Blocking lithium dendrite growth in solid-state batteries with an ultrathin amorphous Li-La-Zr-O solid electrolyte

Jordi Sastre^{1✉}, Moritz H. Futscher¹, Lea Pompizi¹, Abdessalem Aribia¹, Agnieszka Priebe², Jan Overbeck³, Michael Stiefel³, Ayodhya N. Tiwari¹ & Yaroslav E. Romanyuk^{1✉}

Lithium dendrites have become a roadblock in the realization of solid-state batteries with lithium metal as high-capacity anode. The presence of surface and bulk defects in crystalline electrolytes such as the garnet $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) facilitates the growth of these hazardous lithium filaments. Here we explore the amorphous phase of LLZO as a lithium dendrite shield owing to its grain-boundary-free microstructure, stability against lithium metal, and high electronic insulation. By tuning the lithium stoichiometry, the ionic conductivity can be increased by 4 orders of magnitude while retaining a negligible electronic conductivity. In symmetric cells, plating-stripping shows no signs of lithium penetration up to 3.2 mA cm^{-2} . The dense conformal nature of the films enables microbatteries with an electrolyte thickness of only 70 nm, which can be cycled at 10C for over 500 cycles. The application of this material as a coating on crystalline LLZO lowers the interface resistance and increases the critical current density. The effectiveness of the amorphous Li-La-Zr-O as dendrite blocking layer can accelerate the development of better solid-state batteries.

¹Laboratory for Thin Films and Photovoltaics, Empa—Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland. ²Laboratory for Mechanics of Materials and Nanostructures, Empa—Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland. ³Transport at Nanoscale Interfaces Laboratory, Empa—Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland. ✉email: jordi.sastrepellicer@empa.ch; yaroslav.romanyuk@empa.ch

Increasing power requirements in portable devices and the electrification of the automotive industry are pushing the demand for batteries with higher energy capacities and power rates. Solid-state batteries with Li metal as anode are foreseen as the next generation of energy storage devices, given the 10-fold higher capacity of Li metal with respect to traditional graphite anodes^{1,2}. Solid Li-ion conductive electrolytes, which potentially can enable such batteries, have been the subject of considerable interest in recent years. Among different families of solid electrolytes, the lithium garnet $\text{Li}_7\text{La}_3\text{ZrF}_6\text{O}_{12}$ (LLZO) can be regarded as one of the main contestants, owing to its high ionic conductivity up to $10^{-3} \text{ S cm}^{-1}$ and a wide electrochemical stability window, with stability against metallic lithium and high-potential cathodes^{3,4}. This ceramic electrolyte suffers, however, from a major drawback: Its polycrystalline nature makes it prone to the growth of lithium metal dendrites that can short circuit the battery^{5–7}. Although some debate is still ongoing in the research community, the main consensus points toward surface defects, bulk defects, and non-negligible electronic conductivities along the grain boundaries as the reason for lithium metal nucleation and dendrite growth through the solid electrolyte^{8–11}.

Recently, Kim et al. showed that a laser annealing treatment on a bulk LLZO pellet leads to the formation of an amorphized surface and this increases significantly the critical current density (CCD) and lifetime of the solid electrolyte¹². They claim that this in situ formed amorphous surface blocks electron injection and hinders the formation of Li dendrites. However, the laser annealing procedure employed in that work does not allow to control and optimize the properties of the amorphous surface layer. In contrast, ex situ coating processes such as physical vapor deposition guarantee a well-controlled composition and better homogeneity. Kalita et al. first showed the feasibility of preparing amorphous Li-La-Zr-O (aLLZO) thin films by radio frequency (RF) magnetron sputtering and characterized the ionic conductivity of this material as a function of the sputtering power, reporting values in the order of $10^{-7} \text{ S cm}^{-1}$ ¹³. Garbayo et al. further investigated the amorphism in this type of electrolyte thin films prepared by pulsed-laser deposition (PLD) and revealed a relation between the ionic conductivity, the Li concentration, and the formation of glassy states with regards to the processing temperature¹⁴. Both these studies highlighted the potential of the amorphous phase of LLZO, but did not go beyond characterizing stand-alone films nor demonstrated any application either in a thin-film battery configuration or as coating in a bulk solid-state battery. This leaves open the question whether the amorphous phase of LLZO could mitigate the formation of Li dendrites, as it has been shown for other glassy electrolyte materials like Li_3PO_4 and its oxynitride analogous (LiPON)^{15,16}.

In this work, we present a thorough investigation of the chemical structure and electrochemical properties of amorphous Ga-doped Li-La-Zr-O (aLLZO) films prepared by magnetron sputtering. By tuning the excess lithium in the films, the ionic conductivity can be increased over three orders of magnitude, up to $10^{-7} \text{ S cm}^{-1}$, while retaining a negligible electronic conductivity of $10^{-14} \text{ S cm}^{-1}$. In this way, it is possible to prepare ultrathin conformal and grain boundary-free films that can act as an injection barrier for electrons while allowing Li ions to be transported across. The stability of the ultrathin films against metallic lithium is investigated by plating-stripping lithium in half and symmetric cells, showing no interfacial degradation and resistance to short circuits at currents up to 3.2 mA cm^{-2} . Finally, the applicability of this material is demonstrated in the form of surface coating to block the formation of Li dendrites in bulk ceramic LLZO as well as ultrathin solid electrolyte for solid-state microbatteries, showing a functional battery with an electrolyte thickness of only 70 nm.

Results and discussion

Co-sputtering deposition of overlithiated Li-La-Zr-O thin films. aLLZO thin films were deposited at room temperature by magnetron sputtering from a stoichiometric $\text{Li}_{6.25}\text{Ga}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$ target. To control the lithiation level of the amorphous film, a Li_2O target was simultaneously co-sputtered (as shown in Fig. 1a), allowing to tune the mass fraction of LLZO and Li_2O by controlling the sputtering power on each target. This method was previously reported by our group for compensating lithium losses during the preparation of crystallized LLZO thin films^{17,18}. However, besides compensating lithium losses, this approach is also an effective way to tune the Li-ion concentration in the amorphous electrolyte film and modify its electrochemical properties. To characterize the morphology, composition, ionic, and electronic properties, films were prepared on Pt-coated Si and on insulating MgO single-crystal substrates. As seen in the cross-section scanning electron microscopy (SEM) image in Fig. 1b, the as-deposited films, with a thickness of $\sim 70 \text{ nm}$, are homogeneous and conformally cover the substrate. The 3D tomogram in Fig. 1c shows the elemental structure of the interior of the film reconstructed from a gas-assisted focused-ion beam time-of-flight secondary-ion mass spectroscopy (FIB-ToF-SIMS) measurement¹⁹. The measurement reveals a uniform distribution of the matrix elements (La and Zr) of the aLLZO film coated on the Pt-coated Si substrate. Detailed plots of each element's signal and a depth profile can be found in Supplementary Figs. 1 and 2.

