

Previews

Uncovered phase polymorphism steers chemo-mechanics of garnet electrolytes

Yuntong Zhu,¹ Moran Balaish,^{2,3} and Jennifer L.M. Rupp^{1,2,3,4,*}

Understanding and mitigating Li filaments in solid Li⁺ electrolytes is the key to realizing high-energy batteries. In the September 2022 issue of *Nature Materials*, Dixit, Hatzell, and colleagues assessed the grain-level chemo-mechanics of cubic LLZO. Their findings suggest that Li filament formation is correlated with local phase polymorphism, providing guidelines for process optimization.

Safe, reliable, and Li-conductive solid-state electrolytes are considered the key to unlocking the potential of hybrid and solid-state batteries. Solid Li⁺ electrolytes, including garnets and perovskites, are ceramic oxides that are typically processed in the polycrystalline state and consist of heterogeneous grains and grain boundaries. Local variations in the chemical composition and phases can strongly affect the transference number (i.e., ratio of the Li⁺ conductivity to the total conductivity) and mechanics (e.g., fracture toughness and elastic modulus) and define Li-filament formation and shorting at low current densities <5 mA/cm². Studies linking local phase changes and mechanical characteristics to cell-performance metrics (such as critical current densities) are rare but essential to providing engineering roadmaps for the design of solid-state electrolytes. In this respect, Li garnets represent an interesting class of materials for a model study, as small variations in Li-occupied sites and the Li and dopant stoichiometry for a phase can strongly affect their iono-chemo-mechanics.

Over the last decade, garnet-type Li₇La₃Zr₂O₁₂ (LLZO) in its cubic phases (220 space group *I*-43*d* and 230 space group *Ia*-3*d*) has attracted growing interest owing to its high Li-ion conductivity (in

the mS cm⁻¹ range), wide electrochemical stability, good compatibility with Li metal, and non-flammability. Although modeling studies have predicted that cubic-phase LLZO can sustain current densities greater than 100 mA cm⁻² because of the high kinetics at the interface of the Li electrode and garnet electrolyte,¹ discrepancies have been observed, with experimental findings of battery failures below 1 mA cm⁻².^{2,3} One commonly accepted explanation for such failures is that Li penetration can be initiated by surface flaws or defects, leading to localized stress and current inhomogeneity in the ceramic. *In situ* optical curvature measurements coupled with electrochemical tests on LLZO pellets have revealed stress-induced "fracture-like" mechanical responses with the evolution of localized plastic strains at short-circuiting events.³ In a microscopy study, Li-filament evolution was correlated with local inhomogeneities and chemical-composition variations in the grain or grain-boundary localities.³ This finding is consistent with an earlier microscopy study reporting that Li preferentially deposits and grows along the grain boundaries of cubic LLZO phases⁴ due to the increase in electronic (rather than ionic) conductivity at these interfaces relative to that in the bulk grain.⁵ Despite continued efforts, there has been a lack of direct grain-level observation of the phase constitution and

chemo-mechanics of garnet-type Li⁺ electrolytes.

In the September 2022 issue of *Nature Materials*, Dixit, Hatzell, and colleagues assessed the grain-level chemo-mechanical behavior of cubic LLZO ceramic pellets by coupling far-field high-energy diffraction microscopy (FF-HEDM) and tomography during *in situ* operation (Figures 1A and 1B).⁶ The length scales of the chemo-mechanical response, ranging from the angstrom to micrometer scale, were cleverly bridged together by combining mesoscale models via a kinetic Monte Carlo simulation and grain classification with an unsupervised machine-learning algorithm based on stress values. A symmetric Li|LLZO pellet|Li cell suitable for cycling with *in situ* tomography and FF-HEDM was developed, with phase and strain information collected after each lithium stripping and plating step until failure. An unusually high number of grains were identified (≥30,000 grains, with average grain sizes of 55–60 μm), and their full stress tensors were calculated (Figure 1C). Only a small number of grains with minimum and maximum hydrostatic stress showed noticeable changes during the Li stripping and plating cycles, while, importantly, the average hydrostatic and von Mises (shear) stress remained unchanged. These findings imply the presence of local heterogeneities within the garnet ceramics. By coupling FF-HEDM and

