

Early Onset Degradation Mechanism in All Solid-State Batteries Revealed by Operando Photoelectron Spectroscopy

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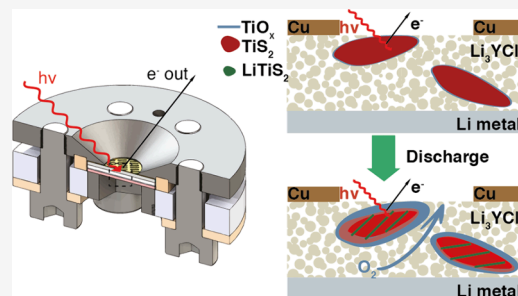


Article Recommendations



Supporting Information

ABSTRACT: Solid-state batteries (SSBs) promise enhanced safety and energy density, yet their long-term stability is limited by poorly understood interfacial degradation. Here, we perform *operando* hard X-ray photoelectron spectroscopy (HAXPES) on device-relevant structures, enabling depth-resolved probing of electrodes during cycling to follow lithiation and interfacial degradation processes in $\text{TiS}_2/\text{Li}_3\text{YCl}_6$ half cells. We identify a reduction process for Li_3YCl_6 . Concurrently, oxygen-containing species are found to migrate toward the cathode current collector, where they react with TiS_2 to form an amorphous TiO_x layer that contributes to capacity fade during extended cycling. Depth-dependent measurements confirm that oxygen enrichment is localized near the surface, establishing a kinetically driven degradation pathway linked to electron injection during discharge. These insights reveal how electrochemically induced migration of oxygen-containing species and interfacial redox can drive degradation in SSBs, providing a mechanistic basis for strategies to improve interfacial stability and cycling performance.



Solid-state batteries (SSBs) are strong contenders for next-generation lithium-ion batteries (LIBs) due to their potential for higher energy and power densities alongside improved safety. These advantages arise from replacing flammable liquid electrolytes with solid ones, enabling the use of lithium metal anodes and bipolar stacking.¹ One challenge of using solid electrolytes is, however, the need for high stacking pressures during operation (up to 70 MPa)² to maintain electrode–electrolyte contact despite cracking or volume changes during (de)lithiation. Probing SSBs under operating conditions is a prerequisite for obtaining relevant information because *post-mortem* analysis can introduce structural and chemical artifacts due to relaxation effects or reaction with residual gases, among others.

While one of the grand challenges in SSB development is to minimize the applied stacking pressure, most new material systems are still investigated under high mechanical loading. These pressures complicate both cell integration at the device level and *in situ* analysis, as they limit access to buried interfaces where degradation occurs. Developing *operando* methods capable of distinguishing surface and buried interface reactions is therefore critical to understand degradation mechanisms limiting SSB performance.

X-ray photoelectron spectroscopy (XPS) is widely used to determine chemical states in electrodes, but its limited probing depths (e.g., maximal 5–10 nm when using $\text{Al K}\alpha$ excitation, $h\nu = 1487.6$ eV) often necessitates sputtering to expose underlying layers, which can induce amorphization, preferentially remove light elements, or cause evaporation of volatile

species such as sulfur under ultrahigh vacuum (UHV) conditions.^{3,4} These artifacts complicate the interpretation of chemical changes at buried interfaces. Hard X-ray photoelectron spectroscopy (HAXPES) overcomes this limitation by employing high energy X-rays that extend the inelastic mean free path of photoelectrons to the order of ten nanometers⁵ and the information depth to multiples of that value, allowing nondestructive access to buried interfaces under realistic conditions.

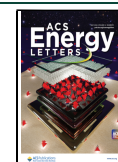
We recently reported a sample environment enabling *operando* HAXPES of solid-state electrochemical cells under applied pressure, which we used to track solid electrolyte interphase (SEI) formation during lithium plating and stripping in lithium symmetric cells with $\text{Li}_6\text{PS}_5\text{Cl}$.⁶ Previous *operando* HAXPES investigations have focused on thin-film or composite oxide cathodes such as LiCoO_2 or Li_2MnO_3 ,^{7–10} and more recently Ni-rich NCM,¹¹ but sulfide-based electrodes have so far remained unexplored. Using TiS_2 as an active material and Li_3YCl_6 as the solid electrolyte, we extend *operando* HAXPES analysis to conventional bulk electrodes in a metal sulfide-based solid-state lithium half-cell.

