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# Influence of Crystallinity of Lithium Thiophosphate Solid Electrolytes on the Performance of Solid-State Batteries

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Solid electrolytes (SEs) largely define the properties of all-solid-state batteries (ASSBs) and are expected to improve their safety, stability, and performance. Their ionic conductivity has much improved in recent years, enabling higher power and energy density. However, more subtle parameters, such as crystallinity, may also influence the electrochemical performance of cells. In this work, the correlation between the performance of ASSBs and thiophosphate SEs having the same stoichiometry, but different crystallinity is investigated. In In/InLi | SE | LiCoO<sub>2</sub>@ LiNb<sub>0.5</sub>Ta<sub>0.5</sub>O<sub>3</sub> model cells, better cycling and rate performance is achieved when using glass/glass-ceramic SEs (e.g., 75Li<sub>2</sub>S·25P<sub>2</sub>S<sub>5</sub> glass, 70Li<sub>2</sub>S·30P<sub>2</sub>S<sub>5</sub> glass, and Li<sub>6</sub>PS<sub>5</sub>Cl glass-ceramic). This can be mostly attributed to the mitigation of contact loss by the glass/glass-ceramic SEs compared to their crystalline SE counterparts. Furthermore, the SE decomposition at typical cathode potentials is investigated by using SE and carbon composites as cathodes. Larger volume changes and more severe decomposition are observed with crystalline SEs in the SE/carbon composite cathode after cycling. The crystalline SEs show higher electronic partial conductivity which results in more degradation in the composite cathode. This work sheds light on optimized composite cathode design for ASSB by carefully choosing solid electrolytes with appropriate mechanical and (electro-)chemical properties.

## achieve high safety and competitive energy and power density.<sup>[1,2]</sup> The solid electrolyte (SE) is the key component in ASSBs and has been extensively explored for several decades.<sup>[3,4]</sup> Among the different types of solid electrolytes, lithium thiophosphates have attracted ever-increasing attention for ASSBs due to their very high ionic conductivity and facile processing at room temperature.<sup>[5,6]</sup> Recent theoretical simulations suggest that the ionic conductivity of SEs in ASSB cathodes needs to reach at least 10<sup>-2</sup> S cm<sup>-1</sup> in order to obtain comparable performance with commercial lithium-ion batteries with liquid electrolytes-a target that may only be achieved with thiophosphate electrolytes.<sup>[7]</sup>

Therefore, significant research effort is spent on improving the ionic conductivity of thiophosphate SEs.<sup>[8,9]</sup> Glasses in the quasi-binary system  $xLi_2S \cdot yP_2S_5$  prepared by mechanical ball milling exhibit a conductivity of up to  $10^{-4}$  S cm<sup>-1</sup> (e.g., 75Li\_2S \cdot 25P\_2S\_5 glass [7525-glass], 70Li\_2S \cdot 30P\_2S\_5 glass [7030-glass]) at room temperature.<sup>[10]</sup>

## 1. Introduction

All-solid-state batteries (ASSBs) using high-voltage/high-capacity cathode materials and a lithium-metal anode are expected to

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The conductivity is enhanced by the precipitation of metastable phases upon heating, forming glass-ceramic dispersions: crystalline phases in an amorphous matrix, in this work denoted as "gc".<sup>[11]</sup> Although very high ionic conductivities above 10 mS cm<sup>-1</sup> have been achieved in some

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quasi-ternary and higher thiophosphate systems (e.g.,  $Li_{6.6}P_{0.4}Ge_{0.6}S_5I$ ,<sup>[12]</sup>  $Li_{5.5}PS_{4.5}Cl_{1.5}$ ,<sup>[13]</sup>  $Li_{10}GeP_2S_{12}$  (LGPS),<sup>[14]</sup> and  $Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$ ,<sup>[15]</sup>), the performance of sulfide-based ASSBs is still not satisfactory due to electrochemical and chemomechanical failure.<sup>[16,17]</sup> For example, Ohtomo et al. have reported that a cell built from graphite,  $LiCoO_2$  (LCO) and 7525-glass shows better cycling performance than the corresponding cell with 70Li<sub>2</sub>S · 30P<sub>2</sub>S<sub>5</sub> glass-ceramic (7030-gc) though the ionic conductivity of the 7525-glass is lower. Sulfur and phosphorus appear to diffuse from the solid electrolyte into LCO for the cell with 7030-gc, while no obvious diffusion occurs with 7525-glass, which might explain better cycling stability of the 7525-glass cell.<sup>[18]</sup>

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Even for SEs with the same stoichiometry, their mechanical and (electro-)chemical properties, such as plasticity, electrochemical stability, ionic and electronic partial conductivity, may vary strongly when the crystallinity changes, which is expected to strongly influence the performance of ASSBs.<sup>[19-21]</sup> For example, Bonnick et al. reported that nano-crystalline Li<sub>3</sub>PS<sub>4</sub>·0.5LiI shows higher ionic conductivity than its amorphous counterpart, leading to higher critical current density of its Li symmetric batteries.<sup>[22]</sup> Due to the better compensation of local mechanical pressure, the cycling performance in ASSBs with glass-type SEs might be better. Systematic studies of the differences between glass-type SEs and their crystalline analogues and their effect on SSB performance have been scarcely reported. To the best of our knowledge, the influence of thiophosphate electrolytes with the same stoichiometry and different crystallinity on the performance of ASSBs has been rarely reported yet.

