Surface-Alloyed Nanoporous Zinc as Reversible and Stable Anodes for High-Performance Aqueous Zinc-Ion Battery

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HIGHLIGHTS

- ZnₓCuᵧ alloy shell was in-situ formed on self-supported three-dimensional nanoporous Zn anode by anionic surfactant-assisted surface alloying of Zn and Cu.
- The self-supported nanoporous ZnₓCuᵧ/Zn anodes exhibit high-rate capability, outstanding reversibility and stability during Zn stripping/plating because of zincophilic ZnₓCuᵧ to guide uniform Zn deposition and facilitate Zn stripping.
- Aqueous Zn-ion batteries assembled with nanoporous ZnₓCuᵧ/Zn anode and KₓMnO₂ cathode achieve specific energy of as high as ~430 Wh kg⁻¹ and retain ~86% after long-term cycles for >700 h.

ABSTRACT Metallic zinc (Zn) is one of the most attractive multivalent-metal anode materials in post-lithium batteries because of its high abundance, low cost and high theoretical capacity. However, it usually suffers from large voltage polarization, low Coulombic efficiency and high propensity for dendritic failure during Zn stripping/plating, hindering the practical application in aqueous rechargeable zinc-metal batteries (AR-ZMBs). Here we demonstrate that anionic surfactant-assisted in situ surface alloying of Cu and Zn remarkably improves Zn reversibility of 3D nanoporous Zn electrodes for potential use as high-performance AR-ZMB anode materials. As a result of the zincophilic ZnₓCuᵧ alloy shell guiding uniform Zn deposition with a zero nucleation overpotential and facilitating Zn stripping via the ZnₓCuᵧ/Zn galvanic couples, the self-supported nanoporous ZnₓCuᵧ/Zn electrodes exhibit superior dendrite-free Zn stripping/plating behaviors in ambient aqueous electrolyte, with ultralow polarizations under current densities up to 50 mA cm⁻², exceptional stability for 1900 h and high Zn utilization. This enables AR-ZMB full cells constructed with nanoporous ZnₓCuᵧ/Zn anode and KₓMnO₂ cathode to achieve specific energy of as high as ~430 Wh kg⁻¹ with ~99.8% Coulombic efficiency, and retain ~86% after long-term cycles for >700 h.

KEYWORDS Nanoporous metal; Zinc-based alloy anode; Aqueous zinc-ion batteries; Surface alloying

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1 Introduction

Highly safe and reliable cost-effective rechargeable batteries hold great promise in many emerging large-scale energy storage applications such as electric vehicles and stationary storage of intermittently available renewable energy sources (e.g., solar and wind) [1, 2]. Lithium-ion batteries as one of the most successful energy-storage devices dominate the present commercial electronics [3], but they are far from meeting future needs of grid-level energy storage due to unsustainability issues, such as high-cost and scarcity of lithium resources, and safety concerns caused by highly toxic and flammable organic electrolytes [1, 3–6]. This dilemma has raised urgent demands for developing alternative battery technologies [3–6], especially safe and low-cost aqueous rechargeable batteries based on non-lithium charge carriers [7–10]. Among various attractive aqueous battery candidates [11–14], aqueous rechargeable zinc-metal batteries (AR-ZMBs) are of considerable interest because multivalent zinc metal (Zn) features high volumetric and gravimetric capacities (5854 mAh cm⁻³ and 820 mAh g⁻¹), low Zn/Zn²⁺ redox potential (~0.76 V versus standard hydrogen electrode, SHE), high Earth abundance and low cost [4, 9, 15–18]. Despite some high-performance cathode materials, such as manganese oxides [19–23], vanadium oxides [24–28] and quinone analogs [29, 30], have been explored to effectively accommodate Zn²⁺ via intercalation or conversion reactions, most AR-ZMBs still exhibit unsatisfactory rechargeability, hindering their practical implementation as power sources for transportation or reliable solutions for grid integration of renewable energy [4]. This is primarily caused by poor reversibility of metallic Zn anode because of its unique metallurgical characteristics and undesirable side reactions (e.g., hydrogen evolution, corrosion and by-product formation), which usually lead to large voltage polarization, dendrite formation and low coulombic efficiency (CE), during the Zn stripping/plating in ambient aqueous electrolytes [16–18, 31–33]. With an aim at improving the reversibility of Zn stripping/plating, many strategies have been proposed to tackle these irreversibility issues [34], and initial strides have been made in electrolyte modulation with additives to regulate solvation/desolvation process of Zn²⁺ [35–40] and/or electrical field distribution of Zn protuberances [41–43], crystallographic plane manipulation to guide epitaxial electrodeposition of Zn [44–46], and interface engineering of artificial solid electrolyte interphase (SEI) to inhibit side reactions [47–55]. Nevertheless, these bulk Zn metal-based anodes still undergo large voltage polarizations particularly at high current densities and thus inevitably trigger side reactions and dendrite formation during the long-term Zn stripping/plating, which result in significant compromise in rate capabilities and cycling stability of AR-ZMBs. Nano-structuring of Zn metals is one of facile strategies to depress the Zn dendrite growth and reduce the voltage polarization by making use of high specific surface area to lower local current density and improve mass transport of Zn²⁺ at electrode/electrolyte interface [56, 57]. However, nano-structured Zn metals usually are of highly chemical activity and undergo severe side reactions because of high-density low-coordination surface atoms [58, 59]. In this regard, it is highly desirable to explore novel Zn-based alloy anodes with highly compatible and stable electrode/electrolyte interfaces for high-performance AR-ZMBs.

In this work, we report self-supported three-dimensional and bicontinuous nanoporous ZnₓCuᵧ/Zn hybrid electrodes, of which the ZnₓCuᵧ alloy shell is in situ formed on nanoporous Zn skeleton by anionic surfactant-assisted surface alloying of Zn and incorporated Cu, as highly reversible and dendrite-free metal anodes of AR-ZMBs. Herein, the anionic surfactant is specifically sodium dodecyl sulfate (SDS) consisting of a hydrophobic hydrocarbon tail and a hydrophilic polar headgroup. In zinc trifluoromethanesulfonate (Zn(OTF)₂) aqueous electrolyte, these SDS molecules graft on the constituent Cu nanoparticle-decorated nanoporous Zn (Cu/Zn) and exclude free water molecules from electrode/electrolyte interface, enabling the formation of ZnₓCuᵧ alloy shell on nanoporous Zn skeleton during Zn stripping/plating processes. As a consequence of the zincophilic ZnₓCuᵧ alloy shell guiding uniform Zn deposition with a nucleation overpotential of as low as zero millivolt and the hetero-structured ZnₓCuᵧ/Zn galvanic couples to facilitate Zn stripping, the nanoporous ZnₓCuᵧ/Zn electrodes exhibit ultralow polarizations under current densities up to 50 mA cm⁻² and exceptional stability for 1900 h during Zn stripping/plating in ambient aqueous electrolyte. These outstanding electrochemical properties enlist AR-ZMB full cells assembled with nanoporous ZnₓCuᵧ/Zn anode and KₓMnO₂ cathode to achieve specific energy of ~430 Wh kg⁻¹ (based on the loading mass of KₓMnO₂ in the cathode) with the CE of as high as ~99.8% and retain ~86% after long-term cycling for more than 700 h.
2 Experimental Section

