## [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 1. In situ optical microscopy observations of the Zn deposition process at a current density of 10 mA cm−2:(a−f) in 2 M ZnSO4 electrolyte and (g−l) in 2 M ZnSO4 electrolyte with 0.05 mM TBA2SO4.

用原位光学显微镜观察了电流密度为10 mA cm2的2 M ZnSO4电解质和0.05 mM TBA2SO4 2 M ZnSO4电解质中Zn沉积过程。

Figure 2. (a) XRD patterns of Zn anodes synthesized in different electrolytes. (b,c,f) SEM images and EDX mapping of Zn anodes synthesized in 2 M ZnSO4 electrolyte. (d,e,g) SEM images and EDX mapping of Zn anodes synthesized in 2 M ZnSO4 electrolyte with 0.05 mM TBA2SO4.

(a)不同电解质合成Zn阳极的XRD谱图。(b,c,f)在2mznso4电解质中合成的Zn阳极的SEM图像和EDX图。(d,e,g)以0.05 mM TBA2SO4为原料，在2 M ZnSO4电解液中合成锌阳极的SEM图像和EDX图。

Figure 3. (a) Voltage profiles of a zinc plating/stripping cycle on the Cu foam in different electrolytes (inset: magnified plating curves at 5 mAh cm−2). (b) Linear polarization curves and (c) chronoamperograms of zinc plates in different electrolytes. (d) Schematics of the Zn2+ ion diffusion and reduction processes on electrodes in 2 M ZnSO4 electrolyte (upper part) and 2 M ZnSO4 electrolyte with 0.05 mM TBA2SO4 (lower part). (e) Model of DFT calculations, showing a hydrated Zn2+ ion passing through the TBA+ cation adsorption layer on a Zn surface. (f) Corresponding potential energy change at a different distance.

(a)不同电解液中泡沫铜上镀锌/剥离循环的电压曲线(插图:5mah cm2放大电镀曲线)。(b)锌板在不同电解质中的线性极化曲线和(c)时安曲线。(d) Zn2+离子在2 M ZnSO4电解质(上)和2 M ZnSO4电解质与0.05 mM TBA2SO4(下)电极上的扩散和还原过程示意图。(e) DFT模型计算，显示水合Zn2+离子通过Zn表面的TBA+离子吸附层。(f)在不同距离对应的势能变化。

Figure 4. Cycling performance comparisons of Zn|Zn and 3D-Zn|3D-Zn symmetric cells in different electrolytes at current densities of (a) 2 mA cm−2 with a fixed capacity of 2 mAh cm−2, (b) 5 mA cm−2 with a fixed capacity of 2 mAh cm−2, (c) 10 mA cm−2 with a fixed capacity of 2 mAh cm−2, and (d) 5 mA cm−2 with a fixed capacity of 5 mAh cm−2. SEM images of (e) Zn plate in normal electrolyte after 20 cycles, (f) 3DZn in normal electrolyte after 20 cycles, (g) 3D-Zn in the TBA electrolyte after 20 cycles, and (h) 3D-Zn in the TBA electrolyte after 150 cycles, all at 2 mA cm−2 for 2 mAh cm−2.

循环性能比较的锌|锌和3 d-zn | 3 d-zn对称的细胞在不同电解质的电流密度(a)马2厘米2固定容量2 mAh厘米2 (b)马5厘米2固定容量2 mAh厘米2 (c)马10厘米2固定容量2 mAh厘米2,马和(d) 5厘米2固定容量5 mAh厘米2。扫描电镜图像(e)正常电解液中锌极板，正常电解液中3DZn，正常电解液中3DZn, TBA电解液中3D-Zn，循环20次，TBA电解液中3D-Zn，循环150次，均为2ma cm2, 2mah cm2。

Figure 5. Schematic illustrations of Zn deposition on Cu foam (a) without or (b) with TBA2SO4 as an electrolyte additive.

