Strategies for the stabilization of metal anodes for Li and Na metal batteries

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Abstract

Li-metal batteries (LMBs) and Na-metal batteries (NMBs) are considered as the promising candidates to replace the conventional Li-ion batteries (LIBs) due to their high theoretical energy density. For LMBs and NMBs, Li metal and Na metal are the ultimate choices to achieve their high energy density due to the high specific capacity, low electrochemical potential and lightweight. However, as alkali metals, both Li and Na metal anodes suffer from serious challenges including 1) Li/Na dendrite formations and short circuits; 2) Low Coulombic efficiency (CE) and poor cycling performance; and 3) Infinite volume changes. This thesis mainly focuses on the design of multiple strategies for the stabilization of Li and Na metal anode for LMBs and NMBs.

The first part in the thesis demonstrates both atomic layer deposition (ALD) Al₂O₃ and molecular layer deposition (MLD) alucone as the protective layers for Li metal anode with effectively suppressed dendrite formation and improved cycle life in different electrolytes (carbonate-based and ether-based).

In the second part, a universal approach has been proposed to achieve a long lifetime and dendrite free Li metal anodes by introducing carbon paper (CP) as an interlayer.

To further improve the electrochemical performances, a bi-functional interlayer of CP with vertical nitrogen-doped carbon nanotubes (NCNTs) was designed for Li metal anode in the third part.

In the fourth part, ALD Al₂O₃ coating was fabricated for the protection of metallic Na anode in the ether-based electrolyte. By protecting Na foil with the ultrathin Al₂O₃ layer, the dendrites and mossy Na formation have been effectively suppressed and life has been significantly improved.

In order to solve the more serious issues in the carbonate-based electrolyte, the inorganic-organic coating alucone coating via MLD was deposited on Na anode, as discussed in the fifth part. The MLD alucone coating shows better performances than the ALD Al₂O₃ coating in the carbonate-based electrolyte.
In the sixth part, a solution-based method was developed to synthesize an artificial protective layer of solid-state electrolyte Na₃PS₄ (NaPS) on the surface of Na metal with more homogeneous Na plating/stripping process, resulting to the suppressed Na dendrite growth.

To further limit the volume change of Na metal anode, in the seventh part, the 3D Na composite electrode using CP-NCNTs as host was fabricated via the thermal infusion method with minimum volume change and dendrite-free Na deposition.

**Keywords**

Li-metal batteries, Na-metal batteries, Li-ion batteries, Li metal anode, Na metal anode, 3D nanostructure, Atomic layer deposition, Molecular layer deposition, Rutherford backscattering spectrometry, Interlayer, Li dendrite, Na dendrite
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5.

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10.

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一切有为法，如梦幻泡影，如露亦如电，应作如是观。
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<tr>
<td>ALD</td>
<td>Atomic layer deposition</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>BJH</td>
<td>Barrett-Joyner-Halenda</td>
</tr>
<tr>
<td>CE</td>
<td>Coulombic efficiency</td>
</tr>
<tr>
<td>CP</td>
<td>Carbon paper</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
</tr>
<tr>
<td>DEC</td>
<td>Diethyl carbonate</td>
</tr>
<tr>
<td>DME</td>
<td>1, 3-dimethoxyethane</td>
</tr>
<tr>
<td>DOL</td>
<td>1, 3-dioxolane</td>
</tr>
<tr>
<td>DEGDME</td>
<td>Diethylene glycol dimethyl ether</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>EC</td>
<td>Ethylene carbonate</td>
</tr>
<tr>
<td>EG</td>
<td>Ethylene glycol</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>EMC</td>
<td>Ethyl methyl carbonate</td>
</tr>
<tr>
<td>EVs</td>
<td>Electric vehicles</td>
</tr>
<tr>
<td>FE-SEM</td>
<td>Field emission scanning electron microscope</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform-infrared</td>
</tr>
<tr>
<td>GLY</td>
<td>Glycerol</td>
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<tr>
<td>Acronym</td>
<td>Full Form</td>
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<tr>
<td>----------</td>
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</tr>
<tr>
<td>LIBs</td>
<td>Li-ion batteries</td>
</tr>
<tr>
<td>Li-S batteries</td>
<td>Lithium sulfur batteries</td>
</tr>
<tr>
<td>Li-metal batteries</td>
<td>LMBs</td>
</tr>
<tr>
<td>LE</td>
<td>Liquid electrolyte</td>
</tr>
<tr>
<td>LFP</td>
<td>LiFePO$_4$</td>
</tr>
<tr>
<td>MLD</td>
<td>Molecular layer deposition</td>
</tr>
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<td>NCNTs</td>
<td>Nitrogen doped carbon nanotubes</td>
</tr>
<tr>
<td>NMBs</td>
<td>Na-metal batteries</td>
</tr>
<tr>
<td>NIBs</td>
<td>Na ion batteries</td>
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<td>NaPS</td>
<td>Na$_3$PS$_4$</td>
</tr>
<tr>
<td>PC</td>
<td>Propylene carbonate</td>
</tr>
<tr>
<td>PVDF</td>
<td>Poly(vinylidene fluoride)</td>
</tr>
<tr>
<td>PVP</td>
<td>Polyvinylpyrrolidone</td>
</tr>
<tr>
<td>RT</td>
<td>Room temperature</td>
</tr>
<tr>
<td>RBS</td>
<td>Rutherford Backscattering Spectrometry</td>
</tr>
<tr>
<td>SEI</td>
<td>Solid electrolyte interphase</td>
</tr>
<tr>
<td>SSEs</td>
<td>Solid-state electrolytes (SSEs)</td>
</tr>
<tr>
<td>SSNMBs</td>
<td>Solid-sate Na metal batteries</td>
</tr>
<tr>
<td>TMA</td>
<td>Trimethylaluminum</td>
</tr>
<tr>
<td>TOF-SIMS</td>
<td>Time-of-flight secondary ion mass spectrometry</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>--------------</td>
<td>--------------------------------------</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>XRR</td>
<td>X-ray reflectometry</td>
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Chapter 1

1 Introduction

1.1 Li metal anode and Na metal anodes

In the past decades, Li-ion batteries (LIBs) have been developed as one of the most successful energy storage devices, particularly for portable electronic devices including mobile phones, laptops and medical microelectronic devices. They have many outstanding features, including high energy density, no memory effect, low maintenance, and little self-discharge. Great efforts have been attempted to further improve the energy density of conventional LIBs. However, the current LIB systems have almost reached a bottleneck with an energy density of 300 Wh Kg\(^{-1}\), which cannot meet the increasing demand of future energy storage devices. In this case, exploring high energy density next-generation batteries systems is urgently required. Li-metal batteries (LMBs), including Li-S batteries, Li-O\(_2\) batteries, and all-solid-state LMBs have received significant attention due to their high theoretical energy densities (2600 Wh Kg\(^{-1}\) for Li-S and 11680 Wh Kg\(^{-1}\) for Li-air).

Furthermore, Li is not regarded as an abundant element in the Earth’s crust, resulting in low availability, high price of Li resources, and increasing prices of LIBs and LIBs, which is not suitable for large scale energy storage devices. To overcome these challenges, Na-metal batteries (NMBs) are considered as great candidates for large scale energy storage systems due to the high abundance, low cost, and suitable redox potential of Na. The earlier studies on high temperature Na-S and Na/NiCl\(_2\) systems have been successfully commercialized, however, the high operating temperature of 300 °C and corrosion issues limit their further application. More recently, other NMBs systems, including room temperature Na-S, Na-O\(_2\), Na-CO\(_2\), and solid-state Na metal batteries have been developed with high energy density.

To achieve high performance LMBs and NMBs, one of the key factors is the Li and Na metal anodes. It should also be noted that the high theoretical specific energy densities of
LMBs and NMBs mentioned above (such as Li/Na-S, Li/Na-O₂ et al) are calculated based on using metallic Li and Na as the anode electrodes. Li metal is an ideal material to achieve high energy density for LMBs with a high specific capacity (3860 mAh g⁻¹), lowest potential (-3.04 V vs. the standard hydrogen electrode) and light weight (0.53 g cm⁻³). Meanwhile, Na metal is the ultimate choice among other anode candidates for NMBs with a high theoretical capacity (1166 mAh g⁻¹) and low electrochemical potential. In this case, the stable performances of the Li and Na metal anodes play the most important roles in the development of high performance LMBs and NMBs.

1.2 Challenges for metallic Li and Na anodes

The Li metal anode has been studied over the past 40 years since the beginning of Li batteries. However, it suffers from serious safety issues which have hindered the development of the Li metal anode for LMBs. The major challenges and issues of the Li metal anode can be summarized as follows:

i) Li dendrite growth

Dendritic deposition of a metal is a common occurrence under high current density during the electrochemical deposition process. Li dendrites have also been widely observed in many studies. Different from other high-redox-potential metals, the mechanism of Li dendrite is more complex due to the interfacial chemistry and reactions at low-redox-potential. Various nucleation models, dendrite growth rate, growth patterns, and influencing factors have been comprehensively proposed and summarized in previous reviews. Generally, the Li dendrite growth is considered as a self-enhanced process. In one theory, the dendrite with high curvature will tend to attract more Li ions during electrochemical plating due to the higher electric fields, which results in the continuous growth of Li dendrites. In another theory, the hemispherical tips of protrusions enable the 3D Li ion diffusion leading to the faster Li electrochemical deposition on the tips, further resulting in Li dendrite growth propagation.

The serious Li dendrite growth will lead to various issues. 1) the sharp and long Li dendrites can penetrate the separator and reach to the cathode side, causing the inner
short circuit of the cells. The short circuits may be accompanied by thermal runaway and may cause fire or explosions. 2) dendrite formation with an increased surface area will result in an increase of side reactions between Li metal and electrolyte, continually consuming of both components.

ii) Solid electrolyte interphase (SEI) layers

Solid electrolyte interphase (SEI) has become a critical component of the battery research. The SEI layer on the Li metal anode is formed by the reduction of the liquid electrolyte. The naturally formed SEI layer on Li metal can prevent further side reactions between the liquid electrolyte and electrode, leading to the long-term stable operation of batteries. However, the unstable SEI layer with non-uniform Li\(^+\) flux distribution can easily cause dendrite growth. Furthermore, the collapse of the SEI film can aggravate local dendrite growth and undesired electrolyte decomposition due to non-homogeneous local current buildup. Meanwhile, electrochemically inert “dead Li” layer formation is another issue due to the Li dendrite detached from the bulk Li surface or current collector. This “dead Li” layer will decrease the Coulombic efficiencies (CEs) and increase the diffusion pathway and resistance of Li ions and electrons, resulting in a large polarization and unsatisfactory energy efficiency.

iii) Large volume change

The volume change of the electrode materials is determined by the ratio between Li and host atoms. For example, the volume change of graphite and Si are 10 % and 400 %, respectively. Due to the “hostless” nature of Li metal, the volume change of it is infinite, which will significantly affect the performances of the cells. Moreover, the “dead Li” with porous structure will further aggravate the large volume change during the Li plating/stripping process.

As an alkali metal, Na metal faces similar problems and challenges during electrochemical cycling. It also can be simply classified as: i) Na dendrite formation and short circuits; ii) unstable SEI formation, low CE and poor cycling performance; iii) Infinite volume changes. Moreover, due to the different chemical, physical and
mechanical properties between Li and Na metal, the Na dendrite and its SEI layer differ slightly from their Li counterparts. Generally, Na dendrites and their related SEI layers are more sensitive to the electrolyte and external environments. In this case, achieving a stable SEI layer and reducing Na dendrite growth will be more challenging compared to the problems associated with Li metal anodes. The detailed discussion will be present in Chapter 2.

1.3 Thesis objectives

In the recent five years, with the fast development of novel techniques and nanomaterials, researchers have attempted to realize this “holy grail” of Li metal and Na metal anodes with different strategies. In order to achieve improved Li and Na metal anodes performances, the authors have devoted significant time to develop different approaches to stabilize both Li and Na metal anodes in terms of the different major challenges listed above. The main research objectives are list below:

Part.1 Different approaches for the stabilization of Li metal anodes

i) To develop both atomic layer deposition (ALD) of Al₂O₃ and molecular layer deposition (MLD) of alucone coating films to stabilize the SEI layer of the Li metal anode. The effects of coating types, thicknesses, electrolytes and understanding of surface/interface chemistry will be established.

ii) To develop conductive carbon paper (CP) interlayer as the host for Li metal anode. The influence of CP layers on the deposited Li morphologies and electrochemical performances will be investigated.

iii) To develop 3D interlayer with N-doped carbon nanotubes for Li metal anode. The effects of surface areas on the electrochemical performances will be demonstrated. Minimum volume change and dendrite-free Li deposition are expected to be achieved.

Part.2 Different strategies for the stabilization of Na metal anodes

iv) To develop both atomic layer deposition (ALD) of Al₂O₃ and molecular layer deposition (MLD) of alucone coating films to stabilize the SEI layer of the Na metal
anode. The influence of coating types, thicknesses, electrolytes and understanding of surface/interface chemistry will be investigated.

v) To develop solid-state electrolyte Na$_3$PS$_4$ (NaPS) as a protective layer for Na metal anode via an in-situ solution-based method. The thickness of NaPS layer will be controlled by adjusting the parameters during the reactions. The thickness effects and surface/interface chemistry change will be discussed in detail.

vi) To develop a 3D carbon host for Na metal anode with minimum volume change and dendrite-free structures. The Na wettability, electrochemical performances and Na deposition morphologies will be investigated.

1.4 Thesis organizations

This thesis consists of 11 chapters (three introductory chapters, seven articles, and one conclusive chapter) and is organized according to the requirements on “Integrated-Article” form as outlined in the Thesis Regulation Guide by the School of Graduate and Postdoctoral Studies (SGPS) of the University of Western Ontario. It includes the following parts specifically.

Chapter 1 gives a brief introduction of Li metal and Na metal anodes and their challenges. Furthermore, the research objectives and the thesis structure are also stated.

Chapter 2 reviews the recent development of Li and Na metal anodes from the fundamental understanding to the various approaches for stabilization. Then, the powerful tools of ALD and MLD and their applications in LIBs are introduced in detail.

Chapter 3 outlines the experimental synthetic approaches of ALD, MLD, CVD and solution-based method, and characterizations techniques applied to characterize the chemical/physical and electrochemical properties of materials and batteries.

Chapter 4 presents the study using atomic layer deposition (ALD) of Al$_2$O$_3$ and molecular layer deposition (MLD) of alucone as protective layer for Li metal anode. Different thicknesses of Al$_2$O$_3$ and alucone are deposited on Li metal anode for
optimization. The surface chemistry and morphology change after cycling are further discussed.

**Chapter 5** demonstrates an effective and universal approach using conductive CP as an interlayer for Li metal anode. The different layers of CP are investigated to meeting the requirements of different capacities.

**Chapter 6** reports a 3D interlayer using the CP with N doped carbon nanotubes (NCNTs). The surface areas of interlayer increases with the longer CVD time for NCNTs grown. Moreover, the surface areas affect the electrochemical performances of composite electrodes. The long life time with high capacity at high current density Li electrode is achieved with minimum volume change and dendrite-free Li deposition.

**Chapter 7** explores the ALD Al₂O₃ as protective coating for Na metal anode in ether-based electrolytes. By protecting Na foil with ultrathin Al₂O₃ layer, the dendrites and mossy Na formation have been effectively suppressed and lifetime has been significantly improved. Furthermore, the thickness of protective layer has been further optimized with 25 cycles of Al₂O₃ layer presenting the best performance for over 500 cycles.

**Chapter 8** demonstrates the inorganic-organic coating alucone coating via MLD for Na anode in carbonate-based electrolyte. By protecting Na anode with controllable alucone layer, the dendrites and mossy Na formation have been effectively suppressed and lifetime has been significantly improved. Moreover, the MLD alucone coating shows better performances than the ALD Al₂O₃ coating in carbonated-based electrolyte.

**Chapter 9** represents a facile and in-situ solution-based method to synthesize an artificial protective layer of solid-state electrolyte NaPS on the surface of Na metal. The thin amorphous NaPS layers on the surface of the Na metal will reduce parasitic side reactions with electrolyte components, increase the homogeneity of the SEI layer and improve the Na⁺ flux to the surface. Meanwhile, the ionically conductive NaPS can eliminate the strong electric field buildup at the surface, resulting in a more homogeneous Na plating/stripping process with suppressed Na dendrite growth.
Chapter 10 fulfills the 3D Na composite electrode using CP-NCNTs as host via the thermal infusion method. As-prepared Na@CP-NCNTs exhibited stable electrochemical plating/stripping performance in symmetrical cells with high capacity at high current density. The 3D skeleton structure was observed to be intact following electrochemical cycling with minimum volume change and dendrite-free in nature.

Chapter 11 summarizes the results, conclusions and contributions of the thesis work. Furthermore, the author states some personal opinions, perspective, and suggestions for future developments of Li and Na metal anodes as well as LMBs and NMBs.
Chapter 2

2 Literature review*

In this chapter, a comprehensive and detailed literature review on the recent developments of Li metal anode, Na metal anode and atomic layer deposition/molecular layer deposition for batteries application are present.

*Parts of this chapter have been published in ACS Energy Letters, 2018, 3, 899–914; Energy & Environmental Science, 2018, 10.1039/C8EE01373J and submitted to Joule
2.1 Li-ion batteries and Li-metal batteries

Over the past decades, the global energy shortage related to the consumption of fossil fuels has become a major concern leading to the demand for alternative clean energy sources\textsuperscript{1-2}. The energy conversion techniques such as wind and solar generated electricity have been thoroughly explored to maximize energy generation. However, they usually provide intermittent energy, which requires highly effective energy storage systems. Rechargeable Li-ion batteries (LIBs) have been developed and are one of the most promising energy storage systems, particularly for portable electronic devices such as laptops, mobile phones, medical microelectronic devices, and even electrical vehicles (EVs). They have many outstanding features, including high energy density, no memory effect, low maintenance, and little self-discharge\textsuperscript{3-6}. The demanding requirements of portable electronic devices has stretched the limits of LIBs, which are currently the predominant choice for energy storage. The global EVs market is also quickly growing, in which the sales of EVs has increased by fifteen times in the past five years \textsuperscript{7}. Moreover, the energy density of current LIBs has already reached to their limitation of 300 Wh Kg\textsuperscript{-1}, which cannot meet the increasing demand of high energy density energy storage device. As the next generation batteries, Li-metal batteries (LMBs), including Li-S, Li-air, and all solid-state LMBs, have received numerous attention due to the high theoretical energy density (2600 Wh Kg\textsuperscript{-1} for Li-S and 11680 Wh Kg\textsuperscript{-1} for Li-air). For all these LMBs, Li metal is an ideal materials to achieve the high energy density due to the high specific capacity (3860 mAh g\textsuperscript{-1}), low potential (-3.04 V vs. the standard hydrogen electrode) and light weight (0.53 g cm\textsuperscript{3}) \textsuperscript{8-11}.

2.1.1 Li metal anode and its challenge

Although Li metal with unique properties are promising for next generation LMBs, utilizing Li-metal anodes have not been successful commercial applied with over 40 years efforts \textsuperscript{12}. There are several issues to hinder the development of Li metal anode for LMBs.

i) Li dendrite growth
During the electrochemical deposition/plating process, dendritic deposition is a common occurred for metal (like Zn, Cu, Ni, et al) under high current density. Li dendrite has also been widely observed in the different studied. Different from other high-redox-potential metals, the mechanism of Li dendrite is more complex due to the interfacial chemistry and reactions at low-redox-potential. Various nucleation models, dendrite growth rate, growth patterns, and influencing factors have been comprehensively proposed and summarized in the excellent reviews \(^{13}\). Generally, the Li dendrite growth is considered as the self-enhanced process. In one theory, the dendrite with high curvature will tend to attract more Li ions during electrochemical plating due to the higher electric fields, which resulting the continuously growth of Li dendrite. In another theory, the hemispherical tips of protrusions enable the 3D Li ion diffusion leading to the faster Li electrochemical deposition on the tips, further resulting the Li dendrite growth \(^{14}\).

The serious Li dendrite growth will lead to various issues. Firstly, the sharp and long Li dendrite can penetrate the separator and reach to the cathode side, causing the inner short circuit of the cells. The short circuits accompany thermal runaway and may cause fire or explosion. Secondly, the dendrite formation with an increased surface area will render the increasing side reaction between Li metal anode electrolyte. It will cause the continually consuming of both Li metal and electrolyte.

ii) Solid electrolyte interphase (SEI) layers

Solid electrolyte interphase (SEI) has become a critical component of the battery research. The SEI layer on the Li metal anode is formed by the reduction of the liquid electrolyte with the ion-conduction and electron-blocking capability \(^{[7]}\). The generated SEI layer on Li metal can prevent further reaction between the electrolyte and electrode, leading to the long-term stable operation of batteries. It is considered that the unstable SEI layer is much easier to cause dendrite growth, in which the collapse of the SEI film can aggravate local dendrite growth and undesired electrolyte deposition due to non-homogeneous local current buildup. Meanwhile, electrochemically inert dead Li layer formation is another issue due to the Li dendrite dropped from the bulk Li surface or current collector. This dead Li layer will decrease the Coulombic efficiencies (CEs) and
increase the increased diffusion pathway and huge resistance of Li ions and electrons, resulting a large polarization and unsatisfactory energy efficiency. Moreover, the ideal SEI on Li metal is considered to be homogeneous in composition, morphology and ionic conductivity as well as with good flexibility.

iii) Large volume change

The volume change of the electrode materials is determined by the ratio between Li atom and host atom. For example, the volume change of graphite and Si are 10 % and 400 %, respectively. Due to the “hostless” nature of Li metal, the volume change of it is infinite, which will significantly affect the performances of the cells. Moreover, the porous Li deposition will make this issue much harsher, promoting more volume increase and decrease during Li plating/stripping process.

Based on the above discussion, in order to achieve high performances Li metal anode, strategies for reducing dendrite growth, stabilizing SEI formation and limiting volume change are urgent to be developed. In the recent years, this area is quickly explored and a lot of approach have been reported. In the next section, the recent progress on the protection of the Li metal anode will be summarized in detail.
2.1.2 Strategies for Li metal anode

2.1.2.1 Protective coating for Li metal anode

Figure 2.1 (a) Schematic diagrams of the different Li anode structures. A thin film of SEI layer forms quickly on the surface of deposited Li (blue). SEM images of Li deposition on a Cu substrate with and without carbon nanosphere modification\textsuperscript{15}. (b) Schematic diagrams of lithium deposition of h-BN film on Cu substrate. Morphology studies of Li metal deposition on bare Cu substrate and h-BN film\textsuperscript{16}. (c) ALD Al\textsubscript{2}O\textsubscript{3} as protective layer for Li metal anode in Li-S batteries and symmetric Li-Li cells\textsuperscript{17-18}.

Artificial SEI fabrication is one of the most effective and popular approach to achieve the stable interface and reduce Li dendrite growth. In the reported literature, different surface modifications are used to create artificial SEI layer on Li metal anode. Some organic coating layers, like macromolecules or polymer, are firstly studied for fabrication of protective layer for Li metal\textsuperscript{19-20}. For example, chlorosilanes vapors is used to reacted with Li foil results in a thin layer consisting of LiCl and lithium alkyl silanolate derivatives that are both protective and ionic conducting\textsuperscript{21}. The protected Li indicates improved thermal stability and smaller initial interfacial impedance. Another study demonstrates similar tetraethoxysilane (TEOS) as precursor leading to a silicate film which effectively stabilizes the lithium surface\textsuperscript{22}. More recently, Susanna et al reports a dip-coating approach to generate protective Fp-silane-derived coatings by direct reaction.
with the surface of Li metal. They attempted three type of Fp-silane, including FpSiMe₃, FpSiPh₃, FpSiMe₂H, with discriminating stability, in which the best compromise was obtained for lithium electrodes dip-coated for 10 min with FpSiPh₃-derived coatings. Based on their study, it is considered that a more stable secondary SEI will be formed due to the physical barrier imposed by the coating between bare lithium and the electrolyte resulting the enhancement of cycle life and stability. The Si based macromolecules shows great potential as precursors for manufacture of protective coating via quite simple ways with improved performances and reduced interfacial impedance. Meanwhile, the optimized coating thickness is one of the key factors for this kind of coating layers. Furthermore, electron-rich function groups is expected to be introduced using different precursors which can offer enhanced conductance compared with methyl-substituted silanes or to the redox-formed compounds of the primary SEI.

Conductive polymer, including polyaniline (PANI), polypyrrole (PPy), poly(3,4-ethylenedioxythiophene) (PEDOT), have been proved to improve the performance for LIBs and Li-S batteries. So, it shows great interests to investigate both electronic and ion conductive polymer as a protection layer for Li metal. Copolymer of PEDOT-co-poly(ethylene glycol) (PEDOT-co-PEG) has been firstly developed for prevent dendrite formation and Li protection. It is a very rational design that this kind of co-polymer includes the electronic conductive part of PEDOT and high ion-conductive polymer of PEG which transports Li ion across the protective layers. Another significant point is the promising mechanically suppressing of Li dendrite growth due to the relative flexible properties of polymer based materials. As a result, the surface morphology of the Li anode with and without the protective layer after 100 cycles indicates obvious difference. The surface of the pristine lithium anode is loosely packed, suggesting serious dendrite growth and corrosion reaction. The protected Li anode shows a relatively smoother and denser surface morphology than the non-protected one. When applied it in Li-S system, the cycle performance and coulombic efficiency of co-polymer coated Li indicates 40 % enhancement compared with uncoated Li, maintaining a high capacity of 875.6 mA h g⁻¹ at 0.2 C after 200 cycles. Very recently, Bucur et al design a novel type of SEI polymer membrane layer containing a pH sensitive interface with the substrate. This type of novel structure can have a dramatic effect on the interface governing the coulombic
efficiency and morphology of lithium depositing. In this case, conductive polymer, especially co-polymer including electronic and ion conductive polymer show great interests as protective coating materials for Li metal.

Except 2D polymer film, the 3D oxidized polyacrylonitrile (PAN) nanofiber layer are demonstrated on top of the current collector by a single-nozzle electrospinning method. After direct deposition of Li on the top of pure Cu foil, it shows a non-uniform structure with long Li filaments on the surface, in which the dendrites with a diameter of ~2 μm can be clearly observed. In contrast, with modification of PAN fibers, Li displays the flat and uniform depositions embedding inside the polymers and fill in the opening spaces among the fiber frames. It indicates that PAN fiber coated electrodes presents a more stable electrochemical cycling performance and longer lifetime. The advantages of PAN nanofibers can firstly be attributed to the polar functional groups on the polymers, which serves as the adhesion sites to bind with Li ions facilitating a relatively homogeneous Li ionic flux. In addition, the oxidized PAN exhibits excellent chemical stability toward electrochemical cycling.

Carbon based film are usually used as a protective layers in tribological, mechanical, electrical and optical applications with chemical inertness and high hardness. Carbon film, such as diamond-like carbon film, are proposed as protective coating for Li metal anode with highly improved performances and reduced dendrite formation. Cui’s group demonstrated another 3D interconnected hollow carbon nanospheres as protective layer on the substrate for Li depositions. The coulombic efficiency of modified Cu electrode is maintained at 99% for more than 150 cycles at 0.25 mA cm⁻² and 98.5% at 0.5 mA cm⁻² compared with rapidly drops of pure Cu electrode. Even at a high current density of 1 mA cm⁻², the modified electrode still maintains the coulombic efficiency of 97.5% for more than 150 cycles. Meanwhile, the SEM images after Li deposition also show dendrite-free structure with interconnected hollow carbon nanospheres coating layer, as shown in Figure 2.1(a). Subsequently, their group reported the hexagonal boron nitride (h-BN) as protective layer on Cu current collectors, as shown in Figure 2.1(b). Li ion can penetrate through the defects of h-BN and be deposited between the ultrathin h-BN and Cu substrate. Smooth Li metal deposition without
dendritic and mossy Li formation was realized, resulting the improve the CEs during electrochemical plating/stripping process.

Li$_3$N with high ionic conductivity and electronic insulativity is considered as promising SEI components for Li metal anode. Meanwhile, Li$_3$N can be easily obtained by reaction of Li and N$_2$ $^{36-38}$. Li$_3$N with polycrystalline has an exceptionally high ionic conductivity ($\sim$10$^{-3}$ S cm$^{-1}$) with potential application as a solid state electrolyte in LIBs $^{38}$. Li$_3$N also can prevent the side reaction between the lithium and the liquid electrolyte, promoting a stable SEI. For example, Wen’s group demonstrates Li$_3$N films coated on Li foil for both Li deposition/dissolution and Li-S batteries $^{37-38}$. It shows a highly improved Li cycling efficiency with 1 h N$_2$ exposing times when using for Li deposition/dissolution. For Li-S battery, Li$_3$N protected Li anode remains as high as 956.6 mA h g$^{-1}$ at 0.2 C with a capacity retention of 79.7% after 200 cycles, while the primitive Li anode shows a capacity of 452.2 mA h g$^{-1}$ under the same testing condition.

Al$_2$O$_3$ as one of most widely studied metal oxide is an electrochemically inactive and ceramic material with a low cost and natural abundance. Al$_2$O$_3$ coating layer has already been applied on different types of batteries. Gao’s group firstly applied a porous Al$_2$O$_3$ layer fabricating on the surface of Li metal anode by using a spin-coating method as protective layer for lithium–sulfur battery $^{39}$. The sulfur cathode with Al$_2$O$_3$ coated lithium anode exhibits improved electrochemical performance, accompanied simultaneously with relatively homogeneous lithium deposition on the anode surface due to the even distribution of Li ion $^{39}$. Meanwhile, Al$_2$O$_3$ is one of the basic materials in the area of atomic layer deposition (ALD). ALD is a thin film deposition technique which is based on the sequential use of self-limiting gas-solid reactions, which will be introduced in the following section in detail $^{40}$. ALD technique has exclusive advantages of extremely uniform and controllable deposition and low deposition temperature $^{41}$, which has been widely studied as surface coating and modification approach for alleviating side reactions and improving the electrochemical performances and even thermal stability of electrode materials both for anodes and cathodes $^{40,42-43}$. Recently, this novel type of thin film is firstly applied as protective layer for Li metal by Alexander et al $^{44}$. They demonstrate a controllable of 14 nm thick ALD Al$_2$O$_3$ layer on Li foil, which can Li ion
transportation and prevent Li metal anode corrosion (Schematic diagram in Figure 2.1(c)). The atmospheric corrosion shows longer life time of ALD Al₂O₃-protected Li compared with Li foil. When using this concept in Li-S system, the ALD Al₂O₃ protection layer increased both initial and long-term capacity of the cell via improved utilization of the sulfur by preventing Li metal anode corrosion and thus enabling cycling with enhanced capacity for up to 100 charge discharge cycles. After that, another study with similar design focus on the Li dendrite prevention process in symmetric Li-Li cells. In their research, different cycles of ALD Al₂O₃ layer with different thickness have been performed, in which 20 ALD cycle with ultrathin ~2 nm limits the onset of dendrite growth and electrolyte decomposition during cycling, which improves lifetime by over 80% (Figure 2.1(c)). Meanwhile, from the morphology of the electrodes after cycling, a remarkably smooth surface of Li foil can be observed compared with extreme surface roughness and porosity of pure Li foil. ALD technique shows great potential for modifying the surface of Li for prevention of corrosion and Li dendrite with improving electrochemical performances in special battery system. However, there is a few report using ALD to deposit protective layers for Li metal anode. More types of coating film on Li metal by ALD are expected with rational design. Firstly, the deposited film should be ion conductive with Li ion or it can react with Li forming ion conducting composites. In this case, solid state electrolyte developed (SSE) by ALD is one of the idea coating film for Li protection. However, the deposition temperature of SSE by ALD is still not low enough related to the milt point of Li metal. Secondly, the film is proposed to form passivating surface when it contact with electrolytes, which can further inhibit decomposition of electrolyte after the initial electrochemical process. The stable SEI film and coating layer can effectively protect Li foil without corrosion of electrolyte, water or air in different kinds of Li-metal batteries.

To combine the advantages of organic and inorganic coating, composite protective layer (CPL) is created for the protection of Li metal. The organic part includes polyers like polyvinylidene fluoride-hexafluoro propylene, PEO, and PVdF-HFP copolymer, and inorganic part consists of metal oxide like Al₂O₃. For example, Kim’s group design the CPL coating composed of Al₂O₃ particles that providing sufficient mechanical strength to suppress the dendrite growth and PVdF-HFP copolymer, which imparts fast Li ion
transport through forming a gel polymer electrolyte with liquid electrolytes. With the introduction of the CPL, the Li dendrite growth and electrolyte decomposition are effectively kept down even at high current densities up to 10 mA cm\(^{-2}\). Testing in LiCoO\(_2\)/Li cell, CPL coated electrode exhibits excellent cycling stability up to 400 cycles at 1 mA cm\(^{-2}\). In addition to solve the problem of incomplete decomposition of Li\(_2\)O\(_2\) at the cathode in Li-O\(_2\) battery, their group further develops 2,2,6,6,-tetramethylpiperidinyl-1-oxyl (TEMPO) as a redox mediator (RM) material and Al\(_2\)O\(_3\)/PVdF-HFP composite as a CPL. The RM can acts as an electron hole transfer agent, which can facilitate the oxidation of insulating solid Li\(_2\)O\(_2\). The CPL coated Li metal electrode is able to suppress the reaction of TEMPO at the Li electrode and extend the RM Li\(_2\)O\(_2\) oxidation over many cycles.

In this part, we summarize the different protective coating layer developed recently on Li metal or other electrodes, including organic, inorganic or the composites. The idea coating structure is considered to include the follow features: 1) the protective layer is expected to have high electronic and ionic conductivity which allow Li ion fast transported through the layers. 2) During the Li deposition process, the volume change is a serious issue that requires flexible and self-healing to accommodate it and impede electrolyte decomposition therefore enhancing coulombic efficiencies. 3) The adhesion sites or free space on films or 3D structure can bind with Li ions facilitating a relatively homogeneous Li formation. In other words, it is important to control the flow of Li ions with the SEI in homogeneities preventing the formation of Li dendrite. 4) The protective coating should be mechanically strong and chemically stable.
2.1.2.2 3D Lithium design

**Figure 2.2** (a) Schematic of the material design and the consequent synthetic procedures from a GO film to a sparked rGO film to a layered Li–rGO composite film. Galvanostatic cycling of a symmetric Li–rGO electrode (blue) and bare Li foil (red) at different current density\(^{40}\). (b) Schematic of the fabrication of the Li-coated PI matrix. Electrochemical characterization in EC/DEC electrolyte\(^{50}\).

One of the key issue for Li metal anode is the serious volume change during electrochemical plating/stripping. Thus, the rational design of 3D host for Li metal is another novel approach to solve this problems. In this case, the 3D pores structures can provide spaces for lithium plating and stripping and inhibit the large volume change of Li metal. Meanwhile, the electrolyte can easily permeate through the pore structure. Recently, Zhang and Guo et al give a detailed summary on the advanced micro/nanostructures for lithium metal anodes\(^{51}\). They reviewed the recent understanding and development of design and realize of different micro/nanostructure for Li metal.
anode, including conductive and non-conductive micro/nanostructure framework and micro/nanostructure solid electrolyte interphase.

For pushing this strategy of 3D host for Li metal anode, Cui’s group put great efforts on this direction. They firstly demonstrated the thermal infusion as a prominent approach to successfully achieve molten Li into lithiophilicity 3D host. One of their typical work was using layered Li-reduced graphene oxide (rGO) electrode via molten Li into rGO film with uniform nanogaps (Shown in Figure 2.2(a)). It is found layered rGO offers a stable scaffold for Li stripping/plating, which significantly mitigates the volume change at the electrode level during cycling. Meanwhile, the excellent lithiophilicity of rGO guarantees uniform Li infusion and deposition and also provides an electrochemically and mechanically stable artificial interface \(^{49}\). As a result, as prepared layered Li-rGO films show highly enhanced electrochemical performances and much longer life time. Cui’s group further introduce a “lithiophilic” coating of Si on the 3D porous carbon matrix to achieve a stable lithium–scaffold composite electrode. The resulting composite electrode possesses a high conductive surface area and excellent structural stability upon galvanostatic cycling. It is also showed stable cycling of this composite electrode with small Li plating/stripping overpotential (< 90 mV) at a high current density of 3 mA cm\(^{-2}\) over 80 cycles\(^{52}\).

Another typical work from Cui’s group is a freestanding and porous metallic lithium anode by infusing molten lithium into a core-shell polyimide(PI)-ZnO matrix (shown in Figure 2.2 (b))\(^{50}\). The polymeric backbone enables uniform lithium stripping/plating, which successfully confines lithium within the matrix, realizing minimum volume change and effective dendrite suppression. The porous electrode reduces the effective current density; thus, flat voltage profiles and stable cycling of more than 100 cycles is achieved even at a high current density of 5 mA cm\(^{-2}\) in both carbonate and ether electrolyte.
2.1.2.3 Other approach

**Figure 2.3** (a) Illustration of the proposed electrochemical deposition processes of Li metal on planar current collector and 3D current collector. Electrochemical performance of planar Cu and 3D Cu current collector\(^5\). (b) Schematic diagram of polydopamine-treated separator and SEM images of Li metal deposition employing polydopamine-treated separator and other separators\(^4\).

Different electrodes, including substrates and current collectors, are one of key components of Li anode, which also have the significant impact for prevention of dendrite. In the initial period of Li plating, the nucleation of Li can be effected by non-uniform distribution of local current density due to the consistent and structure of electrodes, which further determine the morphology of the subsequently plated Li. L. Gireaud et al demonstrated the lithium deposits morphologies on various lithium surface states indicating that the Li dendritic deposits grow preferentially on metal imperfections such as on the electrochemical stripping fingerprints, which locally enhance the current density (current focalization), leading to dendritic growth from these specific domains\(^5\). On the contrary, smooth and rough surfaces imply a homogeneous current density distribution all over the lithium surface leading to dendritic-free mossy lithium deposits.

One approach is to increase the surface areas of substrate simply lowering the deposition/stripping current density. Li powder is considered as the alternative anode materials to Li foil due to the higher surface area\(^6\). Kim et al discussed the dissolution
and deposition behaviour in lithium powder electrode in detail. The dissolution of the lithium powder electrode occurred uniformly in the whole electrode during discharge process, and at low current density, deposition occurred to sustain the initial powder shape during successive charging. In the case of the lithium foil electrode, lithium ions were firstly deposited at scattered pits by means of operating kink site, and then repeatedly grew with a spiral shape, resulting in the production of lithium dendrite. On the other hand, in the case of the lithium powder electrode, lithium ions were uniformly deposited in the depressed parts of the individual powder particle and, therefore, the lithium dendritic growth was remarkably suppressed. Recently, the coated Li powder was introduced to compare with Li foil with respect to cycling stability, coulombic efficiency of lithium stripping/plating, over potential, and morphology changes during cycling. They also can achieve very good properties that there is no dendrite formation for the coated Li powder at low current density even after 100 cycles. Furthermore, the combined effects of current density and total amount of discharge on the formation of dendrites on lithium powder electrodes were examined. It is found that with increasing current density, the amount of discharge needed to guarantee no dendrite formation increases and then decreases; that is, there is a maximum point in the curve. Thus, using Li powder replace of Li foil with increasing surface areas can be an effective way for reducing dendrite formation at low current density. However, it is still a challenge to prevent dendrite on Li powder at high current density. In another research, graphene nanosheets with relative high surface area was applied in term of reducing the current density, thereby dramatically prolonging the dendrite initiation time and decreasing the growth rate of a dendrite, if ever initiated, possibly by a factor of up to $10^{10}$ and $10^5$, respectively.

In principle, the types of substrates also have important influences on the morphologies of the resultant metal deposits. The competitive relationship between crystal nucleation and nucleus growth can be determined by the interaction between the surface atoms of a substrate and the ions to be deposited. Yang et al proposed the “competitive kinetics model” as a novel mechanistic model to explain the electrodeposition of Li$^+$ on general substrates M (except Li) based on the electrochemical kinetic principles. When Li$^+$ is electrodeposited on substrate, two types of interactions occur: interaction between Li$^+$
and surface atoms and interaction between Li$^+$ and Li metal atoms already deposited on the surface of the substrate. Li deposition on the substrate is favorable if the former interaction is stronger than the latter. Therefore, extensive nucleation occurs prior to nucleus growth until the surface of the substrate has been fully covered by the deposited nuclei, which condition benefits uniform deposition. By contrast, if the latter interaction is stronger than the former, the dominant reaction is soon changed to nucleus growth after some Li nucleus have formed on the substrate surface, and this condition is more conducive to dendrite formation $^{61-62}$. Therefore, adjusting the interaction between Li$^+$ and substrate atoms is an effective way to improve Li deposition and stripping. In this case, they developed two types of alloys of Li–Zn and Li$_{22}$Sn$_5$ as substrates compared with Cu disk $^{61,63}$. For example., the interactions between Li+ and the surface atoms of the Li–Zn alloy are obviously different from those on single Zn metal and Li metal substrates because of the inter-constraint between Li and Zn atoms on the alloy surface. As a result, this substrate not only adjusts the Li deposition and stripping kinetics but also changes the reaction mechanism between the freshly deposited Li atoms with the electrolyte. The efficiency of Li deposition/stripping on the Li–Zn alloy substrate remains high at 96.7% after 400 cycles at a current density of 0.1 mA cm$^{-2}$ and 250 cycles at the current density of 0.2 mA cm$^{-2}$.

Some other design, like nanostructured graphene framework $^{64}$, porous graphene network $^{65}$, LiB fibrous structure $^{66}$ and carbon fiber paper $^{67}$ have been applied as dendrite-free current collector or substrate for Li metal battery. The specific structure can acts as a caged entrapment for lithium metal, facilitating extended cycling life, coulombic efficiency or battery performances due to the prevention of dendritic growth. 3D nanostructure is believed to be able to change the plating behaviour of Li metal. Guo et al reports 3D Cu current collector with a submicron skeleton and high electroactive surface area, which can significantly improve the electrochemical deposition behaviour of Li $^{53}$. For Cu foil (Figure 2.3(a)), Li is firstly form small Li dendrites as nucleation, which is a charge centre as the charges accumulate at sharp ends in the electric field with subsequent Li metal deposition to easily form dendrites. However, in the case of 3D Cu nanowire (Figure 2.3(a)), Li is expected to nucleate and grow on the submicron Cu fibres with nano-sized lumps, fill the pores of the 3D current collector, and eventually form a
relatively even Li surface. As the results, Li anode in the 3D current collector can run for 600 h without short circuit and exhibits low voltage hysteresis, which is much more stable than Cu foil.

Separator is one of the most important components in Li metal battery, which is directly bear on the safety issue of batteries. Generally, separator will be impaled when the sharp Li dendrites occur which further lead to the short circuit and other safety problems. The strategy is not only to enhance the properties and stability of separator itself, but also design for diminishing Li-dendrite growth. Along these lines, mussel-inspired polydopamine coated polyethylene (PE) separators have been developed by a simple dip-coating method \(^{54}\). In Figure 2.3(b), it indicates that catechol moieties attached to polydopamine backbones can be seen as adhesion site with extraordinarily strong adhesion causing much-stronger adhesive interactions between Li-metal electrodes and separators, relieving the local surface tension of the Li metal efficiently, which is associated with morphological changes during electrochemical deposition process \(^{54}\). (Figure 2.3(b)) shows the SEM images of the Li surfaces for all of the cells with different separators after first cycles and 20 cycles. It can be obviously seen that the features of the GPE and the bare PE on the surface look increasingly sharper and jagged. Compared with them, the polydopamine-treated-PE cells exhibit smooth surface like flat flakes, which spread uniformly over the entire surface. Furthermore, the cycle life indicates the huge improvements of polydopamine-treated one with GPE and PE separators. The uniform ionic flux prevents Li ions from reacting on the surface of the Li metal in a localized manner, which leads to the suppression of Li-dendrite growth\(^{54}\).

Some other coating layers also have been developed into separator for prevention of Li dendrite \(^{68}\). In one typical study, Hu’s group propose a novel boron nitride (BN) nanosheet coated separator for stable Li metal anodes \(^{69}\). Compared with pristine separator, BN-coated separator lead to uniform deposition/striping of Li due to the smaller total surface area of the initial deposited Li wires and a more homogeneous thermal distribution, decreasing the risk of dendritic Li growth and improving cycling performance. SEM images of Li deposition on Cu foil with pristine separator and BN-coated separator before and after cycling give the evidence for their design. It indicates
the similar phenomenon that the diameter of deposited Li wire becomes much larger when using BN-coated separator, resulting the enhanced coulombic efficiency and high stability especially in high current density even at 1.0 mA cm\(^2\). Another interesting work reported by Cui’s group, in which they developed a bifunctional separator offering a sensing terminal to achieve early detection of lithium dendrites inside batteries. The sensing terminal provides unique signals in form of a remarkable voltage change, indicating imminent penetration of Li dendrites through the separator. This demonstration is very promising of various batteries for enhanced safety and foreseeable dendrites formation.

In this part, we summarize some recent developments of modifying separator for prevention of Li dendrites and improving stability of Li metal. The same idea for coating layer for separator is to relieve the local surface tension and homogeneous thermal distribution of Li leading to the flat flakes or large of Li during the deposition process.

### 2.1.3 Conclusion and perspective

In this section, we summarized the recent achievement on protecting Li metal anodes by the design of protective coating, novel substrate and separators. The rational design of these three features can effectively enhance the electrochemical performance, including CE during Li deposition/dissolution or specific performances in Li-S or Li-air batteries system and reduce the Li dendrites formations. Firstly, the different coating layer, including organic, inorganic and the composites, which are expected to have high electronic and ionic conductivity which allow Li ion fast transported through the layers. It also should be flexible and self-healing to accommodate the serious volume change and impede electrolyte decomposition therefore enhancing coulombic efficiencies. The mechanically and chemically stability is also the important point to evaluate the properties of protective coating. Secondly, the surface area, component and structure of the substrate and current collector have the big influence effect on the dendrites grown during the Li electrochemical deposition process. In principle, the nucleation and local current density of on the surface of current collectors is the key factor for Li dendrites prevention. Thirdly, for separator design, relieving the local surface tension and
homogeneous thermal distribution of Li is the most useful way to the flat flakes or large of Li during the deposition process.

Li metal is an ideal anode for Li-metal batteries, including next generation batteries system, like Li-S and Li-air battery. In order to broaden the applications of Li anodes, more fundamental research are expected to be conducted to address the problems. One important direction still focus on development of new electrolytes (or additives), which can create more stable SEI layer with enough mechanical strength and flexibility. Another breakthrough may come from controllable modification of the surface coating layers. Many effective approaches have been proposed to develop protective structure. However, the thickness, density, ion conductivity etc of coating layer are still need to be explored for optimization. Furthermore, the mechanisms of protection for different coating structure are still not clear, which need further understanding for subsequently rational design of protective layers. For fabrication of protective layer, ALD shows it great potential due to extremely uniform and controllable deposition and low deposition temperature. As discussed above, solid state electrolyte with controllable thickness, high mechanical property and iconic conductive deposited by ALD will be an excellent choice for the protection of Li metal. Similar with polymer based coating structure, thin film prepared by MLD with conductive polymer and inorganic part would be another idea protective coating due to the flexible and self-healing properties. Although there are still many issues to be overcome, we are optimistic that Li metal will be used as an anode in Li metal batteries in the foreseeable future, enabling the next generation of power sources.

