Laminated Zinc-Copper Electrodes as Reversible and Dendrite-Free Anodes for Aqueous Rechargeable Zinc-Ion Batteries

Tian Wang, Daming Yan, Baozhu Yu, Xingchen Zhou, Xiangdong Ding, Yang Yang,* and Junjie Sun*

1. INTRODUCTION

As the international community pays increasing attention to issues such as energy security and environmental protection, it has become particularly important to develop safe, economical, and sustainable energy storage technologies. Battery energy storage technology, which achieves energy storage and utilization by mutual conversion between electrical and chemical energy, is not only a favorable support for reducing fossil fuel dependence and environmental pollution but also an effective solution for grid-connected utilization of intermittent renewable energy.1−3 Lithium-ion batteries (LIBs) have dominated the rechargeable battery market with their good cycling stability and high energy density.4−8 However, flammable organic electrolytes, high cost required for battery design, and insufficient lithium resources pose many economic challenges and safety concerns, limiting further large-scale applications of LIBs. Compared to LIBs, aqueous rechargeable zinc-ion batteries (AR-ZIBs) are considered a highly promising emerging energy storage technology as an energy storage alternative to lithium because of their low cost, high safety, high energy density, and environmentally friendly,9−11 which have become a research hotspot in recent years.

Regarding AR-ZIBs, there has been much research done on cathode materials, including Mn-based oxides and V-based oxides.12−21 However, AR-ZIBs have been plagued by the irreversibility problem of conventional zinc metal anodes regardless of which advanced cathode material is used.9,22,23 For the bare Zn anode, Zn2+ plating/stripping results in a highly irreversible Zn2+ plating/stripping chemistry. Consequently, the symmetric battery based on those anodes could operate steadily to 1000 h in the neutral electrolyte and exhibits excellent cycling durability. Furthermore, the laminated Zn-Cu composite anode and Na2V6O16·3H2O cathode were assembled into a full battery in the neutral electrolyte, which demonstrates outstanding cycling stability within 1000 cycles. And the alkaline full battery can provide ultra-long cyclic stability of 4000 cycles, significantly better than the cell based on the bare Zn anode.

Importantly, the protruding tips not only have higher adsorption, which synergistically induces uniform Zn nucleation, resulting in a highly reversible Zn2+ plating/stripping chemistry. Consequently, the symmetric battery based on those anodes could operate steadily to 1000 h in the neutral electrolyte and exhibits excellent cycling durability. Furthermore, the laminated Zn-Cu composite anode and Na2V6O16·3H2O cathode were assembled into a full battery in the neutral electrolyte, which demonstrates outstanding cycling stability within 1000 cycles. And the alkaline full battery can provide ultra-long cyclic stability of 4000 cycles, significantly better than the cell based on the bare Zn anode.

Keywords: aqueous rechargeable Zn-ion batteries, Zn-Cu composite anode, laminated composite structure, even electric field distribution, reversible Zn2+ plating/stripping
contribute to the aggregation of Zn$^{2+}$ on the initial tips, exacerbating further growth of Zn dendrites and leading to a persistent inhomogeneous electric field on the zinc anode surface.\textsuperscript{25,26} In addition, uneven Zn deposition can also lead to irreversible problems such as dendrite formation and growth, shape deformation, surface passivation, or hydrogen evolution in the Zn anode,\textsuperscript{27,28} resulting in poor stability of Zn metal electrodes in AR-ZIBs. Although the Zn metal can stably undergo redox reactions in neutral solutions due to its high hydrogen evolution overpotential compared to alkaline electrolytes, which can inhibit the Zn dendrite growth to some extent and exhibit higher stability and reversibility, irreversibility issues such as dendrite growth due to uneven plating/stripping of Zn$^{2+}$ still cannot be avoided.\textsuperscript{29} In addition, there always take place uncontrollable shape changes during the repetitive processes of Zn$^{2+}$ plating/stripping, producing a large number of defects and cracks. The structural irreversibility leads to an uneven distribution of Zn$^{2+}$ on the Zn metal surface, which further triggers the growth of Zn dendrites, resulting in significant and rapid capacity decay and a short lifetime of AR-ZIBs.\textsuperscript{30–33} Thus, it is an urgent need to explore new types of zinc-based anode materials, which can overcome these irreversibility problems for building high-performance AR-ZIBs.

