Prediction of a New Material – 
Lithium Phosphorus Oxynitride – Li$_2$PO$_2$N $^a$

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- Motivation for solid electrolytes and LiPON
- Computational methods
- Crystal structures and formation energies of LiPO$_3$ and Li$_2$PO$_2$N
- Summary of electrolyte properties; comparison of simulations and experiments
- Summary and conclusions

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Solid vs liquid electrolytes in Li ion batteries

Solid electrolytes

**Advantages**

1. Excellent chemical and physical stability.
2. Performs well as thin film ($\approx 1\mu$).
3. Li$^+$ conduction only (excludes electrons).

**Disadvantages**

1. Thin film geometry provides poor contact area for high capacity electrodes.
2. Subject to interface stress if electrodes change size during charge and discharge cycles.
3. Relatively low conductivity per unit area.

Liquid electrolytes

**Advantages**

1. Excellent contact area with high capacity electrodes.
2. Can accommodate size changes of electrodes during charge and discharge cycles.
3. Relatively high conductivity per unit area.

**Disadvantages**

1. Relatively poor physical and chemical stability.
2. Relies on the formation of “solid electrolyte interface” (SEI) layer.
3. May have both Li$^+$ and electron conduction.

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Example of solid electrolyte – thin film battery technology


Fig. 2. Schematic cross-section of a thin film lithium battery structure.
Overview of LiPON family of electrolytes

The thin film solid electrolyte LiPON developed at Oak Ridge National Laboratory\textsuperscript{a} is the most widely used solid electrolyte for thin film batteries and a number of other related technologies. While commercial LiPON electrolytes are disordered, much can be learned from related crystalline materials in the \( Li_xPO_yN_z \) family \((x = 2y + 3z - 5)\). In order to systematize the current state of understanding of the crystalline members of the family, it is helpful to visualize a quaternary phase diagram of known materials reported in the literature together with new stable and meta-stable predicted by computer simulation. The corners of the composition tetrahedron indicate the starting materials of \( LiO_{1/2} \), \( LiN_{1/3} \), \( PO_{5/2} \), and \( PN_{5/3} \).

\textsuperscript{a}Bates, Dudney, \textit{et al} Solid State Ionics 53-54, 647 (1992); Dudney Interface 17, 44 (2008)

Natural and synthetic crystalline materials (●), LiPON thin film materials (●), and computer simulated idealized phosphate chain structure materials (■).
Computational methods

• "First principles" simulations using density functional theory\(^a\) to treat the electrons and the Born-Oppenheimer approximation to treat the nuclear positions \(\{\mathbf{R}^a\}\), to determine the "total energy" \(E(\{\mathbf{R}^a\})\) of the system.

• Variety of computer codes – PWscf\(^b\), pwpaw\(^c\), abinit\(^d\)

Results – Quantities derived from \(\min_{\{\mathbf{R}^a\}} E(\{\mathbf{R}^a\})\):

• Stable and meta-stable structures
• Lattice lattice vibration modes and frequencies (\(\nu\))
• Heats of formation (\(\Delta H\))
• Energies for ion migration (\(E_m\)) and for interstitial-vacancy pair formation (\(E_f\))

\(^c\)Tackett et al, Comp. Phys. Comm. 135 348 (2001) pwpaw.wfu.edu
Computational methods – validation

Raman spectra for $\gamma$-Li$_3$PO$_4$

Calculated Raman spectra (red) compared with

Infrared spectra for $\alpha$-P$_3$N$_5$

Phosphate chain material: LiPO$_3$

LiPO$_3$ in $P2/c$ structure; 100 atom unit cell
Chain direction perpendicular to plane of diagram

$P2/c$ LiPO$_3$ can be prepared from a Li$_2$O-P$_2$O$_5$ glass by heating to the crystallization temperature of 486$^\circ$ C.$^a$

**Lattice parameters (in Å) for LiPO$_3$**

<table>
<thead>
<tr>
<th></th>
<th>$a$</th>
<th>$b$</th>
<th>$c$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cal.</td>
<td>13.00</td>
<td>5.30</td>
<td>16.31</td>
<td>98.8$^\circ$</td>
</tr>
<tr>
<td>Exp.$^b$</td>
<td>13.074</td>
<td>5.4068</td>
<td>16.452</td>
<td>99.00$^\circ$</td>
</tr>
</tbody>
</table>

Phosphate chain materials: LiPO$_3$ plus N

LiPO$_3$ in $P2/c$ structure; 100 atom unit cell
Chain direction perpendicular to plane of diagram

$s_1$-Li$_2$PO$_2$N in $Pbcm$ structure; 24 atom unit cell
Chain direction perpendicular to plane of diagram

Ball colors: • = Li, • = P, • = O.

