

Lawrence Berkeley National Laboratory

LBL Publications

Title

In Situ Characterization of Interface Evolution in Argyrodite-Based All-Solid-State Li Batteries

Permalink

<https://escholarship.org/uc/item/7cb9p1cx>

Journal

Small, 20(49)

ISSN

1613-6810

Authors

Huang, Di

Liu, Gao

Tong, Wei

Publication Date

2024-12-01

DOI

10.1002/smll.202406862

Copyright Information

This work is made available under the terms of a Creative Commons Attribution-NonCommercial License, available at <https://creativecommons.org/licenses/by-nc/4.0/>

Peer reviewed

***In Situ* Characterization of Interface Evolution in Argyrodite-Based All Solid-State Li Batteries**

*Di Huang, Gao Liu, and Wei Tong**

Energy Storage and Distributed Resources Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

Email: weitong@lbl.gov

Abstract

Interfacial stability is one of the critical challenges in all solid-state Li metal batteries. Multiple processes such as solid electrolyte decomposition and lithium dendrite growth take place at the solid interfaces during cycling, leading to the overall cell failure. To deconvolute these complex processes, *in situ* characterization is of paramount importance to elucidate the interfacial evolution on the solid electrolyte upon Li plating/stripping. Herein, we develop an all solid-state asymmetric *in situ* cell that allows the direct visualization of the highly localized Li plating/stripping processes under the optical microscope. Moreover, this cell configuration enables reliable post mortem chemical and morphological analysis of the intact solid electrolyte/Li interface. Using combined scanning electron microscopy and energy dispersive X-ray spectroscopy, we observe that the evolution of the Li argyrodite interface is strongly influenced by the current density, particularly in terms of chemical distribution and Li plating morphology. More specifically, the solid interface is LiCl-rich with the formation of Li cubes at low current densities, while high currents result in more uniform elemental distribution and filament morphology. These findings elucidate the dynamic evolution mechanism at solid interfaces and offer valuable guidance for developing stable solid interfaces in all solid-state Li metal batteries.

1. Introduction

All solid-state lithium (Li) metal batteries are considered as one of the next-generation energy storage technologies given their potential advantages over the conventional Li-ion batteries, for example, higher energy density by enabling Li metal anode and better safety by eliminating the use of flammable organic solvents. However, the incorporation of Li metal anode in all solid-state cells is still facing enormous challenges that prevent the practical application. Due to the low reduction potential of Li (-3.05 V vs. RHE), most solid electrolytes (SEs) are thermodynamically unstable toward Li metal, causing complex side reactions such as Li dendrite growth, decomposition of solid electrolytes, formation of solid electrolyte interface (SEI), cracking, and void *etc.*^[1] Lithium argyrodite $\text{Li}_6\text{PS}_5\text{Cl}$ (LPSC) and its derivatives have gained significant attention for their high ionic conductivity ($> 1 \text{ mS cm}^{-1}$) and favored mechanical properties. Unfortunately, this family of solid electrolytes also confronts the similar challenge in chemical stability against metallic Li. At the interface of the anode, LPSC argyrodite can be reduced and form the decomposition products such as Li_2S , P_2S_x , LiCl , P , Li_xP *etc.*^[2] These products are less ionically but more electrically conductive, leading to the severe dendrite formation/growth and short circuit. On the other hand, it has been reported that the LPSC argyrodite exhibits better kinetic stability towards the metallic Li owing to

the SEI formation.^[1d, 3] The idea of taking advantage of the SEI that forms *in situ* as a protective layer on the interface to improve the stability toward Li metal has been explored in other argyrodite derivatives. For example, $\text{Li}_{6+x}\text{PS}_{5-x}\text{N}_x\text{Cl}$ is reported to form ionic conductive Li_3N interlayer, enabling prominent cycling stability.^[4] Similarly, fluorinated argyrodite, $\text{Li}_6\text{PS}_5\text{Cl}_{1-x}\text{F}_x$, can form LiF interlayer to achieve ultrahigh critical current density and cycling stability.^[5] Moreover, the Cl rich LPSC is also reported to archive superior cycling performance towards Li metal anode, owing to the formation of the dense and continuous LiCl -rich interface, preventing the decomposition of the argyrodite electrolyte.^[6] Indeed, the LPSC has been commonly used as a buffer layer between the halide solid electrolytes and Li metal and lithium-indium anodes.^[7] Understanding the interfacial behaviors and their roles in the electrochemistry for this technologically important solid electrolyte is crucial to develop the reliable all solid-state cells with high efficiency and long-term cycling performance.

The interfacial processes in all solid-state cells are complex because the Li plating/stripping is often accompanied by the SE decomposition and SEI formation. To decouple these interfacial behaviors, reliable methodologies are needed to characterize the interfacial evolution and properties between the Li anode and SE. However, the operation of all solid-state cells and their interfacial processes are highly dependent on the stack pressure.^[8] The pressure requirement introduces challenges in developing the *in situ* characterization and even post mortem analysis of solid interfaces because these interfaces are often damaged or buried by the soft lithium metal after cell disassembly. To tackle these issues, the concept of Li-free (also referred to as Li-less) all solid-state cells, in which all the active lithium comes from the cathode material, arouses our interest.^[9] In this cell configuration, Li^+ is extracted from the cathode and directly deposited on the current collector (CC) such as Cu and stainless steel, during charge. This cell architecture removes the physical barrier of the metallic Li anode and makes the visualization of the dynamic Li plating/stripping processes possible. More importantly, the interface between the SE and Li metal anode remains intact after cell disassembly, therefore, it offers an excellent platform to investigate the interfacial evolution.

In this work, we develop a coin-cell type all solid-state cell with a transparent indium tin oxide (ITO) glass window for *in situ* characterization of the Li plating/stripping behavior and post-mortem analysis of the Li and SE interface. Although it's not straightforward to monitor the cell pressure, this coin-cell type configuration is expected to mimic the operation of all solid-state cells under low pressure, close to the practical condition. The asymmetric cell allows us to visualize the Li plating/stripping behaviors under various conditions using the optical microscope. Additionally, the customized all solid-state cell also enables reliable post mortem analysis because the pressure need for all solid-state cell assembly and operation makes the harvesting of the original interphases even more difficult. As a result, we obtain the morphological and chemical information of the interphases between Li and solid electrolyte. The dynamic interfacial evolution on the argyrodite LPSC electrolyte is presented and discussed in this paper. The method presented here can be used to study other solid electrolytes and solid interphases, and thus provides useful guidance for the research in the design of solid interfaces and cells as well as protocol optimization for high-efficiency and long-term cycling all solid-state batteries.

2. Results

In order to monitor the interfacial evolution on the solid electrolyte, we develop an asymmetric cell using the transparent ITO glass window as the current collector, which allows to visualize the Li plating/stripping processes under the optical microscope. The schematic of the asymmetric cell is shown in **Figure 1A**, the hermetic coin-type *in situ* cell is assembled by placing the Li metal on a spacer and spring that provide sufficient internal pressure for the good physical contact of the cell components. After assembling, the cell is cycled at $50 \mu\text{A cm}^{-2}$ with plating for 1 h, and stripping for 1 h with a cut off voltage of 1.5 V (the cyclable capacity is $50 \mu\text{Ah cm}^{-2}$). The thickness of the LPSC pellet is optimized to achieve the good contact and thus a low overpotential. As shown in **Figure 1B**, the optimal asymmetric cell exhibits stable plating and stripping with an overpotential of about 0.5 V for multiple cycles, verifying the proper operation of the cell configuration. In addition, an instant increase in the cell potential at the end of the stripping process signifies no short circuit upon cycling. No additional plateaus beyond the Li plating/stripping ones are observed from the voltage profiles, confirming the electrochemical stability of the ITO glass CC towards metallic Li within the voltage range.^[10]