In Fig. 1d the grazing-incidence X-ray diffractometry (GI-XRD) patterns of the aLLZO film exhibits no sharp reflections but a broad hump, in contrast to the well-defined reflections in the LLZO film crystallized at 700°C (cLLZO) that match well the reference pattern of cubic Ga-doped LLZO (ICSD 430603)²⁰. This confirms the amorphous nature of the as-deposited films, with no long-range order in the crystal structure, and is consistent with the studies of Kalita et al.¹³ and Garbayo et al.¹⁴. To further investigate the short-range order and chemical structure of the films, we performed Raman and Fourier-transform infrared (FT-IR) spectroscopy measurements on the films. The Raman spectra of the aLLZO film presented in Fig. 1e shows a predominant vibrational mode at 800 cm^{-1} that can be attributed to lithium peroxide Li_2O_2 ²¹. This indicates that the formation of lithium peroxide is more thermodynamically favorable than other lithium oxide forms under the oxygen-rich, highly energetic conditions of the sputtering deposition. Kim et al. also reported the presence of Li_2O_2 in the amorphized surface of laser-treated LLZO¹². In contrast to the Raman spectrum of the cLLZO sample, also shown in Fig. 1e, the lack of any sharp peaks characteristic of the garnet crystalline structure further evidences the amorphous disordered structure present in the aLLZO films. Figure 1f shows the FT-IR transmittance spectrum of the film. The lack of features in the region $>1000 \text{ cm}^{-1}$ indicates that the film does not contain carbonate nor hydroxy compounds. In the region $<1000 \text{ cm}^{-1}$, multiple absorptions can be observed, which can be attributed to the Zr²², La^{23,24}, and Li²⁵ bonds with oxygen. Figure 1g visualizes a possible chemical structure consisting of a glass network of disordered Zr-O and La-O chains (network former) and weakly bonded Li cations (network modifier) that can freely migrate along the glassy network, in a similar fashion to other lithium-conductive amorphous oxide electrolytes previously reported²⁶.

The role of excess Li_2O in ionic and electronic conductivity.

The ionic conductivity of the films was measured by impedance spectroscopy using silicon as substrate with Pt as back electrode and patterned Au top electrodes, as illustrated in the inset of Fig. 2a. A Nyquist plot of the impedance response of a selected

Fig. 1 Morphological, phase, and chemical characteristics of the amorphous Li-La-Zr-O ultrathin films. **a** Schematic of the co-sputtering deposition process employed to prepare overlithiated amorphous Ga-doped Li-La-Zr-O (aLLZO) coatings. **b** Cross-section SEM image of the aLLZO film on a Pt-coated Si substrate. **c** Elemental tomogram obtained by GIS-assisted FIB-ToF-SIMS of an aLLZO film deposited on Pt-coated Si. **d** GI-XRD diffractograms of an aLLZO film and a crystallized LLZO (cLLZO) film on single-crystal MgO. A reference pattern for LLZO (ICSD 430603) is included. **e** Raman spectra of the aLLZO and crystallized LLZO films on MgO single-crystal substrates. **f** FT-IR transmittance spectrum of the aLLZO film. **g** Representation of the chemical structure of the amorphous Li-La-Zr-O.

sample is shown in Fig. 2a. The characteristic semicircle arising from the electrolyte response can be modeled with a Randles equivalent circuit²⁷, yielding the electrolyte resistance from which the ionic conductivity can be derived. The tail at lower frequencies is due to the blocking nature of the electrodes and the resulting accumulation of charges at the interfaces. Figure 2b shows the extracted ionic and electronic conductivities at 300 K for samples prepared with different mass fractions of LLZO and Li₂O, regulated by the sputtering rates of both target materials. Films prepared without any Li₂O show poor ionic conductivities below $1 \times 10^{-11} \text{ S cm}^{-1}$. As the fraction of Li₂O is increased, the ionic conductivity increases by three orders of magnitude up to $1 \times 10^{-7} \text{ S cm}^{-1}$ for a mass fraction of 0.66 LLZO:Li₂O. At lower LLZO:Li₂O mass fractions, the ionic conductivity decreases again, although not as abruptly as in the low Li₂O fraction region. In contrast, the electronic conductivity remains fairly constant at $1 \times 10^{-14} \text{ S cm}^{-1}$ for different mass fractions of LLZO and Li₂O, seven orders of magnitude below the best ionic conductivity measured, and about six orders of magnitude below reported values for bulk and thin-film crystalline LLZO^{9,18}.

The ionic conductivity σ depends on both the density of mobile ions and their mobility and can be described with an Arrhenius relationship (Eq. (1)):

$$\sigma = qn\mu = qn\mu_0 \exp \frac{-E_a}{k_B T} \quad (1)$$

where E_a is the activation energy for ion migration, k_B the Boltzmann's constant, T the temperature, and μ_0 a pre-exponential factor²⁸. To determine whether the change in ion conductivity is due to a change in the density or mobility of mobile ions, we performed temperature-dependent impedance spectroscopy and current transient measurements (see “Methods” and Supplementary Figs. 3–5 for details). We find that increasing the amount of Li₂O up to 33% of the total mass increases the density of mobile ions and decreases the activation energy, which increases mobility (Fig. 2c–e). Consequently, we assign the increased ionic conductivity to an increased amount of Li⁺ ions, which reduces the electrostatic interaction between the disordered Zr–O and La–O chains and the mobile Li⁺ ions, resulting in a decrease in activation

Fig. 2 Ionic and electronic transport dynamics of the aLLZO ultrathin films. **a** Nyquist plot of the impedance spectra of an aLLZO film measured with blocking electrodes at room temperature. Inset shows a schematic of the device geometry. **b** Ionic and electronic conductivities of aLLZO films prepared with different mass fractions of LLZO and Li_2O . **c** Activation energy of the ionic conductivity, **d** mobile Li^+ concentration, and **e** Li^+ mobility of aLLZO films with different amounts of Li_2O based on the mean of three measurements each.

Fig. 3 Li stability and short-circuit resistance of the ultrathin aLLZO films. **a** Galvanostatic response of an aLLZO electrolyte film upon electrochemical transport of Li^+ from a Li counter electrode to a Pt working electrode and reversely. Numbers along the plot line indicate the points at which impedance spectroscopy measurements were carried out. **b** Nyquist plot of the impedance response of the aLLZO film in contact with Li metal after multiple steps of plating and stripping. Inset shows the evolution of the electrolyte resistance extracted from the impedance spectra. **c** Galvanostatic response of an aLLZO electrolyte film in a symmetric Li/Li cell configuration. Forward and reverse current densities ranging from 0.2 up to 3.2 mA cm^{-2} were applied in steps of 0.1 mA h cm^{-2} .

energy. This is consistent with findings on other amorphous solid electrolytes such as lithium thiophosphate and LiPON²⁹. Above a critical mass fraction, we assume that the added Li^+ ion forms aggregates, which reduce the ion conductivity, as suggested by the obtained mobile Li^+ ion density, which does not increase further after the critical mass fraction of 0.66 LLZO: Li_2O is reached.

