Linking Solid Electrolyte Degradation to Charge Carrier Transport in the Thiophosphate-Based Composite Cathode toward Solid-State Lithium-Sulfur Batteries

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Solid-state lithium-sulfur batteries (SSLSBs) have the potential to cause a paradigm shift in energy storage. The use of emerging highly-conductive solid electrolytes enables high energy and power densities. However, the need for an intimate mixture of electrolyte and conductive additives to compensate for the insulating nature of cathode active materials \( S_8 \) and \( Li_2S \) induces intense electrolyte degradation. Thus, it is paramount to understand better the electrochemical and transport properties of the cathode composite with extremely high interface density among cathode components. Here, by utilizing a ball-milled composite of the lithium argyrodite \( Li_6PS_5Cl \) and carbon as a model electrode, the stability, reversibility, and transport in the composite as functions of cathode loading, the volume fraction of conducting phase, temperature, and applied potentials are comprehensively investigated. Comparing the onset potentials of electrolyte degradation and the sharp drop in the effective ionic conductivity of the composite determined through transmission-line model analysis, successful enhancement of the capacity retention of SSLSBs is demonstrated by balancing between the attainable capacity and effective carrier transport, achieving a high areal capacity of 3.68 mAh cm\(^{-2}\) after 100 cycles at room temperature. The here-observed analysis is applicable to any solid-state composite with electrically insulating active materials.

1. Introduction

Recent discoveries of various highly conductive solid electrolytes (SEs) have ignited and boosted the research activities in the field of solid-state batteries (SSBs).\(^{[5-9]}\) By employing earth-abundant sulfur as redox-active material, solid-state Li-S batteries (SSLSBs) open up the possibilities for improved safety, environmental friendliness, cost-effectiveness, and high specific energy possibly going beyond the physico-chemical limit of the current lithium-ion batteries.\(^{[16-22]}\) Furthermore, the mechanical rigidity and ion-selectivity of SEs can physically eliminate the shuttle effect, which is a long-standing intrinsic issue in conventional Li-S batteries with liquid electrolytes.\(^{[23-25]}\)

Despite the promising theoretical performance, there are multifold challenges for SSLSBs to become competitive. The ionically and electronically insulating nature of sulfur requires adequate fractions of SEs and conductive additives (e.g., carbon black) in the electrode composite, while a high sulfur loading is desired for high energy density. Chemo-mechanical failure is generally an issue in SSBs, becoming more problematic for Li-S batteries because of large volume changes of about 80% upon cycling.\(^{[26-28]}\) Nevertheless, a functional cathode composite is easily obtained through suitable processing procedures, for example, ball-milling\(^{[29,30]}\) solution processing,\(^{[31,32]}\) and liquid and/or gas phase mixing,\(^{[33,34]}\) especially with well-processable thiophosphate-based electrolytes (e.g. \( Li_6PS_5Cl, \beta Li_3PS_4, Li_{10}GeP_2S_{12} \), and various thiophosphate glasses). A well-mixed composite also appears to reduce the impact of a chemo-mechanical failure.\(^{[26,35-37]}\) The lithium thiophosphates are highly conductive compared to lithium oxide.
SEs and particularly attractive for SSB applications; however, a large interfacial area among the cathode components causes another complication, which is electrolyte degradation.

Lithium thiophosphates are stable only within limited potential windows. The theoretical stability windows of Li₆PS₅Cl and Li₉GeP₂S₁₂, for instance, are reported to be 1.71–2.01 V and 1.71–2.14 V versus Li⁺/Li, respectively.[48] By introducing conductive additives, the “reaction volume”, where both ions and electrons are supplied or extracted, significantly increases and amplifies the influence of SE degradation. A deliberately increased “reaction volume” with carbon additives has even been utilized to experimentally assess a practical stability window, which had not easily been accessible,[49,50] and which seems larger than the thermodynamically calculated windows. An accelerated cell degradation with carbon additives has for instance been shown with Li₉GeP₂S₁₂.[41] The negative impact of electrolyte degradation, consequently, leads to the need for protective coatings.[42] Recently and in contrast, there are also ways to positively exploit this SE degradation. For instance, a mixture of Li₆PS₅ or Li₉GeP₂S₁₂ with carbon additives was employed as cathode composite, which delivers a redox capacity.[43,44] The attainable capacity arises from formation of Sₓ and LiₓP upon cycling, all of which are decomposition products, as well as from the redox activity of thiophosphate structural units.[39,43,45] In order to emphasize that a major part of the redox activity is caused by decomposition products and not the SE itself, we use the term “apparent capacity” in the following. Recently, the apparent redox behavior of Li₆PS₅Cl and Li₉PS₅Br, as well as Li₉PS₅ClₓBr₁₋ₓ, have been reported and the underlying mechanism is actively discussed.[46–49] A successful in situ formation of ionically conductive phases upon cell operation has also been demonstrated by employing PₓSₓBrₓ as an active material.[50] Overall, the mechanistic understanding of lithium thiophosphate degradation and the utilization of their apparent redox behavior are of great interest as a basis for reversible electrode concepts, and a comprehensive investigation of their role in potential SSLSBs, in which a coating of the active material is not applicable, are required.

Besides the mechanistic understanding of the redox steps, an assessment of the charge carrier transport in the composites is vital for Li-S battery development. Figure 1 compares the typical potential profile of conventional Li-S batteries with liquid electrolyte (schematic)[51] and an exemplary SSLSB with Li₆PS₅Cl (this work), visualizing another fundamental challenge in constructing SSLSB. As evident, the solid-state cell shows a considerably higher overpotential, despite comparable delivered cell capacities and conductivities of the employed electrolytes. This higher overpotential in the solid-state analogue is often attributed to the sluggish conversion reaction in solids. Although it is clear that a drastic local reconfiguration of the constituents associated with a conversion reaction requires high activation energies and the difference in the reaction pathways adds complexity as some inclusions may play catalytic roles,[52–55] a rigorous investigation shedding light on the carrier transport in SSBS, especially in the well-processed composite containing substantial density of interface among the components, is missing.