After verifying the cell configuration, we cycle the cells for Li plating/stripping under various current densities from 10 to $200 \mu\text{A cm}^{-2}$. The voltage profiles during the first cycle are presented in **Figure 2**. They all show an instant voltage increase at the end of stripping when all electrochemically active Li is stripped besides those that form dead lithium and consumed by the reactions with the SE. From the voltage profiles, we observe that during the initial stage of plating at $10 \mu\text{A cm}^{-2}$, the cell voltage slowly decreases to -0.5 V (black box in **Figure 2A**), while at higher current densities, the cell potential drops immediately from the open circuit voltage (OCV) to the plating voltage, suggesting more severe side reactions between the SE and Li at $10 \mu\text{A cm}^{-2}$. The cell cycled at $10 \mu\text{A cm}^{-2}$ also exhibits an exceptionally low coulombic efficiency (CE) of 55.7%, in sharp contrast to the CE (92.3%) of the cell cycled at $200 \mu\text{A cm}^{-2}$. The initial CE during Li plating/stripping with the LPSC electrolyte is impacted by the current density. A consensus is that higher current results in more severe side reactions and thus lower CE.^[11] One possible explanation is that the degradation mechanism varies with current density. We note that all the plating/stripping processes are carried out for 1 h, leading to different capacities (the amount of the plated Li), which may have an impact on the CE. To rule out this factor, we assemble two additional cells and cycle them at $200 \mu\text{A cm}^{-2}$ but with different capacities (10 and $100 \mu\text{Ah cm}^{-2}$, **Figure S1**) by controlling the plating/stripping time for 3 and 30 min, respectively, and then compare them with the cells cycled at 10 and $100 \mu\text{A cm}^{-2}$ for 1 h. The CE of all the cells cycled at different current density and time are presented in **Table 1**. It can be seen that the CE increases from 55.7% to 81.0% by increasing the current density from 10 to $200 \mu\text{A cm}^{-2}$ when both cells are cycled at a capacity of $10 \mu\text{Ah cm}^{-2}$. In comparison, at a capacity of $100 \mu\text{Ah cm}^{-2}$, the CE of the cell cycled at $100 \mu\text{A cm}^{-2}$ is 90.3%, showing a small decrease compared to the CE (95.2%) at $200 \mu\text{A cm}^{-2}$. This comparison indicates that the current density has a larger impact on the initial CE.

With the difference in CE at varied current densities, we conduct an *in situ* optical microscopy study to elucidate the Li plating and stripping behaviors (see **Movie S1-4**) during the first two cycles (**Figure 3A**). Representative *in situ* optical images of the SE surface captured during plating/stripping at $10 \mu\text{A cm}^{-2}$ at different time series are shown in **Figure 3B-E**. **Figure 3B, C** shows the 1st plating process from 0 sec to 1 h, followed by the 1st stripping from 0 sec to the end (**Figure 3D, E**), while the 2nd plating and stripping are shown in **Figure 3F, G & H, I**, respectively. The color of the pristine SE under the optical microscope is dark grey. Once the plating starts, small

white spots start to grow on the surface of the SE, which is attributed to the nucleation of the metallic Li. It can be seen that the nucleation process is random and heterogeneous (**Figure 3B**). Upon further plating, these white spots act as the seeds and grow to a larger scale. While the seeds continue to grow, the center area turns to be black and the outer area remains white. Eventually, the large white islands with a black spot in the center are randomly distributed on the surface of the SE (**Figure 3C**). During stripping, the shrinkage of the white islands is expected. However, further expansion of the white islands unexpectedly continues even when the lithium is being stripped from these islands (**Figure 3D, E**). This is likely due to the internal pressure of the *in-situ* cell. As discussed above, the coin-type *in situ* cell can provide the continuous adjustments for the internal pressure. While Li is being stripped from the lithium islands between SE and CC, the residual Li is continuously pressed and spreads to the surrounding area on the surface of SE. As a result, these white islands continue to expand throughout the entire stripping process. At the end of stripping, the color of the central dark areas becomes lighter, while they become dark again during the second plating. The metallic Li continues to grow from the outer areas of the white islands from the previous cycle. While the plating process continues, other white spots appear underneath the islands (blue circles in **Figure 3F, G**). During the 2nd stripping, similar behavior is observed, with the expansion of the outer white areas and the shrinkage of the central dark areas (blue circles in **Figure 3H, I**). Overall, Li eventually forms the isolated islands on the surface of SE.^[8b, 12] In comparison, the plating/stripping processes for the cell cycled at 200 $\mu\text{A cm}^{-2}$ are also investigated (see **Movie S5-6**), which are similar to those at 10 $\mu\text{A cm}^{-2}$. The initial Li plating is nonuniform and localized, though more Li islands form with a larger size of central black spots and these islands grow faster at a high current.

The dark central spots seem to play a critical role in the Li plating/stripping processes. They appear to be the locations where the Li seeds initiate, and then vanish at the end of the stripping. Therefore, we infer that the dark spots are more conductive and act as the conducting channels, while the Li^+ is reduced when electron is conducted through the ITO glass. To gain further information on plating/stripping, the cells are disassembled after the second stripping at 10 $\mu\text{A cm}^{-2}$ and characterized by scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS). We first investigate the “spots” on the ITO glass (**Figure 4**). As revealed in **Figure 4A-C**, the plated area is dominated by two types of features, namely, bumpy core area and smooth outer area, corresponding to the central dark spot and outer white area shown in the optical image (inset in **Figure 4A**), respectively. We observe that the outer area is composed of the dense, thin, and continuous film on the ITO and the central core area is a cluster of the mixed particles and film. We further collect the EDS maps to gain the elemental distribution and chemical information. As revealed by the EDS (**Figure 4D-G**), the cluster of particles in the dark core is dominated by P and S along with sparse Cl, suggesting that the solid electrolyte is attached to the ITO CC and forms the cluster. The P-, S-containing decomposition products such as Li_2S and Li_xP typically form upon contact with Li metal,^[13] which is expected in this work, although they are not readily differentiated from the SE by EDS. However, they are probably the minor components, given the facts that Li starts to grow from the dark core and it provides the essential ion conducting path. Moreover, there are some veins of O in the cluster (**Figure 4H**). The observed O is indicative of metallic Li, which is oxidized upon brief exposure to the inert atmosphere during sample transfer. Therefore, the cluster of the dark core is mixed solid electrolyte and metallic lithium along with its minor decomposition products. In comparison, the outer smooth area exhibits the spatial elemental

segregation and is clearly Cl and O rich (**Figure 4G-H**). Given the absence of P and S, the outer area is mostly composed of the metallic Li and LiCl that forms due to the decomposition of the LPSC electrolyte. We also investigate the Li plating/stripping behavior at a high current density of $200 \mu\text{A cm}^{-2}$ with ITO glass (**Figure S2**) and Cu current collector (**Figure S3**), both of which demonstrate similar phenomena. More precisely, these dark spots resemble the isolated volcano islands as the Li lava erupt through the craters (dark areas) and then form the individual islands. When lithium is extracted during stripping, these craters are the dominating conducting path. As shown in an image of a volcano island on the SE cycled at $10 \mu\text{A cm}^{-2}$ (**Figure S4**), the crater formed in the middle is Cl rich with the absence of other elements. The Li lava, indicated by O map, are situated around the crater on the SE surface, indicated by P and S maps.

To gain better understanding of the interfacial evolution, we take a closer at the SE surface of the cell cycled at $10 \mu\text{A cm}^{-2}$. The SEM images and EDS maps of the representative areas are shown in **Figure 5**. The SE surface largely exhibits a flake-like feature (**Figure 5A**), which is attributed to LiCl according to the elemental maps (**Figure 5B, C**), indicating the formation of LiCl rich interphase at a low current density. Moreover, there are some micro-size Li residual with a cube shape on the surface, showing the morphology of the plated Li.^[14] Note that the SEM image is captured on the SE surface at a higher magnification than the optical image captured on the ITO current collector (**Figure 3**). In contrast, the SE interface formed at $200 \mu\text{A cm}^{-2}$ is remarkably different (**Figure 6A**). Instead of the cube feature, the SE surface is mostly covered by the filaments, suggesting the rapid growth of Li dendrites at a high current. SEM reveals the difference on the SE surface after plating and stripping, while the SE surface is covered by a large amount of Li that shows smooth and dense features (**Figure S5**), which disappear after stripping (**Figure 6A**). The EDS maps (**Figure 6B, C**) show the homogenous distribution of S, P and Cl, with no obvious elemental segregation as observed at $10 \mu\text{A cm}^{-2}$. Therefore, the low current density leads to the decomposition of LPSC electrolyte and segregated LiCl rich interface, while much faster dendrite growth takes place at a high current density. The consumption of the Li for the SEI formation accounts for the low CE at a low current density.

