From Dendrites to Hemispheres: Changing Lithium Deposition by Highly Ordered Charge Transfer Channels

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ABSTRACT: Metallic lithium as an anode is an ultimate ideal for rechargeable lithium batteries with high energy density such as lithium–oxygen batteries and lithium–sulfur batteries. However, the excess reactivity and asymmetrical dissolution–deposition of the metallic lithium anode make it impossible to support a stable long charge–discharge cycling. To protect the metallic lithium anode, apparently it needs to adjust the dissolution and deposition of lithium ions, but more essentially, it should reasonably change the distribution and transport of electrons on the surface and interface of the metallic lithium. In this work, anodic aluminum oxide (AAO) membranes are used to build highly ordered channels on the lithium anode surface in which lithium ions can transfer in the channels and electrons can be



transported by the lithiation reaction of alumina with an oxygen vacancy-involved process. As a result, the cyclic reaction actually is partially transferred to the AAO surface, and lithium deposition occurs there as a hemispherical appearance but not as dendrites. Meanwhile, the highly ordered characteristics provide a physical effect to make the deposited lithium hemispheres a uniform distribution on the AAO surface. The AAO-regulated lithium anodes could be widely used to improve the cycling performance for metal lithium batteries.

KEYWORDS: lithium anode, anodic aluminum oxide, lithiation reaction, oxygen vacancies, dendrite suppression

1. INTRODUCTION

Lithium batteries with high energy density such as lithiumsulfur batteries and lithium-oxygen batteries are considered as the next-generation rechargeable batteries for the growing demands of high-energy batteries.¹ Metallic lithium as an anode with a high theoretical capacity of 3860 mAh/g is a necessary choice for achieving a high energy density of the lithium batteries. However, the excess reactivity and asymmetrical dissolution-deposition in the charge-discharge processes cause a series of problems for lithium batteries.⁴ The dendrites formed by the uneven deposition of the lithium anode surface in the cycle may result in the short circuit of a battery; side reactions of metallic lithium consume excessively an electrolyte to destroy the battery before long; and large volume changes in the lithium anode during dissolutiondeposition can even lead to the collapse of the anode structure. Therefore, protection measures are necessary for the metallic lithium anode in the lithium batteries.

In recent years, some different strategies about the protection of the metallic lithium anode have been attempted. A protective solid-electrolyte interface (SEI) film formed by reactions with electrolyte additives is able to regulate lithium ion deposition on the anode surface. The LiNO₃ additive in lithium–sulfur batteries can preferentially react with lithium to form a stable SEI film on the anode surface to improve the electrochemical performance.³ Some additives such as the alkali metal ions Cs and Rb use their lower reduction potential and positive charge to form a shield at the anode deposition

site to achieve a uniform deposition.⁴⁻⁶ In addition, lithium halide salt can enhance the rapid and uniform diffusion of lithium ions.⁷ It is also found that the highly concentrated electrolyte is effective to improve the cycle stability due to the change of interface reaction environments.⁸ Similar to the strategy of the protective SEI films generated by the reactions between metallic lithium and electrolyte additives, an artificial SEI film with a designed microstructure can restrain the lithium dendrite growth and improve the cycling performance. Many kinds of materials have been tried to use as artificial protective films such as $Al_2O_{3,}^{9-13}$ graphite,¹⁴ carbon nano-tubes,¹⁵ carbon nanofibers,¹⁶ carbon nanospheres,¹⁷ inorganic compounds, or alloy layers of Li,¹⁸⁻²⁰ glass fibers,²¹ and polymerization.^{22,23} Generally, the protective film strategies can change the direct contacts between metallic lithium and electrolyte and regulate the transport and distribution of ions. On the other hand, modifying the lithium anode itself by special structures^{24,25} or alloying^{26–28} can form a more stable and evenly arranged frame to keep the anode's stability in long cycling. In this strategy, the mechanical effect and electron distribution of the anodes are regulated to a certain extent. As

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Figure 1. AAO surface after different cycles. (a) 10, (b) 30, (c) 50, (d) 49.5, and (e) 50 cycles. The histogram shows the diameter distribution and unit area volume of the deposits, which are marked by red circles in panels (d, e). The circulating current density is 0.5 mA/cm^2 , and the deposition and dissolution capacity is 1 mAh/cm^2 .

another rising strategy for the application of the metallic lithium anode, some solid electrolytes are investigated; obviously, the lithium reversible process with the solid electrolytes is different from the dissolution–deposition mechanism in the liquid electrolytes.²⁹ As in this work, researchers have used AAO membranes but as carriers of liquid electrolytes to form solid electrolytes to achieve a uniform deposition,^{30–32} and other solid electrolytes.^{34–37} However, the poor interface contact and unsatisfied stability are still problems for metallic lithium anodes.

