Prediction of a New Material – Lithium Phosphorus Oxynitride – Li_2PO_2N [a]

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- Motivation for solid electrolytes and LiPON
- Computational methods
- Crystal structures and formation energies of $LiPO_3$ and Li_2PO_2N
- 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 accomodate 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.

Example of solid electrolyte – thin film battery technology

A. Patil et al. / Materials Research Bulletin 43 (2008) 1913–1942

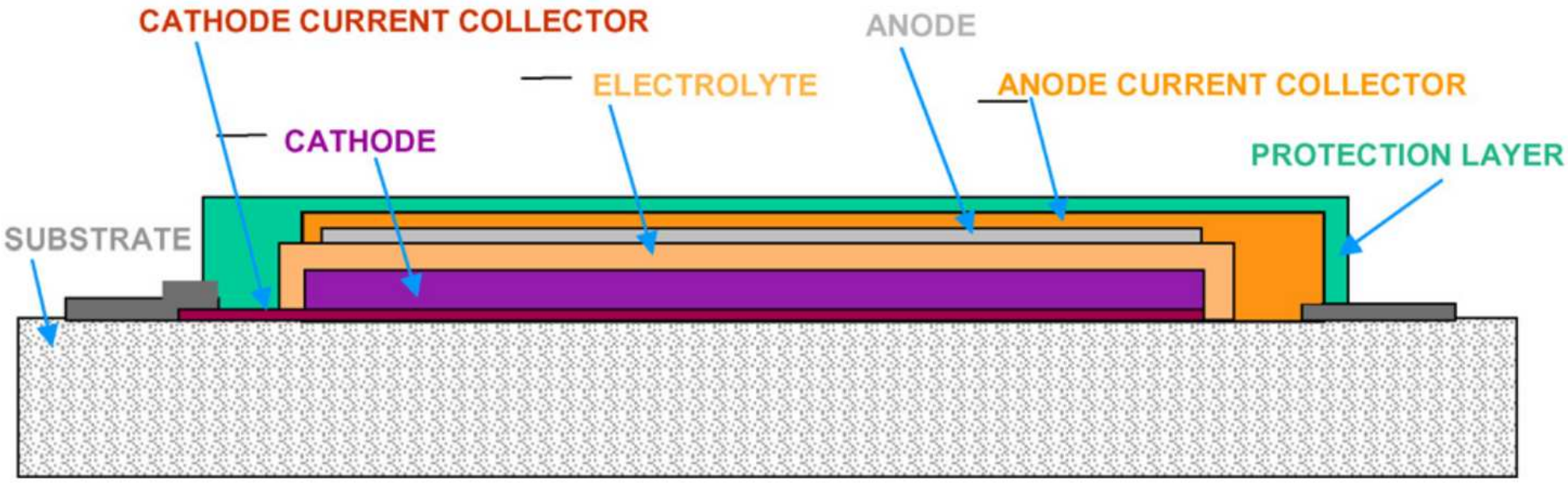
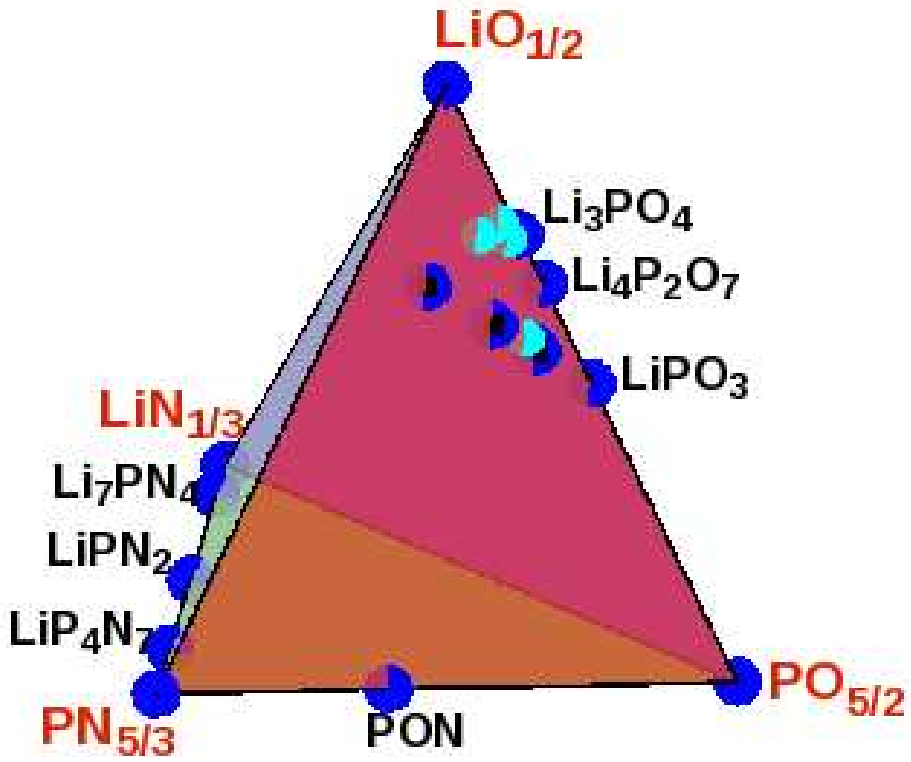