On the whole, the stability of the SE, the reversibility of the redox reactions of the SE and its decomposition products, as well as the charge carrier transport in the composite cathode need to be explored in relation to the Li-S battery performance. We employ a highly conductive lithium thiophosphate Li₆PS₅Cl (Cl-argyrodite) as a model SE. To better resolve the behavior of Li₆PS₅Cl in contact with carbon additives, we first focus on the electrochemical behavior of SE-C composites with a highly microstructured carbon (C). Subsequently, a systematic analysis of the charge carrier transport, that is, the partial electronic and ionic conductivities in the composite, is performed through impedance spectroscopy and DC measurements. The analysis with a transmission-line model (TLM) reveals that a high overpotential in SSLSBs is due to sluggish lithium-ion transport in the composite. By reducing the SE fraction in the composites, a rapid reduction in the lithium-ion conductivity is observed. The activation energy of the lithium-ion transport evaluated directly from the Warburg coefficient gives a clue about the origin of the sluggish lithium storage kinetics. Furthermore, while the oxidative degradation can deliver a reversible capacity and possibly boost the attainable capacity of solid-state cathode composites, impedance measurements after applying different electrode potentials uncover an exponential reduction in the lithium-ion conductivity of the composite, which results in accelerated capacity loss. Finally, SSLSBs with Li₆PS₅Cl-C-S composite cathodes are constructed, achieving an areal capacity of over 4.5 mAh cm⁻² (1350 mAh gₛᵤфизическ相助^{-1}) after 50 cycles, and showing over 80% of capacity retention after 100 cycles. We believe our work can shed light on the limitations of solid-state sulfur composite cathodes, and provide tools to fully exploit their properties toward high-performance SSBS with conversion-type composite electrodes.

2. Results

The results section consists of two major parts: The electrochemical behavior of Li₆PS₅Cl-C composites (in Section 2.1) and the charge carrier transport in the composite cathodes (in Section 2.2). In Section 2.1, the electrochemical behavior
of the ball-milled SE-C composite is investigated. As a basis, the practical stability of Li₆PS₅Cl under oxidative and reductive conditions is tested through step-wise cyclic voltammetry (CV),[39] confirming the apparent redox behavior of the SE-C composite after partial SE decomposition. The magnitude of the apparent redox activity, and its reversibility and impact on cell performance are studied by cycling cells with SE-C composite cathodes with various cut-off potentials. Comparison to recent in-depth analytical investigations is also made, clarifying the underlying reactions delivering the measured capacity. In contrast, Section 2.2 focuses on the charge carrier transport in the cathode composites. First, the applicability of a TLM for the analysis of the obtained impedance spectra is verified. Subsequently, by varying the loading of the SE-C composite, the SE fraction in the composite, temperature, and the applied potential, a systematic investigation of charge carrier transport is conducted through a TLM analysis, providing information such as the effective partial ionic and electronic conductivities within the composites.

2.1. Electrochemical Behavior of Li₆PS₅Cl-Carbon Composites

2.1.1. The Stability and Apparent Redox Activity of Li₆PS₅Cl-Carbon Composites

Step-wise CV, as recently used for evaluating practical stability windows,[39] is conducted on ball-milled Li₆PS₅Cl-C composites to assess the electrochemical behavior. A highly microstructured carbon black with a specific surface area of ≈1400 m² g⁻¹ is employed to provide enough electronic conduction pathways. The CV measurements are performed in a step-wise manner, that is, step-wise CV, and the potential of the working electrode is repeatedly scanned between a fixed cut-off potential and the reversible potential. The reversal potential is consecutively varied every scan until it reaches 0 V versus In/InLi or 3.5 V versus In/InLi for the reduction or oxidation tests. This method provides insight on both the onset potential of the degradation and the redox activity of the degradation products.[39] The scan speed was 0.1 mV s⁻¹ and the reversal potential was varied by 0.1 V after every sweep. It should be noted that all CVs were recorded with an In/InLi anode to minimize side reactions at the anode side. Therefore, unless otherwise specified, the potentials in this manuscript are shown relative to the In/InLi potential (0 V vs In/InLi is 0.62 V vs Li⁺/Li⁻).[56,57] Here, numbers within square brackets, for example, [1], indicate the corresponding area in Figure 2a,b.

As for the reductive step-wise CV shown in Figure 2a, a gradual increase in the cathodic (negative) current [1] below 0.8 V, and its drastic increase below 0.6 V are observed after a small non-Faradaic contribution in the early scans. We assign this reduction reaction to the reduction of P(+)5,[38,48,58] located in the center of the PS₄⁻ tetrahedron in the structure of Li₆PS₅Cl. Therefore, the Li₆PS₅Cl structure collapses upon reduction of P(+)5, resulting in reduced phosphorous compounds Li₃P, LiP, Li₃P₂, or LiP₂, and in the accompanying formation of Li₂S and LiCl. After extensive P(+)5 reduction, an increase in the anodic (positive) current [2] at around the upper cut-off potential is observed. This anodic current may be related to the conversion reaction of Li₂S and Li₃P into Li-thiophosphate glasses, containing thiophosphate polyhedra.[48]

Upon further reductive scans, a broad positive current peak [3] at around 0.4–0.5 V appears, reflecting the oxidation of the reduced phosphorous species (e.g., P(−3) ≈ P(+)3 + (3 + x)e⁻, where x > −3).

The oxidative step-wise CV shown in Figure 2b confirms an apparent redox activity of the SE-C composite appearing after Li₆PS₅Cl oxidation. A slight rise of the positive current [4] is observed with the reversal potential of 1.8 V and it continues to grow up to 2.5 V. As this oxidation proceeds, a new positive current peak [5] at around 2.0 V appears, accompanied by another new negative current peak [5'] at around 1.5 V. These potentials agree with the typical redox potentials of Li-S batteries (Sₓ + 2xLi⁺ + 2xe⁻ = xLi₂S).[26,59,60] implying formation of sulfur upon oxidative degradation as proposed in previous work.[39,61]

Structurally, the argyrodites contain S²⁻ and Cl⁻ anions, besides PS₄⁻ tetrahedra. The so-called free S²⁻ is likely oxidized first, leaving PS₄⁻ tetrahedra behind. Interestingly, a positive current peak [6] at around 2.4 V remains even after the peak height of Li₆S oxidation is saturated, which might reflect a redox process associated with the PS₄⁻ units. The thiophosphate units can be linked (oligomerized) together by releasing sulfur or polysulfides through corresponding redox reactions (e.g., 2PS₄⁻ → P₂S₇⁴⁻ + S + 2xe⁻ = P₂S₇⁴⁻ + 25 + 4e⁻, and even possibly = P₂S₇⁴⁻ + 3S + 6xe⁻).[45,62–64] It is worth mentioning that the apparent redox activity of thiophosphate glasses is reported to occur at slightly higher redox potential than that of elemental sulfur,[64] which corroborates this interpretation. The oxidation of thiophosphate units will probably lead to the formation of polysulfides, based on the recent observation through a combination of X-ray photoelectron spectroscopy (XPS) and the time-of-flight secondary-ion mass spectroscopy.[65] The oxidation of Cl⁻ (2Cl⁻ → Cl₂(g) + 2e⁻) may take place above 4.36 V versus Li⁺/Li (3.74 V vs In/InLi) based on its standard electrode potential; therefore, it does not participate in the electrochemical reaction in the current study. As the degradation proceeds, a small anodic current [7] at around 0.5 V appears, indicating the phosphorus reduction as discussed above [1]; however, it is only visible in the latter scans because of the cathode limiting condition (see Experimental method in Supporting Information).

