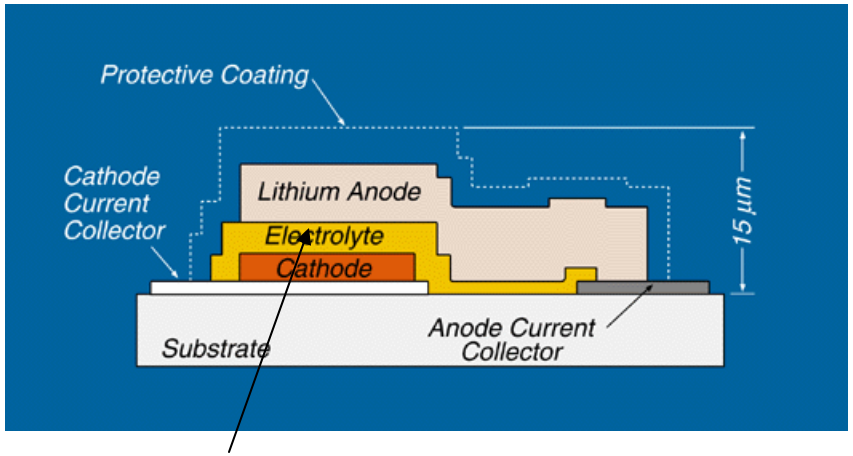
Wake Forest University

First-principles simulations of extended structures in the lithium phosphorous oxynitride electrolytes

Yaojun Du and N. A. W. Holzwarth

The structure of thin film battery[2]



Solid state electrolytes that are physically and chemically stable can be made very thin. Such as LiPON (Li_3PO_4)

The thin film LiPON, having the composition of $Li_{3+x}PO_{4-y}N_z$ with $x = 3z - 2y$ has been developed as a solid state electrolyte for Li ion batteries by ORNL[1].

Conductivities of various LiPON material are measured[1,3]

$$\sigma(T) = \frac{K}{T} e^{-E_A/kT}$$

For various LiPON materials,[1,3-6] the activation energies are determined to be 0.4 – 0.7 eV.

For instance, for $Li_{0.99}PO_{2.55}N_{0.30,}$ Wang et al. measured the activation energy of 0.6 eV.[6]

1. B. Wang et al., J. of Solid State Chemistry **115**, 313 (1995).
2. http://www.ms.ornl.gov/researchgroups/Functional/BatteryWeb/CrossSection.html
3. C. H. Choi et al., Electrochemical and Solid-state Letters, **5**, A14 (2002).
4. Y. Hamon et al., Solid State Ionics **177**, 257 (2006).
5. Wen-Yuan Liu et al., Electrochemical and Solid-state Letters, **7**, J36 (2004).
6. B. Wang et al., Journal of Non-Crystalline Solids **183**, 297 (1995).

Supported by NSF grants DMR – 0405456 + 0427055 and DEAC cluster

Motivation and goal

The goal of this work is to optimize the structure and stoichiometry of LiPON electrolytes for use in Li ion batteries which can achieve the highest ionic conductivity.

A number of groups have addressed this problem experimentally and have found evidence for linear chains of phosphates with bridging -O- and -N- sites and more complicated phosphate structures such as triply coordinated N.[1]

In this talk, we will discuss first-principles simulations on naturally occurring crystals and constructed artificial crystals, focusing on these particular structures and their effects on the migration of Li ions.

Outline

1. Method
2. Optimize the $LiPO_3$ crystal has a linear chain structure (P-O-P) observed in the LiPON glasses.
3. Construction of an artificial $LiPO_3$ crystal which also contains P-O-P chains and which is amenable for NEB treatment.
4. Construction of the Li_2PO_2N crystal which contains P-N-P chains.
5. Characterize the triply-coordinated N based on the α-P_3N_5, Also study its effect on the migration of Li ions.
6. Conclusion.