In this study, the electrochemical performance is compared for glass/glass-ceramic SEs and crystalline SEs using In/InLi | SE | SE/LiCoO<sub>2</sub>@ LiNb<sub>0.5</sub>Ta<sub>0.5</sub>O<sub>3</sub> (denoted as LCO(coated) for the sake of simplicity) cells. The investigated SE pairs are glassceramic Li<sub>6</sub>PS<sub>5</sub>Cl (gc-LPSC) and crystalline Li<sub>6</sub>PS<sub>5</sub>Cl (c-LPSC), 7525-glass and  $\beta$ -Li<sub>3</sub>PS<sub>4</sub>, 7030-glass and Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub>. In situ electrochemical impedance spectroscopy (EIS) and ex situ X-ray photoelectron spectroscopy (XPS) show that physical contact loss is responsible for the poor cycling performance and rate performance of cells with crystalline SEs in spite of the occurrence of interfacial reactions. More severe electrochemical degradation and crack formation occur in the SE/C65 cathode for the Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> | LGPS | SE/C65 cell with crystalline  $\beta$ -Li<sub>3</sub>PS<sub>4</sub> than 7525-glass, which is attributed to the higher electronic conductivity of the  $\beta$ -Li<sub>3</sub>PS<sub>4</sub>. Our results demonstrate that SEs with same stoichiometry and different crystallinity show different mechanical properties, electrochemical window, ionic/electronic conductivity, which affects the performance of ASSBs.

## 2. Results and Discussion

## 2.1. Characterization of Thiophosphate Solid Electrolytes

The  $\beta$ -Li<sub>3</sub>PS<sub>4</sub> solid electrolyte was provided by BASF SE (Ludwigshafen, Germany). The 7525-glass, 7030-glass, gc-LPSC were prepared via ball-milling,<sup>[21]</sup> Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub> was prepared by heat treatment of 7030-glass,<sup>[23]</sup> and c-LPSC was synthesized by solid-state sintering.<sup>[6]</sup> The X-ray diffraction (XRD) patterns (Figures S1–S3, Supporting Information) indicate that 7525-glass, 7030-glass, Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub>, gc-LPSC, and c-LPSC are formed without obvious crystalline impurity phases. More amorphous phase is observed in the XRD pattern of gc-LPSC, while the XRD pattern of the c-LPSC phase indicates a high degree of crystallinity.<sup>[24]</sup> According to impedance measurements of SE pellets (Figure S4, Supporting Information), the measured ionic conductivities at 25 °C are 0.31 mS cm<sup>-1</sup> for 7525-glass, 0.18 mS cm<sup>-1</sup> for  $\beta$ -Li<sub>3</sub>PS<sub>4</sub>, 0.21 mS cm<sup>-1</sup> for 7030-glass, 2.67 mS cm<sup>-1</sup> for Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub>, 1.01 mS cm<sup>-1</sup> for gc-LPSC, and 1.86 mS cm<sup>-1</sup> for c-LPSC.

# 2.2. Electrochemical Performance of In/InLi | SE | LCO(Coated)-SE Cells

#### 2.2.1. Cycling Performance Comparison

**Figure 1**a shows the cycling performance of In/InLi | SE | LCO(coated)/SE ASSB cells with  $\beta$ -Li<sub>3</sub>PS<sub>4</sub> and 7525-glass, respectively. We need to point out that both the SE from separator and cathode are replaced simultaneously. After 100 cycles at 0.1 C, 85% of the initial capacity is retained for the cell using the 7525-glass/LCO(coated) composite. The Coulomb efficiency is close to 99.8%, indicating good reversibility of the ASSB. In comparison, when using the crystalline  $\beta$ -Li<sub>3</sub>PS<sub>4</sub>/LCO(coated) composite, capacity fades to about 70%. The Coulomb efficiency fluctuates between 98% and 99%, indicating worse reversibility of the storage process. Similar observations are made for the gc-LPSC/c-LPSC and 7030-glass/Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub>-based cells (Figure 1b and Figure S5, Supporting Information). For instance, the cell using gc-LPSC as SE shows higher Coulomb efficiency and higher capacity retention than the cell with c-LPSC (Figure 1b).

Further analysis of the derivatives of the charge-discharge curves (Figure 1c,d) reveals clear differences between the cells with 7525-glass and  $\beta$ -Li<sub>3</sub>PS<sub>4</sub> after the 1st and the 100th cycle. In the first charge, both cells show a sharp peak at 3.35 V (vs In/ InLi), which corresponds well with the delithiation process of LCO(coated).<sup>[25]</sup> At the 100th cycle, only a slight shift in the main peak position and a minor decrease of the main peak height is shown in the cell using 7525-glass as SE, which could be related to a minor increase in the overpotential of the cell. In the other cell with  $\beta$ -Li<sub>3</sub>PS<sub>4</sub>, only a very weak peak at around 3.45 V (vs In/InLi) is present after 100 cycles, indicating the increased overpotential and degradation in the ASSB cell, resulting in severe capacity fading. A similar correlation is also found in the LPSC system (Figure 1e,f). A sharp decrease of the main peak occurs in the cell with c-LPSC, while the main peak declines only slightly for the cell with gc-LPSC. It is pointed out that two small peaks at 3.46 V and 3.58 V (vs In/InLi) in both cells with c-LPSC or gc-LPSC before cycling are attributed to the phase transitions between ordered and disordered lithium ion arrangements in CoO<sub>2</sub> framework, which slightly decrease after 50 cycles.<sup>[26]</sup> The results prove better cycling stability of the cells with glass (glassceramic) SE than with their crystalline counterparts.