2.1.2. Reversibility of the Apparent Redox Activity of Li₆PS₅Cl-Carbon Composites

The reversibility of the apparent redox activity along with the SE degradation is investigated by cycling SE-C composites, which do not contain any elemental sulfur, with various cut-off potentials. The results are shown in Figure 2c. Cycling within the potential range of 1–1.8 V delivers only little charges, corroborating the CV results that give no significant Faradaic reaction between 1 and 1.8 V. First, the oxidative degradation is induced by increasing the upper-cutoff potential from 1.8 to 2.4, 2.7, and 3.0 V. The cells start delivering reversible capacities, which increase from 150 to 200 mAh g⁻¹ as the upper cut-off potential is increased. The stable cycling confirms the reversible redox activity of the oxidative degradation products and the attainable capacity depends on the degree of oxidative degradation. In contrast, a much inferior capacity retention is observed upon reductive degradation. By expanding the potential range
to 0–2.7 V, a large capacity of 573 mAh g\textsubscript{SE}\textsuperscript{−1} (7.88 mAh cm\textsuperscript{−2})
is observed in the first charging, following the reductive degradation in the initial discharge delivering 291 mAh g\textsubscript{SE}−1.
Afterward, the capacity rapidly fades as the cycle number increases. This drastic capacity fade likely reflects a progressive reductive degradation. For instance, the reduced phosphorous species of LiP and Li\textsubscript{3}P, which are only obtained upon reductive degradation of Li\textsubscript{6}PS\textsubscript{5}Cl, possess band gaps of 0.81 and 0.74 eV, respectively, enabling a sufficient amount of electronic conduction.[66] The formation of these electronically conductive phases cannot passivate the interface and, eventually, will likely grow through the conductive SEs.[42] However, it is also important to bear in mind that the degree of degradation depends on the size of the interfacial area between SE and carbon, closely related to the specific surface area of the employed carbon additives. With less interfacial area, reductive degradation will show less apparent capacity, highlighting the importance of a choice of carbon additives.[50]

Figure 2d shows representative potential profiles of the cell cycled within 1–3.0 V, visualizing how it evolves upon cycling. The potential profiles of the other cells are shown in Figure S1, Supporting Information. As discussed above, whereas there is only little initial discharge capacity, a reversible capacity appears (≈200 mAh g\textsubscript{SE}−1), following an intense oxidative degradation during the first charge (327 mAh g\textsubscript{SE}−1). Starting from the second cycle, a plateau at around 1.7 V in the charge profile grows as the cycle number increases. For comparison, the potential ranges, in which the redox activities of S\textsubscript{x} and thiophosphate units occur, are shaded in light-gray and dark-gray, respectively, in Figure 2b,d, showing good agreement. The XP spectra of S 2p and P 2p measured before and after cycling further corroborate formation of oxidative degradation products as shown in Figure S2, Supporting Information. The areas under the XPS fits of degradation products increase with cycling up to higher cut-off potentials, reflecting a larger magnitude of oxidation as seen in observed capacities.

There are various proposed mechanisms of the reductive and oxidative degradation and the corresponding apparent redox activity, and the here-observed onset potentials and peak potentials are in good agreement with other experimental reports.[39,48,49] The formation of S, LiCl, and Li\textsubscript{3}PS\textsubscript{4} (or P\textsubscript{2}S\textsubscript{5} at a higher potential) upon oxidative decomposition, and that of
Li₃P, LiCl, and Li₂S upon reductive decomposition, are generally predicted theoretically to cause a much narrower (thermo-
dynamic) stability window. It is worth noting that common
thermodynamic calculations require the crystal structures
of the candidate decomposition products as input, making pre-
dictions including amorphous lithium thiophosphates or
other amorphous phases virtually impossible. While the study
by Schwierert et al. gives a potential explanation on the wider
stability window of Li₃P_{x}S_{5−x}Cl observed experimentally
within the framework of the crystalline solids, the observation of the
critical role of lithium thiophosphate glass formation should
motivate future theoretical work including those glass phases.
It is also important to emphasize that, while the reductive
degradation toward reduced phosphorous species is avoidable,
the oxidative degradation and their apparent redox capacity are
inevitable upon Li-S battery operation, since their potentials
largely overlap. In other words, considering the fact that the
various thiophosphate glasses, for example, (Li₃S)₉(P₂S₅)₁₋₉₇,
possess a considerable variation in their ionic conductivities,
an investigation of the transport in the composite cathode is
essential as they are likely to occur during cycling and degrada-
tion of the crystalline SE.

### 2.2. Charge Carrier Transport in Li₆PS₅Cl-Carbon Composites

#### 2.2.1. Validity of a Transmission-Line Model for Impedance Analysis

Fast ionic and electronic charge carrier transport in the com-
posite cathode is desired for a better Li-S battery performance.
Although the direct measurement of the ionic conductivity
in the SE phase in the composite is challenging, the effective
ionic conductivity, assuming the composite as a single homoge-
neous material, is easily accessible. The effective ionic conduc-
tivity (σ_{eff}^{ion}) of the cathode composite can be obtained through
direct-current (DC) polarization measurements by blocking
the electron transport (e.g., In/InLi|SE|SE-C|In/InLi, see
Figures S3 and S4, as well as Table S1, Supporting Information).
By applying various constant voltages for sufficiently long
time, the ionic resistance of the composite (R_{iion}) is obtained from
the resulting current passing through the composite. Similarly,
an effective electronic conductivity (σ_{eff}^{elec}) can also be obtained
through the electronic resistance (R_{e}) with ion-blocking elec-
trodes (e.g., stainless-steel|SE-C|stainless-steel, see Figure S3,
Supporting Information). The underlying principles have been
well analyzed in detail in the early days of solid-state ionics, but
the measurement of partial conductivities of cathode compos-
ites is not yet a routine method in battery research. With a
given cell constant of the cathode composite layer, the effective
conductivity of the carrier k (= ion or electron) is attained
from σ_{eff}^{k} = 1 \cdot \frac{d}{R_{k} A}, where d, A, and R_{k} are the thickness of the
composite, the electrode area, and the ion or electronic resis-
tance of the composite (= R_{ion} or R_{e}). While this DC polarization
measurement provides direct access to σ_{eff}^{k} of the as-prepared
composite of interest, it is still challenging to address them
during or after the electrochemical treatment, especially with
SEs. Therefore, we assess the effective transport in the com-
posite by utilizing impedance spectroscopy.

