$Li_{14}(PON_3)_2$: Computational study of a possible new electrolyte for Li ion batteries

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Computations were performed on WFU's DEAC cluster.

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- 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

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

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

Solid Electrolyte materials

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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

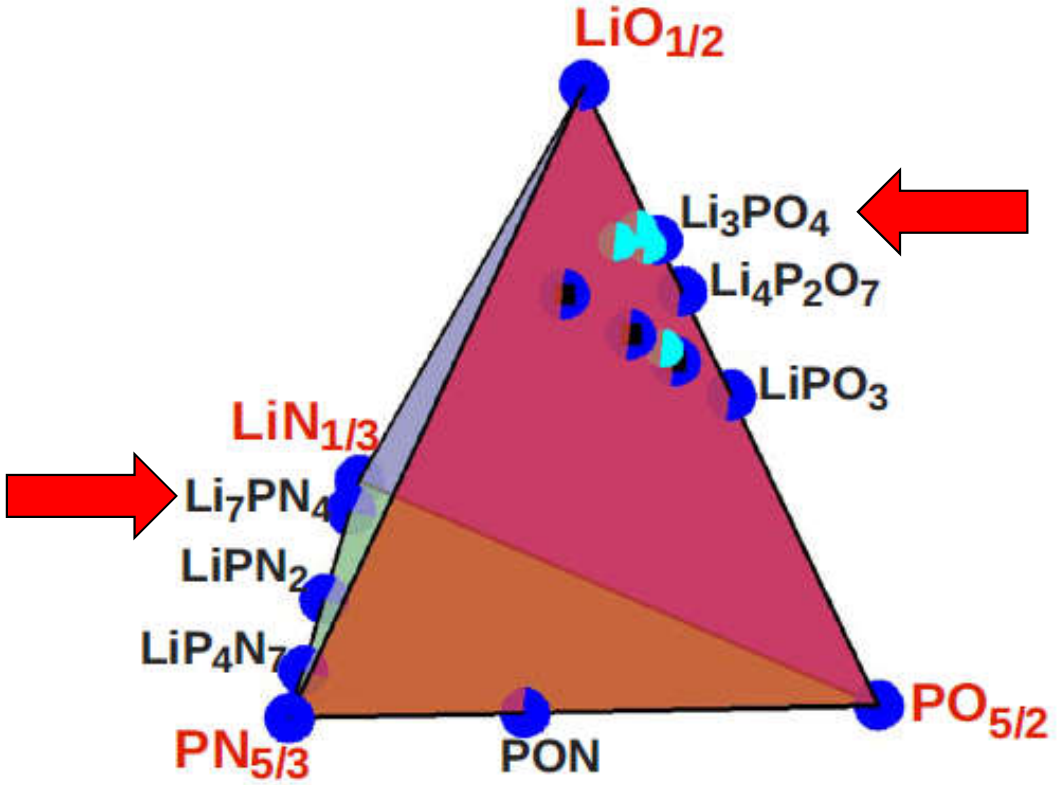
Relatively high ionic conductivity

Excellent contact area with high capacity electrodes

Disadvantages

Poor chemical and physical stability

Relies on the formation of SEI layer



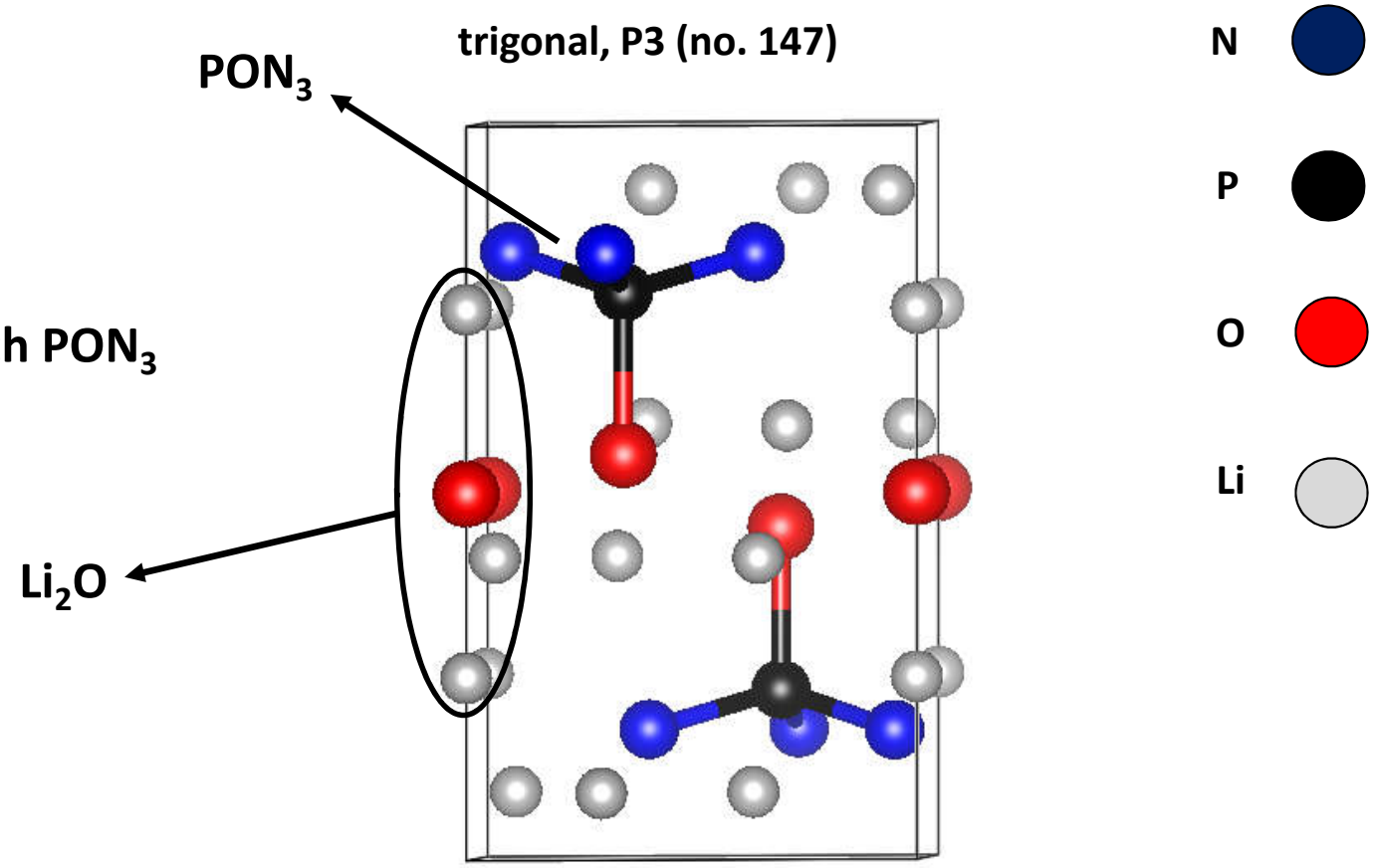
$Li_xPO_yN_z$

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

(Du,PHYSICAL REVIEW B 81, 184106,2010)

