Journal of Advanced Materials Research
http://dx.doi.org/10.62762/JAMR.2025.925427

REVIEW ARTICLE

Metal-Organic Frameworks as Multifunctional Regulators for Zinc Anode Stability in Aqueous Energy Storage Systems

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Abstract

Aqueous zinc-ion batteries (AZIBs) are considered one of the most promising candidates for next-generation energy storage systems, owing to the high safety, low cost, high theoretical capacity (820 mAh g^{-1}), and environmental compatibility. However, the practical implementation of zinc metal anodes still faces challenges such as dendrite growth, hydrogen evolution reaction, and corrosion, which significantly restrict the cycling life and practical usability. To address these issues, metal-organic frameworks (MOFs) with tunable pore structures and ultrahigh specific surface areas have been widely employed for protecting zinc anodes. Therefore, this review systematically summarizes the innovative applications of MOFs in interfacial protection of anodes, three-dimensional host structures, and functional separator design, starting from the fundamental principles and existing problems of AZIBs. Moreover, this review identifies the key issues and challenges in current research and proposes future research directions, aiming to provide new strategic insights into zinc anode protection and promote the high-value application of MOFs materials in the field of energy storage.

Keywords: aqueous zinc-ion batteries, metal-organic frameworks (MOFs), zinc anode protection, interfacial engineering, functional separator design.

Submitted: 21 November 2025
Accepted: 18 December 2025
Published: 26 December 2025

Vol. 1, **No.** 1, 2025.
10.62762/JAMR.2025.925427

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1 Introduction

With the rapid depletion of traditional non-renewable energy sources and the pollution issues arising from fossil fuel combustion, especially the excessive emission of carbon dioxide, severe environmental consequences such as air pollution and the greenhouse

Citation
Zheng, Z., Chen, K., Fang, Y., Zhou, H., Feng, P., Guo, X., & Zheng, Y. (2025). Metal-Organic Frameworks as Multifunctional Regulators for Zinc Anode Stability in Aqueous Energy Storage Systems. *Journal of Advanced Materials Research*, 1(1), 37–55.

effect have become pressing global concerns [1, 2]. Recently, rechargeable secondary batteries have emerged as a promising solution for enabling the large-scale application of intermittent renewable energy and enhancing grid utilization, facilitating the storage and release of energy through the reversible conversion between chemical and electrical energy [3–10]. Typical electrochemical energy storage devices encompass various types of rechargeable secondary batteries, including lithium-ion and lead-acid systems. Among them, lithium-ion batteries have undergone particularly rapid development in recent years, benefiting from high specific energy, a broad operating temperature range, and extended cycle life [11–16]. However, the bottlenecks for the large-scale application of lithium-ion batteries (LIBs) are becoming increasingly apparent. Lithium resources are relatively scarce, with over 70% concentrated in a few countries, leading to high supply chain risks and elevated costs due to expensive raw materials. Furthermore, the flammable organic electrolytes and the propensity for lithium dendrites to cause short circuits and thermal runaway pose significant safety hazards. Inadequate recycling technologies also mean that spent batteries can easily cause secondary pollution. These critical drawbacks hinder the deep application of LIBs in fields such as large-scale energy storage. Against this backdrop, research efforts worldwide have shifted toward aqueous battery systems based on multivalent cations (e.g., Zn^{2+}, Na^+, K^+, Al^{3+}). Among various aqueous systems, aqueous zinc-ion batteries (AZIBs) have shown remarkable potential for development [9, 11, 16]. Zinc offers several distinct advantages over other metals: (I) Zinc is earth-abundant, low-cost, and uniquely suitable for direct use as an anode material, whereas sodium and potassium exhibit violent reactivity with water, aluminum readily forms a passivating oxide layer, and magnesium demonstrates a tendency for aqueous corrosion [12, 13]. (II) With a suitable redox potential (-0.76 V vs. SHE), zinc enables reversible plating/stripping in aqueous electrolytes, while metals such as sodium (-2.71 V), potassium (-2.93 V), magnesium (-2.37 V), and aluminum (-1.66 V) possess redox potentials that are too low for stable operation in aqueous media [12, 13]. (III) Zinc exhibits a high theoretical gravimetric capacity of 820 mAh g^{-1} and an outstanding volumetric capacity of approximately 5850 mAh cm^{-3} [12, 13]. (IV) The inherent safety of aqueous electrolytes, including high ionic conductivity, non-flammability, and low toxicity, combined with the environmental benignity of zinc, makes this battery system particularly attractive for sustainable energy storage [12, 13]. Owing to these collective advantages, AZIBs are regarded as highly promising candidates for future large-scale energy storage applications [17, 18]. However, the practical implementation of zinc metal anodes faces critical challenges such as uncontrolled dendrite growth, hydrogen evolution reaction (HER), and corrosion passivation, which severely limit their cycling longevity and energy density. Previous studies have explored various materials for anode protection, including carbon-based nanomaterials, metal oxides, inorganic non-metallic compounds, and two-dimensional materials [19–22]. Among these, metal-organic frameworks (MOFs) demonstrate superior advantages due to their unique structural and functional properties [23–25].

MOFs are porous materials formed via coordination-driven self-assembly of metal ions/clusters and organic ligands. Their structural diversity stems from the versatile combinations of metal nodes and multidentate organic linkers. By precisely tuning ligand length, functional groups, and metal cluster types, MOFs with hierarchical pore networks, from microporous to mesoporous scales, can be constructed, endowing them with high specific surface areas and customizable surface chemistry [4, 26, 27]. In AZIBs, the confined channels of MOFs guide directional Zn^{2+} migration along predetermined pathways, suppressing disordered dendrite growth, while their hybrid organic-inorganic interfaces regulate zinc ion solvation structures via coordination or hydrogen bonding, reducing side reactions [28–30]. Studies have shown that the multi-level pore structures of MOFs shorten ion diffusion paths and lower desolvation energy barriers, while abundant active sites optimize zinc deposition behavior. For instance, Wang et al. [31] fabricated an anionic MOF-based artificial solid electrolyte interphase in situ on zinc anodes. This protective layer significantly improved Coulombic efficiency and enabled dendrite-free cycling for 5700 hours at 2 mA cm^{-2}, facilitated by continuous sulfonic acid groups guiding rapid directional Zn^{2+} transport. Zhang et al. [32] constructed a bifunctional MOF-E interface layer that provided targeted desolvation sites and fast ion channels, inducing oriented zinc deposition along the (002) crystal plane. The modified Zn||Cu cells maintained 99.7% Coulombic efficiency over 2500 cycles. Furthermore, Zhang et al. [33] identified MOF channel size as a key factor in balancing Zn^{2+} flux and desolvation behavior. The confined spaces in the MOF-5W layer promoted spontaneous desolvation, enabling the electrode to achieve 5000 stable cycles at 40 mA cm^{-2}. These findings underscore the unique advantages of MOFs in addressing interfacial stability and ion transport issues in AZIBs.

Herein, this review begins by elucidating the fundamental challenges and mechanisms of zinc anodes, discusses recent advances in MOF-based stabilization strategies, identifies key challenges and potential directions in the field, and concludes with prospects for MOF materials in zinc anode protection. We aim to provide researchers with novel insights and enhance the applicability and research value of MOF materials in next-generation energy storage systems.

2 Current Status of Aqueous Zinc-Ion Batteries

2.1 Fundamentals of Aqueous Zinc-Ion Batteries

AZIBs are a class of secondary battery systems employing metallic zinc anodes and aqueous electrolytes, and have evolutionary roots intertwined with the origins of electrochemical research. As illustrated in Figure 1, their historical trajectory dates back to 1799 when Italian physicist Alessandro Volta constructed the first electrochemical power source (the Voltaic Pile), using zinc and silver electrodes in a saltwater electrolyte, initiating zinc-based battery research [34, 35]. The Daniell cell, introduced in 1836, significantly improved system stability by physically separating zinc anodes from copper cathodes in zinc sulfate/copper sulfate electrolytes [36]. By 1868, French scientist Georges Leclanché had incorporated alkaline electrolytes into Zn/MnO_2 batteries, establishing the foundation for alkaline zinc-manganese systems [37]. However, traditional alkaline electrolytes frequently induce dendrite growth and hydrogen evolution side reactions, leading to limited cycle life and poor environmental compatibility [38, 39].

To address these limitations, Yamamoto et al. [40] pioneered, in 1988, a rechargeable Zn/MnO_2 battery using neutral/mildly acidic zinc sulfate electrolytes, thereby suppressing dendrites and side reactions and reviving aqueous zinc-ion battery research. The concept of rechargeable zinc-ion batteries was formally established in 2011, shifting research focus to the mechanisms of manganese dioxide cathodes [41]. Nevertheless, uncontrolled dendrite growth, hydrogen evolution reactions, and passivation at zinc anodes critically constrain practical battery lifespan, representing fundamental barriers to technological advancement [42]. Thus, elucidating zinc anode failure mechanisms and developing effective stabilization strategies are crucial for enhancing battery durability and accelerating commercial implementation [43].

