# 示意图

**【锌电沉积-铜箔做基底】**

[1] 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 Letters, 5 (2020) 3012-3020.

Commercial Cu foams were adopted as prototype 3D substrates for Zn electrodeposition because Cu possesses high hydrogen overpotential, high redox potential (0.342 V vs SHE), and, above all, good affinity (zincophilicity) for Zn (Figure S1).23,27 【电沉积-原位光学显微镜】

**【示意图引出】**

[3] F. Xie, H. Li, X. Wang, X. Zhi, D. Chao, K. Davey, S.Z. Qiao, Mechanism for Zincophilic Sites on Zinc-Metal Anode Hosts in Aqueous Batteries, Advanced Energy Materials, 11 (2021).

Therefore, a full-picture of zinc deposition can be illustrated, as is shown in Figure 1d.[43,44] Initially, zinc atoms are adsorbed on the carbon substrate to form a single-atom site. Additional zinc atoms form zinc clusters around these zinc single-atom sites. These clusters expand to form a mesoporous zinc network with further zinc deposition. 【！！！锌初始沉积、成核步骤分析】

**【添加剂作用机理示意图-均匀沉积-对比样和添加剂-沉积-腐蚀-但增加产气-需要解决】**

[12] M.H. Lin, C.J. Huang, P.H. Cheng, J.H. Cheng, C.C. Wang, Revealing the effect of polyethylenimine on zinc metal anodes in alkaline electrolyte solution for zinc-air batteries: Mechanism studies of dendrite suppression and corrosion inhibition, Journal of Materials Chemistry A, 8 (2020) 20637-20649.

The schematics depicting the mechanism for these effects of PEI additive on zinc anodes during the zinc plating and zinc corrosion processes are shown in Fig. 10. 对比样In the process of zinc deposition, as shown in Fig. 10(a), in an additive-free electrolyte, the rapid and inhomogeneous diffusion–deposition behavior of zinc ions promotes the growth of fern-shaped zinc dendrites. 添加剂In contrast, the adsorption of PEI molecules in the process of zinc plating can efficiently buffer the diffusion of Zn2+ species and suppress the zinc electrodeposition kinetics, promoting a more uniform nucleation–growth of zinc to form a flat and dense zinc plating structure. However, an increased HER on the zinc anode within the PEI-containing electrolyte is found by in operando TXM and OM observation, which might result from the side reaction caused by the adsorbed PEI molecules on the zinc anode. In Fig. S6,† the variation in cathodic polarization curves of zinc anodes with PEI additive confirms the result of enhanced HER at the zinc anode from PEI additive; the current density of the HER increases with the PEI concentration in the cathodic scans. 因此，有必要开发一种策略来提高PEI添加剂在高浓度碱性电解质溶液中的稳定性Thus, there is a need to develop a strategy for improving the stability of PEI additive in highly concentrated alkaline electrolyte solution. 【添加剂作用机理示意图-抑制腐蚀】

**【添加剂作用机理示意图-抑制腐蚀】**

[12] M.H. Lin, C.J. Huang, P.H. Cheng, J.H. Cheng, C.C. Wang, Revealing the effect of polyethylenimine on zinc metal anodes in alkaline electrolyte solution for zinc-air batteries: Mechanism studies of dendrite suppression and corrosion inhibition, Journal of Materials Chemistry A, 8 (2020) 20637-20649.

锌电极在碱性电解质中易发生腐蚀On the other hand, as shown in Fig. 10(b), the metallic zinc anode is prone to electrochemical corrosion in concentrated alkaline solution when the batteries are in concentrated alkaline solution when the batteries are in storage,15,35 which would promote the passivation and damage of the electrode surface and result in performance decay.39,40 添加剂By adding PEI in alkaline electrolyte solution, the PEI molecules can adsorb on the zinc anode surface to form a protective layer in the initial oxidation process of zinc. The protection afforded by PEI adsorption can further avoid the direct attack of the alkaline electrolyte solution and thereby mitigate the serious self-corrosion damage of the zinc anode. Nevertheless, the adsorbed PEI layer on the electrode still allows the migration and diffusion of zinc ions during the anodic reaction process, thus maintaining the activity of anodic reaction to a certain extent.

Fig. 10 Schematics for the effects of PEI additive on the (a) zinc anode plating and (b) zinc anode corrosion processes.

【全电池性能】

**【示意图分析】**

[13] J. Zhao, H. Ren, Q. Liang, D. Yuan, S. Xi, C. Wu, W. Manalastas, Jr., J. Ma, W. Fang, Y. Zheng, C.F. Du, M. Srinivasan, Q. Yan, High-performance flexible quasi-solid-state zinc-ion batteries with layer-expanded vanadium oxide cathode and zinc/stainless steel mesh composite anode, Nano Energy, 62 (2019) 94-102.

Fig. 1 shows the typical morphological and structural characterizations of the anode and cathode materials. E-VO shows 3D porous architecture, which consists of the interconnected thin nanosheets with lateral size of several to tens of micrometers (Fig. 1a). Such large lateral size nanosheets easily form a monolithic structure by interconnected with each other, favorable for high conductivity and binder-free electrode fabrication (inset in Fig. 1a and Fig. S1). 【TEM分析】

**【添加剂作用机理示意图-均匀沉积-对比样和添加剂-沉积-腐蚀-但增加产气-需要解决】**

参考修饰词[8] M.H. Lin, C.J. Huang, P.H. Cheng, J.H. Cheng, C.C. Wang, Revealing the effect of polyethylenimine on zinc metal anodes in alkaline electrolyte solution for zinc-air batteries: Mechanism studies of dendrite suppression and corrosion inhibition, J. Mater. Chem. A, 8 (2020) 20637-20649.

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【全电池性能】

# SEM分析

**【SEM和TEM分析】**

[4] H. Yan, S. Li, Y. Nan, S. Yang, B. Li, Ultrafast Zinc–Ion–Conductor Interface toward High-Rate and Stable Zinc Metal Batteries, Advanced Energy Materials, 11 (2021).

SEM image of the Zn-based MMT shows a prominent mica-like structure in Figure S2b, Supporting Information and every MMT flakiness containing numerous lamellae were observed by the bright field TEM image (Figure S2c, Supporting Information). 【！！！厚度分析、结构致密，保水作用】

**【！！！厚度分析、结构致密，保水作用】**

[4] H. Yan, S. Li, Y. Nan, S. Yang, B. Li, Ultrafast Zinc–Ion–Conductor Interface toward High-Rate and Stable Zinc Metal Batteries, Advanced Energy Materials, 11 (2021).

Atomic force microscope was used to determine the thickness of MMT flakiness. As shown in Figure S2f,g, Supporting Information, the thickness of MMT flakiness is about 75–125 nm. To protect Zn anode, a dense interlayer was prepared via a simple doctor blading method (preparation method refers to Supporting Information). As shown Figure 1f, the MMT interlayer with compact structure and without microcrack can densely bond to Zn foil substrate. This structure is beneficial to reduce or even isolate the water in electrolyte for Zn anode. 【！！！接触角证明MMT膜能减弱电解液与基底的接触、保水作用】

**【！！！电沉积过程分析】**

[9] L. Ma, Q. Li, Y. Ying, F. Ma, S. Chen, Y. Li, H. Huang, C. Zhi, Toward Practical High-Areal-Capacity Aqueous Zinc-Metal Batteries: Quantifying Hydrogen Evolution and a Solid-Ion Conductor for Stable Zinc Anodes, Advanced Materials, 33 (2021).

During electrochemical process, the Zn deposition only comes up at a place, where the Zn2+ meets charges. Therefore, the ZnF2 plays a role of regulating the transport of Zn2+ cations toward the electrode surface, without any Zn deposition on ZnF2 surface. The Zn2+ transport flux could be dominated by ZnF2 solid Zn2+-ion conductor during the electrodeposition. 【电荷转移电阻分析】

**【纳米片的优点】**

[13] J. Zhao, H. Ren, Q. Liang, D. Yuan, S. Xi, C. Wu, W. Manalastas, Jr., J. Ma, W. Fang, Y. Zheng, C.F. Du, M. Srinivasan, Q. Yan, High-performance flexible quasi-solid-state zinc-ion batteries with layer-expanded vanadium oxide cathode and zinc/stainless steel mesh composite anode, Nano Energy, 62 (2019) 94-102.

The thin and crumpled nanosheet structure can provide sufficient contact between the electrode material and electrolyte thereby the short ion transfer distance, which is beneficial to achieve high capacity and rate capability. 【TEM分析

**【电沉积用XRD-SEM表征】**

[1] 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 Letters, 5 (2020) 3012-3020.

As-prepared Zn anodes with 3D Cu skeletons (Figure S3) were characterized using XRD spectroscopy and SEM. 【不同电解质电沉积XRD-锌峰表明成功沉积】

**【不同电解质电沉积XRD-锌峰表明成功沉积】**

[1] 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 Letters, 5 (2020) 3012-3020.

Figure 2a illustrates the XRD patterns of Zn anodes prepared in different electrolytes. Except for obvious diffraction peaks from Cu (PDF no. 04-0836) substrates, characteristic peaks of Zn (PDF no. 04-0831) are observed in both Zn anodes, suggesting the successful loading of the Zn metal on the Cu foam. 【！电沉积XRD分析-两个区别-1-在TBA电解液中镀锌阳极表现出较普通电解液中较低的强锌衍射峰；2-固溶CuZn5 (PDF no. 5)的衍射峰在TBA电解液中镀锌阳极中表现更为明显】

**【！SEM图像证实了两种Zn阳极的形貌差异。在电镀过程中，树枝晶生长和增殖导致在正常电解质中形成严重的锌聚集(图2b,c)，而在TBA电解质中，铜泡沫均匀地被锌沉积层覆盖(图2d,e)。】**

[1] 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 Letters, 5 (2020) 3012-3020.

As shown in Figure 2b−e, SEM images confirm the morphology differences between two kinds of Zn anodes. The dendrite growth and the proliferation during plating result in the formation of severe Zn aggregation in the normal electrolyte (Figure 2b,c), whereas the Cu foam is homogeneously covered by a Zn deposit layer in the TBA electrolyte (Figure 2d,e). 【铜基底SEM】

**【铜基底SEM】**

[1] 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 Letters, 5 (2020) 3012-3020.

For comparison, SEM images of the net Cu foam are exhibited in Figure S4. 【mapping-进一步证明添加剂对电沉积的积极作用】

**【XRD、SEM、TEM分析】**

[4] H. Yan, S. Li, Y. Nan, S. Yang, B. Li, Ultrafast Zinc–Ion–Conductor Interface toward High-Rate and Stable Zinc Metal Batteries, Advanced Energy Materials, 11 (2021).

XRD pattern of the as-synthesized MnO2 demonstrate single-crystal β-MnO2 are obtained (JCPDS Card No. that 81-2261).[36] The SEM and TEM image of the prepared β-MnO2 (Figure S16, Supporting Information) exhibits a typical rod structure and uniform size of 1 µm. Similarly, the selected area electron diffraction image also proves that the synthesized MnO2 is single-crystal in nature. In a typical cell, MnO2 or MMT-MnO2 was u sed as a cathode, while bare Zn or MMT-Zn was employed as an anode. 【界面层抑制正极扩散】

**【XRD、SEM、TEM、EDS分析】**

[5] K. Leng, G. Li, J. Guo, X. Zhang, A. Wang, X. Liu, J. Luo, A Safe Polyzwitterionic Hydrogel Electrolyte for Long-Life Quasi-Solid State Zinc Metal Batteries, Advanced Functional Materials, 30 (2020).

The scanning electron microscope (SEM) images show that the micro-flower-like VS2 nanosheets grown uniformly on SS skeleton after 12 h reaction (Figure 4a,b). The crystal structure of VS2 grown on SS substrate is monitored by an X-ray diffraction spectroscopy (XRD; Figure S11, Supporting Information). Excluding SS peak from the substrate, all the characteristic peaks are consistent with the metallic 1T-VS2 with good conductivity. The XRD results show that the VS2 has good crystallinity and pure phase. The detailed structure of VS2 sample is further clarified by high resolution transmission electron microscopy (HRTEM). As shown in Figure 4c, the VS2 nanosheets present a lattice spacing of 0.58 nm, which is in good accordance with the (001) plane of VS2. The energy dispersive spectroscopy (EDS) mapping further reveals the uniform V and S element distribution in the VS2 nanosheets on the SS substrate (Figure 4d). The atomic ratio of S:V collected by EDS mapping is 16:9, which is

consistent with the stoichiometric ratio of VS2 (Figure S12, Supporting Information). 【CV分析电荷存储行为与电容和扩散关系】

**【TEM、SEM分析】**

[6] M. Liu, J. Cai, H. Ao, Z. Hou, Y. Zhu, Y. Qian, NaTi2(PO4)3 Solid-State Electrolyte Protection Layer on Zn Metal Anode for Superior Long-Life Aqueous Zinc-Ion Batteries, Advanced Functional Materials, 30 (2020).

To further identify the clear morphologies, the transmission electron microscope (TEM) and elemental mapping images of nano-NTP are given (Figures S8d and S9, Supporting Information) showing the morphology of ball-like architecture with different grain size (average grain size:100 nm) and 3D porous structure. The scanning electron microscope (SEM) image (Figure S10, Supporting Information) further intuitively shows the 3D porous structure of NTP. The unique high SSA and 3D porous structure of nanoNTP can increase the electrochemical active surface area of Zn anode and then decrease the local current density.[20]【CV分析电解液】

**【SEM分析】**

[8] J. Hao, B. Li, X. Li, X. Zeng, S. Zhang, F. Yang, S. Liu, D. Li, C. Wu, Z. Guo, An In-Depth Study of Zn Metal Surface Chemistry for Advanced Aqueous Zn-Ion Batteries, Advanced Materials, 32 (2020).

SEM images show by-product formation and corrosion on the Zn surface regardless of the presence of a passivation layer (Figure S8, Supporting Information), as further confirmed by the XRD patterns. 【XRD分析】

**【SEM分析】**

[8] J. Hao, B. Li, X. Li, X. Zeng, S. Zhang, F. Yang, S. Liu, D. Li, C. Wu, Z. Guo, An In-Depth Study of Zn Metal Surface Chemistry for Advanced Aqueous Zn-Ion Batteries, Advanced Materials, 32 (2020).

Remarkably, the surfaces of the ZnS@Zn-350 and ZnS@Zn-400 foils changed significantly due to the sulfur-vapor reaction. Unfortunately, the ZnS@Zn-400 foil also suffered from serious distortion due to the deformation of the Zn metal at the high temperature, indicating that the high temperature of 400 °C is unsuitable, too. SEM images show that the Zn surface was evenly covered by ZnS at 350 °C (Figure 3b). 【EDS分析】

**【锌电沉积SEM-表面和截面-不同浓度不同形状-】**

[12] M.H. Lin, C.J. Huang, P.H. Cheng, J.H. Cheng, C.C. Wang, Revealing the effect of polyethylenimine on zinc metal anodes in alkaline electrolyte solution for zinc-air batteries: Mechanism studies of dendrite suppression and corrosion inhibition, Journal of Materials Chemistry A, 8 (2020) 20637-20649.

The SEM images of zinc deposits formed at different PEI concentrations are shown in Fig. 2. Both the top-view and crosssectional images show that the morphology of zinc deposits changes with the PEI concentration. In the case of 0 ppm PEI, the typical dendritic zinc with a distinct fern-shaped morphology is formed at 1.8 V after 1800 s of plating (Fig. 2(a)). However, with a low concentration of PEI additive, the growth of zinc dendrites is suppressed significantly. At a low PEI concentration of 5 ppm, the formed zinc deposits show a porous rock-shaped morphology without the dendritic sharp tip structure and are unevenly distributed on the electrode surface (Fig. 2(b)). In the case of 10 ppm PEI, it shows that the zinc deposits are aggregates of spherical zinc crystals, exhibiting a morphology of randomly stacked spheres (Fig. 2(c)). As the PEI concentration increases to 30 ppm, although some spherical zinc deposits can still be found on the surface, the zinc deposits tend to form a dense film (Fig. 2(d)). As the PEI concentration reaches 50 ppm, the formed zinc film shows a smoother and denser surface morphology (Fig. 2(e)). 【！锌电沉积SEM总结-添加剂修饰锌沉积形貌-通过限制锌扩散动力学抑制枝晶】

# Tafel

**【tafel曲线分析抗腐蚀性能】**

[4] H. Yan, S. Li, Y. Nan, S. Yang, B. Li, Ultrafast Zinc–Ion–Conductor Interface toward High-Rate and Stable Zinc Metal Batteries, Advanced Energy Materials, 11 (2021).

The effect of MMT interlayer for the Zn electrode was quantitatively analyzed by potential polarization in electrolyte (Figure S11, Supporting Information). From the Tafel plots, with the Zn-based MMT layer protection, the self-corrosion potential of electrode increased to −0.743 V and the self-corrosion current reduced to almost an order (10−0.41 vs 100.72 µA cm−2). A larger positive corrosion potential indicates stronger corrosion resistance and a lower corrosion current dictates a lower corrosion rate.[10,13,29] 【开尔文扫描探针分析钝化现象】

**【tafel曲线分析】**

[6] M. Liu, J. Cai, H. Ao, Z. Hou, Y. Zhu, Y. Qian, NaTi2(PO4)3 Solid-State Electrolyte Protection Layer on Zn Metal Anode for Superior Long-Life Aqueous Zinc-Ion Batteries, Advanced Functional Materials, 30 (2020).

Tafel plot experiments in 2 m ZnSO4 + 0.2 m MnSO4 aqueous electrolyte (Figure S13, Supporting Information) show that the corrosion potential of NTP@Zn increases from −0.985 to −0.969 V, compared with the bare Zn. It is generally believed that a more positive corrosion potential indicates less tendency to corrode.

**【tafel曲线分析】**

[9] L. Ma, Q. Li, Y. Ying, F. Ma, S. Chen, Y. Li, H. Huang, C. Zhi, Toward Practical High-Areal-Capacity Aqueous Zinc-Metal Batteries: Quantifying Hydrogen Evolution and a Solid-Ion Conductor for Stable Zinc Anodes, Advanced Materials, 33 (2021).

The corresponding Tafel slope of 425.8 mV dec–1 for Zn@ZnF2 electrode is much higher than that of bare Zn electrode (87.5 mV dec–1), suggesting slow hydrogen evolution reaction kinetics after ZnF2 protection (Figure S15b, Supporting Information). 【！！锌腐蚀分析】

**【！！！保护层的作用】**

[9] L. Ma, Q. Li, Y. Ying, F. Ma, S. Chen, Y. Li, H. Huang, C. Zhi, Toward Practical High-Areal-Capacity Aqueous Zinc-Metal Batteries: Quantifying Hydrogen Evolution and a Solid-Ion Conductor for Stable Zinc Anodes, Advanced Materials, 33 (2021).

The electronically insulated ZnF2 layer can segregate active Zn metal from bulk liquid electrolyte and turn off charges transfer from Zn metal to H2O molecules of electrolyte, thus restraining chemical oxidation and electrochemical hydrogen evolution reaction on Zn@ZnF2 electrode. 【！！！原位光学分析】

**【！！！保护层的好处】**

[11] N. Zhang, S. Huang, Z. Yuan, J. Zhu, Z. Zhao, Z. Niu, Direct Self-Assembly of MXene on Zn Anodes for Dendrite-Free Aqueous Zinc-Ion Batteries, Angewandte Chemie - International Edition, 60 (2021) 2861-2865.

Recently, various strategies have been developed to

inhibit the growth of Zn dendrite, such as the modification of electrolyte,[5] anodes,[3, 6]

the construction of nanostructured Zn and the introduction of protective layers.[7]

Among these strategies, the introduction of protective layer is a promising candidate, where the artificial protective layer will be fabricated onto the Zn anodes to guide the uniform Zn deposition. In general, there are two main routes to construct the artificial protective layer, including ex situ coating and in situ growth.[8]

【！！！原位形成保护层的好处】

**【！！！原位形成保护层的好处】**

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Since the manual coating exists occasionality,

most coating layers produced by ex situ coating often suffer from local inhomogeneity. Therefore, the resultant coating layers would break and wear off during repeated Zn plating/ stripping or at high deposition capacity.[7b]

In contrast, the

in situ formation of interfacial layers is usually achieved by chemical or electrochemical strategies. The resultant interfacial layers will closely contact with Zn anodes, resulting in uniform surface and better stability due to the self-termination effect. Furthermore, such uniform conductive layers are able to uniformize the surface electric field and smooth the Zn deposition on anode surface.[8]

【引出制备方法】

**【！！！腐蚀、界面副反应测试XRD、SEM】**

[7] L. Zhang, B. Zhang, T. Zhang, T. Li, T. Shi, W. Li, T. Shen, X. Huang, J. Xu, X. Zhang, Z. Wang, Y. Hou, Eliminating Dendrites and Side Reactions via a Multifunctional ZnSe Protective Layer toward Advanced Aqueous Zn Metal Batteries, Advanced Functional Materials, (2021).

First, we evaluated the ability of the ZnSe protective layer to eliminate interfacial side reactions. As shown in Figure S15 in the Supporting Information, the Zn foil and Zn@ZnSe were immersed in electrolyte (2 m ZnSO4) for 10 days to detect chemical corrosion. The insets of Figure 4a,b clearly show that the surface of bare Zn changes from silver-gray to dark-gray after prolonged immersion, while the surface of Zn@ZnSe remains almost unchanged. The field-emission scanning electron microscopy (FESEM) images (Figure 4a,b) further show that a large number of loose flaky corrosion byproducts appear on the exposed Zn surface after immersion, which roughens the surface and affects Zn2+ deposition, while the surface of Zn@ZnSe still exhibits densely packed ZnSe nanoparticles without any trace of corrosion. The XRD patterns (Figure 4c) reveal that the loose byproducts on the Zn surface are Zn4SO4(OH)6·5H2O precipitates. The formation process of these byproducts involves the spontaneous release of H2 (HER), which increases the local OH− concentration in the electrolyte; this OH− then reacts with .[17] In con4Zn6OH SO 5HOZnSO(OH)·5H O 2

+− −

4 2

24 46 2

sulfate and H2O to form corrosion products. 【抗腐蚀性能测试】

**【抗腐蚀性能测试】**

[7] L. Zhang, B. Zhang, T. Zhang, T. Li, T. Shi, W. Li, T. Shen, X. Huang, J. Xu, X. Zhang, Z. Wang, Y. Hou, Eliminating Dendrites and Side Reactions via a Multifunctional ZnSe Protective Layer toward Advanced Aqueous Zn Metal Batteries, Advanced Functional Materials, (2021).