Stability against lithium metal plating-stripping. The electrochemical stability of the aLLZO electrolyte was tested by fabricating a half-cell with Pt as a working electrode and metallic Li as a counter and reference electrode. As presented in Fig. 3a, Li^+ was slowly transported towards the Pt electrode applying a low current of $1.25 \mu\text{A cm}^{-2}$ through the cell until approaching 0 V vs. Li/Li^+ . The cell was galvanostatically cycled multiple times

while measuring the impedance after each cycle in order to monitor any possible electrochemical degradation of the electrolyte as a result of the Li redox reactions. Figure 3b shows the Nyquist plot of the impedance and the extracted electrolyte resistance measured during the plating-stripping process. The resistance of the aLLZO film slightly decreases in the first four steps, likely due to an improved interfacial contact at the electrolyte/Pt interface as Li metal gets filled in, and then it stabilizes at a constant value. The stabilization of the electrolyte resistance evidences the electrochemical stability of the aLLZO electrolyte in combination with an Li anode.

The resistance of the aLLZO electrolyte against Li dendrite formation and short circuiting was tested in a symmetrical Li/Li cell, prepared by evaporating metallic Li on sapphire, coating the Li electrode with a thin aLLZO film, and depositing a symmetric Li contact on top. The symmetric cells were cycled at increasing current densities, from 0.2 up to 3.2 mA cm⁻², for five plating-stripping cycles each. For each current density, the transferred capacity was limited to 0.1 mA h cm⁻², equivalent to an Li thickness of 250 nm. Figure 3c shows the voltage response of the symmetric cells upon Li stripping-plating at different current densities. The cell polarization remains stable and scales with the current density without any sign of large voltage fluctuations or drops to 0 V, which would indicate short-circuit formation. The area-specific resistance of the symmetric cell is shown in Supplementary Fig. 6.

Dendrite-blocking coating on bulk crystalline LLZO. The stability against Li metal, dendrite penetration robustness, negligible electronic conductivity of 10⁻¹⁴ S cm⁻¹, and good ionic conduction of the aLLZO ultrathin films here investigated can also be applied as an interface coating for bulk ceramic solid electrolytes, which are employed to fabricate bulk solid-state batteries. Due to the low electronic conductivity, the aLLZO interlayer can prevent the injection of electrons¹⁰, while allowing a fast ionic transport across the interface. Indeed, the inclusion of a 10 nm layer of aLLZO with an electronic conductivity of 1 × 10⁻¹⁴ S cm⁻¹ results in a resistance for electrons of ~100 MΩ cm², which is two orders of magnitude higher than the 1 MΩ cm² of a 0.5-mm-thick LLZO with an electronic conductivity of 5 × 10⁻⁸ S cm⁻¹, as determined by Han et al.⁹. In addition, the amorphous nature of the coating promotes a more homogeneous lithium nucleation at the anode interface, reducing the formation of voids and therefore leading to lower interface resistance and a more uniform distribution of the current.

To test the potential application of the ultrathin aLLZO as interface coating to hinder lithium dendrite formation in bulk ceramic electrolyte, symmetrical cells with crystalline Ga-doped LLZO pellets coated on both sides with a 10-nm aLLZO film were built as shown in Fig. 4a. Figure 4b shows the Nyquist plot of the impedance spectroscopy measurements at room temperature of both the aLLZO-coated and reference (uncoated) symmetric cells. The intercept with the real axis at high frequencies is attributed to the ionic conduction through the bulk. The value for the bulk resistance (~25 Ω cm²) is consistent with the bulk ionic conductivity of the LLZO pellet (~1 × 10⁻³ S cm⁻¹). The semicircles that appear in the Nyquist plot can be attributed to the interface resistance. In the case of the aLLZO-coated cell, one can estimate an interfacial resistance of 3.5 Ω cm², about half the value of that of the uncoated reference. The improved interface resistance can be attributed to an enhanced wettability of the Li metal due to a higher binding energy with the aLLZO coating. This effect is similar to what has been observed even with nonionic conductive coatings like Al₂O₃³⁰.

Li plating-stripping experiments were carried out by galvanostatically cycling the symmetric cells with current densities ranging from 5 μA cm⁻² up to 5.1 mA cm⁻² in steps of 30 min. The measurements were carried out at room temperature and without external pressure, apart from that of the alligator clamp used to contact the cell. Figure 4c, d shows the voltage response and applied current density (dashed line) over time. As expected from the lower interfacial resistance, the aLLZO-coated sample shows significant lower overpotentials than the uncoated one. For example, at 40 μA cm⁻², the overpotential of the aLLZO-coated cell (2.5 mV) is half that of the uncoated reference cell. From 0.16 mA cm⁻², the overpotential of the uncoated cell starts to grow uncontrollably as a result of void formation at the Li/LLZO interface and lower contact area⁵. Eventually, at a current density of 0.64 mA cm⁻², the uncoated cell shunts due to dendrite growth across the ceramic electrolyte. The CCD can be regarded as the upper value of current density applied before a short circuit due to lithium metal penetration is formed³¹. Following this definition, the bare LLZO cell has a CCD of 0.32 mA cm⁻². In the aLLZO-coated cell, the overpotential profile remains stable up to a current density of 0.64 mA cm⁻² and the cell does not start to form microshorts until the applied current density reaches 2.6 mA cm⁻². The CCD of the aLLZO-coated sample is 1.3 mA cm⁻². This experiment proves that the aLLZO coating improves the interface contact between lithium metal and crystalline LLZO and increases the CCD by a factor of 4.

To visualize the formation of Li dendrites, an in-plane plating-stripping experiment with a crystalline LLZO pellet was carried out as illustrated in Fig. 5a. Half of the LLZO pellet surface was coated with a 10-nm aLLZO film (left side) and the other half was left uncoated as the reference (right side). Li metal/Cu contacts were deposited by thermal evaporation with different lateral separations, as seen in the optical image in Fig. 5a. As demonstrated by Kazyak et al.³², such an in-plane geometry is useful to visualize by in-operando microscopy the formation and propagation of Li dendrites in solid electrolytes. In our case, it becomes useful to assess the effect of the aLLZO coating on the formation of Li dendrites.

