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Elucidating Reversible Electrochemical Redox of Li$_6$PS$_5$Cl Solid Electrolyte

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ABSTRACT:

Sulfide-based solid electrolytes are promising candidates for all solid-state batteries (ASSBs) due to their high ionic conductivity and ease of processability. However, their narrow electrochemical stability window causes undesirable electrolyte decomposition. Existing literature on Li-ion ASSBs report an irreversible nature of such decompositions, while Li-S ASSBs show evidence of some reversibility. Here, we explain these observations by investigating the redox mechanism of argyrodite Li$_6$PS$_5$Cl at various chemical potentials. We found that Li-In | Li$_6$PS$_5$Cl | Li$_6$PS$_5$Cl-C half-cells can be cycled reversibly delivering capacities of 965 mAh g$^{-1}$ for the electrolyte itself. During charging, Li$_6$PS$_5$Cl forms oxidized products of sulfur (S) and phosphorus pentasulfide (P$_5$S$_5$) while during discharge, these products are first reduced to Li$_3$PS$_4$ intermediate before forming lithium sulfide (Li$_2$S) and lithium phosphide (Li$_3$P). Finally, we quantified the relative contributions of the products towards cell impedance and proposed a strategy to reduce electrolyte decomposition and increase cell coulombic efficiency.
All solid-state batteries (ASSBs) show great promise to become the next-generation energy storage technology. Compared to conventional liquid electrolyte-based batteries, ASSBs utilizes non-flammable solid state electrolytes (SSEs), which translate to improved safety and the ability to operate over a wider temperature range.\textsuperscript{1-2} As such, recent years has seen much research focused on developing highly conductive SSEs as well as fundamental studies on its intrinsic electrochemical properties. Amongst these electrolytes, argyrodite Li\textsubscript{6}PS\textsubscript{5}Cl has attracted much attention due to its high ionic conductivity (> 1 mS cm\textsuperscript{-1} at 298 K), ease of material synthesis and low temperature processability, which are critical requirements for scalable fabrication of ASSBs.\textsuperscript{3-6} It is also a relatively well studied electrolyte material with detailed experimental literature on its synthesis parameters, crystalline structure and mechanical properties.\textsuperscript{3-6} However, its electrochemical interface and respective decomposition products against electrodes are not as well investigated. Although existing literature on sulfide electrolyte-electrode interface focuses on the chemical reactions against lithium metal anode or layered oxide cathodes\textsuperscript{5, 7-10}, knowledge of its intrinsic interfacial electrochemical properties crucial for designing sulfide-based ASSBs remain lacking.

Like most sulfide-based SSEs, Li\textsubscript{6}PS\textsubscript{5}Cl has a relatively narrow electrochemical stability window, causing it to decompose during cell cycling to form unwanted interfacial oxidation or reduction products.\textsuperscript{11-13} While these oxidation and reduction products have not been fully identified experimentally due to its amorphous and buried nature, they have been predicted by computational density functional theory (DFT) studies done on common SSEs (e.g., Li\textsubscript{10}GeP\textsubscript{2}S\textsubscript{12}, Li\textsubscript{7}P\textsubscript{3}S\textsubscript{11}, Li\textsubscript{3}PS\textsubscript{4}, Li\textsubscript{6}PS\textsubscript{5}Cl).\textsuperscript{13-14} Despite its ability to form passivating interfaces enabling their use in ASSBs without forming electronic pathways that short the cell, their interfacial properties are still unfavorable for cell performance due to large impedance growth and poor 1\textsuperscript{st} cycle columbic efficiencies.\textsuperscript{9, 15} Current reports on sulfide-based Li-ion ASSBs show an irreversible SSE decomposition forming on the interface during the 1\textsuperscript{st} charge.\textsuperscript{9, 16} However, recent studies have suggested the reversible nature of this decomposition, giving rise to high specific cell capacities.\textsuperscript{5-6, 17-19} This electrolyte decomposition-derived capacity is commonly seen in solid-state Li-S battery reports using sulfide-based SSEs, where capacities higher than the cathode’s theoretical capacities of Li\textsubscript{2}S and S were previously reported (Figure 1a). The extra reversible capacity likely arises as result of contributions from reversible electrolyte decomposition beyond the 1\textsuperscript{st} cycle, as both Li-
S and sulfide-based SSE redox ($S / S^2-$) occur simultaneously during cycling over the same voltage range. A summary of capacities for Li-S ASSBs in literature is illustrated in Table S1.