2.1 Materials Preparation

2.1.1 Preparation of Nanoporous Zn-Based Anodes

Precursor alloy of Zn₅₀Al₅₀ (at%) was firstly produced by induction melting of high-purity Zn (99.994%) and Al (99.996%) in high-purity alumina crucible and then pouring in iron casting mold with a cooling rate of ~10 K s⁻¹ [16]. After cutting into sheets, the Zn₅₀Al₅₀ sheets are chemically dealloyed to prepare nanoporous Zn, in which the less-noble Al component was selectively dissolved in N₂-purged KOH solution (1 M) [60, 61]. When rinsed in pure water and ethanol for several times, these nanoporous Zn sheets were immersed in CuCl₂ solution (5 mM) for 15 s to obtain nanoporous Cu/Zn hybrid electrodes via a galvanic replacement reaction. The as-prepared nanoporous Cu/Zn sheets were further washed in pure water to remove residual chemical in nanopore channels and directly used as electrodes in symmetric cells. During the electrochemical Zn stripping/plating, there took place surface alloying of Zn and Cu to form ZnₓCuᵧ/Zn core/shell structure with a three-dimensional nanoporous architecture.

2.1.2 Preparation of KₓMnO₂ Cathode

The KₓMnO₂ nanobelts were prepared by a modified hydrothermal method. Typically, the mixture of KₓMnO₄ (40 mM) and NH₄Cl (40 mM) in a Teflon-lined steel autoclave was heated at 150 °C for 24 h in an oil bath and magnetically stirred at a speed of 250 rpm. The KₓMnO₂-based cathode was prepared by mixing the as-prepared KₓMnO₂ nanobelts with super-P acetylene black conducting agent and poly(vinylidene difluoride) binder with a weight ratio of 70: 20: 10 in N-methyl-2-pyrrolidone (NMP), and then pasted on titanium foil with the loading mass of 1.0 mg cm⁻².

2.2 Physicochemical Characterizations

The microstructural and chemical features of nanoporous Zn, Cu/Zn and ZnₓCuᵧ/Zn sheets were characterized by a field-emission scanning electron microscope equipped with an X-ray energy-dispersive spectroscopy (SEM–EDS, JEOL, JSM-7900F, 15 kV) and a field-emission transition electron microscope (TEM, JEOL, JEM-2100F, 200 kV). X-ray diffraction (XRD) measurements of all specimens were taken on a D/max2500pc diffractometer with a Cu Kα radiation. Raman spectra were measured on a micro-Raman spectrometer (Renishaw) with a 532-nm-wavelength laser at the power of 0.5 mW. X-ray photoelectron spectroscopy (XPS) analysis was conducted on a Thermo ECSALAB 250 with an Al anode. Charging effects were compensated by shifting binding energies based on the adventitious C 1s peak (284.8 eV). Ion concentrations in electrolytes were analyzed by inductively coupled plasma optical emission spectrometer (ICP-OES, Thermo electron).

2.3 Electrochemical Measurements

Coin-type symmetrical cells were assembled with two identical nanoporous Cu/Zn and Zn sheets, as well as bulk Zn sheets with diameter of 1.2 cm and thickness of 100 µm, separated by a glass fiber membrane (GFM), in 1 M Zn(OTF)₂ aqueous solution with or without 1 mM SDS. Electrochemical Zn stripping/plating behaviors of nanoporous Cu/Zn and Zn, and bulk Zn electrodes were measured at various current densities from 0.5 to 50 mA cm⁻². Electrochemical impedance spectroscopy (EIS) measurements of as-assembled symmetric cells were taken over the frequency ranging from 100 kHz to 10 mHz with an amplitude of 10 mV at room temperature. The cycling durability tests were performed at current densities of 0.5 and 50 mA cm⁻². The nucleation overpotentials of electrodes were investigated in a three-electrode cell in which nanoporous Cu/Zn, Zn or bulk Zn foils were employed as the working and counter electrodes, zinc wire as the reference electrode. Within 1 M Zn(OTF)₂ with/without 1 mM SDS, chronopotentiometry measurements were taken at 0.5 mA cm⁻². The Tafel curves were tested in the three-electrode configuration with zinc foil as the counter electrode, zinc wire as the reference electrode, and bulk Zn, nanoporous Zn, nanoporous Cu/Zn and nanoporous ZnₓCuᵧ/Zn as the working electrodes, respectively, within Zn(OTF)₂ aqueous electrolyte. Coin-type full zinc-ion cells were further assembled with the nanoporous Cu/Zn and Zn, bulk Zn as the anode and the titanium foil supported KₓMnO₂ as the cathode, the GFM as the separator, the 1 M Zn(OTF)₂ solution containing with 1 mM SDS and 0.1 M Mn(OTF)₂ as the aqueous electrolyte. The rate capability...
and cycling performance of full cells were carried out on a battery test system.

### 2.4 Theoretical Calculation and Simulation

The density-functional theory (DFT) calculations were performed by using the Dmol3 code. The exchange–correlation potential was based on the functional of Perdew–Burke–Ernzerhof (PBE) of generalized gradient approximation (GGA). The DFT Semicore Pseudopotential (DSPP) method was employed to describe the electron–core interactions. For the basis sets, the double numerical plus polarization (DNP) was used with the real-space global orbital cutoff radius of 4.4 Å. The k-point grid was set at 4 × 4 × 1 for integrating the Brillouin zones. The structures of Zn(002), Cu(111) and ZnCu(110) planes were constructed with five layers, and the bottom two layers of the atoms were fixed. The convergence criterions of the energy, maximum force, and maximum displacement were 1 × 10⁻⁵ Ha, 0.002 Ha Å⁻¹, and 0.005 Å, respectively.

