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Introduction for Anode-Free Batteries

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1.1 Development of Rechargeable Batteries

1.1.1 Brief History of Traditional Rechargeable Batteries

Rechargeable batteries, which realize the highly reversible conversion between chemical energy and electrical energy through Faraday reactions on the electrodes, have a long development history of two centuries. Nowadays, with the increasing demand for higher energy density, improved safety, and sustainable resource utilization, rechargeable batteries have evolved from primitive electrochemical devices to critical technology powering modern society. The genesis of rechargeable batteries can be traced to 1800, when Alessandro Volta invented the "voltaic pile"—the first operational electrochemical cell—comprising alternating zinc and silver disks separated by electrolyte-soaked paper [1]. This breakthrough laid the foundation for electrochemistry, inspiring subsequent innovations. In 1836, John Frederic Daniell developed the well-known Daniell cell, using copper and zinc electrodes and sulfuric acid electrolyte, which delivered sustained currents [2, 3]. In 1859, Gaston Planté invented the first practical rechargeable system, lead-acid battery, which is featured with high power density and low cost and remains widely used in automotive applications nowadays [4]. After that, diverse rechargeable batteries were invented. In 1866, Georges Leclanché developed the zinc-manganese dioxide ($Zn\text{-}MnO_2$) dry cell, which is a precursor to modern alkaline batteries but belongs to a primary battery, greatly advancing portable energy storage technology. In 1878, French engineer Maichéa invented a zinc–air cell with ammonium chloride-based electrolyte, opening an avenue for metal–air batteries [5]. In 1932, Heise and Schumacher created the first alkaline zinc–air battery, which is still a hot research field today [6]. In this period, battery systems were limited by low energy density, short cycle life, and heavy weight, restricting their applications to stationary or large-scale devices.

Early in 1913, the electrode potential of lithium metal was studied by Lewis and Keyes [7], but it was not until the 1970s that lithium batteries were greatly developed. In the 1970s, M. S. Whittingham fabricated the lithium metal battery using titanium disulfide (TiS_2) as the cathode material and metallic lithium as the anode material, laying the foundation for rechargeable lithium batteries [8]. However, the use of metallic lithium anodes led to severe safety issues due to lithium dendrite growth, limiting their practical application. In 1980, Armand proposed the concept of "rocking chair batteries," characterized by the "rocking" movement of lithium ions between the positive and negative electrodes during charge and discharge cycles [9]. On the other hand, the discovery of intercalation compounds paved the way for lithium-ion batteries, which eliminated the safety hazards of metallic lithium anodes in primary batteries. In 1980, J. B. Goodenough and his team developed lithium cobalt oxide ($LiCoO_2$) as a cathode material, which exhibited high specific capacity and structural stability [10]. In 1985, Yoshino of the Asahi Kasei Corporation and Sony developed the first $LiCoO_2$–graphite battery, resolving dendrite growth and cycle stability issues [11]. In 1991, Sony commercialized the first lithium-ion battery, offering an energy density of ~80 Wh kg^{-1}, double that of a typical lead–acid battery, thus revolutionizing portable electronics [12]. After that, lithium-ion battery technology has been rapidly developed, and enormous advancements were achieved in cathode materials (e.g., polyanion compounds [e.g., lithium iron phosphate ($LiFePO_4$)] [13] and nickel–manganese–cobalt oxides (NMCs) [14]), anode material (e.g., carbonaceous materials [15] and silicon-based anodes [16, 17]), and electrolyte formulations [18], which comprehensively enhanced safety, cycle life, and energy density of lithium-ion batteries, driving the adoption of lithium-ion batteries in portable electronics, electric vehicles (EVs), and grid energy storage systems (ESS) [19]. In recent years, solid-state electrolytes have gained extensive attention for their potential to address safety concerns and further boost performance [20]. For the present, lithium-ion batteries have occupied the center stage of the rechargeable batteries market for decades, owing to their high energy density and cycling stability, as well as the reduced cost by sophisticated industrialization.

1.1.2 Development of Metal Batteries

The origin of lithium metal battery dates back to 1913, when Lewis and Keyes fabricated the first lithium metal battery, consisting of metallic lithium electrode, lithium amalgam electrode, and lithium iodide saturated propylamine electrolyte [7]. It was realized that Li is the most electromotive metal, which theoretically suggested the lithium metal as the "ultimate anode" for high-energy-density batteries. However, until the 1970s, the efforts to tackle the problems of lithium metal anode, including dendrite growth and low efficiency of Li stripping/redepositing, yielded little success, which led to a shift in the research direction of batteries from lithium metal batteries to lithium-ion batteries [15]. With the rapid development of lithium-ion batteries, the energy density of single cells has approached their limit of ≈350 Wh kg^{-1} [21]. Therefore, it is necessary to explore battery systems with higher

energy density to meet the growing demand for electrochemical energy in modern society. Lithium metal is known as the "holy grail" of anode materials due to its high theoretical capacity (3860 mAh g^{-1}) and the lowest electrode potential (−3.04 V vs. standard hydrogen electrode [SHE]). Against this background, lithium metal batteries have rekindled people's interest in the 21st century [22]. The primary issues in developing lithium metal batteries are the intractable problems of lithium dendrite growth and low lithium metal stripping/plating efficiency. Since the 2000s, research on constructing room-temperature rechargeable metal batteries has begun to flourish. A series of fundamental studies on electrolyte exploration [23, 24], electrode structure design [25], and lithium metal deposition behavior [26, 27] have started to increase, and knowledge of the electrochemical properties and improvement strategies of lithium metal anodes has greatly enriched. To date, the main strategies for improving the performance of lithium metal anodes include solid electrolyte interphase (SEI) engineering and structure design of lithium metal anode [28, 29]. At present, the operating temperature range of lithium metal batteries has been extended to −40 to 80 °C, the cycle life has exceeded 1000 cycles, and the energy density of single pouch cells is close to 500 Wh kg^{-1} [30–32], showing prospects for practical application. However, further improving the reversibility and safety of lithium metal anodes [33], as well as large-scale preparation of thin lithium metal films to reduce the redundant use of lithium metal [34, 35], still urgently need further exploration.

Despite the great advantage of lithium metal batteries in high energy density, the scarcity of lithium resources and rising material costs have spurred intensive research into post-lithium metal battery technologies. Therefore, leveraging earth-abundant elements and environmentally benign chemistries, various novel rechargeable batteries have been developed as replenishment or alternatives to lithium metal batteries, including sodium metal batteries [36], potassium metal batteries [37], calcium metal batteries [38], magnesium metal batteries [39], aluminum metal batteries [40], and zinc metal batteries [5], have emerged as viable candidates for large-scale energy storage and low-cost applications. Among them, the performances of sodium metal batteries and zinc metal batteries have shown rapid improvement in recent years, demonstrating great prospects for practical application.