Lithium plating-stripping was performed by applying currents in forward and reverse direction between both Li metal contacts. The current and voltage curves as a function of time are presented in Fig. 5b, c. The current density was increased stepwise from 50 μA cm⁻² to 3.2 mA cm⁻² for a total charge transfer of 25 μA h cm⁻², with 15 min rest steps in between. During the plating-stripping process, the surface of the pellet was monitored with an optical microscope in order to observe the nucleation and growth of Li filaments in the bulk ceramic electrolyte. As seen in the voltage plot, high overpotentials are present in both the uncoated and aLLZO-coated test areas, which can be attributed to the geometry of the in-plane measurement and likely poor contact of the evaporated Li due to the lack of externally applied pressure. In the voltage profile of the uncoated pellet, one can observe a continuous spiky behavior, even at the lowest current density, which seems to be related to microshorts (soft short circuits) forming across the Li contacts. This phenomenon can be explained by the high polarization leading to a massive injection of electrons that promotes the nucleation of Li metal in the interior of the ceramic electrolyte. The spiky behavior of the uncoated site repeats itself with increasing current densities and eventually leads to irreversible shunting of the test device at a current density of 1.6 mA cm⁻². In contrast, in the aLLZO-coated side, the voltage profile remains stable throughout the plating-stripping process. At high current densities and despite the enormous overpotential, the aLLZO-coated site maintains a stable polarization. The growth of Li filaments and shunting can also be observed in the in-operando optical microscope images

Fig. 4 Ultrathin aLLZO coating inhibits the growth of Li dendrites in bulk crystalline LLZO electrolyte. **a** Schematic of the through-plane Li/aLLZO/LLZO/aLLZO/Li configuration employed to determine the critical current density. **b** Nyquist plot of the impedance response of the uncoated and aLLZO-coated LLZO pellets. **c, d** Applied current density (dashed line) and voltage response (solid lines) during symmetric galvanostatic cycling of the uncoated and aLLZO-coated LLZO pellets at RT without external pressure applied. Forward and reverse current densities ranging from $5 \mu\text{A cm}^{-2}$ up to 5.1 mA cm^{-2} were applied in steps of 30 min.

recorded during the cycling process (Fig. 5d). In the initial state, the space between the Li metal contacts on both the coated and uncoated sides is free of any inhomogeneity. After reaching the plating-stripping current of 1.6 mA cm^{-2} , the uncoated side shows a large Li dendrite connecting both contacts and some branches of metallic Li that have grown around the edge of the contacts. Conversely, the aLLZO-coated site remains free of Li metal filaments. This experiment demonstrates that the aLLZO coating can prevent the nucleation of Li metal inside the ceramic LLZO and hinder the growth of Li metal dendrites that lead to short circuiting of the cell.

Ultrathin solid electrolyte for microbatteries. The aLLZO films investigated here can also be utilized as ultrathin electrolyte for thin-film solid-state batteries. Microbatteries have been investigated since the early 1990s and have been developed into a commercial product for powering low-power devices such as IoT sensors, wearables, etc.³³. These devices consist of thin-film electrodes (commonly LiCoO_2 (LCO) as cathode and Li metal as anode) and generally employ LiPON films in the range of microns as solid-state electrolyte.

We fabricated a thin-film battery employing sputtered thin-film LCO as cathode material and evaporated Li metal as anode. A 70-nm-thin aLLZO film was employed as a solid electrolyte between the cathode and anode films. To prevent oxidative degradation of the electrolyte in contact with the LCO (see cyclovoltammetry measurement in Supplementary Fig. 7), a 10-nm LiNbO_3 coating was applied by sputtering to the cathode film prior to the aLLZO deposition. The excess Li in the form of Li_2O added to the aLLZO films is likely the cause for the poor electrochemical stability at high potentials. According to first-principle calculations performed by Zhu et al.³⁴, Li_2O is stable against metallic lithium but decomposes at voltages $>3 \text{ V}$ vs. Li/Li^+ . Figure 6a shows a cross-section SEM image of the microbattery, in which the ultrathin aLLZO electrolyte is shown to conformably cover the LCO cathode film and separate it from

the Li metal anode. Note that the poor microstructure of the Li metal is due to the damage produced by the Ga-ion FIB employed to prepare the cross-section³⁵.

Figure 6b shows the voltage curves of the microbattery upon charge-discharge at current densities ranging from $22 \mu\text{A cm}^{-2}$ (1C) to $220 \mu\text{A cm}^{-2}$ (10C). The voltage profiles show the characteristic plateau at 3.9 V vs. Li/Li^+ characteristic of the cathode material employed, indicating unhindered lithium intercalation/deintercalation in and out of the cathode. At lower C rates, overpotentials are moderate ($\sim 50 \text{ mV}$), and as expected, they increase with increasing C rate. The relation between the discharge capacity and the C rate is presented in Fig. 6c. At 1C, the microbattery shows a discharge capacity of $55 \mu\text{A h cm}^{-2} \mu\text{m}^{-1}$, which is equivalent to $\sim 110 \text{ mA h g}^{-1}$, assuming an ideal density of the cathode film. At 10C, the microbattery shows a capacity of $39 \mu\text{A h cm}^{-2} \mu\text{m}^{-1}$, a 70% of the capacity at 1C.

To demonstrate the robustness of the ultrathin aLLZO electrolyte, the thin-film battery was cycled with a current density of 0.2 mA cm^{-2} (10C) for 500 cycles, as shown in Fig. 6d. After 500 cycles ($\sim 100 \text{ h}$ operation), the capacity degrades to $\sim 60\%$ of the initial capacity while retaining a stable Coulombic efficiency of $\sim 97.6\%$. The capacity fading is likely due to interfacial degradation of the electrolyte on the cathode side, but the cell does not show any signs of short circuiting, evidencing high resistance of the aLLZO electrolyte to lithium dendrite formation despite its ultrathin thickness. The high-potential and long-term operation of a microbattery with such an ultrathin sputtered electrolyte is unprecedented and can only be compared to the 90-nm-thick LiPON electrolyte films prepared by atomic layer deposition (ALD) in the work of Pearse et al.³⁶.

Conclusions

We demonstrate that the amorphous phase of garnet LLZO can act as an ultrathin ($<100 \text{ nm}$) solid electrolyte for solid-state microbatteries as well as a coating for increasing the robustness to lithium dendrite growth in bulk ceramic electrolytes. The

Fig. 5 Visualizing dendrite growth in bulk crystalline LLZO electrolyte.

a Optical picture and schematic of the in-plane geometry employed to visualize the formation of dendrites upon Li plating-stripping. Half of a 10 × 10 mm² LLZO pellet was coated with 10 nm aLLZO and Li metal contacts with Cu as current collector were deposited on both sides of the pellet. **b** Current and voltage response during symmetric galvanostatic cycling between two Li metal contacts. Forward and reverse current densities ranging from 0.05 up to 3.2 mA cm⁻² were applied in steps of 25 μ A h cm⁻². **c** Zoom-in of the polarization in the uncoated and coated sites at 0.05 and 1.6 mA cm⁻². **d** Optical images of the LLZO pellet surface on the uncoated and aLLZO-coated side recorded at the beginning of the plating-stripping process and after reaching a current density of 1.6 mA cm⁻². Magnified image shows a Li filament short circuiting the Li contacts in the uncoated side of the pellet.

fabrication process presented in this work allows to increase the lithiation of the films and to enhance their ionic conductivity to values approaching 10⁻⁷ S cm⁻¹. The amorphous nature of the sputtered films results in a grain boundary-free ultrathin electrolyte that can withstand high current densities without short circuiting due to lithium filament penetration. Moreover, the low electronic conductivity of 10⁻¹⁴ S cm⁻¹ blocks injection of electrons, preventing the nucleation of Li metal inside a coated bulk ceramic electrolyte. We believe that aLLZO coatings can have a

significant impact in the development of better solid-state batteries with ceramic electrolytes and lithium metal as anode, allowing higher fast-discharge currents and increasing their lifetime. Future work should focus in implementing and testing this coating material in bulk solid-state batteries.

