Please cite this article in press as: Zhao et al., Addressing Interfacial Issues in Liquid-Based and Solid-State Batteries by Atomic and Molecular Layer Deposition, Joule (2018), https://doi.org/10.1016/j.joule.2018.11.012

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REVIEWS

Review

Addressing Interfacial Issues in Liquid-Based and Solid-State Batteries by Atomic and Molecular Layer Deposition

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Solid-state batteries (SSBs) have attracted increasing attention as one of the most promising next-generation batteries. However, various challenges remain for SSBs toward practical applications. Particularly, the interfacial issues between solid-state electrolyte (SSEs) and electrodes are critical factors affecting the performances of SSBs. Atomic and molecular layer deposition (ALD and MLD) are considered as ideal strategies for overcoming the interfacial issues facing SSBs. In the past years, promising progress has been reported using ALD/MLD to overcome the interfacial drawbacks in SSBs. In this Review, we summarize the recent progress of ALD/MLD techniques in the application of Li batteries, with a special focus on current progress in the shift from liquid to solid cells. Different sections, including the fabrication of interfacial materials, interfacial engineering on SSEs and electrodes, and thin-film/3D SSBs, are discussed in detail. Moreover, the future directions and perspectives of ALD/MLD in interface engineering for SSBs are disclosed.

Introduction

Atomic Layer Depositions and Molecular Layer Depositions

Atomic layer deposition (ALD) is one of the most rapidly developing thin-film deposition techniques of the past decade, attracting increasing attention in different applications due to its unique properties.[1,2] Compared to traditional vapor-phase methods, such as chemical vapor depositions (CVD) and physical vapor depositions, ALD is a self-controlled process in which the growth of the film is dictated by two self-limiting gas-solid surface reactions. ALD techniques depend primarily on binary reaction sequences in which two reactions occur on the surface and deposit a wide range of binary inorganic compounds, including metal oxide, metal nitrides, metal sulfides, and mixed metal oxide.[3] Three key deposition parameters for ALD processes are substrate, temperature, and precursors.[4–6] Concurrently, the ALD technique shows unique properties, including excellent uniformity and conformity, atomic-scale and stoichiometric deposition, and low growth temperatures.[7]

Beyond ALD, molecular layer deposition (MLD) has been further developed by replacing the oxidizing precursor with organic linkers or adding molecular fragments into the film.[8,9] In this case, pure polymer thin films and organic-inorganic hybrid films can be deposited through MLD. The MLD thin films adopt the advantages of ALD and possess additional strengths such as flexibility, low refractive index, and low density.[8,10,11] Several comprehensive review papers, including our recent review papers, have summarized the development of ALD and MLD technique and their wide applications.[12–17]

ALD/MLD for Liquid Lithium-Ion Cells

Lithium-ion batteries (LIBs) have become the most widely used energy storage systems for portable electronic devices and electric vehicles due to their many

Context & Scale

The conventional Li-ion batteries (LIBs) with organic liquid electrolyte have reached their bottleneck in energy density. The flammable non-aqueous liquid electrolytes used in LIBs also cause serious safety concerns, especially for the large-scale battery packs in electric vehicles. In this context, development of solid-state batteries (SSBs) by replacing the liquid electrolyte with solid-state electrolytes (SSEs) is a promising solution to overcome the limitations of the conventional LIBs. However, there are three general challenges regarding the interface between SSEs and electrode materials in SSBs, including mismatch, chemical reactions, and space charge effects. These interfacial issues are key drawbacks of the performances of SSBs.

Atomic layer deposition (ALD) and molecular layer deposition (MLD), two advanced gas-phase thin-film deposition techniques, are considered ideal strategies for overcoming the interfacial issues for SSBs. Unique and beneficial characteristics of ALD/MLD include low growth temperatures, atomic-scale and stoichiometric deposition, and excellent uniformity and conformity, which

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outstanding features, including high energy density, lack of memory effect, and low self-discharge rate.[18–20] Performance of batteries mainly depends on three components: cathode, anode, and electrolyte. The commercial LIBs typically use $LiCoO_2$ as the cathode, graphite as the anode, and a carbonate-based liquid electrolyte. The development of LIBs was a bench-mark advancement from Pd-acid batteries. However, limited by the intrinsic properties of materials and technical limitations, it is difficult for current LIBs to further meet the ever-growing demands for high safety, ultralong lifetime, small size, light weight, and low cost. A key approach to enhance the performance of LIBs is to optimize the properties of the three major components or seek for alternative candidates with better performance. In the past years, various novel electrode materials for cathodes and anodes have been developed to meet the high energy density requirements, but these materials still face serious issues in achieving long-term stability.

Solid electrolyte interphases (SEIs) are generally formed on the electrodes due to interfacial reactions between the liquid electrolytes and electrodes.[21] The properties of an SEI can significantly affect the battery stability. It is believed that a stable SEI can prevent the continuous decomposition of the liquid electrolytes and stabilize the batteries' performances. However, unstable SEIs will cause serious issues in batteries. On the anode side, the cracking and regeneration of unstable SEIs can continuously consume electrolyte and Li ions, leading to low Columbic efficiency.[22] On the cathode side, a poor SEI on the cathode fails to block the hydrofluoric attacks and transition metal dissolution, resulting in rapid failure of the batteries.[23,24] In addition, the volume changes of electrode materials during cycling, particularly for the alloy-based anode (such as Si, Sn, and P) cast significant challenges to SEI preservation. Moreover, the large volume changes can also lead to electrical disconnection from the conductive agents (e.g., carbon black) and the current collectors during the charge/discharge process, further resulting in the poor cycling stabilities.[25,26]

To address the challenges of interfacial issues and large volume change, surface modification to construct a robust artificial SEI on the electrodes is considered an effective approach. The unique properties of ALD/MLD techniques have contributed to significant and proven improvements in batteries applications, typically for LIBs using liquid electrolytes. Generally, the functions of ALD/MLD for liquid cells can be separated into two parts: electrode fabrications and interfacial modifications. Figure 1 presents the development of ALD/MLD for electrode fabrications and interfacial modifications in Li batteries using liquid electrolytes.

Owing to the atom-specific feature, ALD can be used to design and synthesize electrode materials on favorable substrates. Various cathode materials (including V_2O_5, $FePO_4$, $LiCoO_2$, $Li_xMn_2O_4$, and $LiFePO_4$),[34–37] and different anode materials (such as TiO_2, SnO_2, Co_3O_4, $Li_4Ti_5O_{12}$, and metal sulfides)[15,38–41] have been synthesized via ALD for battery applications. For example, two types of SnO_2, amorphous and crystalline, have been deposited on graphene nanosheets (GNSs) by ALD using $SnCl_4$ and H_2O as the precursor (Figure 1). The crystallinity and morphology can be controlled by adjusting the ALD deposition temperatures, and the amorphous SnO_2 on GNSs showed better performance than the crystalline products.[28] This work indicates that ALD can be a powerful tool for fabricating anode materials with controllable morphology, crystallinity, and electrochemical performance. Another typical example is the successful synthesis of $LiFePO_4$ by ALD as a high-performance cathode for LIBs.[27] The amorphous $LiFePO_4$ is deposited by using an ALD sequence of $5\times(FeCp_2\text{-}O_3\text{-}TMPO\text{-}H_2O) + 1 \times (LiO^tBu\text{-}H_2O)$ with a growth rate of

are difficult for other coating techniques. In this Review, we summarize the recent developments of ALD/MLD techniques in the application of Li batteries, with a special focus on the transition from liquid to solid cells. Different sections, including the fabrication of interfacial materials by ALD/MLD, interfacial engineering on SSEs and electrodes, and thin-film/3D SSBs designed by ALD/MLD, are discussed in detail. Moreover, the future directions and perspectives of ALD/MLD in interfacial engineering for SSBs are disclosed.

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https://doi.org/10.1016/j.joule.2018.11.012

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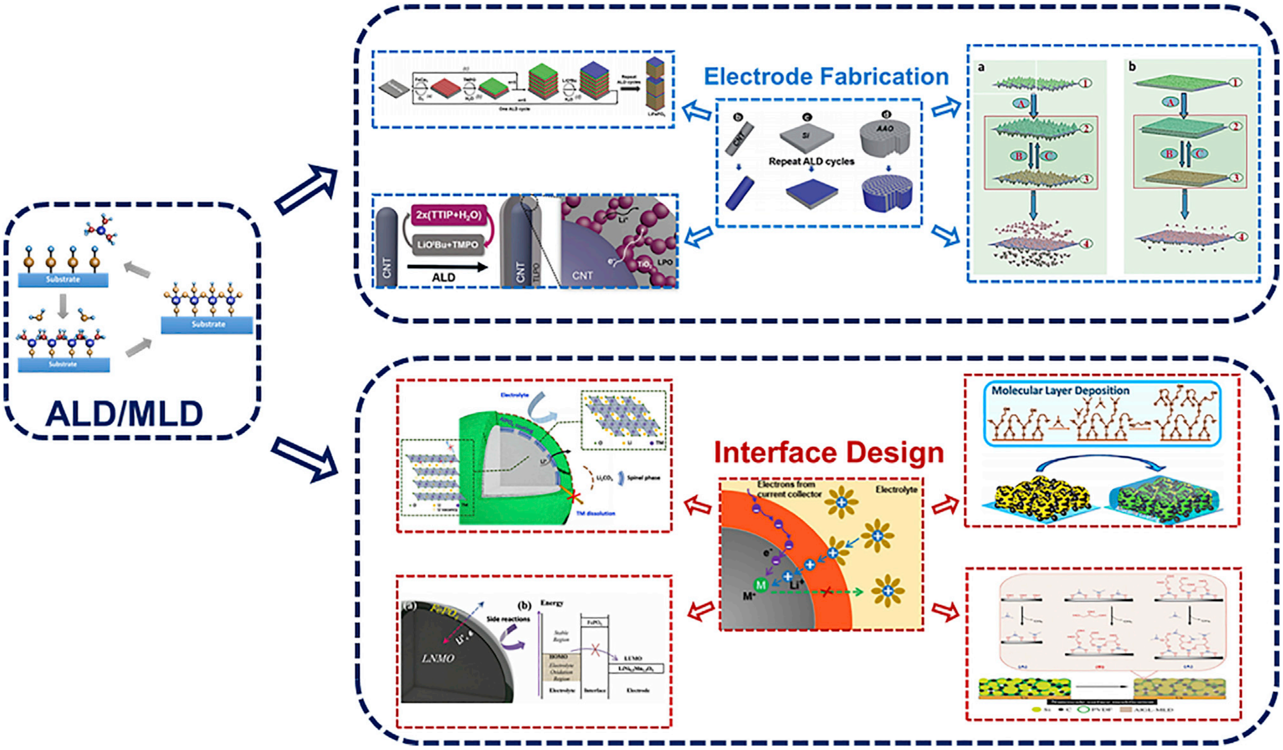