Sodium metal batteries are currently the most studied alkali metal batteries besides lithium metal batteries, owing to the similar electrochemical principles of Na-ion storage to the Li counterparts but with much lower cost of battery materials [41]. However, compared to lithium metal, the larger atomic size (1.06 vs. 0.76 Å for Li), higher atomic weight (23 vs. 6.9 g mol^{-1} for Li), and higher redox potential (−2.71 vs. −3.05 V for Li) of Na metal theoretically compromise the energy density of sodium metal batteries. Combined with the high abundance and low cost of Na minerals, sodium metal batteries could be a cost-effective alternative, in which weight and energy density are minor factors [42]. Intensive researches have been devoted to developing diverse sodium metal-based battery systems, including room-temperature Na–S, Na–O_2, Na–CO_2, and all-solid-state Na metal batteries [36, 43]. The problems for sodium metal anode are similar to those of its lithium

counterpart, including uneven metal deposition and poor metal stripping/plating reversibility [44]. By electrolyte engineering and electrolyte structure design, for the present, sodium metal batteries have gained great advancement in performance. For example, the energy density of a pouch sodium metal battery can reach up to 180 Wh kg^{-1} [45], and the cycling life of the NMC622-based Na metal batteries achieved 1000 cycles with 89.8% capacity retention [46].

Compared with nonaqueous lithium metal batteries and sodium metal batteries, aqueous zinc metal batteries offer unique advantages for stationary storage, including low cost, nontoxicity, nonflammable, and easy recyclability. Zinc metal batteries also have the longest historical lineage among post-lithium-ion systems, dating back to Alessandro Volta's voltaic pile in 1800. After the exploration of various cathode and electrolyte systems, rechargeable Zn–NiOOH batteries were invented in 1899 [47], and the rechargeable Zn–MnO_2 batteries were developed in the 1970s [48], which are still two important categories of zinc metal batteries today. However, the performance of alkaline rechargeable zinc metal batteries remained unsatisfactory, primarily due to issues with zinc anode corrosion, dendrite growth, and cathode instability in alkaline electrolytes [49]. For decades, zinc metal batteries were overshadowed by the rapid development of lithium-ion batteries, which offered higher energy density and better cycling performance. However, the inherent benignity of aqueous zinc metal batteries kept research alive in academic and niche industrial settings [50, 51]. The 2010s marked a renaissance for rechargeable zinc metal batteries, driven by the need for safe, low-cost energy storage. A critical shift from alkaline to neutral or weakly acidic aqueous electrolytes addressed many historical challenges: neutral electrolytes reduce zinc corrosion, while high ionic conductivity (10–100 mS cm^{-1}) enables high power density [52]. In 2012, Xu et al. reported a rechargeable zinc battery using a manganese dioxide (MnO_2) cathode, zinc metal anode, and mild aqueous zinc sulfate or nitrate electrolyte, achieving a discharge capacity of ~100 mAh g^{-1} after 100 cycles at 6C rate [53]. This work sparked intense research interest, leading to rapid advancements in both cathode and zinc anode materials. Key cathode innovations included the development of vanadium-based oxides (e.g., $V_2O_5 \cdot nH_2O$), manganese-based oxides (e.g., α-MnO_2), and Prussian blue analogs (PBAs), offering specific capacities ranging from 200 to 500 mAh g^{-1} [54]. Anode advancements focused on suppressing dendrite growth and side reactions on Zn metal anode [55]. Electrolyte development progressed from liquid to gel and quasi-solid-state systems, improving safety and mechanical stability [56, 57]. The 2020s have seen accelerated industrialization of zinc metal batteries, driven by safety concerns and cost pressures in the energy storage market. Today, zinc metal batteries are emerging as a promising candidate for low-cost, safe energy storage with fast industrialization progressing [58].

1.1.3 The Rise of Anode-Free Batteries (AFBs)

The escalating demand for high-energy-density, low-cost, and safe ESS has driven the continuous evolution of battery technologies. Traditional lithium-ion batteries, despite their widespread application, are constrained by limited energy

density (~300–400 Wh kg^{-1}) due to the low theoretical capacity of graphite anodes (372 mAh g^{-1}) [59, 60]. Metal-based batteries (e.g., lithium metal batteries and sodium metal batteries) address this limitation by using high-capacity metal anodes (e.g., Li: 3860 mAh g^{-1} and Na: 1166 mAh g^{-1}), but their pre-deposited metal anodes introduce critical issues: severe lithium dendrite growth leading to short circuits, high material costs, complex manufacturing processes, and safety hazards [34, 35]. In this context, AFBs have emerged as a game-changing alternative [61].

The development of AFBs is closely associated with advances in the reversible metal electroplating/stripping. As early as the 2000s, researchers began exploring the possibility of using *in situ* deposited metal as anodes in lithium batteries. In 2000, Neudecker et al. reported a "lithium-free" battery without a prefabricated lithium anode, using a Cu current collector to host *in situ* deposited lithium, $LiCoO_2$ cathode and solid lithium electrolyte (LiPON), which laid the conceptual foundation for AFBs [62]. However, this early prototype suffered from poor cycling stability to inadequate reversibility of the anode. Throughout the 2000s, research on AFBs remained sporadic, overshadowed by the rapid development of lithium-ion batteries and conventional lithium metal batteries. A deeper understanding of the behavior of lithium plating and stripping was gained by intensive fundamental works [63, 64]. The main challenges of AFBs included the lack of suitable electrolytes to stabilize metal deposition, poor current collector compatibility, and limited understanding of the interfacial chemistry between metal deposits and electrolytes [65]. The revival of interest in AFBs arose in the 2010s, driven by the growing demand for high-energy-density batteries and advancements in electrolyte chemistry and materials science. Representative studies contributed to the development of AFBs. In 2016, Qian et al. developed an anode-free Cu||$LiFePO_4$ cell using highly concentrated lithium bis(fluorosulfonyl)imide (LiFSI)-1,2-dimethoxyethane (DME) electrolyte, which deliver high initial discharge capacities and an average Coulombic efficiency (CE) of higher than 99.8% during 100 cycling, demonstrating as a performance milestone [66]; in 2018, Nanda et al. reported the first anode-free lithium–sulfur cell comprising an Li_2S cathode and a bare copper foil on the anode side [67]. These early explorations contributed to the comprehension of the basic design principles and identified critical technical bottlenecks for AFBs.

The anode-free post-lithium batteries experienced booming development in the 2010s [68, 69]. The first study was reported in the field of sodium battery in 2017, when Cohn et al. fabricated an anode-free sodium battery based on the electrode consisting of in situ plated sodium on an Al current collector [70]. Then the anode-free sodium batteries experienced fast advancement in the following years [71]. Some state-of-the art works were listed below. In 2023, Wang et al. realized a high CE of 99.80% for potassium-based AFBs at −40 °C by adopting polydimethylsiloxane (PDMS) as an electrolyte additive. Rapid progress has also been achieved in current collector development [72]. In 2024, an anode-free sodium borohydride electrolyte-based all-solid-state battery full cell was fabricated by Deysher et al., which exhibited stable cycling for several hundred cycles [73]. In the same year, Wang et al. reported the first low-temperature anode-free sodium battery by synergetic surface modification of the current collector and electrolyte design,

which achieved a high energy density of 110 Wh kg^{-1} at −40 °C [74]. In 2025, the same group further reported an Ah-level anode-free pouch Na cell with a high cell-level energy density of 209 Wh kg^{-1}, by developing a sole-solvent high-entropy electrolyte [75], demonstrating the great prospect of AFBs for practical application.