泡沫铜上Zn沉积示意图(a)不加TBA2SO4或(b)以TBA2SO4作为电解质添加剂。

【锌电沉积-铜箔做基底】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】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】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】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】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】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】In the comparison of diffraction patterns, two differences are evident: First, Zn anodes plated in the TBA electrolyte show relatively lower intense Zn diffraction peaks compared with those plated in the normal electrolyte; second, the diffraction peaks of the solid solution CuZn5 (PDF no. 351151) are more obvious in Zn anodes plated in the TBA electrolyte (inset in Figure 2a). 【！XRD-锌沉积层薄-这两种差异可以归因于形态演变，因为在TBA电解质中制备的无枝晶锌阳极比在正常电解质中制备的阳极具有更薄的Zn沉积厚度和更大的Cu - Zn界面面积。】According to Zhang’s work, the CuZn5 phase is produced from the dissolution of zinc atoms into the Cu surface.23 Both differences can be attributed to morphology evolution because dendrite-free Zn anodes prepared in the TBA electrolyte possess a thinner Zn deposition thickness and a larger Cu−Zn interface area than anodes prepared in the normal electrolyte. 【！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)。】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】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】As demonstrated in Figure 2f,g, energy-dispersive Xray spectroscopy (EDX) mapping images once again prove the positive role of TBA2SO4 in the synthesis of a dendrite-free zinc anode. 无添加剂-覆盖不全，聚集较厚Without TBA2SO4 additives, the complementary互补的 distributions of Zn and Cu (Figure 2f) were exhibited, indicating the incomplete coverage and thick aggregation of Zn on the Cu foam. 添加剂-均匀分布、薄、By contrast, the homogeneous distributions of Zn and Cu (Figure 2g) reveal a thin and overall coverage of Zn on the Cu foam in the TBA electrolyte, which accords well with the XRD results. 【XPS-锌电沉积】In addition, X-ray photoelectron spectroscopy (XPS) spectra, Raman spectra, and additional XRD patterns of Zn anodes are also presented in Figure S5.In short, it is shown that dendrite-free 3D Zn anodes (hereinafter, 3D-Zn) are successfully synthesized with the inclusion of the TBA2SO4 additive. Note that these 3D-Zn anodes are used in further cell tests. 【！为了深入了解TBA2SO4添加剂对锌沉积的影响，进行了各种电化学分析。】To give deeper insight into the effect of the TBA2SO4 additive on the Zn deposition, various electrochemical analyses were performed. 【电化学稳定窗口-LSV-不锈钢】The electrochemical stability window of 1 M TBA2SO4 solution was evaluated first (Figure S6). It is evident that TBA2SO4 is nonreactive within the electrochemical stability window of water, which verifies that TBA+ cations function as nonredox agents during the Zn plating/stripping process. 【锌沉积溶解CV-两电极-锌作工作电极，铜为参比电极】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。】As shown in the first cycle of galvanostatic plating and stripping (Figure 3a), 98% high Coulombic efficiency is observed in all tests, indicating the good reversibility of Zn deposition on the Cu foam. 然而，随着添加剂浓度的增加，极化电压增强。【添加剂-电沉积-极化电压增大-保护屏障】Nevertheless, an enhanced polarization voltage is exhibited with the increase in additive concentration (inset in Figure 3a). 这可能是由于在电镀过程中TBA+离子在电极表面的竞争性吸附，从而形成了防止Zn2+离子进入和沉积的屏蔽层。It should arise from the competitive adsorption of TBA+ cations on the electrode surface during the plating process, which leads to the formation of a screening layer against Zn2+ ions coming in and depositing. 【添加剂浓度增大，电沉积极化增大】As a consequence, the higher the concentration of TBA2SO4, the higher the polarization voltage. Linear polarization experiments further proved the surface adsorption of TBA+ cations because the corrosion reactions of Zn in the electrolyte were mitigated as TBA2SO4 was added. 【塔菲尔-添加剂腐蚀电流小 对比样大】With the Tafel line extrapolation procedure on linear polarization curves in three electrode cells (Figure 3b), low corrosion currents of 0.26 and 0.28 mA cm−2 were determined for Zn plates in electrolytes with 0.05 and 0.1 mM TBA2SO4, respectively, suggesting a reduced corrosion rate, whereas the Zn plate in normal electrolyte showed a corrosion current of 1.1 mA cm−2. 【计时电流法(CA)表征锌的成核和生长】Furthermore, chronoamperometry (CA) was used to characterize the Zn nucleation and growth because the variation in the current−time profile in CA can sensitively reflect the change in surface morphology in the deposition process. 【计时电流-假定电流密度的增加表示真表面积的增加】A rise in current density is assumed to indicate an increase in true surface area. 【锌电极在不同电解质中的计时电流图如图3c所示。对于**普通电解液**，当过电位为−150 mV时，**电流密度在300 s内单调增加**，表明电极表面有粗糙的(树枝状)Zn沉积】The chronoamperograms of Zn electrodes in different electrolytes are shown in Figure 3c. For the normal electrolyte, the current density increases monotonically within the duration of 300 s at a constant overpotential of −150 mV, suggesting the rough (dendritic) Zn deposition on the electrode surface.24,38−43 【众所周知，在成核过程中，吸附的Zn离子根据表面能和暴露面积最小的原则，倾向于沿表面侧向扩散并聚集到初始核中。在随后的沉积过程中，表面吸附的Zn离子的连续横向扩散和凸起周围的扰动电场进一步放大这些核成为重的树突，如图3d上方所示。】It is well known that during the nucleation process, adsorbed Zn ions tend to diffuse laterally along the surface and aggregate into initial nuclei according to the principle of minimizing the surface energy and the exposed area. In the following deposition, the continuous lateral diffusion of surface-adsorbed Zn ions and a disturbed electric field around protuberances further amplify these nuclei into heavy dendrites, as illustrated in the upper part of Figure 3d. 【对于0.05 mM TBA2SO4的电解液，在沉积初期(60 s内)暂态电流增加后，直到沉积结束，电流密度稳定恒定。】For the electrolyte with 0.05 mM TBA2SO4, after the transient current increase in the early stage of deposition (within 60 s), a stable and constant current density proceeds to the end. 【在此条件下，由于Zn离子和竞争TBA+离子在早期的扩散，首先形成了尺寸更细、面积密度更高的核种子。在随后的沉积过程中，非氧化还原TBA+离子在初始突起附近静电积累，形成具有憎锌斥力机制的屏蔽层，防止Zn2+离子在这些核上聚集和还原(图3d下半部分)因此，阻碍Zn2+横向扩散和抑制尖端效应导致形成光滑的锌沉积层。】Under such conditions, nucleus seeds of a finer size and with a higher areal density form at first due to the diffusion of Zn ions and competitive TBA+ cations in the early stage. In the following deposition, nonredox TBA+ cations electrostatically accumulate in the vicinity of initial protuberances to form a shielding layer with zincophobic repulsion mechanisms, which will prevent Zn2+ ions from aggregating and reducing on these nuclei (lower part of Figure 3d). Consequently, the hindered lateral diffusion of Zn2+ and the inhibited tip effect result in the formation of a smooth Zn deposition layer. 【然而,对于与0.1毫米TBA2SO4电解液,在早期相同的过程后,电流密度开始增加非常缓慢,后者部分电流分布(125−300s),它是可能的,尽管表面Zn2 +离子的横向扩散可能受到吸附稍后通知+阳离子,初始核具有较强的电场仍然更容易生长成树突，因为在较高的添加剂浓度下，突起和平滑区域同时被TBA+屏蔽层覆盖。】However, for the electrolyte with 0.1 mM TBA2SO4, after the same process in the early stage, the current density starts to increase very slowly in the latter portion of the current profile (125−300 s). It is possible that although the lateral diffusion of surface Zn2+ ions could be constrained by adsorbed TBA+ cations, initial nuclei with stronger electric fields are still easier to grow into dendrites because both protuberances and smooth regions are simultaneously covered by a TBA+ shield at higher additive concentrations. 【确定最优浓度-在上述表征和结果的基础上，选择0.05 mM浓度为TBA2SO4添加剂的最佳条件。(更多循环伏安法(CV)和电化学阻抗谱(EIS)数据见图S16和S17】On the basis of the previously described characterizations and results, the concentration of 0.05 mM was selected as the optimal condition for the TBA2SO4 additive. (For additional cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) data, see Figures S16 and S17.) 【TBA+添加剂的优势-添加量少】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】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】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】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】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】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。】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】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。】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】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】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】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。】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】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 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】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】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】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】To investigate the influence of the 3D structure and the TBA2SO4 additive on the cycling performance of the **full cell**, the 3D-Zn anode was coupled to an α-MnO2 cathode to construct a 3D-Zn/MnO2 battery using a 2 M ZnSO4 + 0.1 M MnSO4 electrolyte with or without the TBA2SO4 additive. For comparison, Zn foil (with a capacity of 11.7 mAh cm−2) was also used as the anode to fabricate a Zn/MnO2 battery. αMnO2 nanofibers (Figure S10) were synthesized according to the literature procedures.47 【】The XRD pattern in Figure S11 confirmed the crystalline phase and purity of the as-prepared α-MnO2 (PDF no. 44-0141). 【全电池性能描述-容量、充放电曲线、循环稳定性】At a current density of 1 A g−1, all batteries exhibit a capacity of ca. 220 mAh g−1 after first 20 cycles of activation (Figure S12). A typical charge−discharge curve of the zinc/manganese oxide battery is observed in the 3D-Zn/MnO2 battery with the TBA2SO4 additive (Figure S13). 【电解质添加剂提高全电池性能】More importantly, the 3D-Zn/MnO2 battery with the TBA2SO4 additive shows excellent cycle stability with 94% capacity retention over the following 300 cycles. In contrast, the 3D-Zn/MnO2 battery without the TBA2SO4 additive preserves only 79% of capacity. Moreover, the Zn/MnO2 battery with the planar Zn anode also delivers a poor capacity retention of 35% after 300 cycles. This indicates that both the electrolyte additive and the structural design of the Zn anode are promising for improving the overall battery performance. 【全电池失效分析-XRD、SEM和EDX，并提出了TBA2SO4的作用机制】The post-mortem analysis of full cells via XRD, SEM, and EDX mapping can be seen in the SI (Figures S14 and 15). On the basis of all of the previously described analyses, a probable Zn dendrite inhibition mechanism of TBA2SO4 as an electrolyte additive is proposed. 【无添加剂-锌沉积机理-侧向扩散-枝晶】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】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-】In summary, we proposed an effective, low-cost, and nontoxic cationic surfactant-type electrolyte additive strategy to induce the uniform Zn deposition via the unique zincophobic repulsion mechanism in both the electrode preparation and the battery charge/discharge process. During the plating process, TBA+ cations would electrostatically adsorb and aggregate in the vicinity of protuberances to create the protective TBA+ layers, which could further restrict the lateral diffusion and self-amplifying tip effect by driving the approaching Zn2+ ions to deposit on adjacent flat regions, eventually leading to the dendrite-free homogeneous Zn deposition. In symmetric cells, the as-prepared 3D Zn anode demonstrated remarkable cycle stability for >300 h at a current density of 2 mA cm−2 and excellent rate performance up to 10 mA cm−2. Even at the high current density of 5 mA cm−2 and high capacity of 5 mAh cm−2, the symmetric cell could still stably cycle for >160 h. When assembled with an α-MnO2 cathode in a full cell, it could deliver a lifespan of 300 cycles with 94% capacity retention at a current density of 1 A g−1. Importantly, all of these performances were significantly higher than the control performances in the normal electrolyte, proving once again the improved electrochemical performance with such a novel cationic surfactant-type TBA2SO4 additive. Moreover, in view of the price, toxicity, and the amount used, our proposed cationic surfactant-type electrolyte additive exhibits obvious advantages compared with other types of reported additives. A minimum addition amount of 0.029 g L−1 is achieved in our work, which demonstrates the great potential for practical applications. Our work may provide an effective and scalable electrolyte additive strategy for the production of dendrite-free 3D Zn anodes and longer-life rechargeable ZIBs and ZHBs.

■ ASSOCIATED CONTENT

**【实验部分（SI）】**

Experimental Section 1. Synthesis of dendrite-free 3D zinc anode The deposition was conducted without any oxygen-removal step. Before

electroplating, commercial copper foam (thickness 0.3 mm) was washed with absolute ethanol, 10% hydrochloric acid and deionized water successively to clean the surface. A two-electrode cell system was assembled using the above copper foam as the working electrode and zinc plates as both counter and reference electrodes. The aqueous solution containing 2 M ZnSO4 and 0.05 mM TBA2SO4 (abbreviated as TBA electrolyte in the main text) was used as the electrolyte. 10 mAh cm-2 of zinc was plated by a galvanostatic electrodeposition method at a current density of 10 mA cm-2 for 1 h. The pH of electrolyte slightly increased from 3.71 to 3.82 after deposition. The as-prepared dendrite-free 3D zinc anode was washed by deionized water and ethanol, and then cut into square-shaped pieces with the area of 1 cm2. As for the control group, the electrodeposition was also conducted in 2 M ZnSO4 aqueous electrolyte (abbreviated as normal electrolyte in the main text) for comparison.

3. Material characterization The compositions and microstructures of the 3D zinc anodes were analyzed using

XRD (Rigaku D-Max 2200 VPC) and SEM (FEI Quanta 400 FEG) measurements. Raman spectra were recorded using a FEX (NOST Korea) Raman microscope with a 532 nm diode laser. An ESCALab 250Xi (Thermo Fisher) microprobe was used to record XPS spectra. Real-time observations of zinc deposition on copper foam were investigated by optical microscopy (Motic BA310Met). A transparent optical cell with two-electrode (Cu foam and Zn plate) configuration was placed at specimen stage and kept the Cu foam perpendicular to incident light. Reflected light lamp was used as light source. Meanwhile, galvanostatic deposition was performed with an electrochemical workstation (CHI660E) under the same condition from experimental section 1.

4. Electrochemical measurements Galvanostatic deposition testing was conducted by plating metallic zinc on copper

foam with a fixed capacity of 10 mAh cm-2 at a current density of 10 mA cm-2. The stripping cut-off voltage was set at 1 V vs. Zn2+/Zn. Both Linear polarization and chronoamperometry measurements were conducted on an Autolab electrochemical workstation (Metrohm) using zinc plates as both the working and counter electrodes, and a Ag/AgCl reference electrode, and 2 M ZnSO4 with different concentration of TBA2SO4 as the electrolyte. Linear polarization curves were recorded by voltage scanning between -0.3 and 0.3 V vs the open circuit potential at 1 mV s-1. Linear scan voltammetry (LSC) and cyclic voltammetry (CV) tests were conducted on an Autolab electrochemical workstation (Metrohm). The electrochemical stability window is investigated in a three-electrodes configuration, stainless steel plate as working and counter electrodes, Ag/AgCl as reference electrode. CV tests were conducted in a threeelectrodes configuration, Cu foam as working electrode, Zn plate as counter electrode, Ag/AgCl as reference electrode. Coin cells (CR2032) were assembled for both symmetric and full cells with glass-fiber A as the separator, and all galvanostatic charge and discharge performances were tested on the NEWARE battery testing system. Symmetric cells were assembled using two identical dendrite-free 3D zinc anodes (or zinc plates) and then cycled at different current densities (2, 5 and 10 mA cm-2) for different specific capacities (2 and 5 mAh cm-2). Full cells were assembled using α- MnO2 cathode and dendrite-free 3D zinc anode (or zinc foil with a thickness of 20 μm). The cathodes were prepared by coating the slurry mixture composed of 70 wt % αMnO2, 20 wt % carbon black and 10 wt % polyvinylidene fluoride binder on Ti foil. The loading density (thickness) of MnO2 and 3D-Zn electrodes used in the battery tests are 1 mg cm-2 (20 μm) and 10 mAh cm-2 (3 μm), respectively, keeping the amount of anode excessive. The full cells were cycled in a potential range of 0.8 and 1.9 V vs. Zn2+/Zn.

