A low ride on processing temperature for fast lithium conduction in garnet solid-state battery films

Reto Pfenninger^{1,2}, Michal Struzik^{1,2,5}, Iñigo Garbayo^{2,6}, Evelyn Stilp³ and Jennifer L. M. Rupp^{1,2,4*}

A critical parameter for the large-scale integration of solid-state batteries is to establish processing strategies to assemble battery materials at the lowest processing temperature possible while keeping lithium conduction up. Despite extensive research efforts, integrating ceramic film electrolytes while keeping a high lithium concentration and conduction at a low processing temperature remains challenging. Here, we report an alternative ceramic processing strategy through the evolution of multilayers establishing lithium reservoirs directly in lithium-garnet films that allow for lithiated and fast-conducting cubic solid-state battery electrolytes at unusually low processing temperatures. A lithium-garnet film processed via the multilayer processing approach exhibited the fastest ionic conductivity of $2.9 \pm 0.05 \times 10^{-5}$ S cm⁻¹ (at room temperature) and the desired cubic phase, but was stabilized at a processing temperature lowered by 400 °C. This method enables future solid-state battery architectures with more room for cathode volumes by design, and reduces the processing temperature.

olid-state batteries (SSBs) offer safe alternatives to classical lithium-ion batteries due to the non-combustible nature of the electrolyte, and impart the option for both high-energy and high-power densities1. Recent progress on SSBs identified Ligarnets such as Li₂La₃Zr₂O₁₂ as promising candidates for the electrolyte due to their wide electrochemical stability window², fast Li conductivity^{3,4} of 1 mS cm⁻¹ at room temperature, and non-flammability. Compared with other even faster-conducting SSB electrolytes such as LGPS ($Li_{10}GeP_2S_{12}$) (refs. ⁵⁻⁸) or Li_7P_3S11 (refs. ⁹⁻¹¹), Li-garnets exhibit improved thermodynamic stability, especially towards the Li anode¹²⁻¹⁴. However, one major drawback of Ligarnet electrolytes is that the high Li conductivity requires stabilization of the cubic phase ($Ia\overline{3}d^{4,15}$, or the acentric cubic $I\overline{4}3d^{16,17}$) through doping of the structure with elements on either the Li site $(Al^{3+} and Ga^{3+})^{18-21}$, the La site $(Sr^{2+} and Nd^{3+})^{22-24}$ or the Zr site (mainly Ta⁵⁺)²⁵, and solid-state manufacturing. The current predominant processing strategies are to sinter the initial Li-garnet particles to either a dense pellet^{19,20,26,27} or a tape²⁸⁻³⁰. To activate sufficient grain boundary and volumetric diffusion in densification for either the pellet or the tape, sinter temperatures beyond 1,050 °C are a necessity for cubic Li-garnets.

Exploration of thin-film processing of Li–garnets is an attractive solution to reduce manufacturing temperatures by over 400 °C while maintaining high Li conductivity and reducing the solid electrolyte component thickness from the millimetre to the nanometre scale. Reduced costs for the large-scale production of such electrolytes, as well as greater volumes and increased compatibility with temperature-sensitive electrode materials are desired. For example, by reducing the conventional sinter temperature from 1,050 °C—as is often required to create macroscopic ceramic bodies of cubic Li-garnet from powder-to 660 °C, a much broader choice of electrode materials and interface engineering strategies is within reach³¹. Notably, these are commonly deposited at temperatures of 600-700 °C (for example, Li₄Ti₅O₁₂ and LiFePO₄^{32,33}). In addition, future applications, such as biosensors, wearable computing devices and remote-sensing entities, for which highly integrated microbattery designs are required, would benefit from having access to fastconducting Li-garnet materials in thin-film form. Also, Li-garnet films may bypass traditionally employed electrolyte films, such as lithium phosphorus oxynitride (LiPON)34 for microbatteries, at faster conductivity (2.3×10⁻⁶S cm⁻¹ for LiPON³⁵ versus 1 m S cm⁻¹ for Li-garnets⁴) and over a wider electrochemical stability window^{36,37}. Currently, cells based on LiPON show cyclability over several thousand cycles^{38,39}, and LiPON-based SSBs have already been successfully commercialized⁴⁰. However, the limited electrochemical stability window for LiPON of between 0.68 and 2.63 V³⁶ may only allow for a limited selection of high-voltage cathode materials. In contrast, cubic Li-garnet can be processed as films exhibiting a wide experimental electrochemical stability window of between 0 and 6 V, as was previously shown in a cell employing a metallic Li/ Li₂FeMn₃O₈ high-voltage cathode charged to 5.25 V⁴¹. For LiPON, metallic Li as an anode promotes the inherent formation of a selfpassivation layer consisting of kinetically limiting decomposition products (Li₃N, Li₃P, Li₃PO₄ and Li₂O), which appear on contact and disenable any high-power output applications for LiPON-based designs^{42,43}. The processing of Li-garnet electrolyte layers as films deserves particular attention for both large-scale SSBs employed in electric vehicles (to avoid sintering, simplify co-assembly and reduce costs) and microbatteries towards compatibility with nonheat-resistant electronic circuits⁴⁴.

¹Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA, USA. ²Electrochemical Materials, Swiss Federal Institute of Technology, Zurich, Switzerland. ³Empa, Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland. ⁴Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, MA, USA. ⁵Present address: Faculty of Physics, Warsaw University of Technology, Warsaw, Poland. ⁶Present address: CIC Energigune, Parque Tecnológico de Álava, Miñano, Spain. *e-mail: jrupp@mit.edu

а 50 nm a,Zr,O12 350 nm 25 nm 660 °C b 300 °C Multilaver Merging of deposition individual layers 660 °C Polycrystalline cubic LLZO Direct deposition с

Fig. 1 | Experimental approach for thin-film deposition of Li-garnet. a, Schematic of the experimental approach for the employment of a multilayer structure to deposit cubic $Li_7La_3Zr_2O_{12}$ via PLD. Thin layers of Li_3N were incorporated to compensate for Li loss at elevated temperatures. **b**, Schematic of the two possible approaches to obtaining dense polycrystalline thin films of $Li_7La_3Zr_2O_{12}$ via PLD. *T*, temperature; *t*, time. The first approach (top) employs a subsequent post-annealing treatment, whereas the second approach (bottom) utilizes one-step hot deposition. **c**, Optical microscopy image of a thin film deposited on an MgO substrate.