To verify its applicability, the impedance analysis is first
compared with DC measurements. For that purpose, two sym-
metric cells, as well as a cathode half-cell, are constructed as
shown in Figure 3. This is to focus on the transport in the com-
posite by eliminating the SE/anode interface because the use of
a reference electrode in SSBs is technically demanding.
The thicknesses of the composite cathode layers are determined
from cross section images as shown in Figure S5, Supporting
Information. The resulting impedance spectra are analyzed
with a TLM.

The use of a TLM for the impedance analysis of the porous
electrodes was demonstrated first successfully with conventional
LIBs with liquid electrolyte. Recently, the use of a TLM has
been extended to SSBs with thick electrode configurations, as
well as some exemplary composite electrodes. Figure 4a
is a schematic of the equivalent circuit for the cell (i) with a TLM.
The infinitely long ladder-like circuit, composed of ionic resis-
tances per unit length (r_{ion} = \frac{1}{A \cdot \sigma_{eff}^{ion} (\Omega \ m^{-1})}), electronic resis-
tances per unit length (r_{e} = \frac{1}{A \cdot \sigma_{eff}^{elec} (\Omega \ m^{-1})}), together with the

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**Figure 3.** Schematics of the cells constructed to validate the applied model. The SE-C composites are the same as for the CV measurements and cycling tests (with mass ratio m(SE):m(C) = 90:10). a) A cathode half-cell with In/InLi anode. Total loading of the cathode is 15.3 mg cm⁻² (13.8 mg cm⁻² of SE). b,c) Symmetric cells with 15.3 or 30.6 mg cm⁻² of SE-C composites on both sides. The density of the SE-C composites in the cells can be estimated to 1.70 g cm⁻³, which is almost identical to the density separately measured with the pellet of 150 mg of SE-C composites (1.68 gm cm⁻³). Considering that the theoretical density of the SE is 1.85 g cm⁻³ and the relative density in the cells are 90%, it is safe to assume the density of carbon to be 2.0 g cm⁻³, which is in the range of typical amorphous carbon. [7]
complex transverse impedances \((z_i (\Omega m))\), represents the impedance of the composite cathode \((Z (\Omega))\) as follows,

\[
Z = \frac{r_{\text{ion}}r_e L}{r_{\text{ion}} + r_e} + \frac{\sqrt{z_i}}{\left(r_{\text{ion}} + r_e\right)^2} \left(\frac{r_{\text{ion}}^2 + r_e^2}{z_i}\right) \cosh L \left(\frac{r_{\text{ion}} + r_e}{z_i} + 2r_{\text{ion}}r_e\right)
\]  

(1)

where \(L\) is the total thickness of the cathode composite and \(A\) is the electrode area (0.785 cm\(^2\) in this work). For a non-Faradaic situation, the transverse impedance \(z_i\) part in Figure 4a becomes an interfacial capacitance with a constant phase element CPE \((z_{\text{CPE}})\) defined as:

\[
z_{\text{CPE}} = \left(\frac{1}{\omega}\right)^{\alpha} \epsilon_{\text{dl}}
\]

where \(\omega\) is the angular frequency \((s^{-1})\), \(\alpha\) is a dimensionless ideality factor, and \(\epsilon_{\text{dl}}\) is a frequency-independent interfacial capacitance parameter for the CPE \((S s^{-1} \text{m}^{-1} \text{or} F s^{-\alpha} \text{m}^{-1})\), respectively. The two limits of the real part of \(Z (Z')\) can be analytically solved,

\[
\lim_{\alpha \to 0} Z' = \frac{1}{3} (r_{\text{ion}} + r_e) L
\]

(2)

\[
\lim_{\alpha \to \infty} Z' = \frac{r_{\text{ion}}r_e}{r_{\text{ion}} + r_e} L
\]

(3)

Thus, when \(r_e\) in the composite is negligibly small compared to \(r_{\text{ion}}\), the impedance of the TLM part becomes a third of the total ionic resistance of the cathode layer in the direction of thickness. It should be noted that \(r_e\) was only reliably obtainable in the pristine SE-C composite with 10 wt% of C in this work because \(r_e \ll r_{\text{ion}}\) holds in the other composites with increased \(\sigma_{\text{eff}}\) or decreased \(\sigma_{\text{ion}}\). Therefore, to demonstrate the validity of the general model with \(r_e\), we employ the SE-C composite with the mass ratio \(m\text{(SE)}:m\text{(C)} = 90:10\) here. The ionic and electronic resistances \((R_{\text{ion}} \text{and} R_e)\) in Figure 4c,d are in the dimension of \(\Omega\); \(r_{\text{ion}} L = R_{\text{ion}}\) and \(r_e L = R_e\). For the general mathematical representations and their derivations, we refer the readers to the work by Bisquert et al., Trötzsch et al., Kaiser et al., Siroma et al., Lasia et al., and Barsoukov et al. just to name a few, where a variety of TLMs for different scenarios are theoretically and experimentally summarized.

A Nyquist plot of the measurements and their fits with a non-Faradaic TLM are shown in Figure 4b, demonstrating the goodness of the fits. Representative Kramers–Kronig test results and a Bode plot are shown in Figure S6, Supporting Information, further confirming the validity of the fits and spectra. In the Nyquist plot, a straight 45° line is seen before the sharp capacitive tail appears, which represents a typical impedance spectrum suitable for a non-Faradaic TLM.
stemming from the complex microstructure of the composite. Figure 4c,d shows the extracted $R_{\text{ion}}$, $R_{\text{e}}$, and the effective ionic and electronic conductivities of the SE-C composite $\sigma_{\text{eff}}$ and $\sigma_{\text{eff}}^{\text{eff}}$. Individual fitting results are tabulated in Tables S2–S4, Supporting Information. As expected, the $R_{\text{ion}}$ and $R_{\text{e}}$ values increase linearly as a function of the total thickness of the composite layers. The resulting $\sigma_{\text{ion}}^{\text{eff}}$ and $\sigma_{\text{e}}^{\text{eff}}$ are $(0.20 \pm 0.02)$ and $(1.9 \pm 0.2)$ mS cm$^{-1}$, respectively, and are independent of the thickness as it should be the case. To confirm the results from the TLM analyses, the $\sigma_{\text{ion}}^{\text{eff}}$ and $\sigma_{\text{e}}^{\text{eff}}$ values measured by DC polarization are also shown in Figure 4c,d with dashed straight lines. As explained above, $R_{\text{e}}$ was measured directly with a stainless-steel|SE-C|stainless-steel cell. As for $R_{\text{ion}}$, it is obtained by subtracting the resistance contributions of the InLi|SE interfaces acquired from an In/InLi|SE|In/InLi cell and the SE layers estimated based on its conductivity from the total resistance of an In/InLi|SE|SE-C|SE|In/InLi cell (see Figures S3,S4 and Table S1, Supporting Information for details). As seen in Figure 4c,d, the $\sigma_{\text{ion}}^{\text{eff}}$ and $\sigma_{\text{e}}^{\text{eff}}$ obtained by two different methods show good agreement, corroborating the validity of the TLM analysis of the transport in the SE-C composites. We would like to highlight that the simple semicircle fitting with a parallel circuit of R and CPE, which is a widespread method, can lead to a severe overestimation of $\sigma_{\text{ion}}^{\text{eff}}$ of the composite. As shown in Figure S7, Supporting Information, although no apparent failure is visible in the fitting with a simple R-CPE element, the obtained $\sigma_{\text{ion}}^{\text{eff}}$ of 0.72 mS cm$^{-1}$ is higher than that from the TLM by over a factor of three and leads to a critical misinterpretation (see also Table S5, Supporting Information). Overall, we prove that the TLM analysis offers correct values for the effective partial conductivities and therefore suggest using it as a standard approach. It does not only enable the proper assessment of the transport in the composite at all, but it also allows to evaluate the transport limitations after electrochemical treatment (see Section 2.2.4).