2.2 Na-ion and Na-metal batteries

Because of the high abundance, low cost, and suitable redox potential of Na metal($E_{Na^+/Na}$=−2.71 V vs standard hydrogen electrode), rechargeable Na batteries are considered to be ideal alternatives to LIBs. In the early stage, many studies focused on the high temperature rechargeable Na batteries such as Na-S and Na/NiCl$_2$ systems. These batteries have been commercialized as large scale energy storage systems, however, the high operating temperature of 300 °C and corrosion issues limit their further application. Following a similar mechanism to LIBs, Na ion batteries (NIBs) have been
developed consisting of Na insertion-type electrode materials, in which the Na$^+$ is transported through the liquid electrolyte\textsuperscript{73}. Different materials have been investigated as cathode materials for NIBs, including layered transition metal oxides (NaFeO$_2$, O3-Type Na[Fe$_{1/2}$Mn$_{1/2}$]O$_2$, P3-type Na$_x$CoO$_2$, et al.), polyanionic compounds (NaFePO$_4$, Na$_2$FeP$_2$O$_7$, Na$_3$V$_2$(PO$_4$)$_3$, et al.) and other miscellaneous Na insertion materials \textsuperscript{74-76}. As for the choice of anode materials, the typical graphite found in LIBs cannot be used due to it being less electrochemically active in Na$^+$ systems. In 2000, Dahn’s group firstly reported the electrochemical reversibility of Na$^+$ insertion into hard carbon at room temperature. The hard carbon displayed a capacity of 300 mAh g$^{-1}$, which is superior to that of graphite in Na batteries \textsuperscript{74, 77}. To further improve the capacities of the anode, different alloy materials (such as Sn, Bi, Sb, and P) have been developed using various approaches such as nanostructured or composite materials\textsuperscript{78-82}. Some excellent reviews have summarized the development and understanding of both cathode and anode materials for NIBs in detail \textsuperscript{74, 79, 83-86}. However, the energy densities of the NIBs using current cathode and anode materials are still insufficient and lower than that of commercial LIBs\textsuperscript{84}. In this case, the development of Na-metal batteries (NMBs) with high energy density and low cost are needed to meet the requirements for large scale energy storage systems.

One of the most promising categories of NMBs is the Na-S battery system, which offers a high theoretical capacity and high energy density of $\sim$1672 mAh g$^{-1}$ and 1230 Wh kg$^{-1}$ based on the final discharge products of Na$_2$S\textsuperscript{87}. As mentioned above, high-temperature Na-S batteries operating at 300 °C have been previously developed. The high operation temperature will decrease the energy efficiency of the device and may also cause corrosion in the system\textsuperscript{87}. Researchers are beginning to explore safer and more stable room temperature (RT) Na-S batteries with high energy density. However, the RT Na-S batteries suffer from low electrochemical utilization of the sulfur active material, capacity fading, polysulfide dissolution, and short life times \textsuperscript{87-88}. Efforts have been mainly focused on the design of cathode materials (such as sulfurized polyacrylonitrile, sulfur-carbonaceous composites and sodium polysulfide/sulfide composites) and modification of electrolyte and separators, which have been discussed in detail in a recent review \textsuperscript{88}. 
Another attractive NMB system is the Na-O₂ (or Na-air) battery, which also presents a high energy density of 1602 and 1105 Wh kg⁻¹ based on the discharge products of Na₂O₂ and NaO₂, respectively⁸⁹-⁹². Compared with Li-O₂ batteries, the Na-O₂ system has the advantage of superior energy efficiency due to a lower charging over-potential in the formation of Na₂O₂ discharge products ⁹³-⁹⁷. In 2011, Peled et al. reported the first example of Na-O₂ batteries working at a temperature above the melting point of Na, followed by Sun et al. who demonstrated the first rechargeable Na-O₂ batteries at room temperature in 2012⁹⁸. Since then, these battery systems have achieved growing interests, however, there are still several challenges that need to be addressed in order to obtain long life Na-O₂ batteries. Our previous review gave a comprehensive summary on the challenges in the Na-O₂ battery system, including the control of discharge products, formation of parasitic products, instability of electrolyte, contamination of Na anode and poor cycling life⁹⁸.

Beyond liquid-based NMBs, solid-state Na metal batteries (SSNMBs) have recently become a very hot topic due to their improved safety, high-energy densities, and high-power densities achieved by replacing the organic liquid electrolyte with solid-state electrolytes (SSEs)⁹⁹-¹⁰⁰. Different Na-based SSEs, including solid polymer electrolytes, oxide-based ceramic electrolytes, sulfide-based electrolytes and hybrid solid electrolytes have been developed with enhanced ionic conductivity at RT with good chemical/electrochemical stability⁹⁹, ¹⁰¹-¹⁰⁵. Meanwhile, carbon materials or alloys (such as Na-Sn alloy) have also been used as anode materials in conjunction with SSEs ¹⁰⁶-¹⁰⁷.

### 2.2.1 Na metal anodes

As discussed above, several types of NMBs, including RT Na-S batteries, Na-O₂ batteries and SSNMBs, deliver high theoretical energy densities and have attracted increasing attention as promising alternatives to LIBs for large scale energy storage applications. There is a common point for all these NMBs, in which Na metal is used as the anode. Compared with other anode candidates, Na metal is the ultimate choice among them due to the high theoretical capacity (1166 mAh g⁻¹) and low electrochemical potential. All theoretical specific energy densities of RT Na-S, Na-O₂ and SSNB systems are calculated by using Na metal as the anode.
Similar to the Li metal anode, Na metal also faces several crucial problems and challenges during electrochemical cycling. The major issues of the Na metal anode can be summarized as: 1) Na dendrite formation and short circuits. In a typical cycling process, Na$^+$ will come into contact with electrons from an external circuit during charging and then electrochemically deposit on the surface of Na metal. Similar to the electrodeposition behaviors of Li$^+$ and Zn$^{2+}$, dendritic structures can form on the surface of the Na metal or substrate, which is affected by various factors including current density, anion mobility, electrolyte and deposition capacity. Another critical influence on the Na dendrite formation is the solid electrolyte interphase (SEI). Generally, the SEI layer is formed at the interface between liquid electrolyte (LE) and Na metal anode due to the decomposition of organic electrolyte components on the surface of reactive Na metal. A good SEI layer is considered to be electronically insulating but ionically conductive, which will block further side reactions between LE and Na metal while transporting Na$^+$ during electrochemical cycling. However, an unstable SEI layer will lead to non-uniform Na$^+$ flux, resulting in Na dendrite growth. The accumulation of sharp Na dendrites may penetrate through the separator, causing safety concerns over internal short circuits. 2) Low Coulombic efficiency (CE) and poor cycling performance. The unstable SEI layer will not only cause Na dendrite growth, but also lead to the depletion of electrolyte and electroactive Na during the repeated breakage and repair of the SEI layers during cycling. The consumption of the electrolyte and Na metal will lower the CE and also shorten the life time. Meanwhile, the accumulation of “dead Na” will give rise to large voltage polarizations and increase the resistance of the batteries. 3) Infinite volume changes. The host-less nature of the Na metal anode results in infinite volume changes during repetitive Na plating/stripping processes.

The challenging issues associated with metallic Na anode have also been noticed in practical NMBs. The undesired Na dendrite growth had been observed by Hartmann et al. in the Na-O$_2$ battery system. The porous structure of Na dendrites composed of sodium and oxygen can also be found in the holes of the separator. Another group also reported similar Na dendrite growth in Na-O$_2$ batteries with different discharge capacities. It has now come to attention that the performance of Na-O$_2$ batteries is not
only dependent on the cathode, but also the Na metal anode, which is also a key component that can affect the life time and stability of Na-O₂ cells.

In the initial studies on NMBs, researchers put more emphasis on the development of other cell components, such as cathode materials and electrolyte. The important role of the Na metal anode had been significantly neglected. However, the importance of Na metal anode has been highlighted in recent years and many creative studies have provided possible solutions to address the issues of Na metal. With this in mind, a comprehensive summary is required for a deep understanding on the recent progresses of Na metal anodes, particularly for NMBs. Although this topic has been partial mentioned in an excellent review paper focusing on Li metal anodes, the progress and challenges associate with Na metal anodes has yet to be summarized in detail. Thus, on the basis of this motivation, this review article focuses on the recent developments of metallic Na anodes, including the fundamental understanding, novel characterization methods, and strategies for protection and future perspectives. Our review will accelerate further improvement and application of Na metal anodes from fundamental studies to practical application in NMBs.
2.2.2 Fundamental understanding on Na dendrite formation

2.2.2.1 Properties of Na dendrites

<table>
<thead>
<tr>
<th>Atomic properties</th>
<th>Sodium</th>
<th>Lithium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic radius (empirical)</td>
<td>186 pm</td>
<td>128 pm</td>
</tr>
<tr>
<td>Covalent radius</td>
<td>140 pm</td>
<td>168 pm</td>
</tr>
<tr>
<td>Van der Waals radius</td>
<td>227 pm</td>
<td>150 pm</td>
</tr>
<tr>
<td>First ionization energy</td>
<td>495.8 kJ/mol</td>
<td>520 kJ/mol</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Physical properties</th>
<th>Sodium</th>
<th>Lithium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting points</td>
<td>973 K</td>
<td>454 K</td>
</tr>
<tr>
<td>Boiling points</td>
<td>1515 K</td>
<td>1603 K</td>
</tr>
<tr>
<td>Critical points</td>
<td>2737 K</td>
<td>3220 K</td>
</tr>
<tr>
<td>Heat of vaporization</td>
<td>97 kJ/mol</td>
<td>115 kJ/mol</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mechanical properties</th>
<th>Sodium</th>
<th>Lithium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shear modulus</td>
<td>3.0 GPa</td>
<td>4.2 GPa</td>
</tr>
<tr>
<td>Bulk modulus</td>
<td>6.3 GPa</td>
<td>11 GPa</td>
</tr>
<tr>
<td>Modulus of elasticity</td>
<td>0.6</td>
<td>0.5</td>
</tr>
<tr>
<td>Brinell hardness</td>
<td>0.9 MPa</td>
<td>5 MPa</td>
</tr>
</tbody>
</table>

Figure 2.4 (a) various properties of Li and Na; (b) mechanically stability under quasi-zero electrochemical field for Li and Na dendrites.\footnote{115}

Over the past decades, there have been numerous studies on the formation of Li dendrites, their growth process, surface, and interface chemistry. However, unlike the systematic investigations of the Li anode and Li dendrites\footnote{12, 116-119}, very little research has focused on the properties and process of Na dendrite growth. Belonging to the same group of alkali metals as Li, metallic Na is expected to follow similar principles and mechanisms during electrochemical processes. However, the properties of Na metal are still slightly different from Li metal, which will affect the Na dendrite growth. Figure 2.4 (a) shows the various properties of metallic Na and Li in terms of atomic, physical and mechanical properties. It can be seen that these two alkali metals present different electronic structures and atomic properties. Furthermore, the Na metal intrinsically displays higher chemical activity and lower mechanical properties.

To gain a better understanding on the difference between Na and Li dendrites, Hong et al. carried out an in-operando experiment to study the chemical, mechanical and electrochemical stability of Li and Na dendrites under quasi-zero electrochemical field (QZEF)\footnote{115}. Generally, the QZEF refers to the electrochemical systems when the external
electrochemical process is halted, such as the completion of charge/discharge, interruption of battery operation and massive battery decay under abuse. In their work, similar electrolytes of 1 M LiPF$_6$ in dimethyl carbonate (DMC)/ethylene carbonate (EC) and 1M NaPF$_6$ in DMC/EC were used for Li and Na, respectively. Firstly, both Li and Na dendrites were deposited on the Li and Na electrode under the same condition. To investigate the effects of electrolytes on the dendrites, both electrodes were allowed to settle under QZEF. Interestingly, the Li dendrites showed almost no change under QZEF, but the Na dendrites were gradually dissolved and diminished when settling in electrolyte. Furthermore, a large portion of the Na dendrites had disappeared after 6 h. Secondly, two pieces of fresh Li and Na foils were soaked in the electrolyte to study the chemical stability. The results indicated that the surface of the soaked Na foil possessed rough pits and heaves due to the high activity of Na metal. Thirdly, the mechanical stability of the Li and Na dendrites and their SEI layers were investigated via applying mechanical forces, as shown in Figure 2.4(b). It can be observed that the Li dendrites and their SEI layers are more mechanically stable than Na dendrites due to the robust chemical bonding and lower chemical activity. The weakened mechanical properties of Na dendrites are a critical problem because it can lead to the ceaseless dissolution and damaging of Na dendrites and the development of new SEI, which causes NMBs to have irreversible capacity loss and shortened life times. Lastly, the electrochemical performances had also been investigated using Li-Li and Na-Na symmetric cells. Generally, the Na-Na cells possessed more pronounced voltage hysteresis fluctuations during repeated plating/stripping compared to Li-Li cells, which was attributed to the unstable SEI layer in the similar electrolyte systems.

In comparison to Li metal, Na dendrites and their related SEI layers are more sensitive to the electrolyte and external environments. In this case, achieving a stable SEI layer and reducing Na dendrite growth will be more challenging compared to the problems associated with Li metal anodes.
2.2.2.2 Advanced techniques for the study of Na dendrites

Figure 2.5 Different techniques for Na deposition (plating) studies: (a) in-situ optical images. (b) in-situ AFM. (c) in-situ NMR. (d) in-situ TEM.

Similar to the studies on Li dendrites, advanced techniques for the characterizations of Na dendrite growth and SEI layers are necessary to gain a deep understanding on their fundamental mechanisms and properties. In general, regular techniques have been used to study the Na dendrite and SEI formation, including scanning electron microscopy (SEM), optical microscopy, X-ray photoelectron spectroscopy (XPS), Time-of-flight secondary ion mass spectrometry (TOF-SIMS) and several other methods. It is worth mentioning that our group firstly demonstrate the Rutherford Backscattering Spectrometry (RBS) technique to study the SEI formation on Na metal anodes, which is a very powerful tool to exhibit the compositions and thickness of the SEI layers formed during electrochemical cycling.
Apart from the ex-situ techniques, advanced in-situ techniques are considered to be more promising for observing the plating/stripping behaviors and dendrite growth process of Na metal. Rodriguez et al. demonstrated the in-situ optical imaging of the Na deposition process, as shown in Figure 2.5(a)\textsuperscript{120}. Three types of electrolytes (1M NaPF\textsubscript{6} in (i) EC/diethyl carbonate (DEC); (ii) propylene carbonate (PC)/fluoroethylene carbonate (FEC); (iii) FEC/DEC) are used for their home-made hermetically sealed optical cell. From observation of the in-situ optical images, highly porous Na with mossy and dendritic structures were deposited for all the electrolytes. Meanwhile, the Na dendrites formed in both EC/DEC and PC/FEC were easily expelled into the electrolyte along with gas generations. However, it has also been demonstrated that the issues of porous depositions, gas evolutions and Na loss were reduced when using FEC as the co-solvent.

In-situ atomic force microscopy (AFM) is another useful analytical technique that can provide visualized evidence of electrochemical reactions in batteries system, particularly for changes in surface morphology of the electrode. Recently, Chen’s group reported an in-situ AFM study of Na deposition on a homemade planar electrode in a carbonate-based electrolyte. The schematic of the in-situ AFM setup is shown in Figure 2.5(b)\textsuperscript{121}. In their design, the in-situ AFM included a gold coated homemade planar electrode, a sodium electrode, an O-ring for sealing of the liquid, an AFM probe and an optical camera. They firstly studied the Na deposition behavior by in-situ AFM using an electrolyte consisting of 1 M NaClO\textsubscript{4} in EC/PC (1:1 v). Three stages were visualized in the deposition processes by in-situ AFM combined with optical images. The first stage was the nucleation step appearing in the beginning of Na deposition (100 s). After 300 s deposition, the growth of Na was clearly observed. Subsequently, the Na continues to spread and finally formed a rough layer after 1000 s, followed by the formation of Na dendrites and dead Na layers. FEC was further used in their study as an additive in the electrolyte, which can stabilize the Na deposition and suppress the Na dendrite formations. From the in-situ AFM, the FEC-containing electrolyte demonstrated a more homogeneous morphology and higher modulus than those in the pristine electrolytes. Their work provides a good example of the development of in-situ strategies to study the Na metal anode.
In-situ nuclear magnetic resonance (NMR) spectroscopy is used as a unique and indispensable tool for the nondestructive analysis of battery systems. In previous studies, in-situ NMR has given valuable and quantitative insight with adequate temporal resolution to analyze the Li microstructure (dendritic and mossy Li). Grey and colleagues firstly demonstrated the in-situ $^{23}$Na NMR on a Na metal electrode during electrodeposition of Na (Shown in Figure 2.5(c))$^{122}$. Consistent with the phenomenon observed from other techniques, a high surface area morphology was produced in the continuous galvanostatic plating of Na. Through the use of in-situ $^{23}$Na NMR, it could be observed that the two cells cycled with higher current densities (1 and 2 mA cm$^{-2}$) exhibited similar behavior in terms of their efficiency in removal of the high surface area microstructures. In contrast, a different behavior was seen for the lowest current density studied (0.5 mA cm$^{-2}$), where the efficiency of removal is dramatically increased. Their study suggested that these two regimes are distinguished by both the efficiency in which high surface area deposits can be removed and the time dependence of the nucleation process, both of which are greater at lower current$^{122}$.

The techniques discussed above are suitable to study Na dendrite growth under relatively large scales (micro size), however, the nucleation process of Na deposition is still difficult to be determined. Li et al. presented the first nanoscale-resolution observation of electrochemical Na plating/striping dynamics via in-situ electron microscopies using amorphous carbon nanofibers (CNF) as a current collector$^{123}$. Figure 2.5(d) shows their set up for the in-situ transmission electron microscope (TEM) and SEM. From the in-situ SEM and TEM, it was found that the Na metal is grown and dissolved reversibly as nano/micro-particles at all possible locations around individual CNFs and even throughout their network. Interestingly, Na ions were also transported in the fibers, enabling a more homogeneous Na deposition deep into the interior network. Their works provide some new insights and technical paths in the design of dendrite free Na metal anodes.

As an alternative method of analyzing the Na deposition process, Kondou et al. studied the Na plating procedure in another view by investigating the thermal reactivity of Na metal$^{124}$. From their results, the heat flow profile of sodium plating exhibited lower peak
intensities and larger widths without FEC additive. On the other hand, with FEC, the heat flow profile dramatically changed, exhibiting three-fold increase in peak intensity compared to the FEC-free electrolyte\textsuperscript{124}.

As seen above, many advanced characterization techniques, especially the in-situ techniques, have been proposed to understand the Na dendrite growth and SEI layer formation. Unlike the detailed studies for Li anodes, many fundamental questions have yet to be answered for the Na metal anode and its dendrite growth, which will be discussed in the perspective sections. Meanwhile, any one of these techniques alone is not enough to gain a deep and comprehensive understanding on the surface and interface chemistry of the Na metal anode and its SEI layers, which will require the combination of different analytical techniques in future research. New approaches, such as synchrotron radiation-based techniques, are expected to provide new insight and guidance on the surface chemistry of Na metal anodes.

### 2.2.3 Stabilization of the SEI layer on Na metal anodes

#### 2.2.3.1 Electrolyte modification for stable SEI

**Figure 2.6** (a) Coulombic efficiency of Na plating/stripping in Na/SS cells and photographs of a pristine Na metal electrode and Cu substrates after the initial Na plating with different concentration of electrolytes. (b) Plating–stripping Coulombic efficiencies of Na metal anodes
cycled using (a) 1 M NaPF$_6$ in various electrolyte solvents and (b) 1 M of various electrolyte salts in diglyme$^{125-126}$.

As discussed above, the SEI layer is one of the most important components of the Na metal anode. An ideal SEI should possess high ionic conductivity, sufficient density, small thickness and high flexibility to mechanically suppress the Na dendrite growth$^{8,119,127}$. During electrochemical cycling, the major components of the SEI layer are generated from the reduction of solvents and salts in the organic electrolytes. Thus, the properties of SEI layer are always determined by the organic solvent, Na salt and additives in the electrolytes$^{128}$.

FEC has already been proven as an effective additive to stabilize the SEI on Li metal surfaces, and has also been proposed for Na anodes. In the last section, different groups used FEC as an additive to demonstrate their different in-situ techniques for Na deposition$^{129}$. Another group also demonstrated that the use of FEC as an additive minimizes the irreversible capacity of Na-half cells using Na metal as the anode$^{130}$. From their study, FEC can limit the Na reactivity toward the electrolyte via the growth of a protective layer with an impedance that increases with time. This protective layer mainly consisted of a harder and more homogeneous NaF interface$^{121}$. The NaF coating can provide a homogeneous Na$^+$ flux to the surface of the electrode, resulting in reduced Na dendrite growth and longer life times. More recently, Wang et al. reported a bi-functional electrolyte additive of potassium bis(trifluoromethylsulfonyl)imide (KTFSI) to stabilize Na metal electrodes$^{131}$. In their design, the K$^+$ cations are preferentially adsorbed on the deposited Na and provide electrostatic shielding to suppress dendritic deposition. With the assistance of the bi-functional electrolyte additive, the Na metal anode could realize a long cycle life over hundreds of hours at a high capacity of 10 mAh cm$^{-2}$.

The concentration of the salt in electrolyte will also affect the cycling efficiency of Na metal anodes$^{132-133}$. Lee et al. presented an ultra-concentrated electrolyte composed of sodium bis(fluorosulfonyl)imide (NaFSI) in 1,2-dimethoxyethane (DME) for Na metal anodes coupled with high-voltage cathodes$^{125}$. **Figure 2.6(a)** compares the CE for Na plating/stripping on stainless steel (SS) with different concentrations of salt in the electrolyte. Higher concentration NaFSI-DME electrolytes led to substantially improved
initial CE for Na plating/stripping. Moreover, with the 5M NaFSI-DME electrolyte, a high CE of 99.3% was obtained for 120 cycles at a rate of C/10. Meanwhile, the rate performances (Figure 2.6(a)) had also been drastically enhanced with a CE of 93.8% at a high rate of 2 C using 5M NaFSI-DME electrolyte compared to the conventional dilute 1 M NaPF6-EC/PC electrolyte. However, the highly concentrated electrolyte still possesses shortfalls, such as high viscosity, poor wettability, and high salt cost. In this case, Zheng et al. demonstrated the use of a hydrofluoroether as an “inert” diluent can significantly reduce the salt concentration as well as maintain the high CE134. With their design, a relatively low salt concentration (2.1M NaFSI/DME-bis(2,2,2-trifluoroethyl)ether (1:2)) enabled the dendrite-free Na deposition with a high CE of >99% and greatly enhanced the fast charging (20C) and stable cycling (90.8% after 40 000 cycles) of Na∥ Na3V2(PO4)3 batteries. The bis(2,2,2-trifluoroethyl) ether diluent will not break the localized Na+–FSI–DME solvation structures but improve the interfacial reaction kinetics and interfacial stability of the Na metal anode. Their work has opened a new avenue to tailoring of the electrolyte chemistry with low salt concentrations for developing high-performance NMBs.

It is known that the combination of different electrolyte components, such as the solvent and salt, will further affect the Na deposition behaviour. In 2015, Cui’s group gave a comprehensive study on the electrolyte combinations using different electrolyte salt of NaPF6, NaN(SO2CF3)2 (NaTFSI), NaFSI, NaSO3CF3 (NaOTf) and NaClO4 with solvents such as monoglyme, tetraglyme, EC/DEC and EC/DMC126. Figure 2.6(b) presented the plating-stripping CE of Na metal anodes cycled using 1 M NaPF6 in various electrolyte solvents and 1 M of various electrolyte salts in diglyme, respectively. Generally, the electrolytes of 1M NaPF6 in glymes (mono-, di- and tetraglyme), can enable the highest reversibility and no dendrite structures at room temperature. The SEI formations were also studied using depth profile XPS, in which the uniform inorganic SEI layer made of Na2O and NaF are highly impermeable to electrolyte solvent and conducive to dendrite inhibition.

Other than the conventional electrolytes, significant efforts have been made to develop novel electrolyte systems to achieve high CE and dendrite-free Na depositions. Song et
al. reported a dendrite-free Na-metal electrode employing a non-flammable and highly Na⁺-conductive NaAlCl₄·2SO₂ inorganic electrolyte with enhanced electrochemical performances compared to the conventional organic electrolytes. These remarkable performances can be attributed to the unique nature of the highly concentrated SO₂-based inorganic electrolyte and its intrinsically high Na⁺ conductivity. Subsequently, another novel highly concentrated sodium electrolyte based on liquid ammonia has been reported, which can be described as NaY·xNH₃ (Y: I⁻, BF₄⁻, BH₄⁻). These electrolytes showed excellent properties such as low flammability and high specific ionic conductivity with dendrite-free and highly reversible Na plating/stripping behaviours as well as high CE when performed on a Cu substrate.

**Table 2.1** Summary of the reported literature on electrolyte modification for stable Na metal SEI formation.

<table>
<thead>
<tr>
<th>Na cells</th>
<th>Electrolyte salt</th>
<th>Electrolyte solvent</th>
<th>Additives</th>
<th>Current density (mA cm⁻²)</th>
<th>Capacity (mAh cm⁻²)</th>
<th>CE/life time</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-Cu</td>
<td>1 M NaPF₆</td>
<td>diglyme</td>
<td>-</td>
<td>0.5</td>
<td>1</td>
<td>99.9 % (300 cycles)</td>
<td>126</td>
</tr>
<tr>
<td></td>
<td>1 M NaPF₆</td>
<td>monoglyme</td>
<td>-</td>
<td>0.5</td>
<td>1</td>
<td>99.9 % (300 cycles)</td>
<td></td>
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<tr>
<td></td>
<td>1 M NaPF₆</td>
<td>tetraglyme</td>
<td>-</td>
<td>0.5</td>
<td>1</td>
<td>99.9 % (300 cycles)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 M NaPF₆</td>
<td>EC/DEC</td>
<td>-</td>
<td>0.5</td>
<td>1</td>
<td>&lt; 20% (&lt;25 cycles)</td>
<td></td>
</tr>
<tr>
<td>System</td>
<td>Electrolyte</td>
<td>Solvent</td>
<td>EC/DMC</td>
<td>Volume</td>
<td>Capacity</td>
<td>Life</td>
<td></td>
</tr>
<tr>
<td>----------------</td>
<td>-----------------------------------</td>
<td>---------</td>
<td>--------</td>
<td>--------</td>
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<td>---------------</td>
<td></td>
</tr>
<tr>
<td>Na-Na</td>
<td>1 M NaPF₆</td>
<td>EC/DMC</td>
<td>0.5</td>
<td>1</td>
<td>&lt; 20% (&lt;25 cycles)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 M NaN(SO₂CF₃)₂</td>
<td>diglyme</td>
<td>0.5</td>
<td>1</td>
<td>&lt;10% (&lt;25 cycles)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 M NaFSI</td>
<td>diglyme</td>
<td>0.5</td>
<td>1</td>
<td>&lt;10% (&lt;25 cycles)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 M NaSO₂CF₃</td>
<td>diglyme</td>
<td>0.5</td>
<td>1</td>
<td>&lt; 80% (&lt;125 cycles)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 M NaClO₄</td>
<td>diglyme</td>
<td>0.5</td>
<td>1</td>
<td>&lt;10% (&lt;25 cycles)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na-Na</td>
<td>NaAlCl₄·2SO₂</td>
<td>-</td>
<td>0.75</td>
<td>1.5</td>
<td>95 cycles</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na-Cu</td>
<td>4 M NaFSI</td>
<td>DME</td>
<td>0.2</td>
<td>0.2</td>
<td>99% (300 cycles)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4 M NaFSI</td>
<td>DME</td>
<td>0.5</td>
<td>0.5</td>
<td>99% (300 cycles)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4 M NaFSI</td>
<td>DME</td>
<td>1</td>
<td>1</td>
<td>99% (300 cycles)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na-Al</td>
<td>4 M NaFSI</td>
<td>DME</td>
<td>0.5</td>
<td>0.5</td>
<td>99% (300 cycles)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na-Na</td>
<td>1 M NaPF₆</td>
<td>EC₀.₅DMC₀.₅</td>
<td>3% FEC</td>
<td>0.05</td>
<td>-</td>
<td>600 h</td>
<td></td>
</tr>
<tr>
<td>Na-SS</td>
<td>5 M NaFSI</td>
<td>DME</td>
<td>C/10</td>
<td>-</td>
<td>99.3% (120 cycles)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
In this section, we summarized the recent research progress focusing on the modification of electrolyte components to obtain stable SEI layers for Na metal anodes (Table 2.1).
The promising approaches can be classified as: 1) the rational combination between salt and solvent in the electrolytes, which plays an important role in the electrochemical performances. It is considered that the use of NaPF$_6$ as salt and glymes as solvent will create a uniform inorganic SEI layer consisting of Na$_2$O and NaF, leading to both dendrite-free deposition and long cycling life. 2) The ultra-high salt concentration in the electrolyte can provide remarkable effects to suppress the Na dendrite growth and achieve stable SEI formation. The “inert” diluents in the electrolyte can not only decrease the salt concentrations, but also maintain the excellent plating/stripping behaviours. 3) FEC is widely accepted as the most effective electrolyte additive to produce a stable NaF SEI layer and improve the CE. 4) Beyond the existing electrolytes, novel electrolyte systems with the advantages of low cost, improved safety as well as dendrite-free Na depositions are expected to address the current issues in NMBs.

2.2.3.2 Artificial SEI layers by surface modification

In addition to the in-situ formed SEI layer from the reaction between metallic Na and electrolyte, surface modification with artificial SEI layers is considered as another effective strategy to protect Na metal anodes. The artificial SEI is fabricated prior to cell assembly and can block the direct contact between Na metal and LE, thus preventing the consumption of the electrolytes and electrode materials, heterogeneous deposition, and dendrite formation$^{109}$. Compared to the in-situ formed SEI from the electrolyte components, the artificial SEI possesses more advantages: 1) as discussed in 2.1, the highly chemically active Na metal can react with electrolyte components spontaneously. With the protection of artificial SEI, these side reactions can be effectively blocked. 2) The properties of the artificial SEI can be easily regulated and tailored without any effect from the electrochemical process. Thus, the development of artificial SEI layers has grown very fast in the past year and will be discussed in this section.

To provide guidance for the development of suitable protective films on Na metal anodes, Tian et al. carried out a comprehensive theoretical study on both diffusion and mechanical performance of layered materials to reveal their possibilities as artificial SEI layers for Na metal anodes$^{137}$. From the simulation results, the introduction of defects, the increase of bond length, and proximity effect can improve the conductivity of Na$^+$ ions
and enable lower diffusion barriers with higher diffusion rates\textsuperscript{137}. Generally, the materials with puckering structure, such as phosphorene, SnS, and SnSe, are not good for Na\textsuperscript{+} ion diffusion, and even worse for the strain properties, making them not suitable as artificial protection coatings. Meanwhile, defective h-BN or graphene are also not suitable for Na metal anodes due to the larger radius of Na\textsuperscript{+} resulting in difficult diffusion of Na within the structures. Nevertheless, the simulation results show that both silicene or Si materials are potentially promising artificial SEI coatings for Na metal with relatively high Na diffusion rate and stiffness stronger than common SEI films\textsuperscript{137}. Furthermore, another group screened the Open Quantum Materials Database to identify various coatings exhibiting chemical equilibrium with the Na metal anode\textsuperscript{138}. They identify 118 promising coatings for Na metal anode including binary, ternary, and quaternary compounds, which are listed in their paper.

**Figure 2.7** (a) Schematic showing the procedure used to coat Na with NaBr and its electrochemical performances. (b) A schematic drawing of the polymeric ionic liquid film
formation on Na and its electrochemical performances. (c) Schematic diagram showing the fabrication process of graphene-coated Na and its electrochemical performances\textsuperscript{139-141}.

Chemical reactions with Na metal is an effective approach to fabricate an artificial SEI on the surface. In other words, Na metal is used as a reactant to form the artificial SEI. Archer’s group firstly demonstrated the reaction of metallic Na with bromopropane to undergo the Wurtz reaction as illustrated in the Figure 2.7(a)\textsuperscript{141}. In doing so, NaBr is formed on the surface of Na foil with thicknesses ranging from 2-12 μm. Figure 2.7(a) shows the galvanostatic cycling performance of Na/NaBr and control samples at the current density of 0.5 mA cm\textsuperscript{-2} with the capacity of 0.5 mAh cm\textsuperscript{-2}. From the results, the cell comprising NaBr-coated Na was stable for at least 250 h with minimal rise in cell polarization, producing nearly a 10-fold improvement in the cell lifetime. Furthermore, the in-situ visualization was performed to contrast the electrodeposition stability with and without NaBr layers on the sodium anode. The results showed that the NaBr coating not only restricts dendritic formation, but also prevents unwanted side reactions between the electrode and electrolyte\textsuperscript{141}. Afterwards, their group reported ionic membranes synthesized on a metallic Na anode by an in-situ electro-initiated polymerization method of imidazolium-type ionic liquids containing unsaturated functional groups, as shown in Figure 2.7(b)\textsuperscript{139}. The study showed that the ionic membranes can protect the Na metal against parasitic reactions with liquid electrolyte without compromising ion transport in the SEI. The ionic membrane-protected Na anodes exhibited high CE and stable long-term cycling even at relatively high current densities. Meanwhile, the ionic membranes can reduce the electric field on the surface of Na, resulting in the uniform deposition of Na metal. From their works, the reaction-based method using Na metal as reactant has been proven as a promising alternative strategy to synthesizing artificial SEI layers on the Na metal surface. However, it is still believed that the thickness control is the main challenge for this method in term of unpredictable chemical reactions on the Na surface.

Other approaches have also been reported to modify the surface of Na or create artificial SEI layers for Na metal anodes. Kim et al. demonstrated a multistep approach to fabricate a free-standing composite protective layer that could enable enhanced reversibility of Na metal anode by mechanically suppressing Na dendrite growth and mitigating the
In this work, the as prepared free-standing composite protective layer was laminated on the Na metal electrode by roll-pressing. One of the key factor in their protective layer was the high mechanical strength and high ionic conductivities. Similar ideas have been proposed using ultrathin graphene films as the free standing protective layer on Na metal anode, as shown in Figure 2.7(c). Interestingly, the Na anode stability at different current densities and capacities was dependent on the thickness of the graphene film. To achieve an optimal performance, the thickness of the graphene film was meticulously selected based on the applied current density. It was found that 15 layers of graphene (~5 nm) can significantly enhance the Na cycling behavior at a high current density of 2 mA cm\(^{-2}\) and a capacity of 3 mAh cm\(^{-2}\) over 100 cycles. The stable Na metal anode with a high cycling capacity of 3 mAh cm\(^{-2}\) is more promising in terms of the practical application of NMBs. Another interesting work has been reported by Li and colleagues. In their study, they used a commercial carbon paper (CP) as the protection layer for Na metal anode, in which the CP direct covered the surface of Na foil. The Na anode with CP exhibited significantly improved over-potentials and cycling stability (up to ~1200 cycles). This positive effect was attributed to the large surface area of carbon paper for dissipating current density and its less reactive surface favoring the formation of a stable SEI layer.

<table>
<thead>
<tr>
<th>Na cells</th>
<th>Coating materials</th>
<th>Electrolyte</th>
<th>Current density mA cm(^{-2})</th>
<th>Capacity mAh cm(^{-2})</th>
<th>CE/life time 250 cycles</th>
<th>Ref 141</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-Na</td>
<td>NaBr</td>
<td>1 M NaPF(_6) in EC/PC</td>
<td>0.25</td>
<td>0.25</td>
<td>250 cycles</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 M NaPF(_6) in EC/PC</td>
<td>0.5</td>
<td>0.5</td>
<td>250 cycles</td>
<td></td>
</tr>
<tr>
<td>Material</td>
<td>Interfacial Protection</td>
<td>Electrolyte</td>
<td>Na+ Ions</td>
<td>ClO4⁻ Ions</td>
<td>Protection Time</td>
<td>Ref.</td>
</tr>
<tr>
<td>-------------------</td>
<td>------------------------</td>
<td>--------------------------</td>
<td>----------</td>
<td>------------</td>
<td>----------------</td>
<td>------</td>
</tr>
<tr>
<td>Na-Na Inorganic-organic composite protective layer</td>
<td>1 M NaClO₄ in EC−PC</td>
<td>0.5</td>
<td>1</td>
<td>&gt; 550 h</td>
<td>142</td>
<td></td>
</tr>
<tr>
<td>Na-Na ALD Al₂O₃</td>
<td>1 M NaClO₄ in EC−DEC</td>
<td>0.25</td>
<td>1</td>
<td>400 h</td>
<td>144</td>
<td></td>
</tr>
<tr>
<td>Na-Na Ionic membrane</td>
<td>1 M NaClO₄ in EC/PC</td>
<td>0.1</td>
<td>-</td>
<td>&gt; 250 h</td>
<td>139</td>
<td></td>
</tr>
<tr>
<td>Na-Na Graphene</td>
<td>1 M NaPF₆ EC/DEC</td>
<td>0.5</td>
<td>0.5</td>
<td>200 h</td>
<td>140</td>
<td></td>
</tr>
<tr>
<td>Na-Na Carbon paper</td>
<td>1 M NaClO₄ in PC with 5% FEC</td>
<td>1</td>
<td>1</td>
<td>200 cycles</td>
<td>143</td>
<td></td>
</tr>
</tbody>
</table>
In this part, we have given an overview of the recent developments of the various surface modifications strategies for the protection of Na metal anodes, as summarized in Table 2.2. Based on the fabrication process, the methods can be categorized into the following:

1) **The chemical/physical deposition method (like ALD and MLD).** These deposition methods exhibit the advantages of uniform coverage and precise control over film thickness. In the future, novel coating materials with high Na$^+$ conductivity are expected to be developed for Na metal anode by these methods.

2) **Reaction method using Na as a reactant.** From this process, Na-containing materials or ionically conductive layers can be obtained. However, control over the desired thickness and a deep understanding on the surface/interfacial change are still lacking.

3) **The mechanical transfer method.** Based on this method, a larger variety of materials can be explored with a facile fabrication process. However, the Na metal anode and these protective layers are usually connected by physical contact, which is not as strong as the chemical bonding used by the other two methods.
2.2.4 Nanostructured Na metal anodes

2.2.4.1 Nanostructured current collectors

![Figure 2.8](image)

**Figure 2.8** (a) Schematic of Na deposition on planar and porous Al foils; SEM images of porous Al foils before and after plating/stripping cycling. (b) Schematic illustrations of Na-plating models on different current collectors of Cu foil and 3D Cu nanowires; SEM images of 3D Cu nanowires after Na plating/stripping with different current densities and capacities\cite{145,146}.

Because the spatial inhomogeneity of the Na\textsuperscript{+} distribution on an electrode surface contributes directly to the Na dendrite formation, it is urgent to develop strategies to produce a uniform Na\textsuperscript{+} flux\cite{14,147}. One of the most popular approach is to increase the surface area of the electrode to dissipate the local current density, which can be realized by manipulating the nanostructure of the current collectors. Al foil, the typical current collectors for cathode materials in LIBs, can also serve as a current collector for the anodes in NIBs and NMBs because it will not alloy with Na. However, Na dendrites will be formed on the Al foil due to the inhomogeneous distribution of local current. To achieve dendrite-free Na deposition, a nucleation layer was produced on the Al foil to
assist the sodium seeding process with a lower nucleation energy barrier and improved structure for stable sodium plating\textsuperscript{148}. The results showed that over 1000 plating-stripping cycles with an average CE of 99.8\% was maintained with a low average hysteresis of 14 mV and smooth Na film deposited on the Al current collector. Furthermore, this Na metal-free anode coupled with a pre-sodiated pyrite cathode could provide an energy density of \(\sim 400\) Wh kg\(^{-1}\), which is very promising for future applications. Beyond the planar Al foil, Luo’s group reported porous Al foil as the Na plating substrate to suppress the Na dendrite growth\textsuperscript{146}. Figure 2.8(a) illustrates the schematic of Na deposition on planar and porous Al foils and the SEM images of porous Al foils before and after cycling. From the SEM images, it can be observed that the Na plated on porous Al was homogeneously distributed on the surface of the porous Al without any protuberance. As a result, the Na metal anodes can run for 1000 cycles with a low and stable voltage hysteresis and an average plating/stripping CE above 99.9\% for over 1000 cycles.

Other kinds of nanostructured current collectors have been designed, including 3D Cu with nanowires, porous 3D Ni, carbon nano-template and 3D carbon fiber scaffolds\textsuperscript{145,149-151}. Lu and colleagues reported a facile hydrothermal route to transform commercial Cu foil into 3D Cu nanowires for use as current collector\textsuperscript{145}. Figure 2.8(a) shows the schematic illustrations of Na-plating models on different current collectors of planar Cu foil and 3D Cu nanowires. Thee as-prepared 3D Cu nanowires exhibited an average diameter of 40 nm, which can lead to a more effective electric field. As a result, the 3D Cu nanowires can accommodate a high areal capacity of 3 mA h cm\(^{-2}\) with stable plating/stripping for over 100 cycles. Figure 2.8(a) display the SEM images of the Na plating/stripping on 3D Cu nanowires at different capacities. When increasing the plating capacity to 4 mAh cm\(^{-2}\), the deposited Na showed a nodule-like structure with round-shaped edges on the 3D Cu nanowires.

Generally, the energy barrier between Na and Cu (or Al) is relative high especially in the initial nucleation process, resulting in high over-potentials and non-uniform depositions. In a recent work, macroporous catalytic carbon nanotemplates (MC-CNTs) composed of hierarchically interconnected carbon nanofibers were synthesized from microbe-derived cellulose via simple heating at temperatures from 800 to 2400 °C. Compared with Al foil,
the MC-CNTs delivered lower initial over-potentials, which can be attributed to the lower energy barrier. The MC-CNT fabricated at high temperature (2400 °C) maintained better cycling behavior with a CE of 99.9% over 1000 cycles, and in contrast, the MC-CNT fabricated at 800 °C shows a limited cycling stability (~200 cycles). It is believed that degradation of the graphitic structure for MC-CNT-2400 is significantly retarded in the repetitive cycles, which can cause a remarkable improvement in cycling performances. Recently, another impressive work has been reported by Tang et al.\textsuperscript{152} where they introduced a “sodiophilic” layer of Au-Na alloy on the Cu substrate to significantly reduce the energy barriers and over-potential during the nucleation process. From their results, an average CE of 99.8% can be maintained at a high current density of 2 mA cm\textsuperscript{-2} for 300 cycles.

Table 2.3 Summary of the reported literature on nanostructured current collectors for Na metal anodes

<table>
<thead>
<tr>
<th>Na cells</th>
<th>Current collector</th>
<th>Electrolyte</th>
<th>Current density mA cm\textsuperscript{-2}</th>
<th>Capacity mA h cm\textsuperscript{-2}</th>
<th>CE/life time</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-Al</td>
<td>Al/carbon</td>
<td>1 M NaPF\textsubscript{6} in DEGDME</td>
<td>0.5</td>
<td>0.25</td>
<td>99.8%/(1000 cycles)</td>
<td>148</td>
</tr>
<tr>
<td>Na-Al</td>
<td>Porous Al foil</td>
<td>1 M NaPF\textsubscript{6} in DEGDME</td>
<td>0.5</td>
<td>0.25</td>
<td>99.9%/(1000 cycles)</td>
<td>146</td>
</tr>
<tr>
<td>Na-Al</td>
<td></td>
<td>1 M NaPF\textsubscript{6} in DEGDME</td>
<td>1</td>
<td>0.5</td>
<td>99.8%/(1000 cycles)</td>
<td></td>
</tr>
<tr>
<td>Na-Cu</td>
<td>3D Cu nanowire</td>
<td>1 M NaPF\textsubscript{6} in DEGDME</td>
<td>0.5</td>
<td>0.5</td>
<td>99%/(200 cycles)</td>
<td>145</td>
</tr>
</tbody>
</table>
In this section, we summarize the reported research on the design of nanostructured current collector for NMBs, particularly for anode-free NMBs (Table 2.3). Several works have demonstrated the use of 3D metal and carbon substrates as current collectors to achieve stable performances with high CE of 99 % and superior long life times of over 1000 cycles. However, some challenge still remain: 1) The electrolyte systems used in these studies are among the most stable electrolytes (NaPF₆ in DEGDME), as discussed in 3.1. However, there is no report focusing on the dendrite-free Na deposition and high CE of current collector in carbonate-based electrolyte, which is more popular for cells coupled with insertion-type Na cathodes. 2) The capacities are relatively low (< 1 mAh cm⁻²), which is difficult to meet the requirement for practical applications that require high capacity. 3) Although carbon materials have been used to decrease the energy barriers of Al, large over-potentials are still present under high current density. Thus, there is still room for improvement with respect to the performances via modifying the
current collector with specific materials which have low energy barriers during Na nucleation, such as gold.

2.2.4.2 Nanostructured hosts for Na metal

As discussed above, another serious issue for metallic Na is the relatively infinite volume change, which has only recently begun to be addressed. To overcome this problem, molten Li is introduced into the gaps of nanostructured host materials. Different from the 3D current collector, this strategy is very important for the application of stable Na metal anodes in RT Na-S and Na-O₂ batteries, in which the cathode materials lack prestored Na. Nanostructured carbon materials are the most popular candidate as host due to their low cost, ease of fabrication and stable chemical properties. Luo et al. used...
reduced graphene oxide (rGO) as a host to form a processable and moldable composite Na metal anode, as shown in Figure 2.9(a). Interestingly, it was observed that by controlling the thicknesses of the densely stacked graphene oxide (GO) film, the thicknesses of the Na@rGO can be easily determined, which was found to be 20 times that of the GO films (Figure 2.9(a)). Meanwhile, the shapes and structures of the Na@rGO can be assembled into 1D fibers, 3D monoliths or other 2D shapes by changing the GO precursor. The composites with only 4.5% GO had greatly enhanced mechanical properties, such as hardness, strength, and stability against environmental corrosion compared to pure Na. The as-prepared Na@rGO composite electrodes showed enhanced electrochemical plating/stripping performances in a series of electrolytes, including NaPF$_6$ in diglyme, NaCF$_3$SO$_3$ in diglyme and NaClO$_4$ in EC/PC. The r-GO sheets in the Na@r-GO composite could flatten the surface, leading to a more evenly distributed Na$^+$ flux, further enhancement of the electrochemical performances and suppressed dendrite growth. Moreover, wood-derived carbon materials with channels have also been reported by Hu and colleagues as a 3D host for Na metal. Figure 2.9(b) illustrates the fabrication of the Na-wood composite electrode with the thermal infusion process of molten Na. After melt infusion of Na, the channels of carbonized wood were almost completely filled, as observed by SEM. The electrochemical performances of symmetric cells using Na-wood electrodes and bare Na electrode under different capacity limits are shown in Figure 2.9(b). The Na-wood electrode displayed very stable cycling performance with more than 250 cycles under both testing conditions while the bare Na metal can only run for less than 90 cycles and 50 cycles, respectively. The improved performances can be attributed to the porous channels of the wood-derived carbon, which provide a high-surface-area conductive host that can greatly decrease the effective current density and ensure uniform Na nucleation.

<table>
<thead>
<tr>
<th>Na cells</th>
<th>Host materials</th>
<th>Electrolyte</th>
<th>Current density mA cm$^{-2}$</th>
<th>Capacity mAh cm$^{-2}$</th>
<th>CE/life time Ref</th>
</tr>
</thead>
</table>

Table 2.4 Summary of the reported literature on nanostructured hosts for Na metal anodes.
Herein, we mainly focus on the progress of nanostructured hosts for Na metal anodes, which is still in its infancy. Only a few studies have been reported using carbon materials for the thermal infusion process. Currently, more efforts should be put forward for both the surface chemistry involved in the thermal infusion process and achieving excellent performances with high reversible capacity.

