Calculational Methods

The computational methods used in this work were the same as those used in our previous studies of electrolytes related to LiPON. In Ref. [2], the choice of calculational parameters and the validation of the calculational methods are presented. Briefly, we used density functional theory to treat the electronic states and the Born-Oppenheimer approximation to treat the atomic positions \( \{ \mathbf{R}^a \} \), resulting in a determination of the “total energy” \( E(\{ \mathbf{R}^a \}) \) of the system. The local density approximation (LDA) was used for the exchange-correlation functional. Most of the computations were carried out using the PWscf package; while a few calculations were performed using the abinit and pwpaw packages as well. Visualizations were constructed using the OpenDX and XCrySDEN software packages.

Starting from experimental information for each material or a related material, restricted optimization of the total energy \( E(\{ \mathbf{R}^a \}) \) with respect to the atomic positions \( \{ \mathbf{R}^a \} \) and unit cell parameters, allows us to model stable and meta-stable structures and to estimate the heat of formation (\( \Delta H \)). For each meta-stable structure, a qualitative picture of the valence state distribution can be determined from the averaged partial densities of states \( \langle N^a(\mathbf{E}) \rangle \). In addition, migration energies \( E_{m} \) for Li ion migration were estimated using the “nudged elastic band” method.
Li$_3$PS$_4$ and Li$_3$PO$_4$

Li$_3$PS$_4$ and Li$_3$PO$_4$ are characterized by isolated phosphate or thiophosphate groups. Li$_3$PO$_4$ has been reported in two different orthorhombic crystalline forms – the $\beta$ form$^{12}$ has symmetry $Pmn2_1$ (#31) and the $\gamma$ form$^{13}$ has symmetry $Pnma$ (#62). In our previous work we found that the $\beta$ form is more stable by 0.03 eV per formula unit, while more experimental results are reported for the $\gamma$ form. The crystal structure of Li$_3$PS$_4$ was reported by Mercier $et$ $al.$$^{14}$ to have an orthorhombic symmetry $Pnma$ (#62) which differs from $\gamma$-Li$_3$PO$_4$ structure because of different site occupancies, some of which are fractional. We determined optimized total energies for Li$_3$PS$_4$ in several approximations to the Mercier structure and in the $\beta$ and $\gamma$ structures of Li$_3$PO$_4$, and found the lowest energy structure to be that of $\beta$-Li$_3$PO$_4$. Our results indicate this structure to be more stable than the most stable approximation to the Mercier structure by 0.1 eV per formula unit and more stable than the $\gamma$-Li$_3$PO$_4$ structure by 0.2 eV per formula unit. The comparison of Li$_3$PS$_4$ and Li$_3$PO$_4$ in the $\beta$-Li$_3$PO$_4$ is illustrated in Fig. 1. The lattice parameters of Li$_3$PS$_4$ are found to be roughly 25% larger than those of Li$_3$PO$_4$ and the fractional coordinates are quite similar for the two structures.

In Fig. 2 the partial densities of states of Li$_3$PS$_4$ and Li$_3$PO$_4$ are compared. The S 3$p$ valence bands of Li$_3$PS$_4$ cover a wider range of energies than does the O 2$p$ valence bands of Li$_3$PO$_4$. As noted in our earlier work the two lower bands have $\sigma$ character with significant hybridization with the P 3$s$ and 3$p$ states, while the top of the valence band is has $\pi$ character. It is interesting to note that the magnitudes of the O contributions to $\langle N^a(E) \rangle$ the partial densities of states are generally larger than those of S, indicating that the charge of the O 2$p$ states is more confined within the analysis sphere than is the charge of the S 3$p$ states. While the calculated band gaps within density functional theory are systematically underestimated, it is clear that the gap in Li$_3$PS$_4$ is less than half of that in Li$_3$PO$_4$.

FIG. 1 Ball and stick diagrams for Li$_3$PS$_4$ and Li$_3$PO$_4$ in the $Pmn2_1$ structure ($\beta$-Li$_3$PO$_4$).