To analyze the strategies of lithium anode protection, it can be found what the protective films change mainly is the redistribution of lithium ions in the deposition process, but the deposition still has the same mechanism as the unprotected metallic lithium anode in which the electron distribution guides the sites of lithium ion deposition, while the diffusion of lithium ions decides kinetically the rate of the deposition. This is why lithium dendrites can be found in the protective anodes after a long cycling.² In this work, we propose a simple method to change the distribution and transport of electrons and deposition mechanism of lithium ions in which the electron transport is the rate-controlling step and generates a hemisphere-like lithium deposition, not dendrites. A porous anodized aluminum oxide (AAO) film is directly fitted on the surface of the lithium anode to form highly ordered channels, and its effects in the physical and chemical mechanisms can regulate the surface charge conduction process of the anode. The results are helpful for lithium anode batteries to obtain an improved electrochemical performance and suggest a new insight into the protection of metal lithium anodes.

2. RESULTS AND DISCUSSION

A lithium–lithium symmetric electrolytic cell is used in the experiment to avoid pressure interference during the assembly of the coin cell to observe the true morphology.^{38,39} The AAO film is used to construct an Al_2O_3 protective layer on the surface of the lithium anode, which has a more regular microscopic morphology than the Al_2O_3 layer formed by spin coating⁹ or atomic layer deposition (ALD),¹¹ so the fine morphology and composition changes can be observed. The AAO film has highly ordered channels with a diameter of 390 nm and a wall thickness of about 60 nm (Supporting Information Figure S1). Lithium ions can freely shuttle through the channels after the AAO membrane was infiltrated in the electrolyte and uniformly distributed on the surface of the lithium anode due to the uniformly arranged channels.

Some interesting experimental phenomena are observed with the application of AAO, as shown in Figure 1. Figure 1ac, respectively, shows the surface image of AAO after 10, 30, and 50 cycles. There is not a large amount of deposits on the surface of AAO until about 50 cycles, indicating that the lithium deposition occurs first on the surface of metallic lithium through the AAO channels and deposits on the AAO surface with a processive cycling. It can be inferred that the AAO surface begins to grow deposits only when the deposits of the lithium surface grow into contact with the bottom of AAO (see in the Supporting Information Figure S4, the anode surface deposits grow to contact the bottom of AAO at about 50 cycles). Figure S2 shows that the surface morphology of AAO-protected Li is also significantly different from bare lithium, which means that AAO can regulate the surface deposition morphology of lithium. The morphology difference at 50 cycles is the most obvious, and Figure S2c shows that bare lithium has formed obvious dendritic deposits with a length of more than 10 μ m. While Figure S2f shows that the surface of AAO-protected Li has only particles and short

clusters of deposits with a size of about 1 μ m. Additionally, as shown in Figure S3, only a small amount of dead lithium remains on the AAO surface after cycling at a higher current density and capacity, and the surface of AAO-protected Li does not have dendrites like the bare lithium anode, and the deposit size is also smaller. Figure S4 shows a schematic diagram of the highly ordered channels of AAO uniform with the ion concentration in the horizontal direction and lead to smooth surface deposits. Obviously, the highly ordered channels influence dominantly the morphology of lithium deposition. To investigate the changes of lithium deposition in the charge-discharge process, two differently charged states are compared with each other. Figure 1d is the surface of AAO that is deposited one more time after 49 dissolutiondeposition cycles and is recorded as 49.5 cycles. Also, Figure 1e is the surface of AAO after complete 50 cycles, which means it has one more dissolution process than Figure 1d. It can be observed that the hemisphere deposits on the AAO surface can react reversibly in the charge-discharge processes. The histogram shows the size distribution and volume comparison of AAO surface hemisphere deposits in the Figure 1d and e states, respectively. The hemisphere deposit volume per unit area of the AAO surface in the cyclic state shown in Figure 1d is about 20.5 times that of Figure 1e. Also, the specific hemisphere deposit diameter distribution data are recorded in the Supporting Information Table S1. This means that the lithium deposited on the surface of the AAO can still actively participate in the cyclic reaction, leaving only a small amount of dead lithium (less than 5%). It is worth mentioning that the deposition of the AAO-covered lithium surface after 49.5 cycles is still in uniform cluster growth (Supporting Information Figure S5), but the size is slightly larger than the complete cycle and will be restored to the normal size cluster after another dissolution.

