Design and synthesis of a crystalline LiPON electrolyte

N.A.W. HOLZWARTH, KEERTHI SENEVIRATHNE, CYNTHIA S. DAY, ABDESSADEK LACHGAR, Wake Forest U., MICHAEL D. GROSS, Bucknell U. — In the course of a computation study of the broad class of lithium phosphorus oxy-nitride materials of interest for solid electrolyte applications, Du and Holzwarth, recently predicted a stable crystalline material with the stoichiometry Li$_2$PO$_2$N. The present paper reports the experimental preparation of the material using high temperature solid state synthesis and reports the results of experimental and calculational characterization studies. The so-called SD-Li$_2$PO$_2$N crystal structure has the orthorhombic space group $Cmc2_1$ with lattice constants $a=9.0692(4)$ Å, $b=5.3999(2)$ Å, and $c=4.6856(2)$ Å. The structure is similar but not identical to the predicted structure, characterized by parallel arrangements of anionic phosphorus oxy-nitride chains having planar P–N–P–N backbones. Nitrogen 2p$\pi$ states contribute to the strong bonding and to the chemical and thermal stability of the material in air up to 600$^\circ$ C and in vacuum up to 1050$^\circ$ C. The measured Arrhenius activation energy for ionic conductivity is 0.6 eV which is comparable to computed vacancy migration energies in the presence of a significant population of Li$^+$ ion vacancies.

$^1$Supported by NSF grant DMR-1105485 and by a grant from the Wake Forest University Center for Energy, Environment, and Sustainability.