Influence of Porosity of Sulfide-Based Artificial Solid Electrolyte Interphases on Their Performance with Liquid and Solid Electrolytes in Li and Na Metal Batteries

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ABSTRACT: Realization of all-solid-state batteries combined with metallic Li/Na is still hindered due to the unstable interface between the alkali metal and solid electrolytes, especially for highly promising thiophosphate materials. Artificial and uniform solid-electrolyte interphases (SEIs), serving as thin ion-conducting films, have been considered as a strategy to overcome the issues of such reactive interfaces. Here, we synthesized sulﬁde-based artificial SEIs (Li$_2$S and Na$_2$S) on Li and Na by solid/gas reaction between the alkali metal and S vapor. The synthesized ﬁlms are carefully characterized with various chemical/electrochemical techniques. We show that these artiﬁcial SEIs are not beneﬁcial from an application point of view since they either contribute to additional resistances (Li) or do not prevent reactions at the alkali metal/electrolyte interface (Na). We show that Na$_2$S is more porous than Li$_2$S, supported by (i) its rough morphology observed by focused ion beam-scanning electron microscopy, (ii) the rapid decrease of $R_{\text{interface}}$ (interfacial resistance) in Na$_2$S-covered-Na symmetric cells with liquid electrolyte upon aging under open-circuit potential, and (iii) the increase of $R_{\text{interface}}$ in Na$_2$S-covered-Na solid-state symmetric cells with Na$_2$PS$_4$ electrolyte. The porous SEI allows the penetration of liquid electrolyte or alkali metal creep through its pores, resulting in a continuous chemical reaction. Hence, porosity of SEIs in general should be carefully taken into account in the application of batteries containing both liquid electrolyte and solid electrolyte.

KEYWORDS: porosity, solid-state batteries, sulﬁde-base electrolytes, solid-electrolyte interphase, lithium, sodium

1. INTRODUCTION

Owing to the climate change crisis and energy shortages, efﬁcient energy storage has become an aspirational goal of mankind. The most demanding aspect of “efﬁciency” in energy storage systems, in particular in mobile applications, would most likely be the energy density, which describes the amount of energy stored in a speciﬁc volume/weight. Solid-state batteries (SSBs), combined with alkali metals, have been attracting attention as a new energy storage system that can meet the needs of the times since their volumetric/gravimetric energy density is higher than in conventional Li batteries. However, interfacial issues hinder the application of SSBs, especially for sulﬁde-based solid electrolytes known to have high ionic conductivities in the order of $\sim 10^{-3}$ S cm$^{-1}$. Interfacial issues include high resistances stemming from the imperfect electrode/electrolyte contact, a high activation energy barrier for charge transfer at grain boundaries (or at phase boundaries), and a continuous growth of the solid-electrolyte interphases (SEIs) on reactive alkali metals linked with the formation of mixedconducting SEIs. Additionally, the chemically inhomogeneous interface between alkali metal and the solid electrolyte induces uneven ion transport, leading to the preferential stripping/plating at certain positions and, consequently, the formation of dendrites. Introducing artificial SEIs (i.e., SEIs which are formed ex situ prior to the electrochemical cell assembly), if carefully chosen, can be a strategy to overcome these issues. Chemically stable and homogeneous artiﬁcial SEIs have already been proposed for Li/Na metal batteries when liquid electrolytes are used, demonstrating stable galvanostatic stripping/plating cycleability. Meanwhile, much fewer reports focus on the role of artificial SEIs on the Li/Na metal with reactive solid electrolytes and systematic comparative studies of Li and Na are scarce. The underlying reason might be the complexity of the SSB system, where many chemo-mechanical parameters affecting the cell performance are intertwined with one another. For Li/Na metal batteries where liquid...
electrolytes are employed, mechanical problems are less relevant compared to SSBs since the liquid electrolyte penetrates through the pores and touches all surfaces of the electrode particles evenly, maintaining good contact.\textsuperscript{2} On the contrary, a number of issues in SSBs originate not only from chemical but also from mechanical instabilities of the interfaces. These two effects may also be correlated to each other.\textsuperscript{23} For instance, external pressure applied to the cell and galvanostatic stripping/plating. Growth of the sul-
examined with electrochemical impedance spectroscopy (EIS) and Na system are systematically compared.

and Na2S can be easily synthesized via Li(Na) exposure to sulfur vapor,\textsuperscript{34,35} which has an advantage over the solvent-
mediated method\textsuperscript{36} since only pure S is included as a reactant, avoiding the risk of unwanted side reactions with Li/Na. Also, due to the fact that Li2S and Na2S share similarities in the crystallographic structure and ion conduction behavior, a comparative study of their roles in battery operation may allow exclusion of the chemical factors stemming from the SEI and may provide insights into the morphological/mechanical difference of Li and Na. The sulfide-based layers grown on Li/Na are systematically investigated with focused ion beam-scanning electron microscopy (FIB-SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and time-of-flight secondary ion mass spectroscopy (ToF-SIMS). Finally, their role as artificial SEIs in symmetric Li(Na) metal cells is examined with electrochemical impedance spectroscopy (EIS) and galvanostatic stripping/plating. Growth of the sulfide-based artificial SEIs and electrical conduction behavior in Li and Na system are systematically compared.