The equation is: ++ +↔

trast, there is no corrosion on the immersed Zn@ZnSe surface, and only characteristic peaks of Zn and ZnSe remain, which verifies the excellent corrosion resistance of the ZnSe protective layer. This result is further confirmed in the elemental mapping images of the bare Zn and Zn@ZnSe after immersion (Figure S16, Supporting Information). The linear polarization method can further quantify the corrosion resistance. Figure 4d shows that the corrosion current of Zn@ZnSe (1.69 mA cm−2) is far lower than the 3.81 mA cm−2 corrosion current of bare Zn, indicating a much lower corrosion rate of Zn@ZnSe in the mild aqueous electrolyte.[38] The above results strongly indicate that the ZnSe protective layer can effectively protect Zn from corrosion during storage, which is crucial for practical applications.

【产气分析和循环后性能分析】

# ICP

**【ICP分析】**

[7] Z. Hou, X. Zhang, X. Li, Y. Zhu, J. Liang, Y. Qian, Surfactant widens the electrochemical window of an aqueous electrolyte for better rechargeable aqueous sodium/zinc battery, J. Mater. Chem. A, 5 (2017) 730-738.

On the other hand, the ICP-AES results (Table S2†) show that the concentration of Mn in the electrolyte with added SDS after 2000 cycles was 0.03 mgmL1, which corresponded to 0.2 wt% of Mn in the Na2MnFe(CN)6 material. However, the concentration of Mn in the pristine electrolyte after 100 cycles was 10.0 mgmL1, which was almost 66.0 wt% of Mn in the Na2MnFe(CN)6 material. ICP-AES tests of the cell in the pristine electrolyte or the electrolyte with added SDS in the voltage range of 1.0–1.8 V were also carried out (as shown in Table S3†). After 200 cycles, the Mn concentration was measured. It was found that the concentration of Mn in the electrolyte with added SDS was 0.02 mgmL1, whereas in the pristine electrolyte, it was about 9.5 mgmL1. These results reveal that almost half of Mn was dissolved in the electrolyte after cycling, which thus resulted in a rapid fading of the capacity. The dissolution of the Prussian blue analogue cathode material was the dominant mechanism for the loss of capacity during the charge/discharge process.16 【添加剂作用】

# 保水作用

**【！！！层间含水率的优点】**

[13] J. Zhao, H. Ren, Q. Liang, D. Yuan, S. Xi, C. Wu, W. Manalastas, Jr., J. Ma, W. Fang, Y. Zheng, C.F. Du, M. Srinivasan, Q. Yan, High-performance flexible quasi-solid-state zinc-ion batteries with layer-expanded vanadium oxide cathode and zinc/stainless steel mesh composite anode, Nano Energy, 62 (2019) 94-102.

The higher interlayer water content is beneficial for enlarging the interlayer distance, inhibiting the effective charges of Zn2+ ions and stabilizing the structure, thus favors the larger capacity, higher rate capability, and longer cycling stability. 【XANES分析】

**【！！！保水作用分析】**

[5] K. Leng, G. Li, J. Guo, X. Zhang, A. Wang, X. Liu, J. Luo, A Safe Polyzwitterionic Hydrogel Electrolyte for Long-Life Quasi-Solid State Zinc Metal Batteries, Advanced Functional Materials, 30 (2020).

The interaction between the charged groups in PZHE and water molecules, the hydrogen bonds formed between the hydrophilic groups on the branches and the water molecules synergistically endow PZHE excellent water retention capabilities. At room temperature, the prepared PZHE can hold more than 92% of water in open system for 8 days. 【拉伸能力分析】

**【！！！保水能力与离子电导率】**

[5] K. Leng, G. Li, J. Guo, X. Zhang, A. Wang, X. Liu, J. Luo, A Safe Polyzwitterionic Hydrogel Electrolyte for Long-Life Quasi-Solid State Zinc Metal Batteries, Advanced Functional Materials, 30 (2020).

And both the water retention ability caused by the numerous hydrophilic groups and charged groups in PZHE and the ion transport channels formed with branches in the PSBMA greatly contributes to the high ionic conductivity.[38] 【！！！CV分析电化学窗口与锌的沉积溶解】

# EIS

**【EIS分析】**

[8] J. Hao, B. Li, X. Li, X. Zeng, S. Zhang, F. Yang, S. Liu, D. Li, C. Wu, Z. Guo, An In-Depth Study of Zn Metal Surface Chemistry for Advanced Aqueous Zn-Ion Batteries, Advanced Materials, 32 (2020).

Electrochemical impedance spectroscopy (EIS) measurements of Zn cells were conducted after different numbers of cycles (Figure S6, Supporting Information). 【副产物层分析】

**【锌电极电化学性能测试-阻抗-半圆弧大-表面吸附-抑制腐蚀】**

[12] M.H. Lin, C.J. Huang, P.H. Cheng, J.H. Cheng, C.C. Wang, Revealing the effect of polyethylenimine on zinc metal anodes in alkaline electrolyte solution for zinc-air batteries: Mechanism studies of dendrite suppression and corrosion inhibition, Journal of Materials Chemistry A, 8 (2020) 20637-20649.

Regarding the EIS analysis, Fig. 8(a) shows the Nyquist plots of zinc anodes in 6 MKOH solution with the addition of 0, 10, 30, and 50 ppm PEI at OCP. All plots show a depressed capacitive semicircular loop, which is related to the charge transfer in the corrosion process. 电容回路呈非完全半圆形，这可能与电极表面的粗糙度或不均匀性以及添加剂的吸附有关。The capacitive loops show a non-perfect semicircle which can be attributed to the roughness or inhomogeneity of the electrode surfaces and adsorption of additives.37,38 电容半圆环的直径随PEI浓度的增加而增大，表明由于PEI的吸附，锌阳极的耐蚀性得到了改善The diameter of the capacitive semicircular loop increases with the PEI concentration, indicating an improved corrosion resistance of zinc anodes due to the adsorption of PEI.35 【锌电极电化学性能测试-阻抗-拟合-欧姆阻抗基本相同-界面阻抗变大-腐蚀电阻】

**【锌电极电化学性能测试-阻抗-拟合-欧姆阻抗基本相同-界面阻抗变大-腐蚀电阻】**

[12] M.H. Lin, C.J. Huang, P.H. Cheng, J.H. Cheng, C.C. Wang, Revealing the effect of polyethylenimine on zinc metal anodes in alkaline electrolyte solution for zinc-air batteries: Mechanism studies of dendrite suppression and corrosion inhibition, Journal of Materials Chemistry A, 8 (2020) 20637-20649.

In Fig. S5,† the EIS plots of zinc anodes are fitted to reveal the resistance variation of zinc anodes at different PEI concentrations. The equivalent circuit model for fitting is shown in Fig. S5(a),† where RU represents the ohmic resistance containing the resistances of the current collector, electrolyte, electrode materials, etc., CPE represents the constant phase element, and Rct is the chargetransfer resistance. The fitting curves of EIS plots of zinc anodes for the cases of different PEI concentrations are shown in Fig. S5(b)†. The electrochemical impedance parameters of zinc anodes derived from EIS curve fitting are listed in Table S1.† As presented in Table S1,† the RU values of all the electrodes are almost the same, but Rct of zinc anodes significantly increases from 11.78 to 135.42 ohms with increasing PEI concentration, which indicates an increase of corrosion resistance. Meanwhile, the CPE value of zinc anodes is reduced with the increase of PEI concentration, which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer,37 suggesting that the PEI molecules function by adsorption at the electrode/electrolyte solution interface. 【锌电极电化学性能测试-阳极极化-锌溶解区-钝化区-正移】

**【EIS分析】**

[3] F. Xie, H. Li, X. Wang, X. Zhi, D. Chao, K. Davey, S.Z. Qiao, Mechanism for Zincophilic Sites on Zinc-Metal Anode Hosts in Aqueous Batteries, Advanced Energy Materials, 11 (2021).

In addition to these physicochemical characterizations, the electrochemical impedance spectroscopy (EIS) study (Figure S11, Supporting Information) revealed there is less difference in conductivity between these two carbon-based materials.[52] 【各种表征结合分析】

**【EIS分析离子电导率】**

[5] K. Leng, G. Li, J. Guo, X. Zhang, A. Wang, X. Liu, J. Luo, A Safe Polyzwitterionic Hydrogel Electrolyte for Long-Life Quasi-Solid State Zinc Metal Batteries, Advanced Functional Materials, 30 (2020).

Ionic conductivities of PZHE at different temperatures are confirmed by AC impedance spectroscopy. As shown in Figure 2a, the resistance of the gel electrolyte decreases with the increasing temperature, indicating that the ionic conductivity of PZHE increases with the rise of temperature (Figure S4, Supporting Information). The ionic conductivity of PZHE at 25 and 95 °C is calculated to be 32.0 and 83.5 mS cm−1, respectively. Compared with other gel electrolytes, the PZHE exhibits the highest ionic conductivity to the best of our knowledge (Table S1, Supporting Information). 【！！！保水能力与离子电导率】

**【CV、EIS分析】**

[6] M. Liu, J. Cai, H. Ao, Z. Hou, Y. Zhu, Y. Qian, NaTi2(PO4)3 Solid-State Electrolyte Protection Layer on Zn Metal Anode for Superior Long-Life Aqueous Zinc-Ion Batteries, Advanced Functional Materials, 30 (2020).

To test the performance of the NTP@Zn foil in AZIBs, full cells were fabricated and paired with CNT/MnO2 cathode. As shown in the CV curves in Figure 6a, NTP@Zn/MnO2 battery displayed distinct redox peaks. As is shown in Figure S21, Supporting Information, the surface film (electrode/electrolyte interface) resistance (Rs) of NTP@Zn/MnO2 cell is 4.9 Ω˛, which is much higher than that of 2.2 Ω˛ for bare Zn/MnO2 due to the low conductivity of NTP layer. On the other hand, the chargetransfer resistance (Rct) of NTP@Zn/MnO2 cell is 30 Ω˛, which is much lower than that of 260 Ω˛ for bare Zn/MnO2, since the surface of NTP@Zn show better wettability than that of bare Zn.[9] Figure 6b shows the typical charge/discharge curves of the assembled NTP@Zn/MnO2 battery between 0.8 and 1.85 V at a current rate of 5 C, displaying two flat discharge voltage profiles at 1.4 and 1.2 V. The 1st cycle was the process of low current activation. 【电化学性能分析】

**【锌电极电化学性能测试-阻抗-阳极极化】**

[12] M.H. Lin, C.J. Huang, P.H. Cheng, J.H. Cheng, C.C. Wang, Revealing the effect of polyethylenimine on zinc metal anodes in alkaline electrolyte solution for zinc-air batteries: Mechanism studies of dendrite suppression and corrosion inhibition, Journal of Materials Chemistry A, 8 (2020) 20637-20649.

Fig. 8 shows the electrochemical analysis of the effects of PEI additive on the anodic reaction of zinc anodes. 【锌电极电化学性能测试-阻抗-半圆弧大-表面吸附-抑制腐蚀】

**【初始态阻抗(R0)和稳态阻抗(Rss)分析】**

[4] H. Yan, S. Li, Y. Nan, S. Yang, B. Li, Ultrafast Zinc–Ion–Conductor Interface toward High-Rate and Stable Zinc Metal Batteries, Advanced Energy Materials, 11 (2021).

The initial-state impedances (R0) and steady-state impedances (Rss) of symmetric batteries are analyzed (Figure S4, Supporting Information) and calculated from Nyquist plot (Figure 2c,d.) Thus, the cation transference number of the MMT-Zn electrode was calculated to be 0.82, which was obviously higher than that of the Zn foil (0.22), illustrating the MMT interface serves as a near-single conducting Zn2+ SEI for AZIBs. 【负电荷和填充Zn2+的层状结构的优势分析】

# CV

**【！！！CV分析电化学窗口与锌的沉积溶解】**

[5] K. Leng, G. Li, J. Guo, X. Zhang, A. Wang, X. Liu, J. Luo, A Safe Polyzwitterionic Hydrogel Electrolyte for Long-Life Quasi-Solid State Zinc Metal Batteries, Advanced Functional Materials, 30 (2020).

In addition, cyclic voltammetry (CV) is employed to examine the reversible Zn deposition and dissolution in PZHE and the electrochemical window of PZHE is extended in the wide range of −0.2 to 2 V (Figure 2b). The water in PZHE would not decompose even at high voltage up to 2 V because the water molecules are locked in the PSBMA skeleton through the strong hydrogen bonding and electrostatic interaction. Particularly, for a Zn metal battery system, a high Zn ion transference number (tZn

2+) can ensure a uniform ion distribution at Zn anode interface, thereby achieving high power capacity ZMBs. To confirm the migration of Zn2+, tZn

2+ is calcu− after polymerization. 【离子输运数与PSBMA聚合物网络的空间位阻效应和带电基团对阴离子的静电固定作用】

**【CV分析电荷存储行为与电容和扩散关系】**

[5] K. Leng, G. Li, J. Guo, X. Zhang, A. Wang, X. Liu, J. Luo, A Safe Polyzwitterionic Hydrogel Electrolyte for Long-Life Quasi-Solid State Zinc Metal Batteries, Advanced Functional Materials, 30 (2020).

To analyze the kinetic parameters of the redox reaction of the

VS2 cathode material in PZHE, cyclic voltammetry is performed under various scan rates (Figure 4e). With the increasing scan rate, the oxidation peaks vibrate toward higher voltage and the reduction peaks vibrate toward lower voltage, indicating the increase of the polarization. Two pairs of redox peaks denoted as 1, 2, 3, and 4 are detected during the charge and discharge of the VS2 cathode electrode. The relationship between the peak current (i) and the scan rate (v) can be expressed in Equation (2)[41–43]

ia= vb (2)

where a and b are variables. The value of b varies between 0.5–1. When the value of b is 1, it indicates that the charge storage of the electrode material is controlled by surface capacitance. When the value of b is 0.5, it demonstrates that the charge storage of the electrode material is controlled by the surface diffusion of active ions. In VS2, the b values of the peaks 1–4 are 0.70, 0.63, 0.57, and 0.60, showing that the charge storage behavior is controlled by the cooperation of capacitance and diffusion (Figure 4f).【】 It is impressive that the rate performance and long-cycle performance of the full battery with VS2 cathode are excellent (Figure 4g,h). In addition to VS2, the manganese dioxide (MnO2) is also demonstrated to be a promising cathode material for aqueous ZMBs with high energy densities. The α-MnO2 composite acidified carbon nanotube (CNT) cathode electrode is obtained through a modified hydrothermal method. The conductivity of the α-MnO2 nanorods is elevated by the acidified CNT. XRD and HRTEM are adopted to analyze the structure of the synthesized positive electrode (MnO2@CNT). Excellent crystallinity of the MnO2@CNT was shown in XRD pattern with the diffraction peak of composite cathode well-indexed with the characteristic peak of α-MnO2 (JCPDS: 44–0141; Figure S13, Supporting Information). HRTEM images reveal that the CNTs are dispersed around MnO2, achieving the purpose of improving conductivity (Figure 5a,b; Figure S14, Supporting Information). 【CV分析】

**【CV分析】**

[5] K. Leng, G. Li, J. Guo, X. Zhang, A. Wang, X. Liu, J. Luo, A Safe Polyzwitterionic Hydrogel Electrolyte for Long-Life Quasi-Solid State Zinc Metal Batteries, Advanced Functional Materials, 30 (2020).

Typical electrochemical redox peaks in a voltage range of 0.8 to 1.8 V are observed for MnO2@CNT composite cathode in CV measurements (Figure S15, Supporting Information). Ultra-stable cycling performance is detected for ZMBs assembled with MnO2@CNT cathodes through the galvanostatic charge/discharge curves after different cycles (Figure 5c). 【电池高容量性能分析】

**【！！CV分析扩散动力学】**

[6] M. Liu, J. Cai, H. Ao, Z. Hou, Y. Zhu, Y. Qian, NaTi2(PO4)3 Solid-State Electrolyte Protection Layer on Zn Metal Anode for Superior Long-Life Aqueous Zinc-Ion Batteries, Advanced Functional Materials, 30 (2020).

CVs at various scan rates from 0.1 to 5 mV s−1 were employed to investigate the diffusion kinetics with respect to the zincion diffusion (Figure S5, Supporting Information). The linear relationship with the square root of the scan rates indicates a diffusion-limited process, and the highest slope of NTP@Zn/MnO2 battery represents the fastest zinc-ion diffusion rate, which is consistent with the beneficial zinc-ion diffusion property of NTP@Zn by theoretical calculation. Compared with NTP@Zn, TPO@Zn, and ZPO@Zn, the slope of bare Zn/MnO2 battery is smaller, which indicates the slow ions diffusion. Overall, all of these results clearly indicate that zinc ion has larger diffusion kinetics on the NTP interfacial protection layer.[14] 【XRD分析】

【XRD分析】

[6] M. Liu, J. Cai, H. Ao, Z. Hou, Y. Zhu, Y. Qian, NaTi2(PO4)3 Solid-State Electrolyte Protection Layer on Zn Metal Anode for Superior Long-Life Aqueous Zinc-Ion Batteries, Advanced Functional Materials, 30 (2020).

Meanwhile, to explore the specific process of the transport/mobility of Zn2+ in the NTP coating, NTP@Ti/Zn electrolytic tank cells at 0.05 mA cm−2 after different deposited capacity (Figure 2f) were disassembled for ex situ XRD measurements.【循环后XRD分析】

**【CV分析电解液】**

[6] M. Liu, J. Cai, H. Ao, Z. Hou, Y. Zhu, Y. Qian, NaTi2(PO4)3 Solid-State Electrolyte Protection Layer on Zn Metal Anode for Superior Long-Life Aqueous Zinc-Ion Batteries, Advanced Functional Materials, 30 (2020).

As illustrated in Figure S11, Supporting Information, the electrochemical redox reactions of NTP in 2 m ZnSO4 aqueous electrolyte is analyzed by CV measurement. There is no redox peak in the CV curve. It suggests that the electrochemical redox reactions of NTP layer will not happen as a protection layer. The SEM (Figure S8e,f, Supporting Information) shows the initial characteristic of NTP@Zn foil. 【润湿角测试】

**【全电池CV分析】**

[7] L. Zhang, B. Zhang, T. Zhang, T. Li, T. Shi, W. Li, T. Shen, X. Huang, J. Xu, X. Zhang, Z. Wang, Y. Hou, Eliminating Dendrites and Side Reactions via a Multifunctional ZnSe Protective Layer toward Advanced Aqueous Zn Metal Batteries, Advanced Functional Materials, (2021).

The effectiveness of the ZnSe protective layer was further verified in MnO2||Zn full cells. MnO2@carbon cloth (MnO2@CC) was synthesized by a hydrothermal method, and the mass loading of MnO2 was ≈1.0 mg cm−2. As displayed in Figure S11 in the Supporting Information, the XRD pattern coincides with α-MnO2 (JCPDS No. 44-0141). Figure 3a shows the cyclic voltammetry (CV) curves of the bare Zn||MnO2 and Zn@ZnSe||MnO2 full cells at 0.5 mV s−1 with a voltage range of 1.0–1.8 V. The distinct cathodic and anodic peaks stem from the reversible redox reactions between MnO2 and MnOOH.[35] Moreover, the voltage polarization of Zn@ZnSe||MnO2 is smaller than that of bare Zn||MnO2, implying improved reversibility due to the presence of the ZnSe protective layer.[24,36] This low polarization may be caused by the reduced Rct of Zn@ZnSe||MnO2 (Figure S12, Supporting Information).[27] Figure 3b presents the typical discharge/charge curves of Zn@ZnSe||MnO2 at 0.1C (1C = 308 mA g−2) in the first two cycles, in which the redox plateaus are consistent with those of the CV curves.

【长循环性能分析】

**【CV分析】**

[8] J. Hao, B. Li, X. Li, X. Zeng, S. Zhang, F. Yang, S. Liu, D. Li, C. Wu, Z. Guo, An In-Depth Study of Zn Metal Surface Chemistry for Advanced Aqueous Zn-Ion Batteries, Advanced Materials, 32 (2020).

The cyclic voltammetry (CV) curves of the MnO2/Zn and MnO2/ZnS@Zn-350 batteries are compared in Figure S28 (Supporting Information) and Figure 5d. Clearly, the MnO2/ZnS@Zn-350 battery shows smaller voltage polarization (≈20 mV) than that of the MnO2/Zn battery, indicating its good reversibility due to the ZnS protection. 【！！长循环性能分析】

**【CV分析库伦效率】**

[10] D. Yuan, J. Zhao, H. Ren, Y. Chen, R. Chua, E.T.J. Jie, Y. Cai, E. Edison, W. Manalastas, Jr., M.W. Wong, M. Srinivasan, Anion Texturing Towards Dendrite-Free Zn Anode for Aqueous Rechargeable Batteries, Angewandte Chemie - International Edition, 60 (2021) 7213-7219.

Thecorresponding chronocoulometry curves show that the CEs increase from 92.7%to 97.3% with Zn(OTf)2

within

the first five cycles (Figure 2g and h). On the contrary,the CEs decrease from 93.7%to92.2%with ZnSO4

(Figure S9). and Cu. Thestabilization of

Interestingly,the increasing trends of CEs with cycles are generally observed in the sulfonate-based electrolytes (Figure S9). Such atrend may be associated with the reshaped zinc coordination,[12] facial phenomena.[13f]

and further associated with the interTo verify the advantage of Zn(OTf)2

on

CE, asymmetric cells of Ti j Zn with constant capacity charging/discharging mode were investigated, showing its CE of 100%throughout the cycling, compared with the fluctuated CE between 93.2%and 100%for ZnSO4

(Figure 2i and S10). Thecharacteristics of CEs indicate the advantages of the sulfonate-based electrolytes in solvationdesolvation process,interfacial transport, and deposited texture with exposed surface.

【电化学性能分析】

**【CV分析】**

[11] N. Zhang, S. Huang, Z. Yuan, J. Zhu, Z. Zhao, Z. Niu, Direct Self-Assembly of MXene on Zn Anodes for Dendrite-Free Aqueous Zinc-Ion Batteries, Angewandte Chemie - International Edition, 60 (2021) 2861-2865.

The higher kinetics of MZn60 over pure Zn is also confirmed by cyclic voltammogram d) CV curves of Zn

than that (62 mV) of pure Zn (Supporting Information, Figure S11a). Furthermore, even at higher current densities, such obvious difference is still observed (Supporting Information, Figure S11b–e), indicating that the lower nucleation energy barrier and more uniform nucleation of Zn are achieved in MZn-60 due to the presence of negatively charged oxygen-containing groups on MXene layer and the tight contact between MXene layer and Zn foil.[3]

【！！！原位光学显微镜分析】

**【CV分析】**

[11] N. Zhang, S. Huang, Z. Yuan, J. Zhu, Z. Zhao, Z. Niu, Direct Self-Assembly of MXene on Zn Anodes for Dendrite-Free Aqueous Zinc-Ion Batteries, Angewandte Chemie - International Edition, 60 (2021) 2861-2865.

