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Unveiling the Role of Lithium Iodide in Stabilizing Solid Interfaces in All-Solid-State Li Metal Batteries

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ABSTRACT

A critical challenge in all-solid-state lithium metal batteries (ASSLMBs) is achieving a stable interface between the lithium metal anode and solid electrolyte. Leveraging its success in Li/I₂ batteries, Lithium iodide has garnered significant attentions for its potential to enhance interfacial stability and overall cell performance in ASSLMBs. Here, we elucidate the role of lithium iodide in stabilizing the solid interface in all-solid-state Li metal batteries with Li argyrodite electrolyte, particularly focusing on its influence on lithium deposition behavior and interfacial evolution. Through *in situ* optical imaging, we demonstrate more uniform lithium deposition on iodide-contained argyrodite electrolyte compared to chloride-based counterpart. Complementary density functional theory calculations attribute improved lithium plating behavior to enhanced lithiophilicity and better ionic conductivity of lithium iodide at the solid interface, effectively reducing localized current density. These findings provide useful insights into the mechanisms through which lithium iodide enhances interfacial stability in ASSLMBs.

KEYWORDS: all-solid-state lithium metal batteries, argyrodite electrolytes, solid interfaces, lithium plating/stripping, *in situ* characterization, lithium iodide, lithium wettability

All-solid-state Li metal batteries (ASSLMBs) are widely regarded as the next generation of energy storage devices due to their potential for higher energy density and better safety. Achieving high performance in ASSLMBs hinges on utilizing Li metal anode while enhancing safety through a solid electrolyte (SE) that ideally suppresses Li dendrite growth by replacing flammable organic liquid electrolytes.^{1, 2} For reliable and stable ASSLMBs, SEs must meet several essential criteria: (1) Li ionic conductivity comparable to that of liquid electrolytes ($>1 \text{ mS cm}^{-1}$), (2) excellent chemical and electrochemical stability, especially against high-voltage cathodes and the reactive Li metal anode, and (3) sufficient mechanical properties to enable large-scale manufacturing.^{3, 4} Despite extensive research, no single SE has successfully met all of these requirements. Notably, instability with the metallic Li anode remains a significant challenge for all SE systems, largely due to the low redox potential of Li metal (-3.04 V vs. SHE).⁵ Considerable efforts have been devoted to addressing these challenges through approaches such as SE material engineering, introducing interlayers between the SE and Li, and alloying Li with elements like Ag or In.⁶⁻¹⁰ However, none of these strategies has yet proven to be both technologically effective and commercially viable.

Recently, the incorporation of lithium iodide (LiI) directly within SEs or as an interphase in ASSLMBs has garnered significant attention, as it appears to noticeably enhance the electrochemical properties of SEs and the battery performance. LiI has been used successfully as the solid electrolyte in Li/I₂ pacemaker batteries several decades ago.¹¹ Additionally, LiI has been introduced as a protective layer in Li metal batteries with organic liquid electrolytes to stabilize the solid-electrolyte interface (SEI).^{12, 13} When added to lithium thiophosphates (Li₂S-P₂S₅), LiI enhances chemical and electrochemical stabilities as well as ionic conductivity by tuning the composition of the SEI at the Li and electrolyte interfaces.¹⁴⁻²² In particular, an I-rich lithium argyrodite (Li_{5.6}PS_{4.6}I_{1.4}) has been shown to form an *in situ* LiI-rich interlayer, improving stability against Li metal and enhancing cycling performance (e.g., delivering 128.8 mAh g^{-1} at 0.1C with 79.6% retention after 50 cycles for LiCoO₂/Li₆PS₅Cl/Li cell with Li_{5.6}PS_{4.6}I_{1.4} anode interlayer).²³ More recently, Li-sulfur ASSLMBs using Li₇P₂S₈Br_{0.5}I_{0.5} SE demonstrated excellent cycling stability, e.g., 1440 mAh g^{-1} capacity for 250 cycles, which is attributed to a regenerative nano-LiI interface.²⁴ Similarly, LiI is used as an additive in lithium thioborate electrolyte (Li₁₀B₁₀S₂₀) to modify the grain boundary, achieving an improved conductivity of 1.02 mS cm^{-1} with ~25% LiI by mass compared to 0.38 mS cm^{-1} without LiI.²⁵ However, the mechanism by which LiI enhances the stability of SEs and solid interfaces in ASSLMBs remain poorly understood. Gaining insights into how LiI improves the stabilities of SEs, solid interfaces, and against Li metal as well as their governing factors, is essential to designing effective solid interfaces for reliable and safe ASSLMBs with Li metal anodes.

In situ characterization is essential for probing the dynamic processes at solid-solid interfaces, often referred to as “buried interfaces”, which play a critical role in all solid-state battery performance.^{26, 27} However, even reliable *ex situ* characterization of these interfaces is challenging because of their buried nature and the highly compressed components of all solid-state cells, which make them difficult to access and observe, especially the interface between the solid electrolyte and

Li metal. These difficulties are further amplified in *in situ* studies, which must capture the interfacial phenomena in *real time* under realistic conditions using specialized setups. Recently, Aktekin *et al.* developed an operando approach using hard X-ray photoelectron spectroscopy to study the solid interface between argyrodite and Li metal. This technique can effectively detect the formation of evolution of Li_2S and Li_2O but cannot distinguish chlorides, due to the similar Cl 2p binding energies of $\text{Li}_6\text{PS}_5\text{Cl}$ and LiCl .²⁸

In this study, we employ an *in situ* asymmetric cell developed previously²⁹ to investigate interfacial processes during Li plating and stripping on an iodide-containing argyrodite electrolyte using optical microscopy. We study the interfacial evolution of an iodide-doped argyrodite electrolyte ($\text{Li}_{6-x}\text{PS}_{4+x}\text{ClI}_x$, referred to as LPSCI) to (1) examine the *in situ* formation of lithium halides (LiCl , LiI) at the interface and (2) compare with a chloride-based argyrodite of similar structure and properties. We systematically analyze the interfacial behaviors, including Li plating/stripping and SE decomposition, to clarify the specific role of LiI in stabilizing the solid interface. The LiI phase significantly enhances the uniformity of the Li deposition by improving Li wettability, which in turn minimizes localized current distribution. This study provides clear evidence of LiI 's role in stabilizing solid interfaces in ASSLMBs and underscores the importance of optimizing current distribution to improve interphase formation. Enhancing Li wettability is crucial for developing high-energy ASSLMBs with prolonged lifespan and enhanced safety.

