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/cm² 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) light weight and possibly compact packaging, and (v) a variety of materials that can 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. 3−5 Alloying reactions usually take place between Li and certain metals or semiconductors used as negative electrodes, as M + xLi+ + xe− ⇄ LiₓM, 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, although these materials represent an attractive class of negative electrodes because of 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, 7−10 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 7 and chemical characterization 18 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, nontoxic, and earth abundant, is a promising alternative for ultralightweight negative electrodes...
for portable devices, with theoretical capacity equal to 993 mAh/g for lithium storage. Al metal electrodes have recently presented extremely high-rate capability (charging time of 1 min, with current density of \( \sim 4000 \) mA/g), with specific capacity of about 70 mAh/g, resulting from the intercalation/deintercalation of chloroaluminate anions from the liquid electrolyte into the cathode. Nevertheless, in all-solid-state devices, the alloying reaction between Al and Li leads to the formation of a very stable AlLi alloy \((\text{Al} + \text{Li}^+ + e^- \rightarrow \text{AlLi})\), with consequent pulverization of the negative electrode and rapid loss in capacity in nanoscale devices. However, many details of the degradation mechanism, particularly in thin-film micrometer-size batteries remain unclear, including the effects of an intrinsic Al\(_2\)O\(_3\) layer that covers the negative electrode surface. This oxide layer is present even when fabricating/testing the battery under high-vacuum conditions (10\(^{-7}\) 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 \( \sim 1 \) \(\mu\)m diameter mounds distributed on its surface and composed principally of AlLi alloy, as previously determined, see Figure 1e 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). 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 \((\sim 100\%\) 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 1f.

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 hypothesize that a few-monolayer thick Al–Li–O compound forms on top of the Al electrode, substantially increasing 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 SSLIBs were fabricated by sputtering 300 nm of LiCoO\(_2\) as the positive electrode \((140 \text{ mAh/g})\), 365 nm of LiPON for the electrolyte \((3 \times 10^{-6} \text{ S/cm})\), 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 1b–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 ultrahigh vacuum \((8.5 \times 10^{-11} \text{ Torr})\). 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 \( \sim 1 \) \(\mu\)m diameter mounds distributed on its surface and composed principally of AlLi alloy, as previously determined, see Figure 1e 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). 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 \((\sim 100\%\) 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 1f.

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\(_2\)O\(_3\) layer (Figure 2(a-b)), the oxide is sufficiently thin \((\sim 3\) nm\) to allow electron tunneling.
期间的c-AFM测量。随后的10次充放电循环中，电极表面在30 nA下形成了一层致密且不透射的涂层（图2c,d）。有可能形成一层致密的不透射涂层在Al和AlLi层上可以显著减小表面的电导率，因此必须在电池充放电过程中通过电泳扩散和沉积过程被电极表面捕获。

为了帮助识别不透射涂层的化学成分，我们进行了XPS。O-1s光谱在531 eV处有两个峰，分别对应于Al-2p金属和氧化物峰。然而，在电池放电10次后，氧化物峰并未在放电状态检测到（见图2f）。这个结果表明，在 mound-层形成后，电极表面的耗尽层不会引起任何反应，因为Al和AlLi层之间的反应会随着表面氧化而导致电极和探针之间的界面厚度增加30 nm。通过XPS，图2g显示了在充电和放电过程中的金属Al和氧化物峰。

在c-AFM测量中。这些变化在电极表面的组成和电导率上表明，电极表面的致密涂层在循环中形成，这可以归因于模型中提出的一种机制，其中Li原子反应与AlLi合金形成，导致电池容量的损失。因此可以推测，容量损失是由于电池表面氧化，以及Al合金。这种机制还可能与扩散路径的形成有关，因此对于容量的衰减可能是由于一种组合的机制，包括电极表面的耗尽层以及电池表面的氧化。

图2. Al基电池的表面表征。扫描成像的AFM图像显示了(a)和(b)的原始电池和(c)和(d)的循环电池。图2c,d展示了原始电池和循环电池的O-1s峰，(f) Al金属和氧化物峰，以及(g) Li-1s峰。

图3. 薄膜固态电池的电化学性能。通过400 nm厚Al、400 nm厚Al/Cu、Cu和Si/Cu的电池充电，以及50 nm厚的Si电池，对于被充电的电池，在10 nA下在超真空中进行了放电。图3显示了电池的循环特性。
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. 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%.

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, as shown in the cross-section SEM image of Figure 4b. c-AFM measurements show that the electrical properties of the Si/Cu layer are unaltered upon cycling the battery (see Figure 4c–f). The Si/Cu battery shows an excellent performance, with discharge capacity of ~15 μAh/cm² after 100 cycles at 30 nA (Figure 4g). 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, 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 nanoscale size electrodes, 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. 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 Al2O3, 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/Al2O3 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 nanobattery overcharging. However, for the micrometer-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

\[
(1 + x) Li + \left(1 - \frac{x}{3}\right) Al + \left(\frac{x}{6} + \frac{y}{2}\right) Al_2O_3 \\
\rightarrow Li_2Al_{x}O_{(x+3y)/2} + AlLi
\]

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 possibly 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 indicated by c-AFM measurements. The addition of a Cu protective film did not prevent the capacity loss, due to the presence of an Al2O3 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.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b07058.

Experimental details of battery fabrication, XPS and c-AFM measurements, cross-section SEM of batteries,
cycling curves and Coulombic efficiency for Al and Si negative electrode batteries (PDF)

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Notes
The authors declare no competing financial interest.

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