Thin-film Li–garnets of the composition $\text{Li}_7\text{A}_x\text{La}_3\text{Zr}_2\text{B}_y\text{O}_{12}$ (where A = Al, x = 0 - 0.71, B = Ta or Y, and y = 0 - 0.4) have been synthesized using vacuum-based techniques such as radio frequency sputtering^{45–47}, pulsed laser deposition (PLD)^{48–51}, and wet-chemical synthesis by metalorganic chemical vapour deposition⁵² and solgel methods^{53,54}. The vast majority of Li–garnet thin films reveal an ambient conductivity of $10^{-8}-10^{-6} \text{ S cm}^{-1}$, and predominantly exhibit a crystalline phase (mostly cubic or mixed cubic and tetragonal) after processing at temperatures of $600-1,000 \, ^{\circ}\text{C4}^{4,52,53,55}$, mostly by sol–gel^{53–55} or PLD^{49,51,56} depositions. Compared with tape- or pellet-processed Li–garnets, which are manufactured by sintering of powders at high temperatures, today's state of technology on thinfilm manufacturing results in Li conductivity that is three to five orders of magnitude lower, and presents challenges with respect to

NATURE ENERGY



Fig. 2 | Merging of the multilayered structure. a, SEM image of the multilayer structure deposited at 300 °C, showing the independent layers of delithiated $Li_7La_3Zr_2O_{12}$ and Li_3N deposited on an MgO substrate. We have added a colour code for better visualization of the repeating layers of delithiated $Li_7La_3Zr_2O_{12}$ (green) and Li_3N (orange). **b**, SEM image of the same structure after post-annealing at 660 °C, showing a merged thin film of ~330 nm thickness. The green dotted lines show the borders of the obtained polycrystalline thin film.

the achieved phase purity of the high-conducting cubic phase. In Supplementary Note 1, we summarize the challenges that have been defined for the implementation of Li–garnets as fast Li-conducting solid electrolytes processed at low temperatures. Among them are the delicate phase stabilization in thin films of Li–garnets, particularly at low processing temperatures, as well as strategies to actively avoid Li loss during film manufacturing.

In the present study, we demonstrate a processing method for the manufacture, at the lowest possible processing temperature, of cubic and thin Li–garnet SSB electrolytes, by engineering internal lithiation reservoirs to maintain the critical phase. The presented manufacturing strategy contributes to substantially reduced processing temperatures of cubic Li–garnets, with desirable thin ceramic structures and high Li conduction. The results have implications for our understanding of phase evolution and the avoidance of Li loss in the processing of Li-oxide films in a wider sense, as well as introducing fast-conducting Li–garnet films as a suitable alternative to LiPON for SSBs and other types of lithionic devices.

Manufacturing of lithiated garnet electrolyte films

We explore the deposition of initially multilayered Li₆₂₅Al₀₂₅La₃Zr₂O₁₂ (LLZO)/Li₃N thin films to create an internal reservoir of Li from the Li₃N phases to diffuse and counteract delithiation during LLZO phase formation at elevated temperature (Fig. 1a). Nine repeating layers of LLZO and Li_3N with 50 nm (±10%, all errors are s.d. unless otherwise stated) and $25 \text{ nm} (\pm 10\%)$ thicknesses, respectively, were deposited on top of each other on a polished (001)-orientated MgO substrate by PLD from two own-processed targets. To study the impact of thermal treatment for PLD-deposited thin films of LLZO, we used two different manufacturing paths, both of which resulted in the formation of polycrystalline cubic LLZO thin films (Fig. 1b). In the first approach, PLD multilayer deposition was conducted at 300 °C, followed by an external post-annealing step for 15 min at 660 °C under pure oxygen ($p_0 = 1,013$ hPa). In the second approach, the multilayer PLD deposition was conducted at 660 °C under a low partial pressure of oxygen ($p_0 = 0.04$ hPa). A light microscopy image of the as-deposited film at 300 °C covering an MgO substrate of $\sim 0.9 \times 0.9 \text{ cm}^2$ and processed via the first approach is shown in Fig. 1c. We used scanning electron microscopy (SEM) to investigate the microstructure more closely, and to compare a sample deposited at 300 °C without post-annealing with a film after post-annealing at 660 °C (Fig. 2). The presence of the individual repeated heterolayers of LLZO and Li₃N can be observed by a difference in contrast in the cross-sectional SEM images for the as-deposited film at 300 °C (Fig. 2a). Layers of delithiated LLZO and Li₃N were deposited



Fig. 3 | Negative-ion TOF-SIMS spectrum of a thin film. The garnet film (salmon-shaded area) was deposited at 300 °C as a multilayered structure followed by post-annealing at 660 °C. Platinum electrodes (grey-shaded areas) were deposited on both sides to protect the thin film from exposure and exchange with environmental conditions.

at a thickness ratio of 2:1, resulting in 50 and 25 nm per layer, respectively. The total thickness of the obtained heterostructure was 350 nm (\pm 10%), as measured by SEM, with indications of intimate contact among the layers of garnet and nitride phase, and no signs of pinholes in either. When looking at the same thin film in cross-sectional SEM, after post-annealing at 660 °C under oxygen (Fig. 2b), the film is dense and we can no longer distinguish the layers by inspection of the cross-sectional interface, as in the other specimen. We interpret this as unity of the distinct multilayers after merging at elevated temperatures. To check whether thin-film multilayers directly deposited at 660 °C also resulted in a homogeneous merged thin film of LLZO, we subjected another set of such thin films to inspection by cross-sectional SEM (Supplementary Fig. 1a–c).

To explore the transformation and local chemistry of the initial multilayered structure to a homogeneous film of LLZO, negative-ion time-of-flight secondary ion mass spectrometry (TOF-SIMS) was conducted over a film's cross-section (Fig. 3). A thin film of a multilayer Li₃N/LLZO structure deposited at 300 °C and post-annealed at 660 °C to merge the layers to LLZO was measured between two protective platinum contacts. We tracked the signals of single negatively charged ions of Li-, La-, Zr-, Al- and N- over the LLZO film cross-section. First, analysis of the spectral line clearly indicated the chemical occurrence of the cations Li, La, Zr and Al in the film. Quantitatively, the TOF-SIMS signal of N decreased to <10 counts per measure (c.p.m.) once the post-anneal had been carried out. This indicated clearly that the decomposition of Li₃N over the film thickness had taken place and that nitrogen had left the film. We can clearly track La and Li over the full thickness of the film above 10 c.p.m. Second, we analysed the negative-ion TOF-SIMS signal of aluminium over the film's cross-section, as this is a good marker for Al-doped LLZO. We found for the aluminium a periodic occurrence of four imposed peaks on the spectral line. A similar trend was also seen for Zr, but at a significantly lowered magnitude for zirconium which reveals slight peak elevations coinciding with the aluminium peak positions on the spectral line versus cross-sectional locality of the film. Importantly, the four imposed peaks of the aluminium coincided well with the initial locations of the LLZO layers of the as-deposited multilayers, even though the films were post-annealed. The trend was less obvious for La and Zr, whose signals seemed in

general to be more evenly distributed through the film after postannealing. There has been thorough discussion in the literature on the location and homogeneous distribution of aluminium or gallium dopants used for phase stabilization in pellet manufacturing (sintering)^{27,57-61}. Wachter-Welzl et al.⁶² recently demonstrated the effect of inhomogeneous distribution of aluminium in LLZO as a factor for the observed large spread of measured conductivity values. It has been found that Al and Ga dopants, which both occupy Li sites in the garnet framework—at the tetrahedrally coordinated 24d position⁶¹ or the Li1 site (12a) (in acentric cubic space group $I\overline{4}3d$)¹⁶, respectively-preferably locate inside grain boundaries. Gallium is known to form LiGaO₂ in the vicinity of grain boundaries⁵⁷, whereas Al forms LiAlO₂²⁰. From a ceramics perspective, it makes sense that aluminium accumulates mostly at the original interfaces of the multilayer even after heat treatment (similar to a classic grain boundary interface architecture in a sintered pellet); however, we have yet not compared this finding with the results of other studies.