2.2.5 Practical application of Na anodes in NMBs

In the previous section, we mainly discuss the different strategies to stabilize the Na metal anode. However, most of the studies focus on the electrochemical plating/stripping behaviors in symmetric cells or half cells. In this section, we will summarize the recent works using Na metal electrodes and their practical application in different NMB systems, including Na-CO2, Na-O2 and all-solid-state batteries.
2.2.5.1 Na-O₂ and Na-CO₂ batteries

Figure 2.10 Na metal anode in Na-O₂ batteries: (a) Discharge/charge profiles of a Na–O₂ battery for the last two cycles in DME and diglyme; SEM and EDS mapping images the top-view and cross-section of the Na dendrite in GF separators. (b) Na–O₂ cell discharges at current densities of 25 μA cm⁻² as well as 100 μA cm⁻² with different electrolytes; illustration of sodium SEI formation mechanism and its composition in different DME electrolytes. (c) Schematics of the symmetrical battery design using interlayer for Na metal anode; the rate capability, voltage of the terminal discharge versus the cycle number curves of Na–O₂ batteries with the five blocking interlayers.155-157

As previously discussed, Na-O₂ batteries have attracted increasing attention as an alternative to LIBs due to their high theoretical energy density. Furthermore, Na-O₂ batteries possess the advantage of high energy efficiency due to lower charging overpotential compared to the Li-O₂ system. The improved energy efficiency can be attributed to the reversible electrochemistry of the oxygen/superoxide (O₂/O₂⁻) redox pair (compared to the semi-irreversible oxygen/peroxide (O2/O2²⁻) redox pair in Li-O₂
batteries). Most studies in this field are concentrated on the fundamental understanding of the discharge products, discharge/charge mechanism, cathode design and choice of catalysts.\textsuperscript{95, 158-159} However, the O\textsubscript{2}/O\textsubscript{2}\textsuperscript{-} generated from the cathode may migrate towards the separator and metallic Na because of concentration gradients in the electrolyte. On one hand, the migrated intermediates may precipitate on the non-conductive separator, lowering the CEs of the batteries. On another hand, both O\textsubscript{2}/O\textsubscript{2}\textsuperscript{-} will react with Na metal, resulting in an insulating oxide layer on the Na surface which will block the Na ion transport from the surface to bulk Na. Meanwhile, the Na dendrite growth is another common issue for the Na metal anode, even in Na-O\textsubscript{2} batteries. Furthermore, the Na dendrite growth and O\textsubscript{2} corrosion have been identified in real Na-O\textsubscript{2} cells as one of the most serious issues and limitation on the life time of the batteries.\textsuperscript{113-114, 160} Bi et al. also showed the dendrite formation in Na–O\textsubscript{2} batteries in their paper.\textsuperscript{156} Based on the cell performances, the cycling life of the Na–O\textsubscript{2} batteries using DEM and diglyme as electrolyte fluctuated between 6 cycles to 12 cycles with voltage fluctuations during the charging process, as shown in Figure 2.10(a). After disassembling the failed cells, spots were observed at the surface of glass fibre facing the metal anode, an indication that the Na dendrites caused the shorting of the batteries. From the SEM images in Figure 2.10(a), it was also verified that the Na metal had grown across more than 80% of the thickness of the separator in just a few cycles. As a potential solution, a Na ion selective membrane was employed between two GF separators to prevent dendrite penetration. The Nafion membranes exhibited the good mechanical strength and ionic conductivity of 2.56×10\textsuperscript{-5} S cm\textsuperscript{-1} at RT. The results showed that the incorporation of the Nafion-Na\textsuperscript{+} membranes greatly improves the cyclability of Na-O\textsubscript{2} batteries in both DME and diglyme-based electrolytes. Another group further extended this idea as an “interlayer” for suppressing the Na dendrite formation in Na-O\textsubscript{2} batteries.\textsuperscript{155} They studied several types of polymer films, including fibrillar polyvinylidene fluorid (f-PVDF), compact PVDF (c-PVDF), PVDF with through pores (p-PVDF), polyethylene oxide (PEO), and conventional polytetrafluoroethylene (PTFE). The cycling stability and rate performances of the Na-O\textsubscript{2} batteries using different interlayers are shown in Figure 2.10(c), in which the f-PVDF is superior to the other tested polymers. It was believed that the performance stems from f-PVDF’s uniform fiber structure for Na\textsuperscript{+} distribution and high uptake of
electrolyte for fine electrode-electrolyte contact, stable physical and chemical properties against the robust metal-air conditions, and strong affinity with electrolyte for improved ion conductivity. As an alternative to the introduction of an interlayer between Na and separator, Liang et al. demonstrated a new trilayer separator for Na-O2 batteries. A middle layer of TiO2 nanoparticles were synthesized within the separators to form a sandwich structure. Their results show that the cycling life of Na-O2 batteries can be enhanced from 82 cycles to 137 cycles using the TiO2 sandwich separator, in which the TiO2 nanoparticles can react with Na metal and slow down the Na dendrite growth during cycling.

As previously discussed, the electrolyte components including the solvent and salt have a major influence on the Na deposition behaviour. Luts et al. discovered that the sodium salt anion plays an important role on the performances of real Na-O2 batteries. Figure 2.10(b) show the Na−O2 cell discharges with different electrolytes and an illustration of suggested SEI formation mechanism in the different DME electrolytes. Similarly, NaF formation in the SEI seemed to be a crucial component for improved stability of the Na anode in the Na-O2 batteries. Subsequently, Zhou and colleagues presented a durable protection film containing NaF on the surface of the Na anode to achieve stable Na-O2 batteries. The Na anode with the durable protection film was prepared by discharging and charging a symmetric cell using an ether-based electrolyte (NaCF3SO3 in tetraglyme with 2%FEC). The large amount of NaF in the film endows the metallic Na anode with superior merits to effectively limit the O2 crossover and electrolyte related side reactions, and further suppresses the formation of by-products. Moreover, the formation of Na dendrites can be avoided and long term cycling stability could be achieved without short circuits. In addition, nanostructured porous Al foil and 3D Na@rGO have been investigated in Na−O2 batteries as a proof of concept by Luo’s group.

In addition to Na-O2 batteries, Na-CO2 batteries using greenhouse gas CO2 are also interesting topic as a new type of battery system. The system still poses safety risks from leakage of liquid electrolyte and instability of the metallic Na anode. Chen’s group reported the quasi-solid-state Na-CO2 cells with polymer electrolyte and reduced graphene oxide (rGO) Na anodes. In their study, the rGO-Na anode presented fast and
non-dendritic Na+ plating/stripping behavior. The rationally designed Na-CO$_2$ batteries can be successfully cycled in a wide CO$_2$ partial pressure window with a long life time of over 400 cycles.

Briefly, we summarize the recent works focusing on the metallic Na anode in Na-O$_2$ and Na-CO$_2$ batteries. Differing from the symmetric cells and half cells, the metallic Na not only suffer from the dendritic Na growth, but also possesses other issues such as O$_2$/O$_2^-$ cross over and by-product corrosion. Thus, the metallic Na in the practical Na-O$_2$ and Na-CO$_2$ batteries will be more challenging, in which additional factors need to be taken into consideration when designing the Na metal electrodes.

2.2.5.2 RT Na-S batteries

High temperature Na-S batteries have been previously developed and operate at 300 °C. In this system, both electrodes including the S cathode and Na anode are in a molten state, resulting in low energy efficiency along with corrosion and safety hazards. To overcome these issues, RT Na-S batteries have been firstly demonstrated in 2006$^{88}$. The RT Na-S batteries follow similar working principles with Li-S batteries and share many of the challenges faced by the similar battery system. The main challenges include the insulating nature of the Na$_2$S discharge products; dissolution of polysulfide species; shuttle effects of polysulfides and dendrite formation on Na metal$^{87-88,164}$. The efforts in this field have been primarily focused on the development of functional nanocomposites, utilizing efficient electrolytes, and constructing novel cell configurations to obtain high performance RT Na-S batteries$^{88}$.

However, it also has been noticed that the surface degradation of the Na anode is a major concern for the capacity degradation of the RT Na-S batteries$^{165}$. From the studies by Manthiram’s group, it was shown that the surface of the Na anode became severely rough after cycling (100 cycles) even with the designed functional separator$^{165}$. Therefore, besides the suppression of the polysulfide shuttling effect, protection of the metallic Na anode would be another important research area to achieve long cycle life RT Na-S batteries$^{166}$.
2.2.5.3 All-solid-state Na metal batteries

Figure 2.11 Na metal anode in solid-state batteries: (a) Distribution of different chemical compositions on the surface of the sodium-metal anodes after the cycling tests in both liquid cell and SSBs. (b) Illustrations of three possible interphases between electrolyte and electrode materials: a stable interface (stable), a mixed-conducting interphase (MCI), and the solid electrolyte interphase (SEI) with the corresponding time-dependent resistance is shown below.\textsuperscript{167-168}

SSNMBs are a promising choice for next-generation energy storage devices beyond LIBs because of their enhanced safety and ability to achieve high-energy and high-power densities by replacing the liquid electrolytes with SSEs.\textsuperscript{99, 169-170} From our discussion above, the SEI layer caused by the reactions between Na and liquid electrolyte is the key factor that determines the life time of the Na metal anode. This phenomenon has also been recently proven by Goodenough and colleagues through the use of TOF-SIMS, as shown in Figure 2.11(a).\textsuperscript{167} However, when they replace the liquid electrolyte with a NASICON Na\textsubscript{3}Zr\textsubscript{2}Si\textsubscript{2}PO\textsubscript{12} electrolyte, the side reactions are effectively limited, as revealed by the formation of a passivating interface with a significantly reduced thickness on the surface of the metallic Na anode. The battery performances have also been significantly enhanced in solid-state batteries using the a Na\textsubscript{2}MnFe(CN)\textsubscript{6} cathode.

Despite the benefits of SSNMBs, it should be noted that the interface between SSEs and Na metal anode can still be an issue. Some types of electrolyte may react with Na metal to form unstable interfaces and cause degradation of the SSEs. Janek’s group explored the stability and viability between Na metal and two kind of electrolytes of Na\textsubscript{3}PS\textsubscript{4} and
Na-β″-Al₂O₃. As expected, Na-β″-Al₂O₃ is stable against sodium, whereas Na₃PS₄ decomposes with an overall resistance that increases with time. They also proposed three possible interphases between electrolyte and electrode materials, including the stable interface (stable), a mixed-conducting interphase (MCI), and the solid electrolyte interphase (SEI) (Figure 2.11(b)). Recently, Meng’s group also studied the interface between the sodium anode and sulfide-based solid electrolytes, including Na₃SbS₄, Na₃PS₄, and Cl-doped Na₃PS₄ in SSNMBs. From their results, solid electrolyte interphases between Na₃SbS₄ and Na, as well as Na₃PS₄ and Na, are predicted computationally to be composed of Na₂S and Na₃Sb, Na₂S and Na₃P, respectively, due to the chemical reactions between SSEs and Na metal. Interestingly, Cl-doped Na₃PS₄ shows the presence of an additional compound of NaCl at the interface, which is found to mitigate the decomposition of Na₃PS₄. From their results, new insight and an approach to reduce the chemical reactions and improve the interface stability between SSEs and Na metal has been developed by the doping of other elements.

To engineer the interface between SSEs and Na metal anode, Goodenough and colleagues designed two different approaches to enhance the compatibility of NASICON Na₃Zr₂Si₂PO₁₂ and Na metal. Firstly, it was found that the molten Na cannot wet the surface of NASICON SSEs under low temperature (175 °C), leading to a high resistance between Na metal and SSEs. Promisingly, when increasing the temperature into 380 °C for 30 min, the wettability between Na metal and SSEs significantly improved, resulting in reduced resistance. Another strategy proposed in their paper was the use of a dry polymer as an interlayer between the SSEs and Na metal. This polymer interlayer can not only reduce the large interfacial resistance but also prevent dendrite formation. Excellent cycling performance and high CE SSNMBs were demonstrated with two strategies for good electrochemical stability and high Na deposition efficiency across a Na/SSE interface. Meanwhile, Ong et al. proposed different coating layers on Na metal to prevent the reactions between Na metal and sulfide SSEs based on the first-principles calculations, including Sc₂O₃, SiO₂, TiO₂, ZrO₂, and HfO₂. They explored these coatings and found that the Na₂Ti₃O₇ anode is predicted to be much more stable against a broad range of solid electrolytes compared with other metal oxides.
The development of SSNMBs is still in a very early stage. Significant efforts have been put forward to develop different types of SSEs with high ionic conductivity and chemical/electrochemical stability. However, when metallic Na is used as the anode, the interface between the SSEs and Na metal should be brought to the forefront. Forming a stable interface will be very important to obtaining long life SSNMBs. The surface modifications on Na or SSEs will be an effective approach to prevent these detrimental reactions. Unlike the solid-liquid interphase, the Na deposition behaviours will be determined not only by the surface chemistry of Na metal, but also by the properties of the SSEs. Thus, the Na dendrite growth along the grain boundaries in SSEs will be another potential issues and more experimental works will be needed to gain a fundamental understanding of the process. Lastly, the volume change of Na metal during plating/stripping may still exist in SSNMBs. Potential strategies such as using nanostructured Na metal electrodes are still promising avenues to alleviating this issue.

2.2.6 Conclusion

Figure 2.12 Schematic diagram of the fundamental challenges of Na metal anodes and the protection methods used for their practical application.

In summary, we have provided insight into the development and protection of Na metal anodes for NMBs, as shown in Figure 2.12. Firstly, preliminary mechanisms have been proposed for Na dendrite growth. Particularly, the Na dendrites show weakened chemical, electrochemical and mechanical properties compared to their Li counterparts,
and require stronger protection to inhibit dendrite formation. Meanwhile, the surface modification on Na metal is necessary due to corrosion of Na metal by the electrolyte in the absence of any electrochemical process, which differs from the Li metal electrode.

Secondly, different techniques have been used to study the composition and formation of Na dendrites and its SEI layers, including SEM, optical images, XPS, TOF-SIMS, and RBS. Impressively, various in-situ techniques, such as in-situ optical observation, in-situ AFM, in-situ NMR and in-situ SEM/TEM, have been demonstrated to provide new and more accurate methods of viewing the deposition behaviour of Na metal.

Thirdly, Different strategies have been developed to reduce Na dendrite growth and enable long life Na metal anodes. 1) **Electrolyte modifications.** Since electrolytes play an important role during the SEI layer formation, a lot of studies have focused on the electrolyte modification. From previously reported comprehensive studies, the electrolytes consisting of NaPF$_6$ as a salt and glymes as solvent are the best choice, which can enable the formation of a uniform inorganic SEI layer consist of Na$_2$O and NaF which can inhibit dendrite growth. Furthermore, ultra-high salt concentrations or the introduction of “inert” diluents in the electrolyte have been shown to make remarkable influences on the suppression of Na dendrites and stabilization of the SEI layers. In addition, additives like FEC can also aid in the formation of NaF-containing SEI with improved CE and reduced dendrite growth. Moreover, novel electrolyte systems are still under exploration to further address the current issues in NMBs. 2) **Surface modification.** Three different methods of developing artificial SEI layers on Na metal anode have been identified, including the chemical/physical deposition method, the reaction method using Na as a reactant and the mechanical transfer method. Each of these methods show their own advantages and disadvantages, which are discussed in section 3.2. 3) **Nanostructured current collectors.** 3D current collectors are used to dissipate the local current density and produce uniform Na$^+$ flux for Na metal anode-free Na batteries. Different materials, including Al/carbon films, porous Al films, 3D Cu nanowires, 3D Ni, macroporous catalytic carbon nanotemplates and carbon fibers are reported to achieve very stable performances with high CE. 4) **Nanostructured hosts.** Rationally designed carbon materials, such as rGO, wood-derived carbon and carbon paper with carbon
nanotube matrices, have been used as a host/matrix for the thermal infusion of molten Na. The 3D structure of Na metal composite electrodes exhibit suppressed dendrite growth, enhanced electrochemical performances, and minimized volume change during the plating/stripping process.

Lastly, the current progress of metallic Na anode in different NMBs, like Na-O₂, Na-CO₂ and SSNMBs, have been summarized. 1) In Na-O₂ batteries, the Na metal not only suffers from dendritic Na growth, but also has other issues such as O₂ cross over and by-products of corrosion. One of the most popular approaches to alleviate these issues is to introduce a functional “interlayer” and modify the surface of Na to block the O₂ cross over and reduce the dendrite growth. 2) The SSEs in SSNMBs can prevent the unstable SEI formation compared to liquid-based cells. However, the reactions between SSEs and Na have also been noticed as an issue. Thus, the interface stability between the SSEs/Na is the key to obtaining long life SSNMBs.

2.2.7 Perspective

Although there has been some progress related to the development of Na metal anodes, there are still significant challenges to be overcome, particularly for the practical application of NMBs. Herein, we propose potential directions and perspectives for this field:

1) Better fundamental understandings are needed: Unlike the systematic studies on Li metal anodes, few studies have focused on the fundamental understanding of the Na deposition process. Firstly, the Na deposition structures, including mossy and dendritic Na, should be better defined. Particularly, the relationship between Na deposition with other parameters, such as current density, capacity, temperature and pressure et al. should be further explored. Secondly, the nucleation process of Na is a fundamental aspect that is poorly understood, and more work should include studies on the nucleation locations and times. Thirdly, detailed information related to the SEI formation mechanism, structure, components, and regulation is still inadequate.
2) Advanced characterization techniques and methods: Although different techniques have been applied to study the Na anode, a proper fundamental understanding of Na nucleation, dendrite growth, and chemical/electrochemical reactivity are still unclear, and require advanced techniques and characterization. Firstly, synchrotron radiation-related techniques will be excellent candidates for the study of the SEI layer on Na metal, especially with in-situ capabilities. Secondly, due to the high reactivity of Na metal, cryo-based techniques are an ideal approach to obtaining the most authentic chemical information without any compositional changes of the Na dendrite or SEI layers. Thirdly, any one of these techniques is not enough to have a deep and comprehensive understanding on the surface and interface chemistry for Na anode and its SEI layers, and the combination of different analysis technique in future research will be required.

3) Engineering the SEI: Since the SEI is the key factor for the stability of the Na metal anode, surface modifications with artificial SEI layers have become a promising direction. While several coatings have been explored, other approaches still need to be developed for Na⁺ conductive protective layers, in which sputtering is a good choice to deposit Na-SSEs as artificial SEI on Na metal. Secondly, polymer based thin films with ionic conductivity and high flexibility will be another promising strategy. Particularly, polymer coatings incorporating self-healing functionalities can reconstruct the surface cracks produced during cycling. Thirdly, ALD and MLD are still remarkable to address the issues for Na metal anode, especially with precisely controlled thicknesses. However, new ALD/MLD films need to be developed with improved Na⁺ conductivity, density, and flexibility. Lastly, the combination of different approaches to fabricate hybrid protective layer or composite artificial SEI layers is required, in which the different layers can serve their own functions to form a real and robust protection layer.

4) Nanostructured Na: For NMBs, more than 10 micrometers of Na is ideal for the repeated plating/stripping process. The infinite volume change is still a restriction for long life NMBs. In this case, the rational design of host matrices is critically needed for practical NMBs. The host structure should possess chemical, electrochemical, and mechanical stability. Meanwhile, the weight and volume percentage of the matrix in the whole composites electrode should be limited in order to maximize the energy density of
the cell. Furthermore, although metallic Na is encapsulated in the matrix, the SEI layer will still be formed at the point of contact with the electrolyte. Thus, it would be a better idea to combine the strategies of nanostructured Na with artificial SEI to synergistically improve the stability and electrochemical performances of Na metal anodes.

5) **Different NMB systems:** Apart from the existing issues of Na dendrite growth, dead Na formation and infinite volume change, more serious challenges appear in different NMB systems. For example, the O₂ cross over and by-product corrosion is an obvious issue in Na-O₂ batteries. Furthermore, the interface stability between SSEs and Na metal is another uncertainty in terms of different types of SSEs. In this case, these other factors should be taken into consideration when designing metallic Na anodes for real NMBs.

6) **Practical applications:** Firstly, it should be pointed out that the high CE is very important for practical battery applications. A high CE of > 99.9 % after 1000 cycles at relatively high current density has not been reported yet. Secondly, for the NMBs with different cathodes, the requirements of the areal capacity and thickness of Na metal are different. Thus, the design of Na metal anode should be tailored to the choice of cathode, electrolyte and NMB system.

In conclusion, it seems that the use of only a single approach is not enough to solve all the existing issues of Na metal anodes. Thus, multi-strategy approaches with specific aims will bring the metallic Na anode closer to reality. We believe that with continued efforts, the Na metal anode will act as the “Holy Grail” for the next-generation NMBs for large scale energy storage applications.

### 2.3 Atomic layer deposition and Molecular layer deposition

#### 2.3.1 Atomic layer deposition

Atomic layer deposition (ALD) is one of the most rapidly developing thin film deposition techniques in the past decade, attracting increasing attention in different applications due to its unique properties. Compared to traditional vapor phase methods, such as chemical vapor depositions (CVD) and physical vapor depositions (PVD), ALD is the surface controlled process that the growth of the film is dictated by two self-limited 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 \cite{176}. Three key deposition feature parameters for ALD processes are substrate, temperature and precursors \cite{41,177-178}. Concurrently, the ALD technique shows unique properties, including excellent uniformity and conformity\cite{179}, atomic scale and stoichiometric deposition, and low growth temperatures.

2.3.2 ALD in liquid lithium-ion cells

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.13.png}
\caption{The development of ALD/MLD for electrode fabrication and interface modification in Li battery liquid cells\cite{180-186}.}
\end{figure}

Lithium-ion batteries (LIBs) have become the most widely used energy storage systems for portable electronic devices and electrical vehicles due to their many outstanding features, including their high energy density, lack of memory effect, and small self-discharge\cite{1-3}. The commercialized LIBs include three main components: cathode (LiCoO$_2$), anode (graphite) and electrolytes (liquid carbonate electrolyte). The current LIBs cannot meet the growing demand in terms of improved safety, longer lifetime, smaller size, lighter weight, and lower cost. A key factor to enhance the performance of
LIBs is the amelioration of these three major components’ properties. In the past years, various novel electrode materials, including cathodes and anodes, have been developed to meet the high energy density requirements. However, these materials still face serious issues in achieving long-term stability. One of the major issues in the development of liquid batteries is the interfacial reactions between the electrolyte and electrode. The solid electrolyte interphase (SEI) layers are formed on the electrodes due to these reactions. It is believed that the stable SEI layers can prevent the further decomposition of the liquid electrolytes and stabilize the batteries performances. However, the unstable SEI will cause serious issues for both cathode and anode electrodes in batteries. On one hand, the unstable SEI on anode electrodes can continuously consume electrolyte and Li ions, leading to reduced columbic efficiency of batteries. On the other hand, the unstable SEI on cathode cannot block the transition metal elements dissolving from the cathode materials due to the hydrofluoric generated in the electrolytes, resulting in rapid failure of the batteries.

Another significant challenge for the electrode materials is the volume expansion during cycling, particularly for the alloy-based anode (such as Si, Sn, P et al). The large volume change leads to the electrical disconnection from the conductive agents (e.g. carbon black) and the current collectors during the charge/discharge process, further resulting the poor cycling stabilities. To address the challenges of interfacial issues and large volume expansion, surface modification is considered one of the most effective approaches, creating robust artificial SEI on the electrodes.

The unique properties of ALD techniques have resulted in significant and proven impacts for batteries applications through the use of liquid electrolytes. Generally, the functions of ALD for liquid cells can be separated into two parts: one for electrode fabrications and another for interface modifications. Figure 2.13 presents the development of ALD for electrode fabrication and interface modification in Li batteries using liquid electrolytes.

Firstly, various cathode materials, including V$_2$O$_5$, FePO$_4$, LiCoO$_2$, Li$_x$Mn$_2$O$_4$ and LiFePO$_4$, and different anode materials, such as TiO$_2$, SnO$_2$, Co$_3$O$_4$, Li$_4$Ti$_5$O$_12$ and metal sulfides 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$_2$O as precursor (Figure 2.13). It
was found that the crystallinity and morphology can be controlled by adjusting the ALD deposition temperatures, in which the amorphous SnO$_2$ on GNSs result in better performances than the crystalline products$^{181}$. This work indicates that ALD can be the powerful tool for the fabrication of anode materials with controllable morphology, crystallinity, and electrochemical performance. Another typical example is the successful synthesis of LiFePO$_4$ by ALD as the high performances cathode for LIBs$^{180}$. The amorphous LiFePO$_4$ are deposited by using an ALD sequence of $5 \times (\text{FeCp}_2-\text{O}_3-\text{TMPO-}\text{H}_2\text{O}) + 1 \times (\text{LiO}'\text{Bu-}\text{H}_2\text{O})$ with the growth rate of 0.9 nm/cycles at a temperature of 300 $^\circ$C. Crystalline LiFePO$_4$ is obtained on CNTs after annealing with high capacity, rate capability and ultra-long life time. Besides materials prepared by ALD, Karppinen’s group first demonstrated the fabrication of lithium terephthalate (Li$_2$C$_8$H$_4$O$_4$ or LiTP) as organic LIB electrodes by MLD$^{202}$. It is notable that the Li-terephthalate films without any conductive additives can achieve excellent rate capability. Furthermore, with a protective coating layer of solid state electrolyte of LiPON by ALD, the LiTP organic electrodes can be stabilized with the high capacity and excellent cycle life. These works demonstrate the unique properties of ALD to fabricate both cathode and anode electrodes for LIBs.

Secondly, the interfacial issues and SEI stabilization is one of the key factors for the batteries performances in liquid electrolyte. In this case, surface coating by ALD/MLD is considered the ideal approach to prevent the side reaction and improve the electrochemical performances of the batteries. From 2010, different ALD coatings have been extensively introduced for both cathode and anode electrodes with enhanced performances, including Al$_2$O$_3$, TiO$_2$, ZrO$_2$, TiN, ZnO, LiAlO$_x$, et al$^{43,203}$. Our group has also investigated different complicated coatings, including LiTaO$_x$, FePO$_4$ and AlPO$_x$ on different cathode materials$^{183-184}$, $^{204}$ (LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$, LiNi$_{0.5}$Mn$_{1.5}$O$_4$, Li$_{1.2}$Mn$_{0.54}$Co$_{0.13}$Ni$_{0.13}$O$_2$, shown in Figure 2.13). The robust ALD coating layers lead to various benefits, including the facilitation of fast Li$^+$ ion transportation, preventing metal dissolution, suppressing continuous oxygen release, resulting in significantly improved cycling performances.
Finally, ALD techniques have been proven as a powerful tool for electrode fabrication and interface modification in liquid cells. Specifically, the precisely controllable surface coating by ALD 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.

2.3.3 Molecular layer deposition

Organic-inorganic hybrid materials have recently received increasing attention in various areas such as electronics, photonics, and sensing. Furthermore, the development of novel hybrid materials at the nanoscale with well-defined properties is critical for high-performance applications, especially in the emerging field of energy-related applications like batteries, supercapacitors, and catalysis. Generally, the hybrid organic-inorganic materials can inherit advantageous mechanical, optical, chemical, and electrical properties from the combination of organic and inorganic constituents. In this case, the hybrid materials will show synergistic interactions leading to enhanced properties. There are several methods which have been developed to prepare these hybrid materials, including sol-gel methods, Langmuir–Blodgett (LB) techniques, layer-by-layer assembly, and self-assembly procedures. However, these methods are dependent on solution-based procedures, which face significant challenges in terms of controlling thickness and composition, which are critical parameters for nanoscale applications.

As a novel gas-phase approach, atomic layer deposition (ALD) techniques have been rapidly developed over the past decades. The ALD process is defined as sequential, self-limiting surface reactions that enable the deposition of ultrathin conformal films with atomic level precision on high aspect ratio structures. The ALD techniques are mainly dependent on binary reaction sequences, which occur on the surface of a substrate. A wide range of binary inorganic compounds, including metal oxide, metal nitrides, metal sulfides and mixed metal oxides have been shown using simple reactions based on binary systems. Due to the unique properties of ALD, this novel technique has been widely used in various application areas and, to date, there are several impressive reviews addressing the technique for different applications. Figure 2.14 shows the typical ALD
process of Al₂O₃, using trimethylaluminum (TMA) and water (H₂O) as precursors, which is a well-known procedure in this field.

![Figure 2.14](image)

**Figure 2.14** Schematic of MLD growth using sequential, self-limiting surface reactions; Typical ALD growth mechanism of Al₂O₃ using TMA and H₂O as precursors and MLD growth mechanism of alucone using TMA and EG as precursors.

As an extension of ALD, “molecular” layer deposition (MLD) has been further developed by replacing the oxidizing precursor with organic linkers or the addition of molecular fragments into the film. **Figure 2.14** shows a general schematic representation of MLD growth using sequential, self-limiting surface chemistry. In the 1990s, multiple research groups in Japan developed condensation polymerization reactions for MLD of organic polymers. Subsequently, many types of MLD polymer thin films have been studied, such as polyamide, polyimide, polyurea, polyurethane, polythiourea, and polythiolene. Alternatively, metal-containing MLD (metalcone) can be accomplished by combining a metal precursor, like Al(CH₃)₃, TiCl₄, SnCl₄ et al., with organic linkers such as those used in MLD for organic polymers. Alucoones are one of the most widely studied metalcones among the different metal alkoxides. **Figure 2.14** illustrates the reaction mechanism of the first developed alucone using TMA and ethylene glycol (EG) as precursors. As shown in **Figure 2.14**, EG molecules contain two hydroxyl groups separated by a carbon chain which serve as reactive linkers for condensation reactions with hydroxyl groups on the metal centers, leading to organic-inorganic hybrid
materials. Following the discovery of MLD alucone, several novel metalcones based on different metals (i.e. Zn, Zr, Ti, Hf, Co, Mn, V) and organic molecules (i.e. glycerol (GL), hydroquinone (HQ), hexadiyne diol, polydiacetylene et al.) have been developed\textsuperscript{236-237}. The MLD thin film shows various advantages compared with ALD thin film due to the organic components in the film: 1) Generally, the ALD metal oxide thin films are relatively brittle, in which defects could be generated under straining in the film. On the contrary, the high flexibility of MLD films would reduce the number and size of defects after straining\textsuperscript{238}. Meanwhile, the molecular flexibility will be affected by varying the carbon chain length of organic components in the MLD films (metalcone)\textsuperscript{235}; 2) The density of MLD thin films are much less than the ALD metal oxides\textsuperscript{239}; 3) The MLD thin films, particularly the inorganic-organic metalcone alloy films, display the tunable mechanical properties including the density, refractive index, elastic modulus, and hardness by changing the ratios of organic composition\textsuperscript{240}; 4) The highly porous metal oxides would be produced by removing the organic components from the MLD (metalcone) thin films using thermal or chemical process, in which the porosity are tunable by controlling the MLD process\textsuperscript{241}; and 5) Several types of metalcone alloy show good electrical conductivity, high dielectric constants and refractive indices\textsuperscript{229, 240, 242-243}. However, it still needs to be pointed out that some shortcomings remain for MLD thin film currently. Firstly, the stabilities of some MLD thin film are not satisfactory, as most of the EG-based metalcone is sensitive to air and humidity\textsuperscript{209-210, 244}. Secondly, the restrictive of organic precursors with a sufficient vapor pressure limits the choice for the MLD thin films. Thirdly, porosity of MLD films could lead to the diffusion of gas-phase precursors into the polymer adding the contribution similar to CVD\textsuperscript{225}.

Initially, researchers in this field focused on the development and design of new MLD processes to fabricate thin films. A few good reviews have already summarized the growth mechanism, fabrication and properties of several types of MLD thin films\textsuperscript{209-210, 225, 244-249}. After achieving a better fundamental understanding of this novel technique, MLD has been further applied in various applications, including electronically conducting films, sensors, electronic devices as well as energy storage and conversion\textsuperscript{250-254}. However, there are very few review papers that focus on the utilization of MLD for energy storage and conversion applications. In this review, we compile a comprehensive
summary on the recent development and understanding of MLD in the application of batteries, supercapacitors, catalysis (for water splitting, photodegradation and solar cell) and membranes. The different types of MLD thin films and nanomaterials derived from MLD have been discussed in different sections based on the specific application and properties. Finally, the future direction of MLD in energy related application has been further prospected.

2.3.4 MLD for batteries application

2.3.4.1 MLD for Synthesis of Electrode Materials

![MLD Thin Film](image)

Figure 2.15 Schematic diagram of MLD thin film electrodes: (a) direct use as an electrode for batteries or supercapacitors; (b) Post-treatment to fabricate MLD materials as electrodes for batteries or supercapacitors\(^ {202, 255} \).

ALD has been considered as one of the most promising techniques for the fabrication of thin-film electrodes and solid-state electrolytes for batteries and supercapacitors. Early research has been dedicated to the deposition of different types of metal oxide anode/cathode materials on carbon substrates, including TiO\(_2\), SnO\(_2\), VO\(_x\), Co\(_3\)O\(_4\), et al.\(^ {181, 256-257} \) Furthermore, complicated cathode and solid-state electrolyte compounds containing multiple elements have been further developed by ALD, including LiCoO\(_2\), FePO\(_4\), AlPO\(_4\), LiFePO\(_4\), LiTaO\(_3\), LiPO\(_4\), LiSiO\(_x\) and LiNbO\(_x\) et al.\(^ {180, 196, 258-262} \). This approach for the synthesis of metal oxide-based electrodes is a non-aqueous and versatile process that can enable tailored structures, morphologies, and electrochemical properties.
by tuning the ALD parameters. Based on the previous success of ALD in the application of electrode design for batteries and supercapacitors, researchers are exploring the potential of MLD for similar purposes.

Recently, organic electrode materials have attracted increasing attention as alternatives to the traditional metal-based inorganic electrodes. Organic electrodes possess unique features including low price, environmental friendliness, low weight as well as relatively high theoretical specific capacities due to the low molecular mass with a possibility for multiple redox processes per molecule. As a promising application, thin film organic electrode materials can be used for flexible batteries or supercapacitors. In 2016, Karppinen’s group firstly demonstrated the fabrication of lithium terephthalate (Li$_2$C$_8$H$_4$O$_4$ or LiTP) as an organic LIB electrode by MLD/ALD (Figure 2.15). The as-deposited LiTP organic thin films use Li(thd) (thd=2,2,6,6-tetramethyl-3,5-heptanedionate) and terephthalic acid (benzene-1,4-dicarboxylic acid or TPA) as precursors within the growth temperature range of 200-280 °C. The mechanism of growth was studied by altering the precursor pulse lengths (TPA: 10s and Li(thd): 4s) and growth rate at different temperatures (∼3.0 Å/cycle at 200 °C), verifying the deposition as a typical MLD process. It is very interesting to note that the Li-terephthalate films without any conductive additives can achieve excellent rate capability. Furthermore, with a protective coating layer of solid-state electrolyte (LiPON) by ALD, the LiTP organic electrodes can be stabilized with high capacity and excellent cycle life. Their study provides new insight towards the development of organic thin film electrodes for LIBs by MLD. As another popular MLD thin film, titanicone has also been attempted for use in electrochemical applications. Unfortunately, the titanicone, using tetrakisdimethylaminotitanium (TDMAT) and GL or EG as precursors, is inactive during cyclic voltammetry. Thus, for this concept, there is still significant challenges for the design of structured MLD thin films with electrochemistry activity.

Besides the direct use of MLD thin films as electrodes, another effective approach is to use MLD thin films as a template to fabricate nanocomposites via different post-deposition treatments. Metal organic frameworks (MOFs) and covalent organic frameworks (COFs) are some of the hottest materials for energy storage applications and
have structures similar to many MLD materials, which also contain metal centers with organic linkers or pure organic connections. Numerous nanomaterials or nanocomposites derived from MOFs or COFs have been reported, including porous carbon, heteroatom-doped carbon, nanostructured metal oxides and metal oxide/carbon nanocomposites. Following the same post-treatment methods, MLD thin films can act as sacrificial templates to fabricate various types of thin films. On one hand, porous metal oxides, such as ZnO, SnO$_2$, TiO$_2$, et al., can remain after pyrolysis of the MLD films under air. On the other hand, carbon thin film or metal oxide/carbon nanocomposites will be retained with inert gas flow during the sintering process. Abdulagatov et al. used “titanicone (Ti-MLD)” as a template to yield conducting TiO$_2$/carbon composites after pyrolysis under Ar. It was found that the conductivity of the as-prepared thin film increased with the increasing of pyrolysis temperature, reaching the highest value when heated to 800 °C. Our group also presents a novel way to deposit aluminum alkoxide films with tunable conductivity. The composition of the thin film is tuned by alternating number of EG and Terephthaloyl Chloride (TC) cycles between the cycles of TMA and EG. After sintering at different temperatures, a conductive Al$_2$O$_3$/carbon composite can be achieved, in which the conductivity of the film is related to the aluminium and carbon ratio.

In order to make a comparison between the ALD-TiO$_2$ and MLD-derived TiO$_2$, Kerckhove et al. carried out different treatments of H$_2$O, air and He for the “titanicone” thin films. The results show that both the samples annealed under air and He display enhanced rate performances compared with the respective anatase and amorphous TiO$_2$ references (By ALD). Particularly, the nanocomposites annealed under He had the highest capacity among all treated samples, in which 4.7 times higher capacity (compared to the ALD TiO$_2$) can be achieved with a charge current density of 2 mA cm$^{-1}$. This result is evidence that the inorganic thin film derived from MLD can be more promising than the directly synthesized ALD inorganic thin film. Another interesting work is reported by Qin’s group, who produced N-doped carbon-coated graphene by a carbonization process of MLD thin films. The MLD aromatic polyimide (PI) thin film was deposited on a graphene substrate using pyromellitic dianhydride (PMDA) and 4,4’-diaminodiphenyl ether (ODA) as precursors at 160 °C (Shown in Figure 2.15). After pyrolysis, the N
inherited from the precursor can remain to obtain a N-doped carbon coating on graphene. Due to the unique properties of MLD, the PI layers are coated very uniformly on the surface of graphene and enables a homogenous dispersion of nitrogen atoms in the carbonized products. When used as an electrode materials for supercapacitors, the nanocomposites exhibit remarkable capacitance performance with a high specific capacitance of 290.2 F g\(^{-1}\) at a current density of 1 A g\(^{-1}\) in 6 M KOH aqueous electrolyte, as well as good rate properties and stability.

To summarize, there are very few reports that focus on the application of MLD thin film as electrode materials for batteries and supercapacitor because the technique is still in its infancy. Many researchers in this field are still concentrating on the development of different types of MLD processes. However, the thin films fabricated by MLD or derived from MLD are very promising for use as electrodes for batteries and supercapacitors.
2.3.4.2 MLD Coatings for Anode Materials

Figure 2.16 (a) Schematic of the self-limiting reactions of AIGL used to coat the conventional Si nanocomposite electrodes along with TEM images, EELS elements mapping and cycling
performance. The scale bar in the TEM images is 20 nm; (b) The schematic of MLD coating (AlHQ) and crosslinking process of the AlHQ chains after post-deposition heat treatments for the laminated Si electrode. Cyclic capacity and CE of a Si anode coated with as-deposit AlHQ (blue symbols) are shown and compared to the cyclic capacity and CE of a Si anode coated with Ar-treated AlHQ (green symbols) 186, 266.

The most common commercialized anode material for LIBs is graphite. However, it suffers from a low theoretical capacity (372 mAh g\(^{-1}\)) and poor rate properties, which severely limits further improvement in energy density. Si is now considered as one of the most highly investigated anode materials for LIBs due to its high theoretical capacity of 4200 mAh g\(^{-1}\) 267-269. Regardless of the high capacity, the serious volume change of Si (over ~400%) during the Li alloying and de-alloy process leads to the pulverization and degradation of Si electrodes. In order to solve this issue, several approaches have been attempted in previous studies. One of the most popular techniques is to design nanostructure Si with void spaces, including nanowires, core-shell nanowires and hollow structures to accommodate the volume change. Coating or combining the buffering matrix with Si is another way to relieve the problems associated with volume expansion. Among the various surface coating candidates, the rich chemistry of polymeric materials offer great flexibility which is ideal for the volume change of Si-based materials 270-274. MLD thin films can also be considered as buffer layers for Si nanocomposites due to the mechanically robust and flexible nature, which is not evident in ALD metal oxides. D.M. Piper et al. firstly demonstrated one of the most popular MLD thin films, alucone, as a coating buffer layer for Si nanoparticles 186. **Figure 2.16** shows a schematic of the self-limiting surface reactions involved in the formation of alucone using TMA and GL as precursors. As a result of the deposition process, the Si nanoparticles are coated with thin and conformal layers of Al-GL, which can be observed from the TEM images and confirmed by EESL mapping (**Figure 2.16**). When tested as an anode material for LIBs, the Si/Al-GL nanocomposites exhibit a high specific capacity of nearly 900 mAh g\(^{-1}\) after 150 cycles, and in contrast, the bare Si nanoparticles show a rapid degradation and fail after only 30 cycles. The results indicate that the Al-GL coating provides favorable mechanical properties and flexibility capable of accommodating the volumetric expansion of the Si nanoparticles. Afterwards, the same group developed a new MLD
reaction combining TMA with another aromatic organic diol (HQ) leading to a robust, elastic, and conductive surface coating composed of aluminum dioxybenzene. Figure 3b shows the schematic diagram of the typical MLD process using TMA and HQ as precursor, indicating a controlled layered growth. The linear growth rate of Al-HQ is measured to be 7.5 Å/cycle at the deposition temperature of 150 °C. Interestingly, the Al-HQ thin film are further dehydrogenated when annealing under both inert and air atmosphere. The longitudinal crosslinking reaction of aluminum-dioxybenzene chains occurs due to the dehydrogenation. It is believed that the polydentate Lewis acid-enabled crosslinking structure can create strong covalent bonding on the surface of Si nanoparticles as well as provide higher stability due to the film coating, which is shown in Figure 2.16. They also confirm that the Al-HQ film with heat treatment at 150 °C has the highest Young’s modulus suggesting a more elastic deformation, which is expected to show less accumulative strains and strain energies. Similar to their first work, the Al-HQ coating layer is uniformly distributed on the Si nanoparticles. With the additional benefits arising from the MLD film, the Al-HQ coated Si nanoparticles showed enhanced electrochemical performances compared to the pristine Si nanoparticles. After 200 cycles, the Al-HQ coated (treated at 200 °C) electrodes exhibit a specific capacity of nearly 1500 mAh g⁻¹ and CE in excess of 99%. Furthermore, the as-deposited Al-HQ coated electrodes show a stable capacity of 1000 mAh g⁻¹. Their newly-developed MLD coating of Al-HQ has a capacity three times higher than that of the Al-GL thin film coating. In this case, the post-electrode manufacturing surface modification by MLD is compatible with Si-based materials, and can be further extended to other high capacity materials with large volume changes.
Figure 2.17 (a) Schematics of surface reactions and cycling behavior of silicon nanoparticles with different coating conditions and captured in-situ TEM images showing the lithiation/delithiation behavior of the alucone-coated Si nanoparticles; (b) Time-resolved TEM images show the development of lithiation profiles of the alucone and Al₂O₃-coated SiNWs and schematics of the Li diffusion paths through the SiNWs; average lithiation thickness vs time for the alucone (black square) and Al₂O₃ (red dot) coated SiNWs.

In order to obtain a better understanding of the influence of MLD coating on the performances of Si nanoparticles, Ban et al. collaborated with Wang’s group to display an in-situ TEM analysis on both uncoated and alcuone coated Si nanoparticles. The lithiation and delithiation characteristics of the alucone-coated (Al-GL) Si nanoparticles are revealed by sequential TEM images in Figure 2.17. Compared with pristine nanoparticles, there is no Li₂O formed on alucone-coated Si nanoparticles because of the dramatic removal of SiOx during the alucone coating process. The results indicate that the alucone-coated Si nanoparticles have fast, thorough, and highly reversible lithiation behaviors, which are clarified to be associated with the mechanical flexibility and fast Li⁺ conductivity of the alucone coating. Further studies have been attempted on alucone-coated Si nanowire (SiNWs) by the same group using in-situ TEM. They find distinctly different lithiation profiles between alucone and Al₂O₃, in which alucone is V-shaped and Al₂O₃ is H-shaped, respectively, as shown in Figure 2.17.
To obtain a deeper understanding of alucone-coated Si nanoparticles, Ma et al. examined the film formation, lithiation, and reactivity in contact with an electrolyte solution using density functional theory, ab initio molecular dynamics simulations, and Green’s function theory. It was found that the alucone film is composed of Al-O complexes with 3-O or 4-O coordination. When Li ions are inserted into the film, there is a very strong bonding between the Li and O atoms in the energetically favorable sites. Furthermore, the film becomes electronically conductive after the film is irreversibly saturated with Li atoms. The theoretical results are in agreement with those from morphology and electrochemical analysis.

2.3.4.3 MLD Coatings for Cathode Materials

Figure 2.18 (a) Schematic of alucone MLD thin film formation as a coating layer applied on a C/S cathode; Cycle performances of bare, ALD-Al₂O₃ coated, and MLD-alucone coated C/S cathodes at a current density of 160 mA g⁻¹. (b) Electrochemical cycle performance, discharge-charge profiles, cyclic voltammetric profiles of alucone-coated and pristine C–S electrode and comparison of alucone-coated C–S electrodes running within carbonate based and ether-based electrolyte under 55 °C.
Li sulfur batteries, as one of the most promising next generation batteries system, have been intensively studied because of their high theoretical capacity and energy density. However, the so-called “shuttle effect”, which is caused by the dissolution of polysulfides, lead to the rapid decay in electrochemical performance and CE. Furthermore, the low conductivity and large volume expansion of sulfur is another significant problem for Li-S batteries. In order to solve these issues, surface coating with carbon or metal oxides has proven as an effective approach to prevent the “shuttle effect” and accommodate the large volume expansion. In our earlier work, we studied the coating of sulfur-based electrodes with Al$_2$O$_3$ coatings of varying thickness $^{279}$. Our results showed that 2 cycles of ALD Al$_2$O$_3$ (~0.2 nm) yields the best performance of Li-S batteries. It was found that an ionically conductive layer of AlF$_3$/LiAlO$_2$ is formed during the lithiation process of the surface coating. This ionic conductive layer can not only protect the dissolution of polysulfide, but also enhance the Li ion diffusion, resulting in highly reversible electrochemical performances. Subsequently, we demonstrated that an alucone (Al-EG) thin film coating directly on the sulfur cathode can significantly improve the cycling stability and capability of Li–S batteries (Shown in Figure 2.18. $^{278}$). The thickness of alucone coating has been optimized and investigated for electrochemical performances with 2, 5, 10 and 20 MLD cycles on the surface of sulfur electrodes. Different from the Al$_2$O$_3$ coating layers, all of the alucone coated electrodes show effective enhancement in stability and CE, in which 5 cycles of alucone coating delivers the highest specific discharge capacity of 710 mAh g$^{-1}$ after 100 cycles and stable CE of over 90%. When compared to previous ALD-Al$_2$O$_3$ coatings, MLD-alucone shows superior electrochemical performances, which is shown in Figure 2.18. The morphologies of the pristine electrode and alucone-coated electrode have been examined before and after electrochemical cycling by SEM. The SEM results indicate that the pristine electrode is totally covered with discharge products after cycling, however, the alucone coating can effectively inhibit the discharge products deposition on the surface. It is believed that the reduced dissolution of polysulfide and good mechanical properties of the alucone coating lead to the highly improved electrochemical performances for C/S cathodes.
During our research of alucone-coated C/S electrodes, a more interesting phenomenon has been further explored and revealed in our latest report. We found that alucone coated C/S electrodes can not only display a high specific capacity in ether-based Li-S electrolyte (LiTFSI in DOL/DME), but also can be used in traditional carbonate-based Li-ion electrolyte (LiPF$_6$ in EC/DEC/EMC), which has not been realized before. Furthermore, cycling can also be carried out at high temperature with ultra-long cycle life and stability. Figure 2.18 show the electrochemical performances, in which the alucone-coated electrode delivers an initial capacity of 912 mAh g$^{-1}$ and stabilizes at 429 mAh g$^{-1}$ after 100 cycles. However, the bare C/S electrode drops to 159 mAh g$^{-1}$, indicating the occurrence of irreversible electrochemical processes. Meanwhile, the alucone-coated C/S electrode displays well-defined plateaus during discharge/charge process and the reproducible cathodic/anodic peaks in the CV curves. To demonstrate the electrochemical performances of high temperature Li-S batteries, the alucone-coated C/S electrode has been tested with both ether-based and carbonated-based electrolyte at 55 °C. Impressively, alucone-coated C/S electrodes demonstrate improved capacity and extended cycle life in Li–S batteries using carbonate-based electrolyte. The capacity of the alucone-coated electrode remains at 661 mAh g$^{-1}$ after 50 cycles with a capacity retention of 573 mAh g$^{-1}$ after 300 cycles. The controllable nature of MLD enables the usage of conventional carbon-sulfur cathode materials in traditional carbonate-based electrolyte for Li-S batteries, and provides a facile and versatile method that can be applied to a variety of C–S electrodes without redesigning the carbon host materials.

In this section, the recent development of MLD in the application of energy storage (batteries and supercapacitors) have been summarized in detail. Briefly, the MLD thin film can be used for energy storage applications in terms of three approach: 1) directly use MLD thin film as electrodes; 2) nanocomposites derived from MLD thin films; 3) surface modification by MLD thin film. Although, there are only few reports for MLD thin film in the applications of batteries and supercapacitors and MLD has already shown promising potentials in this areas. These farther efforts will continue to build better design and wider application of MLD thin film for battery and supercapacitor applications, leading to the high performance, long life time energy storage devices.
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Chapter 3

3 Experimental Apparatus and Characterizations Techniques

In this chapter, the different electrode fabrication, as well as physical and electrochemical characterization techniques are states here.
3.1 Experimental apparatus

3.1.1 Atomic layer deposition and molecular layer deposition systems

Figure 3.1 Savannah 200 ALD system (Veeco/carbon nanotube (CNT) division of the Veeco Instruments Inc.)

