

Revealing Interfacial Failure Mechanism of Silicon Based All Solid State Batteries via Cryogenic Electron Microscopy

Corresponding Author: Professor Jianyu Huang

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

This paper investigates the interfacial stability of the Si anode/Sulfide electrolyte system using LGPS and LSPSC electrolytes. The author attributes the observed difference in cycling performance to the formation of distinct interfacial reaction layers (IRLs). Interestingly, they argue that the increase in interface impedance is not the primary cause of capacity decay in either system, which is contrary to conventional understanding in solid state batteries. The study employs advanced low-dose cryo HR-TEM imaging techniques combined with EELS spectroscopy which enable detailed structural and chemical analysis of IRLs in sulfide electrolytes and provide their correlation with electrochemical performance. The findings offer intriguing perspectives on interfacial reactions and their impact on battery performance, contributing to the Si-based sulfide solid-state battery field which is a cutting-edge next generation battery system.

However, there are significant flaws in the interpretation of the results, as discussed below. The author described the interfacial reaction at the Si/LGPS interface as originating from the reaction between Li and LGPS, which means that Li deposition occurs in Si anode. However, since the Si anode undergoes lithiation through Li-Si alloying, it is plausible that the Si/SSE system in this study failed to function as intended. Li plating may instead result from poor interfacial contact, leading to Li metal reduction due to high interface impedance, rather than Li-Si alloying. If this is the case, the reported interfacial reaction cannot reliably represent the stability of Si anode against sulfide electrolytes.

There is a fundamental question regarding whether Li deposition actually occurred and whether the formation of different IRLs was indeed caused by the differences in reactivity between Li metal and the two electrolytes. Regarding the evidence of Li deposition, (Line 186) "EDS mapping of the cracks indicates that the cracks are rich in oxygen, suggesting the growth of Li dendrite along these cracks, as the dendrites were oxidized during the sample transfer." However, the author mentioned that all sample transfer steps are achieved in air-preventing conditions. Even if there was some extent of air exposure, Li cannot be oxidized during the transfer to FIB-SEM as it is buried inside the cell. In SEM-EDS mapping (Figure S5-S8), as the cross-section milling and EDS analysis are conducted in same equipment without transfer, there is no chance to the oxidation of Li metal. Therefore, the author should reconsider the origin of O. In addition, to see what reactions exactly happen on the anode, the author needs to check anode voltage profiles during charging in 3 electrode system.

Given these critical issues, I do not recommend this work for publication in Nature Communications in its current form.

Further comments the author should address and reinforce are listed below.

1. How can the author define IRLs in the LGPS and LSPSC systems as a pure ionic conductor and a mixed conductor, respectively? To support these classifications, the author should provide quantitative measurements of ionic conductivity and electronic conductivity for the IRLs.
2. The description of interfacial layer as pure ionic conductor in Si/LGPS is inconsistent. (Line 191) "This suggests that the interphase layer of pure ionic conductor seems to impede the shuttle of Li dendrites at the interface." (Line 263) "Due to the high electronic conductivity of Li-Ge alloy, the presence of Li-Ge confirming the electrical conductivity of the IRL in ASSBLGPS."
3. Why are the bin intervals in the frequency distribution of crack length (Figure S9b, c) different? Also, one cannot agree they show the different dispersion of crack length.
4. The pristine state of Si/electrolytes should be also analyzed by HR-TEM and EDS.
5. What is the dose-rate during low-dose HR-TEM imaging? How tolerant are the IRL and sulfide electrolytes against e-beam?
6. The author can conduct XRD analysis to support the decomposition of electrolytes and the degradation of Si anode.
7. (Line 267) "The weak crystallinity of Si and the gradient distribution of crystallinity and grain size of Li₂S in the IRL

indicate that the Si/LGPS interface deterioration occurred during the battery cycling." How can the crystallinity and grain size of Si or Li₂S be related to the interface deterioration? The author should provide a detailed description of the relationship.

8. Can the author provide LUMO energies of LGPS and LSPSC which determine the stability of electrolytes?
9. Why are the crystallinity of Si anodes in LGPS and LSPSC electrolytes different? Does it mean that they undergo different lithiation mechanism?
10. The author should provide the preparation procedure of the μ -Si anode and full-cell of solid-state batteries, as well as exact specifications of the cell (areal capacity, dimensions, etc.)
11. The author should provide the experimental procedures for XPS analysis.

Reviewer #2

(Remarks to the Author)

The manuscript entitled " Revealing the Interfacial Failure Mechanism of the Silicon Anode Based All-Solid-State Batteries (ASSBs) via Atomic-Scale Cryo-Electron Microscopy " by Yao et al. conducted atomic-level research on the Si/SSE interface of sulfide-based ASSB by cryo-genic technology. It is interesting that the Si/LSPSC interface comprising nanocrystalline Li₂S, exhibits dense and stable behavior within the ASSB. In contrast, the thickness of the Si/LGPS interface composed of needle-like Li₂S increased by 50 times. The study also demonstrates that the thick interface layer of LGPS-based ASSBs originated from interface reactions does not lead to dramatic increase of interface impedance, which challenges traditional notion that interfacial impedance is the culprit of ASSB failure. Therefore, I suggest that the paper should be published after the authors have addressed the following issues.

1. Regarding the repeated mention of lithium loss in the article, are there any other evidences of lithium-ion loss in the silicon anode besides lithium deposition and the interface reaction between the anode and the electrolyte?
2. The article mentions the uneven distribution of Li₂S in the Si/LGPS interface layer (Figure S13). How can we explain the interface deterioration that occurs during the cycling process of solid-state batteries?
3. Sulfide electrolytes are highly sensitive to air and electron beams. How can the authors ensure that the samples are not affected during the sample preparation process?
4. Why do both interfaces have Li₂S as the main component, but the interface in Si/LSPSC tends to be stable? In other words, how do Li₃P and Li-Ge in Si/LGPS affect the evolution of the interface?
5. Compared to the Si/LSPSC interface (Figure 5a), why are there significant cracks at the Si/LGPS interface (Figure 3a)? Could this be related to the sample preparation process?

Reviewer #3

(Remarks to the Author)

In this manuscript, the authors provide a comprehensive understanding of the solid/electrolyte interface (SEI) structure and chemical components in silicon (Si)-based all-solid-state batteries, using cryo-TEM as a tool. The novel contribution of the study lies in the detailed analysis of the SEI in this system. However, the understanding of the failure mechanism kind of lacks novelty and significance for a publication in Nature Communications. The authors pointed out that the failure mechanism is mainly due to Li inventory loss caused by the unwanted SEI formation, a well-known issue in the battery field. Similarly, the side reaction between the deposited Li and the solid electrolyte at the grain boundaries is another established phenomenon in the field.

The reviewer also has the following questions:

1. Li Deposition in Si-based Batteries: It is widely known that Si anodes have good fast charging/discharging capabilities, which makes significant lithium (Li) deposition in Si-based batteries not very likely. Could the observed Li deposition be a result of unoptimized anode preparation or the use of excessively high current/voltage during cycling? It would be helpful if the authors could provide more detailed information on the anode preparation method and the specific cycling parameters used for the sample preparation, to help clarify whether these factors might influence the observed results.
2. Relevance to Real Applications: In real-world applications of Si anodes in all-solid-state batteries, Si is often mixed with solid-state electrolytes to enhance lithium ionic conductivity, which is not as critical when using liquid electrolytes. However, it appears that in this study, Si is not mixed with the solid electrolyte. This could potentially lead to Li deposition at the interfaces due to the limited ionic conductivity within the Si anode bulk. Consequently, the findings presented in this study may not fully reflect the operational conditions of Si anodes in practical applications. This could limit the broader applicability of the results, and the findings might only be relevant to a smaller audience.
3. Li-Si Alloy and LGPS Interaction: On Page 8, Line 222, the authors claim that Li-Si alloy does not react with LGPS (Li₁₀GeP₂S₁₂). However, there is insufficient evidence to support this argument. Later, on Page 12, Line 355, the authors mention a side reaction between deposited Li and LGPS, but this does not conclusively rule out the possibility of a reaction between the Li-Si alloy and LGPS. Further clarification and stronger evidence are needed to definitively establish whether such a reaction occurs.

Reviewer comments:

Reviewer #1

(Remarks to the Author)

I have carefully reviewed the author's response to my previous comments and the revised manuscript. The author has effectively addressed all of my concerns. The clarifications and additional data demonstrate a clear effort to improve the quality and clarity of the work.

Therefore, I recommend the manuscript to be published in Nature Communications in its present form.

I've thoroughly reviewed the author's response to Reviewer #3 as well. The reviewer agrees that this work reports a new failure mechanism in Si-based solid-state batteries, distinct from lithium-ion batteries with liquid electrolyte, as the author has described in detail. Also, the author has adequately addressed the questions and revised the manuscript accordingly with improved clarity. Therefore, I now find the manuscript suitable for publication in Nature Communications.

Reviewer #2

(Remarks to the Author)

All my concerns have been resolved. The revised manuscript is now acceptable for publication.

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Response to Reviewers' and Editorial Comments

Journal: Nature Communications

Manuscript ID: NCOMMS-24-83108

Title: "Revealing the Interfacial Failure Mechanism of the Silicon Anode Based All-Solid-State Batteries via Atomic-Scale Cryo-Electron Microscopy"

Reviewer #1 (Remarks to the Author):

1. This paper investigates the interfacial stability of the Si anode/Sulfide electrolyte system using LGPS and LSPSC electrolytes. The author attributes the observed difference in cycling performance to the formation of distinct interfacial reaction layers (IRLs). Interestingly, they argue that the increase in interface impedance is not the primary cause of capacity decay in either system, which is contrary to conventional understanding in solid state batteries. The study employs advanced low-dose cryo HR-TEM imaging techniques combined with EELS spectroscopy which enable detailed structural and chemical analysis of IRLs in sulfide electrolytes and provide their correlation with electrochemical performance. The findings offer intriguing perspectives on interfacial reactions and their impact on battery performance, contributing to the Si-based sulfide solid-state battery field which is a cutting-edge next generation battery system.

Response: We thank the reviewer for the interests of our work and for the overall positive comments on our manuscript! Indeed, transmission electron microscopy (TEM) characterizations of interfaces in sulfide based all solid-state batteries (ASSBs) is very challenging due to the extreme air and electron beam sensitivity of sulfide electrolytes. Our study provides quantitative understanding regarding how interface evolution causes capacity decay and failure of ASSBs. Such results are difficult to achieve from other electrochemical characterization techniques and provide important scientific basis for improving the performance of ASSBs.

2. However, there are significant flaws in the interpretation of the results, as discussed below. The author described the interfacial reaction at the Si/LGPS interface as originating from the reaction between Li and LGPS, which means that Li deposition occurs in Si anode. However, since the Si anode undergoes lithiation through Li-Si alloying, it is plausible that the Si/SSE system in this study failed to function as intended.

Response: We thank the reviewer for raising the great question. We acknowledge that there is a lack of clarity regarding the interpretation of the interfacial reaction in the Li/LGPS interface. We have no doubt that the Si anode indeed acted as intended. To illustrate this point, we assembled Li|LGPS|NMC811 cell to compare with the Si|LGPS|NMC811 cell (Figure R1a, b). There exists significant difference between the Si anode and the Li anode, as elaborated in the following.

a. The discharge-capacity profile is very different. Both anodes exhibit two sloping regions (marked by "SR1" and "SR2"): with a slow sloping region (SR1) and a steep sloping region (SR2), and the main discharge capacity of both ASSBs is from the slow

sloping region SR1, which then declines rapidly in the steep sloping region SR2 (Figure R1c). However, the inflection point is very different: for the Li anode, the main capacity is above 3.4 V with a mid-voltage of 3.75 V; while for the Si anode, it is above 3.0 V with a mid-voltage of 3.44 V. There is a 0.31 V difference between the two anodes, which is apparently caused by the initial 0.3 V electrochemical potential of lithiation of Si vs. Li deposition.

b. The Li anode ASSB delivers much higher initial discharge capacity but suffers from rapid capacity decay than the Si ASSB, possibly due to the severe interfacial reaction between Li and the sulfide SSE.

c. The cycle lifetime for the Li anode ASSB is much shorter than that of the Si anode ASSB. This is particularly true for the Li|LGPS|NMC811 cell, which died after only 10 cycles, which was apparently caused by the detrimental interfacial reaction. In the LSPSC-based ASSBs, we obtained similar results where the use of Si anode avoided the interface reactions caused by direct contact between the Li anode and sulfide electrolytes, thereby improving the capacity retention (Figures R1e-h). The related results and discussion have been added in the revised manuscript and supporting information (Page 6 in Revised Manuscript, Figure S3 in Supporting Information).

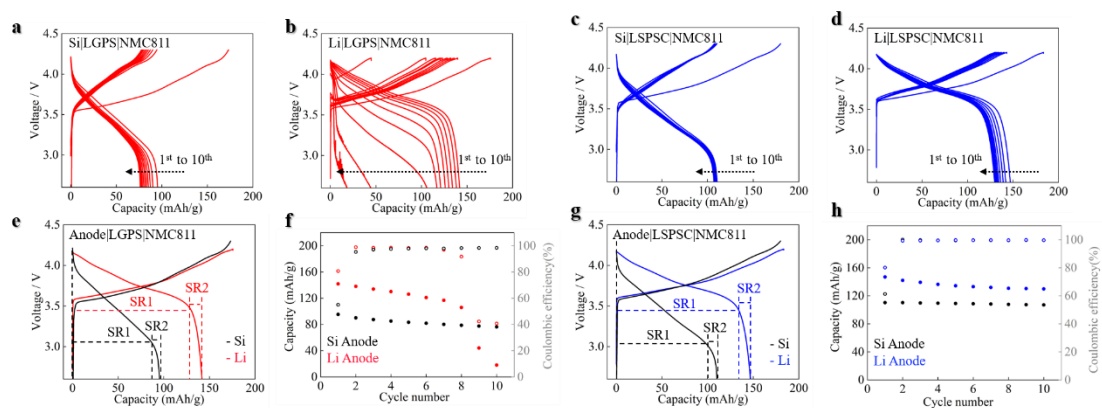


Figure R1. Electrochemical measurements of the Si|sulfide|NMC811 ASSBs and the Li|sulfide|NMC811 ASSBs: (a) Voltage-capacity profile of the Si|LGPS|NMC811 cell. (b) Voltage-capacity profile of the Li|LGPS|NMC811 cell. (c) The 1st cycle voltage-capacity profile with Si and Li anodes in LGPS based ASSBs. (d) The capacity changes with cycle numbers of the ASSBs based on Si and Li anodes with LGPS SSE. (e) Voltage-capacity profile of the Si|LSPSC|NMC811 cell. (f) Voltage-capacity profile of the Li|LSPSC|NMC811 cell. (g) The 1st cycle voltage-capacity profile with Si anode and Li anodes in LSPSC based ASSBs. (h) The capacity changes with cycle numbers of the ASSBs based on Si and Li anodes in LSPSC SSE.

Noteworthy the capacity retention is closely related to the interface reactions. For instance, the interface impedance of the Si|LGPS|NMC811 cell was low, thus exhibiting better capacity retention (Figures R2a, e). In contrast, the interface impedance of the Li|LGPS|NMC811 cell increased significantly with increasing cycling number, which caused continuous capacity decay (Figures R2b, f). The similar is true for the LSPSC based ASSB, i.e. the interfacial impedance of the Si|LSPSC|NMC811 ASSB (Figures

R2c, g) was lower than that of the Li|LSPSC|NMC811 ASSB (Figures R2d, h), thus the former demonstrated better capacity retention than the latter. The obtained results and the related discussion have been added in the revised manuscript and supporting information. (Page 6 in Revised Manuscript, Figure S4 in Supporting Information).