#### 2.2.2. Electrochemical Impedance Spectroscopy

The increase in overpotential is a consequence of the raised internal resistance, as observed by electrochemical impedance

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**Figure 1.** Cycling performance comparison of In/InLi | SE | LCO(coated)-SE ASSB cells at 0.1 C at 25 °C using a) 7525-glass (red) and  $\beta$ Li<sub>3</sub>PS<sub>4</sub> (cyan) as electrolytes, b) gc-LPSC (red) and c-LPSC (cyan) as electrolytes. Differential capacities of c) 7525-glass and d)  $\beta$ -Li<sub>3</sub>PS<sub>4</sub> in ASSBs at the 1st and 100th cycles and e) c-LPSC and f) gc-LPSC in ASSBs at the 1st and 50th cycles.

spectroscopy (EIS, **Figure 2**). The bulk resistance of the solid electrolyte separator is visible at high frequency (>1 MHz). The

interfacial resistance of the SE/LCO(coated) composite lies in the mid-frequency range (600 Hz), and the resistance of the

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**Figure 2.** Nyquist plots of a) In/InLi | 7525-glass | LCO(coated) and b)  $In/InLi | \beta Li_3PS_4 | LCO(coated)$  cells after the 1st and 100th charge, and c) In/InLi | gc-LPSC | LCO(coated) and d) In | c-LPSC | LCO(coated) cells after the 1st and 50th charge at 0.1 C.

In/InLi/SE interface is represented by the semicircle at the low-frequency range (1 Hz).<sup>[27]</sup>

Figure 2a,b shows the Nyquist plots of ASSB cells with 7525glass and  $\beta$ -Li<sub>3</sub>PS<sub>4</sub> electrolytes after cycling, respectively. In Figure 2a, both semicircles at mid- and low-frequency do not change much. Thus, the total internal resistance of the ASSB using 7525-glass remains relatively constant. However, in Figure 2b a rather large semicircle at mid- and low-frequency develops during cycling with  $\beta$ -Li<sub>3</sub>PS<sub>4</sub> as SE. Its impedance shows around eightfold increase as compared to its initial value, as shown in Figure 2b. Interestingly, similar results are obtained for the gc-LPSC, c-LPSC pair, and for the 7030glass, crystalline Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub> pair (Figure 2c,d and Figure S5b,c, Supporting Information). In all cases, the main contribution for the increase of total interfacial resistance is from the SE/LCO(coated) interface. However, the increase of resistance of the LCO(coated)/glass (glass-ceramic) SE interface is slower than that for its crystalline SE/LCO(coated) counterpart (Figures S6-S8 and Table S1, Supporting Information), which could explain higher capacity retention of the cell with glass (glass-ceramic) SE.

#### 2.2.3. Rate Performance Comparison

The rate capability tests are carried out from 0.1 C to 1 C for all ASSB cells. The ASSB with 7525-glass shows superior rate capability compared to the one with crystalline  $\beta$ -Li<sub>3</sub>PS<sub>4</sub> as SE (**Figure 3**a). At 1 C, almost no capacity can be delivered from  $\beta$ -Li<sub>3</sub>PS<sub>4</sub>-containing cells, while still 50 mAh g<sup>-1</sup> of the capacity can be obtained from the cell with 7525-glass. The rapid drop in

capacity at high current density might be greatly affected by the severely hindered Li<sup>+</sup> transfer across the  $\beta$ -Li<sub>3</sub>PS<sub>4</sub>/LCO(coated) interface, which correlates well with the large interfacial resistances discussed before. Moreover, with increasing C-rate, the discharge potential of the cell with  $\beta$ -Li<sub>3</sub>PS<sub>4</sub> is much lower than that of the cell using 7525-glass as SE, which suggests that a larger overpotential is generated at high currents in the  $\beta$ -Li<sub>3</sub>PS<sub>4</sub> system (Figure S9a, Supporting Information). In the LPSC system, the cell with gc-LPSC also shows better rate performance compared to the cell with c-LPSC up to 0.5 C (Figure 3b). However, for the first five cycles at 1 C, the discharge capacity of the cell using c-LPSC is slightly higher than the cell with gc-LPSC.

Figure 3c shows the cycling performance of the In/InLi | SE | LCO(coated)/SE cells with gc-LPSC and c-LPSC at 1 C at 25 °C, respectively. As expected, during the initial tens of cycles, the discharge capacity of the c-LPSC based cell is higher than the cell with gc-LPSC. The higher ionic conductivity of c-LPSC might be one of the reasons. However, the capacity of the c-LPSC-based cell decreases rapidly and becomes much lower than the capacity of the c-LPSC type cell increases strongly after 60 cycles, whereas less change of overpotential is observed in the gc-LPSC type cell (Figure 3d). In addition, a larger increase in the resistance of the LCO(coated)/c-LPSC interface is observed as compared to the LCO(coated)/gc-LPSC system, which may account for the rapid decrease of capacity (Figure 3e, f and Figure S10, Supporting Information).