Atomic layer deposition for air stable samples was conducted in a Savannah 200 ALD system (Veeco/carbon nanotube (CNT) division of the Veeco Instruments Inc.), as shown in Figure 3.1. In this thesis, ALD Al$_2$O$_3$ on carbon paper (CP) was carried out in this system. In a typical process, the ALD Al$_2$O$_3$ deposition was grown on CP at 120 °C by using trimethylaluminium (TMA) and water (H$_2$O) as precursors for 200 cycles.
Atomic layer deposition and molecular layer deposition for air sensitive samples (Li and Na foil) were carried out in a Gemstar-8 ALD system (Arradiance, USA), which is directly connected to an argon-filed glove box (as shown in Figure 3.2).

For the Na protection projects, ALD-Al₂O₃ was directly deposited on the Na foil at 85°C by using TMA and H₂O as precursors. The different cycle numbers of 10, 25 and 50 ALD Al₂O₃ coating were deposited on Na metal. The ALD-Al₂O₃ process used as 0.01 s/40 s/0.01 s/70 s TMA pulse/purge/ H₂O pulse/purge sequence. MLD-Alucone was directly deposited on the as-prepared Na foil at 85 °C by alternatively introducing TMA and ethylene glycol (EG) as precursors. The MLD process used as 0.01 s/40 s/0.01 s/70 s TMA pulse/purge/EG pulse/purge sequence.

For the Li protection projects, ALD-Al₂O₃ was performed using TMA and H₂O as precursors at 120 °C on Li foil. The ALD process used as 0.01 s/30 s/0.01 s/50 s TMA pulse/purge/ H₂O pulse/purge sequence with a growth rate of 0.1 nm/cycle. MLD-Alucone was directly deposited on the Li foil at 120 °C by alternatively introducing TMA and EG as precursors. The MLD process used as 0.01s/40s/0.01s/70s TMA pulse/purge/EG pulse/purge sequence with a growth rate of 0.5 nm/cycle.
3.1.2 Chemical vapor deposition for N doped carbon nanotubes.

Al$_2$O$_3$ was deposited on the CP at 120 °C by using trimethylaluminium (TMA) and water (H$_2$O) as precursors for 200 cycles. Then, the Al$_2$O$_3$ coated CP was loaded into a vertical tube furnace that was ramped from room temperature to 856 °C using an Ar flow of 200 mL min$^{-1}$. Catalyst ferrocene solution (solvent: acetonitrile, concentration: 0.02 g mL$^{-1}$) was then introduced into the quartz tube at a flow rate of 0.1 mL min$^{-1}$ as for 5 min under Ar atmosphere. Following this, imidazole solution is injected into the quartz tube (solvent: acetonitrile, concentration: 0.2 g mL, flow rate: 0.1 mL min$^{-1}$) to grow NCNT bundles for the controlled times followed by cooling to room temperature. The times of grown NCNTs have been adjusted as 10 mins, 20 mins and 30 mins. The obtained samples is named as CP-NCNTs.

3.1.3 Thermal infusion of Na@CP-NCNTs composites

As-prepared CP-NCNTs was cut into 3/8 inch disks and transferred into an Ar-filled glove box with less than 0.1 ppm water and 0.1 ppm O$_2$. Thermal infusion of Na melting was carried out inside the glove box. Bulk Na (from Aldrich) was cut into smaller pieces and placed in a stainless-steel boat and heated on a hot plate until Na began to melt. The prepared CP-NCNTs disk was then placed into the molten Na to obtain the Na@ CP-NCNTs composite electrodes.

3.1.4 Chemical reaction for Na$_3$PS$_4$ on Na metal

The Na$_3$PS$_4$ protective layers were fabricated by the in-situ solution-based method. All the experiment were performed in the Ar-filled glove box (H$_2$O and O$_2$ < 0.1 ppm) to prevent the effects from the moisture and oxygen. Typically, the P$_4$S$_{16}$ powders with controllable amount (10 mg, 20 mg, and 30 mg) were dissolved in 20 mL solvent of diethylene glycol dimethyl ether (DEGDME) with the calculated concentration of 0.5, 1 and 1.5 mg mL$^{-1}$. The prepared P$_4$S$_{16}$-DEGDME solutions were kept in glove box for more than 3 day to obtain the clear liquid with complete dissolution. A fresh Na foil with the diameter of 3/8 inch was prepared with the aid of a homemade press machine by pressing a piece of sodium metal stick (from Aldrich) as a starting sodium metal. Then, a piece of Na foil and 1 mL of P$_4$S$_{16}$-DEGDME solutions (with different concentrations)
were added into a reactor with the controlled reaction times (15 min, 60 min and 90 min). After reaction, the coated Na foil was taken out from the solution and transferred into the heating chamber connected with glove box. The coated Na foil was dried at 80 °C for 2 h to remove the residual solvent of DEGDME.

### 3.2 Characterizations techniques

The physical and chemical properties of the different Li/Na electrodes, such as morphology, structure, components, chemical bonding, surface area, et al. have been determined via varies of analytical techniques, such as scanning electron microscope (SEM), X-ray diffraction (XRD), Raman spectroscopy (RS), Rutherford Backscattering Spectrometry (RBS), X-ray photoelectron spectroscopy (XPS), Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) etc. To investigate the electrochemical properties of as-prepared Li/Na electrode, galvanostatic cycling performance with different current densities, and electrochemical impedance spectroscopy (EIS) were conducted with assembled symmetrical cells.
3.2.1 Physical Characterizations

**Figure 3.3** The Hitachi 3400N Environmental Scanning Electron Microscopy

The morphologies of the samples were characterized by a Hitachi 3400N Environmental Scanning Electron Microscopy at an acceleration voltage of 5 kV, as shown in **Figure 3.3**.
X-ray diffraction (XRD) was used to provide the phase structure information of the prepared electrode. The XRD pattern of the samples were collected on a Bruker D8 Advance Diffractometer using Cu Kα radiation at 40 kV and 40 mA (As shown in Figure 3.4).

X-ray photoelectron spectroscopy (XPS) was used to analyze the chemical composition and bonding by detecting the amount of the escaped electrons from the surface of the samples at a certain excitation energy. The XPS measurements were carried out in Western Surface Science using an Ar glovebox connected XPS (Kratos AXIS Ultra Spectrometer) system for air sensitive samples.
The surface area of the electrodes was calculated by the Brunauer, Emmett, and Teller (BET) model by taking at least six data points where $0.07 < P/P_0 < 0.2$. Pore size distribution was obtained by the Barrett, Joyner, and Halenda (BJH) model using the desorption branch of the isotherm. The photo of Folio Micromeritics TriStar II 3020 Surface Area and Pore Size Analyzer is shown in Figure 3.5.

Raman scattering spectra were recorded using a Nicolet 380 and a HORIBA Scientific LabRAM HR Raman spectrometer system (As shown in Figure 3.6) equipped with a 532.4 nm laser.
Rutherford Backscattering Spectrometry measurements (As shown in Figure 3.7) were conducted using 2.5 MeV He$^+$ beam (Western Tandetron Facility) at several locations on the surface to confirm the uniformity of the thicknesses and composition. All samples were transferred in Ar-filled glove bag with minimum exposure to air. A Sb-implanted amorphous Si sample with a known $4.82 \times 10^{15}$ atoms /cm$^2$ Sb content used for calibration.

Figure 3.7 RBS beamline in Western Tandetron Facility [1]

Figure 3.8 ION-TOF (GmbH,Germany) ToF-SIMS IV in Surface Science Western [2]
The ToF-SIMS measurements were conducted using an ION-TOF (GmbH, Germany) ToF-SIMS IV with a bismuth liquid metal ion source, as shown in Figure 3.8. The base pressure of the analysis chamber was ~10⁻⁸ mbar. The action of the primary ion beam bombardment on the sample surface induces the emission of negative secondary ions. The analysis area was 334 × 334 μm². Sputtering with a Cs⁺ ion beam (3 keV) was used for depth profiling analysis with the sputtering areas of 100 × 100 μm².

### 3.2.2 Electrochemical characterizations

Electrochemical analysis was performance in CR2032 coin-type cells. The coin cells were assembled in an ultra-pure argon filled glove box with a symmetrical Li(Na)/Electrolyte-Separator/Li(Na) system using polypropylene separator (Celgard 2400 or Celgard 3501). Different electrolytes have been applied in different studies, which will be discuss in detail in the different sections.

![Figure 3.9 Land 2001A Battery Test System](image)
The stripping/plating studies were carried out on a Land 2001A Battery Test System (Figure 3.9) or Arbin BT-2000 Battery Test System (Figure 3.10) at room temperature. A constant current was applied to the electrodes during repeated stripping/plating while the potential was recorded over time in the symmetric cell testing. Electrochemical impedance spectroscopy (EIS) was also performed on the versatile multichannel potentiostat 3/Z (VMP3).

3.3 Reference


Chapter 4

4 Robust Metallic Lithium Anode Protected by Molecular Layer Deposition Technique*

Li metal anode is considered as the promising alternative candidate for next generation Li-metal batteries with high specific capacity, low potential and light weight. However, the crucial problem on Li metal anode is one of the biggest challenges. Mossy or dendritic growth of Li occurs in the repetitive Li stripping/plating process with an unstable solid electrolyte interphase layer of non-uniform ionic flux, which can not only lead to the low Coulombic efficiency, but also can create short circuit risks, resulting in possible burning or explosion. In this chapter, we demonstrate the advanced molecular layer deposition (MLD) Alucone protective layer for Li metal anode. By protecting Li foil with controllable Alucone layer, the dendrites and mossy Li formation have been effectively suppressed and lifetime has been significantly improved in different electrolytes (carbonate-based and ether-based). Furthermore, the detailed surface change by advanced characterization techniques of Rutherford Backscattering Spectrometry (RBS). The novel design of molecular layer deposition protected Li metal anode may bring in new opportunities to the realization of the next-generation high energy-density Li metal batteries.

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4.1 Introduction

Recently, the depletion of fossil fuels and environment pollution have become a forefront issue and has become a serious hindrance to the development of a sustainable global economy [1]. Therefore, the exploration and usage of clean and sustainable energy as well as the development of systems and devices for energy storage and conversion is necessary [2]. Rechargeable lithium-ion batteries (LIBs), have drawn great attention recently because of their high energy density, minimal self-discharge and no memory effect, indicating potential application in portable electronics, electric vehicles and renewable energy industries [3]. Compared with commercial LIBs, Li-metal batteries (LMBs), including Li-S batteries, Li-air batteries and all solid-state batteries, have been strongly considered as next generation devices with high theoretical energy density (2600 Wh Kg\(^{-1}\) for Li-S and 11680 Wh Kg\(^{-1}\) for Li-air) [4]. For LMBs, metallic Li is an ideal anode materials due its high specific capacity (3860 mAh g\(^{-1}\)), low potential (-3.04 V vs. the standard hydrogen electrode) and light weight (0.53 g cm\(^{-3}\)) as well as the high energy density of 11680 Wh Kg\(^{-1}\), which is nearly equivalent to gasoline [5]. However, a number of issues, such as dendrite growth and volume change, plague the successful application of lithium metal for practical devices. The constant stripping/plating process of Li in each cycle eventually leads to uneven surface morphology and further the mossy or dendritic Li growth with poor coulombic efficiency (CE) as active lithium is lost to side reactions (Fig.1) [6, 7]. In this case, it can cause two critical problems for Li metal, one is safety hazards because of potential internal short circuits, and another is short cycle life. Even more serious, safety issues like smoke or fire and other hazards will be caused by the dramatic failure of the batteries [7].

One of the key points for metallic Li anode is the formation of a solid electrolyte interphase (SEI) layer, which is formed during the initial charging/discharging processes as a result of reaction between Li metal and different components in the electrolyte. Although the SEI formation will intrinsically consumes both Li anode and electrolyte, leading to lower the CE, it can effectively prevent further contact and reactions between the Li anode and the electrolyte, making the Li anode stable in the electrolyte after a few initial cycles. It is considered that the unstable SEI layer is much easier to cause dendrite
growth, in which the collapse of the SEI film can aggravate local dendrite growth and undesired electrolyte deposition due to non-homogeneous local current buildup.

In the past several decades, researchers have focused on developing various approaches to achieve a stable SEI layer for long life Li metal anode. These strategies can be generally divided into two parts: in-situ SEI formation and ex-situ artificial SEI film [8]. On one hand, the in-situ formation of stable SEI film is developed by adjusting the electrolyte composition and additives [9, 10]. However, it is considered that mechanical strength of these in situ formed protective films is not high enough to withstand the large volume change during Li plating/stripping process [11]. On the other hand, an effective approach is to develop novel coating layers on metallic Li in the form of an ex-situ SEI film to reduce or prevent dendrite growth. Different types of coating layers have been applied on the surface of Li metal for dendrite prevention, including: organic protective layers [12], inorganic protective layers [13], organic-inorganic composite protective layer [14, 15]. For example, a Li-ion conductive inorganic/organic composite protective layer (CPL) has been developed as coating on Li metal anode and has effectively suppressed dendrite growth and electrolyte decomposition, even under high current density [15].

However, challenges still remain for lithium protection and dendrite prevention, in which the controllable and uniform coating under low temperature (lower than the melt point of Li: 180.5 °C) is an issue for applying common method for thin film, e.g. chemical vapor deposition or any wet chemical method. Atomic layer deposition (ALD) can be an ideal technique which can achieve excellent coverage and conformal deposition under relatively low temperatures with precise control over coating thickness at the nanoscale level due to its self-limiting nature [16]. Recently, two different groups have demonstrated ultrathin ALD Al₂O₃ coating film as protective layer for metallic lithium [17]. In their results, the ALD Al₂O₃-protected Li can prevent Li metal corrosion in electrolyte and reduce the dendrite growth as well, which further enhances electrochemical performance with elevated capacity and longer lifetimes. Very recently, our group also successfully demonstrates the ALD Al₂O₃ protecting Na metal anode, which can achieve superior long life time and reduced dendrite growth [18]. Molecular layer deposition (MLD), as an analogy of ALD, can be employed to produce pure
polymeric thin films or inorganic–organic hybrid thin films, which can hold many advantages such as lower growth temperatures, tunable thermal stability, and improved mechanical properties [19, 20]. Furthermore, the toughness and flexibility of polymeric metal thin films by MLD are strengthened with the introduction of C–C and C–O bonds in this system, which is expected to accommodate its huge volume expansion and dendrite growth of Li metal anode [21].

In this chapter, we first demonstrate ultrathin MLD coating as a protective layer for metallic Li anode for improved life time and stability of Li metal anode. Compared with bare Li foil, MLD coating layer can stabilize the SEI film and further change the morphology of lithium growth. Meanwhile, the MLD coating layer can greatly improve the stability in both ether-based (used in Li-S batteries) and carbonate-based (used in Li-ion batteries) electrolyte, which is more promising compared with ALD Al₂O₃ coating. Another interesting phenomenon is that the optimized thickness of MLD coating layer should be adjusted depending on the electrolytes used. Moreover we also discuss the detailed surface change by advanced characterization techniques of Rutherford Backscattering Spectrometry (RBS). To the best of our knowledge, we are the first time to demonstrate a powerful tool of RBS measurement in the field of Li metal anode, which give the guidance to the researchers working in this area.

4.2 Experimental section

**Electrode preparation:** Li foil was purchased China Energy Lithium Co. LTD from with further polishing before using, which is storage in the argon-filed glove box. Molecular layer deposition (MLD) of Alucone coatings were conducted in a Gemstar-8 ALD system (Arradiance, USA) directly connected with argon-filed glove box. Alucone was directly deposited on the Li foil at 120 °C by alternatively introducing trimethylaluminium (TMA) and ethylene glycol (EG) as precursors. The MLD process used as 0.01 s/40 s/0.01 s/0 s TMA pulse/purge/EG pulse/purge sequence with a growth rate of 0.5 nm/cycle. The different cycle numbers of 5, 10, 25 and 50 MLD Alucone coating on Li foil are named as Li@5Alucone, Li@10Alucone, Li@25Alucone, and Li@50Alucone, respectively.
For comparison, ALD Al₂O₃ was performed using TMA and H₂O as precursors at 120 °C. The ALD process used as 0.01 s/30 s/0.01 s/50 s TMA pulse/purge/ H₂O pulse/purge sequence with a growth rate of 0.1 nm/cycle. The different cycle number of 10, 25, and 50 ALD Al₂O₃ has been coated on the Li foil named as Li@10Al₂O₃, Li@25Al₂O₃ and Li@50Al₂O₃, respectively.

**Electrochemical measurements:** The electrochemical analysis were performance in CR2032 coin-type cells. The coin cells were assembled in an ultra-pure argon filled glove box by symmetrical Li/Electrolyte-Separator/Li system using polypropylene separator (Celgard 2400). The electrolyte used in this study was a 1 M LiTFSI salt in dioxolane (DOL): dimethoxyethane (DME) of 1:1 volume ratio with 1% lithium nitrate, which has been used by our group for Li-S studies. The stripping/plating studies were carried out in an Arbin BT-2000 Battery Test System at room temperature. A constant current was applied to the electrodes during repeated stripping/plating while the potential was recorded over time. Another carbonate-based electrolyte is also used for comparison, which is 1 M LiPF6 salt dissolved in ethylene carbonate (EC): diethyl carbonate (DEC): ethyl methyl carbonate (EMC) of 1: 1: 1 volume ratio.

Lithium-sulfur batteries were tested via CR2032 cells using protected Li (Li@50Alucone) and C/S cathode with 1M LiTFSI in DOL: DME 1:1. The C-S composite is synthesized by using commercial carbon black (KJ EC-600, US) mixed with sulfur powder (99.5 %, Sigma-Aldrich) and dried at 80 °C for 12 h to remove moisture. The carbon-sulfur mixture was then transferred to a sealed steel reactor and was heated at 150 °C for 9 h and then 300 °C for 3 h. The obtained carbon-sulfur composites (C-S) maintained 70 wt% sulfur loading. The electrodes were prepared by slurry casting onto aluminum foil. The slurry mass ratio of active material, acetylene black, and polyvinylidene fluoride (PVDF) is 80:10:10. The as-prepared electrodes were finally dried at 80 °C over 12 h under vacuum. The areal loading of sulfur in cathode electrode is about 0.9-1.2 mg cm⁻². Charge-discharge characteristics were galvanostatically tested in the range of 1.0 V - 3.0 V (vs. Li/Li⁺) at room temperature using a Landlike Battery Test equipment.
Characterization: SEM images were taken using a Hitachi 3400N Environmental Scanning Electron Microscopy at an acceleration voltage of 5 kV. Due to the soft properties of Li metal, Swagelok type cells comprised of Li/Electrolyte-Separator/Li system were used to carry out the morphology testing after stripping/plating. The Swagelok cells were disassembled after 30 cycles of stripping/plating process under the different current density. The Alucone coated Li foil are transferred from our ALD glove box directly to an Ar glovebox connected XPS (Kratos AXIS Ultra Spectrometer) system for XPS analysis. Rutherford Backscattering Spectrometry measurements were conducted using 1MeV and 2.5MeV He+ beam (Western Tandetron Facility) at several locations on the surface to confirm the uniformity of the thicknesses and composition. All samples were transferred in Ar-filled glove bag with minimum exposure to air. A Sb-implanted amorphous Si sample with a known $4.82 \times 10^{15}$ atoms /cm$^2$ Sb content used for calibration.

4.3 Results and discussion

![Diagram](image)

Figure 4.1 Schematic diagrams of lithium stripping/plating on bare Li foil and Li foil with MLD coating

The Alucone (Al-EG) film was directly deposited on Li metal anode using trimethylaluminium (TMA) and ethylene glycol (EG) as precursors at 120 °C by a glovebox-integrated ALD tool. The growth rate of Alucone was evaluated by placing a silicon wafer in the deposition chamber at the same time as lithium foil. Alucone growth rate was determined by X-ray reflectometry (XRR) to be $\sim 0.5$ nm/cycle (Figure S4.1).
The influence of Alucone thickness is investigated in detail with 5, 10, 25 and 50 MLD cycles with thickness of 2.5, 5, 10, and 25 nm, respectively (named as Li@5Alucone, Li@10Alucone, Li@25Alucone, and Li@50Alucone). X-ray photoelectron spectroscopy (XPS) is used to investigate the surface of Li foil after Alucone deposition, which is shown in Figure S4.2. Peaks at 70.15, 281.55, and 527.95 eV can be attributed to Al, C and O, respectively. It can be demonstrated that the Alucone coating containing Al and EG has been successfully deposited on the Li foil. Rutherford backscattering spectrometry (RBS) were carried out on Al₂O₃-coated and Alucone-coated Li anodes before and after cycling. Figure S4.3 shows that as-deposited Al₂O₃ film forms a continuous layer ~14 nm thick (assuming \( \text{Al}_2\text{O}_3 = 2.7\text{ g cm}^{-3} \)). Li surface peak is not observed; the best-fit model (Figure S4.3 (b)) assumes formation of the interfacial layer between Al₂O₃ and Li metal or Li surface roughness. Alucone film thickness (Figure S4.3 (d)) is also continuous and slightly thicker for the same number of MLD deposition cycles. Amount of O and C in the Alucone film is consistent with \( \text{Aln(CO)}_m \) stoichiometry, with \( n \approx m=1 \).

Figure 4.2 (a) Comparison of the cycling stability of the Li@10Alucone cycles and the bare Li foil at a current density of 3 mA cm\(^{-2}\) in DOL/DME electrolyte; Voltage profiles of Li@10Alucone cycles and bare Li foil in the first cycles (b) and after 100 cycles (c) at a current density of 3 mA cm\(^{-2}\). (d) Comparison of the cycling stability of the Li@10Alucone cycles and
the bare Li foil at a current density of 5 mA cm\(^{-2}\) in DOL/DME electrolyte; Voltage profiles of Li@10Alucone cycles and bare Li foil in the first cycles (e) and after 100 cycles (f) at a current density of 5 mA cm\(^{-2}\). The amount of Li cycled was 1mAh cm\(^{-2}\).

The galvanostatic cycling performance of Li with MLD Alucone coating layers and bare Li foil were studied in ether-based electrolyte, commonly employed in Li-S batteries (1 M LiTFSI in DOL: DME of 1:1 volume ratio with 1 wt% LiNO\(_3\)). Figure 4.2(a) shows the cycling stability of Li@10Alucone and bare Li foil at a current density of 3 mA cm\(^{-2}\). For bare Li foil, the initial Li stripping/plating over-potential is approximately 50 mV (versus Li\(^+\)/Li) and rapidly increases to over 120 mV (versus Li\(^+\)/Li) after 50 cycles. Following this, the over-potential of bare Li remains at 80 mV (versus Li\(^+\)/Li) for up to 100 cycles. Protected Li, with 10 cycles Alucone, shows a minor initial over-potential of about 100 mV (versus Li\(^+\)/Li), which can be attributed to the formation an ionic conductive SEI film between Alucone and Li. The over-potential of Li@10Alucone decreases after the first few cycles to 40 mV (versus Li\(^+\)/Li) and maintains this over-potential over 100 cycles (50 mV versus Li\(^+\)/Li). Figure 4.2(b, c) shows the detailed voltage profiles of Li@10Alucone and bare Li foil in the first cycle and after 100 cycles. Increasing the current density to 5 mA cm\(^{-2}\), the initial Li stripping/plating over-potential for bare Li increases to 80 mV (versus Li/Li\(^+\)). After 20 cycles, there is a sudden rise of over-potential to 160 mV (versus Li/Li\(^+\)) with following fluctuations in over-potential voltage. Meanwhile, an obvious drop of voltage can be observed for the bare Li foil in around 43 cycles, which could be explained as a soft short-circuit with Li dendrite penetration. However, with 10 cycles of Alucone, the protected Li foil indicates the similar initial over-potential of 100 mV (versus Li/Li\(^+\)) under the current density of 5 mA cm\(^{-2}\). It also can be ascribed to the activated process for Li transportation. The protected Li is extremely stable over 100 cycles with the over-potential of 70 mV (versus Li/Li\(^+\)), which is much lower than that of the bare Li (over 200 mV after 100 cycles). From the voltage profiles of Li@10Alucone at the current density of 5 mA cm\(^{-2}\), a flat voltage plateau at both the charging and discharging states can be retained throughout the whole cycle with minimal increase in hysteresis (Figure 4.2(e, f)). It also should be noticed that the differences in the initial few cycles in the plating/stripping curves are attributed to the lithiation of Alucone and the stable SEI layer formation. To further explain the
performances, electrochemical impedance spectroscopy (EIS) was performed at the point of before cycling and after 50 cycles, as shown in Figure S4.7(a, b, c) and impedance parameters calculated by equivalent circuits for different samples are shown in Tab.S1. Figure S4.7(a) indicates the initial spectra with a slight increase in the impedance for the Li@10Alucone compared with bare Li foil before cycling. After 20 cycles of plating/stripping process (Figure S4.7(b)), the RSEI of both bare Li and Li@10Alucone decreases, in which the resistance of Li@10Alucone is lower than bare Li. Furthermore, resistance of bare Li maintains its resistance value over 50 cycles while Li@10Alucone further decreases (Figure S4.7(c)), demonstrating formation of a stable SEI layer with Alucone protection.

Furthermore, the protected Li foil with 10 cycles Alucone coating shows superior stripping/plating performances with super-long lifetime. Figure S4.4(a) shows the long life cycling performances of Li@10Alucone at the current density of 3 mA cm\(^{-2}\), in which the protected Li can work for more than 500 cycles (500 h) without any short circuit occurring. From the voltage profiles (Figure S4.4 (b)), the curves from the first cycle, 100 cycles, 300 cycles and 500 cycles show a flat plateau at 50 mV (versus Li/Li\(^{+}\)), indicating an extraordinary stable performances with super-long lifetime. Even at high current density of 5 mA cm\(^{-2}\) (Figure S4.4 (c)), there is also no voltage fluctuation up to 500 cycles with flat plateaus occurring at 60 mV (versus Li/Li\(^{+}\)).
In order to understand the influence of MLD Alucone coating on Li dendrite growth, morphology of lithium metal was imaged before and after cycling by SEM. SEM images of bare Li foil are shown in Figure 4.3 (a, b) with a flat surface. After 10 cycles of MLD Alucone coating (Figure 4.3 (c, d)), there is no obvious difference of the quite smooth surface due to the ultrathin thickness of coating layers (~5 nm). After 30 cycles of Li plating/stripping process at a current density of 3 mA cm$^{-2}$, unordered Li dendrite growth can be observed on the bare Li foil (Figure 4.3 (e, f)) with protrusions of over 10 μm occurring. This growth can be attributed to the broken and repeatedly repaired of SEI layer during cycling, resulting in serious growth of sharp Li dendrite. This type of Li dendrite growth can facilely detach from the underlying foil, resulting in the formation of dead Li in subsequent plating and stripping and will consume effective Li and lower the columbic efficiency. Furthermore, the sharp and long dendrite can penetrate the separator, causing short circuit and detrimental safety issues. When increasing the current density to 5 mA cm$^{-2}$, after 30 cycles of plating/stripping similar Li dendrite growth can be observed (Figure S4.8). Promisingly, the morphology of the cycled Li with Alucone coating is drastically different. Figure 4.3 (g, h) shows the SEM images of Li@10Alucone after 30 cycles of stripping/plating under a current density of 3 mA cm$^{-2}$. 

Figure 4.3 Top-view SEM images of bare Li (a, b) and Li@10Alucone cycles (c, d); Top-view SEM images of bare Li (e, f) and Li@10Alucone (g, h) after 30 cycles of stripping/plating in DOL/DME electrolyte at a current density of 3 mA cm$^{-2}$. The amount of Li cycled was 1mAh cm$^{-2}$. 

![Figure 4.3 SEM images of Li and Li@Alucone](image-url)
With the assistance of MLD, the Li dendrites exhibit a nodule-like structure with round-shaped edges and present very dense structure on the surface of Li anode [10]. Even at higher current density of 5 mA cm\(^{-2}\), uniform growth of the reduced Li dendrites can be observed. The larger dimension of nodule-like dendrites can effectively limit their penetration through the separator. Furthermore, this diminished dendrites growth can effectively reduce the high surface area caused by mossy dendrites growth on the bare Li foil (Figure 4.3 (g, h)), which can decrease the contact area between electrolyte and Li. Meanwhile, this kind of structure can be well maintained during the cycling, resulting in better performance and longer life time. It can be considered that with the protection of Alucone, the SEI film is expected to be stabilized with good mechanical strength and ionic conductivity.

The thickness effect of MLD Alucone coating has also been investigated with MLD cycle numbers of 5, 25, and 50 in Figure 4.5. Figure S4.5 (a, e) shows the Li plating/stripping performances of protected Li with 5 cycles Alucone coating. The cycling performances of Li@5Alucone are more stable than the bare Li foil without any fluctuating of voltage. However, the over-potential of Li@5Alucone after 100 cycles at the current density of 3 and 5 mA cm\(^{-2}\) are 70 and 80 mV (versus Li/Li\(^+\)), respectively, which is a little higher than 10 cycle Alucone coated Li foil, demonstrating an increase in hysteresis with less Alucone coatings. When increasing the Alucone coating to 25 cycles (Figure S4.5 (b, f)), the cycling stability during plating/stripping is still very promising compared to bare Li. The over-potential after 100 cycles at a current density of 3 and 5 mA cm\(^{-2}\) are 50 mV and 70 mV, respectively, which are similar with the results of 10 cycles Alucone coating. However, when applying a thicker coating of 50 cycles, although stable plating/stripping performance is achieved, the over-potential is much higher than the protected Li with 10 and 25 cycles of Alucone (Figure S4.6). The results demonstrate that the optimizing of Alucone thickness is an important factor for the electrochemical performances of protected Li foil during plating/stripping process, in which too thin (5 cycles Alucone) or too thick (50 cycles Alucone) coatings can achieve stable cycling performances but higher resistance. Meanwhile, the morphologies of electrodes with 5 cycles and 25 cycles Alucone are also investigated, showing in Figure S4.9 and Figure S4.10. With thinner coating (5 cycles), it has been partial improved for dendrite growth, in which sharp and
long Li dendrite still can be seen on the surface. When increase the thickness into 25 cycles Alucone, the similar structure with dense and shorter rod-like Li is formed which is consistent with the electrochemical performances with different cycles discussed above. So, the optimal thickness of MLD Alucone protective coating layer is 10-25 cycles.

Figure 4.4 (a) Comparison of the cycling stability of the bare Li foil, Li@10Alucone, Li@25Alucone and Li@50Alucone at a current density of 1 mA cm$^{-2}$ in EC/DEC/EMC electrolyte; Voltage profiles of Li foil, Li@10Alucone, Li@25Alucone and Li@50Alucone in the first cycles (b) and after 140 cycles (c) at a current density of 1 mA cm$^{-2}$.

It is well known that dendrite growth in carbonate-based electrolyte is more serious than in ether-based electrolyte. We also applied Alucone coated Li in carbonate-based electrolyte (1 M LiPF$_6$ in EC: DEC: EMC of 1:1:1 volume ratio) to study the Li plating/stripping performances. For pure Li foil, obvious voltage fluctuations can be observed after about 300 h of plating/stripping, with a rapid increase in over-potential occurring, indicating the
ceaseless increase of resistance in the system and short circuit happening during this time (Figure 4.4 (a)). It is very promising that with the protective coating layers of Alucone, the polarization curve is more stable than the bare Li foil (Figure 4.4 (a)). In the above discussion, Li foil with 10 cycles Alucone coating in ether-based electrolyte shows the best plating/stripping performances. Interestingly, in the carbonate electrolyte, 10 cycles of Alucone coating is not enough to form a stable SEI film, and demonstrates a slow rise in voltage. From Figure 4.4 (a), it can be found that when increasing thickness to 50 cycles of Alucone, the most stable plating/stripping performances can be achieved. The voltage profiles in Figure 4.4(b, c) indicate a constant potential with almost no change in Li@50Alucone after 1 cycle and 140 cycles of plating/stripping. Thus, MLD Alucone coating can be an excellent candidate for the protection of Li metal anode for both ether-based and carbonate-based electrolyte with long cycle life and superior stability. Meanwhile, our study also demonstrates that the thickness of Alucone coating should be optimized based on the different types of electrolyte. It can be considered that a thinner coating layer is needed for ether-based electrolyte (DOL/DME), which can easily form a stable SEI layer with Alucone coating (10 cycles). For the carbonate-based electrolyte (EC/DEC/EMC), a thicker coating (50 cycles) is required to form a stable SEI.

![Figure 4.5](image)

**Figure 4.5** (a) Comparison of cycling performance between bare Li, Li@25Al₂O₃ and Li@50Alucone in EC/DEC/EMC electrolyte at the current density of 1 mA cm⁻²; (b) Voltage profiles of Li@50Alucone and Li@25Al₂O₃ after 190 cycles at the current density of 1 mA cm⁻² in EC/DEC/EMC electrolyte.
ALD Al₂O₃ has also been investigated as protective coating for Li metal anode. The same glove-box contact ALD system was applied to deposit Al₂O₃, using TMA and water as precursor at 120 °C, in which the growth rate of Al₂O₃ under this condition is about 0.1 nm per cycles. Firstly, the thickness of ALD Al₂O₃ has also been optimized based on the Li plating/stripping performances in two types of electrolytes. **Figure S4.11** shows the cycling stability of Li foil with different cycles of ALD Al₂O₃ coating, including 10 cycles, 25 cycles and 50 cycles, in which the protected Li metal anode with 25 cycles of Al₂O₃ coating has the best performance and lowest over-potential in the ether-based electrolyte (DOL/DME). In the carbonate-based electrolyte, similar results are present in **Figure S4.12**, in which the optimized thickness of Al₂O₃ coating is still 25 cycles. Then, the comparison between Al₂O₃ and Alucone coating on the plating/stripping performances is shown in **Figure 4.5**. When testing in ether-based electrolyte (DOL/DME), both Al₂O₃ and Alucone show more stable polarization curves compared with bare Li foil. More obvious difference can be observed from **Figure 4.5 (a)** in the carbonate-based electrolyte. As discussed above, the bare Li foil only can be stabilized for 300 h with the unexpected short circuit. With 25 cycles Al₂O₃ coating, although there is no short circuit over 190 cycles, the voltage is continuously raised up after 300 h, declaring the increasing resistance and unstable of SEI film in long time cycling. Promisingly, Li@50Alucone indicates super-stable plating/stripping performances over 480 h (equal to 190 cycles). From the voltage profiles in **Figure 4.5 (b)**, the over-potential of Li@25Al₂O₃ is over 420 mV after 190 cycles, however, it is only 160 mV for Li@50Alucone. From the electrochemical plating/stripping performances, it indicates that optimized Alucone coating is more effective to form the stable SEI layer achieving long life Li metal anode compared with Al₂O₃ in both carbonate-based and ether-based electrolytes. It is believed that Alucone coating is highly stable against liquid electrolyte and acts as a passivating agent to assist Li metal anode to form a stable SEI layer. Meanwhile, Alucone coating is mechanically flexible and allows for repeated Li plating/stripping on the surface of Li foil. Furthermore, it is also considered that after lithiation, Alucone coating has high Li+ conductivity with the porous structure for Li ions transport [19, 22].
In order to elucidate compositional changes following the plating/stripping cycling experiments, RBS measurements were performed for all samples. **Figure 4.6 (a)** shows RBS spectra for bare Li, as well as Li coated with 25 cycles of ALD Al$_2$O$_3$ and 50 cycles of MLD Alucone films all after 10 cycles in carbonate based electrolyte (1M LiPF$_6$ in EC/DEC/EMC). While bare Li show significant penetration of P and F from electrolyte into subsurface layer, as well as oxidation, Al$_2$O$_3$- and Alucone-films act as good protective barriers, with small concentrations of P, F and C localized in the first 70-100 nm from the surface. Notably, Li@50 Alucone film mostly remains as a continuous film as evident from relatively sharp Al, O and C peaks, and very little changes in composition compared to as-deposited Alucone film (see **Figure S4.3 (d)**). In this case, it can be seen that both ALD Al$_2$O$_3$ and MLD Alucone coating can effectively reduce the reactions and penetration of electrolyte with Li metal. Meanwhile, the ALD Al$_2$O$_3$ protective layer will be fractured and MLD Alucone film can remain the better structure after 10 cycles of electrochemical plating/stripping (**Figure 4.6 (e)**), indicating the stronger film of Alucone during cycling. Effects of cycling in DOL/DME electrolyte on elemental depth profiles are illustrated in **Figure S4.13**. More substantial diffusion processes are evident after plating/stripping in more aggressive DOL/DME electrolyte. Al peak is not observed for Li@25 Al$_2$O$_3$ sample, indicating either removal of all Al or significant growth of Li on top Al$_2$O$_3$ layer. Al peak is still detectable for Li@50 Alucone.
sample, however Al depth profile goes deeper, consistent with significant morphological changes detected in SEM and Li diffusion.

For investigating the full cell performances, the Li-S coin cells were assembled with C/S composites as cathode electrode in the ether based electrolyte. The long-term cycling performance of these cells is shown in Figure S4.14. For the bare Li anode, the obvious capacity fade of C/S cathode can be observed due to the self-propagating reaction since the dissolved polysulfides enable to react with Li metal and finally form insulated Li₂S deposited on Li foil. After 100 cycles, the capacity and CE of the cell remain only 486 mAh g⁻¹ and 84%, respectively. Very promising, with MLD Alucone protective coating, the cell can be stabilized after initial 10 cycles and both the reversible capacities and CE have been significantly improved after 100 cycles (711 mAh cm⁻² and 95 %). It can be expected that the MLD Alucone coating can increase the long life time of the cell and improve the utilization of the sulfur by prevention of the corrosion and reaction between Li and polysulfide.

4.4 Conclusion

In conclusion, we firstly demonstrate the use of an MLD protective coating on Li metal anode for long life Li metal batteries. By protected Li foil with ultrathin Alucone layer, the sharp and long dendrites Li formation have been effectively suppressed and life time has been significantly improved. Meanwhile, we reveal a comprehensive study of Alucone coating in both ether-based and carbonated based electrolyte, both resulting in significant improvement on the plating/stripping performance of lithium metal. Remarkably, we also find that the thickness of Alucone coating should be optimized based on the electrolyte employed. Ether-based electrolytes (DOL/DME) demonstrate the best performance when using 10 cycles of Alucone coating and enables the formation of a stable SEI film with restrained dendrite growth. However, for carbonate-based electrolytes (EC/DEC/EMC) a thicker coating of 25 cycles Alucone is needed to achieve stable performance. Furthermore, a comparison between ALD Al₂O₃ and MLD Alucone has also been presented in detail for both electrolyte systems. Based on the plating/stripping performances, Alucone is more promising with longer life time, stable polarization curve and lower internal resistance compared with Al₂O₃, especially in
carbonate-based electrolyte. It is believed that our design of MLD Alucone coated metal Li anode open up new opportunities to the realization of the next-generation high energy density Li metal batteries.

4.5 Acknowledgements

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4.6 Reference


4.7 Supporting Information

Figure S 4.1 (a) XRR data and (b) growth rate of Alucone at 120 °C

Figure S 4.2 XPS Spectrum of Li@10Alucone cycles
Figure S 4.3 RBS spectrum of Li@50Al₂O₃ before plating/stripping (a) and depth profiles (b); RBS spectrum of Li@50Alucone before plating/stripping (c) and depth profiles (d);
**Figure S 4.4** Long life cycling Li strapping/plating performances of Li@10Alucone cycles at the current density of (a) 3 mA cm$^{-2}$ and (b) 5 mA cm$^{-2}$; in DOL/DME electrolyte; (c) and (d) Voltage profiles of Li@10Alucone cycles in the different cycles of 1, 100, 300, 500 cycles at the current density of 3 mA cm$^{-2}$ and 5 mA cm$^{-2}$.

**Figure S 4.5** The cycling stability of the (a) Li@5Alucone cycles and (b) Li@25Alucone cycles at a current density of 3 mA cm$^{-2}$ in DOL/DME electrolyte; Voltage profiles of Li@5Alucone cycles and Li@25Alucone cycles in the first cycles (c) and after 100 cycles (d); the cycling stability of the (e) Li@5Alucone cycles and (f) Li@25Alucone cycles at a current density of 5mA cm$^{-2}$ in DOL/DME electrolyte; Voltage profiles of Li@5Alucone cycles and Li@25Alucone cycles in the first cycles (g) and after 100 cycles (h). The amount of Li cycled was 1mAh cm$^{-2}$. 
Figure S 4.6 (a) Cycling stability of the Li@50Alucone cycles at a current density of (a) 3mA cm$^{-2}$ and (b) 5 mA cm$^{-2}$ in DOL/DME electrolyte; the amount of Li cycled was 1mAh cm$^{-2}$.

Figure S 4.7 Nyquist plot showing electrochemical impedance spectroscopy (EIS) of the bare Li and Li@10 Alucone before cycling (a), after 20 cycles (b) and after 50 cycles (c); the Li@5 Alucone and Li@25 Alucone before cycling (d), after 20 cycles (e) and after 50 cycles (f).
**Figure S 4.8** Top-view SEM images of bare Li (a, b) and Li@10Alucone cycles (c, d) after 30 cycles of stripping/plating in DOL/DME electrolyte at a current density of 5 mA cm$^{-2}$. The amount of Li cycled was 1mAh cm$^{-2}$.

**Figure S 4.9** (a-d) Top-view SEM images of Li@5Alucone cycles after 30 cycles of stripping/plating in DOL/DME electrolyte at a current density of 3mA cm$^{-2}$. The amount of Li cycled was 1mAh cm$^{-2}$. 
Figure S 4.10 (a-d) Top-view SEM images of Li@25Alucone cycles after 30 cycles of stripping/plating in DOL/DME electrolyte at a current density of 3 mA cm\(^{-2}\). The amount of Li cycled was 1mAh cm\(^{-2}\).

Figure S 4.11 (a) Comparison of the cycling stability of (a) the Li@25Al\(_2\)O\(_3\) cycles and bare Li foil; (b) the Li@10Al\(_2\)O\(_3\) and the Li@50Al\(_2\)O\(_3\) cycles at a current density of 3 mA cm\(^{-2}\); (c) the Li@25Al\(_2\)O\(_3\) cycles and bare Li foil; (d) the Li@10Al\(_2\)O\(_3\) and the
Li@50Al2O3 cycles at a current density of 3 mA cm\(^2\); the electrolyte is DOL/DME; The amount of Li cycled was 1mAh cm\(^2\).

**Figure S 4.12** Comparison of the cycling stability of the bare Li@10Al2O3, Li@25Al2O3 and Li@50Al2O3 at a current density of 1 mA cm\(^2\) in EC/DEC/EMC electrolyte.
Figure S 4.13 RBS spectra (a) and calculated depth profiles of bare Li, Li@25Al₂O₃ and Li@10Alucone after 10 cycles of plating/stripping at the current density of 3 mA cm⁻² in the LiTFSI in DOL/DME electrolyte.
Figure S 4.14 Cycle performance of Li-S batteries with the use of MLD alucone protected and bare Li foil with current density of 320 mA g⁻¹.
**Table S 4.1** Impedance parameters calculated by equivalent circuits for different samples.

<table>
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<tr>
<th>Samples</th>
<th>R_ESR Ω</th>
<th>R_SEI Ω</th>
<th>R_CT Ω</th>
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<td>Bare Li before cycling</td>
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<td>Bare Li after 20 cycles</td>
<td>4.61E-08</td>
<td>9.143</td>
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<td>Bare Li after 50 cycles</td>
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<td>1.06E+02</td>
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<tr>
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<td>111.2</td>
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</tr>
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<td>3.52</td>
<td>7.577</td>
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<td>3.583</td>
<td>4.387</td>
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<tr>
<td>Li@10Alucone before cycling</td>
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Chapter 5

5 Carbon Paper Interlayers: A Universal and Effective Approach for Highly Stable Li Metal Anodes*

As discussed in the last chapter, Li metal anode is considered as one of the most promising candidate for next generation Li metal batteries (LMBs) due to the unique properties of high specific capacity, low potential and light weight. However, the crucial problems, including serious Li dendrite growth, undesired side reactions and infinite volume changes, are still big challenges for Li metal anode, which can not only lead to the low Coulombic efficiency, but also can create short circuit risks. The surface modification approach is aimed on addressing the SEI stabilization of Li metal anode. The serious volume change of Li metal anode cannot be relieved by thin film coating. In this chapter, we propose a novel and universal approach to achieve long life time and dendrite free Li metal anodes by introducing carbon paper (CP) as an interlayer. As a result, the as-designed electrodes can deliver extremely high capacity (up to 3 mAh cm\(^{-2}\) and 5 mAh cm\(^{-2}\)), superior stable performances (620 h/265 cycles with 3 mAh cm\(^{-2}\)) and high operational current densities (3 mA cm\(^{-2}\) and 5 mA cm\(^{-2}\)). Meanwhile, the electrodes also can demonstrate high capacity and long life time in full cells using carbon-coated LiFePO\(_4\) (C/LiFePO\(_4\)) as the cathode for Lithium-ion batteries (LIBs) and molecular layer deposition (MLD) coated C/S as cathode for Li-S batteries. These new understandings could open a new window for the fabrication of safe, long life time and dendrite-free Li metal anodes.

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5.1 Introduction

Lithium-ion batteries (LIBs) have been utilized for many applications over the past decades such as portable electronics, electric cars, and large scale energy storage stations [1-3]. Next-generation lithium-based batteries with high energy density, including Li-S, Li-air and solid-state Li batteries, have recently received increasing attention. Among all the anode candidates, Li metal is one of the most promising anodes for lithium-based batteries due to its high theoretical capacity (3860 mAh g^{-1}), low electrochemical potential (-3.04 V vs. the standard hydrogen electrode) and light weight (0.53 g cm^{-3})[4-6]. The rechargeable Li-metal battery (LMB) was initially proposed in the 1970s, however, Li metal anodes hadn’t been further applied in commercial batteries due to safety concerns. The safety issues of the Li metal anode are mainly caused by dendritic Li formation during the electrochemical plating/stripping process [7-9]. The main challenges of Li metal anode can be listed as follows: 1) during the electrochemical plating/stripping process, the mossy and dendritic Li grow. As a result, the Li dendrites may penetrate through the separators, causing short circuits and leading to safety issues [10, 11]. Furthermore, Li dendrites can also become isolated from the bulk Li or current collector and become “Dead Li”, which is electrochemical inactive due to the loss of electronic contact and thus shorten the cycle life of batteries [12]. 2) Side reactions between Li metal and organic electrolytes form unstable solid electrolyte interphase (SEI) layers, which continuously consume the liquid electrolyte and Li metal. This consumption results in rising resistance, lower Coulombic efficiency (CE) and reduced life time of the electrodes [13, 14]. 3) More recently, the infinite volume change of Li metal electrodes during the Li plating/stripping is considered to be a huge problem due to the “hostless” nature [7].

In order to solve these above-mentioned issues and enhance the performances of Li metal electrodes for next-generation LMBs, different strategies have been developed. One of the major efforts focuses on stabilizing the SEI layer through in-situ or ex-situ procedures to achieve suppressed Li dendrite growth and improved life time. On the one hand, the in-situ formation of a stable SEI layer is dependent on the modification of electrolyte components, including organic solvents, Li salts and functional additives [9, 15].
Alternatively, surface protective coating layers have been explored as artificial SEI films to improve the performances [15-18]. Among the reported methods for surface coating, atomic layer deposition (ALD) and molecular layer deposition (MLD) are utilized as the most promising techniques for Li metal surface modification due to their unique properties including excellent coverage, conformal depositions and highly controllable thicknesses [19]. In 2015, two groups demonstrated ultrathin ALD Al₂O₃ thin film as a protective layer for metallic Li. From their results, the artificial SEI layer of Al₂O₃ can successfully prevent the side reactions between the Li metal anode and organic electrolytes and dramatically suppresses the Li dendrite growth [20, 21]. Later in 2016, both our group and Hu’s group had also applied this ALD Al₂O₃ coating for Na metal anodes and tested the performance in two different types of electrolytes (ether and carbonate, respectively), achieving very stable performances and further suppressed Na dendrite growth [22, 23]. Moreover, MLD alumina protective layers, which were firstly reported by our group, have been deposited on Na metal, which exhibits superior electrochemical performances and long life time, especially in carbonate-based electrolyte [24].