2.2.2. The Influence of the Solid Electrolyte Fraction in the Cathode Composite

As mentioned above, $\sigma_{\text{ion}}^{\text{eff}}$ of the SE-C composite with a SE fraction of 90 wt% is measured to be $(0.20 \pm 0.02)$ mS cm$^{-1}$. This value corresponds to only 26% of the measured bulk conductivity $\sigma_{\text{ion}}^{\text{SE}}$ of the ball-milled Li$_6$PS$_5$Cl electrolyte without carbon additives ($\sigma_{\text{ion}}^{\text{SE}} = 0.76$ mS cm$^{-1}$, see Figure S8 and Table S6, Supporting Information), suggesting a strong influence of the microstructure. To further investigate the effect of the SE volume fraction, the conductivity of the SE-C composite with various carbon contents (0, 10, 20, and 30 wt%) were analyzed with a TLM (see also Tables S7 and S8, Supporting Information). As $\sigma_{\text{ion}}^{\text{eff}}$ is much higher than $\sigma_{\text{ion}}^{\text{eff}}$ even with only 10 wt% of carbon, here we focus on the transport of lithium ions. Figure 5a shows $\sigma_{\text{ion}}^{\text{eff}}$ as a function of the volume fraction of SE ($e_{\text{SE}}$), revealing a rapid reduction of $\sigma_{\text{ion}}^{\text{eff}}$ down to $3.3 \times 10^{-2}$ mS cm$^{-1}$ with 30 wt% of carbon. Conventionally, the impact of insulating (and typically spherical) inclusions in an ion-conducting composite is described based on macroscopic conservation laws by

$$ \sigma_{\text{ion}}^{\text{eff}} = \frac{\varepsilon_{\text{SE}}}{\kappa} \sigma_{\text{ion}}^{\text{SE}} $$

(4)

and

$$ \kappa = \gamma \varepsilon_{\text{SE}}^{\beta} $$

(5)

where $\kappa$ is the tortuosity factor, $\sigma_{\text{ion}}^{\text{SE}}$ is the bulk ionic conductivity without inclusions, $\beta$ is the so-called Bruggeman exponent (it

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Figure 5. a) The effective ionic conductivity of the SE-C composite as a function of the volume fraction $e_{\text{SE}}$. In addition to the ball-milled SE without carbon, three composites were prepared with the mass ratio $m$(SE)$:m$(C) = 90:10, 80:20, and 70:30, which are labeled as 9010, 8020, and 7030, respectively. The data point at 1.0 is obtained from the as ball-milled SE without carbon (see also Figure S8, Supporting Information). The dashed curve is based on a Bruggeman model assuming spherical inclusions. The solid curve is with a modified Bruggeman model with $\gamma = 1.53$ and $\beta = 6.97$. The orange circle in (a) represents the estimation purely based on the obtained fits and $e_{\text{SE}}$ of the SE-C-S composite employed in this study. b) The $E_a$ values of the ionic conductivity in both SE-C and SE-C-S composites are extracted from the temperature dependence of the Warburg coefficient and shown here in comparison to the activation energies of some representative amorphous (Li$_2$S)$_{100-x}$(P$_2$S$_5$)$_x$ glasses.[64] Cells with cell (ii) and cell (iii) configurations are constructed with the 90:10 SE-C composite.
is typically denoted as $\alpha$, but $\alpha$ is already used in this work for the ideality of a CPE, and $\gamma$ is a fit parameter. Equation (5) is referred to as the modified Bruggeman model, bridging the tortuosity factor to the volume fraction of the conducting phase, and $\beta$ controls how rapidly $\sigma_{\text{ion}}$ decreases with decreasing $E_{SE}$. Originally, this model has been developed by Bruggeman assuming small and spherical insulating inclusions, leading to\(^{89,90}\) 

$$\kappa = \frac{1}{\kappa_{\text{SE}}} \left( \frac{\sigma_{\text{ion}}}{\sigma_{\text{SE}}} \right)^{1/2}$$  

(6)

This is the case of $\gamma = 1$ and $\beta = 0.5$ in Equation (5). In contrast, the fitting in Figure 5a results in $\gamma = 1.53$ and $\beta = 6.97$. While deviations from the original Bruggeman model have been reported in several recent studies (e.g., experimentally $\gamma = 0.87$ and $\beta = 3.67$ in Froboese et al.\(^{91}\) as well as in theoretical work by Bielefeld et al.\(^{92}\) ), $\beta = 6.97$ indicates a drastic reduction of $\sigma_{\text{ion}}$ in the case of a well-mixed composite with a lithium-conducting thiophosphate, which represents a typical situation of the composite cathodes for SSLSBs.

The cycle capacity from three cells with SE-C composites possessing different mass ratios ($m_{\text{SE}}$:$m_{\text{C}}$) = 90:10, 80:20, and 70:30 and their representative potential profiles are shown in Figure S9, Supporting Information. In general, the composites with $m_{\text{SE}}$:$m_{\text{C}}$ = 90:10 and 80:20 show similar behavior with slightly smaller reversible capacity in the composite with more carbon, the capacity delivered upon the first charging is reduced from 327 to 160 mAh g\(^{-1}\) (SE), possessing different mass ratios ($m_{\text{SE}}$:$m_{\text{C}}$) = 90:10, 80:20, after initial oxidation. However, despite an expected higher interfacial area between SE and C with more carbon, the capacity delivery upon the first charging is further reduced to 87 mAh g\(^{-1}\) (SE) after initial oxidation, and it is expected that some parts of SE are ionically disconnected from the matrix with excess amount of carbon. Although further investigation is required, this indicates that a high Bruggeman exponent $\beta$ in the composite cathodes for SSLSBs is possibly due to an increased fraction of ionically isolated SE, which can effectively increase non-conducting volume and, with it, tortuosity.