Summarizing the electrochemical characterization, the ASSBs with glass/glass-ceramic SEs show superior electrochemical performance compared to cells with the crystalline analogues. In

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**Figure 3.** Rate capability comparisons of a) 7525-glass and  $\beta$ -Li<sub>3</sub>PS<sub>4</sub>, b) c-LPSC and gc-LPSC in ASSBs at 0.1 C, 0.2 C, 0.5 C, and 1 C (1 C corresponds to 1.21 mA cm<sup>-2</sup>). c) Cycling performance comparison of c-LPSC and gc-LPSC in ASSBs at 1 C. d) Charge/discharge curves for ASSBs using c-LPSC or gc-LPSC as SEs after 1st and 60th cycles at 1 C. Nyquist plots of e) In/InLi | gc-LPSC | LCO(coated) and f) In/InLi | c-LPSC | LCO(coated) cells after the 1st and 60th charge.

addition, ASSB cells with crystalline SEs degrade faster, causing increasing internal resistance and larger capacity loss. This motivated us to explore the reasons why glass/glass-ceramic SEs generally outperform their crystalline counterparts, at least in the present model-type In/InLi | SE | LCO(coated)/SE cells.

## 2.3. Chemo-Mechanical Mechanism in InLi | LPSC | LCO(Coated) Cells

According to previous research, contact loss and interfacial reactions occur simultaneously at the LCO(coated)/SE interface and lead to capacity fading of ASSB cells.<sup>[16,25]</sup> However, it is hard to distinguish their contributions to the total increase of interfacial resistance between LCO(coated) and SE. In the following, the individual contributions to cell degradation are separated in an impedance analysis.

We use In/InLi | SE | LCO(coated)/SE ASSB cells with LPSC as SE (Figure S11, Supporting Information) for this analysis

in order to minimize the internal resistance of the cells by the high ionic conductivity of LPSC. In these cells, the interfacial resistance in the 1kHz-100Hz frequency range mainly stems from the LCO(coated)/SE interface. In line with previous reports, we will call the interphase formed between LCO(coated) and SE as cathode/solid electrolyte interphase<sup>[28]</sup> (CEI, Figure S12, Supporting Information). The resistance of the CEI layer (R<sub>LCO/SE</sub>, see Figure S13, Supporting Information) can be simply depicted as  $R_{\text{LCO/SE}} = k d / A$  (d is the thickness of the CEI layer, A is the contact area at the LCO(coated)/ SE interface, and k is a linear pre-factor), describing the mean conductivity of the CEI.<sup>[29]</sup> The ionic transport resistance in the composite cathode  $(R_{gc})$  and charge transfer resistance  $(R_{\rm LCO/SE})$  are shown in Figure S14, Supporting Information. It is obvious that  $R_{\rm gc}$  is smaller than  $R_{\rm LCO/SE}$ , so any reactionzone-like effects can be neglected, meaning that (de)lithiation happens homogeneously in the composite. In addition, the interfacial resistance R<sub>InLi/SE</sub> maintains a constant level during cycling, which proves that the interface between In/InLi anode





Figure 4. a) Interfacial resistance R<sub>LCO/SE</sub> between LCO(coated) and SE (c-LPSC/gc-LPSC). b) Warburg coefficients D<sub>w</sub> of the ASSBs with c-LPSC and gc-LPSC as solid electrolytes, respectively.

and SE is stable.<sup>[30]</sup> Therefore, the major interfacial resistance is derived from the  $R_{\rm LCO/SE}$ .

The interfacial reactions result in growth of the CEI layer, which increases the CEI thickness *d*. According to Equation (1),<sup>[31]</sup> the Warburg coefficient ( $D_w$ ), which is mainly attributed to the solid-state diffusion of Li in LCO(coated), is a function of contact area, assuming that the diffusion coefficient of Li in the LCO(coated) particles is constant. In contrast to  $R_{\rm LCO/SE}$ ,  $D_w$  is only inversely proportional to *A* and is independent of any CEI-related contributions under the assumption that the formation of the CEI does not lead to any constrictions of the ionic transport in the LCO(coated), that is, the CEI layer is homogenously distributed at the LCO(coated)/SE interface.

$$D_{\rm w} = \frac{WRT}{n^2 F^2 A c_0 \sqrt{\widetilde{D_i}}} \tag{1}$$

Therefore, in case there is contact loss between the SE and LCO(coated), one would expect an increase of both  $D_w$  and  $R_{\rm LCO/SE}$ . On the other hand, if there is only the growth of a CEI layer at the SE/LCO(coated) interface, only  $R_{\rm LCO/SE}$  would increase and  $D_w$  would be unaffected. Thus, the combined analysis of charge-transfer and solid-state diffusion allows for the differentiation between the two most prominent degradation mechanisms, that is, contact loss and CEI growth.

