

Electrochemical and Spectroscopic Evaluation of $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ Solid Electrolyte in All-Solid-State Batteries

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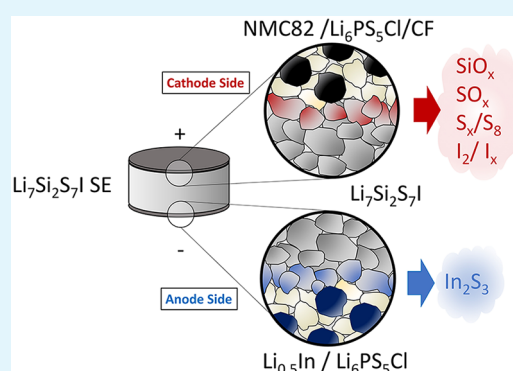
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ABSTRACT: All-solid-state batteries require solid electrolytes with sufficient oxidative and reductive stability; however, the interfacial behavior of emerging silicon-based sulfide electrolytes remains poorly understood. In particular, the electrochemical stability of $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ under practical cell operation and the separate effects of cathode and anode interfaces on performance degradation have not been clarified. Here, we systematically evaluate $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ in $\text{LiNi}_{0.82}\text{Mn}_{0.07}\text{Co}_{0.11}\text{O}_2$ (NMC82) | solid electrolyte | Li-In all-solid-state cells using two- and three-electrode configurations combined with impedance analysis and ex situ Raman and X-ray photoelectron spectroscopy. Three-electrode measurements decouple the interfacial reactions and reveal concurrent interfacial decomposition at both the cathode and anode sides, with dominating effect from the cathode side. Symmetric cell tests using $\text{Li-In}/\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ composite electrodes confirm slight reductive instability against Li-In for $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ as an anolyte. Spectroscopic analysis identifies polysulfides, oxidized iodide, and oxygenated SiO_x and SO_x species at the $\text{Li}_7\text{Si}_2\text{S}_7\text{I}/\text{NMC82}$ interface, as well as In_2S_3 formation at the $\text{Li}_7\text{Si}_2\text{S}_7\text{I}/\text{Li-In}$ interface. Our findings provide mechanistic insight into the interfacial reactions of Si-based sulfide electrolytes and highlight the importance of electrode-decoupled diagnostics for evaluating the compatibility with electrode materials in all-solid-state batteries.

KEYWORDS: all-solid-state batteries, solid electrolyte, $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$, interfacial stability, three-electrode cell, NMC cathode



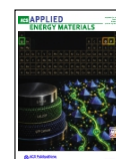
1. INTRODUCTION

All-solid-state batteries (ASSBs) are attractive candidates for next-generation energy storage due to their improved safety and potential for higher energy density enabled by using solid electrolytes (SEs).¹ Achieving practical performance requires SEs with high ionic conductivities at room temperature, good compatibility with high-voltage cathodes, and sufficient reduction stability against anodes.^{2,3} Sulfide-based SEs, such as $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$,⁴ $\text{Li}_7\text{P}_3\text{S}_{11}$,⁵ and argyrodite $\text{Li}_6\text{PS}_5\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$),⁶ are attractive candidates and exhibit high ionic conductivities at room temperature. However, insufficient interfacial compatibility is well recognized in these state-of-the-art SEs, leading to resistive interphases and capacity fading.^{7–11} Among them, $\text{Li}_6\text{PS}_5\text{Cl}$ has been extensively studied together with layered oxide cathode materials.^{12–15} The interfacial instability is related to the intrinsic character of the PS_4^{3-} units and is similarly observed in other thiophosphate-based SEs.^{16,17} Despite efforts on elemental substitution of argyrodites to improve interfacial chemistry,^{18–20} current research suggests the limited impact of this approach on the electrochemical stability,²¹ indicating the need for shifting to alternative structures and compositions while retaining the high ionic conductivity. In all-solid-state batteries using conventional two-electrode configurations, the

capacity fade of the cells arising from both cathode/SE and anode/SE interfaces is convoluted, making it difficult to identify the origin of cell performance loss. Overall, these limitations motivate the search for alternative SE chemistries and the understanding of relevant interfacial processes by decoupling the cathode and anode interfaces.

Recently, a new silicon-based sulfide electrolyte $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ has been developed, exhibiting a high room-temperature ionic conductivity ($\sim 10^{-2} \text{ S cm}^{-1}$) and being composed of earth-abundant elements.^{22,23} The $\text{Si}_2\text{S}_7^{6-}$ -based structural unit in $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$, differing fundamentally from conventional argyrodite electrolytes, is expected to show distinct interfacial chemistry compared to PS_4^{3-} -based electrolytes.^{24,25} This expectation is supported by thiophosphate studies, showing that changes in tetrahedral polymerization alter the local electronic structure

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of P-S units,^{26,27} suggesting that different sulfide connectivities may exhibit different interfacial redox behavior. To date, experimental studies focusing on the stability of Si-containing SEs remain scarce. Hartel et al. explored the performance of $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ as a catholyte using an uncoated $\text{LiNi}_{0.83}\text{Co}_{0.11}\text{Mn}_{0.06}\text{O}_2$ cathode.²⁸ X-ray photoelectron spectroscopy (XPS) analysis revealed the formation of SiO_x species at the $\text{Li}_7\text{Si}_2\text{S}_7\text{I}/\text{LiNi}_{0.83}\text{Co}_{0.11}\text{Mn}_{0.06}\text{O}_2$ interface within the cathode composite, which is associated with performance loss of the cell. In addition, as the catholyte, $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ outperformed $\text{Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}$ when tested in a sulfur cathode, showing that interfacial stability largely depends on active material chemistry and charge cutoff voltage. In all-solid-state batteries, sulfide materials are widely utilized not only as solid electrolytes but also as catholytes to construct composite electrodes. With intimate and high-surface-area contact with the cathode particles, the sulfide catholytes in the cathode/catholyte composites are more prone to oxidative decomposition and interfacial side reactions. Although $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ has been explored as a catholyte, its electrochemical stability when functioning as different components (i.e., separator electrolyte and anolyte) and the corresponding contributions to cell degradation have not been systematically evaluated. Furthermore, cell-level stability is often evaluated using two-electrode cells, which show a convolution of the degradation originating from both the cathode/SE and anode/SE interfaces. Three-electrode cell setups allow deconvolution of impedance and voltage profiles. However, the construction of three-electrode cells in ASSBs is not trivial and requires proper positioning of the reference electrode,^{29,30} the selection of a suitable reference electrode,^{31–35} and the evaluation of the reliability of the reference electrodes for its use in ASSBs.^{32,36,37}

In this work, we systematically investigate the interfacial stability of $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ as the solid electrolyte and anolyte by pairing with a high-Ni layered oxide $\text{LiNi}_{0.82}\text{Mn}_{0.07}\text{Co}_{0.11}\text{O}_2$ (NMC82) cathode and a Li-In composite anode in all-solid-state cells. Three-electrode cells using lithiated Au-reference electrodes, assisted by ex situ Raman and XPS spectroscopy, were used to decouple and quantify the interfacial processes and identify the major origins related to capacity loss and to elucidate the chemical nature of the decomposition products and formation of interphases. The combination of two-electrode, three-electrode, and symmetric cell configurations was deliberately designed to (1) evaluate the electrochemical stability of $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ and its compatibility with different cell components under these distinct roles and (2) decouple the contributions of cathode-side and anode-side degradation, thereby enabling the spatial identification of the dominant interfacial degradation mechanisms. Our findings reveal concurrent oxidative and reductive decomposition from the $\text{Li}_7\text{Si}_2\text{S}_7\text{I}/\text{NMC82}$ and $\text{Li}_7\text{Si}_2\text{S}_7\text{I}/\text{Li-In}$ interfaces, respectively. This study provides direct experimental insight into the interfacial chemistry of silicon-based sulfide electrolytes, elucidating the distinct degradation processes at the cathode and anode interfaces and informing the selection of compatible electrode–electrolyte combinations in all-solid-state batteries.