In this work, we report Zn-Cu composites with alternating Zn and Cu layer structures as dendrite-free and reversible anode materials. The inherent excellent electrical conductivity of the array-distributed two-dimensional copper skeleton in the composite anode ensures a uniform distribution of the surface electric field, and the Zn-Cu intermediate phase throughout the Zn-Cu composite anode can significantly enhance the Zn$^{2+}$ adsorption, which synergistically induces uniform Zn nucleation and inhibits the dendrite growth. Thanks to these advantages, the symmetric battery assembled with laminated Zn-Cu composite anode exhibits low polarization and excellent cycling stability (1000 h of stable operation at 2.5 mAh cm$^{-2}$). In addition, a full battery composed of this anode and Na$_2$V$_6$O$_{18}$·3H$_2$O cathode in the neutral electrolyte has outstanding cycling stability within 1000 cycles. What is more, the obtained laminated Zn-Cu composite anode also exhibits excellent electrochemical performance in alkaline aqueous batteries (long lifespan of 4000 cycles).

2. EXPERIMENTAL SECTION

2.1. Preparation of Laminated Zn-Cu Anodes. High-purity Zn foil (100 μm in thickness) and copper foil (20 μm in thickness) were used to construct the laminated Zn-Cu composite anode. First, the surfaces of both materials were cleaned using alcohol to remove surface impurities. Then, both materials were cut into circular sheets with a diameter of 30 mm and alternately stacked in a mold, followed by applying a force of 30 MPa to the whole material for 30 min. Subsequently, the material together with the mold was directly heated at 240 °C for 1 h, then applied 30 MPa force again, and held the load for 30 min. When the mold cooled to room temperature, the completely cooled Zn-Cu composite was removed from the mold. Finally, the Zn-Cu composite was cut into metal sheets with a thickness of about 800 μm along the vertical direction of its laminated structure, and the composite sheets were further polished to obtain anodic electrodes with an ordered layer structure.

2.2. Preparation of Na$_2$V$_6$O$_{18}$·3H$_2$O Cathodes. Na$_2$V$_6$O$_{18}$·3H$_2$O (NVO) was prepared by a simple stirring method, i.e., 2 g of commercial V$_2$O$_5$ powder was added to 30 mL of aqueous NaCl solution for stirring. After 96 h of vigorous stirring at room temperature, the solution changed from orange to brown. Subsequently, after washing with ethanol and deionized water several times and drying at 80 °C for 12 h in an electric thermostat oven, brown powder of NVO was obtained. To prepare the cathode electrode, the NVO powder, acetylene black, and polytetrafluoroethylene were mixed in alcohol in the weight ratio of 8:1:1 and ultrasonicated for 10 min to mix well, which was coated on stainless steel foil and dried at 60 °C overnight. The mass loading of the NVO electrode was ∼2.6 mg cm$^{-2}$.

2.3. Assembly of Batteries. Two bare Zn or laminated Zn-Cu composite electrodes were used as electrodes, 2 M ZnSO$_4$ was utilized as the electrolyte to assemble neutral symmetric battery. The electrolyte of the alkaline symmetric batteries was composed of 6 M KOH and 0.2 M Zn(CH$_3$COO)$_2$, with the same electrode matching as that in neutral cells. The full batteries were assembled by matching bare Zn anodes and laminated Zn-Cu composite anodes (1 × 1 cm$^2$) respectively with NVO cathodes in the neutral electrolyte or AC cathodes in the alkaline electrolyte. Both symmetric and full cells were assembled and left for 12 h before the relevant electrochemical tests.

2.4. Material Characterizations. The composition of the samples was analyzed with a copper K$_\alpha$ radiation X-ray diffraction (XRD, Bruker D8 ADVANCE). The diffraction patterns ranged from 5 to 80° in steps of 0.02°. The micromorphologies and microstructures of the materials and electrodes were observed with field-emission scanning electron microscopy (SEM, FEI VERIOS 460), and the distribution of elements in electrodes was also analyzed by the corresponding energy-dispersive X-ray spectroscopy (EDS). The microscopic morphology was investigated by an optical microscope (Nikon ECLIPSE MA200).

2.5. Electrochemical Measurements. All galvanostatic charge/discharge tests of the symmetric and full batteries were performed on the Newark Battery Test System (Neware BTS). Cyclic voltammetry (CV) as well as electrochemical impedance spectroscopy (EIS) tests were performed by electrochemical workstation (CHI 660). The scan rates of CV tests were 0.2, 0.3, 0.5, 1, 3, and 5 mV s$^{-1}$, and the frequency range of EIS tests was from 1 MHz to 0.01 Hz. The corrosion tests were performed in a three-electrode system with Zn-Cu or Zn as the working electrode, platinum flake electrode as the counter electrode, and mercureic oxide/saturated glycerol electrode as the reference electrode in the neutral/alkaline electrolyte.