![Figure 1](image.png)

**Figure 1.** (a) Reported 1st cycle discharge capacities of representative solid-state Li-S batteries in literature. Dotted lines represent theoretical capacity of $Li_2S$ and $S$ respectively. (b) Illustration of electrochemical operating windows for $Li_6PS_5Cl$, Li-S and Li-ion chemistries.

The reversible / irreversible observations made in these reports can be rationalized by comparing the operating voltage ranges of batteries used (Figure 1b). Comparing typical voltage ranges used in Li-ion and Li-S batteries against redox potentials of sulfide electrolytes such as $Li_6PS_5Cl$, it becomes clear that oxidative decomposition seen in Li-ion ASSBs would be perceived as irreversible. Likewise, oxidative and reductive decomposition of SSEs in ASSBs with lower voltage operating voltage such as Li-S batteries would be reversible and detected by extra capacities reported from the S or $Li_2S$ cathodes respectively. However, since both SSE decomposition and Li-S redox occur at overlapping voltage windows, it is hard to characterize and deconvolute capacity contributions from each component respectively. Furthermore, there is poor understanding of redox mechanism of $Li_6PS_5Cl$ electrolyte alone, with studies mainly investigating its 1st cycle oxidation against layered oxide electrodes, or its chemical reactions against metallic lithium. Thus, it is vital to investigate the intrinsic electrochemical decomposition of $Li_6PS_5Cl$ itself and its reversibility at typical cathode and anode potentials, without any contributions from the active electrodes.

Here, we use various characterization tools to experimentally observe the decomposition redox of $Li_6PS_5Cl$ and propose a reaction pathway that helps shed light on its capacity contribution. The
decomposition products at various potentials are identified and cell level properties are evaluated by isolating species at the anode and cathode interface respectively to quantify their relative contributions to cell impedance. Finally, we demonstrate a method to reduce electrolyte decomposition in ASSBs and demonstrate its effectiveness in a typical Li-In | Li$_6$PS$_5$Cl | NCM811 cell. This study is fundamentally important to analyze thermodynamically driven interface product formation at electrodes of ASSBs and inform strategies for interfacial engineering and cell design.
Electrochemical Redox of Li₆PS₅Cl. To investigate the reversible decomposition redox of Li₆PS₅Cl, a half cell setup was used with Li-In as the anode and carbon black (CB) (30 wt.%) mixed with Li₆PS₅Cl (70 wt.%) on the cathode. Cyclic voltammetry (CV) was performed on the Li-In | Li₆PS₅Cl | Li₆PS₅Cl-C cell (Figure 2a). Starting at open circuit voltage (OCV), a positive sweep yielded two oxidative peaks (1, 2) at 2.6 V and 3.0 V, while the negative sweep showed two reductive peaks (3, 4) at 2.0 V and 1.1 V respectively. During the second cycle, the first oxidative peak (1’) appeared more intense, which is associated with a higher charging capacity, followed by a smaller oxidative peak (2’). There is a slight shift of the 1ˢᵗ reductive peak (3’) to lower voltage, indicating changes in cell polarisation after oxidation. These observations were also validated with galvanostatic cell cycling (Figure 2b), where increased charge capacity and lowered discharge voltage at the 2ⁿᵈ cycle were found.