FIG. 2 Partial densities of states for Li$_3$PS$_4$ and Li$_3$PO$_4$. 
There has been a number of recent studies of lithium thiophosphate materials with additional sulfur and lithium ions in a structure associated with the mineral argyrodite. The high Li ion conductivity observed in these materials is associated with high-temperature crystalline forms having multiple fractional occupancy sites. However, these materials also have ordered low-temperature structures which we have modeled in this work. The low temperature structure of Li$_7$PS$_6$ has been found to be $Pna2_1$ (#33). The low temperature structure of Li$_6$PS$_5$Cl has not been reported, but it is reasonable to assume that it is similar to that reported for Li$_6$PS$_5$I which forms a monoclinic structure with $Cc$ (#9) symmetry. The calculations optimized the Li$_7$PS$_6$ and Li$_6$PS$_5$Cl structures and the results are illustrated in Fig. 4. For Li$_7$PS$_6$ there are two unbounded S ions associated with each thiophosphate group and for Li$_6$PS$_5$Cl there is one unbounded S ion and one unbounded Cl ion for each thiophosphate group.

FIG. 4 Partial densities of states for Li$_7$PS$_6$ and Li$_6$PS$_5$Cl. Contributions from unbounded S sites are indicated with “(u)”.

Next we consider the partial densities of states of the argyrodite structured thiophosphates, comparing the partial densities of states of Li$_7$PS$_6$ and Li$_6$PS$_5$Cl in Fig. 4. For Li$_7$PS$_6$, the isolated S ions are found to contribute relatively narrow bands near the top of the valence band. For Li$_6$PS$_5$Cl, the isolated Cl ion contributions are at lower energy than those of the isolated S ions.

FIG. 3 Ball and stick diagrams for Li$_7$PS$_6$ in the $Pna2_1$ structure (left) and Li$_6$PS$_5$Cl in the $Cc$ structure (right).
Li$_4$P$_2$S$_6$ and Li$_4$P$_2$O$_6$

The crystal structure of Li$_4$P$_2$S$_6$ was described by Mercier$^{17}$ as hexagonal $P6_3/mcm$ (#193) with half occupancy of the P (4e) sites. Our electronic structure calculations of the 6 possible configurations of this unit cell find the lowest energy structure to be described by the $P31m$ (#162) structure which is a subgroup of the original space group. In this hexagonal group, the Li ions are located at 2c $(1/3,2/3,0)$ and 2d $(1/3,2/3,1/2)$ sites, the P ions are located at 2e $(0,0,z_P)$ sites, and the S ions are located at 6k $(x_S,0,z_S)$ sites. We were also able to simulate a meta-stable phosphate material – Li$_4$P$_2$O$_6$ – with the same structure.

In contrast to the other phosphates and thiophosphates, an interesting characteristic of the optimized Li$_4$P$_2$S$_6$ and Li$_4$P$_2$O$_6$ structures is the presence of a direct bond between two P ions. In Li$_4$P$_2$S$_6$ the P-P bond length is 2.24 Å which is 10% longer than the P-S bond length, while in Li$_4$P$_2$O$_6$ the P-P bond length is 2.10 Å which is 40% longer than the P-O bond length. This is illustrated in Fig. 5.

Partial densities of states for Li$_4$P$_2$S$_6$ and Li$_4$P$_2$O$_6$ are compared. In addition to the bands corresponding to S 3$p$ states, one additional valence band is present due to the filled P 3$s\sigma$ bond, whose contribution is concentrated near the bottom of the spectrum.
\( \text{Li}_4\text{P}_2\text{S}_7 \) and \( \text{Li}_4\text{P}_2\text{O}_7 \)

While to the best of our knowledge, the crystal structure of \( \text{Li}_4\text{P}_2\text{S}_7 \) is unknown, \( \text{Li}_4\text{P}_2\text{O}_7 \) was found to crystallize\(^\text{18}\) in the \( \overline{P}\bar{1} \) structure (\#2). Our simulations confirm this structure and simulations for the corresponding thiophosphate – \( \text{Li}_4\text{P}_2\text{S}_7 \) – show that it has at least a meta-stable state in the same structure.

FIG. 8 Partial densities of states for \( \text{Li}_4\text{P}_2\text{S}_7 \) and \( \text{Li}_4\text{P}_2\text{O}_7 \). Contributions from bridging S or O sites are indicated with “(b)”.