2.6. Calculation Details. Calculations were based on density functional theory (DFT)\textsuperscript{34–35} as implemented in the Vienna Ab initio Simulation Package (VASP).\textsuperscript{36,37} Adsorption energy calculations were performed using generalized-gradient approximation\textsuperscript{38} and the projector augmented plane-wave. The convergence tolerance quality of geometry optimization and the plane-wave energy cutoff was respectively set to 1.0 × 10$^{-7}$ au for energy and 400 eV. All the forces on each atom were limited to 0.01 eV Å$^{-1}$. The Monkhorst–Pack method was utilized to select the k-points for the Brillouin zone, which was set to 6 × 6 × 4$^2$ for Zn (101), 8 × 8 × 4 for Sn (111), and 4 × 2 × 2 for the Zn-Cu (112) model. The adsorption energies (E$_{\text{ads}}$) for the slab model interacting with a Zn ion were calculated with the following equation:

$$E_{\text{ads}} = E_{\text{total}} - E_{\text{slab}} - E_{\text{Zn}}$$

(1)

where $E_{\text{total}}$ is the total energy of the Zn, Cu, or Zn-Cu slab model bound with the Zn ion, $E_{\text{slab}}$ is the energy of the Zn, Cu, or Cu-Zn slab model, and $E_{\text{Zn}}$ is the energy of the Zn ion.

3. RESULTS AND DISCUSSION

3.1. Materials Characterization. As a proof of concept, we chose low-cost pure Zn and Cu as the original materials and produce Zn-Cu composite electrodes with a laminar structure by a simple and scalable method. As illustrated in Figure 1, our designed process for the preparation of the laminated Zn-Cu composite electrode consists of two steps: The zinc and copper foils were alternately stacked in a mold for pressing, sintering, and pressing again, and then cut along the axial direction of the whole material to obtain the Zn-Cu composite electrode.
consisting of a layer of Zn and a layer of Cu interactively arranged and stacked (see the Experimental Section). Figure 2a demonstrates typical XRD patterns of the pure Zn electrode as well as the laminated Zn-Cu composite electrode, where the laminated Zn-Cu composite electrode exhibits characteristic peaks of the Zn phase (PDF # 87-0713) and Cu phase (PDF # 85-1326), illustrating the high purity of the electrode. In addition, it is worthwhile to note that some additional characteristic peaks (e.g., at 42.134°) appear in the XRD patterns of the laminated Zn-Cu composite electrode, which represent the inevitable formation of the zinc-copper intermediate phases (PDF # 41-1435) at the Cu/Zn interface during the preparation of the laminated Zn-Cu composite electrode. The diffraction peak of the zinc-copper intermediate phase is very weak because its content in the laminated Zn-Cu composite anode is very small (relative to the content of Zn and Cu). If too much zinc-copper intermediate phase is formed during the preparation process, this will undoubtedly consume a large amount of the active material Zn. On the other hand, since the intermediate phase at the Zn/Cu interface is very brittle, the excessive zinc-copper intermediate phase tends to lead to sample cracking, which will undoubtedly affect the mechanical strength of the laminated Zn-Cu composite anode. Therefore, the content of the zinc-copper intermediate phase in the laminated Zn-Cu composite anode is required to be low. In addition, to further demonstrate the formation of the zinc-copper intermediate phase, we have performed XRD tests on the composition of the laminated Zn-Cu composite anode at different locations along its cross-sectional direction from the Cu lamellae to the Zn lamellae in turn. The detection surface and detection direction are shown in Figure S1a. During the testing process, the test surface was polished once for each XRD test until the test surface transitioned from the Cu lamellae to the Zn lamellae. As shown in Figure S1b, the diffraction peaks about the zinc-copper intermediate phase at about 42° firstly show a trend from absent to present and gradually increase as the detection position moves from the Cu lamellae to the Zn lamellae (black line to green line). As the detection position gets closer to the Zn lamellae, the diffraction peaks about the zinc-copper intermediate phase show a gradual weakening trend (green line to yellow line). These results fully demonstrate the formation of the zinc-copper intermediate phase in the laminated Zn-Cu composite anode and its formation at the Zn/Cu interface.

The microstructure and morphology of the above two kinds of anode materials were investigated by optical microscopy and SEM. Figure 2b shows representative optical micrographs of the Zn-Cu composite electrode with an ordered laminar structure, in which the Zn and Cu lamellae are alternately distributed and well-defined from each other, i.e., the Zn lamellae (black stripes) with a thickness of about 36 μm are alternately sandwiched by the Cu lamellae (bright white stripes) with a thickness of approximately 20 μm. It is worth stating that since the melting point of Zn is 419.58 °C and it is in a semi-melted state after 1 h of holding treatment at 420 °C, the thickness of Zn lamellae will be thinned to a certain extent during the subsequent 30 min of pressure treatment. Meanwhile, the melting point of Cu is 1083 °C, and it still

Figure 1. Preparation process of the laminated Zn-Cu composite anode.