2. EXPERIMENTAL SECTION

2.1. Synthesis of Li2Sx(Na2Sx) on Li(Na). The Li rod (99.9%, trace metals basis) and Na cubes stored in a mineral oil (99.9%, trace metals basis) were purchased from Sigma-Aldrich and were stored in a glovebox under an Ar atmosphere. S powder (99.998%, trace metals basis, Sigma-Aldrich) was dried in a vacuum oven at 100 °C overnight before use. Li and Na metals were wiped with a tissue paper to remove the residual oil and freshly cut with stainless-steel blades. Subsequently, they were sandwiched between two Celgard separators and roll-pressed to approximately the same thickness (0.15 mm). The Celgard separator was used during pressing since Li and Na adhere strongly to the stainless-steel pressing plate. After the Li(Na) pressing procedure, discs with a diameter of 10 mm were cut and attached to stainless steel discs with a diameter of 18 mm. The stainless-steel discs act as a supporting substrate since the alkali metals easily lose their form. The so-prepared electrodes were placed in homemade glass ampoules with a length of 600 mm together with the S powder. The glass ampoule was immersed in an oven and heated at different temperatures (in the temperature range from 230 °C to 433 K). All processes were performed in a glovebox (both O2 and H2O levels were below 0.1 ppm). A schematic diagram of the Li2Sx(Na2Sx) synthesis is shown in Figure 1.

![Schematic diagram of the synthetic method used for preparation of artificial sulfide-based SEIs](image)

**Figure 1.** Schematic diagram of the synthetic method used for preparation of artificial sulfide-based SEIs. T\textsubscript{li} temperature of sulfur; P\textsubscript{vap} vapor pressure of sulfur; and T\textsubscript{Na} temperature of Li.

2.2. Characterization of Li2Sx(Na2Sx) Formed on Li(Na). For FIB-SEM analysis, samples were transferred from the Ar-filled glovebox to the SEM chamber with a homemade airtight transfer tool. Cross-section images were measured by using a Zeiss Crossbeam scanning electron microscope with a built-in focused ion beam (FIB). FIB cutting was performed using a Ga\textsuperscript{+} beam (accelerating voltage: 30 kV) with a current ranging from 50 pA to 2 nA, depending on the sample and its reactivity.

XPS of Li samples was performed on a Kratos Axis Ultra system with a monochromatic Al K\textsubscript{x} X-ray source. High-resolution data were acquired with a pass energy of 20 eV. Ar\textsuperscript{+} sputtering was performed using a scanned Minibeam III sputter gun (Kratos) with a beam energy of 4 kV and an emission current of 20 mA. XPS data were analyzed with CasaXPS software (version 2.3.23PR1.0 by Casa Software Ltd.). For accurate phase identification, the peak shift due to charging was corrected based on the binding energy of Li2S,\textsuperscript{37} and the phase identification was confirmed again with the binding energy separation between O 1s and Li 1s in Li2O as discussed in the literature.\textsuperscript{38} For fitting of the S 2p peaks, the binding energy difference between the spin−orbit split components (S 2p\textsubscript{3/2} and S 2p\textsubscript{1/2}) and their area ratio were constrained to 1.2 eV and 2:1, respectively.\textsuperscript{39} Samples were transferred to the XPS chamber under an Ar atmosphere in an airtight transfer tool.

ToF-SIMS measurements were carried out using a ToF-SIMS V instrument (ION-TOF) version NCS. Dual beam depth profiles were acquired using a cyclic sputter-probe series. The sputter gun and the analysis gun were operated in the noninterlaced mode with an additional flood gun in order to avoid sample charging. For sputtering, a Cs\textsuperscript{+} source was employed with 2 keV ion energy and 132 nA current on a 500 × 500 μm\textsuperscript{2} crater area. For probing, monatomic B\textsubscript{i}\textsuperscript{+} ions were used, accelerated by 30 keV, with a current of 1.7 pA on a 100 × 100 μm\textsuperscript{2} analysis area. Ions were acquired with negative polarity. Data analysis was carried out using the software Surfacinglab 7.1. The ion intensities were normalized to the total ion count for each sputter
time data point. Samples were transferred under an Ar atmosphere to the chamber using a commercial (ION-TOF) airtight transfer vessel. XRD was measured using an X-ray diffractometer from PANalytical GmbH (Empyrean Series 2) with a Cu Kα radiation energy of 40 kV and a current of 40 mA. The samples were mounted in a dome airtight sample holder from Anton Paar. For phase determination, HighScore Plus software, version 3.0e, was used.

2.3. Synthesis of Li₃PS₄ and Na₃PS₄. β-Li₃PS₄ was synthesized via a solvent-mediated synthesis as reported in the literature.\(^{40-42}\) Li₂S (99.9%, Sigma-Aldrich) and P₂S₅ (98+%, Acros Organics) were mixed in a 3:1 molar ratio and poured to tetrahydrofuran (Fischer Scientific, anhydrous, synthesis grade) with a volume ratio of 1:20. The mixture was stirred for 24 h at room temperature under an Ar atmosphere. Subsequently, the mixture was centrifuged at 9000 rpm for 10 min and dried under vacuum at 140 °C for 24 h.

Na₂PS₄, was synthesized via mechanical ball milling\(^{44,47}\). Na₂S (nonhydrate, extra pure, Fischer Scientific) and P₂S₅ (anhydrous, synthesis grade, Fischer Scientific) were mixed in a 3:1 molar ratio and put in a ZrO₂ jar with five ZrO₂ balls. The ball-to-sample weight ratio was 7:1. The powder mixture was mixed using a planetary mill apparatus (Fritsch, planetary mill apparatus Pulverisette 5) at 250 rpm for 10 min and put in a ZrO₂ jar with five ZrO₂ balls. The ball-to-sample weight ratio was 7:1. The powder mixture was mixed using a planetary mill apparatus (Fritsch, planetary mill apparatus Pulverisette 5) at 250 rpm for 24 h. The samples were neither heat-treated nor exposed to air during the synthesis and handling procedure.