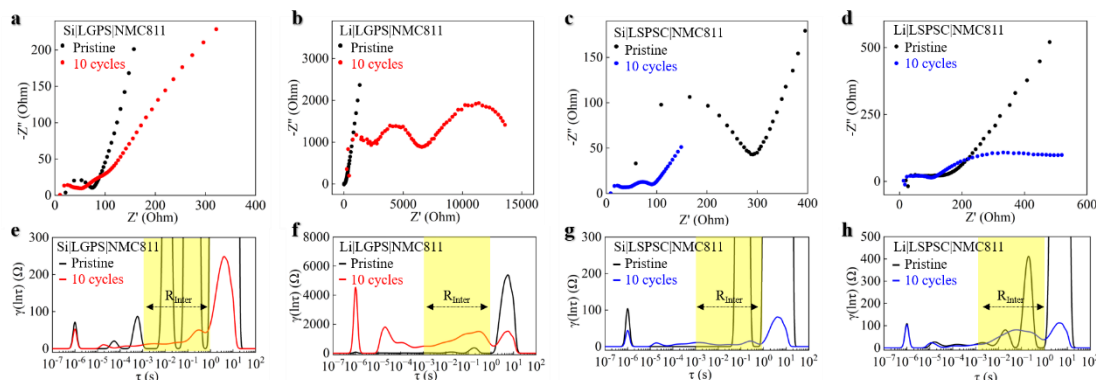


Figure R2. Impedance analysis of the Si|sulfide|NMC811 ASSB and the Li|sulfide|NMC811 ASSB. (a) EIS of the Si|LGPS|NMC811 cell. (b) EIS of the Li|LGPS|NMC811 cell. (c) EIS of the Si|LSPSC|NMC811 cell. (d) EIS of the Li|LSPSC|NMC811 cell. (e) DRT analysis of the Si|LGPS|NMC811 cell. (f) DRT analysis of the Li|LGPS|NMC811 cell. (g) DRT analysis of the Si|LSPSC|NMC811 cell. (h) DRT analysis of the Li|LSPSC|NMC811 cell.

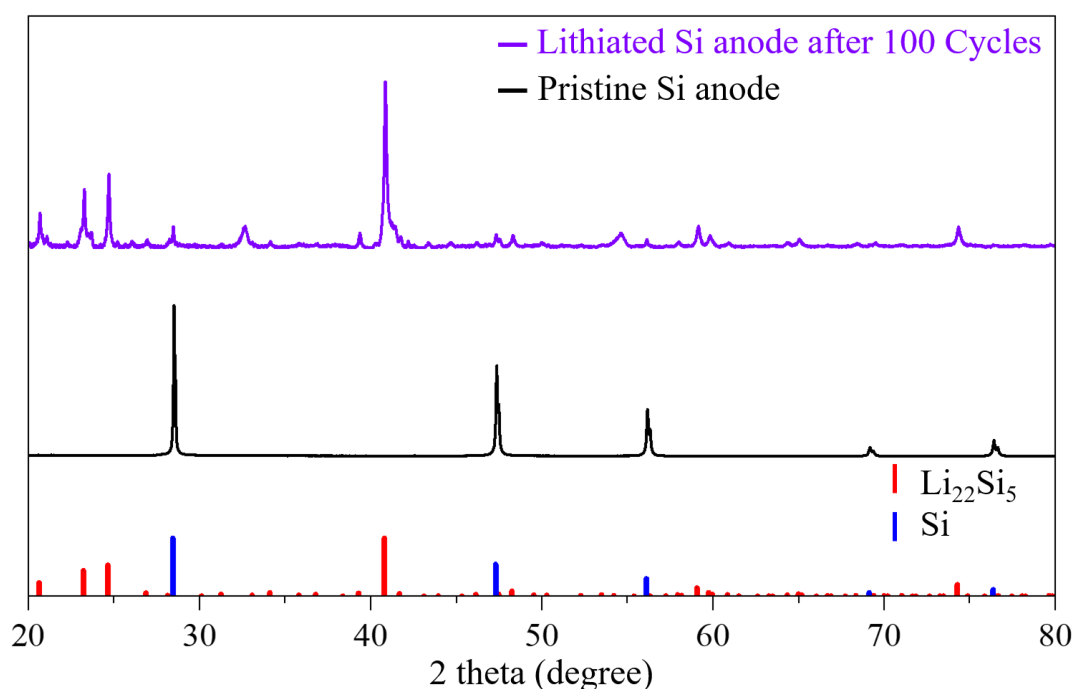


Figure R3. XRD characterization of the pristine Si anode and lithiated Si anode in the Si|LSPSC|NMC811 ASSB.

Furthermore, we characterized the micron-silicon (μ -Si) anode in the fully charged state through X-ray diffraction (XRD) analysis (Figure R3), which indicates the

lithiation of silicon leading to the formation of lithium-silicon alloy. This confirms that the capacity of the ASSB is from Si, not Li. (Page 6 in Revised Manuscript, Figure S5 in Supporting Information).

We acknowledge that the interpretation of the interfacial reaction in our original manuscript is misleading. Indeed, the main interfacial reaction mechanism is originated from the electrochemical reaction of Li^+ from the NMC811 cathode and electrons from the Si anode reacting with the SSE. In the case of the Si|LGPS|NMC811 ASSB, the IRL contains LiGe and LiP alloys which conduct electrons, rendering the interfacial reaction sustainable, resulting in thick IRL layers which consumes the lithium source from the cathode and causes the capacity decay (Figure R4a). Instead, the Li_2S -based IRL hinders the transfer of electrons from the Si anode in the Si|LSPSC|NMC811 ASSB, thereby stabilizing the Si/LSPSC interface and ensuring the stable operation of the ASSB (Figure R4b). We have revised the interpretation in the revised manuscript. (Page 25, Figure 6a and 6f in Revised Manuscript).

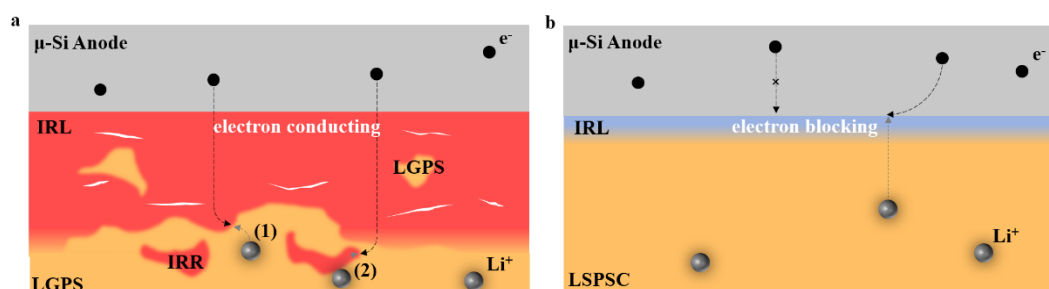


Figure R4. Schematic showing the IRL formation mechanism in the Si/LGPS interface of the Si|LGPS|NMC811 ASSB (a), and the Si/LSPSC interface of the Si|LSPSC|NMC811 ASSB (b). Electrons coming from the anode meet with the Li^+ from the cathode, reacting with the SSEs in the reaction front.

3. Li plating may instead result from poor interfacial contact, leading to Li metal reduction due to high interface impedance, rather than Li-Si alloying. If this is the case, the reported interfacial reaction cannot reliably represent the stability of Si anode against sulfide electrolytes.

Response: As described in our response to the reviewer's question #2, we demonstrate that the Si anode indeed functioned as intended. We do not expect massive Li deposition at the Si/LGPS interface. Note that the Si/LGPS interface maintained an intimate contact and astonishingly uniform after 100 cycles, suggesting little Li deposition at the interface and uniform interfacial reaction (Figures R5a, b). If local Li deposition occurred, we do not expect such uniform IRL formation. Also, if significant lithium deposition occurred at the interface, one would observe voltage fluctuation in the charge-capacity profile (Cao *et al.*, *Adv. Func. Mater.* 2023, 33, 2307998.), which is not the case here.

Furthermore, to demonstrate the impact of lithium deposition on the anode/electrolyte interface and the electrochemical performance, we conducted electrochemical tests on Li|LGPS|NMC811 cell, and characterized the cycled cell with central backscattered electron (CBS) imaging and energy dispersive X-ray

spectroscopy (EDS) mapping. The Li|LGPS|NMC811 ASSB developed a thick IRL with a thickness of 40 μm after only 10 cycles (Figures R5c-f), which is even thicker than that of the Si|LGPS|NMC811 cell after 100 cycles. Furthermore, the IRL contained numerous cracks and was almost pulverized, and it delaminated from the non-reacted LGPS (Figures R5g, h). The IRL of the Li/LGPS interface is entirely different from that of the Si/LGPS interface. In the latter, The IRL is thinner and uniform with only minor cracks, and no pulverization of the IRL was observed. These comparison experiments suggest that no massive Li deposition occurred in the Si/LGPS interface and the Si/LSPSC interface.

Our research has revealed that the utilization of Si anode suppressed the interfacial reactions, ensuring the stable operation of the ASSB. These results also underscore the importance of adopting Si anode in sulfide-based ASSBs. The obtained results and the related discussion have been added in the revised manuscript and supporting information. (Page 6 in Revised Manuscript, Figure S6 in Supporting Information).

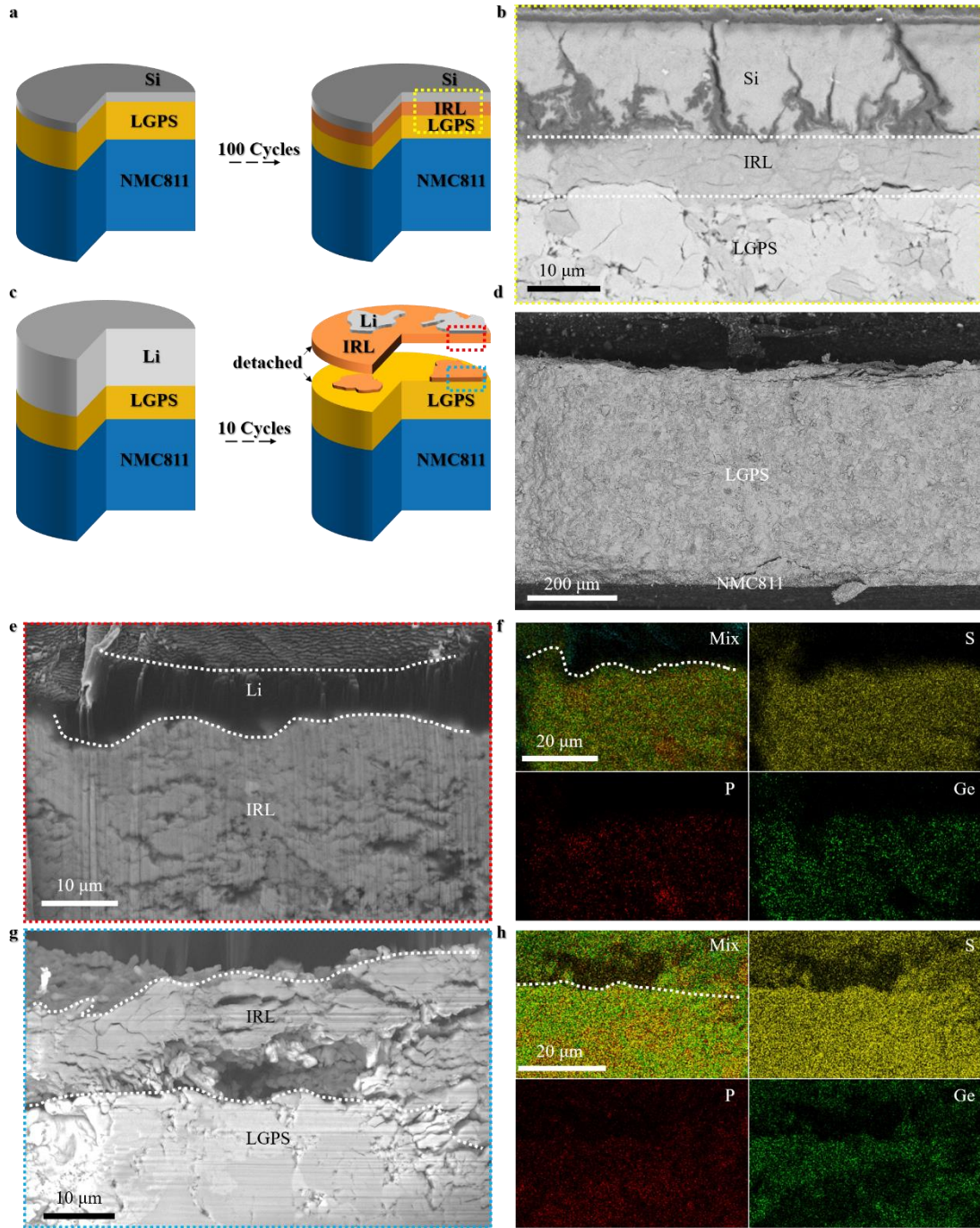


Figure R5. (a) Schematic diagram of the Si|LGPS|NMC811 cell before and after cycling. (b) CBS image of the Si/LGPS interface. (c) Schematic diagram of the Li|LGPS|NMC811 cell before and after cycling. (d) CBS image about the cross section of the entire cell. (e) CBS image of the Li/IRL interface. (f) EDS mapping the Li/IRL interface. (g) CBS image of the IRL/LGPS interface. (h) EDS mapping the IRL/LGPS interface.

4. There is a fundamental question regarding whether Li deposition actually occurred and whether the formation of different IRLs was indeed caused by the differences in reactivity between Li metal and the two electrolytes. Regarding the evidence of Li

deposition, (Line 186) “EDS mapping of the cracks indicates that the cracks are rich in oxygen, suggesting the growth of Li dendrite along these cracks, as the dendrites were oxidized during the sample transfer.” However, the author mentioned that all sample transfer steps are achieved in air-preventing conditions. Even if there was some extent of air exposure, Li cannot be oxidized during the transfer to FIB-SEM as it is buried inside the cell. In SEM-EDS mapping (Figure S5-S8), as the cross-section milling and EDS analysis are conducted in same equipment without transfer, there is no chance to the oxidation of Li metal. Therefore, the author should reconsider the origin of O. In addition, to see what reactions exactly happen on the anode, the author needs to check anode voltage profiles during charging in 3 electrode system. Given these critical issues, I do not recommend this work for publication in Nature Communications in its current form.

Response: We thank the reviewer for the great question! We acknowledge that the original interpretation of results is inaccurate and misleading. The electrochemical stability window of both LGPS and LSPSC is from ~1.71 V to ~2.14 V (Zhu et al., *J. Mater. Chem. A* 2016, 4, 3253-3266; Wang et al., *Matter* 2023, 6, 1096-1124; Wu et al., *Energy Environ. Sci.* 2018, 11, 1803-1810.). In principle, any anodes with an electrochemical potential less than 1.7 V can reduce LGPS and LSPSC and cause their decomposition. Indeed, it was reported that carbon (Tan et al., *Science* 2021, 373, 1494-1499.), Si (Huo et al., *Nat. Mater.* 2024, 23, 543), Li_xSi (Sakuma et al., *Solid State Ionics* 2016, 285, 101; Wang et al., *Chin. Phys. B* 2014, 33, 088201) and Li_xAl (Sakuma et al., *ibid.*) anodes, whose electrochemical potentials are all less than 1.7 V, can all cause the decomposition of the LSPSC SSE. In this context, our original interpretation of the interfacial reaction at the Si/LGPS and the Si/LSPSC interfaces as originating from the reaction between Li and LGPS or LSPSC, respectively, is incorrect. Instead, we believe that the Si/LGPS interfacial reaction was mainly caused by the electrochemical reaction of Li^+ coming from the cathode and e^- coming from the anode with the SSEs, and the reaction products are mainly needle-shaped Li_2S and LiGe in the Si/LGPS interface, which have definite crystallographic orientation relationship, as shown in Figure 3 in our manuscript. Because LiGe is an electronic conductor, the Li/LGPS interfacial reaction is sustainable, causing the formation of the thick IRL layers. In contrast, the interfacial reaction product of the Si/LSPSC interface is mainly Li_2S , which is an electronic insulator, rendering the interfacial reaction unsustainable due to the lack of electron supply to the reaction front. As a result, the IRL in the Si/LSPSC interface is self-limiting and thin.

Following the reviewer's instruction, we did attempt the three-electrode experiments following the procedure used in literature (Kasemchainan et al., *Nat. Mater.* 2019, 18, 1105-1111.), as shown in Figure R6a. During the 1st charging of the Si|LGPS|NMC811 cell using a lithium reference electrode (Figures R6b, c), a continuous voltage drop was observed in the Si anode, indicating gradual alloying of Si with Li. In the second cycle, there was a significant potential drop of the Si anode, suggesting severe degradation of the Si/LGPS and the Li/LGPS interfaces (Figure R6d). For comparison, the potential of the Si anode in the Si|LSPSC|NMC811 cell exhibited slower decline than the Si|LGPS|NMC811 cell, indicating better stability of the

Si/LSPSC interface (Figure R6e). These experiments suggest that the three-electrode measurement cannot clarify whether or not lithium deposition occurred in the interface. However, in our reply to the reviewer's questions #2 and #3, we have confirmed that there is no massive lithium deposition in the interfaces. (Page 8 in Revised Manuscript).