Figure 2. (a) XRD patterns of laminated Zn-Cu composite and bare Zn samples. (b) Optical microscope image of the laminated Zn-Cu composite sample. (c) SEM images of Zn-Cu. (d) Typical SEM image of the laminated Zn-Cu composite sample and EDS element mapping of Cu and Zn.
Figure 3. (a) Schematic diagram of symmetrical battery configuration. Long-term plating/stripping cycling of symmetric batteries of bare Zn and laminated Zn-Cu composite at (b) 2 mA cm\(^{-2}\) and (c) 5 mA cm\(^{-2}\) in aqueous ZnSO\(_4\) electrolyte. (d) Comparison of voltage distribution of the two symmetric batteries at different current densities. (e) Voltage hysteresis of the Zn-Cu//Zn-Cu and Zn//Zn symmetric batteries at various current densities.

For further illustrating the advantages of the laminated Zn-Cu composite electrode, Figure 2c, the laminated Zn-Cu composite electrode shows a relatively smooth surface without any obvious bumps. Similarly, Figure S2 displays the sleek surface of the commercial Zn foil without any bulges. SEM images and EDS further illustrate the unique laminar structure of the Zn-Cu composite electrode with alternating Zn and Cu lamellae, as shown in Figure 2d.

3.2 Symmetric Battery Performance. To research the plating/stripping Zn behaviors of Zn-based anodes, the electrochemical stability of commercial Zn foils and laminated Zn-Cu composite anodes was evaluated for the first time by the galvanostatic cycling test in a typical symmetric cell configuration (Figure 3a). Figure 3b,c shows the comparison of voltage distributions of the Zn//Zn and Zn-Cu//Zn-Cu symmetric battery during the plating/stripping processes in the neutral electrolyte of 2 M ZnSO\(_4\). When the current density is 2 mA cm\(^{-2}\) and the cutoff capacity is 1 mAh cm\(^{-2}\), the Zn-Cu//Zn-Cu symmetric battery shows a relatively stable and flat voltage hysteresis with the polarization voltage of approximately 117 mV (see details in Figure S3).

Impressively, the Zn-Cu//Zn-Cu symmetric battery can maintain an ultrastable cycle of about 1000 h. By comparison, the voltage fluctuation of the Zn//Zn symmetric battery assembled by commercial Zn foils is similar to that of the Zn-Cu//Zn-Cu symmetric battery during the initial cycle (about the first 10 h). However, voltage hysteresis in the Zn//Zn symmetric battery gradually increases with cycle increase (see details in Figure S4), and the cycle curve fluctuates severely and finally fails after 240 h (the hysteresis amount is about 225 mV), which may be related to the internal short circuit due to the dendrites.

Specifically, for the bare Zn anode in the Zn//Zn symmetric cell, Zn\(^{2+}\) is thermodynamically more inclined to nucleate at the dislocation positions and form initial protrusions during the plating/stripping processes, resulting in an uneven electric field distribution on the Zn surface.\(^{24}\) In the subsequent deposition, Zn\(^{2+}\) prefers to accumulate on the initial tip and accumulate for deposition, resulting in a continuous inhomogeneity of the electric field on the Zn anode surface and eventually to the formation of Zn dendrites.\(^{25,26}\) When the Zn dendrites grow to a certain extent, it is easy to cause short circuit of the cell. The lower polarization of the Zn-Cu//Zn-Cu symmetric battery may be because of its unique structure of the laminated Zn-Cu composite electrode. Therein, the array-distributed Cu lamellae homogenizes the electric field distribution on the Zn surface via rapid electronic transmission, which reduces local current density of plating/stripping Zn on the anode surface and thus guides homogeneous Zn deposition during the subsequent plating. When the current density increases to 5 mA cm\(^{-2}\), the Zn-Cu//Zn-Cu symmetric battery still shows outstanding cycle stability and maintains a voltage hysteresis of approximately 157 mV to 1000 h. In stark contrast, the Zn//Zn symmetric battery exhibits obvious voltage fluctuations only at approximately 97 h. Similarly, the Zn-Cu//Zn-Cu symmetric battery shows outstanding stability for more than 900 h at 10 mA cm\(^{-2}\) in Figure S5a, which is superior to that of the Zn//Zn symmetric battery (failed at approximately 323 h) and most previously reported Zn anodes (Table S1).\(^{25,26,241-47}\) All these results indicate that the voltage hysteresis of Zn//Zn symmetric batteries is larger and laminated Zn-Cu composite anodes have better cycling stability than bare Zn anodes in the neutral electrolyte. CV curves show uniform forms (Figure S6). The CE of the Zn-Cu//Zn-Cu symmetric battery remains at 99.97% after about 1000 cycles (see details in Figure S7a), confirming outstanding reversibility of zinc plating/stripping on the laminated Zn-Cu composite anode.