Partial densities of states for \( \text{Li}_4\text{P}_2\text{O}_7 \) and \( \text{Li}_4\text{P}_2\text{S}_7 \) are compared. For these materials, while states with contributions from the P site contribute throughout the valence band, there is no additional valence state due to filled P states as in the case of \( \text{Li}_4\text{P}_2\text{O}_6 \) and \( \text{Li}_4\text{P}_2\text{S}_6 \). On the other hand there are two types of O (S) states. In addition to the normal tetrahedral O (S) site contributions, the “bridging” O (S) site contributions are shown separately on the plot. In particular, there is a band at the bottom of the valence band states which corresponds to states characterized primarily by O 2\( p\sigma \) or S 3\( p\sigma \) contributions for \( \text{Li}_4\text{P}_2\text{O}_7 \) and \( \text{Li}_4\text{P}_2\text{S}_7 \), respectively.
Heats of Formation

In order to assess the chemical stability of the materials, we estimated the heats of formation relative to their decomposition to elemental materials in their standard states as defined in the CRC Handbook, using the methods described in our earlier work. In order to extend the analysis to sulfur containing materials, we needed to estimate the equilibrium energy of the standard state of elemental S, which is the orthorhombic form (α-S) having the structure $Fddd$ (#70).

In order to extend the analysis to Cl-containing materials, we needed to estimate the energy of the standard state of elemental Cl, which is molecular Cl$_2$. Instead of evaluating this energy directly, we estimated it from the total energies of LiCl in the rocksalt structure, LiClO$_4$ in the $Pnma$ (#62) structure, and PCl$_5$ in the $P4/n$ (#85) structure$^{22}$ and the heat of formation data values for these materials given in the CRC Handbook.

From these results, we can make some comments on relative stabilities of these materials. For example, the calculations suggest that Li$_4$P$_2$S$_6$ is more stable than Li$_4$P$_2$S$_7$ in the sense that in their standard states:

$$\Delta H(Li_4P_2S_6) + \Delta H(S) = \Delta H(Li_4P_2S_7) - 0.84 \text{ eV}.$$  

In fact there are literature reports of glassy Li$_4$P$_2$S$_7$, but we know of no reports of crystalline Li$_4$P$_2$S$_6$. By contrast, for the analogous phosphate materials, we find

$$\Delta H(Li_4P_2O_6) + \frac{1}{2}\Delta H(O_2) = \Delta H(Li_4P_2O_7) + 4.21 \text{ eV},$$

suggesting that Li$_4$P$_2$O$_6$ is significantly unstable relative to Li$_4$P$_2$O$_7$. In fact we know of no literature reports of crystalline Li$_4$P$_2$O$_6$ crystals. For the argyrodite material, the calculations also suggest that Li$_4$PS$_6$ is unstable relative to decomposition into Li$_4$PS$_4$ and Li$_4$S in the sense that

$$\Delta H(Li_4PS_6) = \Delta H(Li_4PS_4) + 2\Delta H(Li_4S) + 0.32 \text{ eV}.$$  

In this estimate, we used the $\beta$-Li$_3$PO$_4$ structure to evaluate $\Delta H(Li_4PS_4)$ and the result is within our expected calculation error. The material with chlorine is also marginally unstable relative to decomposition into Li$_3$PS$_4$, Li$_3$S, and LiCl as shown in the

$$\Delta H(Li_3PS_4Cl) = \Delta H(Li_3PS_4) + \Delta H(Li_3S) + \Delta H(LiCl) + 0.38 \text{ eV}.$$  

The calculations also suggest that Li$_7$P$_3$S$_{11}$ is marginally stable with respect to decomposition into Li$_3$PS$_4$ and Li$_4$P$_2$S$_7$ in the sense that

$$\Delta H(Li_7P_3S_{11}) = \Delta H(Li_3PS_4) + \Delta H(Li_4P_2S_7) - 0.06 \text{ eV}.$$  

Again, this is within the expected calculational error.

<table>
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<th>Material</th>
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<th>$\Delta H_{\text{exp}}$ (eV)</th>
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Li Ion Migration Energies

An important question about these materials is how the Li ion migration differs in the phosphate and thiophosphate materials. A measure of the ionic conductivity $\sigma$ as a function temperature $T$ is expected to follow the Arrehenius relation:

$$\sigma \cdot T = K \ n \ e^{-E_m/kT},$$

where $k$ is the Boltzmann constant, $K$ is a material-dependent parameter, $n$ is the number of mobile Li ions or Li ion vacancies, and $E_m$ is the migration energy.