Fig. 2. Schematic cross-section of a thin film lithium battery structure.

Overview of LiPON family of electrolytes

The thin film solid electrolyte LiPON developed at Oak Ridge National Laboratory[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 undertanding 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 $PN_{5/3}$.



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

[a] Bates, Dudney, *et al Solid State Ionics* **53-54**, 647 (1992); Dudney *Interface* **17**, 44 (2008)

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 (ν)
- Heats of formation (ΔH)
- Energies for ion migration (E_m) and for interstitial-vacancy pair formation (E_f)

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[a] Hohenberg and Kohn, *Phys. Rev.*, **136** B864 (1964); Kohn and Sham, *Phys. Rev.*, **140** A1133 (1965); using local density approximation (LDA) (Perdew and Wang, *Phys. Rev. B*, **45** 13244 (1992)

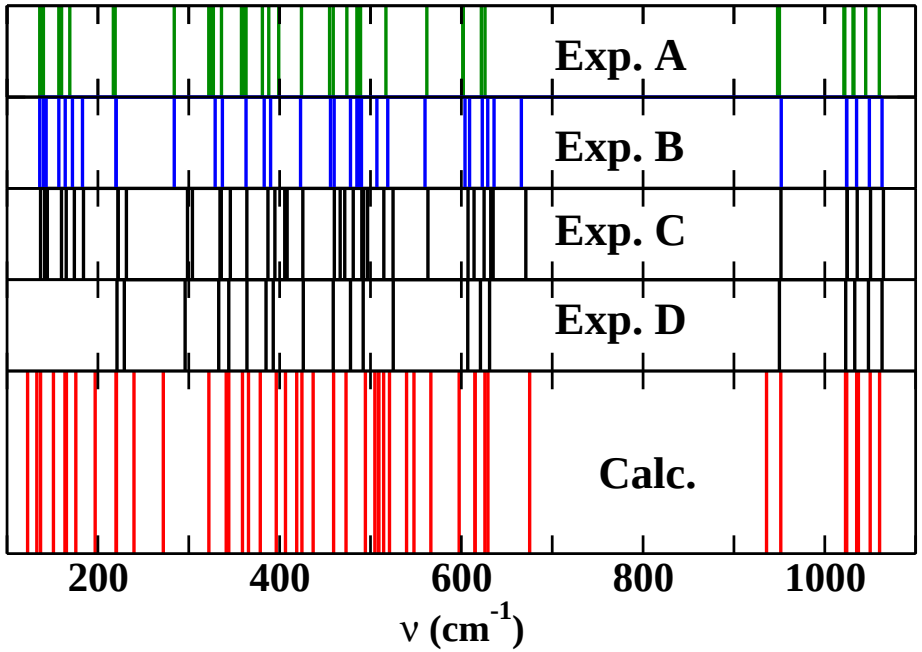
[b] Giannozzi *et al*, *J. Phys.: Condens. Matter* **21** 394402 (2009) `www.quantum-espresso.org`

[c] Tackett *et al*, *Comp. Phys. Comm.* **135** 348 (2001) `pwpaw.wfu.edu`

[d] Gonze *et al*, *Zeit. Kristallogr.* **220** 550 (2005) `www.abinit.org`.