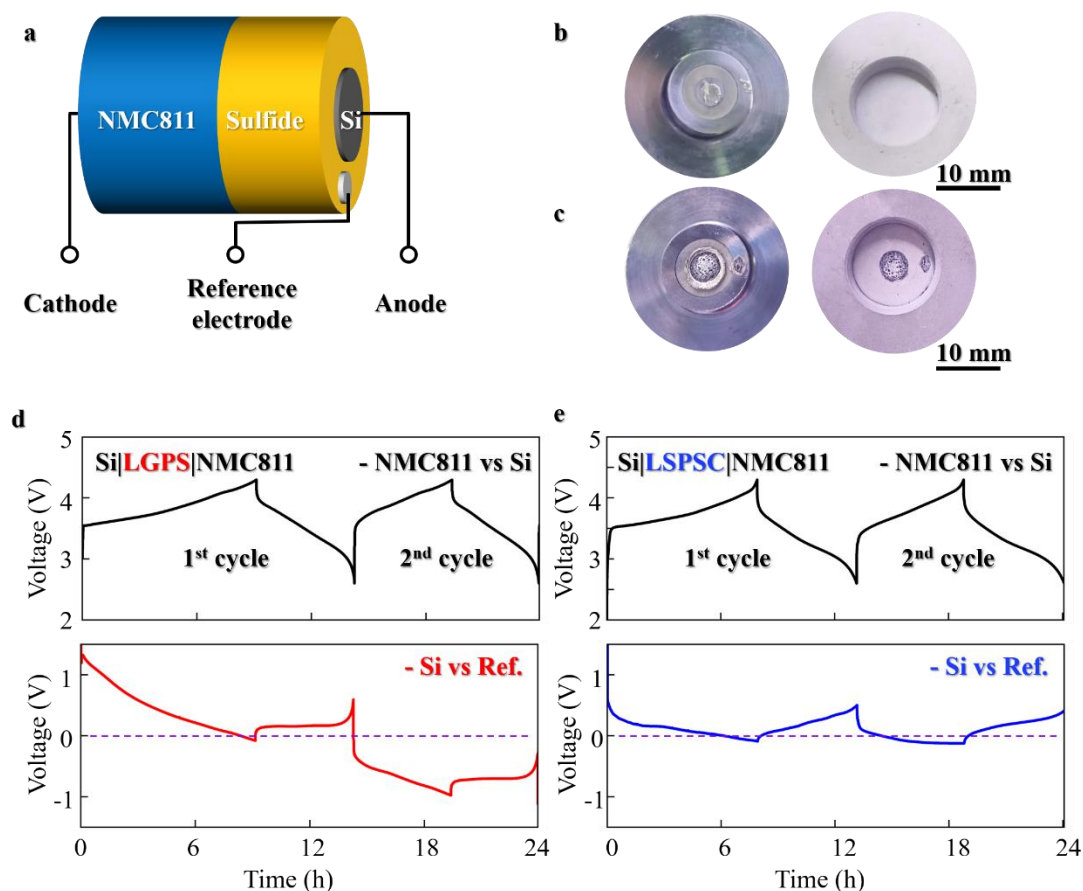


Figure R6. Three-electrode experiments of the Si|LGPS|NMC811 ASSB and the Si|LSPSC|NMC811 ASSB. (a) Schematic of the cell configuration for the three-electrode testing. (b, c) Optical images of the anode/electrolyte interface before and after cycling. (d) Voltage curves of the NMC811 vs Si anode, and the Si vs Reference electrode in the Si|LGPS|NMC811 cell. ("Ref." refers to the reference electrode.) (e) Voltage curve of the NMC811 vs Si anode, and the Si vs reference electrode in the Si|LSPSC|NMC811 cell.

Regarding the reviewer's question about the origin of O, we prepared the Li-Si/sulfide interface buried within the battery in the high vacuum chamber of the Cryo-FIB and characterized the O signal embedded in the internal interface cracks through CBS imaging and EDS mapping (Figure R7). Even under such nuanced sample preparation procedures, O was still detected in the Si anode, and the O element may originate from the oxidation of Li or Li_xSi from the residual gas inside the electron microscope chamber. Even though the sample chamber of the FIB-SEM is in high vacuum, trace O_2 still exists, which causes the oxidation of the dendrites or Li_xSi under the influence of the electron beam. The obtained results and the related discussion have

been added in the revised manuscript and supporting information. (Page 7 in Revised Manuscript, Figure S15 in Supporting Information).

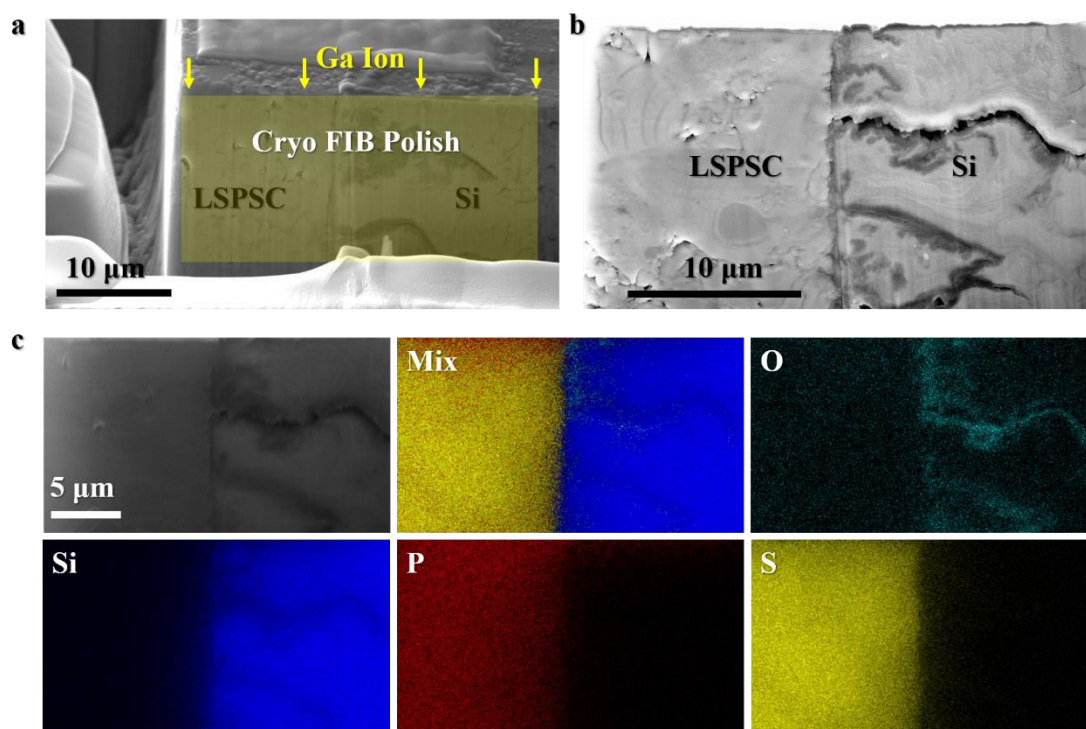


Figure R7. Cryo FIB-SEM characterization of interfaces buried within the battery. (a) Cryo-FIB processed cross-section of the interior of the Si|LSPSC|NMC811 ASSB. (b) CBS imaging of the Si/LSPSC interface. (c) EDS mapping of the Si/LSPSC interface.

Further comments the author should address and reinforce are listed below.

1. How can the author define IRLs in the LGPS and LSPSC systems as a pure ionic conductor and a mixed conductor, respectively? To support these classifications, the author should provide quantitative measurements of ionic conductivity and electronic conductivity for the IRLs.

Response: Thanks for the great question. To address the reviewer's question, we synthesized model SSEs with composition similar to the IRLs and measured their ion/electron transport properties. More specifically, we prepared Li_3P by mixing Li and P in a stoichiometric ratio at 400 °C, and $\text{Li}_{15}\text{Ge}_4$ by mixing Li and Ge in a stoichiometric ratio at 450 °C. Subsequently, we individually ball-milled Li_2S , LiCl , as well as the prepared Li_3P and $\text{Li}_{15}\text{Ge}_7$ at a speed of 500 rpm for 6 hours. Finally, we mixed Li_2S , Li_3P , and $\text{Li}_{15}\text{Ge}_4$ in a stoichiometric ratio of the decomposition products of LGPS (48:8:1), as well as Li_2S , Li_3P , and LiCl in the stoichiometric ratio of the decomposition products of LSPSC (67:10:18) at a speed of 200 rpm for 2 hours to achieve uniformity. Ultimately, we pressed 100 mg of the mixed powders into discs at 720 MPa for testing the electronic and ionic conductivity.

The model IRL in the Si/LGPS interface exhibits an ionic conductivity of 4.08×10^{-6} mS/cm and an electronic conductivity of 1.17×10^{-5} mS/cm (Figures R8a and R8b). The ionic conductivity of the model IRL of the Si/LSPSC interface was measured to be 1.12×10^{-6} mS/cm, with an electronic conductivity of 1.98×10^{-8} mS/cm (Figures R8c and R8d). Apparently the ionic and electronic conductivities of the model IRL for Si/LGPS are of the same order of magnitude, while that for the model IRL of Si/LSPSC differ by two orders of magnitude. Therefore, we define the IRL in the Si/LGPS as a mixed conductor and the IRL of Si/LSPSC as a pure ionic conductor. The obtained results and the related discussion have been added in the revised manuscript and supporting information. (Page 7 in Revised Manuscript, Figure S17 in Supporting Information).

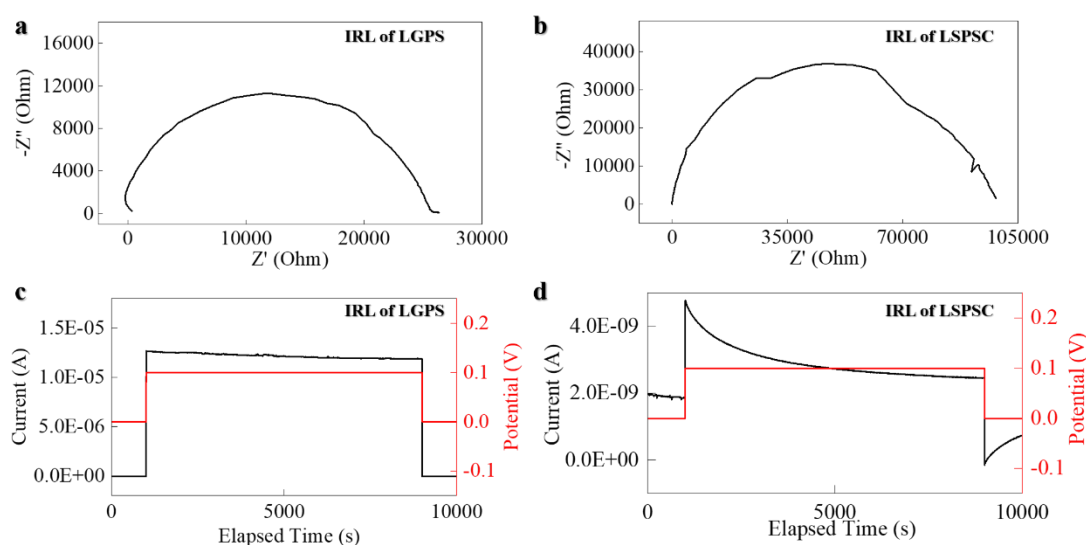


Figure R8. Testing of the ionic conductivity and electronic conductivity of the IRL. (a) The ionic conductivity testing of the IRL about the Si/LGPS interface. (b) The ionic conductivity testing of the IRL about the Si/LSPSC interface. (c) The electronic

conductivity testing of the IRL about the Si/LGPS interface. (d) The electronic conductivity testing of the IRL about the Si/LSPSC interface.

2. The description of interfacial layer as pure ionic conductor in Si/LGPS is inconsistent. (Line 191) “This suggests that the interphase layer of pure ionic conductor seems to impede the shuttle of Li dendrites at the interface.” (Line 263) “Due to the high electronic conductivity of Li-Ge alloy, the presence of Li-Ge confirming the electrical conductivity of the IRL in ASSBLGPS.”

Response: Thanks for pointing out this error. The description at Line 191 of the article is incorrect. The higher O signal at the Si/LSPSC interface than the Si/LGPS interface indicates that the IRL with pure ionic conduction in the Si/LSPSC interface hinders electron transfer between lithium metal and lithium-ion, resulting in more lithium dendrites remaining in the Si anode. The corrected discussion has been corrected in the revised manuscript. (Page 7 in Revised Manuscript).

3. Why are the bin intervals in the frequency distribution of crack length (Figure S9b, c) different? Also, one cannot agree they show the different dispersion of crack length.

Response: Thank the reviewer for the comments. The difference arises from the different number of cracks counted between the two samples, i.e. we counted 77 cracks in the Si/LGPS sample, and 107 cracks in the Si/LSPSC sample. To avoid the statistic error, we counted the same number of cracks from both samples, and the new results are show in Figure R9. From the graph, it can be observed that the crack lengths of the Si anode at the LGPS interface are unevenly distributed in the range of 6 to 15 micrometers, possibly caused by the inhomogeneous stress generated by nonuniform interfacial reactions which is originated from the thicker IRL with nonuniform thickness. In contrast, the distribution of crack lengths at the Si anode interface of LSPSC is relatively even, with a significant number of cracks ranging from 10 to 14 micrometers, accounting for approximately 67%. This is because the lithium flux along the interface is more homogeneous due to the thin and uniform IRL. The corrected results have been added and discussed in the revised manuscript. (Page 7 in Revised Manuscript, Figure S16 in Supporting Information).

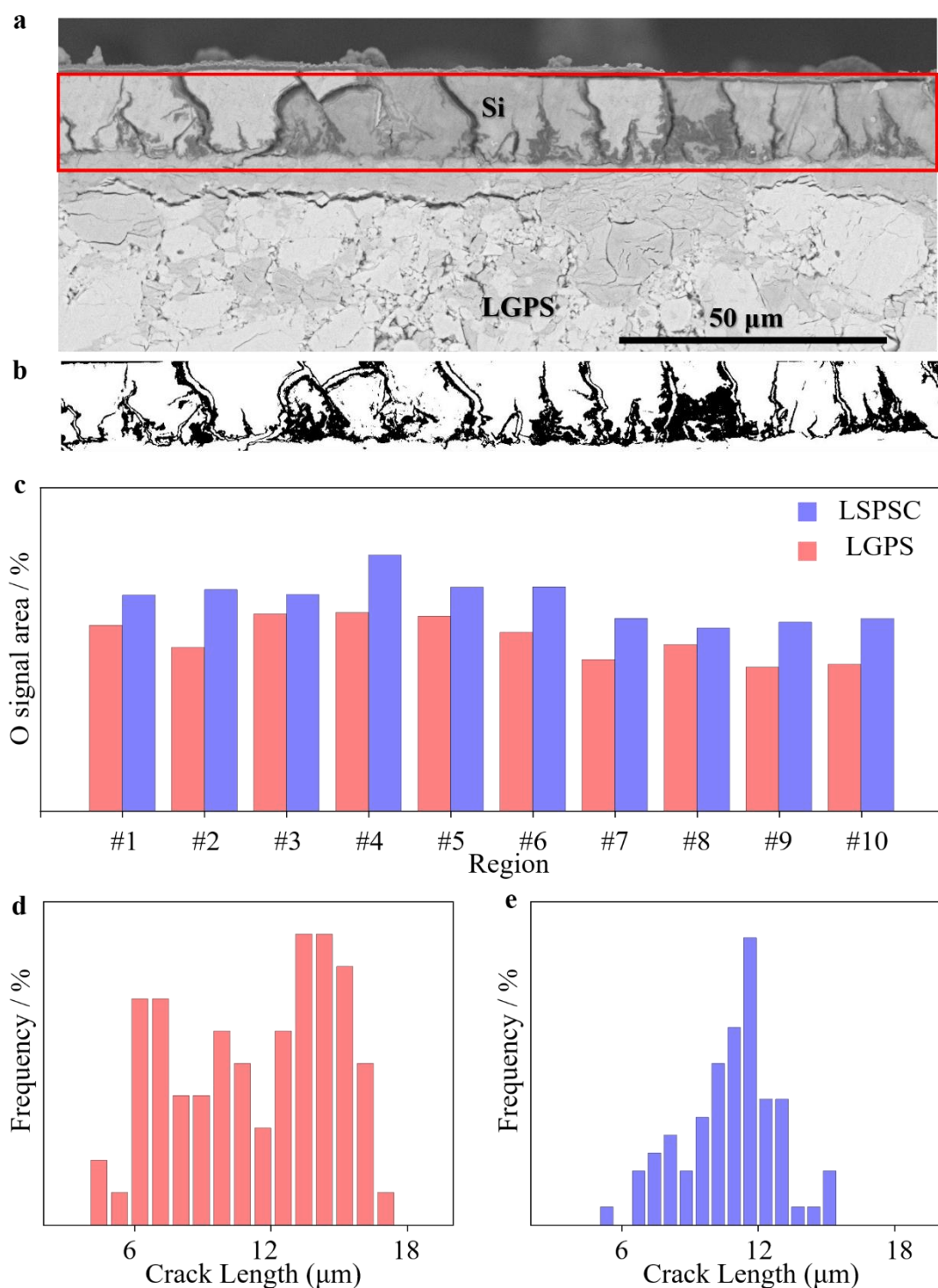


Figure R9. (a) SEM image of the Si/sulfide interface. (b) Using ImageJ to analyze the presence of oxygen and cracks in the anode. (c) Area distribution of the oxygen signal in the EDS mapping of the Si/sulfide interface. Frequency distribution of crack depth in (d) Si/LGPS and (e) Si/LSPSC.

