

# The effects of O vacancies and N dopants on the migration of Li ions in Lithium Phosphorus Oxynitride

Yaojun A. Du\* and N. A. W. Holzwarth†

Department of Physics, Wake Forest University, Winston-Salem, North Carolina 27109, USA

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## I. INTRODUCTION

Lithium Phosphorous Oxynitride (LiPON) has been developed as a promising glassy solid-state electrolyte at Oak Ridge National Laboratory<sup>1-4</sup> to replace liquid and polymer electrolytes. Higher ionic conductivity is desired for LiPON thin-film, since it has relative low ionic conductivity compared to the liquid electrolytes. Ionic conductivity of LiPON highly depends on the details of manufacturing techniques that could produce LiPON film with ionic activation energies ranging from 0.4 eV to 0.7 eV.<sup>2,5-9</sup> On the other hand, Wang *et al.* prepared the polycrystalline  $\text{Li}_{2.88}\text{PO}_{3.73}\text{N}_{0.14}$  that preserves the main structural feature of the crystalline  $\gamma\text{-Li}_3\text{PO}_4$ ; and it has a measured ionic activation energy of 0.97 eV. In this work, we will study the effects of O vacancies and N dopants in polycrystalline  $\text{Li}_{2.88}\text{PO}_{3.73}\text{N}_{0.14}$  as a first step toward understanding the effects of O and N defects in LiPON thin-film.

## II. COMPUTATIONAL METHOD

The stoichiometry of LiPON electrolytes can be expressed as  $\text{Li}_{3+x}\text{PO}_{4-y}\text{N}_z$ . A system with a neutral charge has the relation  $x = -2y + 3z$ . Different N contents may cause an excess of Li ions ( $\text{Li}^+$ ) with  $x > 0$  or a deficit of  $\text{Li}^+$  with  $x < 0$ , which are both extrinsic defects. Based on the crystalline  $\gamma\text{-Li}_3\text{PO}_4$ , we construct simulation cells with the stoichiometries of  $\text{Li}_{3-\frac{1}{16}}\text{PO}_{4-\frac{2}{16}}\text{N}_{\frac{1}{16}}$  to simulate the migration of  $\text{Li}^+$  vacancies in  $\text{Li}_{2.88}\text{PO}_{3.73}\text{N}_{0.14}$ . The nudged elastic band method determines the migration barriers of  $\text{Li}^+$  vacancies.

## III. RESULTS AND DISCUSSIONS

A LiPON electrolyte with a stoichiometry of  $\text{Li}_{3-\frac{1}{16}}\text{PO}_{4-\frac{2}{16}}\text{N}_{\frac{1}{16}}$  can be constructed from a 128-atom supercell of a perfect  $\gamma\text{-Li}_3\text{PO}_4$  by removing an O atom and a Li atom and replacing another O atom by a N atom. If we remove a d-type O atom in  $\gamma\text{-Li}_3\text{PO}_4$ , the remaining structure will relax to a P-O-P structure as shown in Fig. 1(b). If we replace the bridging O atom by a N dopant, the resulting P-N-P structure shown in Fig. 1(a) is more stable and is 2.7 eV lower in total

TABLE I: Bond lengths, bond angles, and relative supercell energies for P-N-P and P-O-P structures.

Type	Bond lengths (Å)*	Bond angle	Energy (eV)
P-N-P	1.63, 1.66	118(°)	0.00
P-O-P	1.66, 1.70	122(°)	2.71

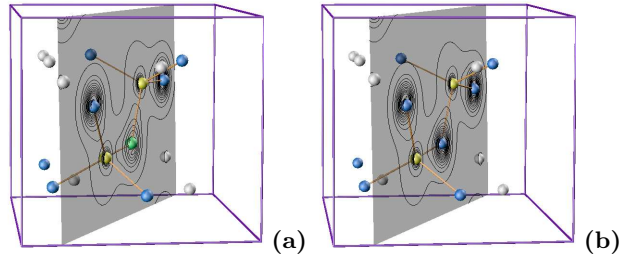


FIG. 1: (Color online) The contour plot of the electronic density of the P-N-P and P-O-P structure. The electronic density is plotted within the planes that includes the P-N-P and P-O-P, as shown in (a) and (b).

energy than the P-O-P structure. Table I summarizes the bond lengths, bond angles, and relative supercell energies associated with the P-N-P and P-O-P structures, indicating that both the bridging N atom and O atom are nearly equally bonded with their two neighboring P atoms. This is further confirmed by the contour plot of the electronic density within the P-N-P and P-O-P plane as shown in Fig. 1. Based on the P-N-P structure, we study a  $\text{Li}^+$  vacancy diffusing far away from the vicinity of the O vacancy following the three crystallographic directions. The migration barriers of 0.83 eV, 1.32 eV and 0.88 eV are computed for the migration along the **a**, **b**, and **c** axis, respectively, which is consistent with the measured 0.97 eV barrier for  $\text{Li}_{2.88}\text{PO}_{3.73}\text{N}_{0.14}$ . Detailed analysis on the migration paths show that the O vacancies provide traps for migrating  $\text{Li}^+$  vacancies.

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\* [duy@wfu.edu](mailto:duy@wfu.edu)

† [natalie@wfu.edu](mailto:natalie@wfu.edu)

<sup>1</sup> J. B. Bates, N. J. Dudney, G. R. Gruzalski, R. A. Zuhr, A. Choudhury, D. F. Luck, and J. D. Robertson, *Solid State Ionics* **53–56**, 647 (1992).

<sup>2</sup> J. B. Bates, N. J. Dudney, G. R. Gruzalski, R. A. Zuhr, A. Choudhury, D. F. Luck, and J. D. Robertson, *Journal of Power Sources* **43–44**, 103 (1993).

<sup>3</sup> B. Wang, B. C. Chakoumakos, B. C. Sales, B. S. Kwak, and J. B. Bates, *Journal of Solid State Chemistry* **115**, 313 (1995).

<sup>4</sup> X. Yu, J. B. Bates, J. G. E. Jellison, and F. X. Hart, *Journal of the Electrochemical Society* **144**, 524 (1997).

<sup>5</sup> C. H. Choi, W. I. Cho, B. W. Cho, H. S. Kim, Y. S. Yoon, and Y. S. Tak, *Electrochemical and Solid-State Letters* **5**, A14 (2002).

<sup>6</sup> Y. Hamon, A. Douard, F. Sabary, C. Marcel, P. Vinatier, B. Pecquenard, and A. Levasseur, *Solid State Ionics* **177**, 257 (2006).

<sup>7</sup> S. Zhao, Z. Fu, and Q. Qin, *Thin Solid Films* **415**, 108 (2002).

<sup>8</sup> W.-Y. Liu, Z.-W. Fu, C.-L. Li, and Q.-Z. Qin, *Electrochemical and Solid-State Letters* **7**, J36 (2004).

<sup>9</sup> F. Vereda, R. B. Goldner, T. E. Haas, and P. Zerigian, *Electrochemical and Solid-State Letters* **5**, A239 (2002).