3. Discussions

Based on the observation from combined SEM and EDS, we propose the interfacial evolution of the LPSC argyrodite during Li plating/stripping (**Figure 7A**). As briefly mentioned earlier, the plating process resembles the eruption of the volcano. At the beginning, Li nucleates at the random spot of the SE surface and acts as the Li seed for further growth. The Li seeds have less energy barrier for Li ion and electron transport,^[15] therefore, the Li and electron flux accumulate on the seeds owing to the fast kinetics. After that, the seeds start to grow on these spots, in the meantime, the SE decomposition and Li dendrite formation also occur on these spots. Therefore, the SE dome is composed of the metallic Li that is entangled with the LPSC electrolyte and its decomposition products. With the continuous plating, the growth of the SE domes pushes away the CC, causing more severe localized current. With the SE dome buildup, only these domes on the interface have effective physical contact between the SE and CC at a low pressure, and they form the craters, as evidenced by the optical microscope and SEM. Upon further plating, the accumulation of Li on these spots raises the local pressure, therefore, the metallic Li starts to spread to its surrounding area, which is the white spot previously captured during the *in-situ* experiments. This process is referred to as the Li eruption. Note that even though the size of the whole plating area increases, the

size of the crater (central dark spot) that provides the Li ion conducting path remains almost unchanged, suggesting the localized current distribution cannot be eliminated during the Li growth. This finding poses a significant challenge to operate all solid-state cell with uniform Li plating/stripping for the practical application. During the stripping process, the plated Li on CC is stripped through the craters. Once the Li around the craters is consumed, the stripping ends and the rest Li located at the outer layer surrounding the craters becomes the dead Li. Our results reveal that these processes are not affected by the current density and CCs (stainless steel^[16], Cu, and ITO).

Although the current has no significant impact on the Li plating/stripping processes, the degradation of the LPSC electrolyte is highly dependent on the current density. The LPSC electrolyte decomposes at a low current and forms more uniform LiCl-rich interface while Li grows into the cube shape. In comparison, the formation of Li filaments with no noticeable LiCl segregation at a high current density suggests a different mechanism for the interfacial evolution (**Figure 7B**). The formation of LiCl (or decomposition of LPSC) and Li plating could be competing processes. At a low current, Li is consumed to form LiCl or other byproducts, while a high current facilitates the formation of Li seeds and their fast growth, resulting in the Li filaments. This observation agrees well with the previous report on stabilizing the interface between the LPSC and Li anode through the formation of LiCl-rich SEI.^[6]

With the highly localized current on these hot spots, one possible solution is to improve deposition kinetics on the surface of the SE. To verify this, we add a layer of the mixed LPSC and carbon fiber (CF) between the SE and CC (inset in **Figure 8**). In principle, the carbon fiber provides more electron conducting path for Li deposition. To build the contrast, we intentionally mix the LPSC and CF roughly to form clusters of different compositions. Under the optical microscope, the dark area features the presence of CF and is more electron conductive. **Figure 8** present the optical images captured during the Li plating at different time series. Instead of the isolated islands, the entire dark area is quickly covered by the plated Li, while other areas remain mostly unchanged except sparse spots. The presence of electrically conductive CF helps homogenize the current distribution and Li plating. However, better electron conduction also leads to the pronounced dendrite growth. **Figure S6** shows the SEM and EDS of the interface on the ITO glass. Similar to the previous results, near the area of the Li dendrite, the segregation of Cl is observed. This study again highlights the importance of the physical contact for better electrical conductivity and more uniform current distribution on the interface. However, the presence of CF promotes the Li growth as well as SE decomposition.

Based on this study, we propose a design strategy for the interface between argyrodite electrolyte and Li anode of all solid-state cells (**Figure 9**). The ideal interphase(s) between the SE and Li is composed of two layers – one layer on the CC side is the electrical conductor that provides good physical contact and shows Li solubility; the layer on the SE side is composed of ionic conductor and chemically compatible with SE. With these interphases, Li plating occurs above the layer on the SE, which avoids the direct contact with the SE and prevents the SE decomposition. The plated Li then dissolves in the interlayer on the CC side, which protects the dissolved Li from further reduction. We note that this interface design is proposed based on the findings using the asymmetric cell with one side being in direct contact with current collector. Despite the limitation in probing the “exact” interface in between SE and Li, the interfacial processes are captured starting from the Li nucleation throughout its growth on the surface of the solid electrolyte.

4. Conclusion

We develop an asymmetric *in situ* cell to investigate the interfacial evolution process on the SE in all solid-state cells using ITO glass as the current collector. The *in situ* cell enables us to visualize the Li plating/stripping behavior under the optical microscope, and it can keep the solid interface intact for characterization. We monitor the Li plating/stripping processes at different current densities and probe the interfacial evolution on the LPSC electrolyte using SEM and EDS. Overall, the Li plating on the argyrodite LPSC electrolyte is heterogeneous and takes place only on random “hot spots”, which are favored by Li growth. This process is referred to as the Li volcanic activity with the “hot spots” as the volcanic craters and Li lava situated around them. High current density facilitates more Li seeds and faster Li growth. However, an exceptionally low CE is obtained at a low current density of $10 \mu\text{A cm}^{-2}$, which correlates well with the slope profile at the beginning of Li plating. Using combined optical microscope and SEM/EDS, we find that the Li plating at a low current is featured by the P, S rich central core and Cl, Li rich outer area, while such elemental segregation doesn’t occur at high currents. In the meantime, Li with a cube shape is deposited at a low current, but high current density leads to the filament morphology. The interfacial evolution on the LPSC electrolyte is highly dependent on the current density, which shows an impact in both the interphases and Li morphology. During stripping, the contact area between the Li metal and CC / SE continues to increase due to the change of the internal pressure. This observation signifies the effect of the stack pressure and/or physical contact on the operation of all solid-state cells, which will be even more challenging for the practical application under a low pressure. Based on these findings, we propose the mechanism regarding the localized Li nucleation and growth, side reactions, and dead Li formation, as well as the strategy to build the stable interface in all solid-state cells. This *in situ* cell set up could be easily adopted to investigate the Li plating/stripping and interfacial processes in other solid electrolytes and solid interfaces.

5. Experimental Section

$\text{Li}_6\text{PS}_5\text{Cl}$ electrolyte was purchased from MSE Supplies LLC and used as received without further treatment. Coin cell parts purchased from Hohsen Corp. along with an ITO glass with a thickness of 1.3 mm and roughness less than $0.15 \mu\text{m}$ were used for the *in situ* optical cell. The ITO glass was cut into small pieces and cleaned with acetone by sonication and then dried overnight before use. A hole with a diameter of 3 mm was punched at the center of the cell lid and then sealed with the ITO glass by epoxy resin. The Li foil with a thickness of $50 \mu\text{m}$ was purchased from MSE Supplies LLC and used as received.

150 mg of SE powder was pressed by the cold hydraulic press into a pellet with a diameter of 12 mm under 350 MPa. A piece of Li foil and ITO were attached on each side of the SE pellet. The *in situ* cell was then assembled carefully. For the cell with a layer of CF, the mixture of CF and LPSC was roughly mixed at a weight ratio of 3: 97, respectively. 140 mg LPSC was then pressed into a pellet under 350 MPa and 10 mg CF/LPSC mixture was added and pressed under 350 MPa again. All the processes mentioned above were operated inside an Ar-filled glove box.