From Figure 2b, the first galvanostatic charge / discharge cycles of the Li₆PS₅Cl-C electrode yielded a large capacity of 354 mAh g⁻¹ and 968 mAh g⁻¹ respectively, while the second cycle yielded 956 mAh g⁻¹ and 1002 mAh g⁻¹ respectively. The first charge voltage plateau starts at the oxidation potential of 2 V, which agrees with DFT calculations in the literature.¹³ This oxidation potential has also been reported in work studying sulfide decomposition in Li-ion ASSBs.¹⁵ Interestingly, a typical discharge cycle (Figure 2b) displays two plateaus, one between 2.2 V to 1.3 V and a second between 1.3 V and 0 V, corresponding to the two reductive peaks in Figure 2a. This indicates two distinct thermodynamically reduction reactions at each respective voltage. Such double discharge plateau has not been observed in previous literature on either sulfide SSE redox studies,¹¹,¹⁹,⁴⁵ or Li-S batteries work using sulfide SSEs⁶,³³ for reasons that will be discussed later.

Theoretical Capacity of Li₆PS₅Cl Oxidation / Reduction

\[ \text{Li}_6\text{PS}_5\text{Cl} \rightarrow \text{LiCl} + \frac{1}{2} \text{P}_2\text{S}_5 + \frac{5}{2} \text{S} + 5\text{Li}^+ + 5\text{e}^- \quad Q_{\text{ox}} / \text{Capacity} = 499 \text{ mAh g}^{-1} \]

\[ \text{Li}_6\text{PS}_5\text{Cl} + 8\text{Li}^+ + 8\text{e}^- \rightarrow \text{LiCl} + \text{Li}_3\text{P} + 5\text{Li}_2\text{S} \quad Q_{\text{red}} / \text{Capacity} = 798 \text{ mAh g}^{-1} \]
Figure 2. (a) Cyclic voltammograms for the first two cycles, voltage was swept between 0 - 4.2 V (vs Li/Li⁺) at 100 μV s⁻¹ starting from OCV. (b) 1ˢᵗ and 2ⁿᵈ voltage profiles of Li-In | Li₆PS₅Cl | Li₆PS₅Cl-C half cell. Cycling was done between 0 to 4.2 V (vs Li/Li⁺) at room temperature and a current density of 0.25 mA cm⁻². (c) 1ˢᵗ Direct discharge curve showing 1 voltage plateau at 1.0 V for excess Li⁺ source, indicating phosphorus species reduction. (d) 1ˢᵗ charge and discharge curves showing 1 voltage plateau at 2.0 V for limited Li⁺ source, indicating sulfur species redox. Marked Numbers 1 to 5 represent potentials where Li₆PS₅Cl was extracted for characterization.

To understand this phenomenon, we hypothesize that after complete oxidation of the Li₆PS₅Cl-C electrode during the first charge, the first discharge plateau is attributed to sulfur species reduction (S → S²⁻) and the second plateau is attributed to phosphorus species reduction (P⁵⁺ → P / P³⁻), as the only species remaining to be reduced is phosphorus. This hypothesis can be verified by directly discharging the Li-In | Li₆PS₅Cl | Li₆PS₅Cl-C cell from OCV as seen in Figure 2c. As the cell at OCV comprises of sulfur in its reduced state (S²⁻) in Li₆PS₅Cl, directly discharging the cell will cause reduction of phosphorus species, as seen in the single discharge plateau at voltages...
below 1.3 V. Based on the previous computational predictions, Li₆PS₅Cl reduction will result in the formation of Li-containing products such as Li₃P, Li₂S and LiCl. To further test this hypothesis, we limit the reaction of phosphorus species, by using a minimal amount of Li-In at the anode (Figure 2d). As the reduction of phosphorus species in Li₆PS₅Cl requires extra Li source to form the respective Li containing products (e.g., Li₃P), these reactions cannot occur if all the Li at the anode are fully consumed. As such, after being fully charged, only one discharge plateau attributed to sulfur redox was seen between 1.3-2.2 V. The galvanostatic data as well as the cyclic voltammogram provides an indication on the SSE redox mechanism, and the respective sulfur and phosphorus reaction potentials vs Li/Li⁺. To support these findings, multiple characterization tools are utilized, and its results are discussed. Extended cycling of the Li-In | Li₆PS₅Cl | Li₆PS₅Cl-C cell can be found in Figure S1.

