1. Introduction

Li metal is an attractive anode material for all-solid-state lithium batteries (ASSLBs) because of its high specific capacity (3860 mAh g\(^{-1}\)) and low electrochemical potential (~3.04 V vs the standard hydrogen electrode).\(^{[1-4]}\) Moreover, the use of intrinsically nonflammable inorganic solid-state electrolytes (SSEs) can theoretically solve the safety issue associated with thermal runaway.\(^{[1,4]}\) Various SSEs have been recently developed, including oxide-, sulfide-, halide-, and borohydride-based SSEs. Sulfide-based SSEs have emerged as one of the most promising candidates for use in ASSLBs due to their mechanical properties and ultrahigh ionic conductivity which can reach as high as 10\(^{-2}\) S cm\(^{-1}\) at room temperature.\(^{[5-8]}\) However, pure Li metal is still unsuitable for real-application in sulfide-based ASSLBs due to the side reactions at the interface.

Similar to conventional liquid-based lithium ion batteries, the first major obstacle for the use of Li metal anodes is the penetration of Li dendrites through the sulfide-based SSEs, which raises safety concerns and often results in the decay of battery performance or even short circuit.\(^{[9,10]}\) Among the typical sulfide-based SSEs, such as Li\(_{10}\)GeP\(_{2}\)S\(_{12}\),\(^{[11,12]}\) Li\(_3\)PS\(_4\) (glass or ceramic),\(^{[13-17]}\) and Li\(_{1+}\)PS\(_{3}\)X (X = Cl, Br, I),\(^{[18,19]}\) the formation of lithium dendrites in Li\(_3\)PS\(_4\) system is well-recognized.\(^{[13-16,20,21]}\) It is proposed that the voids and grain boundaries within the SSEs, as well as the insufficient interfacial contact between Li and SSEs are the two main reasons for lithium dendrite formation in sulfide-based ASSLBs.\(^{[16,22]}\) Thus, there should be a critical current density at which short-circuiting of the cell occurs in the Li\(_3\)S-P\(_2\)S\(_5\)-solid electrolyte system.\(^{[14,15]}\) However, recent reports indicate that the Li dendrites can be formed in Li\(_3\)Ti\(_2\)O\(_12\)/Li\(_3\)S-P\(_2\)S\(_5\)/Li\(^+\) and Se/Li\(_3\)PS\(_4\)/Li\(^+\) ASSLBs using bare Li as the anode, even at a low current density of 50 mA g\(^{-1}\). Another possible reason proposed by Wang and co-workers is the relatively high electronic conductivity (10\(^{-9}\)-10\(^{-8}\) S cm\(^{-1}\)) of Li\(_3\)PS\(_4\).\(^{[16]}\) Though not fully understood yet, the introduction of additives into SSEs similar to Li protection in liquid batteries have been developed. For example, LiI,\(^{[16]}\) LiF,\(^{[23]}\) and P\(_2\)O\(_5\)\(^{[24]}\) have been introduced into Li\(_3\)PS\(_4\) and proven to be effective suppressing lithium
penetration across the Li_{i}PS_{x} SSE layer. Without a method of protecting the SSSEs interface, the evolution of an interfacial layer between sulfide SSSEs and Li metal is caused by the reduction of sulfide-SSSEs. Thus, the interfacial chemistry of the ASSLBs is a dominant factor in determining electrochemical performance and gives rise to the opportunity to develop new strategies to avoid lithium penetration.

Another challenge facing the application of Li metal is its demanding processing requirements. First, Li metal is readily corroded upon exposure to air due to the chemical reaction between Li and H_{2}O, N_{2}, O_{2}, CO_{2}. Therefore, it is difficult to use or store metallic Li for a long time even in a dry-air atmosphere. Moreover, the parasitic reaction of Li with air leads to a nonuniform and ion-impeding surface layer that causes deterioration of electrochemical performance and aggravates Li dendrite growth during cycling due to inhomogeneous electron/ionic current densities at the interface. Until now, a few successful examples of air-stable Li anodes based on the surface coating have been reported. For example, Li_{2}CO_{3} coated Li microparticles are highly stable in dry room. Al_{2}O_{3} protected Li via atomic layer deposition was also reported to improve the stability under ambient conditions (40% relative humidity) for several hours. Other artificial layers such as Li_{2}O has been proposed as passivating coatings to improve the air-stability of Li alloys. A specific structure with densely packed Li alloy nanoparticles encapsulated by large graphitic sheets has also been shown to possess enhanced air stability. However, many coating layers such as Li_{2}CO_{3}, Al_{2}O_{3}, and Li_{2}O exhibit a very low ionic conductivity, which is detrimental to their use in ASSLBs as a result of the high interfacial resistance. In contrast to liquid-based batteries, the Li⁺ conductivity of the protection layer in ASSLBs is essential since the fast electrochemical kinetics only can be guaranteed by effective Li⁺ migration across the interfacial layer. An air-stable and high ionic conductivity material as an artificial protection layer for Li anode in ASSLBs is therefore highly desired. Until now, the use of an air-stable Li anode is yet to be shown in ASSLBs.

