The exchange correlation function is approximated using the local-density approximation (LDA). The choice of LDA functional was made based on previous investigations of similar materials which showed that the simulations are in good agreement with experiment, especially the fractional lattice parameters, the vibrational frequencies, and heats of formation. The simulated magnitudes of the lattice parameters, when systematically scaled by a factor of 1.02, are also in good agreement with experiment.

The calculations were well converged with plane wave expansions of the wave function including $j$\textit{k} + \textbf{G}^2 \leq 64$ bohr$^{-2}$. The Brillouin zone integrals were evaluated by using uniform sampling volumes of 0.006 bohr$^{-3}$ or smaller. Convergence tests showed that increasing the sampling grid by a factor of 8 changed the total energy by less than 0.001 eV for 100 atom supercells. The partial densities of states were calculated as described in previous work, using weighting factors based on the charge within the augmentation spheres of each atom with radii $r_{Li}^{Li} = 1.6$, $r_{P}^{P} = 1.7$, $r_{O}^{O} = 1.2$, and $r_{N}^{N} = 1.2$ in bohr units. The reported partial densities of states curves $\langle N^{\alpha}(E) \rangle$ were averaged over the atomic sites of each type $\alpha$.

Simulation of Li ion migration were performed at constant volume in supercells constructed from the op- timized conventional cells. In modeling charged defects (Li ion vacancies or interstitials), the system was assumed to remain electrically insulating and a uniform background charge was added in order to evaluate the electrostatic interactions. The minimum energy path for Li ion migration was estimated using the “nudged elastic band” (NEB) method as programmed in the QUANTUM ESPRESSO package, using 5 images between each metastable configuration.

**Introduction**

Twenty-five years after the pioneering work at Oak Ridge National Laboratory on LiPON solid electrolytes, new lithium oxonitridophosphate continue to be discovered. LiPON materials have the stoichiometry $\text{Li}_x\text{PO}_y\text{N}_z$ with $x = 2y+3z-5$. The building blocks of these materials are the $\text{PO}_u\text{N}_4$ tetrahedra which are often formed into dimers, trimers, infinite chains, or more complicated intercon-nections. Recently, Baumann and Schnick\cite{10} found an interesting new crystalline LiPON which has the stoichiometry $\text{Li}_{14}\text{P}_2\text{O}_3\text{N}_6$ formed with a trigonal arrangement of isolated tetrahedral (PON$_3$)$^-$ ions stabilized by isolated O$^-$ ions. We report the results of our computationally study of the bulk and interface structures and Li ion migration properties of $\text{Li}_{14}\text{P}_2\text{O}_3\text{N}_6$ in comparison with other LiPON materials also formed from arrangements of isolated oxonitridophosphate tetrahedra such as $\text{Li}_7\text{PN}_4$ and $\text{Li}_3\text{PO}_4$\cite{11,12}.

**Calculational Methods**

The computational methods used in this work are based on density functional theory (DFT), using the projected augmented wave (PAW) formalism. The PAW basis and projector functions were generated by the ATOMPAW code and the crystalline materials were modeled using the QUANTUM ESPRESSO package. Visualizations were constructed using the XCRYSDEN, VESTA software packages.
Structure of the bulk material

Baumann and Schnick\textsuperscript{10} reported the synthesis of Li\textsubscript{14}P\textsubscript{2}O\textsubscript{3}N\textsubscript{6} by heating powders of PO(NH\textsubscript{2})\textsubscript{3} and LiNH\textsubscript{2} in a sealed silica glass ampoule for 24 hours at a temperature of 550 deg. C. The resulting crystals have a trigonal structure characterized by the space group $P\bar{3}$ (No. 147 as listed in the International Table of Crystallography). Figure [1] shows a ball and stick diagram of the structure from two different perspectives. The scale factor of 1.02 used to correct the systematic error on the magnitudes of the lattice constants due to the LDA functional puts the simulated lattice constants within 0.1 Å of the experimental results. The simulated fractional coordinates for the P, O, and N sites are all within 0.01 of the experimental results. For the Li sites, the simulated fractional coordinates differ from the experimental values by a larger amount (0.06 or less). It is our experience\textsuperscript{25} that it is common to find that X-ray analysis is less sensitive to the the Li positions than to the positions of the other elements in the crystal which have larger X-ray cross sections due to their larger atomic numbers $Z$.

Simulations show that the trigonal symmetry is stabilized by the isolated O$^{2-}$ ions located at the 1\textit{b} sites and the corresponding Li$^{+}$ ions located at the 2\textit{c} sites. In addition to its trigonal symmetry, the crystal structure features an interesting arrangement of pairs of PON\textsubscript{3} tetrahedra, forming alternating $c$-axis planes of O$^{2-}$ and N$^{3-}$ ions. The arrangement of the isolated oxonitridophosphate tetrahedra is quite different from other crystalline LiPON materials of this type such as $\beta$- and $\gamma$-Li\textsubscript{3}PO\textsubscript{4} which has been studied previously\textsuperscript{26,27} and Li\textsubscript{7}PN\textsubscript{3}\textsuperscript{28,29}.