Figure 1. The Development of ALD/MLD for Electrode Fabrication and Interface Modification in Li Battery Liquid Cells

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0.9 nm/cycle at a temperature of 300°C. Crystalline $LiFePO_4$ is obtained on carbon nanotubes (CNTs) after annealing and demonstrated high capacity, excellent rate capability, and ultralong lifetime. Besides materials prepared by ALD, Karppinen's group first demonstrate the fabrication of lithium terephthalate ($Li_2C_8H_4O_4$ or LiTP) as organic LIB electrodes by MLD.[42] Notably, the LiTP films can achieve excellent rate capability without any conductive additives. Furthermore, with a protective coating of lithium phosphorousoxynitride (LiPON) solid-state electrolyte (SSE) by ALD, the LiTP organic electrodes can be stabilized with high capacity and excellent cycle life. These works demonstrate the unique advantages of ALD/MLD to fabricate both cathode and anode electrodes for LIBs.

If based on commercial electrode materials, interfacial engineering and SEI stabilization are important approaches to prevent side reactions and improve battery performance in liquid electrolytes. Among all surface-coating methods, ALD and MLD are ideal for fabricating conformal thin-film coatings. Since 2010, different ALD/MLD coatings (e.g., Al_2O_3, TiO_2, ZrO_2, TiN, ZnO, and $LiAlO_x$) have been extensively introduced for both cathode and anode electrodes and demonstrated enhanced performances.[43,44] Our group has also investigated different advanced coatings, including $LiTaO_x$, $FePO_4$, and $AlPO_x$ on different cathode materials[30,31,45] ($LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, $LiNi_{0.5}Mn_{1.5}O_4$, and $Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$, respectively) (Figure 1). The robust ALD coating layers lead to various benefits, including the facilitation of Li^+ ion transportation, prevention of cathode transition metal dissolution, suppression of continuous oxygen release, and eventually improvement on cycling performances. Furthermore, MLD films are explored as promising coatings for electrodes with large volume change such as Si anodes and sulfur cathodes due to the improved mechanical properties and flexibility.[33,46–49] We have previously reported the MLD alucone coating on C/S cathode electrodes with significantly enhance performance for Li-S batteries in an ether-based electrolyte (1 M LiTFSI in DOL/DME), which was superior to bare C/S and ALD Al_2O_3-coated C/S electrodes. Highly reversible electrochemical performance was also achieved in a carbonate electrolyte (1 M $LiPF_6$ in EC/DEC/EMC). A safe and ultra-stable cycle life was demonstrated at high temperatures.[32,50,51]

ALD and MLD techniques are proven as a powerful tool for electrode fabrications and interface modification in LIB applications. Especially, the precisely controllable surface coating by ALD/MLD is one of the most ideal ways to achieve stable SEI layers on electrodes in liquid electrolytes with great enhanced specific capacity, cycling stability, rate capability, and thermal stability. However, it should be noted that there are still several drawbacks of ALD/MLD. One of the major concerns is the slow growth rate. Although various cathode/anode electrode materials have been developed using the ALD/MLD technique, the deposition rates of ALD/MLD films (~Å/cycle) are relatively low. This makes the ALD/MLD synthesized electrodes less commercially viable for standard battery technologies, particularly when compared with composite/powder-based electrodes. Nonetheless, the ALD/MLD electrodes are of potential interest to thin-film batteries and 3D micro-batteries, which will be discussed in the following section. And the ultrathin ALD/MLD films are very promising as the surface/interface modifications for battery applications.

Batteries: From Liquid to Solid

It is generally accepted that the liquid-based LIBs have reached their bottleneck in specific energy and energy density.[52–54] In addition, the flammable, non-aqueous liquid electrolytes used in conventional LIBs have caused serious safety concerns, especially for the large-scale battery packs in EVs.[55] In this context, development of solid-state batteries (SSBs) by replacing the liquid electrolyte with SSEs is a promising solution to the limitations of conventional LIBs.[56,57] SSBs possess many advantages compared with the conventional LIBs[55]: (1) safety is significantly improved by removing the flammable liquid electrolytes; (2) the potential feasibility of Li metal anodes with SSEs can lead to the high energy density for SSBs; and (3) the wide electrochemical voltage window of SSEs can enable the use of high-voltage cathodes high energy density.

However, there are still various challenges confronting SSBs before practical applications. One of the key factors is the SSEs. The developing SSEs include inorganic solid electrolytes (such oxide electrolyte and sulfide electrolyte), solid polymer electrolytes, and composite solid electrolytes.[58,59] Due to continuous efforts in the field, high Li-ion conductivities of $\sim 10^{-2}$ S cm^{-1} have been achieved by the sulfide-based SSEs, which is comparable with the organic liquid electrolyte.[57,60,61] However, there are three general challenges regarding the interface between SSEs and electrode materials, including mismatch, chemical reactions, and space charge effects.[60,62] These interfacial issues between SSEs and electrodes (both cathode and anode) critically impact the stability and lifetime of full cells.[56] Concerning the bulk SSEs, anode/SSE interfaces, and cathode/SSE interfaces, the specific challenges differ. Electrochemical stability windows of SSEs are the first concern. Some SSEs are not stable within the cycling voltage range of typical cathode materials and Li metal anode. Additional interphases are formed due to the decomposition of SSEs when operating beyond the limited

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thermodynamic stability windows. The decomposition interphases will impede the Li^+ transport between the SSEs and the active materials and increase the interfacial resistance, resulting in a shortened lifetime of SSBs. Secondly, even though Li metal is an ideal anode material for high energy density SSBs, side reactions and dendrite growth are the major challenges at Li/SSEs interface. On one hand, most SSEs are subject to reduction into lower valence compound upon contact with Li metal, forming an unstable interface. On the other hand, Li dendrite growth on the Li metal surface and along the grain boundaries of SSEs is another serious issue.[63–67] Thirdly, detrimental side reactions can occur at the cathode/SSEs interface. Space charge effects and mutual diffusion effects can cause large impedance at the cathode/SSE interface, which limits the power density of the SSBs.[68]

To address the interfacial issues and minimize the interfacial resistance between SSEs and electrodes (both cathode and anode), interfacial coating is considered as the most effective approach. The requirements for the interfacial coating materials are high ionic conductivity, chemical/electrochemical stabilities, and proper structures. Firstly, ionic conductivity is required to ensure a smooth Li^+ pathway across the interface so that electrochemical reactions can proceed at the desired rate. Otherwise, insulating coatings such as metal oxides usually introduce extra resistance that impedes the rate performance of batteries when the coating is thick. Secondly, the interfacial coating materials need to be chemically stable in contact with the electrodes and electrochemically stable during cycling. A wide electrochemical window is the key to enable high-voltage cathodes and low-potential Li metal anodes. Finally, the interfacial coating materials should be deposited at relatively low temperature to maintain the structure of cathodes and anodes. High-temperature post-treatment is usually not favored for the same reason that high heat may damage the coating film and structures of electrodes. Different methods, such as sol-gel and pulsed laser deposition, have been used to introduce an artificial interface.[60,69,70] Particularly, ALD/MLD techniques are receiving increasing attentions when moving from liquid LIBs into SSBs due to the unique properties, including atomic-scale and stoichiometric deposition, and excellent uniformity and conformity. Using ALD/MLD to construct a thin artificial interface between SSEs and electrodes is very effective in addressing the interfacial issues of chemical reactions, Li dendrite growth, and space charge effects. Promising progress has been reported using ALD/MLD to overcome the interfacial shortage in SSBs in recent years. In this Review, we summarize the recent development and understanding of ALD/MLD techniques for addressing interfacial issues of Li batteries from liquid to solid. More importantly, since the development of SSBs is still in its infancy, we also propose directions and perspectives of ALD/MLD applications to achieve next-generation SSBs with high stability and long lifetime.

