

Unraveling Asymmetric Macroscopic Reaction Dynamics in Solid-State Li–S Batteries During Charge–Discharge Cycles: Visualizing Ionic Transport Limitations with *Operando* X-Ray Computed Tomography

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By eliminating liquid electrolytes, solid-state Li–S batteries (SSLSBs) deliver emerging high-energy storage solutions with intrinsic safety advantages. However, restricted access to in-battery reaction dynamics has obscured the mechanisms behind critical limitations in rate capability and cyclability. Here, *operando* X-ray computed tomography is employed to capture the evolving through-thickness sulfur-lithiation distribution within composite SSLSB cathodes during cycling, directly linking macroscopic ion transport to cell performance. The observations not only demonstrate that macroscopic ion transport severely restricts the rate capability of SSLSBs, but also disclose a previously unreported charge–discharge asymmetry in reaction heterogeneity that triggers irreversible Li₂S formation. Differential-evolution fitting of the reaction profiles quantified a deterioration in the effective ionic conductivity during charging, which drives the observed asymmetry and likely arises from electrochemical and/or microstructural degradation of the electrolyte. This study establishes a methodology for high-resolution visualization of reaction dynamics within composite cathodes, providing quantitative insights into the macroscopic transport bottleneck based on experimental observations, which are essential for guiding rational electrode design toward enhanced rate capability and cyclability.

1. Introduction

The development of fast ion-conducting solid electrolytes (SEs) has opened new avenues in solid-state battery chemistry, offering a promising alternative to the conventional Li-ion batteries.^[1–4] One of the promising candidates is solid-state Li–S batteries (SSLSBs).^[5–9] They leverage the mechanical rigidity and ionic selectivity of SEs to overcome the shuttle effect,^[10,11] a persistent challenge in conventional Li–S batteries, affording both high safety and outstanding energy density. However, despite these advantages, SSLSBs have not achieved the desired performance goals and require further improvements. Current performance limitations of SSLSBs have been widely attributed to the ionic/electronic insulating nature of sulfur and its lithiated compounds,^[11,12] slow solid-to-solid conversion,^[13–16]

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sluggish Li-ion diffusion within (de)lithiated sulfur,^[17] and contact loss caused by the massive volume changes of sulfur.^[18,19]

To address these inherent challenges arising from insulating nature of active materials, the cathode of SSLSBs necessitates uniform nanoscale compositing of sulfur, SE, and conductive additives, which ensures extensive triple-phase boundaries within the cathode and shortens the diffusion length in the sulfur active material.^[5] However, such nano-structuring simultaneously render ionic and electronic conduction within the cathode highly inefficient. The resulting complex and tortuous transport pathways can reduce the effective ionic conductivity in composite cathodes by two to three orders of magnitude compared to the intrinsic conductivities of the SEs.^[20,21] Furthermore, the resulting high interfacial area density can accelerate electrolyte degradation,^[22] exacerbating the inherently slow macroscopic ion transport within the composite. In some cases, this electrolyte degradation has been intentionally exploited to form redox-active interphases, enabling stable cycling with capacities exceeding 500 mAh g_{cathode}⁻¹.^[22,23] While the electrochemical measurements suggest the macroscopic ion transport is a critical performance bottleneck of the SSLSB, these measurements cannot unambiguously distinguish whether the observed performance limitations stem from macroscopic ionic conduction within the composite or from microscopic diffusion within the sulfur particles themselves. This distinction has become increasingly important for mechanistic understanding in SSLSBs, and also across various cathode chemistries including transition metal-based systems, particularly in the design of high-loading electrodes or cells operated at high current densities, where the demands on mass transport are especially severe.^[24–26]

Recently, Bradbury et al. have provided the first direct evidence that the macroscopic mass transport limitation poses indeed a serious challenge in SSLSBs.^[27] Using *operando* neutron imaging, they directly visualized the reaction front advancing from the SE separator to the current collector side within the electrode, clearly demonstrating that the electrochemical reactions in the cathode were governed by limited macroscopic ion transport. Furthermore, their tomographic analysis revealed irreversible lithium accumulation near the current collector side, suggesting the impact of macroscopic transport limitations on capacity loss. However, these observations were restricted to exceptionally thick (≈ 200 μm) cathodes due to the limited spatial resolution of neutron imaging and thus cannot be generalized to more practical cell configurations with better cyclability or high-rate performance. Consequently, despite growing recognition that macroscopic ion transport is a central limitation in SSLSBs,^[21] it remains unclear how significantly it impacts cells with improved reversibility or under various (dis)charging rates.

To provide deeper insights into these critical challenges, here we conducted *operando* observations of macroscopic reaction heterogeneities within composite SSLSB cathodes using synchrotron X-ray computed tomography (XCT). While XCT has been widely employed to observe morphological changes within batteries,^[28–31] its application for chemical analysis has been limited,^[32] particularly in the context of macroscopic chemical change within electrodes. This study demonstrates for the first time that XCT, when coupled with high-flux synchrotron beams and optimized cell design, can effectively evaluate spatial state-of-charge distribution within well-cyclable cathodes under various

(dis)charging rates with micron-to-submicron spatial resolution. This approach not only provided direct evidence that macroscopic ion transport severely restricts (dis)charge capacities at high rates but also uncovered that reaction heterogeneities within the electrode exhibit asymmetric patterns between charging and discharging, demonstrating that macroscopic ionic transport deteriorates during charging. Furthermore, the high-resolution quantitative visualization capability of XCT enables us to extract key transport parameters, effective ionic conductivity and interfacial charge-transfer kinetics, by fitting the experimentally obtained state-of-charge profiles using a differential evolution algorithm. This quantitative analysis revealed a threefold decrease in effective ionic conductivity within the composite cathode during charging, offering new mechanistic insights into irreversible Li₂S accumulation within the electrode under realistic cell configuration and cycling parameters.

