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Structural stability and electrochemical response of 3D printed and reactively sintered Ga-doped $Li_7La_3Zr_2O_{12}$ electrolytes

Christopher S. Dandeneau [a,*], Rahul Rajeev [b], Adam Gootgeld [a], Dale A. Hitchcock [a], Luke C. Olson [a], Tianyi Zhou [b], Jianhua Tong [b], Kyle S. Brinkman [b], Brenda L. Garcia-Diaz [a]

[a] Savannah River National Laboratory, Aiken, SC 29803, USA
[b] Department of Materials Science and Engineering, Clemson University, Clemson, SC 29634, USA

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ABSTRACT

Cubic Ga-doped $Li_7La_3Zr_2O_{12}$ (LLZO) tubes with one closed end were produced by a 3D printing-reactive sintering process. For the first time, the structural stability of Ga-doped LLZO tubes (relative density: ~88 %, cubic LLZO fraction > 90 %) was evaluated after immersion in eutectic PbLi, a candidate molten breeder, at 350 and 450 °C. The high ionic conductivity cubic LLZO phase was maintained after immersion at 350 °C for 100 h, while secondary phase formation and conversion of cubic LLZO to the tetragonal polymorph was observed after 6 h at 450 °C. Li was successfully pumped through the tubes during linear voltage sweeps at 350 °C, indicating that Ga-doped LLZO is a possible candidate for hydrogen isotope extraction in PbLi via direct electrolysis.

1. Introduction

Eutectic PbLi (Pb-Li: 84.3–15.7 at%) is a primary molten breeder material candidate for use in future deuterium–tritium (D-T) fusion plant designs [1]. As naturally occurring tritium is extremely scarce [2], tritium bred onsite in a fusion plant must be efficiently extracted, sent through the fuel cycle, then utilized as fuel for the burning plasma. A promising tritium extraction technique patented at Savannah River National Laboratory is direct LiT electrolysis [3,4], whereby an electrical potential is applied directly to a molten metallic mixture (PbLi or Li) to electrolytically separate lithium tritide (LiT) formed during tritium breeding. In proof-of-concept experiments conducted with a coin-type cell, thin pellets of cubic $Li_7La_3Zr_2O_{12}$ (LLZO) were utilized as a solid-state Li-ion conductor (i.e., a solid electrolyte).

The viability of LLZO as a Li-ion conductor in molten PbLi depends largely on two factors, namely 1) formation and stability of the cubic LLZO phase, which has a Li-ion conductivity (~10^{-4} S cm^{-1}) that is orders of magnitude higher than that of tetragonal LLZO (~10^{-6} S cm^{-1}) [5], and 2) charge transport behavior that is dominated by the ionic and not electronic conductivity, as this allows a potential to be applied directly in PbLi without shorting.

In this work, the structural stability of 3D printed and reactively sintered Ga-doped LLZO tubes is elucidated for the first time. Previous work demonstrated that Ga-doping on the Li sub–lattice stabilizes the cubic phase and improves ionic conductivity [6,7]. The advantage of reactive sintering is that cubic LLZO phase formation, tube densification, and grain growth all occur in a single sintering step, which significantly reduces fabrication time and cost. The introduction of Ga dopants into the LLZO lattice was successfully employed in our previous work to stabilize the cubic phase [8]. Here, the ability to print structurally stable cubic LLZO tubes with one closed end would greatly facilitate up-scaling of the direct LiT electrolysis process and allow for testing of electrolytes with different geometries. The electrochemical response of immersed Ga-doped LLZO under a linear voltage sweep was also evaluated. To the best of our knowledge, such data have not yet been reported in the literature. In addition to accelerating the development of direct LiT electrolysis as a candidate tritium extraction technology, the results presented here will likely garner interest from researchers involved in the development of electrolytes for all-solid-state batteries.

2. Materials and methods

The 3D printing and reactive sintering process to produce Ga-doped LLZO tubes was derived from earlier work with some modification [9,10]. Processing details are given in the Supplementary Material (see Fig. S1). Tube density was determined by the Archimedes method, while a theoretical density of ~5.35 g/m^3 was calculated from X-ray diffractometry (XRD) data. The relative density of the tubes was determined to

* Corresponding author.
E-mail address: christopher.dandeneau@srnl.doe.gov (C.S. Dandeneau).

