

Ionic Conductive and Highly-Stable Interface for Alkali Metal Anodes

Enzhong Jin¹⁺, Karnpiwat Tantratian²⁺, Changtai Zhao¹, Anastasia Codirezzi⁴, Lyudmila V. Goncharova⁴, Changhong Wang¹, Feipeng Yang³, Yijia Wang¹, Parham Pirayesh¹, Jinghua Guo³, Lei Chen^{2,5*}, Xueliang Sun^{1*}, Yang Zhao^{1*}

¹Department of Mechanical and Materials Engineering
University of Western Ontario, London, Ontario, N6A 5B9, Canada
Email: X. Sun: xsun9@uwo.ca; Y. Zhao: yzhao628@uwo.ca

²Department of Mechanical Engineering
University of Michigan–Dearborn, Dearborn, Michigan 48128, United States
Email: L. Chen: leichn@umich.edu

³Advanced Light Source
Lawrence Berkeley National Laboratory, Berkeley, CA, 94720, United States

⁴Department of Physics and Astronomy
University of Western Ontario, London, Ontario, N6A 3K7, Canada

⁵Michigan Institute for Data Science
University of Michigan, Ann Arbor, Michigan 48109, United States

+ These authors contribute equally to this work

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Abstract

Alkali metals, such as Li and Na metals, are regarded as the most promising candidates for advanced anode for the next-generation batteries due to their high specific capacity, low electrochemical potential, and lightweight. However, critical problems of the state-of-the-art alkali metal anodes, especially dendrite formation and interface stabilization, remain challenging to overcome. The solid electrolyte interphase (SEI) is one of the key factors affecting Li and Na deposition behavior and electrochemical performances. In this study, we successfully developed a facile and universal approach to fabricating ionic conductive interfaces for both Li and Na metal anodes by modified atomic layer deposition (ALD). In this process, the Li metal (or Na metal) plays the role of Li (or Na) source without any additional Li (Na) precursor during ALD. Moreover, we addressed the key questions about the influence of ALD deposition temperature on the compositions and structure of the coatings. The optimized ionic conductive coatings have significantly improved the electrochemical performances. In addition, the electrochemical phase-field model has been performed to prove that the ionic conductive coating is very effective in promoting uniform electrodeposition. This approach is universal and could be potentially applied to other different metal anodes. At the same time, it can be extended to other types of coatings or other deposition techniques.

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1. Introduction

Alkali metal anodes, such as Li and Na metals, with high theoretical capacity, low electrochemical potential, and lightweight, are considered as one of the most promising candidates for the next-generation alkali-metal batteries, including Li/Na-S, Li/Na-O₂, and all-solid-state Li/Na metal batteries^[1]. However, several serious challenges exist for alkali metal anodes, limiting their practical applications. The dendrite growth is one of the major challenges, which leads to undesired safety concerns, low Coulombic efficiency (CE) and inactive "dead Li/Na" layer formation^[2]. The solid electrolyte interphase (SEI) layer, naturally formed due to the chemical/electrochemical reaction between alkali metal and electrolyte, is critical for the electrochemical deposition behaviour and electrochemical performances of the alkali metal anode, in which the structure, composition, and stability of the SEI layer are key factors^[3]. The unstable SEI layer can promote dendrite growth due to the nonuniform ion flux distribution and non-homogeneous alkali metal depositions, leading to the large polarization and the decay of the electrochemical performances^[4]. Tremendous efforts have been attempted to stabilize the SEI via different approaches, including modifying the electrolyte components and creating artificial SEI layers for alkali metal anode. The artificial SEI layers are expected to block the side reactions between electrolyte and alkali metal, stabilize the interface, reduce the dendrite growth, and improve performances^[5]. Many protective layers have been developed for both Li and Na metal anodes, including inorganic layers, organic layers, and organic-inorganic hybrid layers^[6].

Generally, an ideal artificial SEI layer should possess the properties of ultrathin thickness, uniform and complete coating, high ionic conductivity, sufficient density, and good mechanical stability. The fabrication of an ideal artificial SEI layer that can meet all these requirements is a challenge. Atomic layer deposition (ALD) is a unique technique to design the surfaces and interfaces of alkali metal anode at atomic scale with excellent coverage and conformal deposition characteristics under relatively low temperatures with precise control over coating thicknesses^[7]. In the reported literature, several types of films have been fabricated as protective layers for both Li and Na metal anodes by ALD, such as metal oxide, polymers, and hybrid films^[8]. The ultra-thin protective layers by ALD can effectively reduce the dendrite formation and significantly enhance the electrochemical/chemical stability. Although impressive progress has been achieved with ALD-protected alkali metals, challenges remain. Firstly, most of the developed ALD coatings for alkali metals are non-ionic conductive and had to be lithiated/sodiated during the electrochemical plating/stripping

process. The initial lithiation/sodiation steps may cause the non-homogeneous Li/Na depositions on the surface of Li metal. The major limitation to deposit ionic conductive layer on Li/Na metal by ALD is the high deposition temperature (above 200 °C) and high precursor temperature (over 180 °C), which is above the melting point of the alkali metals, such as Li (180.5 °C) and Na metals (97.8 °C)^[9]. Secondly, although some studies reported the ALD metal oxides for Li or Na protection, the influences of the deposition temperature in the ALD process on the compositions and structures of the coating have not been investigated in detail. Thirdly, the chemical composition and micromechanism of metal oxide and solid-state electrolyte as artificial SEI have not been comprehensively understood.

Herein, we propose a universal approach to fabricating ion-conductive coatings for the alkali metal anodes (Li and Na metal as examples) by ALD. In this process, a two-step strategy is developed to obtain the smooth and stable LiAlO_x and NaAlO_x artificial layer for Li and Na metal anodes by the post-lithiation process, respectively. Remarkably, the coating layers are successfully achieved on the surface of metals with excellent quality and significantly improved performances. In addition, we have studied the effects of ALD deposition temperature on the structures of the protective layers and electrochemical performances. The surface and interface chemistry and Li deposition behaviors have been deeply studied by different advanced characteristic techniques. Moreover, the electrochemical phase-field model has been performed to reveal how beneficial the ionic conductive coating is in promoting uniform electrodeposition. On one hand, our design of the ionic conductive protective layer for highly stable alkali metal anodes may open the new window to creating conductive layers on Li and Na metal, which can be extended to other ALD materials or other thin film deposition techniques. On the other hand, this study provides new insight into the temperature effects of Li and Na metal as a substrate during the ALD deposition process.

