

Design Strategies to Enable the Efficient Use of Sodium Metal Anodes in High-Energy Batteries

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Sodium-based batteries have attracted considerable attention and are recognized as ideal candidates for large-scale and low-cost energy storage. Sodium (Na) metal anodes are considered as one of the most promising anodes for next-generation, high-energy, Na-based batteries owing to their high theoretical specific capacity (1166 mA h g⁻¹) and low standard electrode potential. Herein, an overview of the recent developments in Na metal anodes for high-energy batteries is provided. The high reactivity and large volume expansion of Na metal anodes during charge and discharge make the electrode/electrolyte interphase unstable, leading to the formation of Na dendrites, short cycle life, and safety issues. Design strategies to enable the efficient use of Na metal anodes are elucidated, including liquid electrolyte engineering, electrode/electrolyte interface optimization, sophisticated electrode construction, and solid electrolyte engineering. Finally, the remaining challenges and future research directions are identified. It is hoped that this progress report will shape a consistent view of this field and provide inspiration for future research to improve Na metal anodes and enable the development of high-energy sodium batteries.

1. Introduction

Research activities on Na-based batteries started in the 1960s (Figure 1a).^[1–5] High-temperature (HT) sodium-sulfur (Na-S) batteries operating at about 300 °C utilizing molten Na as anode and molten S as cathode were initially developed, owing to the discovery of ceramics with high Na-ion conductivity (e.g., β -Al₂O₃).^[5] However, practical applications of these batteries have been restricted due to safety issues arising from breakage of the ceramic separator leading to unconstrained side reactions.^[2,5] Up to date, research activities on Na-based batteries have mainly focused on lowering the operating temperature to room temperature (RT).^[3]

Recent attempts to develop rechargeable RT Na-based batteries have aimed to use high Na-ion conductive liquid electrolytes (LE) instead of ceramic separators.^[6] Simultaneous research on conventional

Li- and Na-insertion materials started to attract worldwide attention in the late 1970s and early 1980s.^[3] While Li-ion batteries with Li-insertion electrodes have achieved commercial success after their first release in 1991, similar commercialization of Na-ion batteries using Na-insertion electrodes was hindered due to lack of appropriate anode materials.^[7] Owing to abundant resources and worldwide availability of Na, and the wide range of sodium-based solid phases, Na-based batteries are now being reconsidered as ideal candidates for large-scale and low-cost energy storage systems. Since 2009, the number of publications related to Na-based batteries has grown significantly (Figure 1b). Most research activities have been devoted to discovering high-performance anodes to boost the energy density of Na-ion batteries (Figure 1c and Table S1, Supporting Information), because graphite shows much lower storage capability for Na compared to Li.^[8] Hard carbon, phosphorus, metal oxides, metal sulfides, and organic compounds exhibit a much higher capacity but low Coulombic efficiency.^[6,9–12] Furthermore, some of the anode materials suffer from poor electronic conductivity, limited natural abundance, and toxicity, which hinder their practical applications.^[4,13]

Recently, research interests have refocused on the Na metal anode (Figure 1b), owing to its high theoretical specific capacity (1166 mA h g⁻¹) and low electrode potential (–2.71 V

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vs standard hydrogen electrode, SHE) among all known anode materials (Figure 1c). Rechargeable Na-based batteries with Na metal anodes and conventional insertion cathodes could achieve comparable energy densities to the current state-of-the-art Li-ion batteries (with graphite anodes). New types of rechargeable Na-metal-based batteries, such as RT sodium-sulfur (Na-S) batteries, RT sodium-oxygen (Na-O₂) batteries, and RT ZEBRA-type sodium-metal halide batteries, also exhibit potentials to develop high-energy and low-cost energy storage systems. However, there are still some key issues to be solved.^[14–19]

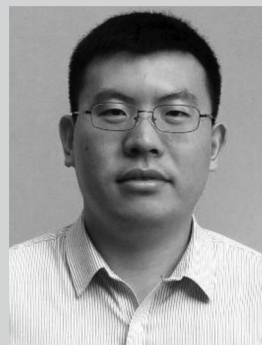
Investigations on Na metal anodes are still in their infancy. To develop better and safer Na metal anodes, it is essential to improve our understanding of the underlying reactions during cycling a battery with Na metal anodes. Herein, we provide an overview on the promises and challenges of Na metal anodes and summarize the design strategies to enable their utilization. We aim to illustrate the rapid progresses that are taking place in this field and thus provide inspiration for future research on Na-based batteries.

2. Challenges of Na Metal Anodes

To effectively use Na anodes in practical rechargeable battery systems, several challenges need to be overcome, the greatest of which are Coulombic efficiency and cyclability.^[4,20,21] High Coulombic efficiency during cycling can minimize the amount of the required active Na in the battery system, reduce the materials cost, and increase the energy density of the entire system. Excellent cyclability is also mandatory to provide enough service life to satisfy customers' requirement. To deal with these issues, it is essential to attain a profound understanding of the plating/stripping behavior of Na-ion/Na, the interfacial chemistry, and the correlations among these aspects.

Meanwhile, the preparation of Na metal foil to assemble Na metal-based batteries is also of paramount importance. Unlike Li metal, Na metal strips are not commercially available. Pure Na metal is highly reactive and must be stored in mineral oil or under inert gas atmosphere. It can quickly react with O₂ and H₂O in the air to form a passivation layer. The high resistance of the passivation layer on the surface of Na metal is detrimental to the electrochemical performance of Na metal anodes.^[22] Currently, Na metal anodes are usually prepared from scraped and polished Na cubes. After rolling the Na cube into a foil using a polyethylene roll and block, Na metal anodes are obtained by punching Na foil. The thickness of the Na foil should be more than 10 μm to achieve good cycling performance.^[20]

Owing to the high reactivity and very negative electrical potential of the Na-ion/Na electrode, most available organic electrolytes can be reduced at the Na surface. Severe side reactions between Na metal and adjacent electrolyte usually generate a thick film defined as “solid electrolyte interphase” (SEI) on the Na metal surface and flammable gases are released.^[23,24] Detailed understanding on how the SEI is formed was gained by Peled et al. as early as in the 1990s.^[24] Without supporting matrix, Na anodes undergo severe volume expansion during plating and volume contraction during stripping, which induces the breakage of the SEI layer and exposes fresh Na to the liquid electrolyte. This effect accelerates further side reactions that deplete the limited Na metal and electrolyte in the



for lithium-based batteries and sodium-based batteries.

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lithium-ion batteries, lithium-air batteries, sodium-ion batteries, lithium-sulfur batteries, supercapacitors, hydrogen storage materials, fuel-cells, graphene, and chemical functionalization of graphene.