For further illustrating the advantages of the laminated Zn-Cu composite anodes to the zinc foil, the electrochemical stability of the bare Zn anode and laminated Zn-Cu composite...
anode was also evaluated in the alkaline electrolyte of 6 M KOH and 0.2 M Zn(CH$_3$COO)$_2$. Impressively, the Zn-Cu∥Zn-Cu symmetric battery still provides a stable polarization voltage of approximately 22 mV for 450 h in an extremely harsh alkaline environment, while the Zn∥Zn symmetric battery exhibits significant voltage fluctuations for approximately 97 h (see details in Figure S5b). Similarly, the CE of the Zn-Cu∥Zn-Cu symmetric battery in the alkaline electrolyte remains at 99.98% after 455 h (see details in Figure S7b), further indicating that the laminated Zn-Cu composite anode after structural modification has a highly reversible plating/stripping process. Apparently, the plating/stripping process on bare zinc foils is unstable. This is because the bare zinc foils act as both the collector and active material in the battery; thus, the electrochemical properties and structure of the bare zinc anodes are changing during plating/stripping on the bare zinc surface, resulting in unstable electrochemical behavior. By comparison, for laminated Zn-Cu composite anodes, the two-dimensional copper skeleton not only always keeps high electrical conductivity but prevents too much structural change in the electrodes during the plating/stripping process. Consequently, the cycling stability of laminated Zn-Cu composite anodes is significantly improved. Figure 3d reflects the comparison of voltage profiles of the Zn∥Zn and Zn-Cu∥Zn-Cu symmetric battery at current densities of 0.2, 0.5, 1, 1.5, and 2 mA cm$^{-2}$ with a constant time of 1 h in the neutral electrolyte. When the current density switches back from 2 to 0.2 mA cm$^{-2}$, the voltage hysteresis of the Zn∥Zn symmetric battery increases from 113 to 171 mV, while that of the Zn-Cu∥Zn-Cu symmetric battery does not change much, proving a good lifetime and rate capability of laminated Zn-Cu composite anodes. Figure 3e shows more visually that the polarization voltages of the Zn-Cu∥Zn-Cu symmetric batteries are all much lower and more stable than those of the Zn∥Zn symmetric cells at different current densities, indicating that the laminated Zn-Cu composite anodes have better electrochemical performance.

3.3. Mechanism Analysis. To examine whether the structurally modified laminated Zn-Cu composite anode had the function of inhibiting the growth of dendrites, we assessed the changes in the morphology and composition of the above-mentioned bare Zn anode and laminated Zn-Cu composite anode after continuous plating and stripping by SEM and XRD. As can be seen in Figure 4a, after 100 cycles of the Zn∥Zn symmetric cell, it is clear that the bare Zn anode surface changes from an initially smooth surface to a rough surface with varying particle sizes because of the inhomogeneous Zn deposition. And further cycling up to 400 cycles, several Zn bulges are observed on the rough surface of the bare Zn anode (see details in Figure S8), indicating Zn dendrite growth on the Zn anode surface and potential internal short circuit. Conversely, the laminated Zn-Cu composite anode still has a relatively uniform and flat surface after 400 cycles (Figure 4b), indicating Zn dendrite growth on the Zn anode surface and potential internal short circuit. Further cycling up to 400 cycles, several Zn bulges are observed on the rough surface of the bare Zn anode (see details in Figure S8), indicating Zn dendrite growth on the Zn anode surface and potential internal short circuit. Consequently, the laminated Zn-Cu composite anode still has a relatively uniform and flat surface after 400 cycles (Figure 4b), indicating Zn dendrite growth on the Zn anode surface and potential internal short circuit. In addition, EIS also demonstrates the excellent stability of the laminated Zn-Cu composite anode during the plating/stripping Zn process.