We synthesize a series of dual halide-rich argyrodites, $\text{Li}_{6-x}\text{PS}_{4+x}\text{ClI}_x$ (LPSCI), via solid-state reaction. The as-prepared materials are referred to as LPSCI-10, LPSCI-30, and LPSCI-50, corresponding to 10%, 30%, and 50% iodide substitution, respectively. The varying iodide content allows the possibility to tune the material properties and interfacial chemistry. X-ray diffraction (XRD) analysis (**Figure 1A**) reveals that the final products are composites composed of two distinct phases of LPSC and LPSI, with a cubic crystal structure belonging to the space group $F\bar{4}3m$ (**Figure 1B**). Increasing iodide content leads to Li_2S impurity, which becomes prominent in LPSCI-50 sample. Therefore, LPSCI-30 that contains minimal Li_2S and a high iodide content is selected for detailed characterization to investigate the influence of lithium iodide that forms as the electrochemical reduction product of the argyrodite at the solid interface in electrochemical performance. Scanning electron microscopy (SEM) (**Figure 1C**) shows aggregated secondary particles at the micrometer scale, typical of solid-state reactions and similar to that of LPSC synthesized under the same condition.³⁰ **Figure 1D, E** present the ionic and electrical conductivity measurements for LPSCI-30 sample, showing an ionic conductivity of 0.94 mS cm^{-1} and electrical conductivity of $6.4 \times 10^{-6} \text{ mS cm}^{-1}$ (**Figure S1**). Conductivities for all LPSCI electrolytes are listed in **Table S1**. For comparison, LPSC exhibits an ionic conductivity of 2.8 mS cm^{-1} and an electrical conductivity of $4.3 \times 10^{-6} \text{ mS cm}^{-1}$. The slightly lower conductivity of LPSCI-30 is expected due to the presence of LPSI phase, which has a comparatively low ionic conductivity ($\sim 10^{-3} \text{ mS cm}^{-1}$) due to limited S^{2-}/I^- anion disorder.^{31,32} Considering the distinct properties of the LPSI phase, LPSCI-30 that exhibits ionic and electrical conductivities close to those of LPSC is suitable for investigating the role of LiI interphase in the electrochemical performance of ASSLMBs.

We then assemble an *in situ* asymmetric cell using the LPSCI-30 electrolyte to visualize the Li plating and stripping processes in *real time*. Notably, this asymmetric *in situ* cell could be regarded as a solid-state half-cell, comprising a Li metal anode, an argyrodite solid electrolyte, and an ITO cathode, if ITO is electrochemically active. **Figure 2A** shows the voltage profiles of the cell during the first cycle at a current density of $10\ \mu\text{A cm}^{-2}$. Starting from an open-circuit voltage of $\sim 2.0\ \text{V}$, the cell voltage drops immediately when applying a negative current, and no distinct voltage plateaus indicative of ITO lithiation are observed.³³ Instead, the cell undergoes an initial Li plating onto the indium tin oxide (ITO) glass current collector for 1 h, followed by Li stripping until all active Li on the ITO is depleted. The immediate voltage increase at the end of stripping clearly indicates the complete Li depletion without any soft or hard short circuit. The cell shows an overpotential of $\sim 70\ \text{mV}$, slightly higher than that with $\text{Li}_6\text{PS}_5\text{Cl}$ ($\sim 50\ \text{mV}$), due to the lower ionic conductivity of LPSCI-30. Upon charging, the *in situ* cell continues to function as expected. Notably, there is a small voltage plateau at the beginning of the plating process, which is observed only at low current densities. Given the low coulombic efficiency, this plateau signifies the formation of lithium halide interphases, resulting from the electrochemical reduction of the solid electrolyte in contact with Li metal.^{29, 34} Li plating and stripping processes are recorded and presented in **Movie S1 and S2**. The voltage profiles cycled at a higher current density ($100\ \mu\text{A cm}^{-2}$) resemble those at $10\ \mu\text{A cm}^{-2}$ and are shown in **Figure S2A**. **Figure 2B-D** display selected optical images obtained from the pristine state to the end of plating process, while **Figure 2E-G** show images captured during stripping. Under optical microscope, the SE appears gray, with white spots representing plated metallic Li. As observed in our previous work, Li deposition on $\text{Li}_6\text{PS}_5\text{Cl}$ electrolyte is random and heterogeneous.²⁹ However, the Li plating behavior is significantly different for iodide-substituted argyrodite. Under the same current density, Li plating on LPSCI-30 is more uniform, with more Li nucleation sites forming on the SE surface, which subsequently grow into a continuous Li layer upon further plating. By the end of plating, the SE surface is almost entirely covered by a uniform Li film (**Figure 2D**), unlike $\text{Li}_6\text{PS}_5\text{Cl}$ electrolyte, where plating forms isolated Li islands. During stripping, the Li deposits in the black spots gradually diminish as Li is removed. As discussed previously, these black spots, formed after Li plating, are SE domes mixed with Li seeds, providing better physical contact between ITO current collector and SE.²⁹ The diminishing black spots during stripping further confirms the presence of more active Li plating sites on the LPSCI-30 interface. The optical images, captured from the top-down view, show the presence of irreversible Li residuals after stripping (**Figure 2G**), which likely exists as a thin surface layer. These results indicate that Li plating on the iodide-substituted argyrodite electrolyte with lithium iodide interphase is more homogeneous and uniform.