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cell. Meanwhile, the uneven SEI layer on the Na anode disturbs uniform Na-ion flux and promotes nonuniform Na plating with the growth of dendrites.

Over the past few decades, many efforts have been devoted to understanding the formation mechanism of Li dendrites. In contrast, there is limited research on the formation and growth mechanism of Na dendrites.^[25,26] **Figure 2** shows the schematic

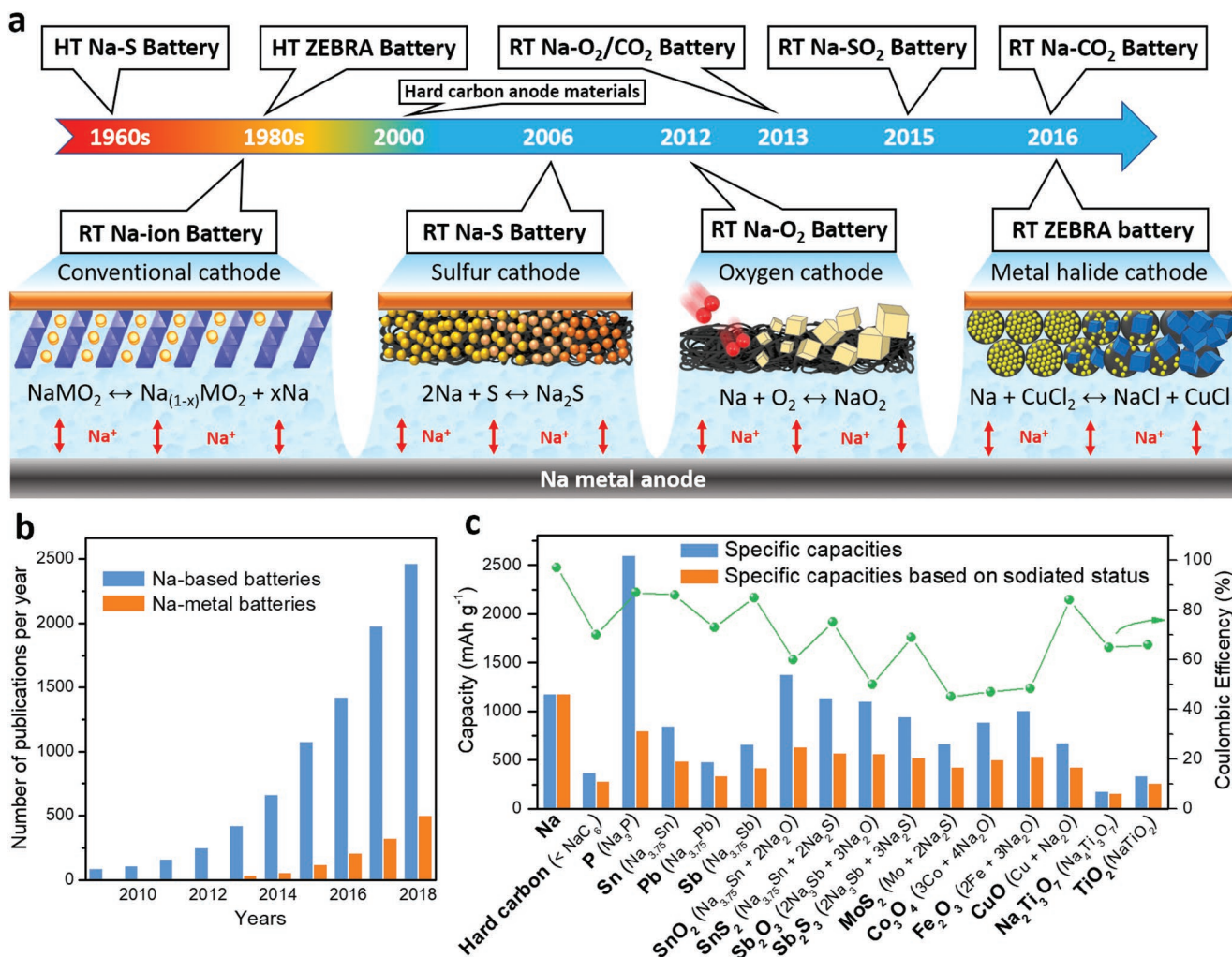


Figure 1. a) Timeline of the development of Na-based batteries with schematics and working principle for four typical rechargeable RT Na-metal batteries.^[1–5] b) Number of publications per year for Na-based batteries and Na-metal batteries. Data were collected from the “Web of Science” with the key words “sodium batteries” and “sodium metal anodes.” c) Theoretical specific gravimetric capacities and corresponding first cycle Coulombic efficiencies of various reported anode materials for RT Na-ion batteries.

illustration for the formation process of Na dendrites. In the initial stage, a layer of uneven SEI forms on the surface of an Na anode, which leads to nonuniform Na plating. Furthermore, the lack of flexibility does not allow the SEI to constrain the volume expansion during Na plating, and therefore, cracks can form easily in the SEI. The enhanced Na-ion flux in cracks accelerates nonuniform Na plating as the energy barrier of Na-ion diffusion in those areas becomes lower.^[27] Consequently, Na dendrites grow abundantly from the cracks upon further Na plating. During the following Na stripping process, the Na dendrites can be isolated easily from the bulk of the anode because the root part of the dendrites are prone to dissolve first. Due to the loss of electric contact, such detached dendrites become “dead” Na. Meanwhile, the volume contraction during Na stripping causes more cracks in the SEI, leading to more pathways for dendrite growth during the following plating process. The repeated plating/stripping of Na-ion/Na leads to accumulation of “dead” Na, formation of more SEI, increased porosity of the Na anode, and the depletion of electrolyte, inducing poor cycling stability.

3. Strategies for Efficient Use of Na Metal Anodes

Many methods that are currently applied for the efficient use of Li metal anodes have been transferred to Na metal anodes. Herein, we highlight several strategies to achieve stable and efficient Na anodes.

3.1. Liquid Electrolyte Engineering

Liquid electrolytes are widely used in RT Na-based batteries. It is essential to control the reactions between the highly reactive Na anode and the liquid electrolyte to achieve stable Na anodes. Solvents, salts, and additives in electrolytes have been intensively investigated to improve the performance of Na anodes because these components in the electrolytes can decompose and be incorporated into the SEI.^[28] Thus, they can be used to tailor the physicochemical properties of the SEI.