Another prominent approach proposed by Cui’s group is the use of thermal infusion to melt Li metal into 3D host structures, including reduced graphene oxide (rGO), porous carbon matrices, and polymeric matrices [25-27]. With this method, one of the major issues regarding the large volume change of lithium can be effectively relieved. Subsequently, other types of 3D hosts have been reported to obtain minimum volume change and longer life time of Li composite electrodes, such as Ni foam [28], Li-ion conductive matrix [29] and wood-derived carbon matrix [30]. However, there are still limitations for the thermal infusion method, in which one concern is the high temperature process required that makes it not easy to be operated and uneconomical. Another shortage is the stringent requirements of the Li wettability on the surface of hosts. Therefore, there are yet remaining challenges for 3D Li composites prepared via thermal infusion method for practical applications in future battery systems. Another interesting work has been reported by Lu’s group, in which the 3D porous current collectors have been mechanically pressed on the Li foil to form 3D Cu/Li composites. As a result, the obtained 3D Cu/Li shows the improved electrochemical performances compared to
planar Cu foil [31]. However, there is still large room for improvement from the achieved performances. Meanwhile, the 3D metal current collectors are relatively heavy, and will lower the energy density of the batteries [32].

In 2012, Manthiram’s group demonstrated microporous carbon paper (CP) as interlayer between cathode and separator for Li-S batteries. The significant enhancement can be achieved on the active material utilization and capacity retention [33]. Subsequently, different carbon fiber-based interlayers have been applied into Li-S batteries to trap soluble intermediate polysulfides, provide space to store electrolyte and reaction production [34-37]. Meanwhile, it has been proven that this kind of carbon fiber-based interlayers also play the positive role in terms of the protection Li metal anodes in Li-S batteries. However, the detailed electrochemical performances and mechanism of Li plating/stripping have not been studied in detail, especially using carbon interlayer on Li metal anode. Herein, we propose a novel and universal approach to achieve long life time and dendrite free Li metal anodes by introducing CP as an interlayer. As a result, the as-designed electrodes can deliver extremely high capacity (up to 3 mAh cm$^{-2}$ and 5 mAh cm$^{-2}$), superior stable performances (620 h/265 cycles with 3 mAh cm$^{-2}$) and high operational current densities (3 mA cm$^{-2}$ and 5 mA cm$^{-2}$). Meanwhile, the electrodes also can demonstrate high capacity and long life time in full LMB cells using carbon-coated LiFePO$_4$ (C/LiFePO$_4$) as the cathode for LIBs and MLD coated C/S as cathode for Li-S batteries. The influence of the number of CPs used for the Li anode interlayer on their electrochemical performance has been investigated. The role of CP in Li deposition/dissolution mechanisms have been further illuminated in detail. These new understandings could open a new window for the fabrication of safe, long life time and dendrite-free Li metal anodes.

5.2 Experimental Section

**Fabrication of Li-CP Composite Electrodes**: the carbon paper (CP, Freudenberg H2315) was cut into 7/16 inch discs by a cutter and then cleaned by water and ethanol followed by drying in a vacuum oven. The weight of one piece of CP is 0.0100 g and the thickness of the CP is ~210 μm. The Li foil (China Energy Lithium Co. LTD) was also cut into the same size of CP without other treatments. The configurations of this concept for different
cells are shown in Figure S4.1. During the assembling of batteries, the CP was aligned and placed on the top surface of the Li foil. Different layers of CP were further carried out for demonstration using the same method to fabricate the Li-CP composites, in which the electrodes with different numbers of interlayers can be named as: Li-CP-1L (1 layer) to Li-CP-5L (5 layers), respectively.

Fabrication of Li-Ni and Li-CC Composite Electrodes: in order to extend the concept of interlayer for Li metal anode, another two types of materials (Ni foam and Carbon cloth (CC)) are used as interlayer to replace the CP with the same configurations during electrochemical testing.

Electrochemical measurements: Electrochemical analysis was performance in CR2032 coin-type cells. The coin cells were assembled in an ultra-pure argon filled glove box with a symmetrical Li/Electrolyte-Separator/Li system using polypropylene separator (Celgard 2400). The electrolyte used in this study was a 1 M LiPF₆ salt dissolved in ethylene carbonate (EC): diethyl carbonate (DEC): dimethyl carbonate (DMC) of 1:1:1 volume ratio. The stripping/plating studies were carried out on an Arbin BT-2000 Battery Test System at room temperature. A constant current was applied to the electrodes during repeated stripping/plating while the potential was recorded over time in the symmetric cell testing. Electrochemical impedance spectroscopy (EIS) was also performed on the versatile multichannel potentiostat 3/Z (VMP3).

To investigate influence of the CP interlayers on the full cell performances, C/LiFePO₄ (LFP) was used as the cathode material. The LFP electrodes were prepared by casting a dimethylformamide (DMF) slurry containing C/LiFePO₄, Super P and poly(vinylidene difluoride) (PVDF) in a weight ratio of 8:1:1 onto carbon-coated Al foil. The cathodes were cut into discs with a diameter of 10 mm and dried at 80 °C prior to use. The areal loading of LFP is about 1.36 mAh cm⁻².

The performance for full cell Li-S batteries were investigated using C-S composites as the cathode electrode. The preparation of C-S cathode electrodes have been reported in our previous study [1]. Commercial carbon black (BP2000, US) was mixed with sulfur powder (99.5 %, Sigma-Aldrich) and dried at 80 °C for 12 h to remove residual moisture.
The mixture was then transferred to a sealed steel reactor and heated at 150 °C for 9 h and then 300 °C for 2 h. The obtained carbon-sulfur composites (C-S) maintained 70 wt% sulfur loading. Electrodes were prepared via slurry casting, with a mass ratio of 80:10:10 between active material, acetylene black, and PVDF-HFP, respectively. The slurry is pasted on commercial carbon paper to avoid active material delamination. The electrodes were cut into disks with a diameter of 10 mm and dried at 80 °C prior to use. The areal loading of C-S composites was about 2.8-3.0 mg cm$^{-2}$. Molecular layer deposition of alucone was performed in a Gemstar-8 ALD system (Arradiance, USA). 10-cycle alucone was directly deposited on C-S electrodes at 100 °C by alternatively introducing trimethylaluminium (TMA) and ethylene glycol (EG). The growth rate for alucone thin film was determined to be ~ 0.3 nm/cycle. Sulfur loading was found to drop ~ by 5 wt% following MLD treatment.

**Characterization:** SEM images were taken using a Hitachi 3400N Environmental Scanning Electron Microscopy at an acceleration voltage of 5 kV. The batteries were first disassembled in the glovebox and then gently rinsed with dimethyl carbonate to remove residual Li salts and electrolyte. To observe the cross-section images of the Li metal, the samples were cut in half using sharp scissors.
5.3 Results and Discussion

Figure 5.1 Comparison of the cycling stability and voltage profiles of Li-CP-1L and the bare Li foil at a current density of 3 mA cm\(^{-2}\) (a), 5 mA cm\(^{-2}\) (b) and rate performances (c) with the capacity limit of 1 mAh cm\(^{-2}\).

The configuration of the designed Li electrodes with CP interlayers is shown in Figure S5.1. Firstly, the CP was cut into a disk shape with the same diameter of commercial Li foil. Before the battery assembly process, the CP interlayers were put onto the surface of Li foil (between Li and separators) and used together as the anode. To evaluate the influence of CP on the electrochemical performance of Li foil, symmetrical coin cells (2032-type) were assembled using a carbonate-based electrolyte (1M LiPF\(_6\) in EC/DEC/DMC) with CP interlayers on the Li foil. The overpotential between the two electrodes in the galvanostatic testing can be separated into two parts: (1) the overpotential associated with the mass-transfer resistance throughout the plating/stripping, and (2) nucleation at the initial stages of deposition, which is affected by the lithiophilicity of the electrode surface [38]. Figure 5.1 shows the electrochemical
plating/stripping performances of the Li foil with one layer of CP as an interlayer (named \textit{Li-CP-1L}) under different current densities with a capacity limit of 1 mAh cm\(^{-2}\). \textbf{Figure 5.1} (a) exhibits the cycling stability and detailed voltage profiles of Li-CP-1L and bare Li foils at a current density of 3 mA cm\(^{-2}\). From the voltage profiles in the 1st cycle, a sharp voltage drop to \(-250\) mV (versus Li\(^+\)/Li) for the bare Li foil is observed at the initial stage of Li plating, which corresponds to the nucleation process. Afterwards, the voltage increases to a stable platform at \(-100\) mV (versus Li\(^+\)/Li). With a more promising electrochemical performance, Li-CP-1L shows a much smaller voltage drop at the initial stage of Li plating (~ \(-50\) mV), indicating homogeneous nucleation with the CP interlayers. Upon further plating, a similar stable platform at 100 mV (versus Li\(^+\)/Li) can be obtained for Li-CP-1L. That the carbon fibers in CP are initially inserted with Li\(^+\) during the first plating process and the stable SEI are induced to form on the surface of CP. In this case, the SEI layers can prevents penetration of solvent molecules and allows interfacial transfer of Li\(^+\), which can provide the homogeneous deposition of Li. From the cycling stability tests, the overpotential of bare Li foil starts to increase after 70 h (70 cycles) and rises to over 700 mV (versus Li\(^+\)/Li) after 150 h (150 cycles) with large polarization in the voltage profiles. In comparison, Li-CP-1L can maintain superior stability and lower overpotentials of 100 mV (versus Li\(^+\)/Li) after 150 h (150 cycles). Even after 300 h (300 cycles), the overpotential of Li-CP-1L is only about 150 mV (versus Li\(^+\)/Li), illustrating the enhanced electrochemical performance enabled by the CP interlayer. \textbf{Figure 5.1(b)} shows the cycling stability and the detailed voltage profiles of Li-CP-1L and bare Li foil at a current density of 5 mA cm\(^{-2}\). When applying a higher current density, the voltage drop for the initial nucleation process is below \(-350\) mV (versus Li\(^+\)/Li) in the 1st cycle for bare Li foil, which is even large than that of the cells cycled at 3 mA cm\(^{-2}\). However, with the CP interlayer, Li-CP-1L shows an initial nucleation potential of \(-80\) mV (versus Li\(^+\)/Li) which stabilizes at \(-150\) mV (versus Li\(^+\)/Li) in the first cycle. During electrochemical cycling at this current density, the stability of bare Li foil is very poor, in which the overpotential starts to increase after only 35 h and rises up to 600 mV after only 50 h with large fluctuations in overpotential voltage. The fluctuating voltage profiles is related to the Li dendrite (mossy) growth, dead Li layer formation and soft short circuiting. For Li-CP-1L, a more stable
performance with less polarization is observed during cycling, in which the overpotential after 140 h is only 240 mV (versus Li+/Li). To further explore the performances under different current densities, the rate behavior of symmetrical cells are presented in Figure 5.1(c). Li-CP-1L demonstrates a significantly lower and more stable voltage polarization at the current density of 1, 3, 5 and 10 mA cm\(^{-2}\). In contrast, the bare Li foil presents a larger overpotential at all current densities, particularly when cycled at 10 mA cm\(^{-2}\). The obvious difference at high current densities can be attributed to the high specific kinetic obstacles, in which the CP interlayer can provide effective pathways for electron/ion transport with favorable electron/ion conductivity.

![Graphs showing cycling stability and voltage profiles of Li-CP-5L and bare Li foil at a current density of 3 mA cm\(^{-2}\) with capacity limits of 3 mAh cm\(^{-2}\) (a) and 5 mAh cm\(^{-2}\) (b).](image)

Figure 5.2 Cycling stability and voltage profiles of Li-CP-5L and bare Li foil at a current density of 3 mA cm\(^{-2}\) with capacity limits of 3 mAh cm\(^{-2}\) (a) and 5 mAh cm\(^{-2}\) (b).

One of the major advantages of using Li metal as the anode for LMBs is the large capacity. It is widely accepted that the areal capacity of a commercial electrode needs to reach at least 3 mAh cm\(^{-2}\) for practical application [7]. Therefore, a capacity limit of 1 mAh cm\(^{-2}\), which is the most popular parameter for demonstrations in the reported literatures, may not meet the requirements for the future batteries applications. In this case, we are also trying to achieve high capacity with enhanced stability by using the CP
interlayer with Li foil. Firstly, the bare Li foil is tested at the current density of 3 mA cm\(^{-2}\) with the capacity limit of 3 mAh cm\(^{-2}\). As expected, the overpotential increases after only 60 h and grows to 1000 mV (versus Li\(^+\)/Li) after 110 h (Figure 5.2(a)). Compared to the behavior of symmetric cells with a lower capacity of 1 mAh cm\(^{-2}\), a larger and faster polarization can be observed at the same current density, indicating the significant amount of mossy and dendritic Li growth during the deposition process. Very interestingly, when using one layer CP as interlayer (Li-CP-1L) with capacity of 3 mAh cm\(^{-2}\), the cycling stability can also be improved with a stable overpotential after 110 h (Seen in Figure S5.2).

In order to further improve the electrochemical performance of the Li anode at large capacity, we apply a simply strategy of increasing the number of CP interlayers. This approach will be shown to be very effective for addressing the challenges of large capacity Li metal anodes, in which the cell configurations are presented in Figure. S1 (b) and the electrochemical performances are shown in Figure S5.2(a) and Figure 5.2(a). The layers of CP are named as Li-CP-3L, Li-CP-4L and Li-CP-5L with 3, 4, and 5 CP interlayers, respectively. It can be seen from Figure.S2 that after 180 h, the overpotential of Li-CP-1L, Li-CP-3L and Li-CP-4L are ~500 mV, 300 mV and 250 mV (versus Li\(^+\)/Li), respectively. Moreover, with 5 CP interlayers, the Li-CP-5L delivers very stable plating/stripping performances and the lowest overpotential of ~240 mV after more than 620 h (Figure 5.2(a)), which is almost 10 times longer life time than that of the bare Li foil. In order to prove the great potential and advantages of multilayer CP for the Li metal anode, a larger capacity of 5 mAh cm\(^{-2}\) is further explored with 5 layers of CP. It can be seen from Figure 5.2(b) that even with a higher capacity of 5 mAh cm\(^{-2}\), the overpotential of Li-CP-5L is still lower than 200 mV (versus Li\(^+\)/Li) after 130 h. Even after 250 h of electrochemical plating/stripping, the Li-CP-5L electrodes still deliver stable performances with a maximum overpotential of 350 mV (versus Li\(^+\)/Li). The electrochemical impedance spectroscopy (EIS) results are shown in Figure.S3 at the point of before cycling and after 50 cycles for different samples (bare Li, Li-CP-1L, Li-CP-3L, Li-CP-4L, and Li-CP-5L) under the current density of 3 mA cm\(^{-2}\) with the capacity of 3 mAh cm\(^{-2}\). It is believed that two distinct semicircles is associated with both the SEI/electrode (high frequency) and the charge transfer (CT)/electrical double layer (EDL).
(lower frequencies). Very promising, even before electrochemical cycling, the resistances have been reduced with the conductive CP interlayers. After 50 cycles of Li plating/stripping, the resistance of bare Li rapidly increases and the Li-CP-5L shows the smallest resistance, which corresponding to the most stable electrochemical performances. The Impedance parameters calculated by equivalent circuits for different samples are shown in Table. S5.1. From Table.S1, it indicates that the R_{SEI} of bare Li foil is much larger than the designed electrodes with CP interlayer after 50 cycles Li plating/stripping process. These results indicate that the CP interlayers can also make a significant influence on the high capacity Li metal anode. Meanwhile, the thickness of CP can be controlled to meet the requirements of the desired capacities. All of the battery testing was carried out in conventional carbonate based electrolyte (1 M LiPF₆ in EC/DEC/DMC of 1: 1: 1 volume ratio), which is considered to be more challenging because of the more serious side reactions and unstable SEI formation compared to ether-based electrolyte systems [9, 26]. To the best out knowledge, our design yields the best performances in symmetric Li/Li cells in carbonate-based electrolyte in term of the large capacity, high current density and longest life time (Table S5.2).
Figure 5.3 Top view SEM images of bare Li foil (a) and Li-CP-1L (b) as well as the cross section view of bare Li foil (c) and Li-CP-1L (d) after 10 cycles with a 1 mAh cm$^{-2}$ capacity limit. Top view SEM images of bare Li foil (e) and Li-CP-5L (d) and cross section views of bare Li foil (g) and Li-CP-5L (h) after 10 cycles with a 3 mAh cm$^{-2}$ capacity limit.

In order to understand the effects of the CP interlayer on the process of Li dendrite growth, the morphologies of deposited Li in different designs are characterized by SEM. As a comparison, the Li deposition behavior of bare Li foil is presented in Figure 5.3 and Figure S5.4-5.5. The first plating and stripping processes of bare Li foil with a capacity of 1 mAh cm$^{-2}$ are shown in Figure S5.4. During the first stripping process
Li is stripped from the surface randomly, generating pits of variable size on the surface. In the first plating process (Figure S5.4(b)), Li is preferentially deposited as mossy-like dendrites due to the inhomogeneous nucleation and growth. When increasing the stripping/plating capacity of Li to 3 mAh cm\(^{-2}\), the holes become larger and the surface of Li becomes rougher during the first stripping process (Figure S5.5(a)).

Likewise, thicker and denser mossy-like Li dendrites can be observed from the first plating process (Figure S5.5(b)). It has previously been shown that the mossy-like Li will produce a dead Li layer and become electrically isolated during cycling and results in low CE, increased polarization and resistance in addition to depletion of the Li inventory [39, 40]. The morphologies of Li deposition for bare Li foil after cycling (10 cycles) is presented in Figure 5.3(a, c). When the capacity of Li is 1 mAh cm\(^{-2}\), a relatively rough surface can be observed from the top-view SEM images and dead Li layers with a thickness of 20 μm can be seen from cross section pictures (Figure 5.3(e, g)). After increasing the capacity to 3 mAh cm\(^{-2}\), large cracks on the top surface of bare Li evolve and thick dead Li layers of ~45 μm are formed after 10 cycles, which is an indication of more serious side reactions and Li dendrite growth.

The influence of CP interlayers on the morphology of Li deposition have also been studied via SEM, as displayed in Figure 5.3 and Figure S5.6-5.9. Firstly, the Li plating/stripping behaviours during the initial cycle are tested with a capacity of 1 mAh cm\(^{-2}\). From Figure S5.6, it can be observed that the morphologies of CP are almost identical in the first cycle. This observation is clearly different compared to the case with bare Li foil, in which there is no pitting behaviour after stripping and mossy-like Li dendrite growth has also been avoided during Li plating (Figure S5.6 (a, b)). The indentations on the surface of Li are cause by the carbon fibers of CP, which aid in delivering uniform local current distributions resulting in homogeneous nucleation and growth of Li during plating and stripping. The phenomenon observed from the SEM results are highly consistent with the first cycle electrochemical potential profiles discussed above. After 10 cycles, the top-view images of CP and the cross-section images of the whole electrode are presented in Figures 5.3(b) and 5.3(d), respectively. As exhibited in Figure 5.3(b), there is still no mossy-like or dendritic Li deposition after 10 cycles, and the Li is plated on the surface or the gaps between the carbon fibers in CP.
The cross section images give consistent evidence, in which Li is filled in the porous spaces between carbon fibers without any dendrite growth, and the dead Li layers are prevented though the use of CP interlayers (Figure 5.3(d)).

Furthermore, more detailed studies on the morphology of 5CP interlayers have been carried out when the capacity is increased to 3 mAh cm\(^{-2}\) (Figure 5.3 (f, h) and Figure S5.7-5.9). In the first cycle, a similar phenomenon can be observed on the surface of Li metal, in which indentations of carbon fibers exist without any holes/pits or mossy-like lithium during stripping and plating. Meanwhile, the morphologies of CP in different layers (1st, 3rd and 5th) are also presented, in which they show near identical structures. After 10 cycles, the Li metal can retain a smooth surface without mossy-like and dendritic Li growth (Figure S5.7(c)). Obvious differences in the plating behaviour can be seen on the different layers of CP after 10 cycles. The inner layers of CP show very similar morphology with the CP in Li-CP-1L, indicating the similar process of SEI formation and Li deposition. However, more pancake-like Li deposition can be observed on the top CP layer in Li-CP-5L with increasing of the capacity. It demonstrates that the extra amount of Li trends to deposit on the top layer of CP and then diffuses into the inner layers, finally reaching the Li metal surface. [41-43].

Figure 5.4 Cycling performance of full cells (C/LiFePO\(_4\) as cathode) using bare Li foil and Li-CP-2L at 1 C; (b, c) Voltage hysteresis profiles of charge/discharge of bare Li foil and Li-CP-2L
in 2rd cycle and after the 150th cycle. (d) Cycling performance of full cells (modified C/S as cathode) using bare Li foil and Li-CP-2L; Voltage hysteresis profiles of bare Li foil (e) and Li-CP-2L (f) in various cycles.

The performance of the Li foil with and without CP interlayers as an anode is further investigated in a full cell using C/LiPFO4 as the cathode. The loading of C/LiFePO4 is over 8 mg cm^{-2} corresponding to an areal capacity of ~1.36 mAh cm^{-2}. Accordingly, we have chosen Li-CP-2L to match this areal capacity, at the same time avoiding an unnecessary increase in weight due to an excessive number of CPs. Figure 5.4 and Figure S5.10 shows the cycling performances of full cells using bare Li foil and Li-CP-2L as anodes at a rate of 1 C, in which the configuration of the cell is shown in Figure. S5.1 (c). In the battery using bare Li foil, the discharge/charge capacity starts fading after 100 cycles, decreasing to about 40 mAh g^{-1} after 300 cycles. However, with an interlayer of CP, the cell maintains an extremely stable capacity of ~ 130 mAh g^{-1} after 380 cycles. Figure 5.4 (c) shows the potential profiles of the cells using bare Li foil and Li-CP-2L as an anode after 150 cycles. An obvious increase in overpotential can be seen for the bare Li electrode, which can be attributed to an increase of surface passivation/pulverization of the lithium. Promisingly, there is almost no change in the overpotential after 150 cycles for the cell with CP interlayers.

Moreover, in our previous study on Li-S batteries, we have successfully developed alucone coated C-S cathode electrodes used in conventional carbonate-based electrolytes with high sulfur loading [44]. The as-prepared sulfur cathodes in carbonate electrolyte have been demonstrated to undergo a solid-phase Li-S redox reaction and therefore the performance of Li metal anode and fast Li/Li^{+} transport are crucial for these types of batteries [44]. The C-S composite loading is around 2.8-3.0 mg cm^{-2}, corresponding to an areal capacity of ~2.5-2.7 mAh cm^{-2}. Figure 5.4(d) shows the cycling performances of full cells using bare Li foil and Li-CP-2L. Interestingly, with the use of Li-CP-2L, the Li-S battery exhibits excellent cycling stability and reversibility. The battery exhibits an initial capacity of over 1200 mAh g^{-1} and maintains 600 mAh g^{-1} after 150 cycles. On the contrary, with the use of bare Li anode, the cycling capacity of the Li-S battery drops very fast, which illustrates the importance of the interlayer to improve the stability of Li-
S batteries. Comparison of discharge-charge profiles of the two Li-S batteries are shown in Figure 5.4(e) and 5.4(f). Impressively, the Li-S battery with the carbon paper interlayers demonstrates stable, flat, and highly reversible discharge-charge potential plateaus, while the potential plateaus of the Li-S cell without an interlayer gradually reduce during cycling. The Li-S full cell demonstration illustrates the excellent performance by the interlayer design and shows potential for use in next-generation lithium metal batteries.

![Figure 5.5](image)

**Figure 5.5** Schematic illustration of the Li stripping/plating behavior occurring on the surface of bare Li foil (a), Li foil with CP interlayers (b); the detailed mechanism of Li deposition on the CP (c).

The CP is demonstrated as an interlayer to significantly improve the stability and lifetime of Li metal anodes. In our design and concept, materials of CP and Li foil are commercialized with an affordable price. Furthermore, the fabrication of the Li-CP composite electrode is facile and easily realized, and can potentially be combined with previously reported approaches including chemical surface modification, electrolyte additives and 3D Li structures. Then, the strong mechanical properties and flexibility of CP make it very promising not only in coin cells but also for use in larger devices without significant changes to the fabrication procedure of commercial batteries. Finally, this approach also can be considered as a universal method by using different materials as interlayers. Another two types of materials (including carbon cloth and Ni foam) are used
as interlayer for Li metal anode (shown in Figure S5.11), demonstrating very stable electrochemical plating/stripping performances compared with Li foil.

The morphologies of Li deposition with and without CP interlayers have been characterized to understand the mechanism and functions of CP during Li-S the Li plating/stripping process. Figure 5.5 shows the schematic illustration of the Li stripping/plating behavior occurring on the surface of the different electrodes. As shown in Figure 5.5(a), the mossy and dendritic Li is formed during cycling of the bare Li foil, resulting in a thicker dead Li layer on the surface. As a result, an increased resistance, lower CE and reduced life time is observed. In contrast, the CP interlayer enables uniform Li deposition without mossy and dendritic growth, which can be attributed to the homogeneous distribution of local current on the CP. Meanwhile, the porous structure of CP provides a transport path for liquid electrolyte and buffer space for Li plating/stripping (Figure 4.5(b-d)).

5.4 Conclusion

In summary, we firstly demonstrate the concept of carbon paper (CP) used as an interlayer for highly stable Li metal anodes. In this novel design, we highlight multiple advantages and performance enhancements including: 1) the fabrication of the Li-CP composite electrode is very facile and easy to be realized, which can be applied in large devices. 2) The as-prepared Li-CP-5L electrode shows superior and stable plating/stripping performances for up to 620 h, which is almost 10 times longer than that of the bare Li foil. To the best of our knowledge, our design presents the best performances in symmetric Li/Li cells in carbonate-based electrolyte in term of the highest capacity, highest current density and longest life time. 3) Ultra-long cycling life and high capacity retention is realized by introducing CP interlayers for Li foil paired with C/LiFePO₄ as the cathode for LIBs and MLD-coated C/S as the cathode for Li-S batteries. 4) There is no observable mossy or dendritic Li formation during the Li deposition process, in which the mechanism and functions of CP during Li plating/stripping process have been highlighted in detail. Herein, our achievement is very promising and provides a facile approach to stabilize Li metal anodes with superior long life time, large capacity and high current density. It is believed that our design of CP
interlayers opens up new opportunities to the realization of next-generation high energy density Li metal batteries.

5.5 Acknowledgements

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5.6 Reference


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[34] L.L. Kong, Z. Zhang, Y.Z. Zhang, S. Liu, G.R. Li, X.P. Gao, Porous Carbon Paper as Interlayer to Stabilize the Lithium Anode for Lithium-Sulfur Battery, ACS applied materials & interfaces, 8 (2016) 31684-31694.


5.7 Supporting information

**Figure S5.1** Schematic diagram of the configurations used for electrode design with CP interlayers: (a) Li-CP-1L; and (b) Li-CP-5L; the Li-ion cell configuration with LiFPO$_4$ as the cathode: (d) Li-CP-2L.

**Figure S5.2** Comparison of the cycling stability (a) and 1$^{st}$ cycle voltage profiles (b) of the Li-CP-1L, Li-CP-3L and Li-CP-4L at a current density of 3 mA cm$^{-2}$ with the capacity limit of 3 mAh cm$^{-2}$. 
Figure S5.3 Nyquist plot showing electrochemical impedance spectroscopy (EIS) of the different samples (bare Li, Li-CP-1L, Li-CP-3L, Li-CP-4L, and Li-CP-5L) before cycling (a) and after 50 cycles (b).
Figure S5.4 Top-view SEM images of bare Li foil after the first stripping (a, b) and plating (c, d) cycles with a capacity of 1 mAh cm$^{-2}$ at a current density of 3 mA cm$^{-2}$.
Figure S5.5 Top-view SEM images of bare Li foil after the first stripping (a, b) and plating (c, d) cycles with a capacity of 3 mAh cm$^{-2}$ at a current density of 3 mA cm$^{-2}$.
Figure S5.6 Top-view SEM images of Li foil in Li-CP-1L after first stripping (a), first plating (b); and CP (facing separator) in Li-CP-1L after first stripping (c), first plating (d) with a capacity of 1 mAh cm\(^{-2}\) at the current density of 3 mA cm\(^{-2}\).

Figure S5.7 Top-view SEM images of surface of Li foil in Li-CP-5L electrode after the first stripping (a), first plating (b) and after 10 charge and discharge cycles (c) with a capacity of 3 mAh cm\(^{-2}\) at the current density of 3 mA cm\(^{-2}\).
Figure S5.8 Top-view SEM images of the first layer CP above lithium in Li-CP-5L electrode after the first stripping (a), first plating (b) and after 10 charge and discharge cycles (c) with a capacity of 3 mAh cm$^{-2}$ at the current density of 3 mA cm$^{-2}$.
**Figure S5.9** Top-view SEM images of the third layer CP above lithium in Li-CP-5L electrode after the first stripping (a), first plating (b) and after 10 charge and discharge cycles (c) with a capacity of 3 mAh cm\(^2\) at the current density of 3 mA cm\(^2\).

**Figure S5.10** Voltage hysteresis profiles of charge/discharge median voltage of Bare Li foil and Li-CP-2 layers for LFP batteries (a) and Li-S batteries (b) in the first cycle and.
Figure S5.11 Comparison of the cycling stability of (a) bare Li and Li@carbon cloth; (b) bare Li and Li@Ni at a current density of 3 mA cm$^{-2}$ with the capacity limit of 1 mAh cm$^{-2}$.

Table S5.1 Impedance parameters calculated by equivalent circuits for different samples.

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<th>Sample Description</th>
<th>R_SEI $\Omega$</th>
<th>R_CT $\Omega$</th>
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<tr>
<td>Bare Li after 50 cycles</td>
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<td>Li-CP-3L after 50 cycles</td>
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<td>Li-CP-4L after 50 cycles</td>
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<td>Li-CP-5L after 50 cycles</td>
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Table S5.2 Summary of the electrochemical plating/stripping performances of Li-Li symmetric cells testing in the reported literature

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<th>Capacities</th>
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<th>Electrolyte</th>
<th>Maximum life time shown</th>
<th>Ref</th>
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<td>Nature Energy, 2017, 6, 17119</td>
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Chapter 6

6. Dendrite-free and minimum volume change Li metal anode achieved by three dimensional artificial interlayers*

In the last chapter, we developed the concept “interlayer” for long-life time Li metal anode. However, the pristine CP using as “interlayer” still cannot meet the requirement of high capacity and high current density. Furthermore, multilayer of CP is requested for the high capacity performances, which will decrease the energy density of the batteries with 5 layers of CP. Herein, we extend the “interlayer” concept to the application of Li metal anodes and rationally design a bi-functional interlayer. The vertical nitrogen-doped carbon nanotubes (NCNTs) are grown on the carbon fibre of carbon papers (CP) to obtain a 3D interlayer for Li metal. Firstly, we demonstrate the relationship between surface area and electrochemical performances on the 3D structure by controlling the growth time of NCNTs. Remarkably, the Li-CP-NCNTs composite electrode can deliver very stable performances over 600 h (~ 900 cycles) and 250 h (~ 750 cycles) at the ultrahigh current densities of 5 mA cm\(^{-2}\) and 10 mA cm\(^{-2}\), respectively, which is two times higher than that of the cell using pristine CP interlayers. Meanwhile, with a high capacity of 3 mAh cm\(^{-2}\), the Li metal anode with CP-NCNTs interlayer delivers a long life time of over 350 h at a current density of 3 mA cm\(^{-2}\). The morphologies of both Li foil and CP-NCNTs interlayers indicate that dendrite-free deposition and minimum volume change with the “bi-functional” interlayers. We believed that these new findings could open a new avenue for achieving long life time, dendrite-free and minimum-volume-change Li metal anodes.

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6.1 Introduction

In the past years, Li-ion batteries (LIBs) have been considered as one of the most successfully developed energy storage devices for portable electronics, electric cars, and large scale energy storage stations. LIBs possess many outstanding features, including high energy density, no memory effect, low maintenance, and minimal self-discharge \([1]\). However, the growing requirements for better LIBs requires constant progress in terms of improved safety, longer lifetime, smaller size, lighter weight, and lower cost. The next generation Li metal batteries (LMBs) such as Li-S, Li-air, and all-solid-state batteries, have recently received more attention due to their higher energy densities \([2, 3]\). As an ideal anode material candidate, Li metal has unique properties such as high theoretical capacity (3860 mAh g\(^{-1}\)), low electrochemical potential (-3.04 V vs. the standard hydrogen electrode), and light weight (0.53 g cm\(^{-3}\)) \([4, 5]\). Although Li metal is considered to be the “Holy Grail” of anode materials, it still has several challenges to be addressed before Commercialization. During the repeated electrochemical plating/stripping process, mossy and dendritic structures are formed on the surface of the Li electrode \([6-8]\). Furthermore, the Li dendrites may penetrate the separator and cause internal short circuits, leading to serious safety concerns. In addition, “dead Li” is formed from the mossy and dendritic Li, which is electrochemical inactive due to the loss of electrical contact and blocking of the Li\(^+\)/electron transportation between the electrolyte and bulk Li \([9, 10]\). During the electrochemical cycling process, side reactions between the electrolyte and metallic Li lead to the formation of solid electrolyte interphase (SEI) layers on the surface of Li metal. The unstable “SEI” will lead to a non-uniform Li ionic flux, resulting in Li dendrite growth \([11, 12]\). Meanwhile, the repeated breaking and repairing of the SEI during cycling will cause the depletion of the electrolyte and Li, which will lower the Coulombic efficiency (CE) and shorten the life time of the Li metal anode \([13]\). Another serious issue of Li metal is the infinite volume change due to its “hostless” nature, which will also significantly affect the performances of the Li metal anode and LMBs \([14, 15]\).

In recent years there have been many approaches proposed to stabilize the Li anode. The stable formation of SEI is one of the key factors to suppressing Li dendrite growth and
improving life time, in which both in-situ and ex-situ procedures have been reported [16]. The modification of electrolyte components, including Li salts, organic solvents, and additives, is an effective strategy to obtain a stable SEI during the electrochemical plating/stripping process. Alternatively, surface coating/modification on the Li metal has been explored as another approach to stabilize the SEI layer as an ex-situ process [17]. Various materials and thin films have been synthesized or deposited on the Li metal anode as protective layers, such as Al2O3, alucone, Li3PO4, Li3PS4, and Li13In13 alloy [18-24]. The robust protective layers can prevent side reactions between liquid electrolyte and Li metal, generate homogeneous Li+ flux, and reduce the Li dendrite growth. Furthermore, a thermal infusion method of melting Li into 3D hosts was developed by Cui’s group as a prominent approach to address the “infinite volume change” of the Li metal anode [25-28]. Different materials have been used as 3D hosts for Li metal, including metal foams, Li-ion conductive matrix, carbon-based matrices, and enabling minimum volume change and longer life times [29-32]. Especially, the carbon fiber based materials received increasing attention. For example, Lu et al demonstrates the carbon paper (CP) with sponge carbon layer (SCCP) as the skeletons for Li metal anode [33]. The additional sponge carbon layer with low electronic conductivity and compact structure enables the uniform Li deposition in the 3D matrix and suppress the dendrite growth. Furthermore, different modifications on CP, such as sliver layer and graphene nanosheets, have been reported to improve the electrochemical performances of the CP [34, 35]. However, there are still some limitations for the thermal infusion method, in which one concern is the high temperature (generally higher than the melting point of Li (180 °C)) process that requires specialized fabrication and is uneconomical. Another shortage is the stringent requirements of the Li wettability on the surface of hosts. Therefore, there are still many remaining challenges for 3D Li composites prepared via thermal infusion method for practical applications in future battery systems.

Recently, we proposed the idea of conductive interlayers (CP) for Li metal anodes with a facile fabrication process [36]. The concept of the “interlayer” was firstly demonstrated by Manthiram’s group where they placed an interlayer between the cathode and separator for Li-S batteries to trap soluble polysulfide intermediates, provide space to store electrolyte and reaction production [37]. Here we extend the interlayer concept to Li
metal anode protection, which can significantly enhance the electrochemical plating/stripping performances and suppress the dendrite growth. It is believed that the bi-functional interlayer can not only enable a uniform Li$^+$ flux on the surface of Li metal, but also serve as the host for Li deposition and restrict the volume change of the Li metal anode spontaneously. However, the reported conductive interlayer is still not good enough under high current density with high capacities for practical applications [36, 38, 39]. Meanwhile, the factors affecting the electrochemical performance of the conductive interlayers are unclear. It is also worth to mention that the introducing of interlayer may decrease both the gravimetric and volumetric energy density of batteries. In this case, the density and thickness of interlayer design is an important factor affecting the gravimetric and volumetric energy density of the cells.

Herein, we demonstrate a bi-functional interlayer using CP as a base material for Li metal anode. The vertical aligned N-doped carbon nanotubes (NCNTs) are grown on the CP to achieve a 3D interlayer structure, named CP-NCNTs. By controlling the time for NCNTs growth, the surface areas of the CP-NCNTs are adjusted, and is related to the electrochemical performances. Promisingly, the design of the CP-NCNTs interlayer can enhance the electrochemical performances and achieve over 600 h cycling time at the high current density of 5 mA cm$^{-2}$. Meanwhile, with a high capacity of 3 mAh cm$^{-2}$, the Li metal electrode with CP-NCNTs interlayer delivers a long life time of over 350 h at a current density of 3 mA cm$^{-2}$. Benefitting from the bi-functional interlayer, both the Li dendrite growth and the volume change have been effectively relieved simultaneously. These new findings could open a new window for the fabrication of safe, long life time, dendrite-free and minimum-volume-change Li metal anodes.

### 6.2 Experimental Section

**Fabrication of CP-NCNTs interlayers:** The growth of N-doped carbon nanotube by spray pyrolysis chemical vapor deposition (SPCVD) method has been reported in our previous studies. ALD coatings were conducted on carbon paper (CP, Freudenberg H2315) in a Savannah 200 ALD system (Veeco/carbon nanotube (CNT) division of the Veeco Instruments Inc.). Al$_2$O$_3$ was deposited on the CP at 120 °C by using trimethylaluminium (TMA) and water (H$_2$O) as precursors for 200 cycles. Then, the
Al₂O₃ coated CP was loaded into a vertical tube furnace that was ramped from room temperature to 856 °C using an Ar flow of 200 mL min⁻¹. Catalyst ferrocene solution (solvent: acetonitrile, concentration: 0.02 g mL⁻¹) was then introduced into the quartz tube at a flow rate of 0.1 mL min⁻¹ for 5 min under Ar atmosphere. Following this, imidazole solution is injected into the quartz tube (solvent: acetonitrile, concentration: 0.2 g mL⁻¹, flow rate: 0.1 mL min⁻¹) to grow NCNT bundles for the controlled times followed by cooling to room temperature. The times of grown NCNTs have been adjusted as 10 mins, 20 mins and 30 mins with the sample names of CP-NCNTs-1, CP-NCNTs-2 and CP-NCNTs-3, respectively.

**Fabrication of Li-CP-NCNTs Electrodes:** As-prepared CP-NCNTs was cut into 3/8 inch discs by a cutter and the Li foil (China Energy Lithium Co. LTD) was also cut into the same size of CP-NCNTs without other treatments. During the assembling of coin cells, the CP-NCNTs interlayer was aligned and placed on the top of the Li foil. Different CP-NCNTs samples were further carried out for demonstration using the same method to fabricate the different composite electrodes, named as: Li-CP-NCNTs-1, Li-CP-NCNTs-2 and Li-CP-NCNTs-3, respectively. The pristine CP was also tested as the interlayer with the same procedure for comparison, named Li-CP. Typically, the weights of the CP and CP-NCNTs-3 are 0.01 g and 0.019 g, respectively.

**Electrochemical measurements:** Electrochemical analysis was performance in CR2032 coin-type cells. The coin cells were assembled in an ultra-pure argon filled glove box with a symmetrical Li/Electrolyte-Separator/Li system using polypropylene separator (Celgard 2400). The electrolyte used in this study was a 1 M LiPF₆ salt dissolved in ethylene carbonate (EC): diethyl carbonate (DEC): dimethyl carbonate (DMC) of 1: 1: 1 volume ratio. The electrolyte amount used for all the samples are ~ 500 uL in order to wet the interlayers. The stripping/plating studies were carried out on a Land 2001A Battery Test System at room temperature. A constant current was applied to the electrodes during repeated stripping/plating while the potential was recorded over time in the symmetric cell testing.
To evaluate Coulombic efficiency (CE), the same CR2032 coin cells were assembled using a Cu foil, CP and CP-NCNTs current collector as the working electrode, a Li foil as the counter electrode, a Celgard 2400 polypropylene film as the separator, and the same electrolyte (1M LiPF$_6$ in EC/DEC/DMC) for the symmetrical cell testing. These batteries were assembled in an Ar-filled glove box and first cycled from 0 to 2 V at 1 mA cm$^{-2}$ for 10 cycles on a Land 2001A Battery Testing System to remove surface contaminations and stabilize the interface. To test CE, a fixed amount of 1 mAh cm$^{-2}$ or 3 mAh cm$^{-2}$ of Li was deposited on the current collector and then stripped away up to 1.5 V at 1 mA cm$^{-2}$ or 3 mA cm$^{-2}$ for each cycle.

To investigate influence of the CP-NCNTs interlayers on the full cell performances, C/LiFePO$_4$ (LFP) was used as the cathode material. The LFP electrodes were prepared by casting a dimethylformamide (DMF) slurry containing C/LiFePO$_4$, Super P and poly(vinylidene difluoride) (PVDF) in a weight ratio of 8:1:1 onto carbon-coated Al foil. The cathodes were cut into discs with a diameter of 10 mm and dried at 80 °C prior to use. The areal loading of LFP is about 10 mg cm$^{-2}$.

**Characterization:** SEM images were taken using a Hitachi 3400N Environmental Scanning Electron Microscopy at an acceleration voltage of 5 kV. The batteries were first disassembled in the glovebox and then gently rinsed with dimethyl carbonate to remove residual Li salts and electrolyte. To observe the cross-section images of the Li metal, the samples were cut in half using sharp scissors. The surface area of the electrodes was calculated by the Brunauer, Emmett, and Teller (BET) model by taking at least six data points where $0.07 < P/P_0 < 0.2$. Pore size distribution was obtained by the Barrett, Joyner, and Halenda (BJH) model using the desorption branch of the isotherm. Raman scattering spectra were recorded using a Nicolet 380 and a HORIBA Scienti跑e LabRAM HR Raman spectrometer system equipped with a 532.4 nm laser.
6.3 Results and Discussion

Figure 6.1 (a) Schematic diagram of the configuration using CP-NCNTs as interlayer for Li metal anode; (b) SEM images of pristine carbon paper; (c) SEM images of CP-NCNTs interlayers.

The configuration of the Li metal electrode using CP-NCNTs as an interlayer is shown in Figure 6.1(a). The CP-NCNTs was put directly on the surface of Li foil (between Li and separators) with the same diameter, and the composites electrodes were used together as the anode. Figure 6.1(b) displays the SEM images of pristine carbon papers. It can be seen that the pristine CP consists of carbon fibres with diameters of ~ 8 μm. The surfaces of the carbon fibres in CP are relatively smooth with some wrinkles. To fabricate the CP-NCNT interlayers, NCNTs were grown on the CP through a one-step spray pyrolysis chemical vapor deposition (SPCVD) method, which was reported in our previous works\(^{40}\). Figure 6.1(c) and Figure S6.1 present the SEM images of CP-NCNTs after SPCVP process. It can be observed that the carbon fibers in CP are totally covered with vertical and dense NCNTs. The lengths and diameters of the NCNTs are around 30 μm
and 100 nm, respectively. From the cross-section images in Figure S6.1, the NCNTs are not only distributed on the surface of CP, but also grown in the inner space of CP.

To understand the relationships between the surface area and electrochemical performances of CP-NCNTs interlayers, the growth times of NCNTs were controlled during the SPCVD process. Different SPCVD times of 10 min, 20 min, and 30 min were carried out for the samples named CP-NCNTs-1, CP-NCNTs-2, and CP-NCNTs-3, respectively. Figure S6.2(a) shows the N\textsubscript{2} adsorption/desorption isotherms for CP-NCNTs-1, CP-NCNTs-2 and CP-NCNTs-3. From the BET analysis, the surface areas of CP-NCNTs-1 to CP-NCNTs-3 increase with SPCVD reaction times, which are 19.8, 20.9, 25.3 m\textsuperscript{2} g\textsuperscript{-1}, respectively. Figure S6.2(b) displays the pore size distributions of the three samples, indicating the similar pore distribution with the average pores widths of about 8 nm. Figure S6.3 shows the Raman spectra of CP-NCNTs-1, CP-NCNTs-2, and CP-NCNTs-3. In the Raman spectra, the peak at about 1591 cm\textsuperscript{-1} (G band) is related to the vibration of sp\textsuperscript{2} bonded carbon atom in 2D hexagonal lattice and the 1329 cm\textsuperscript{-1} (D band) is related to the defects and disorder in the hexagonal graphitic layers. The I\textsubscript{D}/I\textsubscript{G} of CP-NCNTs-3 is about 0.73, which is lower than that of 0.90 for CP-NCNTs-1 and CP-NCNTs-2. Meanwhile, it has been proven in our previous studies that the N-content of the CP-NCNTs-3 is about 4% with the three types of N bonding structures, including pyridinic-N, pyrrolic-N, and graphitic-N\textsuperscript{35}. 
Figure 6.2 Comparison of the cycling stability of the Li-CP and Li-CP-NCNTs-3 at a current density of 5 mA cm$^{-2}$ (a), 10 mA cm$^{-2}$ (b) with the capacity limit of 1 mAh cm$^{-2}$; and at the current density of 3 mA cm$^{-2}$ (c), 5 mA cm$^{-2}$ (d) with the capacity limit of 3 mAh cm$^{-2}$.

To evaluate the influence of the interlayer on the electrochemical performances, symmetrical coin cells (2032-type) with two identical Li-interlayers were assembled using a LiPF$_6$ contained carbonate-based electrolyte (1M LiPF$_6$ in EC/DEC/DMC in 1:1:1 vol%). Two types of interlayers have been investigated for comparison: single layer of CP and single layer of CP-NCNTs. From our previous work, the use of only single layer of CP as an interlayer can improve the electrochemical performances over the bare Li foil, however, the life time and cycling stability at high current density are still insufficient$^{33}$. Figure 6.2 shows the electrochemical plating/stripping performances of the Li foil with one layer of CP (named as Li-CP) and CP-NCNTs-3 (named as Li-CP-NCNTs-3) as interlayers under different current densities with different capacity limits. Figure 6.2(a) exhibits the cycling stability and detailed voltage profiles of Li-CP and Li-
CP-NCNTs-3 at a current density of 5 mA cm\(^{-2}\) with the capacity limit of 1 mAh cm\(^{-2}\). From the cycling stability tests, the over-potential of Li-CP starts to increase after 200 h (~330 cycles) and rises to over 2000 mV (versus Li\(^+/\)Li) after 350 h (~600 cycles) with large polarization in the voltage profiles. Meanwhile, from our previous study, the bare Li foil failed after only 50 h at such high current density\(^{33}\). In comparison, Li-CP-NCNTs-3 can maintain superior stability and lower over-potentials of 200 mV (versus Li\(^+/\)Li) after 350 h (~600 cycles). Even after 580 h (~900 cycles), the over-potential of Li-CP-NCNTs-3 is only about 250 mV (versus Li\(^+/\)Li), illustrating the enhanced electrochemical performance enabled by the CP-NCNTs interlayer. When increasing the current density to 10 mA cm\(^{-2}\), the over-potential of Li-CP starts to increase after only 75 h (~200 cycles) and rises up to over 3000 mV (versus Li\(^+/\)Li) after 180 h (~500 cycles), as shown in Figure 6.2(b). The fluctuating voltage profiles are related to the Li dendrite (mossy) growth, dead Li layer formation and inner short circuiting. Remarkably, the Li-CP-NCNTs-3 can be stable for over 250 h (~750 cycles) at a very high current density of 10 mA cm\(^{-2}\). The results show that with the modification of NCNTs on CP, the stability of the Li-CP-NCNTs can be significantly improved even at ultrahigh current density.