2.2 Fundamentals of Aqueous Zinc-Ion Batteries

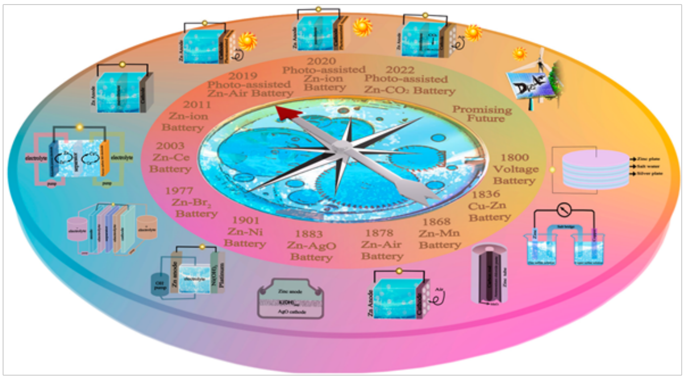

Figure 1. A brief history of the development of AZIBs [35]. Copyright 2022, MDPI.

The core structure of AZIBs comprises four essential components: cathode, anode, electrolyte, and separator [44]. The cathode material, which hosts zinc ions, largely determines the operating voltage and capacity of the battery. It is typically composed of active materials, such as manganese-based oxides, vanadium-based oxides, Prussian blue analogs, or organic compounds, coated on a current collector (e.g., carbon cloth or stainless-steel foil) [45]. The anode is generally made of metallic zinc foil or powder, serving as the zinc source by undergoing oxidation during discharge to release Zn^{2+} [4]. The electrolyte, which bridges the cathode and anode via ion transport, is predominantly aqueous due to the relative stability of zinc in water. Common solute salts include $ZnSO_4$ [46], $Zn(CF_3SO_3)_2$ [47], $ZnCl_2$ [48], $Zn(ClO_4)_2$ [49], and $Zn(CH_3COO)_2$ [50]. The separator–usually a glass fiber or porous polymer membrane (e.g., cellulose)–prevents electrical short circuits while permitting Zn^{2+} transport [51]. AZIBs store and release energy through the reversible migration of zinc ions between the electrodes, as expressed by the following reactions:

$$\text{Anode: Zn} \leftrightarrow \text{Zn}^{2+} + 2e^- \tag{1}$$

$$\text{Cathode: L} + x\text{Zn}^{2+} + 2xe^- \leftrightarrow \text{Zn}_x\text{L} \tag{2}$$

$$\text{Overall: } x\text{Zn} + \text{L} \leftrightarrow \text{Zn}_x\text{L} \tag{3}$$

Taking the Zn//MnO_2 cell as an example (Figure 2):

during discharge, zinc at the anode is oxidized to Zn^{2+}, releasing electrons that travel externally to reduce MnO_2 at the cathode [52]. Simultaneously, Zn^{2+} migrates through the electrolyte and separator, inserting into the structural tunnels of MnO_2 (e.g., the 2×2 tunnels in α-MnO_2) to form a $ZnMn_2O_4$ phase. During charging, an applied voltage extracts Zn^{2+} from the cathode, driving its migration back to the anode for reduction and deposition as metallic zinc, thereby completing the energy storage cycle [53]. But the practical implementation of zinc metal anodes faces significant challenges in cycling stability and safety. A primary concern is the non-uniform zinc deposition during repeated cycling, which promotes dendrite growth. These dendritic structures can penetrate the separator, leading to internal short circuits and potentially triggering thermal runaway. Furthermore, parasitic reactions such as hydrogen evolution and corrosion continuously consume the active zinc and electrolyte, while generating passivation layers (e.g., ZnO) on the anode surface, thereby degrading Coulombic efficiency [54–56]. These interfacial side reactions are not isolated but interact synergistically, exacerbating anode degradation. Thus, a thorough understanding of the failure mechanisms of zinc anodes is essential for developing reliable zinc-based batteries.

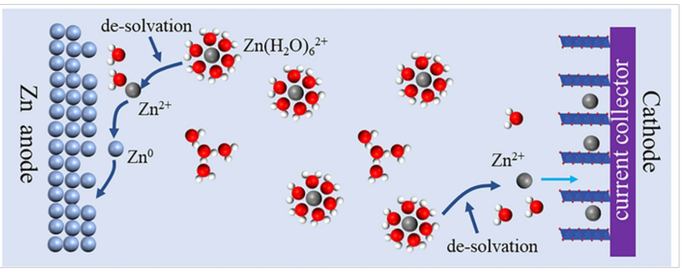

Figure 2. Composition and working principle of the AZIBs [52]. Copyright 2023, Springer Nature.

2.2.1 *Zinc Dendrite Growth*

The implementation of zinc metal anodes in zinc-ion batteries faces substantial challenges, primarily originating from the formation mechanism of zinc dendrites. During electrochemical cycling, the inhomogeneity in zinc deposition/stripping behavior is mainly triggered by unbalanced electric field distribution and uncontrolled two-dimensional diffusion pathways, collectively leading to abnormal Zn^{2+} deposition. From the perspective of nucleation kinetics, metallic zinc tends to form initial nuclei at low-energy sites, and these micron-scale nuclei gradually evolve into dendritic prototypes [57]. Notably, once initial dendritic structures form, their tips develop charge-enriched regions where localized strong electric fields continuously guide Zn^{2+} migration toward the tips via electrostatic attraction, establishing an autocatalytic cycle for dendritic growth [58, 59]. This persistent growth not only causes irreversible active material loss (e.g., "dead zinc" formation) but also raises safety concerns such as internal short circuits [60]. Further studies reveal that zinc deposition morphology is co-influenced by multiple parameters: (I) electrolyte concentration modulates interfacial properties, with higher concentrations suppressing dendrites [61]; (II) elevated temperature reduces nucleation barriers and decreases nucleation density, promoting large-sized nuclei and increasing deposit roughness [62]; (III) low overpotential favors reduced deposition resistance, whereas strong polarization at high current density intensifies localized deposition [63]; (IV) electrode surface roughness induces electric field distortion, triggering preferential deposition at protrusions [64]. Moreover, the coupling among operational parameters is critical: increasing current density not only raises overpotential but also affects electrolyte temperature via Joule heating, and such multi-physics coupling significantly complicates the control of deposition behavior.

2.2.2 *Hydrogen Evolution Reaction (HER)*

The interfacial contact between the zinc metal anode and electrolyte induces side reactions such as hydrogen evolution and electrode corrosion, which severely restrict the electrochemical performance [65]. Although zinc anodes possess a relatively low redox potential (-0.76 V vs. SHE), in neutral or weakly acidic electrolytes, the deposition of zinc ions competes thermodynamically with HER, with the latter being more prone to occur [55]. This competitive mechanism leads to inevitable hydrogen generation at the zinc/electrolyte interface, as described by:

$$3Zn+11H_2O+ZnSO_4 \rightarrow Zn_4SO_4(OH)_6 \cdot xH_2O+3H_2 \uparrow \tag{4}$$

The continuous growth of zinc dendrites significantly increases the electrode/electrolyte contact area, thereby accelerating the kinetics of the hydrogen evolution reaction. It is particularly noteworthy that electrons originally intended for zinc ion reduction are consumed by the HER, resulting not only in irreversible loss of active materials and electrolyte but also a sharp decline in Coulombic efficiency [66]. More critically, the accumulated hydrogen gas in a confined battery system may cause swelling or even rupture of the battery casing, posing serious safety risks.

2.2.3 *Corrosion and Passivation*

Corrosion of zinc anodes constitutes another critical side reaction, arising from the synergistic interplay between chemical and electrochemical processes. Microscopically, inherent physicochemical heterogeneity across the zinc electrode surface induces uneven potential distribution, fostering micro-galvanic cells [67, 68]. This phenomenon drives spontaneous corrosion, which is further accelerated by localized pH elevation (increased OH^- concentration) resulting from hydrogen evolution. The corrosion pathways proceed as follows:

$$Zn^{2+} + OH^- \rightarrow Zn(OH)_2 \rightarrow ZnO + H_2O \qquad (5)$$

$$4Zn^{2+} + 6OH^- + SO_4^{2-} + xH_2O \rightarrow Zn_4SO_4(OH)_6 \cdot xH_2O \quad (6)$$

These in situ generated interfacial species exhibit low solubility and high electrical insulation. When deposited on the electrode, they not only block active nucleation sites, promoting localized dendrite growth, but also create ionic transport barriers at the electrode/electrolyte interface. This leads to severely imbalanced interfacial kinetics and markedly increased charge transfer resistance. More critically, the porous microstructure of these byproducts continuously consumes active electrode materials and electrolyte components, inducing irreversible anode passivation. Ultimately, this results in rapid capacity decay and diminished cycle life [69]. The cascading effect of such interfacial side reactions establishes zinc anode instability as a pivotal bottleneck hindering the practical implementation of aqueous zinc-ion batteries.