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.

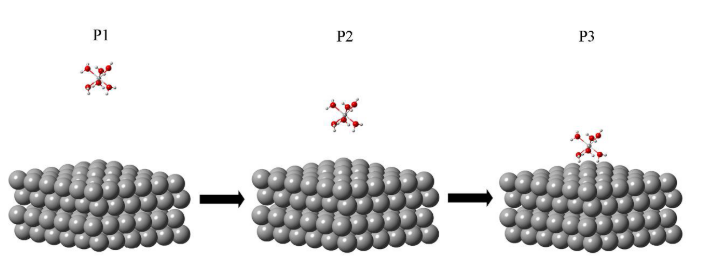


Figure S7. Model of DFT calculations, showing the adsorption process of a hydrated Zn2+ ion towards a neat Zn surface.

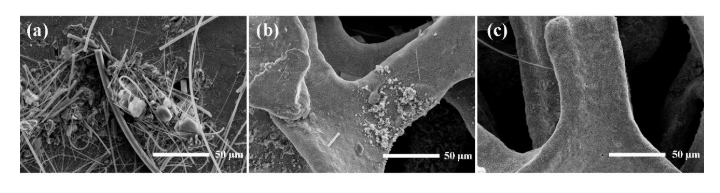


Figure S8. The post-mortem SEM images of (a) Zn plate in normal electrolyte, (b) 3DZn in normal electrolyte, (c) 3D-Zn in the TBA electrolyte, all at 5 mA cm-2 for 2 mAh cm-2.

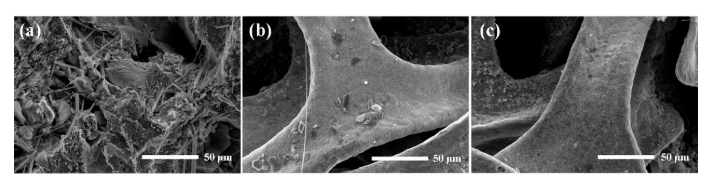


Figure S9. The post-mortem SEM images of (a) Zn plate in normal electrolyte, (b) 3DZn in normal electrolyte, (c) 3D-Zn in the TBA electrolyte, all at 10 mA cm-2 for 2 mAh cm-2.

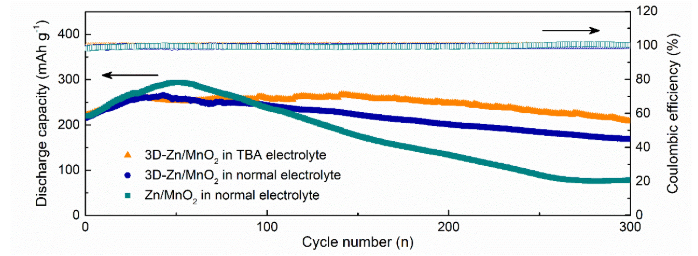


Figure S12. Cycling performance and Coulombic efficiency comparison of Zn/MnO2 and 3D-Zn/MnO2 batteries in the different electrolytes at the current density of 1 A g-1. TBA electrolyte here refers to 2 M ZnSO4 + 0.1 M MnSO4 electrolyte with 0.05 mM TBA2SO4 additive, while normal electrolyte here refers to 2 M ZnSO4 + 0.1 M MnSO4 electrolyte.

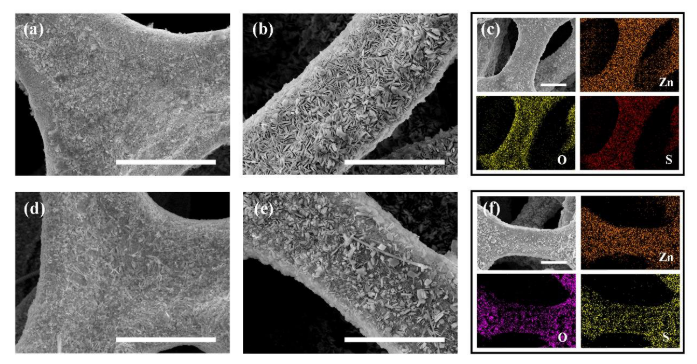


Figure S15. SEM images of 3D-Zn anodes after (a) 100 cycles, (b) 300 cycles in full cells with normal electrolyte; after (d) 100 cycles, (e) 300 cycles in full cells with TBA electrolyte. EDX mapping of 3D-Zn anodes after 300 cycles in full cells with (c) normal and (f) TBA electrolyte. Scale bars in all figures: 50 μm.

The post-mortem analysis of full cells after 100 and 300 cycles was conducted using XRD, SEM and EDX mapping. As shown in Figure S14, the diffraction peaks of corrosion product Zn4(OH)6SO4 was observed for 3D-Zns after 100 battery cycles in the full batteries. Zn4(OH)6SO4 was further hydrated into Zn4(OH)6SO4·5H2O after 300 battery cycles. The similar transformation was also reported by the Sun’s group [R8]. The formation of zinc hydroxide sulfates consumes both active Zn anodes and electrolyte system, which leads to the continuous degradation of battery performance. As seen in Figure S15b, 3D-Zn after 300 cycles is completely covered by abundant Zn4(OH)6SO4·5H2O microsheets in normal electrolyte. These insulative microsheets passivate the 3D-Zn by blocking the diffusion of Zn2+ and decreasing the electron conductivity. Notably, the formation of dendrites can enlarge the intact area between Zn anode and electrolyte, which accelerates the corrosion reactions [R9]. By contrast, with the addition of TBA+, the formation of inactive Zn4(OH)6SO4·5H2O is alleviated (Figure S15e) because of the suppression of Zn dendrite formation. The diffraction peaks of Zn metal and CuZn5 are still detectable in 3D-Zn after 300 cycles in TBA electrolyte (Figure S14b, green pattern), while the diffraction peaks of CuZn5 remain only in 3D-Zn after 300 cycles in normal electrolyte (Figure S14a, green pattern). The EDX mapping tests further prove the alleviated formation of corrosion products on 3DZn in TBA electrolyte. The EDX mapping of 3D-Zn after 300 cycles in normal electrolyte gives an atomic ratio of Zn : O : S = 25 : 56 : 4, while 3D-Zn after 300 cycles in TBA electrolyte gives an atomic ratio of Zn : O : S = 25 : 44 : 2. Lower proportion of S and O elements also reveals the decreased formation of Zn4(OH)6SO4·5H2O in TBA electrolyte.

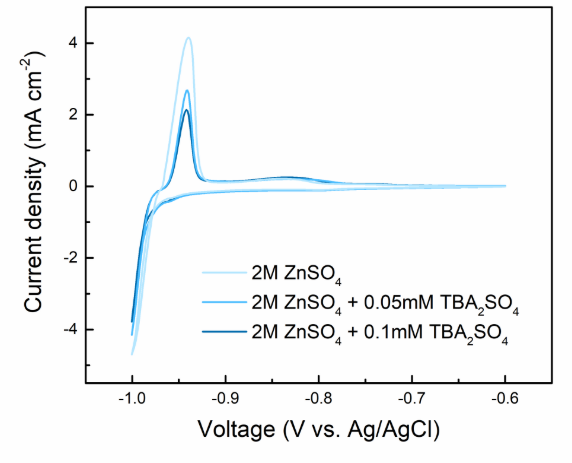


Figure S16. Cyclic voltammetry curves of Zn plating/stripping in different electrolytes using three-electrode configuration (Cu foam as working electrode, Zn plate as counter electrode, Ag/AgCl as reference electrode).

As seen in the figure S16, both cathodic and anodic peak currents are decreased with the addition of TBA+ additive. However, no extra peaks appear with the addition of TBA+ additive, proving the non-reactivity of TBA+ once again.

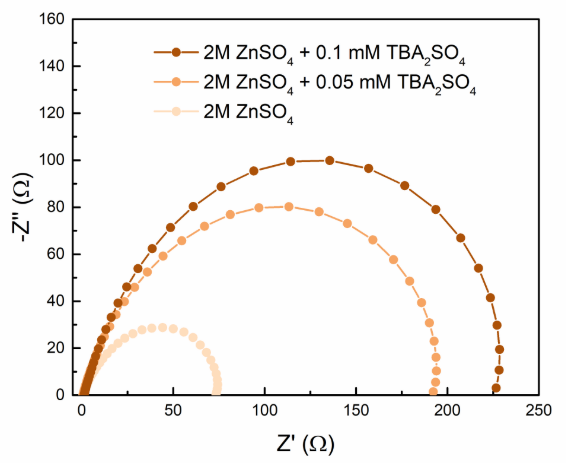


Figure S17. EIS results of the Zn symmetric cells with normal electrolyte or TBA electrolyte.

The addition of TBA+ additive increased the diameter of the semicircle of the Nyquist plots without affecting their characteristic features. This means that the charge transfer resistance of Zn deposition increases due to the adsorption of TBA+ cations on the surface of electrode. More importantly, no extra semicircles appear at high frequencies, indicating again that no TBA-derived layers (or TBA+ reduction products) on electrode surface are formed with the addition of TBA+ additive.