4. The pristine state of Si/electrolytes should be also analyzed by HR-TEM and EDS.

Response: Thanks for the great suggestion. Following the reviewer's suggestion, we analyzed the pristine Si/sulfide interface using cryo-TEM and EDS (Figures R10- R13).

The TEM image shows clearly that the Si/LGPS interface is sharp with intimate contact, and no interface layer was found, indicating no interfacial reaction between Si and LGPS in the pristine sample (Figure R10a, b). EDS (Figure R10c, d), HRTEM (Figure R11a) and its corresponding Fast Fourier Transform (FFT) (Figures R11b, c, d) confirm that no interface reaction took place. The same is true for the Si/LSPSC interface, as verified by SEM (Figure R12a), TEM (Figure R12b), EDS (Figure R12c, d), HRTEM (Figure R13a) and its corresponding FFT (Figures R13b, c, d). As shown, the absence of an interfacial layer between the pristine Si and the sulfide electrolyte demonstrates the chemical stability between Si and the sulfide electrolyte, which is crucial for the stable operation of the Si anode in sulfide-based ASSBs. The obtained results and the related discussion have been added in the revised manuscript and supporting information. (Page 8, Page9, Page11 in Revised Manuscript, Figures S19, S25, S42, S47 in Supporting Information).

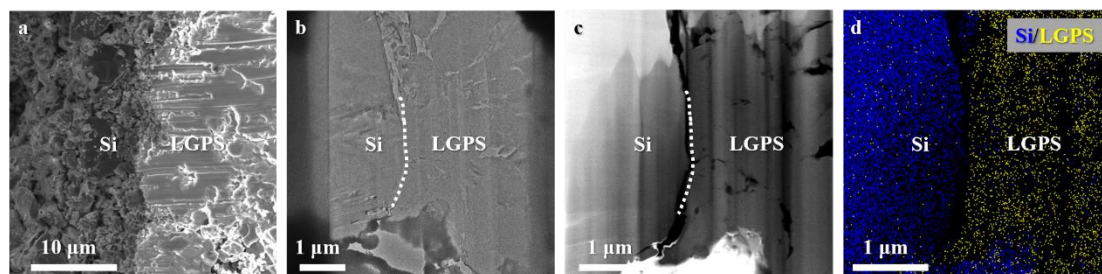


Figure R10. Characterization of the pristine Si/LGPS interface before electrochemical cycling. (a) A cryo-SEM imaging of the Si/LGPS pristine interface. (b) Bright-field image of the Cryo-FIB processed sample transferred to Cryo-TEM. (c) HAADF image corresponding to (b). (d) EDS mapping corresponding to (b) and (c).

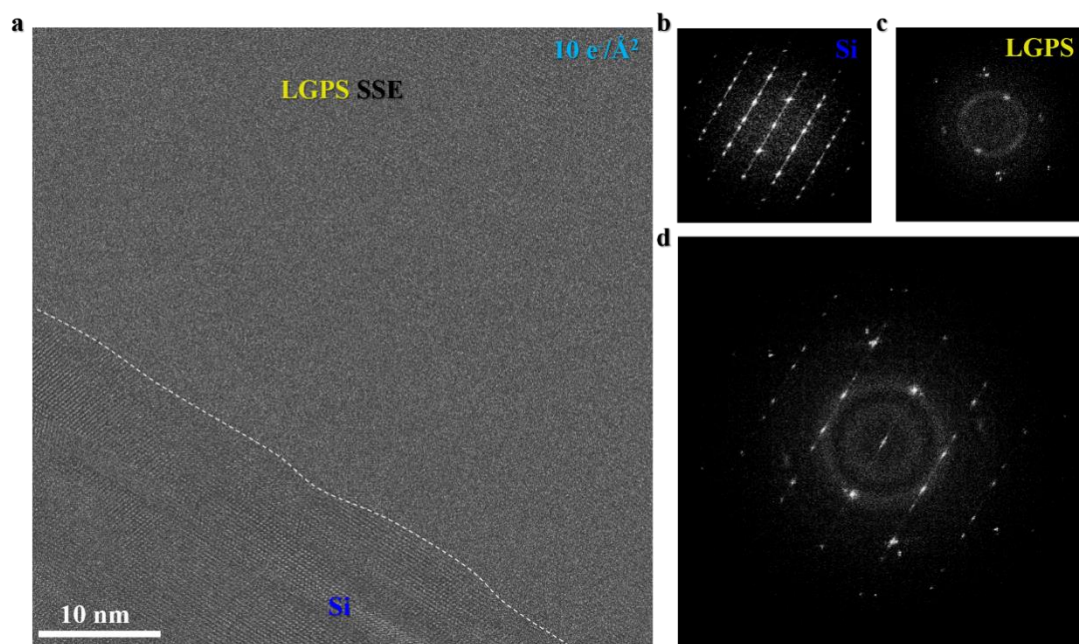


Figure R11. Cryo low-dose HRTEM imaging of the pristine Si/LGPS interface before electrochemical cycling. (a) HRTEM image. (b) FFT of the Si anode. (c) FFT of the LGPS electrolyte. (d) FFT of the entire Si/LGPS interface.

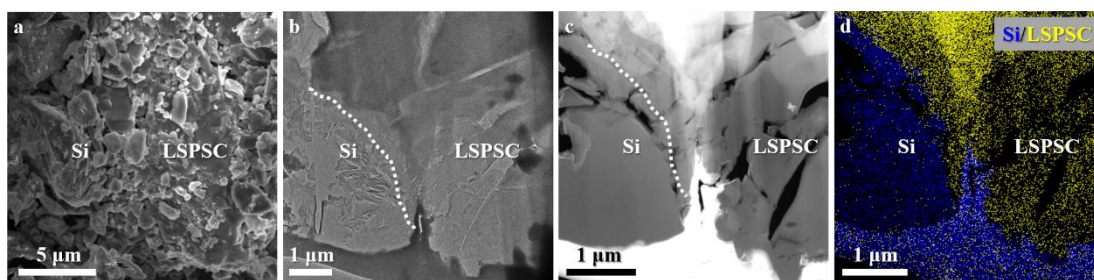


Figure R12. Characterization of the pristine Si/LSPSC interface before electrochemical cycling. (a) A cryo-SEM image of the Si/LSPSC original interface. (b) Bright-field image of the Cryo-FIB processed sample transferred to Cryo-TEM. (c) HAADF image corresponding to (b). (d) EDS mapping corresponding to (b) and (c).

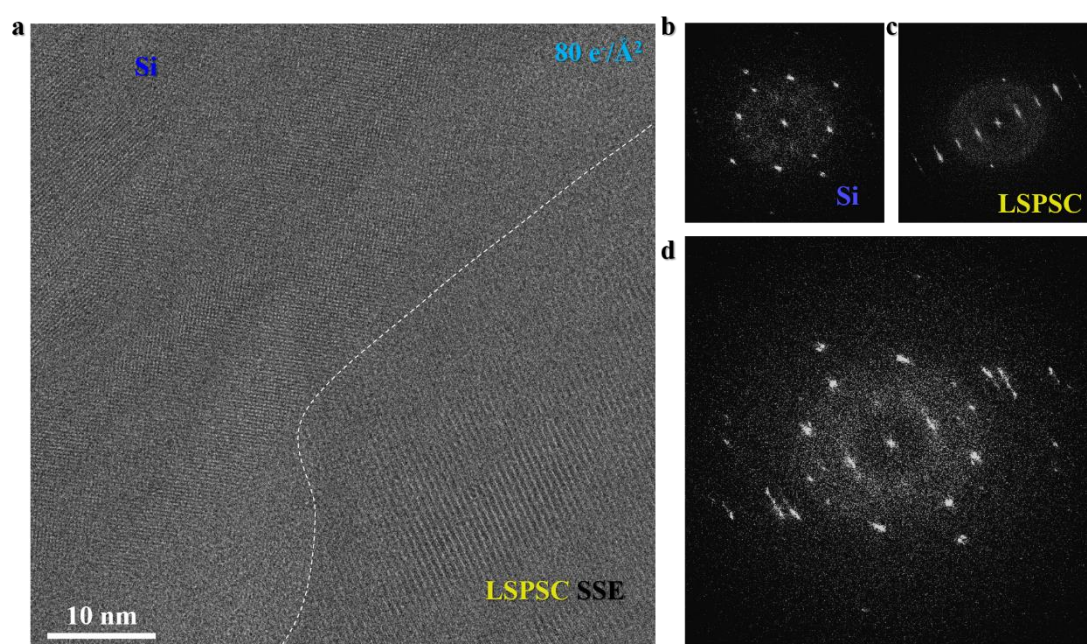


Figure R13. Cryo low-dose HRTEM imaging of the pristine Si/LSPSC interface before electrochemical cycling. (a) HRTEM image. (b) Fast Fourier Transform (FFT) of Si. (c) FFT of LSPSC. (d) FFT of the Si/LSPSC interface.

5. What is the dose-rate during low-dose HR-TEM imaging? How tolerant are the IRL and sulfide electrolytes against e-beam?

Response: The dose rate of low-dose HRTEM imaging is crucial for atomic-level characterization of the interfaces in ASSBs! We first cycled both the Si|LGPS|NMC811 and the Si|LSPSC|NMC811 cells for 100 cycles, then prepared interfaces containing IRL using Cryo-FIB (Figures R14 and R15). We then conducted electron beam damage tests on the LGPS, the LSPSC and the corresponding IRL under frozen conditions. We obtained dose rate appropriate for atomic resolution imaging of sulfide based ASSB and the anode/electrolyte interface at -170 °C. All photos were captured with an exposure time of 1 second. The obtained results and the related discussion have been added in the revised manuscript and supporting information. (Page 8, Page 11 in Revised Manuscript, Figures S20, S43 in Supporting Information).

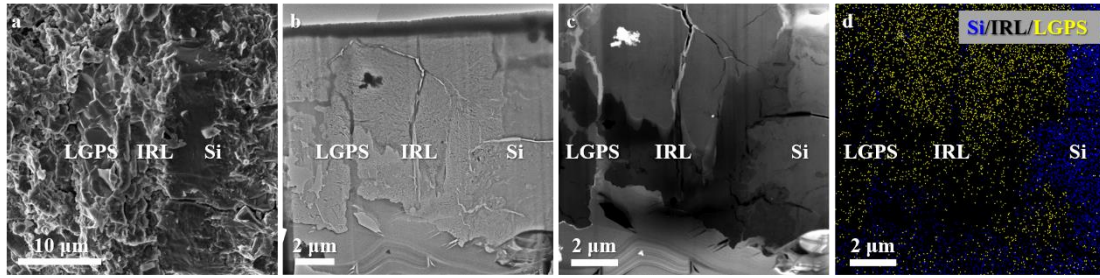


Figure R14. Characterization of the IRL about the Si/LGPS interface. (a) A cryo-SEM image. (b) Bright-field image of the Cryo-FIB processed sample transferred to Cryo-TEM. (c) HAADF image corresponding to (b). (d) EDS mapping corresponding to (b) and (c).

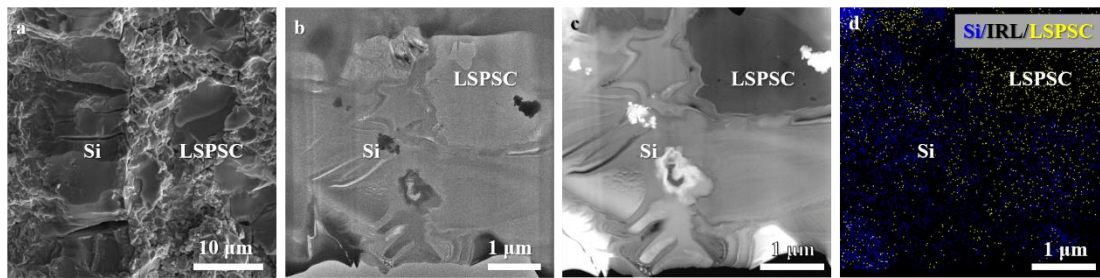


Figure R15. Characterization of the IRL about the Si/LSPSC interface. (a) A cryo-SEM image. (b) Bright-field image of the Cryo-FIB processed sample transferred to Cryo-TEM. (c) HAADF image corresponding to (b). (d) EDS mapping corresponding to (b) and (c).

When imaging the pristine samples at high resolution, we gradually increased the electron beam dose to determine the electron beam tolerance of LGPS and LSPSC. Through testing, we found that LGPS could be stably imaged at $16 \text{ e}^-/\text{\AA}^2$, with gradual amorphization took place with the increasing electron beam dose, and ultimately fully amorphization occurred at $177 \text{ e}^-/\text{\AA}^2$ (Figure R16). During the amorphization process, significant deformation of the LGPS particles was observed (Figure R17). Similarly, we found that LSPSC could be stably imaged at $100 \text{ e}^-/\text{\AA}^2$ and became amorphous at $300 \text{ e}^-/\text{\AA}^2$, with noticeable deformation after irradiation damage (Figure R18). The obtained results and the related discussion have been added in the revised manuscript and supporting information. (Page 8, Page 11 in Revised Manuscript, Figures S22, S23, S45 in Supporting Information).