To further investigate the role of LiI , we disassemble the cell and examine the SE surface morphology and chemistry using SEM and energy dispersive X-ray spectroscopy (EDS). **Figure 3** shows SEM images and EDS maps collected after Li plating and stripping. After Li plating (**Figure 3A**), the SE surface is primarily covered by a metallic Li layer, featured by a morphology consisting of well-formed, dense grains with minimal surface roughness. The presence of metallic Li is confirmed by the O map, due to the oxidation of Li from brief exposure to the ambient atmosphere during sample transfer. We acknowledge the possibility of oxygen adsorption onto the

sample surface during this brief exposure. However, this would likely result in a uniform layer. In contrast, the EDS O mapping shows clear spatial variations that closely match the surface features seen in the SEM images (**Figure 3**). On the other hand, the main elements (S and P) exhibit consistent elemental distribution, different from that of the halides (Cl and I), indicating SE decomposition. Interestingly, Cl and I show different preferences for contact with Li. EDS maps reveal a consistent co-localization of plated metallic Li (inferred from O) and I, with Cl surrounding these regions. These spatial correlations between residual lithium and halides persist even after the stripping process (**Figure 3B**) and similar observations are made at the surfaces of ITO current collector (**Figure S3**) and SE after stripping at a high current density ($100 \mu\text{A cm}^{-2}$) (**Figure S2B**). These results demonstrate a strong correlation between the presence of Li with I on the SE surface, compared to Cl, highlighting a distinct role of LiI in the interface chemistry.

The preference of Li in contact with iodide is crucial for achieving uniform Li plating on the iodide-substituted argyrodite electrolyte. The voltage profiles indicate that the LPSCI-30 SE decomposes at the onset of plating, forming an interphase upon contact with Li. EDS mapping shows a strong correlation between P and S, while they remain segregated from I, confirming the interphase formed through LPSCI-30 decomposition likely consists of lithium halides, such as LiCl and LiI.³⁴ The segregation of lithium halides from argyrodite electrolytes has been observed in previous studies, however, the underlying mechanism remains unclear.^{24, 35} Recent findings indicate that thermal heating may induce such segregation.³⁶ Nevertheless, the Li deposition predominantly occurs in the regions with LiI, enabling more uniform Li coverage on the solid surface of LPSCI-30 electrolyte. This sharply contrasts with the random and localized Li deposition observed on the LPSC electrolyte under identical conditions. Two possible mechanisms may explain this: (1) LiI is more lithophilic than LiCl, and (2) the *in situ* formed LiI-containing interphase is more ionically conductive than LiCl.

To test the first hypothesis, we perform Li wettability experiment on LiCl and LiI pellets by melting a small amount of Li and placing melted Li on the surfaces of LiCl and LiI (**Figure 4A**). The contact angle between liquid Li and LiI is $\sim 120^\circ$, significantly higher than that of LiCl ($\sim 50^\circ$), confirming the more lithophilic nature of LiI than LiCl. We acknowledge that the contact angle may not best represent Li wettability because the results can also strongly depend on other factors, such as surface roughness, geometry and presence of surface impurity. To abstain from these complications, we carry out density functional theory (DFT) calculations to assess the differences in structure and energy of the LiX/Li ($X = \text{I, Cl}$) interfaces. Six distinct interface models are constructed with different crystallographic orientations of LiX, Li metal, and surface terminations. Upon full relaxation, the LiI/Li interfaces generally exhibit lower interfacial energies (**Figure 4B** and **Table S2**), implying a more adhesive nature. In addition, due to the inherent differences in surface stabilities of Li metal and LiX and associated strength of interfacial interaction, various degrees of structural reorganization are observed at the LiX/Li interfaces, as evident in **Figure S4**. Details of interface model construction and the use of cell dimensions are provided in the supplementing information (**Table S3**). At highly reactive interfaces, severe structural deformation is observed. It is possible that the observed high degree of structural disorder is exaggerated with

the use of finite simulation cell, however, because both LiI/Li and LiCl/Li interface models are constructed at the same cell dimension, the results remain valid to compare their relative interfacial reactivity. It is worth noting that for the LiX 001 | Li 111 interface, where higher interfacial energy is observed for LiI/Li, Li metal undergoes severe structural change, almost completely losing its crystallinity starting from the interface into the bulk interior. In contrast, the Li metal layer in the LiCl/Li interface model is less disordered, again indicating less reactivity experienced at the interface. Overall, these DFT calculations confirm that LiI is chemically more reactive with Li metal than LiCl, thereby may contribute to improved wettability at the interface.

To assess Li mobility in LiI vs. LiCl, which are likely to form at the SE/Li metal interface upon SE decomposition, we perform DFT calculation with the nudged elastic band method to compare the activation energy of Li diffusion in bulk LiX model systems. It is found that the energy barriers for single Li-ion migration in LiCl and LiI are 0.528 and 0.423 eV, respectively (**Figure 4C**), which implies fast Li-ion conduction in LiI compared to LiCl. This may in turn facilitate more homogeneous Li deposition due to improved penetration kinetics to reach the current collector. **Figure 4D** presents a schematic illustrating the interfacial mechanisms of LiI and LiCl. Upon initial reduction, the SE forms lithium halides, which segregate from the bulk SE components and accumulate at the interface. The LiI-rich interphase promotes more uniform Li plating due to its higher ionic conductivity and better Li wettability compared to the LiCl-rich interphase.

In this study, we reveal the role of lithium iodide in stabilizing the interface between lithium metal and argyrodite electrolyte in ASSLMBs. We investigate the interfacial processes during Li plating and stripping on an iodide-containing argyrodite electrolyte using *in situ* optical microscopy. Despite the limited spatial resolution (approximately 10 μm), we are able to clearly distinguish contrasting Li plating behaviors and make meaningful comparisons with its iodide-free analog. In comparison, iodide-doped LPSC enables more uniform Li plating on the solid electrolyte, as opposed to the isolated lithium islands formed on chloride-based argyrodite. This interfacial behavior transformation relies on improved interfacial kinetics resulting from the enhanced ionic conductivity and improved Li wettability. Our findings elucidate the role of lithium iodide in enhancing the electrochemical performance of all state-state cells and provide new insights into designing stable solid interphases and interfaces for all-solid-state batteries. The methodologies presented in this work could provide a valuable and practical approach for complementary studies of solid interface formation and evolution when integrated with other *in situ* techniques.