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

【实验方案】Fabricating Nanoporous Zn via RID. We begin by describing the working mechanism of RID based on our understanding of percolation dissolution.24,25 A typical halfreaction of RID goes as MmXx+xm e−→ mM+ xXm−, where MmXx is the compound precursor, M the metal product, and e− the electron from a reducing solution. Unlike most synthesis that dissolves a compound before reducing its metal cations to metal, RID takes a straight route from the compound to the metal. The metal phase will grow from the compound surface once in contact with a reducing solution, first as islands and then as curvy ligaments. With a sufficiently large molar volume change (ΔVm), percolating pores will evolve spontaneously with the dissolution. Meanwhile, if ΔVm is not too large, the metal ligaments, undergoing surface-diffusion-controlled coars-ening, will percolate to retain the shape of the compound. This scenario of percolation dissolution is summarized in Figure 1a. The mechanism informs us of the following criteria for designing a RID reaction. We will need an insoluble MmXx,a sufficiently strong reductant, and a highly soluble anion Xm− to avoid passivation. The nucleation of the metal on MmXx requires low interfacial energy, that is, good wetting, which will also prevent the metal phase from easy detachment from the reacting compound precursor during coarsening. The bounds for ΔVm

can be approximated from continuum

percolation theory26 that suggests a volumetric threshold (pv ∼ 14−16%) for a component to percolate in a random mixture. Therefore, the preferred range of ΔVm is

pV l v <Δ < − pv m (1)

so that under the assumption of no macroscopic volume change, RID can create continuous, open pores to sustain dissolution and a continuous metal phase to yield monolithic material. With the above requirements in mind, we proceed with the fabrication of nanoporous Zn. A seemingly proper choice of a precursor is ZnO, given its low solubility in most solvents. However, in an aqueous solution, we could not identify a sufficiently strong reductant, and in a nonaqueous solution that can accommodate a stronger reductant, the oxide product had a hard time dissolving, leading to a superficial layer of Zn product even after half a day of reaction (Figure S1a). Similar issues occurred if we used ZnS as the precursor (Figure S1b). Therefore, we turned to another common Zn salt, ZnCl2.In dimethoxyethane (DME), ZnCl2 is sparingly soluble, whereas its RID product, Cl−, can readily dissolve with Li+

as the

supporting cation in the solution. ΔVm for the conversion of ZnCl2 to Zn is 80.5%, falling in the desirable range. The wetting angle between Zn and ZnCl2 is about 25° (Figure S2a), making the surface of ZnCl2 a favored site for Zn nucleation. 【实验步骤阐述】The RID experiment is designed as follows. The reductant, naphthalenide, has a relatively short lifetime, so it has to be prepared right before RID by reacting naphthalene with a sheet of Li foil. Li here serves as a convenient source of electrons, although in the future, the oxidation of the solvent in an electrolyzer would make more economic sense at scale. The formation of naphthalenide gave the solution a deep green color, as shown in Figure S2b. The polycrystalline ZnCl2 precursor was prepared in the form of a disk by melting ZnCl2 powder in a copper crucible (the inset of Figure 1b). The ZnCl2 sample, together with the crucible, was then immersed in the reducing solution for ∼3 h. 【实验现象描述：颜色变化】After the reaction, the transparent ZnCl2 disk turned black without losing its integrity (the inset of Figure 1b). Although the sample is brittle, the strength suffices the handling during characterization and later battery assembling, as shown by Figure S2c. The scanning electron microscopy (SEM) image in Figure

1b shows the cross-sectional morphology of the product, a nanoporous structure with slim ligaments. 【EDS和XRD现象描述】We confirmed the bulk composition of the ligaments to be pure Zn with energydispersive spectroscopy (EDS, Figure S3a)and X-ray diffraction (XRD, Figure S3b). The randomly oriented metal ligaments have an average width of around 67 nm (statistics of the ligament width shown in a histogram in Figure S4), smaller than our expectation given much larger ligaments observed for other nanoporous base metals such as Pb and Sn.25,27 【小尺寸原因分析】We attribute this small length scale to two factors. The first is the electrolyte environment where the structure evolved. Surface diffusion of metal in an organic electrolyte can be slower than that in water, which can be further slowed down by a salt layer on the Zn surface formed during the reaction (Figure S2d).27 The second factor is the formation of surface oxide likely during the step of cleaning with ethanol, as confirmed by highangle annular dark-field scanning transmission electron microscopy (HAADF-STEM, Figure 1c). The lattice spacings and the diffraction patterns of the two phases (Figure S5a,b) confirm that a thin, compact layer of ZnO covers the Zn ligament uniformly despite its high curvature. 【尺寸描述】The thickness of the ZnO layer in Figure 1c is around 2.9 nm. The interface between Zn and ZnO appears semicoherent, with the lattice mismatch accommodated by dislocations (Figure S5c).

The nanoporous Zn inherits a large porosity from the large

ΔVm, which can be too big to effectively serve as an anode given the expected decrease in ligament connectivity upon discharging.19 The porosity was estimated by measuring the dimensional changes of the sample, given ΔVm

as the

theoretical porosity with no volume change. The as-prepared porosity is above 80%.24 【问题到解决办法的转折】To tune down the porosity, the most common method is to change the precursor,24 which will require another round of reaction design. An alternative approach is mechanical compression. 【！！！深度放电后形貌保持良好】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】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】The electrochemical tests were performed in a coin cell, comprising an oversized NiOOH cathode, an electrolyte of 6 M KOH saturated with ZnO, and other commercial cell components (Figure 2a). We did not use a symmetric cell with two nanoporous zinc electrodes, as the anode reactions do not require a balance in zincate ions. Instead, the oversized NiOOH cathode allows us to conveniently reach various DoD values and investigate the electrochemical behaviors of the anode. A characteristic curve of voltage versus time is shown in Figure 2b, with a discharging current of 25 mA/cm2 and a charging current of 5 mA/cm2. No voltage hold was necessary in charging given the oversized cathode. We stopped the cycling tests of different cells at different stages (black dots in Figure 2b) and retrieved the anodes for SEM characterization.

【！！！不同放电深度孔结构仍能保持稳定】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】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】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. 【】When l0 is significantly smaller than the change in l, as in the case of the cycled nanoporous Zn, l becomes linearly dependent on t1/4. This relationship implies a quasi-steady-state ligament width (lqs) reached within a typical experimental period of days, which does not grow significantly for a much longer periods (see discussion in the Supporting Information). As the mechanism behind the coarsening would eventually determine the cycling stability of the nanoporous Zn, we carry out the following analysis to further understand how the change of length scales may depend on time and environment. We first focus on Ds, the only material property in eq 2 that depends strongly on the environment. The biggest difference between the nanoporous Zn cycled in the cell and kept in argon is the surface ZnO layer. In the cycling cell, particularly during charging, the layer would be gone, leaving “naked” Zn ligaments to coarsen at a rate more characteristic of metallic Zn in an aqueous solution. The explanation can be supported by the relationship between l and the homologous temperature (TH). TH, a metallurgical term used to predict creep, manifests the empirical proportionality between the activation energy of surface diffusion and the melting point, as both relate to the binding energy.31 We can derive from eq 2 the following relationship between lqs and TH:

log lqs=−

1 4

log

i k

jjjjjjγ 4

aD t kT

s,0

y {

zzzzzz

αTH 4

(3)

where Ds,0 is the maximum surface diffusivity and α is a constant (see Supporting Information for details of the derivation). 【水系和非水系扩散系数不同的影响】Although it is crude to assume the first term on the right-hand side of eq 3 to be a constant, a linear relationship between log(lqs) and TH has been previously shown for many nanoporous metals from aqueous dealloying, replotted as black dots in Figure 3b.27,32 The cycled Zn anode resides nearby. The small initial l of the nanoporous Zn, alongside literature values on dealloying in ether-based solutions, makes another line right below their aqueous counterparts. Both ligament widths of the nanoporous Zn are thus quasi-steady-states, with their difference from the different surface diffusivities in aqueous and nonaqueous solutions. We believe that the above coarsening dynamics, though lowering the specific area, can play important roles in the structural stability. The most obvious benefitis

the

morphological retention despite the length scale change, a phenomenon commonly observed when surface diffusion acts on nanoporous metals.33 It preserves the continuous metal phase, one most needed characteristic for a Zn anode. The second structural outcome is the quasi-steady-state length scale

2408

of ∼500 nm. 【！！！表面扩散与结构改变：通过氧化锌的尺寸进行分析】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】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】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】Before cycling, we ran polarization tests (Figure 4a), which

show a much higher discharging current and power density from the cell with the nanoporous Zn anode. The curve started at a lower open-circuit voltage for the nanoporous Zn as it began with a degree of oxidation higher than that of the Zn powder anode. The powder anode suffers a rapid loss of cell voltage as we ramped up the current density. The large difference in polarization likely originates from two structural differences as we have been highlighting in the work. 【纳米多孔锌性能优异的原因】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】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】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】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】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】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】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】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】RID circumvents the limits by alloy precursors in dealloying and broadens the path toward functional nanoporous structures. The use of nonaqueous solution for RID will enable more choices of insoluble precursors, particularly for the fabrication of nanoporous reactive metals. 【制备材料的实际意义】We demonstrate the application of one such structure in a rechargeable Zn battery. The nanoporous Zn from RID delivered outstanding performance under a practical cycling condition, owing to the structural stability and the large specific area. The results also underscore the dependence of cycling stability on microstructural evolution, a poorly understood topic even for the grand old Zn anode. The nanoporous Zn, with its compositional and structural uniformity and tunability, provides a model system for building structure−property relationships and a starting point for electrode and electrolyte engineering to realize safe and inexpensive Zn batteries.