$Li_{14}(PON_3)_2O$: Computational study of a possible new electrolyte for Li ion batteries

- The First LiPON material with PON_3 Tetrahedra .



(Schnick,Eur. J. Inorg. Chem. 2015, 617-621)

Comparison of different LiPON materials

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trigonal, P3 (no. 147)

Li7PN4, cubic P43n (no. 218)

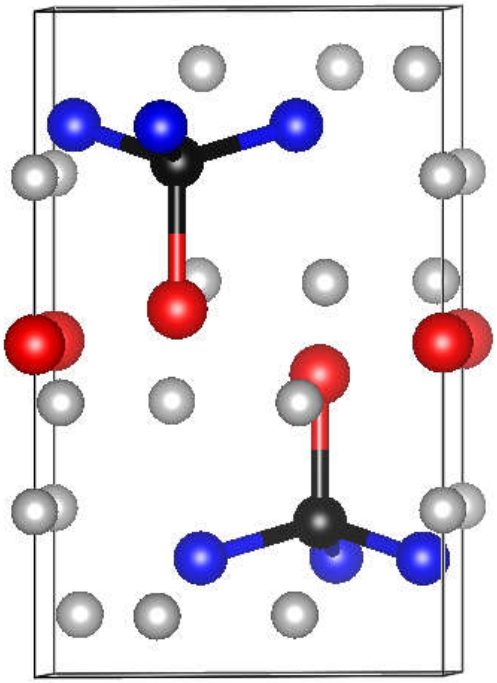
γ – Li_3PO_4 ,orthorhombic Pnma

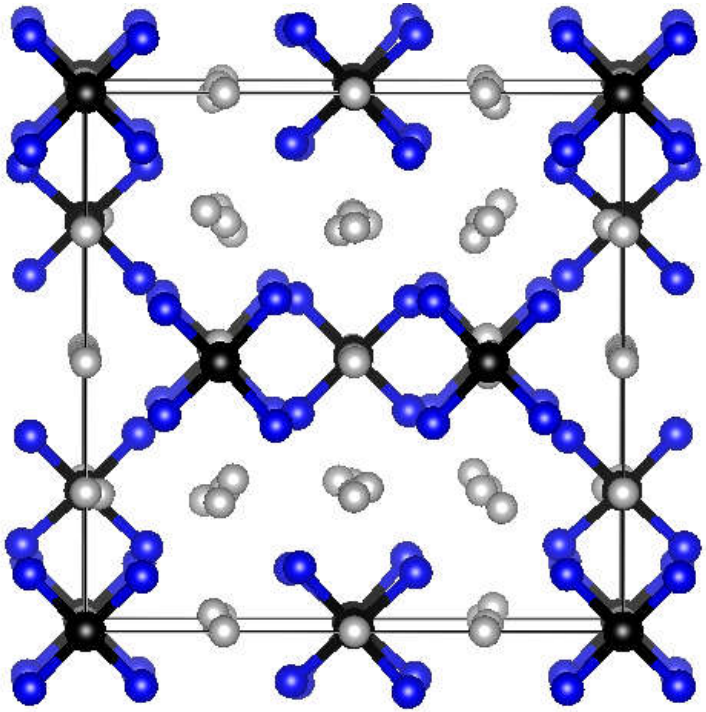
N

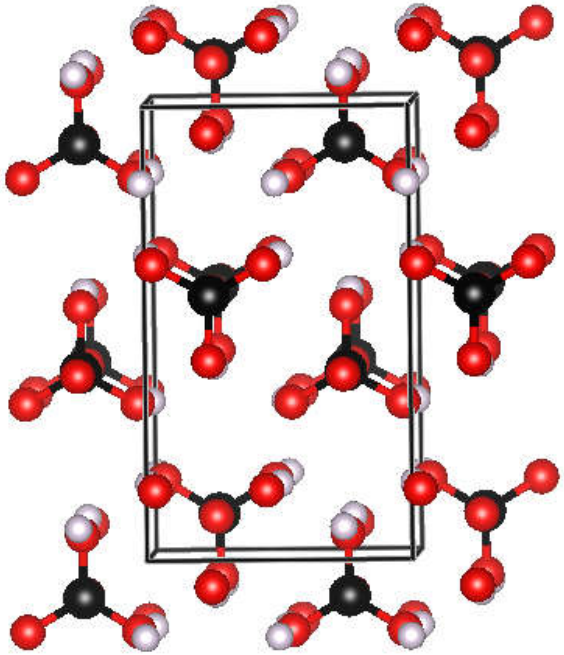
P

O

Li

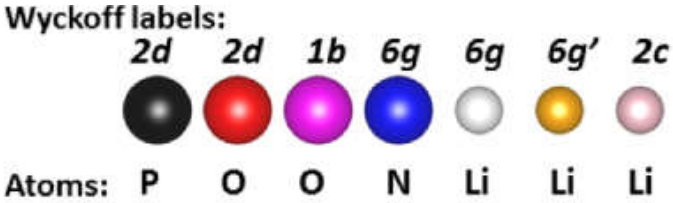


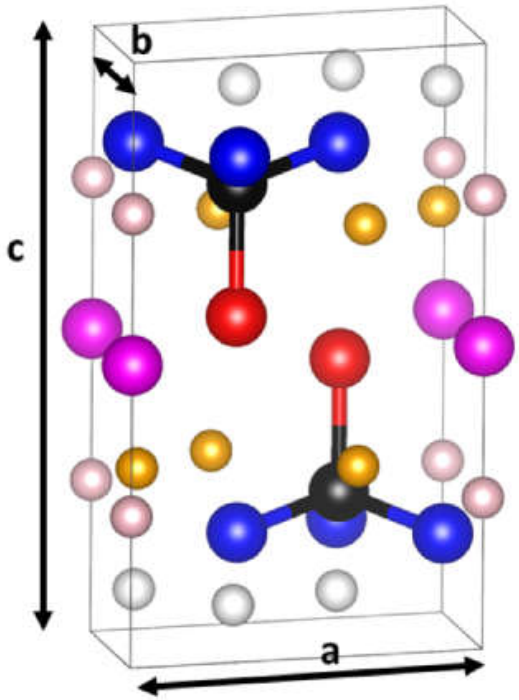


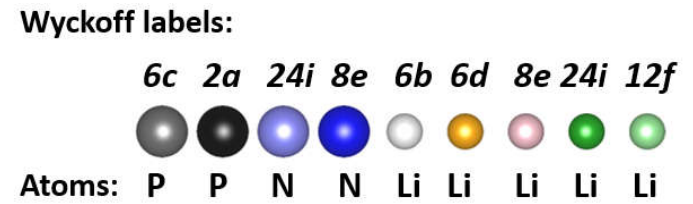


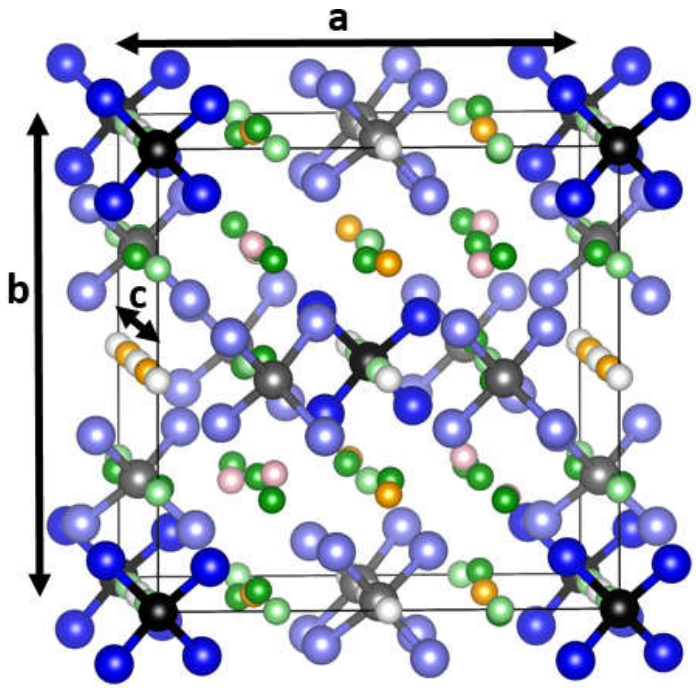
(Schnick,Eur. J. Inorg. Chem. 2015, 617-621)(Schnick ,J of solid state chemistry. 1990, 37,101) (Du,Phys Rev B 76, 174302)