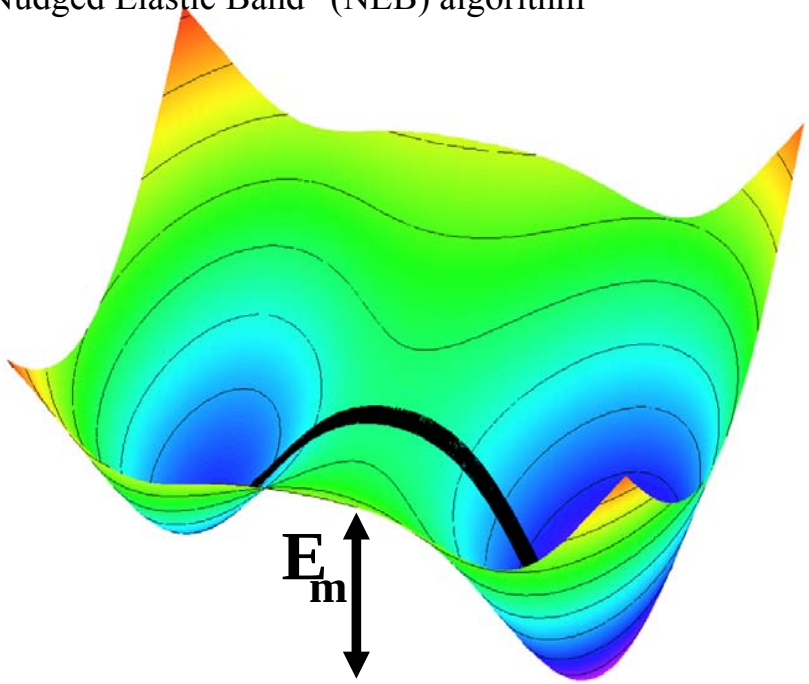
1. B. Wang et al., J. of Solid State Chemistry **115**, 313 (1995).

Method

Quantum ESPRESSO (*PWscf*)[1] package and ultra-soft pseudopotential formalism of Vanderbilt using LDA.

Ionic conductivity via activated hopping

Schematic diagram of minimal energy path, estimated using "Nudged Elastic Band" (NEB) algorithm[2]



Arrhenius relation

$$\sigma \cdot T = K e^{-E_A/kT}$$

Experimental conductivities for single γ-Li_3PO_4 crystals by Ivanov-Shitz et al, *Cryst. Reports* **46**, 864 (2001):

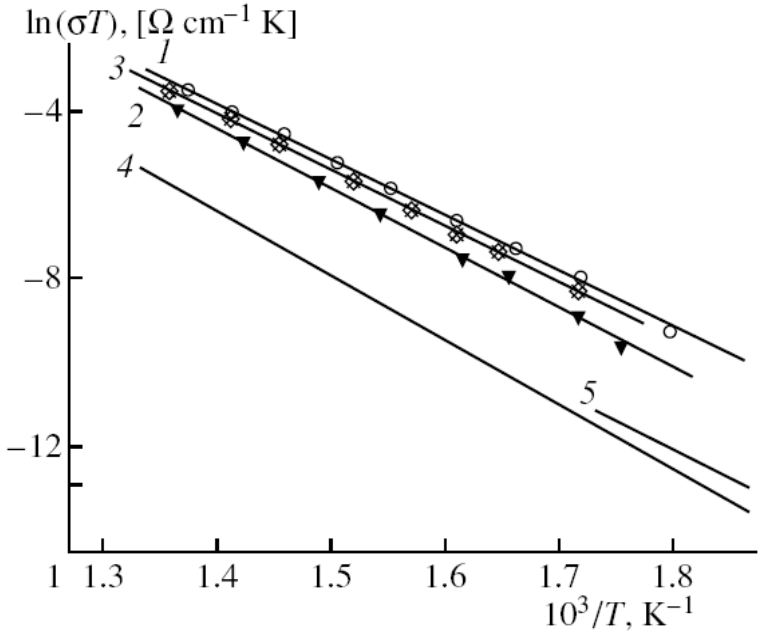


Fig. 2. Temperature dependences of conductivity in γ-Li_3PO_4: (*1*–*3*) for single crystals measured along the (*1*) *a*-axis, (*2*) *b*-axis, (*3*) *c*-axis and (*4*, *5*) for a polycrystal (*4*) according to [4, 5] and (*5*) according to [7].

E_A = 1.14, 1.23, 1.14, 1.31, 1.24 eV for cases 1,2,3,4,5, respectively.

1. www.pwscf.org
2. H. Jónsson *et al.*, in Classical and Quantum Dynamics in Condensed Phase Simulations, edited by Berne, Ciccotti, and Coker (World Scient 1998), p. 385; G. Henkelman *et al, JCP* **113**, 9901, 9978 (2000).

Perfect $LiPO_3$ crystal

The $LiPO_3$ crystal contains linear chains of phosphates connected with bridging -O- sites[1,2].