The EDS mapping of Figure 2a shows that the hemisphere deposit on the AAO film does not involve Al but mainly C and O elements. However, as other morphology, the flaky deposit close to the surface of the AAO film in Figure 2b is enriched in Al and O, but almost no C element was detected. This means that there are two distinct deposits on the surface of the AAO film. The hemisphere deposits containing the C and O



Figure 2. Surface morphology and elemental analysis of AAO after 49.5 cycles. (a) Hemisphere deposit and (b) flaky deposit. (c) Infrared absorption spectrum of AAO after 50 cycles. The circulating current density is 0.5 mA/cm^2 , and the deposition and dissolution capacity is 1 mAh/cm^2 .

elements is the same as the conventional lithium deposition that mainly are the lithium metal and organic/inorganic compounds of lithium.² This also can be proved by the XPS spectra in Figure 3b3, which clearly shows the characteristic peaks of lithium deposits such as Li₂O on the AAO surface. Lithium easily reacts with aluminum to form various compounds such as $\text{Li}_{x}\text{Al}_{y}\text{S}^{19}$ and $\text{Li}\text{AlO}_{2}^{42}$ So the Alcontaining deposit in Figure 2b should be Li,Al₂O₃, which represents a kind of lithium aluminum oxide formed by the Al_2O_3 lithiation reaction.^{11,40,41} The lithiation reaction is a process that the lithium ions in solution dope into Al₂O₃ to form lithium aluminum oxide. We conducted an FTIR test on the AAO after 50 cycles (Figure 2c), and the results proved that there was lithium aluminum oxide on the surface of the AAO. The 400–900 cm^{-1} peak in the fresh AAO sample is produced by the Al-O bond, and it is broadened due to the close positions of the peaks. However, in the AAO after cycling, a series of new and obvious absorption peaks was detected in this interval, which can be identified as the mixed vibration of the Li-O and Al-O bonds in the lithium-doped aluminum oxide. 43 The remaining peaks can be identified as adsorbed impurities or residual organic matter on AAO. The peak at about 1100 cm⁻¹ may be attributed to SiO_2 used as a desiccant in the test chamber of the instrument. The peaks at about 2850 and 1400 cm⁻¹ can correspond to the bonds formed between C, O, and H elements in organic matters, which come from the deposits and electrolyte remaining on AAO. The peaks at about 3450 and 1630 cm⁻¹ respectively represent the O-H and H-OH bonds, which are formed by the adsorbed water from air and its interaction with the hydroxyl group from AAO.⁴³⁻⁴⁶ The lithium deposits that appear on the AAO surface means that electrons from the external circuit can reach the surface of the AAO film. That is, after 50 cycles, when the deposits of lithium anode contact with the AAO, electrons can proceed from the lithium anode, along the anode surface deposits, eventually reaching and "passing through" the AAO film to the surface and allowing lithium ions to deposit. In such an electron transport path, how electrons "pass through" the insulated Al₂O₃ becomes a key issue.

First of all, it should be explained that the deposits grown from the anode surface cannot enter the AAO channel for growth, which means that the electron conduction inside the AAO cannot be simply explained by the "fiber deposit in the channel". The work of Bai⁴⁷ pointed out that at a high current density of 10 mA/ cm^2 , the deposits of the lithium surface can keep out of the channels even in the case of far exceeding the theoretical capacity. So the deposits will not enter the channel at the 0.5 mA/cm^2 current density used in this work, which can be observed from the Supporting Information Figure S6, and there is no deposit in the AAO channels after 50 cycles whether intact or broken, just like the phenomenon observed in the literature.³² This can be attributed to the fact that the deposit size (μ m) is larger than the pore size (nm).¹⁷ Also, although AAO is thin and brittle, it is also sufficient for the anode protection and electrochemical reactions, and Figure S7 shows that the AAO film can remain intact after the cyclic reaction.

The composition phase of AAO is γ -Al₂O₃, which has tetrahedral and octahedral pores in the spinel structure, contains Al atoms and oxygen vacancies that are randomly distributed at these sites.^{48,49} The Al₂O₃ lithiation reaction is a process that the lithium ions in solution dope into Al₂O₃ to



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Figure 3. O1s, Al2p, and Li1s XPS spectra of fresh AAO after the cyclic reaction of AAO and lithium foil. (a1) O1s and (a2) Al2p XPS spectra of fresh AAO. (b1) O1s, (b2) Al2p, and (b3) Li1s XPS spectra of AAO after the cyclic reaction. (c1) O1s and (c3) Li1s XPS spectra of lithium after the cyclic reaction.