¹Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

²Department of Chemistry, Technical University Munich, Garching 85748, Germany

³TUMint. Energy Research GmbH, Lichtenbergstr. 4, Garching 85747, Germany

⁴Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

*Correspondence: jrupp@tum.de

<https://doi.org/10.1016/j.joule.2022.11.009>



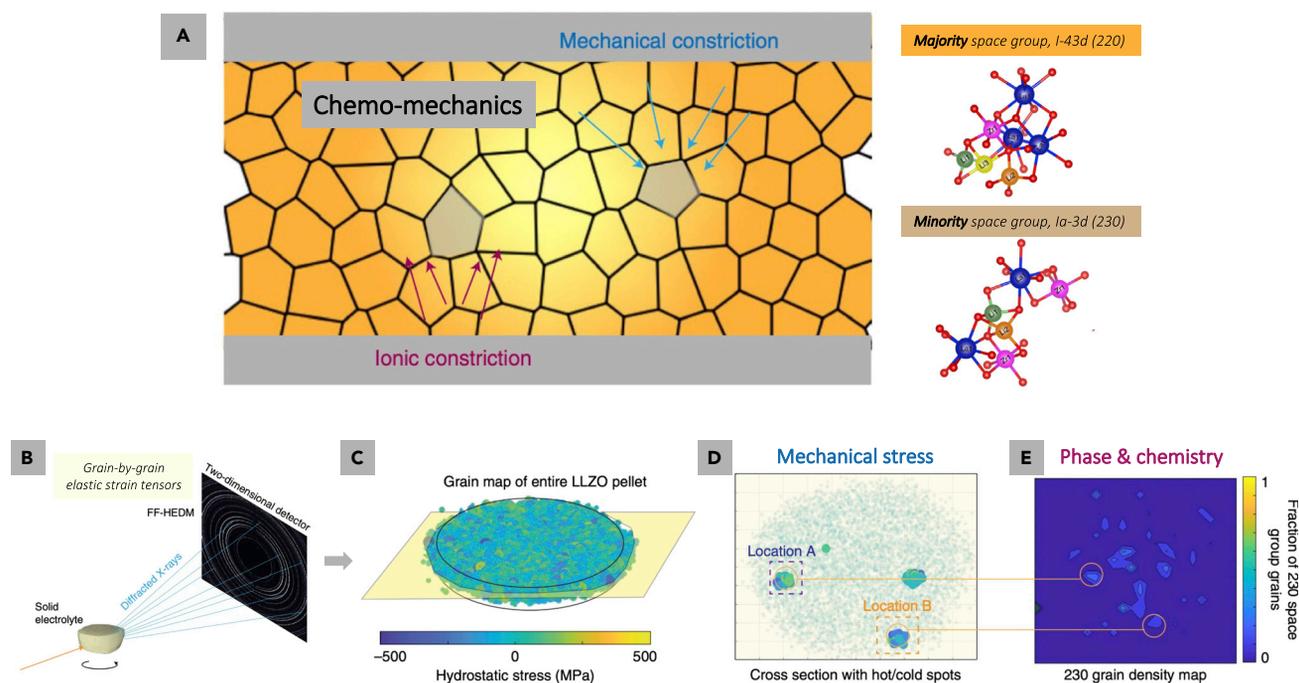


Figure 1. Assessing local phase polymorphism and grain-level chemo-mechanics of cubic LLZO

(A) Schematic highlighting the chemo-mechanics, including the mechanical and ionic constriction effects in pellets due to the presence of a trace secondary phase. Local Li coordination environment in LLZO with the majority of 220 and minority of 230 space groups.

(B) Schematic showing the FF-HEDM technique.

(C) Three-dimensional grain maps for the LLZO sample with the grain color mapped to the hydrostatic stress values.

(D) Cross-sectional map for a thin sub-volume within the bulk of the solid electrolyte as shown in the shaded plane in (A), with high-strain grains (hot spots) and low-strain grains (cold spots) identified with filled markers.

(E) Correlating the location of the identified hot and cold spots with the spatial map of the 230-space-group grain maps. The contour map represents the spatial 230 grain density within the identified sub-volume. Note that only selected hot and cold spots in the shaded plane presented in (A) are correlated with the contour map (E). Additional spots with high 230 grain density that may exist as cold or hot spots in other planes are not detailed here.