CV curves present typical and distinct redox peaks (Figure 5a), corresponding to the reverse conversion reactions between MnO2

and MnOOH,[15] effects of MXene layer on Zn2+

indicating the negligible penetration in Zn/MnO2

batteries. Furthermore, after the first cycle, the following CV curves display similar shapes (Supporting Information, Figure S15), revealing a reversible electrochemical process. 【循环性能分析】

**【CV分析】**

[13] J. Zhao, H. Ren, Q. Liang, D. Yuan, S. Xi, C. Wu, W. Manalastas, Jr., J. Ma, W. Fang, Y. Zheng, C.F. Du, M. Srinivasan, Q. Yan, High-performance flexible quasi-solid-state zinc-ion batteries with layer-expanded vanadium oxide cathode and zinc/stainless steel mesh composite anode, Nano Energy, 62 (2019) 94-102.

The cyclic voltammetry (CV) curves of E-VO electrode at different scan rates were carried out between 0.3 and 1.6 V. There are two distinct pairs of reduction/ oxidation peaks in each of the CV curve, suggesting the two Zn2+ intercalation/deintercalation processes. With the increase of scan rate, the shapes of CV curves are well maintained with a slight peak shift, indicating the structural stability of E-VO cathode (Fig. 2b). 【GCD和CV分析结合】

**【CV分析存储动力学】**

[13] J. Zhao, H. Ren, Q. Liang, D. Yuan, S. Xi, C. Wu, W. Manalastas, Jr., J. Ma, W. Fang, Y. Zheng, C.F. Du, M. Srinivasan, Q. Yan, High-performance flexible quasi-solid-state zinc-ion batteries with layer-expanded vanadium oxide cathode and zinc/stainless steel mesh composite anode, Nano Energy, 62 (2019) 94-102.

Based on the CV curves at various scan rates, the Zn2+ storage kinetics of the two electrodes were studied (Fig. S18). The ratio of capacitive to diffusion contribution to the total capacity can be quantified by separating the capacitive- and diffusion-controlled currents under a certain potential [58,59]. Fig. 4 exhibits the electrochemical kinetics analysis results of the electrodes of E-VO and V2O5 cathodes. For the E98

VO electrode, the capacitive contribution can reach 59% at a slow scan rate of 0.1 mV s−1, which increases with the increasing of scan rate. The higher fraction of capacitive contribution under higher scan rate is ascribed to the faster charging/discharging characteristic for the capacitive storage process than the diffusion controlled process. E-VO electrode exhibits the higher capacitive contributions than those of V2O5 electrode under all the measured scan rates, responsible for its higher rate capability than V2O5 (Fig. 4a). 【容量贡献分析】

**【锌沉积溶解CV-两电极-锌作工作电极，铜为参比电极】**

[1] 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 Letters, 5 (2020) 3012-3020.

The plating and stripping of Zn on a Cu foam in 2 M ZnSO4 electrolyte with different concentrations of TBA2SO4 were conducted in a two-electrode configuration with a fixed plating capacity of 10 mAh cm−2 at a current density of 10 mA cm−2. 【在第一循环中，所有测试的库仑效率均高达98%，说明锌在泡沫铜上的沉积具有良好的可逆性。】

# 长循环

**【！！！循环之前的性能表征】**

[2] C. Wang, G. Zhu, P. Liu, Q. Chen, Monolithic Nanoporous Zn Anode for Rechargeable Alkaline Batteries, ACS Nano, 14 (2020) 2404-2411.

Before engaging cycling experiments of the nanoporous Zn, we take advantage of its uniformity to investigate the structural evolution of a nanostructured Zn anode, a rarely studied but critical factor underlying the cycling stability. We carried out a series of ex situ microscopic characterizations to capture structural changes step by step in discharging and charging processes. 【电池实验条件叙述】

**【！！！不同放电深度孔结构仍能保持稳定】**

[2] C. Wang, G. Zhu, P. Liu, Q. Chen, Monolithic Nanoporous Zn Anode for Rechargeable Alkaline Batteries, ACS Nano, 14 (2020) 2404-2411.

The nanoporous Zn anode experienced significant structural changes but retained the uniform, percolating ligaments, as shown in Figure 2c−f. The ligaments became rougher when discharged to 20% DoD, and the roughness developed into a seemingly secondary porosity at 40% DoD, as a result of both Zn dissolution and ZnO formation. Highlighted in the inset of Figure 2d, the dissolution grows ZnO flowers alongside with pits in the ligaments. The pits and the flowers reside closely, but they can be told apart even at the end of discharging, which we believe is key to stabilizing the structure. 【结构稳定的进一步分析】

**【结构稳定的进一步分析】**

[2] C. Wang, G. Zhu, P. Liu, Q. Chen, Monolithic Nanoporous Zn Anode for Rechargeable Alkaline Batteries, ACS Nano, 14 (2020) 2404-2411.

If the two are far apart spatially, zincate sequestration and ZnO formation must be sluggish, and shape changes would eventually damage the structure. On the contrary, if the two overlap spatially, passivation would take place to prevent deep discharging. Upon recharging, the electrode was able to return to the nanoporous metal structure (Figure 2e). The metal network is upheld throughout the cycling, as also suggested by stable high-frequency impedance measured via electrochemical impedance spectroscopy (EIS, Figure S6a). 【循环后表征分析】

**【循环后表征分析】**

[2] C. Wang, G. Zhu, P. Liu, Q. Chen, Monolithic Nanoporous Zn Anode for Rechargeable Alkaline Batteries, ACS Nano, 14 (2020) 2404-2411.

Through 10 repetitive cycles, the Zn anode remained nanoporous (Figure 2f), but the length scale (i.e. the widths of ligaments and pores) increased. The increase was rapid in the first few cycles, but it then slowed down, apparent from Figure 3a, showing a plot of the ligament width l versus the total time t spent in the cell (statistics of the ligament widths can be found in Figure S4). In the same plot, we show that nanoporous Zn kept in argon (blue dots) and a ZnO-saturated KOH electrolyte (green dots) for a similar period showed much smaller changes. If replotted at a logarithmic scale, the curve of ln(l) and ln(t) shows a slope of∼0.297. This value is close to a quarter and even closer to the scaling exponent estimated from the isothermal coarsening of nanoporous metals,29 suggesting surface-diffusion-controlled coarsening. The length scale change can thus be mathematically described as follows:30 where l0 is the initial ligament width, γ the surface energy, a the lattice constant, Ds

the surface diffusivity, k the Boltzmann

constant, and T the experimental temperature.

**【！！！电解液量控制严格，电极不含任何添加剂：测试更符合实际】**

[2] C. Wang, G. Zhu, P. Liu, Q. Chen, Monolithic Nanoporous Zn Anode for Rechargeable Alkaline Batteries, ACS Nano, 14 (2020) 2404-2411.

The battery was assembled similarly to that in Figure 2a, but with tighter control over the electrolyte volume, whose zincate contributes less than 10% of the overall Zn mass to the cell. This control is to make the test more practically relevant, as advocated by many previous studies.22,36 We did not include any additives in the electrode or the electrolyte, so that the test may reflect the genuine performance of the nanoporous Zn. For comparison, we made an anode from Zn powder (∼150 μm in diameter) and tested it under a similar condition. The cells were discharged to 40% DoD (or a voltage cutoff of 1.35 V) at 25 mA/cm2 and fully charged (or to 1.9 V) at 5 mA/cm2, with no voltage hold or conditioning cycles.

【极化测试对比分析】

**【纳米多孔锌性能优异的原因】**

[2] C. Wang, G. Zhu, P. Liu, Q. Chen, Monolithic Nanoporous Zn Anode for Rechargeable Alkaline Batteries, ACS Nano, 14 (2020) 2404-2411.

The first is the high and stable conductivity of the nanoporous Zn, and the second is its high specific area that offers more sites for charge transfer. The discharging current peaks at ∼100 mA/ cm2 for the nanoporous Zn, which is likely a result of both mass transport limits and passivation. 【！！！电池循环性能分析：天数、理论DOD】

**【！！！电池循环性能分析：天数、理论DOD】**

[2] C. Wang, G. Zhu, P. Liu, Q. Chen, Monolithic Nanoporous Zn Anode for Rechargeable Alkaline Batteries, ACS Nano, 14 (2020) 2404-2411.

Nevertheless, it delivers a peak power over 150 mW/cm2, 4 times higher than that from the Zn powder anode. Figure 4b plots the discharging capacities against the

number of cycles, showing the stable performance of the nanoporous Zn anode. During the 12 day test, the anode consistently delivered a capacity ∼328 mAh/g, 40% of the theoretical value. The corresponding areal capacity is 5.7 mAh/ cm2. The Coulombic efficiency is, on average, 98.8%, much higher than that of a typical Ni−Zn battery,15

as the

conductive anode and the oversized cathode helped suppress hydrogen and oxygen evolutions, respectively. 【能量效率不到100%的分析】

**【对比粉末电极40%DOD很快失效：枝晶导致的】**

[2] C. Wang, G. Zhu, P. Liu, Q. Chen, Monolithic Nanoporous Zn Anode for Rechargeable Alkaline Batteries, ACS Nano, 14 (2020) 2404-2411.

In comparison, the Zn powder electrode could not even reach 40% DoD due to severe polarization in discharging, and its Coulombic efficiency quickly decreased as it reached the 25th cycle, where we suspect that dendrites killed the cell. 【假设负极和负极的重量约占电池重量的39%，电池能量密度高】

**【！！！人工界面保护层，电导率、Zn亲和力和Zn2+迁移对枝晶的形成和生长都至关重要】**

[7] L. Zhang, B. Zhang, T. Zhang, T. Li, T. Shi, W. Li, T. Shen, X. Huang, J. Xu, X. Zhang, Z. Wang, Y. Hou, Eliminating Dendrites and Side Reactions via a Multifunctional ZnSe Protective Layer toward Advanced Aqueous Zn Metal Batteries, Advanced Functional Materials, (2021).

For an artificial interfacial protective layer, the electrical conductivity, Zn affinity and Zn2+ migration are all critical to dendrite formation and growth. 【！！！dft计算分析和细节阐述】

**【锌阳极失效原因】**

[7] L. Zhang, B. Zhang, T. Zhang, T. Li, T. Shi, W. Li, T. Shen, X. Huang, J. Xu, X. Zhang, Z. Wang, Y. Hou, Eliminating Dendrites and Side Reactions via a Multifunctional ZnSe Protective Layer toward Advanced Aqueous Zn Metal Batteries, Advanced Functional Materials, (2021).

This behavior clearly demonstrates an irreversible hard short- circuit phenomenon, suggesting a complete short circuit and the failure of the battery due to the accumulation of dendrites.[41] Thus, under such severe conditions, uncontrollable Zn dendrite growth causes rapid failure of the unprotected Zn anode. Conversely, the Zn@ZnSe cell can stabilize for more than 160 h under these harsh conditions, with an average polarization voltage of only ≈50 mV. Such excellent electrochemical stability exceeds that of most work that has been reported so far (Table S1, Supporting Information) and strongly demonstrates the effectiveness of the ZnSe protective layer in regulating Zn2+ deposition and inhibiting dendrite growth.

2.6. Revealing the Mechanism of Dendrite Inhibition

【！！！人工界面保护层，电导率、Zn亲和力和Zn2+迁移对枝晶的形成和生长都至关重要】

**【！！！抑制枝晶生长的机理分析】**

[7] L. Zhang, B. Zhang, T. Zhang, T. Li, T. Shi, W. Li, T. Shen, X. Huang, J. Xu, X. Zhang, Z. Wang, Y. Hou, Eliminating Dendrites and Side Reactions via a Multifunctional ZnSe Protective Layer toward Advanced Aqueous Zn Metal Batteries, Advanced Functional Materials, (2021).

According to the above analyses, the success of this strategy in regard to dendrite inhibition can be attributed to the following key factors. First, the low Zn affinity of ZnSe leads to an increase in the concentration of Zn2+ at the electrolyte–ZnSe interface, thus promoting a uniform Zn2+ flux. Second, the unbalanced charge distribution on the ZnSe–Zn interface accelerates the migration of Zn ions so that they can be quickly deposited on the Zn metal surface before uniformly nucleating and growing. Finally, the ZnSe protective layer can eliminate interfacial side reactions, including corrosion and H2 evolution, to protect the uniform and undisturbed deposition of Zn2+. Based on these advantages, the ZnSe protective layer can perfectly inhibit the growth of Zn dendrites, thus providing a large improvement in electrochemical performance.

3. Conclusions

【保护层分析结论概括】

**【保护层分析结论概括】**

[7] L. Zhang, B. Zhang, T. Zhang, T. Li, T. Shi, W. Li, T. Shen, X. Huang, J. Xu, X. Zhang, Z. Wang, Y. Hou, Eliminating Dendrites and Side Reactions via a Multifunctional ZnSe Protective Layer toward Advanced Aqueous Zn Metal Batteries, Advanced Functional Materials, (2021).

We demonstrated that the ZnSe layer in situ on a bare Zn surface was an efficient protective layer in AZMBs. The Zn@ZnSe symmetric cell achieved high rate performance and a long lifespan (1500 h, 10 mA cm−2 with 1 mAh cm−2). Even with a large areal capacity (10 mA cm−2, 5 mAh cm−2), it still exhibited excellent electrochemical stability with a low polarization voltage. When further applied in full cells, Zn@ZnSe||MnO2 maintained a high CE near 100% even after 1800 cycles, showing potential for practical application. Based on systematic DFT calculations and various experiments, we demonstrated that the ZnSe protective layer could synchronously achieve anticorrosion and the inhibition of H2 evolution during the whole lifecycle, effectively eliminating the impact of side reactions. More importantly, the low Zn affinity of ZnSe and unbalanced charge distribution between the ZnSe–Se interfaces were two key factors that promoted the increase and uniform distribution of Zn2+ and subsequently accelerated migration and deposition, thereby solving dendrite formation issues. We believe that this strategy for eliminating dendrites and side reactions at a high rate with a large capacity provides a new perspective for the further development of AZMBs.

**【！！！优异离子导电性的作用】**

[8] J. Hao, B. Li, X. Li, X. Zeng, S. Zhang, F. Yang, S. Liu, D. Li, C. Wu, Z. Guo, An In-Depth Study of Zn Metal Surface Chemistry for Advanced Aqueous Zn-Ion Batteries, Advanced Materials, 32 (2020).

The high resistance introduced by the insulating ZnS layer is critical for establishing the necessary potential gradient across the artificial film to drive Zn2+ diffusion through the layer.[24] In addition, the ZnS film features good ionic conductivity (evaluated as ≈1.3 × 10−5 S cm−1, Figure S20, Supporting Information), which facilitates Zn2+ diffusion through this protective anions tend to migrate in the opposite direction from Zn2+ and eventually accumulate at the electrode surface, resulting in a build-up of the concentration gradient. This concentration gradient not only limits the rate at which the battery may be charged or discharged, but also creates a concentration overpotential that limits the operating voltage of the battery, thus limiting the power and energy density of the battery.[25] Notably, Zn2

t + can be dramatically improved to ≈0.78 after introducing the

ZnS layer (Figure S21b, Supporting Information), suggesting that the anions were effectively retarded by this protective layer. 【对称电池测试、原位检测】

**【！！！电化学性能评价电解液】**

[10] D. Yuan, J. Zhao, H. Ren, Y. Chen, R. Chua, E.T.J. Jie, Y. Cai, E. Edison, W. Manalastas, Jr., M.W. Wong, M. Srinivasan, Anion Texturing Towards Dendrite-Free Zn Anode for Aqueous Rechargeable Batteries, Angewandte Chemie - International Edition, 60 (2021) 7213-7219.

Constructing ahighly stable metallic zinc anode requires

exploring the interaction of textured zinc surface in electrolyte.The above-rationalized study indicates the co-functioning of Zn (002) texture as the planar template for further zinc plating and the sulfonate electrolyte as the coordinating agent during plating. It further points out the significance of selection on zinc texture and electrolyte in developing highperformance ZIBs.Founded on the above,weevaluated the performance of the V2

paper as anode and Zn(OTf)2 static charge-discharge (GCD) curves of the V2

O5/Zn full cell by using the (002) zinc as electrolyte.The galvanoO5/Zn cell

exhibit profiles with two sloping discharge/charge regions at 0.6 and 1.0 V(Figure 4a), corresponding to the Zn2+ intercalation/deintercalation processes as established previ ously. [22] At 0.1 A g@1 , a high capacity of 407 mAhg@1 can be delivered. Using the (002) zinc paper, the cellshows a capacity retention of & 168 mAhg@1 (41.3%) at 2 Ag@1 . Also, a stable capacity retention of & 381 mAhg@1 (93.6%) can be achieved when the current was set back to 0.2 A g@1 after rate cycles (Figure 4 b). The cycling stability of the V2O5 /Zn cell with the (002) zinc paper was evaluated. After 2000 cycles at 1 Ag@1, the cell can maintain 64.1% of its maximum capacity with a CE of & 100%, showing its good cycling stability (Fig ure 4 c). In sharp contrast, when the (101) paper was tested for cycling, a sudden drop in capacity was detected only after around 250 cycles accompanied with the fluctuated CEs (Figure S18), which could be attributed to the dendrite induced high corrosion rate. [6a] This demonstrates the supe riority of possessing the Zn (002) texture in aqueous ZIBs.

Conclusion

【电解液诱导晶面取向，结论概括】

**【！！！正负电荷的相互作用】**

[11] N. Zhang, S. Huang, Z. Yuan, J. Zhu, Z. Zhao, Z. Niu, Direct Self-Assembly of MXene on Zn Anodes for Dendrite-Free Aqueous Zinc-Ion Batteries, Angewandte Chemie - International Edition, 60 (2021) 2861-2865.

Simultaneously, a charge interaction is generated between the resultant Zn2+

and the negatively charged

oxygen-containing groups on MXene sheets at the interface, achieving the reduction of the MXene sheets. The removement of negatively charged groups weakens the electrostatic repulsion interaction between the MXene sheets.[10]

【！！自组装过程分析】

**【！！自组装过程分析】**

[11] N. Zhang, S. Huang, Z. Yuan, J. Zhu, Z. Zhao, Z. Niu, Direct Self-Assembly of MXene on Zn Anodes for Dendrite-Free Aqueous Zinc-Ion Batteries, Angewandte Chemie - International Edition, 60 (2021) 2861-2865.

When the

static repulsion between the MXene sheets is less than their bonding interaction, the MXene sheets would be layer-bylayer self-assembled on the surface of Zn foil. After drying, the layered MXene layer is uniformly anchored on the surface of Zn foil (Figure 2a–c). Furthermore, there is a tight contact between Zn foil and MXene layer (Supporting Information, Figure S1), which ensures the interface stability to buffer volume changes of anode during the Zn plating/stripping process. A galvanic cell also suggests that the redox reaction between Ti3

(Supporting Information, Figure S2). Furthermore, the conversion of Ti3

C2Tx to Ti3 C2Txy during assembling can be

reflected by X-ray photoelectron spectroscopy (XPS; Figure 2e). The Ti3

C2Txy film displays a higher Ti/O and C/O

ratios, demonstrating the removal of some oxygen-containing groups during assembly process.[11]

【XPS分析】

**【！！！电荷再分布效应和电子导电性使Zn表面的表面电场均匀化】**

[11] N. Zhang, S. Huang, Z. Yuan, J. Zhu, Z. Zhao, Z. Niu, Direct Self-Assembly of MXene on Zn Anodes for Dendrite-Free Aqueous Zinc-Ion Batteries, Angewandte Chemie - International Edition, 60 (2021) 2861-2865.

The charge redistribution effect and the electronic conductivity of MXene layer uniformize the surface electric field on the Zn surface (Figure 4c and g).[8, 13d]

electric field ensures homogeneous Zn2+

The uniformly distributed deposition on the

surface of Zn, thereby obtaining a flat and smooth surface (Figure 1b, 4d; Supporting Information, Figure S13a). In contrast, the electric field distribution on the surface of pure Zn displays an obvious intensity gradient during Zn plating process (Figure 4e and h). Such enhanced local electric field forms a higher charge region, promoting more Zn2+

deposition nucleation. 【尖端效应的影响】

**【尖端效应的影响】**

[11] N. Zhang, S. Huang, Z. Yuan, J. Zhu, Z. Zhao, Z. Niu, Direct Self-Assembly of MXene on Zn Anodes for Dendrite-Free Aqueous Zinc-Ion Batteries, Angewandte Chemie - International Edition, 60 (2021) 2861-2865.

Owing to the tip effect, these small protuberances gradually evolve into the large and sharp dendrite flakes (Figure 1c, 4 f; Supporting Information, Figure S13b), ultimately leading to the cell failure. These results indicate that the MXene layer really achieves the aim of regulating uniform Zn nucleation and growth. To illustrate the practical application of MZn anodes, we

assembled full cells using MZn-60 as anode and conventional MnO2

as cathode (Supporting Information, Figure S14). Its

【CV分析】

**【循环性能分析】**

[11] N. Zhang, S. Huang, Z. Yuan, J. Zhu, Z. Zhao, Z. Niu, Direct Self-Assembly of MXene on Zn Anodes for Dendrite-Free Aqueous Zinc-Ion Batteries, Angewandte Chemie - International Edition, 60 (2021) 2861-2865.

Moreover, the MZn-60/MnO2

current intensity than the case of the Zn/MnO2

battery displays a higher battery. It

agrees well with the GCD curves (Figure 5b). Even at a high current density of 3 Ag1 maintain 145.7 mAhg1

Figure S16). Furthermore, when the current density returns back to 0.2 Ag1

capacity returns to 281.2 mAhg1

after 40 cycles, the specific discharge . Such excellent rate performance is ascribed to the smaller charge transfer resistance due to the coating of MXene layer (Figure 5d). Besides enhanced rate performance, the MZn-60/MnO2

battery also possesses

long-term cycling stability due to the inhibition of Zn dendrite and side reactions during cycling (Figure 5e; Supporting Information, Figures S17 and S18). Therefore, it delivers

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, its reversible capacity can still (Figure 5c; Supporting Information,

. However, the Zn/MnO2 after 500 cycles.

) and still stabilizes at

after 500 cycles with a retention rate of 81% at battery sharply drops to

【保护层优异性分析，结论概括】

**【！！水凝胶优点】**

[13] J. Zhao, H. Ren, Q. Liang, D. Yuan, S. Xi, C. Wu, W. Manalastas, Jr., J. Ma, W. Fang, Y. Zheng, C.F. Du, M. Srinivasan, Q. Yan, High-performance flexible quasi-solid-state zinc-ion batteries with layer-expanded vanadium oxide cathode and zinc/stainless steel mesh composite anode, Nano Energy, 62 (2019) 94-102.