The obtained fitting parameters enable the estimation of $\sigma_{\text{eff}}$ of any given composite prepared in the same way. For example, $\sigma_{\text{eff}}$ of the SE-C-S composite utilized for SSLSB cells in this work is estimated to be $3.8 \times 10^{-3}$ mS cm\(^{-1}\) with $E_{SE} = 52$ vol% (orange symbols in Figure 5a). While both DC and AC methods could not reliably determine the $\sigma_{\text{eff}}$ of the SE-C-S composite in the current study due to a very long study constant of attaining stationary DC polarization, the here-presented estimation clearly indicates a surprisingly sluggish lithium-ion transport in the composite when the active and electrically insulating material sulfur is present. Indeed, a very long time constant exceeding the limitation of the measurement indirectly confirms sluggish lithium ion transport.

### 2.2.3. Activation Energy of $\sigma_{\text{eff}}$ in the Composite Cathodes

To further explore the origin of the low $\sigma_{\text{eff}}$, the activation energy $E_{a}$ of the lithium-ion conductivity in the composites is evaluated. This should provide information regarding the kinetically limiting (i.e., bottleneck) phases on the lithium-ion transport. Whereas $E_{a}$ is commonly extracted from the Arrhenius plot of the ionic conductivity, here we directly obtain it from the Arrhenius behavior of the Warburg coefficient. This enables the evaluation of the $E_{a}$ of that process with the longest time constant ($\tau$ (s)), as it is the case in SE-C-S composites. As shown in Figure S10, Supporting Information, the typical Nyquist plot of the SE-C-S composite is dominated by the 45° tail, because the time constant $\tau$ of the ion conduction in the composite cathode is longer than the timescale of a reasonable measurement ($\omega^{-1}$ (s)) and not reliably measurable. When the electronic resistance is negligibly small ($r_{e} < < r_{\text{ion}}$), Equation (1) becomes as follows with a time constant $\tau = r_{\text{ion}} e_{\text{dl}} L^{2}$ ($\alpha$ is set to unity, that is, $z_{i} = (j e_{\text{dl}})^{-1}$, as its variation with temperature is minute),

$$Z = r_{e} L + \frac{r_{\text{ion}}}{j e_{\text{dl}}} \coth \left( L^{2} - j e_{\text{dl}} \right) = r_{e} L + \frac{r_{\text{ion}}}{j e_{\text{dl}}} \coth \left( j \omega \tau \right)$$  

(7)

When $\omega \tau \gg 1$, namely $\tau \gg \omega^{-1}$, Equation (7) becomes

$$Z = r_{e} L + \frac{r_{\text{ion}}}{j e_{\text{dl}}} = r_{e} L + \frac{r_{\text{ion}}}{j e_{\text{dl}}} \frac{1}{\sqrt{\omega}} - \frac{1}{\sqrt{\omega} j}$$  

(8)

Thus, from the frequency dependent part, the Warburg coefficient $A_{W}$ (in the dimension of $\Omega$ s\(^{-1/2}\)) is by definition,

$$A_{W} = \frac{r_{\text{ion}}}{j e_{\text{dl}}}$$  

(9)

The details can be found in Supporting Information (Section 12). Considering that there should be no significant morphological changes nor any variation in the permittivity of the components, we can assume a constant $e_{\text{dl}}$ within the measurement temperature range. Furthermore, given that the ionic conductivity decreases exponentially with decreasing temperature, the $r_{e} < < r_{\text{ion}}$ regime can be found below room temperature for the composite with $m_{\text{SE}}$:$m_{\text{C}}$ = 90:10. Thus, by inserting the typical Arrhenius relation ($\sigma_{\text{ion}} = \frac{\sigma_{0}}{T} \exp \left( \frac{E_{a}}{k_{B} T} \right)$), where $\sigma_{0}$ and $k_{B}$ are the pre-exponential factor and the Boltzmann constant), from Equation (9) we obtain,

$$A_{W}^{2} = \frac{1}{2 e_{\text{dl}} \sigma_{0} A} = \frac{T}{2 e_{\text{dl}} \sigma_{0} A} \exp \left( \frac{E_{a}}{k_{B} T} \right)$$  

(10)

Hence, the activation energy can be obtained from the slope of $\ln(A_{W}^{2}/T)$ when it is plotted as a function of $1/T$:

$$\ln \left( A_{W}^{2} \right) = - \ln \left( 2 e_{\text{dl}} \sigma_{0} A \right) + \frac{E_{a}}{k_{B} T}$$  

(11)

Note that Equation (11) is just a rearrangement of Equation (10) to clearly show the $1/T$ dependence. As seen in Figure 6b, a linear relation is confirmed with the experimental $A_{W}$ from the symmetric cells with the SE-C composite (the cells (ii) and (iii)) in Figure 3, as well as the SE-C-S composite. The individual data of Warburg coefficients are tabulated in Table S9, Supporting Information.

Similar $E_{a}$ values for the ionic conductivity are observed in the as-synthesized SE (0.38 eV, see our previous work...
the high $E_a$ (0.52 eV). As the active material shows a much higher resistance because it is clearly indicating that Li$_6$PS$_5$Cl is not the multi-component feature of the SE-C-S composite makes the spectroscopic analysis difficult, this observation is remark-

cally around 0.5–3,[94–96] the here-observed highly tortuous and sluggish lithium-ion transport in the SE-C-S composite anymore. Based on the $E_a$ values of two different amorphous lithium thiophosphates, (Li$_2$S)$_{75}$(P$_2$S$_5$)$_{25}$ (0.40 eV) and (Li$_2$S)$_{60}$(P$_2$S$_5$)$_{40}$ (0.53 eV), reported by Dietrich et al.,[64] the high $E_a$ upon S incorporation may arise from the formation of oxidized amorphous lithium thiophos-

2.2.4. Impact of Solid Electrolyte Degradation on Lithium-Ion Kinetics under Applied Potential

As shown in the previous sections, the lithium-ion transport in the composite is the rate-limiting process; and its kinetics can progressively decline when external potentials are applied. The TLM analysis of impedance data enables the evaluation of the effective transport properties of the composites upon the electro-

Overall, an unexpectedly low effective ionic conductivity of the cathode composites, especially those including sulfur, is revealed in Sections 2.2.2 and 2.2.3. Considering the fact that the values of the Bruggeman exponent ($\beta$ in this work) in conventional Li-S batteries with liquid electrolytes are typically around 0.5–3,[94–96] the here-observed highly tortuous and sluggish lithium-ion transport in the well-processed composite cathode ($\beta$ = 7 with a high $E_a$) contributes to a much larger overpotential in the SSLSBs as emphasized in Figure 1 even with highly conductive lithium thiophosphates. Therefore, although a high sulfur loading and thick-cathode configuration are desired for boosting energy density, those strategies always come along with further increased cell resistance due to the charge carrier transport in the composite, making them challenging.
observed up to 3.0 V (351 mAh g\text{SE}^{-1}) is only slightly larger than the 1st charge up to 3.0 V in the cycling tests (327 mAh g\text{SE}^{-1}). In contrast, the observed cumulative charge down to 0 V (417 mAh g\text{SE}^{-1}) is significantly larger than that of the initial discharge down to 0 V (291 mAh g\text{SE}^{-1}), which is likely due to the progressive formation of electron-conducting interphases. As observed in Figure 2 this progressive degradation is likely responsible for poor cyclability with too deep discharge.