2. Results and Discussion

To visualize reaction heterogeneities within composite SSLSB cathodes using XCT, a cylindrical sample holder with a PEEK housing was developed, as shown in **Figure 1a**. Within this custom holder, a cylindrical SSLSB cell (**Figure 1b**) was fabricated by uniaxial pressing (220 MPa^[33]) of S/C/Li₆PS₅Cl (LPSC) composite powder and LPSC powder, followed by the incorporation of In/Li foil. The nominal sulfur loading in the cathode was set at 5.1 mg cm⁻², with volume fractions of sulfur, LPSC, and conductive additive fixed at $\approx 0.33:0.53:0.15$ (2:3:1 by mass), a ratio previously reported to exhibit favorable performance.^[20] To maintain an inert environment during measurements, the cell was sandwiched between two $\phi 1.5$ mm stainless steel punches with O-ring seals, which not only prevented exposure to air and moisture but also served as current collectors. Additionally, a constant constraint pressure of ≈ 60 MPa was applied to the cell during cycling by applying torque to the holder bolt. This integrated cell-holder design has been confirmed to enable reversible cycling, demonstrating stable electrochemical performance (**Figure S1**, Supporting Information). Prior to XCT measurements, the cell underwent two discharge–charge cycles at 0.1C. It should be noted that the composite cathode layer is placed at the bottom of the cell, as depicted in **Figure 1b**, to mitigate the influence of the volume change of the anode side on the reconstruction of the 3D image.

Monochromatic XCT at 18 keV effectively distinguished individual cell components (**Figure 1c**), with brighter regions indicating higher X-ray absorption. **Figure 1d** illustrates a cross-sectional view near the interface between the LPSC separator layer and the composite cathode layer. The composite cathode layer exhibits a uniform, dense morphology without visible voids. In contrast, inhomogeneous densification is observed in the separator layer, as shown in **Figure 1e**, where electrolytes in the central area appear more densely packed than those in the peripheral regions. This inhomogeneity is commonly encountered in uniaxially compacted powders. However, since ion transport within the separator layer is expected to be significantly faster according to previous studies,^[21] the impact of inhomogeneously densified separator on the cathode composite behavior is anticipated to be negligible. Conversely, the non-uniform thickness and the observed bending of the composite cathode layer (**Figure 1d**) require careful consideration, as a simple cross-sectional slice