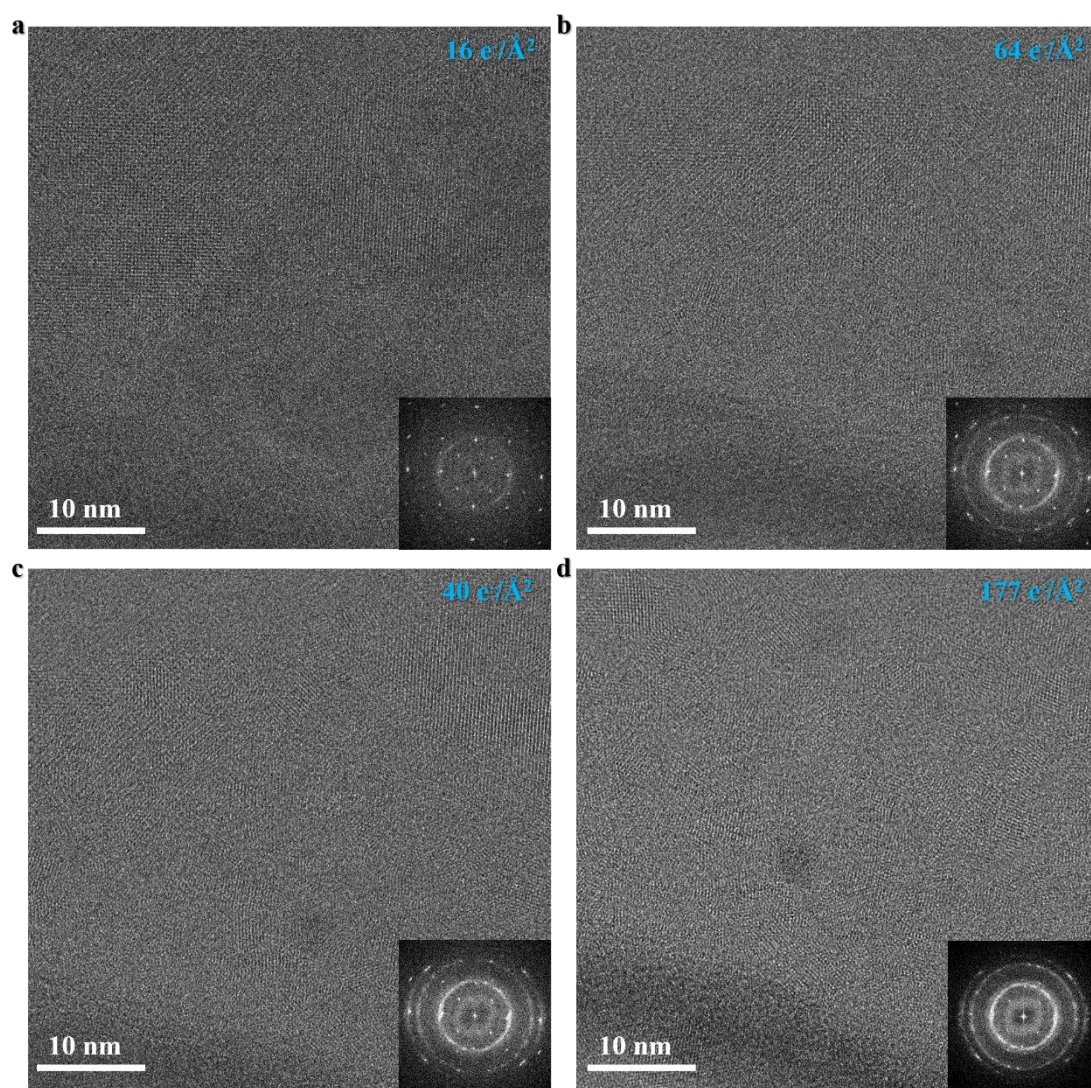


Figure R16. Dose damage test of the LGPS electrolyte. Cryo-HRTEM imaging and its corresponding FFT at: (a) $16 \text{ e}^-/\text{\AA}^2$; (b) $40 \text{ e}^-/\text{\AA}^2$; (c) $64 \text{ e}^-/\text{\AA}^2$. (d) $177 \text{ e}^-/\text{\AA}^2$.

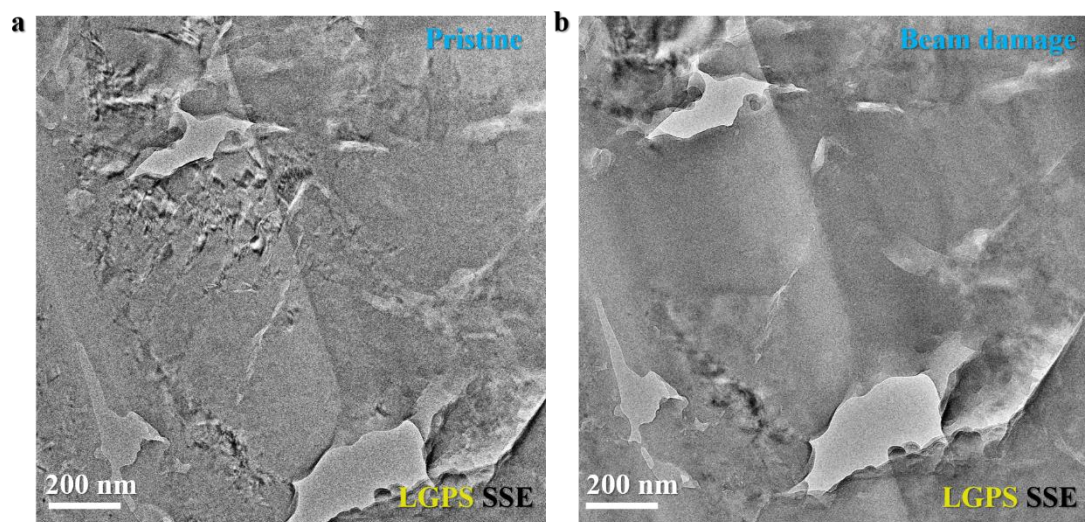


Figure R17. Dose damage test of the LGPS electrolyte. (a) The BF image of the pristine LGPS. (b) The BF image after electron beam irradiation damage.

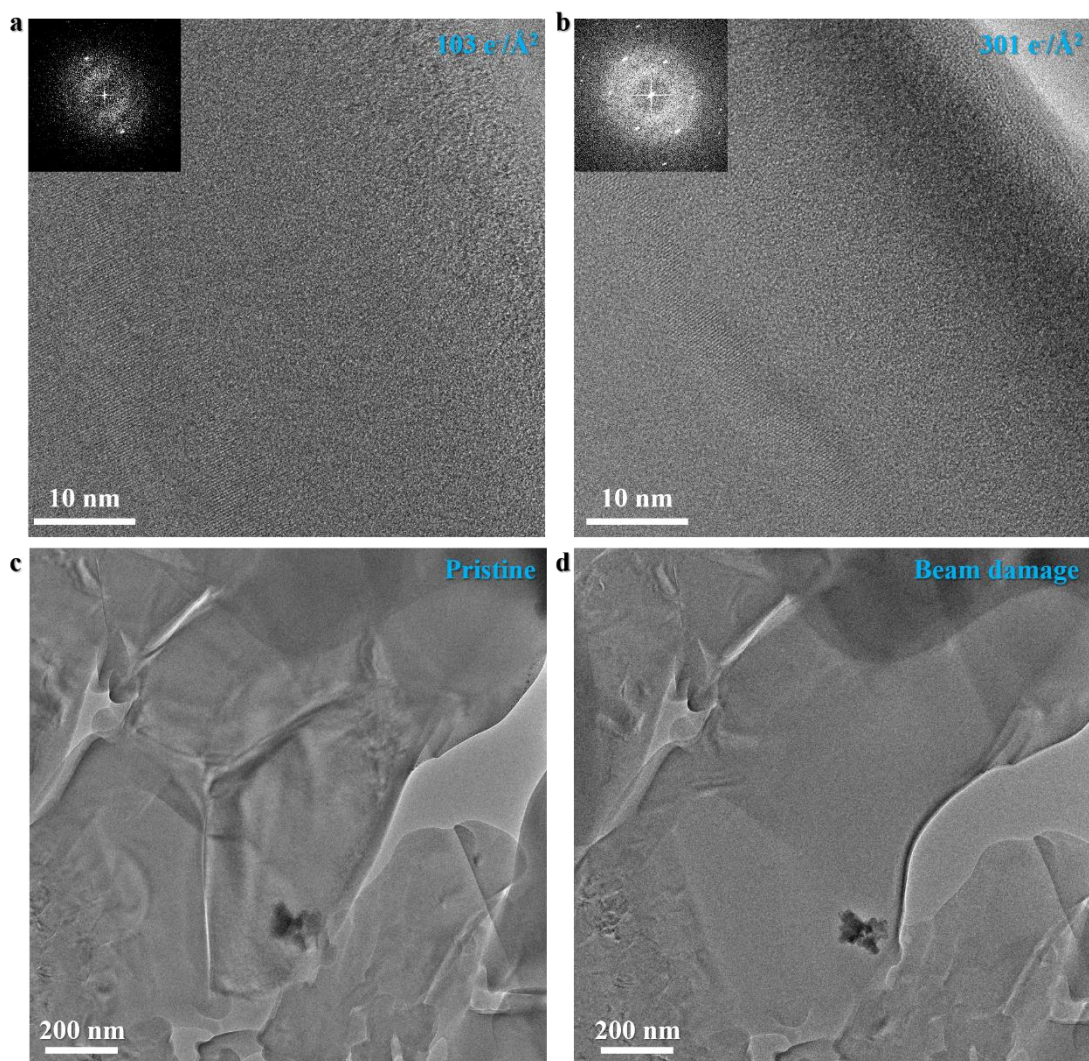


Figure R18. Dose damage test of the LSPSC electrolyte. (a) Cryo-HRTEM imaging and its corresponding FFT at 103 e-/Å². (b) Cryo-HRTEM imaging and its corresponding FFT at 301 e-/Å². (c) The pristine BF image of LSPSC. (d) The BF image of LSPSC after electron beam irradiation damage.

Subsequently, we conducted dose rate tests on samples containing IRL. The LGPS/IRL sample could be stably imaged at 20 e-/Å², with the gradual appearance of voids in LGPS as the electron beam dose being increased, while the IRL remained stable (Figure R19). Surprisingly, the LSPSC/IRL sample exhibited significantly higher electron beam tolerance. At 1100 e-/Å², LSPSC fully amorphized, while the IRL remained stable (Figure R20). The safe dose rate for imaging LSPSC was about 80 e-/Å², and that for LGPS was about 15 e-/Å². While damage of the LGPS-IRL occurred at an electron beam dose of 150 e-/Å², and the LSPSC-IRL remained stable at 1000 e-/Å². The differences in electron beam tolerance between LGPS and LSPSC are interesting and the reason for such difference requires further investigation. Li₂S, as the main component of IRL, exhibits strong electron beam tolerance, which may be related to the structure and bonding of the electrolyte. The obtained results and the related

discussion have been added in the revised manuscript and supporting information. (Page 8, Page 11 in Revised Manuscript, Figures S24, S46 in Supporting Information).

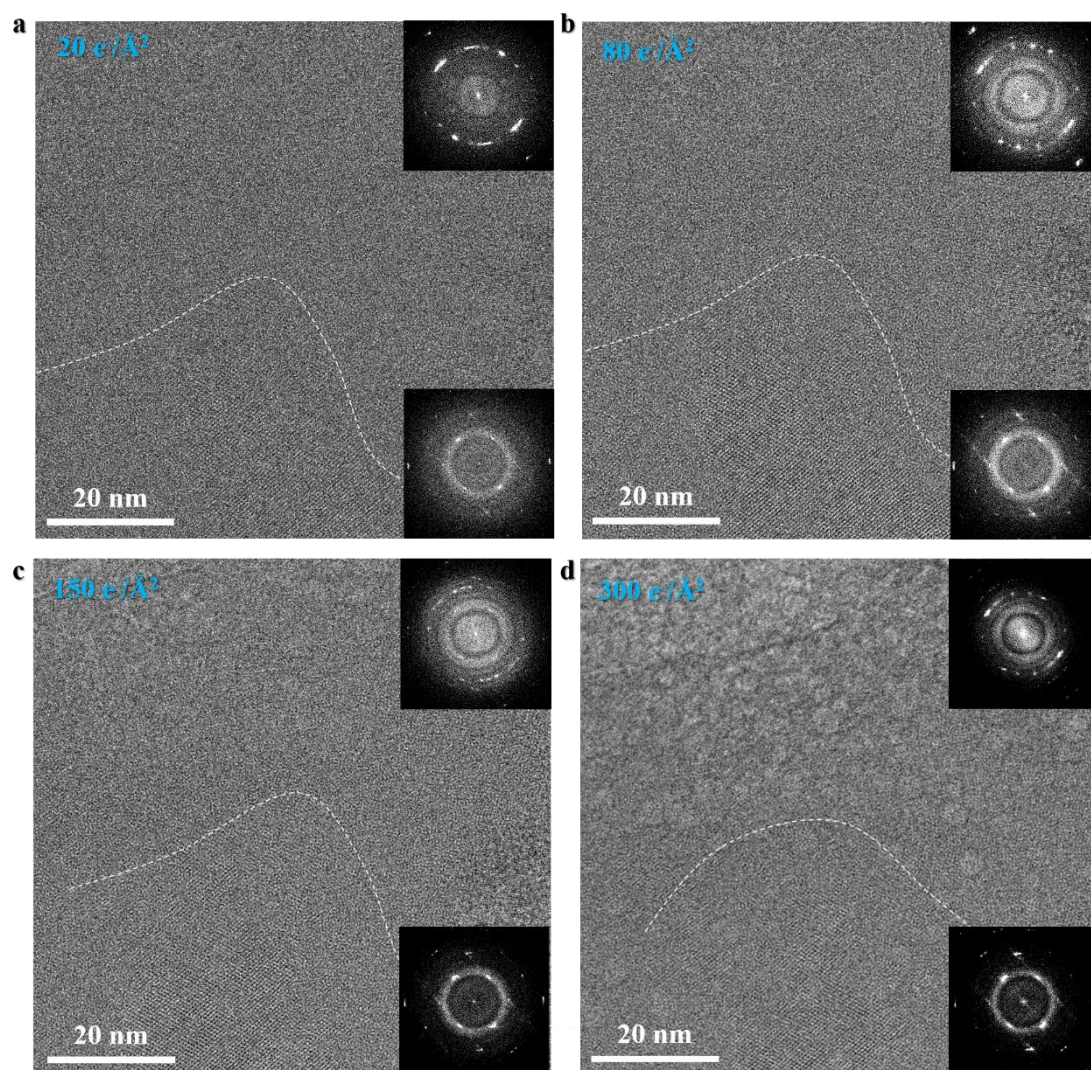


Figure R19. Dose damage test of the IRL of the Si/LGPS interface. Cryo-HRTEM imaging and its corresponding FFT at: (a) 20 $\text{e}^-/\text{\AA}^2$; (b) 80 $\text{e}^-/\text{\AA}^2$; (c) 150 $\text{e}^-/\text{\AA}^2$; (d) 300 $\text{e}^-/\text{\AA}^2$.

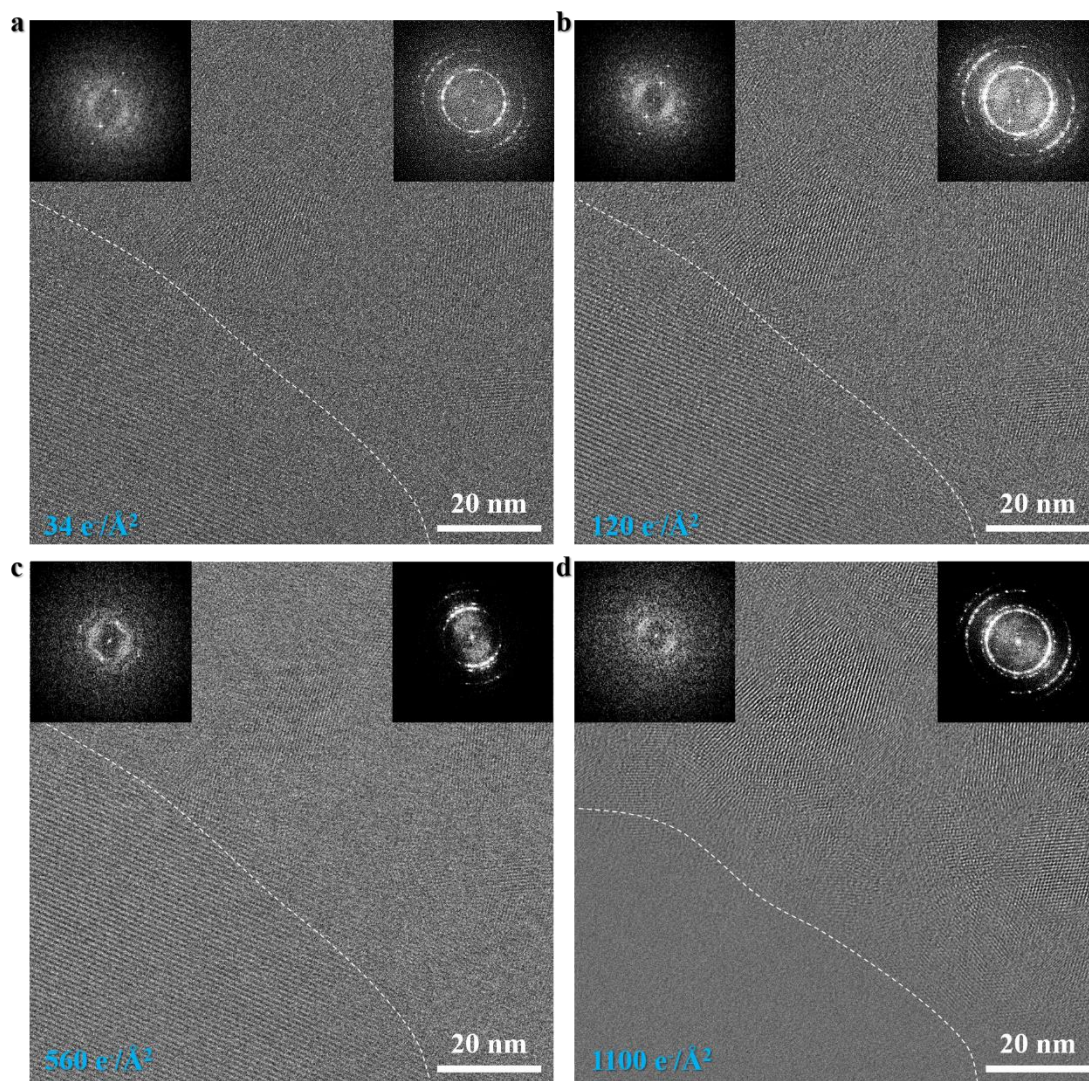


Figure R20. Dose damage test of the IRL of the Si/LSPSC interface. Cryo-HRTEM imaging and its corresponding FFT at: (a) 34 e-/Å²; (b) 120 e-/Å²; (c) 560 e-/Å²; (d) 1100 e-/Å².

