Increasing global demands for energy storage in electric vehicles and the grid necessitate “beyond-lithium-ion” batteries that simultaneously exhibit high capacity, long-term cyclability, and excellent safety. Several candidates, most notably lithium-air and lithium–sulfur batteries, utilize lithium-metal anodes. Although the specific capacity of lithium metal is unrivaled (3860 mAh g$^{-1}$), the capacity fade and risk of catastrophic failure must be overcome. Herein, we describe ultrathin, ionically conducting lithium aluminum sulfide (Li$_x$Al$_y$S) coatings prepared on lithium-metal anodes by using atomic layer deposition, which stabilize the Li–electrolyte interface and reduce (up to five times) the interfacial impedance of lithium–metal anodes in contact with organic electrolyte. We demonstrate that these thin films effectively suppress dendrite formation and preserve a smooth, low-surface-area morphology for electrodeposited lithium metal, thereby doubling the lifetime of Li–Cu asymmetric cells.

Renewable, green alternatives to fossil fuels are needed to address the twin challenges of satisfying the worldwide demand for electrical power and mitigating the threat of global warming. Among the alternatives, solar and wind power appear to be the most promising, but the intermittent and distributed nature of these energy sources demands radical advances in energy-storage technology to facilitate their large-scale deployment. Consequently, tremendous effort is being dedicated toward developing “beyond-lithium-ion” batteries that can meet the demands of transportation and grid storage. A number of candidate technologies, including Li–air and Li–sulfur batteries, hold great promise in this regard, but significant challenges must be overcome before these batteries can be implemented. In particular, the lithium-metal anodes used in both Li–air and Li–sulfur batteries are a source of capacity fade and catastrophic failure.

Lithium metal has an extremely high theoretical specific capacity (3860 mAh g$^{-1}$), low density (0.59 g cm$^{-3}$), and the lowest negative electrochemical potential of any known material ($\sim$3.040 V vs. the standard hydrogen electrode). These attributes make lithium metal extremely attractive as an anode material for rechargeable lithium batteries. Unfortunately, although lithium metal has been investigated as an anode over the last 40 years,$^{[1]}$ its commercialization has been hindered by two severe technical barriers: the growth of lithium dendrites during repeated charge/discharge processes and the low coulombic efficiency (CE) of these processes.$^{[2]}$ The low CE can be partially compensated by using an excess of Li. However, the risk that lithium dendrites can grow to pierce the separator in a battery and reach the cathode, causing an electrical short and possibly fire or explosion, has compelled lithium-ion battery (LIB) manufacturers to adopt graphite anodes (372 mAh g$^{-1}$)$^{[3]}$ rather than lithium, thereby sacrificing capacity in favor of reliability and safety. Although existing LIBs are adequate for portable electronics, they are insufficient to enable the wide-scale implementation of electrical vehicles. Consequently, new battery technologies such as lithium–sulfur (Li–S)$^{[4]}$ and lithium–air (Li–O$_2$)$^{[5]}$ with up to four times higher volumetric energy density compared to LIBs, are undergoing intensive investigation. The success of these new technologies hinges on solving the longstanding challenges posed by lithium-metal anodes.