Herein, we demonstrate the development of an air-stable Li anode with an in situ formed Li_{i}SiS_{y} layer on the surface based on solution reaction. The Li_{i}SiS_{y} layer is fabricated by a simple two-step solution-based reaction process through the chemical reaction among Li, Li_{2}S_{8}, and silicon tetrachloride (SiCl_{4}) (Figure 1a). The in-depth compositions of the Li_{i}SiS_{y} layer were analyzed detailedly by combining synchrotron-based high energy X-ray photoelectron spectroscopy (HEXPS), time-of-flight secondary ion mass spectrometry (TOF-SIMS), and Rutherford backscattering spectrometry (RBS). The air-stable Li_{i}SiS_{y} protective layer can not only block the side reaction between Li and sulfide electrolyte but also allow excellent ion migration across the interface and stable cycling performance in sulfide-electrolyte-based ASSLBs. Symmetric cells configured with a Li_{i}PS_{x} SSE and Li_{i}SiS_{y} protected Li (Li_{i}SiS_{y}-Li) electrodes show stable cycling up to 2000 h. Moreover, all-solid-state LiCoO_{2}/Li_{i}PS_{x}/Li_{i}SiS_{y}-Li cells show a capacity retention of 87.3% for 100 cycles compared to the limited 4 cycle lifetime of the cell using bare Li metal as the anode. These results not only prove the effectiveness of the Li_{i}SiS_{y} protection layer improving the stability of Li metal toward air and sulfide SSE, but also show a promising solution-based route for the in situ formation of protection layers with intimate contact and feasible fabrication process for ASSLBs.

2. Results and Discussion

2.1. Synthesis and Characterization

Figure 1a reveals the in situ fabrication process of the Li_{i}SiS_{y} layer on the surface of metallic Li by the reaction of Li, Li_{2}S_{8}, and SiCl_{4} based on a two-step process (Figure 1a, R1, and R2). In order to obtain a uniform Li_{i}SiS_{y} layer, low concentration of Li_{2}S_{8}/tetrahydrofuran (THF) solution, SiCl_{4}/THF solution, low oxygen content, and a low moisture environment are necessary. Herein, all the reactions were performed in an Ar-filled glovebox (H_{2}O, O_{2} <0.1 ppm). First, polished Li metal was dipped into a Li_{2}S_{8}/THF solution for 12 h to passivate the surface of Li and form a uniform polysulfide layer (Li_{2}S_{8}, R1). Subsequently, the SiCl_{4}/THF solution was added into the resulting solution and shook by hand for ~10 min to perform the second step reaction (R2). The addition of Si–Cl functionality from SiCl_{4} is designed to chemically react with Li_{2}S_{8} and Li metal to form a thermodynamic stable LiCl product and Li_{x}SiS_{y}. LiCl can be dissolved into THF solvent and removed after the cleaning process. Moreover, the thickness of the protected Li_{i}SiS_{y} layer can be adjusted by changing the concentration of Li_{2}S_{8}/THF and SiCl_{4}/THF solutions. Here, we choose to use one concentration (0.025 mol L⁻¹) of Li_{2}S_{8}/NMP solution as an example for detailed analysis (marked as Li-Li_{i}SiS_{y}-1, experimental details are shown in the Supporting Information). After the reaction and washing process, the surface of Li metal changes from metallic luster to gray. Scanning electron microscope (SEM) images of the bare Li electrode demonstrates a smooth and creaseless surface (Figure 1b). After the first reaction step, the surface of the Li electrode becomes more creased and some deposited material can be found (Figure S1, Supporting Information). Further treatment with the SiCl_{4}/THF solution and washing leads to the formation of the Li-Li_{i}SiS_{y}-1 electrode with a porous morphology (Figure 1c). X-ray diffraction (XRD) patterns of the Li-Li_{i}SiS_{y}-1 electrode still reveal the peaks of metallic Li which means that the protection layer is amorphous (Figure S2, Supporting Information).