We formed two conclusions from the negative-ion TOF-SIMS results. First, most of the initial Li₃N layer decomposes (N < 10 c.p.m.) after post-annealing of the original multilayer. We propose that the Li diffuses into the neighbouring Li_{6.25}Al_{0.25}La ₃Zr₂O₁₂, forming phase majority. Second, the Al dopant of LLZO remains close to the original locations of the multilayer interfaces, even after heat treatment and merging of the layers. As an analogy, one can understand this as similar to the increased dopant concentrations present in sintered pellet bodies. Importantly, no major presence of nitrogen is traceable after post-annealing, and all phasecomposing cations are found for the merged LLZO film.

Roles of Li₃N in the synthesis of cubic Li-garnet films

We used ex situ Raman spectroscopy to understand the phase evolution with respect to the temperatures used to anneal the initially multilayered LLZO/Li₃N to single LLZO thin films. The multilayered films of alternating LLZO and Li₃N sequences deposited at 300 °C were selected, and post-annealing temperatures were varied before Raman analysis in a Linkam hot plate stage (Fig. 4a). Close to the original deposition temperature at 300 °C, the multilayered LLZO/Li₃N films revealed a generally broad Raman signal with local maxima around 97, 325, 518 and 665 cm⁻¹. We interpret the characteristic broad peaks observed around 325 and 665 cm⁻¹ as representing the amorphous state of LLZO (as discussed by Garbayo et al.⁵⁰, who reported signatures around 335 and 670 cm⁻¹, respectively). An overlap of the T_{2g} LLZO peak with the strongest longitudinal E_{1g} Raman mode around 350 cm⁻¹ for Li₃N⁶³ exists, which means we cannot confirm the Li₃N phase solely by Raman spectroscopy.

On heating to 425°C, more distinct peaks between 100 and 200 cm⁻¹ appeared—mainly at 122, 159 and 197 cm⁻¹. These indicated the start of an ongoing crystallization process. At 585 °C, characteristic peaks at 106 and 126 cm⁻¹ were assigned to T_{2g} vibrational modes, and triplet peaks at 209, 247 and 288 cm⁻¹ were assigned to T_{2g} , A_{1g} and T_{2g} vibrational modes, respectively^{64,65}. These can be allocated to a full development of the tetragonal LLZO phase64. Notably, at 585 °C, peaks at 247 and 647 cm⁻¹ (both assigned to A_{1g} vibrational modes) also emerged, reducing the overall number of Raman active vibrations. These peaks remained present over all further postannealing up to 710 °C. We interpret this as representing transformation of the film from the tetragonal to the cubic phase of LLZO, which takes place between 630 and 660 °C (note that peaks of the T_{2e} and $E_{\rm g}$ vibrational modes around 107 and 123 cm $^{-1}$, the $A_{\rm 1g}$ and $T_{\rm 2g}$ vibrational modes at 254 and 364 cm⁻¹, and the T_{2g} and E_{g} vibrational modes at 418 and 515 cm⁻¹, respectively, are commonly attributed to Li sublattice vibrations⁶⁴). For temperatures higher than 810 °C, peaks appeared at 299, 394, 492 and 516 cm⁻¹. These can further be assigned to E_{e} , F_{2e} , A_{1g} and F_{2g} vibrational modes, respectively^{50,66}, indicating phase transformation to the delithiated pyrochlore La₂Zr₂O₇ phase (LZO). Inspection of these films by micro-Raman spectroscopy

NATURE ENERGY



Fig. 4 | Exsitu phase evolution. a, Results of exsitu Raman crystallization of separate thin films deposited at 300 °C by PLD, followed by postannealing at the stated temperatures in pure O₂. Films were all measured after they had cooled down to room temperature. Crystallization started to occur at 425 °C. At 585 °C, the tetragonal phase of Li₇La₃Zr₂O₁₂ was fully developed. At 660 °C, transition to the cubic phase was fully completed. At 810 °C, the crystallites of the common delithiated phase $(La_2Zr_2O_7^{66})$ started appearing on the thin film of cubic Li₇La₃Zr₂O₁₂. At 980 °C, a full transformation from Li-garnet to pyrochlore La₂Zr₂O₇ was observed due to Li loss. All reference data were taken from spectra obtained by Tietz et al.⁶⁴ (cubic and tetragonal Li₇La₃Zr₂O₁₂) and Kong et al.⁶⁶ (La₂Zr₂O₇), and stoichiometry and vibrational modes were assigned according to tentative assignments from the literature^{64,66}. The spectrum of the Li₃N PLD target is shown for comparison. b, Thin-film XRD pattern of the film deposited at 660 °C, showing the formation of cubic $Li_7La_3Zr_2O_{12}$, in agreement with Inorganic Crystal Structure Database structure 183607 (ref. 67). An additional diffraction peak at 31.8° was assigned to the presence of the secondary phase of Li₂CO₃, which formed due to long-term exposure to the ambient environment during the measurement. A substrate peak at 29.46° was assigned to MgO and is represented by an asterisk.

revealed that islands with an average diameter of $2-10\,\mu m$ existed, which could be identified as delithiated LZO, whereas the remaining parts of the thin film still showed the full feature-set of cubic LLZO (see Supplementary Fig. 2a,b for details). Hence, a phase separation exists during which local spots of delithiated LZO progress in the LLZO microstructure matrix of the film.



Fig. 5 | Raman spectra of selected thin films deposited by PLD under optimal conditions using three different approaches. Measurements were taken after structures had cooled down to room temperature. Spectra are shown for the traditional deposition, post-annealing and hot-deposition approaches. Reference spectra were taken from Tietz et al.⁶⁴ (cubic and tetragonal Li₂La₃Zr₂O₁₂) and Kong et al.⁶⁶ (La₂Zr₂O₇), and vibrational modes were assigned according to tentative assignments.

We used thin-film X-ray diffraction (XRD) to further probe the occurrence of cubic LLZO, as identified by Raman spectroscopy when post-annealing at 660 °C (Fig. 4b). Diffraction peaks were observed at 16.6, 25.2, 27.2 and 30.6 in 2θ geometry. These peaks agree with the cubic LLZO crystal structure for the Miller indices (211), (321), (400) and (420), respectively, and are also in agreement with Inorganic Crystal Structure Database structure 183607 (ref. ⁶⁷). Two additional peaks at 29.46 and 31.8° represented the MgO substrate and Li₂CO₃⁶⁸ (a known byproduct that forms on exposure of LLZO to moist atmosphere in pellets⁶⁸), respectively (Supplementary Fig. 3).

To probe whether there are differences in phase evolution between the two deposition strategies for thin-film cubic LLZO (that is, grown by PLD or post-annealed at high temperature), we compared the two films directly by Raman spectroscopy. Importantly, we also compared these initial-multilayer processed films with a traditionally processed LLZO PLD film purely deposited from a single LLZO target at the same temperature of 660 °C (Fig. 5). Note that the films deposited at 300 °C and post-annealed were exposed to different oxygen partial pressures compared with the film deposited at 660 °C (1,013 and 0.04 hPa, respectively).