Notably, the failure mechanisms of zinc anodes exhibit significant synergistic coupling: the increased specific surface area caused by dendrite growth accelerates the kinetics of hydrogen evolution, while the localized pH rise (elevated OH^- concentration) resulting from hydrogen evolution further promotes the formation of corrosion products. Simultaneously, the accumulation of byproducts impedes ion transport, disrupting uniform zinc deposition and establishing a self-reinforcing degradation loop of "dendrite growth – intensified side reactions – deteriorated deposition uniformity", as illustrated in Figure 3 [70]. This multifactorial coupled failure mode maintains the electrode interface in a dynamically unstable state, substantially compromising the cycling reversibility of zinc anodes.

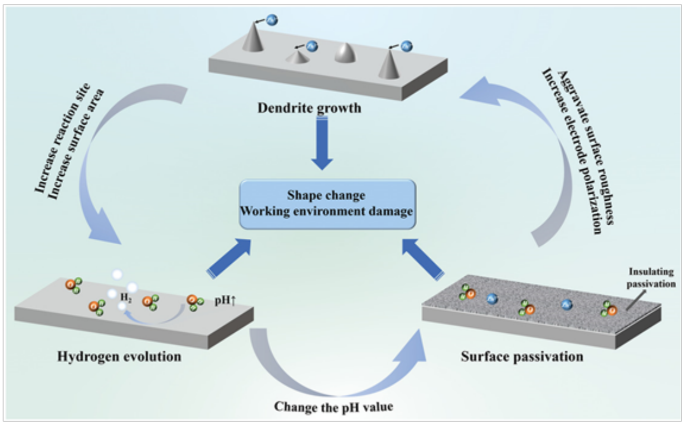

Figure 3. Schematic diagram of the relationship between dendrite growth, hydrogen evolution reaction and corrosion passivation [70]. Copyright 2022, Wiley-VCH.

3 Applications of MOF Materials in Aqueous Zinc-Ion Batteries

3.1 Application of MOFs at Anode Interfaces

Interfacial stability is critical to maintaining the long-term cycling performance of zinc metal anodes. The inherent poor wettability of zinc foil in aqueous electrolytes leads to significant plating/stripping polarization, while its surface defects cause inhomogeneous Zn^{2+} flux, thereby promoting the growth of hazardous zinc dendrites [71]. To address these challenges, MOFs have emerged as promising candidate materials due to their high specific surface area and tailored porosity. These structural characteristics not only shorten ion diffusion pathways and reduce the desolvation energy barrier, favoring homogeneous Zn^{2+} transport and dendrite suppression, but also provide numerous redox-active sites, which enhance reaction kinetics and deliver high specific capacity. Moreover, the reasonable chemical stability of MOFs allows them to form a robust protective coating on the zinc anode, effectively minimizing side reactions [26, 27, 72, 73]. Owing to these synergistic merits, MOF-based coatings have attracted considerable attention for the surface modification of zinc metal anodes.

ZIF-8, a metal–organic framework composed of zinc ions and imidazolate ligands, has attracted broad interest in electrochemical energy storage. It has been demonstrated that combining a ZIF-8-modified Zn anode (denoted as ZIF-8@Zn) with an Mn(BTC) MOF cathode results in a battery system with prolonged cycling stability (Figure 4(a)).

In this configuration, the ZIF-8 interlayer serves to modulate the Zn^{2+} concentration distribution at the electrode interface, thereby suppressing dendrite formation induced by localized electric field enhancement (Figure 4(b)). Post-cycling characterization reveals a homogeneous ZIF-8 coating on the ZIF-8@Zn electrode surface, with no significant protrusions or dendritic structures observed (Figure 4(c-f)). As illustrated in (Figure 4(g)), the porous framework of ZIF-8 guides uniform Zn deposition/stripping behavior, enabling stable cycling for 170 hours with a consistent overpotential of 120 mV at deposition capacities of 0.25 and 0.05 mAh·cm^{-2}.

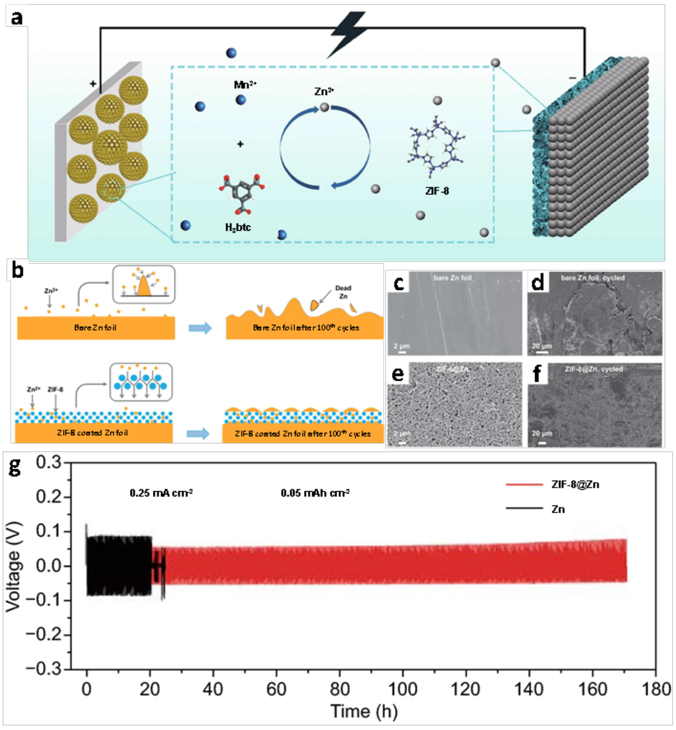

Figure 4. (a) Schematic of the Mn(BTC) cathode//ZIF-8@Zn anode ZIBs. Electrochemical performance of the ZIBs: (b) Schematic illustration for morphology change of the bare Zn foil and ZIF-8@Zn electrodes during repeated Zn stripping/plating process, SEM images of bare Zn electrode (c) Before and (d) After 100 stripping/plating cycles, ZIF-8@Zn electrode (e) Before, and (f) After 100 stripping/plating cycles [74]. Copyright 2020, Springer Nature.

UiO-66, a metal-organic framework constructed from zirconium-oxo clusters and terephthalic acid linkers, is distinguished by its exceptional chemical and structural robustness. In contrast to ZIF-8, which possesses zinc nodes, UiO-66 features stronger Zr-O bonds, granting it superior durability in harsh electrochemical environments, including a wide pH range. This robustness directly contributes to the formation of a stable electrode-electrolyte interface for long-term cycling. To enhance interfacial wettability, researchers have developed alternative design strategies. Liu et al. [75] employed a direct approach to reconfigure the Zn/electrolyte interface. Compared to the poorly wetted bare Zn anode, the microporous MOF-PVDF composite coating provides nanoscale zinc wettability, thereby forming a zincophilic interface and reducing the interfacial charge transfer resistance, as shown in (Figure 5(a-d)). To evaluate the long-term cycling performance, the MOF-PVDF-coated Zn electrode was tested at 1 mA cm^{-2}, demonstrating robust stability over 500 cycles. In contrast, the bare Zn electrode failed after only 150 cycles under identical conditions due to internal short-circuiting (Figure 5(e)).

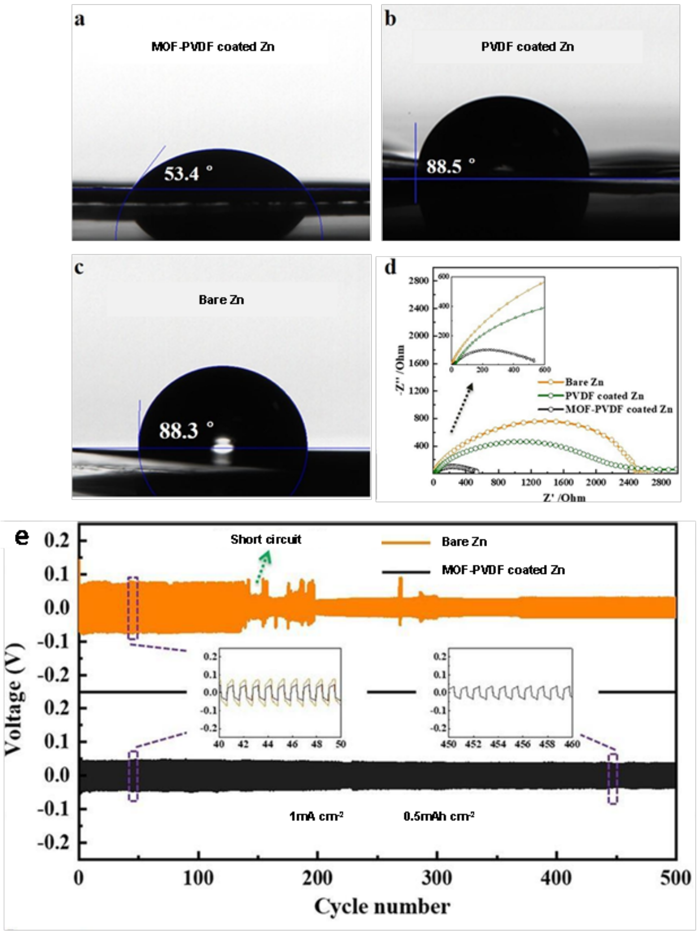

Figure 5. (a)-(c) Images of contact angles between the electrolyte and different anodes. (d) Electrochemical impedance spectra of Zn-symmetric cells with different anodes. (e) Voltage profiles of galvanostatic Zn plating/stripping for different Zn electrodes at 1 mA cm^{-2} [75]. Copyright 2019, American Chemical Society.