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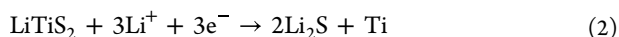
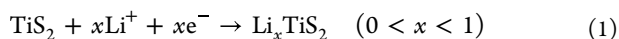
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Here, we employ *operando* HAXPES to investigate electrochemically driven processes in a $\text{TiS}_2|\text{Li}_3\text{YCl}_6$ solid-state half-cell at relevant stacking pressure. We followed the evolution of both the active material and the solid electrolyte during cycling. The measurements reveal reduction of the halide solid electrolyte and concurrent modification of TiS_2 , including migration of oxygen-containing species toward the cathode current collector and formation of TiO_x species. The oxygen-containing species are hypothesized to originate from oxygen-containing interfacial species present within the assembled cell, such as those associated with the surface of the solid electrolyte or other intrinsic oxygen-containing impurities associated with the cell components. This finding identifies a kinetically driven interfacial degradation pathway that contributes to long-term capacity loss, highlighting the ability of HAXPES to disentangle complex interface and bulk reactions in mechanically confined electrochemical systems.

TiS_2 , first investigated by Wittingham in 1975,^{12,13} remains a well-characterized, model intercalation material due to its high specific capacity and electronic conductivity. This makes it an ideal model system for isolating interfacial chemistry without additional variables present in more complex cathode compositions. Furthermore, sulfide-based electrodes more broadly attract significant interest due to their favorable Li^+ diffusion kinetics and improved compatibility with sulfide solid electrolytes compared to oxide cathodes, where oxygen evolution is a known source of interfacial degradation.^{14,15} During lithiation, TiS_2 first undergoes a solid solution mechanism accommodating up to one Li per formula unit ($q_{\text{th}} = 239 \text{ mAh g}^{-1}$, eq 1). Further lithiation can lead to a conversion reaction ($q_{\text{th}} = 680 \text{ mAh g}^{-1}$, eq 2), but in practical cells only the solid solution region is used.^{16,17}



TiS_2 and its lithiated intermediates have high electronic conductivities, which can be modified by controlling the sulfur defect density.¹⁸ This allows TiS_2 electrodes to be assembled without conductive additives, which is beneficial from a characterization perspective for maximizing the spectral intensity of the active material.

The solid electrolyte, Li_3YCl_6 , was chosen to enable clear chemical distinction between active material and electrolyte species. While sulfide cathode active materials (CAMs) are typically paired with sulfide solid electrolytes (SEs) due to their high ionic conductivities and chemical and mechanical compatibility, the presence of common elements complicates XPS analysis. In contrast, Li_3YCl_6 offers high ionic conductivity and oxidative stability alongside a composition that is chemically distinct from TiS_2 . Although halide-based solid electrolytes are known to exhibit limited reduction stability against Li metal, where they form thick and resistive solid electrolyte interphases (SEIs) due to continuous reaction during cycling,^{19,20} their compositional simplicity and oxidative stability make them ideal model systems for probing interfacial redox reactions in SSBs. The $\text{TiS}_2|\text{Li}_3\text{YCl}_6$ composite used here therefore enables direct identification of interfacial processes without elemental overlap, allowing us to decouple the electrochemical evolution of the CAM and SE during cycling.

ELECTROCHEMICAL PERFORMANCE OF THE OPERANDO CELL COMPARED TO A LAB-BASED CELL

To evaluate how interfacial reactions influence macroscopic performance, we compare the electrochemical behavior of the *operando* cell under UHV and Ar to that of a conventional lab-based configuration. The cell measured in UHV clearly shows the lithiation of TiS_2 , which we could probe by HAXPES under *operando* conditions. Figure 1a shows a schematic of a typical

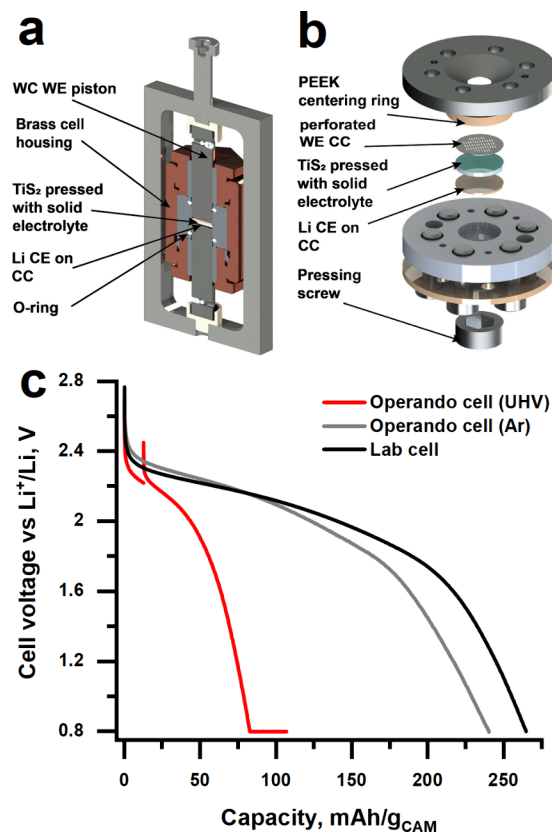


Figure 1. (a) Typical lab-based SSB cell used to apply stacking pressures during the characterization of new electrode materials. (b) Schematic illustration of the developed *operando* cell for SSBs used in this study which allows the application of relevant stacking pressures. (c) Discharge voltage profiles of $[\text{60:40 TiS}_2:\text{Li}_3\text{YCl}_6|\text{Li}_3\text{YCl}_6|\text{Li}]$ cells from a typical lab-based cell, the *operando* cell cycled in an Ar environment, and the *operando* cell cycled under UHV during HAXPES measurements.