The electrochemical characterization was conducted at room temperature using 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 pellet and ITO glass and samples for SEM/EDS analysis were prepared and sealed inside an Ar-filled glove box for the interface characterization. The sealed samples were opened and quickly mounted on the SEM sample stage with a brief exposure (less than 1 min) to the inert atmosphere. SEM/EDS data were collected 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 5 kV.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work is supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231 through the Battery Materials Research (BMR) program. Use of resources at the Molecular Foundry is supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

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

Keywords

All solid-state Li batteries, asymmetric cells, argyrodite electrolyte, solid interfaces, *in situ* characterization, Li plating/stripping

References

- [1] a) A. Banerjee, X. Wang, C. Fang, E. A. Wu, Y. S. Meng, *Chem. Rev.* **2020**, *120*, 6878; b) S. Randau, D. A. Weber, O. Kötz, R. Koerver, P. Braun, A. Weber, E. Ivers-Tiffée, T. Adermann, J. Kulisch, W. G. Zeier, *Nat. Energy* **2020**, *5*, 259; c) H.-D. Lim, J.-H. Park, H.-J. Shin, J. Jeong, J. T. Kim, K.-W. Nam, H.-G. Jung, K. Y. Chung, *Energy Storage Mater.* **2020**, *25*, 224; d) T. Krauskopf, F. H. Richter, W. G. Zeier, J. r. Janek, *Chem. Rev.* **2020**, *120*, 7745.
- [2] a) D. H. Tan, E. A. Wu, H. Nguyen, Z. Chen, M. A. Marple, J.-M. Doux, X. Wang, H. Yang, A. Banerjee, Y. S. Meng, *ACS Energy Lett.* **2019**, *4*, 2418; b) T. T. Zuo, F. Walther, J. H. Teo, R. Rueß, Y. Wang, M. Rohnke, D. Schröder, L. F. Nazar, J. Janek, *Angew. Chem. Int. Ed.* **2023**, *62*, e202213228; c) S. Narayanan, U. Ulissi, J. S. Gibson, Y. A. Chart, R. S. Weatherup, M. Pasta, *Nat. Commun.* **2022**, *13*, 7237.
- [3] L. Ye, X. Li, *Nature* **2021**, 593, 218.
- [4] Y. Liu, H. Su, M. Li, J. Xiang, X. Wu, Y. Zhong, X. Wang, X. Xia, C. Gu, J. Tu, *J. Mater. Chem. A* **2021**, *9*, 13531.
- [5] F. Zhao, Q. Sun, C. Yu, S. Zhang, K. Adair, S. Wang, Y. Liu, Y. Zhao, J. Liang, C. Wang, *ACS Energy Lett.* **2020**, *5*, 1035.

- [6] D. Zeng, J. Yao, L. Zhang, R. Xu, S. Wang, X. Yan, C. Yu, L. Wang, *Nat. Commun.* **2022**, *13*, 1909.
- [7] a) C. Wang, J. Liang, J. Luo, J. Liu, X. Li, F. Zhao, R. Li, H. Huang, S. Zhao, L. Zhang, *Sci. Adv.* **2021**, *7*, eabh1896; b) T. Koç, M. Hallot, E. Quemina, B. Hennequart, R. Dugas, A. M. Abakumov, C. Lethien, J.-M. Tarascon, *ACS Energy Lett.* **2022**, *7*, 2979; c) L. Zhou, T.-T. Zuo, C. Y. Kwok, S. Y. Kim, A. Assoud, Q. Zhang, J. Janek, L. F. Nazar, *Nat. Energy* **2022**, *7*, 83.
- [8] a) E. Kazyak, M. J. Wang, K. Lee, S. Yadavalli, A. J. Sanchez, M. Thouless, J. Sakamoto, N. P. Dasgupta, *Matter* **2022**, *5*, 3912; b) M. Motoyama, M. Ejiri, Y. Iriyama, *J. Electrochem. Soc.* **2015**, *162*, A7067.
- [9] a) M. J. Wang, E. Carmona, A. Gupta, P. Albertus, J. Sakamoto, *Nat. Commun.* **2020**, *11*, 5201; b) C. Heubner, S. Maletti, H. Auer, J. Hüttel, K. Voigt, O. Lohrberg, K. Nikolowski, M. Partsch, A. Michaelis, *Adv. Funct. Mater.* **2021**, *31*, 2106608; c) W. Z. Huang, C. Z. Zhao, P. Wu, H. Yuan, W. E. Feng, Z. Y. Liu, Y. Lu, S. Sun, Z. H. Fu, J. K. Hu, *Adv. Energy Mater.* **2022**, *12*, 2201044.
- [10] M. Awais, D. D. Dowling, M. Rahman, J. G. Vos, F. Decker, D. Dini, *J. Appl. Electrochem.* **2013**, *43*, 191.
- [11] a) C. Luo, Y. Zhu, Y. Wen, J. Wang, C. Wang, *Adv. Funct. Mater.* **2014**, *24*, 4082; b) Q. Zhang, S. Tan, R. G. Mendes, Z. Sun, Y. Chen, X. Kong, Y. Xue, M. H. Rummeli, X. Wu, S. Chen, *Adv. Mater.* **2016**, *28*, 2616.
- [12] B. Neudecker, N. Dudney, J. Bates, *J. Electrochem. Soc.* **2000**, *147*, 517.
- [13] a) C. Yu, F. Zhao, J. Luo, L. Zhang, X. Sun, *Nano Energy* **2021**, *83*, 105858; b) C. Zheng, J. Zhang, Y. Xia, H. Huang, Y. Gan, C. Liang, X. He, X. Tao, W. Zhang, *Small* **2021**, *17*, 2101326.
- [14] M. R. Nadler, C. Kempier, *Anal. Chem.* **1959**, *31*, 2109.
- [15] K. Yan, Z. Lu, H.-W. Lee, F. Xiong, P.-C. Hsu, Y. Li, J. Zhao, S. Chu, Y. Cui, *Nat. Energy* **2016**, *1*, 1.
- [16] Y.-G. Lee, S. Fujiki, C. Jung, N. Suzuki, N. Yashiro, R. Omoda, D.-S. Ko, T. Shiratsuchi, T. Sugimoto, S. Ryu, *Nat. Energy* **2020**, *5*, 299.

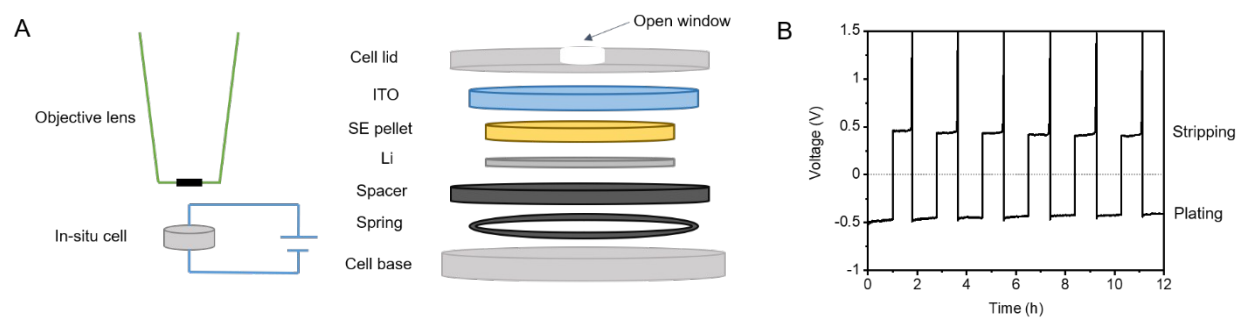


Figure 1. Asymmetric cell for *in situ* characterization using optical microscope. (A) Schematic of the *in situ* cell, and (B) voltage profiles during the initial Li plating/stripping cycles.