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be ~88 % of the theoretical value.

Immersion testing was carried out with eutectic PbLi (Atlantic Metals & Alloys). Differential scanning calorimetry (DSC) data obtained for the ingot (Fig. S2) showed an endothermic peak at ~235 °C, consistent with the melting point of eutectic PbLi [11]. In an inert Ar glovebox, ~50 g of PbLi was placed into a Ta-lined Al_2O_3 crucible. The crucible was then loaded into a custom-built ConFlat cell. Printed Ga-doped LLZO tubes were affixed to the stainless-steel rod of a linear motion thimble (LMT, Nor-Cal Products, Inc.) with Al_2O_3 paste (Ceramabond 552 VFG, Aramco). The LMT was then attached to the lid for controlled immersion of the samples. Three Swagelok ports on the lid of the cell were utilized for inert Ar, exhaust, and a thermocouple. Images of the cell and testing setup are shown in Fig. S3 of the Supplementary Material. Tests were carried out by heating PbLi to 350 or 450 °C in a vertical tube furnace (Carbolite) under Ar, then immersing the specimens.

Immersed regions of the tubes were sectioned and ground with a mortar and pestle for analysis. The crystal structure of specimens before and after immersion was determined via XRD patterns collected with a Rigaku SmartLab instrument (Cu X-ray source). Rietveld refinement carried out with SmartLab Studio II software was utilized for quantification of the phase percentages in collected patterns.

The current responses of tubes after PbLi immersion at 350 °C were recorded with a potentiostat (Biologic, VSP model) during linear sweeps from –5 to 5 V. Printed tubes were affixed to Al_2O_3 tubes (McMaster-Carr) with Al_2O_3 paste. In an inert glovebox, ~0.1 g of Li metal (Sigma Aldrich) was loaded into the Al_2O_3 tube such that it dropped to the bottom of the closed-end Ga–LLZO. A W rod (Eagle Alloys, 99.95 % purity) was then inserted through the Al_2O_3 to the bottom of the Ga-LLZO so that it contacted the Li. An additional W rod served as the anode.

3. Results and discussion

Shown in Fig. 1 are XRD patterns collected for the closed-end Ga-doped LLZO tubes after immersion in PbLi at 350 °C for 24, 50, and 100 h. The pristine tube was ~90 % cubic LLZO, but a sizable fraction of Li_2ZrO_3 (~8%) and a smaller fraction of $LiGaO_2$ phase were detected. The presence of these phases suggests that 20 mol% additional Li precursor may be excessively high. Regardless, Rietveld refinement showed only a minor change in the phase assemblage after immersion for 100 h.

The XRD patterns obtained after PbLi immersion at 450 °C for different durations are displayed in Fig. 2. It is evident that the temperature increase has a profound effect on cubic LLZO phase stability. After immersion for 24 h, a significant fraction of tetragonal LLZO (~35.5 %), the low ionic conductivity LLZO polymorph, was formed. The tetragonal fraction then increases to become the dominant LLZO phase after 50 h of immersion. Furthermore, a color change from yellowish white to black was observed after 50 h (top right of Fig. 2). In previous research on beta-Al_2O_3 immersed in molten Na, a color change from white to grayish black was observed along with an increase in electrical conductivity [12,13]. While electrical conductivity was not measured here, such a scenario would preclude the use of Ga-doped LLZO in direct LiT electrolysis at 450 °C. In earlier work on Al-doped LLZO immersed in molten Li at 300 °C, a color change was associated with electrons trapped at oxygen vacancies; heating in air at 800 °C restored the original color of the material [14]. Here, heating of Ga-doped LLZO immersed for 24 h at 450 °C led to appreciable recovery of the original color and cubic LLZO phase (see Fig. S4).

The initial current response of an immersed Ga-doped LLZO tube at 350 °C during 3 successive voltage sweeps is shown in Fig. 3(a). At negative potentials, Li from inside the tube moves outward towards the larger pool of molten PbLi. The interfacial area between the inner tube surface and small amount of Li inside the tube (~0.1 g) is also quite small, which may explain the negligible currents recorded in this region. At positive potentials, much larger currents of 1.75 – 2.5 mA are observed, possibly because the interfacial area between the pool of molten PbLi (~180 g) and the outside of the tube is much greater. As displayed in Fig. 3(b), linear scans after 12 h of immersion do not differ significantly from the initial scans, suggesting that electrochemical stability is maintained.