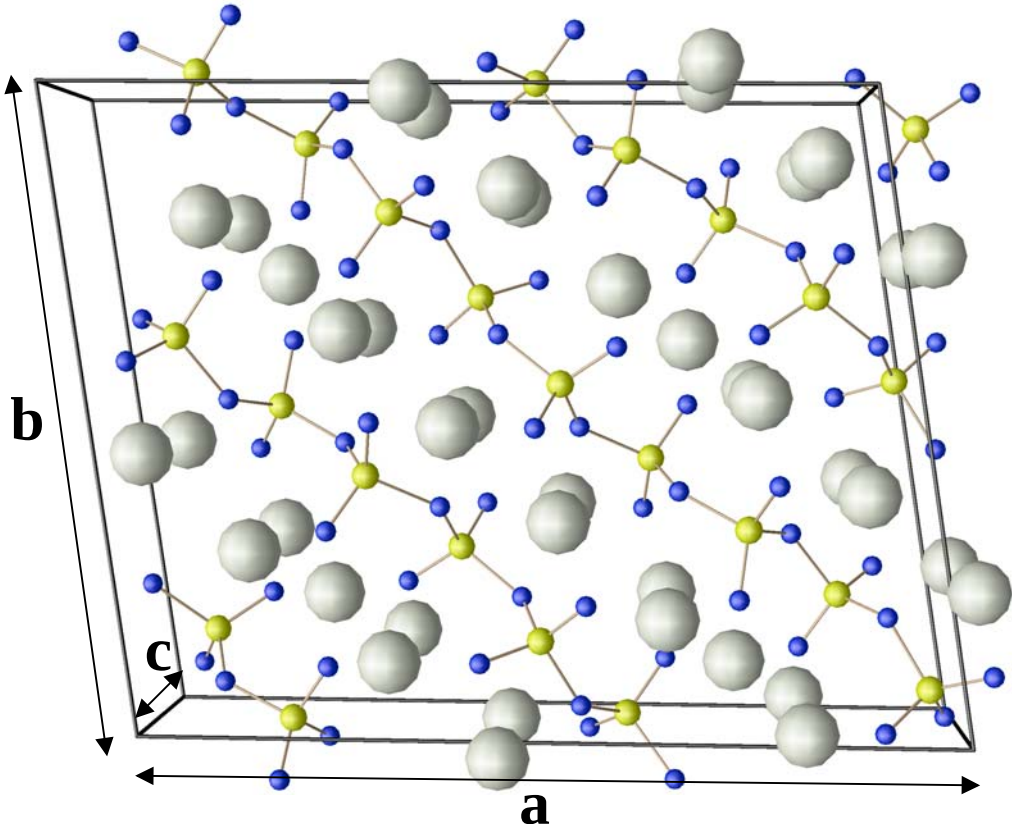
Based on the experiment data, we optimize the primitive cell of a $LiPO_3$ crystal with 100 atoms .

For the bridging O

	This work (LDA)	Experiment[2]
Bond angle (degree)	126.7 – 136.9	127.4 – 137.9
Bond length (Ang.)	1.59-1.61	1.57 – 1.62

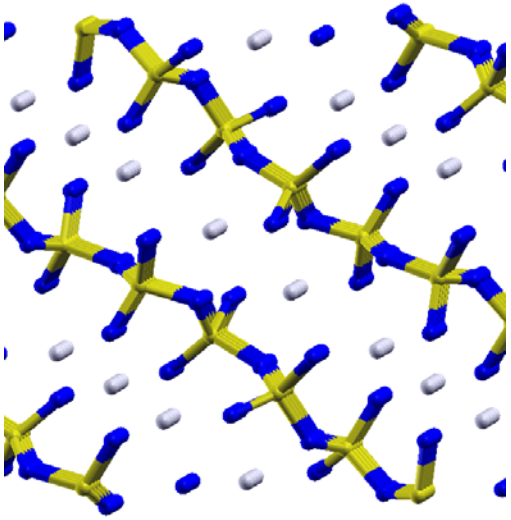
For the tetrahedral O

	This work (LDA)	Experiment[2]
Bond angle (degree)	104.0 –121.2	105.8 –120.5
Bond length (Ang.)	1.49-1.50	1.47 – 1.49

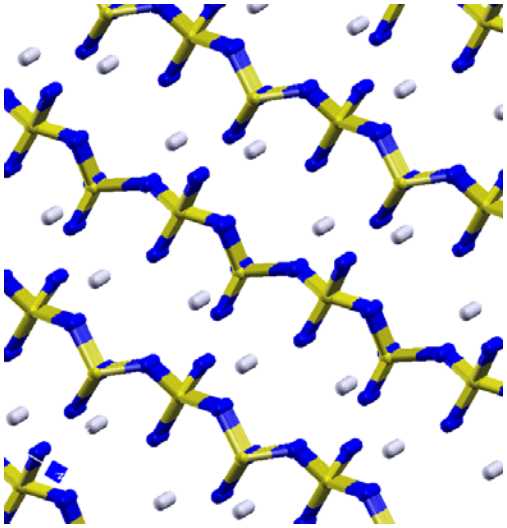


1. B. Wang et al., J. of Non-Crystalline Solids **183**, 297 (1995).
2. E. V. Murashova and N. N. Chudinova, Crysallography Reports **46**, 942 (2001)