Structure analysis

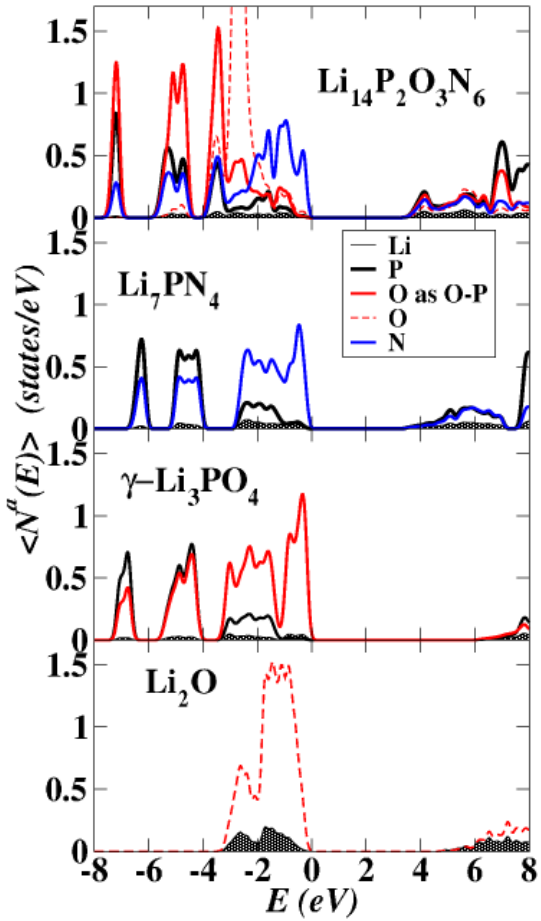








Electronic structure calculation



- 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

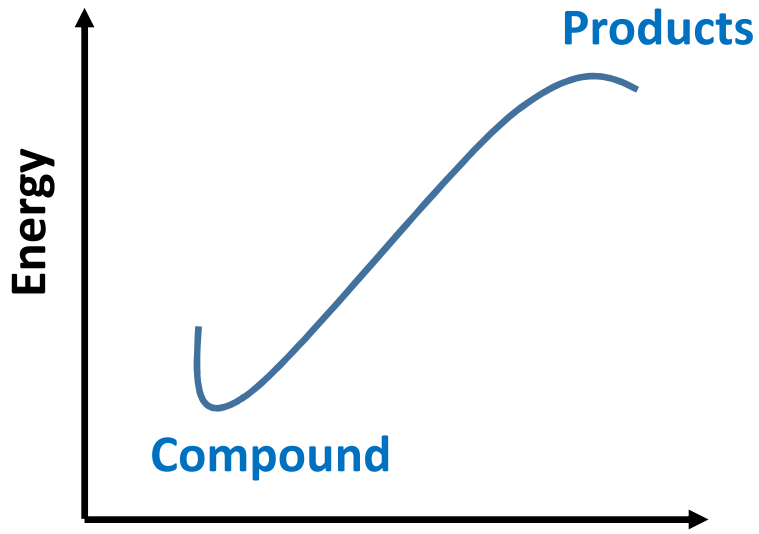
Heat of decomposition calculation

$Li_{14}P_2O_3N_6 \longrightarrow 3Li_2O + 2Li_3N + 2LiPN_2$

$\Delta H_D = -2.93eV$

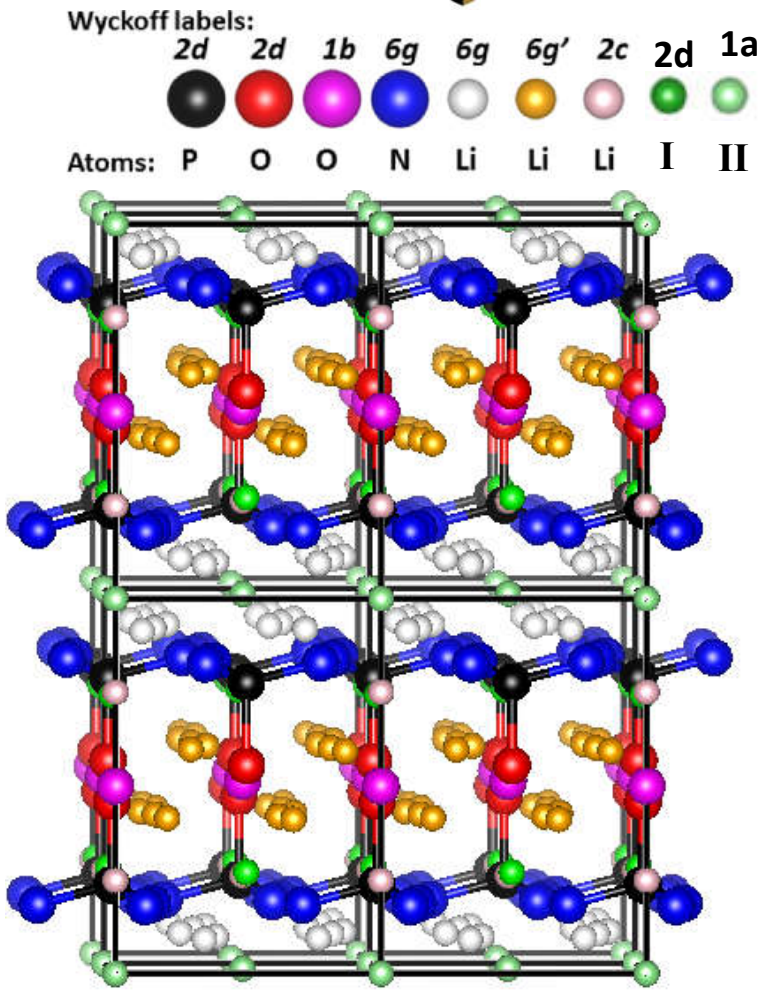
$Li_7PN_4 \longrightarrow LiPN_2 + 2Li_3N$

$\Delta H_D = -2.88\ eV$



$Li_{14}(PON_3)_2$: Li ion migration analysis

Vacancies	