Recently, researchers have revealed that the conventional doctor-blade coating method for constructing MOF interlayers introduces polymer binders, which inevitably block ion transport channels in Zn/Co-MOFs and disrupt Zn^{2+} flux at the interface. To address this issue, Jiang et al. [76] developed a simple, binder-free electrosynthesis strategy to directly fabricate a MOF-based protective layer on the zinc metal anode. Zn||Cu half-cells were assembled to evaluate the reversibility of Zn deposition beneath the MOF layer. The results indicated that although the incorporation of a hydrophobic binder slightly improved deposition reversibility and reduced the corrosion potential, it severely compromised the cycling stability (Figure 6(a–c)).

In contrast, the electro-synthesized Co-ZIF-8 interlayer enabled highly efficient ion transport (Figure 6(d)), endowing the Zn||Zn symmetric cell with a long cycle life of over 1280 hours at a low overpotential (Figure 6(e)).

In contrast to conventional synthesis methods, Sun et al. [77] developed a facile chemical integration strategy to construct a uniform MOF-based interlayer on a Zn substrate via an in situ coordination reaction. This approach enables the localized generation of Zn^{2+} at the electrode interface, which subsequently coordinates with $[Fe(CN)_6]^{3-}$ ions to form a continuous MOF coating (Figure 7(a)).

The 3D open framework of the MOF provides ordered nanochannels that not only homogenize Zn^{2+} flux but also accelerate the desolvation kinetics. Benefiting from the uniform ion transport, effective suppression of side reactions, and enhanced interfacial deposition kinetics, the MOF@Zn anode achieves a high Coulombic efficiency of 99.2% over 1000 cycles (Figure 7(b)) and a remarkable cumulative plating capacity of 5.5 $\mathrm{Ah{\cdot}cm^{-2}}$. Moreover, the MOF@Zn electrode exhibits an ultra-long cycling lifespan exceeding 2100 hours at a current density of 4 $\mathrm{mA{\cdot}cm^{-2}}$ (Figure 7(c)), demonstrating significantly improved interfacial durability.

While the aforementioned studies have demonstrated significant progress in stabilizing Zn anodes via MOF-based protective layers, the simultaneous achievement of rapid ion conduction and precisely guided deposition within a single interphase remains a challenge. To address this, Zhang et al. [32] constructed a bifunctional MOF-E interphase by grafting ethylenediaminetetraacetic acid (EDTA) onto a metal–organic framework (denoted as MOF-E), serving as a dual-functional protective layer for sustainable zinc anodes. This MOF-E-based artificial SEI offers targeted desolvation sites and rapid ion-transport pathways, which effectively mitigates side reactions and promotes oriented Zn deposition along the (002) plane (Figure 8(a-c)). XRD characterization of the deposited Zn layer reveals a strengthened (002) diffraction peak on the MOF-E-modified Cu substrate (Figure 8(d,e)), indicating preferentially oriented crystallization. As shown in Figure 8(e, f), the (002) texture intensity for MOF-E@Cu–Zn reaches 2.25, considerably higher than the value of 1.73 for bare Cu–Zn. The latter also exhibits more scattered (002) signals, suggesting randomly distributed Zn crystallites.

In contrast, the two-dimensional WAXS pattern of the MOF-E-modified electrode displays strong and concentrated diffraction spots around the center (Figure 8(f,g)), confirming a well-aligned Zn texture with dominant (002) orientation. These results collectively demonstrate that the MOF-E interlayer effectively guides the formation of a preferred crystallographic orientation in deposited Zn. As a result, the modified Zn||Cu half-cell achieves an extended cycling life of 2500 cycles with a high Coulombic efficiency of 99.7% (Figure 8(h)). Moreover, the MOF-E-based full cell maintains stable operation over 5000 cycles at a high current density of 8 $\mathrm{A\ g^{-1}}$, demonstrating remarkable rate capability and long-term durability (Figure 8(i)).

MOF interlayers, while promising for addressing zinc dendrite and side reactions, often suffer from structural instability during cycling, limiting their practical adoption. Inspired by the symbiotic structure of Drosera rotundifolia (Figure 9(a)), Han et al. [78] constructed a hierarchical hollow $CuSiO_3$-MOF hybrid via an in situ MOF conversion process. This bio-inspired design offers robust structural integrity, abundant zincophilic sites, strong desolvation capability, and rapid ion migration, collectively enabling highly stable dendrite-free Zn plating/stripping and suppressing H_2O-induced side reactions (Figure 9(b)). As a result, the Zn@$CuSiO_3$-MOF symmetric cell achieves an ultralong cycling lifespan of over 3500 hours with low voltage hysteresis (Figure 9(c)). Notably, even at high depths of discharge (DOD(Zn)) of 45% and 90%, the cell maintains stable operation for 1200 and 400 hours, respectively (Figure 9(d,e)). Moreover, a flexible pouch cell integrated with a C@V_2O_3 cathode exhibits a high rate capacity of 300 $\mathrm{mA\ h\ g^{-1}}$ at 20 $\mathrm{A\ g^{-1}}$, and outstanding cycling stability under both flat and bent conditions (Figure 9(f,g)), highlighting its potential for large-scale energy storage and wearable electronics.

Beyond crystalline ZIF-8 materials, amorphous ZIF-8 demonstrates distinctive merits in protecting zinc

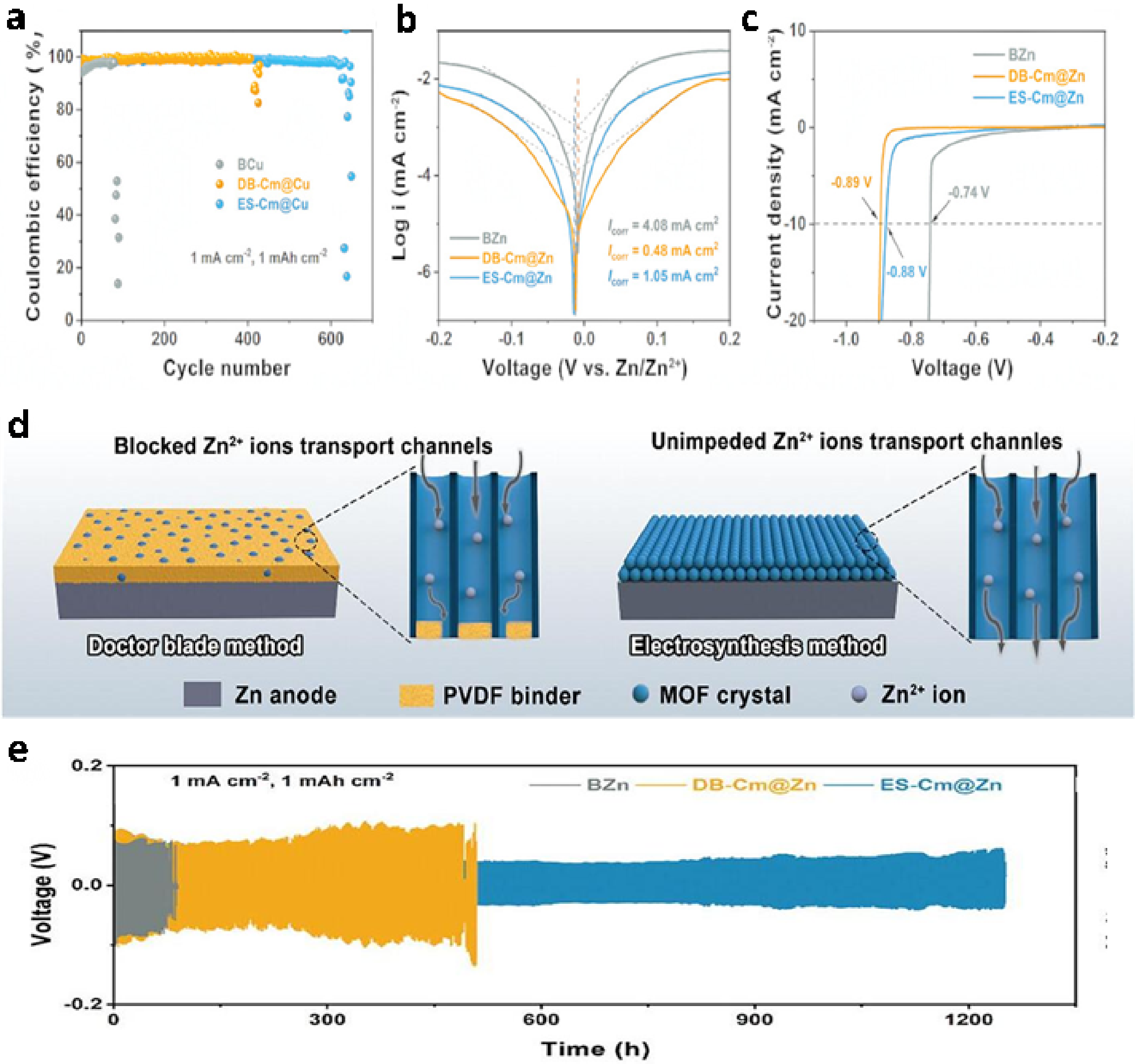

Figure 6. (a) CE results of Zn deposition on BCu, DB-Cm@Cu, and ES-Cm@Cu electrodes at 1 mA cm^{-2}. (b) Tafel curves and calculated corrosion current density on BZn, DB-Cm@Zn, and ES-Cm@Zn anode. (c) Linear sweep voltammetry of Zn||Cu half-cell with different Zn anodes. (d) Schematic illustration of the blocked Zn^{2+} ions transport in MOF interlayers prepared through the doctor blade method (left) and unimpeded Zn^{2+} ions transport in electrosynthetic MOF interlayer (right). (e) Long-term cycling performance of symmetric cells with BZn, DB-Cm@Zn, and ES-Cm@Zn anodes at a current density of 1 mA cm^{-2} [76]. Copyright 2024, Wiley-VCH.

metal anodes. Xiang et al. [20] successfully constructed a continuous amorphous ZIF-8 coating with precisely controlled thickness on zinc substrates through an in situ spraying technique (Figure 10(a)).