Methods

aLLZO sputtering deposition. aLLZO films were deposited at room temperature in an RF magnetron sputtering system (Orion, AJA International Inc.) with a confocal off-axis target configuration. A Li_{6.25}Ga_{0.25}La₃Zr₂O₁₂ target was co-sputtered simultaneously with a Li₂O target (Toshiba Manufacturing Co.) in order to overlithiate the films. The sputtering process was performed at 0.3 Pa using a gas flow of 50 s.c.c.m. Ar and 1 s.c.c.m. Ar:O₂. The deposition rate of each target was controlled independently via the sputtering power and monitored using a quartz crystal microbalance sensor. The deposition time was adjusted to obtain films with thicknesses in the range of 50–100 nm with typical times not exceeding 1 h. Optimized films were prepared with a sputtering power of 1.5 W cm⁻² on the LLZO target and 7.6 W cm⁻² on the Li₂O target and had a thickness of 70 nm. As a reference for crystalline LLZO, films prepared as previously shown by our group were used¹⁸.

Substrates and metal electrodes. Different types of substrates were employed for the different characterization techniques. XRD, Raman and FT-IR measurements were carried out on aLLZO films deposited on (1 0 0)-oriented single-crystal MgO substrates (Jiangyin Maideli Advanced Materials Co., Ltd). Impedance spectroscopy and transient electrical measurements were carried out on aLLZO films deposited on Pt-coated Si substrates. Single-side polished (1 0 0) Si wafers (University Wafer) were first coated with a 60-nm MgO film to improve adhesion and block Li-ion migration into the Si wafer. MgO was deposited from an MgO target (Stanford Advanced Materials) in a CT200 magnetron sputtering cluster tool (Alliance Concept). The sputtering was carried out with a power of 3.1 W cm⁻², a gas flow of 60 s.c.c.m. Ar + 0.5 s.c.c.m. O₂, and a chamber pressure of 0.6 Pa. The wafers were later annealed at 850 °C for 3 h in air. As back electrode, a 20 nm Ti adhesion layer followed by a 300-nm Pt layer were deposited by RF magnetron sputtering in an Orion sputtering system. The Ti and Pt targets (Plasmaterials Inc.) were sputtered with a power of 3 W cm⁻² with a 50 s.c.c.m. Ar flow and a pressure of 0.3 Pa. After depositing the aLLZO films, 50 nm Au contacts with a diameter of 1 mm were deposited on top by thermal evaporation (Nexdep, Angstrom Engineering Inc.) from Au pellets (Kurt J. Lesker Company) with a rate of ~1 Å s⁻¹ at a pressure of ~1 × 10⁻⁴ Pa. For the Li/Pt half-cell measurements, the same type of Pt-coated sapphire substrate was employed and an aLLZO film with about double the standard thickness was deposited on top. On top of the aLLZO film, 5 μ m metallic Li contacts with a diameter of 1 mm were thermally evaporated from a Radak source in an Angstrom Nexdep thermal evaporator. Li granules (Alfa Aesar) were evaporated at a rate of 25 Å s⁻¹ with a background pressure of 1 × 10⁻⁴ Pa. Following the Li evaporation, 100 nm Cu electrodes were also deposited by thermal evaporation at a rate of 1 Å s⁻¹ from Cu pellets (Sigma-Aldrich) without breaking the vacuum. For the Li/Li symmetric cells, instead of the Pt-coated Si substrates, a sapphire single-crystal substrate (MSE Supplies) was coated with 5 μ m Li by thermal evaporation. Sample handling and storage were done in an Ar-filled glovebox line (Inert Corp.) with O₂ and moisture levels below 0.1 p.p.m. The Orion sputtering system and Angstrom Nexdep evaporation system employed are also connected to the glovebox line, thus no exposure to air occurred at any stage of the sample preparation.

Thin-film solid-state battery. LCO with a thickness of 320 nm was deposited at room temperature by RF magnetron sputtering on a Pt-coated sapphire substrate. An LCO target from Toshiba Manufacturing Co. was sputtered with a power of 5.9 W cm⁻² and a voltage bias of 70 V applied to the substrate, at a pressure of 3 Pa and employing a gas flow of 24 s.c.c.m. Ar and 1 s.c.c.m. O₂. Films were post-annealed at 700 °C for 1 h in a tube furnace (Carbolite Gero GmbH, Co.) at atmospheric pressure with an O₂ flow. The cathode film was coated with 10 nm LiNbO₃ by reactive co-sputtering of a Nb target (Plasmaterials Inc.) and a Li₂O target (Toshiba Manufacturing Co.) in an Orion sputtering system with a power of 2.5 and 5 W cm⁻², respectively, a gas flow of 22.5 s.c.c.m. Ar and 2.5 s.c.c.m. O₂, and a chamber pressure of 0.2 Pa. More details on the fabrication and properties of the LCO thin-film cathodes can be found in the work by Filippin et al.³⁷. On top of the LCO cathode film, an aLLZO electrolyte film with a thickness of 70 nm was deposited as described above. The cells were completed with a 2 μ m Li metal anode film deposited by thermal evaporation.

Through-plane and in-plane aLLZO-coated ceramic LLZO pellets. Commercially available Li_{6.25}Ga_{0.25}La₃Zr₂O₁₂ ceramic pellets (Toshiba Manufacturing Co.) with dimensions of 10 mm × 10 mm × 0.5 mm were used for the Li stripping-plating measurements. To remove surface carbonates and other contaminants, the pellets were heat treated between sacrificial LLZO chunks at 400 °C for 3 h in a tube furnace with O₂ flow, following the procedure reported by Sharafi et al.³⁸. The O₂ employed in the heat treatment process had a purity >99.9999%, as specified by the

Fig. 6 Thin-film solid-state battery with an ultrathin aLLZO electrolyte. **a** Cross-section SEM image of the battery stack. **b** Charge-discharge curves at different C rates (1C = 22 μA cm⁻²). **c** Discharge capacity and Coulombic efficiency of the battery at different C rates. **d** Long-term cycling of the battery over 500 cycles at 10C (0.2 mA cm⁻²).

supplier. For the through-plane measurements, both sides of the pellet were coated with 10 nm aLLZO following the procedure previously described. For the in-plane measurement, half of the pellet was coated with 10 nm aLLZO and the other half was left uncoated. Lithium metal was deposited on the samples by thermal evaporation as previously described for the Li/Li symmetric cells. For the through-plane samples, a shadow mask with a diameter of 5 mm was used to define the electrode area on both sides of the pellet. For the in-plane configuration, a shadow mask with 1 mm × 2 mm openings spaced at different distances between each other was employed to define the dimensions of the in-plane Li–Cu contacts. The samples were heated to 150 °C for a few minutes to improve the contact between the Li contacts and the LLZO. The through-plane samples were sandwiched between two Cu-coated metallic spacers and contacted using an alligator clamp. The in-plane sample was contacted using tungsten microprobes.