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Supporting Information Available: Experimental methods. *In situ* optical microscopy observations. Ionic and electronic conductivities. Voltage profiles, SEM images and EDS maps. Interfacial energies and model parameters of Li-halide | Li metal interfaces.

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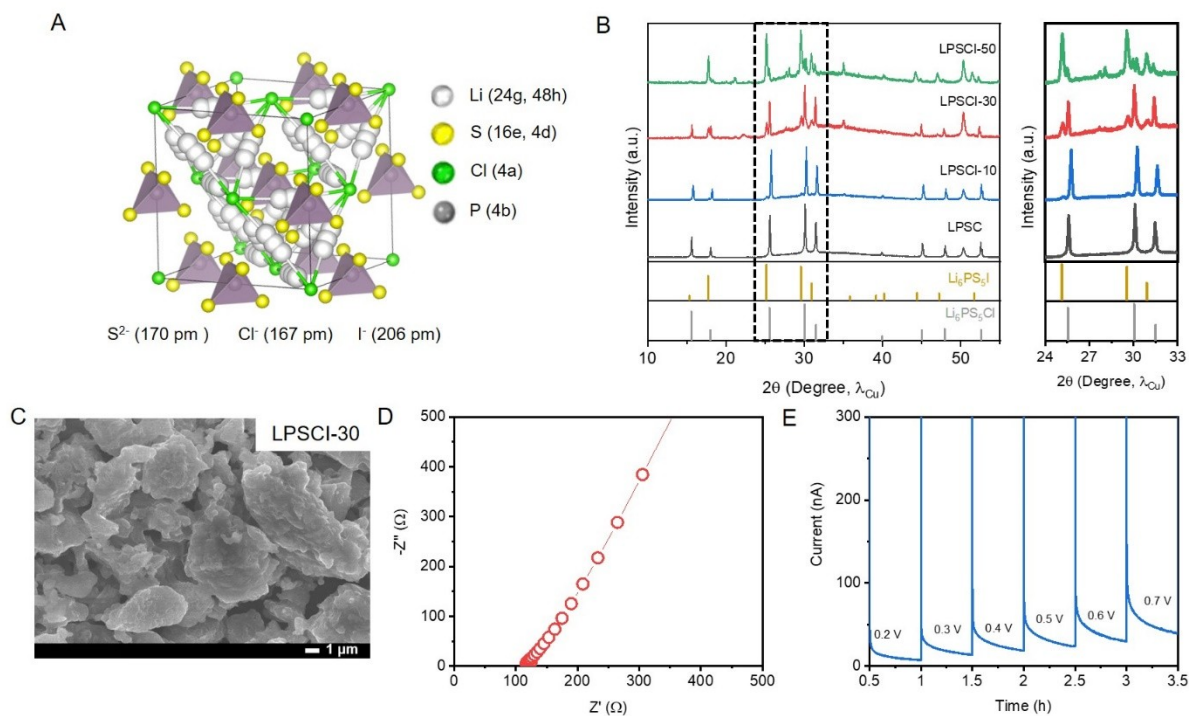


Figure 1. Synthesis and physical properties of $Li_{6-x}PS_{4+x}ClI_x$ (LPSCI) electrolytes. (A) Crystal structure of Li argyrodite (cubic $F\bar{4}3m$). (B) XRD patterns of LPSCI argyrodites with 10%, 30%, 50% iodide substitution, denoted as LPSCI-10, LPSCI-30, and LPSCI-50, respectively. (C) SEM image, (D) Nyquist plot for ionic conductivity, and (E) DC polarization for electrical conductivity of LPSCI-30.

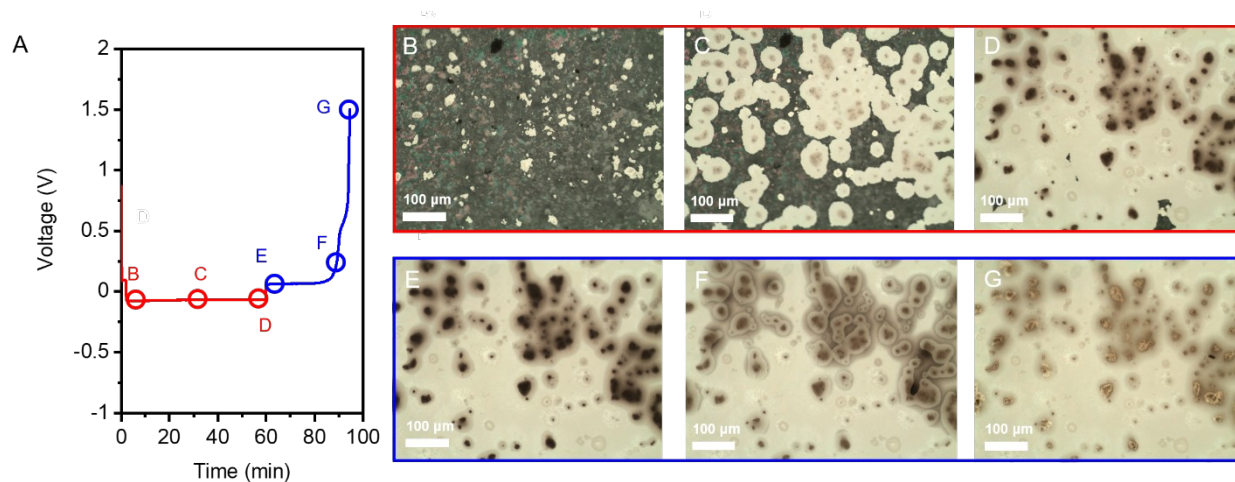


Figure 2. Li plating/stripping on LPSCI-30 argyrodite visualized by *in situ* optical microscopy. (A) Voltage profiles at $10 \mu\text{A cm}^{-2}$ along with the optical images captured at different time series during the 1st plating (B, C, D) and the 1st stripping (E, F, G). The red and blue circles in A indicate the states of charge at which the optical images in (B-D) and (E-G), respectively, were captured.

