Mapping the Nanoscopic Filament Growth Kinetics in Lithium Solid Electrolytes

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**Abstract**

Ceramic lithium conductors such as Li\textsubscript{7}La\textsubscript{3}Zr\textsubscript{2}O\textsubscript{12} (LLZO) are promising solid electrolytes for solid-state batteries. However, the lithium filaments can penetrate the electrolytes at high current densities, leading to cell failure. Due to the limited spatial resolution of macroscopic electrochemical measurement techniques, the nanoscopic growth kinetics of lithium filaments and its physical origin remain unrevealed. Here, we report \textit{in-situ} nanoscale electrochemical characterizations of the filament growth kinetics in LLZO using conductive-atomic force microscope (c-AFM). Significant local inhomogeneity is observed with a hundredfold decrease in the filament triggering bias at the grain boundaries compared with the grain interiors. The origin of the local weakening is assigned to the nanoscopic variation of elastic modulus and surface potential. Further reverse cycles lead to the discovery of the memristive behavior of lithium filament in LLZO based on which a model memristor is designed and demonstrated. A high on/off ratio of \textasciitilde10\textsuperscript{5} is achieved consistently for over 200 cycles.
This work provides insights into the nanoscale electrochemical deposition stability in solid-state batteries and opens up opportunities for novel designs of memristive devices.

**Introduction**

Lithium-ion batteries (LIBs) have been proven a transformative technology and have been dominating the market of portable electronics since its first commercialization. However, recent blooming of the electric vehicle industry and the grid-scale storage call for novel energy storage solutions with aggressive demands on safety, price, and energy density, which is beyond the capability of the current LIBs. Especially, to reach the 500 Wh kg\(^{-1}\) goal, replacing the current graphite anode with lithium metal has been considered critical. Unfortunately, lithium metal is highly reactive and tends to deposit into dendrites during cycling, which inevitably leads to cell failures. Intense research efforts have been made in this regard and multiply strategies have been proposed including tuning the electrolyte composition, coating the lithium metal with artificial layers, designing porous current collectors, and utilizing solid electrolytes (SEs). Among them, replacing the conventional liquid electrolyte with a piece of mechanically strong and lithium conductive solid, i.e., SE, has been regarded the most promising solution to both the safety concerns and energy density issues of LIBs. On the one hand, the SEs are much less flammable compared with the organic liquid electrolyte in LIBs. On the other hand, the high mechanical stiffness of solids have been regarded to be able to restrain the uneven deposition of lithium dendrites (which unfortunately turned out not the case for many SEs).
Figure 1 Illustration of the macroscopic electrochemical measurement setups using (a) porous cathodes and (b) deposited Au electrodes. Illustration of (c) The penetration of lithium filaments in a conventional macroscopic electrochemical measurement setup. (d) Illustration of the nanoscale electrochemical measurement setup used in the current study where the c-AFM tip is used as the WE.