Figure 4. Schematic diagram of the deposition and dissolution on the AAO surface. The inset SEM images are 49.5 cycle AAO (a) surface and (b) cross section; 50 cycle AAO (c) surface and (d) cross section. The circulating current density is 0.5 mA/cm^2 , and the deposition and dissolution capacity is 1 mAh/cm^2 .

form lithium aluminum oxide. Jung's research⁴⁰ shows that in the lithiation reaction, the Li atom constantly replaces the position of the Al atom and bonds with O, resulting in a decrease of the Al–O bond and an increase of the Li–O bond, that is, a decrease in the number of O atoms around the Al. When X = 0 (undoped), the main charge state of Al is +2.4, indicating that the Al atom is surrounded by 4 to 6 O atoms; when $1.4 \ge X \ge 0.2$, the charge state of Al is from +2.4 to 0, indicating an Al atom having 1 to 3 neighbor O atoms; When $X \ge 1.4$, Al exhibits a charge state from 0 to -1.5, indicating an Al atom without an O atom. The value of x in the lithiation reaction is constantly changing and approaches the value of thermodynamic stability, which is about 3.4. So after the lithiation reaction of the following formula occurs at the solid– liquid interface in the AAO tunnels,

$$Al_2O_3 + xLi^+ = Li_xAl_2O_3 + yVo^{++}$$

the oxygen coordination number around Al showed to be insufficient, resulting in additional oxygen vacancies.

The XPS spectra in Figure 3 show the changes before and after the cyclic reaction, clearly proving the occurrence of the lithiation reaction. As shown in Figure 3a1,a2, the spectra peaks of O (531.7 eV) and Al (74.6 eV) of fresh AAO match Al₂O₃ well.^{50,51} After cycling, the surface of AAO shows very obvious changes. As shown in Figure 3b1, the O1s binding energy generally increases, meaning a significant transformation of the surface chemical surroundings for oxygen in the surface of AAO. To analyze comprehensively the results in Figure 3, O1s for AAO after cycling (Figure 3b1) and O1s for lithium after cycling (Figure 3c1) can be fitted as three peaks at 531.3, 532.5, and 533.4 eV, respectively, assigned to Li-O, H-O, and C-O bonds. This is reasonable because the two samples, AAO and lithium, were measured after cycling, and the signals could come from ether electrolytes or lithium deposits.⁵² Theoretically, the signal of oxygen vacancy should appear at the region higher than 531.7 eV (O1s binding energy for AAO), because the defect of oxygen makes a positive chemical shift compared to stoichiometric metal oxides. Unfortunately, at the region, the signal is overlapped with

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the H–O signal, leading in the difficulty to mark separately the oxygen vacancy in Figure 3b1. However, in the AAO after cycling, the existence of lithium is very clear (Figure 3b3, Li1s for AAO after cycling), proving the occurrence of the lithiation reaction between AAO and lithium during the cycles. Further, based on the analysis, Al2p for AAO after cycling (Figure 3b2) can be fitted by the three peaks: besides the Al2p peak for AAO, one with a low binding energy (73.85 eV) is assigned to the formation of oxygen vacancies due to the lithiation reaction, and the other at 75.0 eV is from Al-OH bonds as proved in Figure 3b1.^{53,54} For Li1s, Figure 3b3,c3 shows that the existence of Li-O bonds (55.6 eV) and Li-Li bonds (54.6 eV).⁵⁵ Obviously, Li–O bonds are dominant for the AAO after cycling while much less Li-O bonds exists in the lithium after cycling. Therefore, it can be found that the information from the XPS results can mutually confirm each other to get the reasonable conclusion that the lithiation reaction occurs between AAO and lithium during cycling. The details in the data about the XPS spectra are listed in Table S2, and the general XPS survey spectra are shown in Figure S8.