lab-based cell, illustrating how the bulky housing poses challenges for photon- or electron-based probes to access the electrodes. To overcome this, we developed the cell design presented in Figure 1b, which enables direct probing of the electrode of interest through a perforated current collector that sits at the top of the cell. This perforated current collector is fabricated from 200 μm thick stainless-steel foil that is laser cut to form windows with a dimension of 0.2 mm $\times$ 1.0 mm, which is larger than the typical beam spot at the Sissy endstation at EMIL@BESSY II (up to 0.2 $\times$ 0.1 mm² for hard X-ray energies and 0.1 $\times$ 0.02 mm² for soft X-ray energies) so that the beam can fully fit in the slit without measuring across the current collector material.

Both the lab-based and *operando* cells are assembled in a similar manner, by uniaxial pressing of Li_3YCl_6 solid electrolyte

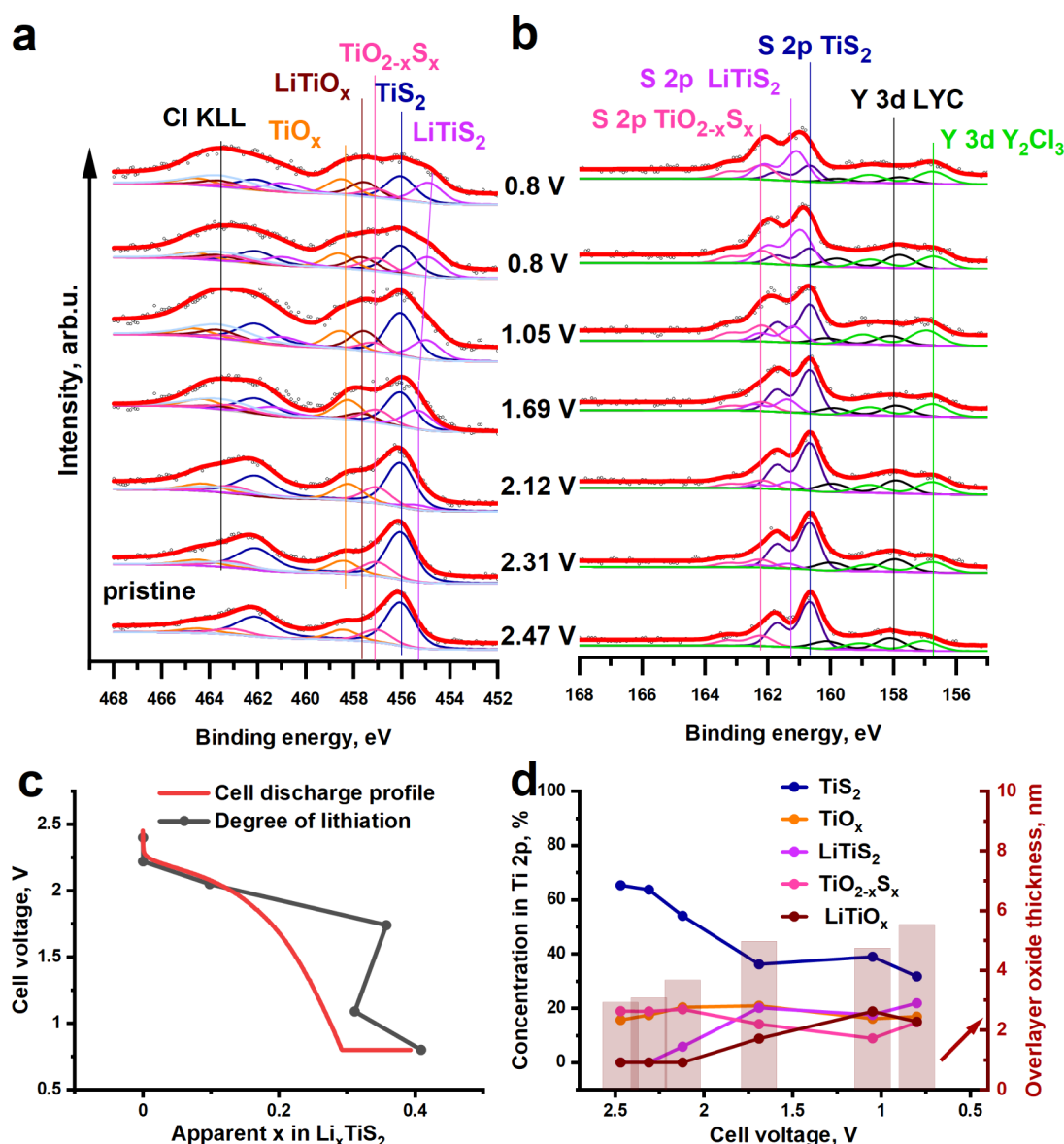


Figure 2. (a) Ti 2p and (b) S 2p spectra from *operando* HAXPES measurements obtained during discharge using a photon energy of 3000 eV. (c) Discharge voltage profile during *operando* measurement compared to the calculated apparent degree of lithiation based on integrated signal intensities of Ti 2p spectra. (d) Change in calculated Ti 2p spectral fractions during discharge highlighting apparent degree of lithiation and oxide formation according to integrated peak intensities and Hill's Equation (red bars for overlayer oxide thickness). OCV measurement was taken at a different spot than the rest of the *operando* measurements. The probing depth for HAXPES measurements with a photon energy of 3000 eV is approximately 14 nm.

with a 60:40 $\text{TiS}_2\text{:Li}_3\text{YCl}_6$ (by weight) composite cathode and Li anode. The main difference in assembly is that for the *operando* cell, a prepressed stack is inserted into the *operando* cell housing, whereas for the lab cell, pressing occurs directly within the cell housing. During electrochemical cycling, a stacking pressure is applied to the *operando* cell via a screw adjusted with a torque wrench (up to 1 N m, corresponding to 80 MPa). Because the *operando* cell housing is not airtight, all measurements must be performed either under inert atmosphere or under UHV conditions.

Figure 1c compares the discharge behavior of a 60:40 $\text{TiS}_2\text{:Li}_3\text{YCl}_6$ | Li_3YCl_6 | Li cell cycled in a typical lab cell to that of a similar cell stack cycled in the *operando* cell under Ar and UHV. All cells show the characteristic sloping behavior of the solid solution lithiation of TiS_2 , indicating that the same electrochemical processes occur. However, the *operando* cell

measured under UHV exhibits a reduced discharge capacity of 83 mAh g^{-1} , compared to 265 mAh g^{-1} for the lab cell and 240 mAh g^{-1} for the *operando* cell cycled under Ar atmosphere (both of which slightly exceed the theoretical capacity of 239 mAh g^{-1} for TiS_2 in the solid solution region). The reduced performance under UHV likely arises from partial loss of interfacial contact due to mechanical relaxation, consistent with the higher overpotential observed.

The dQ/dV curves (Supporting Information, Figure S3) further highlight these differences. The main reduction peak shifts to lower voltage for the UHV measurement, and the shoulder around 1.9 V is absent. The solid-solution lithiation of TiS_2 is known to proceed via a two-step process. For $x < 0.4$, there is a volume expansion and diffusion-limited regime. For $x > 0.4$, there is nearly constant interlayer spacing and a nondiffusion limited regime.²¹ The absence of the 1.9 V feature