SEM imaging. Cleaved cross-sections (Fig. 1b) were imaged with a Hitachi S-4800 field emission gun SEM using an acceleration voltage of 10 kV. FIB cuts (Fig. 6a) were performed and imaged in an FEI Helios NanoLab 660 Dual-Beam SEM and FIB system. The FIBing process was done with a Ga⁺-ion beam at an acceleration voltage of 30 kV with a polishing step at 2 kV. SEM imaging was done with an acceleration voltage of 2 kV.

FIB-ToF-SIMS. The chemical structure of the aLLZO film was characterized using ToF-SIMS^{39,40} allowing both, light and heavy, element distribution to be represented in 3D with high spatial resolution and high mass resolution. In this study, a novel method^{19,41,42} of combining an HV-compatible high-resolution TOF^{43,44} (H-TOF) from TOFWERK (Thun, Switzerland) with an in situ gas injection system (GIS)⁴⁵ incorporated within an FIB/SEM dual-beam instrument from Tescan (Brno, Czech Republic) was used. This technique has been recently reported to provide a significant enhancement of generating secondary ions (up to two orders of magnitude, depending on a material)^{19,42}, resulting in higher signal-to-noise ratio, and therefore increased spatial resolution. Furthermore, a simultaneous co-injection of fluorine gas during a TOF-SIMS measurement shows potential for separating mass interference⁴¹ (which under standard vacuum conditions constitutes one of the main drawbacks of this technique). Finally, the initial studies seem to indicate that fluorine can have the capability of altering the polarity of generated secondary ions during FIB sputtering. This feature, allowing the complete sample's chemical structure to be provided from a single volume (i.e., without any supplementary gas, two separate measurements have to be conducted to show the distribution of positively and negatively ionizing elements; since TOF-SIMS is a destructive technique, the data have to be acquired from different volumes then), was particularly important in the case of the sample investigated in this work as it enabled to detect elements such as Li (which ionizes positively) and Pt and Au (which dominantly ionizes negatively) in the same measurement. The sample surface was bombarded with a continuous monoisotopic ⁶⁹Ga⁺ primary ion beam, which was used as both, a sputtering, and analysis beam. The 20 kV beam energy was applied to ensure high lateral resolution whilst maintaining sufficient depth resolution. The 4D data set, i.e., a 3D (x, y, and z) array with an associated mass spectrum for each data point, was recorded at ~110 ± 1 pA ion current and 32 μs

dwell time from a 10 μm × 10 μm area with 512 × 512 pixels and 2 × 2 binning. Supplementary Fig. 1a shows a secondary electron image of the sputtered crater, with sharp edges and a smooth bottom that indicate no FIB-induced roughness. A XeF₂ precursor was used as a source of fluorine. TOF-SIMS Explorer 1.12.2.0 from TOFWERK (Thun, Switzerland) was used for data collection and analysis. Mass spectra were mass calibrated using the secondary-ion signals of the main sample elements (⁷Li⁺, ²⁴Mg⁺, ⁹⁰Zr⁺, ¹⁹²Pt⁺, and ¹⁹⁷Au⁺), the substrate (²⁸Si⁺), and the primary ion beam (⁶⁹Ga⁺). 3D elemental tomography plots were created using the Mayavi's *mlab* module for Python.

Standard ToF-SIMS depth profiling was performed with a ToF-SIMS 5 system from IONTOF. For sputtering, a Cs⁺-ion gun was employed with an acceleration voltage of 2 kV on an area of 300 μm × 300 μm. The primary ion source used for analyzing was Bi⁺ ions with an acceleration voltage of 25 kV. The negative-charged ions extracted from a 100 μm × 100 μm area within the sputtering crater were used for the analysis. A floodgun was used to avoid surface charging. Supplementary Fig. 2 shows the ToF-SIMS depth profile of extracted negative ions of the oxide compounds composing the aLLZO film (ZrO₂⁻, LaO⁻, and LiO⁻) and the metal electrodes (Au⁻ and Pt⁻). In this case, since the measurement was performed in the negative mode without a GIS system, the oxides of Li, La, and Zr had to be analyzed instead of the individual isotopes because these elements tend to ionize positively.

X-ray diffractometry. XRD diffractograms were acquired in a Bruker D8 Discover XRD system in a GI mode with Cu K_{α1} radiation at an incident angle ω = 2° and measuring in the range 2θ = 10°–60°.

Raman spectroscopy. Raman spectroscopic characterization was performed on a WITec Alpha 300R microscope (300 mm focal length, 600 g mm⁻¹ grating) equipped with a thermoelectrically cooled EMCCD-Detector. Acquisition parameters for excitation at λ = 532 nm were optimized for both amorphous and crystallized samples individually to avoid laser-induced changes (40 mW, 25 s integration time and 20 mW, 1 s integration time, respectively). Objective NA = 0.55). Spectra displayed in Fig. 1e are averages of 25(400) spectra acquired over an area of 100 μm (200 μm) for the amorphous (crystallized) sample. Signatures of cosmic rays and a linear background were removed and scaling is indicated in the panel.

FT-IR spectroscopy. FT-IR measurements were conducted with a BRUKER single reflection attenuated total reflection (ATR) unit (diamond ATR crystal) incorporated in a BRUKER Tensor 27 spectrometer in the wavenumber range of 340–4000 cm⁻¹.

Impedance spectroscopy and current transient measurements. Electrical characterization of the aLLZO films was performed through-plane with Pt as back electrode and Au as top electrode using a Paois measurement system (Fluxim AG). Electrochemical impedance spectroscopy (EIS) spectra were recorded between 100 mHz and 10 MHz with an alternating current amplitude <70 mV. Measurements

were performed in an Ar-filled glovebox at temperatures ranging from room temperature to 200 °C. The temperature was regulated using a Linkam LTSE-420-P heating stage integrated with the measurement system. The temperature on the sample's surface was logged using a PT100 temperature sensor.

The ionic conductivity was extracted from the EIS measurements by fitting the imaginary part of the modulus. Supplementary Fig. 3a–c show representative examples of the imaginary modulus for different LLZO:Li₂O mass fractions. The dots indicate the maximum of the imaginary modulus spectra used to calculate ionic conductivity and activation energy from the Arrhenius plot (Supplementary Fig. 3d).

To quantify the density of mobile ions, we pre-bias the samples at a positive voltage bias for 1 h and then measure the current transient after applying a negative voltage bias of same amplitude as the positive one. The current transient is hence representative to the migration of mobile ions from the Au/aLLZO to the Pt/aLLZO interface. Measured current transients for different voltage biases are shown in Supplementary Fig. 4a, b for two different LLZO:Li₂O mass fractions. After subtracting the background current, the extracted charge is calculated by integration over the measured current transient (Supplementary Fig. 4c). The ion density n is then calculated from the extracted charge ΔC with $\Delta C = qnd$, where q is the elementary charge and d is the thickness of the aLLZO layer. Figure 4d shows the obtained mobile ion densities at different voltage biases. At biases >1.2 V the curve begins to flatten, indicating that most of the mobile ions present in the aLLZO layer are being measured. We use a bias of 2 V for the quantification of the density of mobile ions. We note that larger densities cannot be excluded since larger biases degrade the device. We use the obtained ion density from the transient measurements and the ion conductivity from impedance spectroscopy measurements to calculate the mobility of mobile ions according to Eq. (1).

