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# Tuning Interface Lithiophobicity for Lithium Metal Solid-State Batteries

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ABSTRACT: Solid-state lithium batteries (SSLBs) using garnet electrolytes potentially have a higher energy density and are safer than liquid organic electrolyte Li-ion batteries. However, SSLBs face challenges of Li dendrite and high interface resistance. In this work, we overcome both challenges by doping strontium (Sr) into lithium anodes. Different from all previous metal/metal oxide coating on garnet or Li alloy anodes that form lithiophilic interlayer, Li–Sr/SrO-doped Li <sub>2</sub> O are enriched on the interface forming a lithiophilic/lithiophobic bifunctional layer. The interlayer reduces the interfacial resistance and also suppresses lithium dendrite. The stability of the lithiophobic SrO-doped Li <sub>2</sub> O against Li prevents reducing the garnet and suppresses Li dendrite.	Li metal Li metal Carnet Garnet Lithium Dendrite Suppression Lithiophilic Li-Sr alloy Lithiophobic Li <sub>2</sub> O with SrO Anchors

which distinguishes it from all reported alloy electron-conducting interlayers. The optimized Li–Sr|garnet|Li–Sr symmetric cell achieves a critical current density of 1.3 mA/cm<sup>2</sup> and can be cycled for 1,000 cycles under 0.5 mA/cm<sup>2</sup> at room temperature. The bifunctional lithiophilic/lithiophobic interlayer provides a new strategy for high-performance garnet solid-state lithium batteries.

ithium-ion batteries (LIBs) applications have expanded from electronics to electric vehicles (EVs).<sup>1</sup> To ease the safety concerns<sup>2</sup> and the "range anxiety", the solid-state lithium battery (SSLB) becomes a more attractive choice. The replacement of flammable and toxic liquid electrolyte<sup>3</sup> with solid-state electrolyte (SSE) makes it a safer option. Moreover, the wide electrochemical window of SSE enables the utilization of high-voltage cathodes and Li-metal anodes, which leads to a higher output voltage and thus a higher energy density.

Among all of the inorganic SSE, garnet SSE with a nominal formula Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> (LLZO)<sup>4</sup> demonstrates a high ionic conductivity (1 mS/cm for Ta-doped LLZO<sup>5</sup>) and wide electrochemical window.<sup>4,6</sup> In addition, the high mechanical properties are expected to block the lithium dendrite penetration. Unfortunately, short-circuiting is still observed even at a low current density and a low capacity. Meanwhile, solid-solid contact at LilLLZO also induces a high interface resistance, which accelerates the reduction of the SSE and the dendrite growth. Thus, interfacial engineering that is aiming to minimize interfacial impedances is critical for SSLB. Introducing a lithiophilic interlayer to wet Li metal is proved as an effective strategy to reduce the interface resistance. Various materials, such as Au,<sup>7</sup> Mg,<sup>8,9</sup> Ag,<sup>10</sup> Ge,<sup>11</sup> Al,<sup>12</sup> Si,<sup>13</sup> Al<sub>2</sub>O<sub>3</sub>,<sup>14</sup> and ZnO,<sup>15</sup> have been utilized to form alloys or prelithated layers. In addition, various surface coating technologies, such as sputtering,<sup>18</sup> vapor deposition,<sup>12</sup> metal salt aqueous solution,<sup>16</sup> and atomic layer deposition,<sup>17</sup> are applied to form an interlayer between Li and garnet. Interfacial engineering has successfully reduced interfacial resistance from thousands to single-digit  $\Omega$  cm<sup>2,14</sup> This extremely small interfacial resistance at LilSSE already rivals the ones in conventional LIBs employing liquid electrolytes.<sup>18</sup> However, these interlayers are electronically conductive, which promotes the reduction of solid-state electrolytes and Li dendrite growth. The interfacial engineering seems to be stuck in a new bottleneck since no breakthrough has been obtained using new interfacial materials or coating methods. A strategy forming a stable interlayer that keeps an ionic-conducting nature and separates the lithium plating position away from the SSE is needed.