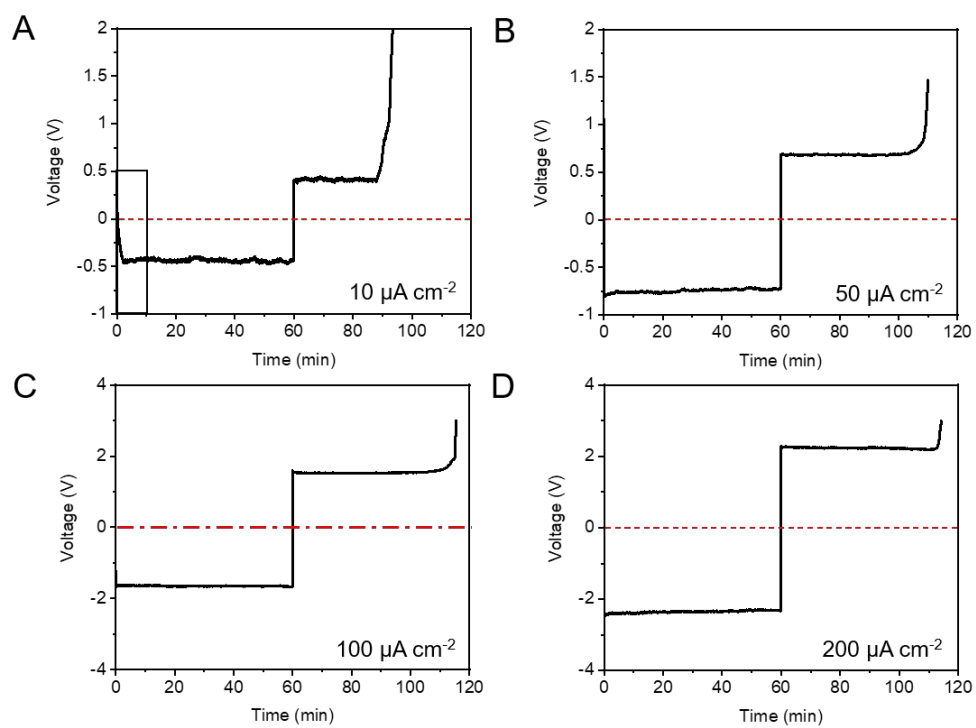


Figure 2. Voltage profiles during the initial cycle at different current densities. (A) 10, (B) 50, (C) 100, and (D) $200 \mu\text{A cm}^{-2}$.

Table 1. The first-cycle CE obtained at different current densities and plating capacities.

Current I ($\mu\text{A cm}^{-2}$)	Capacity Q ($\mu\text{Ah cm}^{-2}$)	Initial CE (%)
10	10	55.7
50	50	83.3
100	100	90.3
200	10	81.0
200	100	95.2
200	200	92.3

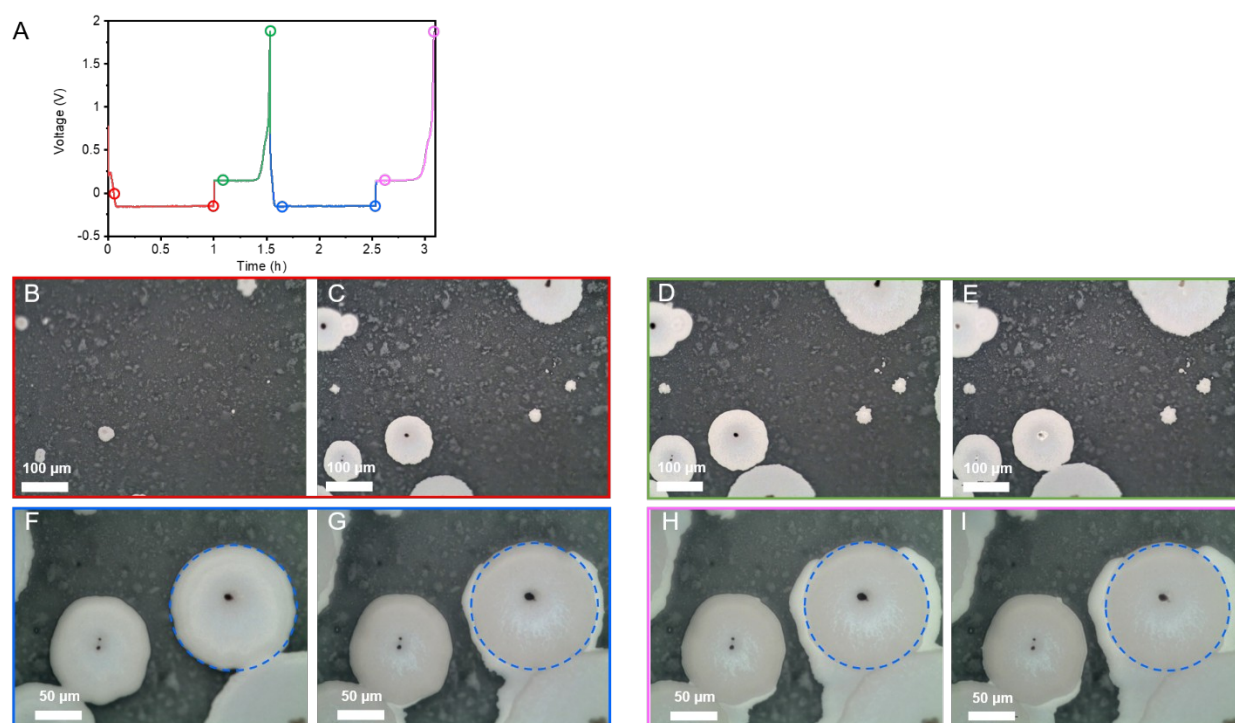


Figure 3. Li plating/stripping on argyrodite electrolyte visualized by *in situ* optical microscopy. (A) Voltage profiles at $10 \mu\text{A cm}^{-2}$ along with the optical images captured at different time series, (B, C) during the 1st plating, (D, E) during the 1st stripping, (F, G) during the 2nd plating, (H, I) during the 2nd stripping. Blue circle in F-G labels the central core formed from the previous cycle.

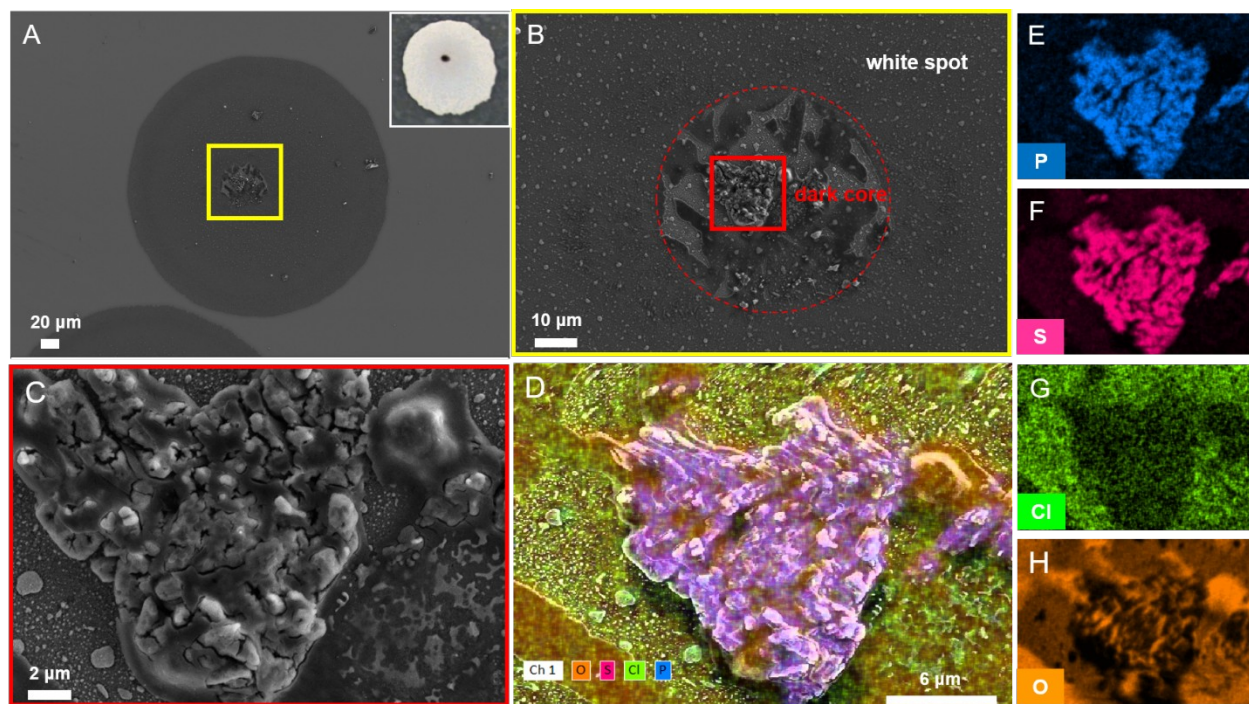


Figure 4. Characterization of the solid interface harvested on ITO current collector after stripping at $10 \mu\text{A cm}^{-2}$. (A-C) SEM image featured by the central core and outer smooth areas, corresponding to the dark core and white spot shown in the optical image (inset in A); and the EDS maps of (D) combined, (E) P, (F) S, (G) Cl, and (H) O, showing the elemental segregation. The cell is cycled at $10 \mu\text{A cm}^{-2}$.