Among the SEs that have been discovered, ceramic oxides are one of the most promising families due to their high ionic conductivity, excellent fire redundancy, good mechanical strength, and the ease of fabrication in air. Especially, lithium-stuffed garnets $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) has been the absolute hot spot of research since its discovery in 2007. When properly doped, such an electrolyte displays a high ionic conductivity of over $10^3$ S cm$^{-1}$ and a Young’s modulus of $\sim$150 GPa. Beyond that, LLZO is one of the very few SEs that are chemically stable toward lithium metal. These properties arouse significant interest in its use in solid-state lithium-metal batteries (SSLMBs). In fact, one of the initial reasons that drives the early researches on LLZO is based on the assumption that the high shear modulus of LLZO could suppress the growth of lithium dendrites, according to the linear elasticity model by Monroe and Newman. Unfortunately, it is later found to be NOT the case, i.e., lithium
metal tends to penetrate LLZO and lead to internal shorts when the SSLMB is subject to high current densities. Significant effort has then been placed in understanding the mechanism behind such lithium penetration. Hu et al. found that LLZO is poorly wetted by lithium metal, even in its molten state. The poor interfacial contact leads to high local current densities and create local “hot spots” for lithium to penetrate. Sharafi and co-workers confirmed that the poor wettability is due to the surface contaminants such as LiOH and Li$_2$CO$_3$. To quantify the capability of LLZO in blocking the dendrites, they further proposed the concept of critical current density (CCD) which is defined as the highest current density before a Li|LLZO|Li cell shorts. Usually, for a LLZO pellet with untreated surface, the CCD does not surpass 0.2 mA cm$^{-2}$. This value is significantly lower than the 2 mA cm$^{-2}$ threshold needed in practice cells. Apart from the contact issues, the local inhomogeneity has also been identified as a source of instabilities for lithium deposition. Importantly, the grain boundary is regarded as the preferential nucleation site due to its high electron conductivity, low elastic modulus, and the low fracture toughness. Recently, Porz et al. proposed a Griffith-like crack extension model where lithium metal infiltrates into the electrolytes through surface defects. Considering the fundamental difference between the lithium penetration in ceramic SEs and its dendritic-like growth in liquid electrolyte, we will follow the term “filament” instead of “dendrite” throughout the article. Based on the understandings, various strategies have been proposed to enhance the stability of the Li|LLZO interfaces and to enlarge the CCD values, including physical/chemical treatment of the interfaces to enhance the interface contact, making composite
anodes to modify its interactions with LLZO, \( ^{28, 29} \) and modifying the grain boundary properties by adding sintering aids. \( ^{30} \) Thanks to these advancements, the CCD can now reach \( \sim 1 \) mA cm\(^{-2} \) and is approaching the practical limit. \( ^{31, 32, 33, 34} \) Despite the significant progress in understanding and the mitigating the filament-like growth of lithium metal in LLZO, to date, its detailed electro-chemo-mechanical origin still remains not fully revealed. Especially, almost all previous analysis are based on macroscopic electrochemical measurements as shown in Figure 1(a) to (b), which lacks the spatial resolution to directly measure the triggering condition and growth kinetics of an individual filament due to its small size as illustrated in Figure 1(c). Moreover, it has long been argued that lithium filament prefers to penetrate the grain boundaries instead of grain interiors.\(^{18} \) However, to what extend such preferential nucleation happens and how it can be quantified still remains to be answered. Beyond that, the nanoscopic driving force of such inhomogeneity is still unresolved which is essential to the future design of interface layers for filament prevention.

In this work, we exploit the extreme spatial resolution of conductive-atomic force (c-AFM) and utilize the AFM tip as the working electrode to perform nanoscale electrochemical characterizations on LLZO as illustrated in Figure 1(d). By applying electric biases on the tip of the c-AFM, we quantitatively measured the electrochemical responses of the lithium plating processes and the filament growth kinetics, with the resolution down to nanoscale. In particular, the intrinsically different responses of grain interior and grain boundaries to electrochemical lithium deposition are revealed for the first time. We found that, the critical electrical bias to induce lithium filament growth
at the grain boundary is $\sim 1/100$ of that in the grain interior. Such a shocking difference points to the fact that the nanoscale inhomogeneity of the LLZO surface results in weak spots which constitutes the easy penetration of lithium metal. To further study the physical driving force of preferential penetration, we carried out ex-situ AFM characterizations on both the electrical and the mechanical response of LLZO surfaces. The results show that the low stiffness at the grain boundary together with variations in the surface potential contributes to the filament growth. More interestingly, the nanoscale electrochemical response under cyclic conditions show the signature memristive switching characteristics. A model memristor is demonstrated based on the tip-to-film configuration with unprecedented stability of over 200 cycles and an on/off ratio up to $10^5$ which is only observed at nanoscale, providing a novel design route for memristive devices beyond the current von Neumann architecture. $^{35,36}$

**Results**

**Figure 2** (a) Illustration of the flow of lithium ions and the electrons during the nanoscale electrochemical measurement. $i_e^{Li\text{ deposition}}$ and $i_e^{filament}$ are the current...
controlled by Li$^+$ conduction before the filament penetration and by the e$^-$ conduction after filament penetration, respective. Illustration of the location of c-AFM tip during the nanoscale measurement (b) at the grain boundaries and (c) at the grain interiors. Typical electrochemical responses, i.e., I-V curves, of the Li|LLZO|tip cells when the c-AFM tip is located at (d) the grain boundaries and (e) the grain interior.