X-ray photoelectron spectroscopy was further employed to confirm the composition of the Li_{i}SiS_{y} layer. Figure 1d–f shows the Li 1s, Si 2p, and S 2p XPS spectra of the Li-Li_{i}SiS_{y}-1 electrode. The XPS spectrum of the Li 1s can be fitted with a Gaussian component peak at 55.2 eV which is related to Li–S bonds (Figure 1d). Moreover, the Si 2p spectrum exhibits several peaks, which can be fitted with two distinct doublets (2P_{1/2} and 2P_{3/2}) (Figure 1e). A special peak of the Si 2P_{3/2} appears at 101.4 eV (pink curves) which can be assigned to Li_{2}SiS_{y} or Li_{x}SiS_{y} [37]. Correspondingly, the S 2p spectrum confirmed the proper assignment with the responsive peaks of S 2P_{3/2} at 161.5 eV (purple curves in Figure 1f). Due to the similar chemical valence of Si and S core in Li_{x}SiS_{y} and Li_{y}SiS_{x}, the XPS peak of Li_{x}SiS_{y} and Li_{x}SiS_{x} component is too closed to be distinguished. Another peak in the Si 2p spectrum at 102.7 eV (dark cyan curves) should be related to the component of SiS_{2} [37]. The S 2p spectrum also suggests the presence of SiS_{2} based
on the S 2p₃/₂ at 163.3 eV (dark cyan curves in Figure 1f). In addition, signals assigned to Li₂S in the spectra could also be observed (with S 2p₃/₂, 160.3 eV, yellow curves in Figure 1f). Thus, it can be concluded that the main chemical compositions of LiₓSiSᵧ protected layer are of Li₂SiS₃/Li₄SiS₄ and SiS₂ together with small amount of Li₂S.

Typically, conventional XPS using Al Kα (1486.6 eV) or Mg Kα (1256.8 eV) source has been used to study the chemical composition of the surface. However, the buried interfaces cannot be studied since the detection depth of the conventional XPS is limited to the first few nanometers in the near-surface region. The use of much higher energy (1.7–10 keV) from a synchrotron radiation source can significantly increase the electron escape depth for both photoelectrons and Auger electrons caused by their increased kinetic energy (Figure 2a). As a result, the tunable kinetic energies allow for variable depth analysis even up to several tens of nanometers. Thus, nondestructive high energy X-ray photoelectron spectroscopy of Li-LiₓSiSᵧ-1 foil was further conducted by using the soft X-ray microcharacterization beamline (SXRMB) at the Canadian Light Source. Figure 2b exhibits the Si 1s and S 1s spectra of the Li-LiₓSiSᵧ-1 foil excited by different photon energies ranging from 3 to 8 keV, which is related to the chemical composition from the surface to the coating at depth.

It can be observed that the Si 1s spectra obtained at 3–8 keV of the Li-LiₓSiSᵧ-1 foil are similar. Two typical peaks at 1842.6 and 1843.7 eV were observed, which can be assigned to SiS₂ and Li₄SiS₄ or Li₂SiS₃, respectively. For the S 1s spectra obtained at 3 keV, an obvious peak at ≈2477 eV caused by the oxidation species of sulfur at the surface of the Li-LiₓSiSᵧ-1 foil is present, which should be due to partial oxidation during transfer. The other three peaks at ≈2473, 2471, and 2469 eV are corresponding to SiS₂, Li₄SiS₄/Li₂SiS₃, and Li₂S, respectively. When the energy of the X-rays is increased, the signal due to oxidized species almost disappears. In contrast, the relative intensity ratio of Li₂S increases progressively at higher
photon energy hence longer probing depth. In addition, the peaks of SiS$_3$, Li$_2$SiS$_4$/Li$_3$SiS$_3$, and Li$_2$S slightly shift to lower energy with the increase in photon energy. The corresponding detailed position and intensities of these peaks are compared in Table S1 and S2 in the Supporting Information. The increase of Li$_2$S content at a greater depth might be caused by residual Li$_2$S$_x$ species that is not fully reacted with the SiCl$_4$/THF solution in R2.

Time-of-flight secondary ion mass spectrometry was further performed to identify the compositions of the Li-Li$_x$SiS$_y$ foil and elemental depth distributions (Figure 2c–f). The TOF-SIMS spectra were collected over time from the ejected secondary ions sputtered by Cs$^+$; and the relative intensity is also related to the weight of the ejected ions. In the initial sputtering region (Figure 2c), a relatively uniform distribution of secondary ions from Li$^+$, Si$^-$, S$^-$, S$_2^-$, and S$_3^-$ species was observed, demonstrating the successful formation of a Li$_x$SiS$_y$ coating on the surface of Li metal. After sputtering for 300 s, the intensity of Li$^+$ is significantly increased, while the opposite trend was presented for the most of other species (Figure 2d). The intensity variation is clarified in Figure 2e,f. Clearly, the signals of S$^-$, S$_2^-$, and S$_3^-$ are relatively high on the surface layer and reduce in the inner layers. While, the signal of Si$^-$ increases along with the sputtering time up to 100 s and then remains steady up to 300 s. The results indicate that the thickness of Li$_x$SiS$_y$ layer should be more than 30 nm estimated by the sputtering rate of 0.1 nm s$^{-1}$. Moreover, Rutherford backscattering spectrometry of Li-Li$_x$SiS$_y$-1 foil was performed to evaluate its thickness. The obvious presence of Si and S peaks in the RBS spectra and simulation profiles in Figure S3 in
the Supporting Information confirm the successful formation of Li$_x$Si$_y$ protection layer on the Li. The O signal should be due to the air exposure during transfer process. The calculated depth profiles based on RBS spectra indicated that the thickness of Li$_x$Si$_y$ layer on the surface Li-Li$_x$Si$_y$-1 foil is ≈150 nm. Combined with the HXPS, TOF-SIMS, and RBS analyses, it can be confirmed that the Li$_x$Si$_y$ layer consists of Li$_2$SiS$_3$/Li$_4$SiS$_4$, SiS$_2$, and small amount of Li$_2$S. The ratio of those components varied with the depth of the Li$_x$Si$_y$ layer, and the Li$_2$S increased as sputtering time progressed. Based on the theory proposed by Wang and co-workers,$^{[9]}$ the electronic conductivity of these components is quite low, and the Li$_2$SiS$_3$/Li$_4$SiS$_4$ components guarantee fast Li$^+$ migration across the interfacial layer, indicating that the Li$_x$Si$_y$ layer should be a promising Li protection layer in ASSLBs.