Computational methods – validation

Raman spectra for γ-Li_3PO_4



Calculated Raman spectra (red) compared with

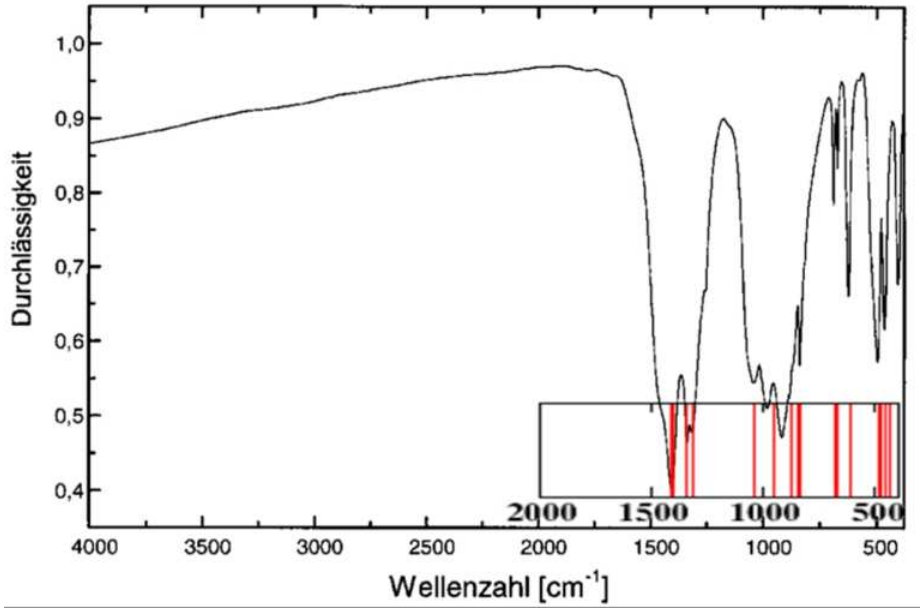
Exp. A: (RT) Mavrin & co-workers, *JETP* **96**, 53 (2003)

Exp. B: (RT) Harbach & co-workers, *Phys. Stat. Sol. B* **66**, 237 (1974)

Exp. C: (LNT) Harbach & co-workers, *Phys. Stat. Sol. B* **66**, 237 (1974)

Exp. D: (LNT) Popović & co-workers, *J. Raman Spec.* **34** 77, (2003)

Infrared spectra for α-P_3N_5

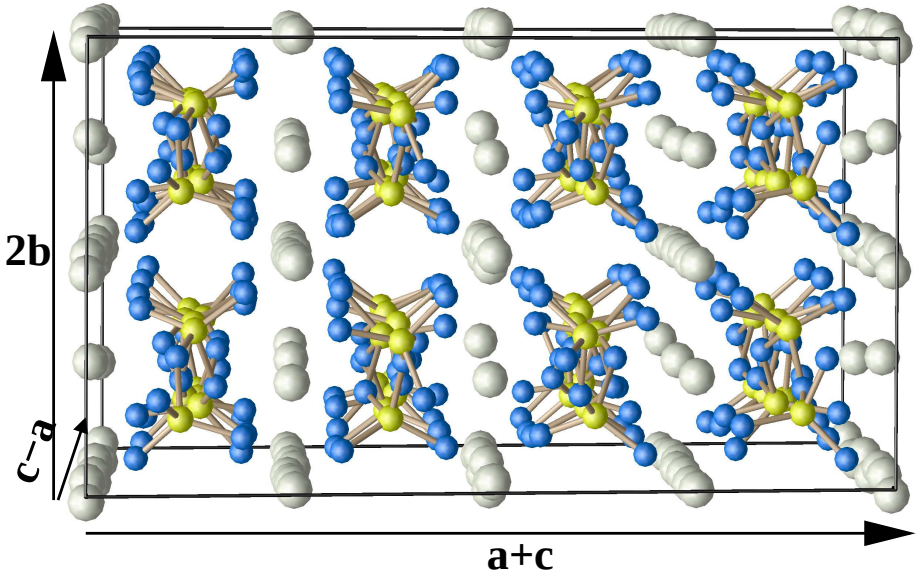


Calculated infrared spectra (red) compared with experiment of Horstmann, Irran, and Schnick, *Z. Anorg. Allg. Chem* **624** 620 (1998).

Phosphate chain material: $LiPO_3$

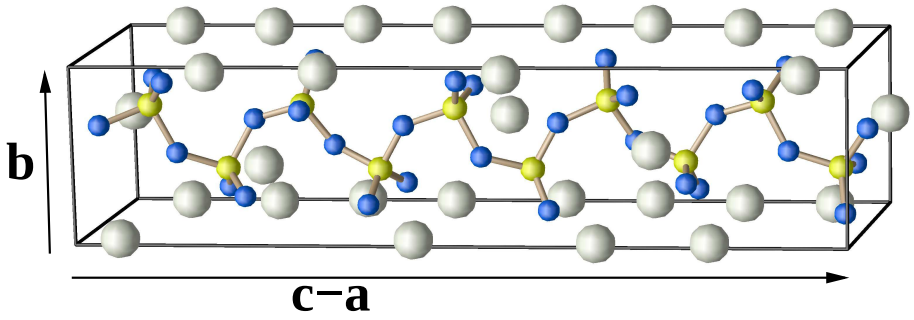
$LiPO_3$ in $P2/c$ structure; 100 atom unit cell