We directly compared the thin films obtained from the two different approaches, the post annealing route conducted at 660 °C towards the hot-deposition at the same temperature, which we rate



Fig. 6 | Ionic transport properties in thin-film Li-garnet. a, Nyquist plots obtained at temperatures of 240 °C (orange) and 281 °C (purple) from the multilayered LLZO thin film after post-annealing at 660 °C. Inset, respective fittings (as determined by a resistor (R) in parallel with a constant-phase element (Q)) are shown by solid lines. Im() indicates the imaginary part of the complex impedance and Re() the respective real part; R_{Ligarnet} indicates the total resistance of the investigated sample. **b**, Temperature dependence of the in-plane total conductivity of selected thin films as a function of the temperature in Arrhenius-type representation.

optimal conditions for both approaches. The spectra for the postannealing and hot-deposition approaches both showed observable peaks of the T_{2g} and E_g vibrational modes around 107 and 123 cm⁻¹, but with more peak overlap in the case of the hot-deposition approach. Vibrational modes A_{1g} and T_{2g} (254 and 364 cm⁻¹) were also present in both cases. However, an additional feature between these two peaks (at 309 cm⁻¹) was identified exclusively for the hotdeposition approach. We interpret this as a minor contribution of the delithiated phase $La_2Zr_2O_7$, for which the characteristic E_g vibration is found around 299 cm⁻¹. The spectrum of a film processed via traditional deposition from a single LLZO target showed broad peaks around 340 and 670 cm⁻¹. Due to the non-distinct features on the observed peaks, we could not identify a particular crystallographic phase being transferred to the thin film in this sample. Thus, the shown multilayer process in this work highlights the requirement for additional Li_3N reservoirs for the successful transfer of Li–garnet to the thin film form by PLD.

In summary, both deposition approaches using multilayers with Li₃N resulted in formation of the cubic phase of LLZO in thin-film form, but for the hot-deposition approach, we observed potential minor phase contributions from the delithiated-phase LZO. This may point to slightly different Li concentrations per volume, even though the main phase of cubic LLZO is maintained. The altered oxygen partial pressures to which the two samples were subjected during fabrication (1,013hPa for the post-annealed sample versus 0.04 hPa for the hot-deposition sample) may have played a key role, even though phase stability was preserved in both. A recent study by Kubicek et al.⁶⁹ suggested altered transport properties as a function of oxygen non-stoichiometry versus Li non-stoichiometry, with relative oxygen vacancy concentrations estimated to be between 2×10^{-7} and 4×10^{-4} for a similar doping concentration (0.15–0.30) Al atoms per formula unit). Owing to observable changes in conduction, we next performed a conductivity study.

Conductivity of cubic-garnet solid-state electrolyte films

We collected electrochemical impedance spectra to measure the total conductivity (bulk and grain boundary contributions) of thin films processed either via the multilayer approach based on Li₃N/LLZO or using the traditional LLZO target alone. Electrochemical impedance measurements were performed in an in-plane geometry, as depicted in the inset of Fig. 6a. Due to the strong overlap of bulk and grain boundary contributions in the Nyquist representation of electrical impedance spectroscopy (EIS), it was not possible to separate and quantify them independently. Consequently, a resistor in parallel with a constant-phase element was used for the fitting, and understood to represent the total Li⁺ conductivity of the film. An example of the collected data points and respective fitting for the post-annealed sample at 240 and 281 °C is shown in Fig. 6a. The calculated conductivities were also plotted in an Arrhenius-style representation (Fig. 6b). Three different thin films were compared, two of which exhibited the cubic phase under Raman spectroscopy (that is, the film that was deposited directly at 660 °C as a multilayered structure with no post-annealing treatment and the film that underwent post-crystallization treatment under pure oxygen for 15 min at 660 °C). When comparing the polycrystalline cubic LLZO thin films fabricated using the multilayer approach (that is, deposited either directly at 660 °C or at 300 °C, with post-annealing under pure O₂ at 660 °C), the thin film deposited at 300 °C achieved the highest total conductivity of $2.9 \pm 0.05 \times 10^{-5} \text{ S cm}^{-1}$ (activation energy, $E_{\text{A}} = 0.46 \pm 0.03 \text{ eV}$) at room temperature (23 °C). The film deposited at 600 °C reached $0.26 \pm 0.05 \times 10^{-5} \text{ S cm}^{-1}$ ($E_{\text{A}} = 0.52 \pm 0.03 \text{ eV}$). The obtained activation energies are within the expected range for thin-film depositions (0.32-0.60 eV^{48,56}; see Fig. 7), but are clearly higher compared with pellets (0.28–0.33 eV^{70,71}), in agreement with previous reports.

For comparison, we included conductivity data obtained from a thin film processed from a LLZO target only (that is, deposited at 660 °C, but without the use of Li₃N for fabrication). In this sample, an extrapolated room temperature conductivity of $5.96 \pm 0.05 \times 10^{-11} \text{ S cm}^{-1}$ and an activation energy of $E_A = 0.72 \pm 0.03 \text{ eV}$ were obtained. In conclusion, thin films that underwent a post-annealing treatment at 660 °C and were deposited at 300 °C revealed higher conductivity values than those that were hot deposited at 660 °C. This could be explained by differences in the oxygen off-stoichiometry between both films, since both post-annealed films were exposed to an ambient pressure of O_2 during thermal treatment at the highest temperature, therefore facilitating transformation and loss of nitrogen compared with the film grown directly at a low partial pressure of oxygen in the PLD vacuum chamber.

In Supplementary Fig. 4, we show how the ionic conductivities of the LLZO films using the Li₃N multilayer and lithiation strategy



Fig. 7 | Processing temperature dependence in Li-garnets. a,b, Comparison of cubic-phase LLZO thin-film (<1µm thickness) Li-ion conductivities (a) and activation energies (b) at room temperature versus the processing/ annealing temperature used. Symbols represent the method of fabrication. Open symbols represent LLZO thin films containing dopants that differ from the one used in this study. Three of the data points for pellets^{70,71,73} represent LLZO pellet conductivities at the doping concentration used in this study (that is, 0.25 Al³⁺ per formula unit), whereas ref. ⁷⁴ used other dopants. Compared with the other thin-film studies presented here^{28,45,48,49,51,53-56,75-77}, the values obtained in this study represent the highest room temperature Li-ion conductivity in thin films of cubic LLZO. The conductivities of selected LiPON thin films^{35,78} are shown for comparison. As shown in **b**, the lowest activation energies reported to date are for sol-gel deposition techniques, followed by PLD deposition. Values for bulk LLZO pellet activation energies^{70,71,73,74,79} are represented respectively. CVD, chemical vapour deposition.

compare with those of LiPON and the standard liquid and polymer electrolytes. Notably, the LLZO films processed using the method presented here reveal a higher conductivity compared with standard LiPON, and may provide future opportunities owing to their greater electrochemical window.

Advantages in Li conductivity

By comparing our results with other cubic LLZO thin films deposited via traditional means (Fig. 7a), it can be concluded that the film processed through the internal building of initial Li₃N reservoirs clearly outperforms in terms of effective conductivity; its performance is close to pellets and tapes, but at a lowered processing temperature. Similar results were found when comparing activation energies for ionic transport (Fig. 7b); the multilayer strategy led to activation energies of 0.46 and 0.52 eV for deposition at 300 °C (+ post annealing) and 660 °C, respectively, compared with 0.72 eV for a thin film without Li_3N .

In summary, we compared the conductivity of three different thin films of LLZO: two employing an Li_3N multilayer acting as a reservoir to counteract Li loss during deposition, and one with no Li_3N . We conclude that the multilayer processing strategies are a viable route for the deposition of highly conductive Li–garnets at significantly lowered processing temperatures.

