

# Tuning the composition and structure of high mobility NASICON-like thin films through atomic layer deposition

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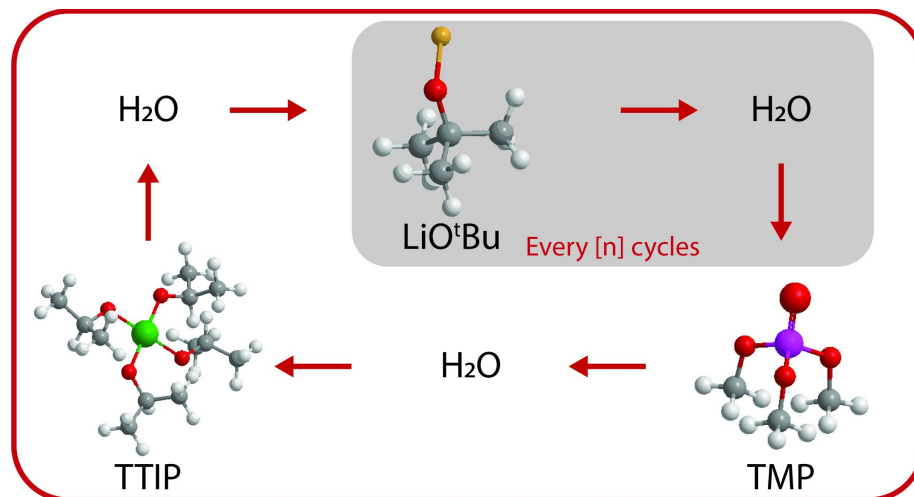
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Fast Li<sup>+</sup> ion conducting thin film solid state electrolytes (SSEs) by atomic layer deposition (ALD) enable high power density, fast time constants, and high operating frequency regimes in solid state ionic devices. However, the ionic conductivity of thin film SSEs fabricated by ALD has been limited by material development challenges, phase purity concerns when dealing with tertiary and quaternary systems, and challenges related to crystallinity. These complexities require careful consideration of the material system, precursor selection, process parameters, and post-annealing conditions to realize ideal ALD thin-film SSE materials with ionic conductivities  $>10^{-6}$  S/cm.<sup>1</sup> Bulk oxide SSEs, such as Li<sub>1+x</sub>Al<sub>x</sub>Ti<sub>2-x</sub>(PO<sub>4</sub>)<sub>3</sub> (LATP) have a NASICON-like crystal structure, show high ionic conductivity when crystalline (10<sup>-3</sup> S/cm), demonstrate air & water stability, and a high voltage stability window.<sup>2</sup> ALD synthesis of LATP can be broken down into well-known constituent processes (e.g., Li<sub>3</sub>PO<sub>4</sub>, Al<sub>2</sub>O<sub>3</sub>, TiP<sub>2</sub>O<sub>7</sub>) which can be combined with respect to stoichiometric ratios.

LATP can be considered Al-doped LiTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (LTP), in which Al<sup>+3</sup> ions partially replace Ti<sup>+4</sup> ions in the NASICON-type structure. This facilitates fast Li<sup>+</sup> ion conduction through the 3D network.<sup>2</sup> With that in mind, an ALD process for LTP was first developed by alternating between Li<sub>2</sub>O and TiP<sub>2</sub>O<sub>7</sub> sub-processes. The Li<sub>2</sub>O sub-process uses lithium *tert*-butoxide (LiO<sup>t</sup>Bu) as the lithium source and water to complete the surface reaction. The TiP<sub>2</sub>O<sub>7</sub> sub-process uses titanium (IV) isopropoxide (TTIP) as the titanium source, trimethyl phosphate (TMP) as the phosphorous source, and water. The growth rate of LTP was measured to be 0.4 Å/cycle at 300 °C. By adjusting the ratio between Li<sub>2</sub>O and TiP<sub>2</sub>O<sub>7</sub> cycles, the Li concentration in LTP can be tuned between 8.4-34.3 at % Li.

A NASICON-type crystalline structure is achieved by post-annealing the LTP films between 650 °C – 850 °C. The ideal annealing temperature was found to be a function of Li-ion concentration. The resulting measured ionic conductivity of partially crystalline LTP thin films is 3.6x10<sup>-5</sup> S/cm at 80 °C. In this talk, we will discuss the complex issues related to process parameters, stoichiometric tunability, and the resulting ionic conductivity when exploring ternary and quaternary LTP/LATP metal phosphates phase space.

1. Meng, X. Atomic layer deposition of solid-state electrolytes for next-generation lithium-ion batteries and beyond: opportunities and challenges. *Energy Storage Mater.* **30**, 296–328 (2020).
2. Xiao, W., Wang, J., Fan, L., Zhang, J. & Li, X. Recent advances in Li<sub>1+x</sub>Al<sub>x</sub>Ti<sub>2-x</sub>(PO<sub>4</sub>)<sub>3</sub> solid-state electrolyte for safe lithium batteries. *Energy Storage Mater.* **19**, 379–400



**Figure 1.** Schematic of supercycling ALD approach for  $\text{LiTi}_2(\text{PO}_4)_3$  utilizing ALD precursors for each sub-process. **(gray)  $\text{Li}_2\text{O}$  sub-process:** lithium tert-butoxide ( $\text{LiOtBu}$ ) as the Li-source, and water. **(white)  $\text{TiP}_2\text{O}_7$  sub-process:** trimethyl phosphate ( $\text{TMP}$ ) as the phosphorous source, titanium (IV) isopropoxide ( $\text{TTIP}$ ) as the titanium source, and water.