Li$_{14}$(PON$_3$)$_2$: Computational study of a possible new electrolyte for Li ion batteries

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Computations were performed on WFU’s DEAC cluster.
• Density functional theory with LDA approximation

• PAW formalism using datasets generated with ATOMPAW code (Holzwarth et al. *CPC* 135, 329 (2001)) [http://pwpaw.wfu.edu](http://pwpaw.wfu.edu)

• Electronic structure calculations performed using QUANTUM ESPRESSO. (Giannozzi et al. *JPCM* 21, 394402 (2009); [http://www.quantum-espresso.org](http://www.quantum-espresso.org))

• Plane wave expansion for wave functions with $|\mathbf{k}+\mathbf{G}|^2 \leq 64$ Ry
Solid Electrolyte materials

**Solid Electrolytes**

**Advantages**
- Excellent chemical and physical stability
- Li conduction only excludes electrons

**Disadvantages**
- Interface stress due to electrode charging/discharging
- Low ionic conductivity

**Liquid Electrolytes**

**Advantages**
- Relatively high ionic conductivity
- Excellent contact area with high capacity electrodes

**Disadvantages**
- Poor chemical and physical stability
- Relies on the formation of SEI layer
$\text{Li}_x\text{PO}_y\text{N}_z$

$(x=2y+3z-5)$

(Du, PHYSICAL REVIEW B 81, 184106, 2010)
Li$_{14}$ (PON$_3$)$_2$O: Computational study of a possible new electrolyte for Li ion batteries

- The First LiPON material with PON$_3$ Tetrahedra.

Comparison of different LiPON materials

trigonal, P3 (no. 147)

Li\(_7\)PN\(_4\), cubic P43n (no. 218)

γ – Li\(_3\)PO\(_4\), orthorhombic Pnma

(Schnick, J. of solid state chemistry. 1990, 37,101)
(Du, Phys Rev B 76, 174302)
Structure analysis

Wyckoff labels:

\[ 2d \quad 2d \quad 1b \quad 6g \quad 6g' \quad 2c \]

Atoms: P O O N Li Li Li

Wyckoff labels:

\[ 6c \quad 2a \quad 24i \quad 8e \quad 6b \quad 6d \quad 8e \quad 24i \quad 12f \]

Atoms: P P N N Li Li Li Li Li

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Electronic structure calculation

- The valence band states are characterized by the 2p states of O and N together with bonding combination of P 3s and 3p states, while the N 2p dominates the top of the valence bands of the Li$_{14}$(PON$_3$)$_2$.

- The conduction band are characterized by the corresponding antibonding states.
Heat of decomposition calculation

Li₁₄P₂O₃N₆ → 3Li₂O + 2Li₃N + 2LiPN₂

ΔH_D = -2.93 eV

Li₇PN₄ → LiPN₂ + 2Li₃N

ΔH_D = -2.88 eV
Li$_{14}$(PON$_3$)$_2$ : Li ion migration analysis

<table>
<thead>
<tr>
<th>Vacancies</th>
<th>Multiplicity and Wyckoff Label</th>
<th>Relative Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4g'</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>4g</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>2c</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></td>
<td>I ≡(1/3,2/3,0.73) (2d)</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>II ≡(0,0,0) (1a)</td>
<td>0.22</td>
</tr>
</tbody>
</table>

➢ Formation Energy of 0.32 eV which involves the pair (g'-I).
Li$_{14}$(PON$_3$)$_2$: Li ion migration analysis

- Vacancy mechanism
Li$_{14}$(PON$_3$)$_2$ : Li ion migration analysis

- Interstitial mechanism
Li$_7$PN$_4$: Li ion migration analysis

Wyckoff labels:

Atoms: P P N N Li Li Li Li

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Li$_7$PN$_4$ : Li ion migration analysis
**Li ion migration summary**