**XPS of Li₆PS₅Cl at various potentials.** To verify specific products of each sulfur or phosphorus species, XPS was conducted at each stage of charge (numbered 1 to 5 in Figure 3) for the S 2p, P 2p, and Cl 2p regions. Cycling profiles from Figure 2a are plotted vertically for ease of reference. At the pristine state, Li₆PS₅Cl comprises of PS₄²⁻ thiophosphate units which can be detected by the characteristic doublet peaks around 161.5 eV in the S 2p region and 131.5 eV in the P 2p region. This was described as terminal S bonds in some literature. No signals from other components are found in the pristine electrolyte. Upon full charge of the Li-In | Li₆PS₅Cl | Li₆PS₅Cl-C cell to 4.2 V, Li₆PS₅Cl decomposes to form oxidised products of elemental S (Figure 3a-2) and P₂S₅ (Figure 3b-2). These findings agree with existing literature studies on the oxidation behaviour of sulfide SSE, as well as computational studies showing Li₆PS₅Cl first forming LiCl and Li₃PS₄, followed by S and P₂S₅ upon further oxidation.
Figure 3. XPS spectra showing the binding energies of Li₆PS₅Cl at different cycling potentials. (a) Sulfur 2p region. (b) Phosphorus 2p region. (c) Cycling voltage profile for reference. (d) XRD patterns at different cycling potentials. Li₂S can be identified as reduced product. (e) Raman Spectra at fully charged state. Sulfur is identified as an oxidized product. Raman Spectra from pristine cathode, sulfur and CB are displayed for reference.
Upon discharge of the cell until 1.3 V (Figure 3c-3), a decrease in peak intensities for S and P$_2$S$_5$ and relative intensity increase of PS$_4^{3-}$ thiophosphate characteristic energies are observed. This indicates a reformation of PS$_4^{3-}$ unit during cell discharge after oxidative decomposition of the pristine electrolyte. While its configuration and structural properties cannot be determined from XPS alone, it clearly suggests that Li$_2$S has not yet been formed after the first discharge plateau. Some residual signal is detected from unreacted P$_2$S$_5$ (Figure 3b-3). As it is believed to have poor reaction kinetics, some P$_2$S$_5$ remains as partially irreversible products of Li$_6$PS$_5$Cl oxidation. Upon further discharge to 0 V, strong signals of Li$_2$S around 160 eV in Figure 3a-4 are observed, while weak signals of reduced phosphorus species and Li$_3$P are detected along with unreacted residual P$_2$S$_5$ in Figure 3b-4. It is worthy to note that due to the low stoichiometric ratio of P to S atoms in Li$_6$PS$_5$Cl, signals from P 2p are weaker in relative intensity and difficult to detect. To verify that signals from P$_2$S$_5$ are attributed to oxidative species formed by charging to 4.2 V, another cell was prepared and directly discharged to 0 V from OCV (Figure 3c-5). As expected, no signals of P$_2$S$_5$ are detected and only Li$_2$S, reduced P and Li$_3$P are found (Figure 3b-5). Binding energies of the Cl 2p region can be found in Figure S2.

Two important observations can be made from the XPS study. (1) The decomposed product species at the oxidized state of 4.2 V and reduced state at 0 V represent the typical interfacial products of Li-ion ASSBs when Li$_6$PS$_5$Cl is used as the electrolyte. The half-cell setup used in this XPS study allows us to electrochemically form the thermodynamically driven interface products at typical voltages of oxide-based cathodes such as LiCoO$_2$ and anodes such as graphite, isolating any effects from the electrode material. (2) This study also demonstrates the reversibility of the electrolyte decomposition, where reformation of PS$_4^{3-}$ units from elemental S and P$_2$S$_5$ acts as an intermediate redox product before formation of Li$_2$S when phosphorus is reduced at lower voltages.