Recently, researchers have come to a consensus that the regular testing parameter of 1 mAh cm\(^{-2}\) cannot meet the requirements for practical applications and does not highlight the potential of large capacity Li metal anodes\(^{36}\). To demonstrate the use of CP-NCNTs interlayers with a practical cycling capacity, the performance of symmetric cells with large capacities of 3 mAh cm\(^{-2}\) and 5 mAh cm\(^{-2}\) was explored. Figure 6.2(c) presents the cycling stability and voltage profiles of Li-CP and Li-CP-NCNTs-3 using a high current density of 3 mA cm\(^{-2}\) and high capacity limit of 3 mAh cm\(^{-2}\). At this condition, the stability of bare Li foil is very poor and overpotential of Li starts to increase after only 35 h. It can be seen that the CP interlayer alone can only stabilize the performances for about 130 h with the over-potential increasing to 1000 mV (versus Li\(^+/\)Li) after 180 h. However, the Li-CP-NCNTs-3 maintains a stable cycling performance with an over-potential of only 450 mV after 350 h, which is almost double the life time of the pristine CP interlayer. After further increasing the current density to 5 mA cm\(^{-2}\) with a high capacity of 3 mAh cm\(^{-2}\), the over-potential of the Li-CP begins to increase only after 100 h, however, the Li-CP-NCNTs-3 can be stabilized over 140 h, as shown in Figure 6.2(d).
**Figure S6.4** displays the cycling performance of Li-CP and Li-CP-NCNTs-3 at current densities of 3 mA cm\(^{-2}\) and 5 mA cm\(^{-2}\) with an ultrahigh capacity of 5 mAh cm\(^{-2}\). The results indicate that even with a high capacity of 5 mAh cm\(^{-2}\), the Li-CP-NCNTs-3 can still provide significantly improved stability and cycling performances compared to Li-CP. Furthermore, the electrochemical results show that the vertical NCNTs can make a significant influence on the performance of high capacity Li metal anodes even at high current densities.

To understand the influence of surface area on the electrochemical performances of the CP-NCNTs interlayers, different electrodes consisting of Li-CP-NCNTs-1, Li-CP-NCNTs-2, and Li-CP-NCNTs-3 were investigated in symmetrical coin cells. **Figure S6.5** shows the comparison of the cycling stability of Li-CP-NCNTs-1, Li-CP-NCNTs-2 and Li-CP-NCNTs-3 at the current density of 2 mA cm\(^{-2}\) with a capacity of 2 mAh cm\(^{-2}\). It can be observed that all of the samples used as an interlayer can effectively enhance the electrochemical performances of the Li metal anode. Furthermore, with an increase of surface area, better performances are achieved for the Li-CP-NCNTs-3. For example, the over-potentials of Li-CP-NCNTs-1, Li-CP-NCNTs-2 and Li-CP-NCNTs-3 are about 250 mV, 200 mV and 150 mV after 225 h, respectively. **Figure S6.6** displays the cycling performances of Li-CP-NCNTs-1 and Li-CP-NCNTs-2 at a higher current density of 3 mA cm\(^{-2}\) with a capacity of 3 mAh cm\(^{-2}\). The results show a similar trend, in which the samples with higher surface area indicate better electrochemical stabilities. These results can be rationalized by the high surface area lowering the local current on the interlayer, leading to a more homogeneous electron/Li\(^+\) distribution with reduced the Li dendrite growth. Meanwhile, the density of CP-NCNTs is around 0.66 g cm\(^{-3}\), which can be considered as the light materials compared with various metal-based interlayer and host for Li metal anode, such Ni, Cu, et al. Thus, the gravimetric energy density using CP-NCNTs interlayer will be higher than the metal-based interlayer and host. Then, in our previous study\(^{36}\), 5 layer of CP are required using as interlayer for Li metal anode to maintain the stable electrochemical performances under high current density and high capacity. Typically, the weight and thickness of 5 layer of CP are 0.05 g and 1050 μm, respectively. After grown NCNTs, the weight and thickness of CP-NCNTs is only 0.019 and 400-450 μm, respectively. Promisingly, the CP-NCNTs interlayer can maintain very
stable performances under high current density and high capacity. In this case, with the design of CP-NCNTs, both volumetric and gravimetric energy density using CP-NCNTs is much higher than that of multi-layer of CP.

Figure 6.3 CE of Li deposition on Cu foil, CP and CP-NCNTs-3 under different cycling conditions: (a) 1 mA cm\(^2\) with a capacity of 1 mAh cm\(^2\); (b) 1 mA cm\(^2\) with a capacity of 3 mAh cm\(^2\); (c) 3 mA cm\(^2\) with a capacity of 1 mAh cm\(^2\); (d) 3 mA cm\(^2\) with a capacity of 3 mAh cm\(^2\). (e) Cycling performance of full cells (C/LiFePO\(_4\) as cathode) using Li foil, Li-CP and Li-CP-NCNTs as anode at 1 C.
To demonstrate its bi-functional interlayer property, a second configuration of the use of CP-NCNTs for Li metal batteries has been also fabricated and examined. In this case, all the designed interlayers have also been investigated as substrates for Li deposition. The cycling Coulombic efficiencies (CE) of Cu foil, CP and CP-NCNTs were carried out under different cycling conditions, as shown in Figure 6.3. All cells containing CP and CP-NCNTs have been activated and stabilized in the first 10 cycles in the voltage range of 0-2 V. From Figure 6.3(a), the Cu foil delivers a low initial CE of ~ 80 % and decreases to only 40 % after 100 cycles. Promisingly, both the CP and CP-NCNTs display better CE than the Cu foil, in which the CE of CP drops to 70 % after 280 cycles, however, the CP-NCNTs can maintain a high CE of 99.5 %. When increasing the current density to 3 mA cm⁻² or capacity to 3 mAh cm⁻² (as shown in Figure 6.3 (b, c)), the CEs and life time of the Cu foil are even lower. The CP-NCNTs always presents the best performances compared to both CP and Cu foil, in which it can be stable for over 130 cycles (CE > 96.7 %) and 300 cycles (CE> 98.6 %) under the conditions of 1 mA cm⁻²/3 mAh cm⁻² and 3 mA cm⁻²/1 mAh cm⁻², respectively. Additionally, when the current density and capacity increase to 3 mA cm⁻² and 3 mAh cm⁻², the CP-NCNTs can deliver an enhanced performance of over 150 cycles while the Cu foil and CP are unstable after only 20 cycles and 100 cycles, respectively (as shown in Figure 6.3 (d)).

The performance of the Li foil with and without CP-NCNTs interlayers as an anode for LMBs was further investigated in a full cell using C/LiFePO₄ as the cathode. The loading of C/LiFePO₄ is ~ 10 mg cm⁻² corresponding to an areal capacity of ~1.7 mAh cm⁻². Figure 6. 3(e) presents the cycling performances of full cells using bare Li foil, Li-CP and Li-CP-NCNTs-3 as the anode at a rate of 1 C (~ 1.7 mA cm⁻²). In the batteries using bare Li foil, the specific capacity drops to 40 mAh g⁻¹ after 150 cycles due to the poor cyclability of the planar Li foil. With one layer of CP as interlayer, the specific capacity keeps around 100 mAh g⁻¹ after 150 cycles, indicating the obvious improvement of CP interlayer. However, the cycling stability is still decreasing after 200 cycles with only one layer of CP due to the high loading and areal capacity of LFP. Promisingly, with the CP-NCNTs interlayer, the full cell can maintain a stable capacity of 130 mAh g⁻¹ over 150 cycles. The cycling stability and capacity retention demonstrates that the bi-functional
CP-NCNTs interlayer can effectively improve the electrochemical performances compared to the pristine Li foil anode in a full cell format.

Figure 6.4 SEM images of the top surface of CP-NCNTs interlayer after 10 cycles of plating/stripping with different capacities of 0.1 mAh cm$^{-2}$ (a, b), 0.5 mAh cm$^{-2}$ (c, d) and 3 mAh cm$^{-2}$ (e, f).

To understand the effects of the CP-NCNTs interlayer on the process of Li plating/stripping, the morphologies of deposited Li in different parts of Li-CP-NCNTs composite electrodes are characterized by SEM. It has been widely reported and also observed in our previous works that the serious Li dendrite growth happens on the surface of Li foil due to the inhomogeneous nucleation and growth$^{36}$. At the same time, dead Li layers are formed on the Li surface causing the volume change and large resistance. Figure S6.7 shows the SEM images of the CP-NCNTs-3 surface and Li foil surface in the Li-NCNTs-3 composite electrode at different stages of cycling. Different from the large pit formations on the bare Li foil in the first stripping process, it can be
obviously seen that the pitting process is avoided (Figure S6.7 (b)). Furthermore, no mossy and dendritic Li growth on the CP-NCNTs-3 interlayer can be seen (Figure S6.7 (a)). In addition, during the first plating process, both the surfaces of CP-NCNTs and Li foil are seen to be relatively smooth without any dendritic and mossy Li growth (Figure S6.7 (e, d)). After 10 cycles of repeated plating/stripping, the surface of CP-NCNTs is uniformly covered with deposited Li and the surface of Li is still very smooth, avoiding Li dendrite growth. The dendrite-free Li deposition is attributed to the uniform local current distributions and homogeneous nucleation and growth of Li caused by the CP-NCNTs interlayers. In addition, the cross-section view SEM images of the CP-NCNTs-3 and Li foil in Li-CP-NCNTs composites are shown in Figure S6.8-6.10. From the cross-section images, it can be observed that the thicknesses of Li foil and CP-NCNTs undergo almost no change in the different cycling stages, such as first stripping (Figure S6.8), first plating (Figure S6.9) and after 10 cycles of plating/stripping (Figure S6.10). Moreover, the top-view and cross-section view SEM images of both Li foil and CP-NCNTs-3 in the Li-CP-NCNTs-3 composite electrode after 100 cycles under the current density of 5 mA cm\(^{-2}\) and 10 mA cm\(^{-2}\) are presented in Figure S6.12 and Figure S6.13, respectively. From the top-view SEM images in Figure S6.12 and Figure S6.13, it can be observed that there is no Li dendrite growth on the surface of both Li foil and CP-NCNTs-3 under the high current density up to 10 mA cm\(^{-2}\) after 100 cycles. Meanwhile, the thickness of CP-NCNTs-3 interlayer remain the similar ranges of ~ 450 μm, indicating the minimize volume change of the electrode after 100 cycles. Thus, with the designed interlayer of CP-NCNTs, the bi-functional properties of the dendrite-free Li deposition and minimum volume change has been realized for Li foil and interlayer during electrochemical plating/stripping.

To further understanding the Li deposition process, the morphologies of CP-NCNTs interlayers with different Li capacities are also investigated in Figure 6.4 and Figure S6.11. Figure 6.4(a, b) displays the SEM images of CP-NCNTs interlayers after 10 cycles of plating/stripping with a capacity of 0.1 mAh cm\(^{-2}\). It can be seen that the NCNTs are still visible and Li is deposited around the surface of the NCNTs. With a deposition capacity of 0.5 mAh cm\(^{-2}\), the Li is deposited along the NCNTs and is further filled in the spaces between the NCNTs (Figure 6.4(c, d)). Subsequently, the bulk Li
almost encompasses the entire surface of NCNTs in the CP-NCNTs without any Li dendrite formation, as shown in Figure 6.4(e, f). From the cross section view SEM images (Figure S6.11), it also can be observed that the volume change of Li is limited in the CP-NCNTs interlayer even with a large capacity of 5 mAh cm⁻². Meanwhile, with the large Li deposition amount during cycling, the thicknesses of Li in CP-NCNTs interlayers increase, as shown in Figure S6.11. Furthermore, with the CP-NCNTs interlayer on the Li foil, the mossy and dendritic Li deposition can be effectively reduced to achieve a dendrite-free structure. Moreover, the volume change of Li during plating/stripping is confined to the void space of 3D CP-NCNTs. Lastly, the Li is nucleated on the surface of NCNTs and further deposited along the NCNTs and the spaces between them, leading to a reduction in local current and homogeneous Li⁺ flux distributions.

6.4 Conclusion

In conclusion, we extend the “interlayer” concept to the application of Li metal anodes and rationally design a bi-functional interlayer using carbon paper as a base material. The vertical NCNTs are grown on the carbon fibres of CP to obtain a 3D interlayer structure for Li metal. Herein, we firstly demonstrated the relationships between surface area and electrochemical performances for the 3D structure by controlling the growth time of NCNTs during the SPCVD process. Impressively, the Li-CP-NCNTs composite electrode can deliver stable cycling performances for over 600 h (~ 900 cycles) and 250 h (~ 750 cycles) at the high current densities of 5 mA cm⁻² and 10 mA cm⁻², which is two times higher than that of the CP interlayers. Meanwhile, with a high capacity of 3 mAh cm⁻², the Li metal electrode with CP-NCNTs interlayer delivers the long life time of over 350 h at a current density of 3 mA cm⁻². The morphologies of both Li foil and CP-NCNTs interlayers indicate that the Li dendrite-free deposition and minimum volume change structure can be obtained with the “bi-functional” interlayers. We believe that these new findings could open a new window for the fabrication of safe, long life time, dendrite-free and minimum volume change Li metal anodes.
6.5 Acknowledgements

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6.6 Reference


6.7 Supporting information

**Figure S6.1** (a-b) Cross-section view SEM images of CP-NCNTs-3; (c, d) top-view SEM images of CP-NCNTs-3
Figure S6.2 N₂ adsorption/desorption isotherms (a) and the pore size distribution based on BJH-method (b) of CP-NCNTs-1, CP-NCNTs-2 and CP-NCNTs-3.

Figure S6.3 Raman spectra of CP-NCNTs-1, CP-NCNTs-2 and CP-NCNTs-3.
Figure S6.4 Comparison of the cycling stability of the Li-CP and Li-CP-NCNTs-3 at the current densities of 3 mA cm$^{-2}$ (a), 5 mA cm$^{-2}$ (b) with the capacity limit of 5 mAh cm$^{-2}$.
Figure S6.5 Comparison of the cycling stability of the Li-CP-NCNTs-1, Li-CP-NCNTs-2 and Li-CP-NCNTs-3 at a current density of 2 mA cm$^{-2}$ with the capacity limit of 2 mAh cm$^{-2}$.

Figure S6.6 Comparison of the cycling stability of the Li-CP-NCNTs-1 and Li-CP-NCNTs-2 at a current density of 3 mA cm$^{-2}$ with the capacity limit of 3 mAh cm$^{-2}$. 
Figure S6.7 The top-view SEM images of CP-NCNTs-3 surface and Li foil surface in the Li-NCNTs-3 composite electrode after first stripping (a, b), first plating (c, d) and 10 cycles of plating/stripping (e, f), respectively. The current density is 3 mA cm$^{-2}$ and the capacity limit is 1 mAh cm$^{-2}$.
**Figure S6.8** The cross section view SEM images of Li foil (a, b) and CP-NCNTs-3 (c, d) in the Li-CP-NCNTs-3 composite electrode after first stripping at the current density of 3 mA cm$^{-2}$ with the capacity of 1 mAh cm$^{-2}$.
Figure S6.9 The cross section view SEM images of Li foil (a, b) and CP-NCNTs-3 (c, d) in the Li-CP-NCNTs-3 composite electrode after first plating at the current density of 3 mA cm\(^{-2}\) with the capacity of 1 mAh cm\(^{-2}\).
Figure S6.10 The cross section view SEM images of Li foil (a, b) and CP-NCNTs-3 (c, d) in the Li-CP-NCNTs-3 composite electrode after 10 cycles of plating/stripping at the current density of 3 mA cm\(^{-2}\) with the capacity of 1 mAh cm\(^{-2}\).
Figure S6.11 The cross section view SEM images of CP-NCNTs-3 in the Li-CP-NCNTs-3 composite electrode after 10 cycles of plating/stripping at the current density of 3 mA cm\(^{-2}\) with the capacity of 1 mAh cm\(^{-2}\) (a) 3 mAh cm\(^{-2}\) (b), 5 mAh cm\(^{-2}\) (c) and 10 mAh cm\(^{-2}\).
Figure S6.12 The top-view and cross-section view SEM images of Li foil and CP-NCNTs-3 in the Li-CP-NCNTs-3 composite electrode after 100 cycles of plating/stripping at the current density of Repeated5 mA cm$^{-2}$ with the capacity of 1 mAh cm$^{-2}$.

Figure S6.13 The top-view and cross-section view SEM images of Li foil and CP-NCNTs-3 in the Li-CP-NCNTs-3 composite electrode after 100 cycles of plating/stripping at the current density of 10 mA cm$^{-2}$ with the capacity of 1 mAh cm$^{-2}$.
Chapter 7

7 Superior Stable and Long Life Sodium Metal Anodes Achieved by Atomic Layer Deposition*

In the last three chapters, we focus on the development of high performances Li metal anode. Na-metal batteries are considered as the promising alternative candidate for Li-ion battery beneficial from the wide availability and low cost of sodium, high theoretical specific capacity, and high energy density based on the plating/striping processes and lowest electrochemical potential. For Na-metal batteries, the crucial problem on metallic Na is one of the biggest challenges. Mossy or dendritic growth of Na occurs in the repetitive Na stripping/plating process with an unstable solid electrolyte interphase layer of non-uniform ionic flux, which can not only lead to the low Coulombic efficiency, but also can create short circuit risks, resulting in possible burning or explosion. In this communication, the atomic layer deposition of Al₂O₃ coating is first demonstrated for the protection of metallic Na anode for Na-metal batteries. By protecting Na foil with ultrathin Al₂O₃ layer, the dendrites and mossy Na formation have been effectively suppressed and lifetime has been significantly improved. Furthermore, the thickness of protective layer has been further optimized with 25 cycles of Al₂O₃ layer presenting the best performance over 500 cycles. The novel design of atomic layer deposition protected metal Na anode may bring in new opportunities to the realization of the next-generation high energy-density Na metal batteries.

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7.1 Introduction

In the past several decades, Li-ion batteries (LIBs) become one of the most widely used energy storage device for portable electronic and electrical vehicles due to their superior features, including high energy density, no memory effect, low maintenance, and little self-discharge [1]. However, the limited resources and uneven distribution of lithium source become a serious challenge for low cost and large scale application of LIBs [2]. The requirements for high-energy and low-cost rechargeable batteries have prompted the replacement of new battery system with conventional LIBs [2, 3]. Na-ion batteries and Na-metal batteries are considered as the promising alternative candidate beneficial from the wide availability and low cost of sodium [4]. Compared with other anodes used in Na-ion batteries, Na metal anode show a high theoretical specific capacity of 1166 mAh g⁻¹ based on the repeated plating/stripping processes and lowest electrochemical potential [5]. Meanwhile, the typical Na-metal batteries, including room temperature Na-S batteries and Na-O₂ batteries, both have a superior theoretical specific energy density (1274 W h kg⁻¹ for room temperature Na-S system and 1605 W h kg⁻¹ if considering Na₂O₂ as discharge product for Na-O₂ batteries, respectively) compared to Li–ion battery systems [5, 6].

For these room-temperature Na metal batteries, main efforts are focusing on the design and fabrication of cathode electrode, however, the crucial problems on metallic Na anode still remain. Similar with Li metal anode: metallic Na reacts with most organic solvents in the liquid electrolyte leading to the formation of solid electrolyte interphase (SEI) layer upon directly contacting and also during the initial charge/discharge processes. The uniform and compact SEI layer effectively prevents the further physical contact between metallic Na and electrolyte, making Na dynamically stable in certain organic solvents. However, mossy or dendritic growth of Na will occur in the repetitive Na stripping/plating process with an unstable SEI layer of non-uniform ionic flux. Dendritic structures are unflavored because they not only lead to the low coulombic efficiency, but also can create short circuit risks when it ultimately penetrate the separator, reaching cathode electrode, further resulting in possible burning or explosion (Figure 5.1). Hartmann et al. observed the undesired growth of Na dendrites during cycling in the Na-
O₂ batteries [7]. The hilly structure of Na dendrite composed of sodium and oxygen also can be found in the holes of separator. Another group also visually investigated the Na dendrite structure in Na-O₂ cell under various discharge capacity cut-off values [8]. Their results all demonstrate that the metallic Na anode is also a serious challenge affecting the performances and lifetime of Na-O₂ batteries beyond cathode electrode.

To data, there are only few reports exploring electrochemical plating/stripping of Na metal at room temperature [9]. Recently, Z.W. Seh et al first reported one type of liquid electrolyte, consist of sodium hexafluorophosphate in glymes (mono-, di-, and tetruglyme), can enable highly reversible and non-dendritic plating/stripping of sodium metal anodes at room temperature [5]. However, it is still believed that the mechanical strength of these in situ formed protective films by adjusting with electrolyte is not yet high enough to withstand the large volume change during the process of Na plating/stripping [10]. Meanwhile, the physical cohesion of these thin films onto Na metal is very limited [11]. Moreover, especially for Na-O₂ batteries, the corrosion of Na metal under O₂ atmosphere can be another issue for the long cycle of cells.

In the previous study on Li metal batteries, the rational design of ex-suit protective coating layers are widely accepted for reducing of dendrite growth and suppressing O₂ corrosion [12]. However, to the best of our knowledge, there is no reference reporting the protective coating on metallic Na for long-life Na metal batteries. The excessively sensitivity and quite low melting point of Na make it difficult to apply the general methods to deposit protective coating layer on the surface of Na metal. Atomic layer deposition (ALD) is a unique technique that can realize excellent coverage and conformal deposition and the thickness of the film deposited by ALD is precisely controllable at the nanoscale level due to its self-limiting nature [13]. A promising feature of ALD is the ability to conformably coat a surface at relatively low temperatures, which can enable the deposition of metals on Na metal, which has a low melting point of 98°C. Our previous work has indicated that an ALD coating layer on the cathode and/or anode material for LIBs prevents direct contact of the electrolyte with the electrode, resulting in the formation of a stable SEI layer thereby increasing the electrochemical performance of the LIB [14]. Recently, two different groups have demonstrated ultrathin ALD Al₂O₃ coating
film as protective layer for lithium metal anode. Their results indicate that ALD protective coating layer can effectively prevent Li metal corrosion in electrolyte and reduce the dendrite growth as well further enhancing electrochemical performances with higher capacity and longer lifetimes [15, 16]. It is also considered that ALD Al$_2$O$_3$ can be a promising candidate for Na protection due to the following reasons: 1) the low reaction temperature of ALD Al$_2$O$_3$, can be deposited within an acceptable temperature range. 2) with electrochemical cycling, Al$_2$O$_3$ will form NaAlOx, which has demonstrated high ionic conductivity [17].

In this chapter, we demonstrated the successful application of the ALD technique to create an ultrathin protective coating on Na metal anode to achieve long lifetime Na metal batteries. Here, it should be mentioned that, after the initial submission of the present paper, Luo et al reported a plasma-ALD process of Al$_2$O$_3$ for Na anode protection [18]. However, our work here reveals more comprehensive study on electrochemical performances and relationship between plating/stripping properties and morphologies. Moreover we also discuss the detailed reaction mechanisms by advanced characterization techniques such as Rutherford Backscattering Spectrometry (RBS) and XPS. To the best of our knowledge, we are the first time to demonstrate a powerful tool of RBS measurement in the field of Li or Na metal anode, which give the guidance to the researchers working in this area.

7.2 Experimental Section

**Electrode preparation:** A fresh Na foil with the diameter of 7/16 inch was prepared with the aid of a homemade press machine by pressing a piece of sodium metal stick (from Aldrich) as a starting sodium metal inside an argon-filed glove box. ALD coatings were conducted on Na foils in a Gemstar-8 ALD system (Arradiance, USA) which is directly connected to an argon-filed glove box. Al$_2$O$_3$ was directly deposited on the Na foil at 85°C by using trimethylaluminium (TMA) and water (H$_2$O) as precursors. The different cycle numbers of 10, 25 and 50 ALD Al$_2$O$_3$ coating on Na metal are named as Na@10Al$_2$O$_3$, Na@25Al$_2$O$_3$ and Na@50Al$_2$O$_3$, respectively.
Electrochemical measurements: The electrochemical analysis was performance in CR2032 coin-type cells. The coin cells were assembled in an ultra-pure argon filled glove box by symmetrical Na/Electrolyte-Separator/Na configuration using polypropylene separators (Celgard 3501). The electrolyte used in this study is 1 M sodium triflate (NaSO\textsubscript{3}CF\textsubscript{3} 98%, Aldrich) dissolved in diethylene glycol dimethyl ether (DEGDME, reagent grade ~98%, Aldrich, pre-dried before usage), which has been also used in our group for Na-O\textsubscript{2} studies \cite{6}. The Na stripping/plating studies were carried out in an Arbin BT-2000 Battery Test System at room temperature. Constant current densities were applied to the electrodes during repeated stripping/plating while the potential was recorded over time. Electrochemical impedance spectroscopy (EIS) was also performed on the versatile multichannel potentiostat 3/Z (VMP3).

Characterization: SEM images were taken using a Hitachi 3400N Environmental Scanning Electron Microscopy at an acceleration voltage of 5 kV. Due to the soft properties of Na metal, Swagelok type cells comprised of Na/Electrolyte-Separator/Na system were used to carry out the morphology testing after stripping/plating. The Swagelok cells were disassembled after 1 cycles or 10 cycles of stripping/plating process under the different current densities. The Na foil and Na@25Al\textsubscript{2}O\textsubscript{3} (before and after plating/stripping) are transferred from our ALD glove box directly to an Ar glovebox connected XPS (Kratos AXIS Ultra Spectrometer) system for XPS analysis. Rutherford Backscattering Spectrometry measurements were conducted using 1MeV and 2MeV He\textsuperscript{+} beam (Western Tandetron Facility) at several locations on the surface to confirm the uniformity of the thicknesses and composition. All samples were transferred in Ar-filled glove bag with minimum exposure to air. A Sb-implanted amorphous Si sample with a known $4.82 \times 10^{15}$ atoms /cm\textsuperscript{2} Sb content used for calibration.
7.3 Results and Discussion

Figure 7.1 Schematic diagrams of Na stripping/plating on bare Na foil and Na foil with ALD coating.

Compared with bare Na foil, the ALD coated Na presents significantly enhanced toward the Na plating/stripping performance. Furthermore, the ALD Al₂O₃ coating thickness has also been optimized in detail. The glovebox-integrated ALD tool was used in this work to directly deposit Al₂O₃ coating layer on Na metal without any air exposure. The typical ALD Al₂O₃ coating process is shown in Figure 7.1 (a) with two half reactions between TMA and H₂O. Based on the growth rate of Al₂O₃ under low temperature, the thickness of 10, 25 and 50 cycles of ALD Al₂O₃ can be defined as 1.4 nm, 3.5 nm, 7 nm, respectively.
Figure 7.2 (a) Comparison of the cycling stability of the Na@25Al$_2$O$_3$ and the bare Na foil at a current density of 3 mA cm$^{-2}$; Voltage profiles of Na@25Al$_2$O$_3$ and bare Na foil in the first cycles (b) and after 100 cycles (c) at a current density of 3 mA cm$^{-2}$. (d) Comparison of the cycling stability of the Na@25Al$_2$O$_3$ and the bare Na foil at a current density of 5 mA cm$^{-2}$; Voltage profiles of Na@25Al$_2$O$_3$ and bare Na foil in the first cycles (e) and after 100 cycles (f) at a current density of 5 mA cm$^{-2}$. The amount of Na cycled was 1 mAh cm$^{-2}$. (g) Long cycle life of Na@25Al$_2$O$_3$ at 3 mA cm$^{-2}$.

Galvanostatic cycling performance of Na with ALD Al$_2$O$_3$ coating layers and bare Na foil were studied in a symmetrical cell configuration using 1 M NaSO$_3$CF$_3$ dissolved in diethylene glycol dimethyl ether. Figure 7.2(a) shows the cycling stability of Na coated with 25 cycles of Al$_2$O$_3$ by ALD (Na@25Al$_2$O$_3$) and the bare Na foil at a current density of 3 mA cm$^{-2}$ with a capacity limitation of 1 mAh cm$^{-2}$. For the bare Na foil, the initial Na stripping/plating overpotential is about 20 mV (versus Na$^+/Na$), and rapidly increases to over 50 mV (versus Na$^+/Na$) after 100 cycles (equal to 100 h). Meanwhile, obvious fluctuating voltage profiles during Na stripping/plating process can be observed, with soft short circuiting of the cell occurring after 50 cycles (equal to 50 h). Interestingly,
Na@25Al₂O₃ demonstrates a similar initial overpotential of about 20 mV (versus Na⁺/Na), but a very negligible change in overpotential following 100 cycles (17 mV versus Na⁺/Na) (equal to 100 h). Detailed voltage profiles of Na@25Al₂O₃ and bare Na foil after the first cycle and following 100 cycles, are shown in Figure 7.2(b, c). For Na@25Al₂O₃, a flat voltage plateau at both the charging and discharging states can be retained throughout the whole cycle without obvious increases in hysteresis. Meanwhile, it also can be noticed that due to the extremely sensitive and highly reducibility of Na metal anode, there is the unstable and change in the voltage profiles at the first cycle, which can be explained as the formation of initial SEI film due to the reaction between surface of Na anode (coated and uncoated) and electrolyte. When increasing current density to 5 mA cm⁻², the initial Na stripping/plating overpotential increases into 160 mV (versus Na⁺/Na) with the highest overpotential exceed 300 mV during cycling (Figure 7.2(d)). Meanwhile, after only 21 cycles (equal to 17 h), a sudden drop of voltage can be observed for the bare Na with fluctuating voltage in the following cycles, which could be explained as a soft short-circuit occurring within the cell as a result of Na dendrite penetration. It is can be found that the life time of bare Na is shortened with increasing current density. However, with 25 cycles of ALD Al₂O₃ coating, the modified Na foil demonstrates reduced lower initial overpotential (38 mV versus Na⁺/Na ), which is extremely stable after 100 cycles with the overpotential of 40 mV (versus Na⁺/Na). In order the show the convinced performances from ALD Al₂O₃ coated Na anode, higher current density (10 mA cm⁻²) is applied, which is shown in Figure S7.1. From the results, the Na@25Al₂O₃ indicates superior stable plating/stripping performances after 150 cycles (equal to 80 h), which is much better than bare Na foil.

To further explain the performances, electrochemical impedance spectroscopy (EIS) was performed at the point of before cycling and after 50 cycles, as shown in Figure S7.5. It is believed that two distinct semicircles is associated with both the SEI/electrode (high frequency) and the charge transfer (CT)/electrical double layer (EDL) (lower frequencies) [16]. Impedance parameters calculated by equivalent circuits for different samples are shown in Table S7.1. The initial spectra in Figure S7.6(a) indicate a slight increase in the impedance for the Na@25Al₂O₃ compared with bare Na foil before cycling. After 50 cycles of plating/stripping process, R_SEI of bare Na showing an obvious increase,
however, Na@25Al₂O₃ indicating a decrease. Meanwhile, the R_{SEI} of Na@25Al₂O₃ becomes smaller than the bare Na foil, which can be attributed to the stable SEI layer with 25 cycles Al₂O₃ coating.

To optimize the thickness of the ALD protective layer on the stripping/plating performance of Na metal, various cycles of ALD Al₂O₃ (10 cycles and 50 cycles) are applied to achieve the controllable thickness of Al₂O₃ layer on Na metal. Compared with bare Na, both Na@10Al₂O₃ and Na@50Al₂O₃ has the significant improvement with lower overpotential and enhanced stability (Figure S7.2 and S7.3). However, a thinner coating of 10 cycles ALD Al₂O₃, voltage fluctuations begin to appear at around 80 cycles (equal to 80 h) with a current density of 3 mA cm⁻² (Figure S7.2(a)). Increasing the current density to 5 mA cm⁻², the Na/Al₂O₃-10 demonstrates an obvious continuous rise in hysteresis (Figure S7.3(a)). Similar results can be obtain with thicker coating of 50 cycles of ALD Al₂O₃. Although enhanced stability can be achieved, the modified Na foil with 50 cycles Al₂O₃ protective layers still shows the higher overpotential and increasing hysteresis compared with 25 cycles ALD Al₂O₃ coating (Figure S7.2(b) and Figure S7.3(b)). The EIS results (Shown in Figure. S7.5 (a, b) and Table. S7.1) also give consistent evidence with the electrochemical performances. For the thinner coating of 10 cycles Al₂O₃, the R_{SEI} shows an obvious decrease after 50 cycles, which is even smaller than bare Na. However, the Na@50 Al₂O₃ demonstrate the increasing of R_{SEI} after 50 cycles of plating/stripping, confirming the increasing resistance and hysteresis compared with bare Na and Na@25 Al₂O₃. Thus, it is very important to optimize the thickness of Al₂O₃ for protect Na. The EIS results indicate the significantly reduced degradation during cycling of optimize thickness of Al₂O₃ coating, leading to lower resistance and increase of lifetime.

With the optimized thickness of ALD Al₂O₃ coating layer (25 cycles), the modified Na foil shows superior stripping/plating performances with super-long lifetime. Even after 500 cycles, there is almost no change in the Na stripping/plating behaviour (Figure 7.2(g)). The flat changing and discharging voltage plateau also can be obtained with different stripping/plating cycles of 200, 250, 300, 350, 400 in the detailed voltage profiles at the current density of 3 mA cm⁻² (Figure S7.4).
Figure 7.3 Top-view SEM images of bare Na (a, b) and Na@25Al₂O₃ (e, f) after 1 cycles of stripping/plating; bare Na (c, d) and Na@25Al₂O₃ (g, h) after 10 cycles of stripping/plating at a current density of 3 mA cm⁻².

In order to understanding the influence of ALD Al₂O₃ coating on the morphologies of Na plating/stripping, the SEM images of the electrodes before and after cycling were analyzed by SEM. Microscopy of the bare Na foil surface are shown in Figure S7.6. Following 25 cycles of ALD Al₂O₃ coating (Figure S7.6), there is no obvious difference of the quite smooth surface due to the ultrathin thickness of coating layers. When a capacity limitation of 1 mAh cm⁻² was used along with a current density of 3 mA cm⁻², two type of Na structures can be observed on the surface, moss like Na (Figure 7.3(a, b)) and dendritic Na (Figure S7.7). For the moss like Na shown in Figure 7.3 (a, b), the sphere-like structure of Na with the sizes about 5 μm can be observed which is forming with the moss like dendrites under nanoscale. More rough structure with dendritic Na can be also found in the top view SEM images (Figure S7.7), which shows the large diameter of a few microns. These type of moss/dendritic Na will further lead to the formation of dead sodium during the plating/stripping process, which will consume effective Na and lower the columbic efficiency. Very interestingly, with ALD Al₂O₃ coating, the morphologies of the plating Na are totally changed compared with bare Na foil. Figure 7.3(e, f) shows the SEM images of Na@25Al₂O₃ after 1 cycles of stripping/plating under
the current density of 3 mA cm\(^{-2}\). With the employed of ALD Al\(_2\)O\(_3\) coating, large island-like Na is produced with a diameter of over 100 \(\mu\)m, in which the surface of the Na island is more smooth without any moss like and/or dendritic Na. The plating behavior of bare and modified Na after 10 cycles have also been studied. After 10 cycles the bare Na suffers from the serious destruction with the appearance of a rough surface littered with cracks (Shown in Figure 7.3(c, d)). However, with 25 cycles of ALD coating, the island-like Na is still stable after 10 cycles of the stripping/plating process. This demonstrates that island-like Na structures can be well maintained during the cycling compared with the moss-like and dendritic Na (Shown in Figure 7.3(g, h)). Increasing the current density to 5 mA cm\(^{-2}\), more outofflatness surface with even big crack can be seen for the bare Na after 1 cycle plating process (Figure S7.10). However, with 25 cycles of ALD Al\(_2\)O\(_3\), the island-like Na can still be achieved with a flat surface at a high current density of 5 mA cm\(^{-2}\) (Figure S7.12). Meanwhile, the SEM images of Na with 10 and 50 cycles of ALD Al\(_2\)O\(_3\) coating have also been tested under different current densities (3 mA cm\(^{-2}\) and 5 mA cm\(^{-2}\)). It can be found that with the assistance Al\(_2\)O\(_3\) coating, the Na dendrite can be effectively inhibited to form the island-like structure, which can play an important role in the improved electrochemical performance (Figure S7.8, 7.9, 7.11, 7.13). The grown of island-like structure on the surface of Na can be attributed to the very uniform and dense Al\(_2\)O\(_3\) coating layer, leading to even distribution of the electric field and further as the large and island-like Na growth.
Figure 7.4 XPS Al 2p, O 1s, S 1s and F 1s spectrum of Na-Al₂O₃ 25; bare Na and Na-Al₂O₃ 25 after 50 cycles of plating/stripping at the current density of 3 mA cm⁻².

XPS testing was employed to determine the chemical nature of the Na surface before and after plating/stripping process (Table S7.2). Figure S7.14 shows the XPS spectra of Na foil with 25 cycles Al₂O₃, bare Na and Na@25Al₂O₃ after 50 cycles of plating/stripping. From the spectra of Na@25Al₂O₃ before cycling, the peaks of Al 2p and Al 2s at 74.18 eV and 116.35 eV demonstrate the successful deposition of Al₂O₃ on the surface of Na foil by ALD. The Na 1s spectrums of all samples have been present in Figure S7.15, which is mainly from the metal Na on the surface of the samples. The detailed XPS spectrum of Al 2p, O 1s, S 1s and F 1s for each samples is shown in Figure 7.4. Bare Na foil after 50 cycles of platting/striping, results in the formation of an SEI composed of organic products including RCH₂ONa (O 1s at 532.79 eV) and inorganic products of Na₂O (O 1s at 530.05 eV), NaF (F 1s at 683.99 eV), Na₂SO₃ and Na₂SO₄ (O 1s at 531.14 and S 2p at 164-172 eV)⁵. Very promising, the Al₂O₃ protective layers can be still remain after 50 cycles of plating/stripping (Figure 7.4(c)), demonstrating the stable properties of Al₂O₃ as an artificial SEI film on the surface. Meanwhile, from the spectrum of O 1s and F 1s, the contents of RCH₂ONa, Na₂O and NaF have been effectively decreased, which declares the less reaction and reduction between the electrolyte and Na foil with the protection of Al₂O₃ coating. More evidence can be found from the spectrum of S 1s, more Na₂SO₄ exist with Al₂O₃ coating, preventing it reduce into Na₂SO₃. It is
considered that the less uniform SEI film of NaSO$_2$CF$_3$ in DEMDME causes more Na exposing to undesirable side reactions with electrolyte, forming more organic reduction products in the SEI and lowering the Coulombic efficiency$^{[5]}$. However, the Al$_2$O$_3$ coating layers can act as the artificial SEI film with electrochemical stable properties during plating/stripping and effectively reduce the reaction between Na anode and electrolyte to form the more stable SEI layer resulting the preventing the Na dendrite growth and improved life time.

Figure 7.5 RBS spectra and calculated depth profiles of bare Na and Na-Al$_2$O$_3$ 25 after 50 cycles of plating/stripping at the current density of 3 mA cm$^{-2}$.

Rutherford Backscattering Spectrometry (RBS) measurements were performed on Al$_2$O$_3$-coated Na (before cycling), and bare Na and Al$_2$O$_3$-coated Na after 50 cycles. Figure S7.16 shows that as-deposited Al$_2$O$_3$ film forms continuous layer ~ 12nm thick, assuming Al$_2$O$_3$ density of 2.7 g/cm$^3$. Absence of surface Na peak indicate that there are no voids in
Al₂O₃ layer. Experimental ion yields are best fitted assuming formation of intermixed ~10nm thick Al₂O₃-Na₂O oxide layer. RBS spectra and calculated depth profiles for samples after cycling are presented in Figure 7.5. Both Al₂O₃-coated and bare Na samples exhibited S peaks due to the interactions with electrolyte during cycling. Al peak is clearly visible in Al₂O₃-coated Na sample after cycling, however Al has a wider depth distribution as it is intermixed with Na-S-O phase. From integrated areal densities for Al peak before and after cycling we estimate that ~85±5 % of as-deposited Al remains on the surface. Amount of S is consistent with our XPS results on similar samples (Figure 7.4). S areal density is a factor of two larger for bare Na sample compared to Al₂O₃-coated Na.

The significant improvement on the electrochemical performances of ALD coated Na electrode can be attribute to the suppressed dendrite growth assistant with ultrathin ALD Al₂O₃ protective coating layer. Obviously, both the initial cycle and 100 cycles overpotential of Na stripping/plating is much smaller for the Al₂O₃ coated Na foil, especially at high current densities (Figure 7.2), which indicate the lower interfacial charge transfer resistance. Meanwhile, the smooth stripping/plating voltage profile of Al₂O₃ coated Na foil also can be contribute to reduced local current density, which further results the flat and smooth surface of the island-like Na formation during plating/stripping process. Furthermore, with the artificial Al₂O₃ coating layers, the side reaction between Na and electrolyte can be effectively reduced to form a sable SEI film. As a result, the modified Na anode can achieve very stable plating/stripping performances under very high current density with superior long life time over 500 h.

7.4 Conclusion

In conclusion, we have successfully demonstrated the concept of ALD Al₂O₃ protective coating on metallic Na foil for long life Na metal batteries for the first time. By protected Na foil with ultrathin Al₂O₃ layer, the dendrites and mossy Na formation have been effectively suppressed and life time has been significantly improved. Based on the plating/stripping tests, the thickness of protective layer have been further optimized, in which with 25 cycles of Al₂O₃ layer indicating the best performance as well as superior
long and stable life time over 500 cycles. The presented design of ALD Al$_2$O$_3$ coated metal Na anode may bring in new opportunities to the realization of the next-generation high energy density Na metal batteries.

7.5 Reference


7.6 Supporting Information

![Graph comparing cycling stability](image)

**Figure S7.1** (a) Comparison of the cycling stability of the Na@25Al₂O₃ and the bare Na foil at a current density of 10 mA cm⁻²; the amount of Na cycled was 1 mAh cm⁻².
Figure S7.2 The cycling stability of the (a) Na@10Al₂O₃ and (c) Na@50Al₂O₃ at a current density of 3 mA cm⁻²; Voltage profiles of (b) Na@10Al₂O₃ and (c) Na@50Al₂O₃ in the first cycles and after 100 cycles stripping/plating at a current density of 3 mA cm⁻².
Figure S7.3 The cycling stability of the (a) Na@10Al₂O₃ and (C) Na@50Al₂O₃ at a current density of 5 mA cm⁻²; Voltage profiles of (b) Na@10Al₂O₃ and (c) Na@50Al₂O₃ in the first cycles and after 100 cycles stripping/plating at a current density of 5 mA cm⁻².
**Figure S7.4** Voltage profiles of Na@25Al$_2$O$_3$ in the 200, 250, 300, 350, 400 cycles stripping/plating at a current density of 3 mA cm$^{-2}$.

**Figure S7.5** Nyquist plot showing electrochemical impedance spectroscopy (EIS) of the bare Na and Na@Al2O3 (10, 25, 50 cycles) before cycling (a) and after 50 cycles (b).
Figure S7.6 Top-view SEM images of bare Na (a, b) and Na@25Al₂O₃ (c, d)

Figure S7.7 Top-view SEM images of bare Na (a, b) after 1 cycle of stripping/plating at a current density of 3 mA cm⁻².
Figure S7.8 Top-view SEM images of Na@10Al₂O₃ after 1 cycle of stripping/plating at a current density of 3 mA cm⁻².
Figure S7.9 Top-view SEM images of Na@50Al₂O₃ after 1 cycle of stripping/plating at a current density of 3 mA cm⁻².
Figure S7.10 Top-view SEM images of bare Na (a, b) after 1 cycle of stripping/plating at a current density of 5 mA cm$^{-2}$. 
Figure S7.11 Top-view SEM images of Na@10Al₂O₃ after 1 cycle of stripping/plating at a current density of 5 mA cm⁻².
Figure S7.12 Top-view SEM images of Na@25Al₂O₃ after 1 cycle of stripping/plating at a current density of 5 mA cm⁻².
Figure S7.13 Top-view SEM images of Na@50Al₂O₃ after 1 cycle of stripping/plating at a current density of 5 mA cm⁻².
Figure S7.14 XPS spectra of Na-Al₂O₃ 25; bare Na and Na-Al₂O₃ 25 after 50 cycles of plating/stripping at the current density of 3 mA cm⁻².

Figure S7.15 XPS Na 1s spectrum of Na-Al₂O₃ 25; bare Na and Na-Al₂O₃ 25 after 50 cycles of plating/stripping at the current density of 3 mA cm⁻².
Figure S7.16 RBS spectrum of Na-Al$_2$O$_3$ before plating/stripping (a) and depth profiles (b).

Table S7.1 Impedance parameters calculated by equivalent circuits for different samples.

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Chapter 8

8 Inorganic-organic Coating via Molecular Layer Deposition Enables Long Life Sodium Metal Anode*

It has been studied that the Na metal anode in carbonate-based electrolyte suffers from more challenges issues than that of in ether based electrolyte. In the last chapter, we developed ALD Al₂O₃ on Na metal anode with stable performances in ether-based electrolyte. In this chapter, we firstly demonstrate the inorganic-organic coating via advanced molecular layer deposition (alucone) as protective layer for metallic Na anode. By protecting Na anode with controllable alucone layer, the dendrites and mossy Na formation have been effectively suppressed and lifetime has been significantly improved. Moreover, the MLD alucone coating shows better performances than the ALD Al₂O₃ coating. The novel design of molecular layer deposition protected Na metal anode may bring in new opportunities to the realization of the next-generation high energy-density NIBs and NMBs.

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8.1 Introduction

Na ion batteries (NIBs), room temperature Na-S and Na-O_2 batteries are highly attractive alternative candidates for future large-scale energy storage and conversion applications comparing with lithium ion batteries (LIBs) due to the wide availability and low cost of metallic sodium [1-6]. In particular, both room temperature Na–S batteries and Na–O_2 batteries have very attractive theoretical specific energy density of 1274 Wh kg^{-1} and 1605 Wh kg^{-1}, respectively [7-9]. Similar as Li metal anode in LIBs, the reaction between metallic Na and commonly employed liquid electrolytes leads to the formation of a solid electrolyte interphase (SEI) on the surface of Na. However, the SEI layer formed in Na carbonate electrolytes is relatively unstable, which leads to non-uniform ionic flux during repetitive Na stripping/plating process as well as low columbic efficiency (CE) and may result in the growth of mossy or dendritic Na causing significant safety issues (Figure 6.1). As indicated in the previous references [10, 11], a number of challenges are still needed to be addressed for the use of metallic Na as an anode in sodium based batteries. Cui’s group reported the obvious dendrite growth, short life time and low CE of NaPF_6 in carbonate based electrolyte (EC/DEC, EC/DMC), in contrast to the significantly improved CE and dendrite free Na growth in NaPF_6-glyme-based electrolyte which can be attributed to the formation of a compact SEI comprising of Na_2O and NaF in the ether-based electrolyte[12].

The use of different coatings to suppress the side reactions and dendrite growth can be another very effective approach for Li and Na anodes. Atomic layer deposition (ALD) possesses the unique advantages of providing an excellent coverage, conformal depositions and highly controllable thicknesses [13, 14]. ALD has been widely studied as a novel coating technique for cathode/anode electrodes in LIBs to prevent the side reactions due to the direct contact of the electrode with the electrolyte and contribute to form a stable SEI layer, which is important to achieve improved electrochemical performances [15-18]. Recent research has revealed that ALD Al_2O_3 coated Li metal can successfully prevent electrolyte corrosion of the anode as well as minimize Li dendritic growth, thereby enhancing electrochemical performance [19, 20]. As for Na anode, our group and Hu’s group have successfully demonstrated the use of ALD Al_2O_3 coating can
also improve the stability of Na anode during stripping/plating prolong its cycling life time and suppress dendrite growth in ether and carbonate solvent electrolyte systems, respectively [21, 22].

Comparing to inorganic coatings, organic coatings or inorganic-organic hybrid coatings may be expected to enable further improved performance of the electrode with huge volume change. Molecular layer deposition (MLD), as an analogy of ALD, can be employed to produce inorganic-organic hybrid or pure polymer thin films with many advantages such as tunable thermal stability and improved mechanical properties [23, 24]. In the typical MLD process, the oxidizing precursor in ALD (like H2O, O2 et al) can be replaced into organic linkers or add a molecular fragment into the film. For instance, Ban et al employed the use of an MLD alucone layer (a hybrid film produced through a reaction between trimethylaluminium and glycerol (Al-GL)) as a surface modifier for conventional nano-Si composites, providing significant improvement to cycling stability, rate, and CE, which can be attributed to the increased toughness and flexibility as a result of C–C and C–O bonds within the alucone film, thereby providing ample room for the huge volume expansion observed for Si anodes [25-27]. Our group has also demonstrated the use of MLD alucone as a coating material to improve the electrochemical performance of carbon/sulfur cathode electrode in Li-S batteries [28, 29]. Therefore, the merits of MLD thin film coating can be also expected to relieve the volume expansion and suppress the dendrite growth for Na anode.