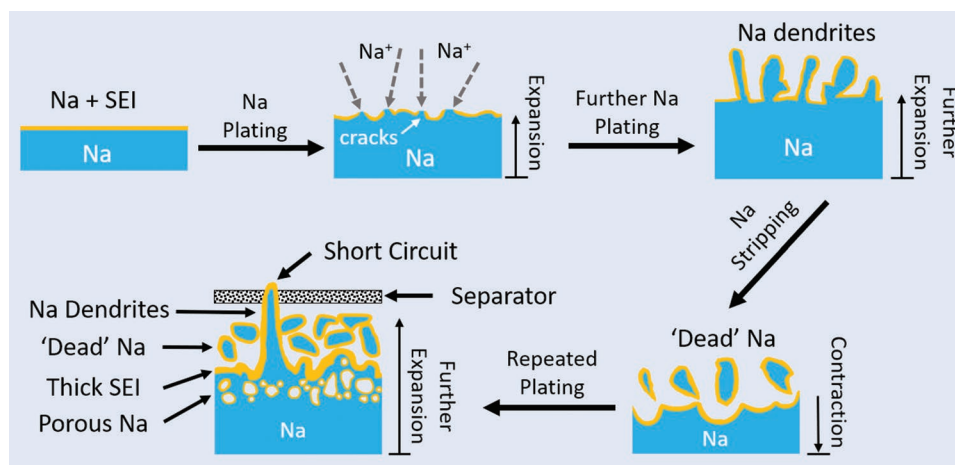


Figure 2. Schematic showing the stripping/plating of Na-ion/Na and Na dendrite formation.

3.1.1. Ether-Based Electrolytes

The Na anodes exhibited limited reversibility during plating/stripping at RT using carbonate-based electrolyte and chloroaluminate ionic liquid electrolytes.^[29–35] Recently, ether-based electrolytes were found to be more compatible for Na-based batteries.^[33,36–38] For example, Cui and co-workers achieved Na anodes with high Coulombic efficiencies and long cycle life by using 1 M sodium hexafluorophosphate (NaPF₆) in bis(2-methoxyethyl) ether (diglyme).^[26] In-depth X-ray photoelectron spectroscopy (XPS) analysis revealed a uniform SEI composed of inorganic sodium fluoride (NaF) and sodium oxide (Na₂O) on the surface of the Na anode. This thin SEI film is highly impermeable to the electrolyte solvent but has good ionic conductivity to facilitate comparatively uniform Na plating underneath.

3.1.2. High-Concentration Electrolytes

The concentration of the electrolyte salt plays a critical role in the electrochemical properties of the liquid electrolyte and influences the formation of dendrites.^[15,39–43] An increase of the initial metal ion concentration in the electrolyte can increase the Sand's time and therefore postpone dendrite formation.^[44,45] Furthermore, elevated concentrations of metal ions in the electrolyte lead to the formation of a unique solvation structure, which reduces the amount of free solvent molecules and therefore mitigates the side reactions between Na metal and organic solvents.^[46–48] Based on this mechanism, a new class of electrolytes called high-concentration electrolytes (HCE) has been developed for alkali metal-based batteries (Figure 3a).^[42,43] Owing to the unique solvation structures and functionalities, HCEs showed not only high stability in contact with Na anodes but also high oxidation durability against high-voltage cathodes. A HCE composed of 5 M sodium bis(fluorosulfonyl)imide in 1,2-dimethoxyethane was applied by Choi and co-workers.^[49] A high Coulombic efficiency of ≈99% was achieved for repeated plating/stripping of Na-ion/Na on a stainless-steel substrate. Although the employment of HCE can enable stable and safe operation of Na anodes, the high cost of the salt, high viscosity,

and poor wettability pose great challenges to their large-scale applications.

Recently, an alternative approach has been developed to resolve these obstacles facing HCE. An “inert” solvent was added to HCEs to form a localized high-concentration electrolyte (LHCE) (Figure 3a).^[50] An “inert” solvent with low dielectric constant and low donor number, such as hydrofluoroethers, showed minimal or no effect on the original solvent structure of the HCE. The LHCE maintained a high Na-ion transference number and showed high stability for Na anodes with reduced viscosity, increased conductivity, and improved wettability. For the long-term cycling performance tests at a high current density of 20 C, Na|Na₃V₂(PO₄)₃ batteries with LHCE showed greatly improved cycling stability owing to the minimized side reactions between the Na metal anode and the electrolyte.^[50]

3.1.3. Electrolyte Additives

Small amounts of additives in electrolytes can modulate the properties of the Na-ion-conducting SEI and significantly increase the Coulombic efficiency of Li/Na anodes.^[25,51–53] Recently, fluorinated compounds have been investigated intensively as electrolyte additives in Li/Na anode research.^[54–56] With the assistance of those additives, a thin and soft SEI with homogeneous structure and high ion transport can form on the anode, which is desirable to suppress dendrite formation. For example, Choi and co-workers added 1 wt% of fluoroethylene carbonate (FEC) to an electrolyte of 1 M sodium bis(fluorosulfonyl)imide (NaFSI) in propylene carbonate (PC)/ethylene carbonate (EC) (1:1).^[57] The decomposition products of the FEC-NaFSI-based electrolyte formed an ionic interlayer with improved mechanical strength and ion permeability of the Na metal anode. This enabled stable plating of Na on a Cu substrate during electrochemical cycling.

A self-healing electrostatic shield mechanism has been proposed to achieve dendrite-free Li plating by adding trace amounts of selected cations to the electrolyte.^[58] Accordingly, this strategy was also applied for Na metal-based batteries.^[59,60] The effective reduction potentials of most alkali metal ions, such