### 3 Results and Discussion

#### 3.1 Characterizations of Nanoporous Hybrid Electrodes

The self-supported nanoporous ZnCu/Zn electrodes are prepared by a facile procedure schematically illustrated in Fig. 1a, in which Cu nanoparticles are uniformly incorporated onto nanoporous Zn via a galvanic replacement reaction and then transformed to ZnCu, alloy shell through surfactant-assisted in situ surface alloying of Cu and Zn during the Zn stripping/plating in Zn(OTF)₂ aqueous electrolyte with SDS additive. Therein, nanoporous Zn precursor sheets are firstly fabricated by chemically dealloying Zn₅₀Al₅₀ alloy composed of intercross-linked hexagonal closest packed (hcp) Zn and face-centered cubic (fcc) Al phases (Fig. S1), wherein the less-noble Al one is selectively etched in a N₂-purged KOH solution (Fig. S2) [60, 61]. Owing to the immiscibility of Al in Zn [16], selective dissolution of Al phase gives rise to interconnective pure Zn skeleton, different from traditional nanoporous metals prepared by chemically dealloying homogeneous solid-solution alloys, in which there generally remain residual less-noble elements due to parting limit effect [62, 63]. Figure 1b shows a typical SEM image of as-dealloyed nanoporous Zn, displaying a three-dimensional nanoporous architecture consisting of interpenetrative channels and interconnective Zn ligaments with characteristic length of ~ 200 nm. Because of the lowest surface energy of (002) plane [44–46], the nanoporous Zn thermodynamically prefers to expose more (002) planes. This is attested by its XRD patterns (Fig. S3a), in which the characteristic diffraction peak of (002) plane exhibits a relatively high intensity compared with the bulk Zn foil (Fig. S3a). When immersed in CuCl₂ solution, Cu nanoparticles with diameter of ~ 50 nm are uniformly incorporated onto nanoporous Zn sheets by a galvanic replacement reaction, as displayed in the representative SEM image of as-prepared nanoporous Cu/Zn (Fig. 1c). With the assistance of SDS molecules that graft on the Cu/Zn surface and exclude free water molecules at electrode/electrolyte interface by making use of their hydrophilic polar headgroups and hydrophobic hydrocarbon tails (Fig. S4), there takes place in situ surface alloying of Cu and Zn to form ZnₙCuₓ alloy shell on nanoporous Zn during the initial electrochemical cycles of Zn stripping/plating in Zn(OTF)₂ aqueous electrolyte with SDS additive [64, 65]. Figure 1d shows a typical SEM image of nanoporous ZnₙCuₓ/Zn electrode after the Zn stripping/plating at 0.5 mA cm⁻² for 10 cycles, where the ligament surface of ZnₙCuₓ/Zn becomes much smoother than the rough surface of as-prepared nanoporous Cu/Zn (Fig. 1c). XPS analysis demonstrates the presence of Zn and Cu with an atomic ratio of 60/40 in the ZnₙCuₓ alloy surface, in addition to the elements in the adsorbed SDS (Fig. S5). Scanning transmission electron microscopy energy-dispersive X-ray spectroscopy (STEM-EDS) elemental mapping illustrates that Cu atoms uniformly distribute along the Zn ligament (Fig. S6). Figure 1e shows a high-resolution TEM (HRTEM) image of ZnₙCuₓ/Zn interfacial region, revealing the seamless integration of ZnₙCuₓ alloy shell on Zn core. Viewed along their <011> and <0001> zone axis, there observe two regions with distinct crystallographic structures corresponding to the cubic Zn₉Cu₇ and the hcp Zn, respectively, which are identified by their characteristic fast Fourier transform (FFT) patterns of the selected areas in Fig. 1e-g. XRD characterization of nanoporous ZnₙCuₓ/Zn electrode further verifies the hybrid structure, with two sets of diffraction patterns: the weak diffraction peaks at 2θ = 43.5°, 63.0° and 79.6° corresponding to the (110), (200) and (211) planes of cubic Zn₉Cu₇, in space group Pm̅3 m (221) (JCPDS No. 02-1231), and the ones else assigned to hcp Zn (JCPDS No.
65-3358) (Fig. 1h), different from the initial nanoporous Cu/Zn with characteristic diffraction peaks of fcc Cu (JCPDS No. 85-1326) (Fig. 1g).

The SDS-assisted in situ surface alloying of Cu and Zn is also demonstrated by XRD characterizations of nanoporous ZnₙCuₓ/Zn. As shown in Fig. S7a, a representative diffraction peak of cubic ZnₓCuᵧ appears at 2θ = 79.6° and gradually increases in intensity, along with the attenuation of Cu diffraction peaks (2θ = 50.4° and 74.1°), during the Zn stripping/plating. Owing to the SDS molecules that essentially inhibit side reactions at the electrode/electrolyte interface, metallic Zn prefers to nucleate and then deposit on Cu
nanoparticles for electrochemically driven surface alloying. As demonstrated in high-resolution Zn 2p and Cu 2p XPS spectra with invariable chemical states (Fig. S8), there do not additionally produce by-products, such as general zinc oxides [9, 15–18, 31, 32]. While in the Zn(OTF)_2 aqueous electrolyte without SDS additive, the nanoporous Cu/Zn still keeps the initial morphology (Fig. S9) and XRD patterns with characteristic diffraction peaks of individual fcc Cu and hcp Zn phases after the Zn stripping/plating for 10 cycles (Fig. S7b), implying that the Cu does not take part in the surface alloying with Zn. This is probably due to the by-product of zinc oxides that are generated little by little to inhibit Zn atom migration in the Zn stripping/plating processes [9, 15–18, 31, 32]. As attested by high-resolution Zn 2p XPS spectra (Fig. S10), the nanoporous Cu/Zn electrode has the oxidized state of surface Zn atoms to remarkably increase compared with its initial surface Zn. When the constituent Cu nanoparticles serve as the nucleation sites, the nanoporous Cu/Zn electrode exhibits the almost same galvanostatic electrodeposition behavior of metallic Zn as the initial one (Fig. 2a), with a nucleation overpotential of ~6.4 mV, the difference between the sharp tip voltage (~25.5 mV versus Zn/Zn^{2+}) and the later stable mass-transfer-controlled overpotential (~19.1 mV) [66, 67]. Because of the lower binding energy of Cu(111) surface (Fig. S11), this value is much lower than bulk Zn foil (41.5 mV) and nanoporous Zn (17.6 mV) (Fig. S12), which are primarily composed of (101) and (002) crystal planes, respectively (Fig. S3). In sharp contrast, the nanoporous Zn_xCu_y/Zn electrode has the Zn nucleation overpotential to gradually decrease to 0 mV (Fig. 2c) and substantially facilitates the nucleation and deposition of metallic Zn because of the lowest binding energy of Zn_xCu_y(110) (Fig. S11). The enhanced kinetics of Zn nucleation and deposition is further demonstrated by EIS.

Fig. 2 Effect of surface Zn-Cu alloying on Zn deposition. a Voltage–time profiles and b EIS spectra of galvanostatic Zn deposition on nanoporous Cu/Zn electrode at 0.5 mA cm\(^{-2}\) after Zn stripping/plating for 0, 5 and 10 cycles without the assistance of SDS, where there does not take place alloying of Zn and Cu. c Voltage–time profiles and d EIS spectra of galvanostatic Zn deposition on nanoporous Zn_xCu_y/Zn electrode after SDS-assisted Zn stripping/plating at 0.5 mA cm\(^{-2}\) for 0, 5 and 10 cycles, which enables the formation of Zn_xCu_y alloy shell via an in situ surface alloying of Zn and Cu. The current density of galvanostatic Zn deposition: 0.5 mA cm\(^{-2}\). e Zn deposition at side site (site 1) and top site (site 2) on the Zn(002) and Zn_xCu_y(110) surfaces with different binding energies. f Comparison of energy difference between site 1 and site 2 at which Zn is deposited on the Zn(002) and Zn_xCu_y(110) surfaces.
analysis of nanoporous Zn,Cu,/Zn electrode (Fig. 2d). In the Nyquist plot, their EIS spectra display single semicircles in high- and middle-frequency range and inclined lines at low frequencies during the Zn stripping/plating processes. Herein, the intersection point on the real axis at the high frequency represents the intrinsic resistance of both electrolyte and electrode \( (R_f) \); the diameter of semicircle in the middle frequencies corresponds to the parallel connection of charge transfer resistance \( (R_{CT}) \) of Zn nucleation/deposition and the constant phase element (CPE); and the slope of the inclined line at low frequencies is the Warburg resistance \( (Z_w) \). Based on the equivalent circuit with these descriptors (Fig. S13a), the EIS spectra of nanoporous Zn,Cu,/Zn electrodes are analyzed using the complex nonlinear least squares fitting method. As shown in Fig. S13b, the nanoporous Zn,Cu,/Zn electrode has its \( R_{CT} \) to decrease to \( \sim 19.8 \, \Omega \) from the initial value of nanoporous Cu/Zn with SDS (\( \sim 29.7 \, \Omega \)), different from nanoporous Cu/Zn without SDS additive, of which the \( R_{CT} \) increases due to the gradual formation of zinc oxides (Figs. 2b and S13c). Furthermore, the Zn atoms thermodynamically prefer to deposit evenly and parallel to the Zn,Cu, alloy surface, effectively inhibiting the formation of Zn dendrites. As illustrated by DFT calculations (Fig. 2e), the Zn,Cu, \((110) \) surface could afford a special deposition location at the side site (site 1) of early stage with an adsorption energy of as low as \( \sim 1.61 \, \text{eV} \), \( \sim 0.46 \, \text{eV} \) lower than the adsorption energy (\( \sim 1.15 \, \text{eV} \)) at the top site (site 2) (Fig. 2f). This implies a more favorable horizontal growth of Zn on Zn,Cu, alloy surface relative to the monometallic Zn(002) plane that features a smooth equipotential surface and compact structure with the energy difference of \( \sim 0.04 \, \text{eV} \) for Zn deposition locations at site 1 and site 2 (Fig. 2e) [44–46]. Owing to the Zn,Cu, alloy shell that can alleviate the Zn corrosion, the nanoporous Zn,Cu,/Zn electrode exhibits a more positive corrosion potential (\( \sim 10 \, \text{mV} \)) and a smaller corrosion current density (3 \( \mu \text{A cm}^{-2} \)) than nanoporous Cu/Zn (\( \sim 18 \, \text{mV} \), 7 \( \mu \text{A cm}^{-2} \)), nanoporous Zn (\( \sim 36 \, \text{mV} \), 9 \( \mu \text{A cm}^{-2} \)) electrodes (Fig. S14).