2. Results and Discussion

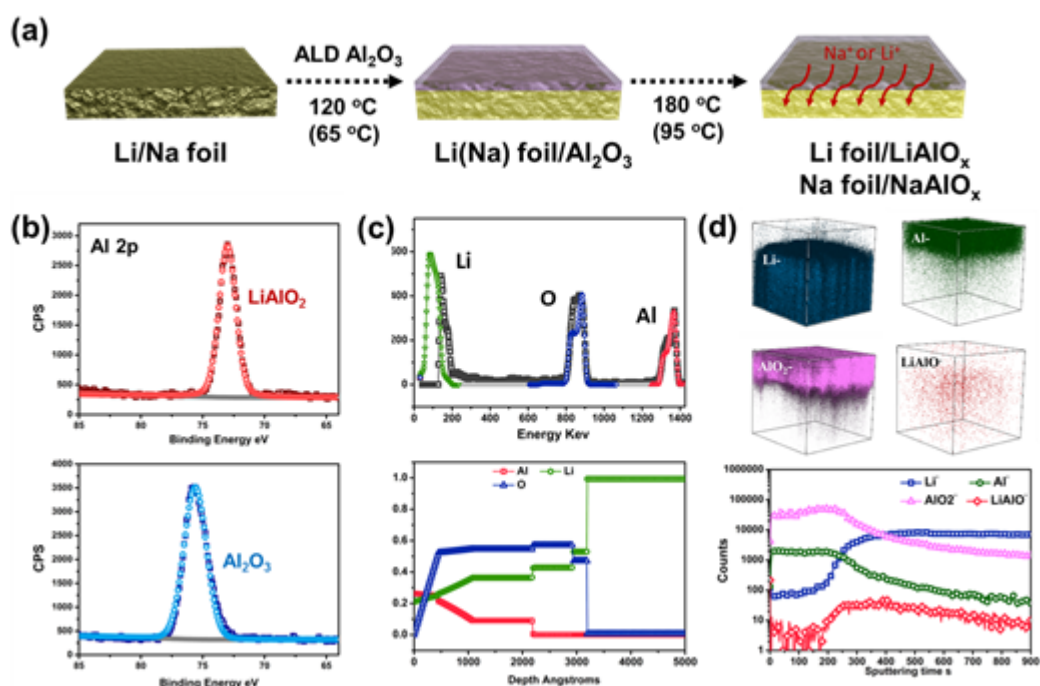


Fig.1 (a) Schematic diagram of the two-step strategy to fabricate the ionic conductive layers on Li or Na metal anodes; (b) The XPS spectrum of Al 2p of Li@200Al₂O₃ and Li@200LiAlO_x-ex; (c) The TOF-SIMS secondary ion images, depth profile of various secondary ion species and corresponding 3D images of Li@200LiAlO_x-ex; (d) The RBS spectra and calculated depth profiles of Li@200LiAlO_x-ex.

The ALD metal oxides have been proven effective artificial SEI for Li metal anode previously. The deposition temperatures of the reported ALD metal oxides are typically below 150 °C. Two important questions remain in this area. Firstly, is it possible to synthesize the lithiated layers on Li metal by ALD without the introduction of an extra Li precursor? Secondly, does the ALD deposition temperature affect the structures or compositions of the coatings? To address these questions, we designed the experiments by controlling the ALD deposition temperatures and developed a new two-step strategy. We first studied the ALD deposition temperature effects for Li metal anodes. The ALD Al₂O₃ was used for demonstration because it is the most popular and effective coating for battery interface modification. The deposition temperature of ALD Al₂O₃ was controlled at 120 °C (below the melting point of Li) and 180 °C (close to the melting point of Li), in which the samples are named as Li@nAl₂O₃ and Li@nLiAlO_x-in (n=ALD cycles, in=in-situ), respectively. For example, the sample with 200 cycles of ALD Al₂O₃ deposited at 120 °C is named as Li@200Al₂O₃ and the sample with 200 cycles of ALD Al₂O₃ deposited at 120 °C is

named as Li@200Al₂O₃-in. Furthermore, the two-step approach was developed, as shown in the schematic diagram in **Fig. 1(a)**. In this two-step approach, the ALD Al₂O₃ was first deposited on Li metal at the regular temperature of 120 °C. Then, the ALD chamber was heated up to 180 °C for the post-treatment and kept for half an hour. The samples obtained by this ex-situ process are named as Li@nLiAlO_x-ex (n=ALD cycles, ex=ex-situ). For example, the sample with 200 cycles of ALD Al₂O₃ deposited by the two-step approach is named as Li@200LiAlO_x-ex. This approach can be extended to other metal anodes (such as Na metal anode) and other coating layers. For example, the ALD Al₂O₃ is firstly deposited on the Na metal anode at relatively low temperatures (65 °C) and then post sodiation process is carried out at the temperature close to the melting point of Na metal (97.8 °C).