Chain direction perpendicular to plane of diagram



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

Single chain view



$P2/c$ $LiPO_3$ can be prepared from a Li_2O-P_2O_5 glass by heating to the crystallization temperature of 486^o C.[a]

Lattice parameters (in Å) for $LiPO_3$

	a	b	c	β
Cal.	13.00	5.30	16.31	98.8^o
Exp.[b]	13.074	5.4068	16.452	99.00^o

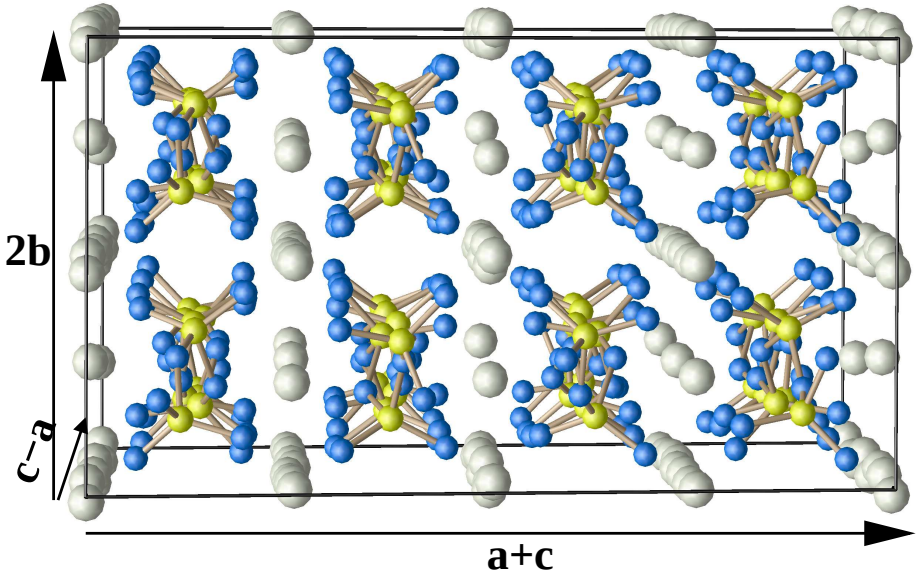
[a] Money and Hariharan, *Appl. Physics A* **88** 647 (2007)

[b] Murashova and Chudinova, *Crystall. Rep.* **46** 942 (2001)

Phosphate chain materials: $LiPO_3$ plus N

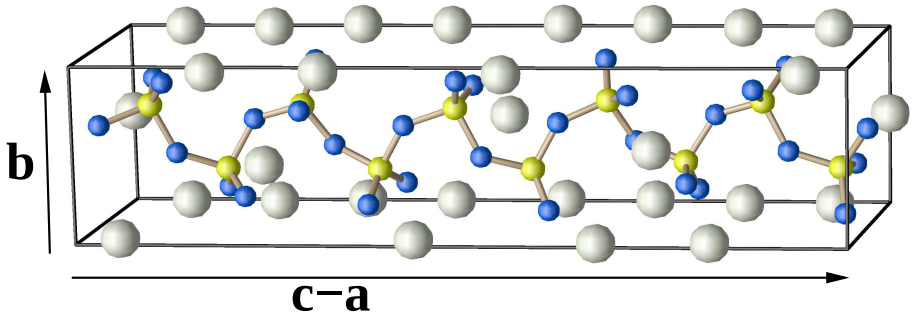
$LiPO_3$ in $P2/c$ structure; 100 atom unit cell