For Li anode, one significant interface resistance comes from the void formation during Li stripping at a high current and capacity due to low Li<sup>0</sup> diffusivity and large volume shrinking. Since the voids cannot be completely healed in the following Li plating process, the void will accumulate into a large hole, increasing the interface resistance.<sup>19,20</sup> If pressure is applied, the plastic deformation capability of the anode also plays an essential role in void evolution.<sup>21</sup> The Li<sup>0</sup> self-diffusivity can be

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Figure 1. Assembling and characterization of Li–SrlLLZTO interface. (a) Digital photographs showing the process of attaching the Li–Sr onto garnet LLZTO pellet. Cross-section morphology (b–e) and Sr elemental mapping (f–i) of the Li–Sr-1%, Li–Sr-5%, Li–Sr-10%, and Li–Sr-20% electrode interface with the LLZTO pellet. The red dashed lines mark the interfaces.

accelerated by the high lithiophilicity at the Li/SSE interface.<sup>9</sup> However, the wisdom of Li dendrite suppression in liquid electrolytes suggests that a lithiophobic SEI is needed to achieve a high critical current density (CCD), which in turn will increase the interface resistance. To simultaneously reduce the interface resistance and also suppress lithium dendrite, a bifunctional surface layer that forms lithiophilic inner-face bonding to Li and lithiophobic out-layer bonding to SSE is desired. To maintain a low interface resistance during longterm lithium plating/stripping cycles, the lithiophilic/lithiophobic bifunctional layer should be stable at the SSElanode interface without diffusion into or reaction with either Li or SSE and should not reduce the diffusivity of Li<sup>0</sup> and/or Li<sup>+</sup>. Although the alloy interface can provide an initial good wettability, the electron-conducting nature of the alloy interfacial layer will facilitate the charge transfer reaction to take place right between the interlayer and the SSE.<sup>22</sup> The deposition of lithium will push the alloy layer away instead of remaining located at the SSElanode interface,<sup>8,23–25</sup> which may not be able to remain a benefit for the long-term operation condition.

The ideal bifunctional interlayer for lithium anode should (1) be stably enriched at the LilSSE interface where the lithiophilic part is toward the inside Li and the lithiophobic part is toward SSE; (2) not reduce the anode  $\text{Li}^0$  diffusivity on the lithiophilic side and not reduce the SSE on the lithiophobic side; and (3) have a plastic deformation capability to accommodate Li volume change. However, such a Li bifunctional layer has not been explored yet.

 $Li_2O$  has a high interfacial energy,  $\gamma$ , and high Li dendrite suppression ability,  $\gamma E_{1}^{26}$  which can function as a lithiophobic interlayer to suppress the lithium dendrite growth, as the interfacial energy and lithiophobicity should reflect each other from energy and macroscopic angles, respectively.<sup>27</sup> However, the low ionic conductivity and high interface resistance at Lil Li<sub>2</sub>O also introduced considerable resistance.<sup>28</sup> In this work, we demonstrated that 1% of strontium and in situ formed SrO can serve as a bifunctional interlayer where SrO-doped Li<sub>2</sub>O retains the high lithiophobic nature of the Li<sub>2</sub>O but reduces resistance due to the formation of a lithiophilic Li-Sr alloy. The unique bifunctional property of Sr-in-Li anodes can reduce the interface resistance and also suppress the Li dendrite, which is distinct from other alloy electron-conductor layers. SrO also shows a robust garnet-philic property as evidenced by the high ionic conductivity of Sr-doped garnet,<sup>29,30</sup> and the high wetting capability of Sr-in-Li on garnet. Using Ta-doped LLZTO (Li<sub>6.5</sub>La<sub>3</sub>Zr<sub>1.5</sub>Ta<sub>0.5</sub>O<sub>12</sub>) as a model solid-state electrolyte,<sup>5</sup> the interface resistance, critical current density, and cycle stability of LLZTO were systematically investigated using bifunctional Sr-in-Li anodes. The mechanism of bifunctional Sr-Li at LilLLZTO was revealed using comprehensive material characterization, electrochemical performance evaluation, and simulation.