Multiplicity and Wyckoff Label	Relative Energy (eV)
$4g'$	0.00
$4g$	0.95
$2c$	0.41
Interstitials	
Fractional Coordinates	Relative Energy (eV)
$I \equiv(1/3,2/3,0.73)$ $(2d)$	0.00
$II \equiv(0\ ,\ 0\ ,\ 0)$ $(1a)$	0.22



➢ Formation Energy of 0.32 eV which involves the pair (**g′-I**) .

$Li_{14}(PON_3)_2$: Li ion migration analysis

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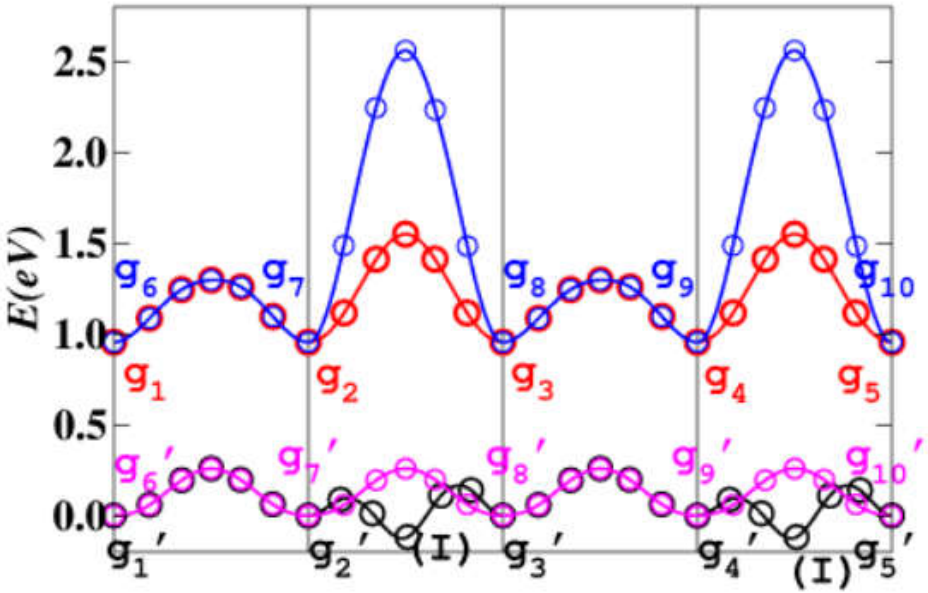
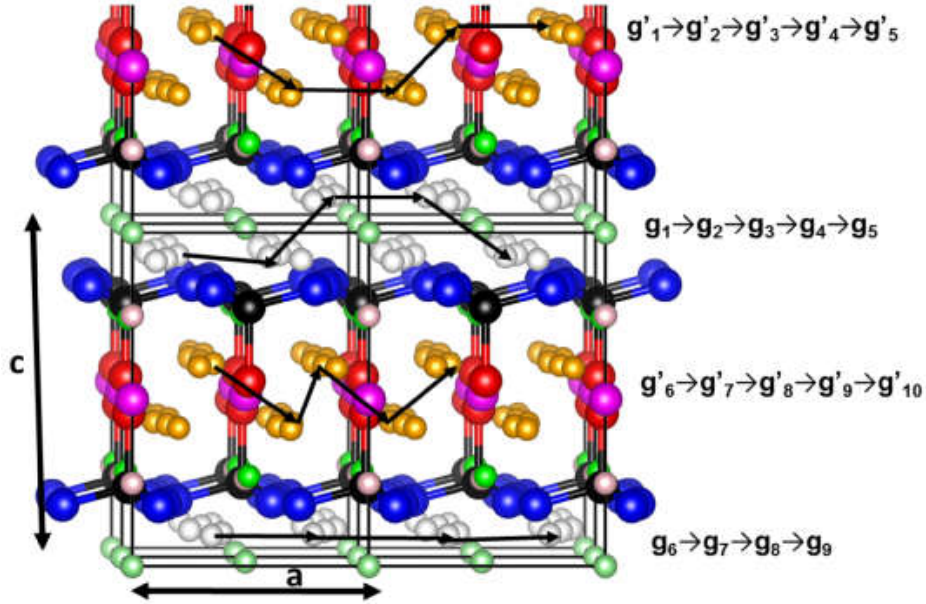
- **Vacancy mechanism**