Energy storage device with flexible nature has attracted increasing

attention in recent years. Aqueous gel electrolyte is considered as a good candidate to replace liquid electrolyte because of the good mechanical properties and relatively safer properties [11,42,62]. 【！！！柔性电池循环性能和器件分析】

**【！！！柔性电池循环性能和器件分析】**

[13] J. Zhao, H. Ren, Q. Liang, D. Yuan, S. Xi, C. Wu, W. Manalastas, Jr., J. Ma, W. Fang, Y. Zheng, C.F. Du, M. Srinivasan, Q. Yan, High-performance flexible quasi-solid-state zinc-ion batteries with layer-expanded vanadium oxide cathode and zinc/stainless steel mesh composite anode, Nano Energy, 62 (2019) 94-102.

Fig. 5 presents the configuration and electrochemical performances of flexible quasi-solid-state Zn/E-VO battery. The flexible Zn/E-VO batteries were assembled by sandwiching quasi-solid-state gelation/Zn(CF3SO3)2 electrolyte between the E-VO cathode and Zn/SS mesh anode (Fig. 5a). As can be seen from Fig. 1b, both the anode and cathode show quite good flexibility. At the current density of 0.1 A g−1, E-VO electrode delivers a capacity of 361 mAh g−1. When the current density increases to 2 A g−1, the capacity still maintains at 115 mAh g−1 (32% of the capacity under 0.1 A g−1), suggesting the good rate capability (Fig. 5c). Such a performance is even comparable to some reported aqueous ZIBs (Table S1) even though the ionic conductivity of gel electrolyte is lower. The DCD curves of the bending and recovering states almost overlap with the initial flat state, indicating the robust performance under deformation (Fig. 5d). At the current density of 1 A g−1, a stable discharge capacity of 183 mAh g−1 is obtained with a capacity retention of 85% after 300 cycles, attesting the excellent cycling stability (Fig. 5e). 【器件展示】

# 能量密度

**【能量效率不到100%的分析】**

[2] C. Wang, G. Zhu, P. Liu, Q. Chen, Monolithic Nanoporous Zn Anode for Rechargeable Alkaline Batteries, ACS Nano, 14 (2020) 2404-2411.

The high specific area of the nanoporous Zn did not seem to provoke severe hydrogen evolution, although in a practical cell where the cathode limits capacity, we may need additives to further

improve the Coulombic efficiency. The energy efficiency was ∼87.6%; the loss likely came from the ionic resistances through two separators and the thick electrodes (Figure S6b). 【对比粉末电极40%DOD很快失效：枝晶导致的】

**【假设负极和负极的重量约占电池重量的39%，电池能量密度高】**

[2] C. Wang, G. Zhu, P. Liu, Q. Chen, Monolithic Nanoporous Zn Anode for Rechargeable Alkaline Batteries, ACS Nano, 14 (2020) 2404-2411.

The capacity delivered by the nanoporous anode can translate roughly to an energy density of 110 Wh/kg in a practical Ni− Zn battery if we assume that a capacity-limiting cathode and the Zn anode make up ∼39% of the weight.20 This performance stands out, particularly among Zn anodes discharged to a high DoD (Table S1). The structural stability is corroborated by post mortem microscopic characterization. 【循环后SEM分析：孔结构完整，但孔径变大】

**【！！！200圈深度循环很有应用意义】**

[2] C. Wang, G. Zhu, P. Liu, Q. Chen, Monolithic Nanoporous Zn Anode for Rechargeable Alkaline Batteries, ACS Nano, 14 (2020) 2404-2411.

Nonetheless, the Zn network in the electrode overcomes 200 deep cycles, which promises highly rechargeable Zn batteries to be fulfilled by future engineering.

CONCLUSIONS

【制备方法的优点概括】

**【！！！锌初始沉积、成核步骤分析】**

[3] F. Xie, H. Li, X. Wang, X. Zhi, D. Chao, K. Davey, S.Z. Qiao, Mechanism for Zincophilic Sites on Zinc-Metal Anode Hosts in Aqueous Batteries, Advanced Energy Materials, 11 (2021).

We propose therefore zinc deposition is induced by initial nucleation sites in the distribution of initial nuclei that impact electrochemical performance.[36,37,41,45,46] Because the distribution of initial nuclei lies in initial nucleation sites, the introduction of zincophilic sites as initial nucleation sites is critical in adjusting the absorbing/bonding ability of hosts.[29,34] 【DFT分析亲锌性】

**【！！！亲锌位点工作机制分析】**

[3] F. Xie, H. Li, X. Wang, X. Zhi, D. Chao, K. Davey, S.Z. Qiao, Mechanism for Zincophilic Sites on Zinc-Metal Anode Hosts in Aqueous Batteries, Advanced Energy Materials, 11 (2021).

Based on these findings, a working mechanism of zincophilic sites is proposed and is illustrated in Figure 3f. Initially, zincophilic sites bond with Zn ions. The pyridine-nitrogen sites form Zn-N bonds with Zn ions. Because of a wide distribution of zincophilic sites, the distribution of Zn nuclei is spacious. Due to these spacious nuclei, the growth of Zn leads to connections nearby to promote Zn clusters that cover the carbon surface, resulting in homogenous deposition of Zn. 【！！！没有亲锌位点导致枝晶的原因】

**【！！！没有亲锌位点导致枝晶的原因】**

[3] F. Xie, H. Li, X. Wang, X. Zhi, D. Chao, K. Davey, S.Z. Qiao, Mechanism for Zincophilic Sites on Zinc-Metal Anode Hosts in Aqueous Batteries, Advanced Energy Materials, 11 (2021).

For a host without zincophilic sites, Zn deposition is as proposed in Figure 3g. Because of the absence of zincophilic sites, the formation of initial nuclei is dense. The dense nuclei give rise to a dense distribution of nucleation sites that triggers the preferential deposition of Zn at tip-spots (nucleation sites).[32] 【！！！有无亲锌位点的原理分析】

**【！！！有无亲锌位点的原理分析】**

[3] F. Xie, H. Li, X. Wang, X. Zhi, D. Chao, K. Davey, S.Z. Qiao, Mechanism for Zincophilic Sites on Zinc-Metal Anode Hosts in Aqueous Batteries, Advanced Energy Materials, 11 (2021).

The result is a non-uniform Zn deposition morphology together with

dendritic zinc. It is concluded, therefore, that the mechanism of zincophilic sites is the formation of bonds between zinc-ion and zincophilic sites. These bonds induce homogenous deposition of Zn and suppresses zinc-dendrite formation. To determine the impact of introducing nitrogen zincophilic sites on electrochemical performance, zinc-metal anode tests were conducted. 【电化学循环分析】

**【电化学循环分析】**

[3] F. Xie, H. Li, X. Wang, X. Zhi, D. Chao, K. Davey, S.Z. Qiao, Mechanism for Zincophilic Sites on Zinc-Metal Anode Hosts in Aqueous Batteries, Advanced Energy Materials, 11 (2021).

The plating and stripping performance of two samples, i.e., C HS and CnC HS, in 100 µL 3.0 m Zn(CF3SO3)2 aqueous electrolyte were investigated using coin-cells with a fixed current density of 4 mA cm−2 and a capacity of 1 mAh cm−2. As is shown in Figure 4a the C HS exhibited a lower average Coulombic efficiency (CE) of ≈93%. The CE of the C HS degraded after 38 cycles, leading to a rapid battery failure. In contrast, the CnC HS with nitrogen-doping exhibited a more stable average CE of ≈95% over 200 cycles. In addition to the coulombic efficiency, the high reversibility of CnC HS as a zinc-metal-anode host is demonstrated by the cyclic voltammetry (CV) as is shown in Figure S17 in the Supporting Information. Further, C HS exhibited an initial coulombic efficiency of 77% while CnC HS exhibited a significantly greater initial coulombic efficiency of 85%. 【氮掺杂增强循环稳定性，分析初始库伦效率低的原因】

**【！！！负电荷吸引锌离子沉积分析】**

[4] H. Yan, S. Li, Y. Nan, S. Yang, B. Li, Ultrafast Zinc–Ion–Conductor Interface toward High-Rate and Stable Zinc Metal Batteries, Advanced Energy Materials, 11 (2021).

Moreover, the phyllosilicate lamella is composed of two layers of silica tetrahedron sandwiched on a layer alumina octahedral,[16a,17] where some Al3+ is substituted by Mg2+, resulting in negative-charged lamella interfaces, as proved by zeta potential of MMT (Figure 1e).[16b,18] Such negatively charged lamella surface ensure a higher concentration of Zn2+ in the surface of anode, enables sufficient zinc ion supplying even in high current density.[16a,19]

2) forms ion-insulating passivation layer, preventing the continuing interconversion of Zn2+ and Zn0, and thus limited the battery rechargeability;[21] 【表面改性作用分析】

**【表面改性作用分析】**

[4] H. Yan, S. Li, Y. Nan, S. Yang, B. Li, Ultrafast Zinc–Ion–Conductor Interface toward High-Rate and Stable Zinc Metal Batteries, Advanced Energy Materials, 11 (2021).

iii) uncontrollable zinc deposition of hexagonal zinc flake (even notorious dendrites growth) causes internal short circuit of battery, leading to rapid battery failure.[22,23] From the perspective of preventing these certainties disadvantages, the as-prepared dense Zn-based MMT interlayer could not only block corrosive aqueous electrolyte, but also serves as pathway for zinc ion transport. 【制备方法的引入】

**【！！！锌离子的逃逸功能】**

[4] H. Yan, S. Li, Y. Nan, S. Yang, B. Li, Ultrafast Zinc–Ion–Conductor Interface toward High-Rate and Stable Zinc Metal Batteries, Advanced Energy Materials, 11 (2021).

As a comparison, the Volta potential of bare Zn, fluctuated in a wide range, average value is 1732 mV (Figure 4f) indicating the non-uniform formatted of a thick passivation film, which significantly increased the escape work of the Zn substrate. Such results can be explained that the Zn-based MMT interlayer isolated the corrosive aqueous electrolyte,[32] maintained the active of Zn anode and alleviated passivation film on the electrode. XRD and SEM were used to intuitively prove the MMT interface suppressing dendrites and alleviating passivation during stripping/plating. 【循环后XRD和SEM分析】

**【电化学性能分析】**

[4] H. Yan, S. Li, Y. Nan, S. Yang, B. Li, Ultrafast Zinc–Ion–Conductor Interface toward High-Rate and Stable Zinc Metal Batteries, Advanced Energy Materials, 11 (2021).

After removing MMT interlayer, the morphology shows small Zn crystal plates of less than 0.5 µm evenly covering on substrate (Figure S14b, Supporting Information). As contract, the surface of the bare Zn appears as big dendrites of more than 5 µm and corrosion holes (Figure 4i; Figure S13, Supporting Information), which is very common in bare Zn electrode. A uniform and dendrite-free morphology is also observed after continuous DOD test, again verifying that the MMT interface can favorably adjust Zn deposition and adapt to volume fluctuations (Figure S15, Supporting Information). All the above results show that stumbling block on Zn anode can be removed by the MMT interface. 【！！！MMT层间传输Zn2+抑制Zn枝晶生长的机理】

**【！！！电池性能优异分析】**

[5] K. Leng, G. Li, J. Guo, X. Zhang, A. Wang, X. Liu, J. Luo, A Safe Polyzwitterionic Hydrogel Electrolyte for Long-Life Quasi-Solid State Zinc Metal Batteries, Advanced Functional Materials, 30 (2020).

A similar phenomenon has been reported in ref. [20]. The excellent cycling performance of ZMBs is mainly attributed to 1) the strong adhesion properties induced by the charged and polar groups in PZHE, which can effectively reduce the interface resistance and improve the kinetics of the electrochemical reaction, 2) the strong water retention capacity of PZHE ensures high ionic conductivity and less corrosion of Zn metal anode

to achieve long-term charging and discharging, and 3) both the VS2 loaded stainless steel mesh and the CNT in the MnO2@ CNT improve the electron conduction in cathode material. Inspired by the development of wearable devices, PZHE promotes the flexible quasi-solid state ZMBs in the future applications. 【切割实验分析】

**【！！！扩散过程受限和临界电流密度效应分析】**

[7] L. Zhang, B. Zhang, T. Zhang, T. Li, T. Shi, W. Li, T. Shen, X. Huang, J. Xu, X. Zhang, Z. Wang, Y. Hou, Eliminating Dendrites and Side Reactions via a Multifunctional ZnSe Protective Layer toward Advanced Aqueous Zn Metal Batteries, Advanced Functional Materials, (2021).

The stability of the Zn anode at a high current density is the key evidence for judging whether the protective layer is effective because dendrite growth is more serious due to the limited diffusion process and critical current density effect.[34] The long-term cycling stabilities of the symmetric cells at a high current density of 10 mA cm−2 with a capacity of 1 mAh cm−2 was further investigated and is displayed in Figure 2e. 【对称电池性能分析】

# 循环后

**【！！！深度放电后形貌保持良好】**

[2] C. Wang, G. Zhu, P. Liu, Q. Chen, Monolithic Nanoporous Zn Anode for Rechargeable Alkaline Batteries, ACS Nano, 14 (2020) 2404-2411.

Figure 1d shows the cross-sectional structure of the nanoporous Zn after being compressed at 6.8 MPa to a porosity of 75%. The deformation was rather uniform, likely owing to the structural uniformity. This specific value of porosity ensures large pore space for mass transports and a high enough volume of metal for electrical conduction, even when it undergoes deep discharging. For example, at 40% DoD and assuming no overall volume change of the electrode, the porosity decreases to ∼69% given that the density of ZnO is lower than that of Zn, but this porosity is still higher than a typical value of a porous anode.28 The volume fraction of Zn decreases from 25 to 16%, close to pv for a percolating Zn phase.

Structural Evolution of the Nanoporous Zn as an Anode.

【！！！循环之前的性能表征】

**【！！！表面扩散与结构改变：通过氧化锌的尺寸进行分析】**

[2] C. Wang, G. Zhu, P. Liu, Q. Chen, Monolithic Nanoporous Zn Anode for Rechargeable Alkaline Batteries, ACS Nano, 14 (2020) 2404-2411.

To coarsen it further by a factor of 2, it would take ∼160 more cycles, which is already an appreciable cycle life for a Zn anode. Last but not least, surface diffusion may have held off another structure-altering dynamics, the electrochemical reaction. We may understand their interplay through the length scales at which they operate. Two notable length scales associated with the reaction are the size and interspacing of the ZnO flowers, both around 100 nm (the shaded area in Figure 3a). This length scale is likely how far the diffusion of zincates can relocate Zn mass. If the ligaments remained ∼70 nm wide, the repetitive dissolution could have either cut them off or induced solid-state Plateau−Rayleigh instability to reshape ligaments into particles as the structural perturbation is larger than the ligament diameter.34 Fortunately, surface diffusion acts quickly to enlarge the ligaments beyond 100 nm and continues to counter any roughening at a similar scale.

【选择碱性锌镍而不选择锌离子：锌的插入和脱出会破坏孔结构】

**【选择碱性锌镍而不选择锌离子：锌的插入和脱出会破坏孔结构】**

[2] C. Wang, G. Zhu, P. Liu, Q. Chen, Monolithic Nanoporous Zn Anode for Rechargeable Alkaline Batteries, ACS Nano, 14 (2020) 2404-2411.

The structural stability promises stable cycling performance, which was indeed achieved in a Ni−Zn battery. We stick to the Ni−Zn chemistry here instead of exploring emerging Zn-ion batteries,35 as the plating and stripping reactions in a neutral electrolyte would destroy the nanoporous structure. 【！！！电解液量控制严格，电极不含任何添加剂：测试更符合实际】

**【循环后SEM分析：孔结构完整，但孔径变大】**

[2] C. Wang, G. Zhu, P. Liu, Q. Chen, Monolithic Nanoporous Zn Anode for Rechargeable Alkaline Batteries, ACS Nano, 14 (2020) 2404-2411.

The inset of Figure 4b shows the structure of the anode retrieved at the end of the 200th cycle (a lower magnification image can be found in Figure S8). The anode, though fragile, retains its integrity. We did not notice any dendrite on the surface of the anode or the separators. The nanoporous structure prevails in the anode. The ligament width stays around 500 nm, but the pores are visibly larger. width stays around 500 nm, but the pores are visibly larger. 【！！！循环过程锌的损失无可避免：锌酸盐的过度饱和】

**【！！！循环过程锌的损失无可避免：锌酸盐的过度饱和】**

[2] C. Wang, G. Zhu, P. Liu, Q. Chen, Monolithic Nanoporous Zn Anode for Rechargeable Alkaline Batteries, ACS Nano, 14 (2020) 2404-2411.

The cross section appears less uniform with big holes. These structural changes, along with the fragility and the increased cell impedance (Figure S6b) suggest a possible loss in Zn mass, which is difficult to avoid given the strong tendency of zincate to supersaturate this electrolyte.37 【！！！200圈深度循环很有应用意义】

**【循环后XRD和SEM分析】**

[4] H. Yan, S. Li, Y. Nan, S. Yang, B. Li, Ultrafast Zinc–Ion–Conductor Interface toward High-Rate and Stable Zinc Metal Batteries, Advanced Energy Materials, 11 (2021).

As shown in Figure S12, Supporting Information, the XRD Patten of MMT-Zn electrode illustrates obvious characteristic peak of metallic zinc with several weaken peaks of passivation products located at 20° and 27°(Zn4SO4(OH)6·4H2O, JPCDS card:44-0673),[33] which can be clear observed in bare Zn anode. The SEM image of Zn-based MMT interlayer after 1000 cycles Zn deposition/dissolution, shows a smooth and compact morphology (Figure 4h;Figure S14a, Supporting Information), which is almost the same with the original electrode (Figure 1f). 【电化学性能分析】

**【！！！MMT层间传输Zn2+抑制Zn枝晶生长的机理】**

[4] H. Yan, S. Li, Y. Nan, S. Yang, B. Li, Ultrafast Zinc–Ion–Conductor Interface toward High-Rate and Stable Zinc Metal Batteries, Advanced Energy Materials, 11 (2021).

Figure 4g shows the mechanism of Zn-based MMT interlayer transporting Zn2+ and suppressing Zn dendrites growth. This interface layer anchors anion to realize a high cation transference number to reduce Zn2+ concentration gradient and the formation of byproducts, and supply interlamellar channel to ensure fast and stable Zn2+ diffusion kinetics to realize uniform Zn2+ deposition. As a result, formation of Zn dendrites is restrained effectively. However, the Zn foil directly contacts with electrolyte resulting in a large number of by-products to form a thick passive film and serious Zn2+ concentration gradients to leading to uneven deposition. To demonstrate the potential practical application of the MMT interface in rechargeable AZIBs. 【全电池分析对锰溶解的抑制作用】

**【钝化膜引出】**

[8] J. Hao, B. Li, X. Li, X. Zeng, S. Zhang, F. Yang, S. Liu, D. Li, C. Wu, Z. Guo, An In-Depth Study of Zn Metal Surface Chemistry for Advanced Aqueous Zn-Ion Batteries, Advanced Materials, 32 (2020).

A dense zinc hydroxycarbonate (i.e., Zn5(CO3)2(OH)6 or Zn4CO3(OH)6·H2O) passivation layer forms on the Zn metal surface once it is exposed to air, which can significantly retard the corrosion process by keeping out moisture and oxygen.[13] Can this passivation film protect the Zn metal or influence the Zn plating/stripping behavior in 1 m ZnSO4 electrolyte? These fundamental issues are still unclear. 【SEM分析】

**【SEM分析】**

[8] J. Hao, B. Li, X. Li, X. Zeng, S. Zhang, F. Yang, S. Liu, D. Li, C. Wu, Z. Guo, An In-Depth Study of Zn Metal Surface Chemistry for Advanced Aqueous Zn-Ion Batteries, Advanced Materials, 32 (2020).

To address these problems, the stability of this oxidation layer was first studied in 1 m ZnSO4. A scanning electron microscope (SEM) image of bare Zn metal without polishing shows a flat surface with some holes (Figure 1a). After deep cleaning, the oxidation layer was removed, with many scratches remaining on the polished Zn metal (Figure S1, Supporting Information), which was confirmed by Fourier transform infrared (FTIR) spectroscopy (Figure S2, Supporting Information). 【腐蚀现象分析】

**【腐蚀现象分析】**

[8] J. Hao, B. Li, X. Li, X. Zeng, S. Zhang, F. Yang, S. Liu, D. Li, C. Wu, Z. Guo, An In-Depth Study of Zn Metal Surface Chemistry for Advanced Aqueous Zn-Ion Batteries, Advanced Materials, 32 (2020).

Bare Zn foil shows an absorption at ≈1500 cm−1, corresponding to the v3 (CO3)2− antisymmetric stretching mode, which is convincing evidence of the presence of a Zn5(CO3)2(OH)6 layer.[14] No obvious absorption can be observed after polishing, indicating that the Zn5(CO3)2(OH)6 layer was thoroughly removed. Both the bare Zn metal and the polished Zn were soaked in 1 m ZnSO4 electrolyte. After one week, the surfaces of both the bare and polished Zn metal incurred a severe corrosion reaction with significant color change (Figure S3, Supporting Information). 【SEM、XRD、FTIR的分析】

**【SEM、XRD、FTIR的分析】**

[8] J. Hao, B. Li, X. Li, X. Zeng, S. Zhang, F. Yang, S. Liu, D. Li, C. Wu, Z. Guo, An In-Depth Study of Zn Metal Surface Chemistry for Advanced Aqueous Zn-Ion Batteries, Advanced Materials, 32 (2020).

The SEM image in Figure 1b shows by-products with the morphology of regular hexagonal flakes that cover the whole surface of the bare Zn, which is similar to what is seen on the polished Zn (Figure S4, Supporting Information), demonstrating that the Zn5(CO3)2(OH)6 layer is highly active in the electrolyte. X-ray diffraction (XRD, Figure S5, Supporting Information) and FTIR measurements were conducted to identify the by-products of both samples. 【EDS分析】

**【EDS分析】**

[8] J. Hao, B. Li, X. Li, X. Zeng, S. Zhang, F. Yang, S. Liu, D. Li, C. Wu, Z. Guo, An In-Depth Study of Zn Metal Surface Chemistry for Advanced Aqueous Zn-Ion Batteries, Advanced Materials, 32 (2020).