## [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).

【制备方法的引出】To investigate the interaction between host and zinc, we employed carbon hollow-spheres (denoted as C HS) derived from resorcinol–formaldehyde (RF) polymer as a model host. The detailed characterizations of precursor and as-prepared carbon spheres are shown as Figures S1 and S2 in the Supporting Information. 【XRD分析】Ex situ X-ray powder diffraction (XRD) studies (Figure 1a) suggested that product plating on carbon host in Zn(CF3SO3)2 aqueous electrolyte is pure zinc-metal. 【TEM分析：三种结构】We conducted ex situ transmission electron microscopy (TEM) to assist understanding of nucleation of zinc on C HS. In the high-resolution high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of carbon loaded with zinc (Figure 1b), three kinds of zinc are to be found: 1) zinc atoms, 2) zinc clusters, and; 3) zinc networks (each indicated by arrows of different colors). In enlarged HAADF-STEM images (Figure 1c), three forms of zinc are shown: 1) singleatoms, 2) clusters, and; 3) porous networks. 【XRD与TEM结合分析】The porous network exhibits a lattice spacing of 0.25 nm, which is assigned to the (002) plane of zinc. This agrees with results from XRD, i.e., that the major product after plating is zinc.[42] 【示意图引出】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】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】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】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】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】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】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】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】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】Detailed characterizations of the precursors are shown in Figure S6 in the Supporting Information. Following the removal of templates, C HS with zincophilic nitrogen sites were obtained (denoted as CnC HS).[49,50] In the scanning electron microscopy (SEM) image (Figure S7a, Supporting Information), it is seen that CnC HS is highly uniform. Additionally, the hollow nature can be readily concluded from inspection of the TEM and scanning transmission electron microscopy (STEM) images (Figure S7b (Supporting Information) and Figure 2e). 【外壳厚度分析】The thickness of the shell is estimated at 20 nm. Additionally, the thickness can be determined from the line-scan energy dispersive X-ray (EDX) analysis and EDX mapping, as is shown in Figure S7c (Supporting Information) and Figure 2f. 【XPS和XAFS证明氮的引入】Furthermore, as is shown in Figure 2g, the existence of nitrogen is demonstrated by the N1s NEXAFS. This confirms the successful introduction of nitrogen-sites on the carbon host.[51] The X-ray photoelectron spectroscopy (XPS) survey results (Figure S8a, Supporting Information) show that the content of nitrogen in CnC HS is 3.53 at% and, that the content of silica in as-prepared CnC HS can be reasonably neglected. Further, the high-resolution N 1s spectrum (Figure S8b, Supporting Information) confirms the presence of nitrogen-doping. This finding agrees well with NEXAFS results. 【碳主体选择原因分析】The Raman spectra, XRD patterns and the nitrogen adsorption isotherm of the as-prepared samples (Figures S9 and S10, Supporting Information) indicated a negligible difference between the pristine carbon host (C HS) and the synthesized CnC HS. This finding makes these two carbon hosts ideal as models to investigate the mechanism of zincophilic sites. 【EIS分析】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】To

provide a comprehensive insight into the interaction between nitrogen-doping carbon and zinc together with

consequent zinc plating, ex situ NEXAFS spectra, in situ Raman spectra, and ex situ SEM images were carefully collated. In the nitrogen 1s NEXAFS spectra (Figure 3a), there are two clear peaks located at 398.1 and 401.1 eV. These peaks can be assigned to pyridinic-nitrogen and graphitic-nitrogen. The pyrrole peak can be overlapped by these two as implied in the XPS findings (Figure S8b, Supporting Information). 【活性位点诱导锌沉积】Nitrogen doping is introduced by the polydopamine precursor.[53,54] As is illustrated by the nitrogen 1s NEXAFS spectra, a significant difference is seen in the intensity of pyridinic-nitrogen (indicated by lavender-blue) and graphitic-nitrogen (light

yellow).

It is concluded that the pyridinic-nitrogen sites are attached by zinc-ion following zinc deposition. Consequently, Zn-N bonds are formed, turning the chemical state of the original pyridinicnitrogen closer to that of graphitic-nitrogen.[55–58] The intensity of the pyridinic-nitrogen peak therefore reduces, while that for graphitic-nitrogen increases. This finding demonstrates that the pyridinic-nitrogen is electrochemically active for zinc nucleation. The carbon 1s NEXAFS spectra (Figure 3b) lead to a similar understanding. The significant change is that the peak located at 290.1 eV (indicated by lavender-blue) disappears following plating of zinc. Compared with the carbon 1s NEXAFS spectra of carbon samples derived from polydopamine (Figure S12, Supporting Information) and C HS (Figure S13, Supporting Information), this peak is assigned as a characteristic peak

from polydopamine-derived carbon sample, or a nitrogendoped carbon-related peak.[55] 【活性位点的电化学活性比较】From comparing the carbon 1s NEXAFS spectra of C HS before and following zinc deposition (Figure S13, Supporting Information), it is concluded that the nitrogen-involved peak disappears more completely in the one of CnC HS. This finding suggests nitrogen sites are more electrochemically active in deposition of zinc. The peak located at 288 eV is assigned to carboxyl functional groups that remain following loading of zinc in carbon 1s NEXAFS spectra of C HS.[53,55] This implies nitrogen sites are more electrochemically active in the deposition of zinc. 【原位拉曼分析电镀行为】In situ Raman spectroscopy was applied to investigate initial plating behavior of zinc on CnC HS. To simulate zinc deposition on CnC HS, several linear-sweep voltammetry (LSV) scans were made. It should be noted that all in situ Raman spectra were normalized to the G-band peak (1580 cm−1) to permit comparison.[59] 【LSV分析活性位点】As is seen in Figure 3c, a peak located at ≈1200 cm−1 decrease gradually with an increasing number of LSV scans. In combination with ex situ NEXAFS results, it is concluded that the peak located at ≈1200 cm−1 is the characteristic peak of pyridine.[60] This suggests that pyridine-nitrogen sites are attached with zinc, together with the formation of Zn-N bonds. 【DFT证明活性位点】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】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】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】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】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】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】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】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】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】As is seen in Figure 4d, CnC HS exhibits a lower plating overpotential of 39 mV compared with 43 mV for C HS. This finding demonstrates the improved nucleation kinetics for CnC HS over C HS, and confirms the impact on overall nucleation kinetics from the nitrogen nucleation sites.[37,61] As is shown in Figure 4e, for galvanostatic cycling testing under various current densities, CnC HS exhibited boosted stability over C HS. Specifically, during an areal capacity of 1 mAh cm−2 under a current density of 2 mA cm−2, large voltage hysteresis occurred in the cycling profiles of C HS, while that for CnC HS remained stable. This finding demonstrates the impact of zincophilic sites in boosting stability of the carbon-host. It is concluded that the introduction of nitrogen sites improves the electrochemical performance of the carbon-host. The lower plating overpotential underscores that the introduction of nitrogen zincophilic sites offer optimized nucleation kinetics. Further, the prolonged cycling performance of CnC HS over C HS is confirmatory evidence of the positive impact of optimized nucleation originating from the introduction of nitrogen sites.

【电池循环性能分析】In an experimental evaluation, CnC HS powder was coated on a titanium substrate and the resulting electrochemical performance as a ZMA was evaluated in an electrolytic Zn-MnO2 battery with simultaneous high-voltage and high energy density.[62–64] The zinc plating profiles on CnC host are presented as Figure S20 in the Supporting Information. As is shown in Figure 4f, the as-prepared zinc-metal anode exhibited excellent capacity retention following 500 cycles. It is seen in the figure that the voltage profiles exhibit a slight difference following 100 cycles. This finding demonstrates the stability of as-prepared zinc-metal anode. It should be noted that CnC HS host with zinc loading exhibited a greater capacity retention than did the C HS host (Figure S21, Supporting Information) which exhibited a capacity decrease following 400 cycles. Further, as is shown in Figure 4g, a Zn-MnO2 battery stack with three cells-in-series successfully lit a standard cell phone (5 V). This finding demonstrates the practical potential for commercial applications.

【锌离子与亲锌位点之间的键合分析】In summary, a mechanism for zincophilic sites on zinc-metal anode hosts in aqueous batteries using carbon-host as a model system is proposed, based on combined multi in situ/ex situ techniques. Based on atomic-level predictions via DFT computation, we experimentally introduced nitrogen sites as zincophilic sites to the model carbon-host. Both ex situ NEXAFS and in situ Raman spectra confirmed zinc ions were bonded with pyridine sites to form Zn-N bonds. These bonds with zincophilic sites induce the critical spacious distribution for initial zinc nuclei. Therefore, hosts with zincophilic sites exhibit a homogenous deposition of Zn, together with boosted electrochemical performance. We conclude that bonding between zinc ions and zincophilic sites is the mechanism for zincophilic nucleation in the ZMA host. Findings will be beneficial to researchers in battery technologies and materials science and in optimizing of zincmetal anodes for practical application in zinc-based batteries.