Li-SrlLLZTO Interface and Li-Sr Anode. Li-Sr alloys with 1, 5, 10, and 20% mole ratio Sr were synthesized by melting Li and Sr at 300 °C. The corresponding Li-Sr alloys were noted as Li-Sr-1%, Li-Sr-5%, Li-Sr-10%, and Li-Sr-20%, respectively. As shown in Figure 1a, when the polished

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Figure 2. Characterization and calculation of the Lilgarnet interface. (a) SEM image of a crater sputtered by the Ga<sup>+</sup>-ion beam on the Li-Sr-1% LLZTO interface showing the cross-sectional surface with an EDS elemental line scanning of the La L along scanning blue line. (b) ToF-SIMS analysis of the Li-Sr-1%|LLZTO interface. (c) XPS spectra of Sr 3d and O 1s on the Li-Sr-1%|LLZTO interface with 3,000 s of Ar<sup>+</sup>ion gun etching to remove the residual anode metal. The Li<sub>2</sub>CO<sub>3</sub> signals are mainly from the environment. (d) Atomic structures of the Li (110)-Li<sub>2</sub>O (111) interface, the Li<sub>2</sub>O (111)-garnet (100) interface, the Li (110)-SrO (100) interface, and the SrO (100)-garnet (100) interface, with the corresponding calculated interface energy  $\gamma$  by DFT. (e) Schematic diagram of the bifunctional lithiophilic/lithiophobic interlayer.

0.82 J/m<sup>2</sup>

LLZTO pellet was immersed into the molten Li-Sr alloy, liquid Li-Sr alloy quickly spread onto the LLZTO surface, indicating a high wettability of Li-Sr alloy with LLZTO.

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The morphology and element distribution of the crosssection of Li-SrlLLZTO interfaces were characterized by scanning electron microscopy (SEM). As shown in Figure 1bi, all of the Li-SrlLLZTO interfaces, regardless of anode composition, demonstrated seamless contact, confirming the high wettability of Li-Sr alloy against LLZTO. However, the microstructure of Li-Sr anodes varies for different ratios Li-Sr. Li-Sr-1% anode showed a monolith metal-like smooth surface, while inhomogeneous blocks and granules were found for Li-Sr-5%, Li-Sr-10%, and Li-Sr-20% anodes. The morphological variation should be attributed to the different phase compositions of Li-Sr alloy. According to the energydispersive X-ray spectroscopy (EDS) mapping, for low Sr contained alloy (1%), Sr mainly segregates at the interface between LLZTO and Li anode. The segregation of Sr at interface is attributed to the high wettability of the Li-Sr alloy to LLZTO due to the strong interaction of Sr with O atom at the interface.<sup>31,32</sup> As the Sr ratio in Li–Sr alloy (Figure 1f–h) increases, more Sr atoms can be found inside the bulk Li anode rather than segregating at the interface. Apparently, a higher

ratio of Sr (>5% Sr) will simultaneously affect the interface contact and the bulk Li anode.

Li-Sr allov

SrO doped Li<sub>2</sub>O

According to the phase diagram in Supporting Information Figure S1, the equilibrium Li-Sr-1% alloy consists of Li metal and a small amount of Li23Sr6 intermetallic compound. Li23Sr6 can react with trace oxygen in the glovebox, forming a lithiophobic Li-Sr-O layer on the Li surface and anchoring to the LLZTO (Figure 1f). With increasing Sr, the content of the Li<sub>6</sub>Sr<sub>23</sub> phase quickly increases and Li<sub>6</sub>Sr<sub>23</sub> will distribute into bulk Li, forming an inhomogeneous composite microstructure (Figure 1g-i). For Li-Sr-20% anode, the main component is the Li<sub>23</sub>Sr<sub>6</sub> phase (Figure S1), which has quite different physical and chemical properties compared with those of Li metal. The morphological and composition variation of the alloys affected the electrochemical performances when serving as anode for SSLBs.