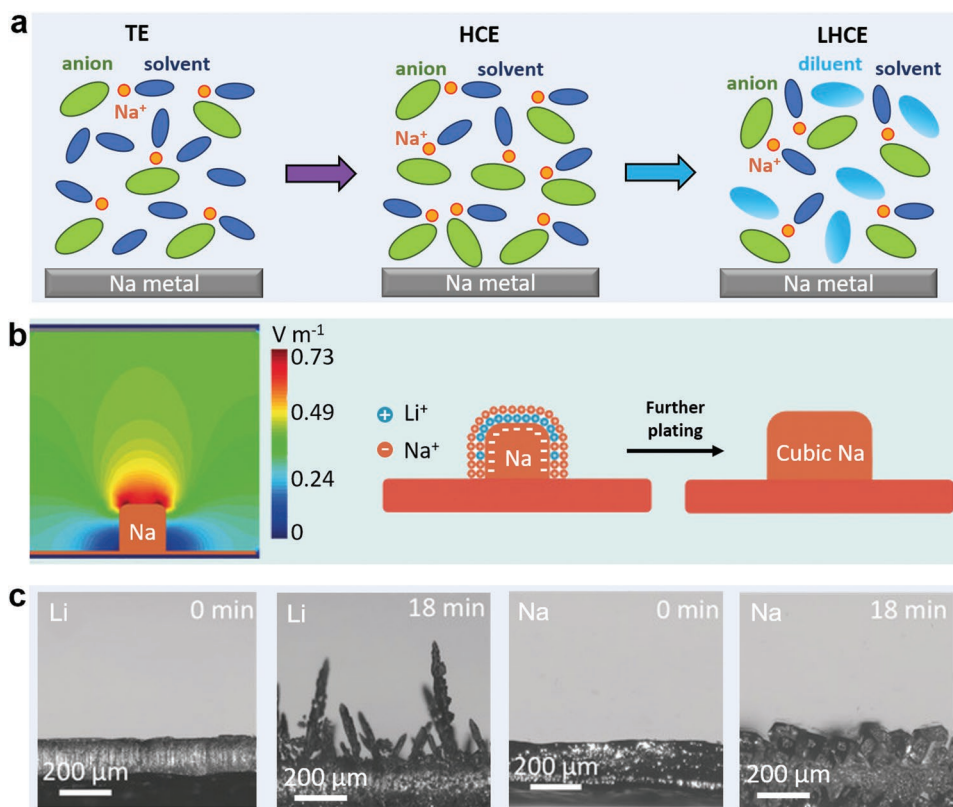


Figure 3. a) Schematics showing traditional electrolyte (TE), high-concentration electrolyte (HCE), and localized high-concentration electrolyte (LHCE). Reproduced with permission.^[59] Copyright 2018, American Chemical Society. b) Simulated electric-field intensity distribution and schematic illustration of Na plating patterns. c) In situ optical observations of Na plating in Li-based electrolyte and Na plating in Li/Na-based hybrid electrolyte. (b,c) Reproduced with permission.^[59] Copyright 2018, Wiley-VCH.

as lithium ions (-3.04 V vs SHE) and potassium ions (-2.93 V vs SHE) are lower than those of sodium ions (-2.71 V vs SHE). The alkali metal ions can be used to provide effective electrostatic shielding to prevent Na dendrite formation without reduction and consumption. As illustrated in Figure 3b, if Na is plated on a Cu substrate, Li-ions will be attracted by the accumulated negatively charged electric field on the tips of the plating regions and form a positively charged electrostatic shield without being reduced. This electrostatic shield forces the incoming Na-ions to diffuse and plate into adjacent regions, effectively suppressing the growth of dendrites on the Na anode surface. For example, Chen and co-workers discovered that Na dendrite formation can be effectively suppressed with the formation of an orderly and compact cubic Na deposition layer in an ether-based hybrid electrolyte (e.g., 0.8 M LiPF₆ and 1.0 M NaPF₆ in dimethoxyethane) (Figure 3c).^[59] Owing to the electrostatic shielding provided by Li-ions, the plating/stripping of Na-ion/Na exhibits high Coulombic efficiencies and low overpotential. Wang and co-workers used potassium bis(trifluoromethylsulfonyl)imide (KTFSI) as a bifunctional electrolyte additive in ether-based electrolyte (1 M sodium trifluoromethylsulfonate (NaOTf) in tetraethylene glycol dimethyl ether (TEGDME)) to improve the Coulombic efficiency and cycling stability of Na anodes.^[60] K-ions provide electrostatic shielding and the TFSI⁻ contributes to the formation of a desirable SEI on Na metal, both of which are favorable for uniform Na plating.

3.2. Na Metal Anode/Electrolyte Interface Engineering

Manipulating the interface between anode and electrolyte, for example by introducing an artificial SEI on top of the Na anode, is a commonly adopted strategy to increase the cycling stability of Na anodes.^[21,61]

An artificial SEI can be constructed on Na anodes via a chemical reaction (Figure 4a).^[62–65] For example, through the reaction of Na with 1-bromopropane, a thin layer of NaBr was coated on a Na anode (Figure 4b).^[66] The NaBr-protected Na metal anode showed a low diffusion barrier for interfacial ion transport, which is beneficial for uniform Na plating. Furthermore, the compact SEI not only restricts dendritic formation but also prevents unwanted side reactions between the electrode and electrolyte. Symmetric cells with NaBr-coated Na electrodes showed stable performance for more than 250 h at the current density of 1 mA cm⁻² without an obvious rise in overpotential.

With the development of advanced thin-film fabrication techniques, a thin and protective layer can be directly coated on Na anodes. Atomic layer deposition (ALD) and molecular layer deposition (MLD) are favorable deposition technologies for uniform and conformal thin film coating.^[34,35,67] Hu and co-workers developed a low-temperature plasma-enhanced ALD (PE-ALD) technology to deposit an ultrathin layer of Al₂O₃ film on Na metal (Figure 4c,d).^[34] With an optimized Al₂O₃ layer