The experimental setup of is shown in Figure 1(d), where we utilize the c-AFM tip as the as the working electrode (WE) and the lithium metal as both the counter (CE) and the reference electrode (RE). By applying a reductive bias on the WE (i.e., negative with respect to Li/Li$^+$), the lithium ions are drawn from the LLZO to the tip of the c-AFM and are reduced to form lithium metal (Li$^0$) as illustrated in Figure 1(d). By varying the applied voltage and mapping it against the measured current, we are able to probe the lithium deposition kinetics at the interfaces between the LLZO and the c-AFM tip at nanoscale as illustrated in Figure 2(a). In principle, when the current is solely contributed by the flow of Li$^+$ ions, it can be used as proxy for the deposition rate of lithium metal. However, such an assumption is only valid at relative low current densities as the lithium metal can penetrate through the LLZO pellet when the electric bias gets large enough. Under such circumstances, the measured current goes through an abrupt change, indicating the transition from pure ionic conduction to a mixed electronic and ionic conduction with the former being the major contributor. In fact, it is to our interest under what electrochemical conditions (i.e., the bias and the current density) the transition happens. We use such a value, i.e., the triggering bias, as the
major proxy to quantify how easy it is for lithium filaments to penetrate through the LLZO as illustrated in Figure 2(a). In particular, for polycrystalline SEs such as LLZO, we care about how the grain interior differs from the grain boundaries as the latter has long being speculated as weak spot for to form lithium filaments while actual quantitative electrochemical measurements have never been reported. To address this, we first did a morphological scan on the LLZO surface to identify the exact location of the grain boundaries and the grain interiors, as illustrated in Figure 2(b) and Figure 2(c). After that, we landed the c-AFM tip to a specific spot of interest, i.e., either the grain boundary or the interior, followed by the electrochemical deposition tests as mentioned previously. The typical electrochemical results of a grain boundary is shown in Figure 2(d). The current does not show significant increase until the bias is lower than -0.12V vs. Li/Li$^+$ where a surge in the conductivity is detected. Such a surge agrees with the metallic filament penetration and is further supported by a back scan where an almost perfect linear relation between the current and the voltage is observed, indicating its pure ohmic nature. The ohmic resistance is calculated to be 116Ω. By further taking into account the electronic conductivity of lithium 1.1·10$^5$ S·cm$^{-1}$, the diameter of the lithium filament is estimated to be ~300 nm, in excellent agreement with previous report by Porz et al. $^{27,37}$ We want to note that due to the extremely small size of the c-AFM tip, it is difficult to measure the current controlled by lithium deposition before the filament penetration. A rough calculation based on the contact area of 30 nm$^2$ (see the method section for the calculation details) and an LLZO ionic conductivity of 5 ·10$^{-4}$ S·cm$^{-1}$ leads to a maximum ionic flow-controlled current of ~2 $10^2$ pA at -10V, which
is well below the detection limit current setup. In contrast, for the grain interiors, despite the high number of trials, we were only able to induce the filament growth for very limited times and all of them are triggered by large biases. A typical case shown in Figure 2(e) where penetration of the metallic filament happens at < -9 V vs. Li/Li⁺. Such an astonishing hundredfold increase in the triggering bias for filament penetration unambiguously points to the fact that the grain boundary is the absolute weak spot for the electrolyte and should be avoided as much as possible.