### 3.2 Electrochemical Properties of Nanoporous Zn-based Electrodes

To investigate the Zn stripping/plating behaviors of nanoporous Zn,Cu,/Zn electrode, electrochemical measurements are carried out on its symmetric cell in 1 M Zn(OTF)_2 aqueous electrolyte with SDS additive. Figure 3a shows the voltage profiles of symmetric nanoporous Zn,Cu,/Zn cell during the Zn stripping/plating processes at various rates from 1 to 100C, comparing with those of symmetric ones based on monometallic nanoporous Zn and bulk Zn electrodes in 1 M Zn(OTF)_2 aqueous electrolyte without SDS additive, respectively. Here 1C represents a one-hour stripping and plating at the current density of 0.5 mA cm\(^{-2}\). Evidently, the symmetric nanoporous Zn,Cu,/Zn cell exhibits relatively flat and symmetric voltage plateaus with an absolute overpotential of \( \sim 19 \, \text{mV} \) at 1C rate, \( \sim 17 \) and \( \sim 28 \, \text{mV} \) lower than those of the symmetric nanoporous Zn (~36 mV) and bulk Zn (~47 mV) ones. This observation implies the synergistic effects of chemical and structural features in nanoporous Zn,Cu,/Zn electrode, i.e., the highly zinccophilic Zn,Cu, alloy shell and the large electroactive surface area [68, 69], which facilitate the Zn stripping and plating with a low voltage polarization. As the rate increases to 5C, 10C and 20C, the nanoporous Zn,Cu,/Zn cell displays steadily increasing voltage hysteresis of \( \sim 7, \sim 13 \) and \( \sim 21 \, \text{mV} \), much lower than the symmetric ones based on nanoporous Zn (~26, ~73 and ~146 mV) and bulk Zn (~73, ~135 and ~280 mV). Even the current density further increases to 50 mA cm\(^{-2}\) (100C), the nanoporous Zn,Cu,/Zn cell still has an overpotential of as low as \( \sim 69 \, \text{mV} \), comparable to the nanoporous Zn cell at 2.5 mA cm\(^{-2}\) (\( \sim 62 \, \text{mV} \)) (Fig. 3b). In view that both nanoporous Zn,Cu,/Zn and Zn electrodes have almost the same nanoporous architecture, the superior rate capability of nanoporous Zn,Cu,/Zn electrode highlights the significant role of Zn,Cu, alloy shell in substantially boosting kinetics of Zn nucleation and deposition. This expectation is further attested by their distinct EIS spectra (Fig. S15a), where the symmetric nanoporous Zn,Cu,/Zn cell has the lowest \( R_{CT} \) value (Fig. S15b).

Figure 3c compares the long-term Zn stripping/plating cycling stabilities of nanoporous Zn,Cu,/Zn and monometallic nanoporous Zn and bulk Zn electrodes in their symmetric cells, which are performed at the rate of 1C with a constant areal capacity of 0.5 mAh cm\(^{-2}\). As a consequence of lowering the current density by increasing the electroactive surface area, nanoporous Zn effectively alleviates the voltage polarization of Zn stripping/plating [68, 69]. This enlists the symmetric nanoporous Zn cell to retain stable voltage profile until for 155 h, outperforming symmetric bulk Zn cell that as usual displays violent fluctuation and high overpotential in a short lifetime. When extending the cycling time, there...
take place severe side reactions of Zn oxidation on nanoporous Zn electrode, which dramatically increases the voltage polarization and then leads to an abrupt failure. Owing to the presence of Zn$_x$Cu$_y$ alloy shell that effectively guides the reversible and dendrite-free Zn stripping/plating, the symmetric nanoporous Zn$_x$Cu$_y$/Zn cell maintains extremely stable voltage profiles at 0.5 mA cm$^{-2}$ for more than 1,900 h, outperforming the monometallic nanoporous Zn. The excellent stability of nanoporous Zn$_x$Cu$_y$/Zn is further confirmed by the negligible change of EIS spectra before and after the

![Graphs and images representing the electrochemical performance of symmetric cells.](https://doi.org/10.1007/s40820-022-00867-9)
Zn stripping/plating for 100 cycles (Fig. 3d). Therein, the
$R_I$ and $R_{CT}$ values only increase by $\sim 1$ $\Omega$ and $\sim 12$ $\Omega$, much
smaller than those of monometallic nanoporous Zn ($\sim 2$
$\Omega$, $\sim 91$ $\Omega$) and bulk Zn ($\sim 12$ $\Omega$, $\sim 236$ $\Omega$) with severe side
reactions of Zn oxidations (Fig. S16). As revealed by Raman
spectrum of nanoporous Zn/Cu/Zn after the long-term
cycling measurement of Zn stripping/plating (Fig. S17a),
there do not display additional Raman bands, in addition
to the characteristic ones of ZnO at $\sim 381$, $\sim 437$, $\sim 580$ and
$\sim 1100$ cm$^{-1}$ with the almost constant intensities [70]. These
observations are different from the observations in nanopo‑
rous Zn and bulk Zn electrodes (Fig. S17b-c), where there
appear neoformative Raman bands at 252, 305 and 837 cm$^{-1}$
corresponding to $\text{Zn}_x(\text{OTF})_y(\text{OH})_{2x-y}n\text{H}_2\text{O}$ [71], in addi‑
tion to more intensive Raman bands of ZnO at $\sim 381$, $\sim 437$,
$\sim 580$ and $\sim 1100$ cm$^{-1}$. The superior stability of nanoporous
Zn/Cu/Zn electrode is further illustrated by the almost same
nanoporous structure after 500 cycles (1000 h) as the initial
one (Fig. S18a). This observation is in sharp contrast with
monometallic nanoporous Zn (Fig. S18b) and bulk Zn elec‑
 trodes (Fig. S18c), which undergoes severe dendrites growth
and cracks when only performing for 150 cycles (300 h) and
50 cycles (100 h), respectively. Even at the rate of as high as
100C (50 mA cm$^{-2}$) (Fig. 3g), the nanoporous Zn/Cu/Zn
does not display evident voltage fluctuation for more than
40,000 cycles of Zn stripping/plating along with the energy
efficiency of $\sim 99.9\%$ (Fig. S19).