## [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).

【涂层改性的阐述】Zn-based MMT interlayer was designed to coat on Zn metal anode (MMT-Zn) and function as a Zn ion-conducive artificial SEI to circumvent the harmful corrosive and formation of by-products, and simultaneously inhibit notorious dendrites growth (Figure 1a).【锌板阳极的缺点】 Generally speaking, three obvious disadvantages could occur in bare zinc anode (Figure 1b): i) highly active zinc metal causes corrosion, leading to loss of active material and production of dangerous hydrogen;[12,20] ii) unexpected side reaction of zinc cation with anion in electrolyte (such as OH− and SO4

freely movable Zn2+.[17] The interlamellar of MMT acts as a freeway for Zn2+ transportation during zinc striping/deposition (Figure 1d). 【！！！负电荷吸引锌离子沉积分析】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】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】As illustrated in Figure 1a,c, the as-prepared interlayer composed of randomly dispersed Zn-based MMT, which was prepared via a simple ion exchange method (shown in Figure S1, Experimental Section, Supporting Information). The crystallize structure of Zn-MMT is a phyllosilicate lamella with XRD patterns were employed to identify of the structure of the obtained Zn-based MMT, as shown in Figure S2a, Supporting Information. 【XRD分析】The XRD pattern of Zn-MMT showed the larger diffraction angle (θ) of ≈7.4°, indicating the smaller layer space of Zn-based MMT, also confirming synthesized of Zn-MMT, because of Zn2+ possessing the smallest radius comparing with Ca2+, K+, and Na+ (Table S1, Supporting Information).[24] 【TEM和mapping分析】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】 In order to prove the MMT laminar is negatively charged and Zn2+ concentrated automatically into inter-lamella space, zeta potential for both commercial and Zn-based MMT in DI water was measured respectively. As shown in the Figure 1e, the zeta potential of commercial MMT lamella is −10.2 mV and that of Zn-based MMT is −2.33 mV, indicating that the automatically concentrated Zn2+ in the MMT inter-lamella space neutralizes the negative charge, therefore causes a positive shift zeta potential. 【SEM和TEM分析】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】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】To demonstrate that the MMT membrane can weaken electrolyte contacting with substrate, the contact angle (CA) test was conducted by dropping the electrolyte (2 m ZnSO4) vertically onto MMT-Zn and bare Zn (Figure 1g). The CA of electrolyte droplet onto MMT-Zn is 132° and bare Zn exhibits a CA of 35°, indicating that Zn-based MMT membrane can isolate bulk of water for Zn foil. Thus, the dense MMT interlayer can store a lot of zinc ions and weaken the contact between water and zinc. 【离子电导率分析】Zn-based MMT layer with varying thickness was employed to demonstrate the ionic conductivity, and the electrochemical impedance spectra of MMT layer is illustrated in Figure S3, Supporting Information. Ionic conductivity (σ) was calculated

according to the equation, σ = l RS (refer to Supporting information). As shown in Figure 2a, it is found that the ionic conductivity is almost unchanged despite varying thickness. An ionic conductivity about 3.9 mS cm−1 was achieved for the Znbased MMT layer. The ionic conductivity of MMT film is higher than that of the solid and molten salt electrolytes reported in literature (refer to Table S2, Supporting Information). 【离子迁移数对电化学性能分析】As well as ionic conductivity, Zn2+ transference number (t+) also played vital role in improving the electrochemical performance of zinc anode since the high cation ability would relieve concentration gradient in interlayer, decrease anion concentration and inhibit side reactions.[25,26] The transfer number of Zn-based MMT layer was measured via a convenient electrochemical method: a potentiostatic polarization (∇V = 10 mV) was employed to measure and calculate the Zn2+ transference number (refer to Supporting Information).[25a] The cation transference number (t+):[25d,27]

t+ =

() ()

∇− ∇−

VI R VI R

/ 00 / ss

ss

where ∇V (10 mV) is the applied potential, I0 is the initial current, Iss is the steady-state current, and R0 and Rss are

the electrode resistances before and after the polarization, respectively.

【初始电流分析极化作用】As displayed in Figure 2b, the initial currents I0 of MMT-Zn and bare Zn electrodes were very similar (18.81 µA vs 18.14 µA). However, the steady-state current (Iss) after potentiostatic polarization for 10 000 s of MMT-Zn was much higher than Zn foil (15.48 µA vs 5.41 µA), indicating that the MMT interface stabilize the electrode surface during the polarization process. 【初始态阻抗(R0)和稳态阻抗(Rss)分析】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】The high ionic conductivity and large transform number of cations is contributed by the unique negative charged and Zn2+ filled layer structure of Zn-based MMT, which played as free way for cation but prevented the anion transport. 【！！！对称电池优势分析】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】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】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】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】The Columbic efficiency (CE) is an important index to evaluate the Zn plating/stripping behavior. Bare Zn||bare Cu and MMT-Zn||MMT-Cu cells were assembled to explore CE (the ratio of stripping capacity to plating capacity) to testify the MMT interface boosting cycle performance.[28] As illustrated in Figure S8, Supporting Information, MMT-Zn||MMT-Cu cell with a long cycling stability is observed, whereas the bare Zn||bare Cu cell suffered a severe overpotential and fast short circuit. The average CE of MMT-Zn||MMT-Cu in 50 cycles is 96.3%. In comparison, the bare Zn||bare Cu can only work for nine cycles with a super low CE. The small overpotential, long cycling life, and high and stable CE also reveal the enhanced reversibility of Zn plating/stripping on the MMT modified electrode. 【抗腐蚀性能测试】To measure the ability of MMT interlayer to inhibit corrosion of anode, we carried out general corrosion experiment and linear polarization test. After immersed into electrolyte for 30 days, the Zn-based MMT layer still contacts closely with the Zn substrate, which well protected the Zn metal anode. When the Zn-based MMT layer is removed, the bright metallic zinc luster and smooth electrode surface can be observed (Figures S9,S10, Supporting Information). As a comparison, corrosion is clearly observed on bare Zn electrode though dim metal surface and accumulation of corrosion products. 【tafel曲线分析抗腐蚀性能】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】Scanning Kelvin Probe technology was employed to study the passivation evolution of the Volta potential of the Zn foil immersed into electrolyte for 144 h, and results are illustrated in Figure 4.[30] The Volta potential map of fresh anode shows in a narrow range and the average values around −1284.7 mV, which is very close to the theoretical Volta potential of zinc metallic (−1320 mV, refer to Supporting Information). After immersed in electrolyte for over 144 h, the Volta potential of MMT-Zn (Figure 4c) and bare Zn (Figure 4e) obviously positive shift to −609.9 and 1732 mV, respectively, which attributed to the passivation film increases the escape work of surface zinc atoms.[31] Moreover, the Volta potential of Zn substrate

with MMT layer protected locate in a narrow range of −700 to −500 mV, which indicated an evenly and thin passivation film. 【！！！锌离子的逃逸功能】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】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】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】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】Full cells were built with the β-MnO2 cathode, which possess a high voltage and high theoretical capacity while commonly troubled by fast capacity fading due to the dissolution of cathode.[34] It’s proved that the Mn2+ dissolution from the MnO2 electrode into the electrolyte was responsible for poor electrochemical performance.[34b] It has been demonstrated that a barrier layer can inhibit the dissolution and shuttle of Mn2+.[35] As for the Mn-based cathode issues, MMT interface is applied in MnO2 cathode to inhibit the Mn2+ migrating into electrolyte (Figure 5a). 【XRD、SEM、TEM分析】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】In order to prove that MMT interface can inhibit Mn2+ diffusing into the electrolyte, MMT-Zn||MnO2 and MMT-Zn||MMT-MnO2 were cycled in 2 m ZnSO4. As shown in Figure S17, Supporting Information, the cathode with MMT interface quickly reaches a stable state with a higher capacity (192 mAh g−1 at the 80th cycle), while the MnO2 cathode shows a lower stable capacity (75 mAh g−1 at the 80th cycle). The MMT-Zn||MMT-MnO2 with more superior cycle performance than MMT-Zn||MnO2 is largely attributable to MMT interface which inhibit discharge product diffusing into the electrolyte. In addition, it is proved by XRD and SEM that MMT interface can stably exist in cathode and anode (Figures S18,S19, Supporting Information). Only the swelling between lamellae occurred during charging/discharging process, which is about 0.13 nm (Table S3, Supporting Information).[37] So, MMT interface can improve cathode stability.

【电化学性能分析】In view of the fact that Mn2+ ion as an additive in the electrolyte can help to inhibit the Mn dissolution in the cathode and improve the cycle performance of full cells.[34] Here, we combine the synergistic effect of MMT interface and Mn2+ additive to improve cycle performance of full cells. 2 m ZnSO4 + 0.1 m MnSO4 was used as the electrolyte for full cells. As shown in Figure 5d, these full cells exhibited a similar initial state (<50 cycles) with an active process and reach maximum capacity about 250–270 mAh g−1 based on mass of cathode active material. Subsequently, the MMT-Zn||MMT-MnO2 cell exhibited an ultra-long cycling stability with large reversible capacity retention over 90% from the stable cycle (210 mAh g−1) to 1000th cycle (195 mAh g−1). Additively, the MMT-Zn||MMT-MnO2 cell exhibited an outstanding CE of around 99.5%. In contrast, the control cells of bare Zn ||MnO2 and MMT-Zn||MnO2 show short service lives with capacity lower than 150 mAh g−1 at the 68th and the 222th, respectively. MMT-Zn||MMT-MnO2 with more superior cycle performance than MMT-Zn||MnO2 is largely attributable to inhibit the discharge product Mn3+ to be converted into Mn2+ and dissolved and diffused into the electrolyte.[33] So, the MMT interface plays a positive role in cathode and anode.