### 2.2. Air Stable Performance

Theoretically, these components in the Li$_x$Si$_y$ layer are chemically inert and impermeable to dry-air and robust against oxidation,$^{[38,39]}$ suggesting that the use of Li$_x$Si$_y$ layer as a protection layer for Li electrode could effectively block the parasitic side reaction in an ambient environment (Figure 3a). Thermal gravimetric analysis (TGA) was first employed to reveal the extent of the chemical reactions between Li and dry-air. The corresponding TGA curves of the bare Li and Li-Li$_x$Si$_y$-1 foil under the dry-air atmosphere for hours at 25 °C are shown in Figure 3a. An ≈1.1% weight increase could be found after 6 h for bare Li foils under the dry-air flow (100 mL min$^{-1}$). Meanwhile, there is almost no weight change observed for the Li-Li$_x$Si$_y$-1 foil during 24 h under the same condition. It can be concluded that Li-Li$_x$Si$_y$-1 foil is more stable than bare Li foil in a dry-air atmosphere.

The chemical composition of the Li-Li$_x$Si$_y$-1 foil after ambient air (humidity around 30%) exposure was further carried out by XPS (Figure 3b,c). The Si 2p spectra (Figure 3b) displayed two doublets (2p$_{1/2}$ and 2p$_{3/2}$). The peaks of Si 2p$_{1/2}$ at 101.4 eV are corresponding to the existence of Li$_2$SiS$_3$/Li$_4$SiS$_4$, and the S 2p spectrum (Figure 3c) further validates the assignment with a peak at 161.4 eV that should be assigned to Li$_2$SiS$_3$/Li$_4$SiS$_4$. There is another peak in the Si 2p spectrum located at 102.3 eV (dark cyan curves, Si 2p$_{3/2}$), which is related to the formation of SiS$_2$. Correspondingly, the S 2p spectrum also

---

**Figure 3.** Air stability of Li-Li$_x$Si$_y$-1 electrode. a) Thermal gravimetric analysis of the Li-Li$_x$Si$_y$-1 electrode and bare Li electrode in air over time, inset is the schematic representation of the Li$_x$Si$_y$ layer as a protection layer for blocking the chemical reaction between Li and air. b,c) XPS spectra of Li-Li$_x$Si$_y$-1 electrodes after ambient air exposure for 5 h. b) Si 2p spectra; c) S 2p spectra. d,e) TOF-SIMS secondary ion images of air-exposed Li-Li$_x$Si$_y$-1 electrodes d) before and e) after Cs$^+$ consecutive sputtering for 300 s (the length of scale bar is 100 μm). f) Depth profile of various secondary ion species obtained by sputtering. g) The 3D view images of the sputtered volume corresponding to the depth profiles in (f).
suggests the presence of SiS₂ based on the S 2p₃/₂ at 163.3 eV (dark cyan curves in Figure 3c). In addition, the S 2p spectrum still contains several weak doublet (S 2p₁/₂ and 2p₃/₂) peaks which are related to the presence of Li₂S and sulfate. It can be concluded that these peaks are similar to the pristine Li-LiₓSiSᵧ₋₁ electrode without air exposure. The observation of relatively lower intensity of SiS₂ and Li₂S species should be caused by their instability toward humidity. Moreover, the TOF-SIMS mapping images of Li-LiₓSiSᵧ₋₁ after ambient air exposure (Figure 3d,e) and elemental depth distributions (Figure 3f,g) collected from the ejected secondary ions sputtered by Cs⁺ were also similar to the results of the freshly prepared Li-LiₓSiSᵧ₋₁ foil shown in Figure 2c–f, further demonstrating the stability of LiₓSiSᵧ layer in air.

