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 Li2O are enriched on the interface forming a lithiopholic/lithiophobic bifunctional layer. The interlayer reduces the interfacial resistance and also suppresses lithium dendrite. The stability of the lithiophobic SrO-doped Li2O against Li prevents reducing the garnet and suppresses Li dendrite, which distinguishes it from all reported alloy electron-conducting interlayers. The optimized Li−Sr/garnetLi−Sr symmetric cell achieves a critical current density of 1.3 mA/cm² and can be cycled for 1,000 cycles under 0.5 mA/cm² at room temperature. The bifunctional lithiophilic/lithiophobic interlayer provides a new strategy for high-performance garnet solid-state lithium batteries.

Lithium-ion batteries (LIBs) applications have expanded from electronics to electric vehicles (EVs). To ease the safety concerns and the “range anxiety”, the solid-state lithium battery (SSLB) becomes a more attractive choice. The replacement of flammable and toxic liquid electrolyte 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 Li₇La₃Zr₂O₁₂ (LLZO) demonstrates a high ionic conductivity (1 mS/cm for Ta-doped LLZO) and wide electrochemical window. In 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 Li/LLZO 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, Mg, Ag, Ge, Al, Si, Al₂O₃, and ZnO, have been utilized to form alloys or prelithiated layers. In addition, various surface coating technologies, such as sputtering, vapor deposition, metal salt aqueous solution, and atomic layer deposition, are applied to form an interlayer between Li and garnet. Interfacial engineering has successfully reduced interfacial resistance from thousands to single-digit Ω cm. This extremely small interfacial resistance at Li/SSE already rivals the ones in conventional LIBs employing liquid electrolytes. 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 Li⁰ 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. If pressure is applied, the plastic deformation capability of the anode also plays an essential role in void evolution. The Li⁰ self-diffusivity can be...
accelerated by the high lithiophilicity at the Li/SSE interface.9 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 long-term lithium plating/stripping cycles, the lithiophilic/lithiophobic bifunctional layer should be stable at the SEI/anode interface without diffusion into or reaction with either Li or SSE and should not reduce the diffusivity of Li0 and/or Li+.

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.22 The deposition of lithium will push the alloy layer away instead of remaining located at the SEI/anode interface,8,23−25 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 Li/SSE interface where the lithiophilic part is toward the inside Li and the lithiophobic part is toward SSE; (2) not reduce the anode Li0 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.

Li2O has a high interfacial energy, γ, and high Li dendrite suppression ability, γE,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.27 However, the low ionic conductivity and high interface resistance at Li/Li2O also introduced considerable resistance.28 In this work, we demonstrated that 1% of strontium and in situ formed SrO can serve as a bifunctional interlayer where SrO-doped Li2O retains the high lithiophobic nature of the Li2O 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,29,30 and the high wetting capability of Sr-in-Li on garnet. Using Ta-doped LLZTO (Li6.5La3Zr1.5Ta0.5O12) as a model solid-state electrolyte,5 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 Li/LiLLZTO was revealed using comprehensive material characterization, electrochemical performance evaluation, and simulation.

Li−SrLLZTO 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...
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.

The morphology and element distribution of the cross-section of Li−Sr|LLZTO interfaces were characterized by scanning electron microscopy (SEM). As shown in Figure 1b−i, all of the Li−Sr|LLZTO 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 energy-dispersive 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.31,32 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.

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 Li6Sr23 phase quickly increases and Li6Sr23 will distribute into bulk Li, forming an inhomogeneous composite microstructure (Figure 1g−i). For Li−Sr-20% anode, the main component is the Li23Sr6 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 Li−Sr|LLZTO 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+ ion beam. The Li−Sr|LLZTO interface can be clearly noticed on the SEM of the crater (marked with a white dashed line) of Figure 2. Characterization and calculation of the Li−garnet interface. (a) SEM image of a crater sputtered by the Ga+ 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+ ion gun etching to remove the residual anode metal. The Li2CO3 signals are mainly from the environment. (d) Atomic structures of the Li (110)−Li2O (111) interface, the Li2O (111)−garnet (100) interface, the Li (110)−SrO (100) interface, and the SrO (100)−garnet (100) interface, with the corresponding calculated interface energy γ by DFT. (e) Schematic diagram of the bifunctional lithiophilic/lithiophobic interlayer.
sticking tendency. (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 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. 