Figures 4a and 4b, respectively, show the change of interfacial resistance  $R_{\text{LCO/SE}}$  and Warburg coefficient  $D_{w}$  (Figure 4b) with increasing cycle numbers. As observed before, in both the gc-LPSC/LCO(coated) and c-LPSC/LCO(coated) cathodes, an increase in R<sub>LCO/SE</sub> is observed, which is slower in case of gc-LPSC. However, there are clear differences in the development of D<sub>w</sub> when comparing gc-LPSC/LCO(coated) and c-LPSC/ LCO(coated). While D<sub>w</sub> of the c-LPSC/LCO(coated) cathode strongly increases with increasing cycle number, it remains more stable for the gc-LPSC/LCO(coated) cathode. This leads to the conclusion that the degradation at the c-LPSC/LCO(coated) interface is strongly affected by contact loss, whereas a high contact area is retained at the gc-LPSC/LCO(coated) interface. The extent of contact loss in the composite cathode may be connected with the particle size distribution. From the XRD results of gc-LPSC and c-LPSC solid electrolytes, it is clear that the gc-LPSC particles are smaller than c-LPSC particles, which is also observed from the SEM images of the c-LPSC and gc-LPSC powder. A size distribution with smaller mean particle size most likely deals better with chemo-mechanical failure.

In order to demonstrate that the interfacial reaction between glass/glass-ceramic SE and crystalline SE in the LCO(coated)/ SE composite cathodes is at a comparable level, ex situ XPS measurements of the composite cathodes before and after cycling were conducted (Figure S15, Supporting Information). The XP spectra were collected after sputtering the cathode for 180 s to minimize the influence of the current collector. 7525-glass (denoted as g-LPS) and  $\beta$ -Li<sub>3</sub>PS<sub>4</sub> (denoted as c-LPS) were chosen here for the sake of simplicity.<sup>[32]</sup>

Comparing the XP spectra of LCO(coated)/c-LPS and LCO(coated)/gc-LPS composite cathodes at various states, there is no obvious difference. Similar observations are made for the LCO(coated)/gc-LPSC and LCO(coated)/c-LPSC composite cathode (Figure S16, Supporting Information). In the studied cases, no carbon was added to the composite. The interfacial reactions may thus be limited due to the poor electronic transport pathway in the composite cathode.<sup>[33]</sup> This corroborates that contact loss is the main reason for the increase of interfacial resistance at the cathode, which reflects the importance of the compatibility of mechanical properties of solid components in ASSBs.

#### 2.4. Influence of Electro-Chemo-Mechanical Degradation of SEs

#### 2.4.1. CV and In Situ Pressure Monitoring

In order to eliminate the influence of LCO(coated) and focus on the properties of the SEs on cell performance,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  | LGPS | SE/C65 cells were fabricated. Carbon C65 was added to investigate the decomposition of the SEs in contact with carbon and increase the quantity of decomposition products to better analyze the process. LGPS, which has much higher ionic conductivity, is utilized here as a separator material to minimize the total impedance of the cell.  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  is used as anode active material for minimizing the volume change at the anode side.<sup>[34]</sup> The volume change of the SE/C65 composite



**Figure 5.** Cyclic voltammetry tests—a) voltage steps and b) current response upon cycling—of ASSB cells using 7525-glass/C65 composite (red) and  $\beta$ Li<sub>3</sub>PS<sub>4</sub>/C65 composite (blue) as working electrodes, and c) the corresponding pressure response. d,e) The SEM images of the corresponding composites after the CV tests. The cutoff voltage is set to be 2.7 V versus LTO, so the same as the electrochemical test with LCO(coated) as active material.

cathode can now be obtained simply by monitoring the total pressure change. The combined CV and in situ pressure results are shown in **Figure 5**a–c.

A high-impedance interphase layer forms as a result of the decomposition of thiophosphate SE during the first two cycles, which leads to a large capacity loss in an ASSB.<sup>[16,27]</sup> Therefore. the CV test was focused on the first two cycles. Significant oxidation occurs in the first positive scan for both materials (Figure 5b). The current begins to rise at a very low voltage ( $\approx 0.3$  V vs LTO), revealing that the whole first positive scan is accompanied by the oxidation of the SE, which is presumably the cause of the additional plateau in the first charge process in an ASSB with carbon additive, as reported before.<sup>[25,27]</sup> Using  $\beta$ -Li<sub>3</sub>PS<sub>4</sub>/C65 as working electrode, the main decomposition appears at around 1.5 V (vs LTO) with a peak current of 0.07 mA, followed by a broader shoulder up to 2.7 V (vs LTO). On the reverse scan, the current remains at 0 mA until 1.0  $\rm V$ (vs LTO), followed by a broad reduction peak until 0 V (vs LTO) and a current of about 0.03 mA. The asymmetric peak in the first cycle suggests that the oxidation products of  $\beta$ -Li<sub>3</sub>PS<sub>4</sub> are not completely reduced in the selected voltage range during the reverse scan. In the second CV cycle, a smaller oxidation peak is observed in the positive scan, indicating that less oxidation takes place, while the asymmetric peak shape remains. The results clearly show that, in the selected voltage range (0–2.7 V vs LTO),  $\beta$ -Li<sub>3</sub>PS<sub>4</sub> is electrochemically oxidized during the charge process. However, the oxidation products are not reversibly reduced at low potential. An interphase is formed, composed of the oxidative products of SE which accumulate during cycling.

