

Low-Temperature Co-Deposited Li-Garnet-Based Composite Cathodes for All-Solid-State Batteries

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Introduction and Motivation

Composite cathode technology:

- All-solid-state batteries offer high energy densities and improved safety compared to conventional lithium-ion batteries.
- Solid electrolytes act as both the separator and the catholyte in all-ceramic composite cathodes.
- Li-garnet solid electrolytes, such as $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, offer high ionic conductivity (1mS cm^{-1}) and stability of 0-5V vs. Li/Li^+ .⁽¹⁾

Challenges in composite cathode fabrication:

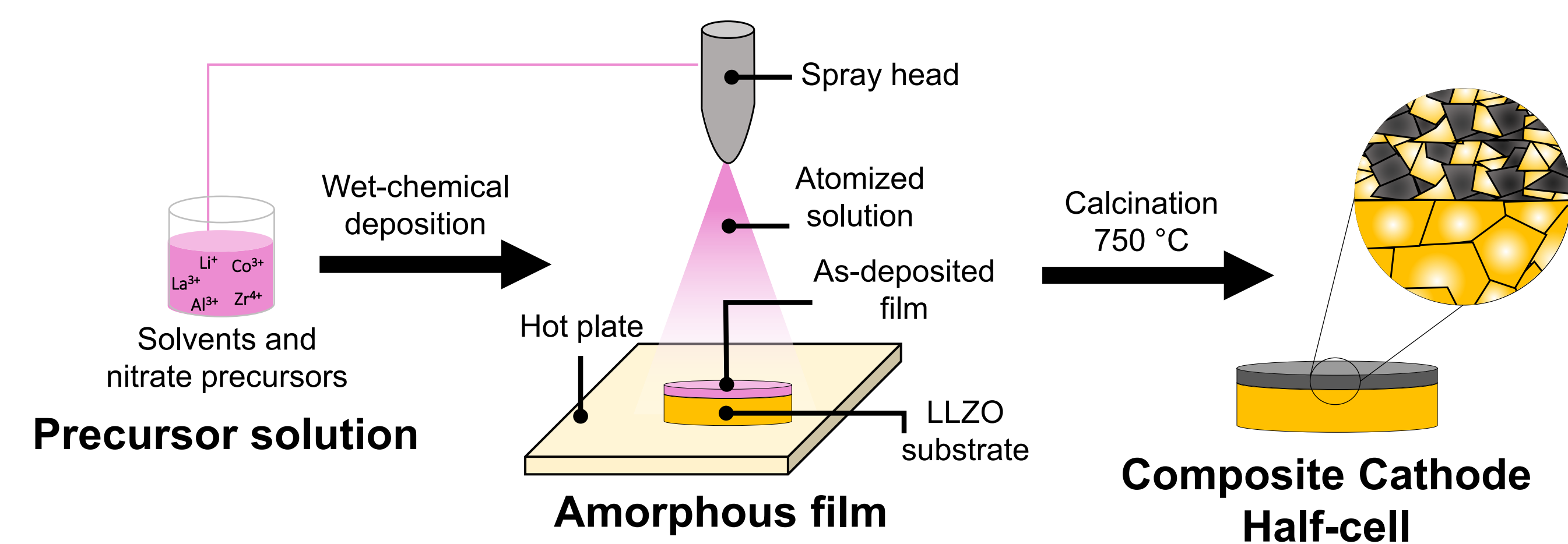
- High processing temperatures of oxide ceramics result in resistive secondary phase formation due to thermal instability of solid electrolyte and cathode materials.⁽²⁾
- High thermal budget, expensive process and limited scalability.
- Interface challenges occur due to poor contact.

Wet-chemical ceramic fabrication:

- Ceramic materials are fabricated from a precursor solution through deposition and annealing.
- Lower processing temperatures reduce thermal instability issues thus side phase formation.
- Scalable fabrication of films with high aspect ratio and intimate electrolyte/electrode contact.