2. METHODS

2.1. Synthesis of $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$

$\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ was synthesized from a solid-state reaction at 450 °C of a pelletized mixture of Li_2S (Alfa, 99.9%), SiS_2 (MSE Supplies, 99.999%, 5% mol excess of SiS_2), and LiI (Merck, 99.99%), following a reported

procedure.²² Subsequent grinding and reheating at 450 °C were done until a phase-pure material was achieved as determined by Rietveld analysis of X-ray diffraction (XRD) data (Figure S1a).

For comparison, commercial $\text{Li}_6\text{PS}_5\text{Cl}$ (D50 ~1 μm) was obtained from MSE Supplies. The phase purity of $\text{Li}_6\text{PS}_5\text{Cl}$ was verified, showing no secondary phases (Figure S1b). Rietveld analysis results are shown in Table S1. Rietveld refinements were carried out using TOPAS Academic.³⁸

2.2. Preparation of Electrode Composites

Cathode composites were prepared by hand grinding $\text{LiNi}_{0.82}\text{Mn}_{0.07}\text{Co}_{0.11}\text{O}_2$ (NMC82, MSE Supplies, D50 ~3–5 μm), $\text{Li}_6\text{PS}_5\text{Cl}$, and carbon fiber (CF, Merck, >98% carbon basis) in a 70:30:2 mass ratio for 10 min until a homogeneous mixture was obtained. Prior to its use, both NMC82 and CF were dried overnight at 200 °C under vacuum within a Büchi oven.

LiIn alloy was prepared by melting the required amount of Li (Goodfellow, 99.9%) and In (Merck, 99.995%) foils in a stainless-steel crucible, which was heated at 250 °C inside an Ar-filled glovebox (O_2 , H_2O < 1 ppm). $\text{Li}_{0.5}\text{In}$ was prepared by mixing the synthesized LiIn and In powder (Merck, 99.99%) in a 1:1 molar ratio. The $\text{Li}_{0.5}\text{In}$ /anolyte anode composites were prepared by hand grinding $\text{Li}_{0.5}\text{In}$ with either $\text{Li}_6\text{PS}_5\text{Cl}$ or $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ in a 60:40 mass ratio, corresponding to a $\text{Li}_{0.5}\text{In}/\text{SE}$ volume ratio of 31:69 for $\text{Li}_6\text{PS}_5\text{Cl}$ and 36:64 for $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$, respectively. After hand grinding, the phases of the anode composites were analyzed by XRD to confirm that the initial phase structures for both $\text{Li}_6\text{PS}_5\text{Cl}$ and $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ were retained (Figure S2).

2.3. Cell Assembly

For all-solid-state battery tests, an airtight pressure cell with a PEEK liner (6 mm internal diameter) and 90%WC–10%Co plungers were used (Figure S3). Initially, 28 mg of the SE powder was gently pressed, followed by the addition of 6.59 mg of the cathode composite (corresponding to a loading of active cathode material 16 $\text{mg}_{\text{NMC82}}\text{cm}^{-2}$), which was spread evenly on the top of the SE layer. Afterward, the cell was flipped, and 29 mg of the anode composite (62 $\text{mg}_{\text{Li-In}}\text{cm}^{-2}$, corresponding to an anode-to-cathode capacity ratio of 2.2 for the assembled cell) was added. The $\text{Li}_{0.5}\text{In}$ anode remained on the In–LiIn two-phase region during the cycling of the cells. Finally, a pressure of 500 MPa was applied and held for 15 min. For the electrochemical tests, the cell was sealed and taken out of the glovebox, with an applied stack pressure of 100 MPa. Cell details with three different configurations are summarized in Table S2.

2.4. Electrochemical Characterization

The all-solid-state cells were cycled at C/10 (1C = 200 mAh g^{-1}) for NMC82 for the first cycle and then at C/5 for the following 100 cycles (unless otherwise specified) between 2.18 and 3.68 V vs. LiIn (i.e., 2.8–4.3 V vs. Li^+/Li) at 30 °C in a temperature chamber. Voltage hysteresis is calculated from the voltage profiles by taking the difference between average charge and discharge potentials.³⁹ Electrochemical impedance was recorded at the end of each discharge with an AC amplitude of 50 mV from 10^5 to 10 Hz.

For $\text{Li}_{0.5}\text{In}/\text{SE}$ symmetric cells, 28 mg of the SE powder was gently pressed, followed by the addition of 29 mg of the anode composite (62 $\text{mg}_{\text{Li-In}}\text{cm}^{-2}$) on both sides. The cells were tested at 30 °C at 0.64 mA cm^{-2} , matching the current density used in the full cells. Impedance was recorded every 20 h from 10^6 to 0.1 Hz. Distribution of relaxation times (DRT) was obtained from the impedance data using a self-tuning hierarchical Bayesian inversion approach.⁴⁰

2.5. Three-Electrode Cell Measurements

The three-electrode cell measurements were carried out, following the method reported by Hertle et al.³⁷ A gold-coated tungsten wire (Au-coated W) of 50 μm in diameter (Goodfellow) was used as the

reference electrode. The reference electrode was embedded inside $\text{Li}_6\text{PS}_5\text{Cl}$ and then sandwiched between two $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ layers to have a configuration of “ $\text{Li}_7\text{Si}_2\text{S}_7\text{I} \mid \text{Li}_6\text{PS}_5\text{Cl} \mid \text{Au-coated W} \mid \text{Li}_6\text{PS}_5\text{Cl} \mid \text{Li}_7\text{Si}_2\text{S}_7\text{I}$ ” (Figure S4) and assembled as described previously.³⁷ 20 mg of $\text{Li}_6\text{PS}_5\text{Cl}$ and 25 mg of $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ were gently pressed to form “ $\text{Au-coated W} \mid \text{Li}_6\text{PS}_5\text{Cl} \mid \text{Li}_7\text{Si}_2\text{S}_7\text{I}$ ”. Then, 29 mg of the $\text{Li}_{0.5}\text{In} + \text{Li}_6\text{PS}_5\text{Cl}$ anode composite was added on top and pressed at 250 MPa. By flipping the cell, 20 mg of $\text{Li}_6\text{PS}_5\text{Cl}$ and 25 mg of $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ were added, followed by 6.59 mg of the cathode composite. The cell was finally pressed at 500 MPa inside an Ar-filled glovebox. For the electrochemical test, the cell was placed in a temperature chamber at 30 °C under a stack pressure of 100 MPa and then cycled using the same testing protocol used for the two-electrode cells.