Simultaneously, a large volume shrinkage occurs during the oxidation of  $\beta$ -Li<sub>3</sub>PS<sub>4</sub>, as shown by the pressure decrease in Figure 5c. The measured pressure follows well with the current-time curve in Figure 5b. The pressure decreases during the positive scan (oxidation) and increases during the negative scan (reduction). A pressure decrease of 0.39 MPa from 1.5 to 2.7 V (vs LTO) was observed in the first oxidation run. During the reverse scan (reduction) the pressure increased by 0.2 MPa. As the measured pressure refers directly to the volume change occurring in the working electrode, the decreased pressure corresponds to the volume shrinkage of SE during oxidation (delithiation). Since the oxidized products cannot be fully reduced in the reverse scan, the SE particles do not return to their original morphology. As a result, the formation and accumulation of an interphase arising from the oxidation of  $\beta$ -Li<sub>3</sub>PS<sub>4</sub> is subjected to the overall volume shrinkage of the working electrode. Consequently, cracks and voids form in and between the  $\beta$ -Li<sub>3</sub>PS<sub>4</sub> particles, as is shown in the SEM images (Figure 5e), where large gaps in the working electrode can be observed after the CV tests. In a real ASSB with cathode active material, void formation leads to contact loss between the SEs and the active materials, resulting in capacity fading, as shown in Section 2.3.

When comparing the first positive CV scans, it is obvious that the peak current and pressure change of the 7525-glass/ C65 cell are only half of the magnitude of its crystalline counterpart,  $\beta$ -Li<sub>3</sub>PS<sub>4</sub>. No further peaks and pressure changes are observed in the following scans. Therefore, the main decomposition of the 7525glass/C65 composite takes place during the first oxidative scan, which leads to relatively small volume

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**Figure 6.** Normalized XP spectra of S 2p of a)  $\beta$ -Li<sub>3</sub>PS<sub>4</sub>/C65 and b) 7525-glass/C65 composite cathodes at different cut-off voltages versus LTO during the charge process, respectively. Simulated structures of c)  $\beta$ -Li<sub>3</sub>PS<sub>4</sub> and d) 7525-glass. Lithium, phosphorus, and sulfur atoms are marked with green, purple, and yellow, respectively.

shrinkage. As a result, only few voids are observed in the composite cathode, as is shown in SEM image (Figure 5d).

#### 2.4.2. Ex Situ XPS Analysis

Much more severe decomposition observed from the current in CV occurs in the  $\beta$ -Li<sub>3</sub>PS<sub>4</sub>/C65 composite cathode than in the 7525-glass/C65 composite in the selected voltage range, which may reflect a more severe decomposition of  $\beta$ -Li<sub>3</sub>PS<sub>4</sub>. In order to prove this, ex situ XPS measurements were carried out for the SE/C65 composite at the charged states of 1.5 V and 2.7 V versus LTO (**Figure 6**a,b).

Comparing the XP spectra recorded at different cut-off voltages using crystalline and amorphous SE in both cases, it is evident that the whole signal is broader at 2.7 V (vs LTO) and shifted toward higher binding energy than at 1.5 V (vs LTO). The broadening indicates further decomposition, that is, oxidation, of the SE with increasing voltage. Combining the CV tests shown in Figure 5, the oxidation peak near 1.5 V can be attributed to the formation of a small amount of P-S-P and  $S_x$ .<sup>[35,36]</sup> In the case of 7525-glass as SE, more P-S-P is formed when the voltage is increased to 2.7 V, while the fraction of the  $S_x$  only increases slightly. Interestingly, when using the  $\beta$ -Li<sub>3</sub>PS<sub>4</sub> in the composite cathode, the peak of  $S_x$  increases strongly when the cell is charged to 2.7 V. According to recent work by Walther et al., adding carbon in the composite cathode amplifies the reaction at the cathode composite interfaces, resulting in formation of more polysulfides.<sup>[33]</sup> This might explain the obvious difference in decomposition between the LCO(coated)-SE cathode and SE-C65 cathode. As both 7525-glass and  $\beta$ -Li<sub>3</sub>PS<sub>4</sub> are made up of the same building block (PS<sub>4</sub><sup>3–</sup>), the more S<sub>x</sub> formed in  $\beta$ -Li<sub>3</sub>PS<sub>4</sub> might relate to the electrochemical stability and electronic conductivity difference as discussed in more detail in the following section.

#### 2.4.3. Electrochemical Window Calculation and Electronic Conductivity

Density functional theory (DFT) calculations were performed to determine the electrochemical windows of the electrolytes. Two models were built, including crystalline  $\beta$ -Li<sub>3</sub>PS<sub>4</sub> and the amorphous phase (Figure 6c,d). The amorphous structures, which represent the 7525-glass solid electrolytes, were first created from molecular dynamics simulations based on a 2×2×1 supercell of the crystal  $\beta$ -Li<sub>3</sub>PS<sub>4</sub> and then optimized by DFT calculations. The redox potential is determined from the Gibbs free energy change of corresponding reductive and oxidative reactions (more details in the Experimental Section). The  $\beta$ -Li<sub>3</sub>PS<sub>4</sub> and 7525-glass electrolytes show a very similar redox potential with a difference within 20 mV (Table 1), which agrees with the CV results. The  $\beta$ -Li<sub>3</sub>PS<sub>4</sub> and 7525-glass electrolytes have similar intrinsic thermodynamic stability. However, from the CV and ex situ XP spectra results,  $\beta$ -Li<sub>3</sub>PS<sub>4</sub> electrolyte decomposes more in the SE/C65 composite cathode. Thus, the improved electrochemical performance of 7525-glass/C65 cathode originates from kinetic effects.