Oxygen vacancies, as a widely studied defect, have been understood how to enhance the electron transport and electrochemical activity.⁵⁶⁻⁵⁹ Oxygen vacancies capturing electrons is an energetically favorable process (the difference between perfect and defect electron affinities and ionization energies).⁴⁹ Therefore, oxygen vacancies can act as electroncapturing centers and as electron-trapping sites and serve as a mobile donor or acceptor for the electron transport.⁶⁰ This view has been confirmed and applied in the proposed insulation surface transition model.⁶¹ Generally, oxygen vacancies caused by the lithiation reaction appear on the surface of the AAO channels, which provide a "springboard" for the electron transport. Eventually, the charge "conduct through" the AAO film, so that the dissolution and deposition reaction of lithium ions can also be performed on the AAO surface.

Therefore, the dissolution-deposition mechanism of the lithium anode with AAO is described as follows (Figure 4). After the anode deposits contact the bottom of the AAO, the lithiation reaction of Al₂O₃ starts, resulting in the increasing of the oxygen vacancy concentration on the channel surface, causing the channel to exhibit an "activity" for the electron conduction. Finally, under the action of the active channels, the dissolution-deposition reaction of lithium ions occurs on the AAO surface, and a hemispherical deposition is obtained, as shown in Figure 4a,b; then as it continues to dissolve, the AAO surface deposits will actively participate in the reaction, making the total volume sharply reduce 95% with good cycle reversibility, as shown in Figure 4c,d. According to the rough calculation, to achieve the charge and discharge capacities (1 mAh/cm²) set in the experiment, about $48 \times 10^7 (\mu m^3/cm^2)$ of pure lithium is needed, and the volume change of the AAO surface deposits is about $21.5 \times 10^7 \ (\mu m^3/cm^2)$. That is, less than half of the reactions occur on the AAO surface. This shows that the application of the AAO film makes the cycle reaction that had all occurred on the lithium anode divide into two parts and one of both transfer to the AAO film surface. This undoubtedly reduces the reaction strength and volume change of the lithium surface, protects the lithium anode, and improves the electrochemical performance.

Another interesting issue is why the lithium deposit on the AAO surface presents a hemispherical morphology. This can be attributed to change of the rate-determining step of the deposition process. As known well, the deposition from the solution to solid involves two stages: nucleation and growth. According to the classical crystallization theory, the driving force during nucleation is the reduction of free energy after the nucleation of the material; and the resistance is the increase of the free energy of the new interface formed. Due to the principle of energy minimization, a sphere has the smallest surface area under the same volume, so the crystals naturally tend to be hemispherical when just nucleated.⁶²⁻⁶⁴ In the subsequent growth process, if the exchange current density is large and the surface diffusion becomes the control step, the crystal nuclei will grow into a dendrite shape, such as the anode surface. The widely accepted theory is the sand time model of Chazalviel,⁶⁵ which believes that the dendrite appearance time is inversely proportional to the current density. However, due to the electrons that are conducted by surface defects, the current density of the AAO surface should be small enough to form a charge transfer-controlled deposition that can maintain the hemispherical growth of crystal nuclei.66,67

Electrochemical measurements are also performed to more fully demonstrate the protective effect of AAO. A half-cell was used to test the Coulombic efficiency of different electrodes. A certain amount of lithium is deposited on a stainless steel (SS) or AAO-coated SS substrate and then dissolved. The ratio of the amount of lithium stripped off to the amount of deposited is the Coulombic efficiency shown in Figure 5a. It can be seen



Figure 5. Electrochemical performance of AAO-protected lithium and bare lithium anodes. (a) Li Coulombic efficiency of Li/SS (stainless steel) cell and Li/AAO-coated SS cell using an ether electrolyte. The circulating current density is 0.5 mA/cm^2 . In one cycle, first discharge to a capacity of 1 mAh/cm^2 and then charge to a cut-off voltage. (b) Exchange current density of different anodes after different times in the electrolyte. (c) Voltage profiles obtained from galvanostatic cycling of cells using bare Li electrodes and AAO-coated Li electrodes at a current density of 1 mAh/cm^2 for a total capacity of 1 mAh/cm^2 .