$Li_{14}(PON_3)_2$: Li ion migration analysis

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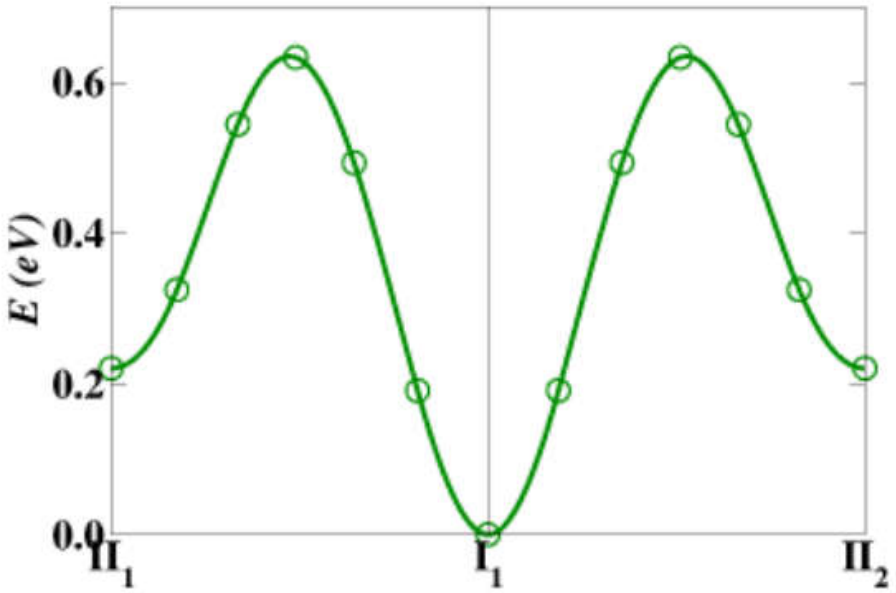
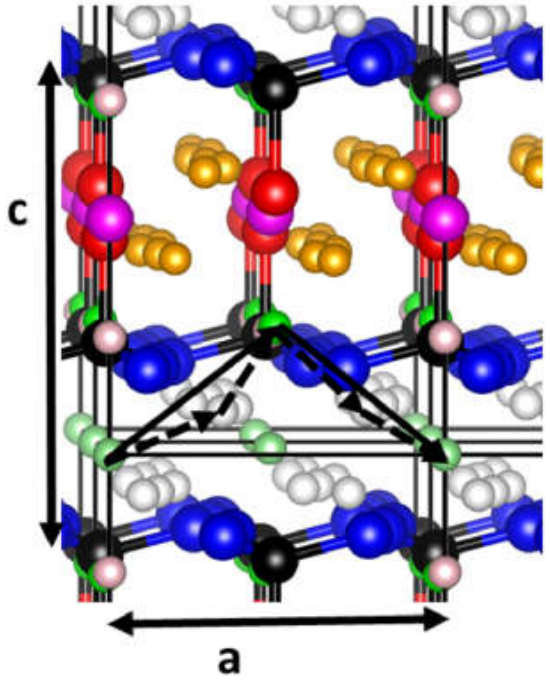
➢ **Interstitial mechanism**

