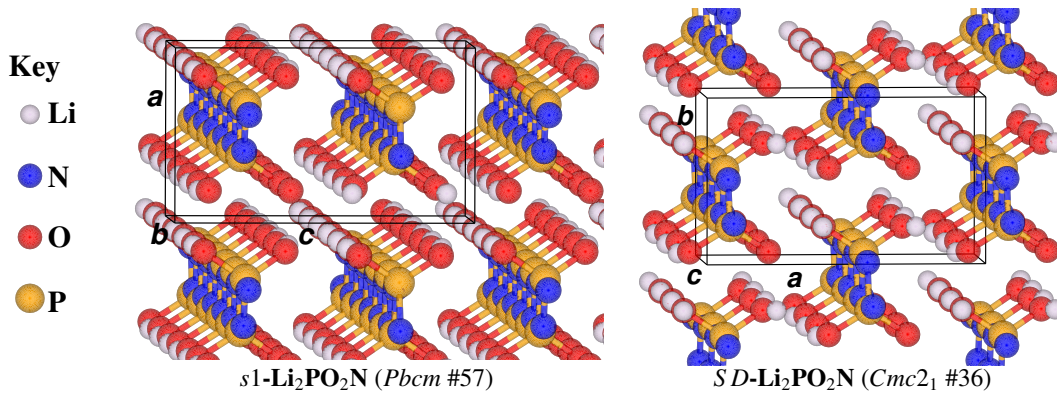


Fig. 3. Ball and stick diagrams of the unit cells of $s_1\text{-Li}_2\text{PO}_2\text{N}$ (4 formula units per unit cell) and $SD\text{-Li}_2\text{PO}_2\text{N}$ (2 formula units per unit cell), each in their indicated space group. The key shown at the left indicates the ball conventions.

introduced into the structure to maintain charge neutrality. The relaxation results were remarkable; showing that the nitrated chain has a very stable structure with a periodic chain composed of $(\text{PO}_2\text{N})_2$ groups. The first optimized structure obtained from the simulation was called $s_1\text{-Li}_2\text{PO}_2\text{N}$ and was found to have 24 atoms per unit cell with the space group *Pbcm* (#57) as visualized in Fig. 3. The most intriguing structural feature of the simulated structure of $s_1\text{-Li}_2\text{PO}_2\text{N}$ compared to its parent LiPO_3 material, is the regularization of the chain structure with a planar -P-N-P-N- backbone. In 2013, a form of $\text{Li}_2\text{PO}_2\text{N}$ was experimentally realized by Senevirathne et. al. (Senevirathne et al. (2013)). The synthesized material, called $SD\text{-Li}_2\text{PO}_2\text{N}$ has the *Cmnc21* (#36) space group and differs from the s_1 structure primarily in the arrangement of the phosphate chains. The solid state synthesis of $SD\text{-Li}_2\text{PO}_2\text{N}$ used the reaction



which is predicted to be exothermic from the computed heats of formation. $SD\text{-Li}_2\text{PO}_2\text{N}$ is visualized in Fig. 3. Subsequent computer simulations verified that the $SD\text{-Li}_2\text{PO}_2\text{N}$ structure is more stable than the $s_1\text{-Li}_2\text{PO}_2\text{N}$ structure by 0.1 eV. Whether $SD\text{-Li}_2\text{PO}_2\text{N}$ will be technologically useful remains to be seen. Preliminary electrochemical experiments Senevirathne et al. (2013) find the ionic conductivity to be quite small.

In addition to modeling idealized pure materials, simulations have contributed to the study of interfaces between the electrolyte and an electrode. We have carried out simulations of the interface between several Li (thio) phosphate materials and anodes composed of pure (metallic) lithium. In Fig. 4 we show examples of idealized structures of interfaces of lithium metal with Li_3PO_4 and with $\text{Li}_2\text{PO}_2\text{N}$ where the calculations easily find idealized interface structures for a variety of initial lithium configurations. The stability of electrolyte interface with Li anodes is consistent with electrochemical measurements on these systems.

While the LiPON family of electrolytes has impressive stability with respect to pure Li anodes, its use has been primarily confined to micro-battery applications because of its low ionic conductivity. Meanwhile Li thiophosphates having the composition Li_vPS_w have shown significant promise as electrolyte materials.