**Figure 3** (a) The morphology change of the LLZO surface before (upper panel) and after (lower panel) the penetration of lithium. (b) The current map of the LLZO surface using c-AFM by applying a +0.1V bias before (upper panel) and after (lower panel) the penetration of lithium. The scale bars in (a) and (b) are 200nm. The filament triggering bias measured (c) with c-AFM tips at different distances to the grain boundaries and (d) with deposited Au electrodes with different sizes. The inset in (d) shows the digital image of the deposited Au electrodes with different sizes.
To further confirm that the surge of the conductivity comes from the formation of metallic lithium filament, we compared the morphology and the conductivity mapping before and after performing the nanoscale electrochemical measurements. As shown in Figure 3(a), several bumps emerged after applying the bias indicating the extrusion of lithium metal. Accompanied with that, the electronic conductivity map (Figure 3(b)) shows that these bumps are highly conductive compared with the other areas, which confirms the formation of electronically conductive path due to the filaments. To further evaluate the sensitivity of our nanoscale electrochemical measurements and to account for the size effect of the WE, we performed electrochemical tests with c-AFM tips at different distances to the grain boundaries and with deposited Au electrodes with different sizes. As shown in Figure 3(c), there is an abrupt increase of the triggering bias when the distance to the grain boundary increased to 100 nm. In fact, when the distance is larger than 100 nm, we can hardly trigger a filament under the -10V limit. On the other hand, when we try to vary the size of the WEs, we found that the transition voltage decreases with the size of the WE, see Figure 3(d). Especially, when the size of the WE reaches the typical size of the LLZO grain, i.e., >10 μm, both the transition biases and the error significantly decrease. This happens because only when the size of the electrode is equivalent to or larger than the typical grain size of LLZO, the probability of it covering at least one grain boundary becomes high. In fact, this observation could serve as another direct quantitative support of the nanoscale inhomogeneity of the LLZO surface and that the grain
boundary in particular is the weak spot of the LLZO SE.

**Figure 4** (a) The morphology and (b) the modulus mapping of the LLZO surfaces. (c) and (d) are the 2D view of selected areas. The scale bars in (c) and (d) are 50 nm. (e) The local modulus as a function of the distance to the grain boundary. (f) The morphology and (g) the surface potential mapping of the LLZO surfaces. (c) and (d) are the corresponding 2D views. The scale bars in (c) and (d) are 500 nm. (e) The surface potential as a function of the distance to the grain boundary. For (e) and (j), the brown and blue bold line in the foreground is the average of the results from 5 separate tests at diffract locations as indicated by the lines in the background. The shaded areas are guide to the eye to indicate the error range.
Considering the hundredfold weakening of the SE at the grain boundary against lithium penetration, we further explored its mechanical and the electrical origin using two different AFM techniques. From the mechanical aspect, there has been several assumptions why the penetration happens among which the softening of the grain boundary is considered the major contributor. Yu and Siegel carried out molecular dynamics simulations on polycrystalline LLZO and found that the shear modulus is significantly lowered by up to 50% at the grain boundaries. They proposed that the inhomogeneity in the elastic properties may result in “soft spots” which could contribute the lithium metal penetration. However, to date, there is no direct experimental result to testify such an assumption due to the lack of spatial resolution to distinguish grain boundaries and grain interiors. We took advantage of the extreme resolution of AFM and performed a nanomechanical test to directly map the mechanical response of LLZO with its nanostructure. Figure 4(a) shows the morphology of a typical LLZO surface and the corresponding elastic moduli are shown in Figure 4(b). The mechanical stiffness is clearly lower at the grain boundaries compared with the grain interiors. In order to avoid the influences of the abrupt changes of surface morphology on the accuracy of elastic property measurement, we specifically chose a relatively flat area and show the results in Figure 4(d) and (e). The decrease at the grain boundaries can be as high as 30% compared with the interior. This is further supported by sampling of the moduli along the vertical lines to the grain boundaries, see Figure 4(f). By averaging 5 individual measurements, the moduli of LLZO decrease from ~145GPa in grain interiors to ~120GPa at grain boundaries. Such results are in good
agreement with the simulations done by Yu et al. \(24\) It is worthwhile to note that, despite the significant drop in the elastic moduli, the value is still significantly higher compared to lithium metal. Therefore, the elastic softening should not be the sole factor that directly controls the filamentary growth. However, the local inhomogeneity may serve as an initiator for the preferential lithium deposition and assists the Griffith-like crack extension mechanism proposed by Porz et al. \(27\) Beside the mechanical origin, the electronic aspects have also been speculated to affect the lithium deposition stability.