The results indicated that the by-product generated on both electrodes was Zn4SO4(OH)6·xH2O, as further confirmed by the energy dispersive spectroscopy (EDS) mapping of S and Zn elements (Figure 1c–e). Accordingly, the Zn5(CO3)2(OH)6 passivation layer cannot function as a protective layer in the electrolyte due to its high thermodynamic activity. The corrosion reaction of bare Zn with a Zn5(CO3)2(OH)6 passivation layer can be expressed as following:

Zn CO OH SO 4H 44 6 22() x

Zn SO OH ·H O2CO Zn 53 2

() ()6 Zn Zn 2e2 ↔++− 2H O2e2OH H22 +↔ +−− 4Zn6OH SO HO Zn SO OH ·H2O 2

++ xx()+↔ +− −

4 2

24 4 6

++ +− → ++

4 2

−+ () 2

x 2H O 2+

(1) (2) (3) (4)

【电化学性能分析】

**【电化学性能分析】**

[8] J. Hao, B. Li, X. Li, X. Zeng, S. Zhang, F. Yang, S. Liu, D. Li, C. Wu, Z. Guo, An In-Depth Study of Zn Metal Surface Chemistry for Advanced Aqueous Zn-Ion Batteries, Advanced Materials, 32 (2020).

The electrochemical performance of symmetrical Zn cells with/without polishing was tested to investigate the influence of the Zn5(CO3)2(OH)6 layer on the Zn electrodeposition behavior. Figure 1f compares the initial charge/discharge voltage profiles of both cells. Remarkably, the bare Zn cell displays a higher voltage hysteresis compared to the polished Zn cell at the start of charge, indicating its higher energy barrier for Zn stripping/ plating due to the passivation layer.[15] As the charge proceeds, the voltage hysteresis of the bare Zn cell decreases, probably due to the dissolution of the passivation layer in ZnSO4 electrolyte, but it increases in the polished Zn cell, indicating the enhanced impedance due to the by-product layer formation. 【EIS分析】

**【副产物层分析】**

[8] J. Hao, B. Li, X. Li, X. Zeng, S. Zhang, F. Yang, S. Liu, D. Li, C. Wu, Z. Guo, An In-Depth Study of Zn Metal Surface Chemistry for Advanced Aqueous Zn-Ion Batteries, Advanced Materials, 32 (2020).

Both bare and polished Zn cells show two different charge transfer steps after one cycle and after 50 cycles, manifesting the additional by-product layer generated during the charge-discharge process. 【光学图像分析】

**【！！！界面性能影响因素】**

[9] L. Ma, Q. Li, Y. Ying, F. Ma, S. Chen, Y. Li, H. Huang, C. Zhi, Toward Practical High-Areal-Capacity Aqueous Zinc-Metal Batteries: Quantifying Hydrogen Evolution and a Solid-Ion Conductor for Stable Zinc Anodes, Advanced Materials, 33 (2021).

As the ZnF2 layer covers the Zn metal electrode surface, the

front interface/phase between the Zn metal and the electrolyte plays a pivotal role in directing the growth mode. Prior to the study of Zn growth, the electrochemical properties of Zn layer are conducted including the ionic conductivity capability, electronic resistivity, and Zn2+ transfer number. 【电导率分析】

**【！！锌倾向于较低能量处生长】**

[9] L. Ma, Q. Li, Y. Ying, F. Ma, S. Chen, Y. Li, H. Huang, C. Zhi, Toward Practical High-Areal-Capacity Aqueous Zinc-Metal Batteries: Quantifying Hydrogen Evolution and a Solid-Ion Conductor for Stable Zinc Anodes, Advanced Materials, 33 (2021).

For the electrode at the plated state, no empty space is observed, and the ZnF2 layer is in intimate contact with the Zn metal (Figure 3j). The outcome originates that the Zn deposition only comes up at a place, where the Zn2+ meets charges. The electronically insulating ZnF2 layer has no relish for Zn nucleation, and the Zn tends to grow on the Zn@ZnF2 interface with lower inserting energy.【！！！向下传导阐述】

**【！！！向下传导阐述】**

[9] L. Ma, Q. Li, Y. Ying, F. Ma, S. Chen, Y. Li, H. Huang, C. Zhi, Toward Practical High-Areal-Capacity Aqueous Zinc-Metal Batteries: Quantifying Hydrogen Evolution and a Solid-Ion Conductor for Stable Zinc Anodes, Advanced Materials, 33 (2021).

Consequently, it prefers to bring Zn2+ ions back into the empty region beneath the ZnF2 layer and

【不对称电池分析】

**【！锌电沉积SEM总结-添加剂修饰锌沉积形貌-通过限制锌扩散动力学抑制枝晶】**

[12] M.H. Lin, C.J. Huang, P.H. Cheng, J.H. Cheng, C.C. Wang, Revealing the effect of polyethylenimine on zinc metal anodes in alkaline electrolyte solution for zinc-air batteries: Mechanism studies of dendrite suppression and corrosion inhibition, Journal of Materials Chemistry A, 8 (2020) 20637-20649.

These images verify that the PEI additive can efficiently modify the morphology of zinc deposits and suppress the dendrite growth through the restriction of zinc diffusion kinetics. 【不同电位锌电沉积-证实沉积动力学对形貌变化和相应的电流密度曲线演化的影响】

**【全电池循环电解质作用分析-锌阳极枝晶问题】**

[2] J. Hao, J. Long, B. Li, X. Li, S. Zhang, F. Yang, X. Zeng, Z. Yang, W.K. Pang, Z. Guo, Toward High-Performance Hybrid Zn-Based Batteries via Deeply Understanding Their Mechanism and Using Electrolyte Additive, Adv. Funct. Mater., 29 (2019).

It is well-known that Zn metal anode suffers from the irreversibility issues caused by the dendrite growth during plating/ stripping process, rendering the cycle performance of aqueous Zn-based batteries highly unstable.[27,28] 【全电池问题-锌枝晶危害-锌枝晶、死锌、消耗电解质、容量】

**【锌电沉积SEM分析-与表面光滑的商用锌箔(图4 d)相比，在含so4添加剂的电解液中电沉积的锌阳极表面形貌粗糙，没有锌枝晶薄片(图4 f)。相反，在不含na2so4添加剂电解质的情况下发现了显著的锌枝晶薄片(图4e)。这些结果与上述理论分析一致。】**

[6] Y. Xu, J. Zhu, J. Feng, Y. Wang, X. Wu, P. Ma, X. Zhang, G. Wang, X. Yan, A rechargeable aqueous zinc/sodium manganese oxides battery with robust performance enabled by Na2SO4 electrolyte additive, Energy Storage Materials, 38 (2021) 299-308.

Compared with commercial Zn foil with a smooth surface ( Fig. 4 d ), the morphology of the Zn anode surface after electrodeposition in the electrolyte containing Na 2 SO 4 additive exhibits a rough feature without Zn dendrite flakes ( Fig. 4 f ). On the contrary, salient Zn dendrite flakes are found in non-containing Na 2 SO 4 additive electrolyte situation ( Fig. 4 e ). These results are consistent with the above theoretical analysis. 【锌电沉积-XRD-进一步收集了Zn阳极在添加或不添加so4添加剂电解质时的XRD谱图，结果表明Zn晶体的生长诱导了(101)择优取向，而so4的加入可以改变锌枝晶的生长模式(图4 g)】

**【SEM-添加剂作用-减缓锌枝晶的生长，这使得锌表面的晶粒更细】**

[7] Z. Hou, X. Zhang, X. Li, Y. Zhu, J. Liang, Y. Qian, Surfactant widens the electrochemical window of an aqueous electrolyte for better rechargeable aqueous sodium/zinc battery, J. Mater. Chem. A, 5 (2017) 730-738.

The addition of SDS to the electrolyte also contributed to the mitigation of the growth of zinc dendrites, which rendered the zinc surface finer-grained, as shown in Fig. S14c.† 【总结-添加剂可以抑制腐蚀和枝晶】

**【全电池SEM结果证明添加剂作用】**

[12] M.H. Lin, C.J. Huang, P.H. Cheng, J.H. Cheng, C.C. Wang, Revealing the effect of polyethylenimine on zinc metal anodes in alkaline electrolyte solution for zinc-air batteries: Mechanism studies of dendrite suppression and corrosion inhibition, Journal of Materials Chemistry A, 8 (2020) 20637-20649.

结果表明，PEI添加剂可以改善锌在高浓度碱性电解质溶液中溶解、迁移和沉积的不均匀性It indicates that the nonuniformity of the dissolution, migration, and deposition of zinc in a highly concentrated alkaline electrolyte solution can be improved by PEI additive. 【全电池SEM-对比样-电极表面恶化-表面积增大-加速钝化和电池衰减】

**【全电池问题-锌枝晶危害-锌枝晶、死锌、消耗电解质、容量】**

[2] J. Hao, J. Long, B. Li, X. Li, S. Zhang, F. Yang, X. Zeng, Z. Yang, W.K. Pang, Z. Guo, Toward High-Performance Hybrid Zn-Based Batteries via Deeply Understanding Their Mechanism and Using Electrolyte Additive, Adv. Funct. Mater., 29 (2019).

The Zn dendrite growth during cycling would eventually result in the internal shorting failure after the separator was pierced. Even before the battery failure, some Zn dendrites turn into “dead” part during the electrochemical reaction, leading to the loss of the capacities and electrolyte consumption.[14] 【全电池-抑制枝晶很重要】

**【无添加剂-锌沉积机理-侧向扩散-枝晶】**

[1] 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 Letters, 5 (2020) 3012-3020.

在成核过程中，吸附在电极表面的Zn2+离子，为了减小表面能和暴露表面积，容易侧向扩散，聚集成分散的大核。As schematically shown in Figure 5, during the nucleation process, to minimize the surface energy and the exposed surface area, the Zn2+ ions adsorbed on the electrode surface are prone to diffusing laterally and aggregating into sparsely dispersed large nuclei. 在后续的电镀过程中，连续的横向扩散和由这些核产生的电场的不均匀分布使得更多的Zn2+离子在已经形成的成核位点上吸附和还原，最终导致表面覆盖着大的Zn枝晶。In the subsequent plating process, the continuous lateral diffusion and the inhomogeneous distribution of the electric field that originated from those nuclei are capable of driving more Zn2+ ions to adsorb and reduce on the already formed nucleation sites, eventually resulting in a surface covered by large Zn dendrites. 【含电解质添加剂-锌成核机理-表面吸附-均匀沉积】

**【含电解质添加剂-锌成核机理-表面吸附-均匀沉积】**

[1] 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 Letters, 5 (2020) 3012-3020.

当电解质中存在适量的TBA2SO4时，Zn2+离子在成核过程中沿表面的横向扩散和聚集受到竞争吸附的TBA+离子的限制，从而形成高面积密度和细尺寸的核。However, when an appropriate amount of TBA2SO4 presents in the electrolyte, the lateral diffusion and aggregation of Zn2+ ions along the surface during the nucleation process are constrained by competitively adsorbed TBA+ cations, which results in the formation of a high areal density and finesize nuclei. 更重要的是，在电场梯度的驱动下，非氧化还原TBA+离子在晶核附近较好地吸附形成TBA+离子层。由于原子核周围有屏蔽TBA+层，接近的Zn2+离子被阻碍并转移到相邻的平板区域，该区域TBA+覆盖最小，直到达到均匀和无枝晶的锌沉积More importantly, driven by the electric field gradient, nonredox TBA+ cations are preferably adsorbed in the vicinity of the nuclei to form a TBA+ cation layer in the following plating process. Because of this shielding TBA+ layer around the nuclei, the approaching Zn2+ ions are hindered and transferred to plate on the adjacent flat region that has minimal TBA+ coverage until a homogeneous and dendrite-free Zn deposition is achieved.

【结论-】

**【TEM和mapping分析】**

[4] H. Yan, S. Li, Y. Nan, S. Yang, B. Li, Ultrafast Zinc–Ion–Conductor Interface toward High-Rate and Stable Zinc Metal Batteries, Advanced Energy Materials, 11 (2021).

To confirm the residency of Zn2+ in the inter-lamella space, the TEM and the corresponding elemental mapping of Zn, Al, O, and Si (Figure S2d,e, Supporting Information) were captured and evidenced homogeneous distribution components.【zeta电位测试证明负电荷存在及现象分析】

**【形貌分析】**

[7] L. Zhang, B. Zhang, T. Zhang, T. Li, T. Shi, W. Li, T. Shen, X. Huang, J. Xu, X. Zhang, Z. Wang, Y. Hou, Eliminating Dendrites and Side Reactions via a Multifunctional ZnSe Protective Layer toward Advanced Aqueous Zn Metal Batteries, Advanced Functional Materials, (2021).

Figure 1g further reveals that this protective layer is composed of uniformly distributed nanoparticles that are closely packed, and the nanoparticle sizes are 100–200 nm. This dense layered structure evenly covers the surface of the Zn foil, with a thickness of ≈0.8 µm (Figure 1h). 【XRD分析】

**【全电池SEM-对比样-电极表面恶化-表面积增大-加速钝化和电池衰减】**

参考修饰词[8] M.H. Lin, C.J. Huang, P.H. Cheng, J.H. Cheng, C.C. Wang, Revealing the effect of polyethylenimine on zinc metal anodes in alkaline electrolyte solution for zinc-air batteries: Mechanism studies of dendrite suppression and corrosion inhibition, J. Mater. Chem. A, 8 (2020) 20637-20649.

As the cell undergoes 10 more cycles at the high current density of 10 mA cm2, in Fig. 11(C(b)), the cycled zinc anode in the PEI-free electrolyte solution shows a serious surface deterioration, forming a more porous electrode surface with numerous deep-pits. 随着电极劣化表面积的增加，锌阳极的钝化速度加快，电池性能下降The increase of surface area with electrode deterioration would accelerate the passivation of the zinc anode and performance decay of batteries.16,41 【全电池SEM-添加剂-均匀-缓解表面恶化】

**【全电池SEM-添加剂-均匀-缓解表面恶化】**

参考修饰词[8] M.H. Lin, C.J. Huang, P.H. Cheng, J.H. Cheng, C.C. Wang, Revealing the effect of polyethylenimine on zinc metal anodes in alkaline electrolyte solution for zinc-air batteries: Mechanism studies of dendrite suppression and corrosion inhibition, J. Mater. Chem. A, 8 (2020) 20637-20649.

However, the cycled zinc anode in the PEI-containing (PEI 30 ppm) electrolyte solution still maintains a good surface morphology due to the protection afforded by PEI adsorption. Only some shallow pits are formed. The results indicate that the PEI additive can effectively alleviate the deterioration of the zinc anode surface in the alkaline electrolyte solution during the practical zinc–air battery cycling, thereby avoiding a severe shape change of zinc anodes and improving the cycling stability. Thus, we speculated that the fast performance decay of cells with PEI additive at the extended cycles under the higher current density of 10 mA cm2 might be caused by the PEI induced intense HER.

【结论】

# 光学显微镜

**【电沉积-原位光学显微镜】**

[1] 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 Letters, 5 (2020) 3012-3020.

To visualize the effect of TBA2SO4 additives, the Zn electrodeposition process was recorded using an in situ optical microscopy setup. 【原位光学对比样-枝晶】

**【原位光学对比样-枝晶】**

[1] 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 Letters, 5 (2020) 3012-3020.

对比样10min后出现斑点As shown in Figure 1a−f, in the absence of TBA2SO4 additives, scattered dark Zn deposit spots appear after 10 min of plating at a current density of 10 mA cm−2. 后长成枝晶或锌突起With the increase in plating time, some deposit spots grow into highly dendritic and mossy Zn protrusions (Figure S2). 对比样更易沉积在突起位置It is evident that Zn ions preferentially deposit on initial protuberant tips, with the stronger electric field on the electrode surface in the normal electrolyte. (See the Experimental Section in the Supporting Information (SI).). 【原位光学-好样-沉积均匀】

**【原位光学-好样-沉积均匀】**

[1] 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 Letters, 5 (2020) 3012-3020.

In sharp contrast, with the addition of TBA2SO4 to the electrolyte, a homogeneous and uniform Zn deposition process is observed, indicating the effective suppression of the dendritic morphology (Figure 1g−l). 高面密度锌沉积Different from sparse Zn deposit spots observed in the early stage of plating (Figure 1b) in the normal electrolyte, high areal density Zn nucleation over the Cu substrate ensures the complete uniform coverage of the Zn coating on the Cu foam (Figure 1j) in the TBA electrolyte. (See the Experimental Section in the SI.)

【电沉积用XRD-SEM表征】

## 【原位光学显微镜分析】

[5] K. Leng, G. Li, J. Guo, X. Zhang, A. Wang, X. Liu, J. Luo, A Safe Polyzwitterionic Hydrogel Electrolyte for Long-Life Quasi-Solid State Zinc Metal Batteries, Advanced Functional Materials, 30 (2020).

To visualize the dynamic stability of symmetric Zn/Zn cells in PZHE and LE, in situ optical microscopy is used to characterize the evolution of Zn deposition morphology at the current density of 5 mA cm−2 (Figure S6, Supporting Information). Not surprisingly, the air bubble generation can be clearly observed in the liquid electrolyte within 20 min (Figure 2f). In contrast, no air bubbles and dendrites are observed in PZHE even after 40 min of deposition because PZHE can retain water molecules in the polymer backbone, which significantly reduces the corrosion and side reactions of Zn metal anode in water (Figure 2e).

【对称电池性能分析】

## 【光学显微镜分析锌沉积】

[6] M. Liu, J. Cai, H. Ao, Z. Hou, Y. Zhu, Y. Qian, NaTi2(PO4)3 Solid-State Electrolyte Protection Layer on Zn Metal Anode for Superior Long-Life Aqueous Zinc-Ion Batteries, Advanced Functional Materials, 30 (2020).

In order to intuitively observe the effect of NTP coating in the uniform deposition of zinc ions, we used optical microscope to observe the zinc-ion deposition behavior at the current density of 10 mA cm−2 on bare Zn and NTP@Zn foils (Figure 5a,b). The bare Zn and NTP@Zn foils did not significantly change in the first 10 min. At the 40th min, it can be observed that the zinc-burr and one bubblet (red circle, side reaction: H2O + 2e− = H2 + OH−) emerged on the surface of the bare Zn foil. With the time prolonging from 80 to 110 min, zinc-burr grew more and more distinctly and the bubblet gradually became larger. On the contrary, the NTP@Zn foil didn’t have obvious dendrite growth, which benefited from the induced uniform deposition effect of the NTP coating. We further observed the morphological evolution by SEM for the bare Ti and NTP@Ti foils at 1 mA cm−2 after 3 h deposition, assembled with the Zn electrode, respectively. For the bare Ti electrode, newly generated messy zinc debris was found on the surface (Figure 5c). In comparison with the bare Ti electrode, the overall morphology of NTP@Zn electrode is smoother, without obvious zinc dendrites formation (Figure 5e).【SEM分析涂层稳定】

## 【！！！原位光学显微镜变化过程分析】

[7] L. Zhang, B. Zhang, T. Zhang, T. Li, T. Shi, W. Li, T. Shen, X. Huang, J. Xu, X. Zhang, Z. Wang, Y. Hou, Eliminating Dendrites and Side Reactions via a Multifunctional ZnSe Protective Layer toward Advanced Aqueous Zn Metal Batteries, Advanced Functional Materials, (2021).

The excellent electrochemical results (Figure 2) discussed above preliminarily indicate that the ZnSe protective layer can inhibit dendrites even at high current densities. To further investigate how the ZnSe protective layer regulates dendrite growth, we observed the dynamic stability of the symmetric cells in situ during the Zn plating process at a high current density (10 mA cm−2) using an optical microscope (Figure S19, Supporting Information). In regard to bare Zn (Figure 5a), the presence of small tips (saddle-brown spots on the surface at 0 min)

due to electrolyte corrosion and surface unevenness leads to inhomogeneous charge distribution and nucleation barriers. After 5 min of Zn plating, obvious protrusions grow along the previous tip sites instead of being uniformly deposited over the whole surface. 【尖端效应的解释】

## 【尖端效应的解释】

[7] L. Zhang, B. Zhang, T. Zhang, T. Li, T. Shi, W. Li, T. Shen, X. Huang, J. Xu, X. Zhang, Z. Wang, Y. Hou, Eliminating Dendrites and Side Reactions via a Multifunctional ZnSe Protective Layer toward Advanced Aqueous Zn Metal Batteries, Advanced Functional Materials, (2021).

This behavior is because the so-called “tip effect” makes it easy for Zn2+ to accumulate on these tips, and the deposition of protrusions further aggravates the uneven distribution of the interfacial electric field and ion flux, leading to the uncontrolled growth of Zn dendrites.[39] After 10 min, the dendrites continue growing, and when the areal capacity is as high as 5 mAh cm−2 (Zn plating for 30 min), the growth of dendrites on the Zn surface is more serious and is accompanied by the formation of H2 bubbles (Figure S20, Supporting Information). After prolonged Zn plating, the bare Zn surface is extremely rough with severe cracking and pulverization, which is also accompanied by uncontrolled dendrite growth (Figure S21a, Supporting Information). In contrast, no obvious protrusions or dendrites appear on the Zn@ZnSe surface during the Zn plating process, and even after 30 min, uniform Zn2+ deposition can still be achieved (Figure 5b). As shown in Figure S21b in the Supporting Information, the surface of Zn@ZnSe is still flat and smooth; thus, dendrite-free Zn plating is realized and suggests that the ZnSe protective layer may effectively regulate the Zn2+ deposition behavior on the Zn surface. 【对称电池测试】

## 【！！！原位光学分析】

[9] L. Ma, Q. Li, Y. Ying, F. Ma, S. Chen, Y. Li, H. Huang, C. Zhi, Toward Practical High-Areal-Capacity Aqueous Zinc-Metal Batteries: Quantifying Hydrogen Evolution and a Solid-Ion Conductor for Stable Zinc Anodes, Advanced Materials, 33 (2021).

The direct proofs for suppressed side reactions and modulated Zn plating/stripping enabled by the ZnF2 layer are obtained from in situ optical visualization observations of Zn deposition. Quite uneven and odd Zn deposits and abundant gas bubbles are observed as early of 15 min after the commencement of deposition with an applied constant current density of 10 mA cm–2 (Figure 4a). For Zn@ZnF2 electrode under the same condition, uniform and compact Zn deposits without any bubbles being observed can be obtained over 45 min process (Figure 4b). It should be mentioned that Zn metal coated with commercial ZnF2 particles displays worse side reaction suppression effect due to loosen architecture of coating layer (Figures S13 and S14, Supporting Information). 【析氢极化曲线】

## 【！！！原位光学显微镜分析】

[11] N. Zhang, S. Huang, Z. Yuan, J. Zhu, Z. Zhao, Z. Niu, Direct Self-Assembly of MXene on Zn Anodes for Dendrite-Free Aqueous Zinc-Ion Batteries, Angewandte Chemie - International Edition, 60 (2021) 2861-2865.