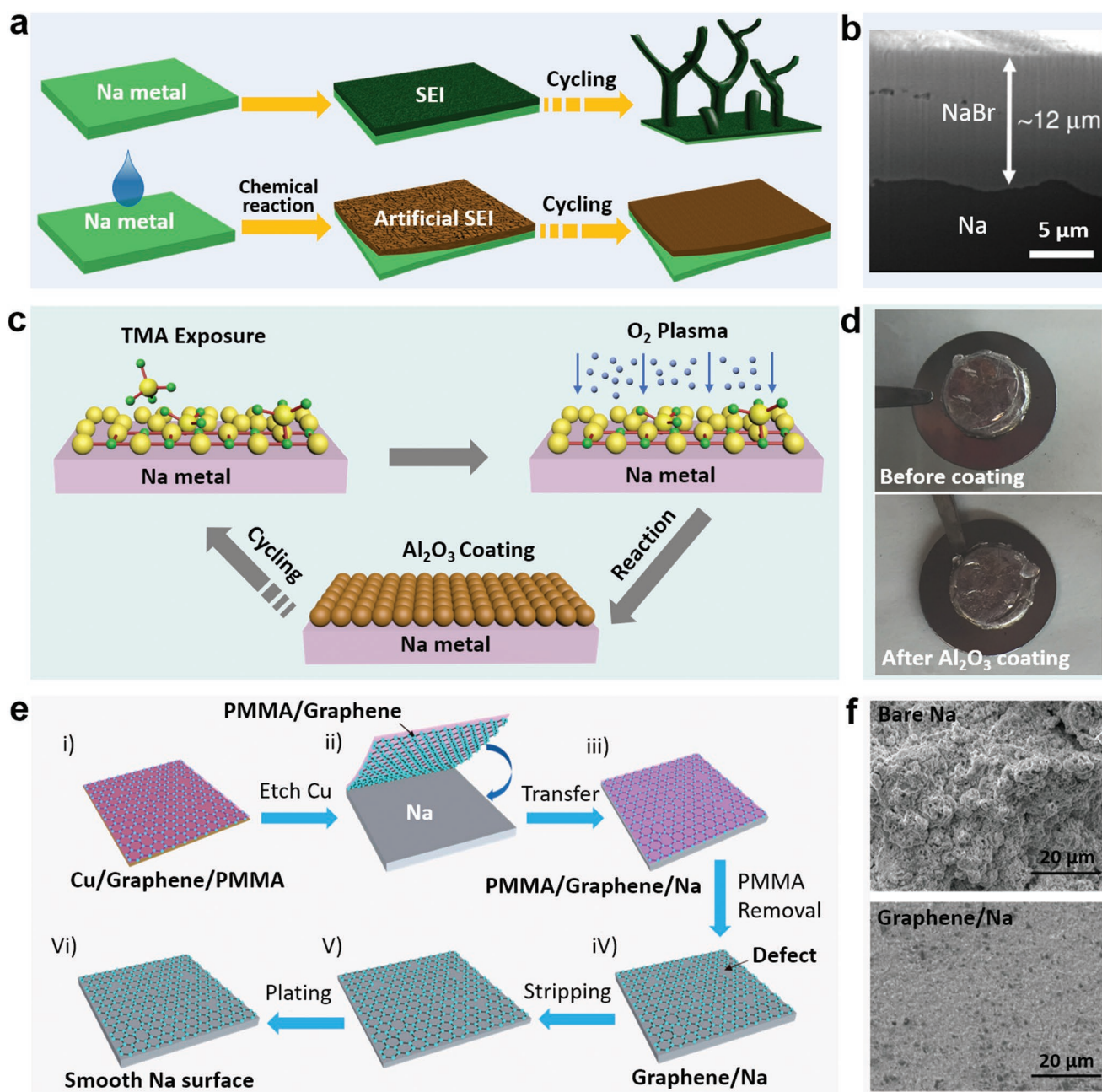


Figure 4. a) Schematic illustration of Na-ion/Na stripping/plating with and without artificial SEI layer. Reproduced with permission.^[62] Copyright 2019, Elsevier. b) Cross-section Cryo-SEM image of a NaBr coating layer on Na anode. Reproduced with permission.^[66] Copyright 2017, Springer Nature. c) Schematic illustration of the low-temperature plasma-enhanced atomic layer deposition (PEALD) process. d) Na anodes before and after coating with Al₂O₃ for 25 cycles. Reproduced with permission.^[34] Copyright 2017, Wiley-VCH. e) Schematic illustration of (i)–(iii) transferring freestanding graphene film onto the Na anode, and (iv)–(vi) the high stability of graphene-coated Na anode during stripping/plating without dendrite formation. f) SEM images of a few-layer graphene-coated Na surface and a bare Na surface after 100 cycles. (e,f) Reproduced with permission.^[69] Copyright 2017, American Chemical Society.

acting as artificial SEI, stable Na anodes have been fabricated, showing significantly improved cycle life compared with bare Na anodes.

A series of 2D materials were investigated as artificial SEIs by Zhang and co-workers through first-principles calculations.^[68] The theoretical simulation results showed that introducing defects, increasing bond length, and metal proximity

have positive effects on the ionic conductivity, which reduced the diffusion barriers and increased the diffusion rate. However, none of the above-mentioned strategies has positive influence on the hardness or the stiffness of the 2D materials, which is thus unfavorable for suppressing Na dendrites. Therefore, it is crucial to achieve a balance between the diffusion and mechanical properties during the design of a 2D material based

