Structure and interface properties of the electrolyte material Li$_4$P$_2$S$_6$*

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*Supported by NSF Grant DMR-1105485. Computations were performed on WFU’s DEAC cluster. ZDH was supported by the HERE program at ORNL. Helpful discussion with Chengdu Liang, Gayatri Sahu, Hui Wang, Melanie Kirkham, Jong Keum, and E. Andrew Payzant at ORNL and William C. Kerr, Keerthi Senevirathne, Cynthia Day, and Abdessadek Lachgar at WFU are gratefully acknowledged.
Why-- • Part of search for ideal solid electrolyte materials for all-solidelectrolyte batteries for all-solid state Li ion batteries
• Reported in by Mercier et. al. , J. Solid State Chemistry 43, 151-164 (1982); hexagonal structure with disorder on the P sites
• Frequently identified as unintended constituent of solid electrolyte preparations; relatively stability in air

What-- Combined experimental and computation study including:
• Structural analysis
• Thermal stability
• Transport properties
Outline

➢ Motivation

➢ Structural analysis

➢ Thermal stability

➢ Ionic conductivity

➢ Summary and conclusions
Motivation for studying Li$_4$P$_2$S$_6$:

- Part of the search for the ideal solid electrolyte material for all-solid state Li ion batteries
- Li$_4$P$_2$S$_6$ frequently identified as unintended stable component of solid electrolyte preparations
- Interesting structural properties, including disorder
- Transport and stability properties

Previous work:


Synthese, structure cristalline et analyse vibrationnelle de l’hexathiohypodiphosphate de lithium Li$_4$P$_2$S$_6$

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Synthesis:

\[2\text{Li}_2\text{S} + \text{P}_2\text{S}_5 \xrightarrow{900^\circ\text{C}} \text{Li}_4\text{P}_2\text{S}_6 + \text{S}\]

Sulfur removed by treatment with solvent; sample prepared for electrochemical applications using ball milling.

Scanning Electron Micrograph of prepared sample:
Computational methods

• Density functional theory with LDA
• PAW formalism using datasets generated with ATOMPAW code
• Electronic structure calculations performed using QUANTUM ESPRESSO and ABINIT codes
• Plane wave expansion for wave functions with $|\mathbf{k} + \mathbf{G}|^2 \leq 64 \text{ Ry}$
• Brillouin zone integration mesh of 0.003 bohr$^{-3}$
• Visualization software: Xcrysden and VESTA; X-ray powder diffract simulated using Mercury
Crystal structure:  Space Group $P6_3/mcm$ (#193)
Projection on to hexagonal plane:
Crystal structure: Space Group $P6_3/mcm$ (#193)
Li$_4$P$_2$S$_6$ units:

2.3 Å
2.1 Å
Crystal structure: Space Group \( P6_3/mcm \) (#193)
Disorder in P-P placements:

Site label \( z \) up

Site label \( z \) down
Structural variation can be mapped on to a two-dimensional hexagonal lattice with each P configuration taking \( \uparrow \) or \( \downarrow \) settings; Li and S configurations fixed.
Examples:

Structure “b”

\[ \Delta E = 0.03 \text{ eV} \]

100% z

Structure “c”

\[ \Delta E = 0 \]

50% z  
50% z

Structure “d”

\[ \Delta E = 0 \]

50% z  
50% z
Temperature dependence of X-ray powder diffraction
## Diffraction analysis

<table>
<thead>
<tr>
<th></th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$Z_P$</th>
<th>$Z_S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp. 298K (X-ray)</td>
<td>6.0709</td>
<td>6.5903</td>
<td>0.1715</td>
<td>0.3237</td>
</tr>
<tr>
<td>Exp. 13K (X-ray)</td>
<td>6.0747</td>
<td>6.5966</td>
<td>0.1715</td>
<td>0.3237</td>
</tr>
<tr>
<td>Exp. 13K (neutron)</td>
<td>6.0761</td>
<td>6.5961</td>
<td>0.1698</td>
<td>0.3284</td>
</tr>
</tbody>
</table>
Comparison of 13 K X-ray data with simulation

Note: simulations scaled by 102% to compensate for systematic LDA error.

Simulations consistent with incoherent average over all P z and z configurations.
**Stability:** \( \text{Li}_4\text{P}_2\text{S}_6 \) is much less reactive than other lithium thio-phosphates, but it decomposes in air, especially at higher temperature.

- **Decomposition products:**
  - \( \text{P}_2\text{O}_5 \)
  - \( \text{Li}_4\text{P}_2\text{O}_7 \)
  - \( \text{Li}_2\text{SO}_4 \)
Ionic conductivity and Activation Energy

2.38 x 10^{-7} S/cm at 25°C and 2.33 x 10^{-6} S/cm at 100°C
Li_4P_2S_6 pressed pellets with blocking (Al/C) electrodes

\[ E_a = 0.294 \text{ eV} \]
Simulations of ion mobility using Nudged Elastic Band Model

Vacancy mechanism: \( \Delta E > 0.6 \text{ eV} \)

Interstitial mechanism: \( \Delta E > 0.1 \text{ eV} \)

Possible interstitial sites
Models of Li$_4$P$_2$S$_6$/Li interfaces -- Surface parallel to P-P bonds:

Surface with vacuum

Surface with lithium
Models of $\text{Li}_4\text{P}_2\text{S}_6$/Li interfaces -- Surface perpendicular to P-P bonds:

- Surface with vacuum
- Surface with lithium
Conclusions:

- Diffraction results are consistent with Mercier’s 1982 analysis with disorder on P sites due to small energy differences of alignment of $P_2S_6$ fragments; remarkably temperature independent.
- Small activation energy ($E_a = 0.3$ eV) for ion conductivity consistent with interstitial mechanism.
- Thermal stability relative to other thio-phosphates.
- Simulations of Li$_4$P$_2$S$_6$/Li interfaces suggest that meta-stable buffer layers may be formed.
- Further processing of materials needed to improve conductivity and stabilize Li/Li$_4$P$_2$S$_6$/Li cells.