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Method to Synthesize Conformal Thin Films of Li7La3Zr2O12 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 (~100) onto which SSE must be conformally deposited.

Among the most promising SSE types in terms of Li-ion conductivity and chemical stability is Li7La3Zr2O12, 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 ZrO2 onto the substrate electrode. This thin film of ZrO2 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 ZrO2 is well established and bypasses the need for multiple ALD sub-cycles. Since the ZrO2 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 ZrO2 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 Li7La3Zr2O12 Powders in Molten LiCl–KCl Eutectic and Facile Densification by Reversal of Li+/H+ 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 ~10-4 to 10-3 S/cm, and controlled thickness from ~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.