<table>
<thead>
<tr>
<th>Material</th>
<th>Mechanism</th>
<th>$E_f$ (eV)</th>
<th>$E_m$ (eV)</th>
<th>$E_m + 1/2 E_f$ (eV)</th>
<th>$E_A$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_{14}$(PON$_3$)$_2$</td>
<td>Vacancy</td>
<td>0.3</td>
<td>0.3</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Li$_{14}$(PON$_3$)$_2$</td>
<td>Kick-out</td>
<td>0.3</td>
<td>0.6</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>Li$_7$PN$_4$</td>
<td>Vacancy</td>
<td>1.9</td>
<td>0.3</td>
<td>1.3</td>
<td>0.48</td>
</tr>
<tr>
<td>Li$_7$PN$_4$ with O</td>
<td>Vacancy</td>
<td></td>
<td>0.5</td>
<td></td>
<td>0.48</td>
</tr>
<tr>
<td>γ-Li$_3$PO$_4$</td>
<td>Kick-out</td>
<td>1.7</td>
<td>0.3</td>
<td>1.2</td>
<td>1.1 – 1.2</td>
</tr>
<tr>
<td>β-Li$_3$PO$_4$</td>
<td>Kick-out</td>
<td>2.1</td>
<td>0.4</td>
<td>1.5</td>
<td></td>
</tr>
</tbody>
</table>
**Li_{14}(PON_3)_2 : Interface with Vacuum**

\[ \gamma = \frac{E_{total} - E_{bulk}}{2A} \]

<table>
<thead>
<tr>
<th>plane</th>
<th>n_f</th>
<th>( \gamma ) (eV/Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(001)_N</td>
<td>1</td>
<td>0.069</td>
</tr>
<tr>
<td>(001)_N</td>
<td>2</td>
<td>0.069</td>
</tr>
<tr>
<td>(001)_N</td>
<td>3</td>
<td>0.069</td>
</tr>
<tr>
<td>(001)_N</td>
<td>4</td>
<td>0.069</td>
</tr>
<tr>
<td>(001)_O</td>
<td>3/2</td>
<td>0.41</td>
</tr>
<tr>
<td>(001)_O</td>
<td>5/2</td>
<td>0.41</td>
</tr>
<tr>
<td>(001)_O</td>
<td>7/2</td>
<td>0.41</td>
</tr>
<tr>
<td>(010)</td>
<td>1</td>
<td>0.10</td>
</tr>
<tr>
<td>(010)</td>
<td>2</td>
<td>0.10</td>
</tr>
<tr>
<td>(010)</td>
<td>3</td>
<td>0.10</td>
</tr>
<tr>
<td>(010)</td>
<td>4</td>
<td>0.11</td>
</tr>
<tr>
<td>(010)</td>
<td>5</td>
<td>0.11</td>
</tr>
</tbody>
</table>
$\text{Li}_{14}(\text{PON}_3)_2$ : Interface with Li

Ideal interface

Strained interface

Interacting interface
$\text{Li}_{14}(\text{PON}_3)_2$ : Interface with Li

(Lepley, PHYSICAL REVIEW B 92, 214201 (2015))

Within any given periodic simulation cell with $n_a$ units of material $a$ and with $n_b$ units of material $b$, we can define an interface energy:

$$
\tilde{\gamma}_{ab}(\Omega, n_a, n_b) = \frac{\tilde{E}_{ab}(\Omega, A, n_a, n_b) - n_a E_a - n_b E_b}{A}
$$

In order approximately remove the effects of lattice strain:

- Design the supercell to be commensurate with lattice $a$
- Now the strain will scale with the amount of material $b$

$$
\Rightarrow \tilde{\gamma}_{ab}(\Omega, n_a, n_b) = \tilde{\gamma}_{ab}^{\text{lim}}(\Omega) + n_b \sigma
$$
Li$_{14}$(PON$_3$)$_2$ : Interface with Li
Li$_{14}$(PON$_3$)$_2$ : Interface with Li

(a)
Summary and Conclusions

- This work report a computational study of the structural and electrolyte properties of the \( \text{Li}_{14}(\text{PON}_3)_2 \) and \( \text{Li}_7\text{PN}_4 \) solid electrolyte materials.

- The conduction process for these LiPON materials was dominated by the vacancy mechanism in comparison to the kick-out mechanism in the \( \text{Li}_3\text{PO}_4 \).

- The calculated range of the activation energies for the \( \text{Li}_{14}(\text{PON}_3)_2 \) was found to be lower than \( \text{Li}_7\text{PN}_4 \) and \( \text{Li}_3\text{PO}_4 \) indicating relatively good conduction properties.

- Both \( \text{Li}_{14}(\text{PON}_3)_2 \) and \( \text{Li}_7\text{PN}_4 \) have a stable interface with metallic Li.