Various strategies have been explored to prevent lithium dendrite growth, but, to date, these have not proved commercializable. Some approaches have utilized micro-structured anodes such as coated lithium powder$^{[6]}$ or a 3D porous current collector$^{[7]}$ to suppress dendrite formation. However, most strategies have focused on improving the stability of the in situ formed solid electrolyte interphase (SEI) layer through electrolyte additives$^{[8]}$ by applying ex situ (i.e. artificial) SEI layers to the lithium metal prior to battery fabrication.$^{[9]}$ For instance, Archer and co-workers achieved stable, long-term cycling of Li by adopting simple liquid electrolytes reinforced with halogenated salt blends,$^{[10]}$ Zhang and co-workers reported that Cs$^+$ additives in the electrolyte can form a positive electrostatic shield around the initial nucleating points for lithium dendrites, which inhibit further growth.$^{[11]}$ Electrolytes with high salt concentration and large Li-ion transference numbers can also effectively suppress lithium dendrite growth.$^{[12]}$ Numerous materials have been investigated as artificial SEI layers, including polymers,$^{[13a,b]}$ SiO$_2$,$^{[14]}$ Li$_2$N,$^{[15a,b]}$ and carbon materials.$^{[16]}$ For instance, Cui and co-workers utilized a monolayer of interconnected hollow carbon nanospheres to protect lithi-
um metal and demonstrated that lithium was deposited underneath the carbon layer without forming dendrites. In addition, monolayer hexagonal boron nitride and graphene can also act as protective layers for lithium metal.

Ideally, artificial SEI layers on lithium metal should be uniform, conformal, ionically conducting, stable against liquid organic electrolytes, and deposited at low temperatures (lithium melts at 180 °C). To this end, atomic layer deposition (ALD) is a promising technique. ALD has attracted increasing attention in the development of next-generation LIBs in recent years, as a means to synthesize nanophase anodes, cathodes, and electrolytes. But the greatest commercial impact for ALD in energy storage is likely through depositing ultrathin protective coatings. Numerous reports exist for ALD coatings on a variety of cathode and anode materials, but only very recently has ALD been investigated for protecting lithium-metal anodes and, thus far, the reports are limited to ALD of Al₂O₃.

Herein, we report the use of ALD solid-state electrolyte thin films to protect lithium-metal anodes and inhibit the growth of Li dendrites. We developed a process for growing ALD lithium aluminum sulfide (LiₓAlₓS) films with precisely controlled thickness and composition and showing a relatively high ionic conductivity of 2.5 \( \times 10^{-7} \) S cm\(^{-1}\) at room temperature. We demonstrate that this material can stabilize the interface between lithium metal and liquid carbonate electrolytes, and effectively suppress lithium dendrite growth.

The LiₓAlₓS ALD was performed by combining an existing process for Li₂S ALD, using lithium tert-butoxide (LTB) and H₂S, with a new process for AlₓSₙ ALD using tris(dimethylamido)aluminum(III) (TMDA-Al) and H₂S. By controlling the ratio of Li₂S to AlₓSₙ ALD cycles, we can deposit LiₓAlₓS films with any composition, as illustrated in Figure 1a. In this work, we focus exclusively on films using an ALD cycle ratio of Li₂S/AlₓSₙ = 1:1.

Figure 1b shows the mass changes observed through in situ quartz crystal microbalance (QCM) measurements during LiₓAlₓS (1:1) ALD at 150 °C. The LiₓAlₓS (1:1) growth is quite linear, and shows mass increases of approximately 13.1 ng cm\(^{-2}\) during each Li₂S cycle and 12.4 ng cm\(^{-2}\) during each AlₓSₙ cycle. Assuming bulk densities for these compounds, these mass changes imply thickness changes of 0.79 Å per cycle for Li₂S and 0.53 Å per cycle for AlₓSₙ, so that the average growth rate was 0.66 Å per cycle. Ex situ spectroscopic ellipsometry (SE) measurements performed on LiₓAlₓS (1:1) deposited on Si(100) yielded a refractive index of \( n = 2.77 \) at 633 nm and a growth rate of 0.50 Å per cycle. This smaller growth compared to the value derived from QCM may result from interactions between the Li₂S and AlₓSₙ to produce a film that is denser than either of the pure compounds. The QCM measurements can also be used to estimate the composition of the LiₓAlₓS (1:1) ALD films. Assuming stoichiometric growth of LiₓS and AlₓSₙ, the QCM measurements for LiₓAlₓS (1:1) imply an atomic ratio of Li/Al of approximately 3.5. Ex situ measurements performed on LiₓAlₓS (1:1) films deposited on Si(100) substrates by using inductively coupled plasma mass spectrometry (ICP–MS) yielded Li/Al = 2.9, which is in good agreement with the QCM measurements.