The electrolyte performance achieved using the Li₃N/LLZO multilayer approach is comparable to the highest conductivity currently achieved using Li–garnets, also on transfer to thin films. Since dense and crack-free electrolyte thin films are key components for integration in high-energy and power-dense energy storage devices, the assembly of SSBs based on the multilayer Li₃N processing technique shown here will allow for processing strategies and design concepts enabling thin electrolytes without the need for traditional sintering (low-temperature processing), and gives room for larger cathode volumes in the overall cell design.

Conclusions

All SSB Li-garnet electrolytes were fabricated through a multilayer processing approach using Li reservoirs (via Li₃N) to establish, at an unusually low processing temperature of 660 °C, thin and dense ceramic films with excellent Li conductivity. This was achieved by employing a multilayer approach combining LLZO with Li₃N layers in PLD, followed by post-annealing that decomposes the Li₃N reservoirs and lithiates the garnet phases, thus compensating for the typical Li loss that occurs during the low-temperature vacuum deposition approach to creating Li-garnet electrolytes. The results clearly show that if such measures are not taken into account during Li-garnet processing, the desired cubic phase cannot be established, or sacrifices have to be made in terms of the electrolyte component volume in the battery cell. These insights into the processing, phase evolution and structure-property stabilization of Li-garnet solid electrolyte films show that it is possible to substantially reduce the standard processing temperature from 1,000 °C (used to synthesize bulky millimetre-thick components (through sintered powders)) to below 700 °C to produce film thicknesses in the nanometre range. Although several issues with the processing technology require attention, this work opens up a route for the fabrication of thin-SSB Li-garnets with very high ionic conductivity processed at low temperatures. The presented processing strategy of controlling lithiation in an oxide material using a nitride may be adopted for other classes of Li oxides, such as electrodes of high energy density, thus counteracting the general concern of Li deficiency on transfer to films. The thin films described here are therefore promising candidates for use in SSBs in electric vehicles, future microbatteries (as they outperform classics, such as LiPON electrolyte films) or other lithionic devices such as Li-operated environmental and chemical sensors72.

Methods

Material synthesis of the PLD targets. To obtain a multilayered thin-film structure, two dense ceramic bodies were fabricated first. These were then used as two separate targets for the deposition of the thin films. We synthesized the PLD target for the Li–garnet thin-film PLD depositions through a nitride-based, modified sol–gel method. Li_{6.25}Al_{0.25}La₃Zr₂O₁₂ powder was synthesized based on a recipe reported by Van den Broek et al.⁷⁰. For this, stable precursor sols were obtained by the dissolution of stoichiometric amounts of LiNO₃ (99.99%; Merck), La(NO₃)₃(H2O)₆ (99.9%; Alfa Aesar) and zirconium(tv) 2,4-pentanedionate (Alfa Aesar) in a water and ethanol mixture that was calcined at 600–650°C after drying. The powders were pressed into pellets by uniaxial pressing followed by isostatic pressing at a pressure of 44 MPa for 3 min. Pellets were then sintered in an alumina crucible inside a bed of parent powder material at 1,050°C for 12h with

 ± 10 °C min⁻¹ heating rate. An Li–garnet target with a diameter of 27 ± 1 mm was obtained with a theoretical density of >85%.

To control the Li–garnet chemistry of the post-annealed thin films, we synthesized a PLD target for Li nitride. Uniaxial pressing of Li₃N powder (Sigma-Aldrich; \geq 99.5%) inside an Ar-filled glovebox at 100 kN for 3 min was followed by isostatic pressing at 440 bar for 3 min. Sintering of the pellet buried in parent powder at 600 °C with \pm 10 °C min⁻¹ heating rate for 6 h under 50 standard cubic centimetres per minute of ultra-pure N₂ led to a pellet with a diameter of 28 \pm 1 mm and a theoretical density of >85%. Exposure of this material to the ambient atmosphere was minimized to prevent potential degradation and chemical reaction in air before PLD system entry.

Thin-film processing of the multilayered electrolyte. Thin-film multilayers of repeating layer sequences of Li₃N and Li_{6,25}Al_{0.25}La₃Zr₂O₁₂ were deposited on (001)-orientated MgO substrates (Crystec) by PLD. The equipment for deposition (PLD; Surface) included a KrF excimer laser with a wavelength of 248 nm at a frequency of 5 or 10 Hz (for Li₃N and Li_{6.25}Al_{0.25}La₃Zr₂O₁₂, respectively). Both PLD targets were thoroughly polished before transfer to the vacuum chamber.

The target-to-substrate distance was kept constant at 70 mm, and background oxygen partial pressures during deposition were fixed at 0.013 hPa for Li625Al025La3Zr2O12 layers and 0.04 hPa for Li3N layers. Each deposited film consisted of nine individual layers. Five were Li625Al025La3Zr2O12 at a film thickness of 50 ± 5 nm. Alternating between them were four intermediate layers of Li₃N with a film thickness of 25 ± 3 nm. The results of changing the Li_{6.25}Al_{0.25}La₃Zr₂O₁₂-to-Li₃N thickness ratio to reduce the content of Li₃N are shown in Supplementary Fig. 5. Regardless of the annealing strategy and active lithiation of the garnet phase, all films were cooled to room temperature under 0.04 hPa O2 inside the PLD vacuum chamber. Li nitride layers were included in the multilayer thin films to overlithiate the Li-garnet multilayer constituents following the decomposition of Li₃N to Li after the annealing stage. To achieve this, we investigated two strategies with slightly different implications for film growth, chemical and structural evolution: (1) we used a deposition temperature of 660 °C; or (2) we cooled the film after deposition at 300 °C to room temperature then subjected it to post-annealing at 660 °C under pure oxygen externally.

Structural characterization of the target and thin-film material. The electrolyte target pellet was characterized by XRD (Bruker D8) with Cu K α radiation in Bragg–Brentano geometry. An extraction voltage of 40 kV at a current of 40 mA was used in the range 2θ =25–55° (see Supplementary Fig. 6 for more details on the phase analysis and literature comparison). Thin-film samples on (001)-orientated MgO were investigated at room temperature using a thin-film XRD diffractometer machine (Bruker D8 DISCOVER) operating with Cu K α radiation in Bragg–Brentano geometry in the range 2θ =15–32.5°. Microstructures of the as-deposited and post-annealed thin films were investigated by cross-sectional SEM (Leo 1530).

Ex situ and in situ Raman spectroscopy. After deposition of the thin films, various post-annealing treatments were performed to analyse the formation of different crystallographic phases as a function of the thermal treatment. To probe the phase evolution of the multilayer to single-phase Li-garnet films, we carried out in situ and ex situ heating/cooling-controlled Raman spectroscopy (WITec) using a heating chamber equipped with an optical window and an active water cooling system (Linkam T95-HT; Linkam Scientific) operating inside a temperature window of 300–980 °C at a rate of ± 10 °C min⁻¹. First, for the ex situ measurements, the as-deposited thin-film samples were heated to the desired temperature under pure O₂ flow, then measured after they had cooled down to room temperature. Optical Raman spectroscopy was conducted with a solid-state laser at a power of 10 mW and a wavelength of 532 nm, with a spectral resolution of 0.7 cm⁻¹ used for near-order structural analysis. Note that the decrease in intensity below 80 cm⁻¹ can be attributed to the edge-filter cut-off for the laser wavelength used, and is therefore attributed to an equipment artefact.