Figure 6c shows the total resistance \(R_{\text{total}} = R_{\text{off}} + R_{\text{anode}} + R_{\text{ion}} + R_c\) of the cell, where \(R_{\text{anode}}\) and \(R_{\text{off}}\) are resistances from SE/anode interface and the separator. While the reductive degradation below 0.4 V causes an increase in the total resistance by a factor of four, the total resistance at 2.5 V is already over two orders of magnitude higher than the original resistance and it continues to grow at higher potentials. As shown in Figure 6d,f, the individual contributions to the total cell resistance can be deconvoluted through a TLM. This deconvolution is only possible between 0 and 2.4 V because the additional resistive contribution that emerges above 2.5 V overlaps with the frequency range of ion transport in the composite. While there are only minute changes in \(R_{\text{off}}\) and \(R_{\text{anode}}\), the value of \(R_{\text{ion}}\) drastically changes from 40 to over 1500 \(\Omega\) at 2.4 V, being the major contributor to the \(R_{\text{total}}\). The corresponding \(\sigma_{\text{ion}}\) at 2.4 V is \(72 \times 10^{-3}\) mS cm\(^{-1}\) (see Figure 6f). Representative Nyquist plots are shown in Figure S11, Supporting Information and the obtained values from both tests are shown tabulated in Tables S10 and S11, Supporting Information.

The gray-shaded areas in Figure 5 are the ranges of potential in which there are no significant changes in \(\sigma_{\text{ion}}\). A wider potential range for the gray area than that of the blue area (the range where no apparent Faradaic current is observed) implies the formation of either ionically or electronically conductive interphases in the early stage of the degradation that do not impede the transport in the composite. In particular, the phase forming with the observed charge between 1.8 and 2.0 V most likely includes lithium thiophosphate glasses that itself are ionic conductors. As for reductive degradation, the formation of electronically conductive compounds can explain the progressive evolution of the interphases. At too high potentials, the strong increase of the resistance suggests detrimental interphases with sluggish lithium ion transport. Although the potential dependence provides only qualitative information regarding the impact on cell cycling, these results clearly tell that, while oxidative SE degradation increases the attainable capacity, a too-high cut-off potential can cause severe degradation, resulting in a higher overpotential, and with it, a poor cell cycling performance. In addition to the inherent sluggish lithium-ion kinetics in the composites, long-term cycling—especially with a high upper cut-off potential—will further deteriorate the ion transport and accelerate cell degradation.

3. Discussion

Several important lessons can be drawn based on the here-presented systematic study of composites with Li\text{PS}_5\text{Cl}:

a) The SE-C composite shows an apparent redox behavior after reductive and oxidative degradation. While the reductive degradation delivers a substantially high capacity of about 570 mAh g\text{SE}^{-1}, it shows a poor retention likely due to the progressive and irreversible electrolyte degradation. In contrast, the apparent redox behavior associated with the oxidative degradation exhibits a less but stable cycling performance with about 200 mAh g\text{SE}^{-1}. These results suggest that the inevitable oxidative degradation during Li-S battery operation can enhance the attainable capacity but the reductive degradation may deteriorate the retention. Therefore, the lower cut-off potential for cycling Li-S batteries needs to be fixed at a sufficiently high potential (>0.8 V vs In/InLi).

b) The impedance analysis with a TLM on SE-C composites reveals that the high overpotential highlighted in Figure 1 is largely due to the sluggish lithium-ion kinetics in the composite. Based on the analysis of \(R_{\text{on}}\), upon sulfur incorporation to obtain the SE-C-S composite, the activation energy becomes higher likely due to the formation of amorphous thiophosphates with higher sulfur content. The analysis of SE-C composites further confirms that the effective ion transport in the composite can progressively deteriorate upon oxidation. These results clearly highlight the sluggish lithium-ion transport in the composite and call for an exploration of i) electrolytes which do not lose ionic conductivity drastically upon processing, ii) electrolytes which decompose into ionically well-conducting interphases, or iii) processing methods which achieve a higher effective ionic conductivity of cathode composites. Whereas for strategy i) processing conditions need to be systematically tested, strategy ii) and iii) may be achieved by modifications to known materials and much faster conductors; however, after these modifications, systematic studies on the transport will be needed.

c) Although a substantially slower lithium-ion transport is limiting the performance of current SSLSBs, this issue may be overcome by reducing the lithium-ion “traveling distances”. By structuring the cathode to implement fast “highways” for lithium ions, the effective traveling distance for lithium ions can be reduced, and with it, the overpotential should also be suppressed. In other words, similar to creating composites with “faster” ionic conductors, creating nano- and microstructured composites with smaller tortuosity may deliver the same results, which are a higher effective ionic conductivity and less sluggish kinetics that exert themselves as a high overpotential.

d) Although the oxidative SE degradation may boost the attainable capacity of Li-S cells, a deteriorating effective ionic conductivity is observed at higher potentials. However, a systematic investigation in this work reveals that the potential window maintaining the \(\sigma_{\text{ion}}\) (a gray area in Figure 6) is slightly wider than the potential window showing the apparent redox behavior of SE-C composite (blue area in Figure 6). This slight margin in the potential window allows us to achieve a higher capacity and a less deteriorated \(\sigma_{\text{ion}}\), simultaneously. Although this optimum cycling parameters for the SE-C-S composite cannot instantly be derived from the results from SE-C composites, the need of optimization is evident.