In the 2020s, AFBs have transitioned from laboratory research to industrialization exploration. With the global push for EVs with longer driving ranges and grid-scale energy storage with lower costs, AFBs have attracted increasing research interest in recent years. In 2024, Contemporary Amperex Technology Co., Ltd. (CATL) revealed a technical route for the design of AFBs, focusing on optimizing the battery configuration. Additionally, several startups (e.g., CATL and QuantumScape) have invested in anode-free technology, aiming to commercialize it for portable electronics and EVs in the near future.

1.2 Fundamentals of AFBs

1.2.1 The Conceptualization of AFBs

The concept of AFBs originated from the pursuit of simplifying metal-based battery designs and addressing the safety issues of pre-deposited metal anodes by eliminating the prefabricated metal anode altogether. Instead, AFBs utilize metal ions dissolved in electrolytes to *in situ* deposit onto a conductive current collector during the first charging cycle, forming a temporary metal anode. This unique design maximizes energy density by reducing the dead weight and volume of the battery. For example, lithium-based AFBs can theoretically reach an energy density of over 500 Wh kg^{-1}, which is ∼100% higher than that of conventional lithium-ion batteries (150–260 Wh kg^{-1}). For sodium-based AFBs, theoretical energy density can reach 300 Wh kg^{-1}, which is 80% higher than that of energy-dense sodium-ion batteries (∼160 Wh kg^{-1}) and comparable to that of lithium metal batteries (∼350 Wh kg^{-1}), but with a lower cost [76]. On the other hand, the removal of the pre-deposited metal anode would greatly reduce the material cost of AFBs. Additionally, the absence of the pre-deposited anode simplifies the battery manufacturing process, reducing the number of production steps (e.g., anode coating and calendering) and equipment requirements. This simplification enables easier scalability and higher production efficiency [61]. Overall, AFBs offer unique advantages over conventional battery systems, making them highly attractive for next-generation energy storage applications.

1.2.2 The Configuration of AFBs

AFBs consist of four basic components: cathode, electrolyte, current collector (replacing the pre-deposited anode), and separator. As shown in Figure 1.1, the metal anode is formed during the battery charging process, when the metal ions in the electrolyte are deposited as metal on the current collector of the negative electrode. The material system is quite similar to that for the corresponding metal batteries, but a metal-rich cathode and highly reversible metal plating/stripping are

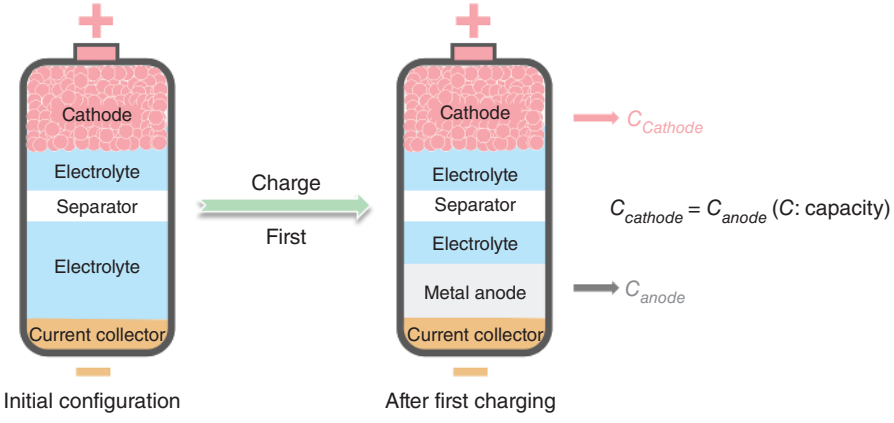

Figure 1.1 Typical configuration of anode-free metal batteries and the in situ formation of a metal anode on the negative electrode during battery charging. *Source:* Wang et al. [69] / with permission of the Royal Society of Chemistry.

necessary for the stable cycling of AFBs. Common material selections for AFBs are briefly introduced as follows.

1.2.2.1 Cathode Materials

The cathode in AFBs serves two key roles: providing a high capacity of metal ions (e.g., Li^+, Na^+, and Zn^{2+}) as the metal source for metal plating on the negative electrode (current collector) and enabling reversible ion intercalation/deintercalation. The ideal cathode material should have high specific capacity, high ionic conductivity, good structural stability, and compatibility with electrolytes. Common cathode materials for lithium-based AFBs include layered oxides (e.g., $LiNi_xCo_\gamma Mn_{1-x-y}O_2$ [NCM] and $LiNi_xCo_\gamma Al_{1-x-y}O_2$ [NCA]) and polyanionic compounds (e.g., $LiFePO_4$ [LFP] and $Li_3V_2(PO_4)_3$ [LVP]). For sodium-based AFBs, the cathodes include layered oxides (e.g., $NaNi_xCo_\gamma Mn_{1-x-y}O_2$ [NCM-Na]), polyanionic compounds (e.g., $Na_3V_2(PO_4)_3$ [NVP]), and PBAs (e.g., $NaFe[Fe(CN)_6]$). For aqueous zinc-based AFBs, the cathodes mainly include zinc-rich or pre-zincificated vanadium oxides (e.g., $Zn_3V_3O_8$) and manganese oxides (e.g., $ZnMn_2O_4$).

1.2.2.2 Electrolytes

Electrolytes in AFBs play a pivotal role in transporting metal ions, enabling uniform metal deposition, and forming a stable SEI layer. The key requirements for AFB electrolytes include high ionic conductivity, good compatibility with cathodes and current collectors, low flammability, and the ability to suppress dendrite growth. Common electrolytes for lithium-based AFBs include high-concentration electrolytes (HCEs, e.g., 4 M LiFSI/DME), localized high-concentration electrolytes (LHCEs), and additive-modified electrolytes (e.g., LiFSI + fluoroethylene carbonate [FEC]). Besides, solid-state electrolytes, such as garnet-type electrolytes (e.g., $Li_7La_3Zr_2O_{12}$, LLZO) and sulfide-based electrolytes (e.g., Li_2S-P_2S_5), have been reported for anode-free lithium batteries, offering high ionic conductivity

($\sim 10^{-3}$ S cm^{-1}) and mechanical strength. For sodium-based AFBs, the electrolytes typically use $NaPF_6$ or NaFSI dissolved in ether solvents (e.g., DME), with additives such as FEC to enhance interface stability. For zinc-based AFBs, aqueous electrolytes (e.g., 2 M $ZnSO_4$ and $Zn(OTf)_2$) are widely used due to their high safety and ionic conductivity. Functional additives or cosolvents are usually used to suppress zinc dendrite growth and side reactions.