**XRD & Raman of Li$_6$PS$_5$Cl at various potentials.** To substantiate these findings, X-ray diffraction (XRD) was conducted for the Li$_6$PS$_5$Cl-C cathode at similar cycling potentials (Figure 3d). At pristine states, diffraction peaks are observed at the characteristic Bragg angles of crystalline Li$_6$PS$_5$Cl as seen in previous studies.$^{3-4, 6}$ Unfortunately, there are little significant changes observed upon cell charging, due to the poor symmetry and amorphous nature of oxidized S and P$_2$S$_5$ products, as reflected by an increased intensity of the amorphous bump between 20-
30° at the 2θ. While any LiCl formed should be crystalline, its relative amounts are too low to be detected and it is likely to be deposited as nano-sized crystals as the SSE was pulverized during ball milling. Only signals from unreacted crystalline Li₆PS₅Cl can be detected. Likewise, the cell discharged to 1.3 V displays no significant change in diffraction patterns. However, the presence of oxidized elemental S can be detected clearly with Raman as seen in Figure 3e. The charged Li₆PS₅Cl-C cathode at 4.2 V vs Li/Li⁺ display signals from oxidized S at 155 cm⁻¹, 220 cm⁻¹ and 475 cm⁻¹, electrolyte PS₄³⁻ at 430 cm⁻¹, as well as the D-band from CB at 1350 cm⁻¹. Upon further discharge to 0V, the relative intensities of Li₆PS₅Cl diffraction peaks start to decrease. As phosphorus reduction in the electrolyte occurs, nanocrystalline Li₂S begins to form and is reflected as broad peaks seen around 26°, 45° and 52° at the 2θ (Figure 3d). A similar trend is observed for the cell that is directly discharged from OCV. These findings are consistent with the XPS analysis discussed earlier, where elemental S is formed as a result of SSE oxidation during charging, Li₂S formation is not observed during discharge until low voltages, where phosphorus reduction occurs. Figure 4a illustrates the proposed reaction pathway of Li₆PS₅Cl reversible electrochemical redox based on the analysis discussed.