For example, the low ionic conductivity of the grain boundary lead to a significant change of the lithium deposition overpotential thereby alternating the local stress distribution which may further results in preferential propagating of filaments. \(13\) The partial electronic conductivity of the grain boundaries may lead to easy recombination of the electrons and the \(\text{Li}^+\) ions to \(\text{Li}^0\) and therefore provide an avenue for lithium nucleation. \(23, 38, 39, 40\) Here, we noticed that due to the electron insulating nature of LLZO, local inhomogeneity of electrical potential may build up at the LLZO|electrode interfaces. Such variance of the electric local electric potential at the interface may give rise to nucleation preferences for lithium. In fact, at grain boundaries, it is known that certain charged depleted or enriched region exist (also known as the space charge layer/space charge region). \(41, 42\) We measure such local variance of electric potential by mapping the surface potential to the morphology using the Kelvin probe force microscopy. \(43\) The results are shown in Figure 4(f) to (j). It is found that the surface potential of LLZO at grain boundaries tends to decrease by \(~10\) mV compared with the grain interiors, see Figure 4(j). Such a decrease corresponds to an e\(^-\) accumulation or
Li+ depletion and is in agreement with a very recent MD simulation by Shiiba et al.\textsuperscript{44} On the one hand, the decrease of Li\textsuperscript{+} concentration may result in lowered conductivity and therefore a preference of lithium extrusion.\textsuperscript{45} On the other hand, as mentioned previously, the variation of the local potential may direct offset the lithium nucleation/deposition potential by up to \textasciitilde15 meV which leads to easier deposition at the grain boundary. However, we must note that the variance of surface potential is relatively small compared with our previous studies on semiconductors and therefore the inhomogeneity of surface potential should only be counted as part of the contributing factors to the uneven deposition.\textsuperscript{46}

\textbf{Figure 5} Illustration of (a), (b) the typical I-V curve of the Li|LLZO|WE memristors and (c) the corresponding internal physical processes. I-V curves of Li|LLZO|WE
memristors with WE being (d) an Au pad with a 500μm-side length and (e) (f) an AFM tip. (g) The I-V curve in log scale for (i). The variation of the on/off ratio with respect to cycle number for Li|LLZO|WE memristors with WE with different sizes. The set and reset potential limits are -0.2V and 1V, respectively.