ALD/MLD to Address Interfacial Problems in SSBs

Interfacial Materials and SSE Fabrication by ALD/MLD

One of the major challenges of SSEs in SSBs is the unstable electrochemical properties at high voltage. Based on Mo's calculation (Figure 2), some common SSEs—including $Li_{10}GeP_2S_{12}$ (LGPS), Li_3PS_4, and $Li_7La_3Zr_2O_{12}$ (LLZO)—show relative low oxidation potential which is likely to decompose at high voltages.[71] As a result, the interfacial resistance is becoming a critical problem for the performance of SSBs. In this case, the interfacial coating with materials of wide electrochemical windows is considered an effective approach to protect the interfacial SSEs and to minimize interfacial resistance due to SSE decomposition. In Mo's calculation

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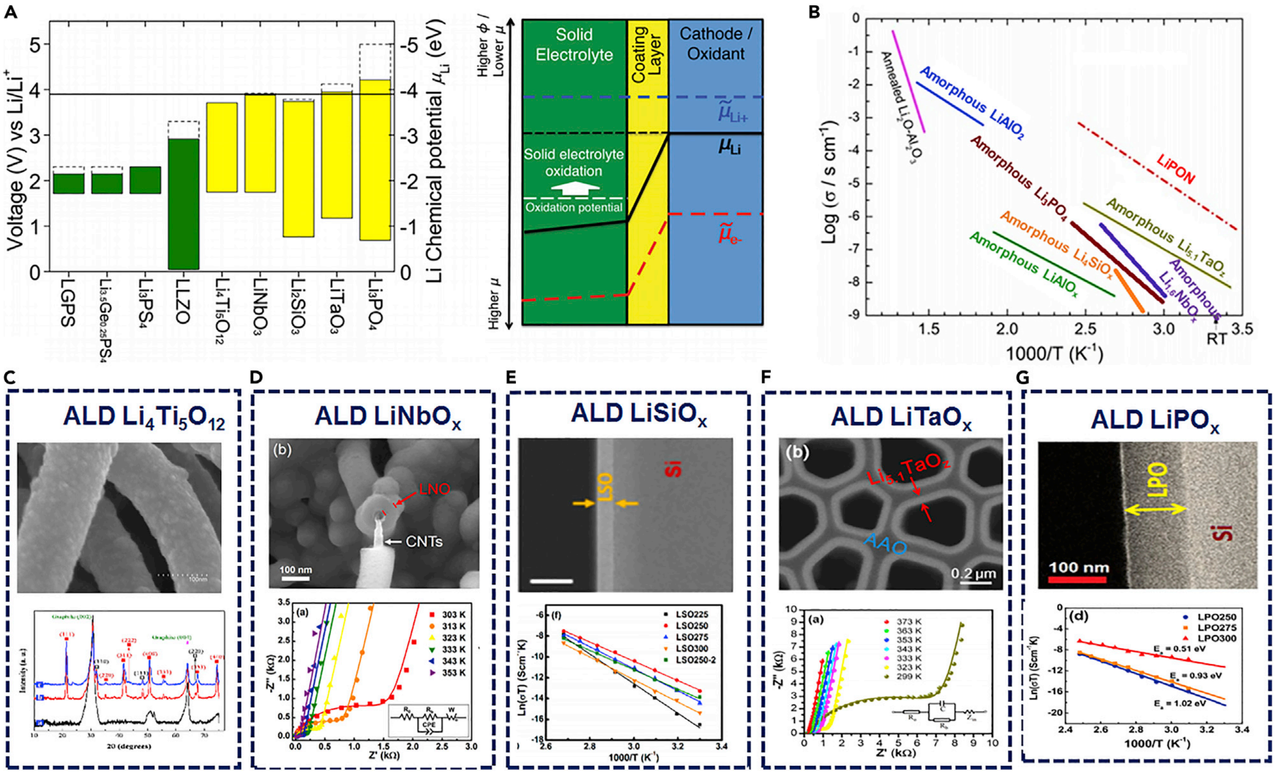

Figure 2. Interfacial Materials and SSEs Fabrication by ALD/MLD

(A) Electrochemical stability window (solid color bars) of commonly used coating layer material and a schematic diagram of the functions of the coating layers in the cathode/electrolyte interface; Reprinted with permission from Zhu et al.[71] Copyright 2015, American Chemical Society.

(B) Ionic conductivities of solid-state electrolytes prepared by ALD in comparison with the commonly used LiPON, reprinted with permission from Liu et al.[15] Copyright 2015, American Institute of Physics.

(C–G) The fabrication of different interfacial materials by ALD for SSBs. (C) $Li_4Ti_5O_{12}$, reprinted with permission from Meng et al.[39] Copyright 2013, The Royal Society of Chemistry. (D) $LiNbO_x$, reprinted with permission from Wang et al.[72] Copyright 2018, American Chemical Society. (E) $LiSiO_x$, reprinted with permission from Wang et al.[73] Copyright 2017, American Chemical Society. (F) $LiTaO_x$, reprinted with permission from Liu et al.[74] Copyright 2013, American Chemical Society. (G) $LiPO_x$, reprinted with permission from Wang et al.[75] Copyright 2015, American Institute of Physics.

(Figure 2A), they investigated the electrochemical stability of several Li-containing materials, such as $Li_4Ti_5O_{12}$, $LiTaO_3$, $LiNbO_3$, Li_2SiO_3, and Li_3PO_4, that are potentially suitable as coating materials. Their results show that these coating materials are generally stable between 2 and 4 V, which covers the typical voltage range for Li-ion cathodes and compensates the instability gap between SSEs and cathodes. Moreover, these materials have poor electronic conductivity and can serve as artificial SEIs to prevent parasitic electrochemical reactions at the interface. Thus, the proposed materials of $Li_4Ti_5O_{12}$, $LiTaO_3$, $LiNbO_3$, Li_2SiO_3, and Li_3PO_4 are promising interfacial materials for cathode/SSE interfaces. Figure 2B summarizes the ionic conductivities of the Li-containing ALD coatings from the reported literatures. These Li-containing materials can also be considered as SSEs. The ionic conductivities of glassy SSEs are in the order $\sim 10^{-8}$ s cm^{-1}, which is still lower than that of the commonly used LiPON in thin-film batteries. Promisingly, these materials are all available through the ALD technique. Figures 2C–2G show the successful fabrications of different interfacial materials ($LiTiO_x$, $LiNbO_x$, $LiSiO_x$, $LiTaO_x$, and $LiPO_x$) achieved by ALD.[39,72–75] For example, ALD $LiNbO_x$ thin films with well-controlled film thicknesses and compositions were deposited by combining the Li sub-cycle (lithium terbutoxide [LiO^tBu] and H_2O) and Nb sub-cycle ($Nb(OEt)_5$ and H_2O) at a deposition temperature of 235°C.[72] Self-limiting behavior and uniform growth at

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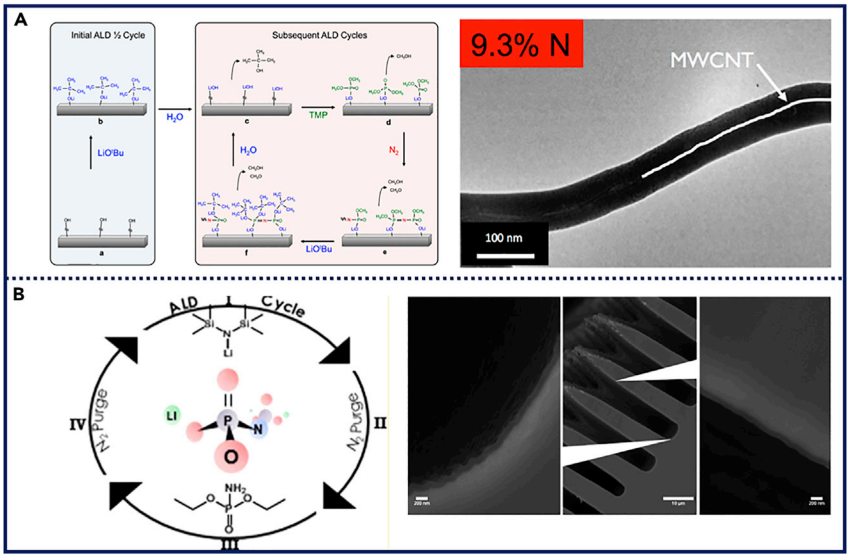

Figure 3. The Fabrication Processes of LiPON by ALD

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(B) Reprinted with permission from Nisula et al.[77] Copyright 2015, American Chemical Society.

different compositions were achieved by varying the sub-cycle combinations of the ALD recipes. Different ratios of Li to Nb sub-cycles were used to tune the thin-film composition, which in turn affected the electrochemical performance and the local electronic structures. Uniform and continuous $LiNbO_x$ thin films were observed on the surface of the CNT and Si wafer substrates, as shown in Figure 2D. Similar to the ALD process for $LiNbO_x$, other materials of $LiSiO_x$, $LiTaO_x$, and $LiPO_x$ can be deposited using the same LiO^{t}Bu precursor for Li in combination with other element-specific precursors, such as tetraethylorthosilane for Si, tantalum(V) ethoxide ($Ta(OEt)_5$) for Ta, and trimethylphosphate (TMPO) for P, respectively.[73–75] The ALD temperatures of these compounds are in the range of 225°C to 300°C for self-limiting growths. From the scanning electron microscopy (SEM) images in Figures 2C–2G, the uniform films were observed not only on Si wafer but also on the high-surface-area substrates such as anodic aluminum oxide templates. With a uniform film-like deposition, these interfacial materials synthesized by ALD can be promising protective coatings to adapt the electrochemical environment for SSEs at high voltages.