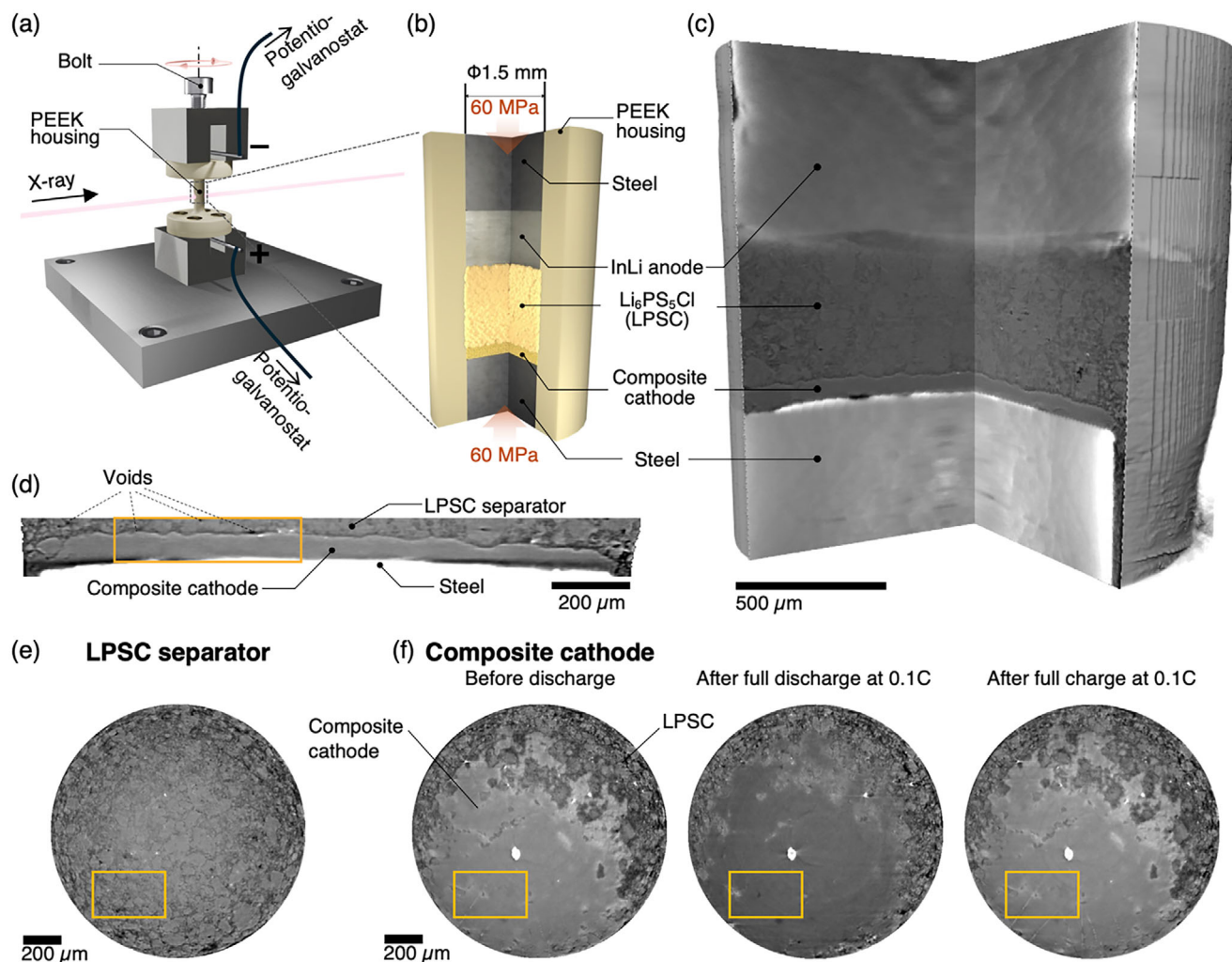


Figure 1. Experimental setup and tomographic analysis of an SSLSB. a) Schematic of the custom-designed sample holder for XCT measurements. b) Schematic of the cylindrical SSLSB cell structure consisting of composite S/C/LPSC cathode, LPSC separator, and In/Li anode. c) 3D reconstruction of the SSLSB cell obtained from XCT measurements. d) Cross-sectional view near the interface between the LPSC separator and composite cathode layers. e) Representative tomographic slice of the LPSC separator layer. f) Representative tomographic slices of the composite cathode layer before discharge, after full discharge and after full charge at 0.1C.

parallel to the X-ray beam may contain overlapping cell components, as highlighted in Figure 1f. To minimize effects arising from morphological heterogeneity, we focused our analysis of X-ray absorbance changes described below on the yellow-framed region in Figure 1d–f. This region was specifically selected because it features a relatively flat LPSC/composite cathode interface, includes the thickest area of the composite cathode layer, and exhibits average LPSC layer density.

Significant changes in the X-ray absorbance of the composite cathode area are clearly observed upon discharge–charge cycles. As shown in Figure 1f, the composite cathode area exhibited markedly reduced X-ray absorbance, becoming darker after full discharge at 0.1C. Upon subsequent full charging, the X-ray absorbance returned to its initial level prior to discharge. These changes in the X-ray absorbance in the composite cathode during cycling are primarily attributed to the sulfur (de)lithiation process. Sulfur undergoes a 78% volume expansion when lithi-

ated to form Li_2S .^[18] The substantial volume expansion and the incorporation of the lighter element Li collectively result in an $\approx 40\%$ decrease in X-ray absorbance for this active material.^[34] Assuming that the reduction of sulfur to Li_2S is the sole cause of changes in the X-ray absorbance within the composite, the X-ray absorbance of the composite cathode per voxel ($1.51\ \mu\text{m}$) is expected to decrease by $\approx 18\%$, from 1.94×10^{-3} to 1.59×10^{-3} , after full discharge (the detailed calculation of the theoretical absorbance values is described in the Experimental Methods in the Supporting Information).

The degree of sulfur lithiation is quantitatively analyzed through the change in the X-ray absorbance in the composite cathode during (dis)charge. Figure 2a shows the discharge–charge curves of the cell at 0.1C, and Figure 2b presents the corresponding X-ray absorbance variations. The discharged capacity of the cell employed for visualization was $\approx 1260\ \text{mAh g}^{-1}$. This deviates from the delivered discharge capacity of an identical