Recently, researchers at ORNL (Liu et al. (2013)) have prepared symmetric electrochemical cells of Li_3PS_4 electrolyte in contact with lithium anodes on either side – $\text{Li}/\text{Li}_3\text{PS}_4/\text{Li}$ – and showed that the cell can be cycled many times with conductivities 1000 times greater than that of the corresponding phosphate electrolytes. These experimental results have provided an interesting puzzle for the computer simulations. Figure 5 shows a computed relaxed structure of a interface lithium metal with Li_3PS_4 electrolyte. In comparison with the phosphate electrolytes, it is apparent that lithium metal reacts with the Li_3PS_4 surface, penetrating into the electrolyte and forming new composites at the interface. Such reactivity seems to contradict the electrochemical experiments for this material. One possible explanation involves the formation of a stabilizing buffer layer. Computationally, we can construct an idealized buffer layer of Li_2S oriented in its non-polar $[1\ 1\ 0]$ direction, placed on the $[0\ 1\ 0]$ surface of $\gamma\text{-Li}_3\text{PS}_4$. The structural optimization results for this structure show that, while the buffer film in this geometry is slightly strained, the system was found to be stable within a binding energy of -0.9 eV. As shown in Fig. 5, the 2-layer Li_2S buffer on the Li_3PS_4

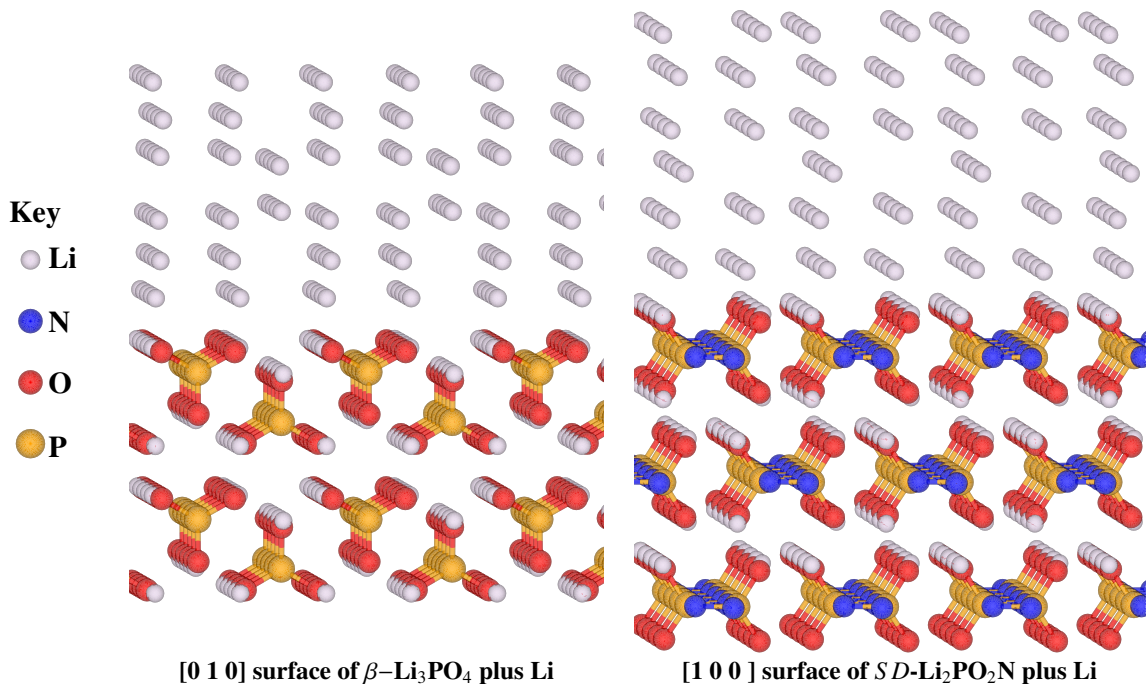


Fig. 4. Ball and stick diagrams of idealized interfaces of Li metal with β -Li₃PO₄ and with *SD*-Li₂PO₂N. The key shown at the left indicates the ball conventions.

electrolyte appears to stabilize the interface with the lithium anode interface to a significant extent. Further study is necessary to determine whether a thicker buffer layer can further stabilize the interface.