This A-ZIF-8 protective layer ingeniously integrates the structural advantages of MOFs with the homogeneous characteristics of amorphous materials. This not only significantly accelerates Zn^{2+} transport kinetics and reduces deposition overpotential but also effectively stabilizes the zinc stripping/plating process and markedly suppresses dendrite formation. The amorphous structure successfully eliminates grain boundaries and crystalline defects, thereby substantially enhancing the coating's mechanical stability and interfacial adhesion strength (Figure 10(b)). Optical characterization clearly demonstrates

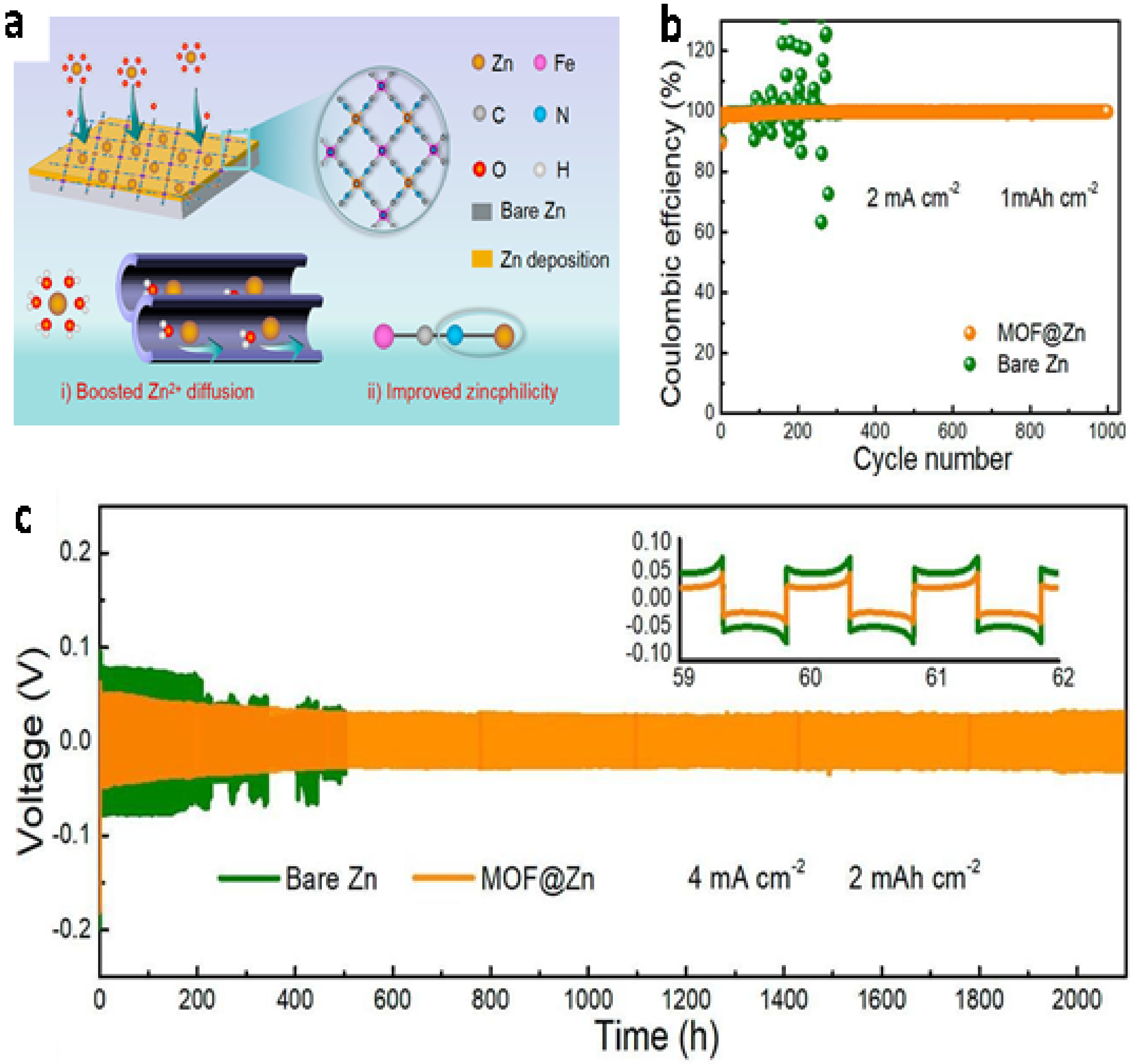

Figure 7. (a) Schematic illustration of the in-situ coordination reaction. (b) Coulombic efficiency of Zn||Cu and MOF@Zn||Cu half-cells at a current density of 2 mA cm^{-2}. (c) Cycling performance of bare Zn and MOF@Zn symmetric cells tested at 4 mA cm^{-2} (2 mAh cm^{-2}) [77]. Copyright 2023, American Chemical Society.

effective suppression of dendritic growth on the zinc electrode surface under the protection of the A-ZIF-8 layer (Figure 10(c)). It indicates that the continuous A-ZIF-8 layer can effectively reduce the energy barrier for Zn nucleation/dissolution and suppress dendrite growth on Ti foil. The symmetric cell (Zn@A-ZIF-8||Zn@A-ZIF-8) assembled with this modified coating achieves an exceptional cycling lifespan exceeding 7900 hours under conditions of 1 mA cm^{-2} current density and 1 mAh cm^{-2} capacity (Figure 10(d)).

3.2 The Application of MOFs in Anode Structural Design

MOFs also offer significant advantages in constructing advanced host architectures for anodes. Three-dimensional porous MOF scaffolds can serve as ideal multifunctional hosts. Their high specific surface area and tunable pore structures not only provide ample space for metal deposition but also guide uniform ion distribution through abundant nucleation sites. This capability enables dendrite-free metal deposition at the bulk scale, presenting