LiPON, one of the most popular SSEs, has been synthesis by ALD.[76,77] Figure 3 illustrates the ALD fabrication processes of LiPON using two different recipes. In Rubloff's work, they use LiO^{t}Bu, H_2O, TMPO, and plasma N_2 ($^PN_2$) as precursors (Figure 3A).[76] Interestingly, they found that the ALD LiPON thin films are polycrystalline, with the N content less than 4.5% and amorphous when the N content is over 4.5%. As a result, the as-deposited ALD LiPON with 5% N can achieve an ionic conductivity of $1.45 \times 10^{-7} \pm 3 \times 10^{-7}$ S cm^{-1}. Almost concurrently, Karppinen's group demonstrated another ALD process of LiPON using lithium hexamethyldisilazide and diethyl phosphoramidate (DEPA) as precursors (Figure 3B).[77] The growth temperature window for this recipe is around 270°C to 310°C with a growth rate of 0.7 Å/cycle. The LiPON thin film deposited at 330°C with a composition of $Li_{0.95}PO_{3.00}N_{0.60}$ showed an ionic conductivity as high as 6.6×10^{-7} S cm^{-1} at 25°C. The successful fabrications of LiPON using ALD achieve highly tunable thickness, tunable N content, and conformal deposition. An electrochemical stability window of 0.68–2.63 V makes LiPON a promising interlayer material for SSEs to address the instability issue toward anodes at low voltage.

Other Li-containing thin films, including $LiAlS_x$ and $LiAlF_x$, have also been synthesized by ALD,[78,79] so have some other popular SSE compositions. Dasgupta's group developed a thermal ALD process for Al-doped LLZO solid electrolytes using LiO^tBu, ozone, tris(N,N′-iisopropylformamidinato)lanthanum, tetrakis(dimethylamido)zirconium, and trimethylaluminum as precursors.[80] After post ALD annealing, the continuous amorphous thin films of LLZO change into island-like structures. In this case, it is considered that the amorphous thin film deposited by ALD/MLD without annealing process is more appropriate for interfacial modifications to ensure full coverage on the surface. More recently, their group presented an ALD process of amorphous lithium borate-carbonate (LBCO) films as SSEs. As-prepared LBCO exhibited ionic conductivities up to 2.2×10^{-6} S cm^{-1}, which is the highest value among all reported ALD ionic conducive films. Based on their results, the ALD LBCO films also exhibited high stability upon exposure to air, and in contact with both Li metal anodes and cathode materials. It is believed that this new material of glassy LBCO will be a very promising interfacial material for both cathode/SSEs and anode/SSEs interfaces.[81]

Based on the calculation of electrochemical stability, several types of Li-containing materials are considered promising candidates as interfacial materials for SSEs, including $LiNbO_x$, $LiSiO_x$, $LiTaO_x$, $LiPO_x$, and LiPON. With the development of ALD techniques, all these materials can be deposited by ALD as amorphous and continuous thin films with a controllable thickness. The as-deposited Li-containing materials are attractive interfacial materials for stabilizing the interface between SSEs and electrodes, which is expected to prevent parasitic reactions and reduce interfacial resistance. The reported works on ALD synthesis of SSEs mainly focus on the electrochemical properties, including ionic conductivity and electrochemical stability. Upon electrochemical cycling, the volume change of the electrodes is one of the major challenges for the lifetime of the cells. However, mechanical properties, in particular toughness of the film, have always been neglected. Considering durability upon battery cycling, the mechanical properties of ALD/MLD films need to be taken into consideration in future studies.

Interface Design on SSE by ALD/MLD

Chemical Reaction Prevention. As discussed in the above sections, one big challenge for SSEs is the chemical compatibility between SSEs and electrodes. The interfacial stability and low interfacial resistance are the key factors to achieving long-life and stable SSBs. Among the potential SSEs, NASICON-type electrolyte LATP ($Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$) has received wide attention due to the relatively high ionic conductivity of 0.1 mS cm^{-1}. Unfortunately, the use of Li metal anode is still hindered by the side reaction between LATP and Li. The Ti^{4+} in LATP is easily reduced to Ti^{3+} in contact with Li metal, forming an unfavorable interphase at the LATP/Li interface. To prevent the chemical reactions and stabilize the interface between LATP and Li metal anode, our group first demonstrated the application of ALD Al_2O_3 coating on LATP electrolyte to realize the stable interface toward Li metal.[82] With an optimized thickness of 150 cycles of Al_2O_3 (as seen in Figure 4), the voltage hysteresis for the Li-Li symmetrical cells during Li plating/stripping is much more stable than the pristine LATP pallet. The evidence can be observed from the high-resolution transmission electron microscopy (HR-TEM) images and electron energy loss spectroscopy mapping, which are shown in Figure 4. The ALD Al_2O_3 protective layers can remain after long cycles with no metallic Li diffusion into the LATP electrolyte with coating layers.

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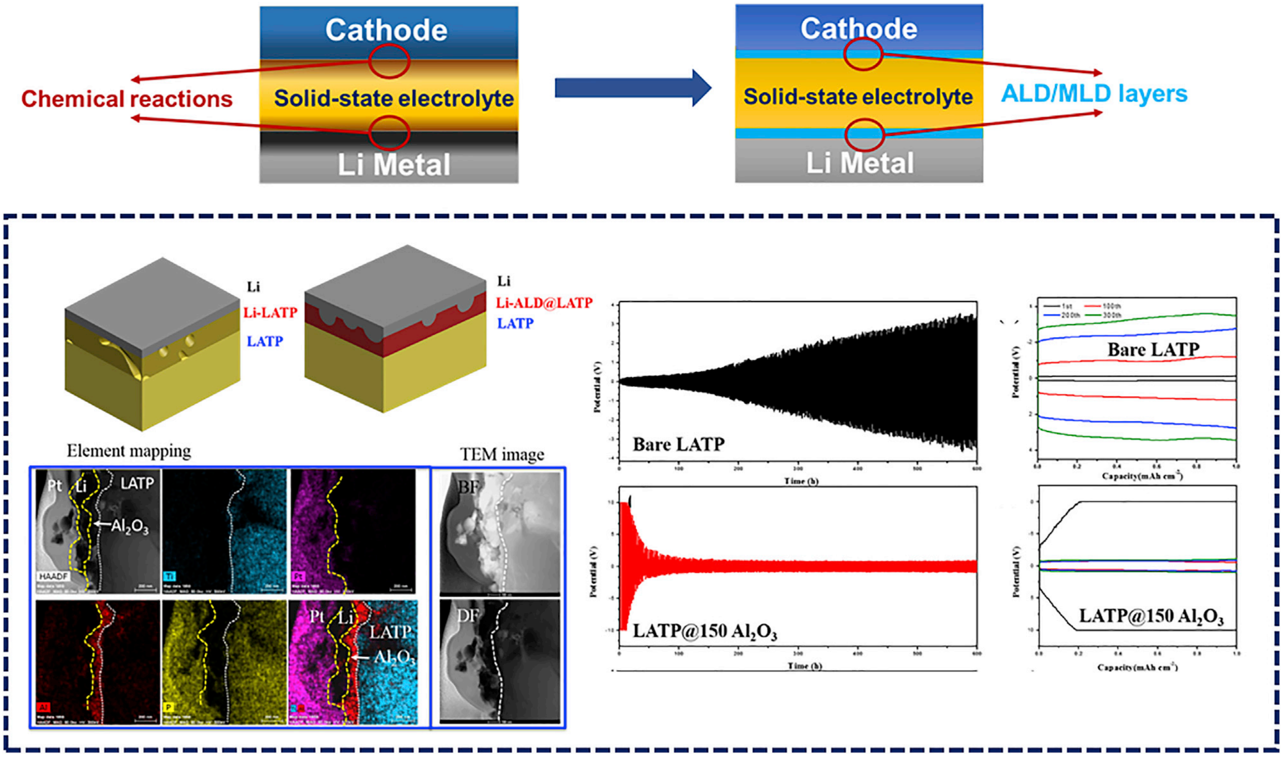

Figure 4. ALD Interface Layers for Chemical Reactions between SSEs and Electrodes (Cathode and Anode)
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In brief, both Li penetration and Ti reduction are prevented by the dense Al_2O_3 coating, which enables the realization of a stable LATP/Li interface. In addition, the Al_2O_3 coating is transformed into a conductive layer of Li-Al-O, which provides Li^+ pathways at the LATP/Li interface, which largely reduces the interfacial resistance. Our work proves the feasibility of ALD protective layer to prevent chemical side reactions and stabilize the Li/SSE interface for achieving long-life SSBs.

Woo et al. also used the ALD Al_2O_3 to prevent the side reactions between $LiCoO_2$ cathode and a sulfide-based $Li_{3.15}Ge_{0.15}P_{0.85}S_4$ SSE.[83] From their results, 90% capacity can be retained after 25 electrochemical cycles using the ALD Al_2O_3-coated $LiCoO_2$, whereas only 70% capacity retention was delivered using uncoated $LiCoO_2$. Interestingly, the ALD Al_2O_3 can effectively mitigate the increase of interfacial resistance for the $LiCoO_2$/$Li_{3.15}Ge_{0.15}P_{0.85}S_4$ SSE interface. Meanwhile, direct evidence from TEM indicated that the thickness of the unfavorable interphase in the SSBs using ALD Al_2O_3-coated $LiCoO_2$ was thinner than that of the SSBs using uncoated $LiCoO_2$. Their results provide guidance that an ALD protective layer is also very effective in blocking side reactions between cathodes and SSEs.

In short, an ultrathin ALD Al_2O_3 coating can effectively prevent the chemical reactions of both oxide- and sulfide-based SSEs with Li metal. The interfacial resistance can be significantly decreased for achieving long-lifetime SSBs with Li anodes. Meanwhile, an ALD Al_2O_3 layer can also block the side reactions between cathodes and SSEs and reduce interfacial side products.