Before running the three-electrode cell, the Au-coated W wire was lithiated at 0.003 mA (or 0.318 mA cm^{-2}) for 10 h using the Li sourced from the anode composite, until the AuLi_3/Li plateau was reached at -0.62 V vs. Li-In (0 V vs. Li^+/Li).³⁷ Although some lithium consumption at the $\text{AuLi}_3/\text{Li}_6\text{PS}_5\text{Cl}$ interface cannot be completely excluded,³⁷ the stability of the reference electrode was verified by monitoring its potential over 10 h (Figure S5). To compensate for possible lithium consumption at the $\text{AuLi}_3/\text{Li}_6\text{PS}_5\text{Cl}$ interface during three-electrode operation, the AuLi_3 layer was relithiated twice for 6 h each to replenish the Li layer (after the initial formation cycle at C/10, and between cycles 11 and 12 at C/5). The lithiation of the Au-coated W wire during the whole experiment consumes only about 3% of the lithium content from the anode composite.

At the end of each charge (3.68 V vs. Li-In), the cell was relaxed for 2 h and then the electrochemical impedance was recorded with an AC amplitude of 50 mV from 1 MHz to 50 mHz. The impedance spectra were fitted from 10^5 to 2 Hz using equivalent circuit models involving resistances (R) and constant phase elements (Q). From high to mid frequency, parallel R - Q was used. The impedance spectra were validated using the Kramers–Kronig (KK) relations. Data points above 10^5 Hz were excluded from fitting due to increased KK residuals and distortion of the high-frequency semicircle associated with non-ideal RQ behavior.

2.6. Raman Measurements

The Raman spectra of pristine and ex situ samples were collected by a Raman microscope (inVia reflex, Renishaw) coupled with an inverted microscope (Leica). A 532 nm laser was used as an excitation source. The laser power was lowered to 5% (< 200 μW) and calibrated by an external Si reference. The laser was focused on the surface of the sample by a 50 $\times$ objective lens (Olympus). The spectra were obtained with a 30 s exposure time and one accumulation from 100 to 1000 cm^{-1} . All the samples were sealed inside home-made airtight Raman cells within an argon-filled glovebox before ex situ characterization. These sealed cells, analogous to those commonly used for operando Raman measurements, effectively minimized exposure to ambient air during sample transfer and measurement.

2.7. X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) measurements were performed using a PHI GENESIS spectrometer. Ex situ samples were retrieved from symmetric cells and full cells after electrochemical testing, mounted under an Ar atmosphere, and transferred into the device using an airtight transfer module. A monochromatic Al $K\alpha$ source (1486.6 eV) was employed at 12.5 W power and 15 kV. The X-ray beam had a diameter of nearly 50 μm in an analysis area of 250×250 μm^2 on the non-tilted samples (90° take-off). The pass energy was set to 27 eV (step 0.1 eV) for detailed spectra collection. Prior to analysis, the sample surfaces were cleaned by Ar^+ sputtering (0.5 kV, 20 s) over a 3×3 mm^2 raster area. Charging was effectively compensated during the measurements utilizing low energy electrons and Ar^+ ions (effective 10 eV, 120 V float).

Data analysis was carried out utilizing CasaXPS (version 2.3.27).⁴¹ All binding energies were referenced to the C 1s peak of adventitious

carbon at 284.8 eV. Peak fitting employed a Shirley background and mixed Gaussian/Lorentzian (GL(30)) line shapes using constrained full width at half-maximum (FWHM). For the In/LiIn peaks in the In-3d detailed spectra, a mixed Gaussian/asymmetric Lorentzian (LA(1.2, 1.5, 60)) was used to account for their characteristic line shape.⁴² Spin-orbit coupling was described by fixed splitting of 1.16 eV for S 2p, 0.6 eV for Si 2p, 7.5 eV for In 3d, 1.6 eV for Cl 2p, and 0.84 eV for P 2p, as well as area ratios constrained to $p_{1/2}:p_{3/2}$ 1:2 and $d_{3/2}:d_{5/2}$ 2:3, respectively.

3. RESULTS

3.1. Performance of $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ in All-Solid-State Cells

To understand the interfacial stability of $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ solid electrolytes, three all-solid-state cells were cycled by combining NMC82/ $\text{Li}_6\text{PS}_5\text{Cl}$ /CF composite cathodes and Li-In/anolyte composite anodes (Figure 1). Due to the reported incompatibility between the $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ catholyte and the uncoated NMC cathode,²⁸ in this work, $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ has been studied as an SE layer and an anolyte. Before testing, purity of the commercial $\text{Li}_6\text{PS}_5\text{Cl}$ was verified by Rietveld refinement analysis of X-ray diffraction (XRD) data (Figure S1), showing no secondary phases detected. AC ionic conductivity measurements for commercial $\text{Li}_6\text{PS}_5\text{Cl}$ were carried out after cold pressing at 500 MPa (95% relative density, Figure S6), yielding a total ionic conductivity of 2.54×10^{-3} S cm^{-1} at room temperature and an electronic conductivity of 7.61×10^{-9} S cm^{-1} (Figure S7). The synthesis and property of the phase-pure $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ have been reported previously.²² Prior to the electrochemical evaluation of $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$, $\text{Li}_6\text{PS}_5\text{Cl}$ was used to optimize the cell parameters in a cell configuration of “cathode composite $\mid$ SE $\mid$ anode composite”, hereafter referred to as Cell 1 (Figure 1a). The mass ratios in the cathode composite of NMC82/ $\text{Li}_6\text{PS}_5\text{Cl}$ /CF were optimized by determining the electronic and ionic conductivities of the cathode composite by DC polarization with ion- and electron-blocking electrodes, respectively (Figure S8). An NMC82/ $\text{Li}_6\text{PS}_5\text{Cl}$ /CF mass ratio of 70:30:2 was selected for the cathode composite, as it showed a low ionic tortuosity factor ($\tau^2 = 3.6(3)$), please refer to the Supporting Information for details) with optimized electronic and ionic conductivities of 0.16 and 2.47×10^{-4} S cm^{-1} , respectively (Table S3).^{43–45} A $\text{Li}_{0.5}\text{In}/\text{Li}_6\text{PS}_5\text{Cl}$ mass ratio of 60:40 was fixed for the anode and was not further optimized.³¹ The reproducibility of the cell performance was verified by running a replicate cell (Figure S9a,b).

To evaluate the interfacial properties of $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$, two cells with the NMC82-based cathode composite and $\text{Li}_{0.5}\text{In}$ /anolyte anode composite were constructed, containing $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ solid electrolyte and $\text{Li}_6\text{PS}_5\text{Cl}$ anolyte for Cell 2 and $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ solid electrolyte and $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ anolyte ($\text{Li}_{0.5}\text{In}/\text{SE}$ mass ratio of 60:40) for Cell 3. Detailed compositions for all the cells are summarized in Table S2. The voltage profiles of Cells 2 and 3 are shown in Figure 1b,c. During formation cycles, the cells show a slightly decreased first discharge capacity following the order: Cell 1 (185 mAh g^{-1}) > Cell 2 (180 mAh g^{-1}) > Cell 3 (175 mAh g^{-1}). The Coulombic efficiencies of these cells are ~ 82 – 84% , indicating initial irreversible decomposition of the $\text{Li}_6\text{PS}_5\text{Cl}$ catholyte in the cathode composite during the formation cycles.^{7,11,46} Long-term cycling of Cell 1 shows a capacity retention of 93.4% at the 100th cycle, suggesting a successful cell configuration. The cells containing $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ (Cells 2 and 3) present a more rapid capacity fade than Cell 1 using only