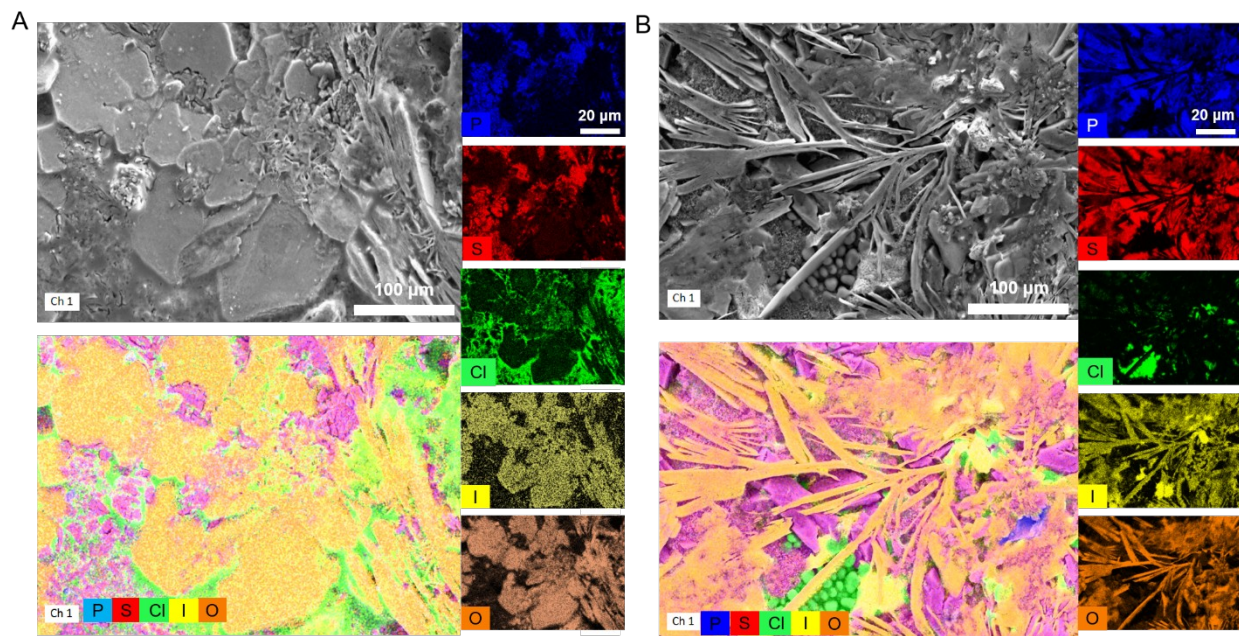


Figure 3. Characterization of the surface of the LPSCI-30 electrolyte cycled at $10 \mu\text{A cm}^{-2}$. SEM image and EDS maps after the 1st plating (A) and the 1st stripping (B).

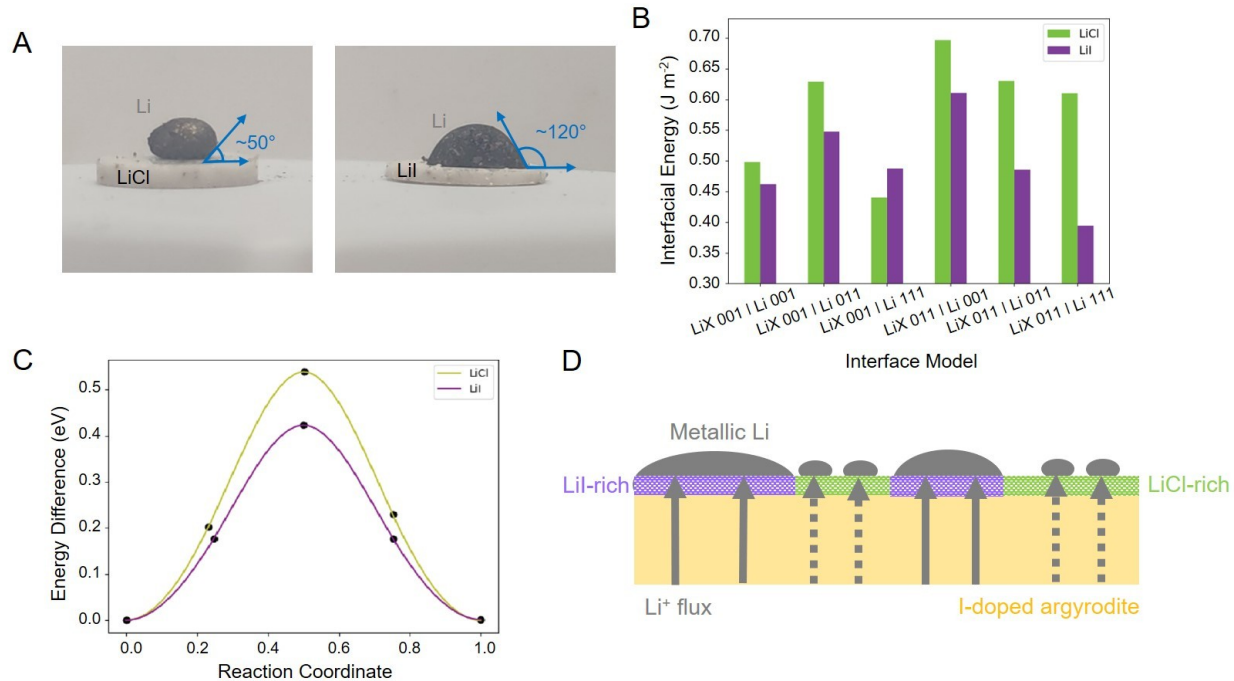


Figure 4. Physical and interfacial properties of lithium halides (LiX, X = Cl and I) at the solid interface of ASSLMs. (A) Contact angel measurement of Li metal with LiX. (B) DFT calculation of interfacial energy for LiX|Li. (C) Energy barrier of Li⁺ diffusion in LiX. (D) Schematic representation of Li diffusion mechanism across the solid interface in a LiX-rich region.