2.4. Cell Assembly and Electrochemical Measurements. CR2032-type coin cells made of stainless steel were assembled with two Li(Na) symmetric electrodes and liquid or solid electrolytes. CR2032-type coin cells made of stainless steel were assembled with two Li(Na) symmetric electrodes and liquid or solid electrolytes. Liquid electrolytes were prepared by dissolving 1 M LiCF₂SO₃ (98%, Sigma-Aldrich) and 1 M NaCF₂SO₃ (99.5%, Solvionic) into triethylene glycol dimethyl ether (triglyme, 99%, Alfa Aesar). The H₂O content in the liquid electrolyte was controlled to be below 1 ppm (using the Karl Fischer titration technique). For the cells with liquid electrolytes, two symmetric electrodes were separated by a 20 μm-thick Celgard separator (H2013) soaked with 20 μL of the liquid electrolyte. Here, a spring was included in the cell for achieving better contact between the different components. For the solid-state cells, the synthesized solid electrolyte powders (Li₃PS₄ and Na₃PS₄) were pressed uniaxially (380 MPa, 10 mm diameter, between 70 and 80% density) in the glovebox and sandwiched between the two Li(Na) electrodes in a coin cell. In solid-state cells, a spring was not used due to the limited cell thickness. In order to determine the ionic conductivity of the solid electrolytes, the pellets were produced in the same way as previously described but were sputtered with Ru (400 nm thickness) on both flat sides in the glovebox.

EIS was performed starting from 10⁶ to 0.1 or 1 Hz, depending on the specific cells. EIS was conducted in the potentiostatic mode, with an amplitude of 0.1 V, using Solartron 1260 and Novocontrol Alpha-A devices. Temperature-dependent EIS measurements were performed in the temperature range from 80 to 0 °C for 1 h for each temperature using an external thermostat (Lauda RC6CP). Impedance spectra were analyzed with ZView software (Scribner Associates, version 3.5c).

3. RESULTS AND DISCUSSION

Figure 1 illustrates the synthesis route for obtaining sulfide-based artificial SEIs on Li/Na. Since the ampoule containing Li/Na and S is long enough, the temperature of Li/Na (T_{Li/Na}) and the temperature of S (T_s) could be regulated separately, allowing subtle control of reaction kinetics by fixing the vapor pressure of S and the reaction constant. The temperature on the Li/Na side of the ampoule was kept at the same or higher value than the temperature on the S side in order to avoid the condensation of S vapor. The expected solid–vapor chemical reaction is as follows\(^{46,49}\):

\[ 2\text{Li}(s) + \frac{1}{8}\text{S}_8(g) \rightarrow \text{Li}_2\text{S}(s) \quad \Delta G^\circ = -466 \text{ kJ mol}^{-1} \]

\[ 2\text{Na}(s) + \frac{1}{8}\text{S}_8(g) \rightarrow \text{Na}_2\text{S}(s) \quad \Delta G^\circ = -398 \text{ kJ mol}^{-1} \]

In contrast to the fact that Li₂S is the only thermodynamically stable phase in the Li–S system,\(^5\) the possibility of formation of sodium polysulfides such as Na₂S₂, Na₃S₄, and Na₅S₇ cannot be excluded in the Na case.\(^5\)
Figure 2 shows the data collected from a variety of materials’ characterization techniques employed on the synthesized artificial SEI films. Cross-section images measured by FIB-SEM in Figure 2a,d reveal the morphology of the Li,S and Na,S films. In both cases, the thickness and morphology of the films depend on the synthesis temperature (see Figures S1 and S2 in the Supporting Information), and the overall observation is that the film thickness increases with increasing  and . In addition, Na,S appears to have a rougher surface than Li,S, which may indicate a higher porosity at the nanoscale. This may be attributable to the inherently partially porous native film on Na,S, which may have led to the porous film even after the chemical reaction. Another contribution could be the molar volume difference between the reactant (Na) and products (Na,S, Na,S, Na,S, and Na,S), described by the Pilling–Bedworth ratio (, relative molar volume increase during sulfidation). For Na,S, is less than 1, suggesting that a porous film is favored, while sodium polysulfides with values greater than 1 induce compressive stress, favoring crack formation in the SEI (see Table S1, Supporting Information). Additionally, energy-dispersive X-ray spectra confirm the existence of S (Figure S3, Supporting Information) in the synthesized layer. The artificial sulfide-based SEI on Na is a crystalline film (Figure 2e), while the one on Li might be amorphous (Figure 2b). However, it should not be neglected that the intensity of the diffracted X-rays is a function of the atomic number. Since Na has a higher atomic number than Li, the probability of X-ray scattering in Na atoms is also higher than in Li, resulting in an increased form factor and scattering intensity. Finally, depth profiling of the chemical composition of the film was performed by XPS and ToF-SIMS. XPS data (Figure 2c) show that the surface of the film on Li is composed of a variety of sulfur-related compounds such as sulfate (SO₄²⁻), sulfite (SO₃²⁻), polysulfide (Li,S,y > 1), and sulfide (Li,S), while the expected Li,S phase is present in the bulk (for more information about phase identification by XPS, see Experimental Section 2.2; Table S2 in the Supporting Information provides the peak positions and the reference of XPS analysis in each phase). A similar chemical complexity was reported for sputter-deposited lithium sulfide films in the literature where the surface was covered with lithium polysulfides and the bulk was composed of Li,S. We could not perform XPS measurements on Na due to its relatively high vapor pressure (~10⁻¹³ mbar⁻¹), which might lead to contaminations of the vacuum chamber. Therefore, ToF-SIMS was applied to characterize the Na,S film on Na (Figure 2f). Note that ToF-SIMS analysis for Na,S on Na is qualitative, not quantitative, since the sample is rough, inhomogeneous, and reactive. As the sputtering in ToF-SIMS progresses, first, the concentration of Na decreases and then gradually increases, while the concentration of S decreases. The results from XPS of Li,S and ToF-SIMS of Na,S imply that a compositional gradient was formed over the film depth, with a higher Na-to-S ratio close to the metal. This is expected from the gradient of the chemical potential of Na and is analogous to the metal-to-oxygen ratio in oxides (e.g., in oxides on Fe).53