Li Wettability. Among all candidates, garnet-type SSEs are one of the most popular oxide-based SSEs for SSBs because of their wide electrochemical windows,

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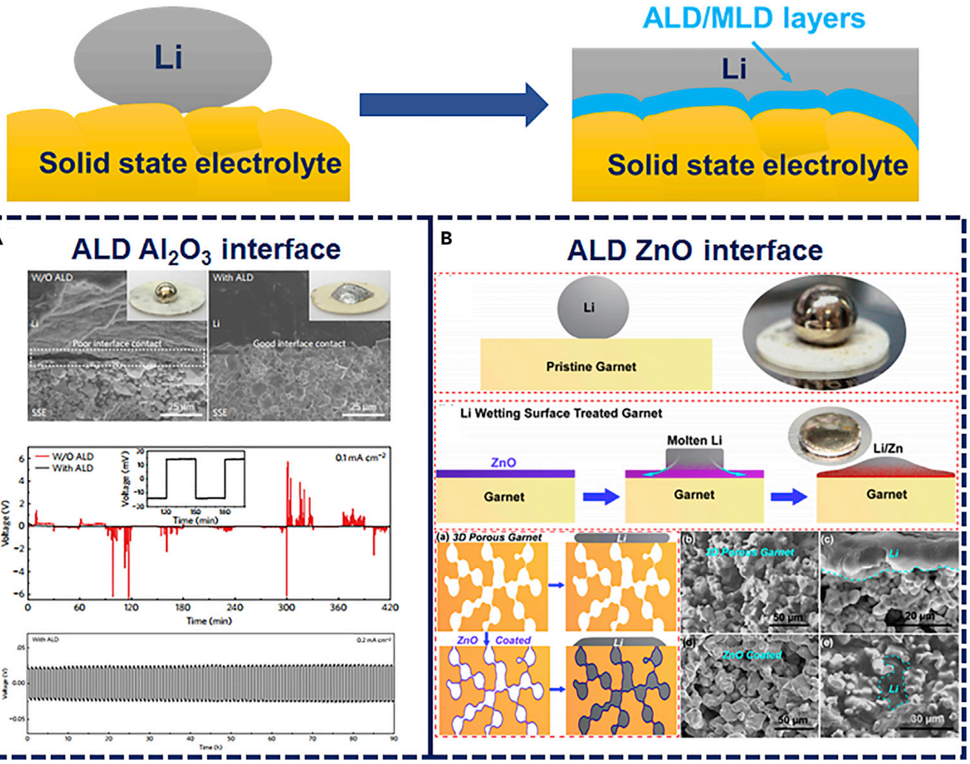

Figure 5. ALD Interface Layer for Improving the Li Wettability of SSEs

(A) ALD Al_2O_3. Reprinted with permission from Han et al.[84] Copyright 2017, Springer Nature.

(B) ALD ZnO. Reprinted with permission from Wang et al.[85] Copyright 2018, American Chemical Society.

stability against Li, relatively high ionic conductivity at room temperature, and stability in air. However, one major challenge is the large interfacial resistance between the garnet SSEs and electrode materials due to its rigid ceramic nature. The high interfacial resistance on the Li side is also caused by the poor wetting properties and the formation of Li_2CO_3 impurity on the SSE surface. To solve this issue, Hu's groups introduced an ultrathin ALD Al_2O_3 coating on $Li_7La_{2.75}Ca_{0.25}Zr_{1.75}Nb_{0.25}O_{12}$ (LLCZN) SSE.[84] Figure 5A presents the improved Li wettability on LLCZN with ALD Al_2O_3 coating. The SEM images in Figure 5A clearly shows the enhancement of interfacial contact by applying the ALD-Al_2O_3 ultrathin layer on the LLCZN surface. When carrying out the Li plating and stripping experiments, the control cell without ALD coating displayed a noisy potential with large voltage polarization indicating uneven ion transport through the interface. However, the ALD Al_2O_3 coating can significantly reduce the resistance and stabilize the LLCZN/Li interface with an overpotential of 13 mV at a current density of 0.1 mA cm^{-2}. Stable cycling performances was demonstrated up to 90 hr with the voltage response at 22 mV at the current density of 0.2 mA cm^{-2}. The interfacial impedance decreased dramatically from 1,710 to 1 Ω cm^2 at room temperature, effectively negating the Li/SSE interfacial impedance. Both experimental and simulation results reveal that the ultrathin ALD Al_2O_3 coating layers achieved to improve Li wettability the garnet SSE. And the lithiated-Al_2O_3 interface can provide effective Li^+ transport between the Li metal anode and SSE.

Moreover, a ZnO thin film deposited by ALD has also been demonstrated by the same group for improving Li wettability on garnet SSEs. The good wetting was due to the ready reactivity of ZnO with Li metal. The interfacial resistance was significantly decreased to as low as ~20 Ω cm^2 (as seen in Figure 5B).[85] More interestingly, they demonstrated the infiltration of Li metal into porous structures of the garnet SSE, which benefited from the gas-phase deposition of the ALD technique to handle complex structures. The Li-filled porous SSE can also potentially serve as a self-supported Li metal composite anode with both high ionic and electronic conductivities for solid-state Li metal batteries. From their results, achieved using ALD Al_2O_3 and ZnO as surface modification layers for garnet SSEs, the Li wettability was significantly improved. Appropriate ALD layers were the key to achieve compact contact between Li and garnet SSEs and low interfacial resistance.

Interface Design on Li/Na Anode by ALD/MLD

Li (Na) metals are considered the most promising anodes for Li (Na)-based batteries with high theoretical capacity, low electrochemical potential, and light weight, especially for the next-generation batteries, including SSBs.[86–88] Fundamentally, the safety issues of the Li and Na metal anodes are mainly caused by the serious metal dendrite formation during electrochemical plating/stripping processes.[87,89,90] There are three main challenges for Li and Na metal anodes during electrochemical cycling in liquid electrolytes.[89,91] Firstly, mossy and dendritic metal deposits will form during the electrochemical plating process, which may penetrate through the separators and cause serious safety issues.[90] Secondly, the unstable SEI layers produced by the side reactions between Li (Na) metal and electrolyte will continuously consume the liquid electrolyte and metal anodes, resulting in large internal resistance, low Coulombic efficiency, and the short lifetime of the electrodes.[92,93] Thirdly, the infinite volume change of metal anodes during the plating/stripping has also been observed recently and considered a significant problem for the "hostless" metal anodes.[88,94,95] To solve the issues and enhance the performance for Li metal anodes, different strategies have been developed to stabilize the SEI. One effective approach is to create an artificial SEI film through surface coating. Among all coating methods, ALD/MLD is considered as an ideal technique for Li and Na metal surface modifications due to their unique properties. In 2015, Kozen et al. first demonstrated the successful application of ALD Al_2O_3 as protective layers on Li metal with exquisite thickness control (Figure 6A).[96] As a result, the ALD Al_2O_3 coating layers can protect the Li surface from corrosions upon exposures to air, sulfur, and electrolyte. When testing in Li-S cells, the ALD-protected Li anode displayed improved capacity retention compared with bare Li metal anodes. Subsequently, Dasgupta's group studied the detailed plating/stripping behaviors for both ALD-treated and untreated Li foils (Figure 6B).[97] With an optimized thickness of ALD Al_2O_3 coating, the electrochemical performance of Li-Li symmetric cells can be significantly enhanced with effectively reduced Li dendrite growth. Furthermore, Chen et al. studied the detailed growth mechanism of ALD Al_2O_3 deposition on Li foil by *in situ* quartz crystal microbalance and found larger growth than expected during the initial cycles.[98] Their results also indicated the enhanced wettability of the Li surface toward both carbonate and ether electrolytes, leading to uniform and dense SEI formation and reduced electrolyte consumption during battery operation.

After that, both our and Hu's group reported the applications of ALD Al_2O_3 coating as protective layers for Na metal anodes (Figures 6C and 6D).[99,100] The ALD Al_2O_3-coated Na anodes presented a significant improvement on the electrochemical plating/stripping performances and suppressed Na dendrite growth in both carbonate- and ether-based electrolytes. Another work, by Elam's group, used an ultrathin ionic conductive Li_xAl_yS coating to stabilize the Li/electrolyte interface and reduce interfacial resistance.[79] When testing in the Li-Cu asymmetric cells, the Li_xAl_yS thin