Chain direction perpendicular to plane of diagram



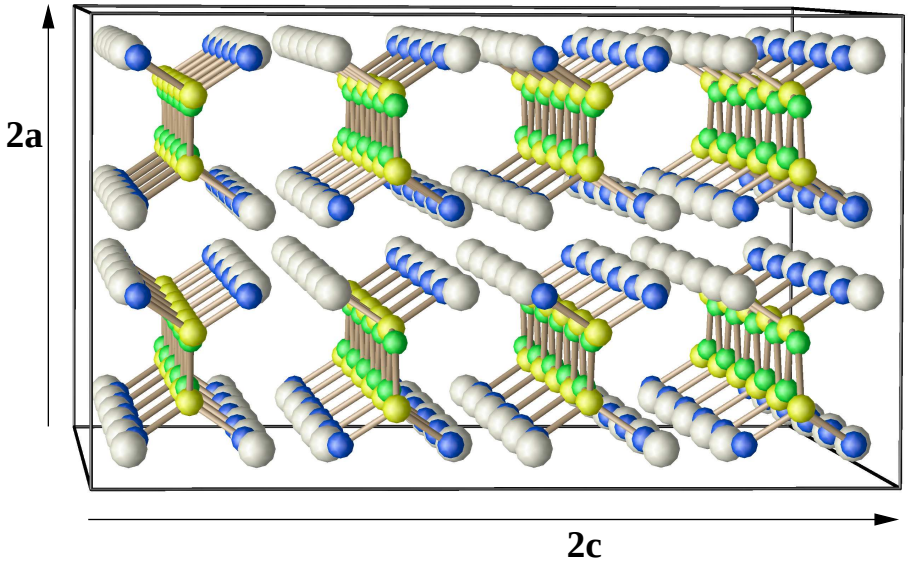
Ball colors: =Li, =P, =O.

Single chain view



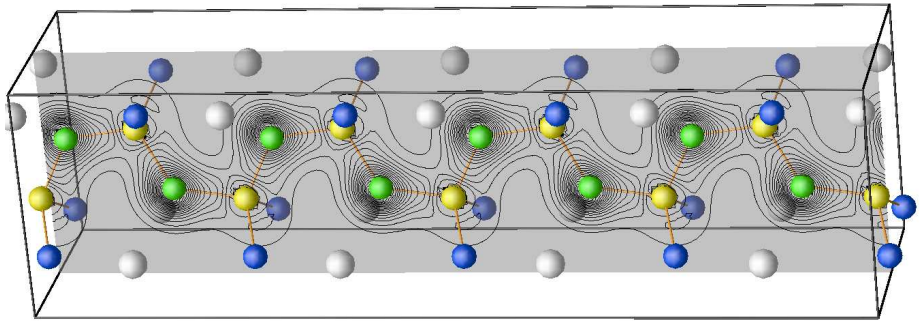
s_1-Li_2PO_2N in $Pbcm$ structure; 24 atom unit cell