2.3. Li Plating and Stripping Performance

To study the electrochemical properties of the Li-LiₓSiSᵧ electrodes, symmetric all-solid-state Li cells were fabricated with commercial Li₃PS₄ as the solid-state electrolyte. Two other Li-LiₓSiSᵧ foils with LiₓSiSᵧ protection layers of different thicknesses were also tested (detailed synthesis is shown in the Supporting Information). The thickness of the LiₓSiSᵧ layer was controlled by utilizing different concentrations of Li₂S₈/THF and SiCl₄/THF solutions. Correspondingly, the Li-LiₓSiSᵧ foils were denoted as Li-LiₓSiSᵧ₋₀.₂₅ and Li-LiₓSiSᵧ₋₀.₅ based on the concentration of the reaction solution. SEM and XRD patterns of these samples are demonstrated in Figure S4–S6 in the Supporting Information. It is revealed that all of these samples show a similar porous and amorphous structure with the same XRD peaks. RBS results in Figure S7 in the Supporting Information proved the thicker LiₓSiSᵧ layer on the surface for Li-LiₓSiSᵧ₋₁ compared to that of Li-LiₓSiSᵧ₋₀.₂₅.

Figure 4 shows the charge/discharge profiles at a constant current of 0.1 mA cm⁻² and a capacity of 0.5 mAh cm⁻² for bare Li and Li-LiₓSiSᵧ electrodes. For the symmetrical all-solid-state Li cells, commercial Li₃PS₄ as SSEs suffer from a short cycling life due to the dendritic formation of Li as shown in Figure 4a, which is consistent with previous reports. All of the...
symmetrical all-solid-state Li cells based on Li-Li$_x$Si$_y$ electrodes exhibited improved Li stripping/plating performance, while there is still a short-circuiting phenomenon for Li-Li$_x$Si$_y$-0.25 and Li-Li$_x$Si$_y$-0.5 electrodes (Figure 4b,c). The most stable performance could be achieved for Li-Li$_x$Si$_y$-1 electrodes as presented in Figure 4d,e. The symmetric Li-Li$_x$Si$_y$-1 cells exhibited an initial overpotential around $\approx$25 mV at 0.1 mA cm$^{-2}$. No short circuit phenomenon was observed even for 2000 h just with only a slight increase in overpotential. Furthermore, the cross section SEM images of Li/Li$_3$PS$_4$ and Li-Li$_x$Si$_y$-1/Li$_3$PS$_4$ after 10 cycles are compared in Figure S8 in the Supporting Information. It can be seen that the close contact between Li-Li$_x$Si$_y$-1 electrode and Li$_3$PS$_4$ electrolyte after cycling, while obvious cracks between bare Li electrode and Li$_3$PS$_4$ electrolyte was observed, which might be caused by the uneven lithium plating/stripping. The rate capability of the symmetrical cell at different current densities up to 1 mA cm$^{-2}$ are presented in Figure S9 in the Supporting Information and also indicates relatively stable voltage polarization. The results demonstrate that the protection of Li-Li$_x$Si$_y$ layer could effectively inhibit short-circuiting for Li$_3$PS$_4$ SSEs in all-solid-state cells, and the thickness of the protection layer also plays a key role in the performance of all-solid-state symmetric cells.

2.4. Composition Evolution upon Electrochemical Cycling

In order to reveal the underlying mechanism of the improved electrochemical performances, we further studied the composition evolution of the bare Li and Li-Li$_x$Si$_y$ electrodes after cycling. To analyze the interlayer composition between Li or Li-Li$_x$Si$_y$ electrode and Li$_3$PS$_4$ SSEs after cycling, symmetric cells with Li and Li-Li$_x$Si$_y$-1 electrodes cycled at 0.5 mA cm$^{-2}$ for 200 cycles were disassembled inside a glove-box for XPS analysis. The intensity of P 2p spectra for bare Li electrode is much higher than that of the Li-Li$_x$Si$_y$-1 electrode (Figure S10, Supporting Information), indicating the more severe interfacial reactions between bare Li and Li$_3$PS$_4$ SSEs occur. As presented in Figure 5a, two sets of the phosphorous species assigned to $-P-S-P-$ and $Li-P-S$ species could

![Figure 5. XPS characterization of bare Li and Li-Li$_x$Si$_y$-1 electrodes after 200 h at 0.1 mA cm$^{-2}$ for 0.5 mAh cm$^{-2}$.](image)

- a) P 2p spectra; b) S 2p spectra.
- TOF-SIMS spectra of bare Li and Li-Li$_x$Si$_y$-1 electrode after 200 h at 0.1 mA cm$^{-2}$ for 0.5 mAh cm$^{-2}$. 