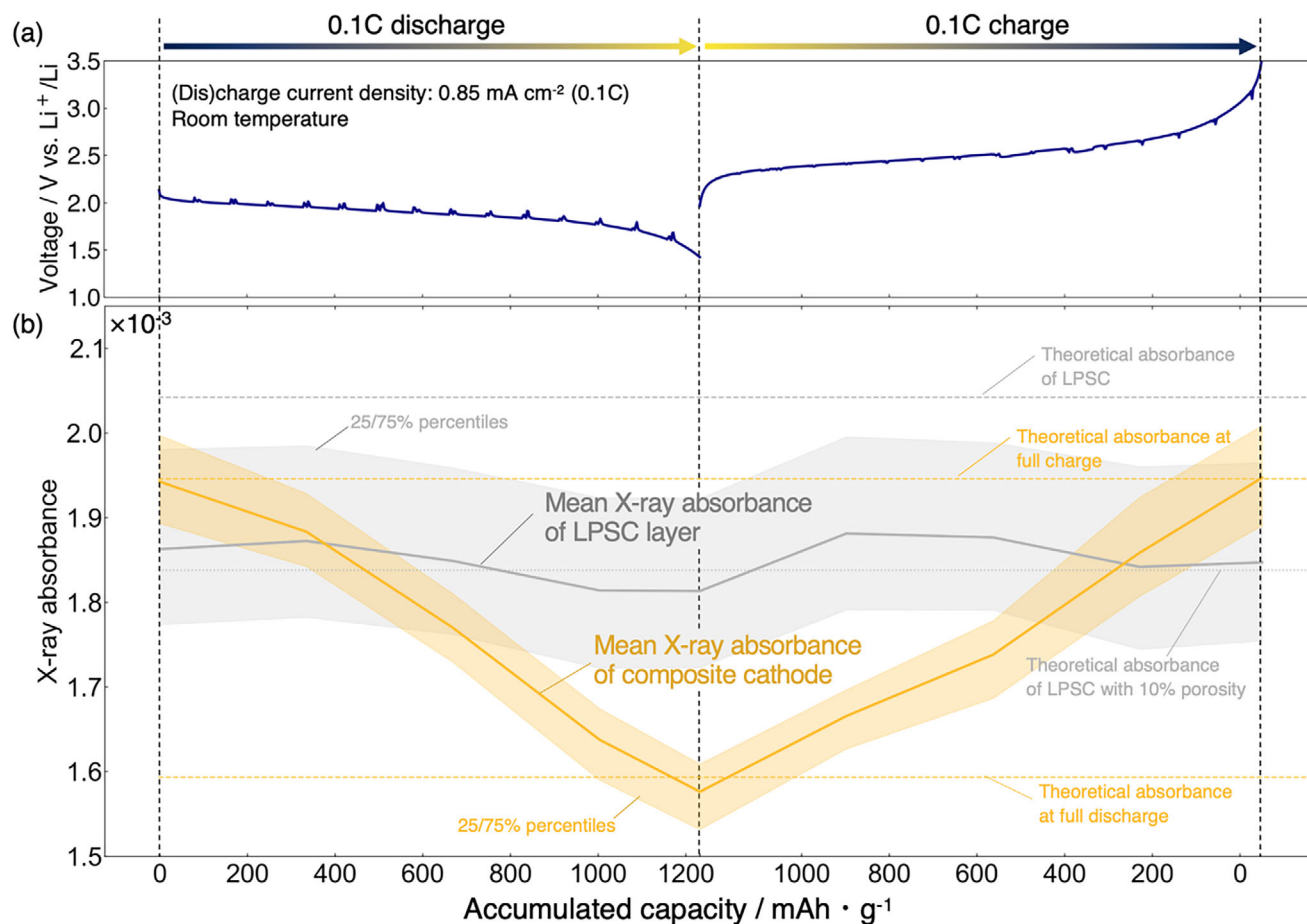


Figure 2. Electrochemical and X-ray absorption characterization of the SSLSB cell. a) Voltage profile during galvanostatic discharge–charge cycling at 0.1C (0.85 mA cm^{-2}) at room temperature. b) Evolution of X-ray absorbance in the composite cathode and LPSC separator regions during 0.1C discharge–charge cycling, showing mean values (solid lines) and 25/75 percentiles (shaded areas).

composite cathode tested beforehand using the same *operando*-cell (Figure S1, Supporting Information) and a $\phi 10\text{-mm}$ cell (Figure S2, Supporting Information), but such a difference in delivered capacity is attributed to deviations in cathode loading from the target value, specifically arising from the challenge of precisely weighing only 0.27 mg of composite cathode for the $\phi 1.5\text{-mm}$ cell (an estimated error based on triplicate cells is 8%). Additionally, minor peaks and dips were observed in the potential profiles, coinciding with the exposure of the cell to the X-ray beam. While these features are likely due to interactions between cell components and the beam, further investigation is required to clarify their exact origin, which is beyond the scope of this study.

As previously mentioned, the region depicted by the yellow frames in Figure 1d–f, encompassing both the composite cathode and LPSC separator layers, was selected as the area of interest for quantifying X-ray absorbance changes, thereby mitigating the impact of morphological heterogeneity. While the LPSC layer showed no distinct (dis)charge-dependent X-ray absorbance variations, the absorbance in the composite cathode area varied almost linearly and reversibly with the progression of (dis)charge (Figure 2b). The average X-ray absorbance in this area before discharge/after charge and after discharge were $\approx 1.94 \times 10^{-3}$ and

1.58×10^{-3} , respectively. These values aligned closely with theoretical expectations for the composite cathode containing S and Li_2S as active materials (1.94×10^{-3} and 1.59×10^{-3} , respectively). Furthermore, the average absorbance in the LPSC area (1.86×10^{-3}) corresponded well to the expected value, assuming 10% porosity,^[34] which qualitatively matched the observed morphology in this area (Figure 1e). Despite prevailing assumptions that the sensitivity of XCT might be insufficient to capture the attenuation changes associated with the lithiation/delithiation of a light element such as sulfur, the present analysis quantitatively confirms that absorbance changes in the composite cathode area are indeed attributable to sulfur (de)lithiation, thus demonstrating the capability of XCT to effectively monitor the lithiation degree of sulfur within composite cathodes.

Now that the degree of sulfur (de)lithiation can be quantitatively assessed through changes in X-ray absorbance, its through-thickness distribution is of particular interest as it sensitively reflects macroscopic mass transport limitations within the electrode.^[27,35,36] Figure 3a shows the X-ray absorbance within the composite cathode as a function of distance from the LPSC/composite cathode interface before discharge. Each line corresponds to the average X-ray absorbance within the region

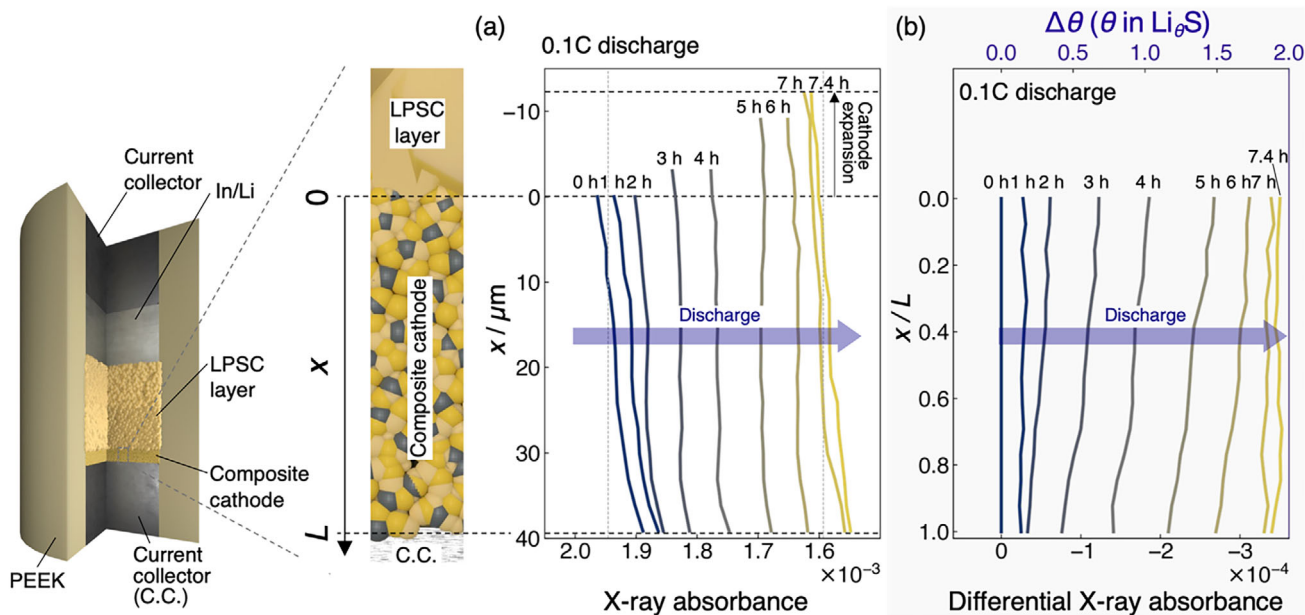


Figure 3. Through-thickness X-ray absorbance profiles of the composite cathode during 0.1C discharge. a) Average X-ray absorbance as a function of distance (x) from the LPSC/composite cathode interface at sequential time points (0–7.4 h). b) Differential X-ray absorbance profiles as a function of normalized distance obtained by subtracting the pre-discharge profile from each discharge point profile. The top axis indicates the corresponding change in lithiation degree of sulfur ($\Delta\theta$ where θ in Li_θS).

of interest (highlighted by the yellow cuboids in Figure 1) at a given depth of discharge at 0.1C. The absorbance profile before discharge showed a slight decrease toward the current collector side. As discharge progressed, the through-thickness X-ray absorbance gradually decreased overall, indicating progressive sulfur lithiation across the entire electrode. This sulfur lithiation concomitantly increased the electrode thickness, causing the LPSC/composite cathode interface to shift toward the LPSC layer (Figure S3, Supporting Information).

To quantitatively assess the degree of sulfur lithiation at a given position x during discharge while excluding the initial spatial variation in the X-ray absorbance, we calculated the differential X-ray absorbance profiles by subtracting the pre-discharge profile from each discharge point profile (Figure 3b). Prior to subtraction, the absorbance profile length at each discharge point was normalized to the pre-discharge profile length (L) to account for the electrode expansion during discharge. This differential analysis isolates absorbance changes solely attributed to sulfur lithiation, allowing estimation of changes in the degree of sulfur lithiation ($\Delta\theta$ where θ in Li_θS). This estimation assumes a linear relationship between absorbance variation and lithiation state (indicated by the top axis in Figure 3b). This analysis reveals that the lithiation progressed almost uniformly throughout the electrode during discharge at 0.1C, reaching nearly full lithiation ($\Delta\theta \approx 2.0$) at the end of discharge. It should be noted, however, that this $\Delta\theta$ represents the average lithiation state at a given position and does not directly correspond to the formation of specific reaction intermediates.

When the discharge rate was increased from 0.1C to 0.2C, 0.4C, and 0.8C, the spatial $\Delta\theta$ distribution became increasingly heterogeneous, as shown in Figure 4a. At higher rates, lithiation progressed preferentially on the LPSC layer side where Li-ions

were supplied, while progression of lithiation was suppressed in regions near the current collector (original absorbance profiles shown in Figure S4, Supporting Information). Considering Newman-type 1D continuum transport models that couple ionic and electronic conduction in composite electrodes,^[37] these observed results clearly demonstrate that macroscopic ion transport acts as the rate-limiting factor in the composite cathode, consistent with findings reported by Bradbury et al.^[27] At discharge rate of $\geq 0.2\text{C}$, $\Delta\theta$ profiles remained heterogeneous even at the end of discharge, indicating that the discharge capacity was limited by these reaction heterogeneities in the cathode. Indeed, as illustrated in Figure 4c, the discharge capacity significantly decreased with increasing discharge rate.

To assess the impact of the reaction heterogeneity on discharge capacity, the discharge capacity of the cell at each rate was compared with those estimated from the integrated value of the $\Delta\theta$ profile after discharge (Figure 4d). The discharge capacity estimated from the $\Delta\theta$ profile at 0.1C ($\approx 1610 \text{ mAh g}^{-1}$) was approximately equal to the theoretical capacity (1672 mAh g^{-1}), which monotonically decreased at higher rates. As shown in Figure 4d, the delivered capacities at each rate were normalized to the discharge capacity at the rate of 0.1 C for direct comparison. The normalized capacities obtained from both X-ray absorbance and electrochemical measurements were in good agreement, indicating that the discharge capacity degradation is closely linked to reaction heterogeneity arising from limited macroscopic ionic transport.

More notably, a striking asymmetry in reaction heterogeneity was observed when comparing the $\Delta\theta$ profiles during discharge and charge processes. Figure 4b shows differential X-ray absorbance profiles between each charging point and the post-discharge state during 0.1–0.8C charging. As expected, an

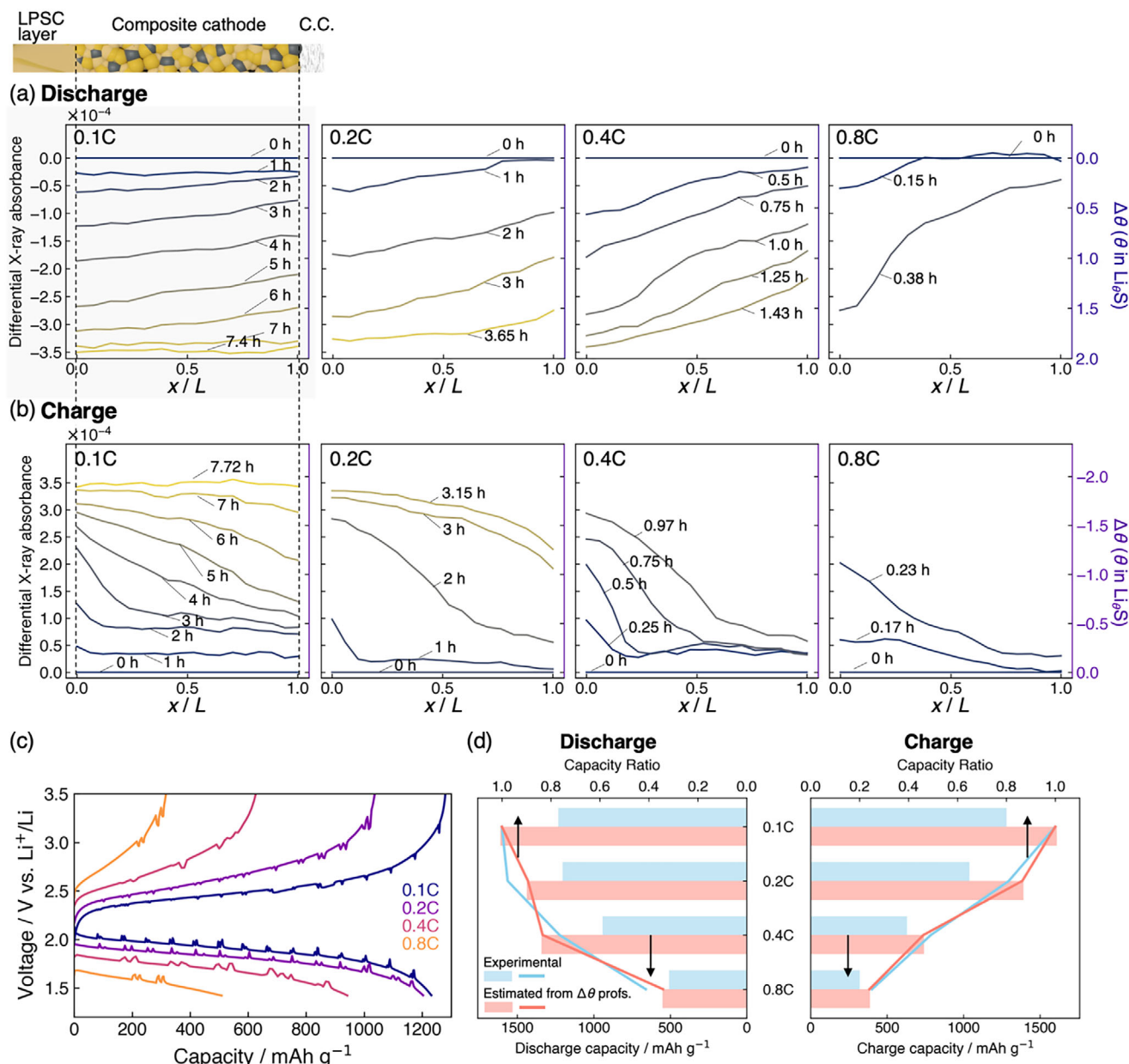


Figure 4. Analysis of the X-ray absorbance profiles at various C-rates and correlation with electrochemical performance. Differential X-ray absorbance profiles as a function of the normalized distance from the LPSC layer to the current collector during a) discharge and b) charge at 0.1C, 0.2C, 0.4C, and 0.8C. c) Charge–discharge curves of the SSLSB cell at 0.1, 0.2, 0.4, and 0.8C. d) Comparison between experimentally measured discharge/charge capacities and those estimated from differential X-ray absorbance profiles, presented both as absolute values and as capacity ratios (normalized to respective 0.1C values).

increase in X-ray absorbance was observed, indicating delithiation of sulfur. After 0.1C charging, the electrode achieved nearly complete charge ($\Delta\theta \approx -2.0$); however, during intermediate charging stages, heterogeneous reaction with preferential sulfur delithiation on the LPSC separator side was clearly observed. This is in marked contrast to the discharge process at the same rate, where sulfur lithiation progressed almost uniformly. At higher charging rates, this heterogeneity was further intensified, creating significant asymmetry between the sulfur lithiation distribution in equivalent-rate discharge. This in-

dicates that the macroscopic ionic transport limitations became more significant during charging compared to discharging. Consequently, the overall $\Delta\theta$ after charging was markedly reduced compared to the same-rate discharge. In alignment with this, the charge capacity of the cell dropped below the discharge capacity at the same rate as shown in Figure 4c. Notably, at 0.4C, the charge capacity decreased to 66% of the discharge capacity. Considering the agreement between the capacity ratios estimated from the $\Delta\theta$ profiles and measured values (Figure 4d), the intensified reaction heterogeneity during charging significantly

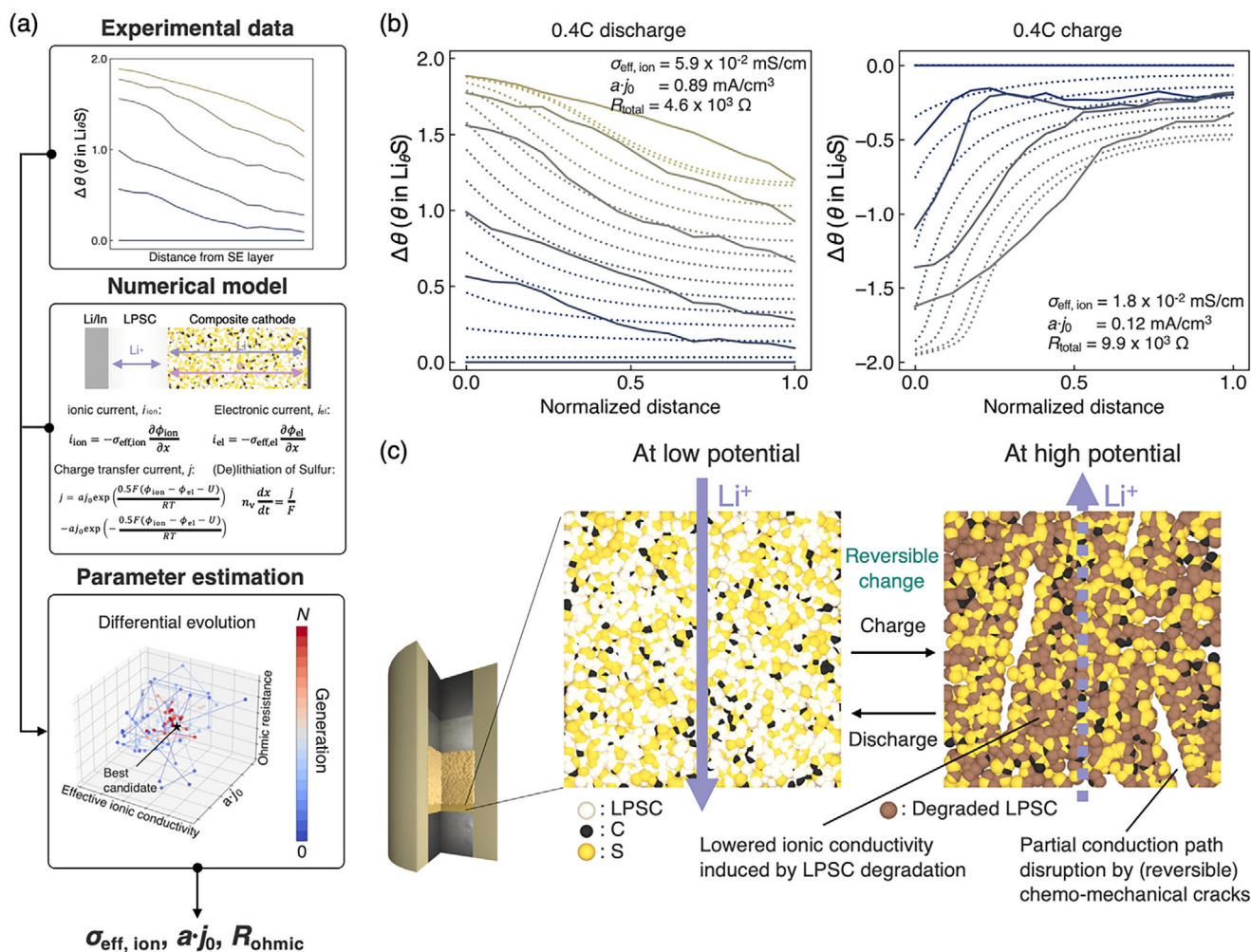


Figure 5. Quantitative analysis of the macroscopic ionic transport limitations during charging and proposed degradation mechanism. a) Parameter estimation methodology using differential evolution algorithm to optimize $\sigma_{\text{eff,ion}}$, $a j_0$, R_{total} based on the obtained $\Delta\theta$ profiles and the numerical model of the SSLSB. b) Comparison between experimentally observed and simulated reaction distribution profiles using optimized $\sigma_{\text{eff,ion}}$, $a j_0$, R_{total} at 0.4C discharge/charge. c) Schematic illustration of the proposed mechanism for macroscopic ionic transport deterioration in the composite cathode at high potential, attributed to reversible electrochemical and/or microstructural degradation of the SE.

contributes to this charge capacity deterioration (a detailed discussion is provided later). Such decrease in charge capacity relative to discharge capacity, namely, the formation of lithiated sulfur that cannot revert to its original state, is recognized as a critical limitation facing SSLSBs.^[35] To date, such irreversible Li₂S formation has often been explained by a decrease in the triple-phase boundary due to chemo-mechanical degradation^[37] or high activation energy barriers for Li₂S conversion.^[38] However, our direct observations clearly reveal that deterioration of macroscopic ionic transport during charging significantly contributes to the accumulation of irreversible Li₂S, complementing existing explanations focusing primarily on interfacial challenges.

The key for further development of SSLSBs is in macroscopic ion transport within the composite cathodes. To quantitatively demonstrate the impact of macroscopic ion transport limitations during charging, we back-calculated the effective ionic conductivity ($\sigma_{\text{eff,ion}}$) within the composite cathode during

(dis)charging from the $\Delta\theta$ profiles using the differential evolution algorithm.^[38] We constructed a 1D numerical model simulating (dis)charge reactions in composite cathodes and searched for the $\sigma_{\text{eff,ion}}$ value that best reproduced both the experimentally obtained $\Delta\theta$ profiles and the (dis)charge capacity. (Figure 5a, see Experimental Section in Supporting Information for details). Our analysis focused on data from 0.4C (dis)charge cycles, where the most significant asymmetry in the $\Delta\theta$ profiles was observed during (dis)charge. For simplicity, we assumed constant $\sigma_{\text{eff,ion}}$ during either discharge or charge and simultaneously estimated the unknown parameters: the product of the interfacial area per unit volume (a) and exchange current density (j_0) — $a j_0$ — and the total resistances external to the composite cathode (R_{total}), such as the LPSC separator resistance and charge transfer resistance in InLi. In particular, $a j_0$ is also a critical parameter determining the interfacial charge-transfer kinetics. Therefore, we simultaneously evaluated changes in this parameter during (dis)charge.

As shown in Figure 5b, the simulated reaction distribution profiles using the optimized parameters reasonably agreed with experimental data at both 0.4C discharge and charge. The estimated $\sigma_{\text{eff,ion}}$ for discharge was $5.9 \times 10^{-2} \text{ mS cm}^{-1}$, which aligned well with the literature value ($3.5 \times 10^{-2} \text{ mS cm}^{-1}$) obtained through DC polarization measurements.^[39] The estimated $\sigma_{\text{eff,ion}}$ for charge was $1.8 \times 10^{-2} \text{ mS cm}^{-1}$, dropping to approximately one-third of its discharge counterpart. The simultaneously estimated a_{j_0} and R_{total} from the charging data were 0.12 mA cm^{-3} and $9.9 \times 10^3 \Omega$, respectively, showing a decrease in a_{j_0} and an increase in R_{total} relative to the discharge values (0.89 mA cm^{-3} and $4.6 \times 10^3 \Omega$). Thus, our parameter estimation indicates that both $\sigma_{\text{eff,ion}}$ and a_{j_0} decreased during charging, suggesting deterioration of both macroscopic ionic transport and interfacial reaction kinetics. Among them, the principal driver of the exacerbated reaction heterogeneity during charging is the degradation of $\sigma_{\text{eff,ion}}$. Indeed, the decrease in a_{j_0} alone cannot replicate this asymmetric reaction pattern during (dis)charge cycles (Figure S5, Supporting Information). Thus, our analysis indicates that the diminished $\sigma_{\text{eff,ion}}$ during charging critically impacts the irreversible Li_2S formation.

A primary candidate responsible for the decrease in $\sigma_{\text{eff,ion}}$ during charging is the degradation of SE at high potentials. Previous studies have demonstrated that electrochemical decomposition of LPSC occurs above its narrow oxidative potential window limit (2.01 V vs. Li^+/Li).^[38] We infer that the resultant low ionic conductivity phases, including various Li-thiophosphates glasses containing PS_4^{3-} , $\text{P}_2\text{S}_7^{4-}$, and $\text{P}_2\text{S}_6^{4-}$ units, restricted macroscopic ionic transport during charging, as illustrated in Figure 5c. On the other hand, these degradation products are known to undergo reversible reduction at low potentials, thereby recovering the $\sigma_{\text{eff,ion}}$ during discharge.^[21] Such reversible redox activity of the degradation products and the associated cyclic changes in $\sigma_{\text{eff,ion}}$ likely causes the formation of asymmetric reaction heterogeneity. Additionally, the volume contraction of sulfur during charge may cause not only a reduction in triple phase boundaries but also partial disruption of ionic conduction pathways, potentially contributing to the decreased $\sigma_{\text{eff,ion}}$ during charging. Thus, our research suggests that the sluggish macroscopic ion transport is not only a standalone issue but is also linked to the electrochemical and microstructural stability of the SE, causing critical problems for SSLSB performance. In other words, the change in the $\sigma_{\text{eff,ion}}$ is a consequence of multi-fold factor, making it to be a universal descriptor for further development.

3. Conclusion

This study demonstrates the utility of XCT for observing macroscopic reaction heterogeneities within composite battery electrodes. Through the development of an experimental setup enabling *operando* synchrotron XCT measurements, we have pioneered visualizing reaction heterogeneities within realistic composite SSLSB cathodes that exhibited stable cyclability and favorable rate capability. Our observation provided direct evidence that macroscopic ion transport within composite cathodes is a critical limiting factor for the rate capability of SSLSBs. More importantly, through XCT visualization, we revealed that this slow macroscopic transport issue is exacerbated during charging, resulting in asymmetric reaction heterogeneities during

(dis)charge cycles, and consequently promoting the irreversible Li_2S formation. The asymmetric macroscopic ion transport limitation appears to be closely related to the electrochemical redox of the SE and/or chemo-mechanical effects, thus necessitating integrated electrode designs that simultaneously ensure efficient ionic transport as well as electrochemical and microstructural stability throughout the electrode.

Supporting Information

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

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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

composite cathode, macroscopic ion transport, *operando* X-ray computed tomography, reaction heterogeneity, solid-state lithium-sulfur batteries

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