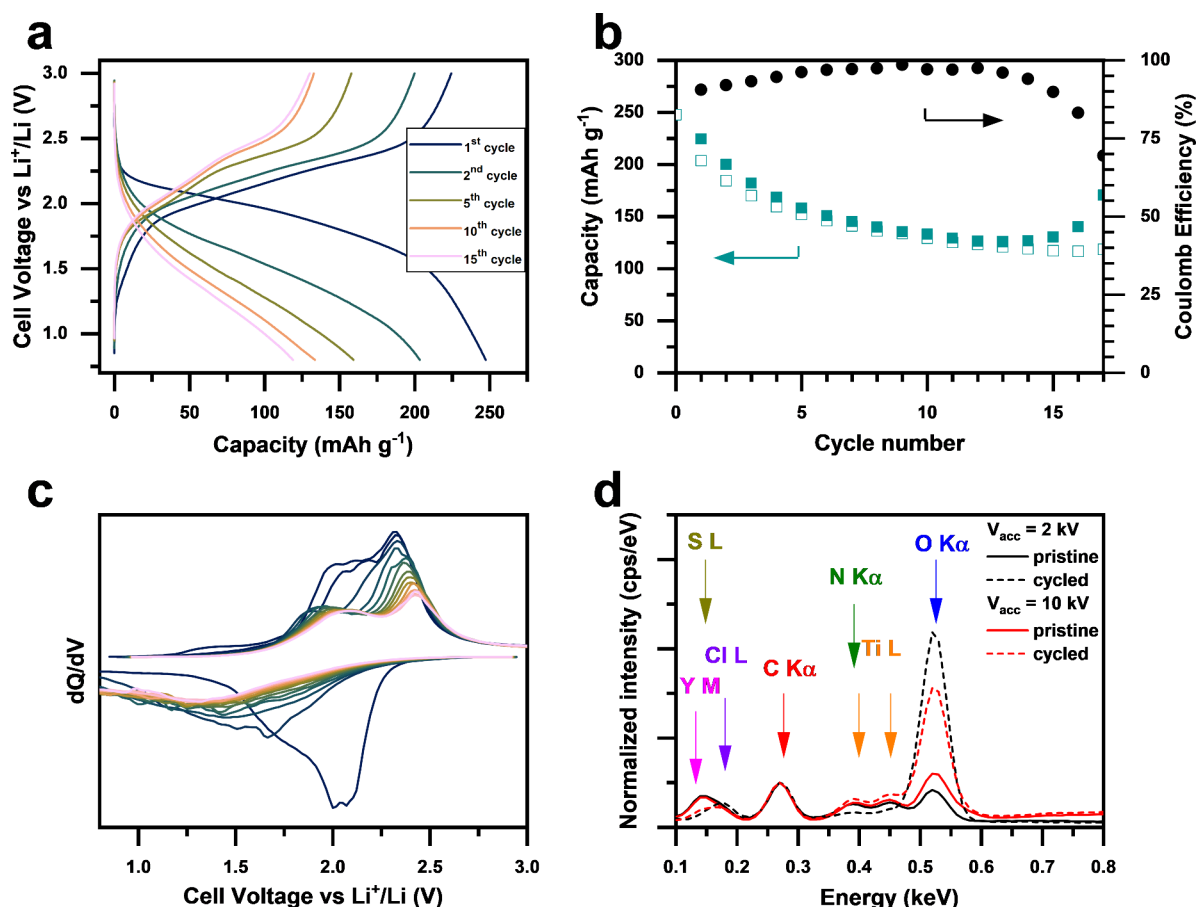


Figure 3. Long-term cycling data (a) voltage profiles, (b) capacity fading curve (closed squares show charge capacity, open squares show discharge capacity) and Coulomb efficiency (black dots), (c) dQ/dV curves, and (d) EDX scan of pristine vs cycled cathodes with different accelerating voltages, normalized to the carbon emission. The probing depths for the oxygen $K\alpha$ emission in the EDX measurements with 2 and 10 kV accelerating voltages is estimated to be 100 and 200 nm, respectively.

thus indicates incomplete lithiation under UHV. Nevertheless, these results confirm that the *operando* cell functions similarly to a conventional lab cell under inert conditions, and that even under UHV, it provides relevant electrochemical and spectroscopic insight into buried interfaces during cycling.

LITHIATION OF TiS_2 PROBED BY *OPERANDO* HAXPES

We first characterized pristine and lithiated reference compounds as well as the Li_3YCl_6 solid electrolyte *ex-situ* to establish the core-level signatures of the relevant species, as discussed in detail in the [Supporting Information](#). These *ex-situ* measurements show the presence of minor oxide species on TiS_2 and provide binding energy references for $Ti^{4+} \rightarrow Ti^{3+}$ reduction and for halide- and oxide-related signals. These spectra serve as essential spectral fingerprints for interpreting the chemical evolution observed under *operando* conditions.

We performed *operando* HAXPES measurements during discharge and followed the evolution of different surface species during lithiation. [Figure 2](#) shows the Ti 2p and S 2p spectra at different states of discharge. In the pristine state, TiS_2 , $TiO_{2-x}S_x$, and TiO_x species are present on the surface, alongside a contribution from the Cl KLL Auger signal of the Li_3YCl_6 solid electrolyte, in agreement with the *ex-situ* spectra.

