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Surface/Interface Effects on High-Performance Thin-Film All-Solid-State Li-Ion Batteries

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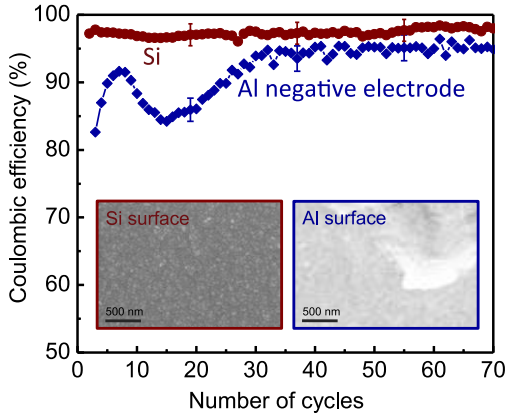
Abstract

The further development of all-solid-state batteries is still limited by the understanding/engineering of the interfaces formed upon cycling. Here, we correlate the morphological, chemical, and electrical changes of the surface of thin-film devices with Al negative electrodes. The stable Al-Li-O alloy formed at the stress-free surface of the electrode causes rapid capacity fade, from 48.0 to 41.5 μAh/cm^2 in two cycles. Surprisingly, the addition of a Cu capping layer is insufficient to prevent the device degradation. Nevertheless, Si electrodes present extremely stable cycling, maintaining >92 % of its capacity after 100 cycles, with average Coulombic efficiency of 98 %.



Keywords energy storage, all-solid-state batteries, thin-films, aluminum, silicon.

In today's society, rechargeable battery technologies with improved performance are urgently needed to address the growing power and energy demands of electric and hybrid vehicles and mobile devices.[1,2] A promising alternative to conventional liquid electrolyte cells is the all-solid-state Li-ion battery (SSLIB), which provides: (i) high power density (> 250 W/kg), (ii) long cycle life, (iii) inherent safety, due to the absence of an organic liquid electrolyte that can cause leakage and fire, (iv) lightweight and possible compact packaging, and (v) allows for a variety of materials to be implemented as the electrodes including those with higher operating voltages.[3-5] As in liquid electrolyte LIBs, in all-solid-state batteries the processes at the negative electrode (commonly denoted as the anode) during the charging step can be classified into essentially 3 different types of reaction: intercalation, conversion, or alloying.[5-7] Alloying reactions usually take place between Li and certain metals or semiconductors used as negative electrodes, as: $M + xLi^+ + xe^- \rightleftarrows Li_xM$, where M refers to Si, Ge, Sn, Al, and their alloys. These reactions are accompanied by substantial volume changes, which can lead to pulverization and the electrical isolation of the active layer, limiting the lifetime of the device under repeated charge/discharge cycles. Therefore, while these materials represent an attractive class of negative electrodes due to their high theoretical capacity, provided that the large strains that accompany Li alloying can be accommodated,[6] it is crucial to engineer the interfaces between the active layers of the devices to prevent undesirable irreversible reactions.

Extensive work has been realized quantifying the volume expansion/contraction during charging/discharging (lithiation/delithiation) of electrode materials in nanoscale devices,[8-10] as well as determining the morphological changes that occur during charging due to stress/strain accumulation resulting from Li alloying.[11-15] In particular, *in situ* transmission electron microscopy (TEM) experiments have been implemented to probe atomic scale processes in real time that take place during the battery charging and discharging.[13,16,17] Further, structural[9] and chemical characterization[17] tools have been combined to demonstrate scenarios where lithiation is irreversible. However, there is still a pressing need to identify how the negative electrode chemical composition changes upon lithiation, because it is closely related to the reversibility of the electrochemical reactions.

Aluminum, low-cost, non-toxic, and earth abundant, is a promising alternative for ultra-lightweight negative electrodes for portable devices, with theoretical capacity equal to 993 mAh/g for lithium storage.[18,19] Al metal electrodes have recently presented extremely high-rate capability (charging time of 1 minute, with current density of ~4,000 mA/g), with specific capacity of about 70 mAh/g, resulting from the intercalation/de-intercalation of chloroaluminate anions from the liquid electrolyte into the cathode.[20] Nevertheless, in all-solid-state devices, the alloying reaction between Al and Li leads to the formation of a very stable AlLi alloy ($Al + Li^+ + e^- \rightleftarrows AlLi$), with consequent pulverization of the negative electrode and rapid loss in capacity in nanoscale devices.[18,21] However, many details of the degradation mechanism, particularly in thin-film micron-size batteries remain unclear, including the effects of an intrinsic Al_2O_3 layer which covers the negative electrode surface. This oxide layer is present even when fabricating/testing the battery under high-vacuum conditions (10 Å of Al_2O_3 forms in <15 min at 10^{-4} Torr).[22]

In this paper we combine X-ray photoelectron spectroscopy (XPS) with local electrical conductivity measurements to characterize the processes that occur on the Al negative electrode outer surface during lithiation in thin-film batteries with the aim of gaining deeper understanding for the rapid loss in capacity. We find that the few-monolayer thick Al-Li-O compound formed on top of the Al electrode substantially increases the electrical resistance at its surface, thus hindering surface-bound charge transport processes and degrading the battery's overall performance. We also demonstrate that coating the Al electrode with a Cu film without breaking vacuum does not resolve the rapid capacity loss. Finally we show that similar SSLIBs fabricated with thin-film Si negative electrodes capped with Cu exhibit remarkably stable performance, retaining >92% of their discharge capacity after 100 cycles, with an average Coulombic efficiency equal to 98%.

Thin-film SSLIB were fabricated by sputtering 300 nm of $LiCoO_2$ as the positive electrode (140 mAh/g), 365 nm of LiPON for the electrolyte (3 x 10^{-6} S/cm), and 400 nm of Al (993 mAh/g) as the negative electrode and the current collector, as shown in Figure 1(a) (see Methods for detailed description of batteries' fabrication). Figures 1(b-d) show

scanning electron microscopy (SEM) images of the morphology of the Al negative electrode surface before (pristine sample) and after cycling the battery under ultra-high vacuum (8.5×10^{-11} Torr). The as-deposited Al surface is smooth, with roughness < 20 nm. The lithiation of the Al layer, accompanied by the volume expansion of the negative electrode, results in the formation of ~1 μm diameter mounds distributed on its surface and composed principally of AlLi alloy, as previously determined - see Figure 1(e) for a cross-section SEM image of all the active layers of the device(with a protective Pt capping layer deposited during the FIB process).[12] AlLi does not form in the bulk of the Al electrode, nor at the LiPON/Al interface; its formation is confined to the outer surface where the large (~100 %) volumetric strain can be best accommodated. The surface segregation of AlLi, however, does not in itself explain the rapid loss in capacity, as shown in Figure 1(f).

Previously, we postulated that formation of the AlLi mounds occurred mainly by surface or grain boundary mediated diffusion, because bulk diffusion coefficients for both Li and Al are very low. Further, we suggested that loss of electrical contact with the negative electrode outer surface segregated AlLi phase did not substantially contribute to the capacity loss, because the mounds remained physically attached to the bulk Al. Because the chemical transformations that accompany charge transfer in SSLIBs with Al negative electrodes occur predominantly on the top surface and because surface diffusion paths for Al and Li are needed for cycling the battery, we have reasoned that loss of surface conductivity could degrade the battery performance. To test this hypothesis, we use conductive atomic force microscopy (c-AFM) to measure the effects of electrochemical cycling on the surface electrical conductivity of the negative electrode, as shown in Figure 2. Prior to lithiation the Al layer is highly conductive. Although the Al outer surface is covered with an intrinsic Al_2O_3 layer (Figure 2(a-b)), the oxide is sufficiently thin (~3 nm) to allow electron tunneling during the c-AFM measurements. Following 10 charge/discharge cycles at 30 nA, the electrode surface becomes insulating throughout and irrespective of morphology, suggesting the formation of a thicker, uniformly distributed insulating layer (Figure 2(c-d)). The presence of an insulating layer on top of the Al and AlLi layers can substantially hinder the charging and discharging

processes because these must be accompanied by electron flow in and out of the negative electrode, respectively.

To help identify the chemical composition of the insulating top layer, we use XPS. The O-1s signature peak at 531 eV from Al_2O_3 is present in both pristine and cycled samples (Figure 2(e)). The spectrum collected on a pristine battery contains both Al-2p metal and oxide peaks. However, after cycling the device 10 times, only the oxide peak is present (even at the discharge state), as shown in Figure 2(f). This result indicates that upon the mounds' formation, the top layers of the electrode are no longer metallic, due to a reaction between Li and both metallic and oxidized Al as well as additional oxygen from the environment. Simultaneously, we detected the Li-1s peak at 55.3 eV, confirming that Li is present on the top surface of the Al layer even after the device is fully discharged [see Figure 2(g)]. The XPS measurements confirm that a new material, composed by Li, Al, and O is present at the top surface of the negative electrode. Further, during the lithiation process the metallic Al from the top layers reacts with Li, suggesting that the Al-Li-O layer is at least 10 nm thick, now unobservable by XPS. This insulating film impedes electronic current flow between the electrode and the probe on the c-AFM measurements. These changes in composition and electrical properties of the negative electrode surface are in agreement with a model we previously proposed, where the Li atoms react with the intrinsic Al_2O_3 layer forming a ternary alloy, as a consequence of the high diffusivity of Li in Al.[12] While the mounds are composed of porous AlLi,[12] the outer shell is formed by an insulating Al-Li-O layer.

The c-AFM and XPS measurements both suggest that cycling of the SSLIB with Al negative electrodes leads to formation of an insulating surface oxide, which could contribute to capacity loss by preventing electron flow to the surface layers where AlLi alloy is formed. Given that additional oxygen (*i.e.* oxygen not present as native Al_2O_3 prior to cycling) must come from the surrounding environment, we can hypothesize that an electrically conducting film which does easily oxidize on top of the Al surface would increase the battery cycle life by preventing, or at least slowing the rate ofAl-Li-O growth. To test this idea, we evaporated a 400 nm thick Cu capping layer immediately after the Al deposition without exposing the samples to the ambient. As shown in Figure

3, the Cu overlayer does not increase the cycle life of the batteries. This result is not entirely surprising given that diffusivity of O in Cu at room temperature is ~10^{-12} cm^2/s,[23] which implies that it would take ~1600 s for oxygen to diffuse through the 400 nm thick Cu layer. This new result suggests that capacity fade is likely due to a combination of reasons, which include loss of surface diffusion paths for the Li in the porous AlLi alloy once the surface is oxidized, as well as loss in electrical conductivity. It is interesting to note that from the charge/discharge curves (not displayed), the charge cycle of the Al/Cu battery does not show a local maximum at 3.8 V compared with that of the uncapped Al-based device, strongly indicating that the existence of the Cu capping layer has altered the electrochemical reactions taking place at the negative electrode and could be another reason for the capacity fade.

Our proposed mechanism implies that if bulk Li diffusion were faster so as not to depend on surface diffusion, capacity retention could be improved. To test this point, we fabricated similar batteries with 50 nm thick Si negative electrodes[24,25] covered with 400 nm thick Cu. Like Al, Si also rapidly forms an insulating surface oxide; however, Li diffusion is ~10 orders of magnitude faster in Si compared to Al[26] and therefore does not depend on surface diffusion mechanism. The SSLIBs with Si electrodes are tested using exactly the same procedure as used with SSLIBs with Al. As shown in Figure 4, these batteries retained over 92% of their capacity after 90 cycles.

Figure 4 shows the morphology and the electrical analysis of the Si negative electrode after cycling the battery in ultra high vacuum and its electrochemical profile. After cycling the device, the interface between the electrolyte and the Si does not present any accumulation of Li,[27] as shown in the cross-section SEM image of Figure 4(b). c-AFM measurements show that the electrical properties of the Si/Cu layer are unaltered upon cycling the battery [see Figure 4(c-f)]. The Si/Cu battery shows an excellent performance, with discharge capacity of ~15 $\mu Ah/cm^2$ after 100 cycles at 30 nA (Figure 4 (g)). As a consequence, the Coulombic efficiency of the device is near 100%. This remarkable improvement in performance is due to the fact that Li diffuses almost 10 orders of magnitude faster in Si than it does in Al,[26] and thus the formation of the surface mounds and the associated trapped Li does not occur in Si (or at a much lower level).

Additionally, an insulating compound analogous to the Al-O-Li, *i.e.* Si-O-Li does not seem to form on the Si electrode surface [see Figure S2]. The SSLIB with Si has an electrochemical performance similar to micron- and nano-scale size electrodes,[28,29] with high cycling stability despite the large volume change that takes place during lithiation. Furthermore, given the same Cu capping layer, the Si-based SSLIB still outperforms the Al/Cu system regarding the capacity retention after long-time cycling. One possible reason for the limited performance of the Al/Cu battery is that the diffusion of Cu into Al may lead to the loss of lithium diffusion path along the Al grain boundaries that constitute the negative electrode, because Cu does not react with lithium ion at low electrical potential.[30] Moreover, as mentioned before, Li diffusion is much faster in Si than in Al, therefore the potential loss of diffusion path along the grain boundaries in the Si film may not have a significant effect on its electrochemical performance. More detailed studies as to how much each factor contributes to the battery overall performance, such as probing a SSLIB with a thick layer of Al_2O_3 and using a current collector with a substantially different coefficient of thermal expansion as the Al, is planned for the near future.

Our systematic study revealed that the Al/Al_2O_3 is the limiting interface for the Li reversible diffusion in SSLIB, instead of the electrolyte/electrode interface. Previously, a P-Si interdiffused layer has been observed at the LiPON/Si electrolyte/negative electrode interface during nano-battery over-charging.[13] However, for the micron-scale devices like the ones probed here, the effect of this interface is negligible compared to the total volume of the negative electrode. For the thin-film SSLIB containing Al, the surface of the material substantially changes upon cycling, forming a new material (Al-Li-O) that traps Li, according to the following chemical reaction:

$$(1+x)Li + \left(1-\frac{x}{3}\right)Al + \left(\frac{x}{6}+\frac{y}{2}\right)Al_2O_3 \rightarrow Li_xAl_yO_{\frac{x+3y}{2}} + AlLi$$

This alloy substantially reduces the surface diffusion paths for the Li in the porous AlLi. Further, even after discharging the batteries, the Al-Li-O is still stuck at the surface of the

electrode, indicating that this material is thermodynamically stable and that the alloying reaction with Li is not reversible.

Summarizing, we investigated the degradation of SSLIBs with Al and Si negative electrodes and identified substantial Li accumulation at the top surface of the Al electrode, accompanied by morphological and electrical changes. The Al layer showed fast capacity fade caused by the formation of a ternary Al-Li-O alloy at the top surface of the negative electrode, as confirmed by XPS measurements. This ternary alloy is thermodynamically stable, does not decompose upon battery discharging, and forms an insulating barrier at the top surface of the electrode, as shown by c-AFM measurements. The addition of a Cu protective film did not prevent the capacity loss, due to the presence of an Al_2O_3 thin layer between the negative electrode and the Cu layers, and the sufficiently rapid oxygen diffusion in Cu at room temperature. By comparison, thin-film Si electrodes showed excellent performance up to 100 cycles, retaining >92% of its discharge capacity, with stable Coulombic efficiency of 98%. The results presented here show the importance of electrode surface and current collector/electrode interface reactions in SSLIB, in addition to those occurring at the electrode/electrolyte interfaces, which are typically the focus of investigation in liquid electrolyte LIBs.

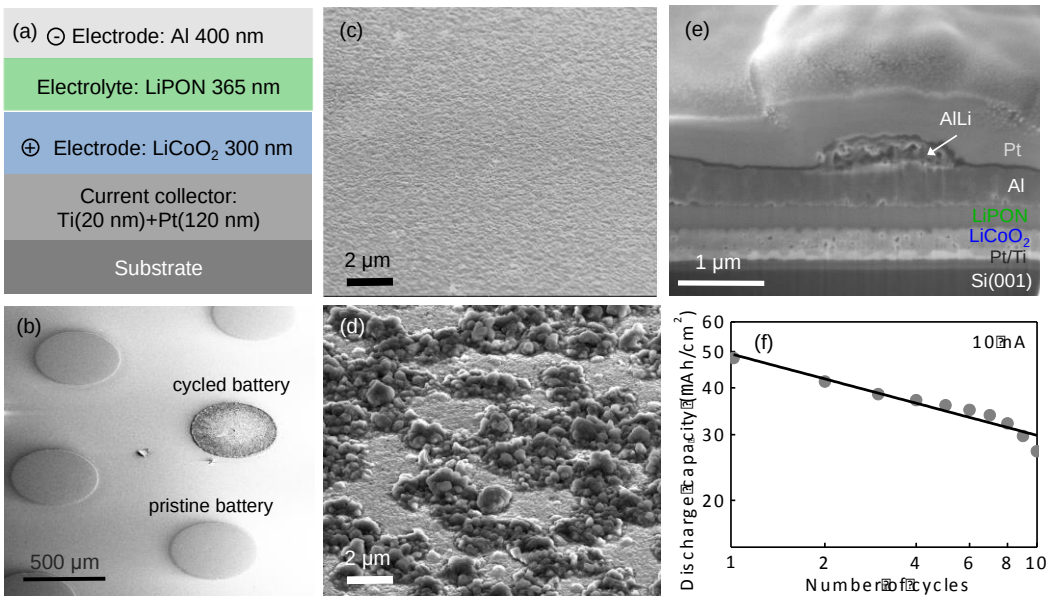


Figure 1. Al negative electrode for all-solid-state batteries. (a) Schematic of all-solid-state batteries with Al negative electrodes. (b) SEM of micron-scale devices showing morphology changes upon cycling. SEM of Al surface for (c) pristine and (d) cycled devices shown in (b). (e) Cross-section SEM image of Al electrode after 10 charging cycles, tilt = 45°. The Pt layer is added uniquely to protect the surface of the battery during the ion milling process and is not an active layer of the device. (f) Discharge capacity as a function of the number of cycles for 10 nA.

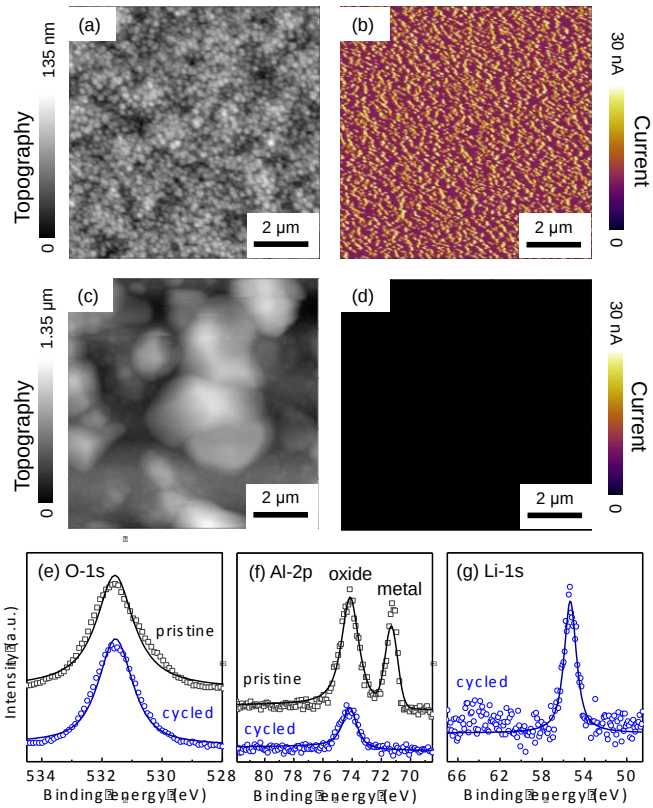


Figure 2. Al-based batteries surface characterization. Topography and conductive atomic force microscopy scans for (a, b) pristine and (c, d) cycled Al-based batteries, respectively, showing complete loss in electronic conductivity upon cycling. XPS of Al negative electrode for pristine and cycled batteries showing (e) oxygen peaks, (f) Al metal and oxide peaks, and (g) Li peak for the cycled device.

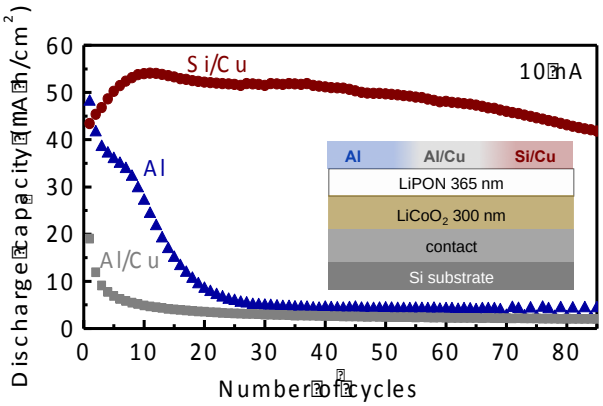


Figure 3. Electrochemical performance of thin-film all-solid-state batteries. Discharge capacity for 400 nm Al, 400 nm Al / 400 nm Cu, and 50 nm Si / 400 nm Cu negative electrodes, for batteries charged at 10 nA in ultra-high vacuum, under identical conditions. Inset: schematic of solid-state devices (out of scale for clarity).

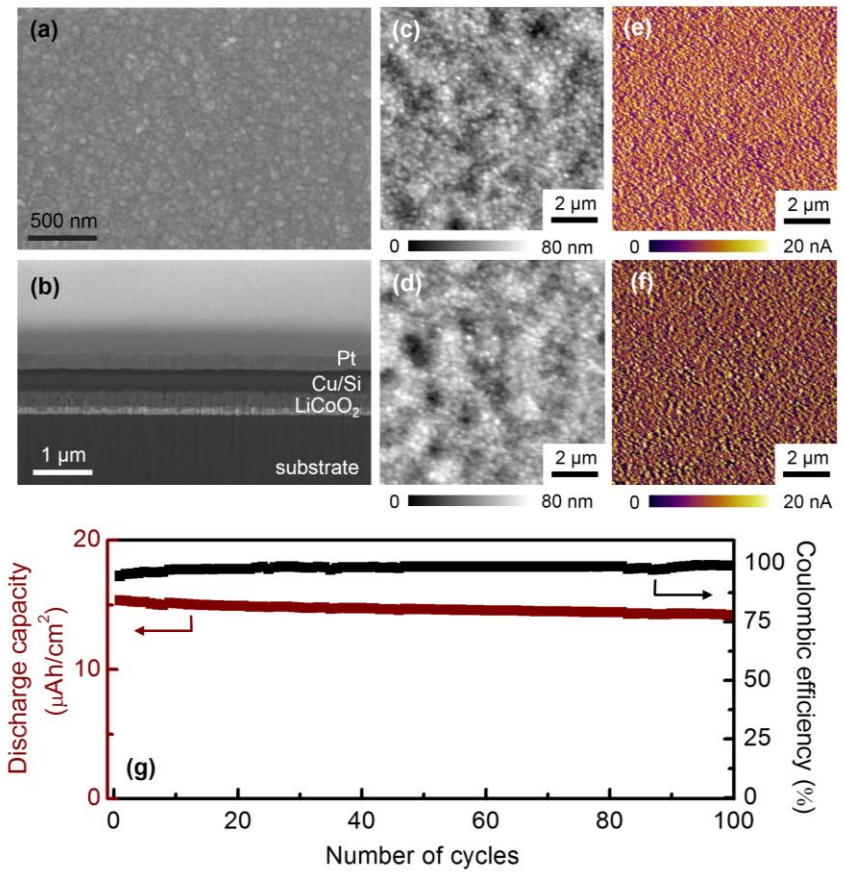


Figure 4. Electrochemical performance of thin-film all-solid-state battery with Si negative electrode. (a) Plane view and (b) cross-section SEM images of Si/Cu negative electrode after 10 charging cycles at 30 nA. A 2 μm thick Pt layer was added to prevent the damage of the Cu/Si top surface during the ion milling process for cross-sectional imaging. Topography and conductive atomic force microscopy scans for (c, e) pristine and (d, f) cycled battery, respectively, showing uniform and constant conductivity upon cycling. (g) Discharge capacity as a function of number of cycles. Capacity retention > 92%, with average Coulombic efficiency = 98%.

Experimental Methods

All-solid-state battery fabrication. The samples were fabricated on a Si (001) substrate with a 100 nm thick SiO_2 layer. 20 nm of Ti and 120 nm of Pt were used as the bottom contact for current collection. 300 nm of crystalline $LiCoO_2$ (cathode) was deposited by sputtering in the same chamber and without exposure to air. The sample was then annealed in ambient oxygen at 700 ^{o}C for 2 hours to smooth the cathode layer. Following the heat treatment, the sample was sputter coated with 365 nm of LiPON (electrolyte) and finally 400 nm of Al, Al/Cu, and Si/Cu negative electrode. Batteries with 0.51 mm in diameter were fabricated by using a steel mask for the top electrode deposition. All SSLIB were cycled under ultra-high vacuum, at 8.5×10^{-11} Torr, to prevent any undesired chemical reactions of lithium on the top surface of the negative electrode, and to exclude the possible influence of humidity on the device degradation.

High-resolution XPS measurements. The XPS data were collected using a 12 kV monochromated Al Kα X-ray source (1486.6 eV), and the analyzer was in hybrid lens mode for survey spectra. High-resolution spectra were collected in the same mode using a step size of 0.1 eV and pass energy of 20 eV. For all measurements, the analysis spot size was 20 μm in diameter as defined by the instrument electron optics. The charge neutralization system was used and all spectra were calibrated to the C 1s hydrocarbon peak at 284.8 eV.

Conductive AFM measurements. The c-AFM measurements were carried out at room temperature using a diamond-coated probe with 83 ± 17 nm in diameter and a cantilever with force constant of 2.8 N/m, at ambient environment. During the measurements, the c-AFM probe was in contact with the negative electrode top surface and the current collector located underneath the positive electrode was grounded. The current pathway was then across all the active layers of the thin-film solid-state-battery. Scans were acquired by using a piezo scanner in closed loop, at 0.4 sec/line. The topography and current signals were acquired simultaneously, in contact mode, under10 V bias applied to the probe.

X-section SEM imaging of batteries. 2 μm thick film of electron-beam and ion-beam Pt was initially deposited to protect the negative electrode surface during the milling process for cross-sectional imaging. Then, the samples were milled by Ga focused ion beam (FIB), using low current to minimize sample damage (9.3 and 0.8 nA).

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Notes

The authors declare no competing financial interest.

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