1.2.2.3 Current Collectors (for Negative Electrode)

The current collector in AFBs serves as the substrate for *in situ* metal deposition, replacing the pre-deposited metal anode. The ideal current collector should have high electrical conductivity, large specific surface area, good compatibility with metal deposits, and the ability to promote uniform nucleation. In general, metallic current collectors are used for AFBs. Copper (Cu) is the most commonly used metallic current collector for lithium- and zinc-based AFBs, due to its high conductivity and compatibility with lithium and zinc deposition. Aluminum (Al) is usually used for sodium-based AFBs owing to the compatibility between Na metal and Al, which do not undergo alloying reactions as well as the low cost and light weight of the Al current collector. The physicochemical properties of the current collector surface are critical to the reversibility of metal plating/stripping. Therefore, modification of current collectors is commonly conducted. Carbon-based materials, including graphene, carbon nanotubes (CNTs), and porous carbon materials, are generally used to modify metallic current collectors, aiming at enhancing surface area and promoting uniform metal nucleation.

1.2.2.4 Separators

The function of separators in AFBs is the same with metal batteries, which includes preventing short circuits between cathode and current collector while enabling metal ion transport. Key requirements include high porosity, good ionic conductivity, thermal stability, and compatibility with electrolytes. Polymer separators are widely used for nonaqueous AFBs, such as polyolefin separators (PE, PP), while cellulose and glass fiber separators are used for aqueous zinc-based AFBs. Modified separators, such as ceramic-coated separators (e.g., Al_2O_3 and SiO_2-coated PE), help in promoting the reversibility of AFBs with improved thermal stability and electrolyte wettability. Functional separators with ion-selective layers (e.g., Nafion-coated separators for zinc-based AFBs) are also reported to suppress unwanted side reactions and enhance ion transport.

1.2.3 The Working Principle of AFBs

The working principle of AFBs is fundamentally different from that of conventional batteries, relying on *in situ* metal deposition onto the current collector during charging and metal dissolution during discharging. The process involves three key steps: metal-ion de/intercalation from/into the cathode, metal-ion transport through the electrolyte, and metal deposition/dissolution on the current collector, accompanied by SEI formation and evolution. The working principle of AFBs can be described as follows.

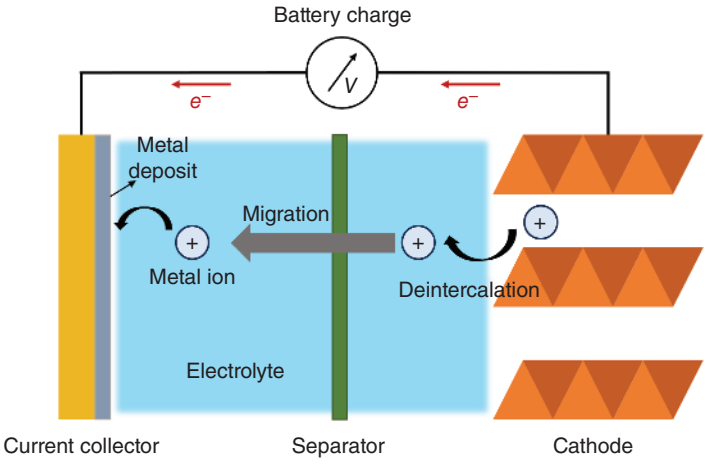

Figure 1.2 The illustration of the charging process of anode-free metal batteries.

Charging Process (illustrated in Figure 1.2):

Cathode reaction: Metal ions (M^{n+}, e.g., Li^+, Na^+, K^+, and Zn^{2+}) deintercalate from the cathode material, and the specific cathode reactions are dependent on the category of electrode material. For example, in a lithium-based AFB with an NCM811 cathode, the charge reaction of the cathode is:

$$LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2 \rightarrow Ni_{0.8}Co_{0.1}Mn_{0.1}O_2 + Li^+ + e^-$$

Metal deposition and SEI formation: The metal ions are reduced into metal deposits at the current collector, forming the temporary metal anode (e.g., Li, Na, K, and Zn). Accompanied by the metal deposition process, electrolyte decomposition occurs at the metal–electrolyte interface, forming a SEI layer. The SEI layer is critical for stabilizing the metal deposit, preventing further electrolyte decomposition, and suppressing dendrite growth. For example, in a lithium-based AFB, the metal deposition at the negative electrode is:

$$Li^+ + e^- \rightarrow Li$$

The SEI layer in alkali metal-based AFBs typically consists of inorganic compounds (e.g., metal fluorides and metal oxides) and organic compounds (e.g., metal alkyl carbonates), formed by the decomposition of electrolyte salts and solvents. For zinc-based AFBs, inorganic species (e.g., zinc fluorides, zinc oxides, and zinc sulfide) are the common components of the SEI layer due to the decomposition of water solvent and other electrolyte components.

Electron conduction and ion transport: Driven by the electric field, electrons flow from the cathode to the anode through the external circuit; meanwhile, the deintercalated metal ions migrate from the cathode through the electrolyte and separator toward the current collector.

Discharging Process (illustrated in Figure 1.3):

Cathode intercalation: Metal ions are intercalated into the cathode material, completing the discharge cycle. For example, in lithium-based anode-free batteries

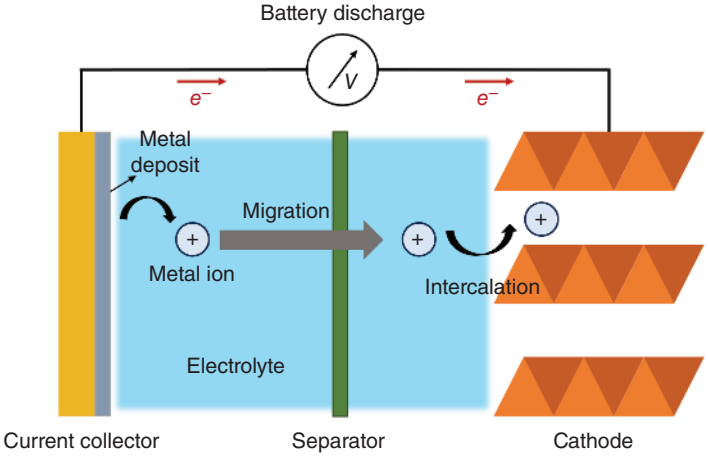

Figure 1.3 The illustration of discharging process of anode-free metal batteries.

with an NCM811 cathode, the cathode reaction is:

$$Ni_{0.8}Co_{0.1}Mn_{0.1}O_2 + Li^+ + e^- \rightarrow LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$$

Metal dissolution: The *in situ* deposited metal layer acts as the anode. The metal layer on the current collector is oxidized, releasing metal ions and electrons. For example, in a lithium-based AFB, the metal deposition at the negative electrode is:

$$Li \rightarrow Li^+ + e^-$$

Electron conduction and ion transport: Driven by the electric field, electrons flow from the anode to the cathode through the external circuit; meanwhile, metal ions migrate from the anode through the electrolyte and separator back to the cathode.