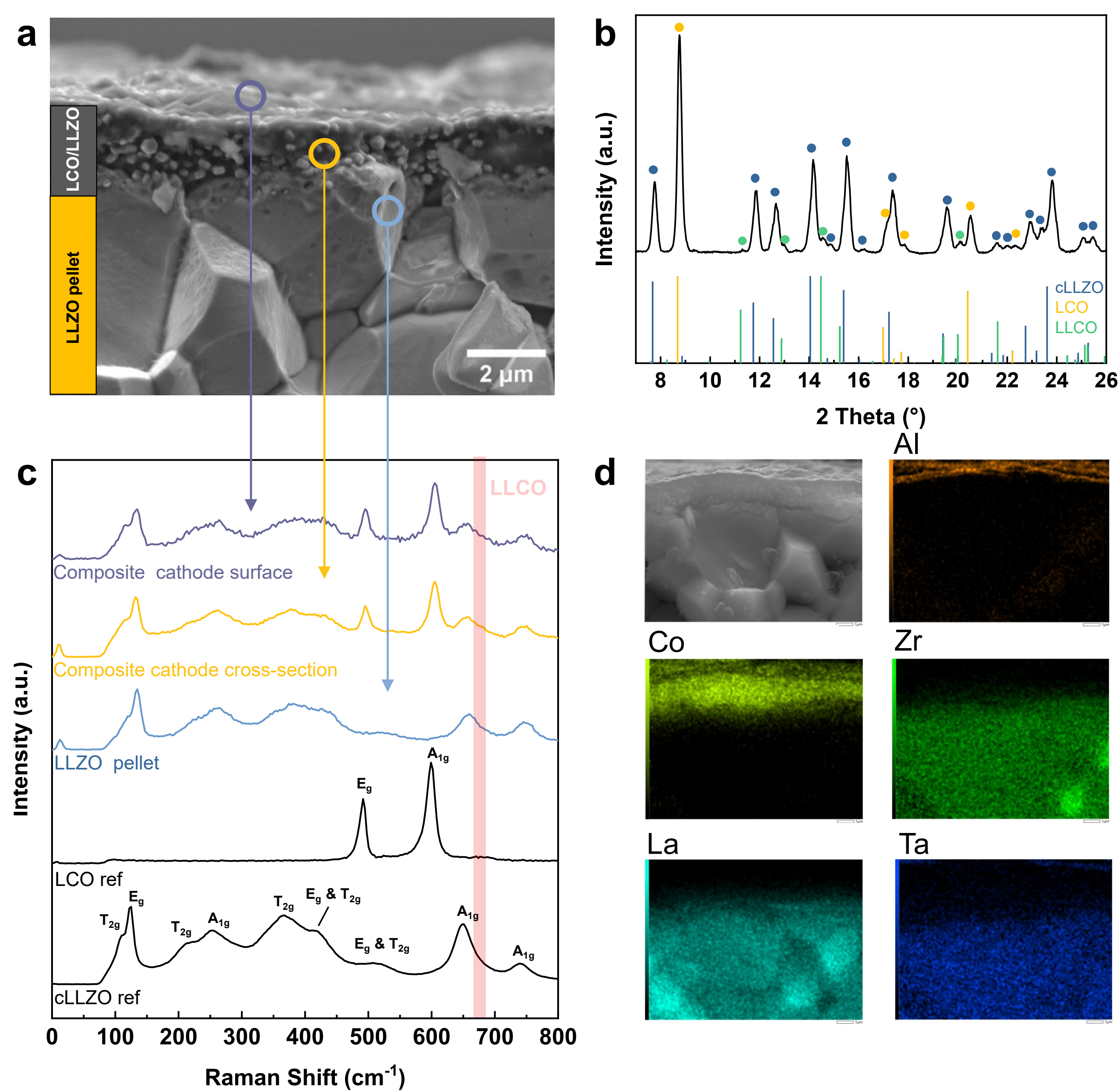
Composite Cathode Fabrication

Novel Wet-Chemical Co-Deposition



Low-temperature direct liquid-to-solid fabrication method. The composite cathode consisting of the two phases of solid electrolyte (Li-garnet, LLZO) and cathode active material (LiCoO_2 , LCO) are fabricated from a single precursor solution.