Solid-state nuclear magnetic resonance (NMR) at mid-discharged state. To further characterize the nature of products at mid-discharge, ⁶Li, ⁷Li, and ³¹P MAS NMR was conducted by comparing pristine Li₆PS₅Cl to the mid-discharged state at 1.3V. ³¹P NMR spectra of the pristine and mid-discharged Li₆PS₅Cl material are shown in Figure 4b. The ³¹P spectra of the pristine Li₆PS₅Cl is typical of that previously shown in literature, with broad features centered at δ = 84.3 ppm and two low frequency shoulders (δ = 82.7 and 81.0 ppm). The broadened features are caused by disorders on the anion sublattice from the substitutional mixing of Cl and S atoms on their respective crystallographic sites around the phosphorus PS₄³⁻ tetrahedron. The ³¹P spectrum of the mid-discharged Li₆PS₅Cl cathode bears the same broadened features as the pristine material with additional broadening at the tails. This difference is attributed to additional high frequency broadening centered around δ = 87 ppm, which falls in between the isotropic chemical shifts observed in crystalline γ-Li₃PS₄ (88.4 ppm) and β-Li₃PS₄ (86.53 ppm) phases. This suggests the formation of isolated PS₄³⁻ tetrahedra with chemical environments more similar to those found in Li₃PS₄ than Li₆PS₅Cl. The broadening at very high (> 90 ppm) and low (< 82 ppm) frequencies are a result of an overall increase in the amorphous content of various PS₄³⁻ and P₂S₇⁴⁻ units and covers a chemical shift distribution typical of Li rich thiophosphate glasses. The
additional broadening observed after cycling suggests the increased presence of distorted PS₄³⁻
tetrahedra similar to that observed in Li₃PS₄ as well as a more heavily disordered thiophosphate
network forming. Assigning definitive isotropic chemical shifts is challenging due to the extremely
broadened features resulting from not only a distribution of bond lengths and angles of the PS₄³⁻
tetrahedra but also as a result of substitutional mixing of S and Cl within the second and third
coordination sphere of Li₆PS₅Cl. However, deconvolution is performed to demonstrate an example
of the rise of the distorted Li₃PS₄ and amorphous lithium thiophosphate components after cycling
(Figure S4a). Evidence of residual Li₂S and LiCl after charge cycling is also found in ⁷Li MAS
NMR (Figure 4b). The ⁷Li spectrum of the pristine material displays a single motional narrowed
Lorentzian peak centered at 1.33 ppm. After cycling, the ⁷Li spectrum displays a shift towards 1.2
ppm and a rise of a broad component between 0.5 and -2 ppm. These changes can be elucidated
by comparison to the ⁷Li chemical shifts for the reference compounds, Li₃PS₄ and LiCl (Figure
S4). The ⁷Li spectrum for Li₃PS₄ displays two peaks at 0.98 ppm and 0.41 ppm while LiCl displays
one peak at -0.99 ppm. The increased intensity of the cycled Li₆PS₅Cl within these regions
indicates the formation of a minor amount of these two compounds. However, a general lack of
distinguishable features outside of the primary Li₆PS₅Cl peak suggests that Li⁺ are exchanging
within the chemical environments of these decomposed products. To obtain better resolution of
these decomposed products, we turn to ⁶Li MAS NMR (Figure 4c) as it offers an increased
sensitivity to changes in the local structure compared to ⁷Li. The relative difference of the primary
Li₆PS₅Cl peak to the reference compounds, Li₃PS₄ and LiCl, is nearly the same as seen in ⁷Li.
Comparing the pristine and cycled Li₆PS₅Cl material reveals the rise of a shallow broad component
similar to that observed in the ⁷Li spectrum. This broad component can be contributed to Li₃PS₄
and LiCl based on similarity of their ⁶Li chemical shifts. The cycled Li₆PS₅Cl also shows a
broadening towards higher chemical shift which was notably absent from the ⁷Li spectrum. This
new feature is close to the chemical shift expected for Li₂S (2.35 ppm)³² suggesting residual
formation of Li₂₋ₓS.
Figure 4. (a) Redox reaction pathway of Li₆PS₅Cl for the 1st charge and subsequent cycles. (b) (Top) ³¹P MAS NMR spectra of pristine and mid-discharged Li₆PS₅Cl. (Bottom) ³¹P MAS NMR spectrum of reference Li₃PS₄ containing both γ and β phases. (c) (Top) ⁷Li MAS NMR spectra of pristine and mid-discharged Li₆PS₅Cl. (Bottom) ⁶Li MAS NMR spectrum revealing the rise of broad peak centered at 0.81 ppm. Expanded chemical shift ranges can be found in SI.

EIS of Li₆PS₅Cl half-cell at various potentials. Next, we investigate the impact of Li₆PS₅Cl decomposition products on cell impedance in typical Li-ion ASSBs. To do so, we conduct electrochemical impedance spectroscopy (EIS) measurements across the Li-In | Li₆PS₅Cl | Li₆PS₅Cl-C cell at different cycling potentials (Figure 5). Considering that charge transfer resistances at the Li-In anode and of the bulk electrolyte do not change significantly, any changes in total cell impedance can be attributed to impedance growth or ionic conductivity changes in the Li₆PS₅Cl-C electrode as redox proceeds.
Figure 5. Nyquist plots at different cycling potentials showing the impedance changes of Li-In | LPSCl | LPSCl-C cell (left). Normalized capacity vs Voltage profiles are displayed for reference (middle). Bar graph shows relative differences in cell impedance at different oxidation or reduction states of Li$_6$PS$_5$Cl-C (right), direct discharge marked as 5 is used at full reduced state for fair comparison.