X-ray photoelectron spectroscopy (XPS) was used to investigate the surface of Li foil after Al₂O₃ deposition under different conditions, which are shown in **Fig. 1(b)** and **Fig. S1-3**. From the full spectrum presented in **Fig. S1-3**, Peaks around 75 eV and 532 eV are attributed to Al and O, respectively. It is demonstrated that the Al₂O₃ contained films have been successfully deposited on the Li foils. **Fig. 1(b)** shows the detailed spectrum of Al 2p for Li@200Al₂O₃ and Li@200LiAlO_x-ex. For the Li@200Al₂O₃ deposited at 120 °C, the peak of Al 2p at 75.6 eV represents the typical chemical state with Al₂O₃ reported in the literature^[10]. After post-annealing above the melting point for Li@200LiAlO_x-ex, the peak of Al 2p slightly shifts to the low binding energy of 72.9 eV, indicating the successful reaction and lithiation between Li metal and Al₂O₃ to form the LiAlO_x. As shown in **Fig. S3**, the peak of Al 2p for Li@LiAlO_x-in is also at 72.2 eV, demonstrating the similar LiAlO_x film formed on the Li surface during the high-temperature ALD deposition process. The soft X-ray Absorption Spectroscopy (XAS) of Near-Edge Structure at Al K edge was carried out to further elaborate on the compositions of the designed samples, as shown in **Fig. S4**. For the standard Al₂O₃ powder sample, the main peak at 1564.7 eV is assigned to transitions from the Al 1s orbitals into Al 3p and O 2p antibonding orbitals of t_{1u} symmetry. In the spectra of LiAlO₂ powder, this main peak slightly shifts to the low energy of 1563.6 eV. Compared to the Li@200Al₂O₃, the pre-edge and main peak features of Li@200LiAlO_x-ex and Li@200LiAlO_x-in also shift to the lower energy, indicating the lithiation of the films causing the observed change in the local electronic structures of Al. Based on the XPS and XAS results, it can be concluded that both the high-temperature ALD and post-annealing processes can lead to the lithiation of Al₂O₃ to form LiAlO_x on the surface of Li foils. Moreover, the X-ray Diffraction (XRD) patterns of Li@200Al₂O₃, Li@200LiAlO_x-ex, and Li@200LiAlO_x-in

are shown in **Fig. S5**. From the XRD results, it can be confirmed that all the films on Li metal are amorphous without any peaks related to Al_2O_3 or LiAlO_2 .

To probe the thicknesses and chemical compositions of the deposited films, the time-of-flight secondary ion mass spectrometry (TOF-SIMS) and Rutherford backscattering spectrometry (RBS) were performed, as shown in **Fig. 1(c, d)** and **Fig. S6-10**. **Fig. S6 (a)** presents the RBS spectra and simulated depth profile of $\text{Li}@200\text{Al}_2\text{O}_3$. Sharp Al and O peaks from the surface can confirm the successful synthesis of an Al-contained layer on Li metal. The thickness of the Al_2O_3 for $\text{Li}@200\text{Al}_2\text{O}_3$ is about 50 nm with another mixture interlayer of 60 nm. After annealing at 200 °C ($\text{Li}@200\text{LiAlO}_x\text{-ex}$), the top surface layer is still around 50 nm and Li content in the top layer significantly increases due to the lithiation process, further confirming the formation of LiAlO_x (As shown in **Fig. 1(c)**). Moreover, the Al also diffuses deeper into the Li foil to form the thicker interlayer of another 100 nm. However, the $\text{Li}@200\text{LiAlO}_x\text{-in}$ film that was deposited at the melting point of Li displays a much thicker layer of LiAlO_x with a thickness above 230 nm, as shown in **Fig. S6(b)**. The Al of $\text{Li}@200\text{LiAlO}_x\text{-in}$ permeates quite deep into the Li foil with another 200 nm layer. Moreover, the O spectrum of $\text{Li}@200\text{LiAlO}_x\text{-in}$ shows that oxygen penetrates above 1 μm on the surface of Li foil. The $\text{Li}@200\text{LiAlO}_x\text{-in}$ was fabricated directly at a high temperature at the melting point of Li metal. In this case, the Li is prone to react with H_2O to form the LiOH and this reaction might cause the continuous corrosion of Li metal to form the thick O-rich interlayer. **Fig. S7** shows the RBS spectra and simulated depth profiles of the $\text{Li}@LiAlO_x\text{-ex}$ with different thicknesses ($\text{Li}@300\text{LiAlO}_x\text{-ex}$ and $\text{Li}@500\text{LiAlO}_x\text{-ex}$). The thickness increases from ~ 80 nm to ~ 100 nm with an increase in ALD cycles from 300 cycles to 500 cycles. From the RBS results, it can be further confirmed that the Li can diffuse and react with Al_2O_3 to form the LiAlO_x for both $\text{Li}@200\text{LiAlO}_x\text{-ex}$ and $\text{Li}@200\text{LiAlO}_x\text{-in}$. However, the in-situ high-temperature ALD process causes the corrosion of Li foil with a much thicker O-rich interlayer formation. Based on this, the two-step approach is more promising to form a smooth LiAlO_x with controllable thickness on Li metal anode.

More detailed information is obtained from TOF-SIMS results, as shown in **Fig.1 (d)** and **Fig. S8**. **Fig. 1(d)** presents the top surface secondary ion images of Li^- , AlO^{2-} , and Al^- and their depth profiles and corresponding 3D reconstructed images for $\text{Li}@200\text{LiAlO}_x\text{-ex}$. From the chemical ion images on the surface of Li, it can be observed that the Li foil is uniformly covered with Al contained films. There is almost no signal of Li^- species detected on the top surface. As expected, the signals of AlO^{2-} and Al^- decrease, whereas the signal of Li^- remains