Figure 3. Electrochemical performance Li−SrLLZTOLi−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.
cell is 1.3 mA/cm² at 0.65 mAh cm⁻², which is an order of magnitude higher than the CCD for Li1.55LLZTOLi (Figure S6) and is one of the highest among all reported alloy-based anode LLZTO. Therefore, SrO-doped LiO₂ 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/cm², 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 Li1.55LLZTOLi, 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 ~1 mA/cm², while for the other three conditions the apparent potential boost occurred at a much lower current of 0.1 mA/cm² since Li1.23Sr6 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–Sr-1%LLZTOLi–Sr-1% cell was decreased from 1.3 mA cm⁻² (Figure 2b) to 0.6 mA cm⁻² (Figure 3e), while the capacity at 1.0 h of plating and stripping time before short-circuit is similar to the capacity of 0.65 mAh/cm² 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–Sr-1%LLZTOLi–Sr symmetric cells under a constant current of 0.2 mA/cm² and capacity of 0.1 mA/cm² were also investigated. As exhibited in Figure 4a, the Li–Sr-1%LLZTOLi–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 mA/cm², the Li–Sr-1%LLZTOLi–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%LLZTOLi–Sr-1% symmetric cell was tested at step-increase currents of 0.1, 0.2, 0.3, 0.4, and 0.5 mA/cm² for 10 cycles at each current density and then moved back to 0.4 mA/cm² (Figure 4b). The Li plating/stripping curve at 0.4 mA/cm² before and after increasing the current is identical, demonstrating a stable Li–Sr1LLZTOLi interface during cycling at different currents.

**Mechanism for the Intense Polarization of Li–Sr LLZTOLi–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 ≥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 over-potential 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 Li1.55LLZTOLi interface between Li1.23Sr6 and Li0.7Sr3 with different lithiation/delithiation potentials (Figure S1) because the Li1.23Sr6 phase may change to Li0.7Sr3 in the Li stripping process, (2) void formation due to reduced Li atom diffusion by Li1.23Sr6 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.
The boosting overpotential can be a sign of overcoming a high energy barrier. We first calculated the equilibrium potentials of Li−Sr alloys since Li23Sr6 phase will convert into Li2Sr3 during Li stripping. The equilibrium potentials of Li2Sr3 and Li23Sr6 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 Li|LLZTO 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.9,20 The void evolution is closely related to the Li atom diffusivity in bulk Li, the lithiophilic/lithiophobic property at the Li−Sr/SrO-doped Li2O|LLZTO interface. A high CCD of 1.3 mA/cm2 for Li−Sr-1% anode at a high capacity of 0.65 mAh/cm2 is attributed to the bifunctional SrO-doped Li2O interlayer that bonds Li to Li2O and also reduces the interface energy at Li2O|LLZTO, decreasing the interface resistance and also suppressing Li dendrite growth. With the increasing of Sr content in Li−Sr anodes, a large amount of Li23Sr6 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 Li23Sr6 phase may also contribute to the low CCD. The brittle Li23Sr6 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.19,21 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

Figure 5. Electrochemical and mechanical stabilities of Li−Sr anodes and Li|LLZTO 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−Sr/SSE interface after two cycles with a current density of 0.2 mA/cm2 and capacity of 0.1 mAh/cm2.

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/cm2 (0.1 C for the first cycle for activation). (e, f) Rate performance for the cell at stepped C-rate.
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–SrLLZTO interfaces. As shown in Figure 5c–f, after Li plating/stripping cycles, Sr is still enriched at LiLLZTO 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–SrLLZTOILiNi0.8Mn0.1Co0.1O2 (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%LLZTOILiNi0.8Mn0.1Co0.1O2 (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 short-circuiting. 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 cycle of 500 cycles for Li–SrLLZTOILiFePO4 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 anode/SSE interface instead of being pushed away; (3) reduce the resistance of the Li2O lithiophobic layer but keep its lithiophobic nature; and (4) have high affinity to garnet. An optimized Li-1% Sr alloy anodeLLZTO can synergistically achieve a low interface resistance and high Li dendrite suppression capability, as evidenced by a high CCD of 1.3 mA/cm² at 0.65 mAh/cm² and a stable cycle of 1,000 cycles (1,000 h) under 0.5 mAh/cm² 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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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., B.Z. conducted the DFT calculations. J.X., N.D.R., S.H., T.D., H.W., and S.L. performed the material synthesis/preparation. X.H., X.J., and C.W. designed the experiments. X.H., X.J., and C.W. conceived and supervised the project.

Notes
The authors declare no competing financial interest.