1.3 The Issues and Strategies of AFBs

1.3.1 Critical Issues for AFBs

Despite the rapid advancement in AFBs, there exist great challenges that hinder their practical application. These challenges mainly originate from the extremely low N/P ratio (the capacity ratio of the negative to positive electrode, theoretically equal to 1:1 after the first battery charging), which results in a high dependence of full cell performance on the performance of either electrode, thus raising rigorous requirements for the reversibility of both electrodes. In practice, the poor reversibility of the metal plating/stripping on the negative side usually acts as the limiting factor to the performance of the full cell. Therefore, the critical issues for anode free is concentrated on the anode side, primarily including metal dendrite, dead metal, and unstable SEI.

1.3.1.1 Metal Dendrite

Metal dendrite growth is the most severe issue for AFBs, as needle-like or mossy metal deposits penetrate separators, causing short circuits and thermal runaway. The core mechanism involves heterogeneous nucleation and uncontrolled growth of metal ions on current collectors, driven by thermodynamic (e.g., surface energy and crystal orientation) and kinetic (e.g., ion diffusion and charge transfer) factors. Thermodynamically, heterogeneous nucleation on current collector is favored over homogeneous nucleation due to lower interface energy increment with a smaller metal surface area in the former case. When the nuclei grow preferentially along crystallographic directions with the highest growth rate, metal dendrite tends to form. Li et al. observed a metal dendrite structure formed by Li plating on a copper current collector in carbonate-based electrolytes using cryo-transmission electron microscopy (cryo-TEM) [77]. Especially, when the AFB is charged at high current density, the increased concentration polarization and more severe electric field distribution at the electrode would exacerbate ion depletion at the electrode surface, thus leading to fast metal dendrite growth, which greatly restricts the rate performance of AFBs. For example, Bai et al. found that mossy lithium forms at low current densities (reaction-limited regime), while dendritic lithium grows at the tip after current density exceeding the critical "Sand's capacity" (diffusion-limited regime), the latter of which is capable of penetrating the separator and causing short circuits [78, 79].

1.3.1.2 Dead Metal

Dead metal refers to metal deposits that are electrochemically inactive on the anode. Generally, dead metal formation follows three primary pathways: (i) cracked or overgrown SEI encapsulates metal deposits, blocking electron transfer and ion diffusion; (ii) dendrite detachment results from weak adhesion between metal deposits and CCs, or the crack of dendrite during uneven stripping; (iii) electrochemically inert or insulating byproducts formed in the side reactions between metal deposits and electrolyte species. The dead metal reduces the CE and capacity by irreversibly consuming active metal ions, and lead to fast degradation of battery performance. For example, Fang et al. quantified the inactive lithium on copper current collector after plating and stripping by titration gas chromatography, and it was found that the amount of dead (inactive) Li was consistent with the capacity loss during battery cycling, indicating the great effect of dead Li on battery performance [80].

1.3.1.3 Unstable SEI

The SEI layer forms at the metal–electrolyte interface during initial charging, serving as a barrier to prevent continuous electrolyte decomposition. An unstable SEI not only leads to irreversible consumption of electrolyte and active materials on the electrodes but also exacerbates dendrite growth and dead metal formation. The poor stability of SEI usually originates from the following factors: (i) the poor mechanical toughness of SEI leads to its cracking during the large volume expansion/contraction of the metal deposit; (ii) the uneven or uncompact structure of the SEI fails to prevent corrosion of the metal electrode and result in growing of byproducts; (iii) the

high solubility of SEI leads to continuous reformation. For example, Kang et al. utilized ^{23}Na solid-state nuclear magnetic resonance spectroscopy (NMR) and *ex situ* electron paramagnetic resonance imaging (EPRI) to monitor SEI evolution and composition during Na plating on copper current collector, and it was found that the incomplete and unstable SEI formation accounted for much of the poor performance of anode-free sodium battery [81].

The metal dendrite, dead metal, and unstable SEI of AFBs are not independent problems but rather highly interconnected. An unstable SEI results in exposure of fresh metal to the electrolyte, promoting heterogeneous nucleation (dendrite growth) and corrosion (dead metal formation), while dendrite growth accelerates SEI degradation due to the high growth rate of the metal dendrites, causing SEI thinning and cracking. Dead metal formation not only reduces ion supply but also impedes uniform metal deposition on the metal anode, thus further promoting dendrite growth. Therefore, overall considerations are necessary to develop strategies for comprehensively addressing these issues.

1.3.2 Strategies for AFBs

To improve the performance of AFBs, various strategies are proposed. Basically, these strategies can be classified into three types, including **current collector engineering, electrolyte modulation**, and **metal ion-supply agents**.

1.3.2.1 Current Collector Engineering

The current collector serves as the substrate for *in situ* metal deposition, and its structure (morphology, porosity) and surface properties (surface energy, conductivity) directly govern the nucleation barrier, current density distribution, and metal-current collector adhesion. Therefore, the engineering of the current collector, which encompasses current collector structure design and surface modification, is critical to improving the performance of AFBs. The core design principles include: (i) lowering the nucleation barrier via surface energy optimization; (ii) promoting the formation of thin, compact, and robust SEI; (iii) accommodating the huge volume change of metal deposit during metal plating/stripping.

Modifying current collector with functional coatings (e.g., metal oxides, carbon, and alloy) or defects is the predominant strategy of current collector engineering, which can tailor surface energy to promote uniform nucleation and even modulate the component and structure of the SEI formed on metal deposit. For example, a lithiophilic current collector was developed by loading NiCdCuInZn-based high entropy alloy on a 3D carbon host (denoted as HEA/C) [82]. The high affinity of the alloy facilitated homogeneous Li nucleation and the 3D structure provide multiple ion transport paths, thereby enabling the anode-free NCM811||HEA/C full cell to deliver a high CE of 99.5% at 1°C after 160 cycles. Carbon materials, such as graphene [83], Ketjenblack [81], and graphitic carbon [84], were widely adopted as the coating layer on metallic current collector, which enabled both smooth metal deposition and improved structural stability of SEI, thus promoting the cycling life of the AFBs.