Figure 4. SEM images of (a) bare Zn and (b) laminated Zn-Cu composite anodes after 100th (left) and 400th (right) zinc plating/stripping cycling tests in the ZnSO$_4$ aqueous electrolyte, respectively. Illustration, 2 µm. (c) Comparison of the initial EIS spectra of Zn∥Zn as well as Zn-Cu∥Zn-Cu symmetric cells. (d) XRD patterns of laminated Zn-Cu composite and bare Zn anodes after 100th plating/stripping cycling tests. (e) Zn 2p XPS spectrum of the bare Zn anode before and after the 100th cycling test. (f) Corrosion curves of laminated Zn-Cu composite and bare Zn anodes.
Moreover, the XRD pattern of the bare Zn anode after 100 cycles (Figure 4d) shows several new diffraction peaks belonging to Zn\textsubscript{6}SO\textsubscript{4}(OH)\textsubscript{6}\cdot5H\textsubscript{2}O (PDF # 39-0688) emerging at 8.068, 16.22, and 24.43°, in addition to the characteristic peaks of Zn, which is considered as a byproduct in the aqueous electrolyte.\textsuperscript{54-56} However, the XRD pattern of the laminated Zn-Cu composite anode after cycling shows only one diffraction peak related to the byproduct at 8.068° and the peak intensity is much smaller than that at the same position on the bare Zn anode surface, showing that the laminated Zn-Cu composite anode has a superior ability to suppress the by-reaction. In addition, it is worth noting that the Zn-Cu composite anode at 100 cycles is in the state of charge completion, and because the Cu is covered by the Zn deposited on the electrode surface at this time, the XRD results of the Zn-Cu composite anode after 100 cycles in Figure 4d do not show any diffraction peaks about Cu. Furthermore, the results of the chemical states of the surface Zn analyzed by X-ray photoelectron spectroscopy (XPS) were consistent with the XRD results. The surface Zn of the bare Zn anode is oxidized due to the formation of Zn\textsubscript{6}SO\textsubscript{4}(OH)\textsubscript{6}\cdot5H\textsubscript{2}O and ZnO after the cycling test\textsuperscript{57,58} which is different from some Zn\textsuperscript{2+} present on the surface of the pristine bare Zn anode (Figure 4e). For the laminated Zn-Cu composite anode after the cycling test, the XPS spectra show that the surface Zn maintains almost the same chemical states as that in the raw electrode (see details in Figure S10a,b). Considering that corrosion of the Zn anode may become a problem for the electrode and thus affect the battery performance, we also investigated the anti-corrosion performance of both anodes through Tafel testing. Figure 4f shows that the corrosion potential of the laminated Zn-Cu anode is −0.3496 V in the neutral electrolyte consisting of 2 M ZnSO\textsubscript{4} which is higher than that of the bare Zn anode (−0.3506 V). Meanwhile, its corrosion current density (7.56 mA cm\textsuperscript{−2}) is much lower than that of the bare Zn anode (10.93 mA cm\textsuperscript{−2}). As comparison, we also evaluated the anti-corrosion performance of both anodes in the alkaline electrolyte (see details in Figure S11). The results show that the laminated Zn-Cu electrode still exhibits higher corrosion potential and lower corrosion current density (−0.5492 V, 16.7 mA cm\textsuperscript{−2}) compared with the Zn anode (−0.5582 V, 20.38 mA cm\textsuperscript{−2}) in the extremely harsh alkaline environment.

To further understand the effect of Cu addition on the system, we start by studying the adsorption of Zn\textsuperscript{2+} on the Zn (101), Cu (111), and Zn-Cu intermediate phase (210) surface. Several high-symmetry adsorption sites such as the top-metal, bridge, and hollow site have been explored at first because such high symmetry points are usually the most stable adsorption sites. The lowest adsorption energy E\textsubscript{ads}, values of one Zn\textsuperscript{2+} on the Zn (101), Cu (111), and Zn-Cu intermediate phase (210) surface are −0.94, −1.01, and −1.25 eV in Figure 5a−c, respectively, all of which are exothermic processes. It can be seen that the adsorption of Zn\textsuperscript{2+} on the Cu surface is slightly more stable than that on the Zn surface, while the adsorption of Zn\textsuperscript{2+} on the Zn-Cu intermediate phase shows the most stable result. In addition, the distance from the adsorbed Zn\textsuperscript{2+} to Zn-Cu intermediate phase surface, 0.61 Å, is the smallest among the three, which identically shows the stronger adsorption capacity of the Zn-Cu intermediate phase to Zn\textsuperscript{2+}. Furthermore, the charge density difference distribution of the Zn-Cu intermediate phase with Zn\textsuperscript{2+} adsorption in Figure 5f shows a more liable transfer of electrons from the adsorbed Zn\textsuperscript{2+} to the Zn-Cu intermediate phase (210) than to the Zn (101) and Cu (111) since bare Zn and Cu have no obvious orbital coupling with the adsorbed Zn\textsuperscript{2+} in Figure 5d,e, substantiating the remarkable zincofilicity of the Zn-Cu intermediate phase (210).