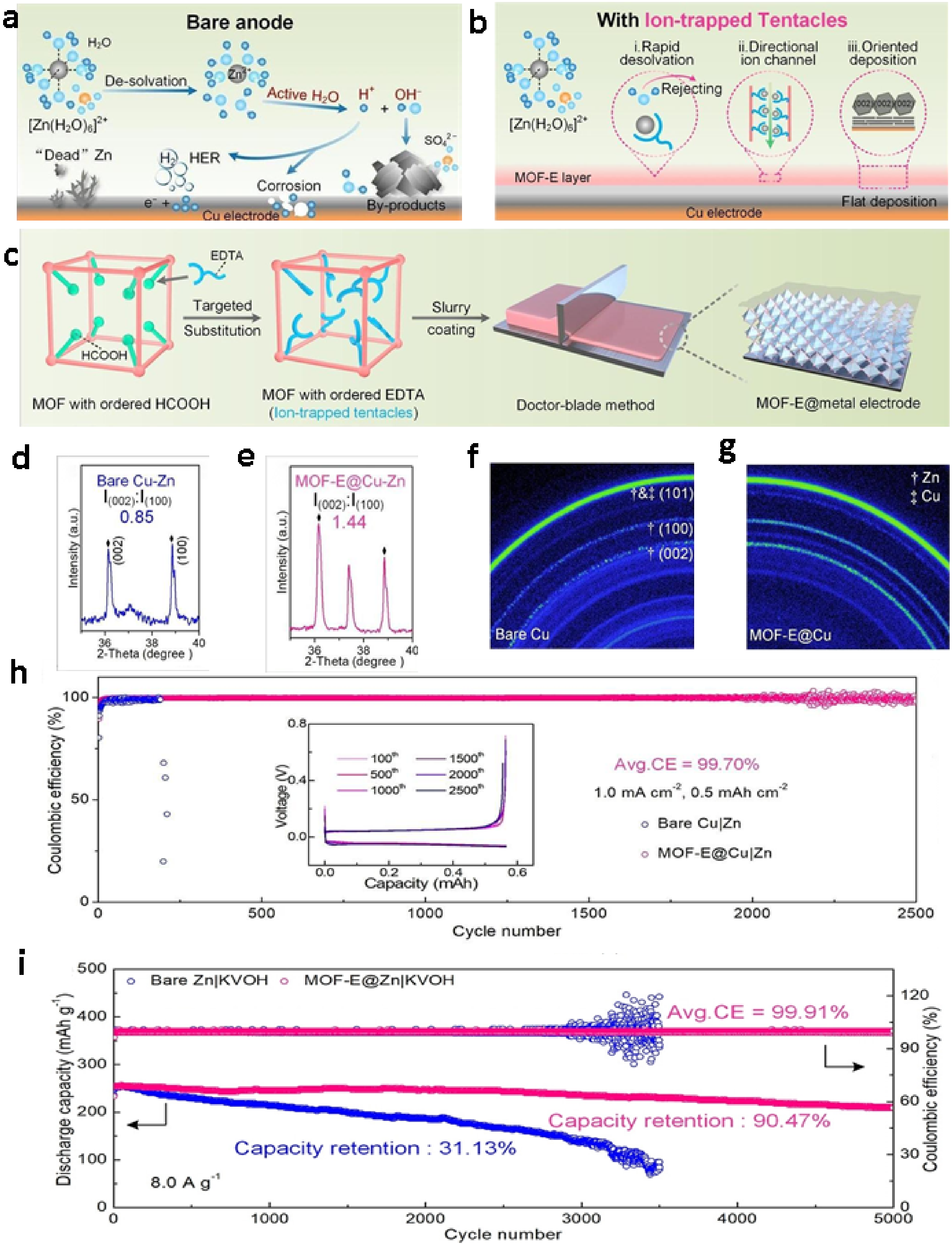

Figure 8. (a) Schematic illustration of Zn deposition on a bare Cu and (b) MOF-E@Cu. (c) Schematic diagram of ordered HCOOH in MOF-808 be substituted by EDTA to form MOF-808 with ordered EDTA (MOF-E) and the process of electrodes preparation. (d,e) XRD patterns of the Zn-deposited bare Cu (d) and MOF-E@Cu (e). (f,g) The WAXS results of Zn deposits on bare Cu (f) and MOF-E@Cu (g). (h) Cycling performance of Zn|Cu and Zn|MOF-E@Cu batteries with selected electrochemical Zn plating/stripping curves of MOF-E@Cu electrode (inset). (i) Long-term cycling performance of different cells [32]. Copyright 2023, Wiley-VCH.

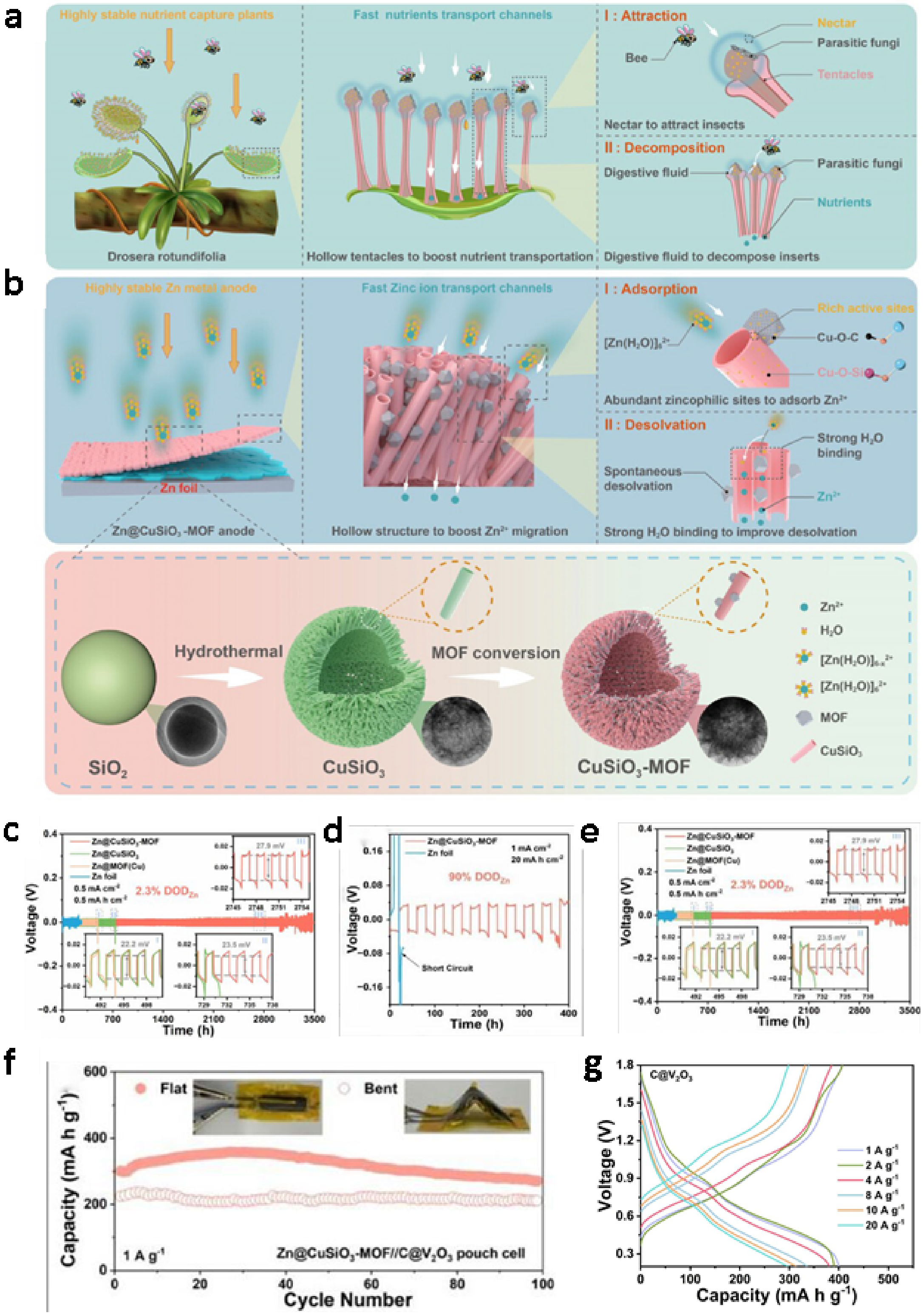

Figure 9. (a) Schematic diagram for the predation process of drosera rotundifolia through attraction, decomposition, and transportation steps. (b) Schematic diagram for the Zn deposition process of Zn@CuSiO$_3$-MOF anode. The bottom shows the schematic illustration for the synthesis of CuSiO$_3$-MOF hybrid through hydrothermal reaction and in situ MOF conversion, as well as their TEM images. (c) Long-term galvanostatic cycling life and selected voltage-time profiles of Zn, Zn@MOF(Cu), Zn@CuSiO$_3$, Zn@CuSiO$_3$-MOF symmetric batteries at 0.5 mA cm^{-2}/0.5 mA h cm^{-2}. (d) Cycling performance of Zn@CuSiO$_3$-MOF and bare Zn symmetric cells at 0.5 mA cm^{-2}/10 mA h cm^{-2} (45% DOD$_{Zn}$), (e) at 1 mA cm^{-2}/20 mA h cm^{-2} (90% DOD$_{Zn}$). (f) cycling behavior at 1 A g^{-1} under flat and bent states of Zn@CuSiO$_3$-MOF//C@V$_2$O$_3$ flexible ZIBs. (g) Battery Capacity Under Different Testing Conditions [78]. Copyright 2025, Wiley-VCH.

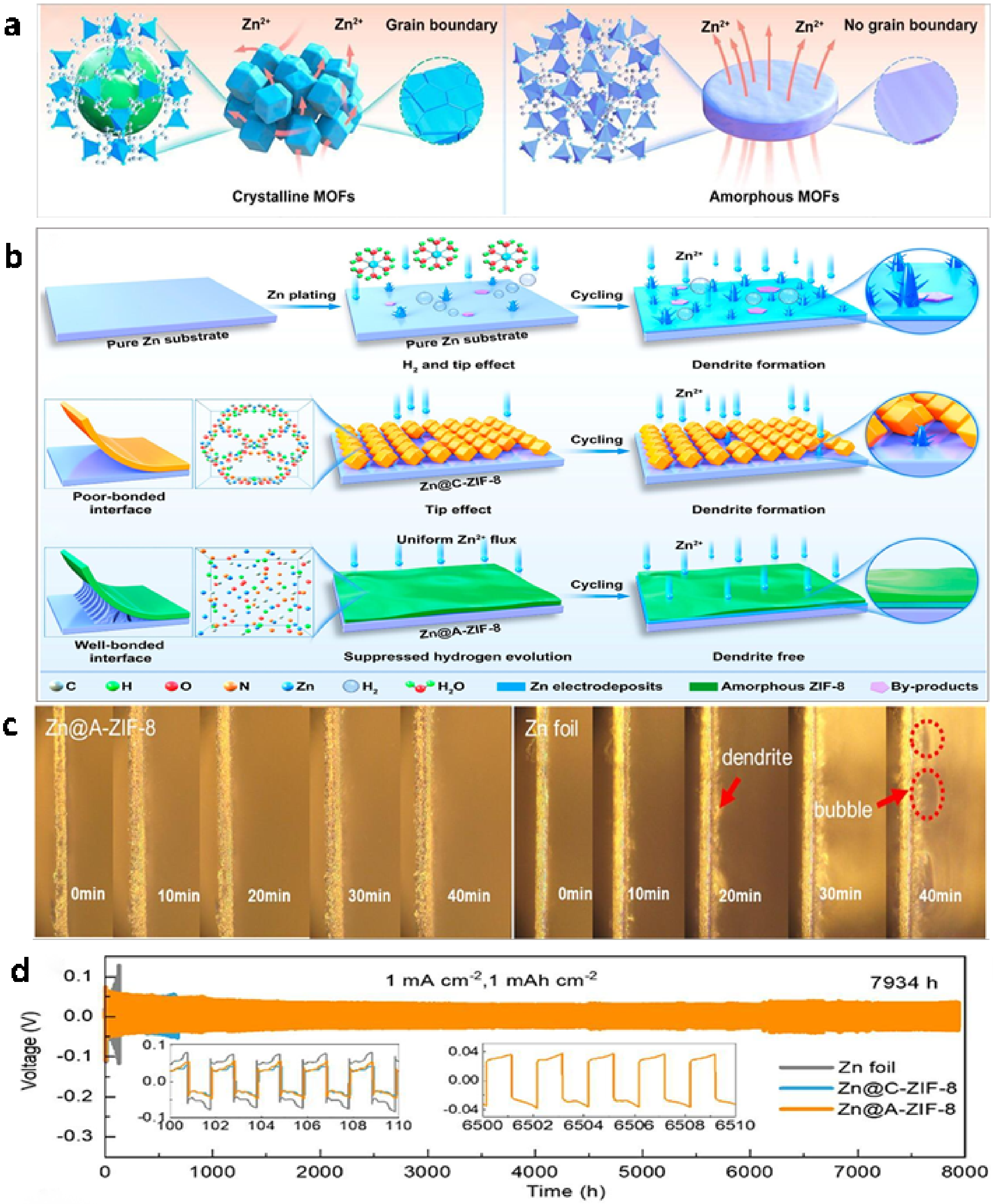

Figure 10. (a) Structural illustration of crystalline ZIF-8 and continuous A-ZIF-8, and their Zn ion conduction. (b) Structure design and elucidation of the suppression mechanism. Schematic comparison of the Zn deposition process on a Zn foil surface and Zn@C-ZIF-8 surface, respectively. Schematic presentation of the Zn deposition process on a Zn@A-ZIF-8 surface. (c) Optical microscopy images of zinc deposition on Zn@A-ZIF-8 and Zn foil at 5 mA cm^{-2}. (d) Electrochemical performance of different Zn anodes. Cycling performance of symmetric cells with different anodes (electrolyte, 2 M $ZnSO_4$ solution; current density, 1 mA cm^{-2}; area capacity, 1 mA h cm^{-2}) [20]. Copyright 2023, American Chemical Society.

a promising pathway for enhancing the cycling longevity and capacity of anodes. Tao et al. [79] constructed a single-atom Cu-modified zinc-based zeolitic imidazolate framework (ZIF-L) nanoarray in situ on a titanium mesh (denoted as CuZIF-L@TM) as a host structure for the zinc metal anode, as illustrated in (Figure 11(a)).

This integrated 3D conductive framework effectively reduces local current density and homogenizes the electric field distribution, thereby alleviating concentration polarization. Furthermore, the hierarchical macroporous array architecture not only provides sufficient space for zinc deposition but also mitigates volumetric variation and structural stress during cycling, enhancing the mechanical stability of the electrode. Combined experimental and theoretical calculations reveal that the atomically dispersed Cu sites in ZIF-L serve as zincophilic centers, guiding uniform and dendrite-free Zn deposition. As a result, the CuZIF-L@TM/Zn electrode exhibits stable cycling for up to 1100 h at 1 mA cm^{-2} with a low overpotential of ~50 mV (Figure 11(b)), and the corresponding full cell assembled with the CuZIF-L@TM/Zn anode maintains excellent capacity retention after 1000 cycles (Figure 11(c)).

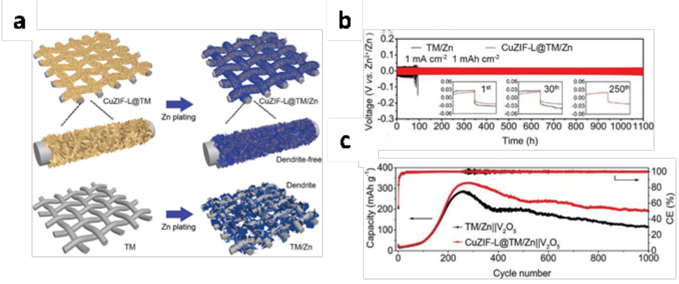

Figure 11. (a) Schematic illustrations of the Zn depositions on CuZIF-L@TM host and TM host. (b) Voltage profiles of symmetric cells using CuZIF-L@TM/Zn or TM/Zn electrodes at a current density of 1 mA cm^{-2}. (c) Cycling performances of TM/Zn||V_2O_5 and CuZIF-L@TM/Zn||V_2O_5 full cells at a current density of 1 A g^{-1} [79]. Copyright 2022, Wiley-VCH.

Wang et al. [80] developed a sandwich-structured zinc anode (BMC@Zn@In) with promising scalability, integrating three functional layers for synergistic performance enhancement. The architecture consists of a MOF-derived ZnO nucleation layer (BMC), a zinc middle layer for regulated deposition, and a stable indium-based protective coating (Figure 12(a)). This hierarchical design enables the symmetric cell to exhibit a depth of discharge of 76% under 6 mA cm^{-2}/12 mAh cm^{-2} (Figure 12(b)) and a minimal polarization of 11 mV at 0.5 mA cm^{-2}, stable cycling for 2000 hours at 1 mA cm^{-2}/0.5 mAh cm^{-2} (Figure 12(c)). When paired with $(NH_4)_2V_{10}O_{25}\cdot 8H_2O$ cathodes or active carbon, the full battery and hybrid supercapacitor achieve cycle lives of 5000 (Figure 12(d)) and 16,000 cycles (Figure 12(e)), respectively, demonstrating remarkable cycling durability.

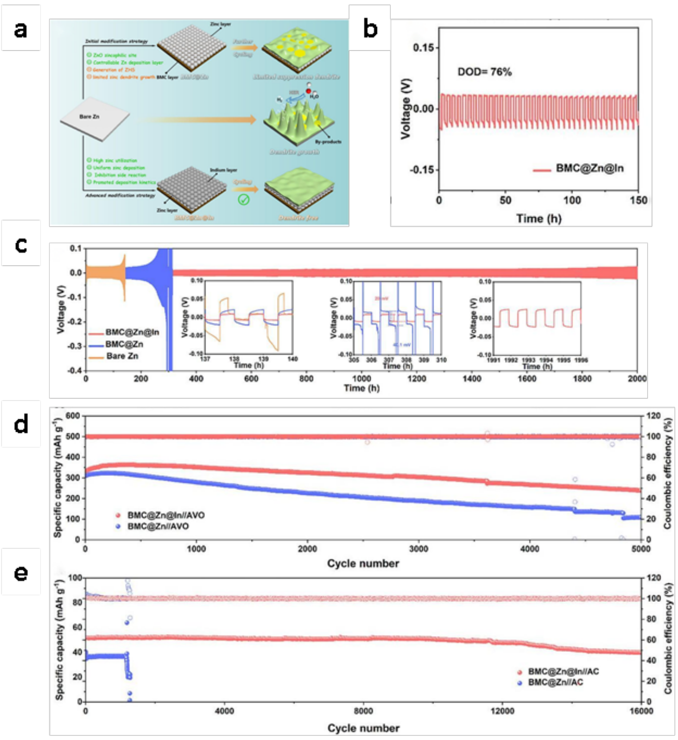

Figure 12. (a) Schematic diagram of electrochemical behavior of various Zn anode types. (b) Cycle performance of symmetric cells with BMC@Zn@In anodes at 6 mA cm^{-2}/12 mAh cm^{-2}. (c) Long cycling performance of symmetric cells with BMC@Zn, BMC@Zn@In anodes, and bare Zn at 1 mA cm^{-2}/0.5 mAh cm^{-2}. (d) Long-term cycling performance of BMC@Zn@In//AVO and BMC@Zn//AVO batteries at 5.0 A g^{-1}. (e) Cycling performance of BMC@Zn@In//AC and BMC@Zn//AC zinc ion capacitors at a current density of 5.0 A g^{-1} [80]. Copyright 2025, Wiley-VCH.

3.3 The Application of MOFs in Separator Functionalization

Incorporating MOFs into battery separators has emerged as an effective strategy for regulating ion transport and stabilizing electrode interfaces. MOF-functionalized separators act not merely as inert barriers but as active ion-regulating centers. Their well-defined porous structures function as molecular sieves that facilitate desolvation and homogenize ion flux, thereby suppressing dendrite formation at its origin. Moreover, the tunable internal surfaces of MOFs can immobilize water molecules and mitigate parasitic reactions, collectively enhancing the overall performance and safety of batteries.

Ultra-thin separators are essential components for achieving high-energy-density zinc-ion batteries, yet their structural integrity is often compromised by zinc dendrite penetration. To address this challenge, Li et al. [81] developed a functional composite separator (FCNF) by engineering an MOF-derived carbon/copper nanocomposite modification layer on a mechanically robust cellulose nanofiber (CNF) substrate (Figure 13(a)). The resulting ultrathin separator, with a thickness of merely 23 μm, exhibits exceptional stability in zinc anode applications while maintaining structural integrity. This innovative design provides an effective solution to dendrite-induced separator failure, demonstrating significant potential for advanced zinc-based energy storage systems. The functional ultrathin FCNF separator demonstrates significantly enhanced cycling stability for zinc anodes under varying current densities and areal capacities when compared to conventional glass fiber separators and unmodified cellulose nanofiber membranes (Figure 13(b-d)). Three-dimensional laser confocal scanning microscopy characterization of zinc deposition morphology reveals that direct deposition on copper substrates generates substantial surface roughness with anomalous protrusions reaching several tens of micrometers in height. In contrast, samples incorporating UCNF and FCNF separators demonstrate remarkably uniform and planar zinc deposition layers with an average surface roughness of approximately 2 micrometers (Figure 13(e-g)).

Ma et al. [82] incorporated an amino-functionalized Zr-based metal-organic framework (UiO-66-NH$_2$) into a lignocellulose separator to enhance the reversibility of zinc electrochemistry. The amino groups not only exhibit zincophilic characteristics but also strongly interact with H$_2$O molecules via hydrogen bonding, thereby regulating the interfacial environment. The abundant sub-nanometer channels within UiO-66-NH$_2$ serve as a desolvation sieve, facilitating Zn^{2+} migration and uniform distribution while promoting efficient ion desolvation (Figure 14(a)). Even at an ultralow thickness of 20 μm, the modified separator significantly improves zinc deposition reversibility and suppresses water-induced hydrogen evolution. As a result, the Zn electrode employing this separator demonstrates a lifespan exceeding 2000 hours at 2 mA cm^{-2} (Figure 14(b)), with remarkable dendrite-free behavior, and remains operational even at an ultrahigh areal capacity of 25 mAh cm^{-2} (Figure 14(c-e)).

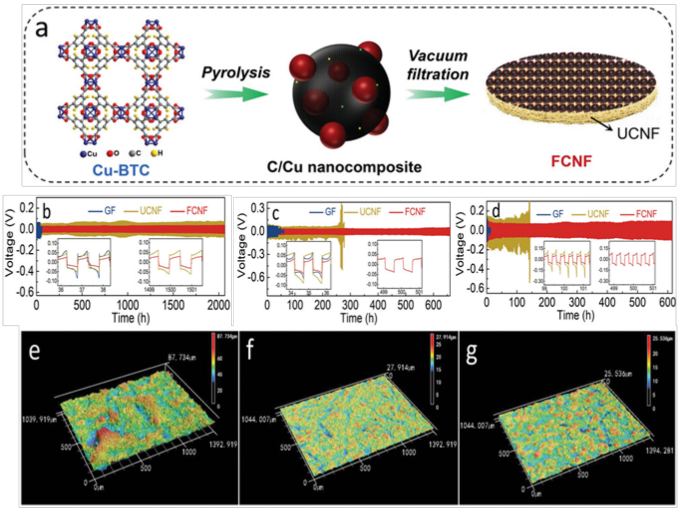

Figure 13. (a) Fabrication schematics (b–d) Cycling stability of the Zn//Zn symmetric cells with different separators under various testing conditions: (b) 1 mA cm^{-2} and 0.5 mAh cm^{-2}; (c) 5 mA cm^{-2} and 2.5 mAh cm^{-2}; (d) 10 mA cm^{-2} and 2 mAh cm^{-2}. (e-g) LCSM images of zinc deposition obtained at 2 mA cm^{-2} and 10 mAh cm^{-2} in Cu//Zn asymmetric cells with the GF (e), UCNF (f), and FCNF (g) separators [81]. Copyright 2023, Wiley-VCH.

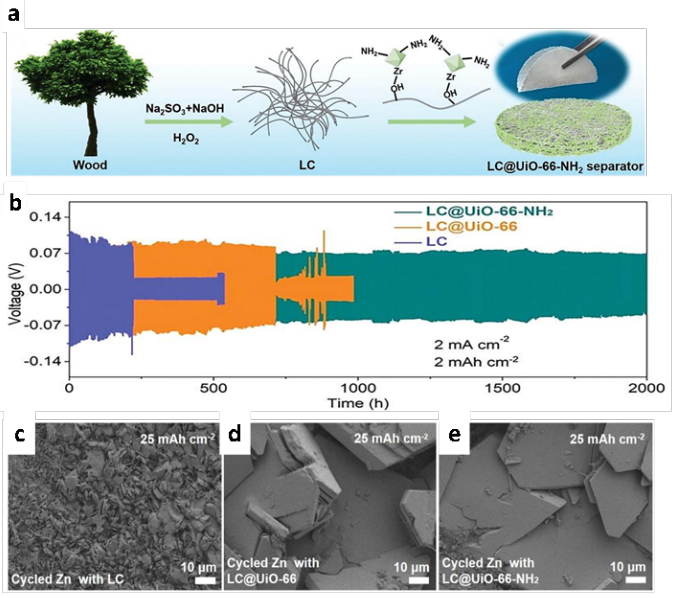

Figure 14. (a) Schematic diagram of the preparation process. (b) Cycling performance at 2 mA cm^{-2} and 2 mAh cm^{-2} when using different separators. SEM images of the Zn electrodes after the plating process with a very large capacity of 25 mAh cm^{-2}: (c) With LC separator, (d) With LC@UiO-66 separator, and (e) With LC@UiO-66-NH$_2$ separator [82]. Copyright 2023, Wiley-VCH.

4 Concluding Remarks and Future Directions

As comprehensively reviewed, metal–organic frameworks (MOFs) have been innovatively applied in three pivotal strategies for protecting zinc anodes: serving as interfacial protective layers, constructing three-dimensional host structures, and designing functional separators. This systematic review comprehensively analyzes the triple protection mechanisms of MOFs for zinc metal anodes. As interfacial protective layers, MOFs guide uniform zinc deposition through well-defined pore structures while their surface functional groups optimize the interfacial environment, significantly suppressing dendrite growth and side reactions. In host structure applications, MOF-based three-dimensional porous frameworks provide sufficient zinc deposition space and achieve controlled deposition behavior through uniformly distributed zincophilic sites, effectively accommodating electrode volume changes. For separator functionalization, MOF-modified separators demonstrate exceptional ion-sieving capabilities, where precisely engineered pore structures facilitate rapid zinc ion transport while blocking reactive species, enabling effective purification of the electrolyte environment. Looking beyond aqueous batteries, MOFs also demonstrate unique capabilities to address the core challenges of conventional solid-state batteries. Their ordered channels can be engineered into dedicated pathways for rapid ion transport, offering a promising solution to overcome the commonly low ionic conductivity of solid electrolytes. Concurrently, the functionalizable internal surfaces of MOFs can improve electrolyte/electrode interfacial compatibility, while their structural flexibility helps accommodate mechanical stress during cycling. These attributes establish MOFs as an innovative material platform for constructing next-generation all-solid-state batteries with high energy density and enhanced safety. Together, these multifaceted protective and conductive mechanisms collectively establish MOFs as versatile materials for comprehensive defense systems in zinc anodes and beyond, offering innovative solutions for developing high-performance energy storage systems.

MOF materials confront fundamental dilemmas in zinc anode protection systems: (I) Ordered pore channels guide directional ion migration yet simultaneously expose excessive active interfaces triggering side reactions; (II) Precisely designed pore size regulation contradicts actual structural defects in synthesis; (III) Dynamic coordination bonds between metal nodes and organic ligands risk dissociation in electrolyte environments; (IV) Hierarchical pores enhance ionic conductivity but potentially compromise mechanical integrity; (V) Intrinsic insulation contradicts the requirement for rapid charge transfer at electrochemical interfaces.

To address the key challenges in MOF-based zinc anode protection systems, researchers should focus on these implementable directions: (I) Development of intrinsically conductive MOF systems through rational molecular design to achieve efficient concurrent electron and ion transport; (II) Establishing comprehensive stability enhancement solutions combining framework optimization and interface modification such as hydroxyl and carboxyl moieties to improve material durability in electrochemical environments; (III) Advancing coordinated design of hierarchical pore structures to balance ion transport rate and selectivity. Through organizing existing research systems and proposing future perspectives, we hope the presented viewpoints and directions will offer valuable references for researchers in the field, inspire novel research strategies, and collectively facilitate the development of high-performance zinc-based batteries.

Data Availability Statement

Not applicable.

Funding

This work was supported by the National Key R&D Program of China under Grant 2024YFB3715000 and the National Natural Science Foundation of China under Grant 22405127.

Conflicts of Interest

The authors declare no conflicts of interest.

Ethical Approval and Consent to Participate

Not applicable.

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