The same experiment was also conducted in situ; however, due to the elevated temperature, increased background noise was present. We therefore focus on ex situ data in this study (but see Supplementary Fig. 7 for further details). In situ Raman spectroscopy was performed to assess the annealing times required for phase formation, and indicated that 15 min annealing was sufficient. We therefore fixed 15 min as the annealing time for the ex situ experiments.

Thin-film negative-ion TOF-SIMS for elemental analysis. To investigate the elemental distribution across the multilayered Li–garnet/Li-nitride thin-film structures, an annealed film in the single Li–garnet phase was analysed using TOF-SIMS (TOF.SIMS; ION-TOF). Special focus was placed on the analysis of nitrogen, to clarify the distribution and content of nitrogen residues released from the dissolved Li₃N layers towards the Li–garnet ones. Since nitrogen is mostly charged negatively, we chose to use negative-ion TOF-SIMS (rather than the more commonly used positive-ion TOF-SIMS). For the TOF-SIMS analysis, a primary beam with 25 keV Bi⁺ primary ions at a measured current of 3.52 pA was used. The sputtering was performed with 2 keV Cs⁺ ions on a grater of 500 μ m \times 500 μ m. The analysis area was 200 μ m \times 200 μ m. The profiling was performed by alternating 2.6 s of sputtering and 100 μ s of analysing, with 0.5 s of waiting and stabilization time in

between. The raster analysis area was random, with a pixel resolution of 128 \times 128. The emission current was set to 1 μ A during the entire measurement.

Characterization of thin-film transport properties. EIS (Zahner IM6) was performed to study impedance and ionic transport processes. Electrodes were fabricated in an in-plane geometry using a shadow mask to sputter Pt electrodes on the Li-garnet films. In the case of Arrhenius-type activated transport properties, temperature was modulated through an atmosphere-controlled and heated Linkam chamber (Linkam Scientific) to measure electrical and electrochemical characteristics in a temperature window of 50-400 °C under a constant dry synthetic air flow of 50 standard cubic centimetres per minute. Pt electrodes were deposited via electron beam evaporation (Plassys MEB 550) on the Li-garnet films. Electrode thicknesses of 100 ± 1 nm were confirmed by quartz crystal frequency thickness monitoring, and shaped through a stainless steel shadow mask to strips with dimensions of $3.25 \text{ mm} \times 0.5 \text{ mm}$ at an electrode separation of 0.25 mm(see inset in Fig. 6a). Before any EIS measurements were performed, we kept an isothermal hold of 15 min to equilibrate the substrate and film. EIS measurements were carried out for the frequency range of 1 Hz to 1 MHz at an a.c. amplitude of 50 mV, and the data were analysed using ZView 3.4F and OriginPro 9.1 software.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Received: 16 August 2018; Accepted: 21 March 2019; Published online: 20 May 2019

References

- Janek, J. & Zeier, W. G. A solid future for battery development. *Nat. Energy* 1, 16141 (2016).
- Thompson, T. et al. Electrochemical window of the Li-ion solid electrolyte Li₂La₃Zr₂O₁₂. ACS Energy Lett. 2, 462–468 (2017).
- Thangadurai, V., Narayanan, S. & Pinzaru, D. Garnet-type solid-state fast Li ion conductors for Li batteries: critical review. *Chem. Soc. Rev.* 43, 4714–4727 (2014).
- Murugan, R., Thangadurai, V. & Weppner, W. Fast lithium ion conduction in garnet-type Li₇La₃Zr₂O₁₂. Angew. Chem. Int. Ed. 46, 7778–7781 (2007).
- 5. Kamaya, N. et al. A lithium superionic conductor. *Nat. Mater.* 10, 682–686 (2011).
- Kato, Y. et al. High-power all-solid-state batteries using sulfide superionic conductors. *Nat. Energy* 1, 16030 (2016).
- Kanno, R. & Murayama, M. Lithium ionic conductor thio-LISICON: the Li₂S GeS₂ P₂S₅ system. J. Electrochem. Soc. 148, A742–A746 (2001).
- Park, K. H. et al. Design strategies, practical considerations, and new solution processes of sulfide solid electrolytes for all-solid-state batteries. *Adv. Energy Mater.* 8, 1800035 (2018).
- Yamane, H. et al. Crystal structure of a superionic conductor, Li₇P₃S₁₁. Solid State Ion. 178, 1163–1167 (2007).
- Mizuno, F., Hayashi, A., Tadanaga, K. & Tatsumisago, M. New, highly ion-conductive crystals precipitated from Li₂S-P₂S₅ glasses. *Adv. Mater.* 17, 918–921 (2005).
- Seino, Y., Ota, T., Takada, K., Hayashi, A. & Tatsumisago, M. A sulphide lithium super ion conductor is superior to liquid ion conductors for use in rechargeable batteries. *Energy Environ. Sci.* 7, 627–631 (2014).
- Richards, W. D., Miara, L. J., Wang, Y., Kim, J. C. & Ceder, G. Interface stability in solid-state batteries. *Chem. Mater.* 28, 266–273 (2016).
- 13. Porz, L. et al. Mechanism of lithium metal penetration through inorganic solid electrolytes. *Adv. Energy Mater.* 7, 1701003 (2017).
- Ma, C. et al. Interfacial stability of Li metal–solid electrolyte elucidated via in situ electron microscopy. *Nano Lett.* 16, 7030–7036 (2016).
- Awaka, J. et al. Crystal structure of fast lithium-ion-conducting cubic Li₇La₃Zr₂O₁₂. Chem. Lett. 40, 60–62 (2011).
- Wagner, R. et al. Crystal structure of garnet-related Li-ion conductor Li_{7-3x}Ga_x La₃Zr₂O₁₂: fast Li-ion conduction caused by a different cubic modification? *Chem. Mater.* 28, 1861–1871 (2016).
- Wagner, R. et al. Fast Li-ion-conducting garnet-related Li_{7-3x}Fe_xLa₃Zr₂O₁₂ with uncommon *I*43*d* structure. *Chem. Mater.* 28, 5943–5951 (2016).
- Bernuy-Lopez, C. et al. Atmosphere controlled processing of Ga-substituted garnets for high Li-ion conductivity ceramics. *Chem. Mater.* 26, 3610–3617 (2014).
- Wolfenstine, J., Ratchford, J., Rangasamy, E., Sakamoto, J. & Allen, J. L. Synthesis and high Li-ion conductivity of Ga-stabilized cubic Li₇La₃Zr₂O₁₂. *Mater. Chem. Phys.* 134, 571–575 (2012).
- Rettenwander, D. et al. Crystal chemistry of "Li₂La₃Zr₂O₁₂" garnet doped with Al, Ga, and Fe: a short review on local structures as revealed by NMR and Mößbauer spectroscopy studies. *Eur. J. Mineral.* 28, 619–629 (2016).
- Rettenwander, D. et al. Structural and electrochemical consequences of Al and Ga cosubstitution in Li₇La₃Zr₂O₁₂ solid electrolytes. *Chem. Mater.* 28, 2384–2392 (2016).

