Taming Zn Electrochemistry with Carbon Nitride: Atomically Gradient Interphase for Highly Reversible Aqueous Zn Batteries

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The irreversibility issues f metallic zinc (Zn) anode of low Coulombic efficiency, persistent parasitic reactions, and severe dendrite growth remain a fundamental, century-old challenge hindering the practical applications in rechargeable aqueous batteries. Herein, a promising atomically gradient solid electrolyte interphase (SEI) strategy is demmonstrated, in which the bottom sublayer of atomic Cu dispersed carbon nitride tightly anchors the whole SEI layer onto Zn anode, whereas the top carbon nitride uniformizes Zn²⁺ flux, facilitates Zn²⁺ diffusion, and detaches the reactive water molecules. Theoretical simulations and structural analysis confirm the strong interactions of this SEI with Zn²⁺ ions that launch an ion-sieving effect to enable single Zn²⁺ ion conduction, and the porous and stiff feature accommodates the deposition stress and volume change under plating/stripping, ensuring consistent conformal contact on the substrate meanwhile suppressing the generation of Zn protuberant tips. Representative X-ray computed tomography study demonstrates the failure mode of the Zn anodes under aqueous electrolyte and verifies the homogeneous Zn electrodeposition behavior and spatially compact metallic structure in the presence of this hydrophobic-zincophilic SEI. Consequently, dendrite-free Zn plating/stripping at \approx 99.2% Coulombic efficiency for 200 cycles, steady charge-discharge for 2000 h, and impressive full cell cyclability are achieved.

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1. Introduction

Although lithium-ion batteries (LIBs) have dominated the current rechargeable energy market for portable devices and electric vehicles, the risk of bursting into flames and the increasing cost of raw materials have stimulated intensive investigations for next-generation rechargeable batteries.^[1-3] Aqueous zinc (Zn) batteries have long been heralded due to their enhanced safety, environmental compatibility, and cost advantage.^[4,5] Metallic Zn is an ideal anode since the intrinsic merits in low redox potential (-0.76 V vs standard hydrogen electrode) and high theoretical capacity (820 mAh g^{-1}),^[6] which offers high energy density to various Zn battery configurations including Zn-ion,^[7-10] Zn-bromine,^[11,12] Zn-iodine,^[13-15] and Zn-iron batteries.^[16] However, the long-standing roadblock to their practical commercialization lies in insufficient cycling stability and low reversibility due to various detrimental side reactions.

Parasitic water decomposition during Zn deposition fluctuates the pH environment in local areas of the Zn surface,^[17,18]

which leads to the inhomogeneous formation of Zn²⁺-insulating passivate layer, $(Zn(OH_4)^{2-}$ to ZnO), the reduction of the Zn reversibility and cycle life, alongside triggers dendrite formation and growth. To alleviate the water-induced side reactions, numerous efforts have been dedicated, including the use of functional electrolyte additives,^[19-23] highly concentrated electrolytes,^[24,25] artificial protective solid/electrolyte interphases (SEI) upon Zn surface,^[26,27] Zn-philic host,^[28] etc.^[29,30] Among them, a Zn²⁺conducting SEI is a simple and effective approach to protecting metallic Zn anode from reactive water and achieving high Zn utilization and reversible Zn stripping/plating. Wang et al.^[31] introduced dimethyl sulfoxide into aqueous ZnCl₂ electrolytes, in which the strong water-dimethyl sulfoxide interaction effectively suppresses the solvated water reduction and the decomposition of solvated dimethyl sulfoxide forms a robust SEI preventing Zn dendrite and further inhibiting water decomposition. Cui et al.^[32] developed an acetamide-Zn(TFSI)₂ eutectic electrolyte to facilitate the formation of Zn fluoride-rich organic/inorganic hybrid SEI. Such protective SEI can functionalize the Zn surface by SCIENCE NEWS ______

stable and favorable Zn²⁺ transport with the low-diffusion barrier, promoting a reversible Zn stripping/plating behavior. Guo et al.^[33] assembled a dense ZnS SEI in situ on the Zn surface, and this artificial layer obtained at 350 °C can suppress Zn corrosion by a physical barrier of reactive water meanwhile inhibit dendrite growth via guiding the Zn electrodeposition. Related SEI construction strategy has just experienced a renaissance to boost the research of utilization of metallic Zn in aqueous Zn batteries,^[34,35] similar to the previous studies on lithium metal anodes. However, the SEI design guidelines and their mechanism explication are still empirical. Understanding the physicochemical properties regarding interphase reactions and further optimizing the SEI layer to ensure long-term cyclability and high reversibility for the Zn anode remains a huge challenge.

We recently reported a dynamic and self-repairing SEI mechanism that the graphitic carbon nitride (g-C₃N₄) quantum dots additives in situ construct a protective SEI on Zn surface during the plating process, while this g-C₃N₄ protective SEI spontaneously redisperses into the electrolyte when reversing the electrical field upon stripping, showing dynamic regeneration in each battery cycle.^[36] Profiting from the intrinsic nature of periodic coplanar zincophilic pores and stiff structure, the g-C₃N₄ SEI separates the forming Zn deposits from the reactive water while keeping the pores for ion-sieving open to enable water-free, single Zn²⁺ ion conduction. Lynden A. Archer's group^[22] also presented a dynamic interphase formed by anisotropic g-C₃N₄ nanostructures in colloid electrolytes, which promotes the spatially compact and vertically aligned Zn electrodeposition. That is the structural features of g-C₃N₄ are desirable for improving aqueous Zn chemistry. Next goal should be to enhance the stability of the g-C₃N₄based artificial SEI to circumvent the failure of the cell resulting from the SEI peeling off. Metal single-atom coordination is a straightforward and effective strategy to partially modulate the electronic structures of g-C₃N₄,^[37-39] and meanwhile retain the structural features toward aqueous Zn chemistry. In addition, the metal affinity of the g-C₃N₄-based SEI can be strengthened by integrating metal single-atom components, which might firmly stabilize the surface protective layer and regulate the deposition behavior.

Herein we developed a gradient-functionalized g-C₃N₄ SEI on Zn surface by incorporating atomically dispersed Cu atoms on $g-C_3N_4$ (Cu@g-C_3N_4). To be specific, the bottom Cu@g-C_3N_4 tightly anchors the entire layer to the Zn foil, assuring the formation of a stable and conformal integrated SEI, whereas the top g-C $_3N_4$ uniforms the Zn²⁺ ion flux, facilitates Zn²⁺ diffusion and endows single Zn²⁺ conduction pathway (Scheme S1, Supporting Information). This SEI layer with gradient distribution from Cu@g-C₃N₄ to g-C₃N₄ (GCuCN) suppresses the side reactions since the ion-sieving effect shielding the reactive water molecules, inhibits the formation and growth of Zn dendrites owing to the stiff nature of $g-C_3N_4$, and alleviates the deposition stress and volume change because of the internally connected porous structures, in concert facilitating highly reversible and uniform Zn deposition-dissolution processes. As a result, a stable cycling of Zn anodes over 2000 h and high Coulombic efficiency of \approx 99.6% were demonstrated in 2 M ZnSO₄. X-ray computed tomography (CT) analysis monitors the failure mode of the Zn anodes under aqueous electrolyte and confirms the protective behavior of our GCuCN SEI layers in a real battery system. The $Zn||MnO_2$ full cell delivers a stable operation for over 500 cycles, while $Zn||V_2O_5$ over 1000 cycles under the GCuCN SEI protection.

2. Results and Discussion

The Cu@g-C₃N₄ was synthesized via the supramolecular anchoring strategy,^[40,41] and the supramolecule assembled through 2,4-diamino-6-phenyl-1,3,5-triazine and cyanuric acid served as active site host, which in situ catches and coordinates Cu2+ ions during the polymerization process. The typical XRD pattern of the Cu@g-C₃N₄ manifests a diffraction peak around 27.5°, in accord with that of pure $g-C_3N_4$, which signifies the characteristic signal of interlayer (002) stacking (Figure S1, Supporting Information). The field emission scanning electron microscopy (SEM) images of both g-C₃N₄ and Cu@g-C₃N₄ shows 2D wrinkled morphologies (Figure S2, Supporting Information). The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of the as-synthesized Cu@g-C₃N₄ reveals that individual Cu atoms were homogeneously dispersed throughout the g-C₃N₄ nanosheets (Figure 1a). The energy-dispersive spectrum (EDS) elemental mappings in Figure S3 (Supporting Information) confirms the existence of Cu in the obtained Cu@g-C₃N₄ and importantly the absence of any observable Cu nanoclusters or nanoparticles. Furthermore, the chemical state and coordination environment of the Cu@g-C₃N₄ was examined by X-ray absorption energy near-edgy structure (XANES) spectroscopy and extended X-ray absorption fine structure (EXAFS) spectroscopy. The electric dipole forbidden 1s \rightarrow 3d pre-edge transitions^[42] at ≈8982.5 eV is clearly distinguished in Cu@g-C₃N₄, and the position is located between those for the benchmark Cu foil and CuO, demonstrating the valence state of the Cu atoms in Cu@g-C₃N₄ is between +1 and +2 (Figure 1b). The Fourier-transformed (FT) k³-weighted extended EXAFS in Figure 1c, with the support of k³-EXAFS in Figure S4 (Supporting Information), discloses a predominant peak located at 1.43 Å for $Cu@g-C_3N_4$, ascribing to Cu-N scattering path. By contrast, the Cu foil exhibits a dominant peak at 2.3 Å. The absence of Cu-Cu contribution in Cu@g-C₃N₄ verifies again the atomic dispersion of Cu atoms, in line with the HAADF-STEM observation. In addition, EXAFS wavelet transform (WT) analysis (Figure 1d) was performed to gain more information on the coordination structures, since it can simultaneously provide both R-space and kspace resolution. With the reference of the Cu foil of an intensity minimum at 7.8 Å⁻¹, the Cu@g-C₃N₄ displays a much lower k-space at ≈ 5.5 Å⁻¹, which is attributable to the Cu-N/C contribution and suggests that Cu exists as a mononuclear Cu center without metallic Cu species.

The interactions of Zn²⁺ ions with g-C₃N₄ and Cu@g-C₃N₄ have first evaluated via density functional theory (DFT) simulations based on the calculated partial density of states (pDOS) and adsorption energies (E_{ads}) of the Zn adatom. For the pristine g-C₃N₄, the valence and conduction bands (Figure 1e, left panel) consist predominantly of nitrogen p_z and carbon p_z states, respectively, showing a bandgap of \approx 1.2 eV. It is indicative that the nitrogen atoms would be the preferred adsorption sites for metal ions.^[43] After adsorbing of a single Zn atom, the pDOS (Figure 1e, middle/right panel) shows semiconductor-to-metal transition with substantial states near the Fermi level, a hallmark

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Figure 1. Structural characterizations of $Cu@g-C_3N_4$. a) High-resolution HAADF-STEM image of $Cu@g-C_3N_4$, the distinct bright dots indicates Cu is atomically dispersed on the g-C₃N₄, b) Cu K-edge XANES spectra, c) FT-EXAFS spectra, d) wavelet transforms for the k³-weighted χ (k) K-edge EXAFS signals of $Cu@g-C_3N_4$ and reference samples including Cu foil, CuO, and CuPc, e) calculated pDOS of g-C₃N₄, 7n atom on g-C₃N₄, and Zn atom on Cu@g-C₃N₄, f) calculated adsorption energy of the Zn atom on Zn (101) and g-C₃N₄, g) differential charge density diagrams of the Zn atom on Zn (101) and g-C₃N₄, g) differential charge density diagrams of the Zn atom on Zn (101) and Zn atom on g-C₃N₄, the isosurfaces are 0.005 *e* bohr⁻³, h) calculated binding energy of g-C₃N₄ and Cu@g-C₃N₄ on Zn (101), and i) differential charge density diagrams of g-C₃N₄ and Cu@g-C₃N₄ layer on Zn (101). The yellow and green isosurfaces correspond to the increase in the number of electrons and the depletion zone, respectively. The isosurfaces are 0.0005 *e* bohr⁻³ for g-C₃N₄ on Zn (101) and 0.005 *e* bohr⁻³ for Cu@g-C₃N₄ on Zn (101). The big violet, gray, small light gray, and blue balls represent Cu, Zn, C, and N atoms, respectively.

of charge transfer between Zn atom and g-C₃N₄/Cu@g-C₃N₄, indicating the pronounced interactions between them. It can also be inferred from the calculated adsorption energies. As shown in Figure 1f, the E_{ads} (Zn on g-C₃N₄) reveals a much higher value (namely, more negative) than the E_{ads} of Zn on Zn(101). Furthermore, differential charge density diagrams show that compared with Zn on Zn(101) (Figure 1g, right panel), charge redistribution between Zn and g-C₃N₄ (Figure 1g, left panel) is more pronounced, which verified a strengthened affinity between Zn²⁺ ions and g-C₃N₄ (Table S1, Supporting Information). These results offer a scenario that the hydrated Zn²⁺ ions could lose coordinated waters in the solvation shell when they move across the

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Figure 2. The morphology and physicochemical properties of the GCuCN@Zn electrode. a) SEM morphology, b,c) cross-section morphologies, and d–f) the corresponding elemental mappings for GCuCN@Zn electrode; images of contact angles of the 2 M ZnSO₄ on g) bare Zn foil, h) GCuCN@Zn foil, i) water wetted then dried GCuCN@Zn foil, j) 2 M ZnSO₄ wetted then dried GCuCN@Zn foil, k) Zn K-edge XANES spectra, and l) FT-EXAFS spectra of 2 M ZnSO₄ wetted GCuCN@Zn, 2 M ZnSO₄, and the Zn foil reference.

g-C₃N₄ layer, enabling only bare Zn²⁺ ions to reach the electrode surface. The ion-sieving effect eventually avoids the active coordinated water contacting the electrode, thereby mitigating the water-induced side reactions. When Zn adsorbs on Cu@g-C₃N₄, the state from Zn locates far from the Fermi level, suggesting a relatively stable Zn²⁺ ion structure across the Cu@g-C₃N₄ layer.

In addition, the stability of g-C₃N₄ and Cu@g-C₃N₄ on Zn foil was also studied. As shown in Figure 1h, the binding energy of Cu@g-C₃N₄ on Zn (101) exhibits a value of -0.69 eV, of great competitive than that of g-C₃N₄ on Zn (101) (-0.21 eV). Bader charge analysis^[44-46] proclaims a charge transfer of 0.05 and 0.08 e/C₃N₄ from Zn (101) to g-C₃N₄ and Cu@g-C₃N₄, respectively (Table S2, Supporting Information). Differential charge density diagrams show that for g-C₃N₄ on Zn (101), the prominent feature is charge redistribution on the topmost Zn layer (Figure 1i, left panel). However, for Cu@g-C₃N₄ on Zn (101), pronounced charge transfer occurs between Cu@g-C₃N₄ and Zn (101), especially in the vicinity of Cu atoms (Figure 1i, right panel) can be noticed. The Cu atom bridges g-C₃N₄ and Zn (101) (Figure S5, Supporting Information), which would effectively tether the entire layer and prevent them from falling off.

As a proof-of-concept example, we then constructed an artificial SEI with a gradient design upon the Zn electrode, comprising the bottom Cu@g-C₃N₄ and upper g-C₃N₄ functional layer (labeled as GCuCN@Zn). From the SEM image in **Figure 2**a, the GCuCN@Zn electrode manifests a flatness and porous morphology. The cross-sectional image shows that the thickness of the GCuCN film is $\approx 9 \ \mu m$ (Figure 2b), and the corresponding EDS

mappings in Figure 2c-f give direct evidence of the expected gradient distribution from inner Cu@g-C₃N₄ to the surface g-C₃N₄ in the film. In addition, the surface wettability was investigated through the contact angle test for the Zn foil with GCuCN coating under 2 м ZnSO₄ electrolyte. As presented in Figure 2g,h, the electrolyte on GCuCN@Zn discloses a higher contact angle of 126.5° relative to that on bare Zn (96.6°), demonstrating a more hydrophobic property on the surface of GCuCN. Considering the negligible factor of PVDF (111.1° as shown in Figure S6, Supporting Information), it can be reasonably attributed to the surface hydrophobic nature of g-C₃N₄-based materials. What is noteworthy is that the contact angle turns to 74.7° on the electrolyte-wetted-then-dried GCuCN@Zn (Figure 2i), whereas keeps negligible change on the reference of the water-wettedthen-dried GCuCN@Zn (Figure 2j). Such a phenomenon can be reasonably attributed to the zincophilic nature of g-C₃N₄-based materials,^[36] owing to the numerous lone pair electrons from structural nitrogen and periodic coplanar pores, which is in concert with the DFT results. Further proof was given by the Zn Kedge XANES analysis in Figure 2k. The pure ZnSO₄ electrolyte shows a white-line peak at 9667.1 eV, while an obvious shift toward lower energy after ZnSO4 adsorbed on GCuCN film can be noticed, demonstrably deriving from the strong interaction between GCuCN and Zn²⁺ ions as verified in DFT computation. This interaction restrains the electron transfer from Zn to O in H₂O, thereby weakening the bonding strength between Zn²⁺ and H₂O.^[31] That is the solvation structure of Zn²⁺ in the electrolyte is modulated when it goes through the GCuCN film. The





Figure 3. Texture formation of GCuCN@Zn electrodes. 2D GIXD patterns of a) pristine GCuCN@Zn and GCuCN@Zn after b) 1st stripping, c) 1st stripping/plating, d) 15th stripping/plating, e) 75th stripping/plating process under 1 mA cm⁻² with 1 mAh cm⁻², f–j) SEM morphologies of GCuCN@Zn after 1st stripping, lst stripping/plating, 75th stripping/plating, 500th stripping/plating process and the Zn deposits under GCuCN SEI after 500th stripping/plating process, k–m) SEM morphologies of bare Zn after 1st stripping, 1st stripping/plating process under 1 mA cm⁻² with 1 mAh cm⁻², high-resolution XPS analyzation of n) Zn $2p_{3/2}$ and o) S 2p of bare Zn and GCuCN@Zn after 15th stripping/plating process under 1 mA cm⁻² with 1 mAh cm⁻².

FT-EXAFS results in Figure 2l unveil more solvation structure information. The distinct increased Zn-O bond proclaims a reduced O-coordination around Zn²⁺, hence the proton activity is impaired and electrochemical water decomposition is suppressed. This suppression effect was then studied by assembling asymmetric Zn||Stainless Steel (SS) cells with and without GCuCN functionalization (Figure S7, Supporting Information). The hydrogen evolution potential on bare Zn is -0.1 versus Zn while the potential on GCuCN@Zn shifts to -0.135 versus Zn, implying the resistance to the competing hydrogen evolution reaction is much improved under the protection of GCuCN on the Zn electrode.

The substantial impacts of the GCuCN SEI on inhibiting side reactions and regulating Zn electrodeposition were identified by 2D synchrotron grazing-incidence X-ray diffraction (GIXD) with a beam size of $\approx 5 \times 7 \ \mu\text{m}$. Figure 3a illustrates the GIXD pattern of pristine GCuCN@Zn, in which the diffraction spots at 2θ angles around 26° can be indexed to the interplanar graphitic stacking of GCuCN and that of 43.4° is assigned to the (101) planes of Zn. After first stripping process, a similar pattern of

GCuCN@Zn is observed in Figure 3b, witnessing an evenly Zn dissolution on each orientation. After first plating process, the GCuCN@Zn shows isotropic Zn scattering with multiple discrete spots at 2θ angles of 36.5°, 39.2°, 43.4°, 54.5°, and 70.1°, assigning to the (002), (100), (101), (102), and (103) planes of Zn (Figure 3c), which confirms the Zn deposits possess a nanocrystalline feature rather than forming Zn agglomerates or Zn protrusions. This suggests a homogeneous Zn growth mode stemming from the high affinity of GCuCN with Zn²⁺ ions that uniformizes Zn²⁺ ion flux and harmonizes ion migration. Continuing the stripping/plating process till 15th cycle, the GCuCN@Zn unveils a polycrystalline ring-like pattern of Zn, and importantly no other species can be detected. Such a phenomenon indicates the suppressed side reactions by the multifunctional GCuCN SEI, in consistent with the DFT computation and XANES analyzation. The adsorbed interaction of Zn2+ ions on GCuCN weakens the water reactivity and the hydrophobic nature of GCuCN synergistically shields the Zn electrode from direct aqueous corrosion. When reaching the 75th cycle, the GCuCN@Zn still only exhibits a polycrystalline crystal structure of metallic Zn ADVANCED SCIENCE NEWS _____ www.advancedsciencenews.com

with strong (101) texture, demonstrating again a stable and reversible Zn stripping/plating process and unearthing an electroorientation of Zn electrodeposits.

The morphology evolution during the stripping/plating on Zn electrode is further characterized using SEM. As shown in Figure 3f and Figure S8 (Supporting Information), a flat and smooth surface can be seen on GCuCN@Zn after first stripping, while the bare Zn unveils an insular dissolution behavior alongside a classical (002) orientation (Figure 3k and Figure S9, Supporting Information). Upon subsequent plating, uniform Zn²⁺ ions move through the GCuCN SEI and are reduced on GCuCN@Zn instead of the irregular accumulation of massive Zn flakes on bare Zn electrode (Figure 3g,l, and Figures S10 and S11, Supporting Information). Note that the deposits on bare Zn are loosely connected and the hexagonal interstices induced during the stripping process remain, a porous electrodeposit structure is created. This is mainly caused by uncontrolled interfacial side reactions and poor Zn anode reversibility, meanwhile may result in aggressive deposition on these small protrusions that evolve into large and sharp dendrite flakes. The observation after the 75th stripping/plating cycle has testified to this hypothesis, where bare Zn is full of abundant cliffy dendrites and dark by-product aggregations (Figure 3m and Figure S12, Supporting Information). In contrast, the GCuCN@Zn preserves an unabridged and glossy surface topography and the GCuCN SEI guarantees a conformal contact with Zn substrate (Figure 3h and Figure S13, Supporting Information). Even after 500 stripping/plating cycles, a flat surface is still obtained on GCuCN@Zn rather than protuberances or dendrites piercing out of the GCuCN SEI (Figure 3i and Figure S14, Supporting Information). Therefore, it can be rationally ascertained our gradient design of GCuCN with hydrophobic and zincophilic properties endows a fine-grain strengthening effect to homogenize the small-sized Zn and a stiff SEI feature to anchor the entire layer to the substrate along with restraining the dendrite growth. To provide insights into the microstructural details of Zn deposits under the GCuCN SEI, we conducted the SEM analysis of the 500 cycled GCuCN@Zn by removing the GCuCN SEI (Figure 3j and Figure S15, Supporting Information). Dense stacked Zn deposits are revealed to be structured aligned on GCuCN@Zn, which is triggered by the reduction of the electric double layer (EDL) thickness of the electrode. According to the Gouy-Chapman-Stern model, the thickness of EDL is constituted of the sum of the Stern layer and the diffusion layer.^[47,48] In a certain electrolyte system, the Stern layer is constant while the diffusion layer can be tuned by modulating the surface charge density. The strengthened interaction of GCuCN with Zn²⁺ ions is capable of increasing the charge density of the electrode, effectively decreasing the thickness of EDL and boosting the uniform deposition. Under the electrical field, migrating of the counter ions inside the EDL contributes to an electro-osmotic flow along GCuCN, inducing an EDL polarization.^[22] Considering the anisotropic structure of GCuCN, the broad surface polarization is able to produce torque to rearrange the Zn²⁺ ions and captain the orientated growth.

Furthermore, X-ray photoelectron spectroscopy (XPS) examination was carried out to scrutiny the surface chemistry of Zn electrode. The bare Zn anode after the 15th stripping/plating manifests a trailing Zn $2p_{3/2}$ XPS signal, which can be deconvoluted into metallic Zn and +2 oxidation state of Zn (Figure 3n). The Zn²⁺ component is ascribed to the by-products, hence as expected, the GCuCN@Zn uncovers a symmetrical Zn $2p_{3/2}$ XPS signal with only a metallic Zn component. This finding is also proved by the S 2p XPS analysis. The bare Zn evinces a distinct sulfate response, indicative of the formation of Zn₄SO₄(OH)₆ xH₂O insulative by-product. In the case of GCuCN@Zn, no sulfate signal can be detected, signifying the importance of integrating the gradient GCuCN SEI on engender the ion-sieving effect to eliminate Zn anode's passivation and corrosion.

Synchrotron X-ray computed tomography (CT) is a nondestructive imaging technique that allows to evaluate the 3D morphological changes inside practical battery systems.^[49–51] We subsequently employed the X-ray CT to capture the full microstructure of GCuCN@Zn electrode and visualize the evolution of morphological features in 3D space. The developed lab-made CT cell is illustrated in Figure 4a, which can achieve ex situ observation of both electrodes in the practical cycled batteries with highresolution scans. Typically, the X-ray beam (mean photon energy is \approx 32 keV in this case) penetrates through the cell and intensity of the transmitted beam is measured by an imaging detector with a high spatial resolution for different rotation positions of the sample. The contrast of X-ray images and reconstructed CT slices are directly related to different attenuation coefficients of Zn, C, O, Si, and S elements. Hence collected, converted and reconstructed data permits to identify different morphological features inside the battery. Figure 4b,c shows the reconstructed images of the bare Zn and GCuCN@Zn symmetric cell after the 75th plating/stripping cycles at 1 mA cm⁻² with 1 mAh cm⁻². Detailed Zn electrode reconstruction reveals the bare Zn possesses a loosely connected dendritic structure with a high amplification (~50 µm, Figure 4d). The large bright islands originate from the preferred Zn^{2+} ions' deposition that facilitates the dendrite growth, and the dark phase contrast region can be identified to be the stronger absorbed $Zn_4SO_4(OH)_6 xH_2O$ product. Moreover, the cross-sectional images offer clear distinctiveness that the theoretically predicted and postmortem electrode analysis verified Zn by-products, Zn dendrites, and dead Zn is capable of being recognizably discriminated. To our best knowledge, this is the first report to observe and detect the internal morphology and structure in the practical cycled battery system in Zn foil symmetric cells. By comparison, the GCuCN@Zn cell retains a relatively flat surface, and the uniform Zn deposits can be found dispersed throughout the cells with bits of some indistinct protuberances after 15th cycles (Figure 4f,g) and even 75th cycles (Figure 4h,i), in line with the above GIXD and SEM observation.

Detailed electrochemical investigations were further implemented. The reversibility of the Zn anode under the GCuCN protection is evaluated by an asymmetric Zn||SS half-cell, as presented in **Figure 5**a. Clearly, the Coulombic efficiency (CE) of bare Zn||SS cell shows an initial value of only \approx 56% and gradually increased to 94.5% within 20 cycles. This arises from a lattice fitting process of the Zn plate/strip behavior on SS foil. However, the stabilized CE is still low because of the poor reversibility of bare Zn caused by the corrosion and side reactions, and it fluctuates greatly after \approx 50 cycles, which is mainly owing to short-circuiting of the Zn||SS cell. In contrast, the cell with GCuCN coated on SS delivers high and stable CE values in the first 20 cycles and keeps for over 200 cycles, denoting a close-to-full control of the reactive waters and good reversibility of metallic Zn

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Figure 4. Synchrotron X-ray computed tomography analysis of GCuCN@Zn symmetric cells. a) The configuration of lab-made X-ray CT cell, 3D X-ray CT tomographic reconstructions of b) bare Zn symmetric cell and c) GCuCN@Zn symmetric cell after 75th plating/stripping cycles at 1 mA cm⁻² with 1 mAh cm⁻², the reconstructed electrode and the cross-sectional images of d,e) bare Zn after 75th plating/stripping cycles, f,g) GCuCN@Zn after 15th plating/stripping cycles, and h,i) GCuCN@Zn after 75th plating/stripping cycles.

under the protection of GCuCN. The charge–discharge voltage profiles for different cycles of these Zn||SS cells are depicted in Figure 5b and Figure S16 (Supporting Information). Note that the voltage hysteresis in Zn||GCuCN@SS is slightly larger than that of bare Zn||SS, suggesting a smaller nucleation size of Zn in the GCuCN@SS system according to the following relationship^[52,53]

$$r = 2\frac{\gamma V_m}{F|\eta|} \tag{1}$$

where *r* is the critical Zn nucleus radius, γ and $V_{\rm m}$ are surface energy and molar volume of the Zn, *F* is the Faraday constant, and η is the nucleation hysteresis. In the case of GCuCN@SS, the decreased Zn nucleus radius endows the feasibility to stabilize fine-grained Zn nuclei and thereby is conducive to the formation of the dense and flat Zn deposits instead of the loose Zn flakes.

The electrochemical evidence of the impact of the GCuCN layer on Zn metal corrosion was studied by linear polarization experiments (Figure 5c). Compared to the bare Zn, the corrosion potential of the GCuCN@Zn is positive-shifted and the corrosion current is downgraded, reflecting a less tendency toward corrosion reactions. The semiconductive nature of the GCuCN layer results in a resistive protecting SEI, as also indicated by a high electrical resistivity (\approx 2450 Ω cm, Figure S17, Supporting Information).^[33,54] Such a high resistance is capable of inducing Zn plating underneath the SEI. The ionic conductivity is estimated as ≈ 0.995 mS cm⁻¹ (Figure S18, Supporting Information), suggesting a fast Zn²⁺ ion diffusion kinetic through the GCuCN SEI. Furthermore, the transference number of Zn^{2+} ($t_{7n^{2+}}$) in the GCuCN is calculated to quantitatively deduce the Zn^{2+} migration and transport (Figure S19 and Table S3, Supporting Information). In a bare Zn symmetric cell, a low t_{Zn2+} of 0.356 is







Figure 5. Electrochemical Zn/Zn^{2+} reactions on GCuCN@Zn electrode. a) Coulombic efficiency measurements of Zn||GCuCN@SS and Zn||SS cells, and b) the corresponding voltage profiles of Zn||GCuCN@SS at various cycles at 1 mA cm⁻² with 0.5 mAh cm⁻², c) the Tafel plots of bare Zn and GCuCN@Zn plate tested at a scan rate of 1 mV s⁻¹, the comparison of long-term galvanostatic Zn stripping/plating in the Zn||Zn symmetric cells and time–voltage profiles under the current density of d) 1 mA cm⁻², e) 3 mA cm⁻², and f) 5 mA cm⁻² with a capacity of 1 mAh cm⁻², g) the rate performance of the Zn||Zn symmetric cells with bare Zn and GCuCN@Zn anode from 0.2 to 5 mA cm⁻².

determined, which agrees with standard aqueous solutions,^[55] owing to that the electrochemical active Zn²⁺ with large solvation shell is much slower than the counter ions.^[56] The low t_{Zn2+} will impose a concentration gradient in the vicinity of Zn anode and build a strong interfacial polarization, hence leading to an exacerbated Zn dendrite propagation. However, t_{Zn2+} can be dramatically strengthened to 0.635 after the incorporation of GCuCN layer. The above support electron transfer impedance, benign ion conduction, and migration on the GCuCN layer, consistent with the requirements of the desired artificial SEI.

As a result, the Zn||Zn symmetric cells comprised of GCuCN@Zn electrodes present much better cycling stability. Illustrated in Figure 5d, the cells with artificial GCuCN SEI can stable cycle over 2000 h at 1 mA cm⁻² with 1 mAh cm⁻², while bare Zn cell delivers a sudden voltage drop after 120 h, ultimately resulting in the cell failure traceable to the dendrite-induced internal short circuit. Even under strict conditions with higher current densities of 3 and 5 mA cm⁻², the GCuCN@Zn still demonstrates striking cyclic stability over at least 1000 cycles without any sign of a short-circuit (Figure 5e,f). On this basis, the rate performance of GCuCN@Zn and bare Zn electrodes are tested and depicted in Figure 5g. As expected, the GCuCN@Zn reveals a much more stable voltage profile from 0.2 to 5 mA cm⁻², and no apparent irreversible voltage is observed.

The recent state-of-the-art SEI protection approaches for enhancing the reversibility of Zn anode in aqueous batteries have been summarized in Table S4 (Supporting Information), and the GCuCN SEI possesses a competitive cycling performance, which benefits greatly from the hydrophobic and zincophilic features of the GCuCN, making the water dipoles detach from the SEI surface, forming a water-poor structure meanwhile keeping high Zn²⁺ conduction and transference number when Zn²⁺ diffuse through GCuCN SEI, which endows an ion-sieving effect to enable water-free, single Zn²⁺ ion conduction. The gradient distribution of GCuCN assures the entire SEI layer tightly anchoring on the Zn foil and maintaining conformal contact owing to the strong interaction of bottom Cu@g-C₃N₄ with metallic Zn. In addition, the affinity of top $g-C_3N_4$ with Zn^{2+} ions is also capable of uniformizing Zn²⁺ ion flux and harmonizing ion migration. Such a configuration sufficiently promotes the

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Figure 6. Electrochemical performance of Zn-ion full batteries. The comparison of electrochemical performance of Zn||MnO₂ full cells with bare Zn and GCuCN@Zn anode. a) CV curves at 0.1 mV s⁻¹, b) Nyquist plots, c) the rate performance, d) typical charge/discharge profiles at 0.1 C, and e) long-term cycling performance at 1 C after 500 cycles. The comparison of electrochemical performance of Zn||V₂O₅ full cells with bare Zn and GCuCN@Zn anode. f) Typical charge/discharge profiles at 0.1 A g⁻¹ and g) long-term cycling performance at 1 A g⁻¹ after 1000 cycles.

homogeneous Zn deposition and eradicates the side reactions and dendrite growth, boosting the electrochemical reaction kinetics and long-term cyclic stability.

Finally, Zn-ion full cells based on MnO2 or V2O5 cathode and GCuCN@Zn anode were fabricated to verify the availability of the artificial GCuCN SEI. Therein, the MnO₂ nanofibers were prepared via a hydrothermal method.^[57] The structure and morphology of the as-synthesized MnO₂ were presented in Figure S20 (Supporting Information). The Zn||MnO₂ full cells were assembled in an electrolyte consisting of 2 M ZnSO₄ + $0.1 \text{ M} \text{MnSO}_4$, in which the MnSO_4 component serves as the inhibitor to alleviate the disproportionation of the cathode.^[58] Cyclic voltammetry (CV) curves in Figure 6a depict that both the Zn||MnO2 and GCuCN@Zn||MnO2 cell exhibit two pairs of anodic/catholic peaks, deriving from the two-step reverse conversion reactions between MnO₂ and MnOOH.^[59] Noticeably, the GCuCN@Zn||MnO2 cell delivers a strengthened current density alongside a positive-shifted Zn²⁺ insertion peak, indicating a slightly enhanced Zn²⁺ insertion reaction kinetics. This can be

also declared through the galvanostatic charge-discharge (GCD) profiles and the electrochemical impedance spectra (EIS) analysis. In detail, the GCD profiles of the GCuCN@Zn||MnO₂ cell reveal a larger initial reversible capacity (282.5 mAh g⁻¹ at 0.1 C) and a lower voltage polarization compared with that of the bare Zn||MnO₂ cell (Figure 6d and Figure S21, Supporting Information). Nyquist plots announce the charge transfer resistance for GCuCN@Zn||MnO₂ is 114.7 Ω , which is similar to that of $Zn||MnO_2|$ (132.3 Ω), while the GCuCN@Zn||MnO_2| illustrates an improved Warburg diffusion behavior (Figure 6b and Table S5, Supporting Information). Accordingly, the GCuCN@Zn||MnO₂ cell presents a patchy rate performance with less capacity fluctuation, whereas the bare Zn||MnO₂ cell falls quickly with the increase of the current density (Figure 6c). For long-term stability, the GCuCN@Zn||MnO2 cell was firstly cycled at 0.1 C for five cycles, and the results at 1C demonstrate a prevailing operating lifespan with a decent capacity retention after 500 cycles, which is due to the restraint of Zn dendrite and side reactions during cycling. To further monitor the effect of the SEI on side

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reactions in full cells, the self-discharge behaviors were explored (Figure S22, Supporting Information). After a rest of 48 h, the GCuCN@Zn||MnO₂ cell can hold 86.26 % of its original capacity, superior to 80.85% of the Zn||MnO₂ cell.

Furthermore, we also considered another conventional cathode of V_2O_5 to match with the GCuCN@Zn anode for the full cell investigation. The commercial V₂O₅ was purchased from Sigma-Aldrich without further purification, and its structure and morphology were characterized in Figure S23 (Supporting Information). As shown in Figure 6f,g, and Figure S24 (Supporting Information), activated at 0.2 A g^{-1} for five cycles at the initial stage, the Zn $||V_2O_5$ cell unveils a capacity of 162.1 mAh g⁻¹ at 1 A g⁻¹ but a rapid capacity degradation after 100 cycles, signifying an exhausted consumption of Zn anode owing to its poor reversibility. In sharp contrast, the GCuCN@Zn||V2O5 cell demonstrates a longer stability and can maintain a residual capacity of 93.5 mAh g^{-1} at 1 A g^{-1} after 1000 cycles, proving again the stable anode interfaces induced by the GCuCN SEI. These results confirm that our GCuCN SEI design can indeed refine the cycle stability and performance of the Zn anode, no matter in symmetric cells or full cells.

3. Conclusion

In summary, we integrate a gradient hydrophobic and zincophilic SEI, comprising of Cu@g-C₃N₄ and g-C₃N₄ form inner to the surface, upon the Zn anode. The DFT computations verified the strong interaction of Cu@g-C₃N₄ with Zn foil and g-C₃N₄ with Zn²⁺ ions, so that the gradient design endows the firm and conformal anchoring of the GCuCN SEI alongside the optimization of the Zn^{2+} solvation structure with reduced water reactivity when diffusing across the GCuCN SEI. The contact angle measurements and X-ray absorption spectroscopy studies substantiate the hydrophobic and zincophilic texture of the GCuCN SEI. The GIXD analysis combined with the postmortem SEM observation and XPS investigation unveils the evenness of the nucleation and importantly the ordered assembly of Zn electrodeposits. Further detailed electrochemical studies prove the expected impact of this GCuCN SEI on uniformizing Zn²⁺ ion flux and harmonizing ion migration, enabling an ion-sieving effect to assure fast single Zn²⁺ conduction, which effectively accelerates the Zn deposition kinetics and hinders the electrolyte-related interfacial side reactions. As a result, the GCuCN@Zn anode exhibits an exceptionally prolonged Zn plating/stripping cycling life of over 2000 h, and a high reversibility over 200 cycles at 1 mA cm⁻² with 0.5 mAh cm⁻². Even under a high current density of 5 mA cm⁻², the GCuCN@Zn anode can maintain stable for over 1000 cycles. Finally, the full cells matching GCuCN@Zn anode with MnO₂ and V₂O₅ cathode deliver a high level of specific capacities and meritorious capacity retention after long-term cycling. This work provides a hierarchical confinement design strategy for Zn anode interphase engineering, opens up the possibility of achieving stable metallic anodes in multivalent aqueous batteries.

4. Experimental Section

Preparation of the Zn Anode with Artificial SEI Layers: 2,4-Diamino-6-phenyl-1,3,5-triazine, cyanuric acid, cupric chloride, divanadium pentaoxide (V_2O_5), and N-methyl-2-pyrrolidone (NMP) were purchased from Sigma-Aldrich. All raw chemicals were used without further purification. First, the 2,4-diamino-6-phenyl-1,3,5-triazine and cyanuric acid were mixed in 50 mL of deionized water at a molar ratio of 1:1. Then the complexes were stirred overnight, and the white supramolecular aggregates were filtered and washed several times with water. After vacuum-dried at 60 °C, the complexes were calcined at 550 °C for 2 h under an Ar atmosphere, obtaining the resulting g-C₃N₄ sample. Furthermore, the dried supramolecular aggregates were mixed with a certain amount of cupric chloride by fine grinding on a mortar and pestle. This mixture was calcined under the same conditions, obtaining the resulting Cu@g-C₃N₄ sample.

The g-C₃N₄ and Cu@g-C₃N₄ were then dispersed in N-methyl-2pyrrolidone with 5 wt% polyvinylidene difluoride (PVDF) by stirring for 12 h. The concentration was 1 wt%, then the slurry was dripped on the Zn foils (with a thickness of 200 μ m) with 15 μ L cm⁻² by a pipette and vacuum-dried at 60 °C for 1 h, leading to an areal mass loading of 0.15 mg cm⁻². For the preparation of the GCuCN interfacial layer, the slurry of 1 wt% Cu@g-C₃N₄ and 1 wt% g-C₃N₄ subsequently dripped onto the Zn foil by a mass loading of 7.5 and 7.5 μ L cm⁻². The modified Zn foil was processed with a lamination step for further application.

Preparation of the α-*MnO*₂ and V₂O₅ *Cathode*: α-MnO₂ was fabricated by a hydrothermal method. In brief, 3×10^{-3} M MnSO₄ H₂O and 2 mL 0.5 M H₂SO₄ were added into 60 mL of deionized water. 20 mL 0.1 M KMnO₄ was added and the mixture was stirred for 2 h, and then transferred to a Teflon-lined autoclave and heated at 120 °C for 12 h. The obtained α-MnO₂ nanowires were collected by filtration, washed with water and isopropanol, and vacuum-dried at 60 °C. The V₂O₅ was purchased without further purification. The α-MnO₂ and V₂O₅ cathode used here comprises 80 wt% α-MnO₂ or V₂O₅, 10 wt% Super P carbon, and 10 wt% PVDF, which were mixed and well dispersed in NMP and cast onto a 12 mm SS current collector. The active mass loading of the α-MnO₂ and V₂O₅ cathode is ≈1.5 and 2 mg cm⁻², respectively.

Electrochemical Measurement: Zn anode was punched into 12 mm slice, and the symmetric and asymmetric cells (CR-2032 type coin cell) were assembled with a glass fiber (GE-Whatman) as the separator and 120 μ L of 2 μ zinc sulfate solution as the electrolyte. Electrochemical cycling tests in Zn||Zn symmetric cells, Zn||SS cells, Zn|| α -MnO₂, and Zn||V₂O₅ cells were recorded on a LANHE CT3002A, Wuhan, China battery test system. The CV and linear sweep voltammetry (LSV) were conducted on a VMP-300 electrochemical workstation (EC-lab, Biologic). The hydrogen evolution performance was collected through LSV with a potential range of -0.9 to -1.6 V versus Ag/AgCl in the 1 m Na₂SO₄ electrolyte at a scan rate of 1 mV s⁻¹.

Materials Characterization: The morphologies of samples were characterized by transmission electron microscopy (JEOL JEM-ARM200CF), field emission scanning electron microscopy (Zeiss Sigma 300), and elemental mapping (Gatan GIF). XPS measurements and depth profile XPS were performed on a Versa probe III (PHI 5000) spectrometer. Analysis was done using CASA XPS. All the XPS spectra were calibrated to the adventitious hydrocarbon (AdvHC) carbon peak at 284.8 eV. X-ray absorption spectroscopy was performed at Hard X-ray MicroAnalysis (HXMA, 06ID-1) beamline at Canadian Light Source. The 2D synchrotron GIXD was collected at Very Sensitive Elemental and Structural Probe Employing Radiation Beamlines (VESPERS, 07B2-1) at Canadian Light Source. The advantage of GIXD technique on flat Zn electrodes is the limited penetration depth of the X-rays into the samples, with the benefit of low background scattering from the substrate. By varying the incident angle, the X-rays' penetration depth can be changed from a few nanometers up to 100 nm. The energy of the X-ray beam used for GIXD is 8 keV and the beam size is pprox5 imes 7 μ m. The GIXD patterns were measured in the incident angle range of 0.2° -2.6°, and the ones measured at 0.8° were shown above. The beam diffracted from the Zn foil was collected by a 2D area detector centered at 40° and located 120 mm away from the sample, which covers a 2heta angular range of 6°-73°. The CT scans were collected at the Canadian Light Source synchrotron facility on the Biomedical Imaging and Therapy beamline (BMIT-BM) with the energy of 32 keV. The mean energy of the filtered white beam was 32 keV. The detector was composed of an Optique Peter

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(France) microscope coupled to the PCO Edge 5.5 sCMOS camera. Effective pixel size was 1.44 μ m and LSO:Tb crystal with 20- μ m thickness was used as a scintillator. Each CT data set consisted of 2500 projections. Collected CT data were preprocessed and reconstructed with the *tofu* software package.^[60]

First-Principles Calculations: First-principles calculations were based on DFT with generalized gradient approximation (GGA)^[61,62] for exchange-correlation potential. The Perdew–Burke–Ernzerholf (PBE) function was used for the GGA as implemented in the Vienna ab initio simulation package (VASP).^[63] The electron–ion interaction was treated using projector-augmented-wave (PAW) potentials^[64] with a plane wavebasis cutoff of 500 eV. The entire Brillouin zone was sampled using the Monkhorst–Pack^[65] method. A vacuum of 15 Å was used to avoid artificial interactions caused by the periodic boundary conditions. All structures were fully relaxed until the force on each atom was less than 0.01 eV Å⁻¹, and the total energy minimization was performed with a tolerance of 10^{-5} eV. Adsorption energy was calculated via the formula $E_{ads} = E_{AB} - E_A - E_B$, where E_{AB} , E_A , and E_B are the calculated energies of AB, A, and B, respectively.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

artificial SEI, graphitic carbon nitride, gradient SEI, zincophilic, Zn anode

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