Besides, electrochemical activation of current collector is also an alternative strategy for current collector engineering. Generally, this strategy is intended to remove the impurities and preform SEI on the current collector outside the battery in electrochemical approaches, thus avoiding the irreversible consumption of metal ion source for the SEI formation in the AFB [85]. Current collectors with 3D porous structure are another popular strategy for current collector. The porous structure not only homogenizes the electric field on the electrode but also provides buffering spaces for the volume changes during metal plating/stripping processes, thus improving the morphology of metal deposit and the structural robustness of the electrode. For example, 3D silver nanowire aerogel (AgNWA) was adopted as the current collector for anode-free zinc batteries, which enabled regulated electric field and improved affinity toward zinc metal, thus enabling a capacity retention of 73% for AgNWA//α-MnO_2 AFB after 600 cycles [86]. In another work, a carbonaceous host (derived from triazole metal-organic framework (MOF) fibers by in situ pyrolysis and denoted as MCNF) containing narrowly distributed mesopores was developed as the 3D porous current collector for anode-free potassium batteries [87]. The porous current collector provided extra voids for accommodating the volume change during metal plating/stripping, which greatly promoted the stability of the anode and supported the stable cycling of anode-free MCNF||Prussian blue (PB) potassium cells for 100 cycles.

1.3.2.2 Electrolyte Modulation

The electrolytes of the AFBs not only serve as the medium for ion transport but also dictate the metal plating/stripping behaviors and the formation of SEI on the anode. Therefore, electrolyte modulation is an important and versatile strategy to improve the performance of AFBs. The principles for electrolyte modulation include: (i) ensuring high electrochemical stability of the electrolyte toward both the cathode and the anode; (ii) forming a protective, ion-conductive, and stable SEI; (iii) enhancing metal-ion transport and solvation/desolvation kinetics to reduce concentration polarization and promote uniform metal deposition.

For the electrochemical stability of electrolytes, current research mainly focuses on the rational selection of solvents, among which the electronic energy levels of solvents provide important references for predicting and explaining the electrochemical stability of electrolytes. Specifically, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of solvent molecules describe the thermodynamic difficulties of electron release and uptake, respectively, which dictate the oxidation and reduction resistances of the solvents [88]. From this perspective, solvent molecules with a large gap between HOMO and LUMO energy levels are generally the preferred choice. For example, oxidation-stable succinonitrile (SN) and moderately solvating carboxylic ester were adopted as cosolvents to enlarge the gap between LUMO and HOMO energy levels of the electrolyte for sodium-ion batteries [89]. Benefiting from the enhanced electrochemical stability of the electrolyte, the formation of electrolyte decomposition product, that is, electron-leaking Na_2CO_3, was greatly suppressed, thereby improving the cycling life of the $Na_3V_2O_2(PO_4)_2F$ (NVOPF)|| hard carbon (HC) full battery.

In view of SEI construction on the negative electrode, electrolyte salts and electrolyte additives as well as solvents are possible regulatory targets. One important regulatory target is the solvation structure of the metal ions, which is believed to directly affect the chemical environment at the electrode interface during SEI generation, thereby determining the final composition and structure of SEI [90]. Therefore, the competitive coordination between solvents and anions to the metal ions has become the key point of research. This can be achieved by deliberately modulating the components of the electrolyte, including the type and concentration of electrolyte salts, solvents, and other additives. To this end, representative electrolyte systems include HCE [91] and LHCE [92]. Weak solvation is usually pursued via increasing the participation of anions in the solvation shell of metal ions, thereby promoting the generation of anion-derived SEI with higher ion conductivity and mechanical robustness. Generally speaking, inorganic substances such as fluoride are considered as components that promote the mechanical strength of SEI [93], while organic components increase the toughness of SEI [72]. In addition to the above methods, electrolyte additives are also important means of regulating SEI. These additives are generally used as sacrificial agents to change the composition and structure of SEI through their preferential decomposition at the electrode. In nonaqueous AFBs, $NaBF_4$ [74], FEC [94], etc., were used as electrolyte additives to regulate the properties of SEI on the metal anodes. In aqueous anode-free zinc batteries, trimethylethyl ammonium trifluoromethanesulfonate ($Me_3EtNOTf$) was reported as electrolyte additives to participate in the regulation of SEI on the Zn anode, which enabled 80% capacity retention of the 50 mAh anode-free $Ti||Zn_xVOPO_4$ pouch cell after 90 cycles at 0.5 mA cm^{-2} [95].

Besides imposing great influence on the SEI properties, electrolytes also directly dictate the kinetic performance of AFBs from the perspectives of ion transport and ion desolvation. For ion transport in the bulk electrolyte, the critical aspects include dissociation ability of solvents on salts and the size of solvation shell of metal ions. High salt dissociation ability and a small-sized metal solvation structure are conducive to the rapid transport of ions in the electrolyte. In terms of electrode reaction kinetics, lower ion desolvation energy facilitates charge transfer of interface ions, thereby promoting rapid deposition of metal ions at the electrode interface. Therefore, weakening the coordination between solvents and metal ions is a common regulatory strategy [96]. Ether solvents, which generally have low dielectric constants and donor numbers, are often used as weak solvating solvents to reduce desolvation energy and promote electrode kinetics [97, 98]. Besides the solvent, the interactions between the metal ions and anions in the electrolyte provide another target for tuning the ion solvation structure. By composing the electrolyte with multiple anions, both the ion transport and ion desolvation kinetics could be largely improved [74, 99].

Overall, the numerous physicochemical properties of each component in the electrolyte may have a significant impact on the performance of AFBs, such as their electronic energy level structure, dielectric constant, dipole moment, polarizability, donor number, and spatial structure. Systematically studying and analyzing the

impact of these characteristics on the performance of AFBs is an important direction of effort in related fields, which would provide solid theoretical guidance for electrolyte strategies of high-performance AFBs.

1.3.2.3 Metal-Ion-Supply Agents

Toward the performance degradation of AFBs caused by irreversible metal ion consumption on the negative electrode, another simple strategy is introducing metal ion-supply agents into the battery. These metal ion-supply agents are usually electrochemically active substances containing metal ions corresponding to the type of battery. Through irreversible electrochemical decomposition during battery charging, they release metal ions and meanwhile produce oxidation products to compensate for the loss of active material in the negative electrode caused by the formation of SEI and irreversible metal plating/stripping. This method essentially increases the actual N/P ratio by introducing additional reversible capacity solely to the negative electrode (during the electrochemical decomposition of metal ion-supply agents, the capacity corresponding to metal ion deposition on the negative electrode is reversible, but the capacity corresponding to the oxidation reaction on the positive electrode is irreversible). These metal ion-supply agents can be added to the cathode or electrolyte. At present, there are relatively few reports on the strategy of metal ion-supply agents, mainly used in alkali metal ion-based AFBs. For example, Li_2S was used as a Li^+ supply agent for an Ah-level anode-free lithium pouch cell based on $LiFePO_4$ cathode and gel electrolyte [100]. This metal supply agent was loaded on the cathode, which not only replenished the Li^+ loss in the battery but also assisted in forming a stable SEI on the anode, thus enabling the quasi-solid-state anode-free pouch lithium battery to operate stably for 500 cycles. In another instance, Zhang et al. adopted $Na_2C_2O_4$ as metal-ion supply agent for anode-free sodium batteries [101]. The metal-ion supply agent was loaded on the cathode and functioned by oxidative decomposition during battery charging, releasing Na^+ and oxidation product CO_2. By this strategy, 97% capacity retention of the AFB was achieved after 80 operating cycles. Ion replenishment reagents have shown preliminary prospects in improving the cycling performance of AFBs. However, the many side effects that ion-replenishment reagents may bring are also worth noting, such as the decrease in battery energy density caused by metal ion-supply agents, and the side reactions between metal ion-supply agents themselves or their decomposition products and battery components. Therefore, there are still challenges in the development and practical application of metal ion-supply agents at present.