The Sr element segregation at LilLLZTO interface for Li-Sr-1% anode was further characterized using depth-profiling time-of-flight secondary-ion mass spectroscopy (ToF-SIMS). As shown in Figure 2a, after removing Li-Sr-1% anode from LLZTO with a scraper, the LLZTO surface was sputtered using Ga<sup>+</sup>-ion beam. The LilLLZTO interface can be clearly noticed on the SEM of the crater (marked with a white dashed

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Figure 3. Electrochemical performance Li–SrlLZTO/Li–Sr symmetric cells. (a) Impedance spectra of the symmetric cells tested at room temperature from 1 MHz to 0.01 Hz (from top panel to bottom panel are Li–Sr-1%, Li–Sr-5%, Li–Sr-10%, and Li–Sr-20%). (b) Li plating/ stripping behavior for these cells at a step-increase current for 0.5 h, with (c) a magnified figure for the first five cycles. (d) Critical current densities and resistances vs the Sr mole ratio in the anode. (e) Li plating/stripping behavior for the cell at a step-increase current for 1.0 h.

line), which ensures the sputtering depth was deep enough to reach the interface as well as the SSE. EDS elemental line scanning was conducted on the line marked in blue (Figure 2a), and the distribution of the La element (red line in Figure 2a) agrees well with the SEM result. Accordingly, the ToF-SIMS analysis in Figure 2b shows a clear rise in the distribution of Zr (90), La (139), Li (7), and O (16) ions that are indicating the ion beam sputtering had reached the LLZTO solid electrolyte. Notably, the Sr (88) ion shows a peak right before the LLZTO phase, which validated the segregation of Sr element on the LilLLZTO interface. The Sr-ion enriched layer is around 250 nm thick, according to the ToF-SIMS analysis.

X-ray photoelectron spectroscopy (XPS) was also conducted with Ar<sup>+</sup> ion gun etching to identify the valence of Sr element in this layer. As shown in Figures S2 and S3, Sr 3d enriched at the 3,000 s cycle, while, after that, a more than 16 times Zr 3d amount and a reduced Sr 3d amount indicated the etching already reached the LLZTO layer. Therefore, the LilLLZTO interface is at the 3,000 s cycle; Sr 3d and Zr 3d here were analyzed in detail. From the Sr 3d spectra (Figure 2c), the peaks for  $3d_{5/2}$  and  $3d_{3/2}$  of SrO<sup>33</sup> were located at 135.3 and 133.5 eV, respectively. O 1s demonstrated that SrO-doped Li<sub>2</sub>O exists on the LilLLZTO interface (Figure 2c). In addition to SrO, LiCO<sub>3</sub> also exists, which may come from atmospheric contamination. The quantification analysis (Figure S4) shows that Li<sub>2</sub>O:SrO composition is roughly 9:1. Li<sub>2</sub>O is lithiophobic with high interfacial energy of  $0.75 \text{ J/m}^2$  and a high Li dendrite suppression ability.<sup>26</sup> However, the low Li-ion conductivity of Li<sub>2</sub>O also induces a large overpotential.<sup>28</sup> Metal oxide doping to Li<sub>2</sub>O can be an effective method to reduce the resistance. SrO is one of the very few metal oxides that is relatively stable against Li with an equilibrium potential of 5.0 mV vs Li,<sup>34</sup> similar to LLZO.<sup>6</sup> In addition, the thermodynamic calculations were done using HSC software<sup>35</sup> (Table S1) and the positive Gibbs energy for the reaction between Li and SrO also verifies the relative stability of SrO against Li. Therefore, SrO-doped Li2O is stable with Li. In addition, SrO-doped Li2O also enhances the wettability with significantly reduced interface