4. Summary and Conclusions

This contribution presents some examples of first principles calculations focused on the development of solid electrolyte materials. Ongoing work focuses on the study of ideal anode/electrolyte interfaces. While typical commercial lithium ion batteries cannot use pure lithium metal anodes, the solid electrolytes, particularly lithium phosphate and lithium phospho-nitride electrolytes are very stable with pure lithium metal anodes. The simulations show that lithium thiophosphate electrolytes are less stable relative to the lithium metal anodes. On the other hand, first principles simulations on this system suggest that protective buffer layers can stabilize the interface. In the experimental system (Liu et al. (2013)), the protective buffer was not intentionally prepared, but seems to have developed spontaneously in the course of the first few electrochemical cycles. The fact that the prepared electrochemical cell can be cycled many times, suggests that the spontaneous buffer layer is quite stable. Further simulations can help sort out more of the detailed mechanisms of this very promising battery material.

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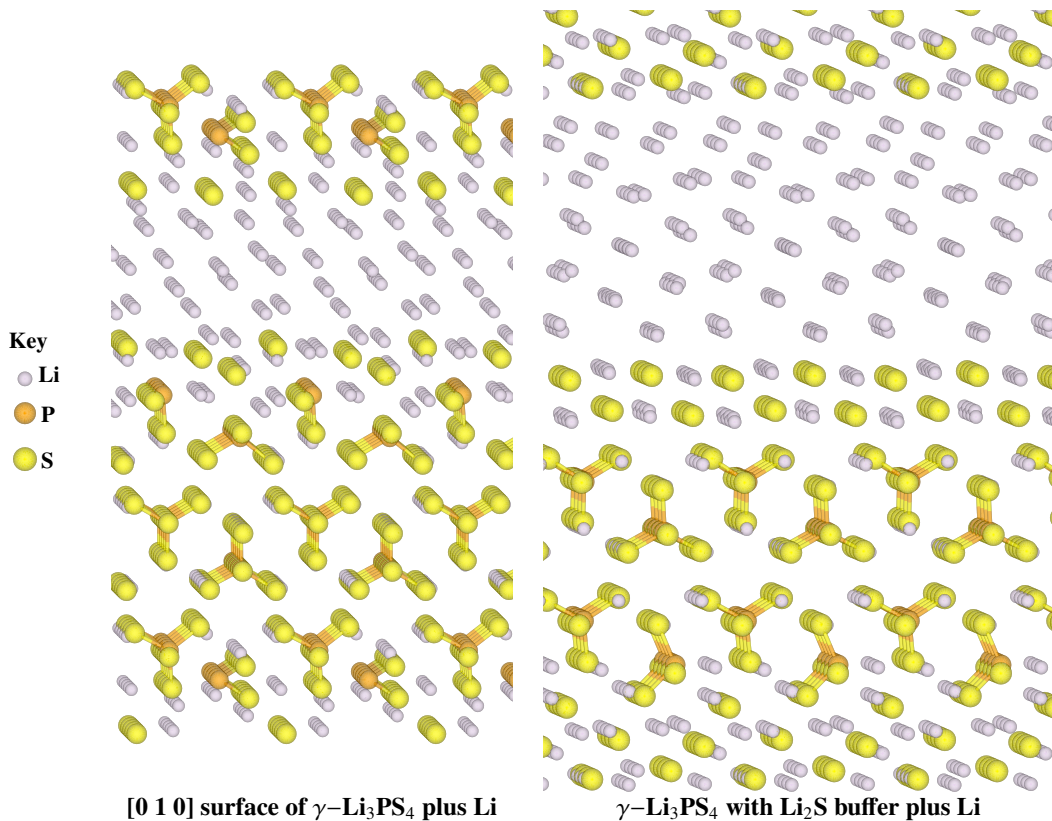


Fig. 5. Ball and stick diagrams of the relaxed geometry of a [0 1 0] surface of γ -Li₃PS₄ exposed to Li anode layers (left) compared with the relaxed geometry of the same surface prepared with an additional idealized buffer layer of Li₂S. The key shown at the left indicates the ball conventions.

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