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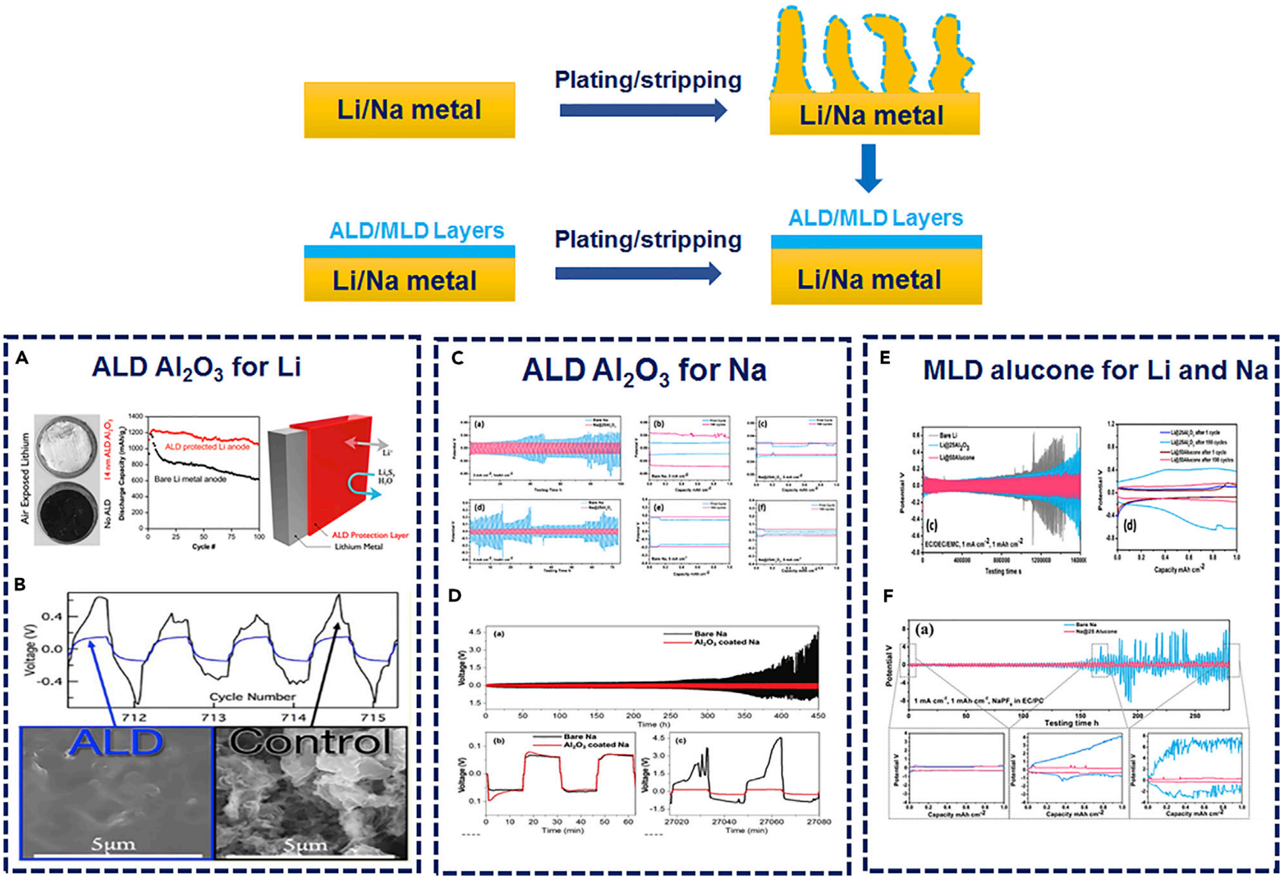

Figure 6. ALD/MLD Protective Layer for Li and Na Metal Anode in Liquid Cells

(A and B) ALD Al_2O_3 for Li metal anode. (A) Reprinted with permission from Kozen et al.[96] Copyright 2015, American Chemical Society. (B) Reprinted with permission from Kazyak et al.[97] Copyright 2015, American Chemical Society.

(C and D) ALD Al_2O_3 for Na metal anode. (C) Reprinted with permission from Zhao et al.[99] Copyright 2017, John Wiley and Sons. (D) Reprinted with permission from Luo et al.[100] Copyright 2017, John Wiley and Sons.

(E) MLD alucone for Li metal anode, reprinted with permission from Zhao et al.[101] Copyright 2017, John Wiley and Sons.

(F) MLD alucone for Na metal anode, reprinted with permission from Zhao et al.[102] Copyright 2017, American Chemical Society.

film can effectively suppress dendrite formation and double the lifetime. All these works offer new possibilities for the realization of practical Li and Na metal anodes.

Moving from ALD to MLD, our group and Elam's group have demonstrated the use of MLD coating of alucone as a protective layer for metallic Li anodes to improve cycling performance.[101,103] Alucone is polymerized ethylene glycol with Al metal centers. In our study, the alucone coatings are deposited at 120°C with a growth rate of 0.5 nm/cycle. Our results show that the MLD coating can stabilize the SEI film and further change the morphology of Li electrochemical deposits compared with bare Li in both ether- and carbonate-based electrolytes. The resulting performance was superior to the ALD Al_2O_3 coatings (Figure 6E). The application of MLD alucone protective coating on Na metal anodes also achieved similar improvements in the electrolyte of $NaPF_6$ in EC/PC (Figure 6F).[102] Compared with pristine Na foil, Na@25alucone showed significantly enhanced electrochemical stripping/plating performance under different current densities from 1 to 3 mA cm^{-2}. With 25 cycles of alucone coating, Na dendrite growth was effectively reduced. Furthermore, MLD alucone protective coatings on Na metal showed better performance

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than the ALD Al_2O_3 coating. It is believed that our designs of MLD alucone-coated Li and Na metal anodes open up new opportunities to the realization of the next-generation high energy density Li and Na metal batteries.

Different ALD and MLD films have been reported as artificial SEIs for both Li and Na metal anodes in recent years. Compared with ALD films (such as Al_2O_3), the MLD films (such as alucone) possess lower density, increased softness, lower modulus, and higher flexibility, leading to better electrochemical performance in the liquid-based electrolytes. However, the currently developed ALD or MLD films are still insufficient for long-life Li and Na metal anodes. It is believed that the ideal artificial SEI for Li and Na metal anodes is multilayer and hybrid designs combining both ALD and MLD. For example, a bilayer artificial SEI consisting of a dense ALD layer and a porous MLD outer layer could be a promising design. On one hand, the dense and ionic conductive ALD films (such as LiF) can be used as the inner layer to transport Li^+ or Na^+ while blocking the pathway of electrons. Electrochemical side reactions between the metal anodes and electrolyte is thus prevented. On the other hand, the highly flexible and porous MLD films are used as an outer shell to provide the channel for electrolyte diffusion and relieve the volume change of Li and Na metals during cycling. This rational multilayer design could be a more effective approach inheriting the advantages from both ALD and MLD techniques.

One of the most popular types of SSEs with outstanding ionic conductivity (10^{-2} S/cm) is sulfide-based SSEs. However, two main challenges hindering the direct use of Li metal with sulfide-based SSBs are Li dendrite growth and side reactions between Li metal and sulfide SSEs.[104] To address these challenges, we first designed an inorganic-organic hybrid alucone coating on Li metal foil by MLD, which could serve as an artificial SEI to block the electron transfer at the anode interface, thus suppressing the interfacial reactions between Li and sulfide-based electrolyte.[105] Figure 7A shows the electrochemical performances of the Li/$Li_{10}SnP_2S_{12}$/Li symmetric cells at a constant current of 0.1 mA/cm^2. The overpotential of Li^+ plating/stripping cycles increased dramatically, indicating the continuous reactions between Li metal and $Li_{10}SnP_2S_{12}$ and accumulation of a highly resistive interphase. After 4,000 min of cycling, the cell was short circuited. Promisingly, with 30 cycles of alucone coating, the overpotential of Li^+ platting/stripping remained almost stable for 10,000 min, strongly indicating the stable electrochemical process at the Li anode interface with $Li_{10}SnP_2S_{12}$ without any inner short circuit. Furthermore, $LiCoO_2$ was used as the cathode to fabricate full SSBs. Figure 7B compares the cycling performance of SSBs using 30alucone-coated Li and bare Li foils as anodes. The stable cycling performance of the SSB with 30alucone-coated Li was in great contrast to the rapid capacity fading of the SSB using bare Li. The SSBs with bare Li anode showed almost no capacity after 60 cycles; however, SSBs with 30aluocne Li presented stable cyclability and still retained a capacity of 60 mAh g^{-1} after 150 cycles. This is a good indication of the reduced interfacial reactions between Li metal and $Li_{10}SnP_2S_{12}$ by the alucone coating. In addition, Li dendrite formation is inhibited as well. This demonstration clearly suggests that Li metal with MLD coating can be successfully applied to Li SSBs without compromising the output voltage, thus guaranteeing the high energy density.

ALD and MLD thin films have been investigated as protective coating layers for both Li and Na metal anodes. All the reported electrochemical performances are tested in liquid electrolyte, including both carbonate- and ether-based electrolytes. Promisingly, the ALD/MLD coating can significantly improve the lifetime of the Li and Na metal anodes and suppress the mossy metal dendrites. It is also expected that the

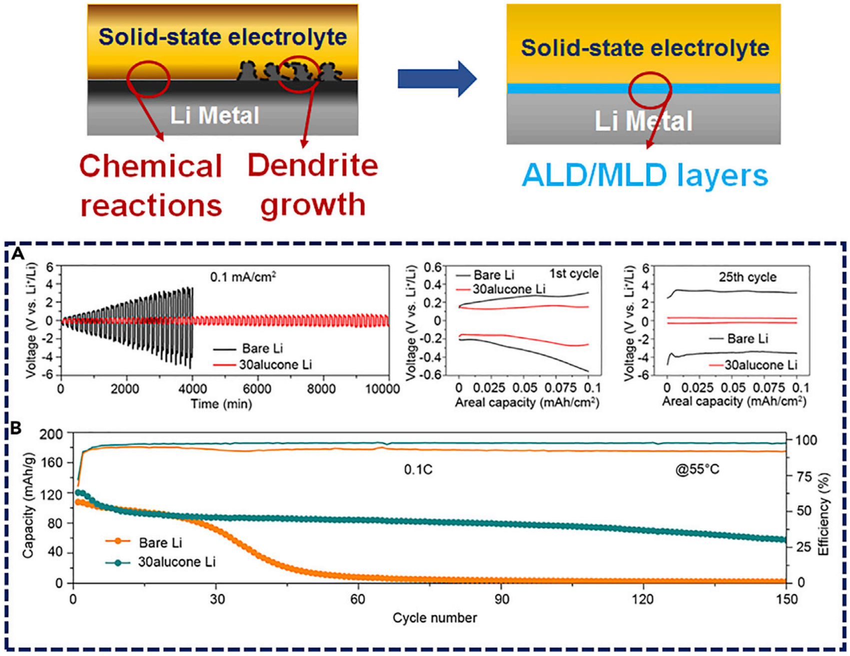

Figure 7. MLD Alucone-Coated Li for Sulfide-Based SSBs

(A) Comparison of the cycling stability between the 30alucone Li and the bare Li foil at a current density of 0.1 mA cm^{-2}. Voltage profiles of the 30alucone Li and the bare Li foil in the first cycle and the 25th cycles.