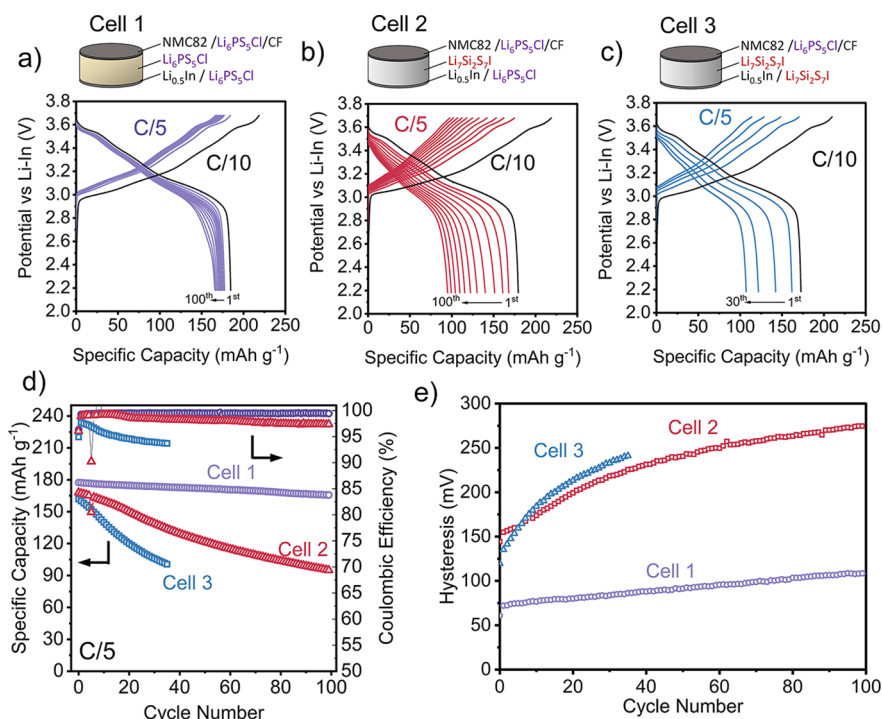


Figure 1. (a–c) Voltage profiles for Cells 1–3, respectively, with cell configurations shown on the top, cycled between 2.18–3.68 V vs. Li-In at 30 °C (1st cycle: C/10, following cycles: C/5, NMC82 mass loading: 16 mg cm⁻²). The profiles are shown every 10 cycles for clarity. (d) Corresponding capacity retention and Coulombic efficiency of the three cells. (e) Voltage hysteresis calculated from the voltage profiles of the cells at C/5.

Li₆PS₅Cl (Figure 1d). As Cell 2 contains Li₇Si₂S₇I only in the SE layer, the performance loss of the cell (a capacity retention of 56.6% at the 100th cycle) is related to the Li₇Si₂S₇I/electrode interfaces. When Li₇Si₂S₇I is also used as an anolyte in Cell 3, the fading becomes more pronounced than that in Cell 2, leading to a capacity retention of 66.2% after 30 cycles. This suggests a poorer interfacial stability of the Li₇Si₂S₇I anolyte with Li_{0.5}In when compared with the Li₆PS₅Cl anolyte.

Furthermore, compared with Cell 1, there is a more pronounced increase in voltage hysteresis for Cells 2 and 3 (Figure 1e). The small difference in initial voltage hysteresis between Cells 2 and 3 is likely related to the intrinsic sensitivity of solid-state cells to interfacial conditions, as subtle variations in electrode–electrolyte contact and local reaction environments can affect the observed electrochemical response. The impedance of the cells recorded at each discharge cycle shows an increase of the interfacial resistance over cycling (Figure S10), following a parabolic rate law for Cells 2 and 3. Such tendency agrees with the observed results of the increase in potential hysteresis, suggesting that the voltage hysteresis is mainly caused by the Li₇Si₂S₇I/electrode interfacial resistance. As such, although Li₇Si₂S₇I has been validated to function as an SE within these cells, the interfacial effects limit the cyclability of the cells when compared with Li₆PS₅Cl. Next, the nature of the electrode interfaces will be investigated to understand the dominant degradation mechanisms.

3.2. Three-Electrode Cell

To deconvolute the respective effects of the cathode and anode interfaces on cell performance degradation, a three-electrode cell was constructed following the procedure reported by Hertle et al.³⁷ Initially, the optimization of the Au reference

electrode was carried out using Li₆PS₅Cl with a cell configuration “Li_{0.5}In + Li₆PS₅Cl | Li₆PS₅Cl | Au-coated W | Li₆PS₅Cl | NMC82 + Li₆PS₅Cl + CF” (Figure S12a,b). For operational stability of the reference electrode, we chose the plateau of −0.62 V vs. Li-In, corresponding to the Li₃Au intermetallic phase.²⁸

The capability to separate the anode and cathode potentials from the three-electrode cells allows the understanding of the capacity fading in Cell 2 (Figure 2a). The anode-side overpotential at the end of discharge (i.e., anode stripping) is more pronounced than that observed during charging and gradually increases with cycling time. This is likely related to the combined effect of partial contact loss and formation of In-rich domains (with low Li⁺ diffusion) during delithiation of the Li_{0.5}In alloy, as it has been reported in other studies.^{47,48} Additionally, the progressive increase in overpotential from both electrodes during cycling indicates the increase of interfacial resistance both at the cathode and anode sides. The increased overpotential upon cycling limits the depth of charge/discharge and accordingly leads to a decrease in accessible capacity.⁴⁷ This can be seen from the trend in the end potentials for charge and discharge shown in Figure 2b. As a result, for the cathode, the end charge potential drifts about −41.4 mV and the end discharge potential drifts about +90.8 mV, limiting the effective potential window for (de)lithiation of the cathode and eventually the accessible capacity of the cell (please refer to the Supporting Information for further discussion).

To understand the origin of the overpotential, impedance from the three-electrode cell over 15 cycles was collected at the end of charge and fitted from 5 × 10⁵ to 2 Hz using two (RQ) circuits in series (Figure S13a). The assignment of each

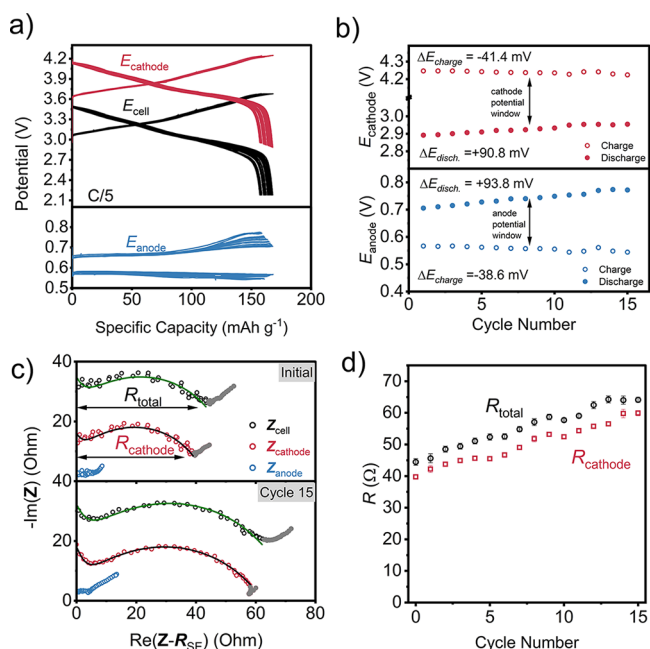


Figure 2. (a) Voltage profiles of the three-electrode cell with “Li_{0.5}In + Li₆PS₅Cl | Li₇Si₂S₇I | Li₆PS₅Cl | Au-coated W | Li₆PS₅Cl | Li₇Si₂S₇I | NMC82 + Li₆PS₅Cl + CF” configuration cycled between 2.18–3.68 V vs. Li-In at 30 °C: overall (black), cathode (red) and anode (blue). (b) Cathode (top) and anode (bottom) potentials at the end of the charge/discharge over cycling. (c) Three-electrode impedance of overall cell (black), cathode (red), and anode (blue) for the 1st and 15th cycles. For clarity, the real part is calibrated by subtracting the resistance of the electrolyte layer (R_{SE}). Solid lines show the impedance fitting. Gray points are excluded for the fitting. (d) Evolution of R_{total} and R_{cathode} over 15 cycles at C/5. R_{total}: total interfacial resistance coming from the cathode and anode interfaces. R_{cathode}: interfacial resistance from cathode interfaces only.