Figure adapted with permission from Dixit et al.⁶

high-resolution X-ray diffraction (XRD), a remarkable observation concerning the nature of the cubic-phase grains was made (Figure 1A): the majority of the grains ($\sim 30,000$) were identified as the cubic phase with 220 space group ($I-43d$), with a minor fraction ($\sim 1,000$ grains) composed of a second cubic phase with 230 space group ($Ia-3d$). The minority 230-space-group cubic phase had a slightly higher ion migration energy barrier (by 0.06 eV) than the majority phase, which can result in more tortuous ion transport pathways. The simulation results revealed notable gradients in both the stress and electric potentials close to the second-cubic-phase regions, suggesting that the local presence of the 230-space-group grains within the bulk material could

be a major cause of the heterogeneity in the mechanics and ion transport. An unsupervised machine-learning algorithm was used to evaluate the spatial distribution of the stress response. No preferential direction of the strain evolution between the pristine and failed samples was observed, suggesting that the failure mechanism is possibly stochastic.

The authors also tracked the grain-level stress response during the onset and stochastic growth of Li filaments. The neighborhoods surrounding the highest-stress-value grains (named “hot spots”) and those surrounding the lowest-stress-value grains (named “cold spots”) both experienced an increase in hydrostatic stress after the

plating experiment, suggesting a transport-driven mechanism where lattice distortion of the grains leads to local increases in stress (Figures 1C–1E). This grain-level observation corroborates the observation of Cho and colleagues³ of stress building up on LLZO prior to short-circuiting. A direct mapping of the grain-specific properties to the tomographic data was conducted to track the local-structure variation upon the growth of Li filaments. The results indicate that the hot spots are strongly correlated with the presence of the minority cubic phase with 230 space group. The presence of the heterogeneous area leads to noticeable structure variation upon cycling, resulting in Li-filament growth or crack formation at exactly these locations. Finally, the

authors compared the Li-ion flow and stress gradient within the bulk LLZO electrolyte. The stress-relaxation pathway was observed to be longer during Li plating than during Li stripping.

This work by Dixit, Hatzell, and colleagues paves important new roads in method development by coupling the experimental approaches of FF-HEDM and tomography with mesoscale simulation and unsupervised machine learning to probe the grain-level chemo-mechanics of polymorphic cubic Li garnets upon *in situ* operation. Through this study, the effects of polymorphic phases on chemo-mechanics and Li-filament formation have been established for solid electrolytes for the example of sintered LLZO pellets with the co-existence of grains with 230 and 220 space groups. The existence of the minor cubic phase and the formation of stress hot spots and cold spots in LLZO have important implications for its manufacture in terms of grain and grain-boundary engineering for future batteries. First, phase homogeneity (i.e., 230 versus 220 space group) of the LLZO powders used for solid-state sintering must be ensured. Optimization of the processing atmosphere, time, and temperature is suggested to gain better control over the O stoichiometry and Li kinetics, especially at elevated sintering temperature (usually >1,100°C for sintering cubic LLZO).⁷ Doping studies to tailor the phase homogeneity are also encouraged to alter the Li-filament growth potential during cycling. Second, alternative sinter-free processing routes at lowered temperature (e.g., 500°C–750°C), such as vacuum-based pulse laser deposition (PLD) and solution-based sequential decomposition synthesis (SDS), are attractive for further study. Specifically, nanocrystalline grains prevail in PLD-⁸ and SDS-processed⁹ films with fast nucleation and diffusion kinetics, and neither route proceeds through an initial particle state or requires high-

temperature sintering; studies on the impact of the processing temperature and route on cubic polymorphism and chemo-mechanics would be of high interest. Furthermore, the use of amorphous Li⁺ electrolytes, such as amorphous LLZO and lithium phosphorus oxynitride (LiPON), could circumvent the issue of phase inhomogeneity, as they present in grain-boundary-free states with homogeneous local chemistry and structure and are therefore less likely than polycrystalline materials to experience stress-induced diffusion.¹⁰ Follow-up studies using the methodology outlined by this work on the chemo-mechanics of amorphous and nanocrystalline Li garnets and beyond, ideally with higher structure homogeneity, would be of interest.