be identified for both samples, which are marked purple and green located at 131.7–131.9 and 132.7–132.9 eV, respectively. Furthermore, the binding energy of the bare Li sample shifts to lower energy compared to that of Li-Li\textsubscript{Si\textsubscript{x}}\textsubscript{S\textsubscript{y}}\textsubscript{-1} electrode, which should be caused by the reduction of Li\textsubscript{3}PS\textsubscript{4} SSEs after direct contact with Li metal. Moreover, the Li-Li\textsubscript{Si\textsubscript{x}}\textsubscript{S\textsubscript{y}}\textsubscript{-1} electrode still displays similar Si 2p and S 2p spectra as shown in Figure S11 in the Supporting Information and Figure 5b with the exception of changes in relative intensity. It should be noted that S 2p3/2 peak centered at \approx 161.5 eV here should be assigned not only to Li\textsubscript{2}Si\textsubscript{3}/Li\textsubscript{4}Si\textsubscript{4} but also to Li–P–S species from the Li\textsubscript{3}PS\textsubscript{4} SSEs. For the S 2p spectrum of bare Li metal, the dominant peaks are attributed to Li\textsubscript{2}S, demonstrating that the Li\textsubscript{3}PS\textsubscript{4} SSEs in direct contact with Li was reduced. The compositions were further studied by TOF-SIMS (Figure 5c). The surface of bare Li or Li-Li\textsubscript{Si\textsubscript{x}}\textsubscript{S\textsubscript{y}}\textsubscript{-1} that is in direct contact with Li\textsubscript{3}PS\textsubscript{4} SSEs was first sputtered by Cs\textsuperscript{+} ions. The existence of CH\textsuperscript{−}, O\textsuperscript{−}, OH\textsuperscript{−}, and C\textsubscript{2}H\textsuperscript{−} species for both samples should be due to the air exposure during transfer. Obviously, strong peaks due to PO\textsubscript{2}\textsuperscript{−}, PSO\textsubscript{−}/PO\textsubscript{3}\textsuperscript{−}, and PS\textsubscript{2}\textsuperscript{−} species could be observed for bare Li, indicating that there should reaction between bare Li and Li\textsubscript{3}PS\textsubscript{4} SSEs during the plating/stripping tests. Comparatively, only a weak signal of S\textsubscript{2}O\textsuperscript{−} and S\textsubscript{3}\textsuperscript{−} for Li-Li\textsubscript{Si\textsubscript{x}}\textsubscript{S\textsubscript{y}}\textsubscript{-1} electrode is observed after cycling, which should originate from the Li\textsubscript{2}Si\textsubscript{3} protection layer since there are no phosphorous species. Based on the surface XPS and sputtered samples with TOF-SIMS results, the Li\textsubscript{2}Si\textsubscript{3} protection layer with optimized thickness could prevent the side reaction between Li and Li\textsubscript{3}PS\textsubscript{4} SSEs that might induce dendrite growth and short circuits.

### 2.5. All Solid-State Li Batteries Performance

The Li electrode with and without Li\textsubscript{Si\textsubscript{x}}\textsubscript{S\textsubscript{y}} layer was used for more in-depth electrochemical studies in full ASSLBs in which the bare Li and Li-Li\textsubscript{Si\textsubscript{x}}\textsubscript{S\textsubscript{y}} anodes were paired with a commercial LiCoO\textsubscript{2} (LCO) cathode and Li\textsubscript{3}PS\textsubscript{4} as SSEs. The detailed assembly process of the full Li-LCO ASSLBs is shown in the Experimental Section. Indeed, the Li-Li\textsubscript{Si\textsubscript{x}}\textsubscript{S\textsubscript{y}} anode shows significantly improved cycling performance than that of the cell with the pristine Li anode. As shown in Figure 6a, the full Li-LCO ASSLBs with pristine Li as the anode is only stable for the initial 50 h at 0.13 mA cm\textsuperscript{−2} (approximately three charge/discharge cycles). After three cycles, the cell exhibits a serious overcharge process which is marked by red arrows in Figure 6a. The overcharge process is related to short-circuiting of the Li anode during charging process. It is one of the reasons why pristine Li is not suitable for ASSLBs when using sulfide as the electrolyte and most of the research is focused on Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12}, indium, or other kinds of alloy as the anode, although Li have the highest energy density. Compared to the pristine Li anode, the Li-LCO ASSLBs with Li-Li\textsubscript{Si\textsubscript{x}}\textsubscript{S\textsubscript{y}} anode reveal a much more stable cycling performance without any overcharging for over 100 cycles (Figure 6b–d). As shown in Figure 6c, it can be revealed that the charge and discharge curves of the full Li-LCO all-solid-state cell with Li-Li\textsubscript{Si\textsubscript{x}}\textsubscript{S\textsubscript{y}} as anode is stable and the capacity is higher than that with pristine Li (Figure 6a). The initial discharge capacity of the Li-LCO ASSLBs with Li-Li\textsubscript{Si\textsubscript{x}}\textsubscript{S\textsubscript{y}} anode reaches 126 mAh g\textsuperscript{−1} at 0.13 mA cm\textsuperscript{−2} and remains at 110 mAh g\textsuperscript{−1} after 100 cycles (Figure 6d). From these results, it can be concluded that the Li\textsubscript{2}Si\textsubscript{3} protection layer on the surface...
of Li metal can effectively avoid dendrite formation and short circuits both in all-solid-state symmetric cells and full cells with high-voltage cathodes. Moreover, even the all-solid-state symmetric cells and full cells with Li-Li$_x$Si$_y$S$_z$-$x$ anode after air exposure can show good electrochemical performance as shown in Figure S12 in the Supporting Information, indicating that the Li$_x$Si$_y$S$_z$ protection layer can also improve the air-stability of Li metal.