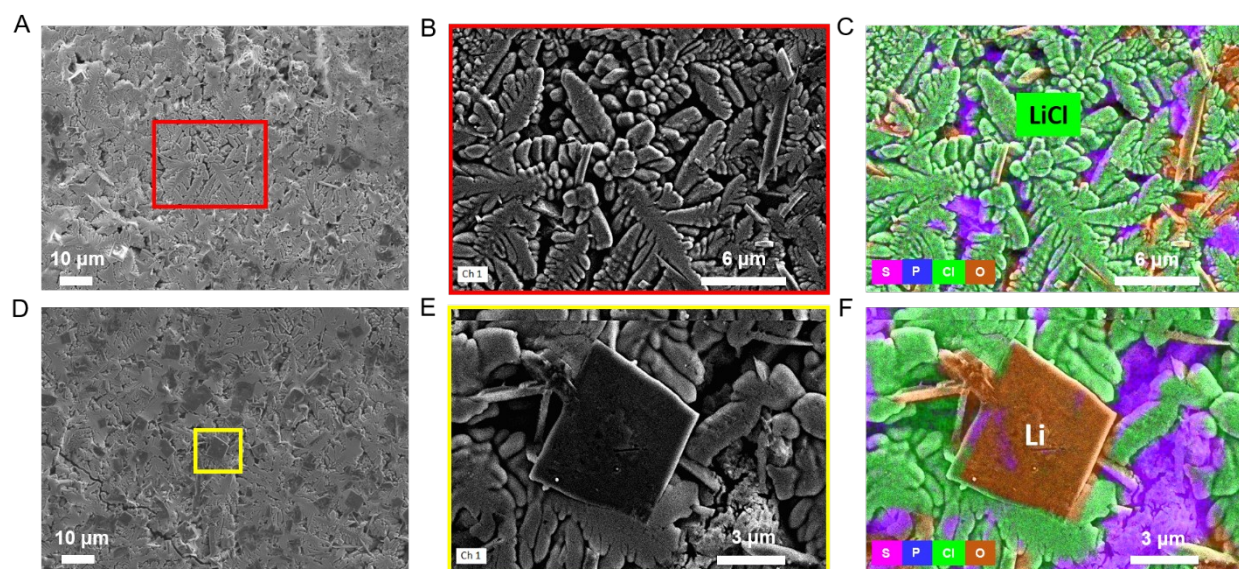


Figure 5. Characterization of the solid interface harvested on argyrodite surface after stripping at $10 \mu\text{A cm}^{-2}$. (A, B) SEM image and (C) combined EDS map, showing the LiCl rich interface with flake-like features, (D, E) SEM image and (F) combined EDS map, showing the Li cube morphology, which is indicated by O upon brief exposure to the inert atmosphere.

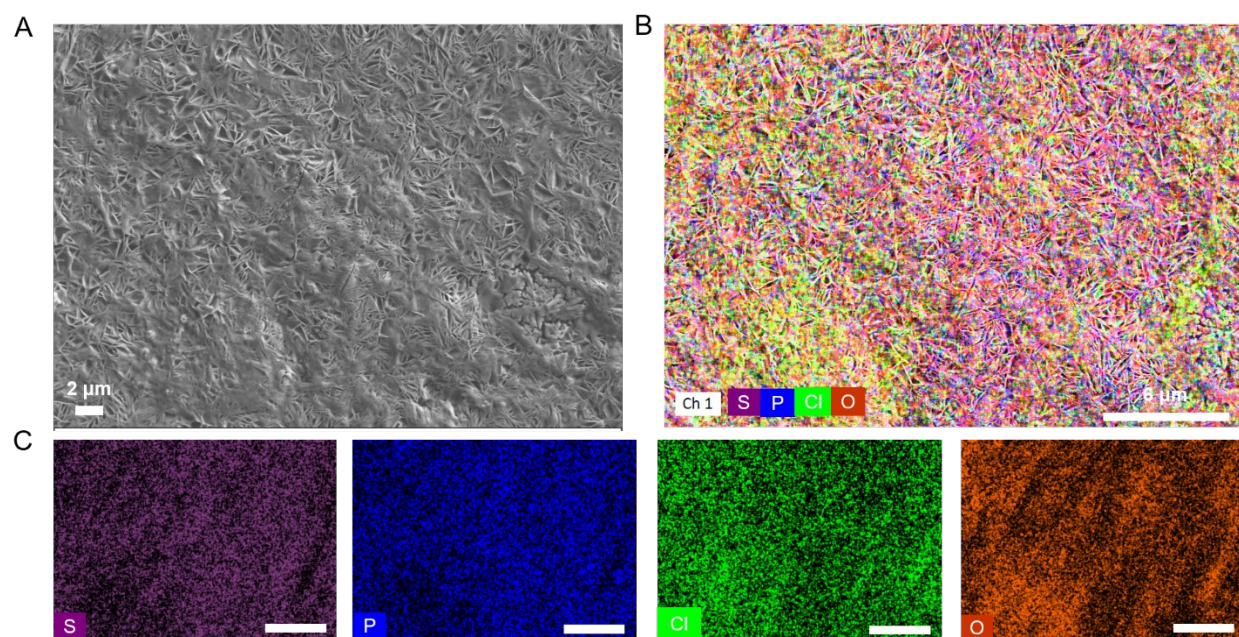


Figure 6. Characterization of the solid interface harvested on argyrodite surface at after stripping at $200 \mu\text{A cm}^{-2}$. (A) SEM image and EDS map of (B) combined, (C) S, P, Cl, and O, showing the filament morphology and uniform elemental distribution, respectively.

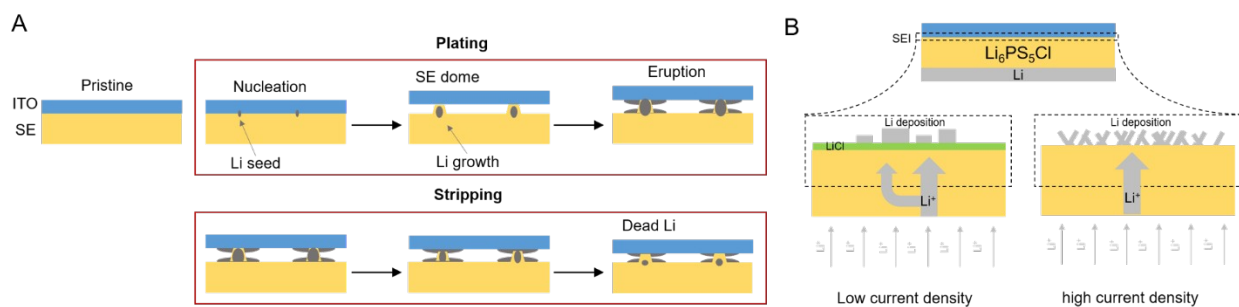


Figure 7. Schematic of the interfacial evolution mechanism during Li plating/stripping on argyrodite electrolyte. (A) Li nucleation and growth on the interface, and (B) interface evolution at different current densities.