constant after 300 s Cs^+ sputtering, which is clearly observed from the depth profiles and corresponding 3D reconstructed images. Moreover, diffusion of Li into the Al-contained films is observed from the 3D reconstructed image, further proving the lithiation of Al_2O_3 . However, it needs to be mentioned that the Li^- count is not high because it is the negative ions. Moreover, the interface between the Al-contained layer and Li surface is relatively smooth, indicating that the post-treatment at high temperature does not affect the morphology of the coating layer and Li surface. As a comparison, the depth profiles and corresponding 3D reconstructed images of Li^- , AlO^{2-} , LiO^- and Al^- for $\text{Li}@200\text{LiAlO}_x\text{-in}$ are shown in **Fig. S8**. Consistent with the RBS result, the in-situ high-temperature ALD process on Li metal leads to the very thick Al-contained film (sputtering time over 800 s). Moreover, there is a very strong LiO^- signal from the top surface penetrating to the bulk Li, demonstrating the corrosion of Li metal by the H_2O precursor. Meanwhile, the deposition of the LiAlO_x film is nonuniform and the interface between Li metal and LiAlO_x is quite rough. The surface morphologies of the different designs were further tested by scanning electron microscope (SEM), as shown in **Fig. S9-10**. From the top view SEM images for $\text{Li}@200\text{LiAlO}_x\text{-ex}$, $\text{Li}@300\text{LiAlO}_x\text{-ex}$, and $\text{Li}@500\text{LiAlO}_x\text{-ex}$, the surfaces of the LiAlO_x protected Li foils are relatively smooth and very similar to the pristine Li foil. However, the surfaces of $\text{Li}@25\text{LiAlO}_x\text{-in}$ and $\text{Li}@100\text{LiAlO}_x\text{-in}$ are quite rough compared to the two steps post-treated samples, which is consistent with the TOF-SIMS analysis.

A similar two-step approach has been applied for Na metal anode to prove the concept and universality. The ALD Al_2O_3 is firstly deposited on the Na metal anode at 65 °C (the sample is named as $\text{Na}@200\text{Al}_2\text{O}_3$) and then the ALD chamber is heated up at 98 °C for sodiation process (the sample is named as $\text{Na}@200\text{NaAlO}_x$). **Fig. S11-12** show the TOF-SIMS results of surface secondary ion images, depth profile, and corresponding 3D images of secondary ion species for $\text{Na}@200\text{Al}_2\text{O}_3$ and $\text{Na}@200\text{NaAlO}_x$, respectively. Compared to $\text{Na}@200\text{Al}_2\text{O}_3$, the Na is successfully diffused into the Al_2O_3 layer to form the NaAlO_x with the post-sodiation process for $\text{Na}@200\text{NaAlO}_x$. The stronger signal from Na secondary ion species in the top coating layer is observed from both depth profile and corresponding 3D images for $\text{Na}@200\text{NaAlO}_x$. The RBS spectra and simulated depth profile of $\text{Na}@200\text{NaAlO}_x$ are shown in **Fig.S13**. The peaks of Al and O from the surface of Na metal further confirm the deposition of Al-based coating on Na metal. With post-treatment at 98 °C, the top NaAlO_x layer is about 40 nm and Na signal is successfully detected in the top layer along with Al-containing coating, which further confirm the formation of NaAlO_x . From the

SEM images for Na@200Al₂O₃ and Na@200NaAlO_x in **Fig. S14**, it can be observed that the surface morphology and structure of the coating layer are not changed with post-sodiation process at melting temperature. The results prove that this two-step approach is universal for fabricating ionic conductive coating layers for alkali metal anodes.

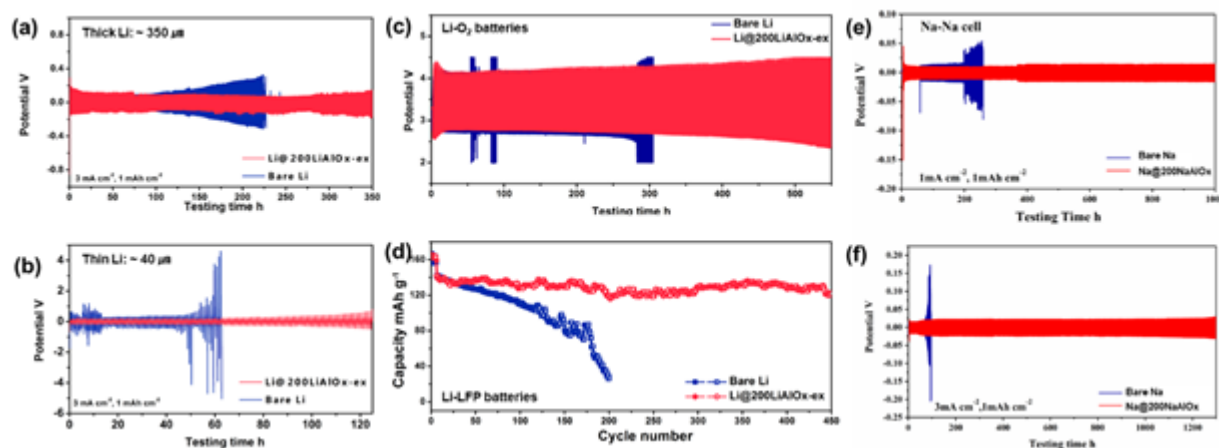


Fig.2 The overpotential of Li/Li symmetric cells using bare Li foil and Li@200LiAlO_x-ex in the carbonate-based electrolyte at the current density of 3 mA cm⁻² with the capacity of 1 mAh cm⁻² with (a) thick Li foil (~350 μm) and (b) thin Li foil (~40 μm). (c) Cycling performances of Li-O₂ full cells (CP-NCNTs as the cathode) using bare Li foil and Li@200LiAlO_x-ex as anode electrode at the current density of 0.1 mA cm⁻². (d) Cycling performances of full cells (C/LiFePO₄ as the cathode) using bare Li foil and Li@200LiAlO_x-ex as anode electrode at 1 C (1 C=170 mA g⁻¹). The overpotential of Na/Na symmetric cells using bare Na foil and Na@200NaAlO_x under the conditions of (e) 1 mA cm⁻²/1 mAh cm⁻² and (f) 3 mA cm⁻²/1 mAh cm⁻²