Material Characterization



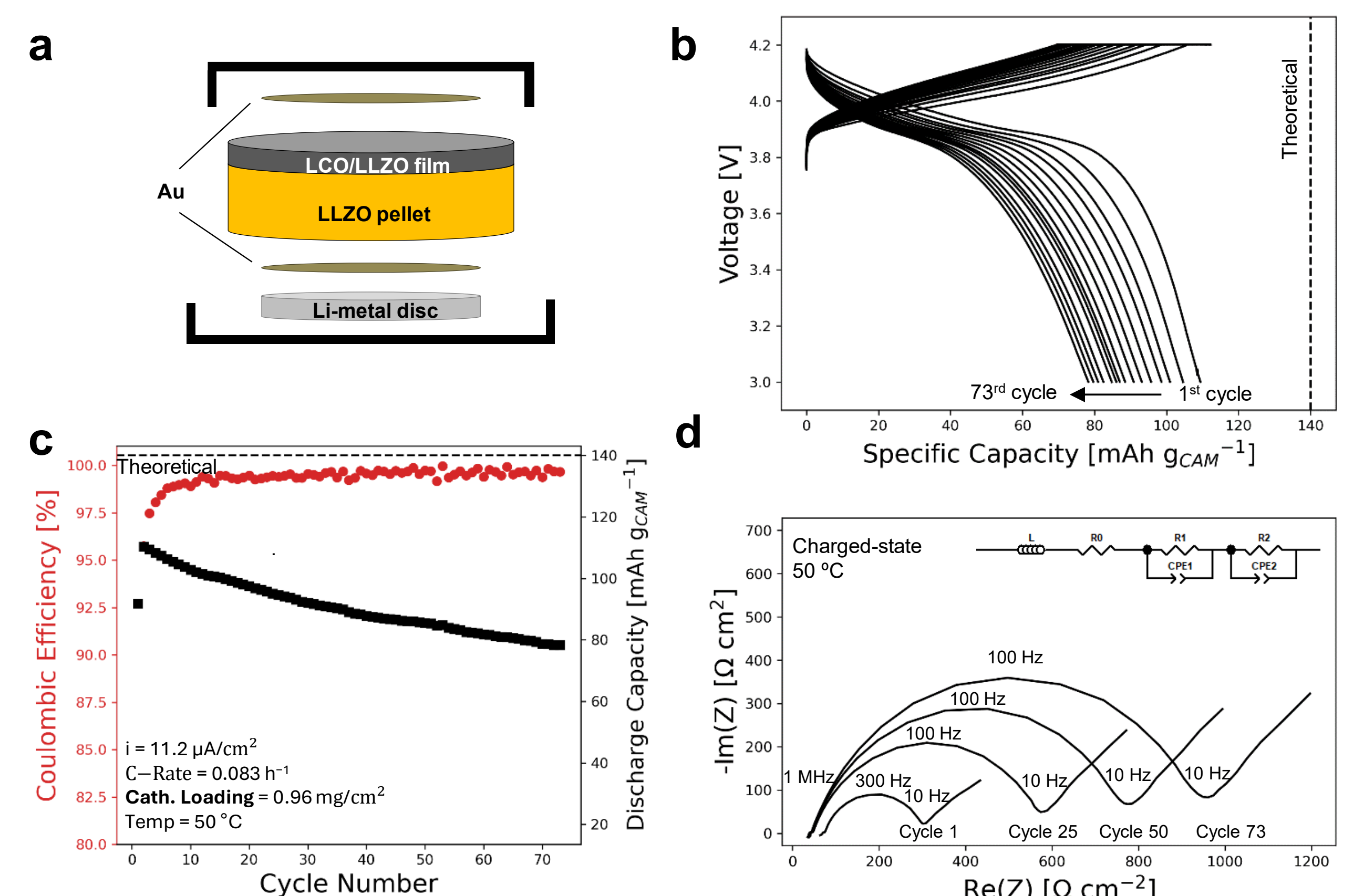
a) Scanning electron microscopy (SEM), b) grazing-incidence XRD, c) Raman spectroscopy and d) energy-dispersive X-ray spectroscopy (EDX) reveal the formation of a dense, crack-free and nano-grained composite cathode film with good adhesion to the pellet substrate. The two phases of solid electrolyte (LLZO) and cathode material (LCO) successfully crystallize with minimal undesired formation of secondary phases.

Conclusion

We present a novel wet-chemical fabrication method for ceramic composite cathodes. Crystalline phases of solid-electrolyte (Li-garnet, LLZO) and cathode active material (LiCoO_2) are obtained with minimal formation of secondary phases even though deposited from a single precursor solution. All-solid-state batteries assembled with a Li-metal anode show a high discharge capacity of $110.5\text{ mAh g}_{\text{CAM}}^{-1}$ and a record capacity retention of 71% after 73 cycles.