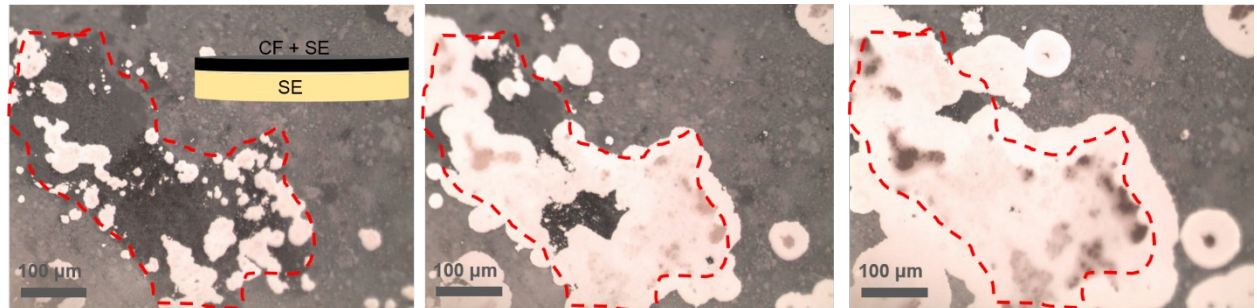


Figure 8. Optical images captured at different time series during the Li plating on argyrodite mixed with carbon fiber, showing more current distribution and uniform plating with enhanced electrical conductivity.

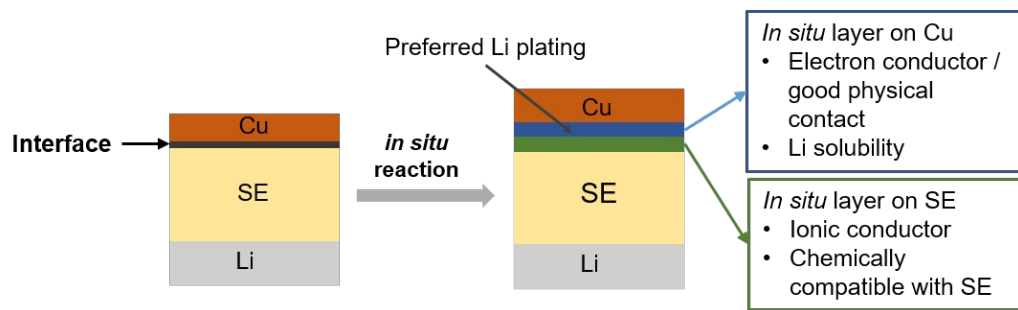
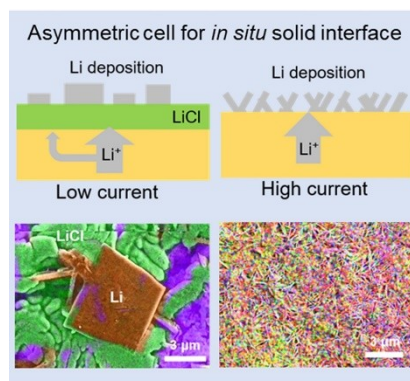


Figure 9. Design considerations for solid electrolyte and Li anode interface in all solid-state batteries.

TOC summary



An asymmetric *in situ* all solid-state cell allows visualization of Li plating/stripping behaviors on solid electrolyte and intact solid interface for reliable analysis. The interface is highly localized and

strongly dependent on current density. At a low current, it is LiCl-rich with Li cube morphology, while high currents result in more uniform elemental distribution and filament morphology.

Supporting Information for

***In Situ* Characterization of the Interface Evolution for Argyrodite-Based All
Solid-State Li Batteries**

*Di Huang, Gao Liu, and Wei Tong**

Energy Storage and Distributed Resources Division, Lawrence Berkeley National Laboratory,
Berkeley, California 94720, United States

Email: weitong@lbl.gov

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.

Movie S3. *In situ* optical microscopy observation, showing the Li plating behavior during the 2nd cycle at 10 $\mu\text{A cm}^{-2}$. The movie clip is accelerated by 100 times.

Movie S4. *In situ* optical microscopy observation, showing the Li stripping behavior during the 2nd cycle at 10 $\mu\text{A cm}^{-2}$. The movie clip is accelerated by 100 times.

Movie S5. *In situ* optical microscopy observation, showing the Li plating behavior during the 1st cycle at 200 $\mu\text{A cm}^{-2}$. The movie clip is accelerated by 100 times.

Movie S6. *In situ* optical microscopy observation, showing the Li stripping behavior during the 1st cycle at 200 $\mu\text{A cm}^{-2}$. The movie clip is accelerated by 100 times.

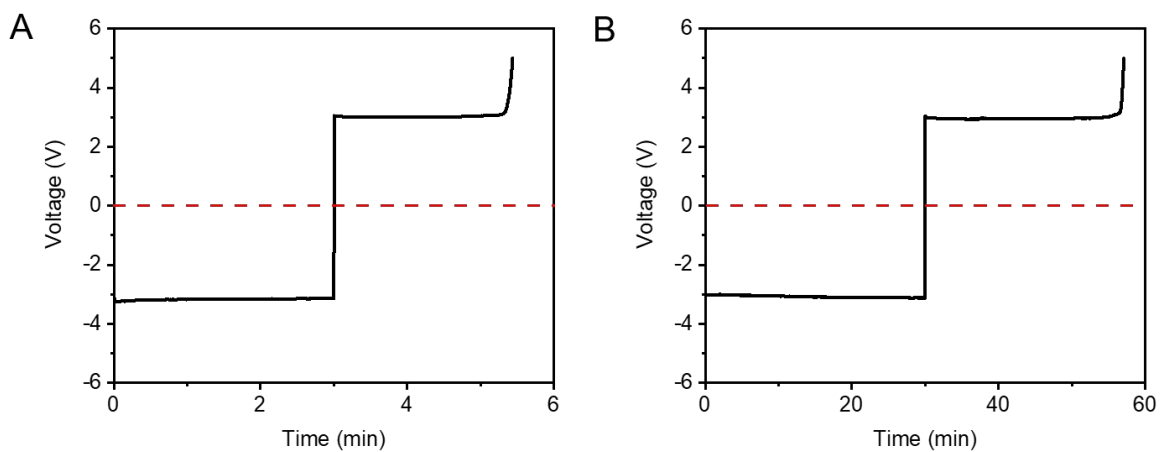


Figure S1. Voltage profiles during the initial plating/stripping at a current density of $200 \mu\text{A cm}^{-2}$ for a plating capacity of (A) 10 and (C) 100 $\mu\text{Ah cm}^{-2}$.

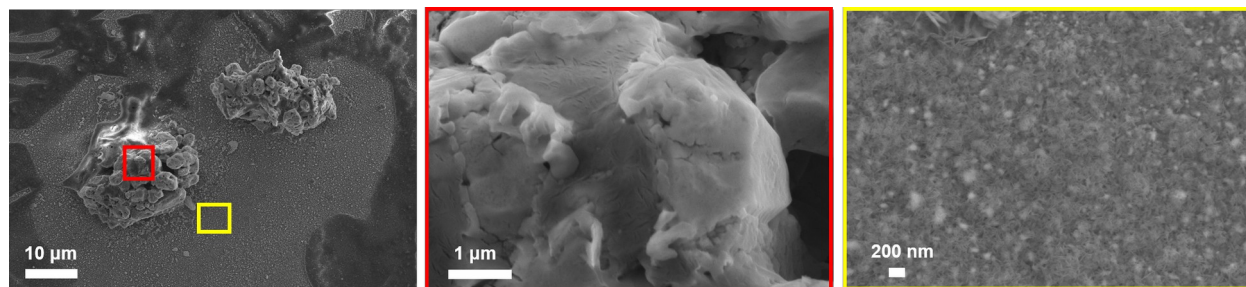


Figure S2. SEM images of the solid interface on ITO current collector after stripping at $200 \mu\text{A cm}^{-2}$.

