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## Method to Synthesize Conformal Thin Films of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ on Surfaces and Three-Dimensional Substrates

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3D battery electrodes with solid-state electrolytes (SSE) are an attractive architecture for next-generation Li-ion energy storage due to their superior safety characteristics and potential for high power/energy densities. These electrodes are structured as arrays of plates or pillars with high aspect ratios ( $\sim 100$ ) onto which SSE must be conformally deposited.

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Among the most promising SSE types in terms of Li-ion conductivity and chemical stability is  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ , or LLZO. However, these properties are only exhibited in the crystalline form of LLZO, requiring high temperatures ( $>1000$  degrees C) and long sintering times (24+ hours) to produce. Furthermore, the 3D electrode geometries present unique challenges for SSE deposition: Although atomic layer deposition (ALD) can achieve desirable conformality, the required thickness of the SSE deposition—between 1 and 10 microns—exceeds typical ALD limits by 1-2 orders of magnitude. Recent efforts to integrate the ALD process with crystalline LLZO required complex layering sub-cycles and were unable to produce quality films. Therefore, in order for LLZO to confer its advantages to 3D electrodes, a process must be able to effectively form and conformally deposit crystalline LLZO at thicknesses up to 10 microns.

Researchers at Arizona State University have developed a novel process that combines the conformal nature of ALD but incorporates a synthetic method that enables the formation of high-quality, crystalline LLZO. First, ALD is used to deposit a coat of  $\text{ZrO}_2$  onto the substrate electrode. This thin film of  $\text{ZrO}_2$  serves as a seed layer for a topochemical, molten-salt-mediated conversion process which results in the formation of a thin film of crystalline LLZO. Further film growth in the salt melt can yield thicknesses on the order of several microns.

Performing ALD for  $\text{ZrO}_2$  is well established and bypasses the need for multiple ALD sub-cycles. Since the  $\text{ZrO}_2$  seed layer does not need to be crystalline, ALD can be performed at a lower temperature which can preserve the integrity of the interface between the  $\text{ZrO}_2$  and the active electrode material. The crystalline LLZO that results from molten salt synthesis has ionic conductivity comparable to materials prepared by solid-state reaction.

Related publications:

[Synthesis of Fine Cubic Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> Powders in Molten LiCl–KCl Eutectic and Facile Densification by Reversal of Li<sup>+</sup>/H<sup>+</sup> Exchange](#)

[Reduction in Formation Temperature of Ta-Doped Lithium Lanthanum Zirconate by Application of Lux–Flood Basic Molten Salt Synthesis](#)

Potential Applications:

- Solid-state electrolytes
- 3D battery electrodes
- Microbatteries

Benefits and Advantages:

- Innovative – Greatly simplifies current LLZO formation processes by hybridizing ALD with molten salt synthesis.
- Practical – Formed LLZO is highly crystalline with ionic conductivity  $\sim 10^{-4}$  to  $10^{-3}$  S/cm, and controlled thickness from  $\sim 0.1$  to 10 microns.
- Superior – Process requires less reaction time than ALD-based LLZO deposition, while delivering crystallinity and ionic conductivity that outperforms ALD, chemical vapor deposition (CVD), and sputtering methods.