3. Conclusions

In summary, we have successfully demonstrated that the in situ formed Li$_x$Si$_y$S$_z$ protection layer on the surface of Li can stabilize the Li$_3$PS$_4$/Li interface. Moreover, the Li$_x$Si$_y$S$_z$ protection layer is stable toward air. In-depth analyses using synchrotron HEXPS, TOF-SIMS, and RBS confirm the compositions of different chemical species within the Li$_x$Si$_y$S$_z$ protection layer. The Li$_x$Si$_y$S$_z$/Li$_3$PS$_4$ species ensure fast ionic migration across the protection layer, and the Li$_x$S in contact with Li metal prevent further interfacial reactions. Thus, the Li$_x$Si$_y$S$_z$ protection layer can effectively prevent the reduction of Li$_x$PS$_4$ by Li metal. The reaction between Li$_2$S$_8$, SiCl$_4$, and Li in THF solvent based on the formation of Li$_x$PS$_4$ is shown in Figure S12 in the Supporting Information, indicating that the reaction is very slow, and followed by the addition of 1 mL SiCl$_4$/THF solution. This display of the in situ formation of a protective layer can provide new insights into the interfacial reactions. Thus, the Li$_x$Si$_y$S$_z$ protection layer can effectively avoid dendrite formation and short circuits both in all-solid-state symmetric cells and full cells with high-voltage cathodes. Moreover, even the all-solid-state symmetric cells and full cells with Li-Li$_x$Si$_y$S$_z$-$x$ anode after air exposure can show good electrochemical performance as shown in Figure S12 in the Supporting Information, indicating that the Li$_x$Si$_y$S$_z$ protection layer can also improve the air-stability of Li metal.

4. Experimental Section

Materials: Sulfur (S, sublimate), lithium sulfide (Li$_2$S, 99%), tetrahydrofuran, and silicon tetrachloride were purchased from Aladdin Industrial Corporation (USA); lithium foil (diameter 10 mm and thickness was 250 µm) was purchased from China Energy Lithium Co., Ltd. Commercial LiCoO$_2$ electrode materials came from China Automotive Battery Research Institute (China). Commercial Li$_3$PS$_4$ electrolyte was purchased from MSE supplies LLC.

Preparation of Li-Li$_x$Si$_y$S$_z$ Electrode: The Li$_x$Si$_y$S$_z$ protection layer on the surface of Li metal was synthesized by using the two steps in situ reaction between Li$_2$S$_8$, SiCl$_4$, and Li in THF solvent based on the following two reaction equations

\[
\text{Li + Li}_2\text{S}_8 = \text{Li}_3\text{PS}_4
\]

(1)

\[
\text{Li}_2\text{S}_8 + \text{SiCl}_4 = \text{Li}_3\text{PS}_4
\]

(2)

In order to obtain a uniform Li$_x$Si$_y$S$_z$ layer on the surface of Li metal, low concentrations of Li$_2$S$_8$/THF and SiCl$_4$/THF solutions, low oxygen content, and a low moisture environment are necessary. Here, all the reactions were performed in Ar-filled glove-box (H$_2$O, O$_2$ < 0.1 ppm). Typically, 23 mg Li$_2$S, 112 mg S, and 20 mL THF solvent was added into a glass bottle and stirred for 12 h to make a clear Li$_2$S$_8$/THF solution (0.025 mol L$^{-1}$). 0.12 mL SiCl$_4$ was added into 20 mL THF solution to form a clear SiCl$_4$/THF solution (>0.05 mol L$^{-1}$). The first reaction step was using Li$_2$S$_8$ and metallic Li. A piece of metallic Li foil (polished by a toothbrush) and 1 mL of Li$_2$S$_8$/THF solution were added together into a clean glass bottle, following by standing for 12 h. The color of the solution was yellow and did not change during the standing process. This reaction was very slow, and followed by the addition of 1 mL SiCl$_4$/THF solution into the resulting solution. The solution was shaken by hand for ~10 min to perform the second step reaction. When adding SiCl$_4$/THF solution, the color of the solution changed from yellow to pale yellow. After shaking, the color of the solution changed to bright yellow, which indicated the completion of the reaction. Then, the resulting Li foil was further washed with THF solvent and then dried for 1 h at 60 °C in Ar-filled glove-box. The surface color of the resulting Li foil changed from a shiny metal luster to gray. In order to control the thickness of the Li$_x$Si$_y$S$_z$ layer, the concentration of the Li$_3$PS$_4$/THF solution was changed from 0.25, 0.5, and 1 time of 0.025 mol L$^{-1}$. (The concentration of the SiCl$_4$/THF solution was two times of the concentration of Li$_3$PS$_4$/THF solution.) The achieved Li-Li$_x$Si$_y$S$_z$ foil was marked as Li-Li$_x$Si$_y$S$_z$-$x$, Li-Li$_x$Si$_y$S$_z$-$0.25$, Li-Li$_x$Si$_y$S$_z$-$0.5$, and Li-Li$_x$Si$_y$S$_z$-$1$ based on the concentration of Li$_3$PS$_4$/THF solution.