To characterize the electrical properties of the LiₓAlₓS (1:1) ALD film, we performed electrochemical impedance spectroscopy (EIS) measurements on 50 nm films deposited on SiO₂/Si.

**Figure 1.** a) Schematic illustration of LiₓAlₓS ALD; b) in situ QCM measurements of LiₓAlₓS ALD performed at 150 °C using (LTB-H₂S)/(TDMA-Al-H₂S) = 1:1; c) Arrhenius plot for temperature-dependent ionic conductivity measured using a 50 nm LiₓAlₓS film.
substrates patterned with micrometer-scale interdigitated Pt electrodes in the temperature range of 180–300 °C. The resulting Nyquist plots (Figure 2) are composed of one semicircle and a tail. This finding indicates that our LiAlS ALD films are amorphous, as crystalline materials would show two semicircles corresponding to separate contributions from grains and grain boundaries.[13] The low-frequency tail is attributed to ionic blocking by the Pt electrodes. The ionic conductivity was calculated from the impedance data by fitting the equivalent circuit shown in the inset of Figure 2, where is the resistance, CPE is the constant phase element, and the subscript “el” represents the electrode.[14] The temperature dependence of the ionic conductivity follows Arrhenius behavior, as shown in Figure 1c, and yields an activation energy of approximately 0.48 eV. The extrapolated room-temperature ionic conductivity is $2.5 \times 10^{-7}$ S cm$^{-1}$ and is among the highest reported for ALD solid-state electrolytes.[15] Moreover, the ionic conductivity could likely be improved by optimizing the composition of the LiAlS films.

Next, we investigated the interfacial stability of lithium-metal anodes coated by the LiAlS ALD film in contact with a commercial carbonate-based electrolyte ($1 \text{ M LiPF}_6$ in EC/EMC 3:7) by fabricating Li electrolyte/Li symmetric batteries and performing AC impedance measurements. As shown in the inset of Figure 3a, the impedance spectra are modeled by using an equivalent circuit composed of the electrolyte resistance $R_{\text{el}}$, the resistance across the SEI $R_S$ with capacity CPE$_S$, and the charge-transfer resistance at the electrodes $R_T$ with capacity CPE$_{CPE}$. The AC impedance data in Figure 3a show only one semicircle, indicating that the time constants for CPE$_S$ and CPE$_{CPE}$ are nearly identical and cannot be resolved in these measurements. Figure 3b shows the $R_S$ values for the symmetric batteries derived from the AC impedance measurements as a function of the storage time. After 68 h of storage, the control sample with pristine Li showed a much higher $R_S$ value of approximately 2500 ohms compared to that for the Li protected by the LiAlS ALD film (ca. 500 ohms). Moreover, the $R_S$ for pristine Li continued to increase throughout the test, whereas the coated Li stabilized after approximately 20 h. The continual increase in $R_S$ for pristine Li indicates continual SEI formation from the reaction between the bare lithium and the electrolyte. Evidently, LiAlS can protect the Li from direct contact with the electrolyte to produce a thinner and more stable SEI.

The CE is a defining parameter for determining battery lifetime. In our study using asymmetric Li/Cu cells, the CE is defined as the ratio of lithium stripped from the Cu electrode to lithium deposited on the Cu electrode during each cycle. Figure 3c shows the CE versus cycle number for asymmetric Li/Cu cells, using both pristine Cu electrodes and Cu coated with LiAlS ALD films (1:1). The Li/pristine Cu cell shows a gradual decrease in CE over the first 90 cycles, followed by a precipitous drop at around 135 cycles. In comparison, the Li/LiAlS-coated Cu cell shows a very stable CE, extending until 170 cycles. The maximum CE values in Figure 3c are only around 80%, as a result of the carbonate-based electrolyte used.[9] A much higher CE of approximately 97% was achieved by using an ether-based electrolyte (Figure 4), but the behavior was very similar: the LiAlS-protected Cu electrode maintained a high CE for over 700 cycles compared to only 400 cycles for the pristine Cu. In summary, the LiAlS ALD film on the Cu electrode allows the Li/Cu cells to maintain a high and stable CE and long-term cyclability in both carbonate- and ether-based electrolytes.

