Garnet-Type Li^+ Conductor for Solid-State Li-Metal Batteries

*Purna Chandra Rath, Cheng-Chia Chen, Chih-Yang Huang, An-Yuan Hou, Wen-Wei Wu, Jeng-Kuei Chang**

Department of Materials Science and Engineering, National Yang Ming Chiao Tung University, Hsinchu, Taiwan
jkchang@nycu.edu.tw
**Corresponding Author*

Abstract

The development of solid-state electrolytes (SSEs) is crucial for realizing next-generation high-energy-density and high-safety lithium-metal batteries (LMBs). The chemical composition design and synthesis route are known to be the determining factors for SSE properties. One of the most promising SSEs for LMB applications is garnet-type Li^+-conducting oxide synthesized via a solid-state reaction. This study performs an *in situ* TEM investigation of $Li_{6.25}Ga_{0.25}La_3Zr_2O_{12}$ (Ga-LLZO) growth during a high-temperature calcination process. At 750 °C, an intermediate phase, $La_2Zr_2O_7$ (LZO), is formed through epitaxial growth along the crystallographic orientations of $(\bar{1}11)_{LZO}//(\bar{1}11)_{ZrO2}$ and $[211]_{LZO}//[101]_{ZrO2}$. The incorporation of Li and Ga into LZO is found to occur at 900 °C. The LZO transforms into Ga-LLZO via a layer-by-layer diffusion process that takes place along the $[01\bar{1}]$ direction. The Ga doping can stabilize the cubic structure of Ga-LLZO at a temperature of 900 °C (while a temperature of >1100 °C is needed to obtain cubic LLZO) and eliminate the formation of the unwanted tetragonal phase. This dynamic microstructure evolution of Ga-LLZO is examined at an atomic scale. This study opens up a new route to better characterize and understand SSE materials, providing opportunities for further tailoring SSE properties.

Keywords: operando analysis, solid-state electrolyte, calcination, phase transition