It is interesting to note that during the nanoscale electrochemical measurement, the formation of the metallic filament displayed certain reversibility, i.e., when a reverse bias is applied, the metallic filament tends to be absorbed by the electrolyte and the short circuit is reversed. In fact, such a phenomena has been observed in a number of recent work. Wang et al. carried out in-situ neutron depth profiling of the Li|LLZO interface and observed “dynamic short circuiting” where during lithium plating of a half-cell, the short circuit can be temporarily eliminated. 47 Krauskopf and co-workers further confirmed such a dynamic process by carrying out galvanostatic electrochemical impedance spectroscopy. 37 A number of other recent studies also support their observations and all of these results all point to the fact that the short circuit in lithium SSBs, to some extent, can be reversed. 37, 48 We took a step further and show that the filament growth in LLZO follows a memristive behavior and the reversibility is highly dependent on the size of the electrode. At extreme cases of c-AFM tips, the reversibility of the memristive switching is very stable and may open up new opportunities for using lithium SEs in neuromorphic computing, i.e., a new computing architecture beyond von Neumann, which is well beyond the conventional usage in energy storage such as batteries. 49
Figure 5 (a) and (b) illustrates the typical I-V curve of a Li|LLZO|WE cell where the WE is Pt or any other non-reactive metal. When a negative bias (vs. Li/Li⁺) is applied, the Li⁺ ions are drawn from LLZO towards the WE and are being reduced to form metallic lithium as shown in Figure 5(c). During this stage, the current is controlled by the ionic conductivity of LLZO and is sometimes not measurable with the nanoelectrochemical measurement setup. This stage corresponds to the off state or the high resistance state (HRS) of an asymmetrical memristor. When the negative bias becomes larger, the lithium filament start to grow and penetrates the LLZO pellet to form an electronically conductive path. During this stage, the measured current goes through an abrupt change and the nominal resistance becomes orders of magnitude higher compared with that at small bias. Such a transition corresponds to the ‘set’ stage of a memristor where the resistance becomes significant smaller as illustrated in Figure 4(d). In fact, the stage after setting corresponds to the low resistance state (LRS) or the on state, see Figure 4(e). The LRS can be further reversed back to its HRS state by applying a reverse positive bias. Depending on the size of the electrode, the reversibility can be varied. As illustrated in the fourth panel of Figure 4(c), if the size of the electrode is too large and the set bias is too high, the filament becomes too thick and the electrical potential is offset by the high electron conductivity and there is not enough driving force to strip lithium away from the filament so as to break it for high resistance. Therefore, the memristor fails and cannot go back to its off states, as shown in Figure 4 (e). In order to compare the electrochemical behavior of Li|LLZO|WE cells with different WE sizes, we prepared a number of WEs with a wide range of typical lengths.
For macroscopic WEs, we deposited Au on the entire side of a LLZO pellet. Such a WE has an area of 1.12 cm$^2$. For smaller WEs with side lengths ranging from 500μm to 200μm, we used masks to shade part of the LLZO pellet as shown in the inset of Figure 2(i). For microscopic WEs, we used a tungsten probe where the contact area is approximated to be several μm$^2$ to tens of μm$^2$. For the nanoscale WE, we used the c-AFM tip where the contact area is ~30 nm$^2$. The typical cyclic curves of the Li|LLZO|WE cells are shown in Figure 4(d) to (f). In Figure 4(d), the side length of the WE is 500μm which resembles the macroscopic case. During the initial cycle, we indeed see and onset of the cell. However, the ratio between the HRS and LRS state (the on/off ratio) is relatively small and did not go beyond 10. Moreover, the memristive switching does not display good reversibility. In fact, after being set for the first time, it can hardly be reset. This is in agreement with most macroscopic observations where the short circuit is detrimental to an SSB and can hardly be fully reversed. 50 However, if the size of the WEs shrinks to nanoscale, the reversibility is much better. Figure 4(e) shows the results for the case using the c-AFM tip as WE. Despite that the set bias becomes smaller during the initial several cycles, it eventually stabilized at ~0.25V and reset of the memristor is always successful. In fact, the on/off ratio within an operating voltage window of ±0.25V kept almost constant after the first 10 cycles. We further tried to maximize the memristive switching performance of the Li|LLZO|tip device by limiting the set and reset voltages. As shown in Figure 4(f), when the voltage range is between -0.2V and +1V, the SE-based memristor displays extreme stability where the resistance of the LRS and HRS keep almost constant. Figure 4(g) gathers the
cyclic stability of the on/off ratio of the memristive device based on LLZO with different electrode sizes. The initial on/off ratio decreases with the sizes of the electrode and the stability to hold such on/off ratio scales with the inverse of the electrode sizes as well. Only at nanoscale, stable memristive switching can be achieved. In fact, the memristor based on the nanoelectrode displays a rather high on/off ratio of $10^5$ for 200 cycles. This may open up design opportunities for novel architectures of memristive devices beyond cross-bars.