Herein, we demonstrate, for the first time, the application of MLD alucone as a protecting layer for Na metal anode cycled in carbonate based electrolyte (NaPF6 in EC/PC). Compared to bare Na and ALD Al2O3 coated Na, MLD coated Na shows significantly enhanced electrochemical stripping/plating performances under various current densities and results in the formation of a smooth Na surface following plating and stripping and can effectively reduce the formation of Na dendrites. Also should mention that we carried out mechanistic study by XPS and RBS.
8.2 Experimental section

**Electrode preparation:** A fresh Na foil with the diameter of 7/16 inch was prepared with the aid of a homemade press machine by pressing a piece of sodium metal stick (from Aldrich) as a starting sodium metal inside an argon-filed glove box. Molecular layer deposition (MLD) of Alucone coatings were conducted in a Gemstar-8 ALD system (*Arradiance, USA*) directly connected with argon-filed glove box. Alucone was directly deposited on the as-prepared foil at 85 °C by alternatively introducing trimethylaluminium (TMA) and ethylene glycol (EG) as precursors. The MLD process used as 0.01 s/40 s/0.01 s/70 s TMA pulse/purge/EG pulse/purge sequence. The different cycle numbers of 10, 25 and 40 MLD Alucone coating on Na foil are named as Na@10Alucone, Na@25Alucone, and Na@40Alucone, respectively.

For comparison, ALD Al₂O₃ was performed using TMA and H₂O as precursors at 85 °C. The detailed experiment have been reported in our previous work.

**Electrochemical measurements:** The electrochemical analysis was performance in CR2032 coin-type cells. The coin cells were assembled in an ultra-pure argon filled glove box by symmetrical Na/Electrolyte-Separator/Na configuration using polypropylene separators (Celgard 3501). The electrolyte used in this study is 1 M Sodium hexafluorophosphate (NaPF₆ 98%, Aldrich) dissolved in ethylene carbonate (EC) and propylene carbonate (PC) with volume ratio of 1:1. The Na stripping/plating studies were carried out in an Arbin BT-2000 Battery Test System at room temperature. Constant current densities were applied to the electrodes during repeated stripping/plating while the potential was recorded over time.

**Characterization:** SEM images were taken using a Hitachi 3400N Environmental Scanning Electron Microscopy at an acceleration voltage of 5 kV. Due to the soft properties of Na metal, Swagelok type cells comprised of Na/Electrolyte-Separator/Na system were used to carry out the morphology testing after stripping/plating. The Swagelok cells were disassembled after 10 cycles of stripping/plating process. The Na foil and Na@25Alucone (before and after plating/stripping) are transferred from our ALD glove box directly to an Ar glovebox connected XPS (Kratos AXIS Ultra
Spectrometer) system for XPS analysis. Rutherford Backscattering Spectrometry measurements were conducted using 2.5 MeV He\(^+\) beam (Western Tandetron Facility) at several locations on the surface to confirm the uniformity of the thicknesses and composition. All samples were transferred in Ar-filled glove bag with minimum exposure to air. A Sb-implanted amorphous Si sample with a known \(4.82 \times 10^{15}\) atoms /cm\(^2\) Sb content used for calibration.

**Calculations:** Density functional theory (DFT) calculations have been carried out using the projector-augmented plane-wave (PAW) method as implemented in the Vienna Ab Initio Simulation Package (VASP). The exchange-correlation energy functional was described by using the generalized gradient approximation of Perdew-Burke-Ernzerhof (GGA-PBE). We used the Monkhorst–Pack scheme with a mesh of \(3 \times 4 \times 1\) \(k\)-points and an energy cutoff of 400 eV. The convergence criteria for total energy was set at \(10^{-5}\) eV. The Na(100) surface was modelled using a 5 layers slab using a \(4 \times 3\) unit cell. The bottom three layers of the Na(100) slab was fixed at the bulk structure. For the AIMD-NVT simulation we used the Nosé–Hoover thermostat, a time step of 1 fs, and GGA-PBE as well as the same energy cutoff and \(k\)-points as DFT calculations.
8.3 Results and discussion

Figure 8.1 (a) Schematic diagrams of Na stripping/plating on bare Na foil and Na foil with MLD alucone coating; (b) 3D and top views of adsorption of a single Alucone molecule on the Na(100) surface. The calculated Bader charges for labeled atoms are listed in Table. S1.

The MLD alucone thin film was deposited on fresh Na metal using sequential exposures of trimethylaluminium (TMA) and ethylene glycol (EG) at 85 °C in a glovebox-integrated ALD tool. A typical MLD process of alucone deposition has been verified recording the mass gain per MLD cycle via in-situ quartz crystal microbalance (QCM) sensor measurements at 85 °C (shown in Figure S8.1). The mass gain maintains a constant value (Δ~60 ng cm⁻²) from cycle to cycle for both TMA and EG at 85°C, which is similar to the reported value in the literature (Figure S8.1(b)). To confirm the uniform and conformal nature of the alucone MLD process, 100cy of deposition was conducted on nitrogen doped carbon nanotubes, as shown in Figure S8.2. To investigate the influence
of alucone film’s thickness on the electrochemical plating and stripping of Na anode, 10, 25 and 40 MLD cycle coatings were conducted and named as Na@10Alucone, Na@25Alucone, Na@40Alucone, respectively. X-ray photoelectron spectroscopy (XPS) was used to detect the surface composition of MLD coated Na (Figure S8.3(a)), confirming the presence of Al, C and O. The C 1s XPS spectra of Na@25Alucone is shown in Figure S8.3(c), in which the peak at 285 eV is attributed to adventitious C-H species and peak at 286.5 eV is attributed to C-O species, respectively. Meanwhile, the O 1s spectra and Al 2p spectra are shown in Figure S8.3(b, d), which are very similar with the peaks in Al₂O₃ films. It can be concluded that the MLD alucone coating containing Al and EG has been successfully deposited on Na foil. For comparison, Na coated with ALD Al₂O₃ has been also fabricated.

To confirm the strong interaction between the protecting alucone layer with the surface of Na, we have studied structure, energetics, and Bader charges for adsorption of a alucone molecule on Na(100) using density functional theory (DFT) and ab initio molecular dynamics (AIMD) calculations. We chose the Na(100) surface because an ab initio thermodynamics study on Li shows that (100) has the highest contribution among the low-index facets to the particle of Li [30]. To determine the most favorable structure we have first performed DFT calculations for adsorption of alucone from its O2 side (See Figure 8.1(b)) to four possible different binding sites (top, short-bridge, long-bridge, and 4-fold hollow) on the surface. Afterwards, we have performed AIMD-NVT simulations for 11 ps at 600 K for the DFT-determined minimum energy structure (4-fold hollow site). Finally, we have carried out a DFT calculation for the final structure of the AIMD simulation. The structure that was determined in this way (See Figure 8.1(b)) is 0.73 eV more favorable than that was obtained in the DFT calculation before the AIMD simulation. As can be seen in Figure 8.1(b), the molecule adsorbs parallel to the surface so that Al and O atoms can interact with Na surface atoms. Hence, the calculated adsorption energy of 5.50 eV for alucone/Na(100) is very strong. Afterwards, we analyzed the Bader charges (see Table S8.1). A total electron transfer of 2.87 eV from the surface to the molecule is found, confirming the strong adsorption energy. Table S8.1 indicates that the main electron transfer from the surface is toward Al and O2. There are
also small electron transfers from Na(100) to other O atoms (0.14 $|e|$ – 0.24 $|e|$). Therefore, the strong interaction between alucone and Na is due to the O–Na and Al–Na bonds.

**Figure 8.2** (a) Comparison of the cycling stability of the Na@25alucone and the bare Na foil at a current density of 1 mA cm$^{-2}$; Potential profiles of Na@25alucone and bare Na foil at the three different stages. (b) Comparison of the cycling stability of the Na@25alucone and the bare Na foil at a current density of 3 mA cm$^{-2}$; Potential profiles of Na@25alucone and bare Na foil at three different stages. The amount of Na cycled was 1 mAh cm$^{-2}$. 
Galvanostatic cycling of MLD alucone coated Na and bare Na foil was studied using a symmetrical cell configuration (MLD coated) Na / carbonate electrolyte + separator / (MLD coated) Na, using the electrolyte of 1 M NaPF₆ dissolved in 1:1 (v:v) EC:PC. Figure 8.2(a) presents a comparison of the cycling stability of Na@25alucone and bare Na foil at a current density of 1 mA cm⁻² with a capacity limitation of 1 mAh cm⁻². For bare Na foil, an initial stripping/plating overpotential of about 200 mV (versus Na⁺/Na) is observed. The subsequent over-potentials gradually increase to over 4000 mV (versus Na⁺/Na) after about 160 h. Furthermore, rapid uncontrolled fluctuations of the plating/stripping curves can be observed, with soft short circuiting of the cell occurring after 160 h. Interestingly, Na@25alucone demonstrates a similar initial overpotential of about 200 mV (versus Na⁺/Na), but demonstrates negligible change in the over-potential over the following 270 h (300 mV versus Na⁺/Na). Detailed potential profiles of Na@25alucone and bare Na foil at a current density of 1 mA cm⁻² at three different stages are shown in Figure 8.2(a). For Na@25alucone, a virtually flat voltage plateau is observed during both charging and discharging states and is retained throughout the cycle life with negligible increase in hysteresis. However, the bare Na displays a significant increase as well as unstable overcharging potential after 160 h and 270 h. When increasing the current density up to 3 mA cm⁻², the bare Na foil shows the larger overpotential than Na@25alucone during initial cycle and starts to increase after 80 h (Figure 8.2(b)). Meanwhile, the overpotential of bare Na foil rises up to over 1500 mV after 100 h. However, Na@25alucone demonstrates reduced lower initial overpotential (200 mV versus Na⁺/Na), which is extremely stable after 100 h with the overpotential of 400 mV (versus Na⁺/Na). A similar phenomenon can be observed from the voltage plateau in the three different stages at the current density of 3 mA cm⁻². The voltage hysteresis gradually increase in the cells made with bare Na metal and ultimately fails after 80 h.

To find the optimized MLD alucone thickness, various cycle numbers of alucone MLD (10 cycles and 40 cycles) were performed on Na. Figure S8.4 and Figure S8.5 displays the electrochemical plating/stripping performances and potential profiles of Na@10alucone at a current density of 1 mA cm⁻² and 3 mA cm⁻². The results indicate that a thinner MLD coating of 10 alucone cycles can also prevent an increase in overpotential with prolonged cycling and contributes toward preventing mossy and dendritic growth,
but cannot retain as good prolonged performances as Na@25alucone. Similarly, results can be obtained with a thicker coating of 40 cycles of MLD alucone. Although enhanced stability can be achieved, the modified Na foil with 40 cycles of alucone coating consistently demonstrates elevated over-potential and increasing hysteresis compared with 25 cycles MLD alucone coating (Figure S8.6).

In order to understand the improved performance of MLD alucone coated Na electrode comparing to bare Na, the morphologies of bare Na and Na@25alucone before and after cycling were analyzed by SEM. Figure 8.3 compares the SEM images of bare Na and Na@25alucone after 10 cycles of electrochemical plating/stripping at a current density of 1 mA cm\(^{-2}\) with the capacity limit of 1 mAh cm\(^{-2}\). From top view SEM images (Figure 8.3 (a-c)), moss-like and 3D sphere-like structures of Na dendrites of the thickness of approximately 10 μm can be clearly observed for bare Na. Furthermore, following electrochemical cycling, the surface of Na metal appears to have increased surface roughness as well as high surface area comprising of porous SEI material (Figure S8.7).
Cross-sectional SEM images of cycled bare Na have also been investigated and are displayed in Figure 8.3 (d-f). From Figure 8.3 (d), a clear distinction between Na dendrite growth and subsurface bulk Na can be seen, in which the Na dendrite layer is approximately 150 μm. The high surface area Na dendrite can also be observed in Figure 8.3 (e, f). These types of moss/dendritic Na will further lead to the formation of dead sodium during the plating/stripping process, which will consume effective Na and decrease CE. Interestingly, through the use of an alucone coating, the surface morphology of electrochemically cycled Na is relativity smoothed and does not have any high surface area moss/dendritic Na, as shown in Figure 8.3(g-i) and Figure S8.7. Meanwhile, the cross-section view of Na@25alucone (Figure 8.3 (i-l)) displays a negligible gap between plated Na and bulk Na, indicating uniform electrochemical deposition of Na. It can be certified that with alucone layer, the Na dendrite can be effectively reduced to form the smooth surface on Na metal, which can play an important role in the improved electrochemical performance.

**Figure 8.4** XPS F 1s, O 1s and Na 1s spectrum of bare Na and Na@25alucone after 10 cycles of plating/stripping at the current density of 1 mA cm⁻².

XPS testing was employed to determine the surface chemical nature of bare Na and Na@25alucone electrodes after 10 cycles of electrochemical plating and stripping. The F 1s, O 1s and Na 1s XPS spectra of each sample are shown in Figure 8.4. In the F 1s spectrum, the peak at 686 eV occurs in both samples, which is due to residual NaₓPF₆ and
Na$_3$PO$_2$F$_2$ on the surface. However, an extra F peak of 683 eV can be observed from Na@25alucone after cycling, which can be assigned as the Na-F (NaF) peak. For the O 1s spectra, there are no obvious O peaks in the bare Na after cycling, however, the O 1s peak of 530.9 eV in Na@25alucone after cycling is the formation of Na$_2$O-like phase in the SEI layers. Meanwhile, the content of F, O and Na in bare Na sample is much less than the Na@25alucone indicating unstable SEI formation on bare Na. This causes additional Na to be exposed to electrolyte, resulting in undesirable side reactions occurring, consuming both active Na and electrolyte thus, lowering the columbic efficiency of the cell. Furthermore, the non-uniformity of the SEI results in non-uniform Na$^+$ flux and dendritic growth of Na metal, causing constant breaking and re-forming of the SEI$^{12}$. However, the SEI in Na@25alucone mainly consist Na-O (530.9 eV) and Na-F (683.9 eV), which is considered as stable SEI components and highly impermeable to the electrolyte solvent, resulting in uniform Na$^+$ flux and reduced dendrite growth of Na metal$^{12}$. 
Rutherford backscattering spectrometry (RBS) measurements were performed on bare Na and Na@25alucone electrodes before and after 10 plating/stripping cycles to confirm film thicknesses and deduce elemental depth profiles. Figure S8.10 show RBS spectrum for alucone-coated Na foil before electrochemical plating/stripping and calculated depth profiles. As evident from sharp Al, C and O surface peaks, alucone layer ~ 60 nm thick was developed on the Na surface after 25 MLD alucone cycles. Several samples with 25, 50 and 75 MLD deposition cycles were analyzed by RBS to determine alucone growth rate. Assuming a change in composition due to Na diffusion into alucone layer after deposition, the MLD growth rates of 0.62-1.0 nm/cycle were calculated which are a factor of ~ 20% higher compared to Li and ~ factor of ~ 20% higher compared to the rate observed by SEM on carbon tubes and presented in Figure S8.2. It is considered that the higher growth rate of alucone on Na can be attributed to the reactions of Na and EG in
the initial cycles leading to a thicker layer, which has also been observed and determined by Elam’s group for ALD Al$_2$O$_3$ coating on Li$^{31}$. Na profile goes all the way to the surface. In addition Al profile goes deeper (200-300nm) into Na foil, consistent with morphological feature observed in SEM and Al(C$_x$O$_y$)/Na interdiffusion. Remarkably Al peaks and associated depth profiles do not change dramatically after 10 cycles of stripping/plating (Figure 8.5). P and F contents are higher in SEI layer for alucone covered Na compared to a bare Na sample, after electrochemical cycling, which is also consistent with XPS results presented above. P and F from NaPF$_6$ penetrate well into Al(C$_x$O$_y$) layer and are likely to contribute to overall stability of SEI. Notably, Na concentrations on the surface do not change significantly after electrochemical cycling, another argument towards enhanced stability of SEI in Na@alucone samples.

For comparison, 30 cycles of ALD Al$_2$O$_3$ was also been deposited on the surface of metallic Na, using TMA and water as precursors at 85 $^\circ$C$^{21}$. Figure S8.8 shows the electrochemical plating/stripping cycling performance of Na@30Al$_2$O$_3$ under a current density of 1 mA cm$^{-2}$ and 3 mA cm$^{-2}$. It can be found that the lifetime of Na@30Al$_2$O$_3$ can be partially enhanced compared to bare Na. However, the alucone coated samples still outperforms ALD Al$_2$O$_3$. It is believed that the alucone coating is highly stable against liquid electrolyte and acts as a passivating agent to assist Na metal anode to form a stable SEI layer. Furthermore, an alucone coating is mechanically flexible$^{25}$ and allows for repeated Na plating/stripping on the surface of Na foil with significant roughness.

### 8.4 Conclusion

In conclusion, we demonstrate the first use of an inorganic-organic MLD-alucone protecting layer on metallic Na anode for long life Na metal batteries. By protecting Na foil with an ultrathin alucone layer, the formation of mossy and dendrite-like Na is effectively suppressed and life time significantly improved. Furthermore, a comparison between ALD Al$_2$O$_3$ and MLD alucone has also been investigated, demonstrating that the alucone coated Na outperforms ALD Al$_2$O$_3$ by displaying prolonged life time and stable polarization curves. It is believed that our design of alucone coated metal Na anode opens
up new opportunities to the realization of next-generation high energy density Na metal 
batteries.

8.5 Acknowledgements

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Canada (NSERC), the Canada Research Chair Program (CRC), the Canada Foundation 
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8.6 Reference

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8.7 Supporting Information

Figure S8.1 Mass gain and reactor pressure during sequential TMA and EG exposures.

Figure S8.2 SEM images of 100 cycles Alucone on N doped carbon nanotubes.
Figure S8.3 XPS spectra of Na@25Alucone before cycling
Figure S8.4 The cycling stability of the Na@10Alucone at a current density of 1 mA cm$^{-2}$; Voltage profiles of Na@10Alucone in three different stage after stripping/plating at a current density of 1 mA cm$^{-2}$.

Figure S8.5 The cycling stability of the Na@10Alucone at a current density of 3 mA cm$^{-2}$; Voltage profiles of Na@10Alucone in three different stage after stripping/plating at a current density of 3 mA cm$^{-2}$.
Figure S8.6 The cycling stability of the Na@40Alucone at a current density of 3 mA cm\(^{-2}\).

Figure S8.7 Top-view SEM images of bare Na after 10 cycles of stripping/plating at a current density of 1 mA cm\(^{-2}\) with the capacity of 1 mAh cm\(^{-2}\).
Figure S8.8 Top-view SEM images of bare Na@25Alucone after 10 cycles of stripping/plating at a current density of 1 mA cm$^{-2}$ with the capacity of 1 mAh cm$^{-2}$.

Figure S8.9 The cycling stability of the Na@30Al$_2$O$_3$ at a current density of 1 mA cm$^{-2}$ and 3 mA cm$^{-2}$. 
Figure S8.10 RBS spectrum of Na@25Alucone before plating/stripping (a) and depth profiles (b).
Table S 8.1 Changes in Bader charges of atoms in the Alucone molecule and topmost layers of Na(100) after adsorption (Δq in e). The atom numbers are labeled in Fig. 1.

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Chapter 9

9 In situ formation of controllable Na-P-S as protective layer for Na metal anode *

In the last two chapters, we developed the gas-phase thin film deposition method of ALD and MLD for the protection of Na metal anode. However, it will be challenging to directly deposit solid-state electrolyte as coating for Na metal anode by ALD and MLD. In this chapter, we demonstrate for the first time a facile and in-situ solution-based method to synthesize an artificial protective layer of Na₃PS₄ (NaPS) on the surface of Na metal. Promisingly, the thickness and composition of the NaPS can be controlled through adjustment of the precursor concentration and reaction times. The thin amorphous NaPS layers on the surface of the Na metal will reduce parasitic side reactions with electrolyte components, increase the homogeneity of the SEI layer and improve the Na⁺ flux to the surface. Meanwhile, the ionically conductive NaPS can eliminate the strong electric field buildup at the surface, resulting in a more homogeneous Na plating/stripping process with suppressed Na dendrite growth. The design of the NaPS-coated Na anode opens up new opportunities for the realization of next-generation high-energy density Na metal batteries.

*A version of this chapter has been submitted*
9.1 Introduction

Na-ion batteries (NIBs) and Na metal batteries (NMBs) are considered as promising alternatives to the conventional Li-ion batteries for large-scale energy storage applications due to the wide availability and low cost of sodium sources [1]. In addition, NMBs, including room temperature Na-S and Na-air batteries, show high theoretical specific energy densities of 1274 Wh kg⁻¹ and 1605 Wh kg⁻¹, respectively [2]. Metallic Na is the ultimate choice among all the possible anode candidates due to its high theoretical capacity and low electrochemical potential [3]. However, metallic Na suffers from several challenges during electrochemical cycling, including: 1) The high reactivity between Na and liquid electrolyte causes the formation of a solid electrolyte interphase (SEI) on the surface of Na metal. The unstable SEI layers lead to continuous consumption of liquid electrolyte and shortening of the cycling life time [4]. 2) The inhomogeneous ionic flux on the surface of Na will result in mossy or dendritic Na growth, which can further lead to the formation of “dead Na”, lower the Coulombic efficiency (CE) and cause safety concerns due to the risk of dendrite growth and short-circuiting [5]. 3) The hostless nature of the Na metal anode results in large volume changes during repetitive Na plating/stripping processes [6].

To date, different approaches have been proposed to address the aforementioned challenges of metallic Na, including electrolyte modifications, the design 3D hosts and current collectors, and surface coating/modifications [7]. In previous studies, it has been demonstrated that using ultra-concentrated electrolytes or additives such as fluoroethylene carbonate (FEC) can stabilize the SEI layer and reduce dendrite growth [8]. Alternatively, surface coating/modification is another effective strategy to achieve stable artificial SEI layers which can suppress Na dendrite growth and increase the life time of NMBs [9]. In our previous studies, we demonstrated inorganic Al₂O₃ and organic-inorganic hybrid alucone (Al-ethylene glycol) thin films as protective layers for Na metal anodes, achieving enhanced electrochemical stability and cycling life in the ether-based and carbonate-based electrolytes, respectively [10]. In order to achieve ideal artificial SEI layers, a high ionic conductivity coating which can lead to the uniform
distribution of ion flux and localized current densities should be developed. Recently, Nazar’s group described an efficient way to stabilize Li plating using the Li$^+$ ion solid electrolyte Li$_3$PS$_4$ as a surface modification for Li metal anodes [11]. The Li$_3$PS$_4$ layer was chemically and electrochemically stable over repeated plating/stripping cycles and delivered more stable plating/stripping performances compared to control Li foils. To the best of our knowledge, there are still no reports using Na$^+$ ion conductive solid-state electrolytes (SSEs) as an artificial protective layer to address the instability and dendrite growth of Na metal anode.

Herein, we demonstrate a facile and in-situ solution-based approach to fabricate the SSEs protective layer of Na$_3$PS$_4$ (NaPS) on the surface of Na metal. Promisingly, the thickness and composition of the NaPS can be controlled through adjustment of the concentrations of the precursors and reaction times. The thin amorphous NaPS layers on the Na (Na@NaPS) will reduce the reactions with the electrolytes and increase homogeneity of the SEI layers and Na$^+$ flux. Meanwhile, the NaPS as the protective layer at the surface, resulting in homogeneous Na plating/stripping processes and suppressed Na dendrite growth. Our design of SSE NaPS-coated Na anode opens up new opportunities for the realization of next-generation high energy density Na metal batteries.

9.2 Experimental section

Preparation of Na@NaPS: The typical P$_4$S$_{16}$ was synthesized by using the previous report [12]. The Na$_3$PS$_4$ protective layers were fabricated by the in-situ solution-based method. All the experiment were performed in the Ar-filled glove box (H$_2$O and O$_2$ < 0.1 ppm) to prevent the effects from the moisture and oxygen. Typically, the P$_4$S$_{16}$ powders with controllable amount (10 mg, 20 mg, and 30 mg) were dissolved in 20 mL solvent of diethylene glycol dimethyl ether (DEGDME) with the calculated concentration of 0.5, 1 and 1.5 mg mL$^{-1}$. The prepared P$_4$S$_{16}$-DEGDME solutions were kept in glove box for more than 3 day to obtain the clear liquid with complete dissolution. A fresh Na foil with the diameter of 3/8 inch was prepared with the aid of a homemade press machine by pressing a piece of sodium metal stick (from Aldrich) as a starting sodium metal. Then, a piece of Na foil and 1 mL of P$_4$S$_{16}$-DEGDME solutions (with different concentrations) were added into a reactor with the controlled reaction times (15 min, 60 min and 90 min).
After reaction, the coated Na foil was taken out from the solution and transferred into the heating chamber connected with glove box. The coated Na foil was dried at 80 °C for 2 h to remove the residual solvent of DEGDME. The experiment design of different P$_4$S$_{16}$ concentration and reaction time are shown in Table. S1.

**Electrochemical measurements:** The electrochemical analysis was performance in CR2032 coin-type cells. The coin cells were assembled in an ultra-pure argon filled glove box by symmetrical Na/Electrolyte-Separator/Na configuration using polypropylene separators (Celgard 3501). The electrolyte used in this study is 1 M sodium hexafluorophosphate (NaPF$_6$ 98%, Aldrich) dissolved in ethylene carbonate (EC) and propylene carbonate (PC) with volume ratio of 1:1. The Na stripping/plating studies were carried out in a Land Battery Test System at room temperature. Constant current densities were applied to the electrodes during repeated stripping/plating while the potential was recorded over time.

To investigate the full cell performances, the carbon coated NaCrO$_2$ (NaCrO$_2$/C) was synthesized by solid-state reaction as described previously [13-14]. The NaCrO$_2$/C electrodes were prepared by casting a dimethylformamide (DMF) slurry containing NaCrO$_2$/C, Super P and poly(vinylidene difluoride) (PVDF) in a weight ratio of 8:1:1 onto carbon-coated Al foil. The cathodes were cut into discs with a diameter of 10 mm and dried at 80 °C prior to use. The areal loading of NaCrO$_2$/C is about 6-8 mg. The full batteries were tested also via CR2032 cells using Na@NaPS-3 as anode and NaCrO$_2$/C as cathode in a Land Battery Test System at room temperature. The electrolyte used in full cells was 1 M sodium perchlorate (NaClO$_4$, Aldrich) dissolved in propylene carbonate (PC) with 2 % of fluoroethylene carbonate as additive.

**Characterization:** The cells were disassembled after stripping/plating process and then sealed with the Ar-filled tubes before characterization. SEM images were taken using a Hitachi 3400N Environmental Scanning Electron Microscopy at an acceleration voltage of 5 kV. The Na foil and Na@NaPS-3 (after plating/stripping) are transferred from our ALD glove box directly to an Ar glovebox connected XPS (Kratos AXIS Ultra Spectrometer) system for XPS analysis in the Surface Science Western. Rutherford
Backscattering Spectrometry measurements were conducted using 2.5 MeV He\(^+\) beam (Western Tandetron Facility) at several locations on the surface to confirm the uniformity of the thicknesses and composition. All samples were transferred in Ar-filled glove bag with minimum exposure to air. A Sb-implanted amorphous Si sample with a known \(4.82 \times 10^{15}\) atoms /cm\(^2\) Sb content used for calibration. The ToF-SIMS measurements were conducted using an ION-TOF (GmbH, Germany) ToF-SIMS IV with a bismuth liquid metal ion source. The base pressure of the analysis chamber was \(~10^{-8}\) mbar. The action of the primary ion beam bombardment on the sample surface induces the emission of negative secondary ions. The analysis area was \(334 \times 334\) μm\(^2\). Sputtering with a Cs\(^+\) ion beam (3 keV) was used for depth profiling analysis with the sputtering areas of \(100 \times 100\) μm\(^2\).

9.3 Results and discussion

![Figure 9.1](image)

Figure 9.1 (a) Schematic diagram of the in-situ fabrication process of NaPS on Na foil; (b) RBS spectra and calculated depth profiles of Na@NaPS-3; (c) the thicknesses of different samples
related to the precursor concentrations and reaction times; (d) XPS survey spectra and P 2p and S 2p high-resolution spectra for Na@NaPS-3;

The SSEs NaPS protective layers are formed by a simple in-situ solution-based method. As shown in Figure 9.1(a), sulfur-rich phosphorus sulfide molecules (P_4S_{16}) are used as precursors to react with Na metal directly in a diethylene glycol dimethyl ether (DEGDME) solvent. The reaction between Na metal and P_4S_{16} is shown as:

\[
12 \text{Na}^+ + \text{P}_4\text{S}_{16} = 4 \text{Na}_3\text{PS}_4
\]

Due to the high reactivity between Na metal and P_4S_{16}, the reactions are expected to be controlled with different precursor concentrations and reaction times. The experimental design parameters are shown in Table S9.1. Firstly, the concentrations of the P_4S_{16} precursor in DEGDME are controlled at 0.5 mg mL^{-1}, 1 mg mL^{-1}, and 1.5 mg mL^{-1} and used with a constant reaction time of 15 min. The samples in this experiment are named as Na@NaPS-1, Na@NaPS-2 and Na@NaPS-3, respectively. Secondly, the samples with constant concentrations of 1.5 mg mL^{-1} are used to study the effect of longer reaction times (60 min and 90 min), and these samples are named as Na@NaPS-4 and Na@NaPS-5, respectively.

Rutherford backscattering spectrometry (RBS) measurements were performed on Na@NaPS-1 to Na@NaPS-5 to confirm the film thicknesses on the Na and deduce the elemental depth profiles. Figure 9.1(b) shows the RBS spectrum and simulated depth profiles for Na@NaPS-3. The presence of P and S peaks from the surface can confirm the successful synthesis of the NaPS films on the Na foil. Figure S9.1 show the RBS spectrums and simulated depth profiles for another samples of Na@NaPS-1 (a), Na@NaPS-2 (b), Na@NaPS-4 (c), and Na@NaPS-5 (d). Notably, by increasing the concentration of P_4S_{16} in DEGDME, the thickness of the NaPS coating increases from 120 nm to 220 nm, as shown in Figure 9.1(c). Meanwhile, the content of both P and S increase as well (Table. S9.2). When keeping the concentration of P_4S_{16} constant at 1.5 mg mL^{-1}, the RBS results indicate that the ratio of Na to P and S stays constant and the thicknesses increase to 300 and 380 nm for Na@NaPS-4 and Na@NaPS-5 with increasing reaction times (Figure 9.1 (c) and Table S9.2). Thus, it can be concluded from
the RBS results that the thickness and composition of the NaPS films can be controlled by adjusting the concentration of $P_4S_{16}$ and reaction times.

To further confirm the chemical compositions of the NaPS films, X-ray photoelectron spectroscopy (XPS) was carried out for typical samples of $P_4S_{16}$, Na@NaPS-1, Na@NaPS-3 and Na@NaPS-5. Figure S9.3 (a) and (b) shows the high-resolution XPS spectrum of S 2p and P 2p for the $P_4S_{16}$, respectively. The peaks of S 2p$_{1/2}$ and 2p$_{3/2}$ at 164.8 eV and 163.6 eV corresponds to the P-S-P bonding in $P_4S_{16}$. Meanwhile, the peaks of P 2p$_{1/2}$ and 2p$_{3/2}$ at 135.2 eV and 134.4 eV can be assigned to the P-S in $P_4S_{16}$. Figure 9.1 (d) and Figure S9.2 present the XPS survey spectra for Na@NaPS-1, Na@NaPS-3 and Na@NaPS-5, where the S and P peaks can be obviously observed, consistent with the RBS results. From the high-resolution P 2p spectra for Na@NaPS-3, several peaks in the high-resolution P 2p spectra can be fitted with different distinct doublets. The double peaks of P 2p$_{1/2}$ and 2p$_{3/2}$ at 133.8 eV and 133.0 eV can be assigned to phosphorous in $PS_4^{3-}$ [11]. Meanwhile, the peaks at 133.0 eV and 132.21 eV is related to the bond of P-S in $P_2S_{7}^{4-}$ [15]. In the S 2p spectra, the S 2p$_{1/2}$ and 2p$_{3/2}$ peaks at 162.5 eV and 161.6 eV are responsive with P=S bond in the $PS_4^{3-}$ species. Very interesting, from the high-resolution P 2p spectra for Na@NaPS-1 (Figure S9.3(d)), not only $PS_4^{3-}$ peak can be observed, but also the un-reacted $P_4S_{16}$ peak exists, indicating the incomplete reaction between Na and $P_4S_{16}$ with low concentration of precursor and shorter reaction time. However, the P 2p spectra for Na@NaPS-5 is almost the same with Na@NaPS-3, indicating that the final products of the coating layer is mixed by both Na$_3$PS$_4$ and Na$_4$P$_2$S$_7$. All the XPS results indicate that the Na$_3$PS$_4$ films are successfully synthesized on the surface of Na foils through the in-situ solution-based method.
Figure 9.2 (a) TOF-SIMS chemical ion images of the Na⁺, P⁻, S⁻, S₂⁻, S₃⁻ species for Na@NaPS-3 (Blue circle: sputtering areas); The analysis area was 300 x 300 μm² and the sputtering areas of 100 x 100 μm². (b) cross-section ion images of S⁻ species for Na@NaPS-3; (c) TOF-SIMS depth profiles of Na⁺, P⁻, S⁻, S₂⁻, S₃⁻ species for Na@NaPS-3.

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) was performed to further probe the compositions of the NaPS film and the element depth distributions. Figure 9.2 (a) shows the secondary ion images of Na⁺, P⁻, S⁻, S₂⁻ and S₃⁻ with the magnified images on the edges after sputtering. Because of the sample exposure to air during the transferring process, the surfaces of the samples are oxidized and no species related to Na₃PS₄ films can be observed at the initial stage of analysis. However, after sputtering by Cs⁺ ions, the different negative ions of P⁻, S⁻, S₂⁻ and S₃⁻ are visible from the edge of the sputtering areas, which are attributed to the Na₃PS₄ film on Na foil. Figure 9.2 (b) presents cross-section ion images of S⁻ species for Na@NaPS-3, indicating the formation of a continuous Na₃PS₄ film from the surface down to the bulk Na. Figure S9.4 displays similar ion images of Na⁺, P⁻, S⁻, S₂⁻ and S₃⁻ for Na@NaPS-1 and Na@NaPS-5, demonstrating the same Na₃PS₄ film formed with different experimental conditions. The
TOF-SIMS depth profiles of Na\textsuperscript{−}, P\textsuperscript{−}, S\textsuperscript{−}, S\textsubscript{2}\textsuperscript{−} and S\textsubscript{3}\textsuperscript{−} for Na@NaPS-3 are shown in Figure 9.2(e). As expected, the signals of P\textsuperscript{−}, S\textsuperscript{−}, S\textsubscript{2}\textsuperscript{−} and S\textsubscript{3}\textsuperscript{−} decrease whereas the signal of Na\textsuperscript{−} remains consistent after 800 s Cs\textsuperscript{+} sputtering. The TOF-SIMS analysis demonstrates that Na (or Na\textsuperscript{+}) species exists from the surface of the Na\textsubscript{3}PS\textsubscript{4} coating layer down to the bulk Na metal. Figure S9.5 shows the depth profiles of Na@NaPS-1 and Na@NaPS-5, where it can be observe that bulk Na can be reached after sputtering times of 200 s and 1300 s, respectively. The TOF-SIMS analysis further confirms that with increasing concentration of P\textsubscript{4}S\textsubscript{16} and reaction times, the NaPS films grow thicker.

Through combination of characterization techniques such as RBS, XPS and TOF-SIMS, it can be concluded that Na\textsubscript{3}PS\textsubscript{4} films with controlled thicknesses have been successfully synthesized on Na foil by the in-situ solution-based method. Moveover, from the XRD patterns in Figure S9.6, the as-prepared Na\textsubscript{3}PS\textsubscript{4} are amorphous without any characteristic XRD signatures. The three main peaks in the XRD patterns are attributed to the cubic Na metal\textsuperscript{[7]}\textsuperscript{[7]}. The morphologies of Na@NaPS-1, Na@NaPS-3 and Na@NaPS-5 are presented in Figure S9.7 and Figure S9.8. From the top view SEM images in Figure S9.7 (a,b and c, d), smooth and continuous films are formed on the surface for both Na@NaPS-1 and Na@NaPS-3. However, a rougher surface with larger particles sizes is obtained with longer reaction time and higher precursor concentration for Na@NaPS-5 (Figure S9.7 (e, f)). From the cross-section SEM images (Figure S9.8), the NaPS layer grows thicker from Na@NaPS-1 to Na@NaPS-5. In brief, the trend of the thickness as the function of the concentration of P\textsubscript{4}S\textsubscript{16} solution and the reaction time is well consistent from the RBS, TOF-SIMS, and SEM results.
Figure 9.3 (a) Comparison of the cycling stability and potential profiles of the Na@NaPS-3 and bare Na foil at a current density of 1 mA cm⁻² with the capacity of 1 mAh cm⁻²; (b) The cycling stability and potential profiles of the Na@NaPS-3 and bare Na foil at a current density of 3 mA cm⁻² with the capacity of 1 mAh cm⁻²; (c) The cycling stability and potential profiles of the Na@NaPS-3 and bare Na foil at a current density of 1 mA cm⁻² with a capacity of 3 mAh cm⁻².

Galvanostatic cycling of Na₃PS₄ coated Na and bare Na foils was studied using a symmetrical cell configuration of Na@NaPS/separator/Na@NaPS, using a 1 M NaPF₆ electrolyte dissolved in 1:1 (v:v) EC:PC. Figure 9.3 (a) presents a comparison of the cycling stability of Na@NaPS-3 and bare Na foil at a current density of 1 mA cm⁻² with a capacity of 1 mAh cm⁻². The thicknesses effects of NaPS on the electrochemical performances will be discussed in the following part. For pristine Na foil, the initial stripping/plating over-potential is about 200 mV (versus Na⁺/Na). Subsequently, the over-potential starts to increase after 150 h and reaches 4000 mV after 160 h. It can be
observed that the pristine Na foil suffers from unstable voltage profile fluctuations, resulting in short circuiting of the cell. Promisingly, the Na@NaPS-3 delivers the slightly larger over-potential in the first plating process and then stabilizes in the following cycles with an over-potential of 300 mV (versus Na⁺/Na), which can be sustained for more than 270 h. The potential profiles of Na@NaPS-3 and bare Na foil are also shown in Figure 9.3(a), in which the Na foil displays unstable over-potentials with large polarization and Na@NaPS-3 presents smoother profiles with negligible increase in hysteresis. When increasing the current density to 3 mA cm⁻², the over-potential of pristine Na is seen to rapidly increase after only 70 h (Figure 9.3(b)). Furthermore, the over-potential reaches over 5000 mV (versus Na⁺/Na) after 115 h, which is the voltage cut-off limitation in the testing. Promisingly, the Na@NaPS-3 maintains improved stability at higher current density with a lower over-potential of 500 mV after 140 h. In the previously reported literatures, the cycling capacity of metal anodes (for both Li and Na metal anode) in symmetrical cell testing is usually around 1 mAh cm⁻² or even lower, which cannot meet the requirements for practical applications. Herein, we also demonstrate the Na@NaPS-3 with a large capacity of 3 mAh cm⁻² compared with bare Na foil under the same testing conditions. Figure 9.3(c) presents the cycling stability and voltage profiles of both Na@NaPS-3 and bare Na foil using the high capacity limit of 3 mAh cm⁻² under the current density of 1 mA cm⁻². The bare Na foil exhibits unstable plating/stripping behavior after 100 h of cycling with increasing over-potentials which rise to 3000 mV after 180 h (Figure 9.3(c)). However, the Na@NaPS-3 displays a stable cycling performance with an over-potential of only 300 mV after 250 h, which is almost 10 times lower than what was observed for bare Na foil. Based on these observations, the NaPS coating is an excellent protective layer for Na metal anode in applications that require a large capacity.

To understand the relationships between thickness, composition and electrochemical performance, the other samples of Na@NaPS-1, Na@NaPS-2, and Na@NaPS-4, Na@NaPS-5 were studied under a current density of 1 mA cm⁻² with cycling capacities of 1 mAh cm⁻² and 3 mAh cm⁻². Figure S9.9 shows the electrochemical performances of samples obtained with lower P₄S₁₆ concentrations for Na@NaPS-1 and Na@NaPS-2. From the results, it can be seen that both Na@NaPS-1 and Na@NaPS-2 exhibit better
performances than that of the bare Na foil, in which the stability of Na@NaPS-2 appears to be enhanced compared to Na@NaPS-1. However, they are still not comparable to Na@NaPS-3. From the discussion above, the NaPS coating becomes thicker with an increase in P_4S_{16} concentration. Furthermore, we find that the thicknesses of the NaPS protective layers have a significant influence on the electrochemical performances. The higher P_4S_{16} concentrations leading to thicker coatings (Na@NaPS-3) shows the best benefits in term of the plating/stripping performances. Furthermore, the cycling stabilities of the samples of Na@NaPS-4, Na@NaPS-5 with longer reactions are presented in Figure S9.10. The performances of Na@NaPS-4 and Na@NaPS-5, appear to be inferior to the bare Na foil. This result indicates that the coating thickness (from RBS and SIMS results) and surface roughness (from SEM results) are critical parameters and excessive coating can lead to poor electrochemical performances. Thus, the Na@NaPS-3 with the Na_3PS_4 layer of ~220 nm displays the best electrochemical performances with respect to cycling current density and capacity.

The performance of the bare Na foil and Na@NaPS-3 as anodes for NMBs was further investigated in a full cell using a NaCrO_2/C cathode. The loading of NaCrO_2/C is ~ 8 mg cm^{-2} corresponding to an areal capacity of ~1.1 mAh cm^{-2}. Figure S9.11 presents the cycling performances of full cells using bare Na foil and Na@NaPS-3 as the anode at a rate of 1 C (~ 1.1 mA cm^{-2}). In the batteries using bare Na foil, the specific capacity drops to 35 mAh g^{-1} after 75 cycles due to the poor cyclability of the planar Na foil. Promisingly, the Na@NaPS-3 anode can enable full cells that can maintain a stable capacity of 106 mAh g^{-1} over 75 cycles. The cycling stability and capacity retention demonstrates that the NaPS protective layer can effectively improve the electrochemical performances compared to the Na foil in a full cell format.
Figure 9.4 Top-view SEM images of the bare Na foil (a) and Na@NaPS-3 (b) after 10 cycles of stripping/plating; (c) XPS spectra and P 2p, S 2p and F 1s spectrum of Na@NaPS-3 after cycling. (d) TOF-SIMS chemical ion images of the Na\textsuperscript{+}, P\textsuperscript{5+}, S\textsuperscript{6-}, and S\textsuperscript{2-} species for Na@NaPS-3 after cycling (Blue circles correspond to the sputtering areas); The analysis area was 300 × 300 μm\(^2\) with a sputtering area of 100 × 100 μm\(^2\); (e) TOF-SIMS depth profiles of F\textsuperscript{−}, Na\textsuperscript{+}, P\textsuperscript{5+}, S\textsuperscript{6-}, S\textsuperscript{2-} and PF\textsubscript{6}\textsuperscript{−} species for Na@NaPS-3 after cycling. All the cells are tested at a current density of 1 mA cm\(^{-2}\) with a capacity of 1 mAh cm\(^{-2}\).

In order to understand the enhanced performance of NaPS-coated Na anode compared to the pristine Na foil, the morphologies of Na@NaPS-3 and Na foil after cycling were analyzed by SEM. Figure 9.4 (a, b) compares the SEM images of Na@NaPS-3 and Na foil after 10 cycles of electrochemical plating/stripping at a current density of 1 mA cm\(^{-2}\) with the capacity limit of 1 mAh cm\(^{-2}\). From the SEM images shown in Figure 9.4 (a), Na dendrites with moss-like structures of approximately 10-20 μm can be clearly observed for bare Na foil after cycling. Meanwhile, the surface of the Na foil becomes very rough and porous with the formations of dead Na. These types of moss/dendritic Na will further lead to the formation of dead sodium during the plating/stripping process, which will decrease CE and consume active Na as well as electrolyte. More SEM images of Na foil after cycling are shown in Figure S9.12. Large moss-like and porous dead Na
particles are observed from different areas on the Na foil. Promisingly, with the NaPS coating layers, the surface morphology of Na after electrochemical plating/stripping is relatively smooth and does not possess any high surface area porous structures, as shown in Figure 9.3(b). The flake-like coating layers can be clearly seen from the surface of Na@NaPS-3, indicating that the NaPS protective layers remain after cycling. Figure S9.12(e-g) displays similar SEM images of Na@NaPS-3 after cycling from another area of the electrode demonstrating the relatively uniform and smooth surface enabled by the NaPS protection layers.

XPS testing was performed to determine the surface chemical nature of Na foil and Na@NaPS-3 electrodes after electrochemical plating and stripping. The full XPS spectra and high resolution XPS spectrum of P 2p, S 2p and F 1s of Na@NaPS-3 after cycling is shown in Figure 9.4(c). From the full XPS spectra, both S 2p and P 2p peaks arising from the NaPS film can be observed after cycling. In the F 1s spectrum, the peak at 686 eV is due to residual Na$_x$PF$_y$ and Na$_x$PO$_y$F$_z$ generated from electrolyte on the surface, which is consistent with the peaks at 137 eV for the P 2p spectrum. It is apparent that both the S 2p and P 2p peaks are similar to that of the spectrum from the original Na@NaPS-3 samples in Figure 9.1, which are attributed to the characteristic signal of PS$_4^{3-}$ in the Na$_3$PS$_4$ films. The XPS results show that the NaPS protective layers are very robust and can retain its structure after electrochemical cycling.

Furthermore, TOF-SIMS was employed to study the surface and elemental depth distributions of Na@NaPS-3 after cycling. Figure 9.4(d) show the ion images of Na$^-$, P$^-$, S$^-$ and S$_2^-$ of Na@NaPS-3 after electrochemical cycling (images before and after depth profile sputtering). From the ion images before depth profile sputtering, signals arising from P$^-$ and S$^-$ species are seen to be distributed uniformly on the surface. After sputtering by Cs$^+$ ions, the different negative ions of P$^-$, S$^-$, S$_2^-$ present stronger signals from the edge of the sputtering areas, indicating the NaPS film is electrochemically stable and remains intact. Figure 9.4(e) shows the depth profiles of F$^-$, Na$^-$, P$^-$, S$^-$, S$_2^-$ and PF$_6^-$ for Na@NaPS-3 after cycling. Combined with the ion images in Figure S9.14 of F$^-$ and PF$_6^-$, the top surface of the Na@NaPS-3 after cycling is covered with the salt of NaPF$_6$, which is also consistence with XPS results. After sputtering, the NaPF$_6$ is almost
completely removed and the signal of other species of $P^-$, $S^-$ and $S_2^-$ significantly increase. After 350 s, the concentration of $P^-$, $S^-$, and $S_2^-$ ions from the NaPS film decrease, indicating that the thickness of the NaPS film has a very small change after cycling when compared with the profiles in Figure 9.2 (c).

9.4 Conclusion

In conclusion, we firstly demonstrate a facile and in-situ solution-based method to fabricate a solid-state electrolyte $Na_3PS_4$ protective layer on the Na metal anode for long life Na metal batteries. The thickness and chemical composition of the NaPS layers can be controlled by adjusting the precursor concentrations and reaction times, and has been optimized in our study. By protecting the Na foil with $Na_3PS_4$, the mossy and dendrite-like Na growth is effectively suppressed. From the symmetric cell testing, Na@NaPS-3 displays the most stable electrochemical performances with lower polarization compared with Na foil. Meanwhile, the optimized Na@NaPS-3 can achieve much better performances with the large capacities and current densities required for practical applications. It is believed that our design of $Na_3PS_4$-coated Na anode can open up new opportunities for the realization of next-generation high energy density Na metal batteries.

9.5 Acknowledgements

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9.6 Reference


9.7 Supporting Information

Figure S 9.1 RBS spectra and calculated depth profiles of Na@NaPS-1 (a), Na@NaPS-2 (b), Na@NaPS-4 (c) and Na@NaPS-5 (d).