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Table 1. Electrochemical window of the  $\beta\text{-}\text{Li}_3\text{PS}_4$  and 7525-glass electrolytes.

Models	Reduction potential (V vs Li/Li <sup>+</sup> )	Oxidation potentia (V vs Li/Li+)
$\beta$ -Li <sub>3</sub> PS <sub>4</sub> , 2 × 2 × 1 supercell	1.725	2.305
7525-glass, $2 \times 2 \times 1$ supercell	1.737	2.286

A higher electronic conductivity of the SE can change the kinetics of SE oxidation, as extraction of lithium requires both ion and electron transport, resulting in stronger decomposition of SE in the composite cathode due to faster decomposition reaction kinetics.<sup>[37]</sup> According to DC polarization measurements with blocking electrodes (Figure S17, Supporting Information),  $\beta$ -Li<sub>3</sub>PS<sub>4</sub> ((6.34 ± 3) × 10<sup>-10</sup> S cm<sup>-1</sup>) has a higher electronic conductivity than the 7525-glass ((1.37 ± 0.6) × 10<sup>-10</sup> S cm<sup>-1</sup>). As a result, more serious interfacial reactions were observed in the  $\beta$ -Li<sub>3</sub>PS<sub>4</sub>/C65 cathode than in the 7525-glass/C65 cathode (Figure 6a,b). Consequently, besides the electrochemical window, the electronic partial conductivity of SEs is a very important factor when considering decomposition reactions of composite cathodes.

## 3. Conclusions

In summary, In/InLi | SE | LCO(coated)-SE ASSB cells with glass or glass-ceramic SEs show higher Coulomb efficiency, slower increase of interfacial resistance, and better cycling and rate performance when compared to cells built with their crystalline analogues. Even though high ionic conductivity of crystalline SEs may result in initially high absolute capacity at high C-rate, it does not guarantee high capacity retention of the cells. Ex situ XPS results reveal that no obvious discrepancy of interfacial reactions in the LCO(coated)/SE composite cathodes appears between SEs with different crystallinity. The crystalline SE show more contact loss between SEs and LCO(coated) upon cycling as compared to the glass-type SE, which might be the main factor accounting for these performance differences.

In addition, LTO | LGPS | SE/C65 model cells were used to investigate the influence of mechanical and (electro-)chemical properties of SEs themselves on the performance of ASSBs. Larger volume shrinkage and more cracks occurred in cells with  $\beta$ -Li<sub>3</sub>PS<sub>4</sub> than with 7525-glass. From a thermodynamic perspective, theoretical and CV results reveal that the electrochemical window of 7525-glass SE is slightly narrower than that of the  $\beta$ -Li<sub>3</sub>PS<sub>4</sub>, which we consider as insignificant. However, the decomposition of  $\beta$ -Li<sub>3</sub>PS<sub>4</sub> is stronger than that of the 7525-glass, which is due to the higher electronic conductivity of  $\beta$ -Li<sub>3</sub>PS<sub>4</sub>. Typically, crystalline phases have higher electronic partial conductivities than their amorphous analogues, which means that crystalline SE are more prone to degradation by oxidation in general. More ionic/electronic insulating polysulfides  $(S_x)$  form in the  $\beta$ -Li<sub>3</sub>PS<sub>4</sub>-C65 cathodes, which is revealed by ex situ XPS characterization.

Our work deepens the understanding of the influence of the (electro-)chemical and mechanical properties of different SEs on the performance of ASSBs and opens a new way for designing high-performance ASSBs. Clearly, the high ionic conductivity of crystalline SE alone is not enough to achieve high-performance cathodes. More subtle phenomena need to be considered in addition.

## 4. Experimental Section

Solid Electrolytes: The crystalline  $\beta$ -Li<sub>3</sub>PS<sub>4</sub> solid electrolytes were provided by BASF SE. The 7525-glass, Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub>, 7030-glass70Li<sub>2</sub>S·30P<sub>2</sub>S<sub>5</sub>, c-LPSC electrolytes were prepared according to the previous work.<sup>[6,21,23]</sup> The gc-LPSC electrolyte was synthesized by ball milling a mixture of Li<sub>2</sub>S (Alfa, 99.9%), P<sub>2</sub>S<sub>5</sub> (Sigma-Aldrich, 99%) ,and LiCl (Alfa Aesar, 99%) at 500 rpm for 150 cycles using a planetary ball mill apparatus (Fritsch Pulverisette 7).

Cell Assembly: For the galvanostatic cycling tests, the In/InLi | SE | LCO(coated)-SE ASSB cells were assembled as follows. First, 80 mg of SE powder was compressed in a PEEK housing with a diameter of 10 mm by hand. The LCO(coated)-SE composite cathodes were prepared via hand-mixing the LCO(coated) (prepared according to the previous work<sup>[38]</sup>) and SE in a weight ratio of 70:30. Then, 10 mg of the composite cathode was spread onto one side of the electrolyte pellet and pressed at 3.5 tons. Afterward, the indium foil with a diameter of 8 mm was put on the other side of the pellet, followed by pressing at 1.5 tons. For the CV and in situ pressure tests, the LTO | LGPS | SE-C65 cell assembly steps were the same as described above. The SE-C65 cathode was prepared by hand-mixing SE and C65 in a weight ratio of 75:25, and the composite anode was prepared by mixing LTO, LGPS, C65 in a weight ratio of 30:60:10. The mass of the cathode, electrolyte, and anode layer is 10, 80, and 20 mg, respectively. All the procedures were conducted under argon atmosphere in a glove box ( $[O_2] < 1$  ppm,  $[H_2O] < 1$  ppm).