In order to examine the role of the synthesized films (Li,S and Na,S) on Li and Na as protective layers, they were assembled into symmetric cells (Figure 3a) with glyme-based liquid electrolytes, one of the most commonly used electrolyte classes for Li–S and Na–S batteries.57,58 The combination of a trflate salt and triglyme was chosen since a small interfacial resistance, , has been reported in this case, especially for Na.59,60 In both cases, a decrease of the interfacial resistance was observed for open-circuit potential (OCP) aging of cells (Figure 3b,c) together with a change to yellow or orange-like color of the electrolyte solution (when performed in a beaker cell), which most likely indicates the dissolution of the polysulfide species.61,62 This behavior (i.e., decrease with time) was also reported in the literature when Li,S was synthesized on Li and tested in battery cells.34 In the case of Na symmetric cells with Na,S, the interfacial resistance becomes as small as ~5 Ω after 24 h. This might indicate that the molar proportion of sodium polysulfide is higher in Na,S than in Li,S, or this could simply be due to the smaller amount of Na,S compared to Li,S (thinner layer). Another realistic picture is that the electrolyte penetrates through the pores (or cracks) in the surface films, reacting with fresh Li/Na, resulting in the formation of a different type of SEI, and finally leading to a mechanical detachment of the already existing artificial SEIs (Li,S and Na,S). If this is true, the more rapid decrease of interfacial resistance in the case of the Na symmetric cell with Na,S (Figure 3c) compared to the Li symmetric cell with Li,S (Figure 3b) indicates that the Na,S film is much more porous than Li,S. This is also expected, based on the fact that Na,S appears to be rougher than Li,S, as observed by FIB-SEM (Figure 2a,d). A more detailed investigation, such as quantitative analyses for the determini-
nation of the amount of different sulfide phases in Li₅S₄ and Na₅S₄ films and cryo-TEM to observe their porosity, would assist in the clarification of the origin of the different electrochemical behaviors of Li₅S₄ and Na₅S₄. This is, however, beyond the scope of the here-presented work. Additionally, highly concentrated electrolytes [i.e., 5 M lithium bis-(trifluoromethanesulfonyl)imide (LiTFSI) in dioxolane/dimethylether (DOL/DME) (1:1 vol) and 5 M sodium bis-(fluorosulfonyl)imide (NaFSI) in DME], which were reported to show excellent electrochemical performance in batteries, would assist in the clarification of the origin of the different electrochemical behaviors of Li₅S₄ and Na₅S₄. This is, however, beyond the scope of the here-presented work.

Figure 4. Investigation of the time-dependent growth of interfacial contributions with EIS under open-circuit conditions in Li₅Li₃PS₄Li and Li₅Li₃Li₃PS₄Li, Li₅Li₃Li₃PS₄Li. (a,d) Nyquist plots showing all contributions. (b,e) Change in interface resistances ($R_{\text{interface}}$) over time. (c,f) Change in capacitances corresponding to the interface ($C_{\text{interface}}$) over time. More details on the $E_{\text{d}}(\text{interface})$ values can be found in the Supporting Information (Figure S8).

Figure 5. Investigation of the time-dependent growth of interfacial contributions with impedance spectroscopy under open-circuit conditions in Na₅Na₃PS₄Na and Na₅Na₅S₄Na₃PS₄Na₅Na. (a,d) Nyquist plots showing all contributions. (b,e) Change in interface resistances ($R_{\text{interface}}$) over time. (c,f) Change in capacitances corresponding to the interface ($C_{\text{interface}}$) over time. More details on the $E_{\text{d}}(\text{interface})$ values can be found in the Supporting Information (Figure S8).
were employed in Li and Na symmetric cells with and without artificial SEIs (Figure S9, Supporting Information). In all cases, increase of $R_{\text{interface}}$ was observed, especially for the Na case, which implies that the highly concentrated electrolyte is still reactive, rendering a fair comparison between Li$_3$S$_4$ and Na$_3$S$_4$ difficult.

We can circumvent the issue of the dissolution of the polysulfide species by using solid-state cells. Sulfide-based solid electrolytes $\beta$-Li$_2$PS$_4$ and cubic Na$_2$PS$_4$ were synthesized via a solvent-mediated synthetic route and a mechanical ball milling procedure, respectively. XRD of the synthesized solid electrolytes identifies that the crystal phases ($\beta$-Li$_2$PS$_4$ and cubic Na$_2$PS$_4$) are formed (Figure S4a,c, Supporting Information). We measured the ionic conductivities of $\beta$-Li$_2$PS$_4$ and cubic Na$_2$PS$_4$ to be $1.47 \times 10^{-4}$ and $1.55 \times 10^{-4}$ S cm$^{-1}$ (see Figure S4b,d, Supporting Information), by EIS with blocking Ru electrodes, respectively. Subsequently, symmetric cells consisting of Li(Na) electrodes with Li$_3$S$_4$(Na$_3$S$_4$) artificial SEIs and Li$_2$PS$_4$(Na$_2$PS$_4$) were assembled. We compare the EIS behavior of these cells with those of the bare Li/Na symmetric cells (Li/Li$_2$PS$_4$/Li and Li/Li$_3$S$_4$/Li/Li$_2$PS$_4$/Li) in Figure 4 and the analogous system with Na in Figure 5). In the Li case, three semicircles (Figure 4a,d) were observed, indicating at least three different charge transport processes appearing at different relaxation times (see Figure S5a, Supporting Information, where the equivalent circuit model used for fitting the impedance spectra is suggested). Ionic transport through the bulk solid electrolyte appears at the highest frequency (>20 kHz) as confirmed from the measurement with blocking electrodes (Figure 4b, Supporting Information). The semicircle at medium frequencies (maximum frequency between 6 and 20 kHz) corresponds to the interfaces between Li and Li$_2$PS$_4$ as they continuously change over time. We believe that the change in the interfacial resistance ($R_{\text{interface}}$) over time in the cell with bare Li (Figure 4b) is most likely due to the continuous formation of SEIs by a chemical reaction between Li and Li$_2$PS$_4$ according to$^{28}$

$$8\text{Li} + \text{Li}_2\text{PS}_4 \rightarrow \text{Li}_3\text{P} + 4\text{Li}_2\text{S} \quad \Delta G^0 < 0$$

The origin of the smallest semicircle appearing at low frequency (<10 Hz) is not clear, but we suspect it stems from the imperfect solid contact or the charge transfer at the interface. Note that only the interfacial resistance changes over time, while the other two resistances (bulk conduction through the solid electrolyte, which appears at higher frequency, and contact resistance/charge transfer at lower frequency) stay constant over time (more details in Figure S6, Supporting Information).

The observed changes in the values of interfacial resistances ($R_{\text{interface}}$) over time starkly vary in the two different systems. The $R_{\text{interface}}$ value decreases in the case of a symmetric cell with bare Li (Figure 4b), which is counter-intuitive considering the fact that predominantly resistive phases (thermodynamically expected to produce more Li$_2$S than Li$_2$P with a molar ratio of 4:1, $\sigma$(Li$_2$S) $\sim$ 10$^{-11}$ S cm$^{-1}$ and $\sigma$(Li$_2$P) $\sim$ 10$^{-13}$ S cm$^{-1}$) are formed. This may be attributable to the creep of Li through the SEI due to the external pressure built up in the coin cell. Another possibility is the partial electronic conductivity of Li$_2$P. If this is a considerable value, Li$_2$P would allow for significant chemical diffusion through the SEI, resulting in further chemical reactions. Therefore, the value of $R_{\text{interface}}$ will decrease if the SEI morphologically rearranges in time in such a way that the contact between the Li$_2$P phases improves or Li$_2$P becomes connected in parallel to the other existing phases. The symmetric cell with the artificial Li$_3$S$_4$ SEI shows opposite behavior compared to the one with bare Li, where the value of $R_{\text{interface}}$ increases with time (first 100 h, Figure 4e). This indicates a continuous formation of resistive phases, which may be Li$_2$S and/or LiOH produced by a chemical reaction between the protruded Li and polysulfides or a reaction between the residual H$_2$O (on the surface of Li$_3$S$_4$) and Li$_2$PS$_4$. Another possibility is crack formation in the artificial Li$_3$S$_4$ SEI during the electrochemical cell assembly; this would most likely influence the $R_{\text{interface}}$ values of the initial measurement. Note that in both cases, the activation energy of conduction ($E_a$) is measured to be 0.54−0.58 eV, suggesting that both Li$_2$P ($E_a = 0.44$ eV$^{50}$) and Li$_2$S ($E_a = 0.90$ eV$^{50}$) contribute to the electrical conduction. The calculated capacitance of the order of 10$^{-9}$ F in the case of the symmetric cell with Li$_3$S$_4$ (Figure 4e) is in good agreement with the expected capacitance if the thickness of Li$_3$S$_4$ measured by FIB-SEM (Figure 2a) is taken into account together with the dielectric constant of Li$_2$S ($\varepsilon = 11$). Symmetric cells with bare Li show capacitance values one order of magnitude higher than the one with Li$_3$S$_4$, indicating a thinner SEI or considerable contributions from the grain boundaries. Based on the previous literature dealing with the Li/Li$_2$PS$_4$ interface, in which almost no degradation is observed by FIB-SEM,$^{66}$ it is more likely that a very thin SEI forms in the case of the symmetric cells with bare Li.

Figure 5 shows the impedance evolution over time in the Na symmetric cells with and without the artificial sulfide-based SEI (Na$_3$PS$_4$/Na and Na$_3$PS$_4$/Na$_3$S$_4$/Na$_3$S$_4$/Na). In both cases, two semicircles were observed (Figure 5a,d) in the impedance spectra, which were fitted with an equivalent circuit model including two RC parallel circuits in series (Figure S6b, Supporting Information). The semicircle appearing at high frequency (>100 kHz) corresponds to the ionic transport through the bulk solid electrolyte, while the semicircle at low frequency (<100 kHz) represents the interface between Na and the solid electrolyte as it changes gradually over time (Figure S6, Supporting Information). The expected interface reaction is symmetric to the one of Li.$^{29}$ The interfacial resistance ($R_{\text{interface}}$) increases continuously for both the pristine Na symmetric cells and the ones with a Na$_3$S$_4$ layer (Figure 5b,e). There have been reports in the literature about the increase of $R_{\text{interface}}$ in Na$_3$PS$_4$.$^{24,67}$ The underlying reason is suspected to be the partial electronic conductivity of Na$_3$P affecting the interface evolution similarly as described for the Li case,$^{66−69}$ but the defect chemistry of this compound has not been experimentally confirmed due to its explosiveness and the potential risk of releasing a toxic gas (PH$_3$). Another possibility is that Na creeps through the pores of the artificial SEI, reacting with Na$_3$PS$_4$ instantly upon contact and producing another SEI. This issue is still under discussion, though, because it is generally believed that the metal creep induces a drop in $R_{\text{interface}}$ in electrochemical cells due to the high electrical conductivity of metals.$^{24}$ Regardless of the similarity in the $R_{\text{interface}}$ growth behavior of Na symmetric cells with and without a Na$_3$S$_4$ layer, the values of the interfacial capacitance are rather different. $C_{\text{interface}}$ in a symmetric bare Na (without the artificial SEI) cell is in the order of 10$^{-10}$ F and its value stays more or less constant over time (Figure 5c), while $C_{\text{interface}}$ in a symmetric Na cell with a Na$_3$S$_4$ layer increases over time and finally reaches values in the order of 10$^{-8}$ F (Figure 5f). Since it is unlikely that the thickness of the SEI
The remarkable fact is that the Li temperature.

This may be attributable to the Na (0.65 eV) and even higher than the one of both Na3P (0.13 eV) and Na2S (0.59 eV).31 This may be attributable to the lower activation energy compared to Na2S or (ii) the Na di species have an inherently higher activation energy value than in the cell without the Na3S layer.

The notable difference in Na cells compared to Li cells is that the overpotential increase was observed in both cases (e.g., cells with and without Na3S) as the stripping/plating progresses. The increase of overpotential on electroplating most likely indicates that Na+ diffusion is the rate-limiting factor rather than the Na nucleation,70–72 which might be attributed to the highly resistive SEI between Na and the electrolyte in both cases of the cell, that is, with and without Na3S. Based on the galvanostatic stripping/plating results, it is concluded that the Na3S layer does not play a significantly different role in Na+ conduction compared to the SEI layer formed by the contact between Na and Na3PS4, highly likely due to the porosity of Na3S.

### 4. CONCLUSIONS

Artificial sulfide-based SEIs (Li2S and Na3S) were synthesized on Li and Na by a chemical reaction between Li2S and Na vapor. Chemical characterizations of these artificial SEIs suggest that they consist of polysulfides (Li2S and Na3S, y > 1) and sulfides (Li2S and Na2S) with compositional gradients (Li/Na and S over the film depth), and a similar chemistry was observed in sputter-deposited lithium sulfide thin films in the literature.53 Given the fact that lithium polysulfide species are thermodynamically unstable as solid-state compounds,53 it is likely that various lithium polysulfide species exist as metastable phases only in the vicinity of the surface. The combination of morphology observation by FIB-SEM upon synthesis and OCP aging in symmetric cells with liquid organic electrolytes implies that Na3S is more porous compared to Li2S, which might be due to the different R_PIL of Li2S and Na3S.

Finally, galvanostatic stripping/plating of the four different systems (LiILi, PSLi, LiILiS, LiILiPSLi, LiILiS, and Li and the sodium variants) was performed (Figure 6) in order to determine their practical capability for battery application. For the Li case, the artificial SEI (i.e., Li2S) induces a considerably higher overpotential (Figure 6a, red) compared to the situation without Li2S (Figure 6a, black). Such an overpotential is especially large at the very first stage of stripping/plating (~0.05 V) and gradually decreases afterward, implying that the nucleation energy barrier is higher compared to the case of bare Li. After nucleation started, the voltage of the cell with Li2S (red) is still higher than that of the cell with bare Li (black), implying that the artificial SEI layer (Li2S) is more resistive than the interface formed by the contact between Li and Li2PS4. This higher overpotential in the Li2S case is consistent with the impedance results shown in Figure 4. A remarkable fact is that the LiILi, PSLi, LiILiS, LiILiPSLi, LiILiS, Li and Li3PS4 cells operate in a stable manner without a significant overpotential increase on galvanostatic cycling, implying that both the naturally formed SEI and the artificial SEI act as stable passivation layers in a chemo-mechanical sense. In the Na case, symmetric cells with and without the artificial SEI (Na3S) both show similar cycling behavior (Figure 6b) in terms of overpotential values and the degree of overpotential increase on galvanostatic cycling, which is also in agreement with the resistance measured by EIS in Figure 5. In addition, the degree of overpotential increase is comparable under the OCP condition and under current application, implying that the applied current does not accelerate the growth of the SEI. The notable difference in Na cells compared to Li cells is that the overpotential increase was observed in both cases (e.g., cells with and without Na3S) as the stripping/plating progresses. The increase of overpotential on electroplating most likely indicates that Na+ diffusion is the rate-limiting factor rather than the Na nucleation,70–72 which might be attributed to the highly resistive SEI between Na and the electrolyte in both cases of the cell, that is, with and without Na3S. Based on the galvanostatic stripping/plating results, it is concluded that the Na3S layer does not play a significantly different role in Na+ conduction compared to the SEI layer formed by the contact between Na and Na3PS4, highly likely due to the porosity of Na3S.

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Na2S/Na polysulfides \( R_{PB} (Li,S) = 1.06, R_{PB} (Na,S) = 0.89,\)
\( R_{PB} (Na,S) = 1.16, R_{PB} (Na,S) = 1.79,\) and \( R_{PB} (Na,S) = 2.17.\) Note that this statement is only valid for the artificial SEI synthesized by the solid–vapor chemical reaction method. When the artificial SEIs are used in solid-state electrochemical cells, they do not provide advantages in terms of chemical stability of the interface or overpotential during striping/plating. However, systematic comparison between Li and Na suggests that Na is much more reactive than Li against thiophosphate solid electrolytes, leading to the statement that Na requires an improved protection layer in terms of density and chemical stability. Also, we speculate that the reason why Na2S did not behave as a good protection layer in a solid-state electrochemical cell is most likely due to its nanoporosity, which could be proven by cryo-TEM in future work. We again stress the importance of examining the porosity of SEIs, not only for the ones formed by the contact between Li/Na and electrolytes but also for artificial SEIs in both liquid and solid electrolytes. Additionally, the effect of external pressure needs to be systematically investigated in the future in order to examine how Li/Na creep influences the interfacial resistance.

**ASSOCIATED CONTENT**

† Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c23923.

Cross-section images of Li\(x\)Sy on Li synthesized at various temperatures measured by FIB-SEM; cross-section images of Na\(x\)Sy on Na synthesized at various temperatures measured by FIB-SEM; comparison of \( R_{PB} \) of Li\(x\)sulfides and polysulfides; energy-dispersive x-ray spectra of Li\(x\)Sy on Li and Na\(x\)Sy on Na; binding energies and full width at half-maximum of the S 2p3/2 peak for identification of different species by XPS; XRD patterns and EIS spectra of the synthesized \( \beta \)-Li3PS4 and cubic Na3PS4; equivalent circuit models for fitting the spectra of Li symmetric cells with Li3PS4 and Na symmetric cells with Na3PS4; evolution of the different resistance over time in the four systems; evolution of the different capacities in the four systems; Arrhenius plots and determination of the activation energy of electrical transport through the bulk SEI; and EIS results of symmetric Li and Na cells with highly concentrated electrolytes (PDF)

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**REFERENCES**

(1) Kalair, A.; Abas, N.; Saleem, M. S.; Kalair, A. R.; Khan, N. Role of Energy Storage Systems in Energy Transition From Fossil Fuels to Renewables. Energy Storage 2021, 3, No. e135.

(2) Janek, J.; Zeier, W. G. A Solid Future for Battery Development. Nat. Energy 2016, 1, 16141.

(3) Mantiram, A.; Yu, X.; Wang, S. Lithium Battery Chemistries Enabled by Solid-state Electrolytes. Nat. Rev. Mater. 2017, 2, 16103.

(4) Banerjee, A.; Wang, X.; Fang, C.; Wu, E. A.; Meng, Y. S. Interfaces and Interphases in All-Solid-State Batteries with Inorganic Solid Electrolytes. Chem. Rev. 2020, 120, 6878–6933.

(5) Famprakis, T.; Canepa, P.; Dawson, J. A.; Islam, M. S.; Masquelier, C. Fundamentals of Inorganic Solid-Electrolyte Batteries. Nat. Mater. 2019, 18, 1278–1291.

(6) Lotts, B. V.; Maier, J. Relevance of Solid Electrolytes for Lithium-based Batteries: A Realistic View. J. Electroceram. 2017, 38, 128–141.

(7) Wenzel, S.; Sedlmaier, S. J.; Dietrich, C.; Zeier, W. G.; Janek, J. Interfacial Reactivity and Interphase Growth of Argyrodite Solid Electrolytes at Lithium Metal Electrodes. Solid State Ionics 2018, 318, 102–112.

(8) Popovic, J. The Importance of Electrode Interfaces and Interphases for Rechargeable Metal Batteries. Nat. Commun. 2021, 12, 6240.

(9) Tikekar, M. D.; Choudhury, S.; Tu, Z.; Archer, L. A. Design Principles for Electrolytes and Interfaces for Stable Lithium-metal Batteries. Nat. Energy 2016, 1, 16114.

(10) Xu, R.; Cheng, X.-B.; Yan, C.; Zhang, X.-Q.; Xiao, Y.; Zhao, C.-Z.; Huang, J.-Q.; Zhang, Q. Artificial Interphases for Highly Stable Lithium Metal Anode. Matter 2019, 1, 317–344.

(11) Cheng, X.-B.; Zhang, R.; Zhao, C.-Z.; Wei, F.; Zhang, J.-G.; Zhang, Q. A Review of Solid Electrolyte Interphases on Lithium Metal Anode. Adv. Sci. 2016, 3, 1500213.

(12) Kang, D.; Xiao, M.; Lemmon, J. P. Artificial Solid-Electrolyte Interphase for Lithium Metal Batteries. Batter. Supercaps 2021, 4, 445–455.

(13) Zhai, P.; Liu, L.; Gu, X.; Wang, T.; Gong, Y. Interface Engineering for Lithium Metal Anodes in Liquid Electrolyte. Adv. Energy Mater. 2020, 10, 2001257.

(14) Fan, L.; Li, X. Recent Advances in Effective Protection of Sodium Metal Anode. Nano Energy 2018, 53, 630–642.

(15) Lee, B.; Paek, E.; Mitlin, D.; Lee, S. W. Sodium Metal Anodes: Emerging Solutions to Dendrite Growth. Chem. Rev. 2019, 119, S416–S460.
(54) Honig, R. E. *Vapor Pressure Data for the More Common Elements*; Radio Corporation of America, RCA Laboratories, Industry Service Laboratory, 1957.

(55) Hauffe, K. Scaling Processes in Metals and Alloys with Formation of Thick Protective Layers. In *Oxidation of Metals*; Springer US: Boston, MA, 1995; pp 144–364.

(56) Xiao, C.; Usiskin, R.; Maier, J. Passivation Layers in Lithium and Sodium Batteries: Potential Profiles, Stabilities, and Voltage Drops. *Adv. Funct. Mater.* 2021, 31, 2100938.

(57) Manthiram, A.; Fu, Y.; Chung, S.-H.; Zou, C.; Su, Y.-S. Rechargeable Lithium—Sulfur Batteries. *Chem. Rev.* 2014, 114, 11751−11787.

(58) Wang, Y.; Zhang, B.; Lai, W.; Xu, Y.; Chou, S. L.; Liu, H. K.; Dou, S. X. Room-Temperature Sodium-Sulfur Batteries: A Comprehensive Review on Research Progress and Cell Chemistry. *Adv. Energy Mater.* 2017, 7, 1602829.

(59) Seh, Z. W.; Sun, J.; Sun, Y.; Cui, Y. A Highly Reversible Room-Temperature Sodium Metal Anode. *ACS Cent. Sci.* 2015, 1, 449−455.

(60) Lutz, L.; Alves Dalla Corte, D.; Tang, M.; Salager, E.; Deschamps, M.; Grimaud, A.; Johnson, L.; Bruce, P. G.; Tarascon, J.-M. Role of Electrolyte Anions in the Na−O2 Battery: Implications for NaO2 Solvation and the Stability of the Sodium Solid Electrolyte Interphase in Glyme Ethers. *Chem. Mater.* 2017, 29, 6066−6075.

(61) Fan, X.; Sun, W.; Meng, F.; Xing, A.; Liu, J. Advanced Chemical Strategies for Lithium−Sulfur Batteries: A Review. *Green Energy Environ.* 2018, 3, 2−19.

(62) Kumar, D.; Rajouria, S. K.; Kuhar, S. B.; Kanchan, D. K. Progress and Prospects of Sodium−Sulfur Batteries: A Review. *Solid State Ionics* 2017, 312, 8−16.

(63) Suo, L.; Hu, Y.-S.; Li, H.; Armand, M.; Chen, L. A New Class of Solvent-in-Salt Electrolyte for High-Energy Rechargeable Metallic Lithium Batteries. *Nat. Commun.* 2013, 4, 1481.

(64) He, J.; Bhargav, A.; Shin, W.; Manthiram, A. Stable Dendrite-Free Sodium−Sulfur Batteries Enabled by a Localized High-Concentration Electrolyte. *J. Am. Chem. Soc.* 2021, 143, 20241−20248.

(65) Nazri, G. Preparation, Structure and Ionic Conductivity of Lithium Phosphide. *Solid State Ionics* 1989, 34, 97−102.

(66) Kato, A.; Kowada, H.; Deguchi, M.; Hotehama, C.; Hayashi, A.; Tatsumisago, M. XPS and SEM Analysis between Li/Li3PS4 Interface with Au Thin Film for All-Solid-State Lithium Batteries. *Solid State Ionics* 2018, 322, 1−4.

(67) Wenzel, S.; Leichtweiss, T.; Weber, D. A.; Sann, J.; Zeier, W. G.; Janek, J. Interfacial Reactivity Benchmarking of the Sodium Ion Conductors Na3PS4 and Sodium β-Alumina for Protected Sodium Metal Anodes and Sodium All-Solid-State Batteries. *ACS Appl. Mater. Interfaces* 2016, 8, 28216−28224.

(68) Eichhoff, H.; Dietrich, C.; Klein, W.; Zeier, W. G.; Fässler, T. F. On the Crystal Structure and Conductivity of Na3P. *Z. Anorg. Allg. Chem.* 2021, 647, 28−33.

(69) Yu, X.-L.; Giorgi, G.; Ushiyama, H.; Yamashita, K. First-Principles Study of Fast Na Diffusion in Na3P. *Chem. Phys. Lett.* 2014, 612, 129−133.

(70) Chen, K.-H.; Wood, K. N.; Kazyak, E.; LePage, W. S.; Davis, A. L.; Sanchez, A. J.; Dasgupta, N. P. Dead Lithium: Mass Transport Effects on Voltage, Capacity, and Failure of Lithium Metal Anodes. *J. Mater. Chem. A* 2017, 5, 11671−11681.

(71) Wang, H.; Matios, E.; Luo, J.; Li, W. Combining Theories and Experiments to Understand the Sodium Nucleation Behavior towards Safe Sodium Metal Batteries. *Chem. Soc. Rev.* 2020, 49, 3783−3805.

(72) Barton, J. L.; Bockris, J. O. The Electrolytic Growth of Dendrites from Ionic Solutions. *Proc. R. Soc. A* 1962, 268, 485−505.

(73) Adelhelm, P.; Hartmann, P.; Bender, C. L.; Busche, M.; Eufinger, C.; Janek, J. From Lithium to Sodium: Cell Chemistry of Room Temperature Sodium−Air and Sodium−Sulfur Batteries. *Beilstein J. Nanotechnol.* 2015, 6, 1016−1085.