Figure S 9.2 XPS spectra of Na@NaPS-1, Na@NaPS-3 and Na@NaPS-5.
Figure S 9.3 XPS S 2p spectrum of P₄S₁₆ (a), Na@NaPS-1 (c) and Na@NaPS-5 (e); XPS P 2p spectrum of P₄S₁₆ (b), Na@NaPS-1 (d) and Na@NaPS-5 (f).

Figure S 9.4 TOF-SIMS chemical ion images of the Na⁺, P⁺, S¹⁻, S₂⁻, S₃⁻ species for Na@NaPS-1 (a) and Na@NaPS-5 (b). The analysis area was 334 × 334 μm² and the sputtering areas of 100 × 100 μm².
**Figure S 9.5** TOF-SIMS depth profiles of Na\(^-\), P\(^-\), S\(^-\), S\(_2\)\(^-\), S\(_3\)\(^-\) species for Na@NaPS-1 (a) and Na@NaPS-5 (b).
Figure S 9.6 XRD patterns of bare Na, Na@NaPS-3 and Na@NaPS-5.

Figure S 9.7 Top-view SEM images of Na@NaPS-1 (a, b), Na@NaPS-3 (c, d) and Na@NaPS-5 (e, f).
Figure S 9.8 Cross-section view SEM images of Na@NaPS-1 (a), Na@NaPS-3 (b) and Na@NaPS-5 (c).

Figure S 9.9 Comparison of the cycling stability of Na@NaPS-1 (a) and Na@NaPS-2 (b) at the current density of 1 mA cm$^{-2}$ with the capacity 1 mAh cm$^{-2}$; Comparison of the cycling stability of Na@NaPS-1 (c) and Na@NaPS-2 (d) at the current density of 1 mA cm$^{-2}$ with the capacity 3 mAh cm$^{-2}$. 
Figure S 9.10 Comparison of the cycling stability of Na@NaPS-4 (a) and Na@NaPS-5 (b) at the current density of 1 mA cm$^{-2}$ with the capacity 1 mAh cm$^{-2}$; Comparison of the cycling stability of Na@NaPS-4 (c) and Na@NaPS-5 (d) at the current density of 1 mA cm$^{-2}$ with the capacity 3 mAh cm$^{-2}$.

Figure S 9.11 Cycling performance of full cells (NaCrO$_2$/C as cathode) using bare Na foil and Na@NaPS-3 at 1 C. The loading of NaCrO$_2$/C is about ~8 mg cm$^{-2}$, corresponding to the areal capacity of ~1.1 mAh cm$^{-2}$. 
**Figure S 9.12** Top-view SEM images of the bare Na foil (a-c) and Na@NaPS-3 (e-g) after 10 cycles of stripping/plating at a current density of 1 mA cm$^{-2}$ with the capacity of 1 mAh cm$^{-2}$.

**Figure S 9.13** XPS spectra and P 2p (a), S 2p (b) and F 1s (c) spectrum of bare Na foil after cycling.
**Figure S 9.14** TOF-SIMS chemical ion images of the $F^-$ and $PF_6^-$ species for Na@NaPS-3 after cycling. The analysis area was $300 \times 300 \, \mu m^2$ and the sputtering areas of $100 \times 100 \, \mu m^2$. 
Table S 9.1 Experimental design to control the factors of precursor concentration and reaction time

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Table S 9.2 Compositions of P and S in different samples based on XPS results

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<th>S At% (XPS)</th>
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<tr>
<td>Na@NaPS-3</td>
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<td>1.4 %</td>
</tr>
<tr>
<td>Na@NaPS-5</td>
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<td>2.4 %</td>
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Chapter 10

10 High Capacity, Dendrite-free Growth and Minimum Volume Change Na Metal Anode*

In the last three chapters, we developed different method, including ALD, MLD and solution-based method to fabricate protective layer on Na metal anode. However, another big issue of volume change of Na metal anode cannot be addressed by surface modification method. In this chapter, we demonstrate the rational design of a carbon paper (CP) with N doped carbon nanotubes (NCNTs) as a 3D host to obtain Na@CP-NCNTs composites electrodes for NMBs. In our design, 3D carbon paper plays a role as a skeleton for Na metal anode while vertical N doped carbon nanotubes can effectively decrease the contact angle between CP and liquid metal Na, which we term as being “Na-philic”. In addition, the cross-conductive network characteristic of CP and NCNTs can decrease the effective local current density, resulting in uniform Na nucleation. Therefore, the as-prepared Na@CP-NCNTs exhibits stable electrochemical plating/stripping performance in symmetrical cells even when using a high capacity of 3 mAh cm$^{-2}$ at high current density. Furthermore, the 3D skeleton structure was observed to be intact following electrochemical cycling with minimum volume change and dendrite-free in nature.

*A version of this chapter has been published in *Small*, 2018, 14, 1703717
10.1 Introduction

Li ion batteries (LIBs) are a widely popularized energy storage device for use in portable devices and electrical vehicles [1-4]. However, low cost and large scale application remains a significant challenge for LIBs due to the limited and uneven distribution of lithium sources [5, 6]. As a promising alternative, Na-ion batteries (NIBs) and Na metal batteries (NMBs) have received a great deal of attention due to sodium’s wide availability and low cost. Furthermore, Na metal anode is considered as an attractive candidate compared with other anodes for NMBs due to its high theoretical specific capacity of 1166 mAh g\(^{-1}\) and lowest electrochemical potential. Meanwhile, both Na–S batteries and Na–O\(_2\) batteries using Na metal as anodes demonstrate a high theoretical specific energy density of 1274 Wh kg\(^{-1}\) and 1605 Wh kg\(^{-1}\), respectively [7-13].

Currently, research efforts in the development of NMBs are primarily focused on the design and fabrication of cathode materials, with little emphasis directed toward the development of Na anode electrode materials. However, similar to issues faced with the use of Li metal anode, crucial problems for metallic Na anode remain. Many of these issues are by side reactions occurring between Na metal and the organic liquid-based electrolyte [14-18]. Moss-like and dendritic Na is often observed to be deposited during repetitive Na plating/stripping process with an unstable solid electrolyte interphase (SEI) layer forming on the surface of Na metal anodes. Continuous moss-like and dendritic Na growth will lead to two serious problems: 1) internal short circuit of the battery, presenting serious safety concerns; 2) accumulation of “dead Na” as well as consumption of electrolyte, leading to poor coulombic efficiency (CE) [6, 19, 20]. Furthermore, the host-less nature of using pure Na metal as an anode results in large infinite volume changes to occur during electrochemical plating/stripping process and presents a difficult materials challenge problem.

To date, there are only few reports exploring the electrochemical plating/stripping properties of Na metal at room temperature. Cui’s group firstly reported the in-situ formation of a stable SEI layer by altering components of the electrolyte. Their study demonstrate that mono-, di-, and tetraglyme sodium hexafluorophosphate can enable the reversible and non-dendritic plating/stripping of sodium metal anode [21]. Another
strategy is the use of a coating layer to stabilize SEI formation and suppress unwanted side reactions. Atomic layer deposition (ALD) is a technique that provides excellent coverage with conformal deposition in highly controllable manner and can be conducted at relative low deposition temperatures. These features make ALD an ideal technique for Na anode protection [22, 23]. Recently, both Hu’s and our group have successfully demonstrated the application of ALD Al₂O₃ coating layers for the enhancement of electrochemical stability of Na metal anode and suppressed dendrite growth with prolong cycling life time in carbonate and ether based electrolyte systems, respectively [20, 24]. Furthermore, our group firstly report the use of inorganic-organic coating (alucone) via molecular layer deposition (MLD) as a protective layer for metallic Na anode. By protecting Na anode with an alucone layer, dendrite and mossy Na formation was effectively suppressed, resulting in prolonged lifetime of Na metal anode.

These strategies are suitable in solving the issue of unstable SEI formation, thereby reducing Na dendrite growth, however, they do not address the large volume changes due to “the host-less” nature of using metallic Na as an anode. To overcome the volume change of Na, it is expected to design different 3D host to hold Na metal with buffering spaces. Get inspiration from the Li protection field, a novel strategy of “thermal infusion” has been reported to achieve 3D scaffold supported Li electrode with minimum volume change and long life time [25]. It has been studied that the wettability between melting metal with the scaffold structure is a key factor in allowing for metal diffusion into the host material. To modify the surface of substrate into “metal-philic”, coating layers or N doped sites are effective to improve the wettability, resulting in uniform nucleation and deposition of metal on the surface [26-28]. Subsequently, Chen’s group and Hu’s group reported two types of Na anodes with 3D structures (Na-reduced graphene oxide and Na-carbonized wood), in which confining Na metal anode in a 3D host can significantly enhance stability [19, 29]. Despite this, the research and development for the use of Na metal anode remains in its infancy and achieving highly stable Na metal anode with high capacity, minimum volume change and a dendrite free structure remains elusive. Meanwhile, similar phenomenon with lithiophilic, we name “Na-philic” here has not been explored in the previous study.
Herein, we demonstrate the rational design of a carbon paper (CP) with N doped carbon nanotubes (NCNTs) as a 3D host to obtain Na@CP-NCNTs composites electrodes for NMBs. In our design, 3D carbon paper plays a role as a skeleton for Na metal anode while vertical N doped carbon nanotubes can effectively decrease the contact angle between CP and liquid metal Na, which we term as being “Na-philic”. In addition, the cross-conductive network characteristic of CP and NCNTs can decrease the effective local current density, resulting in uniform Na nucleation. Therefore, the as-prepared Na@CP-NCNTs exhibits stable electrochemical plating/stripping performance in symmetrical cells even when using a high capacity of 3 mAh cm\(^{-2}\), which is highest in the reported literatures using carbonate based electrolyte. Furthermore, the 3D skeleton structure was observed to be intact following electrochemical cycling with minimum volume change and dendrite-free in nature.

10.2 Experimental Section

**Fabrication of CP-NCNTs Composite skeleton:** ALD coatings were conducted on CP in a Gemstar-8 ALD system (Arradiance, USA). Al\(_2\)O\(_3\) was deposited on the CP at 120 °C by using trimethylaluminium (TMA) and water (H\(_2\)O) as precursors for 200 cycles. Then, the Al\(_2\)O\(_3\) coated CP was loaded into a vertical tube furnace that was ramped from room temperature to 856 °C using an Ar flow of 200 mL min\(^{-1}\). Catalyst ferrocene solution (solvent: acetonitrile, concentration: 0.02 g mL\(^{-1}\)) was then introduced into the quartz tube at a flow rate of 0.1 mL min\(^{-1}\) as for 5 min under Ar atmosphere. Following this, imidazole solution is injected into the quartz tube (solvent: acetonitrile, concentration: 0.2 g mL\(^{-1}\), flow rate: 0.1 mL min\(^{-1}\)) to grow NCNT bundles for 30 min followed by cooling to room temperature. Typically, a 30 minute growth yielded NCNT bundles with a length of around 20 μm.

**Fabrication of Na@CP-NCNTs Composite electrodes:** As-prepared CP-NCNTs was cut into 3/8 inch disks and transferred into an Ar-filled glove box with less than 0.1 ppm water and 0.1 ppm O\(_2\). Thermal infusion of Na melting was carried out inside the glove box. Bulk Na (from Aldrich) was cut into smaller pieces and placed in a stainless-steel boat and heated on a hot plate until Na began to melt. The prepared CP-NCNTs disk was then placed into the molten Na to obtain the Na@ CP-NCNTs composite electrodes. The
weight of the CP and CP-NCNTs are 0.01 g and 0.019 g, respectively. After Na thermal diffusion, the weights of Na in the composite electrodes of Na@CP-NCNTs are around 0.039-0.042 g. In this case, the theoretical specific volumetric and gravimetric capacity of the anode is 65 mAh cm⁻² and 928 mAh g⁻¹, respectively.

**Electrochemical measurements**: Electrochemical analysis was performed using CR2032 coin-type cells assembled in an ultra-pure Ar filled glove box. The cells followed a symmetrical configuration of Na/Electrolyte-Separator/Na with the use of a polypropylene separator (Celgard 3501). The electrolyte used in this study was 1 M sodium hexafluorophosphate (NaPF₆ 98%, Aldrich) dissolved in ethylene carbonate (EC) and propylene carbonate (PC) with volume ratio of 1:1. Na stripping/plating studies were carried out in an Arbin BT-2000 Battery Test System at room temperature. Constant current densities were applied to the electrodes during repeated stripping/plating while transient potential was recorded over time.

**Characterization**: SEM images were taken using a Hitachi 3400N Environmental Scanning Electron Microscopy at an acceleration voltage of 5 kV. Due to the soft properties of Na metal, Swagelok type cells comprised of Na/Electrolyte-Separator/Na system were used to carry out the morphology testing after stripping/plating. Swagelok cells were disassembled after 10 cycles of stripping/plating in an Ar filled glove box and gently rinsed using dimethyl carbonate to remove residual Na salts and electrolyte. SEM cross-section images of Na metal was obtained by slicing the electrode in half with the use of a sharp scissor. XPS testing was carried out using an Ar glovebox connected to an XPS (Kratos AXIS Ultra Spectrometer) system. XRD testing was obtained using a Bruker D8 Advance XRD system equipped with a Cu-Kα X-ray source. Raman spectroscopy was performed using an air-sensitive holder on a HORIBA Scientific LabRAM HR system.

**Theoretical Section**: Density functional theory (DFT) calculations were carried out using the projector-augmented plane-wave (PAW) method as implemented in the Vienna Ab Initio Simulation Package (VASP) [32]. We used Perdew-Burke-Ernzerhof [33] exchange-correlation functional, a 5×5 unit cell of nanoribbon, a 2×1×1 k-point mesh,
and an energy cutoff of 450 eV. We have considered vacuum spaces of $\sim 15 \text{ Å}$ and $\sim 14 \text{ Å}$ for the separation of nanoribbon edges and planes to exclude image-image interaction. The convergence criteria for total energy was set at $10^{-4}$ eV.

### 10.3 Results and discussion

**Figure 10.1** Schematic diagram of (a) the fabrication procedure of Na@CP-NCNTs; (b) the Na stripping/plating behavior occurred on the surface of Na foil and Na@CP-NCNTs.

To encapsulate Na metal into a 3D conductive scaffold, the “Na-philic” NCNTs were introduced to increase the Na wettability of CP. **Figure 10.1** shows the schematic diagram of the fabrication procedure of Na@CP-NCNTs composites. To assist with the
growth of vertical carbon nanotubes, Al₂O₃ was initially deposited on the surface of CP using ALD. NCNTs were obtained through a one-step spray pyrolysis chemical vapor deposition (SPCVD) method, which has been reported in our previous study [12]. Finally, encapsulation of Na metal into the 3D CP-NCNTs structure was accomplished using a thermal infusion process of melting Na in an Ar-filled glovebox. Interestingly, without NCNTs, pristine CP was found to be “Na-phobic” and displayed a large contact angle between the substrate and melted Na (Figure S10.1(a)). Promisingly, after functionalizing the CP with NCNTs, the contact angle between Na and CP-NCNTs was effectively reduced (Seen in Figure S10.1(b)) and Na was found to instantaneously diffuse into the 3D CP-NCNTs, as shown in Figure S10.1 (c-e). These results demonstrate that NCNTs possess the ability to change Na wettability properties of CP from “Na-phobic” into “Na-philic.”

The morphology of obtained CP-NCNTs composites was investigated via SEM, as shown in Figure S10.2. Following the SPCVD process, individual cross-stitched carbon fibers are covered uniformly with vertical NCNTs up to 20 μm in length. Figure S10.3 shows the Raman spectra of pristine carbon paper and fabricated CP-NCNTs. The peak at about 1591 cm⁻¹ (G band) is related to the vibration of sp² bonded carbon atom in 2D hexagonal lattice and the 1329 cm⁻¹ (D band) is related to the defects and disorder in the hexagonal graphitic layers. The I_D/I_G of CP-NCNTs is 0.71 while the value of CP is 0.95, suggesting a greater degree of graphitization of carbon deposit during SPCVD and growth of carbon nanotubes [30]. In addition, XPS analysis of the CP-NCNTs shown in Figure S10.4 indicates the N content of the samples to be 4.7 % (Table S10.1). The typical high-resolution XPS spectra of N 1s for CP-NCNTs is shown in Figure S10.4b, The peaks at 398.2, 399.2, and 400.7 eV are attributed to pyridinic-N, pyrrolic-N, and graphitic-N, and the peak at 404 eV is assigned to terminal N−O bonding. Following the thermal infusion process, Na fills the voids of porous structure CP-NCNTs, as seen from SEM images presented in Figure S10.5. Furthermore, cubic Na metal peaks are observed in the X-ray diffraction (XRD) pattern for Na@CP-NCNTs composite (Figure S10.6), providing further confirmation for the presence of Na. XPS analysis of Na@CP-NCNTs is presented in Figure S10.7, in which the Na 1s and C 1s signals are present, further confirming the successful encapsulation of melted Na into the CP-NCNTs host.
Figure 10.2 Comparison of the cycling stability of the Na@CP-NCNTs and the bare Na foil at a current density of 3 mA cm\(^{-2}\) (a), 5 mA cm\(^{-2}\) (b) and the rate performances (e); (b-c, e-f) Voltage profiles of the Na@CP-NCNTs and the bare Na foil.

To evaluate the electrochemical performance of Na@CP-NCNTs, symmetrical coin cells (2032-type) with two identical Na@CP-NCNTs were assembled using a NaPF\(_6\) contained carbonate-based electrolyte (1M NaPF\(_6\) in EC/PC). In our previous study we demonstrated that NaPF\(_6\) based carbonate-based electrolyte faces a greater number of issues compared to its ether-based analogue. Figure 10.2 (a) displays the cycling stability of Na@CP-NCNTs composites and bare Na foil at a current density of 3 mA cm\(^{-2}\). It is considered that the definition of voltage hysteresis is admitted as the mass-transfer resistant throughout the whole process. For the bare Na foil, an initial over-potential of 400 mV (versus Na\(^+\)/Na) is observed alongside a gradually increasing over-potential up to 1000 mV. For comparison, as-prepared Na@CP-NCNTs composites exhibit very stable performance, with an over potential of only 60 mV in the first cycle and slightly increasing to 150 mV after 130 h of stripping and plating. Furthermore, the Na@CP-NCNTs composites display very stable performance and can maintain an over-potential of 200 mV after 180 h of cycling. Further increasing the
current density to 5 mA cm\(^{-2}\), the over-potential of bare Na foil begins increasing after 90 h with fluctuating voltage profiles and rising to over 1000 mV after 140 h (Figure 10.2 (b-d)). The appearance of fluctuating voltage profile can be attributed to detrimental Na dendrite (mossy) growth and rapid formation of dead Na, resulting in soft short circuiting. Promisingly, Na@CP-NCNTs composites can achieve stable plating/stripping performances at this elevated current density with the low over-potential of 120 mV after 140h of cycling. Meanwhile, the long cycling performance is presented in Figure S10.8 at the current density of 1 mA cm\(^{-2}\) with the capacity of 1 mAh cm\(^{-2}\). The results presented here demonstrate that the as-prepared electrodes show very stable performance up to 350 h of continuous stripping/plating with minimum changes to the voltage hysteresis. To further explore the electrochemical performance Na@CP-NCNTs rate analysis of symmetrical cells was conducted and is presented in Figure 10.2(e-g). The novel composite demonstrates both lower and more stable voltage polarization curves at a current density of 1, 3, 5 and 10 mA cm\(^{-2}\) compared to bare Na. The obvious difference can be attributed to high specific kinetic obstacles faced when using elevated current density. However, the Na@CP-NCNTs composites are capable of operating stably at high current density due to their high electron/ion conductivity providing ample avenues for electron/ion transport.
Herein, we demonstrate the Na@CP-NCNTs composites with a large capacity of 3 mAh cm$^{-2}$ as compared with bare Na foil under the same testing conditions. In the presented literatures, the capacity of reported electrodes in symmetrical cell testings is always around 1 mAh cm$^{-2}$ or even lower for both Li and Na anode, which cannot meet the requirements for practical applications and display the major advantages of large capacities (Seen in Table.S). Figure 10.3 presents cycling stability and voltage profiles of both Na@CP-NCNTs and bare Na foil using a high current density of 5 mA cm$^{-2}$ and high capacity limit of 3 mAh cm$^{-2}$. The bare Na foil exhibits unstable plating/stripping behavior after 40 h of cycling with increasing over-potential increase to 2000 mV after 90 h (Figure 10.3). However, the Na@CP-NCNTs composites maintains a stable cycling performance with an over-potential of only 200 mV after 90 h, almost 10 times lower.
than what was observed for bare Na foil. Based on these observations, Na@CP-NCNTs composite is an excellent candidate for use in applications that require a large capacity.

Figure 10.4 (a) Top-view SEM images of Na@CP-NCNTs after different stripping amount of Na in the first cycle (0.5 mAh cm$^{-2}$, 1 mAh cm$^{-2}$, 3 mAh cm$^{-2}$); (b) Top-view SEM images of Na@CP-NCNTs after different cycles with the capacity of 1 mAh cm$^{-2}$ (1, 5, 10 cycles)
Figure 10.5 (a) Cross section-view SEM images of Na@CP-NCNTs after different stripping amount of Na in the first cycle (0.5 mAh cm$^{-2}$, 1 mAh cm$^{-2}$, 3 mAh cm$^{-2}$); (b): Cross section-view SEM images of Na@CP-NCNTs after different cycles with the capacity of 1 mAh cm$^{-2}$ (1, 5, 10 cycles).

In order to understand the effects of Na stripping and plating, morphology of our novel composite and bare Na foil was imaged following stripping of Na (0.5 mAh cm$^{-2}$, 1 mAh cm$^{-2}$, 3 mAh cm$^{-2}$) in the first cycle. Figure S10.9 and Figure S10.10 displays cross-section and top view SEM images of bare Na foil tested under the various conditions. Top-down SEM images demonstrate the appearance of large grooves following Na stripping. Furthermore, these grooves increase in size when the capacity is increased from 0.5 mAh cm$^{-2}$ to 3 mAh cm$^{-2}$. However, the surfaces of Na@CP-NCNTs following stripping 0.5 mAh cm$^{-2}$ and 1 mAh cm$^{-2}$ is much smoother compared to bare Na, indicating uniform distribution of ions/electrons. This advantageous effect may arise from the presence of vertical NCNTs (Figure 10.4(a)). Interestingly, further increasing the stripping capacity to 3 mAh cm$^{-2}$, partial CP-NCNTs morphology can be clearly observed, indicating favourable structure retention following the high temperature thermal infusion process and electrochemical plating/stripping. Furthermore, cross-section SEM images of the Na@CP-NCNTs following stripping (Figure 10.5(a)), exhibit minimum volume change, demonstrating its favourable properties.
Further SEM measurements were conducted on bare Na foil and Na@CP-NCNTs composite after varying amounts of electrochemical cycling (1, 5, 10 cycles) using a fixed capacity of 1 mAh cm\(^{-2}\). **Figure S10.11** shows the micrographs of bare Na foil electrode (a) and Na@CP-NCNTs composites electrode (b) after 10 cycles of electrochemical plating/stripping. Our results show that the bare Na foil electrodes are covered with dark slurry which can be considered as the dropped dead Na in the electrolyte. In contrast, the Na@CP-NCNTs composites electrodes reveal the presence of pristine Na metal, indicating decreased production of dead Na. Cross-section SEM images of bare Na foil after 1, 5, and 10 cycles are shown in **Figure S10.12**. Following the first cycle, the surface of Na foil turns rough but the thickness of the foil has almost no change. However, after 5 electrochemical plating/stripping cycles, a thick layer of dead Na, ~30 μm in thickness, can be seen in **Figure S10.12** (b). This layer is a result of detrimental side reactions occurring between Na and the organic electrolyte, leading to continuous formations of mossy-like or dendritic Na. With prolonged cycling of 10 cycles, the layer of dead Na drastically increases in thickness (**Figure S10.12** (c)), indicating large volume changes occurring for Na foil during cycling. The corresponding top view SEM images of Na foil after 1, 5, and 10 cycles are outlined in **Figure S10.12**. With sustained electrochemical cycling, the appearance of mossy-like or dendritic Na growth becomes more obvious as the surface begins to increase in roughness, suggesting continuously side reactions and unstable SEI layer formation. Conversely, top view SEM images (**Figure 10.4(b)**) of Na@CP-NCNTs electrodes after cycling, display a relatively smooth surface and lack any mossy or dendritic Na, indicating uniform Na deposition during electrochemical plating/stripping. Cross section SEM images for Na@CP-NCNTs electrodes, shown in **Figure 10.5(b)**, exhibit a highly stable structure with negligible change in thickness. Briefly, our design of CP-NCNTs hosted Na metal anodes demonstrates a dendrite free electrode with minimal volume change with different stripping capacities and stripping/plating cycle numbers.
Figure 10.6 Atomic structures and binding energies (BE) of Na at different N-doped graphene locations.

To study the effect of N dopant on binding energy (BE) of Na on CNTs we use an H-terminated nanoribbon (NR) with a width of 11.38 Å as model system. NRs are choosen so that we can also model N dopant at the edges of CNT by replacing an H-C pair with an N atom. Since we are only interested in chemisorption of Na, dispersion correction for the Van Der Waals interaction is not considered. Calculated BEs of Na (with respect to a bulk Na) on C atoms and N dopants at different positions, with respect to the edges as well as pyridinic and pyrrolic N sites, are listed in Figure. 6. Our calculations show that BEs on N dopants (Figure 10.6 (b)-(e)) or C atoms (Figure 10.6 (f)-(g)), which are not at the edges, are positive. However, a calculated BE of −0.64 eV for Na adsorption to N dopants at the edges of NR is strong (Figure 10.6 (a)). Pyridinic (Figure 10.6 (h)) and pyrrolic (Figure 10.6 (i)) sites with three N atoms provide an even stronger BE of −1.82
eV and –1.92 eV, respectively. This represents a value which is almost three times higher than the BE of Na to one edge N dopant. This result shows a significant improvement of bond strength between Na and carbon-based materials such as CNTs by N doping.

The SEM and simulation results represent a strong consistency to the electrochemical performance obtained here in. Using this data, we present a schematic illustration in Figure 10.1(b) to represent our interpretation for the unique phenomenon observed when using this novel Na@CP-NCNTs composite electrode compared to bare Na foil. For the bare Na foil, shown in Figure 10.1(b), the serious mossy-like and dendritic Na is produced during electrochemical plating/stripping process due to the serious side reaction with components within the electrolyte. Furthermore, rapid and prolonged formation of dead Na results in the formation of a high surface area SEI layer that consumes active Na as well as drains the cell of electrolyte. This causes the resistance of the cell to increase and diminishes cell performance. In contrast, the 3D skeleton of the CP-NCNTs electrode allows for uniform deposition of Na and lacks any surface features related to mossy or dendritic Na. During electrochemical cycling, Na is easily and uniformly removed from the skeleton structure and deposited back on the CP-NCNTs during plating. With uniform deposition occurring using a robust structure, the as-prepared Na@CP-NCNTs electrodes indicate minimum dendrite growth and volume change, resulting in excellent electrochemical performance with long life time and allows for the use of large capacity.

10.4 Conclusion

In conclusion, we demonstrate a unique structure of CP with NCNTs as a 3D skeleton for stable use of Na metal anode using high current density and cycling capacity. In our rational design, 1) the growth of vertical NCNTs can effectively change the Na wettability of CP from “Na-phobic” into “Na-philic”; 2) the highly conductive networks from CP and NCNTs provides homogeneous local current allowing for uniform Na stripping and plating; 3) the Na@CP-NCNTs composites show stable electrochemical plating/stripping performances under different current density, even up to 5 mA cm\(^{-2}\). Furthermore, we also are the first to demonstrate the stable use of a high capacity of 3 mAh cm\(^{-2}\) using our unique Na@CP-NCNTs electrode. 4) The 3D skeleton structure remains intact after cycling with minimum volume change. It is believed that our design
of 3D host with “Na-philic” properties opens up new opportunities to the realization of next-generation high energy density Na metal batteries.

10.5 Acknowledgements

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10.6 References


[21] Seh, Z. W.; Sun, J.; Sun, Y.; Cui, Y., ACS central science 2015, 1 (8), 449-55.


10.7 Supporting information

Figure S10.1 Photographs of melt Na on carbon paper (a) and CP-NCNTs (b); the thermal infusion process of Na into CP-NCNTs (c-e).

Figure S10.2 SEM images of NCNTs-CP grown by CVD method.
Figure S10.3 Raman spectrum of CP and CP-NCNTs

Figure S10.4 (a) XPS spectrum of CP-NCNTs; (b) XPS N 1s spectrum of CP-NCNTs
Figure S10.5 SEM images of as-prepared Na@CP-NCNTs

Figure S10.6 XRD patterns of CP, CP-NCNTs and Na@CP-NCNTs
Figure S10.7 XPS spectrum of Na@CP-NCNTs

Figure S10.8 Long cycling stability of the Na@CP-NCNTs electrodes at a current density of 1 mA cm^{-1} with the capacity limit of 1 mAh cm^{-2}.
Figure S10.9 Cross section-view SEM images of bare Na foil after different stripping amount of Na in the first cycle ((a) 0.5 mAh cm$^{-2}$, (b) 1 mAh cm$^{-2}$, (c) 3mAh cm$^{-2}$).

Figure S10.10 Top-view SEM images of bare Na foil after different stripping amount of Na in the first cycle ((a) 0.5 mAh cm$^{-2}$, (b) 1 mAh cm$^{-2}$, (c) 3mAh cm$^{-2}$).
**Figure S10.11** Photographs of bare Na foil (a) and Na@CP-NCNTs (b) after 10 cycles electrochemical plating/stripping at the current density of 3 mA cm$^{-2}$ with capacity limit of 1 mAh cm$^{-2}$.

**Figure S10.12** Cross section-view SEM images of bare Na foil after different cycles with the capacity of 1 mAh cm$^{-2}$ at the current density of 3 mA cm$^{-2}$ ((a)1, (b)5, (c)10 cycles).
Figure S10.13 Top-view SEM images of bare Na foil after different cycles with the capacity of 1 mAh cm\(^{-2}\) at the current density of 3 mA cm\(^{-2}\) (a)1, (b)5, (c)10 cycles).
Table S10.1 The concentration of the element for CP-NCNTs from the XPS results

<table>
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<th>Element</th>
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<tr>
<td>Fe 2p</td>
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<tr>
<td>O 1s</td>
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<tr>
<td>N 1s</td>
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<td>C 1s</td>
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Chapter 11

11 Conclusion and Future Perspectives

This chapter summarized conclusions and contributions of this thesis, and personal statement and suggestions for future work were presented.

*Part this chapter has been published in Energy & Environmental Science, 2018, 10.1039/C8EE01373J
11.1 Conclusion

Lithium-ion batteries (LIBs) have been developed over the past decades to be one of the most successful energy storage devices for various application, including portable devices and EVs. However, the energy density of current LIBs has almost reached their limitation, which cannot meet the increasing demands of high energy density energy storage devices. LMBs, including Li-S, Li-air and all solid-state Li-metal batteries, are considered as promising candidates with high theoretical energy density for the next-generation batteries systems. Furthermore, Li is not regarded as an abundant element in the Earth’s crust, making the resource limited and high in price. This results in an increasing price of LIBs, which limits the application of LIBs in large scale energy storage systems. Na-based batteries, particularly Na-metal batteries (NMBs), have been developed in the recent year for application in large scale energy storage systems due to the high abundance, low cost, and suitable redox potential of Na. The most attractive NMBs include Na-S, Na-air, Na-CO2 and all-solid-state Na metal batteries. To reach the high energy density of LMBs and NMBs, Li metal and Na metal are the ultimate choice for anodes, respectively. Both the Li metal anode and Na metal anode show high specific capacity, low electrochemical potential and light weight. The properties and performances of Li and Na metal anode are recognized as one of the key factor for the high performance LMBs and NMBs. However, both Li and Na metal anodes suffer from serious challenges during electrochemical processes. Generally, the issues can be summarized as: i) Li/Na dendrite formation and short circuits; ii) unstable SEI formation, low CE and poor cycling performance; iii) Infinite volume changes.

This thesis work is mainly focused on the surface/interface and skeleton design for both Li and Na metal anodes. A series of experiments have been carried out in this study to fabricate different surface coatings and skeletons for Li and Na metal anodes. Different chemical, physical and electrochemical characterizations were conducted to determine the relationships of physical properties of the as-prepared materials and electrochemical performance of Li and Na metal anodes. Moreover, the underlying mechanisms of materials and their electrochemical reactions were explored, such as the surface and interface change with different coating layers; the thickness effect of the protective layer.
in different electrolyte systems; the relationship between the surface area and electrochemical performances of the host structure; etc. In summary, this study focused on Li and Na anodes for LMBs and NMBs and works on four major parts: surface modification, skeletons design, physical/electrochemical characterization, and understanding of the underlying mechanisms. The detailed study gained a better understanding for Li and Na metal anodes in liquid electrolyte, and it is believed that these designs and analysis bring new insights for Li and Na metal anodes in their applications.

Both atomic layer deposition (ALD) of Al₂O₃ and molecular layer deposition (MLD) alucone were deposited as protective layers for Li metal anode. Generally, by protecting Li foil with Al₂O₃ and alucone, the electrochemical performances and lifespan have been improved. Furthermore, a comprehensive study of Al₂O₃ and alucone coating in both ether-based and carbonated-based electrolyte, both resulting in significant improvement on the plating/stripping performance of lithium metal. The thicknesses of alucone have been optimized in both types of electrolyte. Furthermore, a comparison between ALD Al₂O₃ and MLD Alucone has also been presented in detail for both electrolyte systems. Based on the plating/stripping performances, alucone was more promising with longer life time, stable polarization curve and lower internal resistance compared with Al₂O₃, especially in carbonate-based electrolyte.

The concept of conductive carbon paper (CP) interlayer has been demonstrated for highly stable Li metal anodes. The fabrication process of Li-CP composite electrolyte is very facile and easy to be realized. The as-prepared Li-CP-5L electrode shows superior and stable plating/stripping performances for up to 620 h, which is almost 10 times longer than that of the bare Li foil. To the best of our knowledge, our design presents the best performances in symmetric Li/Li cells in carbonate-based electrolyte in term of the highest capacity, highest current density and longest life time. There is no observable mossy or dendritic Li formation during the Li deposition process, in which the mechanism and functions of CP during Li plating/stripping process have been highlighted in detail.
In order to achieve higher energy density using interlayers, the 3D bi-functional interlayer was fabricated using vertical NCNTs grown on the carbon fibres of CP. The relationships between surface area and electrochemical performances were demonstrated for the 3D structure by controlling the growth time of NCNTs during the SPCVD process. Impressively, the Li-CP-NCNTs composite electrode can deliver stable cycling performances for over 600 h (~ 900 cycles) and 250 h (~ 750 cycles) at the high current densities of 5 mA cm$^{-2}$ and 10 mA cm$^{-2}$, which is two time higher than that of the CP interlayers. Meanwhile, with a high capacity of 3 mAh cm$^{-2}$, the Li metal electrode with CP-NCNTs interlayer delivers the long life time of over 350 h at a current density of 3 mA cm$^{-2}$. The morphologies of both Li foil and CP-NCNTs interlayers indicate that the Li dendrite-free deposition and minimum volume change structure can be obtained with the “bi-functional” interlayers.

The ALD Al$_2$O$_3$ film was deposited on metallic Na for long for long life Na metal batteries in ether-based electrolyte. By protected Na foil with ultrathin Al$_2$O$_3$ layer, the dendrites and mossy Na formation have been effectively suppressed and life time has been significantly improved. Based on the plating/stripping tests, the thickness of protective layer have been further optimized, in which with 25 cycles of Al$_2$O$_3$ layer indicating the best performance as well as superior long and stable life time over 500 cycles. The Al2O3 coating remained after cycling and the side reaction between Na and electrolyte can be effectively reduced to form a sable SEI film.

The organic-inorganic MLD alucone protecting layer on metallic Na anode was developed in carbonated-based electrolyte. By protecting Na foil with an ultrathin alucone layer, the formation of mossy and dendrite-like Na is effectively suppressed and life time significantly improved. Furthermore, a comparison between ALD Al$_2$O$_3$ and MLD alucone has also been investigated, demonstrating that the alucone coated Na outperforms ALD Al$_2$O$_3$ by displaying prolonged life time and stable polarization curves.

A facile and in-situ solution-based method was reported to fabricate a solid-state electrolyte Na$_3$PS$_4$ protective layer for Na metal anode. The thickness and chemical composition of the NaPS layers can be controlled by adjusting the precursor
concentrations and reaction times, and has been optimized in our study. By protecting the Na foil with Na$_3$PS$_4$, the mossy and dendrite-like Na growth is effectively suppressed. From the symmetric cell testing, Na@NaPS-3 displays the most stable electrochemical performances with lower polarization compared with Na foil. Meanwhile, the optimized Na@NaPS-3 can achieve much better performances with the large capacities and current densities required for practical applications.

To relieve the volume change of the Na metal anode, a unique structure of CP with NCNTs as a 3D skeleton for stable use of Na metal anode was designed. The growth of vertical NCNTs can effectively change the Na wettability of CP from “Na-phobic” into “Na-philic”. The highly conductive networks from CP and NCNTs provides homogeneous local current allowing for uniform Na stripping and plating. Furthermore, the Na@CP-NCNTs composites show stable electrochemical plating/stripping performances under different current density, even up to 5 mA cm$^{-2}$. Furthermore, we also are the first to demonstrate the stable use of a high capacity of 3 mAh cm$^{-2}$ using our unique Na@CP-NCNTs electrode. The 3D skeleton structure remains intact after cycling with minimum volume change.

### 11.2 Contributions to this field

1. **Developing ultrathin films as a protective layer for Li and Na metal anodes.** In this thesis, we demonstrate the ALD Al$_2$O$_3$ as protective layer for Na metal anode with significant improved electrochemical performances, which is one of first two reports in this field published in the same year (my work *Advanced Materials*, 2017, 29, 1606663; work from another group *Advanced Energy Materials*, 2017, 7, 1606526). Furthermore, MLD alucone has been used, for the first time, as the coating layers for both Li metal anode and Na metal anode, resulting in enhanced plating/stripping performances, especially in carbonate-based electrolyte (*Small Methods*, 2018, 2, 1700471; *Nano Letters*, 2017, 17, 5653). These studies may result in new opportunities by using ALD and MLD as protective layers to the realization of the next-generation high-energy-density Li and Na metal batteries.
2. **In-situ solution-based method to fabricate the Na3PS4 as protective layer for Na metal anode.** In this thesis, the solution-based method is firstly proposed to synthesize the Na3PS4 as protective layer for Na metal anode, using Na metal as reactant in the reaction. This study may open the new window to develop the solid-state electrolyte modified Na metal electrode for the next generation solid-state Na metal batteries.

3. **A universal and effective approach of development of conductive interlayers for Li metal anodes.** In this thesis, the new concept of “interlayer” has been proposed, for the first time, as the universal approach to achieve long life time and dendrite free Li metal anodes (Nano Energy, 2018, 43, 368). Furthermore, this concept has been extended to a 3D bi-functional interlayer (Energy Storage Materials, 2018, 15, 415). The relationship between surface area and electrochemical performances on the 3D structure has been studied in detail. This approach could be a facile way to fabricate the large-scale Li metal anode with long-life time and high capacity.

4. **High Capacity, Dendrite-free Growth and Minimum Volume Change Na Metal Anodes.** The concept of “Na-phobic” and “Na-philic” has firstly been identified for Na metal anode using vertical NCNTs to tune the wettability of carbon paper host (Small, 2018, 14, 1703717). The 3D skeleton structure was observed to be intact following electrochemical cycling with minimum volume change and was observed to be dendrite-free in nature.

5. **Deep understanding of the surface and interface chemistry on the Li and Na metal anodes.** The surface and interface chemistries of the Li and Na anodes have been deeply investigated by different techniques, including X-ray photoelectron spectroscopy (XPS), Time-of-flight secondary ion mass spectrometry (TOF-SIMS) and Rutherford Backscattering Spectrometry (RBS). It is worth to mention that, for the first time, the powerful technique of RBS has been introduced in this field, which can provide the important information of the SEI compositions and thicknesses as shown in the publications above.
11.3 Perspectives

Although there has been some progress related to the development of Li and Na metal anodes, there are still significant challenges to be overcome, particularly for the practical application of LMBs and NMBs. Herein, we propose potential directions and perspectives for this field:

1) **Better fundamental understandings are needed:** Although some studies have been carried out in the past year for the mechanism study on Li metal anode, more detailed fundamental understanding are needed in the future, such the SEI formation, composition, etc. Moreover, few studies have focused on the fundamental understanding of the Na deposition process. For example, the Na deposition structures, including mossy and dendritic Na, should be better defined. Particularly, the relationship between Na deposition with other parameters, such as current density, capacity, temperature and pressure et al. should be further explored. Then, the nucleation process of Na is a fundamental aspect that is poorly understood, and more work should include studies on the nucleation locations and times. Lastly, detailed information related to the SEI formation mechanism, structure, components, and regulation is still inadequate.

2) **Advanced characterization techniques and methods:** Although various techniques have been applied to study both Li and Na anode, a proper fundamental understanding of Li and Na nucleation, dendrite growth, and chemical/electrochemical reactivity are still unclear, and require advanced techniques and characterization. Firstly, synchrotron radiation-related techniques will be excellent candidates for the study of the SEI layer on Li and Na metal anodes, especially with in-situ capabilities. Secondly, due to the high reactivity of Li and Na metal, cryo-based techniques are an ideal approach to obtaining the most authentic chemical information without any compositional changes of the Li and Na dendrites or SEI layers. Thirdly, any one of these techniques is not enough to have a deep and comprehensive understanding on the surface and interface chemistry for Li and Na anodes and its SEI layers, and the combination of different analysis technique in future research will be required.
3) Engineering the SEI: Since the SEI is the key factor for the stability of the Li and Na metal anodes, surface modifications with artificial SEI layers have become a promising direction. While several coatings have been explored, other approaches still need to be developed for Li$^+$ and Na$^+$ conductive protective layers, in which sputtering is a good choice to deposit Li-SSEs and Na-SSEs as artificial SEI on Li and Na metals. Secondly, polymer based thin films with ionic conductivity and high flexibility will be another promising strategy. Particularly, polymer coatings incorporating self-healing functionalities can reconstruct the surface cracks produced during cycling. Thirdly, ALD and MLD are still remarkable to address the issues for Li and Na metal anodes, especially with precisely controlled thicknesses. However, new ALD/MLD films need to be developed with improved Li$^+/Na^+$ conductivity, density, and flexibility. Lastly, the combination of different approaches to fabricate hybrid protective layer or composite artificial SEI layers is required, in which the different layers can serve their own functions to form a real and robust protection layer.

4) Nanostructured Li and Na: For LMBs and NMBs, more than 10 micrometers of Li and Na is ideal for the repeated plating/stripping process. The infinite volume change is still a restriction for long life LMBs and NMBs. In this case, the rational design of host matrices is critically needed for practical LMBs and NMBs. The host structure should possess chemical, electrochemical, and mechanical stability. Meanwhile, the weight and volume percentage of the matrix in the whole composites electrode should be limited in order to maximize the energy density of the cell. Furthermore, although metallic Li and Na is encapsulated in the matrix, the SEI layer will still be formed at the point of contact with the electrolyte. Thus, it would be a better idea to combine the strategies of nanostructured Li and Na with artificial SEI to synergistically improve the stability and electrochemical performances of Li and Na metal anodes.

5) Different LMBs and NMB systems: Apart from the existing issues of Li and Na dendrite growth, dead Li and Na formations and infinite volume change, more serious challenges appear in different LMBs and NMB systems. For example, the O$_2$ cross over and by-product corrosion is an obvious issue in Li-O$_2$ and Na-O$_2$ batteries. Furthermore, the interface stability between SSEs and Li and Na metals is another uncertainty in terms
of different types of SSEs. In this case, these other factors should be taken into consideration when designing metallic Na anodes for real LMBs and NMBs.

6) Practical applications: Firstly, it should be pointed out that the high CE is very important for practical battery applications. A high CE of > 99.9 % after 1000 cycles at relatively high current density has not been reported yet. Secondly, for the LMBs and NMBs with different cathodes, the requirements of the areal capacity and thickness of Li and Na metals are different. Thus, the design of Li and Na metal anode should be tailored to the choice of cathode, electrolyte and LMBs/NMB system.

In conclusion, it seems that the use of only a single approach is not enough to solve all the existing issues of Li and Na metal anodes. Thus, multi-strategy approaches with specific aims will bring the metallic Li and Na anodes closer to reality. We believe that with continued efforts, the Li and Na metal anode will act as the “Holy Grail” for the next-generation LMBs and NMBs for large scale energy storage applications.
Appendices

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Yang Zhao, Xueliang Sun, Molecular Layer Deposition Technique for Energy Conversion and Storage, ACS Energy Letters, 2018, 3, 899–914
Appendix C: Permission from John Wiley and Sons for Published Article on Advanced Materials

Published papers:

Yang Zhao, Lyudmila V. Goncharova, Andrew Lushington, Qian Sun, Hossein Yadegari, Biqiong Wang, Wei Xiao, Ruying Li, Xueliang Sun, Superior Stable and Long Life Sodium Metal Anodes Achieved by Atomic Layer Deposition, Advanced Materials, 2017, 29, 1606663
Appendix D: Permission from American Chemical Society (ACS) for Published Article on Nano Letters

Published papers:

Yang Zhao, Lyudmila V. Goncharova, Qian Zhang, Payam Kaghazchi, Qian Sun, Andrew Lushington, Biqiong Wang, Ruying Li, Xueliang Sun, Inorganic-organic Coating via Molecular Layer Deposition Enables Long Life Sodium Metal Anode, Nano Letters, 2017, 17, 5653–5659
Appendix E: Permission from Elsevier for Published Article on *Nano Energy*

**Title:** Carbon paper interlayers: A universal and effective approach for highly stable Li metal anodes

**Author:** Yang Zhao, Qian Sun, Xia Li, Changhong Wang, Yipeng Sun, Keegan R. Adair, Ruying Li, Xueliang Sun

**Publication:** Nano Energy

**Publisher:** Elsevier

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Published papers:

*Yang Zhao*, Qian Sun, Xia Li, Changhong Wang, Yipeng Sun, Keegan R. Adair, Ruying Li, Xueliang Sun, Carbon Paper Interlayer: An Universal Approach for Highly Stable Li Metal Anode, *Nano Energy*, 2018, 43, 368-375
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*Yang Zhao*, Lyudmila V. Goncharova, Qian Sun, Xia Li, Andrew Lushington, Biqiong Wang, Ruying Li, Fang Dai, Mei Cai, Xueliang Sun, Robust Metallic Lithium Anode Protected by Molecular Layer Deposition Technique, *Small Methods*, 2018, 2, 1700417
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*Yang Zhao*, Xiaofei Yang, Liang-Yin Kuo, Payam Kaghazchi, Qian Sun, Jianneng Liang, Biqiong Wang, Andrew Lushington, Ruying Li, Huamin Zhang, Xueliang Sun, High Capacity, Dendrite-free Growth and Minimum Volume Change Na Metal Anode, *Small*, 2018, 14, 1703717
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*Yang Zhao*, Xiaofei Yang, Qian Sun, Xuejie Gao, Xiaoting Lin, Changhong Wang, Yipeng Sun, Keegan R. Adair, Ruying Li, Mei Cai, Xueliang Sun, Dendrite-free and minimum volume change Li metal anode achieved by three dimensional artificial interlayers, *Energy Storage Materials*, 2018, DOI: 10.1016/j.ensm.2018.07.015
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Publications: (A) Peer-reviewed Journal Papers Based on This Thesis (First Author)

1. Yang Zhao, Keegan R. Adair, Xuéliang Sun, Recent developments and insights into the understanding of Na metal anodes for Na-metal batteries, Energy & Environment al Science, 2018, 11, 2673-2695

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2. **Yang Zhao**, Xueliang Sun, Highly Efficient Protection by Atomic Layer Deposition/Molecular Layer Deposition for Lithium and Sodium Metal Anode, 2017 MRS Fall Meeting, Nov 26th-Dec 1st 2017, Boston

3. **Yang Zhao**, Ali Fathalla Abdulla, Xia Li, Qian Sun, Zhongxin Song, Ruying Li and Xueliang Sun, Metal Organic Framework Derived Nanomaterials in the Application of Lithium-Ion and Sodium-Ion Battery, 18th International Meeting on Lithium Batteries(IMLB2016), Chicago, USA, June 19-24, 2016