resistance (discussed in the following section) by reducing the interface energy between  $Li_2O$  and LLZTO, as demonstrated by the density functional theory (DFT) calculation. Figure 2d demonstrated that  $Li_2O$  is garnet-phobic due to the high interfacial energy of  $1.03 \text{ J/m}^2$  with garnet. Since the  $Li_2O$  layer on the molten Li surface is unavoidable even in the glovebox, the molten Li with  $Li_2O$  surface cannot wet the LLZTO. Since SrO has low interface energy with garnet ( $0.82 \text{ J/m}^2$ ) and low interfacial energy against Li ( $0.26 \text{ J/m}^2$ ), SrO-doped  $Li_2O$  functions as an anchor to bond both Li anode and LLZTO, which significantly reduce the interface resistance. In addition, the lithiophobic SrO-doped  $Li_2O$  with low electronic conductivity can also suppress the reduction of LLZTO and Li dendrite growth (Figure 2e).

Electrochemical Behavior of Li-SrlLLZTOLLi-Sr Symmetric Cells. The Li plating/stripping behavior of Li–Sr alloy anodes with different Li-Sr ratios was evaluated at room temperature using symmetric cells. The interfacial resistance before cycling was first measured using electrochemical impedance spectra (EIS). EIS plots (Figure 3a) of Li-Srl LLZTOILi-Sr cells demonstrated that Li-Sr-1% anode has the lowest impedance, and the total impedance of symmetric cells increase with Sr content in Li. The first semicircle (~1 kHz) of EIS plots is attributed to the total resistance of the LLZTO pellets (bulk and grain boundary), which is about 130–135  $\Omega$  cm<sup>2</sup> due to the difference of LLZTO pellets, which is consistent with conductivity measurement of LLZTO (Figure S5) and reported results.<sup>36</sup> The interfacial resistances (1 kHz to 0.1 Hz) increase with Sr content, but they are still much smaller than that of LilLLZTOLLi cells (Figure S6). The resistance from 1 kHz to 0.01 Hz vastly increases with the increase of Sr content in the anode as 14, 40, 45, and 57  $\Omega$  cm<sup>2</sup> for Li-Sr-1%, Li-Sr-5%, Li-Sr-10%, and Li-Sr-20% anodes, respectively (Figure 3d), indicating that excess Li<sub>23</sub>Sr<sub>6</sub> in bulk Li can reduce the Li atom diffusion.

The CCD was evaluated using Li–SrlLLZTOLLi–Sr cells by a step-increase current for a fixed 0.5 h of Li plating and 0.5 h of Li stripping. As shown in Figure 3b, the CCD for Li–Sr-1%



Figure 4. Cycling stability of Li–SrlLLZTOlLi–Sr symmetric cells. (a) Long-term cycling performance at  $0.2 \text{ mA/cm}^2$  with different Li–Sr anodes. (b) Rate performances of Li–Sr-1% lLLZTOlLi–Sr-1% symmetric cell from 0.1 to 0.5 mA/cm<sup>2</sup>. (c) Long-term cycling performance of Li–Sr-1% lLLZTOlLi–Sr-1% symmetric cell at 0.5 mA/cm<sup>2</sup>. Insets are the magnifications of the voltage profiles of 1–10 and 950–1000 cycles.

cell is  $1.3 \text{ mA/cm}^2$  at 0.65 mAh cm<sup>-2</sup>, which is an order of magnitude higher than the CCD for LilLLZTOLLi (Figure S6) and is one of the highest among all reported alloy-based anodel LLZTO.<sup>22</sup> Therefore, SrO-doped Li<sub>2</sub>O bifunctional layer has a high Li dendrite suppression capability. Nevertheless, the CCD for the cells with Li-Sr-5%, Li-Sr-10%, and Li-Sr-20% anodes are only 0.40, 0.30, and 0.25 mA/cm<sup>2</sup>, which are in line with resistance increase with Sr content in the EIS measurement (Figure 3d). Detailed analysis of Li plating/stripping curves of all Li-Sr anodes shows a rapid increase in the slope of the voltage profiles at the latest stripping state right before short circuit. The rapid increase of voltage can be induced by void formation. The void formation reduced the contact area at LilLLZTO, which increases the local current density, thus reducing the CCD. For example, for Li-Sr-1% anode, the transformation from flat voltage plateau to drastic polarization did not happen until a current density of  $\sim 1 \text{ mA/cm}^2$ , while for the other three conditions the apparent potential boost occurred at a much lower current of 0.1 mA/cm<sup>2</sup> since  $Li_{23}Sr_6$ in bulk Li may reduce the Li atom diffusion (Figure 3c). When the Li plating/stripping time was extended from 1.0 to 2.0 h, CCD of Li-SrlLLZTO/Li-Sr cell was decreased from 1.3 mA  $cm^{-2}$  (Figure 2b) to 0.6 mA/cm<sup>2</sup> (Figure 3e), while the capacity at 1.0 h of plating and stripping time before shortcircuit is similar to the capacity of 0.65 mAh/cm<sup>2</sup> measured at a shorter time of 0.5 h (Figure 3b), indicating that the amount of transported Li species controlled the void formation and also Li dendrite growth for the Li-Sr-1% anode.