The constructed $LiPO_3$



Naturally existing $LiPO_3$

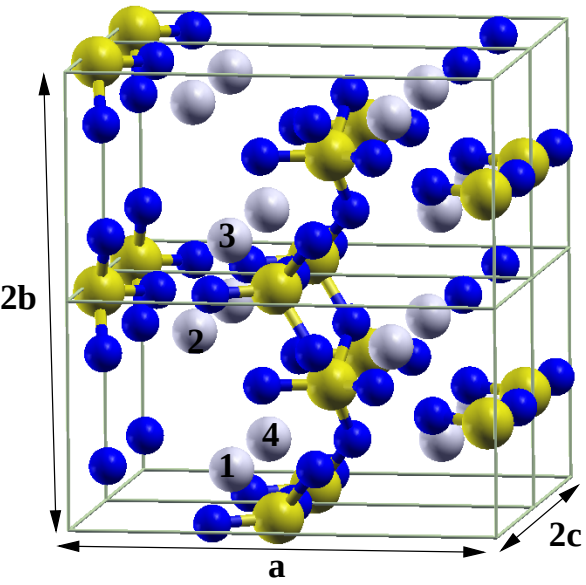


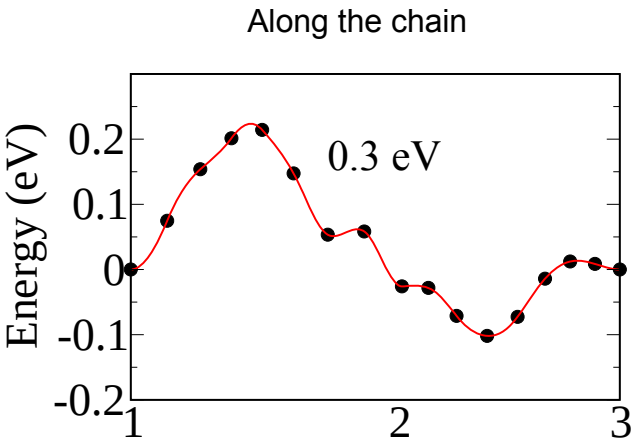
Artificial $LiPO_3$

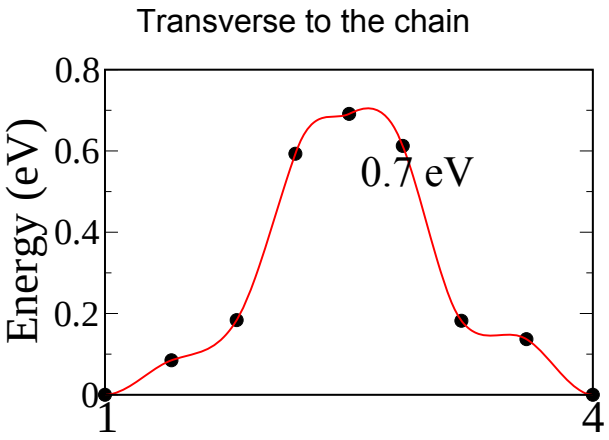
Comparison between the artificial and natural $LiPO_3$

	Total energy (eV/f.u.)	Volume $(a.u.)^3/f.u$	Bond Angle (Bridging O)	Bond Length (Bridging O)	Bond Angle (Tetrahedral O)	Bond Length (Tetrahedral O)
Artificial	0.2	386.5	131.5 – 134.4	1.60 – 1.62	101.2 – 122.1	1.49
Natural	0	375.2	126.7 – 136.9	1.59 – 1.61	105.8 – 120.5	1.49-1.50