6. The author can conduct XRD analysis to support the decomposition of electrolytes and the degradation of Si anode.

Response: Thanks for the reviewer's suggestion. Macroscopic characterization using XRD is crucial for the comprehensive understanding of sulfide/anode interfaces. To address this, we assembled Si|sulfide|NMC811 ASSBs and conducted XRD analysis before and after cycling at the anode/electrolyte interface.

After 100 cycles, a significant amount of Li_2S appeared in the Si/LGPS interface, while the peak intensity of Si decreased significantly (Figure R21). In the meantime, XRD analysis reveals a higher degree of amorphization of the Si adjacent to LGPS after 100 cycles. This indicates that more amorphization of the Si anode occurred at the Si/LGPS interface with more pronounced interface deterioration.

In contrast, the Si/LSPSC interface shows a very weak peak of Li_2S after 100 cycles. These results indicate that the Si/LGPS interface experienced substantial electrolyte decomposition and the Si anode decayed after cycling, while the Si/LSPSC interface exhibited relatively minor degradation after cycling. The obtained results and the related discussion have been added in the revised manuscript and supporting information. (Page 6 in Revised Manuscript, Figure S2 in Supporting Information).

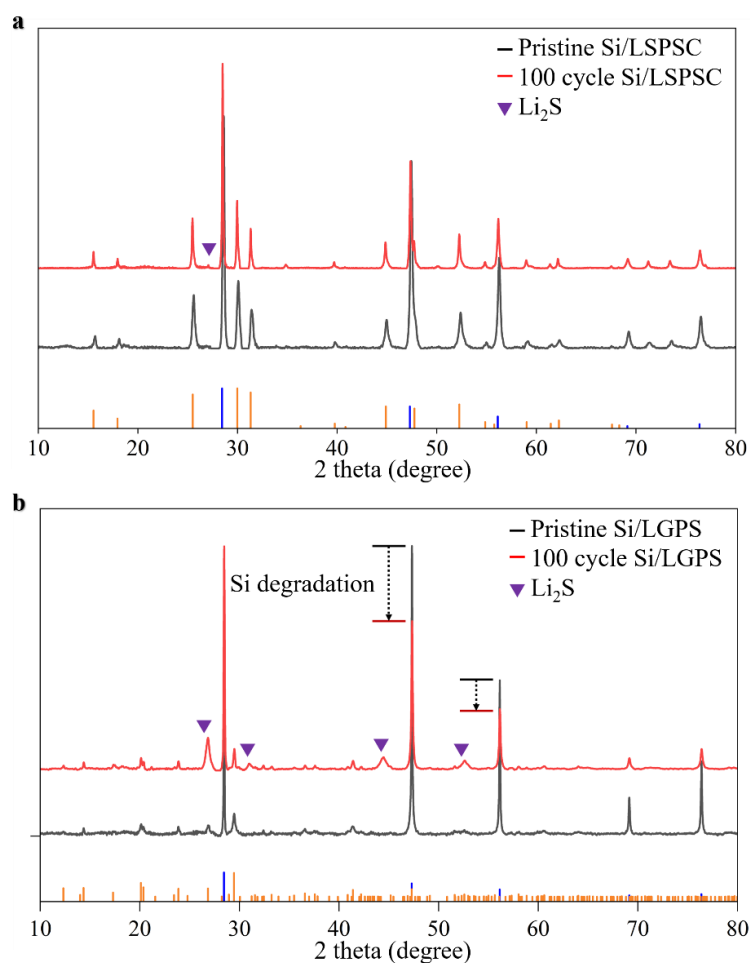


Figure R21. XRD characterization of the Si/electrolyte interface before and after cycling. (a) XRD of the Si/LSPSC interface before and after cycling. (b) XRD of the Si/LGPS interface before and after cycling.

7. (Line 267) “The weak crystallinity of Si and the gradient distribution of crystallinity and grain size of Li_2S in the IRL indicate that the Si/LGPS interface deterioration occurred during the battery cycling.” How can the crystallinity and grain size of Si or Li_2S be related to the interface deterioration? The author should provide a detailed description of the relationship.

Response: Thanks for the question. The size distribution of Li_2S particles at the Si/LGPS IRL interface is indeed an intriguing discovery. In the IRL, Li_2S particles closer to the electrolyte layer exhibit larger sizes, while those closer to the Si anode side are smaller. This indicates that during the interface growth process, decomposition of the electrolyte leads to the formation of larger Li_2S particles, which gradually evolve into smaller ones through continuous electrochemical cycling.

Therefore, small-sized Li_2S represents the later-formed Li_2S , while large-sized Li_2S signifies newly generated Li_2S . The spatial distribution of Li_2S particle sizes to some extent reflects the aging of the IRL over time as electrochemical processes progress. The related discussion has been added in the revised manuscript. (Page 10 in Revised Manuscript, Figures S28, S31 in Supporting Information).

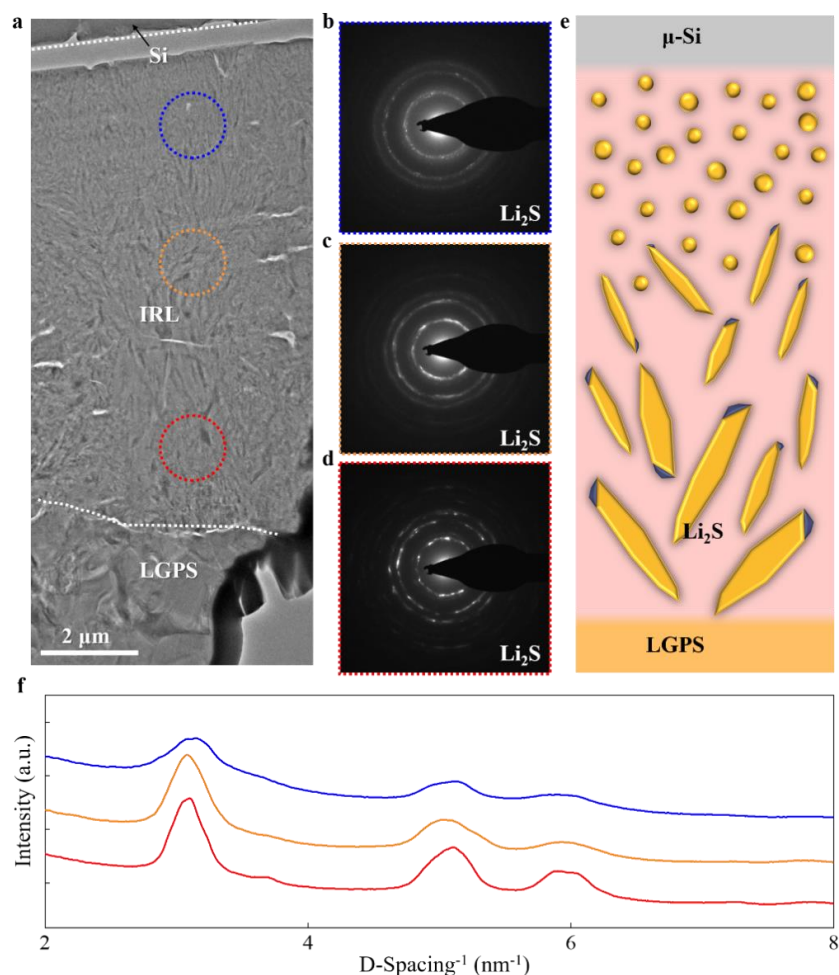


Figure R22. (a) Bright field image of the Si/LGPS interface. (b-d) EDP evolution of the interphase. (e) Schematic of the Li_2S shape and distribution. (f) Diffraction integral diagram about the IRL of the Si/LGPS interface.

8. Can the author provide LUMO energies of LGPS and LSPSC which determine the stability of electrolytes?

Response: Thank you for the question. The electrochemical stability window of LGPS ranges from 1.71 to 2.14V, while the electrochemical stability window of $\text{Li}_6\text{PS}_5\text{Cl}$, a structure similar to LSPSC, ranges from 1.71 to 2.01V (Zhu *et al.*, *J. Mater. Chem. A* 2016, 4, 3253-3266; Wang *et al.*, *Matter* 2023, 6, 1096-1124; Wu *et al.*, *Energy Environ. Sci.* 2018, 11, 1803-1810.). Based on the HOMO-LUMO energy levels, the Li-Si/sulfide electrolyte interfaces are thermodynamically unstable, however, the in-situ formed SEI product extends a wider electrochemical stability window. For example, the electrochemical stability windows of Li_2S , Li_3P and LiCl range from 0 to 2.1V, from 0 to 0.9 V, and from 0 to 4.2 V, respectively. These IRL product provides a kinetic stability at low potentials for the Li-Si/sulfide electrolyte. (Peljo *et al.*, *Energy Environ. Sci.* 2018, 11, 2306-2309; Richards *et al.*, *Chem. Mater.* 2016, 28, 266-273; Zhu *et al.*, *ACS. Appl. Mater. Inter.* 2015, 7, 23685-23693.), which is similar to our results. The Li-Si/LSPSC interface shows higher stability than the Li-Si/LGPS interface. (Page 8 in Revised Manuscript).

9. Why are the crystallinity of Si anodes in LGPS and LSPSC electrolytes different? Does it mean that they undergo different lithiation mechanism?

Response: Thanks for the great question. The difference in the crystallinity of Si anode is ascribed to the different lithiation degree. Previous in-situ TEM results demonstrate that the crystallinity of the Si anode is related to the degree of lithiation of Si (Liu *et al.*, *Nat. Nanotechnol.* 2012, 7, 749-756.). Moreover, the thicker IRL in the Si/LGPS interface impedes the extraction of lithium-ion from the Si anode, resulting in incomplete delithiation of the Si anode at 2.6 V. Therefore, compared to the Si anode in the Si/LSPSC interface, there is a certain degree of amorphization about Si anode in the Si/LGPS interface. The related discussion has been added in the revised manuscript. (Page 10 in Revised Manuscript).

10. The author should provide the preparation procedure of the $\mu\text{-Si}$ anode and full-cell of solid-state batteries, as well as exact specifications of the cell (areal capacity, dimensions, etc.)

Response: In our assembly process, we first pre-pressed 100 mg of the electrolyte particles into 10 mm discs under 120 MPa pressure. Subsequently, we uniformly prepared 2 mg of micrometer-sized Si anode particles onto the electrolyte disc with 240 MPa, and finally pressed 20 mg of mixed cathode on the other side using 720 MPa pressure, resulting in an area load of 17.8 mg/cm². This description is incorporated into the revised manuscript or supporting information. The related discussion has been added in the revised manuscript. (Page 15 in Revised Manuscript, Figure S63 in Supporting Information).

11. The author should provide the experimental procedures for XPS analysis.

Response: The experimental procedure for XPS involved disassembling the solid-state battery inside a glovebox to expose the interface layer between the Si anode and the electrolyte. Subsequently, the sample was transferred to the XPS for testing under inert

gas protection to avoid the effect of air. After electrochemical cycling, clear peaks of Li_2S were observed in the interfaces of LSPSC and LGPS through fitting, similar results were obtained for Li-Ge and Li_3P (Figure 2 and Figure 4 in our manuscript). The related discussion has been added in the revised manuscript. (Page 8 in Revised Manuscript).

Reviewer #2 (Remarks to the Author):

The manuscript entitled " Revealing the Interfacial Failure Mechanism of the Silicon Anode Based All-Solid-State Batteries (ASSBs) via Atomic-Scale Cryo-Electron Microscopy " by Yao et al. conducted atomic-level research on the Si/SSE interface of sulfide-based ASSB by cryo-genic technology. It is interesting that the Si/LSPSC interface comprising nanocrystalline Li_2S , exhibits dense and stable behavior within the ASSB. In contrast, the thickness of the Si/LGPS interface composed of needle-like Li_2S increased by 50 times. The study also demonstrates that the thick interface layer of LGPS-based ASSBs originated from interface reactions does not lead to dramatic increase of interface impedance, which challenges traditional notion that interfacial impedance is the culprit of ASSB failure. Therefore, I suggest that the paper should be published after the authors have addressed the following issues.

Response: We are very grateful to the referee for his/her overall positive comments on our work! All the referee's concerns are addressed in our revised manuscript, and a point-to-point response is listed in the following.

1. Regarding the repeated mention of lithium loss in the article, are there any other evidences of lithium-ion loss in the silicon anode besides lithium deposition and the interface reaction between the anode and the electrolyte?

Response: We thank the referee for the great question! In liquid-based silicon anode batteries, the cracking and growth of the solid electrolyte interface (SEI) are important mechanisms leading to the failure of the Si anode. The surface state of the Si anode is closely related to the growth of the SEI. Therefore, we characterized the original Si anode particles using STEM-EELS and STEM-EDS mapping and found an uneven amorphous Si oxide layer of 3-5 nm on the surface (Figure R23). To study the changes in these oxide layers, we cycled the Si anode in a Si|LGPS|NMC811 cell for 30 cycles. Through STEM-EELS mapping, we observed an interface layer of 20-50 nm between Si particles. EELS analysis indicates that this interface layer is related to Li-Si-O (Figure R24). This suggests that besides lithium deposition and interface reactions in the Si anode, part of the irreversible capacity loss is attributed to the irreversible lithiation of the oxide layer on the Si anode surface. Furthermore, the 1st cycle Coulombic efficiency of Si is usually around 70% in ASSB, suggesting besides the formation of SEI, a significant amount of lithium-ion is trapped in silicon, making the full retraction of the lithium-ion virtually impossible. The obtained results and the related discussion have been added in the revised manuscript and supporting information. (Page 13 in Revised Manuscript, Figures S61, S62 in Supporting Information).

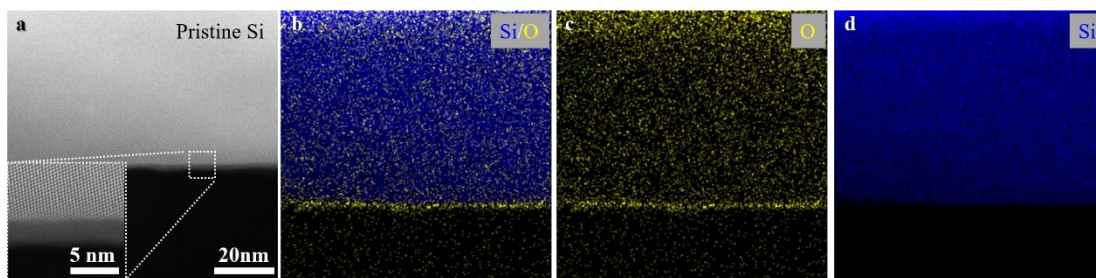


Figure R23. Atomic-level characterization of the oxide layer on the surface of the Si anode. (a) STEM-HAADF imaging. (b) Si/O overlaid EDS mapping. (c) O EDS mapping. (d) Si EDS mapping.

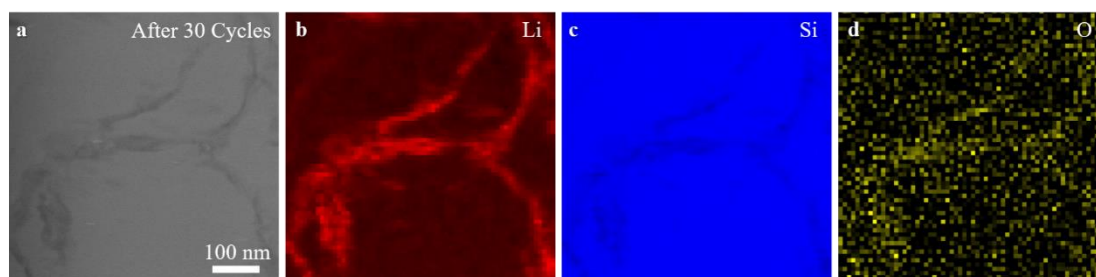


Figure R24. The μ -Si anode of the Si|LGPS|NMC811 ASSB after 30 cycles and its elemental distribution. (a) Cryo-STEM ADF imaging. (b) Li EELS mapping. (c) Si EELS mapping. (d) O EELS mapping.