Chain direction perpendicular to plane of diagram



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

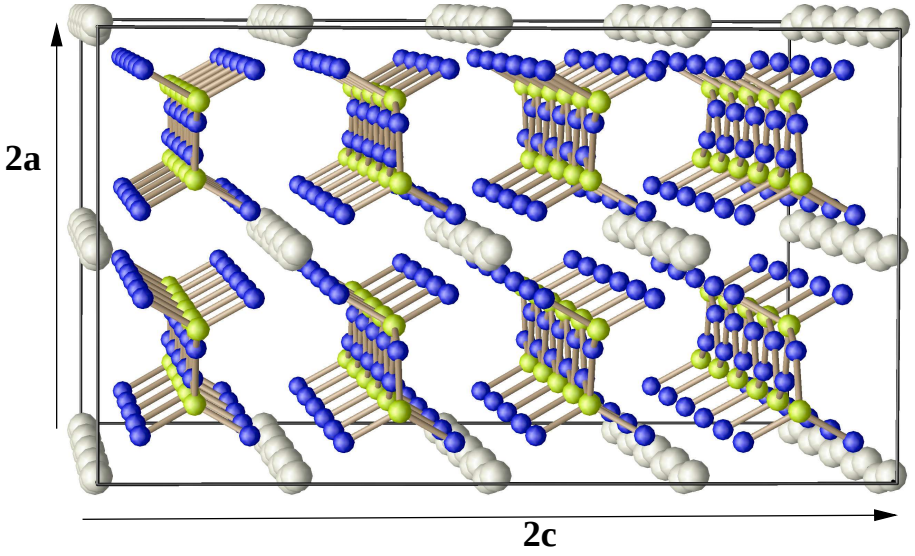
Single chain view



Phosphate chain materials: s_1-$LiPO_3$ and s_1-Li_2PO_2N

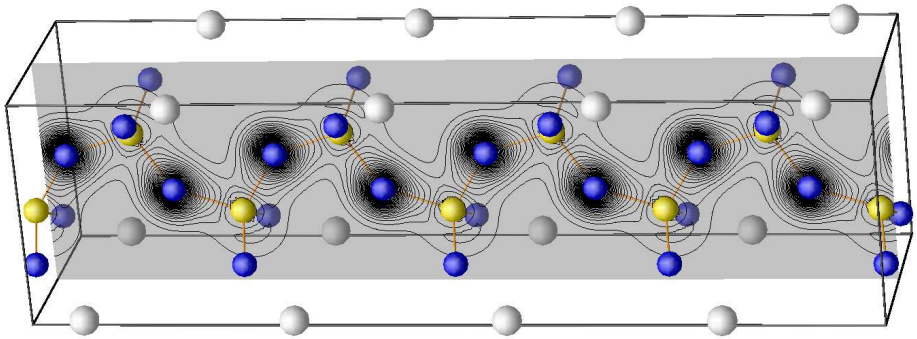
s_1-$LiPO_3$ in *Pbcm* structure; 20 atom unit cell

Chain direction perpendicular to plane of diagram



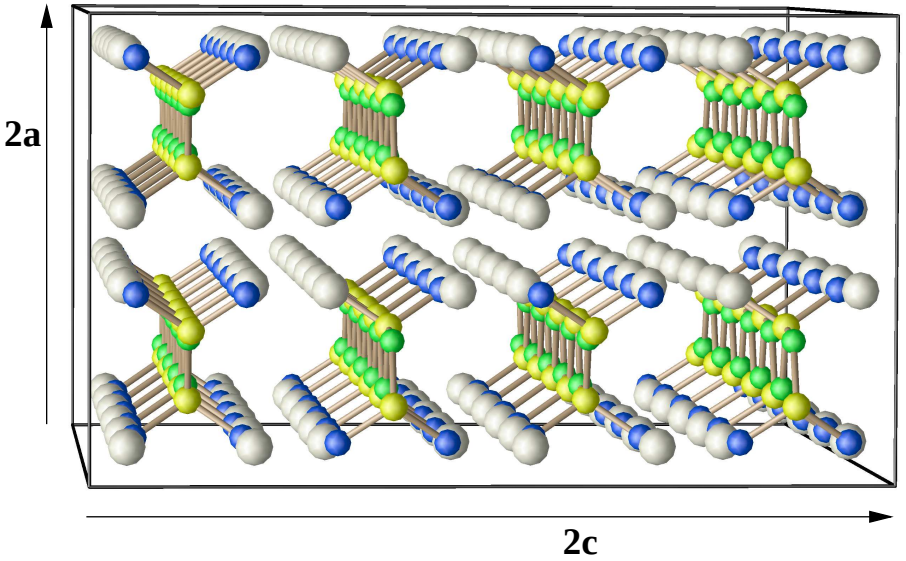
Ball colors: =Li, =P, =O.

Single chain view



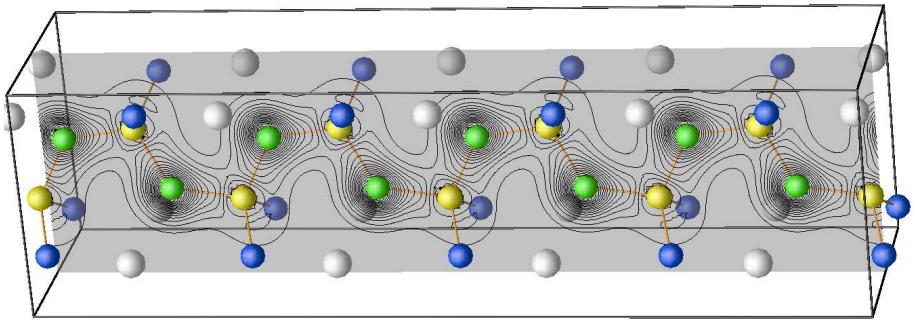
s_1-Li_2PO_2N in *Pbcm* structure; 24 atom unit cell