For the 3000 eV kinetic energy Ti 2p *operando* HAXPES data ([Figure 2a](#)), the spectra remain largely unchanged during

the initial stages of discharge until the cell reaches approximately 2.1 V, which coincides with the observed voltage plateau in [Figure 1c](#). At this point, a new photoemission line emerges, shifted by 0.7 eV to lower binding energy relative to the TiS_2 Ti 2p_{3/2} line at 455.3 eV, which we assign to Li_xTiS_2 . This signal continues to grow and shift to lower binding energies during lithiation, shifting by up to −1.2 eV at the final measured discharge state (0.8 V). At the same time, the TiO_x contribution to the Ti 2p_{3/2} signal (458.3–458.6 eV) increases, as does the intensity of the Cl KLL Auger signal. The gradual shift of the TiO_x signal to higher binding energies indicates formation of thicker and more stoichiometric titanium oxide with x close to 2.²² The remaining photoemission features in the Ti 2p_{3/2} region can be attributed to TiS_2 , $TiO_{2-x}S_x$, and Li_xTiO_x at 456.1, 457.1, and 457.7 eV, respectively.

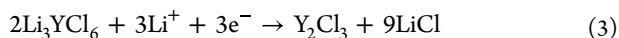
The calculated apparent degree of lithiation during discharge is shown in [Figure 2c](#) alongside the discharge profile (for details on the calculation of the apparent degree of lithiation, refer to the [Supporting Information](#)). At 0.8 V, the composition corresponds to $Li_{0.3}TiS_2$, which increases to $Li_{0.4}TiS_2$ after a potentiostatic hold,²¹ noting that some capacity contributions below 1.5 V may also arise from TiO_x lithiation and solid electrolyte degradation processes. Peak fitting analysis also allows extraction of atomic fractions ([Figure 2d](#)), showing a decrease in the TiS_2 fraction that coincides with an increase in $LiTiS_2$, as expected. We also

observe a general increase in oxide-related species, including TiO_x , $\text{TiO}_{2-x}\text{S}_x$, and LiTiO_x during discharge.