【充放电曲线分析电化学性能】The galvanostatic charge and discharge profiles of the full cells are plotted in Figure 5b and Figure S20, Supporting Information. At the first cycle, the cells exhibit characteristic initial discharge/charge curves of MnO2 and show an obvious order of overpotential. In the subsequent cycle, the MMT-Zn||MMTMnO2 always keeps the smallest voltage hysteresis among the full cells (Figure 5c; Figure S14i, Supporting Information). This is a result of MMT layer inducing high concentration Zn2+ into interlamellar channel, which reduce the diffusion length for Zn2+, resulting in small voltage hysteresis. The galvanostatic charge and discharge profiles fully prove that the Zn-MnO2 battery can be greatly improved with the MMT interface. In order to probe MMT interface influence on morphology for anodes and cathodes in full cells, the cycled batteries were disassembled to observe the morphology. 【电极形貌变化分析】The MMT-Zn anode showed a dense flake with size less than 250 nm (Figure S21c,d, Supporting Information). Nevertheless, the bare Zn anode morphology consists of polygonal flakes which will likely be stacked into dendrites (Figure S21a,b, Supporting Information). So, the MMT interface as a near-single cation conductor improves anode performance in full cells. The MnO2 electrodes undergo marked changes in morphology after cycling. The pristine micrometer fibers are transformed to short submicron fibers with a small part of particles in MMT-MnO2 electrode (Figure S22b,d, Supporting Information). But for MnO2 electrode, the main part of the after-cycling morphology is nanoparticles (Figure S22b,d, Supporting Information). Nanoparticles formed by the cathode are one of the possible factors contributing to the full-cell capacity decay. The change state of MnO2 morphology proves that MMT interface can improve the cathode stability. The mass of MMT interface is about 0.32 mg for 1.5 µm. 【容量对比分析性能】In order to certify MMT-MnO2 cathode with outstanding capacity, we compared the capacity based on (MMT + MnO2) mass in MMT-Zn||MMT-MnO2 with that of based on MnO2 mass (2 mg) in MMT-Zn||MnO2 (Table S5, Supporting Information). It’s found that the MMT-MnO2 has superior advantage after the 150th cycle (177 vs 174 mAh g−1 at the 150th cycle; 179 vs 126 mAh g−1 at the 400th cycle). 【负载量和容量分析】Furthermore, we also design a cathode with more loading MnO2 (8.5 mg) in full cells. As shown in Figure S23, Supporting Information, MMT-Zn||MMT-MnO2 has a higher and more stable capacity based on MnO2 mass than MMTZn||MnO2 (based on MnO2 mass, 144 mAh g−1 vs 73 mAh g−1 at 400th cycle). As shown in Table S6, Supporting Information, the MMT-MnO2 cathode constantly keeps higher capacity than MnO2 cathode. Therefore, even if the MMT interface on the cathode surface adds to the parasite weights, the MMT-MnO2 cathodes still have a distinctive advantage. 【器件展示阐述】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】In a nutshell, the improved performances of MMT-Zn||MMTMnO2 full cell can be attributed to the following five functions of Zn-based MMT interface: 1) negative-charged MMT lamella surface facilitating the Zn2+ concentration to relieve uneven plating/stripping realizing a dendrite-free morphology, 2) positive-charged lamella edges anchoring anion to realize a high cation transference number (t+ ≈ 0.82) to inhibit side reactions, 3) compact, hydrophobic, and without microcrack properties isolating aqueous in electrolyte to alleviate corrosion, 4) interlamellar channel reducing the diffusion length for Zn2+ to ensure fast and stable Zn2+ diffusion kinetics, and 5) inhibiting Mn3+ to be converted into Mn2+ diffusing into electrolyte.

3. Conclusion

【结论分析】In summary, a versatile Zn-based MMT interface is applied to the Zn battery to obtain a remarkably improved durability of rechargeable AZIBs. The Zn-based MMT interface which acts as an artificial SEI to inhibit formation of dendrites and by-products on Zn anode, ensures water isolation and alleviates the corrosion of Zn anode. It can realize Zn2+automatically-concentration on the Zn anode surface, and its lamella structure endows a freeway for Zn2+ migration which ensures a high Zn2+ transference number (t+ ≈ 0.82) and ionic conductivity (σ ≈ 3.93 mS cm−1) electrochemical process. In addition, MMT interface is applied to the MnO2 cathode to inhibit dissolution of Mn2+. Our results show that the symmetrical batteries render a dendrite-free plating/ stripping with a small and ultra-stable overpotential (50 mV) and a long-life span at 1 mA cm−2/0.25 mAh cm−2 and with 100 mV overpotential at ultrahigh cycling current and capacity of 10 mA cm−2/45 mAh cm−2 (cycling over 1000 h, 77% DOD). MMT-Zn||MMT-MnO2 delivers an ultra-long cycle life and ultrahigh capacity (1100 cycles with 191.5 mAh g−1 at 2 C). Zn-based MMT interface is promising for next-generation rechargeable AZIBs that require high stability and durability.

## [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).

【FTIR分析制备样品】Fourier-transform infrared spectra (FTIR) was used to elucidate the polymerization mechanism of [2-(methacryloyloxy) ethyl] dimethyl-(3-sulfopropyl) (SBMA) monomer (Figure 1c). The strong characteristic absorption peak at 3400 cm−1 is ascribed to -OH generated from the absorbed moisture in the air. The absorption peak at 1489 cm−1 belongs to C-N+ group. Two absorption peaks at 1179 and 1040 cm−1 are attributed to the SO3−group, separately. In addition, the monomer SBMA has a C-N+ characteristic absorption peak at 1306 cm−1, while the peak is very weak for PSBMA due to the electrostatic supply effect of N+ on SO3 region, the SBMA monomer exhibits a stretching vibration peak of C=C group at 810–840 cm−1, while the peak disappears in the PSBMA polymer, demonstrating the SBMA monomer solution forms a homogeneous and transparent PSBMA hydrogel after heating[39] (Figure 1e; Figure S1, Supporting Information). 【！！！保水作用分析】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】When keeping open at 50 °C for 24 h, the water content for PZHE can still remain above 87% (Figure 1d). As a kind of hydrogel containing chemical crosslinks, PZHE delivers excellent mechanical properties. After 20 times twisting tests, the prepared PZHE can quickly return to its original state (Figure S2, Supporting Information). High stretchability up to 200% strain is also obtained due to the chemical bonds and hydrogen bonds in the 3D network, ensuring the structural integrity in PZHE (Figure S3, Supporting Information). 【切割试验分析】Based on the mechanism shown in Figure 1a, when PZHE is cut into two parts, the charged groups on the branches of PSBMA can rejoin the two parts of the gel through electrostatic interaction. What is more, hydrogen bonds between SO3− group on the branches and the water molecules can also re-establish the PZHE. To further validate the self-healing phenomenon at the interface of cutting surface, PZHE with dye additives and normal PZHE are prepared (Figure 1f). Two pieces of gel are cut from the middle position, and the normal gel and the dyed gel are quickly connected together. After standing for 24 h, the tensile test is carried out with tweezers and 200 g of mass can be sustained for the gel after healed that demonstrate the recovery of its original mechanical strength. 【EIS分析离子电导率】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】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】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】Amplifying the peak of the fingerprint

lated by Equation (1)[40] tR R

Zn 2+ = cell DC /where Rcell is the total cell resistance before polarization, RDC = VDC/IDC, and VDC is the applied potential, IDC is the stable current (Figure 2c,d; Figure S5a,b, Supporting Information). The tZn

2+ increases significantly from 0.252 in liquid electrolyte (LE) to 0.656 in PZHE. The promotion of the ion transport number may be attributed to the steric hindrance effect of the PSBMA polymer network and the electrostatic effect of the charged groups to immobilize the anions. 【原位光学显微镜分析】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】Electrochemical performance and the interface stability between Zn and PZHE electrolyte is tested in Zn/PZHE/Zn symmetric cells. At current density of 0.5 mA cm−2, the symmetric Zn/PZHE/Zn cells remain stable at an ultra-low hysteresis of 220 mV for more than 3500 h. The time–voltage curves maintain its shape even after 7000 cycles (Figure 3a).

Significantly, when the current density increases to 1 and 3 mA cm−2, the Zn symmetric cells can still cycle stably for 1900 and 500 h (Figure 3b,c), which proves a good cycle stability of ZMBs in PZHE. Nevertheless, for Zn/LE/Zn symmetric cells, the battery cannot cycle stably for more than 90 and 40 h at current densities of 0.5 and 1 mA cm−2, respectively (Figure S7, Supporting Information). 【对称电池循环后电极分析】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】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】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】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】And high specific capacity of 200 mAh g−1 with the Coulombic efficiency of above 99% is obtained after 600 cycles at the current density of 1.5 A g−1 (Figure 5d). There may be two reasons for the increase in full battery capacity. First, the temperature at the later stage of the test is higher than the temperature at the earlier stage. The increase in temperature leads to faster zinc ion intercalation reaction on the cathode, which leads to higher specific capacity. Besides, the carbon nanotubes contained in the MnO2@CNT cathode will be the substrate of electro-deposited MnOx. The increase in MnOx brings an increase in specific capacity of full cell. The CNT contributes capacity in the later stage. 【！！！电池性能优异分析】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】In this work, VS2/PZHE/Zn flexible quasi-solid state battery is assembled in an open-air system. It is surprising that the quasi-solid state ZMBs are still capable of driving electronic devices after several times cutting. After four times cutting, almost half amounts of the remaining ZMBs still work well (Figure 6a–e). It is worth noting that the open-circuit voltage of ZMBs still maintain more than 89.2% after four times cutting, which proves that there is small current leakage of the quasi-solid state ZMBs during cutting and gives a promising future for flexible wearable devices that need to be tailored to various shapes (Figure 6f). 【柔性电池测试】As shown in Figure 7a, the assembled quasi-solid state battery has a specific capacity of 89 mAh g−1 even after 100 charge and discharge cycles under a current density of 0.5A g−1. And the quasi-solid state ZMBs with low-voltage VS2 cathode can meet the high-voltage demands of future flexible devices in series. Compared with a single quasi-solid state ZMBs, the output voltage of the battery after series connection is 2 V (Figure 7b; Figure S16, Supporting Information). Unlike the traditional coin, cylindrical, or rectangular-shape batteries,