Nyquist plot of the pristine cell at OCV shows a total cell resistance of approximately 45 Ω, which translates into the expected Li$_6$PS$_5$Cl conductivity on the order of ~10$^{-3}$ S cm$^{-1}$. However, when the cell is charged, the total cell resistance increases by two orders of magnitude, as reflected in Figure 5 (left). This results from formation of highly insulating products of S and P$_2$S$_5$, etc.
dramatically increasing the charge transfer resistance in the cathode. However, when the cell is discharged to 1.3V, the total cell impedance falls to 139 Ω as seen in the bar chart of Figure 5 (right), regaining almost all the conductive properties of the electrolyte in the cathode. This is due to the reformation of conductive Li$_3$PS$_4$ found in the previous section. It is likely that the impedance measured at 1.3V is higher than the pristine state due to incomplete reaction of the oxidised products found in Figure 3b as well as contributions from LiCl formed during redox. Upon full discharge to 0V, the total cell impedance increases to 400 Ω (Figure 5) which is an increase of less than 1 order of magnitude compared to the pristine state. The large changes in impedances measured across the cell during cycling provides us an indication of the effects of SSE decomposition on ASSB cell performance.

Li$_6$PS$_5$Cl reductive decomposition. From these results, it can be inferred that impedance growth in ASSB full cells during cycling is largely attributed to oxidation decomposition of SSE at high voltages. By comparison, reduction decomposition of SSEs at anodes such as graphite contributes less to cell resistance. This likely results from the formation of Li$_3$P, which was previously reported to have some Li$^+$ conductive properties. Additionally, based on literature work studying Li-S chemistries, Li$_2$S at discharged states was found to have comparatively lower charge transfer resistances compared to elemental S at charged states when measured with similar impedance methods. To further substantiate this, impedance growth of an anode composite comprising 60 wt% carbon graphite was measured before and after lithiation (Figure S5). As expected, impedance growth at the anode was still significantly less compared to the cathode composite comprising only 1wt% CB after charging. EIS measurements were also done on pure interfacial components prepared in their stoichiometric formation ratios. The results showed some ionic conductive properties of reduced species (~10$^{-6}$ S cm$^{-1}$), while the oxidized species were found to be entirely insulative (Figure S6).

Li$_6$PS$_5$Cl oxidative decomposition. While SSE decomposition brings about negative effects on electrode charge transfer resistance and overall cell impedance, its impact is more pronounced at the cathode where oxidative decomposition occurs. As such, strategies to mitigate SSE oxidative decomposition in ASSBs are vital. Although it is difficult to change the decomposition thermodynamics of sulfide-based SSEs, it is possible to control its kinetics by tuning the morphology or specific surface area of carbon used. With reduced surface area, the SSE would
have less exposure to electronically conductive surfaces. Without sufficient electronic pathway for redox to occur, the kinetics of SSE decomposition can be significantly reduced.

**Figure 6.** SEM images of: (a) carbon black (b) vapor grown carbon fibre showing differences in morphology and size. (c) Charge voltage profiles of Li-In | Li₆PS₅Cl | Li₆PS₅Cl-C cells using 30 wt% carbon black (surface area: ~ 80 m²/g) vs vapor grown carbon fibre (surface area: ~ 24 m²/g)). (d) Charge & discharge voltage profiles of Li-In | Li₆PS₅Cl | NCM811 cells using 1 wt.% of carbon black vs vapor grown carbon fibre.