All-Solid-State Battery Performance

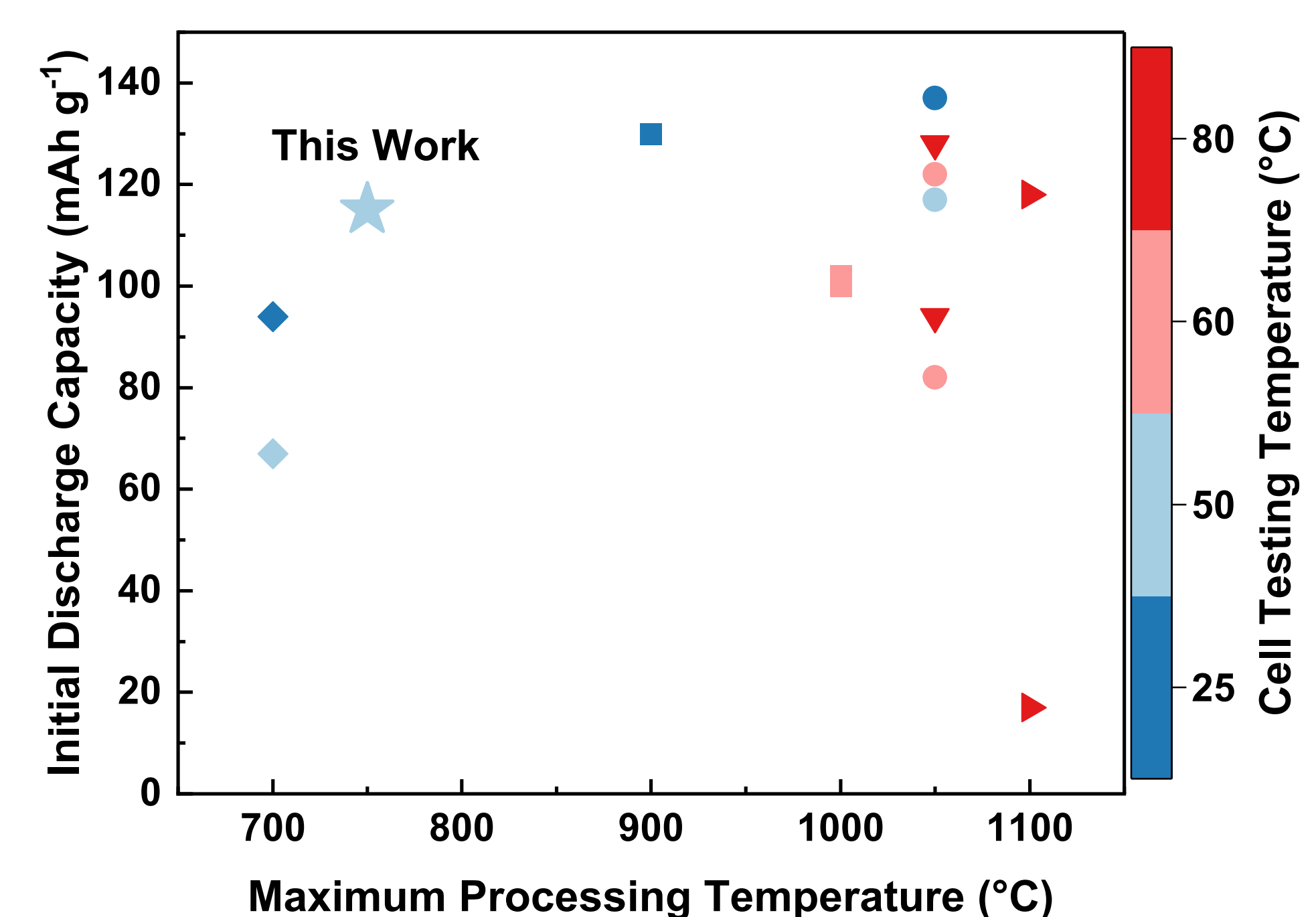
Electrochemical Performance



Key performance results:

- Initial discharge capacity: $110.5\text{ mAh g}_{\text{CAM}}^{-1}$ at a cathode loading of $0.95\text{ mg}_{\text{CAM}}\text{ cm}^{-2}$
- 79 % utilization of the cathode active material
- Record capacity retention: 71 % ($78.3\text{ mAh g}_{\text{CAM}}^{-1}$) after 73 cycles
- Decreasing capacity due to gradually increasing LLZO/LCO interfacial resistance

Performance Classification



The here presented all-solid-state battery shows a remarkably high discharge capacity with respect to the fabrication temperature. This is enabled by a low LLZO/LCO interfacial resistance due to the intimate contact of all components and reduced secondary phase formation.

Outlook

Overall, we see strong potential for wet-chemical deposition methods to fabricate composite cathodes in a scalable process. The here presented method provides a platform to explore the potential of other cathode materials and the fabrication of low-temperature oxide based all-solid-state batteries with only wet-chemically fabricated solid electrolyte and composite cathode components in the future.