Electrochemical Measurements: The In/InLi | SE | LCO(coated)-SE ASSBs cells were tested in a homemade cell at a constant pressure of ~70 MPa at 25 °C using VMP-300 Biologic, VMP-3, and MACCOR potentiostats/galvanostats in a voltage range of 2.0–3.6 V (vs In/InLi), corresponding to 2.6–4.2 V (vs Li<sup>+</sup>/Li). The impedance of the cells after cycling was measured using a VMP-300 Biologic potentiostat/ galvanostat in the frequency range of 7 MHz–100 mHz at 25 °C. The impedance measurements of the In/LiIn | SE | LCO(coated)-SE cells were conducted using VMP-300 Biologic potentiostat/galvanostat in the frequency range of 7 MHz–300 µHz at 25 °C.

The CV measurements of the LTO | LGPS | SE-C65 were conducted using a potentiostat (VMP-300 Biologic) at a scan rate of 0.1 mV s<sup>-1</sup> within the voltage range of 0–2.7 V at 25 °C. Meanwhile, the operando pressure monitoring of these cells was performed with a homemade apparatus.<sup>[20,34]</sup> The initial cell pressure was fixed at around 60 MPa by tightening the frame.

To obtain the partial ionic/electronic conductivities of the SEs, 80 mg of the SE powder was pressed into a pellet. Two stainless steel disks were attached to the pellet as current collectors. The AC impedance measurements were conducted in the frequency range of 7 MHz–1 Hz at RT. The direct-current (DC) polarization tests were conducted with applied constant voltages of 0.4 V, 0.6 V, and 0.8 V for 6 h, respectively.

*Characterization*: The surface morphology of the samples was examined by scanning electron microscopy (SEM, Zeiss Merlin) at an acceleration voltage of 5 kV. The X-ray diffraction diffractometer Rigaku D/max-2500 diffraction meter with a Cu K<sub> $\alpha$ </sub> radiation source was used to identify the phase of the samples. The samples were sealed in an airtight container covered with a Kapton polyimide thin film to prevent unwanted reactions with moisture and air.

An X-ray photoelectron spectroscopy spectrometer (PHI 5000 VersaProbe II) with a monochromatized Al K $\alpha$  source (1486.6 eV) was used to obtain the surface chemistry of the samples. The samples were transferred using a transfer module filled with argon atmosphere. The pass energy was 23.5 eV. The sample surface was cleaned via Ar<sup>+</sup> sputtering with an acceleration voltage of 0.5 kV for 180 s. A dual beam charge neutralization was applied for charge compensation. The

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sputtered area was (2 × 2) mm<sup>2</sup>. Data evaluation was performed with the software CasaXPS (version 2.3.22, Casa Software Ltd) using Gaussian-Lorentzian line shapes (GL(30)) and a Shirley background. Common curve fitting restrictions were used such as upper FWHM limits, fixed area ratios (e.g., p orbitals 1:2) and fixed spin-orbit splitting.<sup>[33]</sup>

DFT Calculations: The redox potential of  $\beta$ Li<sub>3</sub>PS<sub>4</sub> and 7525-glass was calculated based on density functional theory (DFT) performed in the Vienna Ab initio Simulation package (VASP).<sup>[39]</sup> The projector augmented wave (PAW)<sup>[40]</sup> pseudopotentials and the Perdew–Burk–Ernzerhof generalized gradient approximation functional<sup>[41]</sup> were adopted. The self-consistent field (SCF) and geometry convergence tolerance were set to  $1 \times 10^{-5}$  and  $1 \times 10^{-4}$  eV, respectively. Besides, the energy cutoff was set to be 520 eV. In order to model the 7525-glass structures, a  $2 \times 2 \times 1$  supercell of  $\beta$ -Li<sub>3</sub>PS<sub>4</sub> was built and then heated at 298 K to produce amorphous structures. The redox potential of  $\beta$ -Li<sub>3</sub>PS<sub>4</sub> and 7525-glass was calculated according to the following reduction and oxidation reactions:<sup>[42]</sup>

$$Li_3PS_4 + 5Li = 4Li_2S + P \tag{2}$$

$$2Li_{3}PS_{4} = 3S + P_{2}S_{5} + 6Li$$
(3)

## **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**

W.Z. and S.W. designed the experiments. S.W., W.Z., and D.D. prepared the samples and conducted the main experiments and analyses. F.H.R. carried out the SEM measurements. S.W. and W.Z. prepared the XPS samples, S.O. and R.K. conducted the XPS measurements, and F.W. and R.K. analyzed the data. A.G. prepared the gc-LPSC powders, S.W. carried out the XRD measurements, and A.G. conducted the XRD refinement. S.W. conducted the in situ impedance test of the cell, and R.R. analyzed the data. X.C. and Q.Z. conducted the theoretical calculation of the electrochemical window of solid electrolytes. S.W., W.Z, X.C, R.R., C.-W.N., W.G.Z., F.H.R., and J.J. wrote the manuscript. All authors discussed the results and contributed to the preparation of the manuscript.

## Data Availability Statement

Research data are not shared.

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