2. The article mentions the uneven distribution of Li_2S in the Si/LGPS interface layer (Figure S13). How can we explain the interface deterioration that occurs during the cycling process of solid-state batteries?

Response: We thank the referee for the great question! Firstly, after 100 cycles, the interface layer of the Si/LGPS interface contains a larger-sized Li_2S with an average particle size of 150 nm near LGPS, while Li_2S near the Si anode is in nanoscale with a mean particle size of 30 nm. In contrast, the Li_2S particles are larger than 30 nm near the Si anode (Figure R25) after 30 cycles, which differs from the results after 100 cycles, indicating that Li_2S in the interface layer gradually refined during continuous electrochemical cycling. Therefore, the uneven distribution of Li_2S in the IRL originates from the electrolyte fatigue induced by electrochemical cycling. The smaller the Li_2S particles, the more the grain boundaries, and the presence of more grain boundaries may impede the transport of lithium-ion within the interface layer. The obtained results and the related discussion have been added in the revised manuscript and supporting information. (Page 10 in Revised Manuscript, Figure S31 in Supporting Information).

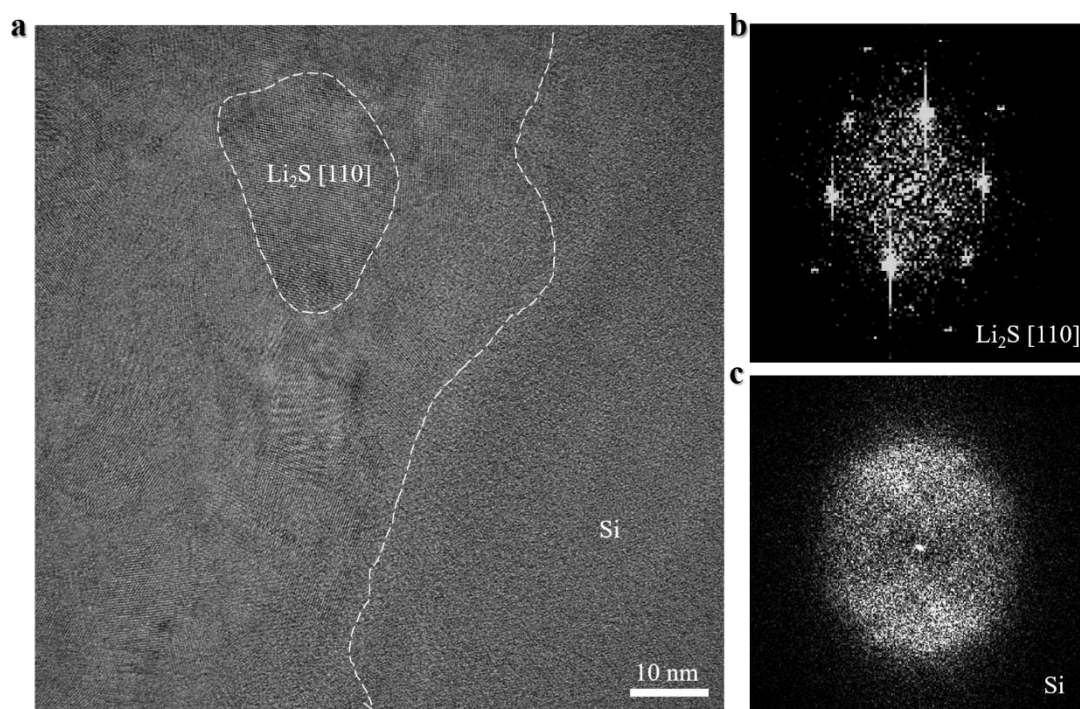


Figure R25. Cryo-HRTEM revealing the Si/LGPS interface of the Si|LGPS|NMC811 ASSB after 30 cycles. (a) Cryo-HRTEM image of the IRL in the Si/LGPS interface. (b) FFT of Li_2S in the IRL. (c) FFT of Si at the interface.

3. Sulfide electrolytes are highly sensitive to air and electron beams. How can the authors ensure that the samples are not affected during the sample preparation process?

Response: Thanks for the great question. In order to preserve the pristine interface of an ASSB, we have developed a nuanced cryogenic sample preparation and transfer protocol. By conducting FIB sample sectioning at -170°C , we minimized the ion beam damage to the sample and prevented the sample from reacting with the residual gas inside the FIB chamber. The cryo-sectioned sample was then transported to a cryo-TEM sample holder using a dedicated cryo-transfer device, during which the sample was emersed in liquid nitrogen throughout the transfer process, thus ensuring that the FIB lamella was not affected by air exposure. Finally, the TEM observations were conducted at -170°C , which minimized the impact of the electron beam damage on the sample to the greatest extent possible (Figure R26). The related discussion has been added in the revised manuscript. (Page 6 in Revised Manuscript, Figure S8 in Supporting Information).

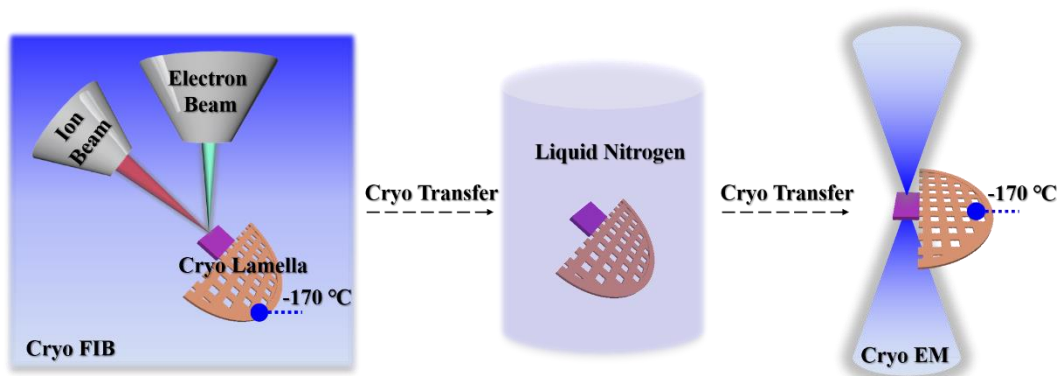


Figure R26. Preparation, transfer, and characterization processes of the sulfide-based ASSB interfaces.

4. Why do both interfaces have Li_2S as the main component, but the interface in Si/LSPSC tends to be stable? In other words, how do Li_3P and Li-Ge in Si/LGPS affect the evolution of the interface?

Response: Thanks for the great question. Although the main component in both interphase is Li_2S , the thickness of the interface layer in the Si/LGPS is 50 times greater than that in the Si/LSPSC. From a microscopic perspective, during the electrochemical decomposition of LGPS, Li_3P and Li-Ge nanocrystals are continuously generated. Both Li_3P and Li-Ge have higher electronic conductivity than Li_2S . Therefore, as electron transport pathways, the dispersed Li_3P and Li-Ge nanocrystals enable electrons to transfer to the reaction front of the LGPS, thereby promoting the continuous decomposition of LGPS. And we conducted tests of model IRL of LSPSC and LGPS, demonstrating that the IRL of LGPS exhibits high electronic conductivity, which renders the interfacial reaction sustainable and causes continuous consumption of Li ions, in turn thicker IRL (Figure R8). The related discussion has been added in the revised manuscript. (Page 7 in Revised Manuscript, Figure S17 in Supporting Information).

5. Compared to the Si/LSPSC interface (Figure 5a), why are there significant cracks at the Si/LGPS interface (Figure 3a)? Could this be related to the sample preparation process?

Response: Thanks for the great question! Yes, the delamination at the Si/LGPS interface could be related the sample preparation process. The Si/LGPS interface is a solid-solid contact, and during the disassemble of the ASSB, separation between the anode the electrolyte occurs frequently. Another reason for the more cracks in the Si/LGPS interface may be related to the large stress generated by the lithiation/delithiation of Si and the reaction between lithium-ion and LGPS electrolyte. Our previous in-situ experiments indicate that LGPS particles undergo significant deformation during lithium-ion electrochemical insertion, which generates large stress in the interface and in turn more cracks (Zhao *et al.*, *Nano Lett.* 2021, 22, 411-418.). Furthermore, the Si/LGPS IRL is much thicker than the Si/LSPSC IRL, indicating sever interfacial reaction in the former. In contrast, the Si/LSPSC interface is stable and the IRL is very

thin, which generates less stress in the interface, thus fewer cracks. The related discussion has been added in the revised manuscript. (Page 6 in Revised Manuscript, Figure S6 in Supporting Information).

Reviewer #3 (Remarks to the Author):

In this manuscript, the authors provide a comprehensive understanding of the solid/electrolyte interface (SEI) structure and chemical components in silicon (Si)-based all-solid-state batteries, using cryo-TEM as a tool. The novel contribution of the study lies in the detailed analysis of the SEI in this system. However, the understanding of the failure mechanism kind of lacks novelty and significance for a publication in Nature Communications. The authors pointed out that the failure mechanism is mainly due to Li inventory loss caused by the unwanted SEI formation, a well-known issue in the battery field. Similarly, the side reaction between the deposited Li and the solid electrolyte at the grain boundaries is another established.

Response: We thank the referee for pointing out the novelty of our manuscript! Indeed, atomic scale characterization of interfaces in sulfide electrolyte based ASSBs are extremely challenging due to the air and beam sensitivity of the sulfide electrolyte. Nevertheless, there is an urgent demand for in-depth understanding to the interfaces of sulfide based ASSBs. Indeed, in their seminal work regarding the Si/sulfide interface, Huo et al stated that “The SEI components, their microstructure and growth rate on cycling, therefore, require a better understanding” (*Huo et al., Nat. Mater. 2024, 23, 543-551.*). In a similar vein, when discussing the interfaces in sulfide based ASSBs, Sakuma et al commented that “However, even though the anode and the solid electrolyte interface play key roles in the battery performance, there is little information available concerning the effects of various combinations of materials and the associated decomposition processes at the anode/electrolyte interface” (*Sakuma et al., Solid State Ionics 2016, 285, 101-105.*). In this context, our report constitutes a timely contribution to the important topic in ASSBs, i.e. the interface issue. As also pointed out by Reviewer 1: “The findings offer intriguing perspectives on interfacial reactions and their impact on battery performance, contributing to the Si-based sulfide solid-state battery field which is a cutting-edge next generation battery system.” Indeed, Si-based sulfide ASSB is an important battery system to realize high energy density and long cycle life of ASSBs. However, its electrochemical performance is plagued by various interface issues, and atomic scale characterization of Si/sulfide interfaces has not been possible due to the extreme air and electron beam sensitivity. The results we presented here represents the first atomic scale studies of Si/sulfide interfaces. Thanks for the cryo-TEM technology, which has been broadly used in biology sciences, but it is in its infancy in materials sciences. Our results demonstrate the potential of the application of cryo-TEM in addressing the most challenging issues in materials sciences, which will undoubtedly stimulate further research in this field.

Moreover, the cryo-TEM results reveal distinct different IRL structures in the LGPS and LSPSC systems, and uncover their correlation with electrochemical performance, which reveal quantitatively what causes capacity decay in Si anode based ASSBs, and provide important scientific bases to improve the Si-based sulfide ASSBs. For example, based on our observation that the Si/LSPSC interface is more stable than the Si/LGPS interface, we introduced a thin LSPSC layer in the Si/LGPS system, and the Si|LSPSC|LGPS|NMC811 ASSB exhibits much better electrochemical performance

than the Si|LGPS|NMC811 ASSB. Through cryo-HRTEM observation, we reveal the spatial inhomogeneity of Li₂S distribution within the IRL between Si and LGPS (Figure S28 in our manuscript). Specifically, the Li₂S grain size near the anode surface is smaller than that at the reaction front of IRL. Moreover, with increasing electrochemical cycling, the Li₂S grains undergo progressive refinement (Figure S31 in our manuscript). This natural "electrochemical grain refinement" may be beneficial for ionic transport during the cycling of ASSB. Under low electron dose conditions, we have observed lattice distortions in the electrolyte at the reaction front induced by electrochemical reactions (Figure S32 in our manuscript), as well as a coherent relationship between Li₂S and LiGe within the IRL (Figure S36 in our manuscript).

In short, the cryo-TEM studies of interfaces in Si-based sulfide ASSB have never been reported and are entirely new. These studies provide important sciences to improve the performance of Si-based sulfide ASSBs.

Regarding the novelty of our manuscript, we believe that the reviewer misunderstood our results. The reviewer is correct that one of the major failure mechanisms in **liquid electrolyte** lithium-ion batteries (**LELIBs**) is the loss of lithium-ion due to continuous SEI formation and destruction, which consumes both Li and the liquid electrolyte. Si is a very good example of this. During cycling, Si cannot form stable SEI, and during charging, large volume expansion breaks the SEI formed in the previous cycling, which exposes fresh Si to the electrolyte (*He et al., Nat. Nanotechnol. 2021, 16, 1113-1120.*). The newly exposed Si forms new SEI in the subsequent charging, and this process repeats, causing rapid capacity decay (*Jin et al., Adv. Energy Mater. 2017, 7, 1700715; Chae et al., Joule 2017, 1, 47-60.*). Nevertheless, **it is not clear whether similar failure mechanism operates in ASSBs**. In fact, it is generally accepted that the major failure mechanism in ASSBs is associated with the high interfacial impedance and lithium dendrite growth. Because of the solid-solid contacts among the various components, ASSBs usually exhibit large interfacial impedance. The bad contacts at the anode/SSE interfaces cause local high impedance, in turn high polarization, which become the hot spot for Li dendrite nucleation. Once the dendrites penetrate the entire SSE, the ASSB shorts and fails.

Our result provides the first direct evidence that interface impedance is not the major issue, it is the continuous and sustainable interfacial reactions that consume the Li inventory from the cathode that causes crack and capacity decay. This failure mechanism is entirely new, and it is at odd with general notion that interfacial impedance is the problem in ASSB. We should point out that this failure mechanism is also different from that in LELIBs. In the case of Si anode in LELIBs, the failure is caused by the loss of active material, i.e., pulverization of Si that causes failure. In ASSB, it is the sustainable interfacial reaction which consumes both Li inventory and the SSE, causing capacity decay and ASSB failure. In ASSB, Si is not pulverized. We have no doubt that the results reported here provide new understanding to the failure mechanisms of Si-based sulfide ASSBs, which provide important sciences to guide the development of high performance ASSBs.

Additionally, we have conducted supplementary experiments addressing all the reviewer's queries. Below, we provide a detailed point-by-point response.

The reviewer also has the following questions:

1. Li Deposition in Si-based Batteries: It is widely known that Si anodes have good fast charging/discharging capabilities, which makes significant lithium (Li) deposition in Si-based batteries not very likely. Could the observed Li deposition be a result of unoptimized anode preparation or the use of excessively high current/voltage during cycling? It would be helpful if the authors could provide more detailed information on the anode preparation method and the specific cycling parameters used for the sample preparation, to help clarify whether these factors might influence the observed results.

Response: We apologize for the lack of clarity regarding the Li deposition. We do not expect massive Li deposition at the Li/LGPS interface. This is because the IRL is astonishingly uniform in thickness (Figure R5b), indicating a uniform interfacial reaction of lithium-ion and electrons with SSE. If local Li deposition occurred, we do not expect such uniform IRL formation.

The IRL formation is essentially an electrochemical process. We believe that the Li/LGPS interfacial reaction was mainly caused by the electrochemical reaction of Li^+ and e^- with LGPS, and the reaction products are mainly needle-shaped Li_2S and LiGe which have definite crystallographic orientation relationship, as shown in Figure 3 of our manuscript. Because LiGe is an electronic conductor, the Li/LGPS interfacial reaction is sustainable, causing the formation of the thick IRL layers.

The ASSBs assembly and testing procedure are the following. During solid-state battery testing, we compressed 100 mg of electrolyte into a 10 mm disc under 120 MPa pressure. The anode consists of 2 mg of pure micrometer-sized Si compressed at 240 MPa pressure, while the cathode, made up of a mixture of 20 mg NMC811 and LSPSC electrolyte, was compressed at 720 MPa pressure (Figure R27). The N/P ratio was 2.5 (calculated based on the theoretical capacity of 3500 mAh/g about Si anode). The final electrochemical tests were conducted at 1C, and the electrochemical cycling window was 2.6-4.3V. The related discussion has been added in the revised manuscript. (Page 15 in Revised Manuscript, Figure S63 in Supporting Information).