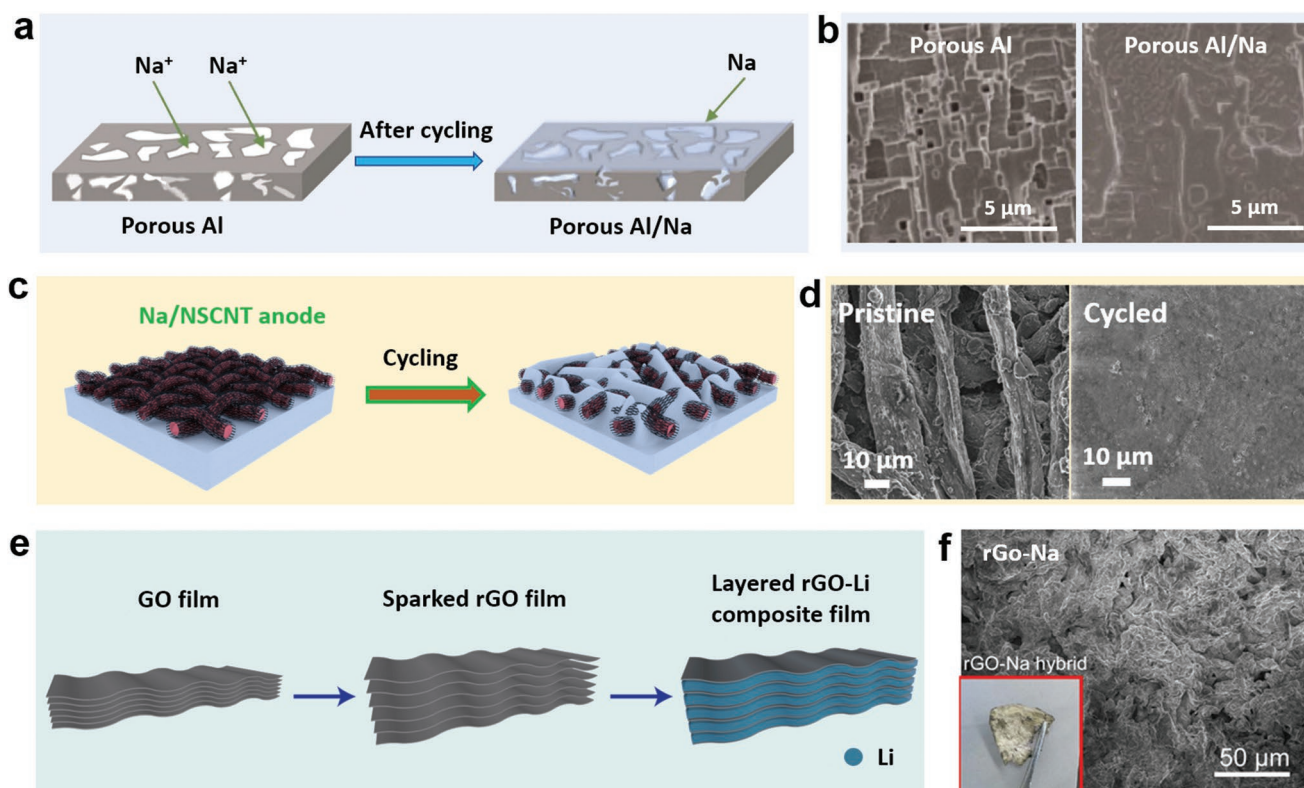


Figure 5. a) Schematic illustration of Na plating on porous Al. b) Top-view SEM images of porous Al foils before and after repeated Na-ion/Na stripping/plating. (a,b) Reproduced with permission.^[74] Copyright 2017, American Chemical Society. c) Schematic illustration of the Na/nitrogen and sulfur codoped carbon nanotube paper (Na/NSCNT) anode during stripping/plating without dendrite formation. d) Ex situ SEM images of Na/NSCNT anode before and after 20 cycles. (c,d) Reproduced with permission.^[76] Copyright 2018, Wiley-VCH. e) Schematic illustration of the synthesis procedures for a layered reduced graphene oxide (rGO)-Li composite film. Reproduced with permission.^[81] Copyright 2016, Springer Nature. f) SEM image with corresponding inset photograph of a rGO-Na anode. Reproduced with permission.^[82] Copyright 2017, National Academy of Sciences, USA.

artificial SEI. Furthermore, in practical applications, the thickness of the artificial SEI is another important parameter that needs to be considered. Li and co-workers directly applied free-standing graphene films with tunable thickness onto Na anodes and systematically investigated the influence of the thickness of the graphene film on the stability of Na anodes (Figure 4e,f).^[69] The electrochemical performances of cells with graphene film protected Na anodes showed that a thickness difference of only a few nanometers ($\approx 2\text{--}3$ nm) can have a decisive influence on the stability and rate capability of the Na anode. A few-layer graphene film (≈ 2.3 nm in thickness) is well suited for a Na anode working at relatively low current density (≤ 1 mA cm⁻²), whereas a multilayer graphene film (≈ 5 nm in thickness) would be the best option to protect Na anode during operation at high current density (2 mA cm⁻²).

3.3. Nanostructured Sodium Metal Anodes

3.3.1. Current Collector and Interlayer Engineering

Uniform Na plating can be achieved by increasing the surface area of the electrode to dissipate local current density through manipulating the nanostructure of the current collectors.^[70,71] Various 3D porous current collectors were applied to achieve

dendrite-free Na plating.^[72,73] Replacing commercial Al foil with porous 3D Al foil yielded uniform Na deposition without obvious dendrite formation (Figure 5a,b). The Li|porous Al half cells can run for 1000 cycles with a low and stable voltage hysteresis and an average plating/stripping Coulombic efficiency above 99.9% for over 1000 cycles.^[74]

Another effective approach to enhance uniform Na plating is to place a piece of conductive and porous paper on the top of Na anode as a “sodiophilic” interlayer to facilitate Na nucleation without dendrite formation.^[75,76] Recently, Wang and co-workers used nitrogen and sulfur codoped carbon nanotube (NSCNT) paper as an interlayer to control Na plating behavior and suppress the formation of Na dendrite.^[76] As shown in Figure 5c,d, the N- and S-containing functional groups on the carbon nanotubes guide the Na nucleation behavior and endow uniform Na plating while ensuring excellent cycling stability.

3.3.2. Nanostructured Hosts for Na Metal

To overcome the volume change upon repeated plating/stripping of Na-ion/Na, 3D porous hosts have been designed to accommodate the cycled Na.^[77–80] Overall, an ideal host should exhibit good “sodiophilicity” to facilitate Na metal infusion,

high surface area to reduce local current density, and good stability to avoid side reactions with electrolytes.

So far, several hosts have been designed for Li-based composite anodes, which demonstrated significantly improved electrochemical performances.^[25] For instance, freestanding and flexible reduced graphene oxide (rGO) and Li metal (rGO-Li) anodes were fabricated by Cui and co-workers (Figure 5e).^[81] Following a similar strategy, rGO-Na anodes were also developed to enhance the cycling stability of a Na-CO₂ battery (Figure 5f).^[82] By adding only 4.5% of rGO, the Na@rGO composite prepared by Luo and co-workers exhibited low reactivity towards their electrolyte and significantly enhanced tensile strength and hardness.^[83] Moreover, wood-derived porous carbon materials with vertical channels were reported by Hu and co-workers as a 3D porous host for Na metal.^[84] Sun and co-workers further developed this infusion strategy and prepared Na/N-doped carbon nanotube (NCNT) decorated carbon paper (CP) (Na@CP-NCNTs) anodes for Na-metal batteries.^[85]

3.4. Solid-State Electrolyte Engineering

Since Na metal anodes undergo unwanted side reactions with liquid electrolytes, it is crucial to assess whether solid electrolytes (SEs) can replace them in practical applications. SEs are envisaged to play an important role for future batteries by performing two tasks: (i) being a physical barrier to diffusion of unwanted side products from cathode to anode; (ii) posing a mechanical barrier to the formation of dendrites. **Figure 6** outlines this dual role of the SEs, whereas the minimum requirement for a SE is high ionic conductivity for Na-ions. The following section will give a brief overview of some popular Na-ion-conducting SEs. We discuss their physicochemical and mechanical properties for successful use as envisaged protective layer for solving the aforementioned challenges.

3.4.1. Preventing “Cross-Talk” and Dendrite Growth

Various reaction intermediates or discharge products can be dissolved in the commonly used LE. These dissolved species, such as polysulfides in Na-S batteries and superoxide in Na-O₂ batteries, freely diffuse and migrate from one electrode to the other, allowing, what is known as “cross-talk” between the electrodes (Figure 6).^[15,18,86] All-solid-state batteries with SEs would be the ideal solution to this problem since they immobilize any species except the intended metal ion to transport. However, inorganic SEs often suffer from sluggish transport and poor interface kinetics.^[87] Furthermore, discharge products of metal air batteries, such as Li₂O₂ and NaO₂, are electrical insulators and therefore require liquid electrolytes to solvate reactants, intermediates, or redox mediators.^[88,89] For this purpose, the so-called hybrid battery setup (Figure 6) was introduced. It comprises solid electrolyte as an ion-selective barrier to separate the liquid electrolyte in anode and cathode thus preventing the unwanted shuttling of soluble species to the metal anode.^[90,91]