Fig [1]. (a) Ball and stick diagram of the $P\bar{3}$ structure of a unit cell of Li\textsubscript{14}P\textsubscript{2}O\textsubscript{3}N\textsubscript{6}, viewing the $c$-axis along the vertical direction, using the indicated ball conventions to distinguish the inequivalent sites, labeled according to their Wyckoff letters. (b) Projection of 4 unit cells of Li\textsubscript{14}P\textsubscript{2}O\textsubscript{3}N\textsubscript{6} perpendicular to the $c$ axis to show the trigonal symmetry.
Electronic Structure of the bulk materials

It is interesting to compare the electronic structure of Li$_{14}$P$_2$O$_3$N$_6$ with other oxonitridophosphates composed of isolated tetrahedra and related materials. The corresponding partial densities of states are given in Fig [2]. The valence band states are characterized by the 2$p$ states of O and N together with bonding combinations the the P 3$s$ and 3$p$ states while the conduction bands are characterized by the corresponding antibonding states. The N 2$p$ states dominate the top of the valence band for Li$_{14}$P$_2$O$_3$N$_6$. The O 2$p$ contributions to Li$_{14}$P$_2$O$_3$N$_6$ are of two types. The occupied states associated with P-O bonds contribute to the bottom of the valence band, while the non-bonded O 2$p$ states contribute to the middle of the valence band. Knowing that LDA calculations typically underestimate band gaps, we can safely conclude that the four materials are good insulators, having band gaps larger than 3 eV.

Related to the electronic structure is the stability of the compounds relative to decomposition. These can be roughly estimated from the calculated total energies, assuming that vibrational energies including zero point energies can be neglected. For example, we considered the following possible decomposition reaction.

$$\text{Li}_{14}\text{P}_{2}\text{O}_{3}\text{N}_{6} \rightarrow 3\text{Li}_{2}\text{O} + 2\text{Li}_{3}\text{N} + 2\text{LiP}_{2}\text{N}_{2} - 2.92\text{eV}. \quad (1)$$

The negative energy on the right side of the equation indicates that Li$_{14}$P$_2$O$_3$N$_6$ is stable with respect to decomposition into these binary and ternary products. In anticipation of the study of interfaces of this electrolyte with Li metal, we also considered the energy associated with reaction with Li metal as follows.

$$\text{Li}_{14}\text{P}_{2}\text{O}_{3}\text{N}_{6} + 16\text{Li} \rightarrow 3\text{Li}_{2}\text{O} + 6\text{Li}_{3}\text{N} + 2\text{Li}_{3}\text{P} + 3.1\text{eV}. \quad (2)$$

Fig [2] Partial density of states plot for the LiPON materials Li$_{14}$P$_2$O$_3$N$_6$ and Li$_7$PN$_4$ in comparison with $\gamma$-Li$_3$PO$_4$ and Li$_2$O. Oxygen contributions from isolated O$^{2-}$ ions and from oxygens associated with P-O bonds are distinguished with dashed and full red lines, respectively. In each plot, $E = 0$ is aligned at the top of the valence band.
Li ion migration mechanisms in Li$_{14}$P$_2$O$_3$N$_6$

Li ion migration in Li$_{14}$P$_2$O$_3$N$_6$ was investigated using supercells based on $2 \times 2 \times 1$ multiples of the unit cell. Table summarizes the 3 inequivalent vacancy energies relative to the $g'$ site vacancy and 2 inequivalent interstitial energies relative to the $I$ site interstitial. The placements of these defect sites are illustrated in Figs. [3a] and [3c] in an orthorhombic construction of the hexagonal unit cell.

<table>
<thead>
<tr>
<th>Vacancies</th>
<th>Multiplicity and Wyckoff Label</th>
<th>Relative Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$4g'$</td>
<td></td>
<td>0.00</td>
</tr>
<tr>
<td>$4g$</td>
<td></td>
<td>0.95</td>
</tr>
<tr>
<td>$2c$</td>
<td></td>
<td>0.41</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Interstitials</th>
<th>Fractional Coordinates</th>
<th>Relative Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I$</td>
<td>$(13,23,0.73)$ ($2d$)</td>
<td>0.00</td>
</tr>
<tr>
<td>$II$</td>
<td>$(0, 0, 0)$ ($1a$)</td>
<td>0.22</td>
</tr>
</tbody>
</table>

In order to study likely migration pathways, using the NEB method$^{24}$, we considered a range of near neighbor hops between defect sites, the large range of the relative energies of the unique vacancy configurations listed in Table [1]. For the vacancy mechanism four different paths were found as shown in figure [3a]. For the interstitial and the kick-out mechanism two paths were found as shown in figure [3c]. The corresponding migration energies for the vacancy and the kick-out mechanisms are shown in figure [3b] and [3d] respectively. The NEB calculation shows that the favorable conduction mechanism is the vacancy mechanism which takes place near the oxygen plane with $E_m = 0.3$ eV.