In addition to the CE, the voltage hysteresis during Li deposition/stripping is another revealing parameter for long-term cyclability. We define hysteresis as the potential difference between Li stripping and Li deposition. For the Li/Cu cell with pristine Cu, the hysteresis increases with cycling, reaching 380 mV after 160 cycles (Figure 3d). We attribute this increase to the degradation and consumption of the electrolyte.[9, 15] For LiAlS-protected Cu, however, the hysteresis is much more stable, remaining at approximately 120 mV over 120 cycles, and increasing only slightly to 157 mV after 160 cycles. These findings support the hypothesis that the LiAlS ALD film inhibits any reaction between the electrodeposited Li and the electrolyte.

To investigate the origin of the improved electrochemical cycling performance imparted by the LiAlS ALD film, scanning electron microscopy (SEM) was performed on the Li electrodeposited onto pristine Cu and LiAlS-coated Cu (Figure 5). As expected, the Li deposited on pristine Cu shows numerous long filaments or nanowires[9, 10] (Figures 5a and 5c). It is easy to imagine that these 0.1–0.2 μm needle-like Li structures could easily puncture a separator in a Li battery, resulting in short circuit and failure. In addition, these structures dramatically increase the Li surface area compared to a planar foil, which would rapidly consume electrolyte to form a SEI. In contrast, the surface of the ALD LiAlS-coated Cu remains relatively flat with no obvious Li dendrites after lithium deposition (Figure 5b). Figure 5d shows a cross-sectional SEM image of the ALD LiAlS-coated Cu after lithium deposition, and illustrates that the Li is much denser compared to the pristine Cu.
(Figure 5c). It can be concluded that the ALD-derived solid-state electrolyte Li$_x$Al$_y$S film can suppress Li dendrite growth.

In summary, we successfully synthesized Li$_x$Al$_y$S solid-state electrolyte thin films through ALD. These films show a high ionic conductivity of $2.5 \times 10^{-2}$ S cm$^{-1}$ at room temperature and are highly effective in stabilizing the interface between lithium metal and liquid organic electrolytes. In addition, Li$_x$Al$_y$S can effectively suppress lithium dendrite growth during Li dep-
osition/stripping processes. These solid electrolyte ALD coatings show promise for improving the performance of Li–S and Li–O₂ batteries.

**Experimental Section**

We utilized a custom viscous-flow, hot-walled ALD reactor composed of a stainless-steel flow tube with a length of 100 cm and an inner diameter of 5 cm. Ultrahigh purity Ar (99.999%) was used as the carrier gas at a mass flow rate of 252 sccm and a pressure of 1.2 Torr. The Li₂S ALD [12] was performed by using alternating 5 s exposures to lithium tert-butoxide (LTB, 98%, Strem Chemicals, Inc., USA) and hydrogen sulfide (1% H₂S in Ar, Matheson Tri-gas, USA), with 5 s Ar purging periods between each dose. The AlₓSᵧ ALD was accomplished by using alternating exposures to 5 s tris(dimethylamido)aluminum(III) (TDMA-Al, Sigma–Aldrich Co., USA) and 10 s H₂S, separated by 5 s Ar purging periods. The solid LTB and TDMA-Al were heated to 140 and 80 °C, respectively, in stainless-steel reservoirs, and 36 sccm Ar was diverted through each reservoir during the respective precursor dose. The LiₓAl₃Sᵧ ALD was performed by alternating between the LTB-H₂S exposures for LiₓS ALD and the TDMA-Al-H₂S exposures for AlₓSᵧ with every ALD cycle. In situ QCM measurements were performed to investigate the LiₓAl₃Sᵧ ALD. These experiments used RC™ Quartz, 6 MHz quartz sensors (Colnatec, Inc.) mounted in a Maxtek BSH-150 sensor head. The sensor head was modified to purge the back side of the crystal with Ar to ensure that ALD only occurred on the front side. [17] The QCM thickness monitor (Maxtek TM-400) reported mass changes in units of ng cm⁻², and these values were multiplied by the bulk densities of 1.66 and 2.32 g cm⁻³ for LiₓS and AlₓSᵧ, respectively, to obtain the corresponding thickness changes.