In AR-ZIBs, energy is stored/delivered mainly by Zn electrochemical plating/stripping processes. For the bare Zn anode, Zn\textsuperscript{2+} is thermodynamically more inclined to nucleate at dislocation positions and form initial protrusions during the plating/stripping processes, resulting in an uneven distribution of electric field on the Zn anode surface.\textsuperscript{24} Importantly, the protruding tips not only have higher potentials but also consist of high-density low-coordination steps and tangles with lower activation energy, both of which contribute to the aggregation of Zn\textsuperscript{2+} on the initial tips and intensify further growth of Zn dendrites.\textsuperscript{25,26} To make matters worse, the weak interaction between the Zn substrate and the deposited Zn leads to a
uniform Zn zincophilicity of the Zn-Cu intermediate phase ensure the array-distributed two-dimensional copper skeleton and the contrast, the inherent excellent electrical conductivity of the utilization and cell life are affected by a significant tip effect. By anode surface. After long and repeated cycles, the Zn anode sustainably nonuniform electric field distribution on the Zn

sustainably nonuniform electric field distribution on the Zn anode surface. After long and repeated cycles, the Zn anode utilization and cell life are affected by a significant tip effect. By contrast, the inherent excellent electrical conductivity of the array-distributed two-dimensional copper skeleton and the zincophilicity of the Zn-Cu intermediate phase ensure the uniform Zn\(^{2+}\) plating/stripping on the laminated Zn-Cu composite electrode surface. Moreover, high corrosion resistance of the laminated Zn-Cu composite anode further prolongs the lifespan of the anode.

3.4. Full Battery Performance. To further determine the practicality of the laminated Zn-Cu composite anode in AR-ZIBs, the Zn||NVO and Zn-Cu||NVO full batteries were assembled in the neutral electrolyte using 0.4 mm bare Zn and Zn-Cu as the anode respectively and Na\(_2\)V\(_2\)O\(_5\)·3H\(_2\)O (NVO) as the cathode (Figure 6a). NVO was prepared by a simple liquid–solid mixing method,\(^{59}\) only adding V\(_2\)O\(_5\) powder to aqueous NaCl solution and stirring (see the Experimental Section). With increasing mixing time, the solution color changed from orange to brown (see details in Figure S12), which was attributed to the insertion of sodium ions into the V\(_2\)O\(_5\) layers and the formation of nanoribbon morphology through a dissolution–recrystallization process.\(^{60,61}\) Figure S13 shows the XRD patterns of the prepared sample, which match well with the characteristic peaks of Na\(_2\)V\(_2\)O\(_5\)·3H\(_2\)O (PDF # 16-0601), which proves the successful synthesis of the cathode materials. Figure 6b compares the representative CV curves of the Zn||NVO and Zn-Cu||NVO full cell in the neutral electrolyte, and both demonstrate two pairs of typical redox peaks, illustrating that the effect of Cu lamellae on the type of the redox reaction of cells is almost negligible. Among them, the two pairs of redox peaks located at 0.56/0.75 and 0.85/1.04 V in the Zn-Cu||NVO cell can be attributed to the reversible redox reactions that the insertion/extraction process of Zn\(^{2+}\) and H\(^+\) into/from NVO corresponds to the changes in the valence of vanadium from V\(^{5+}\) to V\(^{4+}\) and V\(^{4+}\) to V\(^{3+}\), respectively.\(^{54}\) Likewise, the same process occurs in the Zn||NVO cell. Furthermore, it can be seen in Figure S14 that using different anode materials, viz., the laminated Zn-Cu composite anode and bare Zn with a single-phase structure, makes them demonstrate different voltammetric behaviors. The potential difference between the reduction peak and the oxidation peak in the CV curve of the Zn-Cu||NVO full battery is smaller than the Zn||NVO full battery (190 vs 320 mV), indicating that the laminated Zn-Cu composite anode is more favorable for the Zn storage/delivery and has better reversibility than the bare Zn foil. Thus, the Zn-Cu||NVO full cell shows superior rate performance at scan rates from 0.2 to 5 mV s\(^{-1}\) (see details in Figure S15). It is worth stating that the copper skeleton in the 2D laminated Zn-Cu composite electrode does not involve in electrochemical reactions, which is further confirmed by the similar charge/discharge curves of two cells (Figure 6c).\(^{62}\) The EIS analysis further verifies the expectation that the laminated Zn-Cu composite anode improves the Zn plating/stripping kinetics, where the R\(_{CT}\) value (charge transfer resistance) of the Zn-Cu||NVO battery is much lower than the Zn||NVO battery (Figure 6d). To test the strengths of the laminated Zn-Cu composite over bare Zn anodes, the durability of Zn||NVO as well as Zn-Cu||NVO full batteries was tested through the galvanostatic charge/discharge test. From Figure 6e, it can be seen that the Zn-Cu||NVO cell shows superior cycling stability within 1000 cycles at 0.2 A g\(^{-1}\). In sharp contrast, the capacitance of the Zn||NVO cell decays by nearly 50% after about 200 cycles, which may be due to the irreversibility issues of bare Zn. This is further confirmed by the cross-sectional SEM images of the bare Zn and laminated Zn-Cu anodes after long-term cycling. Apparently, after about 980 cycles, the bare Zn anode surface accumulated significant Zn protrusions (Figure S16a), indicating the growth of Zn dendrites. In sharp contrast, the laminated Zn-Cu anode maintained a relatively uniform and flat surface after 1032 cycles (Figure S16b), indicating that it can maintain structural stability and highly reversible electrochemical behavior during the repeated Zn plating/stripping process.

To further determine the long-term cycle stability of our prepared laminated Zn-Cu composite electrode, we choose...
commercial activated carbon (AC), which was known to have excellent stability, as the cathode and assembled Zn||AC battery with bare Zn and Zn-Cu||AC battery with laminated Zn-Cu composite anode in the aforementioned alkaline electrolyte. Like the neutral cells, the Zn||AC and Zn-Cu||AC full cells also exhibit similar CV curves and galvanostatic charge/discharge curves in an alkaline environment (see details in Figure S17a), once again indicating that the contribution of the Cu lamellae to the capacitance of the reaction is negligible. Impressively, the Zn-Cu||AC cell maintains superior stability over 4000 cycles under an extremely harsh alkaline environment (see details in Figure S17c), while the Zn||AC cell shows severe degradation after 1300 cycles. The capacitance of the Zn||AC cell returns to its initial state when a new bare Zn anode is used; however, capacitance degradation occurs after 800 cycles once again. This may be due to the irreversibility problems of the bare Zn anode, as well as further demonstrate that the structurally modified laminated Zn-Cu composite anode significantly improves the reversibility of the redox reactions during the repeated Zn plating/stripping processes.

4. CONCLUSIONS

In summary, we have developed a laminated Zn-Cu composite anode with alternating Zn and Cu lamellae as an effective strategy to solve the irreversibility problem caused by dendrite growth during Zn plating/stripping processes, thus achieving reversible deposition/striping of Zn. Through a series of characterizations and DFT calculations, the role of the inherent excellent electrical conductivity of the array-distributed two-dimensional copper skeleton and the zinchalcity of the Zn-Cu intermediate phase on the uniform plating/stripping of Zn$^{2+}$ are elucidated. The symmetric cell based on laminated Zn-Cu composite anodes can operate steadily for 1000 h in the neutral electrolyte and exhibits excellent cycling durability. What is more, the symmetric battery can still work for 450 h in an extremely harsh alkaline environment and exhibits almost 100% coulombic efficiency. In addition, when incorporating the Zn-Cu composite anode with a Na$_2$V$_6$O$_{16}$·3H$_2$O cathode in the neutral electrolyte and the AC cathode in the alkaline electrolyte, the as-fabricated full cells show excellent long-term cycling stability, significantly better than the batteries based on bare Zn anodes.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaem.3c00855.

Further material characterizations including SEM images, CV curves, XRD patterns, EIS spectra after cycles, XPS data, voltage distribution of symmetric cells, corrosion curves, CV curves at various scan rates from 0.2 to 5.0 mV s$^{-1}$, cross-sectional SEM images after long-term cycles, cycling performance in the alkaline electrolyte, and comparison of our present work with previously reported Zn anodes (PDF)

AUTHOR INFORMATION

Corresponding Authors
Yang Yang – State Key Laboratory for Mechanical Behavior of Materials, School of Material Science and Engineering, Xi’an Jiaotong University, Xi’an 710049, P.R. China; Email: yangyymse@mail.xjtu.edu.cn
Junjie Sun – State Key Laboratory for Mechanical Behavior of Materials, School of Material Science and Engineering, Xi’an Jiaotong University, Xi’an 710049, P.R. China; Email: sunjunjie1987pd@mail.xjtu.edu.cn

Authors
Tian Wang – State Key Laboratory for Mechanical Behavior of Materials, School of Material Science and Engineering, Xi’an Jiaotong University, Xi’an 710049, P.R. China
Daming Yan – State Key Laboratory for Mechanical Behavior of Materials, School of Material Science and Engineering, Xi’an Jiaotong University, Xi’an 710049, P.R. China
Baozhu Yu – School of Science, Xi’an University of Technology, Xi’an 710048, China
Xingchen Zhou – State Key Laboratory for Mechanical Behavior of Materials, School of Material Science and Engineering, Xi’an Jiaotong University, Xi’an 710049, P.R. China
Xiangdong Ding – State Key Laboratory for Mechanical Behavior of Materials, School of Material Science and Engineering, Xi’an Jiaotong University, Xi’an 710049, P.R. China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsaem.3c00855

Author Contributions
*T.W. and D.Y. contributed equally to this work.

Notes
The authors declare no competing financial interest.

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