First-principles simulations of extended phosphorus oxynitride structures in LiPON glasses

YAOJUN DU, N. A. W. HOLZWARTH, Wake Forest University — The thin film electrolyte LiPON, having the composition of Li$_{3+2+x}$PO$_{4+y}$N$_z$ with $x = 3z - 2y$, was developed at Oak Ridge National Lab in the 1990's for use in solid state batteries and related applications. In an effort to understand and to optimize properties of this electrolyte material, we expanded previous studies of isolated defects in crystalline Li$_3$PO$_4$ to focus on more complicated phosphate structures based on combinations of tetrahedral P–O bonds and bridging P–O–P bonds. For example, crystalline LiPO$_3$ and P$_2$O$_5$ are composed of phosphate structures with linear and branched chains, respectively. Both these and related structures derived from substituting O with N and adjusting mobile Li ion concentrations approximate components found in LiPON films. In the simulated structures, we find that N is energetically more stable at bridging bond sites than at tetrahedral sites by 2-3 eV and that the Li ion migration energies are 0.5–0.6 eV, similar to values measured in LiPON films.

1Supported by NSF Grants DMR-0405456, 0427055, and 0705239.
2N. J. Dudney, Interface 17:3, 44 (2008) and listed references.

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Date submitted: 20 Nov 2008