Supporting Information for

Unveiling the Role of Lithium Iodide in Stabilizing Solid Interfaces in All-Solid-State Li Metal Batteries

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Experimental Methods

LPSCI powders were synthesized via a solid-state reaction. Raw materials, including Li_2S , LiCl , LiI , and P_2S_5 , were sealed inside an Ar filled glovebox at specific molar ratios and ball-milled in a zirconium jar at 550 rpm for 24 h. The milled powder was then pressed into pellets and annealed at 550 °C for 3 h in a tube furnace under Ar atmosphere. After annealing, the sample was grounded into powder and stored inside the Ar glovebox. Ionic and electrical conductivities were measured using electrochemical impedance spectroscopy (EIS) and direct current (DC) method, respectively. Ionic conductivity was calculated using the equation: $\sigma = l/RA$, where l is the pellet thickness, R is the bulk resistance measured by EIS, and A is the pellet area. Electrical conductivity was measured using the same equation, and R is indicated by the slope between the voltage and the current. X-ray diffraction (XRD) patterns were collected in an airtight holder on the Bruker D2-Phaser with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) from 10 to 55°.

An *in situ* asymmetric solid-state cell was assembled using a configuration described in our previous report.¹ The indium tin oxide (ITO) glass allows for visualization of Li plating/stripping behaviors. The electrochemical characterization was conducted at room temperature using a biologic workstation. Galvanostatic charge/discharge were carried out at different current densities and the Li plating/stripping processes were monitored using a Nikon LV100 digital microscope with the Lumenera INFINITY 3 camera and 10x/20x objective lens. After cycling, the cells were disassembled to harvest the SE pellet and ITO current collector for the interface characterization. Scanning electron microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDS) maps were obtained on the Zeiss Gemini Ultra-55 Analytical Field Emission Scanning Electron Microscope coupled to a Bruker X-Ray Energy Dispersive Spectrometer at the voltage of 10 kV.

DFT calculations were performed using the Vienna Ab Initio Simulation Package (VASP) with the Perdew, Burke, and Ernzerhof (PBE) type generalized gradient approximation (GGA) approximation.² The projector augmented wave (PAW) pseudopotentials were used to represent ion-electron interactions for all elements³ and to account for dispersion interactions, the DFT-D3 method with a Becke-Johnson damping function was employed.⁴ A plane-wave basis set with a cutoff energy of 600 eV was utilized, with proper k-point sampling to ensure numerical convergence. For all structural relaxations, the energy and forces were converged to 10^{-6} eV and 0.01 eV/Å, respectively. For the calculations of Li-ion diffusion, the climbing-image nudged elastic band method⁵ was used with a background charge of -1 implemented in a 215-atom supercell to model Li^+ migration to the nearest vacancy site. The activation energies were obtained when the residual forces on each moving image along Li-ion migration path are smaller than 0.05 eV/Å.

Movie S1. *In situ* optical microscopy observation, showing the Li plating behavior during the 1st cycle at 10 $\mu\text{A cm}^{-2}$. The movie clip is accelerated by 100 times.

Movie S2. *In situ* optical microscopy observation, showing the Li stripping behavior during the 1st cycle at 10 $\mu\text{A cm}^{-2}$. The movie clip is accelerated by 100 times.

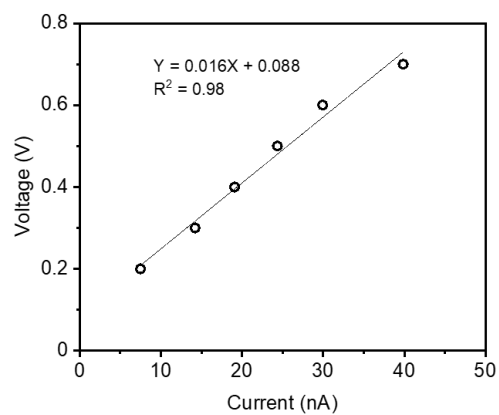


Figure S1. Electrical conductivity of LPSCI-30 electrolyte, indicated by the slope between the voltage and current measured from DC polarization.