Symmetrical cells were assembled to evaluate the Li plating/stripping behavior of the different designs of the coating layers. **Fig. S15** shows the electrochemical performances of the Li@100Al₂O₃, Li@100LiAlO_x-in, and Li@100LiAlO_x-ex in the symmetrical cells. At the current density of 1 mA cm⁻² with the capacity of 1 mAh cm⁻², the Li@100Al₂O₃ displays the over-potential of ~ 200 mV over 400 h. In the reported literature, the thin Al₂O₃ with few nanometers can improve the cycling performances, however, thick Al₂O₃ may lead to even worse performance due to ionic insulative Al₂O₃ with nonuniform Li deposition (Fig. S16). The Li@100LiAlO_x-in deposited at high temperature presents better performances compared to the Li@100Al₂O₃ with the stable over-potential over 600 h. Remarkably, the Li@100LiAlO_x-ex shows the best performance of over 800 h among all the samples. After

increasing the current density into 5 mA cm^{-2} , the advantage of $\text{Li}@100\text{LiAlO}_x\text{-in}$ is not as obvious as at low current density, in which the electrochemical performance of $\text{Li}@100\text{LiAlO}_x\text{-in}$ is slightly better than that of the $\text{Li}@100\text{Al}_2\text{O}_3$. The reason could be that although the Al_2O_3 for $\text{Li}@100\text{LiAlO}_x\text{-in}$ was lithiated under the high-temperature ALD, the continuous corrosion of Li metal by H_2O lead to the O-rich interlayer and nonuniform LiAlO_x layer with a rough surface. Promisingly, the $\text{Li}@100\text{LiAlO}_x\text{-ex}$ keeps the superiority compared to the other two designs. In this case, it can be concluded that the two-step approach ($\text{Li}@n\text{LiAlO}_x\text{-ex}$) with a post-treatment can be considered as the effective approach to lithiate the Al_2O_3 to form LiAlO_x on the Li metal surface with high uniformity and controlled thicknesses. In addition, the thickness of $\text{Li}@n\text{LiAlO}_x\text{-ex}$ was further optimized, as shown in **Fig. S16**. Various thicknesses of 50, 100, 150, 300 and 500 cycles of LiAlO_x were deposited on the Li anodes. At different current densities (1 mA cm^{-2} and 3 mA cm^{-2}), the optimized thickness of the LiAlO_x is around 150-300 ALD cycles.

As discussed above, the two-step approach with post-treatment produces high quality and precisely controlled LiAlO_x coating on the Li surface. In this case, we picked up the $\text{Li}@200\text{LiAlO}_x\text{-ex}$ as an example of the battery performance study. **Fig. 2(a)** and **Fig. S17(a)** show the cycling stability of bare Li foil and $\text{Li}@200\text{LiAlO}_x\text{-ex}$ at different conditions using conventional Li foil with a thickness of $350 \mu\text{m}$. At the current density of 1 mA cm^{-2} with the capacity of 1 mAh cm^{-2} (**Fig. S17**), the initial Li stripping/plating over-potential of bare Li foil is approximately 50 mV (versus Li^+/Li) and rapidly increases to over 200 mV (versus Li^+/Li) after $\sim 650 \text{ h}$. Then, the overpotential of bare Li foil keeps over 300 mV and is fluctuant. In contrast, $\text{Li}@200\text{LiAlO}_x\text{-ex}$ displays significant improvement in cycling stability. The overpotential of $\text{Li}@200\text{LiAlO}_x\text{-ex}$ is stable with a low overpotential of 100 mV after 1000 h without any short circuit. **Fig. 2(a)** displays the symmetrical cell performances of bare Li foil and $\text{Li}@200\text{LiAlO}_x\text{-ex}$ at a higher current density of 3 mA cm^{-2} . The bare Li foil still shows the increased overpotential and subsequently short-circuited after $\sim 225 \text{ h}$. In comparison, the $\text{Li}@200\text{LiAlO}_x\text{-ex}$ displays improved stability with a stable overpotential over 350 h . For more practical applications, thin Li foil is requested to obtain high energy density. In this case, we also used the thin Li foil with a thickness of $40 \mu\text{m}$. The electrochemical performances of the symmetrical cell for the bare Li foil and $\text{Li}@200\text{LiAlO}_x\text{-ex}$ using thin Li foil are shown in **Fig. 2 (b)** and **Fig. S17 (b)**. In **Fig. S17 (b)**, the overpotential of the bare thin Li foil started to increase after 200 h and reached 1000 mV after 225 h , indicating the depletion of the Li metal and formation of dead Li layers. As a

comparison, the thin Li@200LiAlO_x-ex is stable over ~ 330 h without any short circuit. The bare thin Li foil is extremely unstable at the high current density of 3 mA cm⁻², as shown in **Fig. 2(b)**. The lifetime of the bare thin Li foil is less than 50 h. However, the cycling stability of the thin Li@200LiAlO_x-ex is over 120 h and about two times higher than that of the thin Li foil. It is also worth mentioning that the electrochemical performances of the thin Li even with coatings are generally worse than the thick Li due to the consumption of Li metal and electrolyte, which has been widely recognized in this field.

In order to further demonstrate the unique properties of the LiAlO_x coating, different full cell systems have been investigated using bare Li foil and Li@LiAlO_x-ex electrodes as the anode. Based on the symmetric cell performances discussed above, the Li@200LiAlO_x-ex electrode is used as an example for the full cells. The electrochemical performances of the Li-O₂ batteries were performed by using 2016-type coin cells of a carbon-based cathode (N-doped carbon nanotube grown on carbon paper, NCNTs-CP), an electrolyte of LiClO₄ in tetraethylene glycol dimethyl ether (TEGDME) and a bare Li foil or protected Li foil (Li@200LiAlO_x-ex) as the anodes. **Fig. 2 (c)** and **Fig.S18** present the charge-discharge profiles and cycling performances of the Li-O₂ cells using bare Li foil and Li@200LiAlO_x-ex as anodes, respectively. For the bare Li anode, the performance of the Li-O₂ cell is less than 280 h (140 cycles). However, the protected Li of Li@200LiAlO_x-ex delivers a significantly improved cycling stability of ~ 550 h (300 cycles), which is two times higher than that of the cell using a bare Li anode. The results reveal that the LiAlO_x coating can effectively mitigate the degradation of Li anodes against O₂ corrosion and Li dendrite formation. Furthermore, the Li-LiFePO₄ (LFP) batteries were demonstrated in **Fig. 2 (d)**. The LFP cells were firstly activated at 0.1 C for 5 cycles and then cycled at 1 C for long-term cycling performance. In the cell using bare Li foil, the discharge/charge capacity starts fading after 100 cycles and decreases to about 30 mAh g⁻¹ after 200 cycles. However, using Li@200LiAlO_x-ex as the anode, the cell maintains an extremely stable capacity of ~ 120 mAh g⁻¹ after 450 cycles.