(B) Cycle performance of all-solid-state lithium ion batteries using 30alucone Li and the bare Li foil as anode electrodes. Reprinted with permission from Wang et al.[105] Copyright 2018, Elsevier.

ALD/MLD-protected Li/Na also can show effective functions in SSBs in terms of solving the issues including preventing the chemical reactions between Li/Na and SSEs, reducing the Li/Na dendrite growth, stabilizing the interface and lowing the interfacial resistances. We believe that the ALD/MLD-protected Li/Na metal anodes can not only play a crucial role in liquid cells but also become a rising star in SSBs.

In this section, we mainly summarize the recent development of ALD/MLD addressing the interfacial issues in SSBs with three parts including interfacial materials fabrication, interface design on SSEs, and interface design on Li/Na metal. The current achievements show that different thin ALD/MLD layers are very promising for solving the challenges of side reactions, interfacial resistance, Li wettability, and dendrite growth. However, there are still many areas to be explored in this field. To be an ideal interfacial layer for SSBs, the ALD/MLD films should meet the following requirements:

(1) Wide electrochemical windows. At the interface between cathode and SSEs, the ALD/MLD films should be electrochemically stable at high voltages. Among the candidates, Li_3PO_4 presents the highest upper limit up to 5 V and can be a promising interfacial material for high-voltage cathodes. On the anode side, ALD/MLD films are required to remain electrochemical stable down to at least 0 V to be compatible with Li metal anodes.
(2) High ionic conductivity. The ALD/MLD films should have sufficient ionic conductivities to allow fast Li^+ transport across the electrode/SSE interfaces (including both anode/SSE and cathode/SSE interfaces). Considering the currently developed ALD/MLD materials, the ionic conductivities are

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generally around 10^{-6} to 10^{-8} S cm^{-1}, which are still lower than that of typical films prepared by sol-gel methods. Therefore, it is an urgent task to develop ALD/MLD films with high ionic conductivities for high-performance SSE interfacial materials.

(3) Good mechanical properties. Volume change is always a critical problem for both cathodes and anodes during electrochemical cycling. The ALD/MLD buffer layers between SSEs and electrode with good mechanical properties shall help to relieve the volume change during cycling. Particularly, as the protective layers for Li and Na metal anodes, the ALD/MLD films with high flexibility and high toughness would be beneficial to address the challenges of both Li/Na dendrite growth and volume changes

(4) Friendly film growth conditions. The ALD/MLD films are usually deposited under relatively low temperatures compared with other techniques such as CVD. However, the growth conditions of ALD/MLD for Li and Na metals and SSEs are more challenging due to the low melting points of Li and Na metals and high sensitivity of SSEs (particularly sulfide-based SSEs).

ALD/MLD for Thin-Film Batteries and 3D SSBs

In addition to the efforts in addressing interfacial issues for SSBs, ALD and MLD are promising techniques to fabricate solid-state thin-film batteries and 3D micro SSBs.[106] As discussed before, ALD and MLD are capable of fabricating conformal coatings on complex 3D structures at relatively low temperatures. It is possible to perform uniform depositions on a variety of surfaces, such as flexible polymer and fiber substrates. This is particularly suitable for fabricating thin-film SSBs and 3D SSBs.[107]

Recently, Karppinen's group demonstrated an all solid-state thin-film battery using MLD lithiated p-benzoquinone (Li_2Q) as cathode and ALD LiPON as SSE.[108] The resulting cell was able to reach 50% of the full capacity in less than 0.25 s, with energy and power densities of 108 mW hr cm^{-3} and 508 W cm^{-3}, respectively. This organic SSB could be a good configuration for fundamental studies, which eliminates the effects of conductive additives. However, it should be pointed out that the cycle life of the current device still leaves much room for improvements in the future.

LiPON has been developed as the SSEs for thin-film batteries in the past year. Pearse et al. firstly demonstrated the thermal ALD LiPON working in a full SSB.[109] The ALD LiPON was deposited using LiO^tBu and DEPA as precursor at a deposition temperature of 300°C. The resulting ionic conductivity was $(6.51 \pm 0.36) \times 10^{-7}$ S^{-1} at 35°C. The thin-film devices were fabricated using $LiCoO_2$ as the cathode and Si as the anode operating at current densities up to 1 mA cm^{-2}. Moreover, another interesting work reported the plasma-assisted ALD of LiPO(N) in Li-ion half cells comprising TiO_2/LiPO(N) and $LiMn_2O_4$/LiPO(N) and in high-aspect ratio pillar arrays.[110] Moreover, Pearse et al. reported a 3D SSB fabricated by ALD, in which the strategy for fabricating and testing conformal 3D SSBs is schematically presented in Figure 8A. Figure 8B shows an optical photograph of the finished battery "chip."[111] As shown in the cross-sectional TEM image in Figure 8C, the 3D battery consisted of 40 nm of Ru, 70 nm of V_2O_5, which was subsequently electrochemically lithiated to LiV_2O_5, 40–100 nm of Li_2PO_2N, 10 nm of SnN_x and 25 nm of TiN. The corresponding compositions and ALD recipes for each layer are summarized in Figure 8D. Impressively, the 3D SSBs consisting of the LiV_2O_5-SnN_x couple delivered stable capacities of 2.6 μAh cm^{-2} for a long lifetime of up to 100 cycles. Meanwhile, the areal discharge capacity of these cells can be scaled up by 9.3 times that of planar cells through integration with 3D substrates using ALD.

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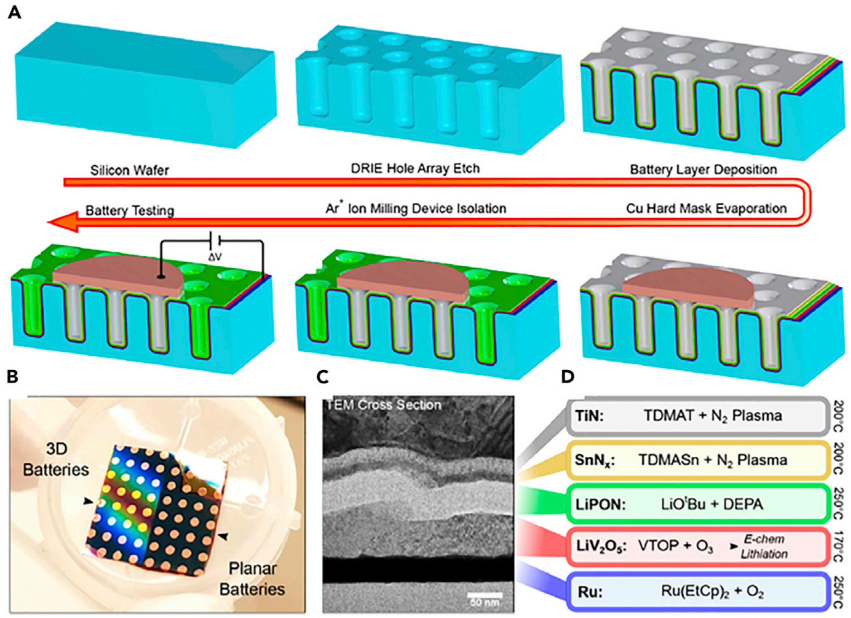

Figure 8. Fabrication and Characterization of 3D Solid-State Thin-Film Batteries

(A) Schematic of fabrication of devices.

(B) Optical photograph of finished battery "chip."

(C) Cross-sectional TEM image of an all-ALD solid-state battery.

(D) Overview of ALD chemistry and process temperature for each layer. Reprinted with permission from Pearse et al.[111] Copyright 2018, American Chemical Society.

The 3D structure benefits from the rate performance and round-trip efficiency of the cell. Their work provided a new opportunity for realization of long-sought 3D SSBs by ALD technique.

Conclusions and Perspectives

The recent renaissance of SSBs has made it a hot topic in the field of energy storage. High safety and high energy density are the key attractions for SSBs to be one of the most promising systems for next-generation batteries, especially for applications in EVs. However, practical applications of SSBs are still hampered by major challenges as we discussed in the above sections. ALD and MLD techniques are considered as an ideal strategy to overcome these issues in SSBs, particularly for intractable interfacial problems. Notable potentials benefit from the unique properties of ALD and MLD, such as low growth temperatures, atomic-scale and stoichiometric depositions, and excellent uniformity and conformity. These advantages are unreachable using other common coating methods.