Simulations of the Li ion migration within the constructed $LiPO_3$



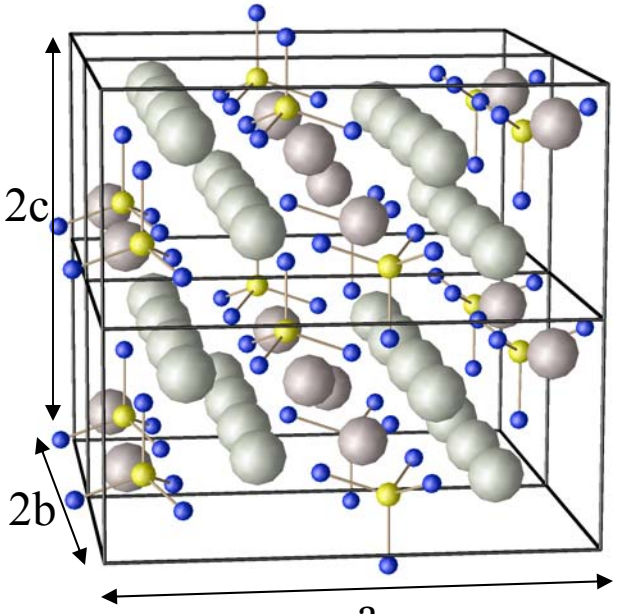




	This work (eV)	NMR[1] (eV)	Impedance[2] (eV)
E_m (eV)	0.3 – 0.7	0.66	0.76

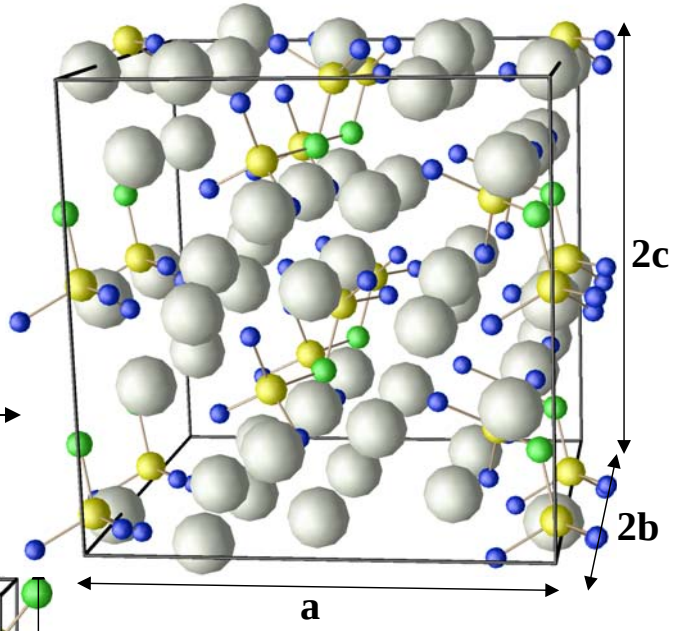
1. Sandra et al., Phys. Rev. B, **77**, 104301 (2008).
2. B. K. Money and K. Hariharan, Appl. Phys. A, **88,** 647 (2007).

ɔn of N-containing phosphate chains



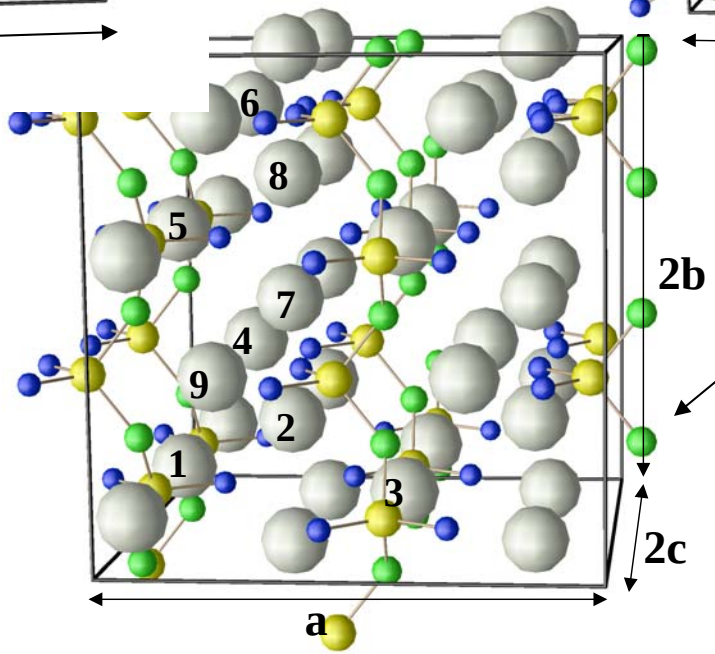
γ-Li_3PO_4

Remove 2 O atoms and 2 Li atoms, and substitute 2 O atoms by 2 N atoms respectively to obtain



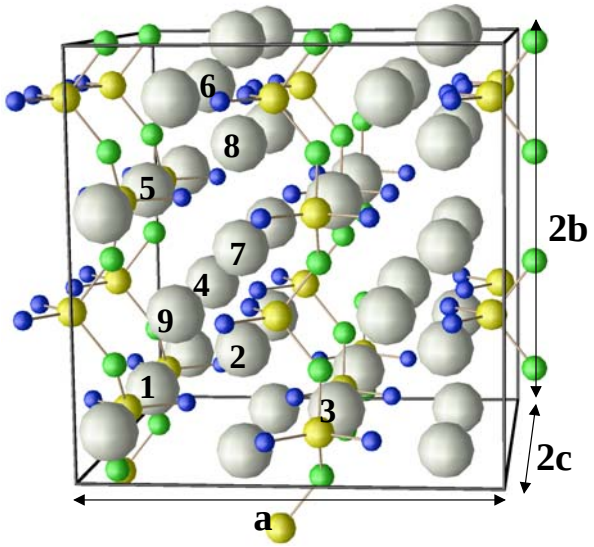
$Li_{5/2}PO_3N_{1/2}$

Remove 2 O atoms and 2 Li atoms, and substitute 2 O atoms by 2 N atoms respectively to obtain