In this initial study, we focus on the migration energy $E_m$ for Li ion vacancy migration in idealized crystals of Li$_4$P$_2$O$_7$ and Li$_4$P$_2$S$_7$. These two materials form similar stable and meta-stable crystals with $P\overline{1}$ symmetry. For the simulations, we constructed $1 \times 2 \times 2$ supercells and studied the migration of a Li ion vacancy between 6 sites separated by roughly 3.0 Å and 3.6 Å for Li$_4$P$_2$O$_7$ and Li$_4$P$_2$S$_7$, respectively. The sites do not span a complete path within the supercell but do cover a representative range of crystal environments. The 6 sites are illustrated in Fig. 9 for the Li$_4$P$_2$S$_7$ supercell. A corresponding geometry was used for the Li$_4$P$_2$O$_7$ supercell.

The band occupancies of the supercell states were adjusted in order to approximate an insulating environment for ion migration, and the excess charge was compensated by adding a uniform charge of the opposite sign. The 6 optimized configurations for a Li ion vacancy were used as the end points for the NEB calculation in which 7 intermediate images were used to approximate the minimum energy path. The energy path diagram is shown in Fig. 9, comparing the results for Li$_4$P$_2$S$_7$ and Li$_4$P$_2$O$_7$.

As is evident from the energy path diagram shown in Fig. 9, the energy landscape for this system is complicated. However, the results indicate a clear qualitative result that the migration energy barriers for Li ion vacancy migration in Li$_4$P$_2$S$_7$ is less than half that in Li$_4$P$_2$O$_7$. For the particular migration path chosen, we find the migration energy barriers to be $E_m = 0.3$ eV for Li$_4$P$_2$S$_7$ and $E_m = 0.8$ eV for Li$_4$P$_2$O$_7$. 

FIG. 9 Left: Li ion vacancy sites used in migration energy study in Li$_4$P$_2$S$_7$. Similar sites were used for Li$_4$P$_2$O$_7$. Right: Energy path diagram for Li ion vacancy migration in Li$_4$P$_2$S$_7$ and Li$_4$P$_2$O$_7$. The integer labels on the the horizontal axis correspond to the 6 vacancy sites indicated in the structural diagram. Between each pair of optimized vacancy configurations are 7 NEB image configurations along the minimum energy path. The continuous line is constructed with a spline interpolation between the image energies.
Summary and Conclusions

This study has found some interesting similarities and differences between the phosphate and thiophosphate materials. Our structural optimizations were generally in good agreement with the experimental structures, although there are some differences. For example, our calculations for Li$_4$PS$_4$ indicated that the most stable structure is that of $\beta$-Li$_4$PO$_4$, while the experiment indicated a structure similar to $\gamma$-Li$_4$PO$_4$ with partial occupancies of some of the sites. A similar discrepancy was found for the structure of Li$_3$P$_2$S$_6$. These differences are undoubtedly related to real temperature effects which are not considered in the simulations.

In general, a greater variety in the bonding configurations of the thiophosphates is observed compared with those of the phosphates. The argyrodite structures with unbounded S and Cl groups within the crystal and increased concentrations of Li ions are very intriguing.

In addition to our analysis of the optimized structures and their stabilities, we have presented some preliminary results pertaining to Li ion vacancy migration within a representative set of materials. We find that the energy barriers for Li ion vacancy migration in Li$_4$PS$_4$ to be less than half that for Li$_3$P$_2$O$_7$. This result is consistent with the experimental observation of increased ionic conductivity in the thiophosphate materials compared with those of the phosphates. Our analysis suggests that one factor contributing to the lowered potential barriers in the thiophosphates is the more diffuse valence charge distribution near the O sites compared with the compact valence charge distribution near the S sites.

Acknowledgements

This work was supported by NSF grants DMR-0427055 and 0705239 and by the Wake Forest University DEAC computer cluster. We would like to thank Dr. F. Stadler for informing us about the argyrodite materials.

Bibliography

[9] OpenDX The Open Source Software Project Based on IBMs Visualization Data Explorer is available from the website http://www.opendx.org.