that the Coulombic efficiency of the AAO-protected SS is higher and more stable. Especially after the initial cycle, the AAO-protected SS shows a stable Coulombic efficiency close to 99% and can be maintained in long cycles, while the Coulombic efficiency of a bare SS fluctuates around 80%. This proves that AAO shows a positive impact on the cycle performance. The bare lithium electrode will face an uneven deposition and morphological changes during the cycle, which will produce negative effects such as "dead Li", resulting in a lower and unstable Coulombic efficiency. Figure Sb shows the exchange current density of different electrodes calculated from the Tafel plots of Figure S9. When the electrode just

contacts with the electrolyte (0 h), the exchange current density of bare lithium is higher than that of AAO-protected Li, meaning a higher reactivity. After 4 h, a side reaction occurred on the lithium surface to form an SEI film, and the decrease in the reaction activity caused a rapid decrease in the exchange current density of bare lithium. On the other hand, the exchange current density of AAO-protected Li decreased slowly and kept higher in a longer test. This shows that AAO can suppress the undesirable side reaction between lithium and an electrolyte and keep the electrode with a higher reaction activity and cycle efficiency. Figure 5c shows the electrochemical performance of symmetrical batteries measured by galvanostatic cycling. The voltage changes over time in the cycles of different electrodes are used to monitor the cycle life and stability of the electrodes. The protection of AAO has a positive effect, showing smaller voltage changes and better stability than bare Li, and a longer cycle life can be expected.

3. CONCLUSIONS

In summary, anodized aluminum oxide (AAO) membranes are used to establish highly ordered active charge transfer channels on the surface of lithium to achieve anode protection. For the first time, the phenomenon of electron conduction in the lithium surface Al_2O_3 layer and the lithium deposition on it are observed clearly. Comprehensive mechanisms about the lithium reaction and vacancy-assisted electron transfer are proposed. This is a new finding and very important for the protection of a lithium anode. Combined with the physical effect of AAO-ordered channels on the uniform distribution of lithium ions, the results could be commonly used in lithium anode battery systems to achieve good protection and obtain an improved electrochemical performance.

4. EXPERIMENTAL SECTION

4.1. Preparation of AAO-Covered Lithium Anodes. The porous anodized aluminum film (Shenzhen Topmembranes Technology Co., Ltd.) used had a diameter of 13 mm, a thickness of 50 μ m, a hole pitch of 450 nm, and a pore diameter of 390 nm. The AAO film is first cleaned with ultrasonic waves to remove impurities from the surface, then placed directly on the lithium in an argon atmosphere glove box.

4.2. Material Characterization. The symmetric electrolytic cells were prepared for the morphology observation, which were assembled in an argon glove box. The electrolyte was prepared by dissolving 1.0 M LiTFSI and 0.4 M LiNO3 into the mixture of 1,3-dioxolane (DOL) and dimethylether (DME) with a volume ratio of 1:1. One of the two electrodes is pure lithium, and the other is lithium, which is covered by AAO. All the samples in Figures 1, 2, and 4 and Figures S2 and S5-S7 are cycled to the capacity of 1 mAh/cm2 at a current density of 0.5 mA/cm². Also, the samples in Figure S3a-c are cycled to the capacity of 2 mAh/cm² at a current density of 1 mA/cm², and the samples in Figure S3d-f are cycled to the capacity of 4 mAh/cm² at a current density of 2 mA/cm^2 . After the cycle, the electrodes were removed, rinsed with DME, and then dried. SEM (JEOL-7800F) and corresponding EDS were used to obtain the morphologies and elemental distribution of the electrodes. The XPS analysis is performed by an X-ray photoelectron spectrometer (ESCALAB 250Xi). The FTIR data is tested at room temperature, the wave number range is fixed at 400-4000 cm⁻¹, the background is subtracted twice, and the accuracy is controlled at 1 cm⁻¹. The characteristic absorption peak is analyzed by the KBr tablet method using a Tensor 27 infrared spectrometer.

4.3. Electrochemical Measurement. The 2032-type coin cells were assembled by using a Celgard 2400 as a separator (18 mm) and the above electrolyte. Li Coulombic efficiency testing used Li/SS (stainless steel) and Li/AAO-coated SS as electrodes. The circulating

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current density is 0.5 mA/cm². In one cycle, first discharge to a capacity of 1 mAh/cm² and then charge to a cut-off voltage. Voltage profiles were obtained from galvanostatic cycling of symmetry cells using bare Li electrodes or AAO-coated Li electrodes at a current density of 1 mA/cm² for a total capacity of 1mAh/cm². The linear sweep voltammetry (LSV) test and Tafel plot were conducted as following: the three-electrode system was used, including the working electrode (bare Li or AAO-coated Li), counter electrode (Li foil, 14 mm), and reference electrode (Li slip). The sweep speed is 1 mV/s. The LSV measurements were performed using an LK2000 work-station.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c20099.

SEM images of AAO and lithium anode, schematic diagram of lithium deposition process, XPS data of AAO, Tafel plots, distribution statistics, and proportion of the elements (PDF)

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Notes

The authors declare no competing financial interest.

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