**Discussions**

We performed nanoscopic electrochemical measurement of filament growth kinetics in LLZO using the c-AFM tip as the working electrode. The extreme size of the electrode enabled us to achieve unprecedented spatial resolution to distinguish the inhomogeneity on the nanoscale. The grain boundaries of polycrystalline LLZO is now unambiguously confirmed as the weak spot to induce filament growth with a critical overvoltage that is hundredfold smaller than that of the grain interior. The electromechanical origin of such weakening effect is further probed using nanomechanical tests and surface potential mapping where we observed a reduction in stiffness of up to 40% and a drop of the surface potential of ~15 meV at the grain boundaries, respectively. More importantly, the highly stable reversible memristive behavior of lithium filament is found at nanoscale. A high on/off ratio of $10^5$ for the 200 cycles based on the tip-to-film design may serve as the playground for future memristive device design beyond crossbars. This work not only provides new insights into the filament growth in solid
electrolytes for the development of SSBs but also opens up exciting opportunities of utilizing lithium solid electrolyte for memristive switching, which is beyond the current application in SSBs.

Methods

Sample preparation. The composition is Li_{6.5}La_{3}Zr_{1.5}Ta_{0.5}O_{12}, where the Ta doping helps stabilize the cubic phase. It is named as LLZO throughout the article for simplicity despite the Ta dopant. The solid electrolyte was synthesized via a conventional solid-state reaction where LiOH·H_{2}O (≥ 99.0%, Sigma-Aldrich), La₂O₃ (99%, Sigma-Aldrich), Ta₂O₅ (≥ 99.99%, Ourchem), and ZrO₂ (<100 nm, Sigma-Aldrich) are used as starting materials. After weighing stoichiometric amount the starting materials with 10% Li-excess and wet ball-milling with isopropanol, the mixed power was dried and sintered at 900 °C in air for 12 h followed by pelletization with another 10 wt.% LiOH·H₂O added. Finally, the green pellets were sintered at 1140 °C for 16 h in MgO crucibles which were covered with a lid. Mother powder was added on top of the pellet to minimize the Li loss. The prepared disks were then sanded down to the thickness of 300μm. 50nm thick Au was then deposited on one side of the pellet and a lithium foil was attached to the same side as the counter and the reference electrode followed by melting at 300 °C. This step ensures a good contact of the counter and the reference electrode.

AFM and nanoelectrochemical measurements. The topography and AFM current-voltage (I-V) curves were measured with a Benyuan system (CSPM5500, China) in a
glove box (O2 and H2O <1ppm) with Keithly 2400 sourcemeter as the electrochemical measurement unit. All metal Pt probes with tip radius of 20nm (25PT300B, Rocky Mountain nanotechnology, USA) were used for CP-AFM measurement. The modulus and SKPM measurement were performed with a Demension Icon system (NANOSCOPE V7-B, Bruker, USA). Pt coated Si probes with a tip radius of 20nm (SCM-PIT-75, 75kHz, 2.8N/m) were used. Topography images and modulus images or SKPM images were taken simultaneously at a scan rate of 1Hz. During the nanocelectrochemical measurements, the current is limited to 1mA and the voltage to 10V to avoid damage to the AFM tip.

**Calculation of the contact area.** The contact area between LLZO and the AFM-tip is calculated using the following relation derived from Herzian contact mechanics: \(^{52}\)

\[
A = \pi \left( \frac{3P_{\text{eff}}r}{4E^*} \right)^{2/3}
\]

where \(r\) is the tip radius, \(P_{\text{eff}}\) is the tip pressure force, and \(E^*\) is the effective modulus of LLZO, which we estimate to be \(~60\text{GPa}.\) \(^{53}\) The tip radius is about 20 nm and the tip pressure is about 400 nN calculated from our force curve measurement. From this calculation we assess the contact area in our studies to be \(~30\text{ nm}^2.\)

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**Author contributions**

Z.L. and Z.Y. contributed equally to this work. Z.L. conceived the idea, carried out the electrochemical tests, and analyzed the data. Z.Y. and W.L. carried out the AFM tests.
C.L., K.W., and J.H. prepared the samples. C.Y. conceived the idea and analyzed the data. All co-authors took part in the writing and revision of the manuscript.