3.1. Cycling Optimization and the Current Status of Solid-State Li-S Batteries with Thiophosphate Solid Electrolytes

Clearly optimization of operating conditions is needed and based on the above results, cells with the SE-C-S composite
were prepared and cycled with various cut-off potentials (0–3, 1–3.0, and 1–2.7 V) to find the optimum potential window for cycling a given composite cathode. A rather high amount of sulfur is loaded, which should deliver an areal capacity of 5.68 mAh cm\(^{-2}\) with the theoretical capacity (1672 mAh g\(_{\text{sulfur}}\)\(^{-1}\)), in contrast to the typically reported sulfur loading ranging from 1 to 3 mAh cm\(^{-2}\). The utilized sulfur loading is in the range of the proposed areal capacity to be competitive for EV application.\(^{[51,97]}\)

![Figure 7](https://example.com/f7.png)

**Figure 7.** a) The delivered capacity and its retention from solid-state Li-S batteries cycled under optimized conditions. Restricting the lower and upper cut-off potentials to 1 and 2.7 V significantly improves the cyclability. b) The conversion efficiency \(\Phi_C\) indicates progressive degradation when the cell is discharged down to 0 V. c) The Coulombic efficiency \(\Phi_Q\) shows non-complete discharge especially in the later cycles when the cell is cycled up to 3.0 V, reflecting a drastic increase in the overpotential as shown in d). e) Restricting the upper cut-off potential to 2.7 V suppresses the high overpotential. f) The achieved areal capacities after cycling are compared to the reported values from the thiophosphate-based SSBs with conversion-type electrodes. The reports at room temperature with larger than 50 cycles\(^{[26,31,60–109]}\) are summarized based on the work by Yang et al.\(^{[110]}\) The additional data are listed in Table S12, Supporting Information in the same manner as ref. [110].

The cycling performance can be further understood with cycling efficiencies, namely the conversion efficiency \(\Phi_C\) and the Coulombic efficiency \(\Phi_Q\), as shown in Figure 7b,c. As defined in IUPAC and our previous work,\(^{[26]}\) \(\Phi_C\) and \(\Phi_Q\) are

\[
\Phi_C = \frac{Q_{c,n}}{Q_{d,n-1}}
\]

and

\[
\Phi_Q = \frac{Q_{d,n}}{Q_{c,n}}
\]

where \(Q_{c,n}\), \(Q_{d,n}\), and \(Q_{d,n-1}\) are a charge and discharge capacity in \(n\)th cycle, and discharge capacity in \((n-1)\)th cycle, respectively. One cycle consists of a charging and the following discharging step. As in Figure 7b, the low \(\Phi_C\) with 0–3.0 V is responsible for its low retention, indicating the irreversibly large discharge capacity compared to the following charge capacity. This is in line with the progressive degradation confirmed in the SE-C composites, which is particularly large in the early cycles. In contrast, a lower \(\Phi_Q\) is observed in the cell
cycled within 1–3.0 V, especially in the later cycles, implying that the charged capacity is not fully delivered in the following discharge. While the oxidative degradation adds a reversible capacity from SE in Li-S cells, it deteriorates the lithium-ion transport, making the full discharge more difficult. The incomplete discharge, in turn, limits the capacity in the following charge, resulting in the progressive reduction in the achievable capacity in the long run. The significantly higher overpotential upon cycling is clearly visible in Figure 7d,e, showing the potential profiles of 5th and 50th cycles. These cycling data further corroborate that lower effective ionic transport in the composites, here resulting from decomposition, affect the overpotentials in these SSBs. By restricting the cycling potential between 1 and 2.7 V, both the $\Phi_C$ and $\Phi_Q$ are improved, achieving optimized high capacity retention. The potential profiles of other representative cycles are also shown in Figures S12 and S13, Supporting Information.

The aforementioned improvements enable the capacity retention of 106.9% upon the 50th discharge with respect to the initial discharge capacity, achieving 1350 mAh g$_{sulfur}^{-1}$ (4.59 mAh cm$^{-2}$). Note that the capacity delivered from the cell cycled within 1–2.7 V is increased in the early cycles by 0.99 mAh cm$^{-2}$ (from 4.29 to 5.28 mAh cm$^{-2}$). Assuming that this increase is solely from the oxidative SE degradation in the cathode, the calculated specific capacity of SE is 194 mAh g$_{SE}^{-1}$ (mass of SE is 5.30 mg cm$^{-2}$), which is in good agreement with the value observed in SE-C cycling shown in Figure 2c. Although the exact fraction of SE degraded in the composite is undefined, the result confirms its contribution exist in SE-C-S cells, as well as SE-C cells. The results with 1–2.7 and 1–3.0 V are reproduced as shown in Figure S14, Supporting Information with a different batch of SE-C-S composite, confirming the reproducibility.

In the end, the observed cycling performance is compared with that of the state-of-the-art thiophosphate-based SSBs with conversion-type electrodes cycled at room temperature in Figure 7f (see also Table S12 and Figure S15, Supporting Information). The extended cycling shows the capacity retention of 81.8% at 100th cycle with respect to the initial discharge capacity (see Figure S14, Supporting Information), resulting in an outstanding areal capacity in the 100th cycle (1083 mAh g$_{sulfur}^{-1}$, 3.68 mAh cm$^{-2}$). This highlights the potential of SLSBs and necessity of the careful cycling parameter optimization to assess best possible cycling in a given system.

4. Conclusions

In this work, we performed a comprehensive study on the stability, reversibility, and lithium-ion transport of the composite cathode for SLSBs as a function of the cathode loading, the SE fraction in the composite, temperature, and applied potential, by employing a ball-milled composite of Li$_6$PS$_5$Cl and high-surface-area carbon as model system. The reductive SE degradation is progressive, leading to poor capacity retention. In contrast, the oxidative degradation results in delivering a highly reversible apparent redox capacity; however, it slows down lithium-ion transport and increases the cathode overpotential. Based on the impedance analysis with a TLM, the lithium-ion kinetics in the SE-C composite is very sluggish before electrochemical treatment, which becomes worse after intensive oxidation due to the limiting effective ionic conductivity. In other words, the electrochemical stability window may be narrow—however, the “stability window for effective conductivity” is wider in the here-presented Li$_6$PS$_5$Cl-carbon composite. The optimal potential window for cell cycling, achieving a boosted capacity without significantly deteriorating the lithium-ion transport, is found by potential-dependent impedance analysis. In addition, the direct measurement of the activation energy of ion transport in the composite is successfully demonstrated, paving the way for identifying the phases responsible for the sluggish ion transport. Especially for a system where chemically specific analysis is challenging, such as the multi-component cathode composite in this work, the electrochemical observation may offer hints to further understand the underlying mechanisms.

Through cycling parameter optimization, capacity retention of 81.8% in the 100th cycle with 3.68 mAh cm$^{-2}$ is achieved, which is one of the highest areal capacities achieved so far in literature for this type of SSBs. Our work provides not only the necessary experimental methods to comprehensively investigate the composite cathode but also the best route to obtain the highest achievable performance from the given system. We hope our work can guide the field toward high-performance SLSBs, by optimizing cycling conditions as well as finding composite and architecture strategies to increase the effective ionic conductivity in solid-state battery electrode composites.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

S.O. designed the study, synthesized the materials, prepared the cathode composites, performed electrochemical and spectroscopic measurements, and analyzed the data. S.O. and C.R. constructed test cells. G.F.D. performed DC measurement. S.O., J.J., and W.G.Z. wrote the manuscript. All authors discussed the results.

Data Availability Statement

Research data are not shared.
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