To further prove the concept, the Na-Na symmetrical cells were assembled to evaluate the Na plating/stripping behavior. **Fig. 2(e)** presents the electrochemical performances of the bare Na foil and Na@200NaAlO_x in the symmetrical cells under the condition of 1 mA cm⁻²/1 mAh cm⁻². The initial overpotential of bare Na foil is approximately 20 mV (versus Na⁺/Na) and rapidly increases to over 40 mV (versus Na⁺/Na) after ~ 200 h. After about 280 h, a sudden drop of the overpotential is observed, indicating the short circuit occurs for the bare Na. Very promisingly, for the Na@200NaAlO_x, the cell demonstrates stable

performance for over 1000 h with a low overpotential of 20 mV. When the current density was increased to 3 mA cm^{-2} , the overpotential of the bare Na increased dramatically up to 150 mV after only 100 h and a short circuit occurred shortly thereafter, as shown in Fig. 2(f). For the $\text{Na}@200\text{NaAlO}_x$, even at a higher current density of 3 mA cm^{-2} , the overpotential is extremely stable over 1200 h without any short circuit. The electrochemical performances for both Li and Na metal anodes demonstrate that the $\text{LiAlO}_x/\text{NaAlO}_x$ coating can effectively improve the stability of Li/Na metal anode in different systems and shows potential for use in next-generation Li/Na-metal batteries. Particularly, LiAlO_x coating derived from the two-step process demonstrates unique properties and superior performances compared to the Al_2O_3 and LiAlO_x deposited directly at high temperatures. It is further proof that this approach is universal to be extended to different alkali metal anodes.

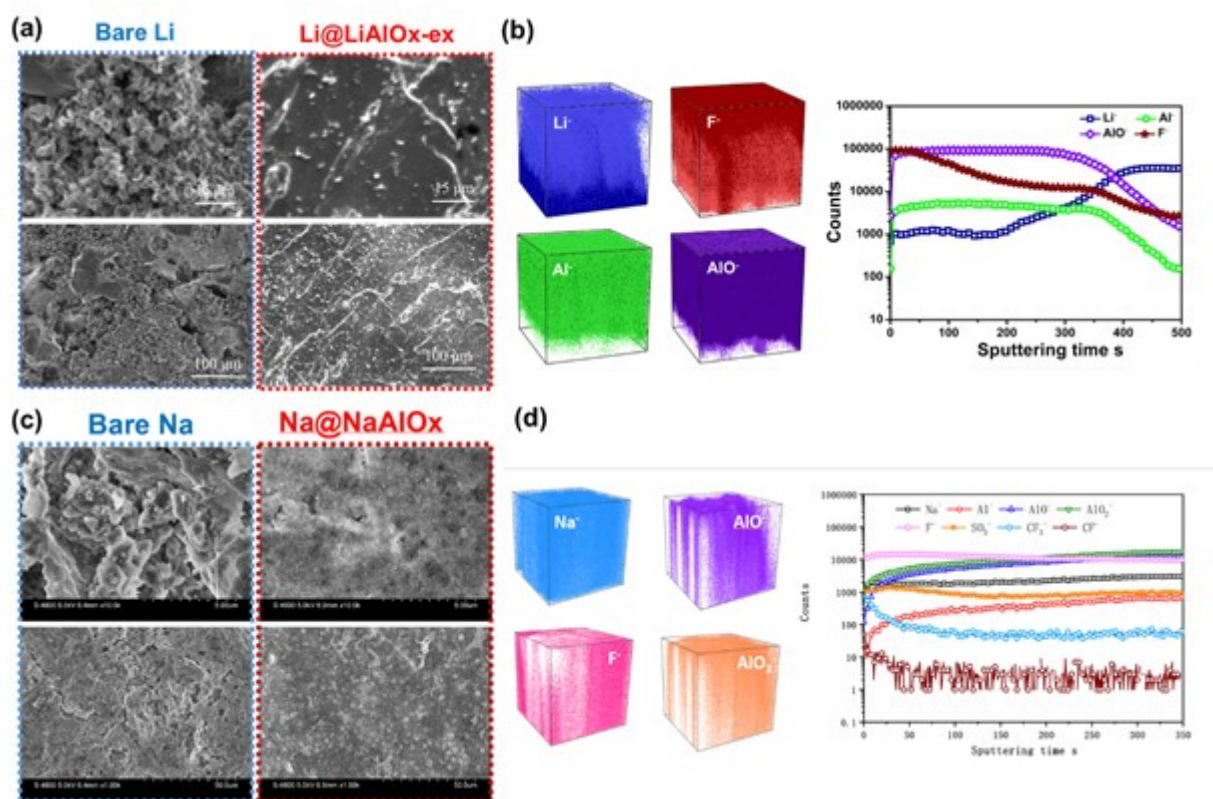


Fig.3 Top-view SEM images of (a) bare Li foil and Li@200LiAlO_x-ex after electrochemical cycling (50 cycles) ; (b) The TOF-SIMS depth profiles and corresponding 3D reconstructed images of Li@200LiAlO_x-ex after electrochemical cycling. Top-view SEM images of (c) bare Na foil and Na@200NaAlO_x after electrochemical cycling (50 cycles) ; (d) The TOF-SIMS depth profiles and corresponding 3D reconstructed images of Na@200NaAlO_x after electrochemical cycling.