The cycling stability of Li–SrlLLZTOILi–Sr symmetric cells under a constant current of 0.2 mA/cm<sup>2</sup> and capacity of 0.1 mAh/cm<sup>2</sup> were also investigated. As exhibited in Figure 4a, the Li–Sr-1%ILLZTOILi–Sr-1% symmetric cell demonstrated an excellent stability for 1,000 cycles with a neat and flat potential profile. In contrast, an intense polarization occurs in the Li–Sr-5% and Li–Sr-10% cells and follows with a short-circuit within the first five cycles. Even when current density increases to 0.5  $\text{mA/cm}^2$ , the Li–Sr-1%|LLZTO|Li–Sr-1% symmetric cell still shows superior cycling stability without any intense polarization for 1,000 cycles (Figure 4c), which is one of the best among reported planar garnet type solid-state electrolytes work at room temperature (Table S2).

The rate performance of Li–Sr-1%lLLZTOlLi–Sr-1% symmetric cell was tested at step-increase currents of 0.1, 0.2, 0.3, 0.4, and 0.5 mA/cm<sup>2</sup> for 10 cycles at each current density and then moved back to 0.4 mA/cm<sup>2</sup> (Figure 4b). The Li plating/stripping curve at 0.4 mA/cm<sup>2</sup> before and after increasing the current is identical, demonstrating a stable Li–SrlLLZTO interface during cycling at different currents.

Mechanism for the Intense Polarization of Li-Srl LLZTOILi-Sr Cells. As shown in Figure 3c and Figure 4a, in the first few cycles, a flat and similar potential profile was found for all cells. However, the polarization quickly increases for Li-Sr anodes with Sr content  $\geq$  5%, as demonstrated by either an increase of current density or constantly current cycling. The interpretation of this strong polarization (Figure S7) is crucial for the understanding of the failure mechanism. As the current density increases in a linear step in the CCD test, the ionic transportation inside SSEs should also render linear overpotential according to the Nernst-Planck equation, which is not the case for this intense polarization. The increase in Li plating/stripping overpotential at the latest Li plating/stripping stage can potentially be attributed to (1) phase transformation at the LilLLZTO interface between Li23Sr6 and Li2Sr3 with different lithiation/delithiation potentials (Figure S1) because the Li<sub>23</sub>Sr<sub>6</sub> phase may change to Li<sub>2</sub>Sr<sub>3</sub> in the Li stripping process, (2) void formation due to reduced Li atom diffusion by  $Li_{23}Sr_6$  phase in bulk Li, and (3) formation of cracks in the bulk Li-Sr anodes due to the large volume changes during Li plating/stripping.



Figure 5. Electrochemical and mechanical stabilities of Li–Sr anodes and LilLLZTO interface. (a) DFT calculation for the equilibrium potentials of Li–Sr alloys. (b) Digital pictures of Li–Sr alloys with significantly different ductility and malleability after pressing. (c–f) Morphologies and Sr elemental mapping of Li–SrlSSE interface after two cycles with a current density of 0.2 mA/cm<sup>2</sup> and capacity of 0.1 mAh/cm<sup>2</sup>.