NATURE ENERGY

- 22. Howard, M. A. et al. Synthesis, conductivity and structural aspects of Nd_3Zr_2 $Li_{7-3x}Al_xO_{12}.$ J. Mater. Chem. A 1, 14013–14022 (2013).
- 23. Dumon, A., Huang, M., Shen, Y. & Nan, C.-W. High Li ion conductivity in strontium doped Li₂La₂Zr₂O₁₂ garnet. *Solid State Ion.* **243**, 36–41 (2013).
- 24. Zeier, W. G., Zhou, S., Lopez-Bermudez, B., Page, K. & Melot, B. C. Dependence of the Li-ion conductivity and activation energies on the crystal structure and ionic radii in Li₆MLa₂Ta₂O₁₂. ACS Appl. Mater. Interfaces 6, 10900–10907 (2014).
- 25. Li, Y., Han, J.-T., Wang, C.-A., Xie, H. & Goodenough, J. B. Optimizing Li⁺ conductivity in a garnet framework. *J. Mater. Chem.* **22**, 15357–15361 (2012).
- Rettenwander, D. et al. Synthesis, crystal chemistry, and electrochemical properties of Li_{7-2x}La₃Zr_{2-x}Mo_xO₁₂ (x=0.1-0.4): stabilization of the cubic garnet polymorph via substitution of Zr⁴⁺ by Mo⁶⁺. *Inorg. Chem.* 54, 10440–10449 (2015).
- Allen, J. L., Wolfenstine, J., Rangasamy, E. & Sakamoto, J. Effect of substitution (Ta, Al, Ga) on the conductivity of Li₇La₃Zr₂O₁₂. *J. Power Sources* 206, 315–319 (2012).
- Yi, E., Wang, W., Kieffer, J. & Laine, R. M. Flame made nanoparticles permit processing of dense, flexible, Li⁺ conducting ceramic electrolyte thin films of cubic-Li₂La₃Zr₂O₁₂ (c-LLZO). J. Mater. Chem. A 4, 12947–12954 (2016).
- 29. Fu, K. Toward garnet electrolyte-based Li metal batteries: an ultrathin, highly effective, artificial solid-state electrolyte/metallic Li interface. *Sci. Adv.* **3**, e1601659 (2017).
- Fu, K. Three-dimensional bilayer garnet solid electrolyte based high energy density lithium metal-sulfur batteries. *Energy Environ. Sci.* 10, 1568–1575 (2017).
- Miara, L. et al. About the compatibility between high voltage spinel cathode materials and solid oxide electrolytes as a function of temperature. ACS Appl. Mater. Interfaces 8, 26842–26850 (2016).
- 32. Hirayama, M., Kim, K., Toujigamori, T., Cho, W. & Kanno, R. Epitaxial growth and electrochemical properties of Li₄Ti₅O₁₂ thin-film lithium battery anodes. *Dalton Trans.* 40, 2882–2887 (2011).
- 33. Lu, Z. G., Cheng, H., Lo, M. F. & Chung, C. Y. Pulsed laser deposition and electrochemical characterization of LiFePO₄–Ag composite thin films. *Adv. Funct. Mater.* 17, 3885–3896 (2007).
- 34. Lacivita, V. et al. Resolving the amorphous structure of lithium phosphorus oxynitride (LiPON). J. Am. Chem. Soc. 140, 11029–11038 (2018).
- Yu, X., Bates, J. B., Jellison, G. E. & Hart, F. X. A stable thin-film lithium electrolyte: lithium phosphorus oxynitride. *J. Electrochem. Soc.* 144, 524–532 (1997).
- 36. Zhu, Y., He, X. & Mo, Y. Origin of outstanding stability in the lithium solid electrolyte materials: insights from thermodynamic analyses based on first-principles calculations. ACS Appl. Mater. Interfaces 7, 23685–23693 (2015).
- Oudenhoven, J. F. M., Baggetto, L. & Notten, P. H. L. All-solid-state lithium-ion microbatteries: a review of various three-dimensional concepts. *Adv. Energy Mater.* 1, 10–33 (2011).
- Bates, J. B., Dudney, N. J., Neudecker, B., Ueda, A. & Evans, C. D. Thin-film lithium and lithium-ion batteries. *Solid State Ion.* 135, 33–45 (2000).
- 39. Li, J., Ma, C., Chi, M., Liang, C. & Dudney, N. J. Solid electrolyte: the key for high-voltage lithium batteries. *Adv. Energy Mater.* **5**, 1401408 (2015).
- 40. Patil, A. et al. Issue and challenges facing rechargeable thin film lithium batteries. *Mater. Res. Bull.* **43**, 1913–1942 (2008).
- Han, X. et al. Negating interfacial impedance in garnet-based solid-state Li metal batteries. *Nat. Mater.* 16, 572–579 (2017).
- Schwöbel, A., Hausbrand, R. & Jaegermann, W. Interface reactions between LiPON and lithium studied by in-situ X-ray photoemission. *Solid State Ion.* 273, 51–54 (2015).
- 43. Schichtel, P. et al. On the impedance and phase transition of thin film all-solid-state batteries based on the $\rm Li_4Ti_5O_{12}$ system. J. Power Sources **360**, 593–604 (2017).
- 44. Dai, J., Yang, C., Wang, C., Pastel, G. & Hu, L. Interface engineering for garnet-based solid-state lithium-metal batteries: materials, structures, and characterization. *Adv. Mater.* **30**, 1802068 (2018).
- Rawlence, M. et al. Effect of gallium substitution on lithium-ion conductivity and phase evolution in sputtered Li_{7-3x}Ga_xLa₃Zr₂O₁₂ thin films. ACS Appl. Mater. Interfaces 10, 13720–13728 (2018).
- Kalita, D. J., Lee, S. H., Lee, K. S., Ko, D. H. & Yoon, Y. S. Ionic conductivity properties of amorphous Li–La–Zr–O solid electrolyte for thin film batteries. *Solid State Ion.* 229, 14–19 (2012).
- Nong, J., Xu, H., Yu, Z., Zhu, G. & Yu, A. Properties and preparation of Li–La–Ti–Zr–O thin film electrolyte. *Mater. Lett.* 154, 167–169 (2015).
- 48. Tan, J. & Tiwari, A. Fabrication and characterization of Li₂La₃Zr₂O₁₂ thin films for lithium ion battery. *ECS Solid State Lett.* **1**, Q57–Q60 (2012).
- Kim, S., Hirayama, M., Taminato, S. & Kanno, R. Epitaxial growth and lithium ion conductivity of lithium-oxide garnet for an all solid-state battery electrolyte. *Dalton Trans.* 42, 13112–13117 (2013).
- Garbayo, I. et al. Glass-type polyamorphism in Li-garnet thin film solid state battery conductors. *Adv. Energy Mater.* 8, 1702265 (2018).