Ball colors: • = Li, • = P, • = O, • = N.

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Phosphate chain materials: $s_1^-\text{LiPO}_3$ and $s_1^-\text{Li}_2\text{PO}_2\text{N}$

$s_1^-\text{LiPO}_3$ in $Pbcm$ structure; 20 atom unit cell
Chain direction perpendicular to plane of diagram

Ball colors: •=Li, •=P, •=O.

$s_1^-\text{Li}_2\text{PO}_2\text{N}$ in $Pbcm$ structure; 24 atom unit cell
Chain direction perpendicular to plane of diagram

Ball colors: •=Li, •=P, •=O, •=N.
Phosphate chain materials: LiPO$_3$ and Li$_2$PO$_2$N

Comparison of different structural forms of LiPO$_3$ and Li$_2$PO$_2$N in terms of their heats of formation ($\Delta H_{\text{cal}}$) and volumes $V_{\text{cal}}$ (per formula unit).

<table>
<thead>
<tr>
<th>Material</th>
<th>Structure</th>
<th>$\Delta H_{\text{cal}}$ (eV)</th>
<th>$V_{\text{cal}}$ (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiPO$_3$</td>
<td>$P2/c$ [#13]</td>
<td>-12.80</td>
<td>56</td>
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<tr>
<td>$s_1$-LiPO$_3$</td>
<td>$Pbcm$ [#57]</td>
<td>-12.73</td>
<td>58</td>
</tr>
<tr>
<td>$s_2$-LiPO$_3$</td>
<td>$Aem2$ [#39]</td>
<td>-12.73</td>
<td>58</td>
</tr>
<tr>
<td>$s_3$-LiPO$_3$</td>
<td>$Pmc2_1$ [#26]</td>
<td>-12.70</td>
<td>67</td>
</tr>
<tr>
<td>Li$_2$PO$_2$N</td>
<td>$Pbcm$ [#57]</td>
<td>-12.42</td>
<td>57</td>
</tr>
<tr>
<td>$s_2$-Li$_2$PO$_2$N</td>
<td>$Aem2$ [#39]</td>
<td>-12.45</td>
<td>57</td>
</tr>
<tr>
<td>$s_3$-Li$_2$PO$_2$N</td>
<td>$Pmc2_1$ [#26]</td>
<td>-12.08</td>
<td>66</td>
</tr>
</tbody>
</table>
**s$_1$-Li$_2$PO$_2$N: Can it be made?**

Possible exothermic reaction pathways:

\[
\frac{1}{5}P_2O_5 + \frac{1}{5}P_3N_5 + Li_2O \rightarrow Li_2PO_2N + 2.5 \text{ eV.}
\]

\[
LiPO_3 + Li_3N \rightarrow Li_2PO_2N + Li_2O + 4.5 \text{ eV.}
\]

\[
LiNO_3 + Li + P \rightarrow Li_2PO_2N + \frac{1}{2}O_2 + 7.0 \text{ eV.}
\]

Ball colors: grey = Li, yellow = P, blue = O, green = N.

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Partial densities of states analyses

LiPO₃

Li₂PO₂N

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Summary and conclusions

- We have carried out a comprehensive survey of crystalline members of the LiPON family, including both known and predicted materials.

- Having demonstrated good agreement with experimental measurements of some structural parameters, heats of formation, and lattice vibrational spectra, we have developed some confidence in the plausibility of our predictions.

- In particular, we have identified several stable/meta-stable phosphonitride chain structures having the stoichiometry Li$_2$PO$_2$N, the most stable of which are characterized by a planar -N-P-N-P- backbone. **These highly symmetric structures have yet to be experimentally realized.**

- Further work is needed to investigate the electrolyte properties of these materials, particularly their Li ion conductivities.