To quantify the electronic conductivity, we measure the steady-state current 1 h after applying both a positive and a negative bias of 1.2 V. This is shown in Supplementary Fig. 5a, b as an example, with the obtained electronic conductivities summarized in Supplementary Fig. 5c. In order to cancel out the effect of the internal electric field due to the different metals used as contacts and possible interfacial effects, we take the mean over both values. The mean values are then used to quantify the activation energies and electronic conductivities, as shown in Supplementary Fig. 4d. For all the samples with different LLZO:Li₂O mass fractions, we obtain an activation energy of 0.35 ± 0.9 eV and an electronic conductivity of $(2.2 \pm 1.4) \times 10^{-14} \text{ S cm}^{-1}$, which remains fairly constant for the different mass fractions.

Galvanostatic and potentiostatic cycling of Pt/Li half-cells and symmetric Li/Li cells.

To assess the stability vs. metallic Li, the half-cell was galvanostatically cycled with a current of $1.25 \mu\text{A cm}^{-2}$ around 0 V vs. Li/Li⁺ in steps of 1 h. EIS was measured after each step. The resistance of the aLLZO films to Li dendrite penetration was investigated by galvanostatically plating-stripping Li in a symmetric Li/Li cell. The symmetric cells were cycled at increasing current densities from 0.2 up to 3.2 mA cm^{-2} for five plating-stripping cycles at each current density value. The transferred capacity was limited to 0.1 mA h cm^{-2} , equivalent to a Li thickness of 250 nm.

To determine the electrochemical stability of the aLLZO electrolyte, the films were measured in galvanostatic and potentiostatic mode in a Pt/Li half-cell. To determine the stability at high potentials, a cyclic voltammetry (CV) measurement was performed between 1 and 5 V vs. Li/Li⁺ at a rate of 2 mV s^{-1} .

Galvanostatic cycling of thin-film batteries.

Charge–discharge curves of the full thin-film battery with aLLZO as electrolyte were recorded in galvanostatic mode within a potential range of 3–4.25 V vs. Li/Li⁺. The cells were tested with charge–discharge current densities ranging from $22 \mu\text{A cm}^{-2}$ (1C) to 0.22 mA cm^{-2} (10C). Long-term cycling was performed at 0.22 mA cm^{-2} for 500 cycles (~100 h). The oscillations in the discharge capacities are due to temperature variations inside the glovebox between day and night.

Through-plane Li plating-stripping of Li/crystalline LLZO/Li symmetric cells.

Through-plane Li plating-stripping was performed on an aLLZO-coated LLZO pellet and an uncoated pellet as reference. Prior to the plating-stripping process, EIS was measured at room temperature with an amplitude of 10 mV and a frequency range of 1 MHz to 1 Hz. The cells were galvanostatically cycled with symmetric current densities ranging from $5 \mu\text{A cm}^{-2}$ up to 5.1 mA cm^{-2} in steps of 30 min. The measurements were carried out at room temperature and without external pressure, apart from that of the alligator clamp used to contact the cell.

In-plane Li plating-stripping with in-operando microscopy. In-plane Li plating-stripping was performed on the aLLZO-coated and aLLZO-uncoated sides of the ceramic LLZO pellet using the Li metal contacts with a spacing of 0.5 mm. Plating-stripping of Li was performed at current densities ranging from $50 \mu\text{A cm}^{-2}$ to 3.2 mA cm^{-2} for a total charge transfer of $25 \mu\text{A h cm}^{-2}$, with 15 min rest steps in between. During the Li plating-stripping process, a Dino-Lite AM73115MZT digital microscope was used to monitor the surface of the LLZO pellet.

Data availability

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

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References

- Janek, J. & Zeier, W. G. A solid future for battery development. *Nat. Energy* **1**, 16141 (2016).
- Albertus, P., Babinec, S., Litzelman, S. & Newman, A. Status and challenges in enabling the lithium metal electrode for high-energy and low-cost rechargeable batteries. *Nat. Energy* **3**, 16 (2018).
- Samson, A. J., Hofstetter, K., Bag, S. & Thangadurai, V. A Bird's-eye view of Li-stuffed garnet-type Li₇La₃Zr₂O₁₂ ceramic electrolytes for advanced all-solid-state Li batteries. *Energy Environ. Sci.* **12**, 2957–2975 (2019).
- Wang, C. et al. Garnet-type solid-state electrolytes: materials, interfaces, and batteries. *Chem. Rev.* **120**, 4257–4300 (2020).
- Krauskopf, T., Richter, F. H., Zeier, W. G. & Janek, J. Physicochemical concepts of the lithium metal anode in solid-state batteries. *Chem. Rev.* **120**, 14463–14477 (2020).
- Huang, W. L. et al. Can we find solution to eliminate Li penetration through solid garnet electrolytes? *Mater. Today Nano* **10**, 100075 (2020).
- Hatzell, K. B. et al. Challenges in Lithium metal anodes for solid-state batteries. *ACS Energy Lett.* **5**, 922–934 (2020).
- Porz, L. et al. Mechanism of Lithium metal penetration through inorganic solid electrolytes. *Adv. Energy Mater.* **7**, 1701003 (2017).
- Han, F. et al. High electronic conductivity as the origin of lithium dendrite formation within solid electrolytes. *Nat. Energy* **4**, 187–196 (2019).
- Song, Y. et al. Probing into the origin of an electronic conductivity surge in a garnet solid-state electrolyte. *J. Mater. Chem. A* **7**, 22898–22902 (2019).
- Liu, H. et al. Controlling dendrite growth in solid-state electrolytes. *ACS Energy Lett.* **5**, 833–843 (2020).
- Kim, J.-S. et al. Origin of intergranular Li metal propagation in garnet-based solid electrolyte by direct electronic structure analysis and performance improvement by bandgap engineering. *J. Mater. Chem. A* **8**, 16892–16901 (2020).
- Kalita, D., Lee, S., Lee, K., Ko, D. & Yoon, Y. Ionic conductivity properties of amorphous Li–La–Zr–O solid electrolyte for thin film batteries. *Solid State Ion.* **229**, 14–19 (2012).
- Garbayo, I. et al. Glass-type polyamorphism in Li-garnet thin film solid state battery conductors. *Adv. Energy Mater.* **8**, 1702265 (2018).
- Westover, A. S., Dudney, N. J., Sacci, R. L. & Kalnaus, S. Deposition and confinement of Li metal along an artificial Lipon–Lipon interface. *ACS Energy Lett.* **4**, 651–655 (2019).
- Deng, T. et al. Tuning the anode–electrolyte interface chemistry for garnet-based solid-state Li metal batteries. *Adv. Mater.* **32**, 2000030 (2020).
- Sastre, J. et al. Aluminum-assisted densification of cosputtered lithium garnet electrolyte films for solid-state batteries. *ACS Appl. Energy Mater.* **2**, 8511–8524 (2019).
- Sastre, J. et al. Lithium garnet Li₇La₃Zr₂O₁₂ electrolyte for all-solid-state batteries: closing the gap between bulk and thin film Li-ion conductivities. *Adv. Mater. Interfaces* **7**, 2000425 (2020).
- Priebe, A., Utke, I., Pethö, L. & Michler, J. Application of a gas-injection system during the FIB-TOF-SIMS analysis—influence of water vapor and fluorine gas on secondary ion signals and sputtering rates. *Anal. Chem.* **91**, 11712–11722 (2019).
- Wagner, R. et al. Crystal structure of garnet-related Li-ion conductor Li_{7–3x}Ga_xLa₃Zr₂O₁₂: fast Li-ion conduction caused by a different cubic modification? *Chem. Mater.* **28**, 1861–1871 (2016).
- Gittleton, F. S. et al. Raman spectroscopy in Lithium-oxygen battery systems. *ChemElectroChem* **2**, 1446–1457 (2015).
- Kanade, K. G., Baeg, J. O., Apte, S. K., Prakash, T. L. & Kale, B. B. Synthesis and characterization of nanocrystallized zirconia by hydrothermal method. *Mater. Res. Bull.* **43**, 723–729 (2008).
- Xu, Z. et al. Synthesis of hollow La₂O₃:Yb³⁺/Er³⁺/Tm³⁺ microspheres with tunable up-conversion luminescence properties. *RSC Adv.* **3**, 8407–8416 (2013).
- Tian, J. et al. High surface area La₂Sn₂O₇ pyrochlore as a novel, active and stable support for Pd for CO oxidation. *Catal. Sci. Technol.* **5**, 2270–2281 (2015).
- Wijaya, O. et al. A gamma fluorinated ether as an additive for enhanced oxygen activity in Li–O₂ batteries. *J. Mater. Chem. A* **3**, 19061–19067 (2015).
- Ren, Y. et al. Oxide electrolytes for Lithium batteries. *J. Am. Ceram. Soc.* **98**, 3603–3623 (2015).