Fig [3] Panels (a) and (c) show ball and stick models of several supercells of Li$_{14}$P$_2$O$_3$N$_6$ using the same ball conventions as in Fig [1]. with the addition of type $I$ and $II$ interstitial sites shown in bright and pale green, respectively. The $a$ and $c$ axes are indicated in the diagrams while the third axis of the diagram is perpendicular to the other two, specifically constructed in the $a + 2b$ direction. Panels (b) and (d) show energy path diagrams from NEB simulations of Li ion migration between metastable vacancy or interstitial configurations indicated by the vertical lines.
**Li electrolyte interface in Li$_{14}$P$_2$O$_3$N$_6$**

We prepared two series of configurations of interfaces of Li$_{14}$P$_2$O$_3$N$_6$ with Li as shown in Fig 4 (a) and (b) and the corresponding plots of the surface energy versus the number of metallic lithium atoms $n_b$ are evaluated as plotted in Fig [4c]. Interface configurations $\Omega_1$ and $\Omega_2$ have approximately the same density of the Li atoms per unit volume 0.05-0.06 atoms/Å$^3$, close to the density of bulk Li. The estimated strains of the two configurations are $\sigma(\Omega_1) = 0.0004$ eV/Å$^2$ and $\sigma(\Omega_2) = 0.0014$ eV/Å$^2$, consistent with the notion that the more regular structure of configuration $\Omega_1$ produces smaller strain. The strain corrected interface energy, $\gamma_{ab}^{lim}$, for the two configurations is found to be approximately 0.05 eV/Å$^2$. This value is similar to the corresponding values of 0.03-0.04 eV/Å$^2$ reported by Lepley$^{21}$ for interfaces of $\beta$- or $\gamma$- Li$_3$PO$_4$ with Li metal.

The partial densities of states for the interface Fig [4a] with $n_b = 36$ are shown in Fig [4d]. The partial densities of states for the interior of the electrolyte is very similar to that of the bulk structure of Li$_{14}$P$_2$O$_3$N$_6$ shown in Fig [2]. The metallic Li states are physically separated from the electrolyte, but energetically overlap with the top of the Li$_{14}$P$_2$O$_3$N$_6$ valence band by approximately 1 eV. The partial densities of states associated with the Li ions at the interface of the electrolyte and the metallic Li, show that they have more electronic charge than the Li$^+$ ions in the interior of the electrolyte. The “Electrolyte Li” curve in the top portion of the plot Fig [4d] is the same as the “Li” curve in lower portion of the plot representing ionic Li within the interior of the electrolyte. The “Interface Li”. Also shown in the top portion of the plot Fig [4d] are the “Interface Li” contributions corresponding to Li sites nearest the electrolyte and the “Metallic Li” contributions corresponding to the interior of the metallic Li region of the supercell.
Summary and Conclusions

The results of the reported simulations suggest that the nitrogen rich crystalline lithium oxonitridophosphate material of this study – Li$_{14}$P$_2$O$_3$N$_6$ – show promising properties as solid electrolyte for Li ion batteries, possibly for use with Li metal anodes.

Simulations of idealized interfaces constructed for Li$_{14}$P$_2$O$_3$N$_6$/Li is structurally metastable and electrically insulating. The partial densities of states associated with the interfaces show small effects in their electronic structures, while the partial densities of states associated with the interior of the electrolyte is identical to it bulk values. The partial densities of states associated with the metallic Li layers show that the Fermi level of the system lies well within the band gap of the interior layers of the electrolyte. While the total energy results for these LiPON electrolytes suggest exothermic reactions with Li under equilibrium conditions such as shown in Eq [2]. These simulations show that LiPON/Li interface are likely to be practically stable as has been shown in experimental demonstrations.

The simulations also suggest that the activation energies for Li ion migration in the nitrogen rich electrolyte is also quite promising. We found that the most efficient predicted activation energy for Li ion migration in Li$_{14}$P$_2$O$_3$N$_6$ is 0.3-0.4 eV for a pure vacancy mechanism involving g′ site Li ions. The predicted activation energy for Li ion migration in Li$_{14}$P$_2$O$_3$N$_6$ is lower than the experimentally measured values for Li$_7$PN$_3^{31}$ and for γ-Li$_3$PO$_3^{32}$ as well as the $E_A = 0.6$ eV values measured for typical amorphous LiPON films.

References


Acknowledgements

This work was supported by NSF grant DMR-1507942. Computations were performed on the Wake Forest University DEAC cluster, a centrally managed resource with support provided in part by the University. We would also like to thank Dr. Nicholas Lepley for the use of his unpublished simulations of a -Li 3 PO 4 /Li interface.