Furthermore, more direct evidence for modulating Zn plating by MXene layer is obtained from the in situ optical visualization observations. The MZn-60 shows a smooth dendrite-free surface in plating process (Figure 4a). In contrast, some small protrusions appear on pure Zn surface as early as 10 min and gradually evolve into Zn dendrite (Figure 4b). Zn nucleation and deposition depend on the electric field distributions at the interface between anode and electrolyte. In order to illustrate the role of MXene layer in controlling the electric field distribution at interface between anode and electrolyte, a theoretical simulation was carried out by COMSOL (Supporting Information, Figure S12). 【！！！电荷再分布效应和电子导电性使Zn表面的表面电场均匀化】

## 【！！！电荷再分布效应和电子导电性使Zn表面的表面电场均匀化】

[11] N. Zhang, S. Huang, Z. Yuan, J. Zhu, Z. Zhao, Z. Niu, Direct Self-Assembly of MXene on Zn Anodes for Dendrite-Free Aqueous Zinc-Ion Batteries, Angewandte Chemie - International Edition, 60 (2021) 2861-2865.

The charge redistribution effect and the electronic conductivity of MXene layer uniformize the surface electric field on the Zn surface (Figure 4c and g).[8, 13d]

electric field ensures homogeneous Zn2+

The uniformly distributed deposition on the

surface of Zn, thereby obtaining a flat and smooth surface (Figure 1b, 4d; Supporting Information, Figure S13a). In contrast, the electric field distribution on the surface of pure Zn displays an obvious intensity gradient during Zn plating process (Figure 4e and h). Such enhanced local electric field forms a higher charge region, promoting more Zn2+

deposition nucleation. 【尖端效应的影响】

## 【尖端效应的影响】

[11] N. Zhang, S. Huang, Z. Yuan, J. Zhu, Z. Zhao, Z. Niu, Direct Self-Assembly of MXene on Zn Anodes for Dendrite-Free Aqueous Zinc-Ion Batteries, Angewandte Chemie - International Edition, 60 (2021) 2861-2865.

Owing to the tip effect, these small protuberances gradually evolve into the large and sharp dendrite flakes (Figure 1c, 4 f; Supporting Information, Figure S13b), ultimately leading to the cell failure. These results indicate that the MXene layer really achieves the aim of regulating uniform Zn nucleation and growth. To illustrate the practical application of MZn anodes, we

assembled full cells using MZn-60 as anode and conventional MnO2

as cathode (Supporting Information, Figure S14). Its

【CV分析】

# 对称电池

**【DFT计算与实际区别-与模拟系统不同的是，实际溶液中TBA+层的屏蔽效果会增强，因为Zn阳极表面吸附的TBA+离子层密度更大。】**

[1] 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 Letters, 5 (2020) 3012-3020.

Different from the simulated model system, the shielding effect of the TBA+ layer will be enhanced in a practical solution because of the denser TBA+ cation layer adsorbed on the Zn anode surface. 【对称电池-通过长期恒流循环试验评价3D-Zn阳极的电化学稳定性和性能】

**【对称电池-通过长期恒流循环试验评价3D-Zn阳极的电化学稳定性和性能】**

[1] 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 Letters, 5 (2020) 3012-3020.

Symmetric cells were assembled to evaluate the electrochemical stability and performance of 3D-Zn anodes using long-term galvanostatic cycling tests. 【对称电池参数设置-对称电池在不同电解质下的电压分布，电流密度为2ma cm−2，比容量为2mah cm−2。】

**【对称电池参数设置-对称电池在不同电解质下的电压分布，电流密度为2ma cm−2，比容量为2mah cm−2。】**

[1] 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 Letters, 5 (2020) 3012-3020.

Figure 4a shows the voltage profiles of a symmetric Zn|Zn cell and 3D-Zn|3D-Zn cells in different electrolytes at a current density of 2 mA cm−2 and a specific capacity of 2 mAh cm−2. 【对称电池分析-在正常电解液中，第26周(51 h)和第36周(72 h)电压曲线开始迅速波动，随后出现短路】

**【对称电池分析-在正常电解液中，第26周(51 h)和第36周(72 h)电压曲线开始迅速波动，随后出现短路】**

[1] 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 Letters, 5 (2020) 3012-3020.

显然，与平面锌板相比，3D-Zn阳极的寿命略有延长，但在没有TBA2SO4添加剂的情况下，仍然存在严重的枝晶生长。In the normal electrolyte, the voltage profiles of Zn|Zn and 3D-Zn|3D-Zn cells start to fluctuate very soon and subsequently short out in the 26th (51 h) and 36th cycles (72 h), respectively. It is evident that 3D-Zn anodes present slightly extended lifespans compared with planar Zn plates but still suffer from severe dendrite growth without the TBA2SO4 additive. 【对称电池分析-TBA电解质】

**【对称电池分析-TBA电解质】**

[1] 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 Letters, 5 (2020) 3012-3020.

循环150次(300 h)以上时，电压曲线稳定，无短路迹象，表明在电解质添加剂的帮助下，3D-Zn电极的循环稳定性大大提高。In contrast, the 3D-Zn|3D-Zn cell in the TBA electrolyte displays a stable voltage profile with no sign of short-circuit for over 150 cycles (300 h), indicating the much improved cycling stability of the 3D-Zn electrode with the assistance of the electrolyte additive. 【对称电池-不同电流密度性能分析】

**【对称电池-不同电流密度性能分析】**

[1] 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 Letters, 5 (2020) 3012-3020.

Noticeably, with a fixed specific capacity of 2 mAh cm−2,Zn| Zn cells display a prolonged lifespan of 77 cycles (62 h) at 5 mA cm−2 and 632 cycles (252 h) at 10 mA cm−2 in the normal electrolyte (Figure 4b,c). 【对称电池-符合已报道的成核生长理论，即大电流密度下高的成核过电位和大量的活性位点会导致小的成核尺寸和均匀的沉积层。】

**【对称电池-符合已报道的成核生长理论，即大电流密度下高的成核过电位和大量的活性位点会导致小的成核尺寸和均匀的沉积层。】**

[1] 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 Letters, 5 (2020) 3012-3020.

This trend obeys the reported nucleation and growth theory that a high nucleation overpotential and massive active sites at a large current density bring about a small nucleation size and a uniform deposition layer.23,43−45 【对称电池循环性能对比】

**【对称电池循环性能对比】**

[1] 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 Letters, 5 (2020) 3012-3020.

As for 3D-Zn anodes, despite the successful avoidance of short-circuiting, a gradual increase in the polarization after long-time stable cycling (ca. 300 h) is observed in the normal electrolyte, whereas symmetric cells with the TBA electrolyte can cycle stably for over 570 cycles (456 h) at 5 mA cm−2 and 1000 cycles (400 h) at 10 mA cm−2. With increasing the areal specific capacity to 5 mAh cm−2 (Figure 4d), remarkable cycle stability for 80 cycles (160 h) still can be achieved for the 3D-Zn|3D-Zn cell in the TBA electrolyte when the Zn plate and the 3D-Zn anode in the normal electrolyte rapidly fail in the 11th (21 h) and 18th cycles (36 h), respectively. Clearly, a high cycling capacity will accelerate the dendrite growth and shorten the cell lifespan.46 【SEM表征-进一步研究对称电解槽中锌阳极在电镀/剥离循环后的形貌变化】

**【SEM表征-进一步研究对称电解槽中锌阳极在电镀/剥离循环后的形貌变化】**

[1] 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 Letters, 5 (2020) 3012-3020.

SEM characterizations were carried out to further investigate the morphological changes of Zn anodes in symmetric cells after plating/stripping cycling. 【无添加剂-锌沉积SEM】

**【无添加剂-锌沉积SEM】**

[1] 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 Letters, 5 (2020) 3012-3020.

As shown in the ex situ SEM images of Zn electrodes after 20 plating/stripping cycles (Figure 4e−g), the Zn plate and 3D-Zn anodes cycled in the normal electrolyte exhibit rough surfaces with massive dendrites and large aggregations, which can penetrate the separator and bridge the electrodes easily. 【好样-锌沉积SEM】

**【好样-锌沉积SEM】**

[1] 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 Letters, 5 (2020) 3012-3020.

With regard to 3DZn anodes cycled in the TBA electrolyte, a dense and smooth surface remains, even after 150 cycles (Figure 4h). 【对称电池循环后SEM对比】

**【对称电池循环后SEM对比】**

[1] 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 Letters, 5 (2020) 3012-3020.

The postmortem SEM images of Zn anodes cycled at 5 and 10 mA cm−2 in symmetric cells are presented in Figures S8 and S9. 【引出全电池测试及组成】

## 【氮掺杂增强循环稳定性，分析初始库伦效率低的原因】

[3] F. Xie, H. Li, X. Wang, X. Zhi, D. Chao, K. Davey, S.Z. Qiao, Mechanism for Zincophilic Sites on Zinc-Metal Anode Hosts in Aqueous Batteries, Advanced Energy Materials, 11 (2021).

This finding demonstrates boosted reversibility from introduction of nitrogen-sites. The relatively lower initial coulombic efficiency might originate from some side reactions such as the hydrogen evolution reaction and/or the formation of undesirable, inactive products.[5,9] These data demonstrate, therefore, that nitrogen-doping on the host enhances cycling stability of the zinc-metal anode. The symmetric cells were also used to investigate the stability of zinc-metal anode on different carbon hosts. 【对称电池数据分析】

## 【对称电池数据分析】

[3] F. Xie, H. Li, X. Wang, X. Zhi, D. Chao, K. Davey, S.Z. Qiao, Mechanism for Zincophilic Sites on Zinc-Metal Anode Hosts in Aqueous Batteries, Advanced Energy Materials, 11 (2021).

From this the symmetric battery test (Figure 4b), it was concluded that CnC HS improve the cyclic stability as zincmetal anode host compared with C HS. It should be noted that a gradual increment in voltage hysteresis occurred after 3000 min in the symmetric cell test with C HS. The galvanostatic profile of C HS fluctuates after 4000 min. This finding indicates an opencircuit which led to failure of the battery. The symmetric cell for CnC HS was cycled over 7000 min, demonstrating stable cycling performance. 【电压分布分析亲锌位点作用】

## 【电压分布分析亲锌位点作用】

[3] F. Xie, H. Li, X. Wang, X. Zhi, D. Chao, K. Davey, S.Z. Qiao, Mechanism for Zincophilic Sites on Zinc-Metal Anode Hosts in Aqueous Batteries, Advanced Energy Materials, 11 (2021).

The voltage profiles under different current densities were recorded to investigate the impact of nitrogen-doping under different current densities (Figure 4c; Figure S18, Supporting Information). From the voltage profiles, it was seen that CnC HS exhibited a lower overpotential of 20 mV compared with that for C HS of 27 mV at the current density of 0.5 mA cm−2. This finding demonstrates that the nitrogen sites boosted electrode kinetics of Zn nucleation/deposition. The overpotential for CnC HS increased to 36 and 40 mV at, respectively, current densities of 2.0 and 4.0 mA cm−2. This compared with, respectively, 52 and 96 mV for C HS. The average lower overpotentials for CnC HS under various current densities than the ones of C HS (shown in Figure S19 in the Supporting Information) confirm boosted performance as hosts of the zinc-metal anode. The Zn plating overpotentials for CnC HS and C HS were used to reveal the difference in nucleation of zinc on these two carbon hosts. 【亲锌位点电化学性能分析】

## 【！！！对称电池优势分析】

[4] H. Yan, S. Li, Y. Nan, S. Yang, B. Li, Ultrafast Zinc–Ion–Conductor Interface toward High-Rate and Stable Zinc Metal Batteries, Advanced Energy Materials, 11 (2021).

The electrochemical performance of Zn-based MMT interlayer protected Zinc anode (MMT-Zn) was evaluated in symmetric cell, as shown in Figure 3. The plating/stripping performance of MMT-Zn||MMT-Zn symmetric cell exhibits a stable voltage profile over 1000 cycles without fluctuation at a low current density of 1 mA cm−2 with a low area capacity of 0.25 mA h cm−2. More voltage profile detail is enlarged in Figure 3b–d, the voltage hysteresis of MMT-Zn electrode is around 50 mV and maintained entire cycling process, which indicates the stable interface of modified zinc anode. That is because the uniform MMT interlayer can contribute to high Zn2+ concentration that acts as an available Zn2+ source for plating, high cation transference number and anchored anion reduces the formation of byproducts, and interlamellar channel ensures a freeway for Zn2+ to deliver an ultra-stable and small overpotential for MMT-Zn electrode. 【低极化表明Zn的成核和生长能垒较低，促进了相对均匀的金属电镀过程】

## 【低极化表明Zn的成核和生长能垒较低，促进了相对均匀的金属电镀过程】

[4] H. Yan, S. Li, Y. Nan, S. Yang, B. Li, Ultrafast Zinc–Ion–Conductor Interface toward High-Rate and Stable Zinc Metal Batteries, Advanced Energy Materials, 11 (2021).

Low polarization indicates a low energy barrier for Zn nucleation and growth, and promotes a relatively uniform metal plating process to guide a dendrite-free morphology.[11] That is to say, MMT interface suppresses formation of passivation film and dendrites during the stripping/plating process. As comparison, bare Zn electrode has a voltage hysteresis increase from around 70 mV at initial to 84 mV at 47 cycle, and 2.65 V at 126–130 cycles, which attributed to the gradually formation of uneven, compact, and non-ionic conductive passivation layer. The remarkably improved cycling stabilities of the MMTZn||MMT-Zn cells are also observed at much higher current densities of 2 and 10 mA cm−2 (Figure S5, Supporting Information). The polarization of MMT-Zn||MMT-Zn remains stable after 240 h at current density of 2 mA cm−2, and even at an ultrahigh current density of 10 mA cm−2, the polarization still remains constant till 95 h (450 cycles). In contrast, the polarization of bare Zn electrode can only remain in stable within 45 and 18 h (at 2 and 10 mA cm−2), and gradually increased and fluctuated in the subsequent. 【深DOD测试稳定性】

## 【深DOD测试稳定性】

[4] H. Yan, S. Li, Y. Nan, S. Yang, B. Li, Ultrafast Zinc–Ion–Conductor Interface toward High-Rate and Stable Zinc Metal Batteries, Advanced Energy Materials, 11 (2021).

Cycling stabilities have been further investigated by the DOD test in symmetrical cells

(Figure 3e). With a high current density of 10 mA cm−2 and a high areal capacity of 45 mA h cm−2, which corresponds to 77% theoretical DOD (refer to calculation of the DOD in Supporting Information), the MMT-Zn electrode can work more than 1000 h with a steady polarization voltage (Figure S6, Supporting Information). However, due to the dendrite and passivation of bare Zn electrode during cycling, the polarization voltage of bare Zn electrode fluctuates severely.

【对称电池分析】

## 【对称电池分析】

[4] H. Yan, S. Li, Y. Nan, S. Yang, B. Li, Ultrafast Zinc–Ion–Conductor Interface toward High-Rate and Stable Zinc Metal Batteries, Advanced Energy Materials, 11 (2021).

In order to prove that thicker MMT interface can improve electrochemical performance, Zn electrode with 40 µm protective layer was assembled into symmetrical cells. A longer and more stable cycle performance than that with 1.5 µm protective layer (360 h vs 240 h at 2 mA cm−2, 125 h vs 90 h at 10 mA cm−2) is shown in Figure S7, Supporting Information. The above results indicate that a thicker MMT interface can still achieve an efficient and stable electrochemical performance. 【CE分析性能优势】

## 对称电池循环后电极分析】

[5] K. Leng, G. Li, J. Guo, X. Zhang, A. Wang, X. Liu, J. Luo, A Safe Polyzwitterionic Hydrogel Electrolyte for Long-Life Quasi-Solid State Zinc Metal Batteries, Advanced Functional Materials, 30 (2020).

Observing the morphology of Zn metal anode after cycling at a current density of 0.5, 1, and 3 mA cm−2, dense deposition morphology can be observed even after 3500, 2000, and 500 h cycle in PZHE (Figure 3d–f; Figure S8, Supporting Information), indicating that the PZHE may homogenize the ion distribution near Zn metal anode surface. Based on the comparison between Figures S9 and S10, Supporting Information, the surface of symmetrical cell using PZHE contains less sulfate radicals, indicating that the charged groups in PZHE immobilize the anions and evenly distribute the Zn2+ on anode. What is more, PZHE immobilizes the water molecules through hydrogen bonding and electrostatic interaction for less side reactions and corrosion. The synergistic effect enables the Zn/PZHE/Zn symmetric cells with excellent long cycling performance. Vanadium disulfide (VS2) is a promising cathode material for aqueous ZMBs, which can be well matched with Zn metal anode. Herein, the VS2 positive material is prepared on a stainless steel (SS) mesh through a hydrothermal synthesis method. The SS with good conductivity is used as a conductive skeleton. 【XRD、SEM、TEM、EDS分析】

## 【对称电池性能分析】

[7] L. Zhang, B. Zhang, T. Zhang, T. Li, T. Shi, W. Li, T. Shen, X. Huang, J. Xu, X. Zhang, Z. Wang, Y. Hou, Eliminating Dendrites and Side Reactions via a Multifunctional ZnSe Protective Layer toward Advanced Aqueous Zn Metal Batteries, Advanced Functional Materials, (2021).

After three cycles of activation at 0.5 mA cm−2, the Zn@ZnSe symmetric cell exhibits an ultralong and stable lifespan (1500 h) at 10 mA cm−2, while the Zn cell has a sharp increase and fluctuation in voltage after only 120 h. The stable cycling life of the Zn@ZnSe cell is almost 12.5 times longer than that of the Zn cell. It is worth noting that the polarization voltage of the Zn@ZnSe symmetric cell is as low as 82 mV after 378 h of operation, which is only 21.4% of the Zn cell (383 mV) (the inset of Figure 2e). Moreover, even after 1500 h, the polarization voltage of the Zn@ZnSe cell increases by only 23 mV (to 105 mV), which is superior to that of most Zn anodes in aqueous Zn-ion batteries (Table S1, Supporting Information). This result is key evidence that the ZnSe protective layer can effectively inhibit the growth of Zn dendrites and the occurrence of side reactions during long-term cycling at a high rate. The above result was further validated by the electrochemical impedance spectroscopy (EIS) curves of the symmetric cells before and after cycling (Figure S10, Supporting Information).

2.3. Electrochemical Properties of the Full Cells

【全电池CV分析】

## 【对称电池测试】

[7] L. Zhang, B. Zhang, T. Zhang, T. Li, T. Shi, W. Li, T. Shen, X. Huang, J. Xu, X. Zhang, Z. Wang, Y. Hou, Eliminating Dendrites and Side Reactions via a Multifunctional ZnSe Protective Layer toward Advanced Aqueous Zn Metal Batteries, Advanced Functional Materials, (2021).

To further verify whether the ZnSe protective layer can still function at a high rate with a large areal capacity, a cycling test of the symmetric cells was carried out at 10 mA cm−2 with 5 mAh cm−2. Figure 5c shows that the bare Zn cell has an irreversible polarization voltage surge after only 5 cycles and continues to fluctuate until a short circuit occurs only 25 h later. Figure S22 in the Supporting Information clearly shows that starting from 25 h, the overpotential drops sharply from over 2.5 V to ≈50 mV, which is mainly because Zn dendrites pierce the separator, allowing the cathode and anode to be in direct contact.[40] It should be noted that in the first 10 h after the short circuit (25–35 h), although the curve fluctuates, the stripping/plating process still has a certain reversibility, clearly demonstrating a soft short-circuit phenomenon caused by the recoverable local contact. However, as cycling continues (35–40 h), it is apparent that the voltage signal appears to be a basically constant low value (the response signal is a straight line), and the specific value only depends on the magnitude or direction of the applied current (inset of Figure 5c). 【锌阳极失效原因】

## 【锌阳极失效原因】

[7] L. Zhang, B. Zhang, T. Zhang, T. Li, T. Shi, W. Li, T. Shen, X. Huang, J. Xu, X. Zhang, Z. Wang, Y. Hou, Eliminating Dendrites and Side Reactions via a Multifunctional ZnSe Protective Layer toward Advanced Aqueous Zn Metal Batteries, Advanced Functional Materials, (2021).

This behavior clearly demonstrates an irreversible hard short- circuit phenomenon, suggesting a complete short circuit and the failure of the battery due to the accumulation of dendrites.[41] Thus, under such severe conditions, uncontrollable Zn dendrite growth causes rapid failure of the unprotected Zn anode. Conversely, the Zn@ZnSe cell can stabilize for more than 160 h under these harsh conditions, with an average polarization voltage of only ≈50 mV. Such excellent electrochemical stability exceeds that of most work that has been reported so far (Table S1, Supporting Information) and strongly demonstrates the effectiveness of the ZnSe protective layer in regulating Zn2+ deposition and inhibiting dendrite growth.

2.6. Revealing the Mechanism of Dendrite Inhibition

【！！！人工界面保护层，电导率、Zn亲和力和Zn2+迁移对枝晶的形成和生长都至关重要】

## 【！！！人工界面保护层，电导率、Zn亲和力和Zn2+迁移对枝晶的形成和生长都至关重要】

[7] L. Zhang, B. Zhang, T. Zhang, T. Li, T. Shi, W. Li, T. Shen, X. Huang, J. Xu, X. Zhang, Z. Wang, Y. Hou, Eliminating Dendrites and Side Reactions via a Multifunctional ZnSe Protective Layer toward Advanced Aqueous Zn Metal Batteries, Advanced Functional Materials, (2021).

For an artificial interfacial protective layer, the electrical conductivity, Zn affinity and Zn2+ migration are all critical to dendrite formation and growth. 【！！！dft计算分析和细节阐述】

## 【对称电池测试、原位检测】

[8] J. Hao, B. Li, X. Li, X. Zeng, S. Zhang, F. Yang, S. Liu, D. Li, C. Wu, Z. Guo, An In-Depth Study of Zn Metal Surface Chemistry for Advanced Aqueous Zn-Ion Batteries, Advanced Materials, 32 (2020).

To confirm the suppression of Zn dendrite growth by the ZnS artificial layer, transparent symmetric cells were assembled to in situ monitor the Zn plating/stripping behavior using an optical microscope equipped with a digital camera. A high current density of 5 mA cm−2 with 10 min of intermittence was applied to repeatedly conduct plating/stripping measurements. 【循环后SEM分析】

## 【循环后SEM分析】

[8] J. Hao, B. Li, X. Li, X. Zeng, S. Zhang, F. Yang, S. Liu, D. Li, C. Wu, Z. Guo, An In-Depth Study of Zn Metal Surface Chemistry for Advanced Aqueous Zn-Ion Batteries, Advanced Materials, 32 (2020).