Monroe and Newman proposed that inhomogeneous plating on a Li metal anode can be prevented if the shear modulus G of the separator is greater than that of Li metal ($G > 1.8 G_{\text{Li}}(T)$), where T is the temperature at which the Li electrode is operated.^[92] At room temperature, this condition is met at $G \approx 6$ GPa. Later, Balsara and co-workers used nanostructured lamellar block copolymer electrolytes to verify the proposed values by Monroe and Newman.^[93] Since, most inorganic SEs have a very high Young’s modulus in the range of 10–200 GPa, they meet the aforementioned condition for G very well.^[94,95] However, several experimental reports suggest even robust SEs succumb to short-circuit due to dendrite formation.^[96,97] A certain elasticity of the SEs applied should prevent them from breaking.^[98] Similar principles of failure are applicable for dendrite growth through Na-ion-conducting SEs that are used as protective layer on Na anodes.^[99]

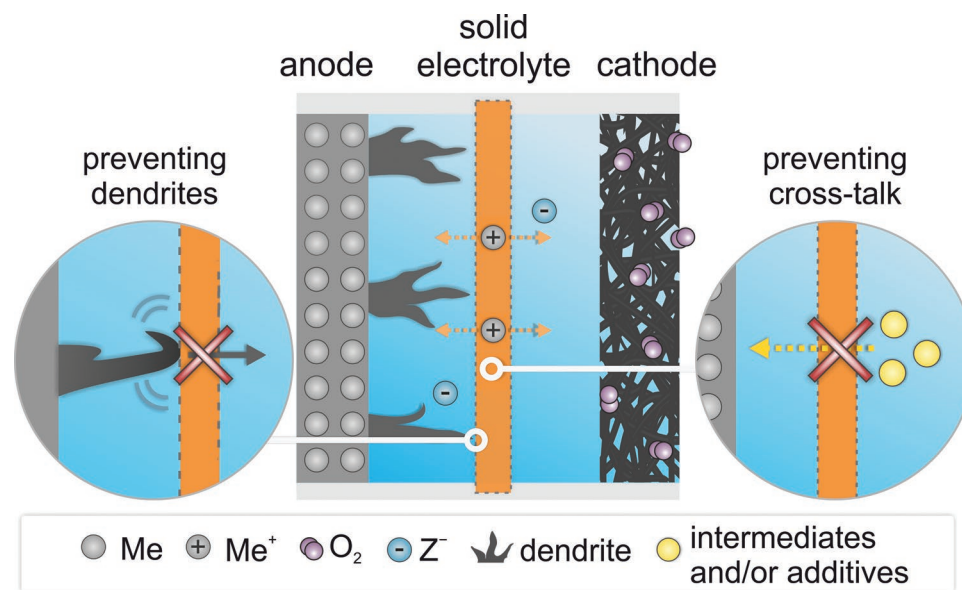


Figure 6. Schematic diagram of a battery with liquid electrolyte using solid electrolyte as a protective layer on a metal anode serving the multiple purposes of (1) preventing the transfer of unwanted species to the highly reactive metal anode to stop deleterious side reactions and (2) reducing the growth of dendrites due to high mechanical strength of the solid electrolyte.

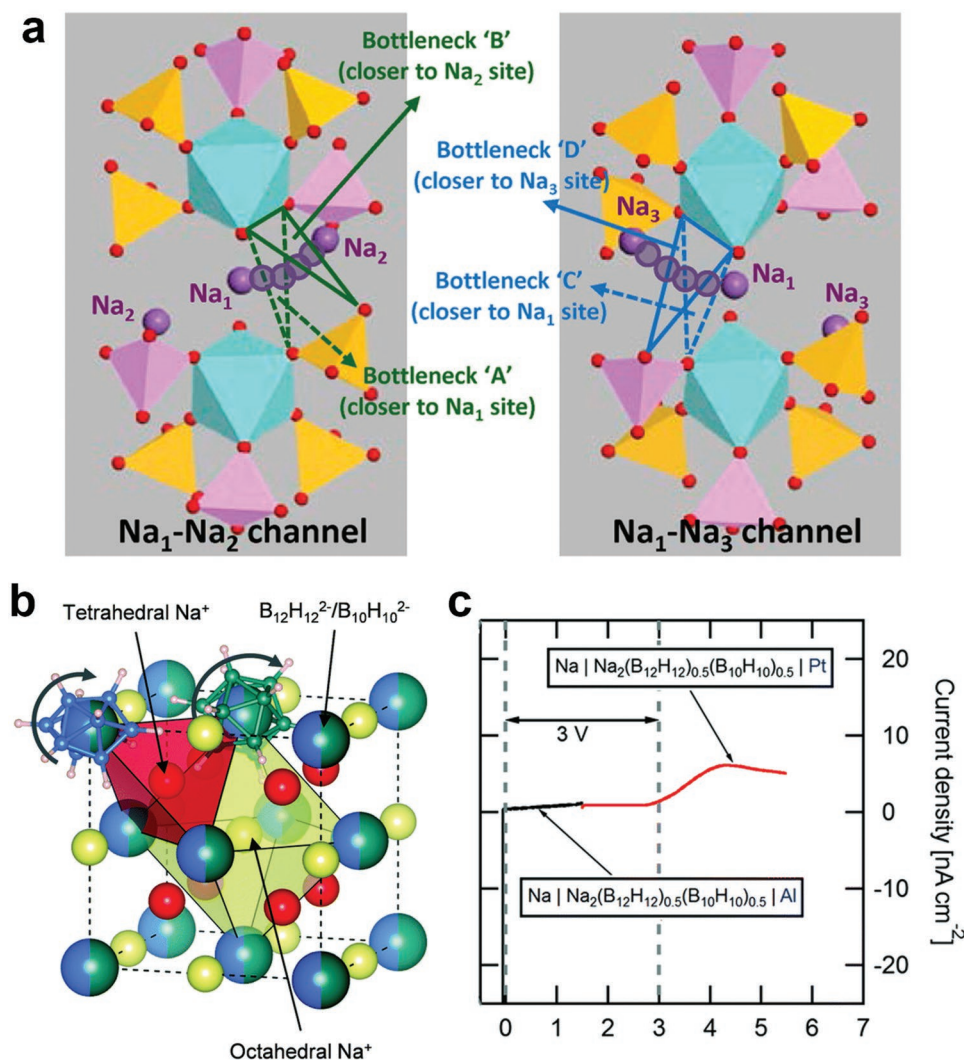


Figure 7. a) Structure of monoclinic NASICON showing the four different types of bottlenecks in Na-ion transport. Reprinted with permission.^[103] Copyright 2016, American Chemical Society. b) Simplified structure of Na₂(B₁₂H₁₂)_{0.5}(B₁₀H₁₀)_{0.5}—a highly promising type of SE; c) cyclic voltammetry tests showing the electrochemical stability window. The large B₁₂H₁₂²⁻ and B₁₀H₁₀²⁻ ions freely rotate allowing high mobility of Na-ions. (b,c) Reproduced with permission.^[108] Copyright 2017, The Royal Society of Chemistry.