The O 1s spectra (Figure S11) support these assignments, showing an increase in TiO_x -related components with lithiation. Using a uniform-film approximation (details of Hill's Equation are provided in the Supporting Information), we estimate that the oxygen-containing Ti-related overlayer thickness increases from ~ 2 nm in the pristine state to ~ 5 – 6 nm at the end of discharge within the probed volume. At this thickness, titanium oxides can behave as a bulk-like layer, reducing electronic and ionic conductivity and contributing to the buildup of interfacial impedance. *Operando* synchrotron-based XPS measurements with 1230 eV excitation energy further support that the increased oxide composition is a surface phenomenon (see increased amount of TiO_x and LiTiO_x for 1230 eV data in Figures S11 and S12). This phenomenon is discussed further, below.

■ ELECTROCHEMICAL REDUCTION OF THE Li_3YCl_6 SOLID ELECTROLYTE

Intercalation of Li^+ ions in TiS_2 is accompanied by the reduction of Li_3YCl_6 , which is confirmed by changes in the related Cl 2p and Y 3p core-level photoemission lines (Figure S12a,b). The reduction of Li_3YCl_6 was previously studied in $\text{Li}|\text{Li}_3\text{YCl}_6|\text{Li}_3\text{YCl}_6\text{-C}$ half cells with an onset potential of 2.7 V vs Li^+/Li , where LiCl , Y^0 , and Y_2Cl_3 were proposed reduction products.²³ This suggests that reduction of Li_3YCl_6 in our study should yield similar species. However, the Cl 2p peak position remains largely unchanged, shifting by only 0.2 eV to higher binding energies at the end of discharge. Because Li_3YCl_6 , LiCl , and Y_2Cl_3 exhibit similar Cl 2p binding energies (198.8–198.9 eV²⁰), they can be difficult to distinguish experimentally within the beamline resolution of 0.3 eV at the given excitation energy. In contrast, the Y 3p spectra reveal a new component shifted by -1.2 eV relative to pristine Li_3YCl_6 , consistent with changes observed in the Y 3d region. The large chemical shift to lower binding energy points toward yttrium reduction, consistent with Y_2Cl_3 formation.²³ We therefore propose the final observed reduction reaction in eq 3.



Reduction of Li_3YCl_6 begins at 2.3–2.1 V and reaches $\sim 60\%$ conversion within our probing volume near the cathode current collector at 0.8 V. While this bulk uniform process should conserve the overall Cl:Y ratio, the observed 50% increase in the Cl 2p/Y 3p intensity ratio (Figure S12c) suggests surface segregation of LiCl , as previously reported for Li_3YCl_6 .²⁴ The metallic Y^0 species proposed in earlier studies²³ is not observed here, as the chemical shift of the new Y 3p component is inconsistent with the ~ 4 eV shift expected for Y^0 . This discrepancy may arise from the different reduction potential in this study (0.8 V) as compared to the Li^0 plating experiment (effectively setting the surface to 0 V).

■ OXYGEN MIGRATION FROM BULK DURING ELECTROCHEMICAL CYCLING

To better understand the observed oxygen migration, we cycled a TiS_2 electrode in a lab-based cell until it developed a soft short (~ 17 cycles), evident from the divergence of charge and discharge capacities and the drop in Coulomb efficiency (Figure 3b), which occurs due to the instability of the $\text{Li}/\text{Li}_3\text{YCl}_6$ interface. The cathode was then analyzed by SEM/

EDX with different accelerating voltages to probe the depth-dependent composition. Figure 3a shows progressive polarization of the voltage profiles over 15 cycles, while Figure 3b shows the associated capacity fading and Coulomb efficiency. The dQ/dV plots in Figure 3c reveal that the first cycle exhibits the expected high capacity TiS_2 behavior with both intercalation and capacitive features.²¹ In subsequent cycles, the reduction peak shifts dramatically to lower potentials and the oxidation peak to higher potentials, both with decreasing intensity. After the third cycle, the capacitive shoulder nearly disappears and a new oxidation feature emerges around 2.0 V. These trends are consistent with electrode passivation by a more insulating layer that is not fully isolating, which we attribute to oxygen migration toward the cathode current collector during cycling.²⁰

Operando HAXPES already revealed the growth of this TiO_x layer during the first discharge, reaching a thickness of ~ 4 nm by 0.8 V (Figure 2d), which was possible due to the highly surface-sensitive nature of the measurements. Continued oxygen migration in later cycles led to the appearance of a new redox species attributed to lithiation of TiO_x ,^{25,26} which was also evident in the *operando* HAXPES spectra. *Ex-situ* XRD and SEM/EDX characterization after ~ 17 cycles (Figures S14 and S15, respectively) show the cathode becoming more amorphous, with decreased reflection intensity and broadening of the LiTiS_2 reflections. A shift of the main 00l reflection to lower 2θ angles (14.06° vs 15.80° for TiS_2 and 14.51° for synthesized LiTiS_2) corresponds to an interlayer spacing of 6.29 Å, which is larger than both the pristine TiS_2 (5.61 Å) and LiTiS_2 (6.10 Å), which points toward a structural expansion consistent with partial oxygen incorporation into the TiS_2 lattice, possibly involving transient oxysulfide species.