27. Bredar, A. R. C., Chown, A. L., Burton, A. R. & Farnum, B. H. Electrochemical impedance spectroscopy of metal oxide electrodes for energy applications. *ACS Appl. Energy Mater.* **3**, 66–98 (2020).
28. Famprikis, T., Canepa, P., Dawson, J. A., Islam, M. S. & Masquelier, C. Fundamentals of inorganic solid-state electrolytes for batteries. *Nat. Mater.* **18**, 1278–1291 (2019).
29. Grady, Z. A., Wilkinson, C. J., Randall, C. A. & Mauro, J. C. Emerging role of non-crystalline electrolytes in solid-state battery research. *Front. Energy Res.* **8**, 218 (2020).
30. Han, X. et al. Negating interfacial impedance in garnet-based solid-state Li metal batteries. *Nat. Mater.* **16**, 572–579 (2017).
31. Ruan, Y. et al. A 3D cross-linking lithiophilic and electronically insulating interfacial engineering for garnet-type solid-state lithium batteries. *Adv. Funct. Mater.* **31**, 2007815 (2021).
32. Kazyak, E. et al. Li penetration in ceramic solid electrolytes: operando microscopy analysis of morphology, propagation, and reversibility. *Matter* **2**, 1025–1048 (2020).
33. Dudney, N. J. Solid-state thin-film rechargeable batteries. *Mater. Sci. Eng. B* **116**, 245–249 (2005).
34. Zhu, Y., He, X. & Mo, Y. First principles study on electrochemical and chemical stability of solid electrolyte–electrode interfaces in all-solid-state Li-ion batteries. *J. Mater. Chem. A* **4**, 3253–3266 (2016).
35. Lee, J. Z. et al. Cryogenic focused ion beam characterization of lithium metal anodes. *ACS Energy Lett.* **4**, 489–493 (2019).
36. Pearse, A. J. et al. Nanoscale solid state batteries enabled by thermal atomic layer deposition of a lithium polyphosphazene solid state electrolyte. *Chem. Mater.* **29**, 3740–3753 (2017).
37. Filippin, A. N. et al. Ni–Al–Cr superalloy as high temperature cathode current collector for advanced thin film Li batteries. *RSC Adv.* **8**, 20304–20313 (2018).
38. Sharaifi, A. et al. Surface chemistry mechanism of ultra-low interfacial resistance in the solid-state electrolyte $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$. *Chem. Mater.* **29**, 7961–7968 (2017).
39. Benninghoven, A., Rudenauer, F. G. & Werner, H. W. *Secondary Ion Mass Spectrometry: Basic Concepts, Instrumental Aspects, Applications and Trends* (Wiley, 1987).
40. van der Heide, P. *Secondary Ion Mass Spectrometry: An Introduction to Principles and Practices* (Wiley, 2014).
41. Priebe, A., Pethö, L. & Michler, J. Fluorine gas coinjection as a solution for enhancing spatial resolution of time-of-flight secondary ion mass spectrometry and separating mass interference. *Anal. Chem.* **92**, 2121–2129 (2020).
42. Priebe, A., Xie, T., Pethö, L. & Michler, J. Potential of gas-assisted time-of-flight secondary ion mass spectrometry for improving the elemental characterization of complex metal-based systems. *J. Anal. At. Spectrom.* <https://doi.org/10.1039/D0JA00372G> (2020).
43. Whitby, J. A. et al. High spatial resolution time-of-flight secondary ion mass spectrometry for the masses: a novel orthogonal ToF FIB-SIMS instrument with in situ AFM. *Adv. Mater. Sci. Eng.* **2012**, 1–13 (2012).
44. Alberts, D. et al. Design and performance of two orthogonal extraction time-of-flight secondary ion mass spectrometers for focused ion beam instruments. *Instrum. Sci. Technol.* **42**, 432–445 (2014).
45. Wang, Z. M. *FIB Nanostructures* (Springer Science, Business Media, 2014).

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Author contributions

J.S. conceived, designed, and carried out the experimental work, and prepared the manuscript; M.H.F. carried out and analyzed the transient electrical measurements, and assisted in the manuscript preparation L.P. helped in the thin-film fabrication and EIS measurements; A.A. carried out the FT-IR measurements; A.P. carried out the FIB-ToF-SIMS measurements; J.O. carried out the Raman measurements; M.S. carried out the FIB-SEM measurements; A.N.T. supervised the project and reviewed the manuscript; Y.E.R. helped in the experimental conception, supervised the project, and reviewed the manuscript. All authors contributed to the manuscript writing and revision.

Competing interests

The authors declare no competing interests.

Additional information

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Correspondence and requests for materials should be addressed to J.S. or Y.E.R.

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