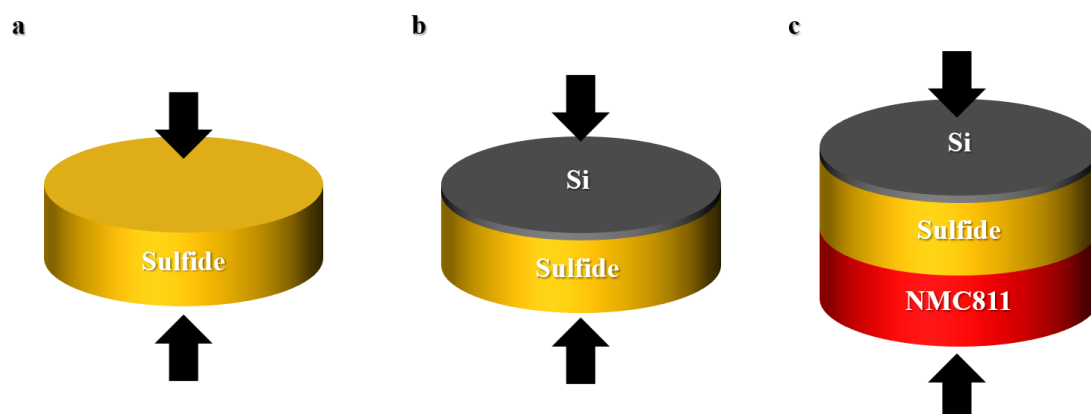


Figure R27. Assembly process of the ASSB. (a-c) Schematic showing the ASSB assembly steps.

2. Relevance to Real Applications: In real-world applications of Si anodes in all-solid-state batteries, Si is often mixed with solid-state electrolytes to enhance lithium ionic conductivity, which is not as critical when using liquid electrolytes. However, it appears that in this study, Si is not mixed with the solid electrolyte. This could potentially lead to Li deposition at the interfaces due to the limited ionic conductivity within the Si anode bulk. Consequently, the findings presented in this study may not fully reflect the operational conditions of Si anodes in practical applications. This could limit the broader applicability of the results, and the findings might only be relevant to a smaller audience.

Response: Thank for the comment. Researchers have indicated that compared to liquid-state batteries, the operation of pure Si anodes in solid-state batteries is a superior choice. The introduction of carbon will increase the decomposition of sulfides. In addressing how to optimize the performance of Si anode in ASSBs, we designed both pure Si and Si mixing with sulfide anodes. We observed a significant capacity decay of the full cell with the introduction of the electrolyte into the Si anode, particularly in the Si+LGPS|LGPS|NMC811 ASSB (Figure R28). In impedance tests, we discovered that in the LSPSC system, the pure ionic conductivity of the SEI ensured the stable operation of both pure Si and Si+LSPSC anodes. Conversely, in the LGPS system, the mixed conductivity of the SEI led to the continuous increase of interface impedance, with significant differences in electrochemical cycles (Figure R29). This indicates that pure Si anodes is a better choice for ASSB. Similar conclusion was reached in Huo et al.'s and Meng et al.'s work (*Huo et al., Nat. Mater.* 2024, 23, 543-551; *Tan et al. Science*, 2021, 373, 1494-1499.). The obtained results and the related discussion have been added in the revised manuscript and supporting information. (Page 12, Page 13 in Revised Manuscript, Figures S55, S56 in Supporting Information).

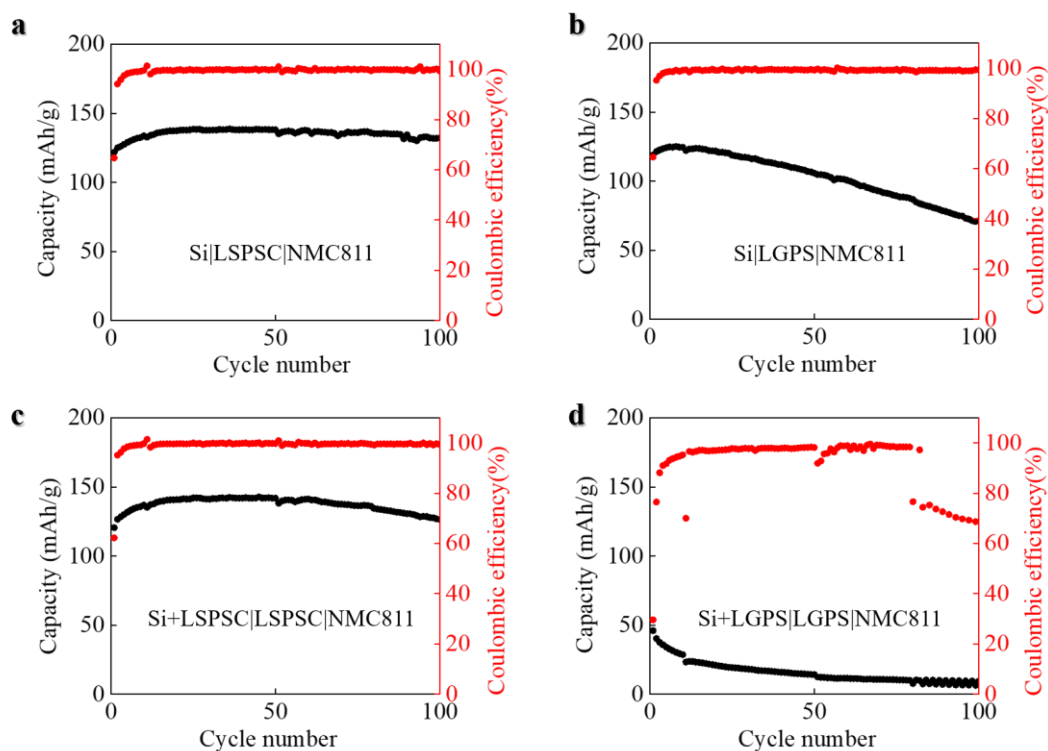


Figure R28. Electrochemical tests of ASSBs assembled with pure Si and Si + sulfide SSE anodes. (a) Si|LSPSC|NMC811. (b) Si|LGPS|NMC811. (c) Si+LSPSC|LSPSC|NMC811. (d) Si+LGPS|LGPS|NMC811.

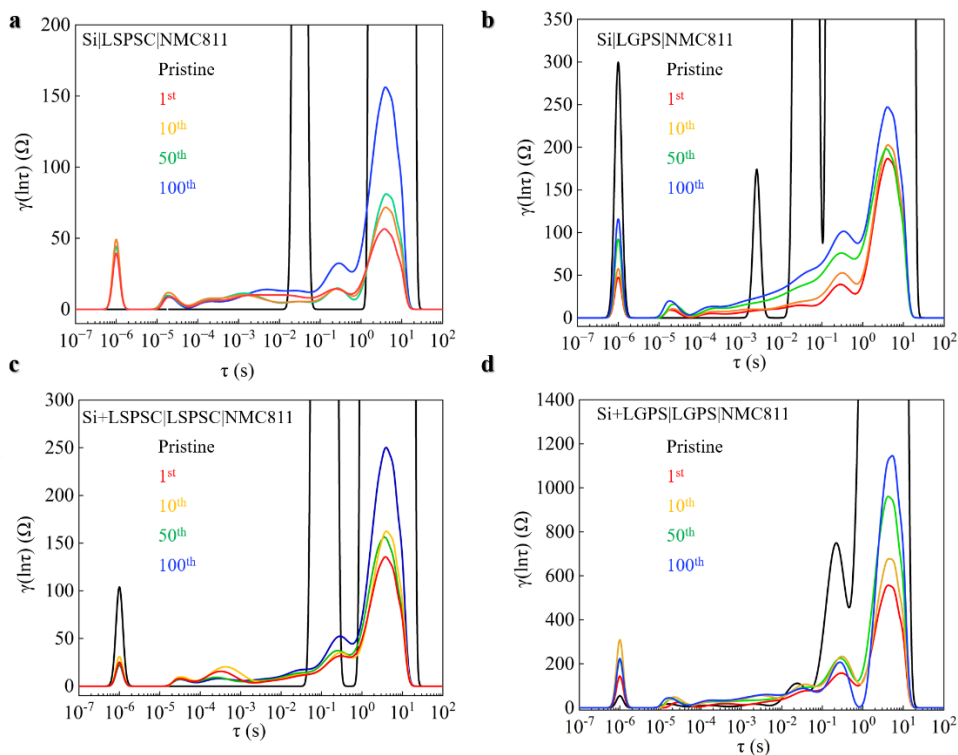


Figure R29. DRT analysis of ASSBs assembled with pure Si and Si mixed with sulfide SSE anodes. (a) Si|LSPSC|NMC811. (b) Si|LGPS|NMC811. (c) Si+LSPSC|LSPSC|NMC811. (d) Si+LGPS|LGPS|NMC811.

3. Li-Si Alloy and LGPS Interaction: On Page 8, Line 222, the authors claim that Li-Si alloy does not react with LGPS ($\text{Li}_{10}\text{GeP}_2\text{S}_{12}$). However, there is insufficient evidence to support this argument. Later, on Page 12, Line 355, the authors mention a side reaction between deposited Li and LGPS, but this does not conclusively rule out the possibility of a reaction between the Li-Si alloy and LGPS. Further clarification and stronger evidence are needed to definitively establish whether such a reaction occurs.

Response: Thank for the great comment. We acknowledge that the original statement is incorrect. We changed the statement to: “In terms of the electrochemical stability between Li-Si alloy and LGPS, it is more stable than the Li/LGPS interface.” First, we monitored the impedance variation of the $\text{LiSi}|\text{LGPS}|\text{LiSi}$ symmetric cell and the $\text{Li}|\text{LGPS}|\text{Li}$ symmetric cell under static conditions, where the impedance of the $\text{LiSi}|\text{LGPS}|\text{LiSi}$ cell was lower, while the impedance of the $\text{Li}|\text{LGPS}|\text{Li}$ cell increased to 2000 ohm in just seven days (Figures R30a-d). In the electrochemical cycling of LGPS based ASSB at 0.1 mA/cm^2 , the overpotential of the ASSB with Li as the electrode continuously increased with running time, while the overpotential of the ASSB with LiSi as the electrode remained essentially unchanged. The polarization of the $\text{Li}|\text{LGPS}|\text{Li}$ symmetric cell with pure Li anode continued to increase, suggesting irreversible electrochemical degradation at the Li/LGPS interface (Figure R30e). The significant increase in impedance also indicates the continuous deterioration of the Li/LGPS interface. Therefore, in comparison to the Li/LGPS interface, the $\text{Li}_x\text{Si}/\text{LGPS}$ interface demonstrates electrochemical stability (Figures R30f-i).

Skuma et al. (*Solid State Ionics* 2016, 285, 101-105.) and Wang et al. (*Chin. Phys. B* 2024, 33, 088201.) report that Li_xSi anode does cause sulfide electrolyte decomposition. The electrochemical stability window of both LGPS and LSPSC is from $\sim 1.71 \text{ V}$ to $\sim 2.14 \text{ V}$ (Wang et al., *Matter*, 2023, 6, 1096-1124; Binninger et al., *J. Mater. Chem. A* 2020, 8, 1347-1359; Peljo et al., *Energy Environ. Sci.* 2018, 11, 2306-2309; Wu et al., *Energy Environ. Sci.* 2018, 11, 1803-1810.). In principle, any anodes with an electrochemical potential less than 1.7 V can cause decomposition of LGPS and LSPSC. The obtained results and the related discussion have been added in the revised manuscript and supporting information. (Page 8 in Revised Manuscript, Figure S18 in Supporting Information).

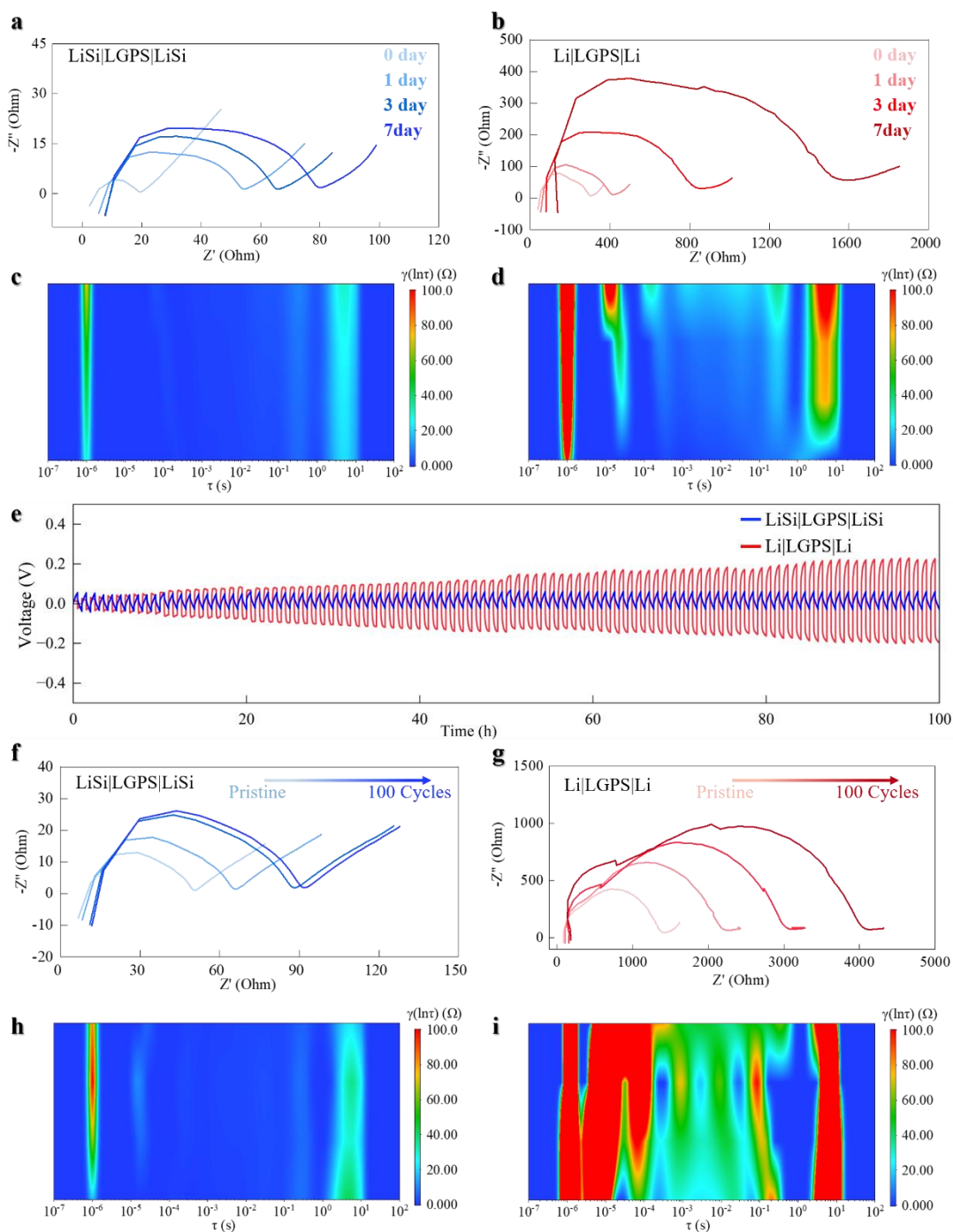


Figure R30. Electrochemical tests of ASSBs assembled with Li and LiSi anodes. (a) Impedance variation of the LiSi|LGPS|LiSi ASSB under static conditions. (b) Impedance variation of the Li|LGPS|Li ASSB under static conditions. (c) DRT analysis corresponding to the impedance tests of the LiSi|LGPS|LiSi cell under static conditions. (d) DRT analysis corresponding to the impedance tests of the Li|LGPS|Li cell under static conditions. (e) Current-voltage curves of the Li|LGPS|Li and LiSi|LGPS|LiSi symmetric cells. (f) Impedance tests of the LiSi|LGPS|LiSi cell at different operating times. (g) Impedance tests of the Li|LGPS|Li cell at different operating times. (h) DRT analysis corresponding to the impedance tests of the LiSi|LGPS|LiSi cell. (i) DRT analysis corresponding to the impedance tests of the Li|LGPS|Li cell.