When performing EDX analysis with different accelerating voltages, we can effectively probe different depths of our cathode material, with lower voltages providing more surface-sensitive information due to a reduced probing depth. In Figure 3d, EDX spectra can be found with 2 and 10 kV accelerating voltages. In both cases, there is a significant increase in the oxygen signal when comparing the pristine to cycled electrodes. It can also be seen that the relative intensity increase is greater in the case of 2 kV accelerating voltage, which supports that the oxygen is concentrated near the surface. This highlights the progressive growth of the oxide layer, where the initial growth was found in the very near-surface region in the initial discharge by HAXPES, but the oxide is found to continue to grow, with EDX showing the progressive growth from the current collector interface into the bulk after many cycles.

The observation of oxygen migration during electrochemical cycling is not unusual in itself and has been reported previously for TiS_2 cathode active materials with liquid electrolyte, where the electronic structure of TiS_2 was lost after many cycles due to the transformation of TiS_2 to Ti-O related compounds.²⁷ However, our observation that oxygen already begins to migrate toward the cathode current collector during the first discharge is surprising. This corresponds to the onset of TiS_2 reduction, where negatively charged anions, e.g., O^{2-} , would be expected to migrate toward the anode based on the direction of electron motion in the external circuit. At first it seemed that the preference to the cathode current collector could simply be related to adventitious oxygen from the environment that was able to attack exposed TiS_2 from the laser cut holes on the cathode current collector, but this can be readily excluded due

to the UHV environment, and is further supported by the long-term cycling experiments that do not use an open cell configuration. The oxygen-containing species therefore most likely originate from within the cell interior and redistribute from the bulk under electrochemical driving forces. While we cannot fully exclude residual moisture contributions from the cell housing, e.g. from PEEK components which were dried overnight at 60 °C prior to assembly, the electrochemically activated nature of the oxygen uptake process points toward contributions from the active cell components as the primary source.

To identify the oxygen source, we performed EDX on pristine and ball milled TiS_2 and Li_3YCl_6 (see Figure S16). TiS_2 showed minor oxygen contamination after ball milling, while Li_3YCl_6 already contained small amounts of oxygen before processing that did not increase significantly afterward. In all cases, the oxygen signal was lower than in the cycled electrode, indicating additional oxygen accumulation during cycling. This observation suggests that the oxygen incorporated during cycling does not solely originate from processing-induced surface contamination, but rather from oxygen-containing species inherently present within the assembled cell. From *operando* HAXPES at OCV (see Figure 2d), we know that processing introduced oxysulfide terminations on the TiS_2 surface (as $\text{TiO}_{2-x}\text{S}_x$), where the pristine TiS_2 surface contains 56% TiS_2 , 7% $\text{TiO}_{2-x}\text{S}_x$, and 37% TiO_x . In the assembled cell, the composition shifted to 65% TiS_2 , 16% $\text{TiO}_{2-x}\text{S}_x$, and 19% TiO_x as calculated from the Ti 2p core level spectra fitting (see Supporting Information for details).

The formation of oxysulfide species, $\text{TiO}_{2-x}\text{S}_x$, results in electronically and chemically heterogeneous regions on TiS_2 , where mixed anion coordination generates undercoordinated or distorted Ti centers. These sites will promote increased reactivity with electronegative species such as O^{2-} due to their increased electron density and altered local bonding environments. *Operando* HAXPES measurements show that the Li_3YCl_6 also degrades during discharge, but to oxygen-deficient species including Y_2Cl_3 and LiCl , (see Figure S12), but no noticeable increase of yttrium oxide species were observed. Their absence, supported by the smaller than expected chemical shift (−1.2 eV instead of −2.5 eV), indicates that oxygen in Li_3YCl_6 likely exists as weakly bound adsorbed oxygen or hydroxide species. Such weakly bound species may become mobile along microstructural pathways (e.g., grain boundaries or interfacial regions) during electrochemical polarization.