To prepare LiₓAlₓSᵧ ALD samples for testing, 50 nm films were deposited on Li and Cu foils at 150 °C. Both LiₓS and AlₓSᵧ are extremely air-reactive. Consequently, the coated foils were unloaded from the ALD reactor into an Ar-purged glove bag, and placed in Ar-filled, sealed glass containers for transport into the glove box. The Li foils were loaded into the ALD reactor by using a similar protocol. Film thicknesses were determined from LiₓAlₓSᵧ ALD films deposited on Si(100) substrates by using spectroscopic ellipsometry (J. A. Woollam Co. alpha-SE) performed in an Ar-purged glove bag.

To prepare samples for ionic conductivity measurements, 50 nm LiₓAlₓSᵧ ALD films were deposited onto SiO₂/Si substrates patterned with micrometer-scale interdigitated Pt electrodes [18] (Alta Microtec, Inc.). These interdigitated Pt electrodes provide a 40 000 x enhancement in ionic current compared to a simple arrangement of two electrodes in square geometry. In-plane ionic conductivity measurements were performed on the coated substrates in an Ar-filled glovebox using EIS. Contact to the Pt electrodes was made by using microprobes, and the sample was placed on a hot plate to facilitate measurements in the temperature range of 180–300 °C. EIS was performed by applying 5 mV amplitude in a frequency range of 1 MHz–0.1 Hz, using a Solartron 1260 impedance/gain phase analyzer combined with a Solartron 1287 electrochemical interface.

CR2032-type coin cells were fabricated to facilitate impedance measurements and electrochemical cycling tests. Li/Li symmetric cells were assembled with Li metal as both the working and counter electrodes. For the Li/Cu cells, the pristine Cu or LiₓAlₓSᵧ-coated Cu foil was used as the working electrode, and Li foil was used as the counter and reference electrodes. Celgard 2400 membrane was used as the separator, whereas Cu foil served as substrates for the Li-metal deposition. The electrolyte used was 1 M LiPF₆ in EC/EMC (3:7). To standardize the testing, 30 µL of electrolyte was used in each coin cell. EIS of Li/Li cells was measured by using a Solartron 1260 impedance/gain phase analyzer combined with a Solartron 1287 electrochemical interface. Spectra were recorded from 1 MHz to 0.1 Hz with the amplitude of 5 mV. The spectra were fit by using the equivalent circuit in Figure 2a. For the electrochemical cycling testing of the Li/Cu cells, the current density for lithium deposition and stripping was set to 0.5 mA cm⁻². In each cycle, 1 C cm⁻² (0.28 mA h cm⁻²) of lithium metal was deposited on the Cu electrode and then stripped until the potential reached 1.0 V versus Li⁺/Li. The charge/discharge testing was performed by using an Arbin 2043 electrochemical tester.

The morphology of the electrodeposited lithium was characterized by using SEM (Hitachi S-4700). After a single half-cycle of lithium electrochemical deposition, the Li/Cu coin cells were disassembled to collect the lithium-metal film deposited on the Cu electrodes. Then, the electrolyte on the lithium surface was flushed away with DME. After drying, the Cu samples were transported to the scanning electron microscope in Ar-filled glass containers and quickly loaded into the microscope to minimize air exposure.

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