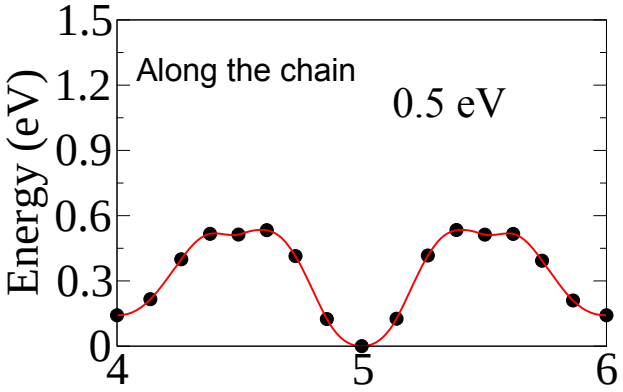


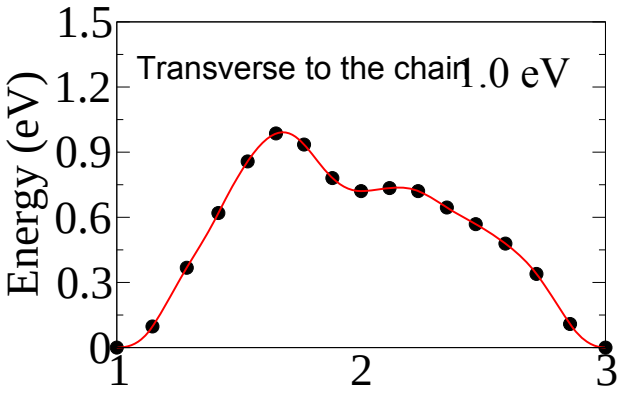
Li_2PO_2N

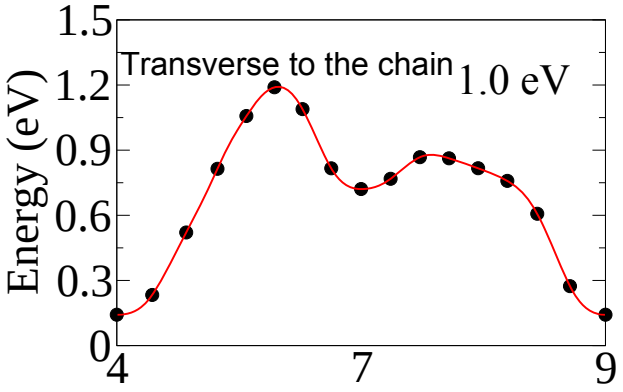
Simulations of the Li ion migration within the constructed Li_2PO_2N



	Bridging N (P-N-P)	Tetrahedral O
Bond angle (degree)	130.9	103.2—114.8
Bond length (Ang.)	1.62 – 1.63	1.54 – 1.55





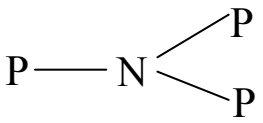


Migration within the chain structure

We have characterized the bonding situations of P-O-P and P-N-P structures and have shown that Li ion vacancies can diffuse along the P-O-P and P-N-P with migration barriers of 0.3 eV and 0.5 eV, respectively. On the other hand, if the Li ion vacancies diffuse perpendicular to the chain structures, the migration barrier will raise to 0.7 eV and 1.0 eV, respectively.