Upon lithiation of TiS_2 , which is first observed spectroscopically in this cell at 2.1 V, the TiO_x species are found to increase. We attribute this to a surface reconstruction process whereby oxygen is incorporated into TiS_2 , consistent with the transient formation of an amorphous oxysulfide ($\text{TiO}_{2-x}\text{S}_x$) intermediate. This is consistent with partial sulfur replacement by oxygen and the formation of a mixed-anion coordination environment around Ti atoms. It is thermodynamically favorable, as Ti–O bonds (bond dissociation energy ~ 670 kJ/mol) are significantly stronger than Ti–S bonds (~420 kJ/mol),²⁸ consistent with the more negative formation enthalpy of TiO_2 ($\Delta H_f \sim -944$ kJ/mol)²⁹ compared to TiS_2 ($\Delta H_f \sim -410$ kJ/mol).³⁰ Although oxygen substitution is expected to occur gradually under equilibrium conditions, it is accelerated during lithiation due to the progressive reduction of Ti, which increases its chemical reactivity and promotes binding with electronegative species. This mechanism also suggests that

partially oxidized or oxysulfide-rich TiS_2 regions may be preferentially lithiated compared to pristine TiS_2 due to altered electronic and ionic properties, although confirming this hypothesis would require *operando* studies with improved spectroscopic time resolution to better track the lithiation sequence across compositionally distinct TiS_2 regions.

The oxygen concentration becomes enriched near the current collector interface because this is where electron injection occurs during discharge, and the closest TiS_2 particles to the electron injection interface are the first to react. While electron injection occurs throughout the percolated network of the composite cathode, the driving force for oxygen-related interfacial reactions is greatest near the current collector, where the ohmic drop is smallest and the local electrochemical overpotential is therefore highest. This nonuniform potential distribution across the cathode thickness produces a spatial gradient in the local reaction driving force, rationalizing the preferential accumulation of oxygen-containing species near the current collector interface. This process continues during cycling until a TiO_x degradation layer is formed. This layer lacks crystalline reflections by XRD (Figure S14) and is likely amorphous, as also supported by the observed increased polarization during cycling and the new redox feature that emerges in the third cycle that resembles am- TiO_2 (de-)lithiation from the literature.^{25,26}

Observation of oxygen migration during cycling from within the cell interior is important for understanding degradation pathways in SSBs. Through *operando* HAXPES measurements we found that this oxygen migration process already begins during the first discharge. This early onset coincides with the lithiation plateau of TiS_2 , suggesting a coupling between Ti reduction and the local incorporation of oxygen at the solid–solid interface. Our results point to the formation of a mixed-anion $\text{TiO}_{2-x}\text{S}_x$ oxysulfide phase at the $\text{TiS}_2/\text{Li}_3\text{YCl}_6$ interface. This transformation is thermodynamically driven by the stronger bonding enthalpy of Ti–O compared to Ti–S, and kinetically promoted by electron injection from the current collector during discharge. Over extended cycling, a gradient in oxygen concentration emerges, with TiO_x enrichment localized near the current collector interface. This indicates a persistent electron-assisted oxygen migration pathway that continues beyond the initial electrochemical formation of the interface. The resulting amorphous TiO_x -rich layer contributes to increased polarization and long-term capacity fading, highlighting the importance of interfacial redox and anion exchange reactions in dictating the stability of solid-state battery architectures. The oxygen migration mechanism identified here is expected to be relevant to sulfide electrode materials more broadly, and since the key mechanistic observations occur within the solid-solution intercalation regime, the conclusions are expected to hold across a range of sulfide-based cathode materials and operating voltage windows, providing a foundation for future studies on higher energy density sulfide systems. By elucidating this mechanism, our results provide a framework for developing strategies to suppress electron-assisted oxygen migration and improve interfacial stability in future SSB designs.

■ ASSOCIATED CONTENT

Data Availability Statement

Raw data is available on the Zenodo repository and can be accessed at DOI: [10.5281/zenodo.18711105](https://doi.org/10.5281/zenodo.18711105).

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsenenergylett.6c00551>.

Experimental details, calculation of TiO_x thickness, comparison of dQ/dV curves for different sample environments, XRD patterns of pristine and cycled samples, comparison of O 1s, S 1s, S 2p, Ti 2p, and Cl 2p HAXPES spectra with 3000 and 1230 eV kinetic energies for ex-situ samples highlighting surface species and Auger transition, Cl 2p and Y 3p spectra for Li_3YCl_6 solid electrolyte with 3000 eV excitation energy, survey spectra for TiS_2 powder with 1230 eV kinetic energy and the operando cell at OCV with 3000 eV kinetic energy, O 1s operando HAXPES spectra with 3000 eV kinetic energy, O 1s, S 2p, and Ti 2p operando HAXPES spectra with 1230 eV kinetic energy, plot of normalized Cl 2p/Y 3p ratio, plot of binding energy differences at given potentials, SEM and EDX mapping, EDX spectra with different accelerating voltages, beam damage analysis based on Ti 2p comparison spectra, mass-spectrum of the analysis chamber of the SISSY 1 endstation, binding energy table (PDF)

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Notes

The authors declare no competing financial interest.

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