This work further suggests that local phase polymorphism and structural heterogeneities are important drivers for the formation of Li filaments in cubic Li garnets. Earlier microscopy studies have suggested that defects and grain boundaries with variations in electronic conductivity could be more vulnerable sites for filament propagation.^{4,5} By combining the findings of this work with previous observations, a more comprehensive picture of the electro-chemo-mechanics of grains versus grain boundaries can be obtained. Engineering strategies to synthesize pure 220-space-group Li-garnet ceramics are encouraged, which could be achieved by altering the synthesis protocols to attain further control of the chemo-mechanics. Collectively, these works help form guidelines for Li-ceramic engineering of ideal grain chemistries and phases to close the gap between the experimentally measured and theoretically predicted high critical current densities for future batteries.

DECLARATION OF INTERESTS

The authors declare no competing interests.

REFERENCES

1. Krauskopf, T., Mogwitz, B., Hartmann, H., Singh, D.K., Zeier, W.G., and Janek, J. (2020). The Fast Charge Transfer Kinetics of the Lithium Metal Anode on the Garnet-Type Solid Electrolyte Li₆25AlO₂₅La₃Zr₂O₁₂. *Adv. Energy Mater.* 10, 2000945. <https://doi.org/10.1002/aenm.202000945>.
2. Tsai, C.L., Roddatis, V., Chandran, C.V., Ma, Q., Uhlenbruck, S., Bram, M., Heitjans, P., and Guillon, O. (2016). Li₇La₃Zr₂O₁₂ Interface Modification for Li Dendrite Prevention. *ACS Appl. Mater. Interfaces* 8, 10617–10626. <https://doi.org/10.1021/acsmi.6b00831>.
3. Cho, J.H., Kim, K., Chakravarthy, S., Xiao, X., Rupp, J.L.M., and Sheldon, B.W. (2022). An Investigation of Chemo-Mechanical Phenomena and Li Metal Penetration in All-Solid-State Lithium Metal Batteries Using In Situ Optical Curvature Measurements. *Adv. Energy Mater.* 12, 2200369. <https://doi.org/10.1002/aenm.202200369>.
4. Gao, H., Ai, X., Wang, H., Li, W., Wei, P., Cheng, Y., Gui, S., Yang, H., Yang, Y., and Wang, M.S. (2022). Visualizing the failure of solid electrolyte under GPa-level interface stress induced by lithium eruption. *Nat. Commun.* 13, 5050. <https://doi.org/10.1038/s41467-022-32732-z>.
5. Han, F., Westover, A.S., Yue, J., Fan, X., Wang, F., Chi, M., Leonard, D.N., Dudney, N.J., Wang, H., and Wang, C. (2019). High electronic conductivity as the origin of lithium dendrite formation within solid electrolytes. *Nat. Energy* 4, 187–196. <https://doi.org/10.1038/s41560-018-0312-z>.
6. Dixit, M.B., Vishugopi, B.S., Zaman, W., Kenesei, P., Park, J.S., Almer, J., Mukherjee, P.P., and Hatzell, K.B. (2022). Polymorphism of garnet solid electrolytes and its implications for grain-level chemo-mechanics. *Nat. Mater.* 21, 1298–1305. <https://doi.org/10.1038/s41563-022-01333-y>.
7. Wang, C., Ping, W., Bai, Q., Cui, H., Hensleigh, R., Wang, R., Brozena, A.H., Xu, Z., Dai, J., Pei, Y., et al. (2020). A general method to synthesize and sinter bulk ceramics in seconds. *Science* 368, 521–526. <https://doi.org/10.1126/science.aaz7681>.
8. Pfenninger, R., Struzik, M., Garbayo, I., Stilp, E., and Rupp, J.L.M. (2019). A low ride on processing temperature for fast lithium conduction in garnet solid-state battery films. *Nat. Energy* 4, 475–483. <https://doi.org/10.1038/s41560-019-0384-4>.
9. Hood, Z.D., Zhu, Y., Miar, L.J., Chang, W.S., Simons, P., and Rupp, J.L.M. (2022). A Sinter-Free Future for Solid-State Battery Designs. *Energy Environ. Sci.* 15, 2927–2936. <https://doi.org/10.1039/d2ee00279e>.
10. Balaish, M., Gonzalez-Rosillo, J.C., Kim, K.J., Zhu, Y., Hood, Z.D., and Rupp, J.L.M. (2021). Processing thin but robust electrolytes for solid-state batteries. *Nat. Energy* 6, 227–239. <https://doi.org/10.1038/s41560-020-00759-5>.