To understand the influence of the LiAlO_x layers on the Li deposition behavior, the morphology of Li metal was imaged by SEM after cycling. **Fig. S19** shows the SEM images of pristine Li foil after the different depths of electrochemical cycling (10 cycles, 20 cycles, and 30 cycles) at a current density of 1 mA cm^{-2} with a capacity limit of 1 mAh cm^{-2} . The mossy Li and dead Li layers are formed within 10 cycles, becoming more serious after deeper cycling. With 50 cycles of Li plating/stripping (**Fig. 3 (a)**), a porous mossy structure with a rougher surface and obvious cracks are observed on the Li. These issues cause the increasing polarization of the cell and finally lead to short circuit. In comparison, the morphologies of the $\text{Li@200LiAlO}_x\text{-ex}$ are drastically different, as shown in **Fig. S19** and **Fig. 3 (a)**. With the different cycling stages (10 cycles, 20 cycles, and 30 cycles), as shown in **Fig. S20**, no visible morphological change can be observed from the surfaces of the $\text{Li@200LiAlO}_x\text{-ex}$. After 50 cycles of Li plating/stripping, the Li dendrite growth and dead Li formation are effectively reduced with the LiAlO_x coating, which leads to significantly enhanced electrochemical performances.

Besides the morphology, the chemical compositions of the SEI are another critical factor for the Li deposition behavior and electrochemical performances. To understand the compositional changes following the plating/stripping cycling experiments, TOF-SIMS measurements were carried out. **Fig. S21** presents the TOF-SIMS results (including surface chemical ion images, depth profiles and corresponding 3D reconstructed images) of bare Li foil after plating/stripping cycling experiments at a current density of 1 mA cm^{-2} with a capacity limit of 1 mAh cm^{-2} . The bare Li shows significant penetration of F from electrolyte with a long sputtering time (over 500 s), which is related to the thick dead Li layer formation. However, as shown in **Fig. 3(b)** and **Fig. S22**, the LiAlO_x coating remains on the top surface and with only slight changes compared to the spectra before cycling, in which the sputtering time is around 400 s. From the TOF-SIMS analysis of the SEI, it is found that the LiAlO_x coating is robust and chemical/electrochemical stable during the Li plating/stripping process. To have a better understanding and comparison of the SEI, the XAS at Al K-edge was performed for $\text{Li@200Al}_2\text{O}_3$, $\text{Li@200LiAlO}_x\text{-in}$, and $\text{Li@200LiAlO}_x\text{-ex}$ after cycling. After cycling, the XAS spectra of Al K-edge (**Fig. S23**) become broader, with the peak shifts to higher energy compared to that of before cycling. Moreover, the intensities of spectra for $\text{Li@200Al}_2\text{O}_3$ and $\text{Li@200LiAlO}_x\text{-in}$ dramatically decrease compared to that of

Li@200LiAlO_x-ex, indicating the degradation of the coating layers during cycling. It further confirms that Li@200LiAlO_x-ex is the most stable protective layer during cycling.

Similarly, the surface morphology and composition for bare Na and Na@200NaAlO_x after electrochemical cycling were further investigated. **Fig. 3 (c)** shows the top view SEM images of bare Na and Na@200NaAlO_x after cycling. For the bare Na, the mossy Na is formed after the cycling, and the surface of the Na becomes rough with cracks. Remarkably, the surface of the Na@200NaAlO_x after cycling is much smoother without any dendritic and mossy Na formation, which is one of the reasons for the significantly enhanced electrochemical performances. The chemical composition of the interface was studied by TOF-SIMS, as shown in **Fig. S24** and **Fig. 3 (d)**. For the bare Na after cycling, strong signals of F⁻, CF₃⁻, SO₃⁻ secondary ion species are observed, demonstrating the decomposition of the electrolyte components as well as the thick dead Na layer growth. As a comparison, the AlO⁻ and AlO₂⁻ secondary ion species from the NaAlO_x layer remain with minor changes, indicating that the NaAlO_x protective layer is extremely stable during the electrochemical cycling, consistent with the results of electrochemical performances. The RBS spectra and simulated depth profile of Na@200NaAlO_x after cycling are shown in **Fig.S25**. From the RBS depth profile, it can be confirmed that the thickness of the NaAlO_x layer remains as 40 nm as the top layer, further indicating the robust behavior of the NaAlO_x during electrochemical cycling.

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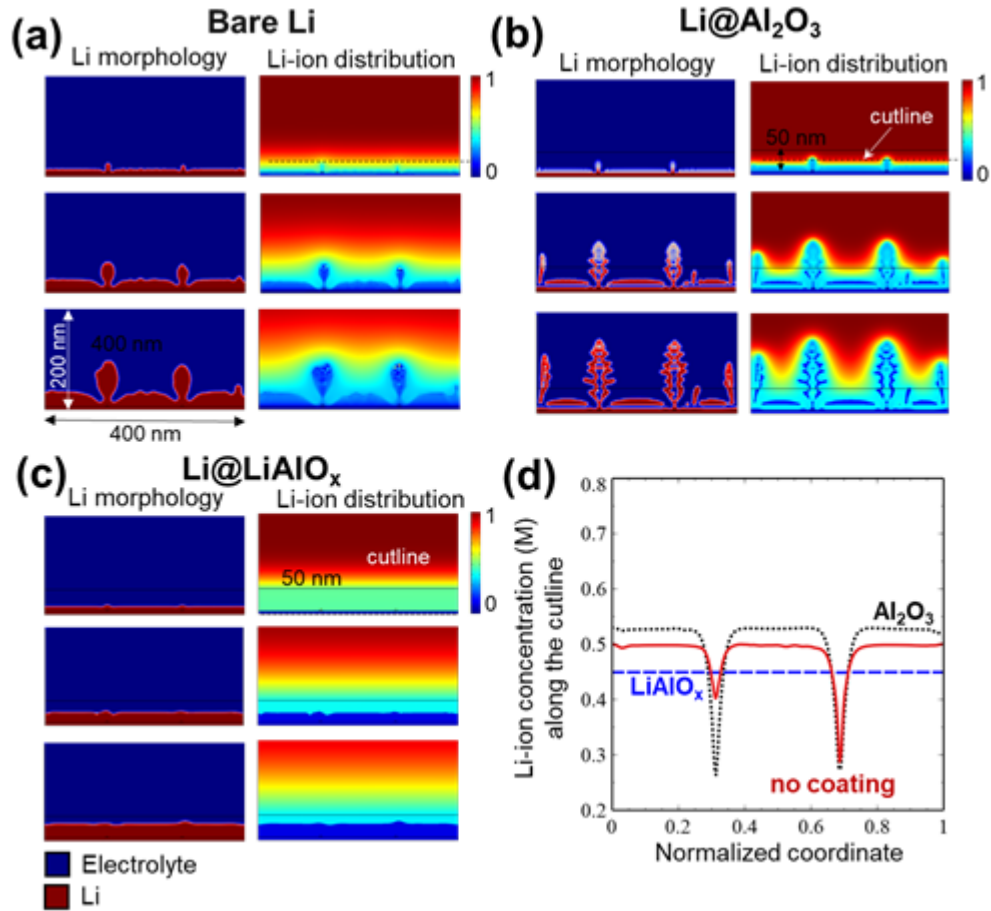