Figure 6. Electrochemical performance of Li–Sr-1% LLZTO NMC811 cells. (a) Schematic diagram of a Li–Sr LLZTO NMC811 cell. (b) Impedance spectra of the cell tested at room temperature before (black circle) and after 100 cycles (red circle). (c, d) Cycle performances for the cell at 0.2 C with cathode loading of 0.8 mAh/cm<sup>2</sup> (0.1 C for the first cycle for activation). (e, f) Rate performance for the cell at stepped C-rate.

The boosting overpotential can be a sign of overcoming a high energy barrier. We first calculated the equilibrium potentials of  $Li_{23}Sr_6$  and  $Li_2Sr_3$  using DFT since  $Li_{23}Sr_6$  phase will convert into  $Li_2Sr_3$  during Li stripping. The equilibrium potentials of  $Li_2Sr_3$  and  $Li_{23}Sr_6$  are 27.8 and 25.7 mV, respectively (Figure 5a). The 2.0 mV potential difference cannot cause a significant potential increase at the latest Li stripping state right before short-circuit.

The void formation at the LilLLZTO interface may be responsible for the polarization at the latest Li stripping stage, where the Li vacancy diffusion inside the alloy electrode cannot keep the pace of the current increasing.<sup>9,20</sup> The void evolution is closely related to the Li atom diffusivity in bulk Li, the lithiophilic/lithiophobic property at the Li–SrlSrO-doped Li<sub>2</sub>OlLLZTO interface. A high CCD of 1.3 mA/cm<sup>2</sup> for Li–Sr-1% anode at a high capacity of 0.65 mAh/cm<sup>2</sup> is attributed to the bifunctional SrO-doped Li<sub>2</sub>O interlayer that bonds Li to

 $Li_2O$  and also reduces the interface energy at  $Li_2OILLZTO$ , decreasing the interface resistance and also suppressing Li dendrite growth. With the increasing of Sr content in Li–Sr anodes, a large amount of  $Li_{23}Sr_6$  phase is distributed inside Li, reducing the Li diffusivity, thus forming voids at the early stage of Li stripping and thus a low CCD.

The cracks formed inside the Li–Sr bulk due to the poor mechanical property of the  $Li_{23}Sr_6$  phase may also contribute to the low CCD. The brittle  $Li_{23}Sr_6$  phase in Li–Sr anodes will crack during the significant volume change in Li plating/ stripping, which also blocks the Li atom diffusion to the interface and reduces the contact area.<sup>19,21</sup> The deformation capability of Li–Sr anodes with different Sr content was evaluated using a facile pressing test. As shown in Figure 5b, the flow and elastic behavior exhibit noteworthy differences by pressing the Li-metal ball, as well as the Li–Sr-alloy balls under 2 MPa. The Li-metal and the Li–Sr-1% alloy demonstrate

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good ductility and form thin foils with a smooth surface and metallic luster, while the Li-Sr-5%, -10%, and -20% alloys render wrinkles, cracks gaps, and even fracture. As shown in Figure S8, the pressed Li-Sr-20% has a sharp fracture and part of it even shattered into small pieces. Although a precise or quantitative study on the deformation property is absent, the contract is distinct. A significantly worse ductility and malleability can be anticipated with the increase of the Sr ratio in Li-Sr alloy, which would introduce more detrimental cracks during cycling. The postmortem SEM was taken after the cycling test to analyze the morphology and element distribution evolution of the cross-section of Li-SrlLLZTO interfaces. As shown in Figure 5c-f, after Li plating/stripping cycles, Sr is still enriched at LilLLZTO interface without being pushed away due to the high stability of the SrO anchor, which is totally different from those electron-conducting alloy coatings. However, gaps can be clearly seen between the LLZTO and anode for the Li-Sr-10% and -20% cells, as evidence of void formation and contact loss. Cracks and holes also appeared in Li–Sr anode bulk with Sr > 5%.