1.4 Progress in Upscaling of AFBs

1.4.1 Challenges in Upscaling from Coin Cells to Pouch Cells

AFBs have attracted extensive attention in the field of electrochemical energy storage due to their advantages of high energy density, simplified structure, and

reduced cost. Coin-type AFBs have laid a solid foundation for basic research on electrode materials, electrolyte compatibility, and interfacial stability. However, scaling up from coin-type to pouch-type configurations is not a simple dimensional expansion but involves a series of challenges derived from differences in cell structure, component configuration, and operating conditions. These challenges directly restrict the electrochemical performance and practical application of pouch-type AFBs.

The most significant difference between coin-type and pouch-type cells lies in their structural dimensions and assembly methods, which lead to distinct differences in ion transport paths, current distribution uniformity, and mechanical stress distribution. Figures 1.4 and 1.5 show the large difference in the typical structures and configurations between the coin cells and pouch cells. For coin-type AFBs, the electrode area is small (usually several square centimeters), the ion transport distance is short, and the current distribution is relatively uniform under low areal capacity conditions. In contrast, pouch-type AFBs require large electrode areas (tens to hundreds of square centimeters) to meet the practical energy demand, which significantly increases the ion transport resistance and causes uneven current distribution. This unevenness easily leads to local overconcentration polarization and uneven deposition of metal ions (e.g., Li and Na) on the current collector, resulting in the formation of dendrites. Moreover, high mass loading on the electrode (tens of milligram per square centimeters) for pouch-type batteries result in high areal capacities, which greatly challenges the integrity of SEI and uniformity of metal deposition. Unstable SEI films will continuously consume the electrolyte and active metal ions, and uneven metal deposition may exacerbate

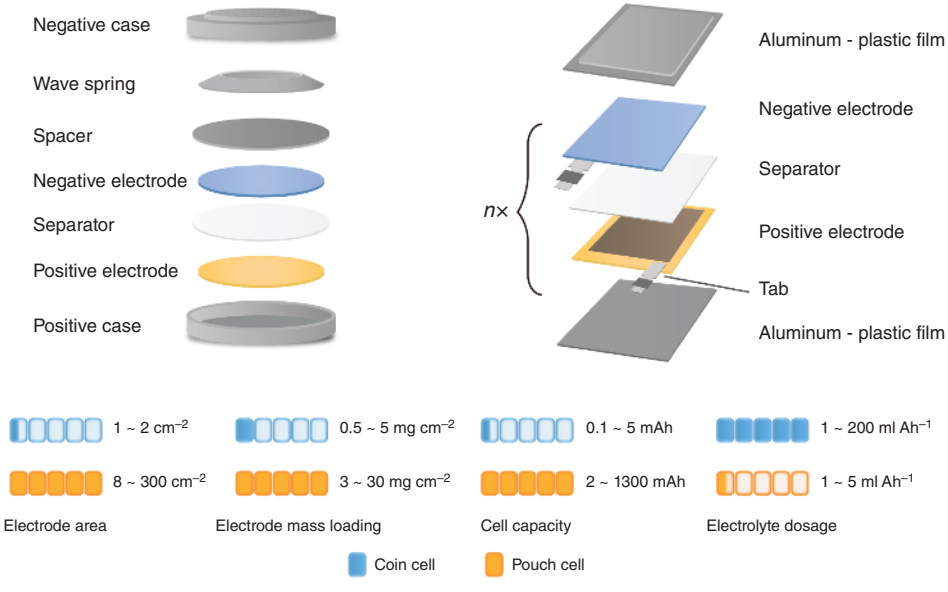

Figure 1.4 The comparison between the structure of coin cells and pouch cells.
Source: Wang et al. [102] / with permission of John Wiley & Sons.

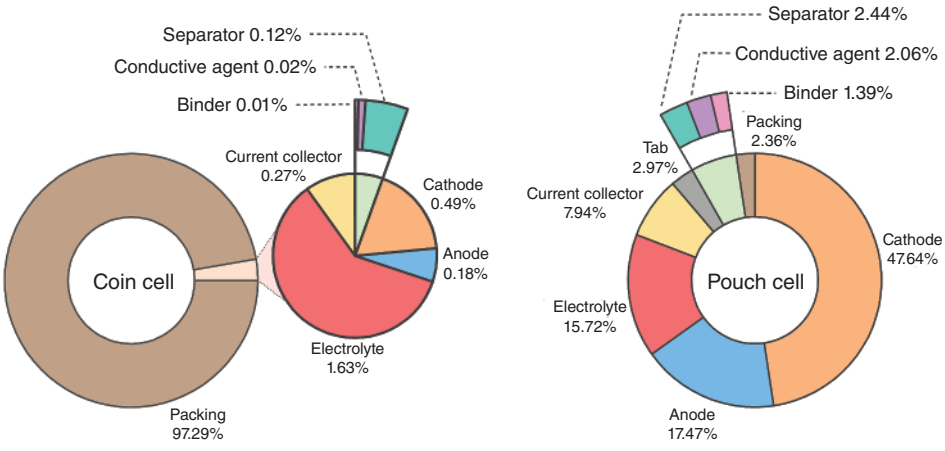

Figure 1.5 The comparison between the configuration of coin cells and pouch cells. *Source:* Wang et al. [102] / with permission of John Wiley & Sons.

metal dendrite growth and dead metal accumulation, which not only reduces the reversibility of the battery but also poses safety hazards such as short circuits.

Besides, the large volume change during battery cycling also raises greater challenge to the structural stability of the pouch-type cells. For example, the volume change originating from the metal plating/stripping can reach up to 20% for an anode-free lithium cell at an areal capacity of 4 mAh cm^{-2} [103]. During the repeated plating and stripping of the metal at large areal capacities, the large volume change of the electrode interface will generate cyclic mechanical stress, which may cause the separation of the electrolyte–electrode interface. The rigid shell of coin-type cells can provide a relatively stable mechanical support, reducing the impact of volume changes on the interface. In contrast, the flexible packaging of pouch-type cells makes them more susceptible to mechanical stress during cycling.

In addition, the component configuration optimization is crucial for the performance of AFBs, and the requirements for components (cathode, electrolyte, and current collector) change significantly when scaling up to pouch-type cells. Especially, to pursue high-energy-density AFBs, it is necessary to fabricate AFBs with harsh configurations (e.g., high mass loading, lean electrolyte, and high stack numbers), which would undoubtedly pose more severe challenges to material development, battery configuration design, and battery manufacturing processes.