Due to its nanosized particles (**Figure 6a**), carbon black has a higher specific surface area (80 m² g⁻¹) that promotes decomposition kinetics of SSEs compared to other types of carbon such as vapor-grown carbon fiber (VGCF) with lower surface area (24 m² g⁻¹) (**Figure 6b**). Such differences were also detected with Raman, where VGCF exhibits significantly lowered D / G band ratios compared to CB. (**Figure S3**). **Figure 6c** illustrates the effect of using 30 wt.% of both types of carbon in the Li-In | Li₆PS₅Cl | Li₆PS₅Cl-C cell charged at 0.25 mA cm⁻². The cell using CB showed much higher decomposition capacity and faster decomposition kinetics compared to
the cell using VGCF. The sharp vertical voltage line at the end of the plateau of SSE-CB composite also indicates a complete reaction of SSE in the composite, while the VGCF composite shows a higher polarization indicating decreased decomposition kinetics. The effect of using lower surface area carbon can also be seen in Figure 6d, which compared the 1st cycle cell voltage curves of a Li-In | Li_{6}PS_{5}Cl | NCM811 half-cell using 1 wt.% of each carbon type in the oxide cathode. The cell using VGCF carbon additive shows a reduced electrolyte decomposition profile offset (inset), as well as a higher 1st cycle columbic efficiency compared to CB. Additionally, the discharge curve from the cell using VGCF also displays lower cell polarization. This results from lower cell impedance due to reduced SSE decomposition compared to the cell using CB. Extended cycling capacity retentions can be found in Figure S7.

As such, scientific efforts to improve the performance of ASSBs such as widening of SSE’s electrochemical stability window and/or reducing cell polarization growth over extended cycling can be directed toward reducing electrolyte oxidative decomposition. However, this is challenging to overcome, as the oxidative decomposition during the 1st charge is an unavoidable thermodynamic property of the electrolyte. Existing methods to apply surface coatings on the cathode particles can only reduce the interfacial reactions between the electrolyte and electrode but cannot prevent the formation of highly resistive oxidized SSE products. Current efforts to tackle this by controlling the decomposition kinetics should go beyond carbon optimization or using materials with lower specific surface area at the cathode, as carbon still plays an important role in capacity utilization of layered oxide cathodes. Other strategies are needed to either improve the intrinsic property of the SSE or further reduce its decomposition kinetics. New methods may include surface or bulk modification of SSE particles to improve their stability at high voltage or developing better conductive networks to maintain electronic pathway between cathode particles with minimal exposure to the SSE.
In summary, this study elucidates the redox behaviour and the mechanisms of Li₆PS₅Cl solid electrolyte decomposition. We found that Li₆PS₅Cl decomposition is irreversible in Li-ion batteries due to the high voltage ranges used. When lower voltage cycling is done, large reversible capacities of 965 mAh g⁻¹ from the electrolyte alone are observed. To investigate this reversible decomposition, XPS, XRD, Raman and NMR characterizations were conducted at various voltages of a Li-In | Li₆PS₅Cl | Li₆PS₅Cl-C cell, where its oxidation and reduction products were identified experimentally. It was found that oxidised products of elemental S and P₂S₅ undergo an intermediate transition product of Li₃PS₄ before being reduced to Li₂S and Li₃P. Subsequently, the impedance contributions of reductive and oxidative decomposition products were measured using EIS measurements. It was found that the cell impedance and polarisation growth in typical Li-ion ASSBs are a result of SSE decomposition at the cathode, where reductive SSE decomposition have less effects on overall cell impedance. Alternative types of low specific surface area carbon are proposed to reduce SSE decomposition, and its effect was demonstrated in a Li-In | Li₆PS₅Cl | NCM811 cell. The principles of SSE redox and its mechanism found in this study can be further extended toward new electrolyte material selection or modification, that mitigates SSE oxidation decomposition and thus improves cycle performance of ASSBs.
ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental Details, Literature Li-S ASSBs summary table, Li₆PS₅Cl-C half-cell cycling with different voltage windows, XPS binding energies of Cl 2p regions, Raman spectra of carbon black vs vapor grown carbon fiber, NMR Chemical Shifts of ³¹P and ⁶,⁷Li reference materials, Anode vs Cathode impedance growth comparison, Reduced vs Oxidized species impedance comparison, Extended half cell cycle capacity retention.

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Notes

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REFERENCES


**TOC Figure**

![TOC Figure](image-url)