Electrochemical Behavior of the Proof-of-Concept Li-SrlLLZTOLLiNi<sub>0.8</sub>Mn<sub>0.1</sub>Co<sub>0.1</sub>O<sub>2</sub> (NMC811) Cells. Since Li-Sr-1% anode shows the high CCD, high cycling stability with LLZTO electrolyte, it was selected for additional cell evaluation. Li-Sr-1%|LLZTO|LiNi<sub>0.8</sub>Mn<sub>0.1</sub>Co<sub>0.1</sub>O<sub>2</sub> (NMC811) cells were assembled as the schematic diagram demonstrated in Figure 6a, with liquid electrolyte wetted cathode interface (Table S3) to eliminate the cathode side contact influence. The cell provides 192 mAh/g at 0.2 C from 2.7 to 4.3 V (Figure 6c) with a capacity retention of 82% after 100 cycles (Figure 6d). The EIS plots (Figure 6b) before and after 100 cycles indicate a small resistance reduction without shortcircuiting. The initial Coulombic efficiency of 91.68% at 0.1 C and average Coulombic efficiency of 99.82% for the rest cycles at 0.2 C were displayed. The cell delivered discharge capacities of 192.1, 174.4, 153.0, 132.2, and 107.0 mAh/g at 0.1, 0.2, 0.3, 0.4 and 0.5 C (Figure 6e). The capacity quickly recovered to 175.2 mAh/g when the current was set back to 0.1 C (Figure 6f). Long cycling of 500 cycles for Li-SrlLLZTOlLiFePO<sub>4</sub> cell is also presented in Figure S9. These results indicate Li-Sr-1% is a stable anode (Figure S10) against LLZTO during cycling. However, further optimizations of liquid-free cathode interface engineering are still needed to realize practical applications of all-solid-state lithium-metal batteries (ASSLB).

Solid-state Li-metal batteries face two critical challenges of Li dendrite growth and high interface resistance. To suppress Li dendrite growth, the interface should be lithiophobic (dendrite-phobic), while low interface resistance requires a lithiophilic (wetting) interface. The dilemma between interface wetting and dendrite-phobicity was solved with a unique combination of strontium and in situ formed SrO, which facilitate a bifunctional lithiophilic/lithiophobic interlayer combining low interface resistance and high dendrite suppression capability. SrO is stable with Li and facilitates the contact between anode and LLZTO by reducing the interface energy between Li2O and LLZTO. It serves as an anchor which allows the Li to be deposited between the interfacial layer and the anode that (1) suppress the lithium nucleation and dendrite propagation on SSE; (2) keep the interfacial layer stable on the anodelSSE interface instead of being pushed away; (3) reduce the resistance of the  $Li_2O$ lithiophobic layer but keep its lithiophobic nature; and (4) have high affinity to garnet. An optimized Li-1% Sr alloy

anodelLLZTO can synergistically achieve a low interface resistance and high Li dendrite suppression capability, as evidenced by a high CCD of  $1.3 \text{ mA/cm}^2$  at  $0.65 \text{ mAh/cm}^2$  and a stable cycle of 1,000 cycles (1,000 h) under  $0.5 \text{ mA/cm}^2$  at room temperature. This work provides a new strategy and sheds light on enhancing the performance of SSLBs.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.1c02122.

Experimental details; (Figures S1–S10, Table S1–S3) phase diagram of the Li–Sr system, XPS spectra and the quantification of the interface, thermodynamic calculations result, Arrhenius plot, digital photographs, electrochemical performances, reported results (PDF)

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## **Author Contributions**

X.H., X.J., and C.W. designed the experiments. X.H., X.J., H.W., and S.L. performed the material synthesis/preparation. X.H. and X.J. conducted electrochemical experiments. X.J. and B.Z. conducted the DFT calculations. J.X., N.D.R., S.H., T.D., and B.L.L. performed SEM, XPS, and ToF-SIMS. X.H., K.G., and B.N. performed XPS analysis. X.H. wrote the draft manuscript. All authors revised the manuscript. C.W. conceived and supervised the project.

## Notes

The authors declare no competing financial interest.

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