process at different frequency ranges is based on previous studies.^{49–52} The low frequency tail (<2 Hz) is related to diffusion processes from both electrodes. The high-frequency region (>10⁵ Hz) contains the contribution of the SE (with capacitance, C ≈ 10⁻¹⁰ F). As the Au reference electrode is positioned in the middle of the multilayer separator Li₇Si₂S₇I|Li₆PS₅Cl|Li₇Si₂S₇I, dividing it into two approximately equal parts, the total resistance of the multilayer SE (R_{SE}^{cell}) is about twice the resistance of the R_{SE}^{cathode} (R_{SE}^{cell} ≈ 2R_{SE}^{cathode}, Figure S12b). Over cycling, both R_{SE}^{cell} and R_{SE}^{cathode} increase due to the interfacial reaction between Li₆PS₅Cl and Li₇Si₂S₇I (Figure S13b). A symmetric cell with the configuration “current collector | Li₇Si₂S₇I | Li₆PS₅Cl | Li₇Si₂S₇I | current collector” further confirms this interfacial degradation (Figure S14). Chemical incompatibility between different SEs has been previously reported in previous studies.^{53,54} The mid-frequency region (10⁵ to 2 Hz) is related to the interfaces on both the cathode and anode sides (R_{total}, C ≈ 8 × 10⁻⁶ F, Figure 2c). The total interfacial impedance (R_{total}) is dominated by the impedance at the cathode side (R_{cathode}), showing +34% increase in R_{cathode} after 15 cycles (Figure 2d). As such, the observed potential drifts in Figure 2b are most likely dominated by interfacial instability at the Li₇Si₂S₇I/NMC82 interface. However, additional degradation processes, including mechanical contact loss, particle fracture, or microstructural

evolution, may also contribute to the observed capacity fade.⁴⁹ The capacity trend of the three-electrode cell is consistent with that of Cell 2, which features the same SE-layer/electrode interfaces, and is therefore considered representative of the interfacial evolution occurring at the Li₇Si₂S₇I interfaces (Figure S9c,d).

3.3. Li_{0.5}In-Anolyte |SE| Li_{0.5}In-Anolyte Symmetric Cells

To further corroborate the instability of Li₇Si₂S₇I found at the anode side, galvanostatic cycling of the “Li_{0.5}In + Li₇Si₂S₇I | Li₇Si₂S₇I | Li_{0.5}In + Li₇Si₂S₇I” symmetric cell was performed at 30 °C (Figure 3a). Li₆PS₅Cl was used for comparison in the same cell configuration. The cell was tested at 0.64 mA cm⁻², matching the current density in operating the all-solid-state cells as discussed above. The voltage profiles showed a steady increase in overpotential for both Li₇Si₂S₇I and Li₆PS₅Cl. Moreover, compared with Li₆PS₅Cl, Li₇Si₂S₇I shows higher plating/stripping overpotential and faster increase in overpotential over cycling (Figure 3b). The evolution of the impedance of the cells was recorded every 20 h during cycling (Figure S16). To identify potential interfacial contributions, the distribution of relaxation times (DRT) was evaluated using a self-tuning hierarchical Bayesian inversion approach (eq 1):

$$Z(\omega) = \int_0^{\infty} \frac{\gamma(\ln\tau)}{1 + j\omega\tau} d\tau \quad (1)$$

where Z(ω) is the measured impedance, and γ(lnτ) represents the distribution of relaxation time τ. The DRT analysis reveals that Li₇Si₂S₇I is less stable against Li_{0.5}In, as evidenced by a growing contribution in the relaxation time range of 10⁻² to 10⁰ s. Based on previous DRT analyses of In/LiIn-containing solid-state batteries, responses between 10⁻² and 10⁰ s are associated with charge transfer at the Li-In/SE interface.^{55,56} DRT peaks above 1 s correspond to low-frequency diffusion response. The corresponding interfacial resistance versus time for both cells is displayed in Figure 3c, which increases linearly with time showing a slope of 0.33 Ω h⁻¹ for Li₇Si₂S₇I and 0.05 Ω h⁻¹ for Li₆PS₅Cl. By focusing on the role of the anolyte materials and SE/Li_{0.5}In interfaces in both symmetric cells, this experiment explains the different capacity fading behavior observed between Cell 2 and Cell 3.

Raman spectroscopy was performed on Li_{0.5}In/anolyte anode composites before (hand-ground mixture) and after cycling in both full (Figure S17) and symmetric cells (Figure 3d,e). After hand grinding, Raman bands from Li_{0.5}In (a weak band centered at 120 cm⁻¹) and SE can be resolved (Figure 3d,e).⁵⁷ For the hand-ground Li_{0.5}In + Li₆PS₅Cl (Figure 3d), the intense band located at 421 cm⁻¹ corresponds to the A₁ symmetric stretching mode of the PS₄³⁻ tetrahedra in Li₆PS₅Cl.⁸ Additional bands at 314 and 346 cm⁻¹ (marked with *) can be tentatively assigned to In-containing decomposition products, such as In₂S₃ or InCl₃.^{57,58} The presence of these bands even before cycling indicates chemical instability between Li₆PS₅Cl and Li_{0.5}In. The hand-ground Li_{0.5}In + Li₇Si₂S₇I shows the presence of the main band at 383 cm⁻¹ related to Si₂S₇⁶⁻ units in Li₇Si₂S₇I.²² Additionally, a shoulder at 273 cm⁻¹ reveals the formation of a secondary phase due to the reaction between Li₇Si₂S₇I and Li_{0.5}In. XRD analysis on the hand-ground composites (Figure S2) shows that the bulk structures of Li₆PS₅Cl and Li₇Si₂S₇I remain after grinding,

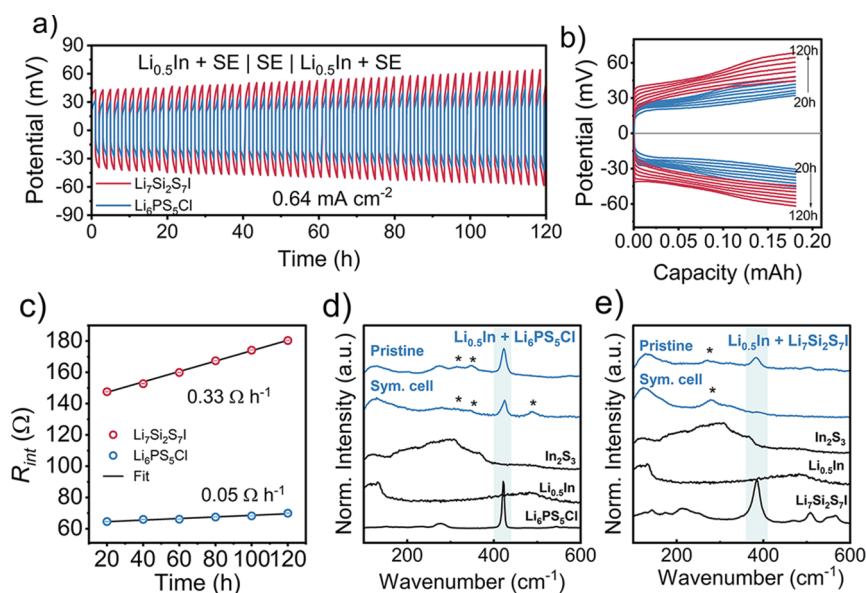


Figure 3. (a) Plating/stripping tests of $\text{Li}_{0.5}\text{In}$ -anolyte |SE| $\text{Li}_{0.5}\text{In}$ -anolyte symmetric cells at 0.64 mA cm^{-2} and 30°C , containing $\text{Li}_6\text{PS}_5\text{Cl}$ and $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$. (b) Overpotential of the cells, showing data every 20 h. (c) Evolution of the interfacial resistance (R_{int}) of the cells. (d, e) Raman spectra of the $\text{Li}_{0.5}\text{In}$ + anolyte anode composites before and after cycling in the symmetric cell for $\text{Li}_6\text{PS}_5\text{Cl}$ and $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$, respectively. In_2S_3 , InCl_3 , $\text{Li}_{0.5}\text{In}$, $\text{Li}_6\text{PS}_5\text{Cl}$, and $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ are shown as references. Asterisks indicate new species formed, while shadowed regions indicate the main Raman bands for the SEs.

indicating that the degradation only occurs at the $\text{Li}_6\text{PS}_5\text{Cl}/\text{Li}_{0.5}\text{In}$ and $\text{Li}_7\text{Si}_2\text{S}_7\text{I}/\text{Li}_{0.5}\text{In}$ interfaces.

After cycling in both full cells (Figure S17) and symmetric cells (Figure 3d,e), the most prominent band of the anolyte remains for $\text{Li}_6\text{PS}_5\text{Cl}$ (421 cm^{-1}) but disappears for the $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ -based composite (383 cm^{-1}). This suggests that the decomposition layer formed on $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ particles upon prolonged contact with $\text{Li}_{0.5}\text{In}$ is of greater thickness than for $\text{Li}_6\text{PS}_5\text{Cl}$, hiding the main $\text{Si}_2\text{S}_7^{6-}$ band. The decomposition layer might be amorphous,^{7,59} which cannot be resolved by Raman. A new band at 488 cm^{-1} appears in the $\text{Li}_6\text{PS}_5\text{Cl}$ composite and suggests the presence of S-S bonding within thiophosphate-derived interfacial species, such as S-S-bridged P-S environments.⁶⁰

To obtain chemical information about degradation products at the SE- $\text{Li}_{0.5}\text{In}$ interface, XPS from the cycled symmetric cells was collected on the composite electrodes. The surface of the samples was sputtered to remove surface contamination formed during storing and handling of the samples in the glovebox. Figure 4 shows the In-3d and S-2p spectra of the composites after cycling at 0.64 mA cm^{-2} compared to the pristine $\text{Li}_{0.5}\text{In}$, $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$, and $\text{Li}_6\text{PS}_5\text{Cl}$. Additional XPS traces for Cl 2p and P 2p for $\text{Li}_6\text{PS}_5\text{Cl}$, and I 3d and Si 2p for $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ can be found in Figure S18. The In 3d spectrum of the pristine $\text{Li}_{0.5}\text{In}$ alloy shows mainly one doublet characteristic of Li_xIn alloy phases (441.8 and 449.3 eV , Figure 4a).⁶¹ After cycling, the $\text{Li}_{0.5}\text{In}/\text{Li}_6\text{PS}_5\text{Cl}$ composite shows additional components, which are in line with the formation of In_2S_3 (445.0 and 452.5 eV)⁶² and InCl_3 (446.3 and 453.8 eV).⁶³ The formation of InCl_3 is further supported by the Cl 2p trace (Figure S18),⁶⁴ showing a different Cl environment than the Cl^- anion in $\text{Li}_6\text{PS}_5\text{Cl}$ (198.6 and 200.2 eV) or LiCl , which appear at the same binding energy.⁶⁵ The $\text{Li}_{0.5}\text{In}/\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ composite also showed an additional In 3d component at higher binding energies supporting the formation of In_2S_3

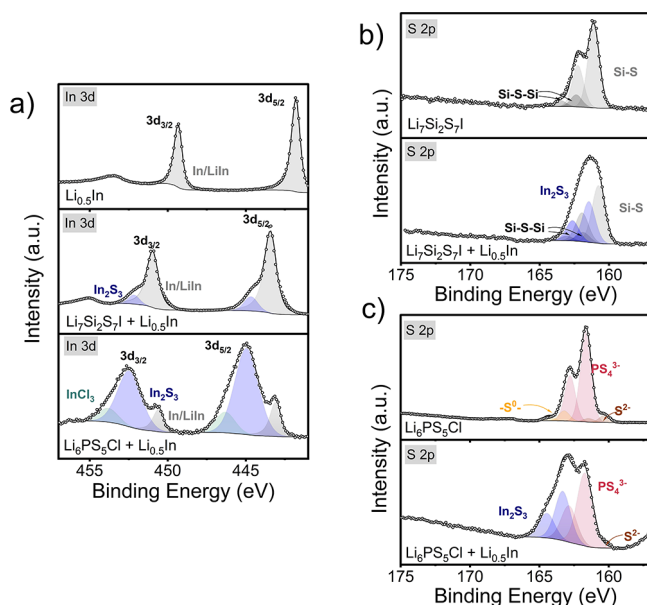


Figure 4. Fitted XPS spectra of $\text{Li}_{0.5}\text{In}$ -anolyte |SE| $\text{Li}_{0.5}\text{In}$ -anolyte symmetric cells after cycling at 0.64 mA cm^{-2} and 30°C , containing $\text{Li}_6\text{PS}_5\text{Cl}$ and $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$: (a) Comparison between In 3d detailed spectra of $\text{Li}_{0.5}\text{In}/\text{SE}$ composite anodes after cycling with pristine $\text{Li}_{0.5}\text{In}$ and (b, c) comparison between S 2p detailed spectra of $\text{Li}_{0.5}\text{In}/\text{SE}$ composite anodes of symmetric cells with pristine SEs.

(444.7 and 452.2 eV), in agreement with Raman band assignment. Both composites showed a shift of the In 3d signal of the Li-In alloy toward higher binding energies relative to the pristine $\text{Li}_{0.5}\text{In}$ alloy. This may arise from a decrease in the lithium content of the alloy due to the reductive side reactions with the SE. Previous XPS studies have demonstrated that increasing

lithiation of Li-In alloy phases results in a shift of the In 3d signal toward lower binding energies. Therefore, a loss of lithium from the alloy would be expected to shift the In 3d peak toward higher binding energies.^{66–68}

The S 2p spectra of the cycled $\text{Li}_{0.5}\text{In}/\text{Li}_6\text{PS}_5\text{Cl}$ composite reveal new shoulders appearing at higher binding energies corresponding to the In_2S_3 phase (163.3 and 164.4 eV)⁶² in addition to the signals due to free S^{2-} (160.0 and 161.1 eV) and PS_4^{3-} (161.7 and 162.9 eV) in $\text{Li}_6\text{PS}_5\text{Cl}$ (Figure 4b).⁶⁵ Additionally, P 2p reveals the presence of reduced phosphorus environments (130.0 and 130.8 eV, Figure S18) originated from the reduction of P(+V) in $\text{Li}_6\text{PS}_5\text{Cl}$ that is reported to take place close to the working potential of the Li-In anode.^{7,69} The comparatively improved interfacial stability of $\text{Li}_6\text{PS}_5\text{Cl}$ may be related to the formation of an interphase containing ionically conductive Li_3P , as previously reported for $\text{Li}_6\text{PS}_5\text{Cl}$ in contact with lithium metal.⁶⁹ Such an interphase may help maintain interfacial Li^+ transport and mitigate impedance growth despite the occurrence of ongoing interfacial reactions. In a similar way, the S 2p trace from $\text{Li}_{0.5}\text{In}/\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ composites shows a shoulder attributed to In_2S_3 overlapping with the bridging and terminal sulfide signals in $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$. No substantial change was observed for Si 2p and I 3d after cycling (Figure S18), indicating the absence of reduced Si species and I^- -containing decomposition products. The remaining Si-S contribution in the XPS spectra may be related to an amorphous decomposition layer containing Si-S fragments at similar binding energies, rather than preservation of the original $\text{Si}_2\text{S}_7^{6-}$ structural motif. Overall, the XPS results support the conclusion that reductive contact with $\text{Li}_{0.5}\text{In}$ induces the decomposition of $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$, leading to the formation of an indium sulfide-rich

interphase. Together with the suppression of the Raman-active $\text{Si}_2\text{S}_7^{6-}$ band after cycling and the rapid increase in interfacial resistance observed in symmetric cells, these results indicate substantial interphase growth and progressive passivation of $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ at the anode side.

3.4. Ex Situ Analysis on the Full Cells

Ex situ Raman spectra were recorded for Cell 2 and Cell 3 to understand the changes in the cell components (Figures 5 and S17). As the cathode composite is the same for both cells, both spectra in Figure S17a,c showed similar characteristic bands of PS_4^{3-} in $\text{Li}_6\text{PS}_5\text{Cl}$ (421–425 cm^{-1}) and $A_{1g} + E_g$ modes of NMC82 (350–700 cm^{-1}).⁷⁰ Shifts toward lower wavenumber values (417 cm^{-1}) of the PS_4^{3-} band of the $\text{Li}_6\text{PS}_5\text{Cl}$ particles were observed, indicating the formation of Li_3PS_4 due to the decomposition of $\text{Li}_6\text{PS}_5\text{Cl}$.⁷ Additionally, the formation of S_8 was observed with characteristic bands at 154, 219 (S-S-S bending), and 471 cm^{-1} (S-S stretching),^{71–73} agreeing with previous reports.^{7,9,11}

To study the cathode/SE interfaces, the surface of the SE layer facing the cathode (delaminated cathode layer after cell disassembly) is selected for Raman analysis (Figure 5a,b). In Cell 2, the absence of the Raman band of the $\text{Si}_2\text{S}_7^{6-}$ units at 386 cm^{-1} indicates the degradation of $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ (Figure 5a). Additionally, a broad band centered at 459 cm^{-1} is consistent with sulfur-rich (S_x) polysulfide species formed at high oxidation potentials over 100 cycles at C/5.^{9,28} The remaining bands denoted by asterisks could be related to the formation of oxidized iodide species (e.g. I_5^- or I_2), known to form in solid-state systems through oxidation of I^- ,⁷⁴ or oxygenated phases (e.g., containing SO_x or $\text{SiS}_{4-x}\text{O}_x$ units) formed at the interface

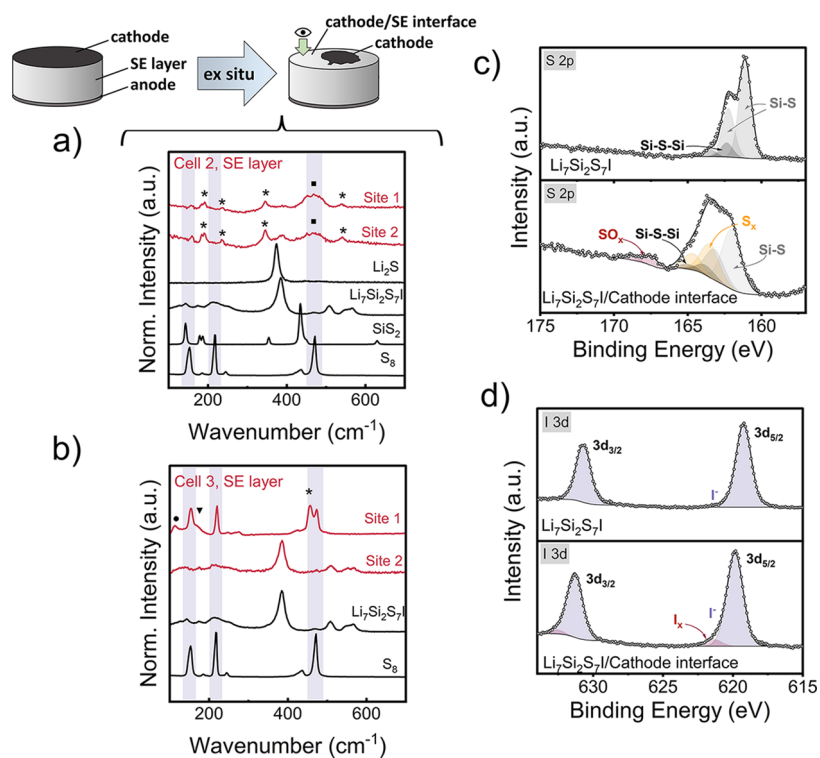


Figure 5. Ex situ spectroscopic analysis of the cathode-SE layer interface of Cells 2 and 3. Raman spectra of (a) Cell 2 and (b) Cell 3. Asterisks indicate new unidentified bands while $\blacksquare$, $\bullet$, and $\blacktriangledown$ symbols indicate assigned bands from S_x , I_3^- , and I_5^- , respectively. XPS spectra of the pristine $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ and $\text{Li}_7\text{Si}_2\text{S}_7\text{I}/\text{cathode interface}$ of Cell 2 after the electrochemical cycling in Figure 1 (c) S 2p spectra and (d) I 3d spectra.

with NMC82 as found in thiophosphate-based cathode composites.⁹ Alternatively, they may originate from other Li-Si-S-I phases generated during oxidation; however, comparison with reported Li-Si-S phases does not permit a definitive assignment.⁷⁵ Cell 3, in contrast, showed S_8 coming from the oxidation of the sulfide SE, together with low-frequency bands at 112 and 166 cm^{-1} , which are tentatively assigned to polyiodide species I_3^- and I_5^- , respectively (Figure 5b). Due to its shorter cycle life (36 cycles), less deterioration of the $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ SE at the interface was identified, being possible to locate the characteristic $\text{Si}_2\text{S}_7^{6-}$ signal at some points of the interface.

The anode composite of Cell 2 has a similar Raman spectrum to those observed for the Li-In symmetric cells with $\text{Li}_6\text{PS}_5\text{Cl}$, featuring bands at $\sim 120\text{ cm}^{-1}$ corresponding to $\text{Li}_{0.5}\text{In}$ and at $\sim 300\text{ cm}^{-1}$ related to the In_2S_3 decomposition product (Figure S17b). The doublet at 457 and 480 cm^{-1} denoted with asterisks has not been identified. The anode composite of Cell 3 showed a complete disappearance of $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ bands (Figure S17d), which likely accounts for the rapid capacity fading observed in Figure 1d.