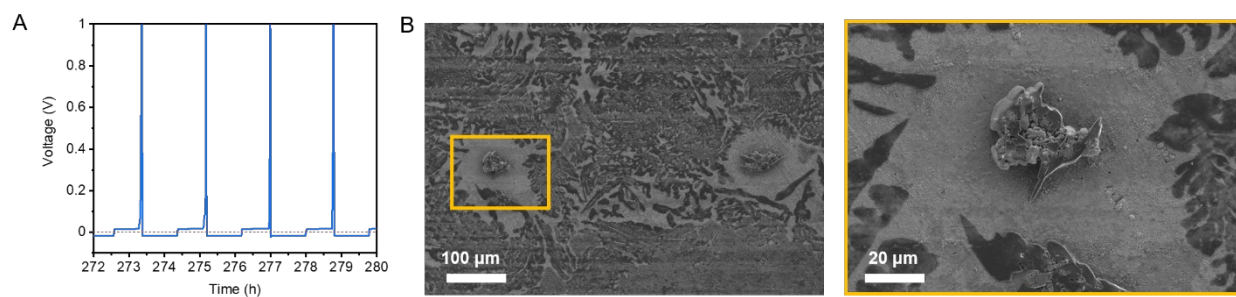


Figure S3. Solid interface characterization of an asymmetric cell using Cu current collector. (A) Voltage profiles and (B) SEM images of the solid interface on Cu after stripping at $100 \mu\text{A cm}^{-2}$.

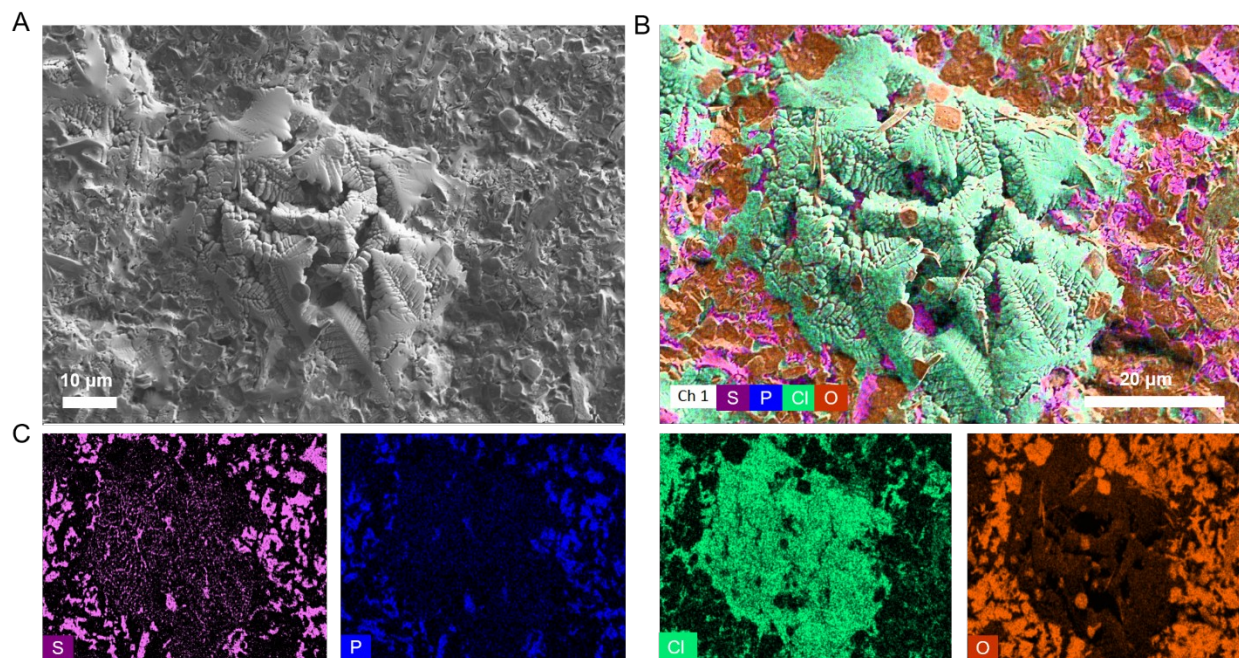


Figure S4. (A) SEM image and EDS map of (B) combined, (C) S, P, Cl, O element collected on the argyrodite surface after stripping at $10 \mu\text{A cm}^{-2}$, showing the Li volcanic activity, where the crater is LiCl rich and Li is situated around the crater.

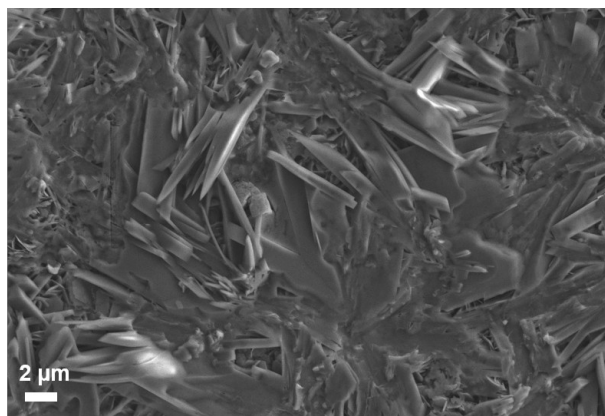


Figure S5. SEM image of the SE surface after the 1st Li plating at 200 $\mu\text{A cm}^{-2}$.

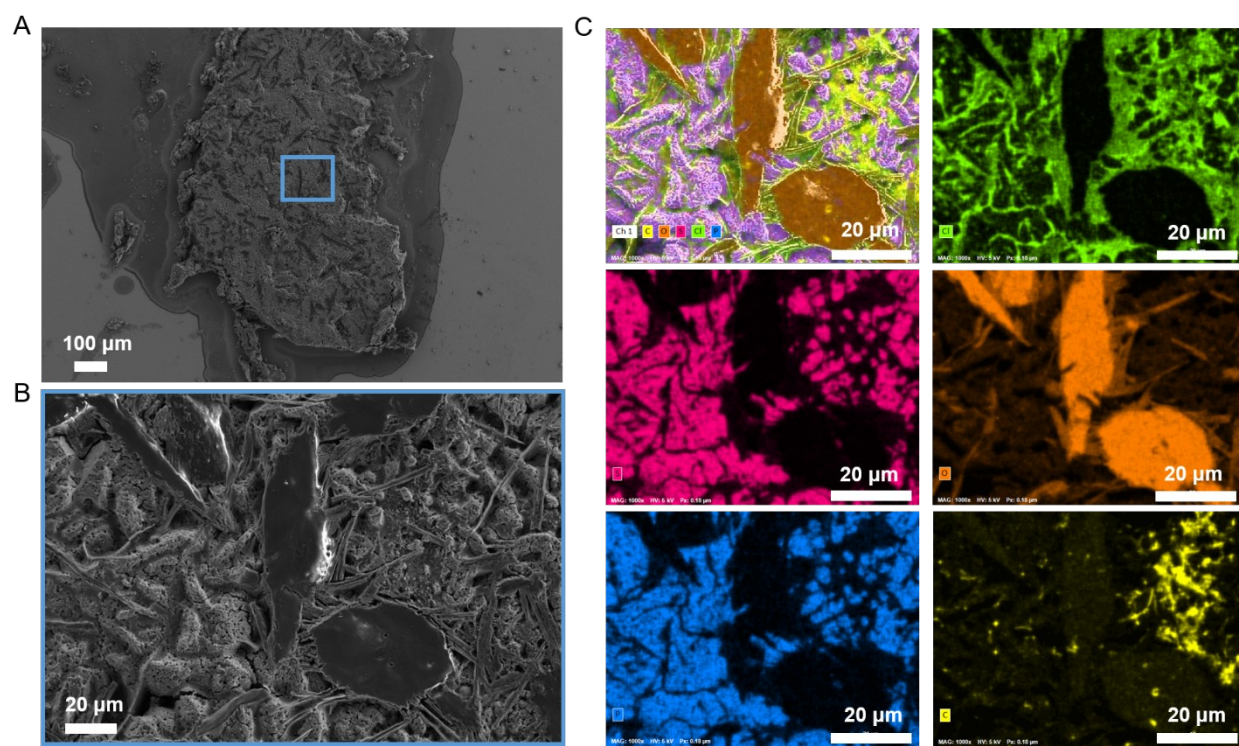


Figure S6. (A, B) SEM images and (C) EDS maps of the solid interface on ITO side in all solid-state cell with the presence of argyrodite mixed carbon fiber.