1.4.2 Progress in Pouch-Type AFBs

Until now, the progress in pouch-type AFBs is mainly focused on the fields of lithium-ion batteries and sodium-ion batteries [102, 104]. It was not until 2018 that the first report on anode-free pouch lithium batteries was released. This report described the cycling performance of high-voltage $LiNi_{0.5}Mn_{0.2}Co_{0.3}O_2$ (NCM532) cathode paired with a Cu current collector [105]. In 2019, Weber et al. developed a dual-salt LiDFOB/$LiBF_4$ liquid electrolyte to support an anode-free lithium

pouch cell to obtain 80% capacity retention after 90 cycles [106]. In 2021, Li_2O was introduced as a preloaded sacrificial agent on a $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ cathode, which enabled a 2.46 Ah anode-free pouch lithium cell with an energy density of 320 Wh kg^{-1} [107]. In 2022, a quasi-solid-state anode-free pouch lithium battery exhibited a high energy density of 1323 Wh L^{-1}, based on lithium sulfide-based cathodes and polymeric gel electrolytes [108]. In 2023, a cathode pre-lithiation strategy was adopted to extend the lifespan of anode-free lithium pouch batteries, and a high 97% capacity retention was obtained after 50 cycles with a Li-rich $Li_2Ni_{0.5}Mn_{1.5}O_4$ cathode [109]. In recent years, engineering of current collectors and separators has also manifested great prospect for high-performance anode-free pouch lithium batteries, which achieved 99.1% capacity retention after 50 cycles and a high energy density of 450 Wh kg^{-1}, respectively [110, 111].

The development of anode-free pouch sodium batteries only started in recent years. In 2022, a pioneering work on current collector interfacial engineering demonstrated the feasibility of upscaling anode-free sodium batteries [84]. In 2024, several breakthroughs in the field of anode-free pouch sodium batteries were reported. Cu_3P-modified current collectors enabled a high CE of 99.92% for Na plating/stripping, thus supporting the 15 mAh pouch battery to operate stably for 170 cycles [112]. To improve the reversibility of metal plating/stripping at the anode, the solvation structure of metal ions was modulated by introducing ether-based diluents into the electrolyte, such as 1,3-dioxolane (DOL) [113] and 2-methyltetrahydrofuran (Me-THF) [93]. High-capacity retention of 95% was achieved for the anode-free pouch sodium battery at −25 °C after 100 operating cycles, and even at −55 °C, the CE of a anode reached 99.5% [113]. In the same year, a combination of electrolyte modulation and current collector modification was proposed by Zhu et al., which enabled a high specific energy density of 110 Wh kg^{-1} for an Ah-level anode-free pouch battery at −40 °C [74]. Toward the inadequate high-voltage capability of traditional electrolytes, construction of a robust cathode electrolyte interphase (CEI) as well as SEI by elaborate electrolyte modulation was proved to be a feasible strategy. Weakly solvating anion-stabilized (WSAS) electrolyte [114], "liquid-in-solid" electrolyte [115], and sole-solvent high-entropy electrolyte [75] were developed by different research groups and greatly advanced the performance of anode-free pouch-type sodium batteries both at room temperature and low temperatures. As a benchmark performance of anode-free pouch sodium batteries, a cell-level energy densities of 209 Wh kg^{-1} at 25 °C was reported, which approaches to that of traditional lithium-ion batteries (around 250 Wh kg^{-1}) [116], demonstrating great application of the anode-free pouch sodium batteries. On the other hand, the development of anode-free pouch batteries of other metal ions is still in their infancy [68]. Overall, the upscaling of AFBs is speeding up in the academic field, and through strategies such as electrode interface modification and electrolyte engineering, the anode-free pouch batteries may well experience booming development in the future.

1.4.3 Industrialization of AFBs

AFBs have broad industrialization prospects due to their high energy density and low cost, which are attributed to the simplified battery structure and manufacturing process, as well as reduced material costs. Due to the removal of the metal anode, the energy costs of AFBs can be up to ~30% lower than that of traditional NCM-based lithium-ion batteries, without considering the lifespan of the batteries [61]. Owing to the simplified manufacture, it is estimated that the production cost of AFBs can be reduced compared with that of traditional lithium-ion batteries. Moreover, the energy density of AFBs can reach more than 500 Wh kg^{-1} [61], which is significantly higher than that of traditional lithium-ion batteries. With the increasing demand for high-energy-density energy storage devices in EVs, consumer electronics, and large-scale ESS, AFBs are expected to become a new generation of high-performance battery technology.

In recent years, the industrial field has increased its investment in the research and development of AFBs, especially lithium- and sodium-based AFBs. A few enterprises have launched related research projects, and some important advances have sprung up. For example, in November 2024, Beijing Xibei Power Technology Co., Ltd. (Xibei Power), a high-tech enterprise specializing in the development of sodium-ion batteries and cathode materials, successfully developed an anode-free pouch-type 25 Ah sodium-ion battery product with an energy density of 230 Wh kg^{-1}, through the combined design of high-entropy cathode materials, high-voltage electrolyte, and electrode interfaces [117]. This technology greatly simplifies the production process, reducing the investment in personnel and equipment by approximately 40% and the floor space requirement by around 12%. In April 2025, CATL, a global leading battery manufacturer, officially released its anode-free lithium battery technology. By designing nanoscale interface structures and optimizing ion conduction pathways, the performance of the AFB can be greatly improved [118]. It has solved the problem of cyclic decay in lithium metal anodes, increased ion conductivity by 100 times, reduced active ion consumption by 90%, and improved storage performance by 300%. The volumetric energy density has increased by 60%, and the weight energy density has increased by 50%. When combined with high-performance cathode materials, astonishing energy density as high as 1000 Wh L^{-1} can be achieved. In November 2025, Jiangsu Hid.Func. Technology Co., Ltd. (Hid.Func.), an enterprise integrating the R&D, manufacturing and sales of advanced sodium-ion batteries in China, has made a significant technological breakthrough by developing an anode-free semisolid-state sodium battery [119]. This innovative battery delivers an energy density of 310 Wh kg^{-1}, outperforming not only current mainstream sodium-ion batteries but also some of the commercial lithium-ion batteries. More notably, in September 2025, QuantumScape, a leading US-based solid-state battery startup backed by Volkswagen Group, achieved a historic milestone by successfully demonstrating a Ducati V21L motorcycle powered by its QSE-5 anode-free solid-state batteries, marking the transition of lab-scale AFBs to real-vehicle applications [120]. The QSE-5 batteries boast an energy density of 844 Wh L^{-1}, which can charge from 10% to 80% in 12 minutes and support

continuous 10C discharge [121]. At present, the industrialization of AFBs is still in its infancy. With the increasing research works in AFBs from both academia and industry, it can be expected that the applications of AFBs will be seen in our daily lives in the near future.

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