The $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ /cathode interface of Cell 2 was also studied by XPS (Figures S5c,d and S19). S 2p suggests the presence of both polysulfide species (163.5 and 164.7 eV)⁹ and sulfate/sulfite groups (167.5 and 168.8 eV) due to the oxidation of sulfur.⁶⁵ Interestingly, the I 3d reveals the formation of oxidized iodine species (621.3 and 632.7 eV), consistent with the possible formation of I_2/I_3^- upon cycling, which has been proposed as a redox mediator in Li-S ASSB.⁷⁶ Although the shift of the I 3d peak after cycling could be consistent with changes in the local iodide environment, the similar binding energies of iodide in $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ and LiI prevent unambiguous identification of LiI formation from XPS alone.⁷⁷ Oxygen-containing sulfur species are also suggested by the additional characteristic signal (531.0 eV) in the O 1s trace.⁷⁸ Si 2p revealed the formation of SiO_x species (102.2 and 102.8 eV), as indicated in the previous $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ study,²⁸ which is likely related to the impedance rise in the cathode interface. This observation, together with the attenuation of the $\text{Si}_2\text{S}_7^{6-}$ Raman signature after cycling, is consistent with oxidation-induced breakdown of the Si-S-Si connectivity.

Overall, the combined electrochemical and spectroscopic results demonstrate that $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ undergoes both reductive and oxidative decomposition against $\text{Li}_{0.5}\text{In}$ and NMC82, respectively, which leads to an increase in interfacial resistance and eventually accelerated capacity fade and increased voltage hysteresis in both Cells 2 and 3. Three-electrode measurements are effective to decouple these interfacial reactions at the cathode and anode interfaces. Spectroscopic evidence from Raman and XPS suggests polysulfide formation at the cathode side, alongside the emergence of decomposition products tentatively assigned to oxygenated SiO_x and SO_x species, as well as oxidized iodine species.

The proposed reaction pathways hypothesized from spectroscopic evidence are summarized by the schematic in Figure 6. Together, these results directly link spatially separated interfacial chemistry to apparent electrochemical performance, such as interfacial impedance, voltage polarization, and capacity loss in all-solid-state batteries. Although ex situ Raman and XPS provide valuable insights into the chemical evolution of cycled electrodes, they cannot fully distinguish species formed during electrochemical cycling from those arising during relaxation or post-mortem processes. Therefore, the observed sulfur-, oxygen-, silicon-, and iodine-related signatures are considered

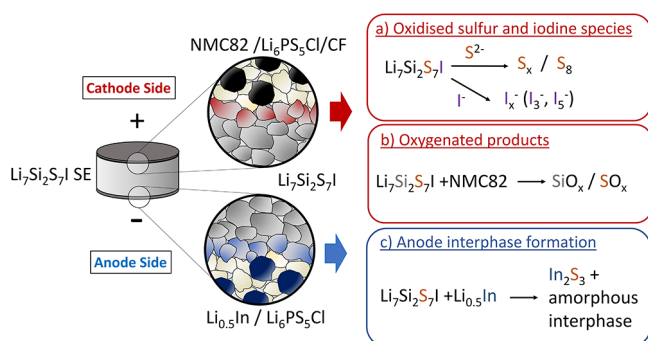


Figure 6. Proposed dominant degradation processes of $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ at the cathode and anode facing interfaces during cycling. The pathways are proposed based on the Raman and XPS analyses and are intended to illustrate the dominant degradation processes rather than balanced overall reaction mechanisms. (a) Oxidation of $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ at the cathode-facing interface, leading to oxidation of sulfide and iodide species. (b) Decomposition promoted by contact with the NMC82 cathode, resulting in the formation of oxygenated sulfur and silicon species (SO_x and SiO_x) and progressive degradation of the $\text{Si}_2\text{S}_7^{6-}$ framework. (c) Reductive decomposition of $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ at the $\text{Li}_{0.5}\text{In}$ -facing interface, involving the formation of In_2S_3 together with additional amorphous thiosilicate-derived decomposition products.

evidence for the involvement of these chemical species, while specific phase assignments and reaction pathways remain tentative. Operando techniques will be valuable for directly tracking species evolution, minimizing potential air expose during handling, and further validating the proposed mechanism.

In summary, these findings highlight three key interfacial design strategies for earth-abundant Si-based sulfide electrolytes: suppressing cathode-side oxidation of sulfide, iodide, and thiosilicate species; regulating iodide redox activity under high-voltage operation; and forming anode interphases that are ionically conductive yet electronically insulating. Cathode coatings, interlayers, or catholyte designs that minimize S_x/SO_x , SiO_x , and oxidized iodine formation, together with anode protection strategies that suppress reductive decomposition and In_2S_3 formation, will be critical for enhancing the stability of silicon-containing SEs.

4. CONCLUSIONS

The performance of silicon-based sulfide electrolyte $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ was investigated as the SE layer and anolyte in cells with the NMC82 cathode and Li-In anode. By combining two-electrode cycling, three-electrode diagnostics, symmetric cells, and spectroscopic analysis, we decoupled the degradation pathways and quantified their respective contributions. Our results demonstrate that $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ undergoes both oxidative decomposition at the $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ /NMC82 interface and reductive instability against $\text{Li}_{0.5}\text{In}$, with progressive interfacial resistance growth at both electrodes. Importantly, three-electrode analysis reveals that cathode impedance constricts the effective potential window, thereby exacerbating the apparent capacity fade. Raman and XPS suggest polysulfide formation at the cathode side, alongside the emergence of decomposition products tentatively assigned to oxygenated SiO_x and SO_x , and oxidized iodine species. At the anode side, the formation of In_2S_3 and the attenuation of the $\text{Si}_2\text{S}_7^{6-}$ bands indicate surface degradation of $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$. These findings elucidate the electrochemical stability

limits of thiosilicate-based electrolytes and highlight that interface decoupling is essential for accurate electrochemical evaluation when selecting compatible electrode–electrolyte combinations in all-solid-state batteries.

■ ASSOCIATED CONTENT

Data Availability Statement

The data that support the findings of this research will be made openly available via the University of Liverpool open research platform Liverpool Elements on acceptance of the publication.

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsaem.6c01833>.

XRD analysis of the SEs and $\text{Li}_{0.5}\text{In}$ /anolyte composites, cell setup, lithiation profile of the Au reference electrode, AC/DC conductivity data on the SEs, DC conductivity, and tortuosity factor analysis of the NMC82/ $\text{Li}_6\text{PS}_5\text{Cl}$ /CF cathode composite, evolution of interfacial resistance on Cells 1–3 during cycling, voltage trace of the three-electrode cells, additional impedance data from the three-electrode cell of Figure 2, $\text{Li}_7\text{Si}_2\text{S}_7\text{I}/\text{Li}_6\text{PS}_5\text{Cl}$ interfacial stability test, DRT evolution of the $\text{Li}_{0.5}\text{In}$ /anolyte symmetric cells, ex situ Raman spectra on cycled Cells 2 and 3, XPS detail spectra of the SEs and the $\text{Li}_{0.5}\text{In}$ /anolyte composites after cycling in symmetric cells (Cl 2p, P 2p, I 3d, and Si 2p), and XPS detailed spectra of pristine $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ and at the cathode/SE layer interface after cycling in Cell 2 (O 1s and Si 2p) (PDF)

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Notes

The authors declare no competing financial interest.

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