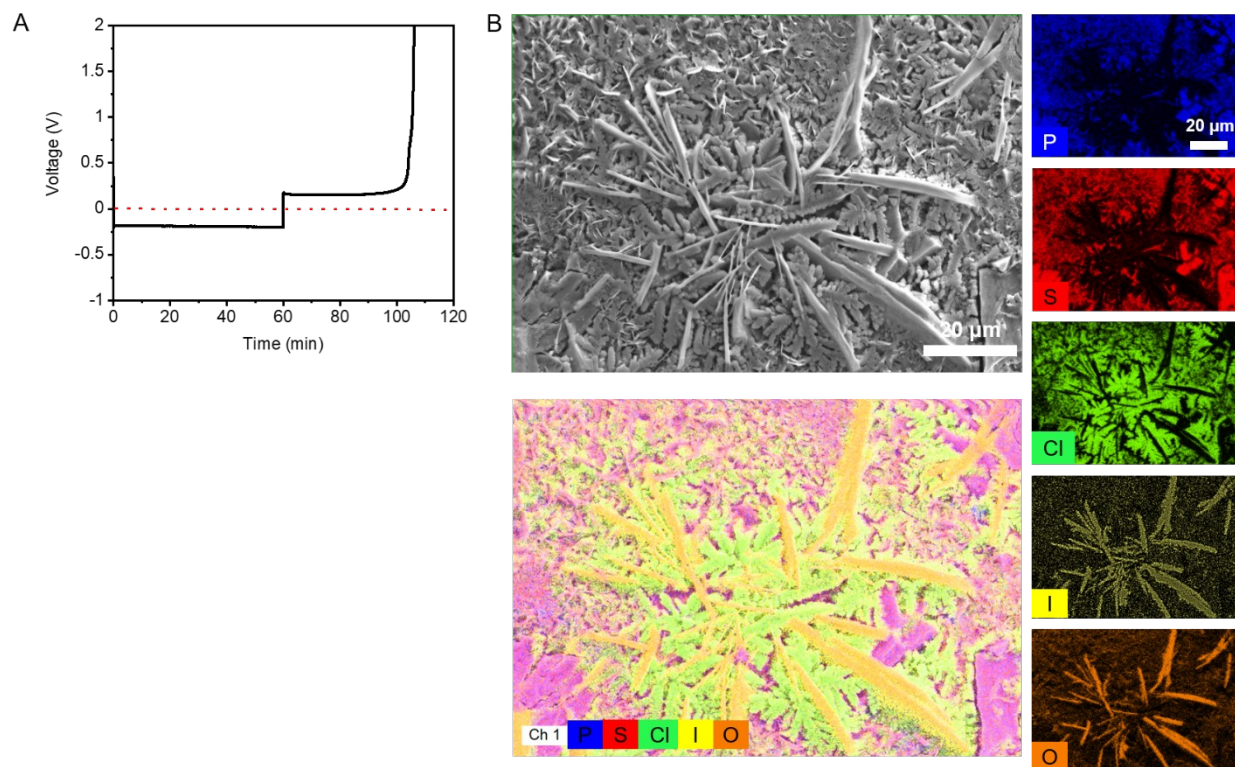


Figure S2. (A) Voltage profiles of the asymmetric cell cycled with LPSCI-30 electrolyte at 100 mA cm^{-2} . (B) SEM image and EDS maps collected on the LPSCI-30 electrolyte after the 1st stripping.

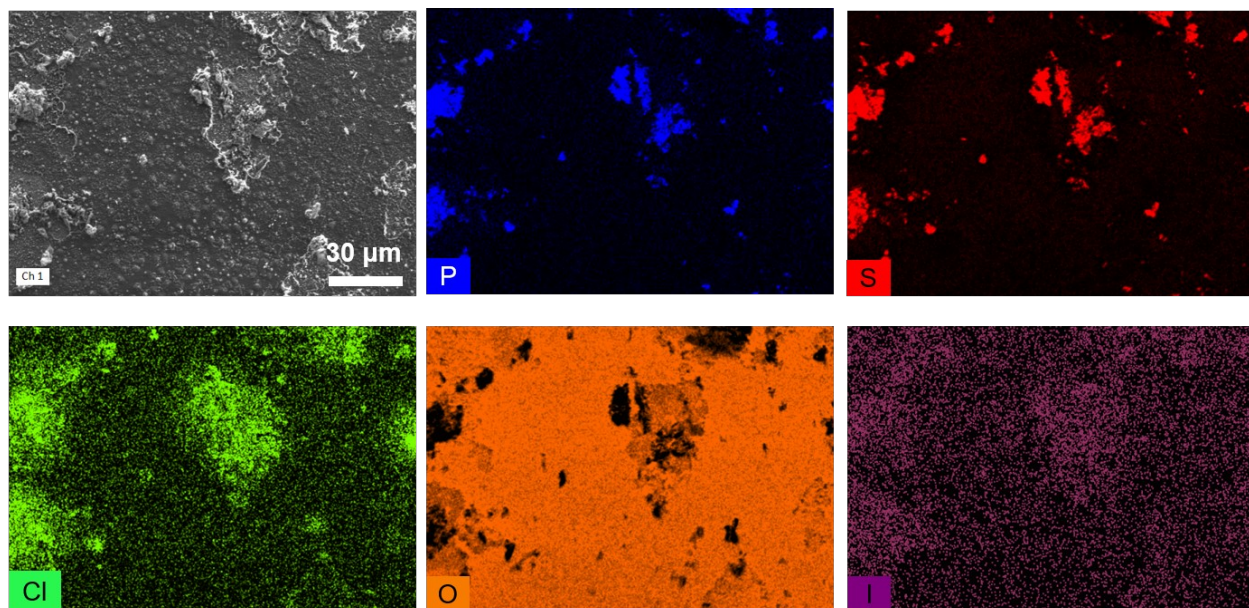
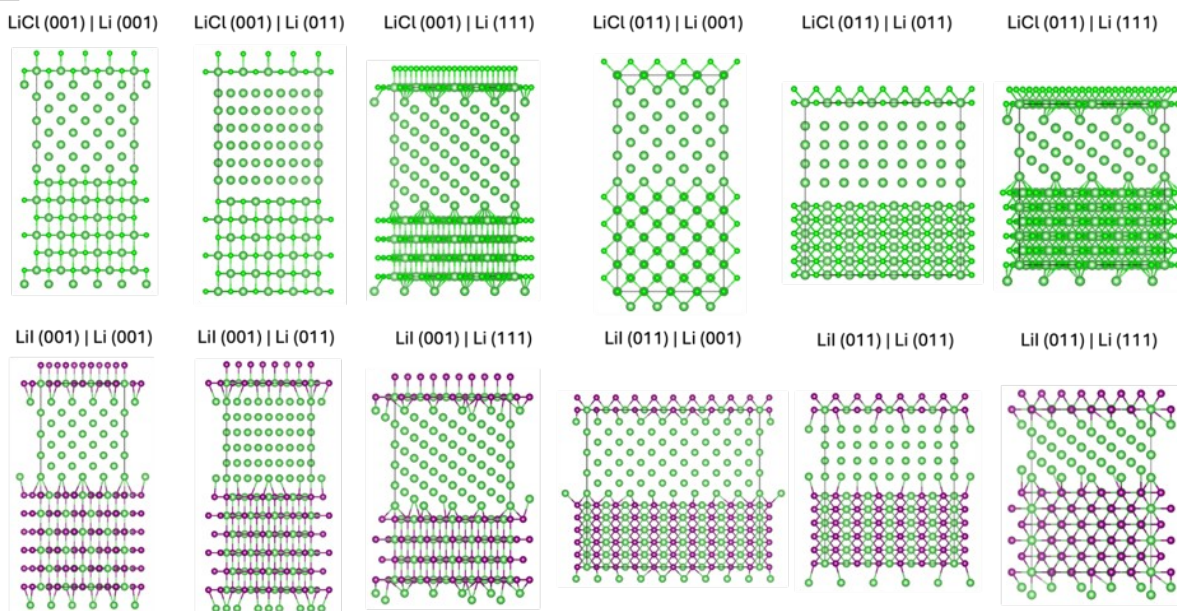


Figure S3. SEM image and EDS maps collected on the ITO after the 1st stripping with LPSCI-30 electrolyte.