4. Conclusions

For the first time, the structural stability of Ga-doped LLZO tubes

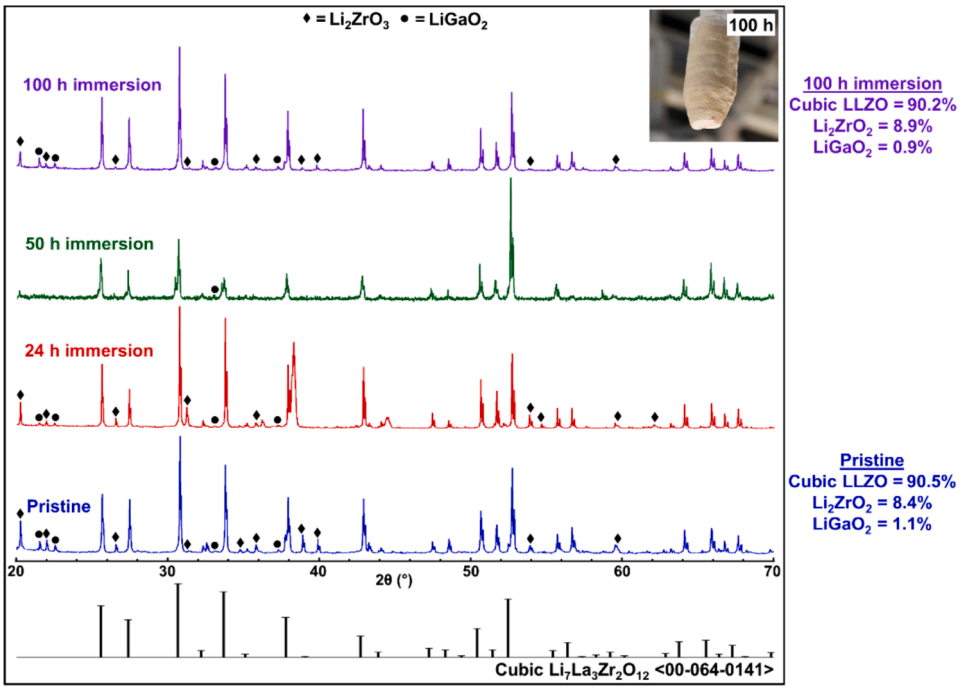

Fig. 1. XRD patterns of Ga-doped LLZO tubes after immersion in PbLi at 350 °C for different time durations; a photograph of the sample immersed for 100 h is shown in the top right.