3.4.2. Optimizing Properties of Solid Electrolytes

SE materials for Na-based batteries can be mainly categorized into organic (i.e., polymer-based^[100]) and inorganic. Polymer-based SEs exhibit good film-forming properties and good contact between anode and electrolyte, but they suffer from poor ionic conductivity at room temperature, poor mechanical strength, and low ion transference number.^[100] Inorganic SEs on the other hand exhibit high conductivity, high transference number, and very high mechanical strength, but many SE phases are chemically reduced by Na metal and degrade quickly. For a more comprehensive overview on SE materials, we refer the reader to recent literature.^[18]

Na-β''-Al₂O₃ is the best-known SE material with a Na-ion conductivity of 7.80 mS cm⁻¹ (for powder samples), which is enough to make it commercially viable.^[101] The NASICON structure type Na₃Zr₂Si₂PO₁₂ with open 3D channels for the transport of Na-ion is the second best SE material with a

specific conductivity of 0.56 mS cm⁻¹ and an activation energy of 0.37 eV for the transport of ions.^[102] The NASICON structure has four different “bottleneck regions” that connect the adjacent sites in the Na-ion conduction pathway as illustrated in Figure 7a.^[103] The size of the bottleneck region, and therefore the ionic conductivity, can be increased either by using a smaller ion like Sc³⁺ compared to Zr⁴⁺ or by simply using 10% excess of Na in Na₃Zr₂Si₂PO₁₂.^[102–104] Among the oxide SEs, Na-β''-Al₂O₃ is known to be stable in contact with Na metal while NASICON-type electrolytes react with Na to form a thin passivation layer, which can then function as a stable interphase to prevent further reaction. Such interphase formation in situ can improve the contact between SE and Na and allows for better charge transfer kinetics, but it may also lead to impedance increase depending on the composition of the interphase.^[105]

Going from oxide to sulfides, the larger ionic radius of S atoms not only reduces its electrostatic interaction with Na-ion

but also makes the anion lattice more dynamic (or deformable) due to its high polarizability. Sulfide SEs therefore generally exhibit higher ionic conductivity compared to oxides. For the same reason, they are more malleable, enabling not only easy device fabrication, but also low grain boundary resistance. Na₃PS₄ is one of the most common sulfide SEs.^[106] However, sulfides in general suffer from poor chemical stability and low electrochemical stability as compared to oxides. The electrochemical stability of most sulfide SEs lies between 2.3 and 2.7 V (vs Na⁺/Na).^[107]

Another interesting class of SEs is the class of complex hydrides, for example, NaAlH₄ and Na₃AlH₆, which were shown to have an ionic transference number for Na-ions close to 1.^[108] Hydrides with large anions, such as Na₂(B₁₂H₁₂)_{0.5}(B₁₀H₁₀)_{0.5}, show a very high ionic conductivity of 0.9 S cm⁻¹ at RT since they possess a highly flexible ionic lattice (Figure 7b). However, like sulfides, these electrolytes suffer from a narrow electrochemical stability window of around 3 V (Figure 7c). The promising aspect of these hydride systems is that they are not only chemically stable and inert to O₂ and H₂O at RT but also stable in contact with Na, which has been one of the major bottlenecks for the use of SEs in metal anode-based batteries.

4. Outlook and Future Perspectives

Developing efficient and stable Na anodes in Na-based batteries is one of the ultimate, yet challenging goals for the development of high-energy low-cost energy storage systems. What has been achieved for Li anodes can be extended to Na anodes. However, the lack of fundamental understanding of the cell chemistry of Na-based systems requires more in-depth investigations. With the aid of cutting-edge characterization technologies, further research on experimental and theoretical studies must be conducted to unravel the Na nucleation and growth mechanism and its relationship to SEI formation.

To optimize liquid electrolytes, the choices of electrolyte salts and solvents are decisive for the quality of the SEI that forms on top of the Na metal anode. By increasing the concentration of electrolyte salts, the electrochemical properties of the liquid electrolyte can be optimized, and the formation of Na dendrites can be effectively suppressed. In addition, the properties of SEIs can be tailored by adding small amounts of electrolyte additives as film-forming agents. However, side reactions between electrolytes and other battery components and increased costs induced by the additives need to be carefully evaluated.

To construct artificial SEIs with enhanced properties, a thin coating film on Na anode should possess not only high ionic conductivity but also appropriate flexibility with a high elastic modulus and a compact structure. With the development of advanced thin-film coating technologies, such as ALD, MLD, spin coating, doctor-blade coating, and roll-press processing, it is expected that large-scale manufacture of artificial SEI protected Na anodes will be feasible in the future.

Designing a suitable host for Na metal is necessary to constrain the severe volume change during repeated Na stripping/plating process. The host materials should possess good

“sodiophilicity” to facilitate Na metal infusion, and a high surface area to reduce local current density. They also need to exhibit good chemical, electrochemical, and mechanical stability to avoid side reactions with electrolytes. Meanwhile, the weight and volume percentage of the host in the composite electrode should be carefully controlled to maximize the energy density of the entire battery. In our opinion, the cost and feasibility for mass production of the host materials, especially components such as graphene and carbon nanotubes, need to be considered for the future fabrication of Na metal-based batteries.

To realize different Na-based battery systems such as high-energy Na-O₂ batteries and Na-S batteries, further challenges need to be resolved. For instance, “cross-talk” between the electrodes induces continuous side reactions on the surface of Na metal anodes as illustrated in Figure 6. Therefore, practical Na metal-based batteries might be realized via SEs. The SEs can thereby serve the dual purpose of providing a barrier with high mechanical strength to prevent dendrite growth and to stop shuttling of species between the electrodes to prevent unwanted side reactions. After years of extensive investigations, SEs with ionic conductivity comparable to (or at least close to) that of liquid electrolytes have been developed. Currently, it might be time to concentrate research efforts on further open issues, such as the chemical stability of interphases and the electrochemical stability window of SEs. The chemical stability needs to be assessed on different sides of the interphases: (a) in contact with metal anode, (b) against a cathode for an all-solid-state battery, (c) in contact with organic electrolytes and redox mediators for metal-oxygen batteries, and (d) against polysulfides and other reaction intermediates for metal-sulfur batteries.

Since we have shown the rapid progress in various fields of applied research on advanced materials for Na metal anodes, we believe that the mutual challenges that persist can be jointly tackled in the future with interdisciplinary research. In the end, this will help to propel the highly promising Na-based battery technologies.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

artificial solid electrolyte interphases, dendrite growth, electrode engineering, electrolyte engineering, sodium metal anodes

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