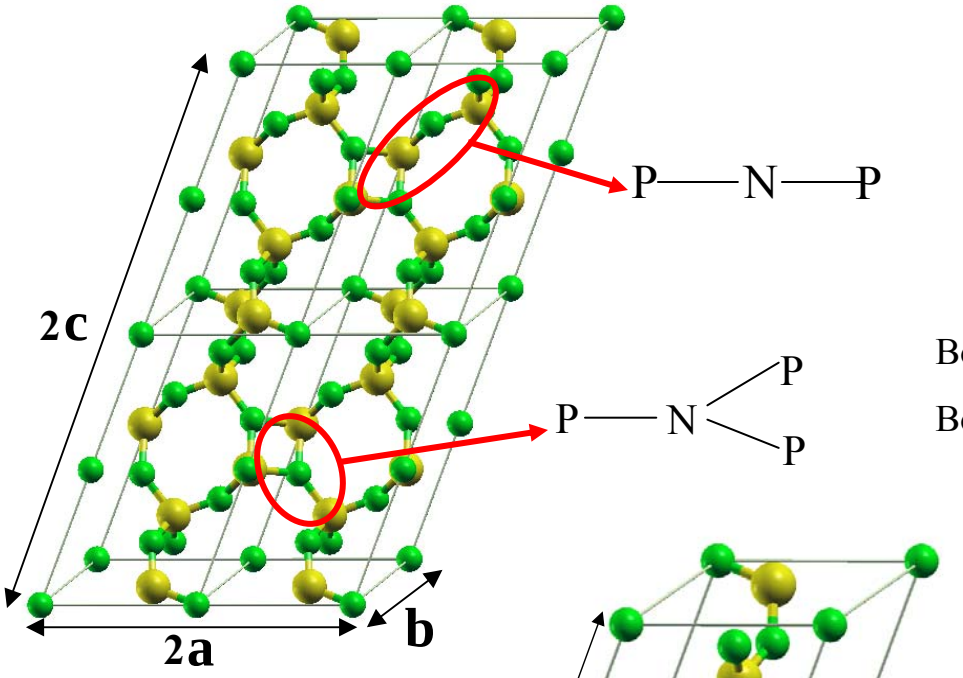
Next, we have will characterize the bonding situations of the triply coordinated N based on the α-P_3N_5 crystal, and study Li ion migration within the crystal.

The ratio between the doubly coordinated N and triply coordinated N is 0.3.[1]

Triply coordinated N 

1. B. Wang et al., Journal of Non-Crystalline Solids **183**, 297 (1995).

Migration of Li ions within the α-P_3N_5 structure



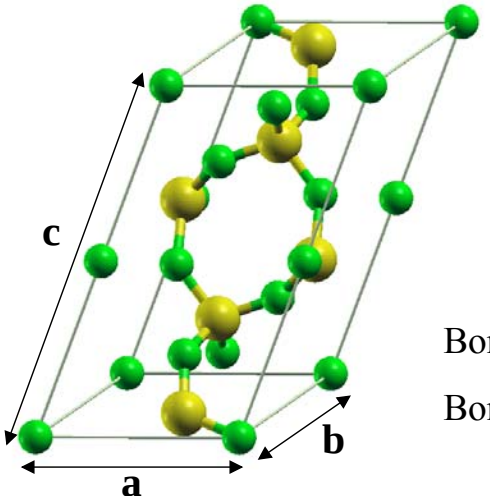
Doubly Coordinated N

P—N—P

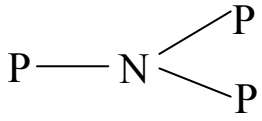
Bond Length: 1.55 and 1.56 Ang.

Bond Angle: 142.5 and 180 degree.

Six member ring that is proposed by Veprek[2].



Triply Coordinated N[1]