In this Review, we summarize the recent developments and understandings of ALD and MLD techniques in the applications of batteries, with a special focus on the transition from liquid to solid electrolytes (as shown in Figure 9). ALD processes of potential SSEs and interfacial materials, including $Li_4Ti_5O_{12}$, $LiTaO_3$, $LiNbO_3$, Li_2SiO_3, Li_3PO_4, LiPON, and LLZO have been developed over the past years. Amorphous structures and uniform depositions are generally achieved. In addition, the ALD Al_2O_3 coatings demonstrate important functionalities on different SSEs (LATP and LGPS) to prevent chemical reactions between the SSEs with Li metal. The interfacial resistance can be significantly decreased to achieve longer lifetime. Moreover, different ALD metal oxides (e.g., Al_2O_3 and ZnO) are applied as surface

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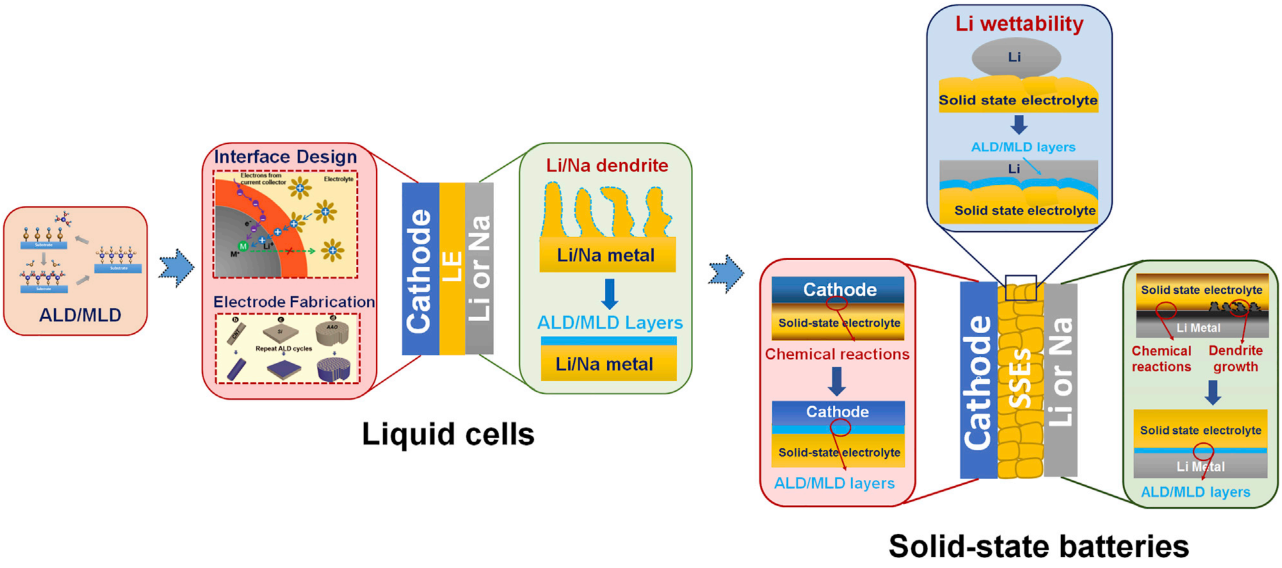

Figure 9. Schematic Illustration of ALD/MLD for Liquid Cell and SSB Applications

modifications on garnet SSEs to enhance Li wettability and decrease interfacial resistance between garnet SSEs with Li. In liquid cells, various ALD and MLD thin films (Al_2O_3, alucone, and $LiAl_xS_y$) are used as the protective layers for Li and Na metal anodes in the last 3 years. The ALD- or MLD-protected Li and Na metal anodes generally present improved stability, longer lifetime, stabilized SEI formation, and suppressed Li/Na dendrite growth.

Although promising results have been achieved using ALD and MLD techniques for SSBs, there are still challenges to be overcome and new properties to be developed in the future. The potential directions and perspectives are listed in detail as follows:

(1) To date, metal oxides (e.g., Al_2O_3 and ZnO) are the most widely reported ALD interfacial materials for SSB applications. Although the ALD metal oxides can effectively prevent the reactions between SSEs and electrodes to stabilize the interface, the low ionic conductivity or even non-ionic conductivity of the metal oxides usually requires a lithiation process in the initial cycles, which will consume Li in the cells and cause a large initial resistance. Based on the previous studies in liquid cells and simulation results, Li-containing thin films, such as $LiTaO_3$, $LiNbO_3$, Li_2SiO_3, and LiPON, with relatively high ionic conductivity, can be a better choice for interfacial materials than metal oxides. For example, $LiNbO_3$ prepared by other methods (such as sol-gel and pulsed laser deposition) are proposed as buffer materials on $LiCoO_2$ to decrease the charge effects between $LiCoO_2$ and sulfide electrolytes and improve performance.[112,113] Likely, ALD $LiNbO_3$ is expected to show further enhanced performance compared with other approaches due to the thinness and conformality of ALD films. However, all these thin films, such as $LiTaO_3$, $LiNbO_3$, Li_2SiO_3, and LiPON, are not yet widely used as interfacial materials in SSBs. In this context, the Li-containing ALD thin films shall receive more attention in the near future.

(2) The electrochemical stability windows of the ALD Li-containing thin films are mainly in the range of 2–4 V, which is suitable for cathode/SSE interfaces. However, these ALD Li-containing thin films still require more efforts to

enable feasibilities at low potentials (0–1 V). Based on the calculations, Li compounds, such as LiF, LiCl, LiBr, Li_3OCl, and Li_3N, show low-potential stabilities around 0–1 V, which can be appropriate interfacial materials between SSEs and anodes, especially Li metal anodes.[114] Some of these compounds (such as LiF[115,116]) have been fabricated by ALD, but the rest are still unreported. Therefore, ALD processes on the unreported compounds and their applications as SSB interfacial materials show potential for high impacts. In addition to ALD films, polymeric thin films and inorganic-organic hybrid thin films also possess stable electrochemical windows at low potentials. Thus, MLD thin films with high ionic conductivity can be another promising option for SSE/anode interfacial materials in SSBs. However, more research efforts are required for the development of novel MLD films.

(3) The ALD/MLD-protected Li and Na metal anodes have been studied in the past 3 years in liquid cells that achieved highly stable SEI, effectively improved lifetime, and suppressed Li/Na dendrite growth. Our group recently made the first demonstration using MLD-protected Li for sulfide-based SSBs. Predictably, the ALD/MLD-protected Li/Na metal anodes can also make a notable enhancement on the electrochemical performance in SSBs in terms of mitigating chemical side reactions and dendrite formation. The relatively low deposition temperatures of ALD/MLD can realize various types of protective layers on the low-melting-point Li and Na metals. Currently, feasible thin films are still limited to common metal oxides or metalcones. One future target is to develop low-temperature Li compounds, such as LiF, LiCl, LiBr, Li_3OCl, and Li_3N, by ALD, which can be directly applied as a protective layer for Li metal. The Li-containing MLD thin films is another promising possibility that needs to be explored for Li metal anode with high flexibility and ionic conductivity.

(4) One key advantage of ALD and MLD is the precise control of thickness down to the nano level. Related to the intrinsic properties of the deposited materials, the thinness of ALD/MLD interfacial layers can be an important factor for achieving good battery performance. Typically, the ionic conductivities of ALD/MLD films for Li-containing compounds are around $10^{-7}\sim10^{-8}$ S cm^{-1}, which are still lower than that of the films prepared by sol-gel methods. And the ALD/MLD metal oxide films are generally ionic insulating. Therefore, the additional interfacial resistance cannot be neglected if the ALD/MLD layers are too thick. In addition to the initially large overpotential caused by thick coatings, the consumption Li during the initial lithiation of the coating also depends on the coating thickness. However, the mechanical integrity of ALD/MLD layer cannot be retained if the protective films are too thin, causing cracks on the interface and re-emerging side reactions. In this context, the optimization and balance of the ALD/MLD layer thickness are very important for future studies.

(5) Another interesting direction is the all solid-state thin-film batteries fabricated by the ALD and MLD techniques. ALD/MLD techniques can realize 3D microbatteries with more complicated designs due to the unique properties of ALD.[117] Although the ALD/MLD processes for different components, including cathode, anode, and SSEs, are achievable separately, the fabrication of practical whole cells is very challenging.[118]

(6) Mechanism studies, especially on the interfacial effects between SSEs and electrodes, are of great interest to the field for achieving high-performance SSBs. Various characterization techniques, including synchrotron radiation-based X-ray techniques, HR-TEM, Rutherford backscattering spectroscopy, etc., are very powerful tools to analyze the interfacial differences between

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SSEs and electrodes with or without ALD/MLD coating layers. In particular, *in situ* analyses are vital for understanding the mechanism during electrochemical cycling for SSBs, which should give critical guidance for researchers working in this area.[119–124] Particularly, the ALD/MLD technique is an ideal method for fabricating well-defined interfaces for the better understanding of the mechanisms using different ways of characterization due to the highly controlled deposition properties. This offers opportunities for designing specific *in situ* experiments.

(7) ALD/MLD reactors with rotary and roll-to-roll functions have been developed for large-scale particle samples and flexible substrate in the past years.[125–128] These features will facilitate the scale-up of interfacial modifications and battery fabrication for SSBs by ALD/MLD.

Foreseeably, ALD and MLD techniques have the potential to play an important role in addressing the interfacial challenges in SSBs. We believe that the successful applications of ALD/MLD in SSBs will offer new opportunities to the realization of next-generation SSBs with high energy density and high safety.

ACKNOWLEDGMENTS

This research was supported by the Natural Science and Engineering Research Council of Canada (NSERC), the Canada Research Chair Program (CRC), the Canada Foundation for Innovation (CFI), and the University of Western Ontario (UWO). We gratefully acknowledge Dr. Qian Sun and Jing (Erica) Luo for their constructive suggestion and discussion.

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