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Energetics of ionic transport on $\text{Li}_w\text{Si}_x\text{P}_{1-x}\text{O}_y\text{N}_z$ amorphous and glassy electrolytes

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Lithium phosphorous oxynitride (LiPON), having an amorphous structure, was first synthesized at the Oak Ridge National Laboratory in the 1990s. Its development has arisen from the pursuit of solid electrolytes stable against lithium metal (Li) to fabricate micro-batteries employing by radio-frequency (RF) magnetron sputtering. Strictly speaking, LiPON is not thermodynamically stable against Li. However, a passivating solid electrolyte interphase emerging between Li and LiPON comprises decomposition products (Li_3N and Li_2O) thermodynamically stable against Li. Along with the suitable electrochemical stability, the low electronic ($<10^{-10} \Omega^{-1}\cdot\text{cm}^{-1}$) and moderate ionic ($>10^{-6} \Omega^{-1}\cdot\text{cm}^{-1}$) conductivity have been also refereed as key properties for its applications as thin-film electrolytes.

The relationships between sputtering conditions, chemical composition, local structure, and ionic conductivity of LiPON thin films have been intensively explored and reported in literature. Most studies converge on the fact that the ionic conductivity can be enhanced by increasing the nitrogen concentration up to a saturation point. Moreover, as an attempt to increase even more the ionic conductivity of LiPON thin films, several other derived systems were proposed based on the partial replacing of phosphorus by another network glass former, such as, boron, germanium, silicon, and sulfur. This approach stems from the well-known phenomenon so called mixed network former effect, firstly reported on glassy bulk systems, which can lead to decrease de activation energy and increase the ionic conductivity. Among all the reported systems, the replacement of P by Si seems to show the most important increment of ionic conductivity that is linked to a drop of the activation energy for the ion conduction process.

The activation energy (E_a) for ionic conductivity is actually constituted of two distinct contributions namely, migration (ΔH_m) and defect formation (ΔH_f) enthalpies, according to the following equation: $E_a = \Delta H_f/2 + \Delta H_m$. These quantities are linked to structural features of the electrolyte that in turn are strongly affected by chemical composition, and synthesis route. The debate

regarding the $\text{Li}_w\text{Si}_x\text{P}_{1-x}\text{O}_y\text{N}_z$ system is centered on the resulting structure once nitrogen and silicon are incorporated and on its structural role regarding the ionic transport. Another exciting discussion is oriented towards the similarities and fundamental differences in terms of structure and ionic transport of this amorphous thin film electrolytes and their glassy bulk counterparts. Therefore, the major aim of this discussion is to shed light on the interplay of chemical composition, local structure and ionic transport on $\text{Li}_w\text{Si}_x\text{P}_{1-x}\text{O}_y\text{N}_z$ amorphous thin films prepared by RF magnetron sputtering and glassy electrolytes prepared by the classical melt-quenching approach.

Herein, we apply a methodology based on impedance spectroscopy analyses to determine the partial contributions of defect formation and migration enthalpies to the overall activation energy for ionic conduction. The main results evince that the well-known decrease in activation energy and enhancement of the ionic conductivity caused by the incorporation of nitrogen in amorphous LiPON is due to a drop in the migration enthalpy while the defect formation enthalpy remains nearly the same. Likewise, the increase of Li/P ratio on $\text{Li}_w\text{PO}_y\text{N}_z$ amorphous thin films tend to decrease significantly the migration enthalpy. A more intricated behavior is observed when P is replaced by Si on $\text{Li}_w\text{Si}_x\text{P}_{1-x}\text{O}_y\text{N}_z$ amorphous thin films. In this case, a minimum in the dependence of the migration enthalpy on composition is spotted around a P/Si ratio close to the unity. Finally, an astonishing difference arises when comparing the defect formation and migration enthalpies of $\text{Li}_w\text{PO}_y\text{N}_z$ amorphous thin films and $\text{Li}_w\text{PO}_y\text{N}_z$ glassy bulk electrolytes. While the activation energy on $\text{Li}_w\text{PO}_y\text{N}_z$ amorphous is amply controlled by the migration enthalpy, on $\text{Li}_w\text{PO}_y\text{N}_z$ glassy bulk electrolytes the defect formation enthalpy is larger than the migration enthalpy. The variation of these quantities with the chemical composition and the synthesis route of these electrolytes is correlated with structural aspects unveiled by nuclear magnetic resonance spectroscopy or previously published literature experimental results and simulations.