Characterizations: The structure and morphology of the as-prepared Li-Li$_x$Si$_y$S$_z$ were characterized by X-ray diffractometer (Philips X’Pert Super diffractometer with Cu Ka radiation) and scanning electron microscopy (a Hitachi S-4800). The chemical information of the as-prepared Li-Li$_x$Si$_y$S$_z$ foil was characterized by X-ray photoelectron spectrometer (ESCALAB 250 spectrometer, Perkin-Elmer). The XPS spectra were fitted with Gaussian–Lorentzian functions and a Shirley-type background. The spin–orbit split peaks for Si 2p (2p$_{3/2}$, 2p$_{1/2}$) were constrained using a separation of 0.86 eV and the intensity ratio of 2p$_{3/2}$/2p$_{1/2}$ of about 0.52. The spin–orbit split peaks for S 2p (2p$_{3/2}$, 2p$_{1/2}$) were constrained using a separation of 1.21 eV and the intensity ratio of 2p$_{3/2}$/2p$_{1/2}$ of about 0.54. The chemical information of the as-prepared Li-Li$_x$Si$_y$S$_z$ foil with deep profile was tested by time-of-flight secondary ion mass spectrometry, Rutherford backscattering spectrometry, and high-energy X-ray photoelectron spectroscopy. The TOF-SIMS measurements were performed on an ION-TOF (GmbH, Germany) ToF-SIMS IV with a bismuth liquid metal ion source, the pressure of the chamber was around 10$^{-8}$ mbar. Sputtering with a Cs$^+$ ion beam (3 keV) was applied for depth profiling analysis, corresponding to sputtering areas of 100 × 100 µm$^2$. The thickness of Li$_x$Si$_y$S$_z$ layer was characterized by RBS using 1 and 2 MeV He$^+$ beam (Western Tandetron Facility at University of Western Ontario) at several locations on the surface. A Nb-implanted amorphous Si sample (with Nb content of 4.82 × 10$^{15}$ atoms cm$^{-2}$) was used for calibration. High-energy X-ray photoelectron spectroscopy was performed on the soft X-ray microcharacterization beamline at the CLS30 under different energies. Electrochemical Characterizations: Symmetrical all-solid-state Li/Li$_3$PS$_4$/Li cells were assembled with bare Li metal and Li$_x$Si$_y$S$_z$ protected Li as the electrodes, and commercial Li$_3$PS$_4$ as the solid-state electrolyte. The cathode composites were prepared by hand mixing process of LiNbO$_2$ coated LiCoO$_2$ and Li$_3$PS$_4$ in a weight ratio of 7:3. For the assembly of ASSLBs with LiCoO$_2$ cathodes, the solid-state electrolyte layer was prepared by pressing 100 mg of Li$_3$PS$_4$ at 2 ton inside a polystyrafluoroethylene (PTFE) die (diameter of 10 mm). Then, 10 mg of the cathode composites were dispersed on the surface of the solid-state electrolyte uniformly and pressed at 2 ton. Finally, one piece of bare Li anode or Li$_x$Si$_y$S$_z$ protected Li was attached on the other side of the solid-state electrolyte layer and pressed at 1 ton. The active LiCoO$_2$ loading was about 8.92 mg cm$^{-2}$. All the electrochemical tests were conducted using a Land cycler (Wuhan, China) at room temperature.

Supporting Information

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

Acknowledgements

J.L. and X.L. contributed equally to this work. This work was supported by the Natural Science and Engineering Research Council of Canada (NSERC), the Canada Research Chair Program (CRC), the Ontario Research Fund, the Canada Foundation for Innovation (CFI), the China
Automotive Battery Research Institute Co., Canada MITACS fellowships, the Canada Light Source at University of Saskatchewan (CLS), and the University of Western Ontario.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

air stable, all-solid-state batteries, Li$_3$PS$_4$, lithium metal anodes, sulfide electrolytes

Received: July 1, 2019
Revised: July 28, 2019
Published online: