



Constructing anion-enriched interfacial microenvironment for superior reversible anode-free zinc batteries

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ARTICLE INFO

Keywords:

Zinc batteries

Anode-free

HKUST-1

Anion- π interactions

Porous architecture

ABSTRACT

Anode-free configuration stands as a decisive route toward maximizing the energy density of aqueous zinc batteries. Its realization, however, requires a near-perfect coulombic efficiency, which is very challenging in aqueous electrolytes due to water-related interfacial side reactions and dendritic Zn growth. To tackle these challenges, we engineer an anion-trapped interfacial microenvironment via a $\sim 3\ \mu\text{m}$ Cu-based organic framework layer (HKUST-1) with three-dimensional pore structure. This functional layer exhibits a high compatibility to various conventional electrolyte systems, while its 3D porous architecture topologically guides uniform Zn deposition. More critically, the abundant electron-deficient aromatic rings within HKUST-1 layer enable strong anion- π interactions, reversing the interfacial zeta potential from $-2.08\ \text{mV}$ to $+13.08\ \text{mV}$, thereby driving the selective adsorption and localization of Zn salt anions. The achieving anion-trapped interfacial microenvironment restructures the interfacial Zn^{2+} solvation sheath and promotes the formation of a robust solid-electrolyte interphase (SEI) film. Together, these features establish a stable interphase that enables high-rate and highly reversible Zn plating/stripping process. As a result, the anode-free full cells achieve exceptional reversibility with an average coulombic efficiency of 99.7% over 500 cycles and the anode-free $\text{Zn}-\text{I}_2$ cells can even maintain 100% capacity after 1500 cycles at $-20\ ^\circ\text{C}$. This strategy of anion-trapped interfacial microenvironment based on anion- π interaction provides new insights for anode-free zinc batteries, enabling the fabrication of energy storage technologies with high safety and high energy density.

1. Introduction

The escalating demand for grid-scale energy storage has intensified the research for battery technologies that are safe, low-cost, and environmentally friendly. Aqueous zinc batteries (AZIBs) have emerged as a transformative candidate technology, leveraging the inherent advantages of Zn metal anode, including high theoretical capacity ($820\ \text{mAh g}^{-1}$), low redox potential ($-0.76\ \text{V}$ vs. SHE), high natural abundance, and low cost [1–7]. However, the commercialization of conventional AZIBs is hindered by the water-related interfacial side reactions (e.g.: corrosion, hydrogen evolution reactions) and dendritic Zn growth, which result in low coulombic efficiency (CE) and poor cycling life. To compensate for the irreversible Zn consumption caused by such

interfacial instability, a substantial excess of Zn metal anode ($50\text{--}200\ \mu\text{m}$ in thickness) is usually used, which severely constrains the volumetric energy density and cost-effectiveness [8–12]. In this context, the anode-free configuration, which directly plates/strips Zn on a bare current collector, represents a decisive route toward maximizing the energy density of this promising battery chemistry. Nonetheless, its successful implementation relies on an extremely stringent prerequisite: a near-perfect CE ($\text{CE} > 99.7\%$) over extended cycling to match the limited Zn reservoir.

Achieving such high reversibility in aqueous media remains a formidable challenge. The thermodynamic instability of Zn metal anode in aqueous electrolytes intensifies water-induced parasitic reactions at the interface. Simultaneously, the inherently heterogeneous Zn

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<https://doi.org/10.1016/j.cej.2026.180598>

Received 2 June 2026; Received in revised form 31 July 2026; Accepted 10 August 2026

Available online 11 August 2026

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nucleation and growth on foreign substrates, like copper, exacerbate dendrite formation [13–25]. These coupled issues lead to rapid capacity fade of AZIBs and are particularly fatal in anode-free systems, where any irreversible loss directly depletes the finite Zn inventory. Recent efforts to stabilize Zn plating/stripping have focused on interface engineering, including chemical interface modification of Cu current collectors and developing electrolyte additives. For example, aromatic molecule-based self-assembled 4-mercapto-pyridine monolayers have been employed to enhance charge transfer and Zn deposition kinetics [26]. Surface homogenization via Cl atomic layers has also been proposed to induce dense Zn growth along favorable crystallographic planes [27]. Similarly, substrates functionalized with aluminium fluoride hydroxide (Cu@AOF) can guide lateral Zn^{2+} flux and promote planar Zn deposition [28]. Although effective, these approaches largely operate through cation-centric mechanisms, treating anions as passive bystanders. Yet, beyond Zn^{2+} , the interfacial behavior of anions, key constituents in the electric double layer and the Zn^{2+} solvation sheath, has been largely overlooked in interfacial design. Thus, precisely controlling the anion microenvironment at the electrode interface remains an underexplored avenue. It can fundamentally suppress parasitic reactions and achieve the near-perfect CE for anode-free AZIBs.

Herein, we construct an anion trapped interfacial microenvironment to fundamentally address the coupled challenges in anode free AZIBs. This is achieved by engineering a thin, uniform, dense metal-organic framework (MOF) layer of HKUST-1 directly on the Cu current collector. This functional layer serves a dual purpose: its three-dimensional porous architecture topologically guides uniform Zn deposition; its abundant electron-deficient aromatic rings within the HKUST-1 framework establish strong anion- π interactions, which actively reverse the interfacial zeta potential from negative to positive (+13.08 mV). This reversal drives the selective adsorption and localization of electrolyte anions, creating an anion-enriched interface microenvironment, which performs two critical functions (Fig. 1): i) it restructures the interfacial Zn^{2+} solvation sheath, forming water-scarce Helmholtz plane and reducing interface side reactions; ii) it facilitates the formation of a robust, anion-derived inorganic-rich SEI. Consequently, the synergistic

effect guides dendrite-free Zn plating/stripping with exceptional reversibility. Benefiting from this rationally designed anion trapped interfacial microenvironment, the anode-free Zn|Cu half cells achieve an average CE of 99.7% over 500 cycles. When paired with an I_2 cathode, the anode-free Zn- I_2 cells maintain $\sim 100\%$ of its capacity after 1500 cycles even at a low temperature of -20°C . This work underscores the pivotal yet underappreciated role of anions in interfacial stability and introduces anion- π interaction as a powerful molecular tool for precise interfacial microenvironment engineering, providing a new design principle for high-energy, long-life AZIBs.

2. Results and discussion

2.1. Construction and characterization of the in situ-grown HKUST-1 layer

Building upon the design principle of an anion-trapped interfacial microenvironment, we first established a robust and uniform HKUST-1 functional layer on the current collector. By immersing the clean copper foil in the growth solution, when the copper atoms on the surface of the copper foil come into contact with the hydrogen peroxide (H_2O_2) in the solution, they will be oxidized to Cu^{2+} . The Cu^{2+} ions coordinate and combine to form HKUST-1 nanocrystals attached to the surface of the copper foil. HKUST-1, a Cu-based metal-organic framework (MOF), is constructed from Cu^{2+} and organic linkers, forming a three-dimensional porous structure with large and accessible channels. This well-defined architecture makes it particularly suitable for regulating ion transport and metal deposition behavior in electrochemical systems. As shown in Fig. 2a, a dense and adherent HKUST-1 film was fabricated on the Cu foils via an in-situ growth strategy [29]. This method offers a distinct advantage by fostering strong chemical bonding between the MOF and the substrate, which is critical for preventing particle detachment during long-term electrochemical cycling and ensuring mechanical integrity of the interface. SEM characterization revealed that the HKUST-1 particles grown on the Cu surface exhibited a well-defined polyhedral morphology (Fig. 2a). Corresponding EDS mapping confirmed the

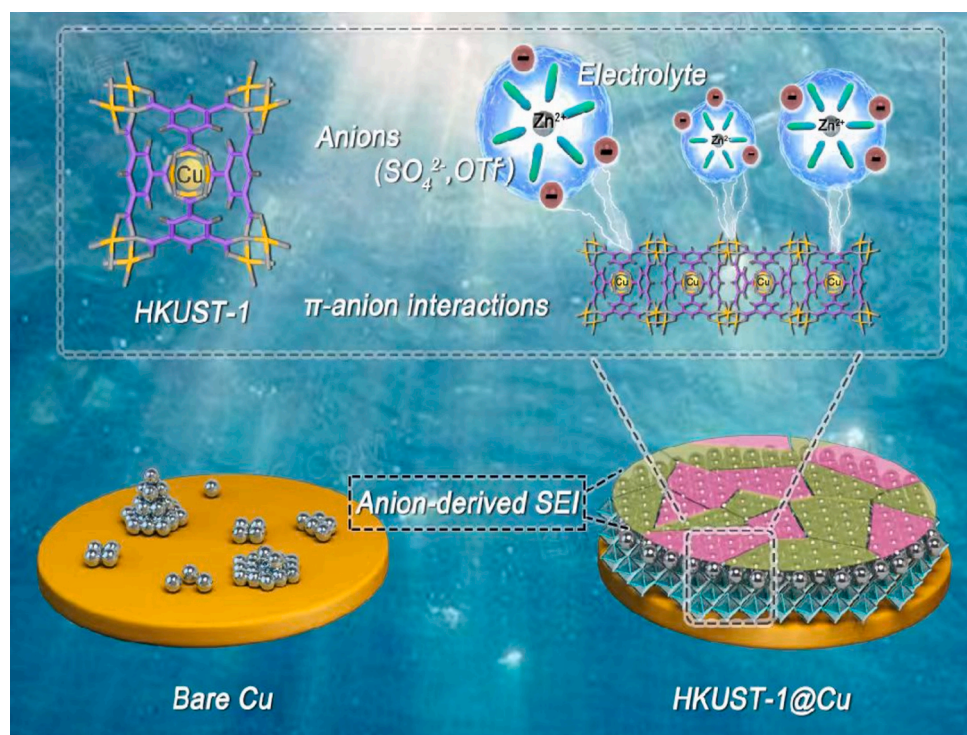


Fig. 1. Schematic representation of π -anion interactions on the HKUST-1@Cu surface.

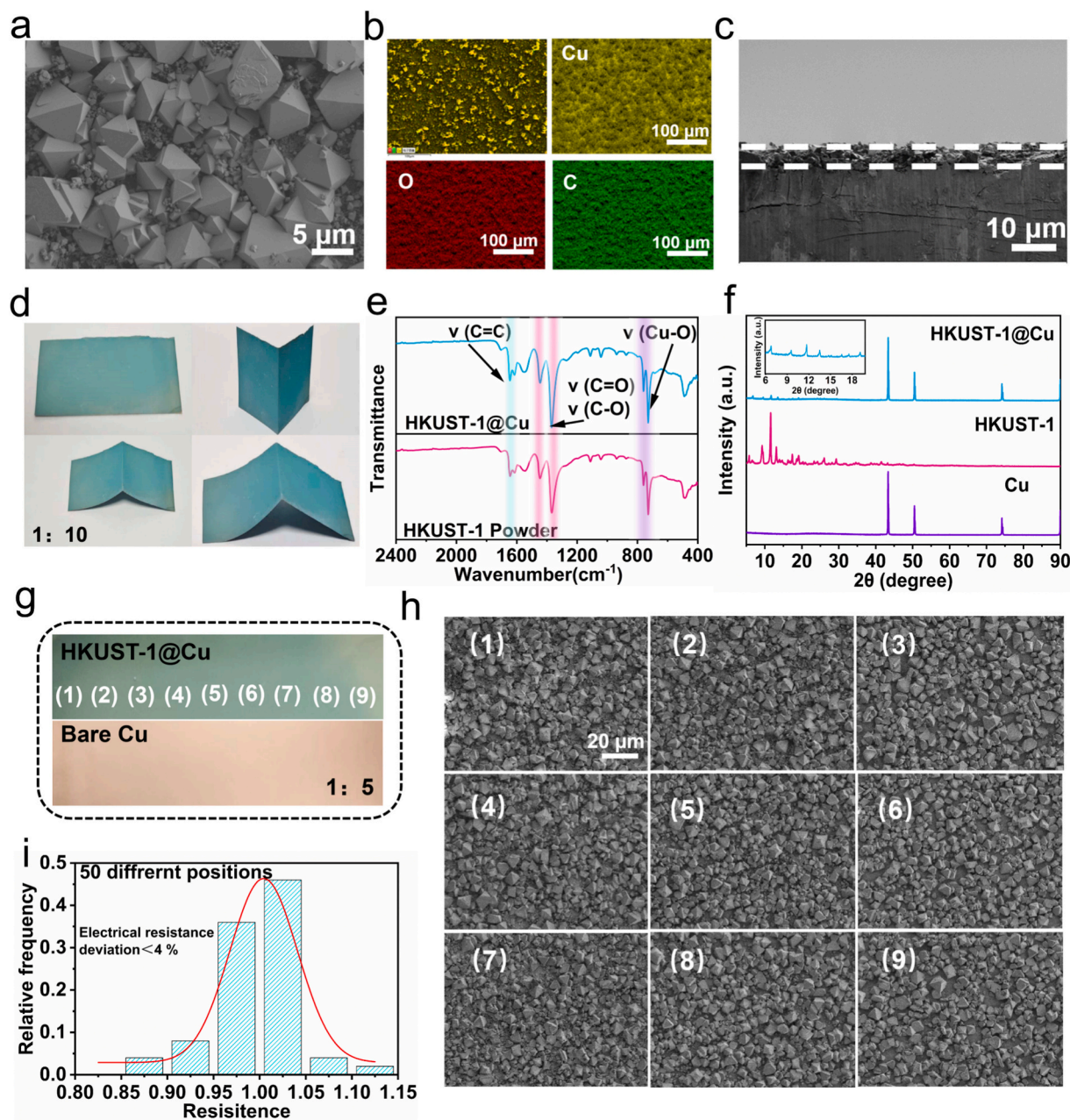


Fig. 2. Construction and characterization of the in situ-grown HKUST-1 layer. a, b) SEM images and EDS mapping results of HKUST-1@Cu. c) SEM image of the cross section of HKUST-1 layer. d) Verify its good adhesion by bending it. e) FTIR spectrum of HKUST-1@Cu layer and HKUST-1 powder. f) XRD comparison results related to HKUST-1@Cu. g) Digital photo of the pristine HKUST-1@Cu and Bare Cu. h) SEM of the 9 surface sites of HKUST-1, scale bar: 20 μm. i) The distribution of resistances at 50 different positions on a large area of HKUST-1@Cu.

homogeneous distribution of C, O and Cu elements across the surface, corroborating the complete and uniform coverage of the HKUST-1 layer (Fig. 2b). Cross-sectional SEM further showed that the thickness of the HKUST-1 layer was ~3 μm, making it one of the thinnest interphase layers in anode-free AZIBs (Fig. 2c). Furthermore, the robustness of the HKUST-1 interface layer was tested through repeated folding. As shown in Fig. 2d, after multiple folds and curls, the HKUST-1 particles remain firmly anchored to the substrate, indicating a strong interfacial adhesion rather than a mere physical attachment. To further examine the mechanical integrity of the HKUST-1 layer at the bending region, an enlarged SEM image of the folded area was provided in Fig. S1. The HKUST-1 layer maintains an intact surface morphology without obvious cracks or delamination, further confirming its good mechanical robustness under bending deformation. Meanwhile, XPS analysis was

employed to gain deeper insights into the bonding environments and structural evolution of HKUST-1@Cu before and after cycling, as shown in Fig. S2. The presence of characteristic Cu²⁺ signals in the Cu 2p spectrum, alongside the clear signatures of Cu–O–C bonds in both the C 1 s and O 1 s spectra, confirms that HKUST-1 was chemically grafted onto the Cu surface via Cu–O–C linkages rather than merely physically attached. After cycling, the main characteristic peaks associated with the organic linkers, including C–C, C–O, C=O and Cu–O–C, are well retained, indicating that the HKUST-1 framework is not obviously damaged during the interfacial reaction process. These results further confirm the structural stability of the HKUST-1 interfacial layer under electrochemical cycling conditions.

More critically, the in-situ growth process preserved the intrinsic crystalline structure of HKUST-1. As shown in Fig. 2e-f, both FT-IR

spectroscopy and XRD patterns of the HKUST-1 layer aligned perfectly with those of pristine HKUST-1 crystals, confirming that the synthesis process did not induce phase impurities or structural degradation, thereby ensuring the functional units, particularly the electron-deficient aromatic rings, remain intact for subsequent anion regulation. Furthermore, to explore the scalability and large-scale preparation of this in-situ growth strategy, a large-area HKUST-1 interphase layer of $2 \times 8 \text{ cm}^{-2}$ was prepared on a Cu foil (Fig. 2g). The high consistency of this process was evidenced by SEM, which showed identical crystal morphology across 9 randomly selected locations (Fig. 2h). FT-IR spectroscopy further verified the structural integrity of the HKUST-1 film, with characteristic vibrations of C=O, C–O, and Cu–O bonds matching those of phase-pure HKUST-1 (Fig. S3). Remarkably, resistance measurement between the top and bottom surfaces of the HKUST-1 film displayed exceptional uniformity with a small deviation $<4\%$ across 50 different positions, demonstrating outstanding large-area uniformity of the interfacial layer and underscoring the scalability of the in-situ growth strategy (Fig. 2i).

2.2. Anion-trapped interfacial microenvironment

Beyond the structural uniformity, the chemical functionality of the HKUST-1 interface was then thoroughly investigated. Firstly, the interfacial wettability was probed through contact angle measurements. As shown in Fig. 3a and Fig. S4, compared to the bare Cu substrate (contact angle: 74.3°), the HKUST-1 interface layer exhibited low contact angle and high compatibility to various conventional electrolyte systems, which promoted uniform electrolyte infiltration and enabled rapid Zn^{2+} transport kinetics at the interface. Besides, the specific surface area of the HKUST-1 interface layer was $353.93 \text{ m}^2 \text{ g}^{-1}$ by using N_2 adsorption at 77 K. And the analysis of low-pressure adsorption data demonstrated that the average pore size was 23 Å, which was much larger than the diameters of Zn^{2+} and was conducive to guiding uniform Zn deposition (Fig. 3b–c).

More importantly, the key functional units of abundant 1,3,5-benzenetricarboxylic acid (H_3BTC) linkers within HKUST-1, whose electron-deficient aromatic rings can trap a large quantity of Zn salt anions via anion- π interactions, helping to form a robust, anion-derived inorganic-rich SEI layer during electrochemical cycling [30]. It should be noted that the anion- π interaction is broadly applicable to various anions, but the interaction strength depends on the intrinsic properties of the anions, such as charge density, polarizability, hydration/desolvation energy, and steric configuration. Generally, anions with delocalized charge, suitable polarizability, or accessible oxygen-containing groups tend to be more readily trapped by electron-deficient aromatic rings. Therefore, common Zn salt anions in aqueous zinc batteries, such as OTf^- and SO_4^{2-} , can interact with the H_3BTC linkers, although their interaction strengths may vary due to their different solvation structures. This was further quantitatively supported by the quadrupole moment (Q_{zz}) [31]. As shown in Fig. 3d, the H_3BTC linker exhibited a significantly higher Q_{zz} value (-39.63) than bare benzene (-83.38) because of its abundant carboxyl groups, indicating a substantially enhanced capability for interacting with anions. Furthermore, Fig. 3e demonstrated that the Zn salt anions interacted favorably with the H_3BTC linker with overlapping electron clouds, wherein the interaction distance was shorter than the sum of van der Waals radii.

Direct experimental evidence confirmed the formation of this unique anion-trapped interfacial microenvironment. Zeta potential measurements revealed a decisive reversal from -2.08 mV (bare Cu) to $+13.08 \text{ mV}$ for HKUST-1 interface layer, signaling the creation of a positively charged surface that electrostatically attracted Zn salt anions (Fig. 3f). Besides, when using $\text{Zn}(\text{OTf})_2$ as Zn salt, NMR spectroscopy provided a molecular-level insight, in which a significant upfield shift of the OTf^- signal indicated a shielding effect on F atoms, characterizing the anion- π complexation (Fig. S5). Furthermore, the HKUST-1@Cu electrode was immersed in a $2.0 \text{ M Zn}(\text{OTf})_2$ electrolyte and subsequently rinsed

thoroughly with deionized water. The FT-IR spectrum of the rinsed electrode still exhibited the characteristic vibration bands associated with CF_3SO_3^- and $-\text{CF}_3$ groups, confirming the persistent adsorption of OTf^- on HKUST-1 through anion- π interaction (Fig. 3g). At the same time, ultraviolet-visible (UV-vis) absorption spectroscopy displayed a distinct red shift upon introducing $\text{Zn}(\text{OTf})_2$ to HKUST-1 interface layer, also unequivocally demonstrating the formation of anion- π interaction (Fig. 3h).

The formation of the SEI layer results from a dynamic structure of the electrolyte at the interface. The interface solvation differences between the two were explained by molecular dynamics simulations of the transient structure at the interface (Fig. 3i). Near the bare Cu interface, the coordination number of OTf^- in the solvation structure is 0.55, whereas the anion- π interaction on the HKUST-1@Cu surface led to the formation of an anion-rich solvation shell near the surface ($\text{CN}_{\text{OTf}} = 0.78$) (Fig. 3j–k). As shown in Fig. 3l, the anion-rich electrode surface formed a stable electrochemical architecture. Normalized density distributions also revealed significantly reduced aqueous phase on the HKUST-1 surface compared to Bare Cu, substantially mitigating surface side reactions (Fig. 3m).

Collectively, these multi-faceted characterizations established that the in situ-grown HKUST-1 layer did not merely act as a physical coating. Instead, it actively engineered an anion-trapped interfacial microenvironment through potent anion- π interactions. This microenvironment, characterized by localized anion enrichment in Helmholtz plane, was pivotal for reducing interface side reactions, regulating Zn^{2+} deposition and the formation of stable SEI film.

2.3. Nucleation and interfacial stabilization

Having established the formation of an anion-enriched interface microenvironment, we next explore its advancement in enhancing the reversibility of Zn plating/stripping process. DFT calculations were first performed to compare key interfacial properties on bare Cu surfaces and the HKUST-1 interface layer. As shown in Fig. 4a, HKUST-1 interface layer exhibited the strongest binding energy with Zn than that Cu planes, which substantially reduced the nucleation barrier and encouraged uniform initial deposition. Furthermore, the calculated diffusion energy barrier for Zn on the HKUST-1 surface was remarkably low ($\sim 0.085 \text{ eV}$), favoring lateral Zn growth (Fig. 4b). Meanwhile, compared to bare Cu foils, the Cu electrode with HKUST-1 modification demonstrated a much lower overpotential in the initial voltage-capacity curves of half cells, highlighting its advantages in reducing nucleation barrier and charge-transfer resistance (Fig. 4c).

These predictions were directly validated by in situ optical microscopy. As shown in Fig. 4d, while severe roughening and Zn dendrite growth rapidly occurred on bare Cu electrode, the electrode surface after modifying HKUST-1 layer maintained exceptional smoothness throughout plating, demonstrating effective guidance for uniform Zn deposition. Charge transfer resistance (R_{ct}) and apparent barrier (E_a) data further confirmed the enhanced charge transfer efficiency and accelerated de-solvation process. As shown in Fig. S6, after modifying the HKUST-1 layer, it can be observed that the symmetrical cells exhibited significantly reduced semi-circular features in the EIS spectra, indicating lower interfacial charge transfer impedance. Further analysis of temperature-dependent kinetics yielded an apparent activation energy (E_a) of $12.27 \text{ kJ mol}^{-1}$ for de-solvation, significantly lower than that on bare Cu, confirming the rapid de-solvation kinetics [32,33].

The composition of the resulting SEI was investigated by XPS. After 30 plating/stripping cycles, the S 2p spectrum of HKUST-1@Cu exhibited OTf^- -derived sulfur species (S(VI)) and ZnS (S^{2-}), while the F 1s spectrum showed C–F species and ZnF_2 (F^-), indicating the preferential reduction of adsorbed OTf^- anions (Fig. 4e and f). This anion-derived SEI film was critical for suppressing water-induced side reactions and dendritic Zn growth, as well as enhancing de-solvation kinetics. At the same time, the stability of SEI film during cycling was

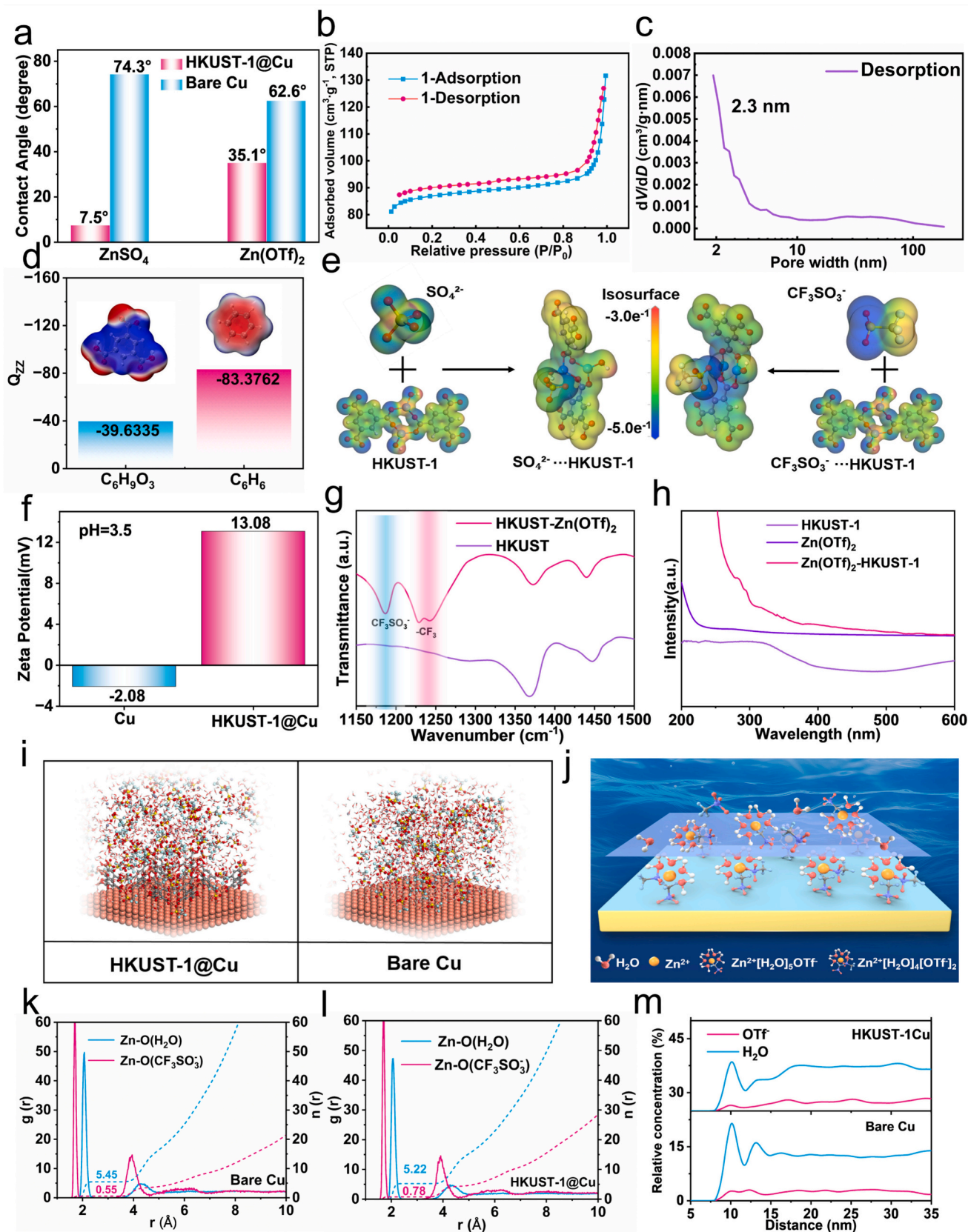


Fig. 3. Anion-trapped interfacial microenvironment. a) The contact angles of HKUST-1@Cu and bare Cu in the two electrolytes. b-c) Brunauer-Emmett-Teller (BET) analysis, b) Specific surface area, c) Average aperture. d) Comparison of Q_{zz} values for benzene rings and H_3BTC . e) The electrostatic interactions of SO_4^{2-} and OTf^- with HKUST-1, respectively. f) Zeta potential of HKUST-1@Cu and bare Cu surfaces. g) FTIR spectra of pristine HKUST-1@Cu and Bare Cu surfaces after immersion in 2.0 M Zn(OTf)_2 electrolyte. h) UV-vis absorption spectra between HKUST-1 and Bare Cu. i) Transient images of the interface in HKUST-1@Cu and bare Cu obtained through molecular dynamics simulations. j) Schematic diagram of anion-rich solvation structure at the interface. k-m) RDF and coordination

number obtained from MD simulations. k) HKUST-1@Cu. l) Bare Cu. m) Normalized density distributions of H_2O and OTf^- on the surfaces of HKUST-1@Cu and Bare Cu.

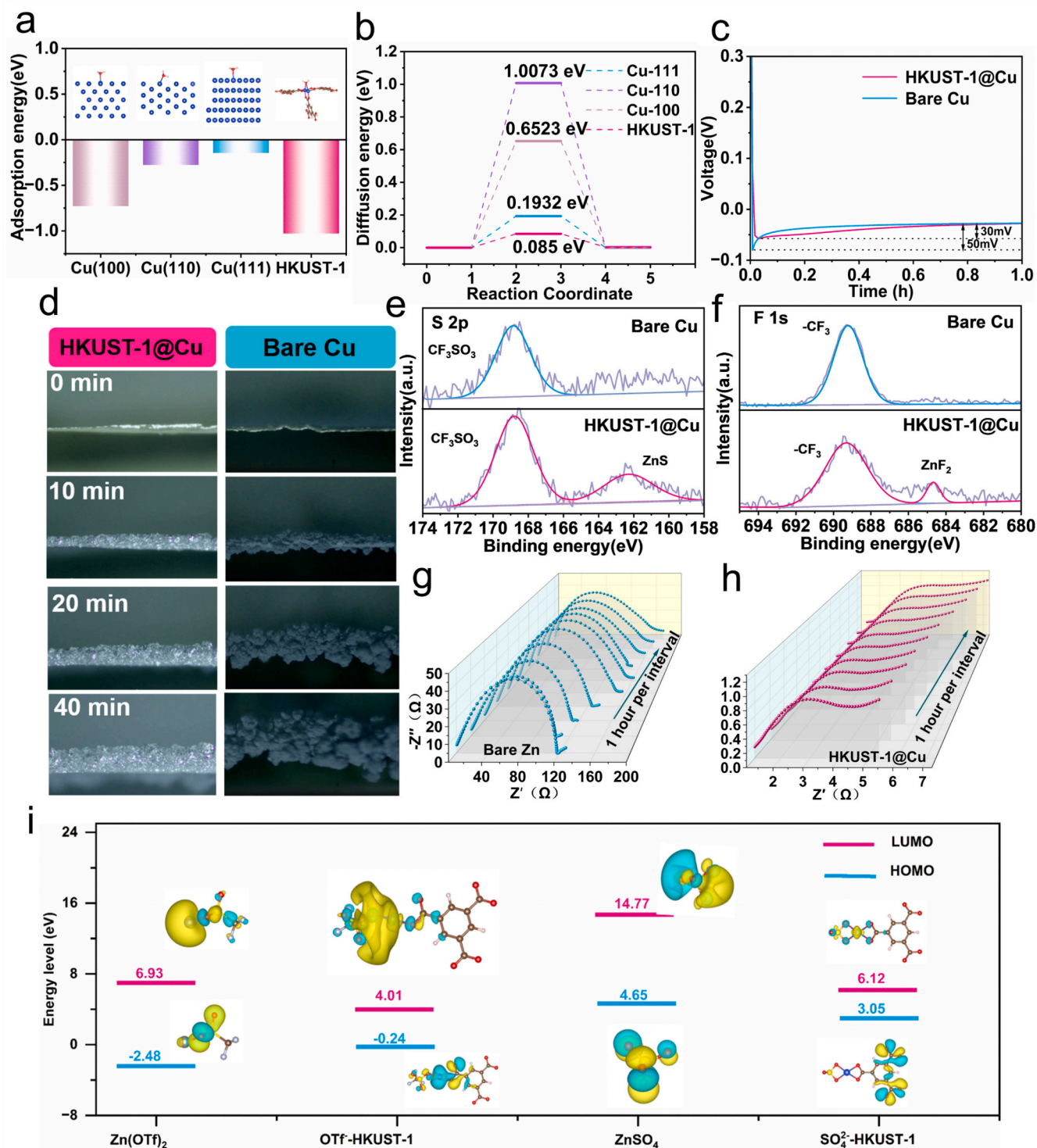


Fig. 4. Nucleation and interfacial stabilization. a) Binding energies of Zn atoms adsorbed on different structures. b) Migration energy barriers for Zn on different structures. c) The nucleation overpotential of HKUST-1@Cu and bare Cu. d) In situ optical imaging of zinc deposition on HKUST-1@Cu and bare Cu. e-f) High-resolution S 2p and F 1 s XPS spectra of Bare Cu and HKUST-1@Cu after cycling. g-h) In-situ EIS test results for HKUST-1@Cu and bare Cu. i) HKUST-1 and the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of anions.

also analyzed by in situ electrochemical impedance spectroscopy (EIS) [34]. As shown in Fig. 4g-h, the interfacial impedance of the Cu

electrode with HKUST-1 modification remained stable over time, corresponding to stable SEI film, in stark contrast to the continuously

increasing impedance of bare Cu, which suffered from by-product accumulation. Distribution of relaxation times (DRT) analysis identified that the timescale for surface ion migration (τ_2) remained consistently faster and more stable on HKUST-1@Cu, underscoring sustained interfacial kinetic advantages (Fig. S7).

Finally, DFT calculations provided a fundamental rationale for the SEI formation. The lowest unoccupied molecular orbital (LUMO) energy of Zn salt anions (e.g., SO_4^{2-} , Otf^-) underwent a significant decrease upon adsorption on HKUST-1 interface layer (Fig. 4i). This reduction in LUMO energy facilitated the preferential reduction of these anions at the interface, thermodynamically favoring the formation of the stable SEI components (ZnS , ZnF_2).

Collectively, these results unveiled a coherent mechanism: the anion-trapped microenvironment not only regulated ion transport and deposition morphology but also actively fostered the formation of a self-limiting, robust SEI, thereby achieving the exceptional interfacial stability required for anode-free AZIBs.

2.4. Electrochemical performance and cycling stability

The stable interfacial properties of HKUST-1 layer directly translate into the electrochemical stability. Firstly, we compared the Zn deposition process on bare Cu and HKUST-1@Cu at varying deposition capacities. As shown in Fig. 5a, as capacity increased, bare Cu surfaces

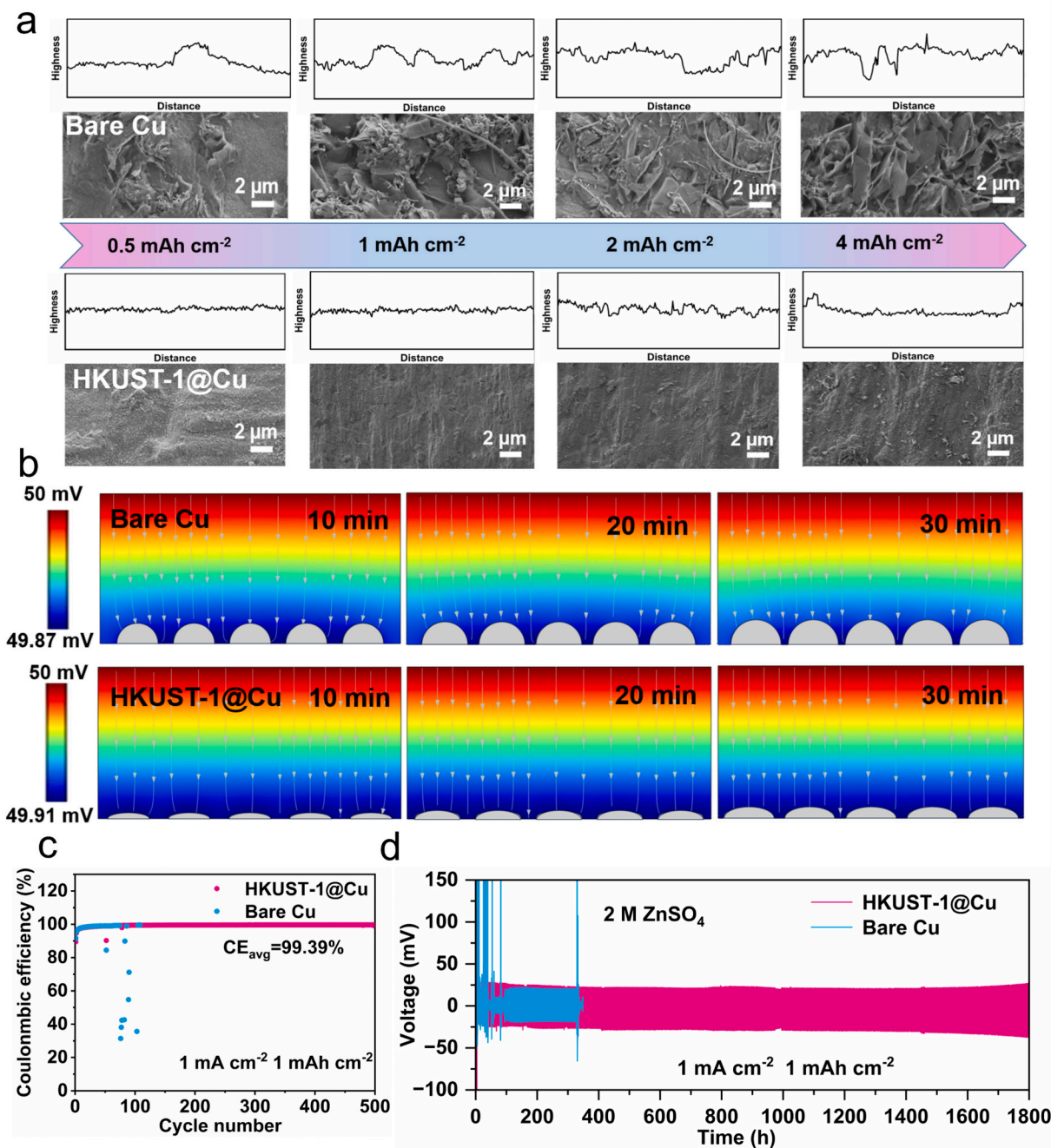


Fig. 5. Electrochemical performance and cycling stability. a) SEM images and statistical data on the surface of Zn anodes with different deposition capacities. b) Simulated electric field distribution of HKUST-1@Cu and Bare Cu. c) The cycling performance of Cu | Zn half cells. d) Cycling performance of symmetrical batteries in 2.0 M ZnSO₄ electrolyte.

developed pronounced dendritic structures and copious by-products, accompanied by a sharp rise in roughness (Fig. S8). In stark contrast, the electrode surface with HKUST-1 modification remained remarkably smooth and free of large-scale parasitic precipitates, demonstrating effective suppression of irregular growth. We also performed corresponding COMSOL electric field simulations. As shown in Fig. 5b, when the deposition time was increased from 10 min to 30 min, the electric field in bare Cu exhibited a chaotic enhancement state, leading to irregular Zn^{2+} protrusions and random concentration distributions. In

stark contrast, HKUST-1@Cu induced uniform Zn deposition throughout the entire deposition time. Furthermore, upon electroplating at 1.0 mAh cm^{-2} , Zn preferentially filled the pores and interstitial spaces of the HKUST-1 layer, leading to a progressively planarized surface (Fig. S9). This regulated deposition was facilitated by a lower nucleation overpotential, indicative of reduced kinetic barriers and enhanced Zn^{2+} migration. After Zn deposition, the stability was further evidenced by immersing in a corrosive electrolyte environment. It can be clearly observed that after immersion, the HKUST-1@Cu surface retained its

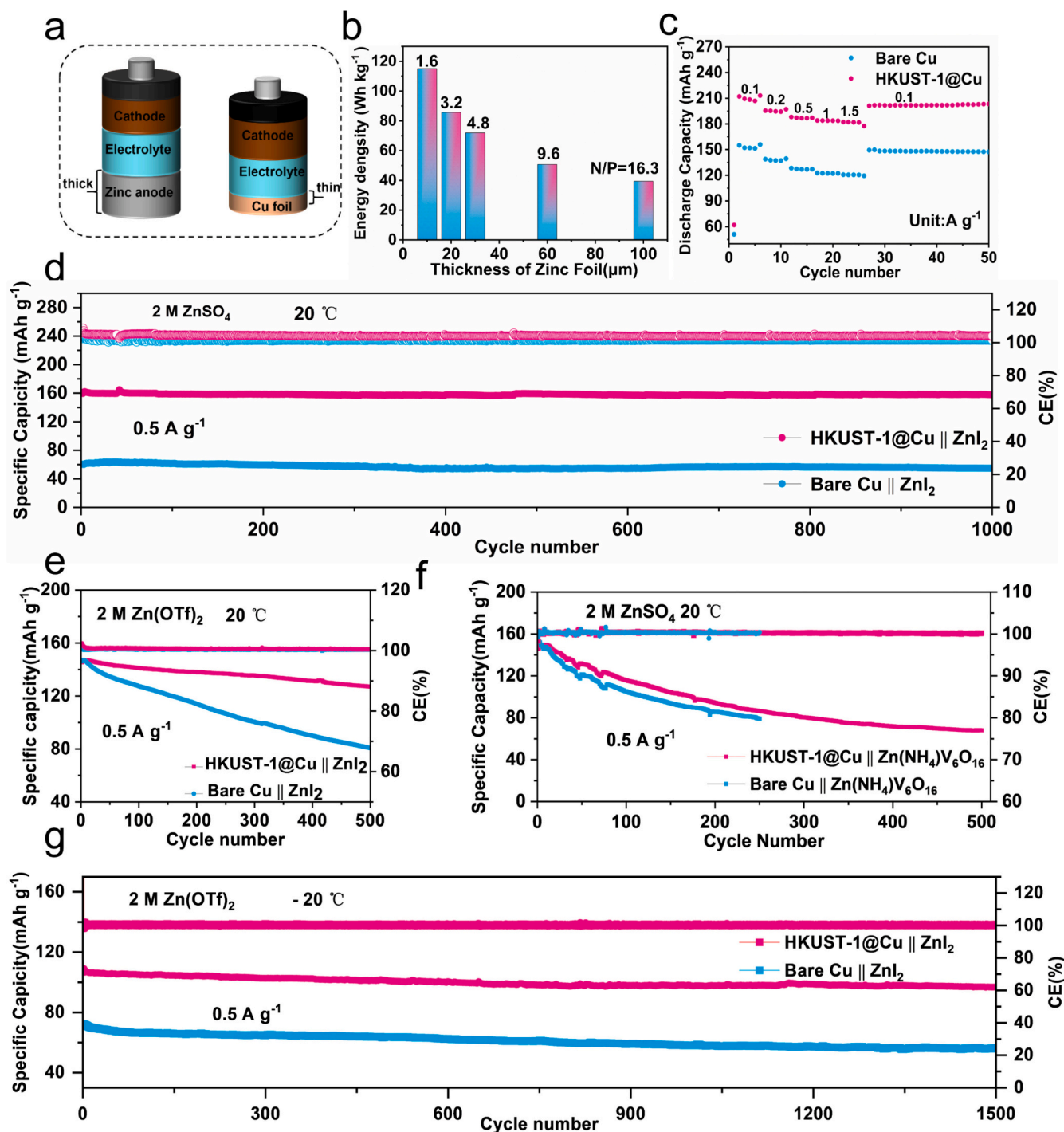


Fig. 6. Full cells of the anode-free configuration. a) Schematic Diagram of Conventional ZMB and AFZMB Structures. b) Theoretical maximum energy density achievable with zinc foil of different thicknesses. c) Rate performance of full cells. d) Long-term cycling performance of the entire battery with ZnI₂ cathodes in a 2 M ZnSO₄ electrolyte. e) Long-term cycling performance of the entire battery with ZnI₂ cathodes in a 2 M Zn(OTf)₂ electrolyte. f) Long-term cycling performance of the entire battery with Zn(NH₄)₂V₆O₁₆ cathodes in a 2 M ZnSO₄ electrolyte. g) Cycling performance of ZnI₂ cathodes at -20 °C.

smoothness, whereas bare Cu was covered with hexagonal plate-like dendrites (Fig. S10).

These advantages culminate in exceptional electrochemical performance. CE, a key parameter for evaluating the Zn plating/stripping reversibility, remained high and stable at $\sim 99.5\%$ over 500 cycles for HKUST-1@Cu, while cells with bare Cu suffered rapid failure within 100 cycles (Fig. 5c). In symmetric cell tests, HKUST-1@Cu delivered outstanding cycling stability in both ZnSO_4 and $\text{Zn}(\text{OTf})_2$ electrolyte systems (Fig. 5d and Fig. S11). Although slight voltage fluctuations were observed around 320 h in the $\text{Zn}(\text{OTf})_2$ system, the enlarged voltage profile in Fig. S11 confirms a regular charge/discharge behavior without obvious short-circuit or cell failure, further demonstrating the stable Zn plating/stripping process on HKUST-1@Cu. To further evaluate the performance of the HKUST-1 coating under increased areal-capacity conditions, the symmetric cells were tested at 2 mA cm^{-2} and 2 mAh cm^{-2} in 2 M ZnSO_4 electrolyte. The HKUST-1@Cu-based symmetric cell exhibited stable cycling for 250 h, whereas the bare Cu-based symmetric cell showed pronounced voltage fluctuations and failed after approximately 50 h (Fig. S12), further confirming the improved interfacial stability enabled by the HKUST-1 coating. After cycling 50 cycles, AFM confirmed that the HKUST-1@Cu electrode maintained significantly lower surface roughness compared to bare Cu, a key factor enabling sustained stable cycling. (Fig. S13). Furthermore, XPS analysis revealed no obvious compositional change in the HKUST-1 layer after cycling, attesting to its exceptional electrochemical and structural integrity (Fig. S14).

In general, these results underscored that the engineered HKUST-1 interface actively orchestrated a synergistic effect: homogenizing the electric field and ion flux to prevent dendrites, while its chemical stability and anion-regulating capability effectively suppressed corrosive side reactions, thereby creating a durable and self-regulating interphase for AZIBs with high reversibility and long-term stability.

2.5. Full cells of the anode-free configuration

The ultimate validation of the anion-trapped interfacial microenvironment strategy lies in its full-cell performance. Thus, systematic electrochemical characterizations were conducted to compare the performance differences between full cells assembled with HKUST-1@Cu composite electrodes and bare Cu. Schematic diagrams of conventional AZIBs and anode-free AZIBs were illustrated in Fig. 6a, replacing a thick Zn foil ($50\text{--}200 \mu\text{m}$) in traditional AZIBs with a thin, anode-free Cu dramatically increased the energy density. In our $\text{Zn}||\text{Zn}(\text{NH}_4)\text{V}_6\text{O}_{16}$ system, this anode-free configuration achieved a near-ideal N/P ratio of ~ 1.6 , a critical step toward practical high-energy-density batteries (Fig. 6b).

Electrochemical evaluation confirmed the superior functionality of the HKUST-1 interlayer. While cyclic voltammetry confirmed that the HKUST-1 layer did not alter the bulk redox mechanism of cathodes like $\text{Zn}-\text{I}_2$, its impact on interfacial kinetics was profound (Fig. S15). The full cells with HKUST-1@Cu electrode exhibited markedly smaller voltage polarization and exceptional rate capability, with 98% capacity recovery when the current density was returned to 0.1 A g^{-1} , underscoring the structural stability and highly reversible reaction kinetics (Fig. 6c).

Most notably, the HKUST-1@Cu-based full cells delivered extraordinary cycling stability, retaining a capacity of 160 mAh g^{-1} for over 1000 cycles at 0.5 A g^{-1} with nearly 100% capacity retention (Fig. 6d). This performance far surpassed the rapid degradation observed in the full cells using bare Cu electrode, directly attributing the long-term reliability to the robust SEI film derived by the anion-trapped interfacial microenvironment strategy. Enhanced storage stability further demonstrated practical utility: after 48 h of shelving, the HKUST-1@Cu cell maintained 88.36% of its initial capacity, significantly higher than the 79.53% for bare Cu, indicating effective suppression of open-circuit side reactions (Fig. S16).

Then, the versatility and environmental adaptability were also rigorously tested. Consistent performance superiority was maintained with alternative electrolytes and different cathodes, including $\text{Zn}||\text{Zn}(\text{NH}_4)\text{V}_6\text{O}_{16}$ (Fig. 6e-f) [35,36]. Remarkably, leveraging the advancement in suppressing parasitic reactions, the HKUST-1@Cu-based anode-free AZIBs achieved 1500 stable cycles with high-capacity output even at -20°C (Fig. 6g). This exceptional low-temperature performance underscored the design's robustness and significantly broadened its application prospects in extreme environments. Collectively, the anion-trapped microenvironment engineered by the HKUST-1 layer was not merely a conceptual advance but a practical enabler. It transformed the anode-free configuration from a challenging concept into a viable battery technology, achieving unprecedented cycling life, rate capability, and environmental resilience.

3. Conclusion

In summary, we have developed an effective interfacial engineering strategy that enables highly reversible anode-free AZIBs through the in-situ construction of a HKUST-1 layer. The dense and uniform HKUST-1 coating serves not only as a physical barrier but also as a functional interface that fundamentally regulates the electrode-electrolyte microenvironment. Key to this design is the abundance of electron-deficient aromatic rings within the HKUST-1 layer, which establishes strong anion- π interactions. These interactions actively reverse the interfacial zeta potential from -2.08 mV to $+13.08 \text{ mV}$, driving the selective adsorption and localization of Zn salt anions. The resulting anion-enriched interface simultaneously restructures the Zn^{2+} solvation sheath to promote de-solvation and facilitates the formation of a robust, anion-derived SEI film rich in ZnS and ZnF_2 . This synergistic mechanism ensures uniform, dendrite-free Zn deposition while effectively suppressing water-induced corrosion and hydrogen evolution. Consequently, the anode-free $\text{Zn}-\text{I}_2$ full cell delivers exceptional cycling stability, retaining nearly 100% of its capacity over 1000 cycles at 0.5 A g^{-1} at room temperature and sustaining stable operation for 1500 cycles even at -20°C . The strategy also proves versatile, enabling stable cycling with different cathodes. Our work thus introduces anion- π interaction-mediated microenvironment regulation as a powerful molecular tool for interfacial design, paving the way for practical, high-energy-density anode-free AZIBs.

CRedit authorship contribution statement

Bao Li: Writing – original draft. **Shuai Liu:** Supervision, Data curation. **Xueqing Chen:** Data curation. **Rujian Fu:** Data curation. **Mengfan Zhao:** Data curation. **Lifeng Hou:** Writing – review & editing. **Shi Wang:** Writing – review & editing. **Zhong Jin:** Writing – review & editing. **Qian Wang:** Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 22402146, 22572140, U24A6002), the Beijing Natural Science Foundation Xiaomi innovation joint Foundation (L223011), Young Elite Scientists Sponsorship Program by CAST (2022QNR001), Shanxi energy internet research institute (SXEI2023A004), Open Research Fund of Guangdong Advanced Carbon Materials Co., Ltd. (Kargen-2024B0905), the special fund for Science and Technology Innovation Teams of Shanxi Province (202204051001004).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2026.180598>.

Data availability

Data will be made available on request.

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