Fig.4 The simulated spatiotemporal evolution of the morphological for deposits Li and the distribution of Li-ion concentration under different coatings: (a) bare Li, (b) $\text{Li@Al}_2\text{O}_3$, and (c) Li@LiAlO_x . (d) The plot of Li-ion concentration near the interface at the beginning of the Li deposition process, showing the high ionic diffusivity layer is beneficial for homogenizing the Li-ion distribution, which is a key driving force for uniform Li deposition.

To confirm the benefit of highly ionic conductive coating layer, the electrochemical phase-field model was performed. The approximated Li-ion diffusion coefficient of each coating used in this study are as follows: LiAlO_x ($1.4 \times 10^{-11} \text{ m}^2\text{s}^{-1}$) \gg uncoated surface ($4.6 \times 10^{-13} \text{ m}^2\text{s}^{-1}$) $>$ Al_2O_3 ($1.0 \times 10^{-13} \text{ m}^2\text{s}^{-1}$)^[11]. **Fig.4 (a)-(c)** illustrate the simulated spatiotemporal evolution of deposits Li and the associated Li-ion distribution during Li plating under different coating conditions. Despite the same initial surface morphology for all studies, in which two small Li perturbations are introduced, Li@LiAlO_x shows the surface of deposited Li remains uniform throughout the Li plating process, which is consistent with the experimental characterization that no dendrite after cycling is observed under the LiAlO_x

coating (**Fig.3 (a)** or **Fig. S19**). This is thanks to the intrinsic nature of the highly ionic conductive layer. Once Li-ions are reduced to Li atoms by the charge transfer reaction at the electrode surface, Li-ions in the coating layer (or electrolyte) quickly diffuse to the interface to replace the depleted Li-ions. Thus, the homogeneous distribution of Li-ions along the interface is well-maintained. On the other hand, when Li-ion diffusion near the interface is slow, bare Li as an example, the gradient of Li-ion concentration closed to the interface is evident, as shown in **Fig.4 (d)**. The variation of Li-ion concentration along the interface contributes to the nonuniform driving force for Li electrodeposition, thus resulting in the dendritic morphology of Li. The results agree with the experimental observation in **Fig.3 (a)** or **Fig. S18**, showing porous mossy Li structure after cycling. Moreover, for Li@Al₂O₃, whose coating layer is considered thick and highly non-ionic conductive, the Li dendrite quickly grows due to the significant Li-ion concentration gradient, substantially deteriorating cyclic performance (**Fig. S14**).

Conclusion

In conclusion, we successfully developed a universal approach to deposit ionic conductive interfaces for the alkali metal anodes by ALD. In the unique two-step ALD process, there is no Li/Na precursor required during deposition and Li/Na metal plays the role of Li/Na source. The LiAlO_x/NaAlO_x coatings derived by a two-step strategy are uniform, smooth, and highly controllable. The ionic conductive coating layers can significantly improve the electrochemical performances of the Li and Na metal anodes in symmetric cells and full cells. Multiple evidence reveals that the ionic conductive coatings are chemically and electrochemically stable during electrochemical plating/stripping and can reduce the Li/Na dendrite growth and dead Li/Na layer formation, resulting in performance improvement. We further investigated the influence of the ALD deposition temperatures on the Li metal anode's morphology, composition, and performance. Although the LiAlO_x is also directly achieved with a high-temperature ALD process (Li@nLiAlO_x-in), the surface of Li metal turns rough and corroded when the deposition temperature is above the melting point. We believe that this work can not only open a new window on creating ionic conductive layers on alkali metal without alkali precursor but also provides new insight into the temperature effects during the ALD deposition process when using temperature-sensitive alkali metal as a substrate.

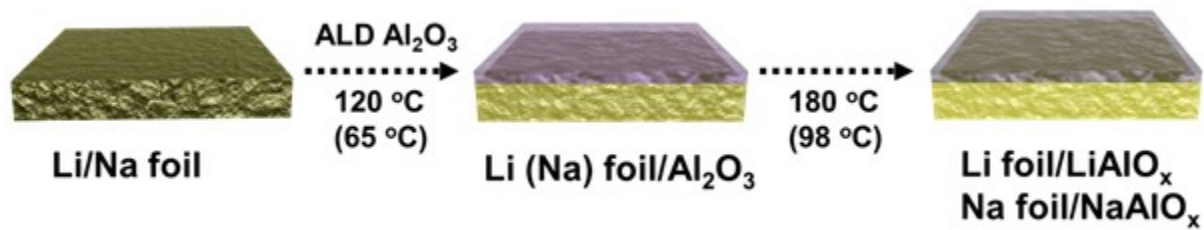
Acknowledgments

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We developed a facile and universal approach to fabricating ionic conductive interfaces for alkali metal anodes by modified atomic layer deposition (ALD). The optimized ionic conductive coatings have significantly improved the electrochemical performances. This approach could be potentially applied to other different metal anodes. At the same time, it can be extended to other types of coatings and deposition techniques.

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