

# Tuning the Particle Morphology of Garnet-type Solid Electrolytes

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Super-ionic conductivity of Li ions in solids, greater than 1 mS/cm, has stimulated renewed interest in solid-state Li-ion batteries, which would have substantial advantages in terms of safety and lifetime.

While significant attention has been paid to the optimization of the Li-ion conductivity, the electrochemical stability of solid electrolytes against the electrodes have been largely neglected. Although the garnet  $\text{Li}_7\text{La}_3\text{Zr}_4\text{O}_{12}$  is a fast-ionic conductor and is believed to be stable against the Li-metal anode,<sup>1-3</sup> recent reports suggest that Li dendrites propagate through the grain boundaries, compromising device safety and performance.<sup>4</sup>

First-principles density functional theory-based calculations are applied to provide insights into the  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  particle morphology and composition under various physical and chemical conditions.

Our findings show Li segregation at the  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  surfaces, suggesting Li-rich grain boundaries, including experimental conditions comparable with synthesis and sintering. On the basis of our results, we propose practical strategies to curb Li segregation at the  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  interfaces. By studying the surface phase diagram of  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ , we find that Li segregation can be curbed by suitably tuning of the ceramic synthesis conditions. Finally, we observe that particle compositions of  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  are altered under a voltage, with Li segregation at the exterior occurring at high voltages (> 3 V). These findings contribute towards the rationalisation of the synthesis and operation of solid electrolytes for solid-state batteries.

## References:

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