Chain direction perpendicular to plane of diagram



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

Single chain view

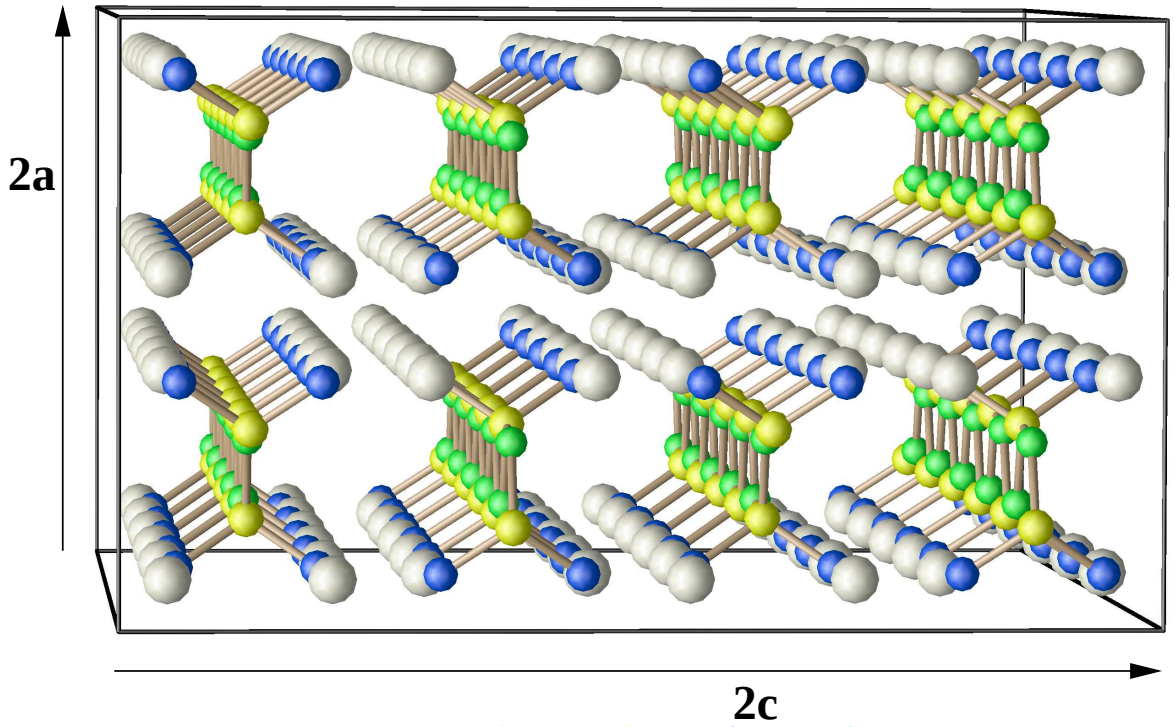


Phosphate chain materials: $LiPO_3$ and Li_2PO_2N

Comparison of different structural forms of $LiPO_3$ and Li_2PO_2N in terms of their heats of formation ($\Delta H_{\rm cal}$) and volumes $\mathcal{V}_{\rm cal}$ (per formula unit).

Material	Structure	$\Delta H_{\rm cal}$ (eV)	$\mathcal{V}_{\rm cal}$ ($\mathring{A}^3$)
$LiPO_3$	$P2/c$ [#13]	-12.80	56
s_1-$LiPO_3$	$Pbcm$ [#57]	-12.73	58
s_2-$LiPO_3$	$Aem2$ [#39]	-12.73	58
s_3-$LiPO_3$	$Pmc2_1$ [#26]	-12.70	67
s_1-Li_2PO_2N	$Pbcm$ [#57]	-12.42	57
s_2-Li_2PO_2N	$Aem2$ [#39]	-12.45	57
s_3-Li_2PO_2N	$Pmc2_1$ [#26]	-12.08	66

s_1-Li_2PO_2N: Can it be made?



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

Possible exothermic reaction pathways:

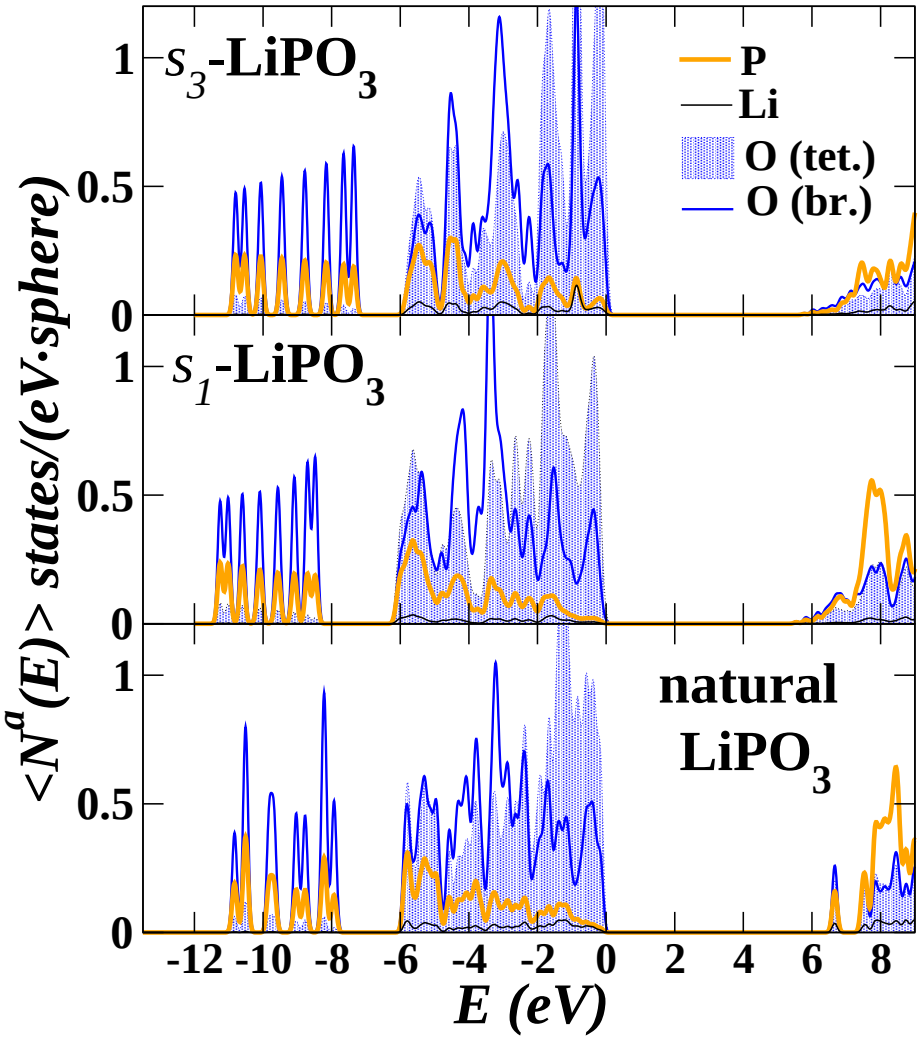
$$\tfrac{1}{5}P_2O_5 + \tfrac{1}{5}P_3N_5 + Li_2O \rightarrow Li_2PO_2N + 2.5\ \text{eV}.$$

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

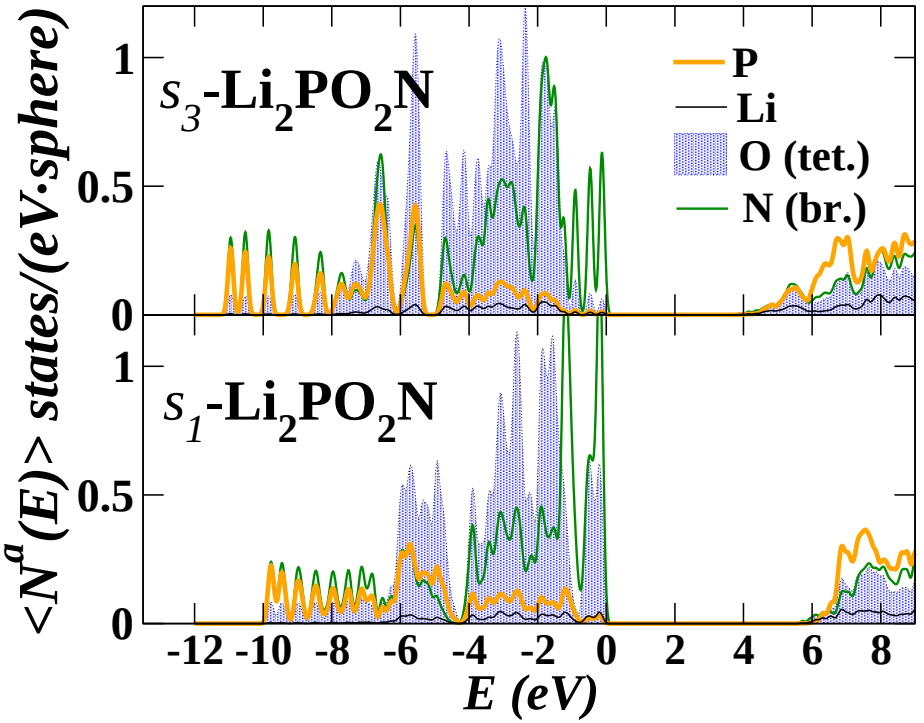
$$LiNO_3 + Li + P \rightarrow Li_2PO_2N + \frac{1}{2}O_2 + 7.0\ \text{eV}.$$

Partial densities of states analyses

$LiPO_3$



Li_2PO_2N



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 paprameters, heats of formation, and lattice vibrational spectra, we have developed some confidence in the plausibility of our predictions.
- In particular, we have identied several stable/meta-stable phosphonitride chain structures having the stoichiometry Li_2PO_2N, 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.