3.3 Electrochemical Performance of AR-ZMB Full
Cells

Full AR-ZMB cells are assembled with nanoporous Zn/Cu/
Zn electrode as the anode and K$^+$-preintercalated $\alpha$-MnO$_2$
(K,MnO$_2$) nanobelts as the cathode, a mixture solution of
1 M Zn(OTF)$_2$, 0.1 M Mn(OTF)$_2$ and 1 mM SDS as the
aqueous electrolyte (nanoporous Zn/Cu/Zn//K,MnO$_2$).
Therein, the K,MnO$_2$ nanobelts are prepared by a modified
hydrothermal method (Fig. S20) and then mixed with super‑
P acetylene black conducting agent and poly(vinylideneflu‑
oride) binder on titanium foil [16, 72]. Figure 4a shows a
representative cyclic voltammetry (CV) curve of full AR‑ZMB
device of nanoporous Zn/Cu/Zn//K,MnO$_2$ at a scan
rate of 0.1 mV s$^{-1}$, displaying primary redox peaks at 1.55
and 1.47 V that correspond to the intercalation/deinterca‑
lation of Zn$^{2+}$ [16, 19–22]. Although the nanoporous Zn/Cu/
Zn//K,MnO$_2$ AR-ZMB has the same K,MnO$_2$-based cath‑
edote material as the nanoporous Zn/K,MnO$_2$ and bulk Zn/
K,MnO$_2$ ones, it exhibits superior voltammetric behaviors,
with a higher current density and a smaller redox peak volt‑
age difference, at various scan rates from 0.1 to 5 mV s$^{-1}$
(Fig. S21). These observations imply the significant role
of nanoporous Zn/Cu/Zn hybrid anode in improving rate
capability of AR-ZMBs by virtue of the synergic effect of
Zn,Cu$_x$ alloy shell and nanoporous architecture on Zn
stripping/plating kinetics. Figure S22a-c shows the voltage
profiles for the galvanostatic charge and discharge of nano‑
porous Zn,Cu/Zn//K,MnO$_2$, nanoporous Zn$_x$/K,MnO$_2$ and
bulk Zn//K,MnO$_2$ AR-ZMBs at various specific currents
from 0.1 to 5 A g$^{-1}$, displaying obvious voltage plateaus that
are consistent with the corresponding redox peaks in their
corresponding CV curves (Fig. S21a-c). Here the applied
specific current and the achieved capacity are calculated by
the loading mass of K,MnO$_2$ in the cathode. Evidently, the
use of nanoporous Zn,Cu$_x$/Zn anode not only increases the
charge/discharge capacities but also improves the energy
efficiency of AR-ZMB by lowering the voltage polarization.
As shown in Fig. 4b, the discharge capacity of nanoporous
Zn,Cu/Zn//K,MnO$_2$ AR-ZMB can reach $\sim 325$ mAh g$^{-1}$ at
the specific current of 0.1 A g$^{-1}$, higher than those of nano‑
porous Zn//K,MnO$_2$ ($\sim 295$ mAh g$^{-1}$) and bulk Zn//K,MnO$_2$
one ($\sim 268$ mAh g$^{-1}$). Even as the specific currents
increase to 5 A g$^{-1}$, the nanoporous Zn,Cu/Zn//K,MnO$_2$ AR-ZMB
still achieves the charge/discharge capacities of $\sim 165$/$\sim 164$ mAh g$^{-1}$, with a Coulombic efficiency of as high as $\sim 99.2\%$
(Fig. 4d), $\sim 2.3$- and $\sim 3.8$-fold higher than the values of
nanoporous Zn//K,MnO$_2$ ($\sim 71$/$\sim 71$ mAh g$^{-1}$) and bulk
Zn//K,MnO$_2$ ones ($\sim 42$/$\sim 40$ mAh g$^{-1}$). The superior rate
capability of nanoporous Zn,Cu/Zn//K,MnO$_2$ AR-ZMB is also demonstrated by the EIS spectrum in the Nyquist
plot (Fig. 4c), where the $R_{CT}$ value is only $\sim 14$ $\Omega$, much
lower than those of nanoporous Zn//K,MnO$_2$ ($\sim 38$ $\Omega$) and
bulk Zn//K,MnO$_2$ ($\sim 103$ $\Omega$) ones, respectively (Fig. S23).
When increasing Zn utilization in nanoporous Zn,Cu/Zn
electrode to $\sim 37.6\%$, the overall energy density of nanopo‑
orous Zn,Cu/Zn//K,MnO$_2$ full cell can reach $\sim 204$ Wh kg$^{-1}$
(Fig. S24). The self-discharge performance of nanoporous
Zn,Cu/Zn//K,MnO$_2$ cell is shown in Fig. S25. The voltage of the cell evidently drops to 1.531 V in $\sim 15$ h, which is
due to the pseudocapacitive discharge behavior. While in
the subsequent $\sim 485$ h, the nanoporous Zn,Cu/Zn//K,MnO$_2$
 cell exhibits a very low self-discharge rate (0.18 mV h$^{-1}$)
because of ultralow insertion kinetics of Zn$^{2+}$ [16]. Owing to the highly zincophilic Zn$_x$Cu$_y$ alloy shell guiding the reversible and dendrite-free Zn stripping/plating, the nanoporous Zn$_x$Cu$_y$/Zn/K$_x$MnO$_2$ AR-ZMB also exhibits exceptional long-term stability during the galvanostatic charge/discharge cycling measurements. As shown in Fig. 4e, it achieves initial charge/discharge capacities of ~320~319 mAh g$^{-1}$ (i.e., specific energy of ~430 Wh kg$^{-1}$) at 0.2 A g$^{-1}$ and still retains ~86% (~278~278 mAh g$^{-1}$) after more than 700 h, along with the Coulombic efficiency of as high as ~99.8%. Even at the specific current of as high as 1 A g$^{-1}$, the capacity retention of nanoporous Zn$_x$Cu$_y$/Zn/K$_x$MnO$_2$ AR-ZMB can reach ~84% after 800 cycles. However, the nanoporous Zn$_x$/K$_x$MnO$_2$ and bulk Zn/K$_x$MnO$_2$ devices undergo fast capacity degradation in 100 h probably due to the poor reversibility of nonmetallic Zn (Figs. 4e and S26).

4 Conclusions

In summary, we have developed three-dimensional and bicontinuous nanoporous Zn$_x$Cu$_y$/Zn hybrid electrodes for the use as highly reversible and dendrite-free Zn anode in aqueous rechargeable zinc-metal batteries. By making use of amphiphilic properties of SDS, there form a hydrophilic SDS/Cu/Zn interface to substantially inhibit side reactions and thus facilitate in situ surface alloying of Cu and Zn during Zn stripping/plating. Owing to the nanoporous architecture to reduce the current density per electrochemical surface area and the Zn$_x$Cu$_y$ alloy shell to guide uniform and horizontal Zn deposition with a zero millivolt nucleation overpotential and facilitate Zn stripping via the formation of Zn$_x$Cu$_y$/Zn galvanic couples, the symmetric nanoporous Zn$_x$Cu$_y$/Zn cell exhibits highly reversible and dendrite-free Zn stripping/plating behaviors in 1 M Zn(OTF)$_2$ aqueous
electrolyte, with ultralow polarizations and stable voltage profile under various current densities up to 50 mA cm\(^{-2}\). It maintains stable Zn stripping/plating for as long as 1900 h at 0.5 mA cm\(^{-2}\) and for 40,000 cycles at 50 mA cm\(^{-2}\), respectively, outperforming the symmetric cells based on monometallic nanoporous Zn and bulk Zn. These outstanding electrochemical properties enlist AR-ZMB full cells with nanoporous Zn,Cu/zinc anode and K\(_2\)MnO\(_2\) cathode to achieve specific energy of ~430 Wh kg\(^{-1}\) (based on the loading mass of K\(_2\)MnO\(_2\) in the cathode) with the Coulombic efficiency of as high as ~99.8% and the retention of ~86% for more than 700 h.

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References

1. B. Dunn, H. Kamath, J.M. Tarascon, Electrical energy storage for the grid: a battery of choices. Science 334(6058), 928–935 (2011). https://doi.org/10.1126/science.1212741
2. Z.P. Cano, D. Banham, S. Ye, A. Hintennach, J. Lu et al., Batteries and fuel cells for emerging electric vehicle markets. Nat. Energy 3(4), 279–289 (2018). https://doi.org/10.1038/s41560-018-0108-1
3. Y. Sun, N. Liu, Y. Cui, Promises and challenges of nanomaterials for lithium-based rechargeable batteries. Nat. Energy 1, 16071 (2016). https://doi.org/10.1038/energy.2016.71
4. Y. Tian, G. Zeng, A. Rutt, T. Shi, H. Kim et al., Promises and challenges of next-generation “beyond Li-ion” batteries for electric vehicles and grid decarbonization. Chem. Rev. 121(3), 1623–1669 (2021). https://doi.org/10.1021/acs.chemrev.0c00767
5. J.Y. Hwang, S.T. Myung, Y.K. Sun, Sodium-ion batteries: present and future. Chem. Soc. Rev. 46(12), 3529–3614 (2017). https://doi.org/10.1039/C6CS00776G
6. W. Zhang, Y. Liu, Z. Guo, Approaching high-performance potassium-ion batteries via advanced design strategies and engineering. Sci. Adv. 5(5), eaav7412 (2019). https://doi.org/10.1126/sciadv.aav7412
7. H. Kim, J. Hong, K.Y. Park, H. Kim, S.W. Kim et al., Aqueous rechargeable Li and Na ion batteries. Chem. Rev. 114(23), 11788–11827 (2014). https://doi.org/10.1021/cr500232y
8. G. Liang, F. Mo, X. Ji, C. Zhi, Non-metallic charge carriers for aqueous batteries. Nat. Mater. 6(2), 109–123 (2021). https://doi.org/10.1038/s41578-020-00241-4
9. Y. Liu, X. Lu, F. Lai, T. Liu, P.R. Shearing et al., Rechargeable aqueous Zn-based energy storage devices. Joule 5(11), 2845–2903 (2021). https://doi.org/10.1016/j.joule.2021.10.011
10. Y. Sui, X. Ji, Anticatalytic strategies to suppress water electrolysis in aqueous batteries. Chem. Rev. 121(11), 6654–6695 (2021). https://doi.org/10.1021/acs.chemrev.1c00191
11. J. Yang, B. Yin, Y. Sun, H. Pan, W. Sun et al., Zinc anode for mild aqueous zinc-ion batteries: challenges, strategies, and perspectives. Nano-Micro Lett. 14, 42 (2022). https://doi.org/10.1007/s40820-021-00782-5
12. H. Dong, O. Tutusaus, Y. Liang, Y. Zhang, Z. Lebens-Higgins et al., High-power Mg batteries enabled by heterogeneous enolization redox chemistry and weakly coordinating electrolytes. Nat. Energy 5(12), 1043–1050 (2020). https://doi.org/10.1038/s41560-020-00734-0
13. C. Wu, S. Gu, Q. Zhang, Y. Bai, M. Li et al., Electrochemically activated spinel manganese oxide for rechargeable aqueous aluminum battery. Nat. Commun. 10, 73 (2019). https://doi.org/10.1038/s41467-018-07980-7
14. B. Li, X. Zhang, T. Wang, Z. He, B. Lu et al., Interfacial engineering strategy for high-performance Zn metal anodes. Nano-Micro Lett. 14, 6 (2022). https://doi.org/10.1007/s40820-021-00764-7
15. Q. Ran, H. Shi, H. Meng, S.P. Zeng, W.B. Wan et al., Aluminum-copper alloy anode materials for high-energy aqueous aluminum batteries. Nat. Commun. 13, 576 (2022). https://doi.org/10.1038/s41467-022-28238-3
16. S.B. Wang, Q. Ran, R.Q. Yao, H. Shi, Z. Wen et al., Lamella-nanostructured eutectic zinc–aluminum alloys as reversible and dendrite-free anodes for aqueous rechargeable batteries. Nat. Commun. 11, 1634 (2020). https://doi.org/10.1038/s41467-020-15478-4

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17. X. Jia, C. Liu, Z.G. Neale, J. Yang, G. Cao, Active materials for aqueous zinc ion batteries: synthesis, crystal structure, morphology, and electrochemistry. Chem. Rev. 120(15), 7795–7866 (2020). https://doi.org/10.1021/acs.chemrev.9b00628

18. N. Zhang, X. Chen, M. Yu, Z. Niu, F. Cheng et al., Materials chemistry for rechargeable zinc-ion batteries. Chem. Soc. Rev. 49(13), 4203–4219 (2020). https://doi.org/10.1039/c9cs00349e

19. H. Pan, Y. Shao, P. Yan, Y. Cheng, K.S. Han et al., Reversible aqueous zinc/manganese oxide energy storage from conversion reactions. Nat. Energy 1, 16039 (2016). https://doi.org/10.1038/nenergy.2016.39

20. J. Huang, Z. Wang, M. Hou, X. Dong, Y. Liu et al., Poly-aniline-intercalated manganese dioxide nanolayers as a high-performance cathode material for an aqueous zinc-ion battery. Nat. Commun. 9, 2906 (2018). https://doi.org/10.1038/s41467-018-04949-4

21. X. Tang, D. Zhou, B. Zhang, S. Wang, P. Li et al., A universal strategy towards high-energy aqueous multivalent-ion batteries. Nat. Commun. 12, 2857 (2021). https://doi.org/10.1038/s41467-021-23209-6

22. D. Feng, T.N. Gao, L. Zhang, B. Guo, S. Song et al., Boosting high-rate zinc-storage performance by the rational design of Mn2O3 nanoporous architecture cathode. Nano-Micro Lett. 12, 14 (2020). https://doi.org/10.1007/s40820-019-0351-4

23. X.Z. Zhai, J. Qu, S.M. Hao, Y.Q. Jing, W. Chang et al., Layered birnessite cathode with a displacement/intercalation mechanism for high-performance aqueous zinc-ion batteries. Nano-Micro Lett. 12, 56 (2020). https://doi.org/10.1007/s40820-020-0397-3

24. D. Kundu, B. Adams, V. Duffort, S.H. Vajargah, L.F. Nazar, A high-capacity and long-life aqueous rechargeable zinc battery using a metal oxide intercalation cathode. Nat. Energy 1, 16119 (2016). https://doi.org/10.1038/nenergy.2016.119

25. Y. Zhang, F. Wan, S. Huang, S. Wang, Z. Niu et al., A chemically self-charging aqueous zinc-ion battery. Nat. Commun. 11, 2199 (2020). https://doi.org/10.1038/s41467-020-16309-5

26. Y. Yang, Y. Tang, G. Fang, L. Shan, J. Guo et al., Li+ intercalated V2O5·nH2O with enlarged layer spacing and fast ion diffusion as an aqueous zinc-ion battery cathode. Energy Environ. Sci. 11(11), 3157–3162 (2018). https://doi.org/10.1039/c8ee01651h

27. S.B. Wang, Q. Ran, W.B. Wan, H. Shi, S.P. Zeng et al., Ultra-high-energy and -power aqueous rechargeable zinc-ion microbatteries based on highly cation-compatible vanadium oxides. J. Mater. Sci. Technol. 120, 159–166 (2022). https://doi.org/10.1016/j.jmst.2022.01.007

28. Q. Li, X. Rui, D. Chen, Y. Feng, N. Xiao et al., A high-capacity ammonium vanadate cathode for zinc-ion battery. Nano-Micro Lett. 12, 67 (2020). https://doi.org/10.1007/s40820-020-0401-y

29. Y. Liang, Y. Jing, S. Gheytani, K.Y. Lee, P. Liu et al., Universal quinone electrodes for long cycle life aqueous rechargeable batteries. Nat. Mater. 16(8), 841–848 (2017). https://doi.org/10.1038/nmat4919

30. Q. Zhao, W. Huang, Z. Luo, L. Liu, Y. Lu et al., High-capacity aqueous zinc batteries using sustainable quinone electrodes. Sci. Adv. 4(3), eaao1761 (2018). https://doi.org/10.1126/sci‑adv.aao1761

31. G. Fang, J. Zhou, A. Pan, S. Liang, Recent advances in aqueous zinc-ion batteries. ACS Energy Lett. 3(10), 2480–2501 (2018). https://doi.org/10.1021/acsenergylett.8b01426

32. W. Lu, C. Zhang, H. Zhang, X. Li, Anode for zinc-based batteries: challenges, strategies, and prospects. ACS Energy Lett. 6(8), 2765–2785 (2021). https://doi.org/10.1021/acsenergylett.1c00939

33. L. Ma, M.A. Schroeder, O. Borodin, T.P. Pollard, M.S. Ding et al., Realizing high zinc reversibility in rechargeable batteries. Nat. Energy 5(10), 743–749 (2020). https://doi.org/10.1038/s41580-020-0674-x

34. Z. Yi, G. Chen, F. Hou, L. Wang, J. Liang, Strategies for the stabilization of Zn metal anodes for Zn-ion batteries. Adv. Energy Mater. 11(1), 2003065 (2021). https://doi.org/10.1002/aenm.202003065

35. F. Wang, O. Borodin, T. Gao, X. Fan, W. Sun et al., Highly reversible zinc metal anode for aqueous batteries. Nat. Mater. 17(6), 543–549 (2018). https://doi.org/10.1038/s41563-018-0063-z

36. M. Yan, N. Dong, X. Zhao, Y. Sun, H. Pan, Tailoring the stability and kinetics of Zn anodes through trace organic polymer additives in dilute aqueous electrolyte. ACS Energy Lett. 6(9), 3236–3243 (2021). https://doi.org/10.1021/acsenergylett.1c01418

37. C. Liu, X. Xie, B. Lu, J. Zhou, S. Liang, Electrolyte strategies toward better zinc-ion batteries. ACS Energy Lett. 6(3), 1015–1033 (2021). https://doi.org/10.1021/acsenergylett.0c02684

38. Y. Zhu, J. Yin, X. Zheng, Y. Lei et al., Concentrated dual-cation electrolyte strategy for aqueous zinc-ion batteries. Energy Environ. Sci. 14(8), 4463 (2021). https://doi.org/10.1039/d1ee01472b

39. B. Zhang, L. Qin, Y. Fang, Y. Chai, X. Xie et al., Tuning Zn2+ coordination tunnel by hierarchical gel electrolyte for dendrite-free zinc anode. Sci. Bull. (2022). https://doi.org/10.1016/j.scib.2022.01.027

40. L. Li, S. Liu, D. Ba, W. Liu, Q. Gui et al., Electrolyte concentration regulation boosting zinc storage stability of high-capacity K0.486V2O5 cathode for bendable quasi-solid-state zinc ion batteries. Nano-Micro Lett. 13, 34 (2021). https://doi.org/10.1007/s40820-020-00554-7

41. P. Sun, L. Ma, W. Zhou, M. Qiu, Z. Wang et al., Simultaneous regulation on solvation shell and electrode interface for dendrite-free Zn ion batteries achieved by a low-cost glucose additive. Angew. Chem. Int. Ed. 60(33), 18247–18255 (2021). https://doi.org/10.1002/anie.202105756

42. A. Bayaguud, X. Luo, Y. Fu, C. Zhu, Cationic surfactant-type electrolyte additive enables three-dimensional dendrite-free zinc anode for stable zinc-ion batteries. ACS Energy Lett. 5(9), 3012–3020 (2020). https://doi.org/10.1021/acsenergylett.0c01792

43. Z. Wang, L. Dong, W. Huang, H. Jia, Q. Zhao et al., Simultaneously regulating uniform Zn2+ flux and electron conduction
by MOF/rGO interlayers for high-performance Zn anodes. Nano-Micro Lett. 13, 73 (2021). https://doi.org/10.1007/s40820-021-00594-7

44. J. Zheng, Q. Zhao, T. Tang, J. Yin, C.D. Quilty et al., Reversible epitaxial electrodeposition of metals in battery anodes. Science 366(6465), 645–648 (2019). https://doi.org/10.1126/science.aax6873

45. J. Zheng, Y. Deng, J. Yin, T. Tang, R. Garcia-Mendez et al., Textured electrodes: manipulating built-in crystallographic heterogeneity of metal electrodes via severe plastic deformation. Adv. Mater. 34(1), 2106867 (2021). https://doi.org/10.1002/adma.202106867

46. M. Zhou, S. Guo, J. Li, X. Luo, Z. Liu et al., Surface-preferred crystal plane for a stable and reversible zinc anode. Adv. Mater. 33(21), 2100187 (2021). https://doi.org/10.1002/adma.202100187

47. L. Kang, M. Cui, F. Jiang, Y. Gao, H. Luo et al., Nanoporous CaCO3 coatings enabled uniform Zn stripping/plating for long-life zinc rechargeable aqueous batteries. Adv. Energy Mater. 8(25), 1801090 (2018). https://doi.org/10.1002/aenm.201801090

48. N. Zhang, S. Huang, Z. Yuan, J. Zhu, Z. Zhao et al., Direct self-assembly of MXene on Zn anodes for dendrite-free aqueous zinc-ion batteries. Angew. Chem. Int. Ed. 60(6), 2861–2865 (2021). https://doi.org/10.1002/anie.202012322

49. K. Wu, J. Yi, X. Liu, Y. Sun, J. Cui et al., Regulating Zn deposition via an artificial solid-electrolyte interface with aligned dipoles for long life Zn anode. Nano-Micro Lett. 13, 79 (2021). https://doi.org/10.1007/s40820-021-00599-2

50. X. Yang, C. Li, Z. Sun, S. Yang, Z. Shi et al., Interfacial manipulation via in situ grown ZnSe cultivator toward highly reversible Zn metal anodes. Adv. Mater. 33(52), 2105951 (2021). https://doi.org/10.1002/adma.202105951

51. J. Hao, B. Li, X. Li, X. Zeng, S. Zhang et al., An in-depth study of Zn metal surface chemistry for advanced aqueous Zn-ion batteries. Adv. Mater. 32(34), 2003021 (2020). https://doi.org/10.1002/adma.202003021

52. X. Wang, J. Meng, X. Lin, Y. Yang, S. Zhou et al., Stable zinc metal anodes with textured crystal faces and functional zinc compound coatings. Adv. Funct. Mater. 31(48), 2106114 (2021). https://doi.org/10.1002/adfm.202106114

53. Z. Guo, L. Fan, C. Zhao, A. Chen, N. Liu et al., A dynamic and self-adapting interface coating for stable Zn-metal anodes. Adv. Mater. 34(2), 2105133 (2021). https://doi.org/10.1002/adma.202105133

54. Y. Jiao, F. Li, X. Jin, Q. Lei, L. Li et al., Engineering polymer glue towards 90% zinc utilization for 1000 hours to make high-performance Zn-ion batteries. Adv. Funct. Mater. 31(49), 2107652 (2021). https://doi.org/10.1002/adfm.202107652

55. S. Xie, Y. Li, X. Li, Y. Zhou, Z. Dang et al., Stable zinc anodes enabled by zincophilic Cu nanowire networks. Nano-Micro Lett. 14, 39 (2022). https://doi.org/10.1007/s40820-021-00783-4

56. H. Zhao, Y. Lei, 3D nanostructures for the next generation of high-performance nanodevices for electrochemical energy conversion and storage. Adv. Energy Mater. 10(28), 2001460 (2020). https://doi.org/10.1002/aenm.202001460

57. W. Guo, Z. Cong, Z. Guo, C. Chang, X. Liang et al., Dendrite-free Zn anode with dual channel 3D porous frameworks for rechargeable Zn batteries. Energy Storage Mater. 30, 104–112 (2020). https://doi.org/10.1016/j.ensm.2020.04.038

58. C. Li, X. Xie, H. Liu, P. Wang, C. Deng et al., Integrated ‘all-in-one’ strategy to stabilize zinc anodes for high-performance zinc-ion batteries. Natl. Sci. Rev. 9(3), nwab177 (2022). https://doi.org/10.1093/nsr/nwab177

59. Y. An, Y. Tian, S. Xiong, J. Feng, Y. Qian, Scalable and controllable synthesis of interface engineered nanoporous host for dendrite-free and high rate zinc metal batteries. ACS Nano 15(7), 11828–11842 (2021). https://doi.org/10.1021/acsnano.1c02928

60. H. Shi, Y.T. Zhou, R.Q. Yao, W.B. Wang, Q.H. Zhang et al., Intermetallic Cu3Zr clusters anchored on hierarchical nanoporous copper as efficient catalysts for hydrogen evolution reaction. Research 2020, 2987234 (2020). https://doi.org/10.34133/2020/2987234

61. H. Shi, Y.T. Zhou, R.Q. Yao, W.B. Wang, X. Ge et al., Spontaneously separated intermetallic Cu3Mo from nanoporous copper as versatile electrocatalysts for highly efficient water splitting. Nat. Commun. 11, 2940 (2020). https://doi.org/10.1038/s41467-020-16769-6

62. I.C. Oppenheim, D.J. Trevor, C.E.D. Chidsey, P.L. Trevor, K. Sieradzki, In situ scanning tunneling microscopy of corrosion of silver-gold alloys. Science 254(5032), 687–689 (1991). https://doi.org/10.1126/science.254.5032.687

63. J. Erlebacher, M.J. Aziz, A. Karma, N. Dimitrov, K. Sieradzki, Evolution of nanoporosity in dealloying. Nature 410(6827), 450–453 (2001). https://doi.org/10.1038/35068529

64. X.Y. Lang, H.Y. Fu, C. Hou, G.F. Han, P. Yang et al., Nanoporous gold supported cobalt oxide microelectrodes as high-performance electrochemical biosensors. Nat. Commun. 4, 2169 (2013). https://doi.org/10.1038/ncomms13169

65. F. Jia, C. Yu, Z. Ai, L. Zhang, Fabrication of nanoporous gold film electrodes with ultrahigh surface area and electrochemical activity. Chem. Mater. 19(15), 3648–3653 (2007). https://doi.org/10.1021/cm0704251

66. K. Yan, Z. Lu, H.W. Lee, F. Xiong, P.C. Hsu et al., Selective deposition and stable encapsulation of lithium through heterogeneous seeded growth. Nat. Energy 1, 16010 (2016). https://doi.org/10.1038/nenergy.2016.10

67. R. Zhang, X.R. Chen, X. Chen, X.B. Cheng, X.Q. Zhang et al., Lithiophilic sites in doped graphene guide uniform lithium nucleation for dendrite-free lithium metal anodes. Angew. Chem. Int. Ed. 56(27), 7764–7768 (2017). https://doi.org/10.1002/anie.201702099

68. J.F. Parker, C.N. Chervin, E.S. Nelson, D.R. Rolison, J.W. Long, Wiring zinc in three dimensions re-writes battery performance—dendrite-free cycling. Energy Environ. Sci. 7(3), 1117–1124 (2014). https://doi.org/10.1039/c3ee43754j

69. J.F. Parker, C.N. Chervin, I.R. Pala, M. Machler, M.F. Burz et al., Rechargeable nickel–3D zinc batteries: an energy-dense,
safer alternative to lithium-ion. Science 356(6336), 414–417 (2017). https://doi.org/10.1126/science.aak9991

70. R. Zhang, P.G. Yin, N. Wang, L. Guo, Photoluminescence and Raman scattering of ZnO nanorods. Solid State Sci. 11(4), 865–869 (2009). https://doi.org/10.1016/j.solidstatesciences.2008.10.016

71. C. Liu, W. Xu, C. Mei, M. Li, W. Chen et al., A chemically self-charging flexible solid-state zinc-ion battery based on VO₂ cathode and polyacrylamide–chitin nanofiber hydrogel electrolyte. Adv. Energy Mater. 11(25), 2003902 (2021). https://doi.org/10.1002/aenm.202003902

72. Z. Lv, Y. Luo, Y. Tang, J. Wei, Z. Zhu et al., Editable supercapacitors with customizable stretchability based on mechanically strengthened ultralong MnO₂ nanowire composite. Adv. Mater. 30(2), 1704531 (2018). https://doi.org/10.1002/adma.201704531