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REFERENCES
(1) Diouf, B.; Pode, R. Potential of Lithium-Ion Batteries in Renewable Energy. Renewable Energy 2015, 76, 375–380.
(2) Feng, X.; Ouyang, M.; Liu, X.; Lu, L.; Xia, Y.; He, X. Thermal Runaway Mechanism of Lithium Ion Battery for Electric Vehicles: A Review. Energy Storage Mater. 2018, 10, 246–267.
(3) Auburch, D.; Zinigrad, E.; Cohen, Y.; Teller, H. A Short Review of Failure Mechanisms of Lithium Metal and Lithiated Graphite Anodes in Liquid Electrolyte Solutions. Solid State Ionics 2002, 148 (3–4), 405–416.
(4) Murugan, R.; Thangadurai, V.; Weppner, W. Fast Lithium Ion Conduction in Garnet-Type Li7La3Zr2O12. Angew. Chem., Int. Ed. 2007, 46 (41), 7778–7781.
(5) Li, Y.; Han, J.-T.; Wang, C.-A.; Xie, H.; Goodenough, J. B. Optimizing Li+ Conductivity in a Garnet Framework. J. Mater. Chem. 2012, 22 (30), 15357–15361.
(6) Han, F.; Zhu, Y.; He, X.; Mo, Y.; Wang, C. Electrochemical Stability of Li10GeP2S12 and Li7La3Zr2O12 Solid Electrolytes. Adv. Energy Mater. 2016, 6 (8), 1501590.
(7) Tsai, C.-L.; Roddatis, V.; Chandran, V. C.; Ma, Q.; Uhlenbruck, S.; Bram, M.; Heitjans, P.; Guillon, O. Li7La3Zr2O12 Interface Modification for Li Dendrite Prevention. ACS Appl. Mater. Interfaces 2016, 8 (16), 10617–10626.
(8) Fu, K.; Gong, Y.; Fu, Z.; Xie, H.; Yao, Y.; Liu, B.; Carter, M.; Wachsmann, E.; Hu, L. Transient Behavior of the Metal Interface in Lithium Metal–Garnet Batteries. Angew. Chem., Int. Ed. 2017, 56 (47), 14942–14947.
(9) Krauskopf, T.; Mogwitz, B.; Rosenbach, C.; Zeier, W. G.; Janek, J. Diffusion Limitation of Lithium Metal and Li–Mg Alloy Anodes on LLZO Type Solid Electrolytes as a Function of Temperature and Pressure. Adv. Energy Mater. 2019, 9 (44), 1902568.
(10) Feng, W.; Dong, X.; Li, P.; Wang, Y.; Xia, Y. Interfacial Modification of Li/Garnet Electrolyte by a Lithiophilic and Breathing Interlayer. J. Power Sources 2019, 419, 91–98.
(11) Luo, W.; Gong, Y.; Zhu, Y.; Li, Y.; Yao, Y.; Zhang, Y.; Fu, K.; Pastel, G.; Lin, C.; Mo, Y.; Wachsmann, E. D.; Hu, L. Reducing Interfacial Resistance between Garnet-Structured Solid-State Electro-
(27) Chen, J.; Li, Q.; Pollard, T. P.; Fan, X.; Borodin, O.; Wang, C. Electrolyte Design for Li Metal-Free Li Batteries. *Mater. Today* **2020**, 39, 118−126.

(28) Lorger, S.; Usiskin, R.; Maier, J. Transport and Charge Carrier Chemistry in Lithium Oxide. *J. Electrochem. Soc.* **2019**, 166 (10), A2215−A2220.

(29) Thangadurai, V.; Weppner, W. Li6Al2Ta2O12 (A = Sr,Ba): Novel Garnet-Like Oxides for Fast Lithium Ion Conductors. *Adv. Funct. Mater.* **2005**, 15 (1), 107−112.

(30) Thangadurai, V.; Weppner, W. Li6Al2Nb2O12 (A = Ca, Sr, Ba): A New Class of Fast Lithium Ion Conductors with Garnet-Like Structure. *J. Am. Ceram. Soc.* **2005**, 88 (2), 411−418.

(31) Cheng, K.; Xu, H.; Zhang, L.; Du, Y.; Zhou, J.; Tang, S.; Chen, M. Numerical Simulation of the SrZrO3 Formation in Solid Oxide Fuel Cells. *J. Electron. Mater.* **2019**, 48 (9), 5510−5515.

(32) Risold, D.; Hallstedt, B.; Gauckler, L. J. The Strontium-Oxygen System. *CALPHAD: Comput. Coupling Phase Diagrams Thermochem.* **1996**, 20 (3), 353−361.

(33) Van Doveren, H.; Verhoeven, J. A. T. H. XPS Spectra of Ca, Sr, Ba and Their Oxides. *J. Electron Spectrosc. Relat. Phenom.* **1980**, 21 (3), 265−273.

(34) Li, H.; Balaya, P.; Maier, J. Li Storage via Heterogeneous Reaction in Selected Binary Metal Fluorides and Oxides. *J. Electrochem. Soc.* **2004**, 151 (11), A1878.

(35) Roine, A. HSC - SOFTWARE VER. 3.0 FOR THERMODYNAMIC CALCULATIONS. *Proceedings of the International Symposium on Computer Software in Chemical and Extractive Metallurgy* **1989**, 15−29.

(36) Huang, X.; Lu, Y.; Guo, H.; Song, Z.; Xiu, T.; Badding, M. E.; Wen, Z. None-Mother-Powder Method to Prepare Dense Li-Garnet Solid Electrolytes with High Critical Current Density. *ACS Applied Energy Materials* **2018**, DOI: 10.1021/acsaem.8b00976.