- Park, J. S. et al. Effects of crystallinity and impurities on the electrical conductivity of Li-La-Zr-O thin films. *Thin Solid Films* 576, 55-60 (2015).
- Katsui, H. & Goto, T. Preparation of cubic and tetragonal Li₂La₃Zr₂O₁₂ film by metal organic chemical vapor deposition. *Thin Solid Films* 584, 130–134 (2015).
- Tadanaga, K. et al. Preparation of lithium ion conductive Al-doped Li₇La₃Zr₂O₁₂ thin films by a sol-gel process. J. Power Sources 273, 844–847 (2015).
- Bitzer, M., Van Gestel, T., Uhlenbruck, S. & Buchkremer, H.-P. Sol-gel synthesis of thin solid Li₂La₃Zr₂O₁₂ electrolyte films for Li-ion batteries. *Thin Solid Films* 615, 128–134 (2016).
- Chen, R.-J. et al. Sol-gel derived Li-La-Zr-O thin films as solid electrolytes for lithium-ion batteries. J. Mater. Chem. A 2, 13277-13282 (2014).
- Rawlence, M., Garbayo, I., Buecheler, S. & Rupp, J. L. M. On the chemical stability of post-lithiated garnet Al-stabilized Li₂La₃Zr₂O₁₂ solid state electrolyte thin films. *Nanoscale* 8, 14746–14753 (2016).
- El Shinawi, H. & Janek, J. Stabilization of cubic lithium-stuffed garnets of the type "Li,La₃Zr₂O₁₂" by addition of gallium. *J. Power Sources* 225, 13–19 (2013).
- Buschmann, H. et al. Structure and dynamics of the fast lithium ion conductor "Li₂La₃Zr₂O₁₂". *Phys. Chem. Chem. Phys.* 13, 19378–19392 (2011).
- 59. Rettenwander, D. et al. Site occupation of Ga and Al in stabilized cubic Li_{7-3(x+y)}Ga_xAl_yLa₃Zr₂O₁₂ garnets as deduced from ²⁷Al and ⁷¹Ga MAS NMR at ultrahigh magnetic fields. *Chem. Mater.* **27**, 3135–3142 (2015).
- 60. Rettenwander, D., Geiger, C. A., Tribus, M., Tropper, P. & Amthauer, G. A synthesis and crystal chemical study of the fast ion conductor Li_{7-3x}Ga_xLa₅Zr ₂O₁₂ with x=0.08 to 0.84. *Inorg. Chem.* 53, 6264–6269 (2014).
- Rettenwander, D. et al. DFT study of the role of Al³⁺ in the fast ion-conductor Li_{7-3x}Al³⁺_xLa₃Zr₂O₁₂ garnet. *Chem. Mater.* 26, 2617–2623 (2014).
- Wachter-Welzl, A. et al. The origin of conductivity variations in Al-stabilized Li₇La₃Zr₂O₁₂ ceramics. *Solid State Ion.* **319**, 203–208 (2018).
- Chandrasekhar, H. R., Bhattacharya, G., Migoni, R. & Bilz, H. Infrared and Raman spectra and lattice dynamics of the superionic conductor Li₃N. *Phys. Rev. B* 17, 884–893 (1978).
- Tietz, F., Wegener, T., Gerhards, M. T., Giarola, M. & Mariotto, G. Synthesis and Raman micro-spectroscopy investigation of Li₂La₃Zr₂O₁₂. *Solid State Ion.* 230, 77–82 (2013).
- Larraz, G., Orera, A. & Sanjuán, M. L. Cubic phases of garnet-type Li₇La₃Zr₂O₁₂: the role of hydration. *J. Mater. Chem. A* 1, 11419–11428 (2013).
- 66. Kong, L. et al. A novel chemical route to prepare La₂Zr₂O₇ pyrochlore. J. Am. Ceram. Soc. **96**, 935–941 (2013).
- Xie, H., Alonso, J. A., Li, Y., Fernández-Díaz, M. T. & Goodenough, J. B. Lithium distribution in aluminum-free cubic Li₇La₃Zr₂O₁₂. *Chem. Mater.* 23, 3587–3589 (2011).
- Cheng, L. et al. Interrelationships among grain size, surface composition, air stability, and interfacial resistance of Al-substituted Li₂La₃Zr₂O₁₂ solid electrolytes. ACS Appl. Mater. Interfaces 7, 17649–17655 (2015).
- Kubicek, M. et al. Oxygen vacancies in fast lithium-ion conducting garnets. Chem. Mater. 29, 7189–7196 (2017).
- Van den Broek, J., Afyon, S. & Rupp, J. L. M. Interface-engineered all-solidstate Li-ion batteries based on garnet-type fast Li⁺ conductors. *Adv. Energy Mater.* 6, 1600736 (2016).
- 71. Matsuda, Y. et al. Phase formation of a garnet-type lithium-ion conductor $Li_7 = -3xAl_1La_3Zr_2O_{12}$. Solid State Ion. 277, 23–29 (2015).
- Struzik, M., Garbayo, I., Pfenninger, R. & Rupp, J. L. M. A simple and fast electrochemical CO₂ sensor based on Li₇La₃Zr₂O₁₂ for environmental monitoring. *Adv. Mater.* **30**, 1804098 (2018).
- Zhang, Y. et al. Effect of lithium ion concentration on the microstructure evolution and its association with the ionic conductivity of cubic garnet-type nominal Li₂Al_{0.25}La₃Zr₂O₁₂ solid electrolytes. *Solid State Ion.* **284**, 53–60 (2016).
- Shin, D. O. et al. Synergistic multi-doping effects on the Li₇La₃Zr₂O₁₂ solid electrolyte for fast lithium ion conduction. *Sci. Rep.* 5, 18053 (2015).
- Djenadic, R. et al. Nebulized spray pyrolysis of Al-doped Li₂La₃Zr₂O₁₂ solid electrolyte for battery applications. *Solid State Ion.* 263, 49–56 (2014).
- Jonson, R. A. & McGinn, P. J. Tape casting and sintering of Li₇La₃Zr_{1.75}Nb_{0.25}Al_{0.1}O₁₂ with Li₃BO₃ additions. *Solid State Ion.* **323**, 49–55 (2018).
- Yi, E., Wang, W., Kieffer, J. & Laine, R. M. Key parameters governing the densification of cubic-Li₇La₃Zr₂O₁₂ Li⁺ conductors. *J. Power Sources* 352, 156–164 (2017).
- Bates, J. B. et al. Fabrication and characterization of amorphous lithium electrolyte thin films and rechargeable thin-film batteries. *J. Power Sources* 43, 103–110 (1993).

NATURE ENERGY

ARTICLES

79. Ohta, S., Kobayashi, T. & Asaoka, T. High lithium ionic conductivity in the garnet-type oxide $\text{Li}_{7-X}\text{La}_3(\text{Zr}_{2-X}, \text{Nb}_X)O_{12}$ (X=0–2). *J. Power Sources* **196**, 3342–3345 (2011).

Acknowledgements

The authors thank the Competence Center Energy and Mobility and Swiss Electrics for funding the project 'All solid state Li-ion batteries based on new ceramic Li-ion electrolytes' (proposal 911). J.L.M.R. thanks Lincoln Laboratory project ACC 697 (2018) and the Thomas Lord Foundation for financial support.

Author contributions

R.P., M.S., I.G. and E.S. carried out the experiments. R.P., M.S., I.G., E.S. and J.L.M.R. performed the analysis and discussed the data. R.P. and J.L.M.R. wrote the manuscript with help from all of the co-authors.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information is available for this paper at https://doi.org/10.1038/ s41560-019-0384-4.

Reprints and permissions information is available at www.nature.com/reprints.

Correspondence and requests for materials should be addressed to J.L.M.R.

Publisher's note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

© The Author(s), under exclusive licence to Springer Nature Limited 2019