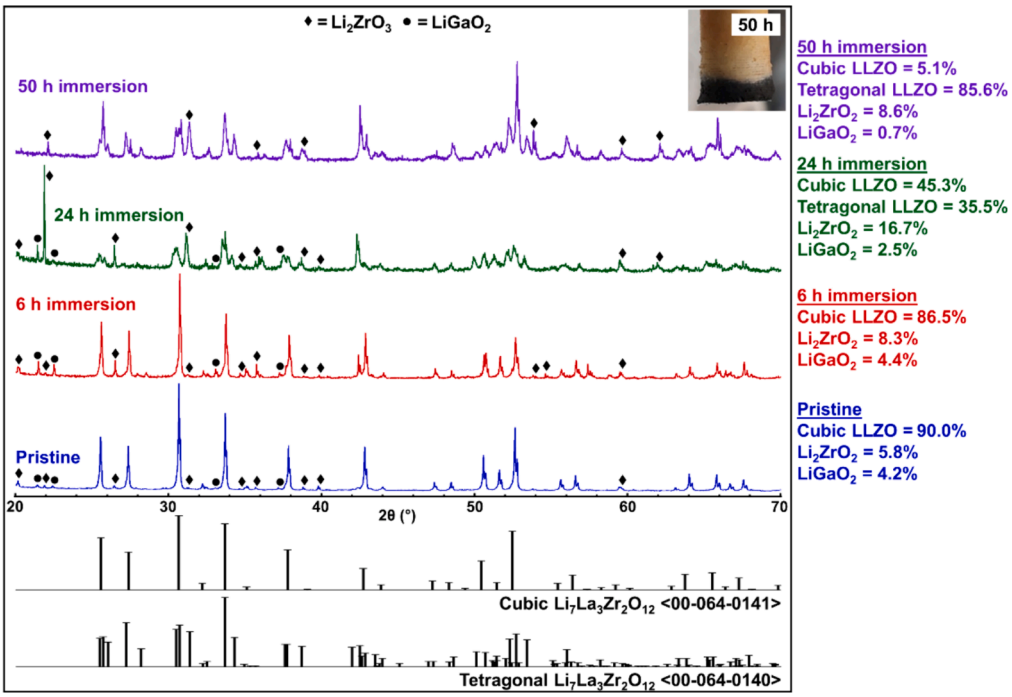

Fig. 2. XRD patterns of Ga-doped LLZO tubes after immersion in PbLi at 450 °C; a photograph of the specimen immersed for 50 h is displayed in the top right.

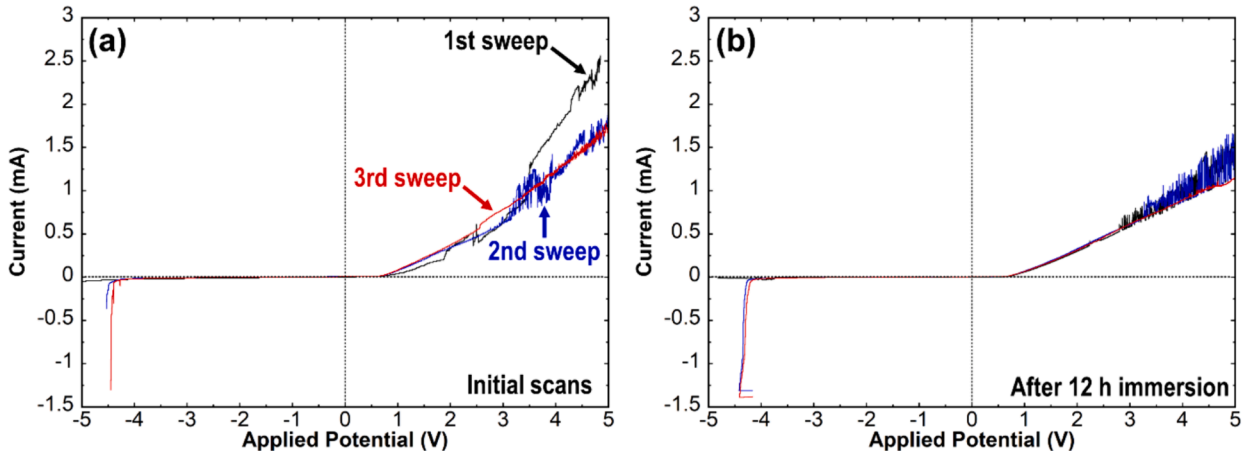

Fig. 3. Current response of immersed Ga-doped LLZO during a linear potential sweep from −5 to 5 V: (a) initial results and (b) data collected after 12 h of immersion.

produced by 3D printing and reactive sintering was evaluated before and after molten PbLi immersion. Based on the results, the printed tubes could possibly be utilized as electrolytes for direct LiT electrolysis of molten PbLi mixtures, provided the temperature is held below 450 °C. Linear potential sweeps at 350 °C showed that Li could be pumped through the electrolyte under an applied potential. As reliable and efficient tritium extraction techniques are in high demand by the fusion community, Ga-doped LLZO is promising candidate for use in direct LiT electrolysis.

CRediT authorship contribution statement

Christopher S. Dandeneau: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis. **Rahul Rajeev:** Investigation, Formal analysis. **Adam Gootgeld:** Writing – review & editing. **Dale A. Hitchcock:** Writing – review & editing. **Luke C. Olson:** Writing – review & editing. **Tianyi Zhou:** Investigation, Formal analysis. **Jianhua Tong:** Resources, Methodology. **Kyle S. Brinkman:** Writing – review & editing, Supervision, Project administration. **Brenda L. Garcia-Diaz:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matlet.2024.137240.

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