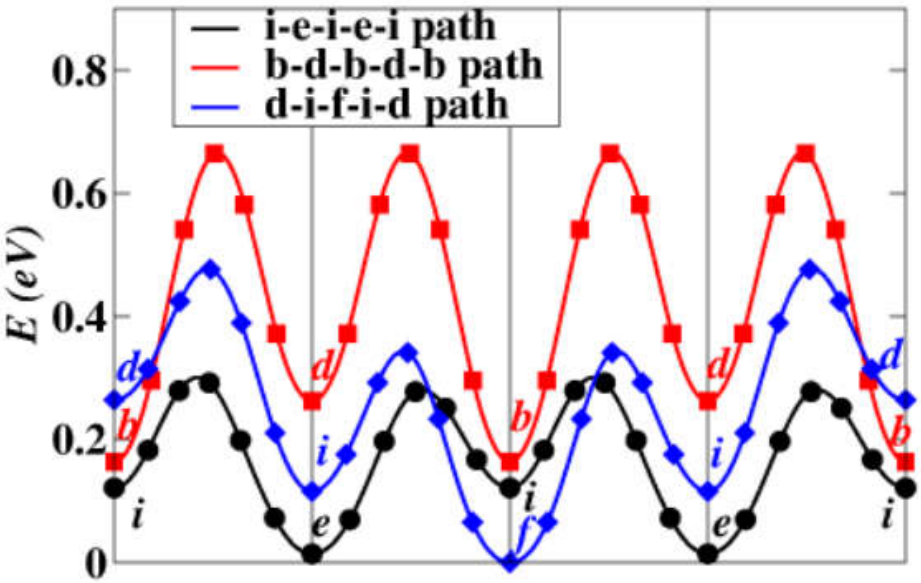




$II_1 \rightarrow I_1 \rightarrow II_2$

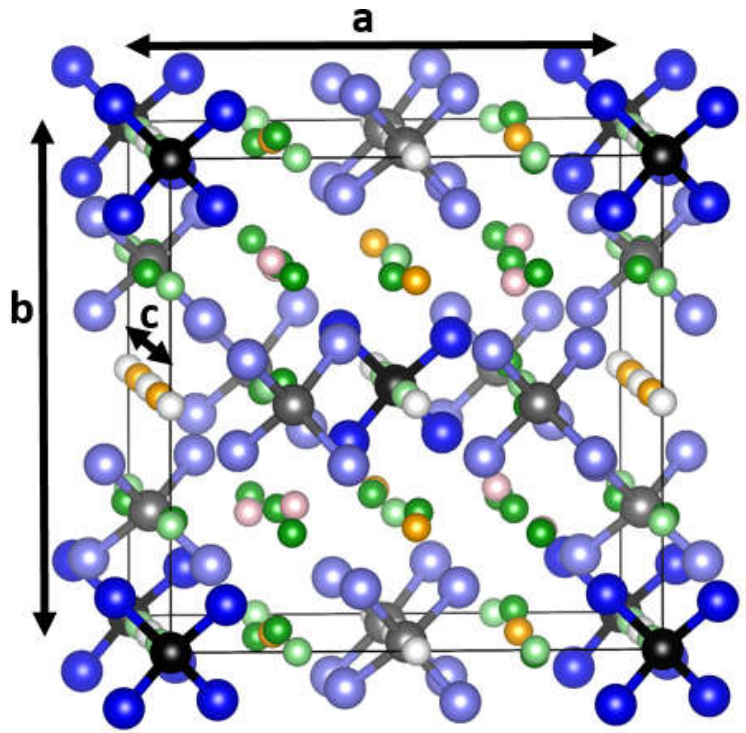
$(II_1 \rightarrow g_a \rightarrow I_1)$
$\rightarrow (I_1 \rightarrow g_b \rightarrow II_2)$

Li_7PN_4 : Li ion migration analysis

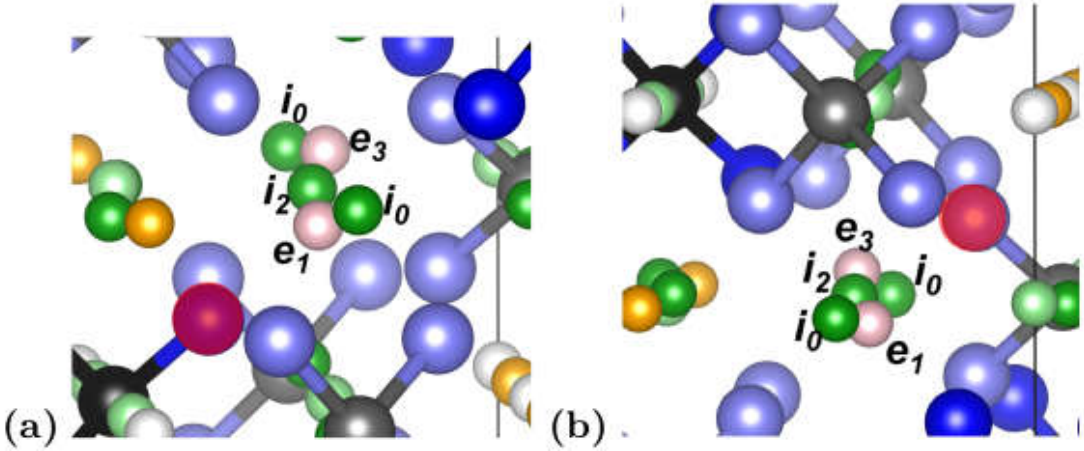


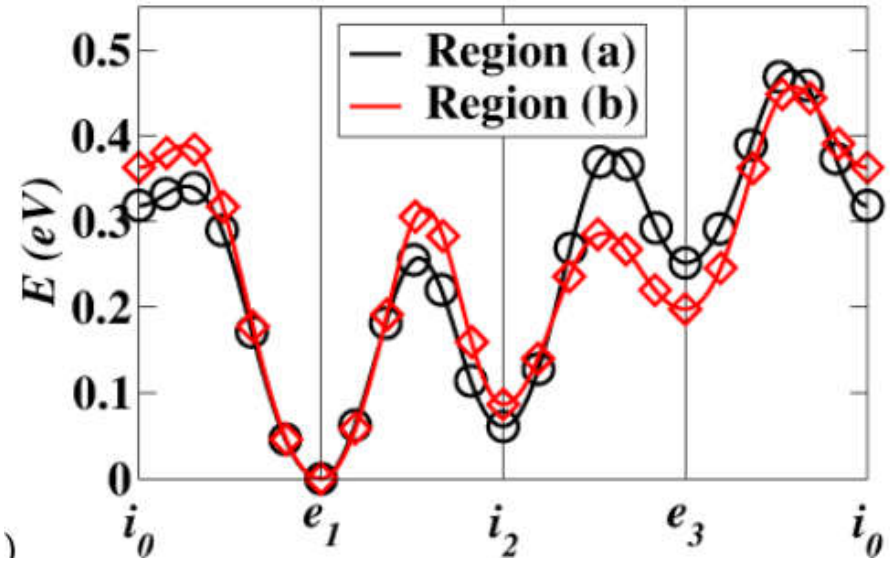
Wyckoff labels:

	6c	2a	24i	8e	6b	6d	8e	24i	12f
Atoms:	P	P	N	N	Li	Li	Li	Li	Li



Li_7PN_4 : Li ion migration analysis





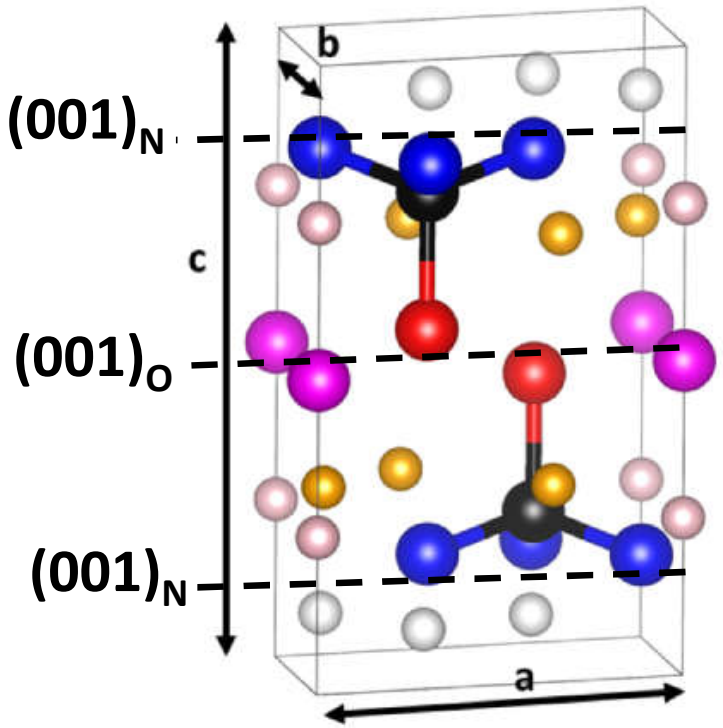
Li ion migration summary

		Simulation			Experimental
Material	Mechanism	E_f (eV)	E_m (eV)	E_m +1/2 E_f (ev)	E_A (eV)
$Li_{14}(PON_3)_2$	Vacancy	0.3	0.3	0.4	
$Li_{14}(PON_3)_2$	Kick-out	0.3	0.6	0.7	
Li_7PN_4	Vacancy	1.9	0.3	1.3	0.48
Li_7PN_4 with O	Vacancy		0.5		0.48
Υ-Li_3PO_4	Kick-out	1.7	0.3	1.2	1.1 – 1.2
β-Li_3PO_4	Kick-out	2.1	0.4	1.5	

$Li_{14}(PON_3)_2$: Interface with Vacuum

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

plane	n_f	γ (eV/A^2)
$(001)_N$	1	0.069
$(001)_N$	2	0.069
$(001)_N$	3	0.069
$(001)_N$	4	0.069
$(001)_O$	3/2	0.41
$(001)_O$	5/2	0.41
$(001)_O$	7/2	0.41
(010)	1	0.10
(010)	2	0.10
(010)	3	0.10
(010)	4	0.11
(010)	5	0.11



$Li_{14}(PON_3)_2$: Interface with Li

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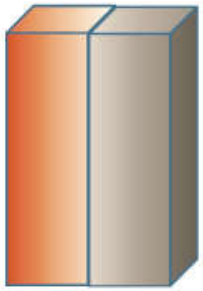
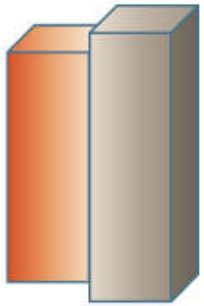
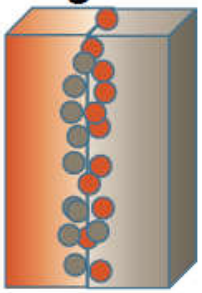
Ideal interface



Strained interface



Interacting interface



$Li_{14}(PON_3)_2$: Interface with Li

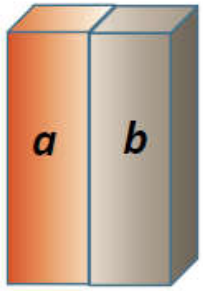
(Lepley, PHYSICAL REVIEW B 92, 214201 (2015))

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:

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

area of interface within supercell

bulk energies

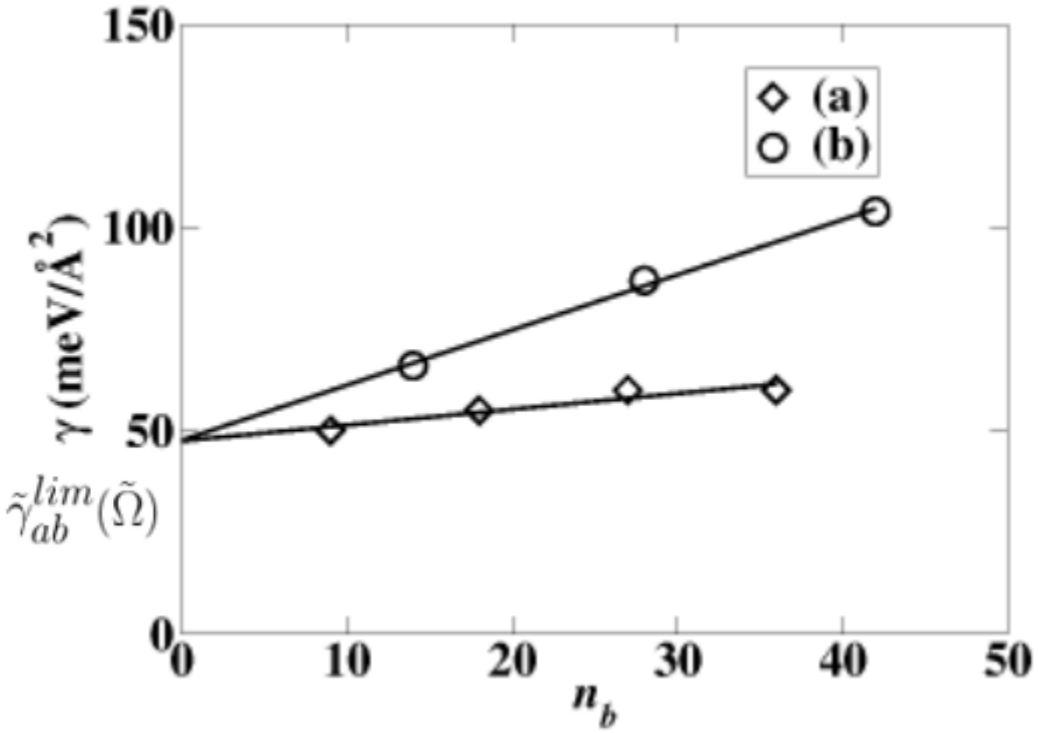


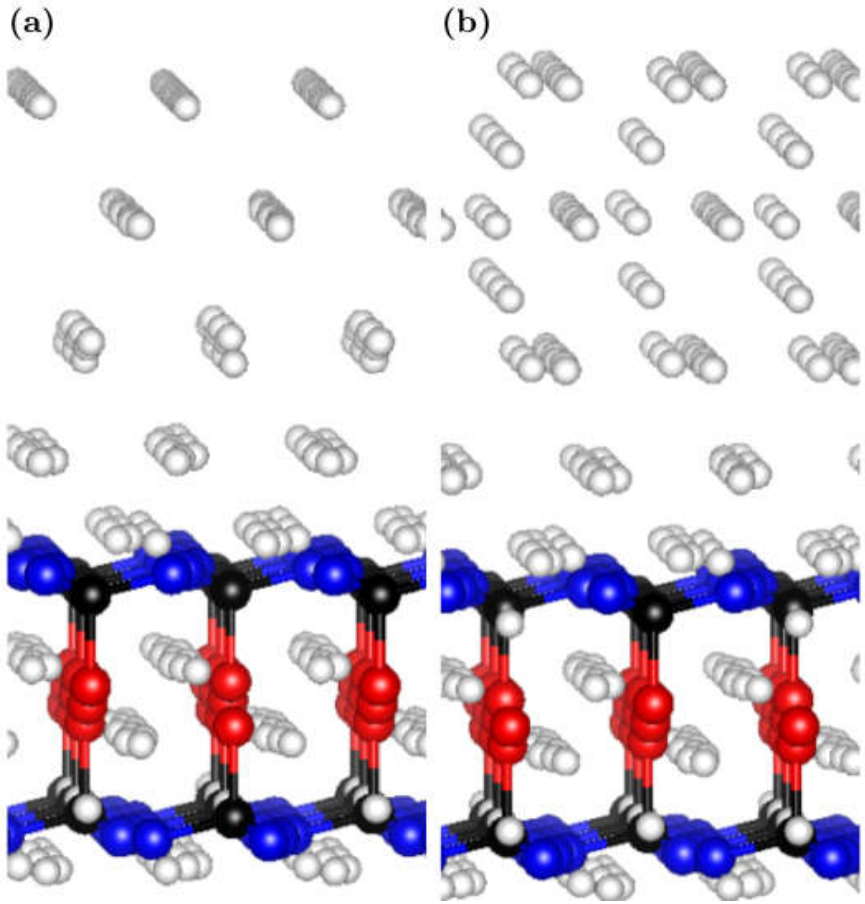
In order approximately remove the effects of lattice strain:

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

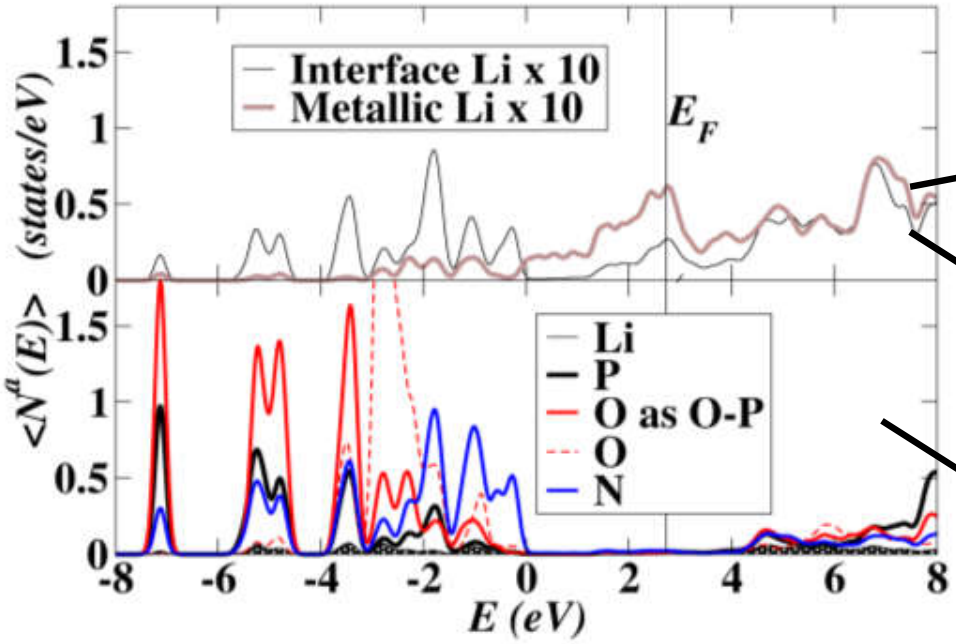
$$\Rightarrow \tilde{\gamma}_{ab}\left(\tilde{\Omega}, n_a, n_b\right) = \tilde{\gamma}_{ab}^{\lim}\left(\tilde{\Omega}\right) + n_b \sigma$$

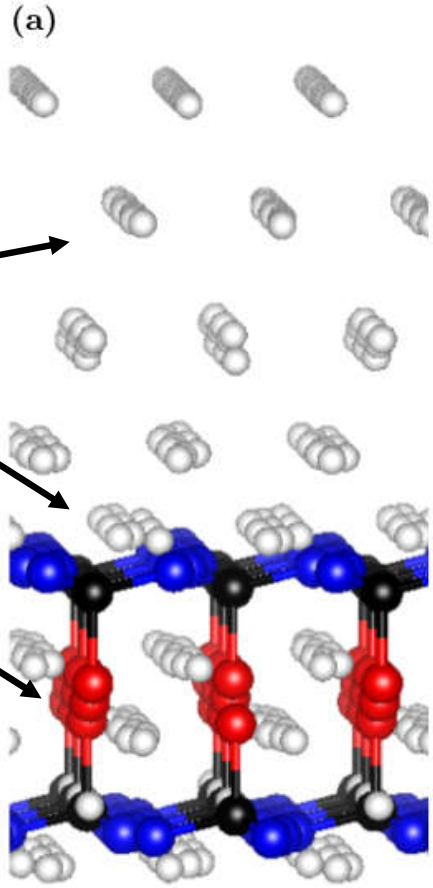
$Li_{14}(PON_3)_2$: Interface with Li





$Li_{14}(PON_3)_2$: Interface with Li





Summary and Conclusions

- This work report a computational study of the structural and electrolyte properties of the $Li_{14}(PON_3)_2$ and Li_7PN_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 Li_3PO_4 .

- The calculated range of the activation energies for the $Li_{14}(PON_3)_2$ was found to be lower than Li_7PN_4 and Li_3PO_4 indicating relatively good conduction properties .

- Both $Li_{14}(PON_3)_2$ and Li_7PN_4 have a stable interface with metallic Li .