Figure 4a presents images of a bare Zn electrode after different plating/stripping cycles. Before cycling, the bare Zn electrode displays a smooth edge. After 50 cycles, protrusions start to grow along the edge of the bare Zn electrode, which evidences uneven Zn plating. These protrusions gradually turns into Zn dendrites on the Zn electrode with further cycling. In strong comparison, the ZnS@Zn-350 electrode exhibits smooth Zn plating and stripping in Figure 4b. There is still no sign of protrusions or Zn dendrite generation, even after 250 cycles. SEM was further conducted to observe the Zn electrodeposition with/without the ZnS protective layer. Zn deposition was conducted under 1 mA cm−2 with the deposition capacity of 1 and 2 mA h cm−2, respectively. 【截面SEM分析】

## 【对称电池分析】

[8] J. Hao, B. Li, X. Li, X. Zeng, S. Zhang, F. Yang, S. Liu, D. Li, C. Wu, Z. Guo, An In-Depth Study of Zn Metal Surface Chemistry for Advanced Aqueous Zn-Ion Batteries, Advanced Materials, 32 (2020).

The stability of Zn metal anode with/without a ZnS layer was evaluated by long-term galvanostatic cycling of the symmetrical cells (Figure 5a). After cycling for ≈100 h at 2 mA cm−2, a sudden reduction of the polarization voltage appeared in the bare Zn cell, which might be ascribed to a dynamic dendrite-induced short circuit. In contrast, the ZnS@Zn-350 cell displayed prolonged cycling stability for more than 1100 h. Figure 5b compares the first charge-discharge voltage profiles of both cells. The ZnS@Zn-350 cell delivers a polarization voltage of ≈98 mV, much lower than that of the bare Zn cell (≈153 mV), indicating its low energy barrier for Zn deposition. Even after 40 cycles, the bare Zn cell still maintains a large polarization voltage (Figure S23, Supporting Information). One of the probable reasons for the high energy barrier is that the accumulation of detrimental by-products may

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block the conduction of ions.[28] 【倍率性能分析】

# DFT

**【TBA+添加剂的优势-添加量少】**

[1] 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 Letters, 5 (2020) 3012-3020.

It is noteworthy that compared with other electrolyte additives that have been reported for Zn dendrite inhibition, a minimum addition amount of 0.029 g L−1 is achieved in our work by virtue of the unique zincophobic repulsion ability of the surface-adsorbed cationic surfactant-type additive TBA+. 【与其他添加剂对比-价格，毒性和用量】

【与其他添加剂对比-价格，毒性和用量】

[1] 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 Letters, 5 (2020) 3012-3020.

Considering the price, toxicity, and amount used, our proposed cationic surfactant-type electrolyte additive exhibits obvious advantages compared with other reported types of additives, showing great potential for practical applications (Table S1). 【为验证表面吸附TBA+离子对Zn2+离子镀过程的疏锌排斥机制，进行了DFT计算】

**【为验证表面吸附TBA+离子对Zn2+离子镀过程的疏锌排斥机制，进行了DFT计算】**

[1] 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 Letters, 5 (2020) 3012-3020.

To verify the zincophobic repulsion mechanisms of surfaceadsorbed TBA+ cations on the plating process of Zn2+ ions, DFT calculations were conducted. 【DFT计算描述-计算模型】

**【DFT计算描述-计算模型】**

[1] 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 Letters, 5 (2020) 3012-3020.

As shown in Figure 3e, our calculation model consists of a single TBA+ cation adsorbed on the Zn(0002) surface and a moving hydrated Zn2+ ion. 【DFT结果-锌离子向电极表面迁移能垒高，表明TBA+离子对Zn2+离子扩散有屏蔽作用】

**【DFT结果-锌离子向电极表面迁移能垒高，表明TBA+离子对Zn2+离子扩散有屏蔽作用】**

[1] 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 Letters, 5 (2020) 3012-3020.

As the calculated potential energy results presented in Figure 3f show, there is an energy barrier of ∼0.55 eV when a hydrated Zn2+ ion passes through the TBA+ cation layer toward the Zn surface, indicating a shielding effect of the TBA+ cation on Zn2+ ion diffusion. 【迁移能垒对比解释】

**【迁移能垒对比解释】**

[1] 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 Letters, 5 (2020) 3012-3020.

这个能量势垒会导致锌在TBA+覆盖区域缓慢沉积。相比之下，我们也模拟了水合Zn2+离子在整洁的Zn表面没有TBA+离子的吸附过程(图S7)，计算结果给出了平滑的势能下降曲线(图3f)，表明Zn2+在整洁的Zn表面的吸附过程具有动态优势。It is clear that this energy barrier would lead to a sluggish Zn deposition in the TBA+ covered area. In comparison, the adsorption process of a hydrated Zn2+ ion on a neat Zn surface without a TBA+ cation was also simulated (Figure S7), and the calculation results gave a smooth potential energy decrease curve (Figure 3f), indicating a dynamically favored Zn2+ adsorption process on a clean Zn surface. 【DFT计算与实际区别-与模拟系统不同的是，实际溶液中TBA+层的屏蔽效果会增强，因为Zn阳极表面吸附的TBA+离子层密度更大。】

5. DFT calculation method

Density function theory calculations were performed by using the CP2K package

[R1]. PBE functional [R2] with Grimme D3 correction [R3] was used to describe the system. Kohn-Sham DFT was used as the electronic structure method in the framework of the Gaussian and plane waves method [R4,5]. The Goedecker-Teter-Hutter (GTH) pseudopotentials [R6,7], DZVP-MOLOPT-GTH basis sets [R4] were used to describe the molecules. A plane-wave energy cut-off of 500 Ry has been employed. All the simulation has been carried out within a 13.65×15.76×353 box under

periodic boundary condition. On the Z direction, there is about 15 Å vacuum to decouple the interaction between the images. A four-layer Zn (0002) surface has been used to model the surface and the bottom two layers are kept fixed to maintain bulk property. To gain more insight, we further carry out DFT simulation. The distance between

Zn(H2O)6 2+ and Zn (0002) surface is shown in Figure 3e. When the Zn(H2O)6 2+ is adsorbed on the Zn surface, the Zn-Znsur distance is about 4 angstrom. To gain more insight into the interaction between Zn(H2O)6 2+ complex and Zn surface, we further scan the distance from 4 to 14 angstrom with respect to the Zn surface.

## 【DFT分析亲锌性】

[3] F. Xie, H. Li, X. Wang, X. Zhi, D. Chao, K. Davey, S.Z. Qiao, Mechanism for Zincophilic Sites on Zinc-Metal Anode Hosts in Aqueous Batteries, Advanced Energy Materials, 11 (2021).

We, therefore, conducted DFT computations to compare zincophilic ability of nitrogen and carbon in graphene models (Figure S3, Supporting Information). 【计算内容分析】

## 【计算内容分析】

[3] F. Xie, H. Li, X. Wang, X. Zhi, D. Chao, K. Davey, S.Z. Qiao, Mechanism for Zincophilic Sites on Zinc-Metal Anode Hosts in Aqueous Batteries, Advanced Energy Materials, 11 (2021).

As is shown in Figure 2a, atomic charges of graphene and nitrogen-doped graphene were estimated by Bader charge analysis.[47] As is seen in the figure, there is an apparent significant redistribution of charge density following the introduction of an electronegative N-atom. According to the Bader charge analysis, the calculated Bader charge on nitrogen is −1.1741 e. The carbonatom at a corresponding position exhibits a charge density of 0.0036 e. Therefore, the introduction of nitrogen significantly changes the charge distribution of graphene to create a site with increased zincophilicity.[6,37,41,48] The configurations of zinc adsorption on different sites on carbon substrates are illustrated

in Figure S4 in the Supporting Information. 【理论模型电子累积与消耗】

## 【理论模型电子累积与消耗】

[3] F. Xie, H. Li, X. Wang, X. Zhi, D. Chao, K. Davey, S.Z. Qiao, Mechanism for Zincophilic Sites on Zinc-Metal Anode Hosts in Aqueous Batteries, Advanced Energy Materials, 11 (2021).

According to the theoretical model results, shown as Figure 2b, the charge transfer from N-doped graphene to zinc on different adsorption sites is more negative than that between zinc and graphene. In the charge transfer results, the yellow-color and light bluecolor regions in Figure 2c represent, respectively, electron accumulation and depletion. 【电荷密度分析价键结合】

## 【电荷密度分析价键结合】

[3] F. Xie, H. Li, X. Wang, X. Zhi, D. Chao, K. Davey, S.Z. Qiao, Mechanism for Zincophilic Sites on Zinc-Metal Anode Hosts in Aqueous Batteries, Advanced Energy Materials, 11 (2021).

In the figure (indicated by red) of the charge density between zinc-atom and graphene model without nitrogen-doping, most of the electron accumulation of zinc is located at the top of the zinc atom. 【锌吸附分析：氮的引入促进了锌的结合】

## 【锌吸附分析：氮的引入促进了锌的结合】

[3] F. Xie, H. Li, X. Wang, X. Zhi, D. Chao, K. Davey, S.Z. Qiao, Mechanism for Zincophilic Sites on Zinc-Metal Anode Hosts in Aqueous Batteries, Advanced Energy Materials, 11 (2021).

Whereas in the nitrogendoped graphene model (indicated by lavender blue), the charge density between zinc-atom and nitrogen-doped graphene is significantly denser. This finding confirms that the introduction of nitrogen boosts the binding between the carbon substrate and zinc. 【结合能分析亲锌性的改善】

## 【结合能分析亲锌性的改善】

[3] F. Xie, H. Li, X. Wang, X. Zhi, D. Chao, K. Davey, S.Z. Qiao, Mechanism for Zincophilic Sites on Zinc-Metal Anode Hosts in Aqueous Batteries, Advanced Energy Materials, 11 (2021).

As is shown in Figure 2d, the binding energies of zinc-atom on different adsorption sites on graphene are, respectively, 0.030 (Top), 0.014 (Hollow), and 0.029 (Bridge) eV. For the adsorption sites on N-doped graphene, the corresponding binding energies are, respectively, −0.072 (Top), −0.089 (Hollow), and −0.076 (Bridge) eV.[6,37,41] This finding underscores that the introduction of nitrogen-doping changes the interaction of zinc and carbon substrate from zincophobic to zincophilic.

【石墨烯上的氮位比碳位更亲锌】

## 【石墨烯上的氮位比碳位更亲锌】

[3] F. Xie, H. Li, X. Wang, X. Zhi, D. Chao, K. Davey, S.Z. Qiao, Mechanism for Zincophilic Sites on Zinc-Metal Anode Hosts in Aqueous Batteries, Advanced Energy Materials, 11 (2021).

Based on the consequent increased local charge densities, charge transfer, and favorable thermodynamics, it is proposed that nitrogen-sites are more zincophilic than carbon-sites on graphene. This finding, therefore, makes this a suitable zincophilic model site to investigate the mechanism of zincophilic sites. Because introducing nitrogen sites boosted zincophilicity of the carbon host, carbon spheres with nitrogen zincophilic sites were synthesized following a layer-by-layer strategy, as is illustrated in Figure S5 in the Supporting Information. 【形貌形成原因分析】

## 【DFT证明活性位点】

[3] F. Xie, H. Li, X. Wang, X. Zhi, D. Chao, K. Davey, S.Z. Qiao, Mechanism for Zincophilic Sites on Zinc-Metal Anode Hosts in Aqueous Batteries, Advanced Energy Materials, 11 (2021).

It is concluded that, as the intensities of Raman spectra are normalized to G-band peak, the intensity of pyridine decreases faster than the G band peak of graphene (≈1580 cm−1). This finding demonstrates that pyridine-nitrogen sites are more electrochemically active than the graphitic carbon. The electrochemical activity of pyridinic nitrogen was confirmed by DFT computation (Figure S14, Supporting Information). As is shown in Figure S15 in the Supporting Information, the pyridine nitrogen site (hollow-1) exhibited greater charge transfer and stronger binding energy than other adsorption sites (Figure 2). Further, the recovery of the pyridine-nitrogen peak in the in situ Raman spectra (Figure S16, Supporting Information) following an entire zinc plating/stripping process demonstrates reversibility of the zincophilic site. 【SEM分析亲锌位点促进锌均匀沉积】

## 【SEM分析亲锌位点促进锌均匀沉积】

[3] F. Xie, H. Li, X. Wang, X. Zhi, D. Chao, K. Davey, S.Z. Qiao, Mechanism for Zincophilic Sites on Zinc-Metal Anode Hosts in Aqueous Batteries, Advanced Energy Materials, 11 (2021).

To explore the impact of the zincophilic sites, and the formation of Zn-N bonds, ex situ SEM was conducted to gain an understanding at a more macroscopic level. From ex situ SEM image with lower magnifications (Figure 3d), most of the zinc deposited on CnC HS substrate exhibits a planar-morphology. The SEM image of C HS substrate (Figure 3e) suggested that a significant amount of zinc-dendrite is generated following the deposition of zinc. This finding suggests that the zincophilic site guides the growth of zinc deposition, and induces a homogenous deposition.[6,13,16]

【！！！亲锌位点工作机制分析】

## 【！！！亲锌位点工作机制分析】

[3] F. Xie, H. Li, X. Wang, X. Zhi, D. Chao, K. Davey, S.Z. Qiao, Mechanism for Zincophilic Sites on Zinc-Metal Anode Hosts in Aqueous Batteries, Advanced Energy Materials, 11 (2021).

Based on these findings, a working mechanism of zincophilic sites is proposed and is illustrated in Figure 3f. Initially, zincophilic sites bond with Zn ions. The pyridine-nitrogen sites form Zn-N bonds with Zn ions. Because of a wide distribution of zincophilic sites, the distribution of Zn nuclei is spacious

. Due to these spacious nuclei, the growth of Zn leads to connections nearby to promote Zn clusters that cover the carbon surface, resulting in homogenous deposition of Zn. 【！！！没有亲锌位点导致枝晶的原因】

## 【！！！没有亲锌位点导致枝晶的原因】

[3] F. Xie, H. Li, X. Wang, X. Zhi, D. Chao, K. Davey, S.Z. Qiao, Mechanism for Zincophilic Sites on Zinc-Metal Anode Hosts in Aqueous Batteries, Advanced Energy Materials, 11 (2021).

For a host without zincophilic sites, Zn deposition is as proposed in Figure 3g. Because of the absence of zincophilic sites, the formation of initial nuclei is dense. The dense nuclei give rise to a dense distribution of nucleation sites that triggers the preferential deposition of Zn at tip-spots (nucleation sites).[32] 【！！！有无亲锌位点的原理分析】

## 【！！！有无亲锌位点的原理分析】

[3] F. Xie, H. Li, X. Wang, X. Zhi, D. Chao, K. Davey, S.Z. Qiao, Mechanism for Zincophilic Sites on Zinc-Metal Anode Hosts in Aqueous Batteries, Advanced Energy Materials, 11 (2021).

The result is a non-uniform Zn deposition morphology together with

dendritic zinc. It is concluded, therefore, that the mechanism of zincophilic sites is the formation of bonds between zinc-ion and zincophilic sites. These bonds induce homogenous deposition of Zn and suppresses zinc-dendrite formation. To determine the impact of introducing nitrogen zincophilic sites on electrochemical performance, zinc-metal anode tests were conducted. 【电化学循环分析】

## 【DFT计算分析】

[6] M. Liu, J. Cai, H. Ao, Z. Hou, Y. Zhu, Y. Qian, NaTi2(PO4)3 Solid-State Electrolyte Protection Layer on Zn Metal Anode for Superior Long-Life Aqueous Zinc-Ion Batteries, Advanced Functional Materials, 30 (2020).

As the solid-state electrolyte protection layer for Zn metal anode, zinc-ions’ migration and electronic conductivity play an important role in the dynamic plating/stripping process of Zn metal and charge-transfer resistance, which is the same as Li anode.[13] To screen out fast zinc-ion conductivity and weak electronic conductivity, we carried out DFT calculations. The calculated density of states in Figure 2a exhibit that the band gap of NTP, TPO, and ZPO are all between 0.5 and 4.5 eV, indicating that these three phosphates having weak conductivity are all semiconductors. The crystal structures in Figure S1, Supporting Information, were used for calculations. The lantern framework of NTP is consisted of octahedral TiO6 and tetrahedral PO4. Na atoms in the formation of six-coordination Na-O exist in the crystal voids. The crystal structure analysis shows that the remaining voids consist of eight oxygen atoms can be used for the migration of zinc ions (Figure S2, Supporting Information). Octahedral TiO6 and tetrahedral PO4 also exist in TPO (Figure S3, Supporting Information). The structure of ZPO containing tetrahedral ZnO4 and PO4 is completely different from that of NTP and TPO. The tetrahedral void shown in Figure S4, Supporting Information, can accommodate zinc ion.【迁移势垒分析】

## 【迁移势垒分析】

[6] M. Liu, J. Cai, H. Ao, Z. Hou, Y. Zhu, Y. Qian, NaTi2(PO4)3 Solid-State Electrolyte Protection Layer on Zn Metal Anode for Superior Long-Life Aqueous Zinc-Ion Batteries, Advanced Functional Materials, 30 (2020).

After determining the capacity of zinc ions in the interstitial site, the proposed migration pathways of zinc ion between adjacent voids are hinted in Figure 2b–d for NTP, TPO, and ZPO, respectively. The calculated migration barriers exhibited in Figure 2e imply that compared with TPO and ZPO with high migration barrier of 0.86 and 1.30 eV, respectively, the migration barrier is reduced to 0.52 eV in NTP, suggesting the fastest zinc-ion diffusion in NTP. The lower migration barrier means a faster ion migration and charge rate, which both contribute to the improved zinc stripping/plating kinetics. 【！！CV分析扩散动力学】

## 【！！！dft计算分析和细节阐述】

[7] L. Zhang, B. Zhang, T. Zhang, T. Li, T. Shi, W. Li, T. Shen, X. Huang, J. Xu, X. Zhang, Z. Wang, Y. Hou, Eliminating Dendrites and Side Reactions via a Multifunctional ZnSe Protective Layer toward Advanced Aqueous Zn Metal Batteries, Advanced Functional Materials, (2021).

DFT calculations were performed to systematically and deeply analyze the mechanism of dendrite inhibition at the atomic level. First, the calculated density of state (DOS) (Figure 6a) shows that the band gap of ZnSe is 2.17 eV, implying that ZnSe is a semiconductor with weak electrical conductivity. For such an insulating protective layer, better Zn2+ migration is needed to realize the effective regulation of Zn dendrites.[42] Next, we calculated the adsorption energy of Zn atoms to investigate the Zn affinity of ZnSe. Different from previous reports, we adopted a polyatomic adsorption system instead of a monatomic adsorption system because polyatomic adsorption is closer to the actual state. Zn and ZnSe were simulated by slab models of the (001) surface (common facet) and (111) surface (exposed facet; Figure S23, Supporting Information), respectively, as shown in Figure S24 in the Supporting Information. Figure 6b,c displays the optimized configurations of Zn atoms adsorbed on the surfaces of Zn and ZnSe. The adsorption energy between Zn atoms and the Zn (001) surface is −1.136 eV, much higher than that between Zn atoms and the ZnSe (111) surface (−0.293 eV), indicating that ZnSe has a lower Zn affinity. This result is mainly because the electron density around the exposed Zn atom of the ZnSe (111) surface is reduced due to the effect of bonding with the Se atom, so that the ZnSe (111) surface is more repulsive to the adsorbed Zn atoms. The low migration barrier (0.76 eV) of Zn ions on the ZnSe (111) surface further illustrates the low Zn affinity of ZnSe (Figure 6d). The migration pathway of Zn ions on the ZnSe (111) surface is exhibited in Figure S25 in the Supporting Information. Such a low Zn affinity can ensure that Zn2+ does not tend to deposit on the protective layer and invalidate the protection. More importantly, this low Zn affinity can promote the enrichment of Zn2+ at the interface between the anode surface, and electrolyte, increasing the interfacial Zn2+ concentration, which is conducive to the uniform nucleation and deposition of Zn2+.[14] 【保护层对迁移行为的计算】

## 【保护层对迁移行为的计算】

[7] L. Zhang, B. Zhang, T. Zhang, T. Li, T. Shi, W. Li, T. Shen, X. Huang, J. Xu, X. Zhang, Z. Wang, Y. Hou, Eliminating Dendrites and Side Reactions via a Multifunctional ZnSe Protective Layer toward Advanced Aqueous Zn Metal Batteries, Advanced Functional Materials, (2021).

We further studied the Zn2+ migration behavior through the ZnSe protective layer on the Zn surface. The interface between Zn and ZnSe was simulated by combining slab models of the Zn (001) and ZnSe (111) surfaces. 【电荷分布变化促进Zn2+快速迁移分析】

## 【电荷分布变化促进Zn2+快速迁移分析】

[7] L. Zhang, B. Zhang, T. Zhang, T. Li, T. Shi, W. Li, T. Shen, X. Huang, J. Xu, X. Zhang, Z. Wang, Y. Hou, Eliminating Dendrites and Side Reactions via a Multifunctional ZnSe Protective Layer toward Advanced Aqueous Zn Metal Batteries, Advanced Functional Materials, (2021).

Figure 6e shows that the Se atoms (from the ZnSe layer) and Zn atoms (from the Zn anode) at the interface have bonding interactions. These interactions change the charge distribution of the interface and results in an unbalanced charge distribution, as shown in the electron density difference maps (Figure 6f,g). The local internal driving force induced by an unbalanced charge distribution can promote the rapid migration of Zn2+ toward the anode to realize uniform Zn2+ deposition under the protective layer and the inhibition of dendrite growth.[27,43,44] In contrast, this driving force for positively charged Zn2+ is instead repulsive for negatively charged anions (SO42− and OH−), which prevents them from approaching the Zn metal surface, thus ensuring that they cannot trigger side reactions. 【dft计算插层能】

## 【dft计算插层能】

[7] L. Zhang, B. Zhang, T. Zhang, T. Li, T. Shi, W. Li, T. Shen, X. Huang, J. Xu, X. Zhang, Z. Wang, Y. Hou, Eliminating Dendrites and Side Reactions via a Multifunctional ZnSe Protective Layer toward Advanced Aqueous Zn Metal Batteries, Advanced Functional Materials, (2021).

To verify that these charge distribution changes can promote rapid Zn2+ migration and deposition to the anode surface, the Zn2+ intercalation energy was further calculated. Figure S26 in the Supporting Information shows that the intercalation of Zn2+ on the bare Zn surface needs to overcome an energy barrier of 0.889 eV, while on the Zn surface with bonded Se atoms, the intercalation of Zn2+ only requires an energy barrier of 0.186 eV, implying faster Zn2+ migration and deposition on the Zn surface with bonded Se atoms.[27] These results further illustrate that the ZnSe protective layer plays an important role in promoting the migration and deposition of Zn2+. 【离子迁移数计算】

## 【离子迁移数计算】

[7] L. Zhang, B. Zhang, T. Zhang, T. Li, T. Shi, W. Li, T. Shen, X. Huang, J. Xu, X. Zhang, Z. Wang, Y. Hou, Eliminating Dendrites and Side Reactions via a Multifunctional ZnSe Protective Layer toward Advanced Aqueous Zn Metal Batteries, Advanced Functional Materials, (2021).

The Zn2+ transference number (tZn +2 ) was calculated to quantify the

ability of the ZnSe protective layer to promote Zn2+ migration. As shown in Figure S27 in the Supporting Information, tZn +2 increases significantly from 0.22 in the bare Zn symmetric cell to 0.43 in the Zn@ZnSe symmetric cell, which strongly illustrates the effectiveness of the ZnSe protective layer. 【！！！抑制枝晶生长的机理分析】

## 【！！！抑制枝晶生长的机理分析】

[7] L. Zhang, B. Zhang, T. Zhang, T. Li, T. Shi, W. Li, T. Shen, X. Huang, J. Xu, X. Zhang, Z. Wang, Y. Hou, Eliminating Dendrites and Side Reactions via a Multifunctional ZnSe Protective Layer toward Advanced Aqueous Zn Metal Batteries, Advanced Functional Materials, (2021).

According to the above analyses, the success of this strategy in regard to dendrite inhibition can be attributed to the following key factors. First, the low Zn affinity of ZnSe leads to an increase in the concentration of Zn2+ at the electrolyte–ZnSe interface, thus promoting a uniform Zn2+ flux. Second, the unbalanced charge distribution on the ZnSe–Zn interface accelerates the migration of Zn ions so that they can be quickly deposited on the Zn metal surface before uniformly nucleating and growing. Finally, the ZnSe protective layer can eliminate interfacial side reactions, including corrosion and H2 evolution, to protect the uniform and undisturbed deposition of Zn2+. Based on these advantages, the ZnSe protective layer can perfectly inhibit the growth of Zn dendrites, thus providing a large improvement in electrochemical performance.

## 【！！！DFT分析成键作用】

[8] J. Hao, B. Li, X. Li, X. Zeng, S. Zhang, F. Yang, S. Liu, D. Li, C. Wu, Z. Guo, An In-Depth Study of Zn Metal Surface Chemistry for Advanced Aqueous Zn-Ion Batteries, Advanced Materials, 32 (2020).

According to a previous report,[20] the Zn (002) facet is transformed into ZnS (002) at the interphase of ZnS@Zn, as illustrated in Figure 3g. DFT calculations revealed that the bonding interaction occurs between the S atoms and Zn atoms in the Zn metal, which modifies the charge distribution (Figure 3h) and further leads to an unbalanced charge distribution at the interphase (Figure 3i). 【！！！不平衡电荷分布的作用】

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The unbalanced charge distribution not only accelerates the Zn2+ diffusion at the ZnS@Zn interphase, but also enhances the adhesion of the ZnS layer to the Zn metal.[21] Rolling and twisting experiments were also conducted to evaluate the adhesion between the ZnS layer and the Zn metal. As depicted in Figure S15 (Supporting Information), the ZnS@Zn-350 foil keeps its surface integrity after twisting to various degrees, suggesting good adhesion between the ZnS layer and the Zn metal.

【浸泡实验】

## 【DFT分析】

[9] L. Ma, Q. Li, Y. Ying, F. Ma, S. Chen, Y. Li, H. Huang, C. Zhi, Toward Practical High-Areal-Capacity Aqueous Zinc-Metal Batteries: Quantifying Hydrogen Evolution and a Solid-Ion Conductor for Stable Zinc Anodes, Advanced Materials, 33 (2021).

In theory, the corresponding differential charge density distribution of Zn@ ZnF2 is calculated by the density functional theory (DFT) to elucidate mechanism for the interaction between F atoms of ZnF2 layer and Zn atoms of Zn metal. Figure 2f displays that the geometrically optimized F element can distinctly induce charge transfer and redistribution at the Zn/ZnF2 interface. 【！！！二维等高线图切片电荷密度差分布分析扩散能垒】

## 【！！！二维等高线图切片电荷密度差分布分析扩散能垒】

[9] L. Ma, Q. Li, Y. Ying, F. Ma, S. Chen, Y. Li, H. Huang, C. Zhi, Toward Practical High-Areal-Capacity Aqueous Zinc-Metal Batteries: Quantifying Hydrogen Evolution and a Solid-Ion Conductor for Stable Zinc Anodes, Advanced Materials, 33 (2021).

We further slice the charge density difference distribution with 2D contour map showing the Zn-F bonds in Figure 2g. The unbalanced charge distribution can be clearly observed, with positive charge being accumulated around the Zn layer and negative charge distributed around Zn-F bonds. This can promote the formation of substantial Zn@ZnF2 interface and fast Zn2+ diffusion on the surface. Thus, the F atoms of ZnF2 layer can tightly bond with Zn atoms of Zn metal. The Zn2+ deposition mechanism is revealed by calculating the diffusion energy barrier of single Zn2+ on ZnF2(002) surface and ZnF2 bulk by the climbing image nudged elastic band method. As shown in Figure 2h, the energy barrier for Zn2+ diffusion on ZnF2 (002) surface is calculated to be 0.27 eV, while Zn2+ hopping in bulk ZnF2 represents a barrier as high as 0.76 eV determined by the same methods (the corresponding atomic structures are shown in Figure 2h (inset)), indicating that exposed ZnF2 (002) surface can greatly enhance the Zn2+ diffusion. 【！！！计算分析动力学】

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[9] L. Ma, Q. Li, Y. Ying, F. Ma, S. Chen, Y. Li, H. Huang, C. Zhi, Toward Practical High-Areal-Capacity Aqueous Zinc-Metal Batteries: Quantifying Hydrogen Evolution and a Solid-Ion Conductor for Stable Zinc Anodes, Advanced Materials, 33 (2021).

【！！！界面性能影响因素】

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[9] L. Ma, Q. Li, Y. Ying, F. Ma, S. Chen, Y. Li, H. Huang, C. Zhi, Toward Practical High-Areal-Capacity Aqueous Zinc-Metal Batteries: Quantifying Hydrogen Evolution and a Solid-Ion Conductor for Stable Zinc Anodes, Advanced Materials, 33 (2021).

As the ZnF2 layer covers the Zn metal electrode surface, the

front interface/phase between the Zn metal and the electrolyte plays a pivotal role in directing the growth mode. Prior to the study of Zn growth, the electrochemical properties of Zn layer are conducted including the ionic conductivity capability, electronic resistivity, and Zn2+ transfer number. 【电导率分析】

# 器件

## 【器件展示阐述】

[4] H. Yan, S. Li, Y. Nan, S. Yang, B. Li, Ultrafast Zinc–Ion–Conductor Interface toward High-Rate and Stable Zinc Metal Batteries, Advanced Energy Materials, 11 (2021).

In order to demonstrate the practical application of MMT-Zn||MMT-MnO2, we lighted up the “ZIB”-shape parallel light-emitting diodes via two MMT-Zn||MMT-MnO2 coin cells connected in series. 【改性界面功能分析】

## 【！！！柔性电池循环性能和器件分析】

[13] J. Zhao, H. Ren, Q. Liang, D. Yuan, S. Xi, C. Wu, W. Manalastas, Jr., J. Ma, W. Fang, Y. Zheng, C.F. Du, M. Srinivasan, Q. Yan, High-performance flexible quasi-solid-state zinc-ion batteries with layer-expanded vanadium oxide cathode and zinc/stainless steel mesh composite anode, Nano Energy, 62 (2019) 94-102.

Fig. 5 presents the configuration and electrochemical performances of flexible quasi-solid-state Zn/E-VO battery. The flexible Zn/E-VO batteries were assembled by sandwiching quasi-solid-state gelation/Zn(CF3SO3)2 electrolyte between the E-VO cathode and Zn/SS mesh anode (Fig. 5a). As can be seen from Fig. 1b, both the anode and cathode show quite good flexibility. At the current density of 0.1 A g−1, E-VO electrode delivers a capacity of 361 mAh g−1. When the current density increases to 2 A g−1, the capacity still maintains at 115 mAh g−1 (32% of the capacity under 0.1 A g−1), suggesting the good rate capability (Fig. 5c). Such a performance is even comparable to some reported aqueous ZIBs (Table S1) even though the ionic conductivity of gel electrolyte is lower. The DCD curves of the bending and recovering states almost overlap with the initial flat state, indicating the robust performance under deformation (Fig. 5d). At the current density of 1 A g−1, a stable discharge capacity of 183 mAh g−1 is obtained with a capacity retention of 85% after 300 cycles, attesting the excellent cycling stability (Fig. 5e). 【器件展示】

## 【器件展示】

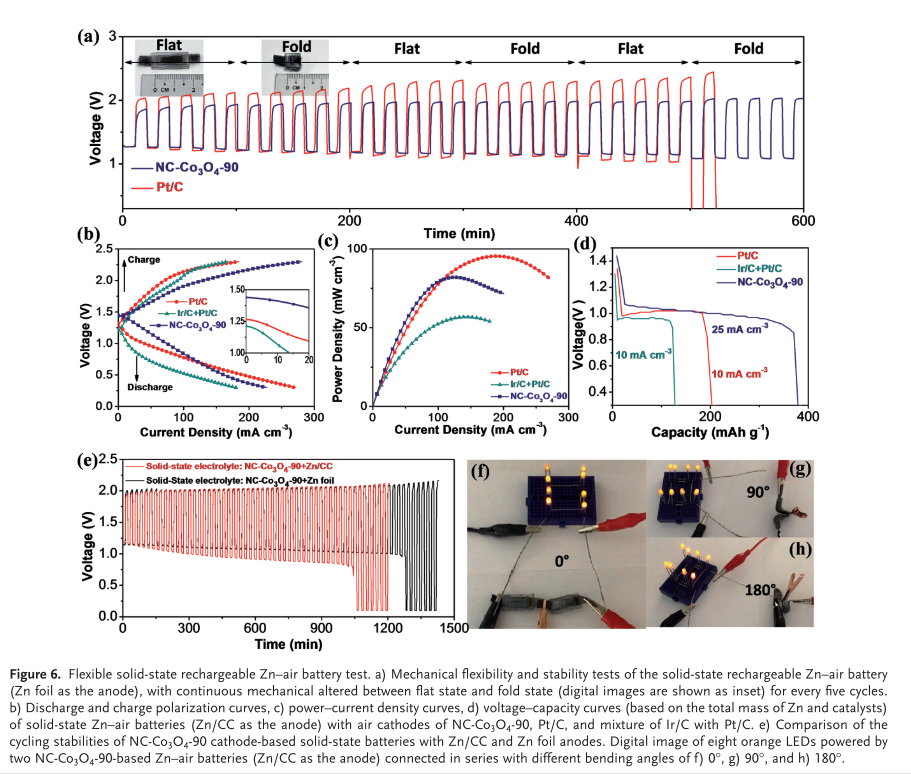
[13] J. Zhao, H. Ren, Q. Liang, D. Yuan, S. Xi, C. Wu, W. Manalastas, Jr., J. Ma, W. Fang, Y. Zheng, C.F. Du, M. Srinivasan, Q. Yan, High-performance flexible quasi-solid-state zinc-ion batteries with layer-expanded vanadium oxide cathode and zinc/stainless steel mesh composite anode, Nano Energy, 62 (2019) 94-102.

The demonstration shows one blue LED light up by two flat or bending quasi-solid-state Zn/E-VO batteries (insets in Fig. 5e). These results indicate a potential application of quasi-solid-state Zn/E-VO battery in flexible energy storage fields.

3. Conclusion In summary,【混合价态水间层分析，结论概括】

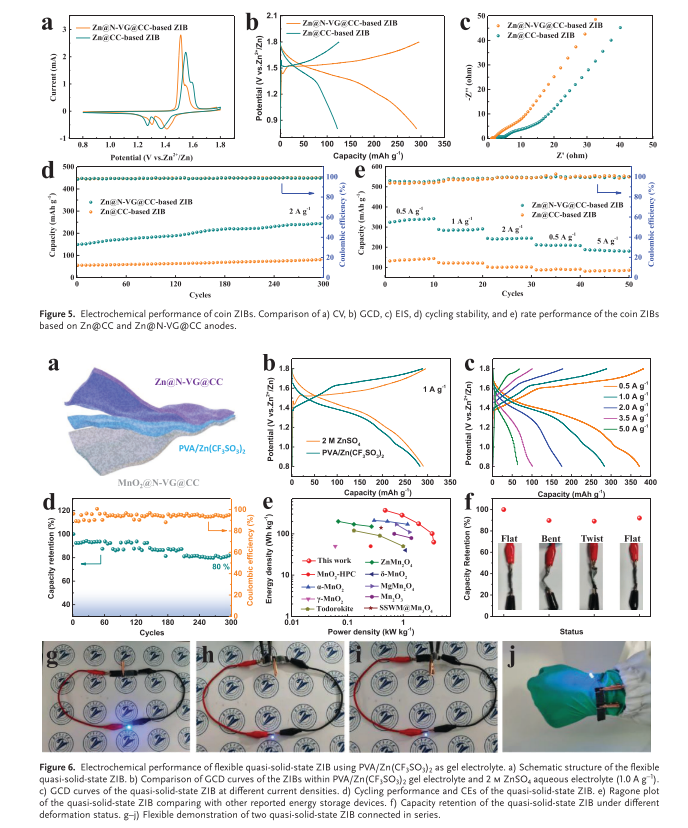
**【图6-弯折循环曲线、能量密度、器件展示】**

[14] C. Guan, A. Sumboja, H. Wu, W. Ren, X. Liu, H. Zhang, Z. Liu, C. Cheng, S.J. Pennycook, J. Wang, Hollow Co3O4 Nanosphere Embedded in Carbon Arrays for Stable and Flexible Solid-State Zinc–Air Batteries, Advanced Materials, 29 (2017).



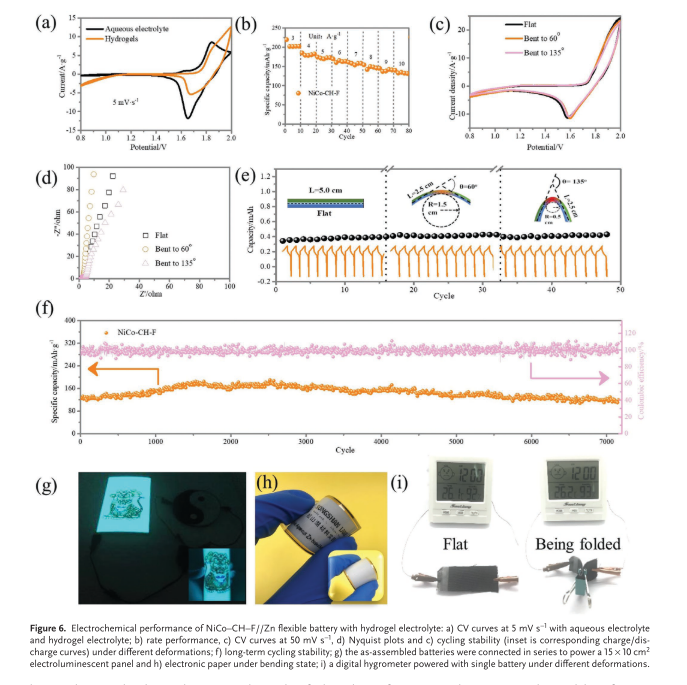
**【图5-CV、EIS、倍率、循环、弯折、器件展示、能量密度、电池示意图】**

[2] Q. Cao, H. Gao, Y. Gao, J. Yang, C. Li, J. Pu, J. Du, J. Yang, D. Cai, Z. Pan, C. Guan, W. Huang, Regulating Dendrite-Free Zinc Deposition by 3D Zincopilic Nitrogen-Doped Vertical Graphene for High-Performance Flexible Zn-Ion Batteries, Advanced Functional Materials, 31 (2021).



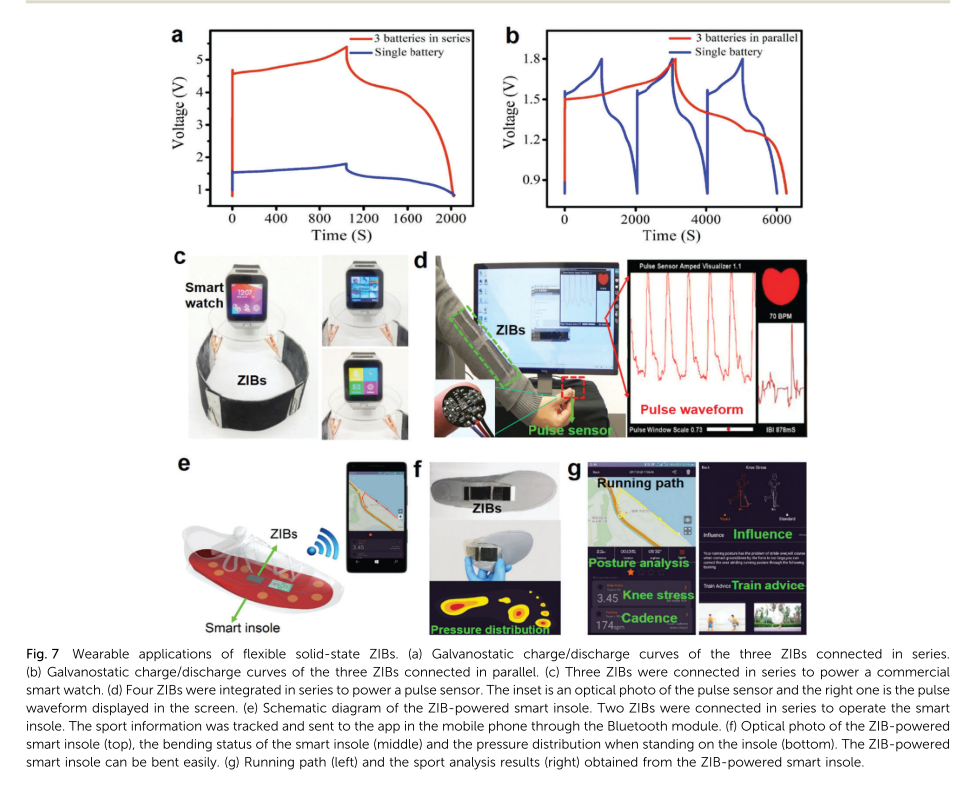
**【图6-循环、阻抗、倍率、弯折、器件展示】**

[5] X. Li, Y. Tang, J. Zhu, H. Lv, L. Zhao, W. Wang, C. Zhi, H. Li, Boosting the Cycling Stability of Aqueous Flexible Zn Batteries via F Doping in Nickel–Cobalt Carbonate Hydroxide Cathode, Small, 16 (2020).



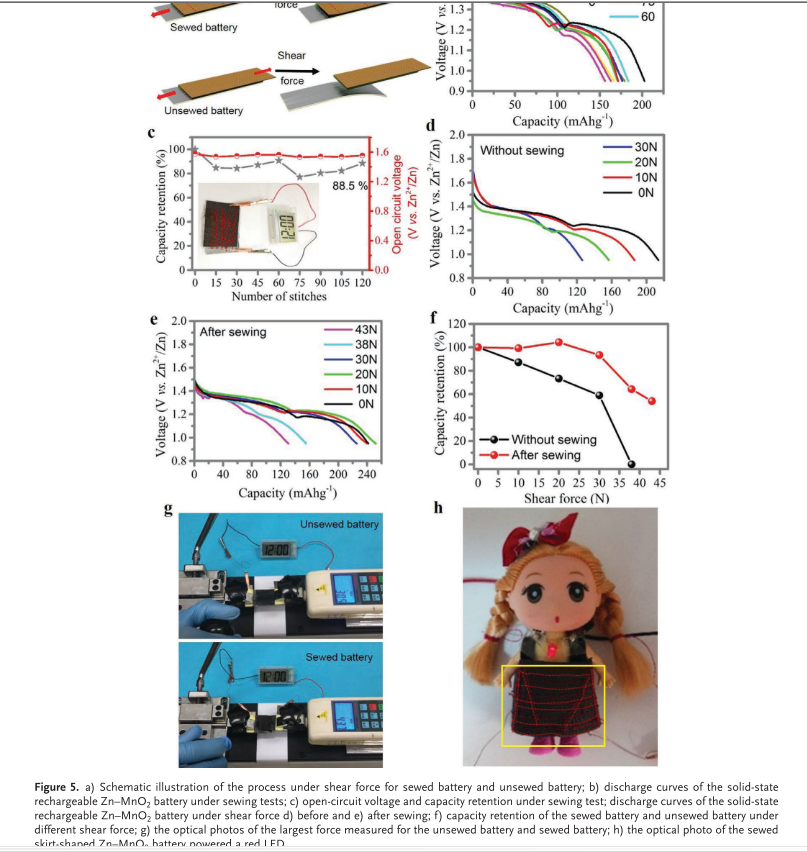
**【图7-器件展示】**

[12] H. Li, C. Han, Y. Huang, Y. Huang, M. Zhu, Z. Pei, Q. Xue, Z. Wang, Z. Liu, Z. Tang, Y. Wang, F. Kang, B. Li, C. Zhi, An extremely safe and wearable solid-state zinc ion battery based on a hierarchical structured polymer electrolyte, Energy and Environmental Science, 11 (2018) 941-951.



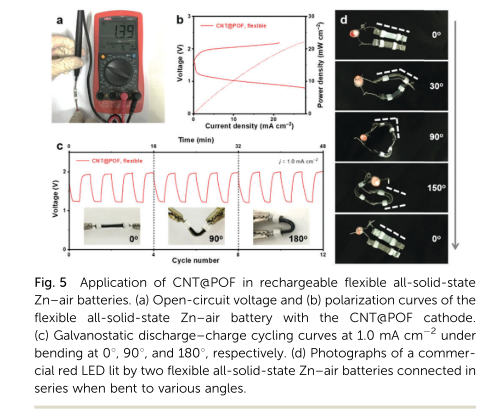
**【图5-器件展示】**

[16] D. Wang, H. Li, Z. Liu, Z. Tang, G. Liang, F. Mo, Q. Yang, L. Ma, C. Zhi, A Nanofibrillated Cellulose/Polyacrylamide Electrolyte-Based Flexible and Sewable High-Performance Zn–MnO2 Battery with Superior Shear Resistance, Small, 14 (2018).



**【图5-电压测试、弯折性能】**

[22] B.Q. Li, S.Y. Zhang, B. Wang, Z.J. Xia, C. Tang, Q. Zhang, A porphyrin covalent organic framework cathode for flexible Zn-air batteries, Energy and Environmental Science, 11 (2018) 1723-1729.



**【图6-电池示意图、弯折性能、极化曲线、循环曲线、器件展示】**

[24] W. Liu, B. Ren, W. Zhang, M. Zhang, G. Li, M. Xiao, J. Zhu, A. Yu, L. Ricardez-Sandoval, Z. Chen, Defect-Enriched Nitrogen Doped–Graphene Quantum Dots Engineered NiCo2S4 Nanoarray as High-Efficiency Bifunctional Catalyst for Flexible Zn-Air Battery, Small, 15 (2019).