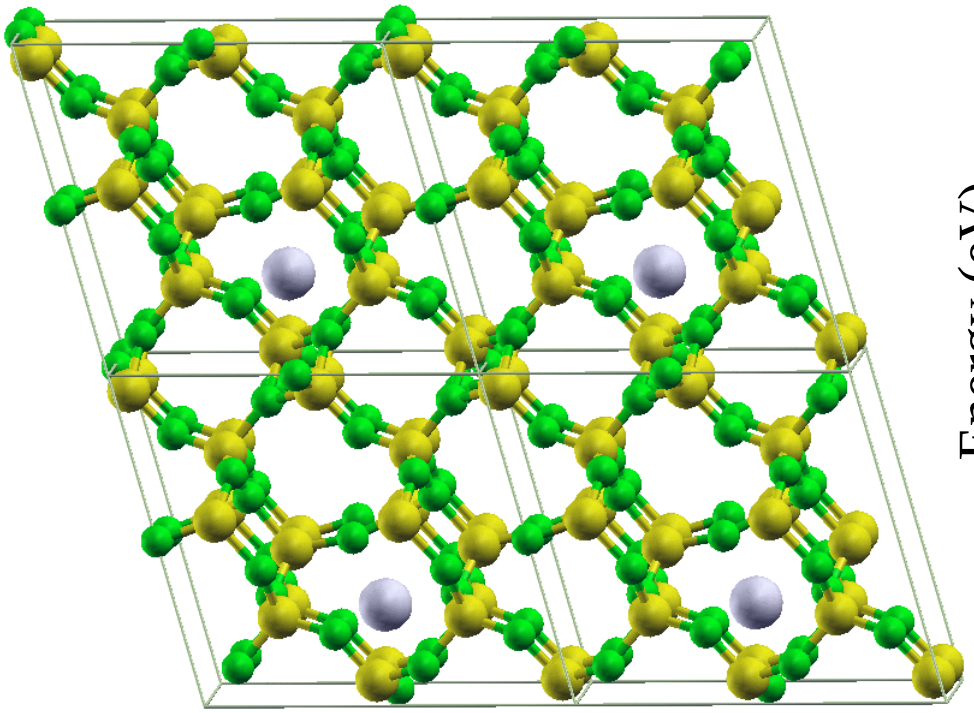


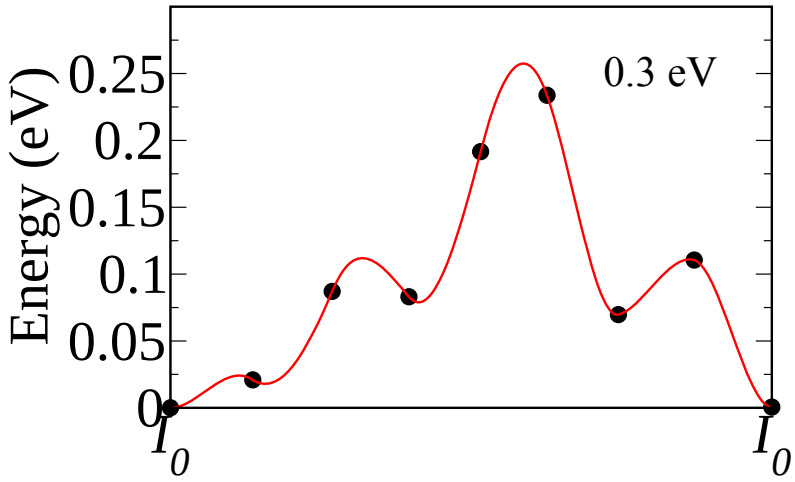
Bond Length: 1.66, 1.69, and 1.71 Ang.

Bond Angle: 127.2, 97.2, and 135.6 degree.

1. B. Wang *et al.*, J. of Non-Crystalline Solids **183**, 297 (1995).
2. S. Veprek *et al.*, Philosophical Magazine B **43,** 527 (1981).

Migration of Li ions within the α-P_3N_5 structure





Conclusion

1. We have constructed $LiPO_3$ with a 20-atom primitive cell. It contains the linear bridging structure of P-O-P that has the bond angle of 131.5 – 134.4 degree and the bond length of 1.60 – 1.62 Ang. On the other band, the naturally existing $LiPO_3$ has the bond angle of 126.7 – 136.9 degree and the bond length of 1.59-1.61 Ang.

2. We have constructed Li_2PO_2N with a 24-atom primitive cell. It contains the linear bridging structure of P-N-P that has the bond angle of 131.5 – 134.4 degree and the bond length of 1.60 – 1.62 Ang.

3. In both the constructed $LiPO_3$ and Li_2PO_2N, we have show that the linear structures of P-O-P and P-N-P provide 1D diffusion channel for Li ions. We expect that the migration barrier within $LiPO_3$ glasses to be 0.7 eV which is consistent with the experimental results.

4. Li ion can be inserted into the α-P_3N_5 crystal and has a migration barrier of 0.3 eV. However, the connection between our results and the triply coordinated N within the LiPON material has yet to be confirmed.

Summary of migration energies for Li ion vacancies in $Li_{3+x}PO_{4-y}N_z$ with $x = 3z - 2y$

x	y	z	form	E_{exp}(eV)	E_m(eV)
0	0	0	γ-Li_3PO_4	1.1[1,a]	0.7
-2	1	0	$LiPO_3$ (P-O-P)	0.66 – 0.76[5,6]	0.5 – 0.7
-1	1	2	Li_2PO_2N (P-N-P)		0.5 – 1.0[b]
-3	4	5/3	α-P_3N_5		0.3[b]

[a] The 1.1 eV activation energy includes the formation energy of intrinsic defects and the migration energy for an interstitialcy mechanism. (see Phys. Rev. B **76,** 174302 (2007)).

[b] For various LiPON materials,[2-4] the activation energies are determined to be 0.4 – 0.7 eV.

1. A. K. Ivanov-Shitz et al., Crystallogr. Rep. **46**, 864 (2001).
2. Y. Hamon et al., Solid State Ionics **177**, 257 (2006).
3. C. H. Choi et al., Electrochemical and Solid-state Letters, **5**, A14 (2002).
4. Wen-Yuan Liu et al, Electrochemical and Solid-state Letters, **7**, J36 (2004).
5. Sandra et al., Phys. Rev. B, **77**, 104301 (2008).
6. B. K. Money and K. Hariharan, Appl. Phys. A, **88,** 647 (2007).

Future work

We will consider other materials such as P_2O_5, $LiPN_2$, and Li_7PN_4.