A Pre-relaxation



■ Li ■ Cl ■ I

B After-relaxation

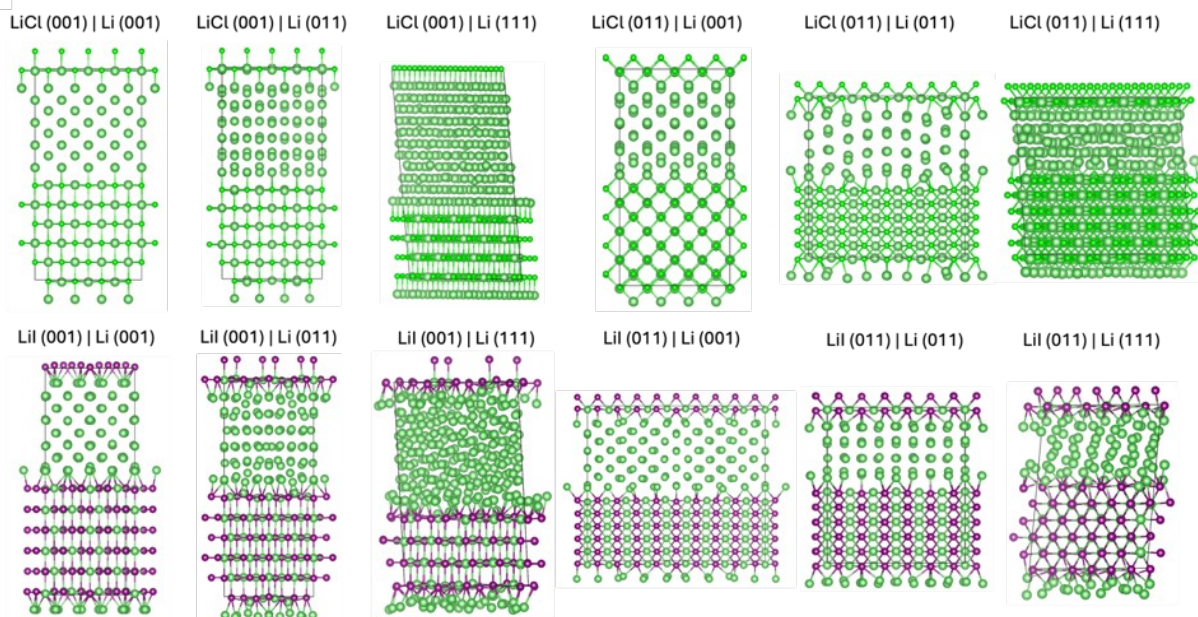


Figure S4. Structure representation of Li-halide | Li metal interface models. (A) Pre-relaxed and (B) post-relaxed atomic configurations of each interface model.

Table S1. Ionic and electronic conductivities of the as-prepared LPSCI argyrodites with 10%, 30%, 50% iodide substitution, denoted as LPSCI-10, LPSCI-30, and LPSCI-50, respectively.

Sample	Ionic Conductivity (S cm ⁻¹)	Electrical Conductivity (S cm ⁻¹)
LPSCI	2.8×10^{-3}	4.3×10^{-9}
LPSCI-10	2.6×10^{-3}	2.3×10^{-9}
LPSCI-30	0.9×10^{-3}	6.4×10^{-9}
LPSCI-50	0.3×10^{-3}	10.1×10^{-9}

Table S2. Calculated interfacial energies of Li-halide (LiX) | Li metal interfaces.

Interface Model	LiCl (J m⁻²)	LiI (J m⁻²)
LiX (001) Li (001)	0.4984	0.4621
LiX (001) Li (011)	0.6293	0.5478
LiX (001) Li (111)	0.4407	0.4878
LiX (011) Li (001)	0.6972	0.6108
LiX (011) Li (011)	0.6306	0.4860
LiX (011) Li (111)	0.6106	0.3948

Table S3. Model parameters of Li-halide | Li metal interfaces.

Slab A	Slab B	a (Å)	b (Å)	$\bar{\epsilon}$ (%)	γ (°)	# of atoms	k-point mesh (a, b, c)
LiCl (001)	Li (001)	14.144	14.144	1.17	90	320	$3 \times 3 \times 2$
LiI (001)	Li (001)	13.629	13.629	2.31	90	248	$3 \times 3 \times 1$
LiCl (001)	Li (011)	20.308	10.147	1.14	45	336	$2 \times 3 \times 1$
LiI (001)	Li (011)	13.998	18.695	2.06	82	360	$3 \times 2 \times 1$
LiCl (001)	Li (111)	35.013	8.878	3.58	154	392	$1 \times 6 \times 2$
LiI (001)	Li (111)	20.582	15.972	2.34	128	344	$2 \times 3 \times 2$
LiCl (011)	Li (001)	14.582	14.146	4.02	90	320	$3 \times 3 \times 2$
LiI (011)	Li (001)	32.676	12.836	2.99	65	472	$1 \times 3 \times 2$
LiCl (011)	Li (011)	13.135	20.224	3.15	79	296	$3 \times 2 \times 2$
LiI (011)	Li (011)	14.251	20.153	2.81	90	272	$3 \times 2 \times 2$
LiCl (011)	Li (111)	20.590	17.844	3.04	63	392	$2 \times 3 \times 2$
LiI (011)	Li (111)	34.179	9.336	2.25	155	272	$1 \times 4 \times 2$

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