which are not competent to suffer any damage, quasi-solid state batteries can normally drive electronic devices under various extreme conditions such as cutting, soaking, freezing, washing, and hammering. 【电池浸泡性能分析】For example, as a flexible device, the quasisolid state ZMBs may be exposed to a large amount of water in some accidental operation. To evaluate the waterproof and stability in water of the quasi-solid state battery, the assembled quasi-solid state ZMBs are soaked and washed in deionized water in a plastic container for 30 min (Figure S17, Supporting Information). The electronic meter can still work normally with the battery after soaking. For the sake of further evaluating the battery performance after immersion, the quasi-solid state ZMBs are cut off from two places then immersing in deionized water for 5 min (Figure 7c). It is impressive that the battery can still drive the device normally. For simulating the effect of water washing on the quasi-solid state flexible battery, the quasisolid state battery can power the electronic watch after being immersed in water and stirred vigorously for 5 min, which proves that the battery has good waterproof and mechanical stability (Figure S18, Supporting Information).【锤击实验】 To investigate whether the ZMBs can bear the hit or accidental fall from a high altitude that is likely to appear for the flexible devices in practical application, the quasi-solid state ZMBs are assembled for the severe hammering tests (Figure S19, Supporting Information). After 30 times of hammers, obvious pits are detected on the surface of the ZMBs, however, the battery is still able to power electronic devices demonstrating the excellent durability of the quasi-solid state ZMBs. 【高温实验】Thermal safety is another important requirement for the flexible batteries in practical wearable applications, however, the conventional organic electrolyte systems are very sensitive to high temperature. To verify the fire resistance of the assembled ZMBs, ZMBs are exposed to fire through an alcohol lamp (Figure S20, Supporting Information). Under the condition of continuous heating for 5 min, the quasi-solid state battery is still competent to drive the electronic watch, exhibiting outstanding fire durability. 【低温实验】Besides, for aqueous batteries, the battery will always fail below 0 °C due to the freezing of water molecules, which is fatal to flexible devices. As a demonstration, the quasi-solid state battery is left to retain at −20 °C for 4 h to demonstrate the anti-icing performance of ZMBs and it is still capable of powering the electronic watch (Figure 7d). The low temperature anti-icing performance roots in the interaction between the charged groups, hydrophilic groups in PZHE and water molecules which hinder the extension of hydrogen bonds during the freezing process of water molecules, leading to the quasi-solid state batteries still worked at −20 °C. 【自修复性能】To demonstrate the self-healing applications, two quasi-solid state ZMBs are connected in series to run the electronic watch (Figure 7e). By cutting the two batteries apart, the digital numbers on the screen of the electronic watch disappear immediately. However, when the broken section is reconnected for a few seconds, the electronic watch is driven afresh with the clearly visible digital numbers appeared on the screen, demonstrating a remarkable self-healing performance of the quasi-solid state batteries. Such an outstanding self-healing performance can be attributed to the electrostatic interaction and hydrogen bonding between the PZHE skeleton and water molecules, which ensures the quick healing of the quasi-solid state battery after injuring (Figure 1a).

【柔性性能概括】In summary, we have successfully fabricated a highly safe and long-life rechargeable Zn metal battery with a (PZHE). The gel electrolyte formed by PZHE framework encapsulating water molecules displays record high ionic conductivity of 32.0 mS cm−1 and ion transference number of 0.656, excellent self-healing and mechanical properties. The PZHE effectively reduces the side reactions and corrosions between water molecules and Zn metal anode, thus achieving a symmetric battery with ultra-long cycling life up to 3500 h. ZMBs consisting of PZHE and the heavily loaded VS2 cathode remain the capacity retention of 83% after 500 cycles. And Zn/PZHE/ MnO2 cells possess a specific capacity of 200 mAh g−1 even after 600 charge/discharge cycles. The flexible quasi-solid state ZMBs with PZHE exhibit excellent processability, self-healing property and safety, which can drive the electronic device operating even after being subjected to cutting, soaking, hammering, washing, burning, and freezing. It is believed that the quasi-solid state flexible ZMBs with such an excellent safety, superior self-healing and remarkable electrochemical performance can pave the way for the next generation promising wearable energy storage devices.

## [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).

2.1. NTP@Zn Anode

【DFT计算分析】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】 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】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】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】 Figure 2g shows that the diffraction peaks of basic zinc sulfate don’t generate. It means that the main side reactions are suppressed in the process of deposition. In addition, it was not found on the cycled NTP@Zn (Figure S23, Supporting Information). On the other hand, the main diffraction peaks of NaZnPO4 are found in 29–31° and 34–36° (Figure S6, Supporting Information).[15] And the other peaks have migration to the right during the Zn2+ plating on NTP@ Ti foil. The peak displacement of high angle (49–51°) is larger than that of low angle (23–25°). It suggests that d-spacing is reduced, which is attributed to the adsorption or insertion of Zn2+ (0.75 Å) in the Ti4+ (0.6 Å) place of NTP. 【电解质电感耦合等离子体测试】Then, inductively coupled plasma tests of the electrolyte after deposition indeed find the Ti element (Figure S7, Supporting Information), which is attributed to dissolution of superficially exposed titanium cation in the presence of sulfate anions.[16] It will make the surface of NTP coating show electronegativity, and further promotes the internal transport/mobility of Zn2+ in the NTP coating.[17]

【XPS分析】The surface chemical composition and local coordination environment information of the as-prepared samples are tested by XPS (ESCALAB 250 spectrometer, PerkinElmer) in Figure 3. The oxidation states and existence of Zn in cycled NTP nanoparticles are elucidated through Zn 2p spectra in Figure 3b.[18] And the interference of ZnSO4 electrolyte in the surface of NTP layer is also eliminated through S 2p scan (Figure 3d). After cycled, the characteristic peak positions of Na 1s has obvious movement from 1072 to 1073 eV in Figure 3a, which is attributed to the effects of Zn2+ and Na+ when Zn2+ transports between TiO6 octahedra and PO4 tetrahedra. The larger nuclear charge number of Zn2+ will lead to the valence electron transfer of Na+, which finally brings the binding energy of Na 1s to shift toward the high field. Meanwhile, the effects also exist in the Zn2+ and O element, which affects the binding energy of O 1s to shift toward the low field in Figure 3c, from 531 to 530.4 eV due to the strong electron absorption of O element.【XRD、TEM分析】 In addition, the interplanar d-spacing will broaden when

Zn2+ diffuses in the interstices of NTP due to its electrostatic repulsive force.[19] After Zn plating/stripping cycling on

NTP@Zn foil, as shown in Figure 3e, the XRD peaks of NTP@ Zn have migrated to the low degrees, suggesting that the interplanar d-spacing of NTP (washing repeatedly by N-methyl-2-pyrrolidone (NMP) and ethanol, from cycled NTP@Zn) was broadened. It has also been found that the interplanar d-spacing of NTP shifts from 0.367 (PDF#72-2457) to 0.379 nm through the HRTEM image (Figure 3f) after Zn plating/stripping cycling. The XRD pattern of NTP shows that the main peaks can be indexed to the rhombohedral structure (PDF#72-2457) (Figure S8a, Supporting Information). The regular and uniform internal arrangement of atoms in NTP can be proved by the sharp diffraction peaks in the XRD pattern. The N2-adsorption/ desorption curve gives the Brunauer–Emmett–Teller specific surface area (SSA) of 89.19 m2 g−1 (Figure S8b, Supporting Information). Average pore size and BJH desorption pore volume (Vpore) of the nano-NTP were determined to be 40 nm and 1 cm3 g−1 (Figure S8c, Supporting Information). 【TEM、SEM分析】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】 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】The thickness of NTP coating was about 20.77 µm through the measure of cross section that could be controlled by the concentration and amount of paint. The surface of NTP coating was flat and dense. The wetting angles (Figure S12, Supporting Information) of one purified water droplet on bare Zn foil (a, 83.19°) and NTP@Zn foil (b, 56.73°) demonstrate that the electrolyte is more likely to infiltrate NTP@Zn foil. The full cell consisted of NTP@Zn foil electrode will have a smaller interface transfer resistance. 【tafel曲线分析】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.

2.2. The Stability and Reversibility of NTP@Zn Electrode

【电池循环性能分析】Galvanostatic Zn plating/stripping was carried out by using CR2016 coin cells to confirm the stability of NTP@Zn electrode. Figure 4 shows the galvanostatic cycling cycling performance of bare Zn|2 m ZnSO4|bare Zn symmetric cell only having 80 h cycling, NTP@Zn|2 m ZnSO4|NTP@Zn symmetric cell achieving 260 h cycling at a current density of 1 mA cm−2 and NTP@Zn|2 m ZnSO |NTP@Zn symmetric cell at different current density of 0.2–5 mA cm−2 achieving 200 h cycling. 【对称电池性能分析】At the very beginning, the NTP@Zn symmetric cell demonstrated much lower polarization than the bare Zn one (40 vs 100 mV, Figure 4b). During 80 h of stripping/plating, a fluctuating polarization voltage (20–100 mV) was detected in the bare Zn symmetric cell. Rather, the NTP@Zn symmetric cell exhibited a stable polarization voltage (30–50 mV) (Figure 4a). After 210 h of stripping/plating, the polarization voltage of the NTP@Zn symmetric cell was 30 mV (Figure 4c). The low polarization indicates a low energy barrier for metal nucleation, and may promote a relatively uniform metal plating process.[21] 【长循环性能分析】Long-term galvanostatic cycling reversibility of symmetrical Zn cells with coated Zn foils manifest stable diffusion of zinc-ion batteries in the coating of NTP. With increasing current density from 0.2 to 5 mA cm−2, the polarization curves still keep a better stability and reversibility in each 20-stripping/plating cycles on the NTP@Zn symmetric cell (Figure 4d), compared with the bare Zn symmetric cell (Figure S14, Supporting Information). The elemental mapping of NTP@Zn (Figure S15, Supporting Information) and NTP nanoparticle (Figure S16, Supporting Information) after 240 h cycle show that Zn element is very uniform in NTP@Zn and NTP nanoparticle. It suggested that the diffusion of Zn2+ in NTP could lead to an even deposition of Zn. 【光学显微镜分析锌沉积】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】 Furthermore, the SEM and EELS-mapping image (Figure S22, Supporting Information) showed that the Zn was mainly distributed between the Ti foil and NTP protection layer after the Zn2+ deposition, suggesting good zinc-ion conductivity and weak electronic conductivity of NTP coating. In addition, bare Zn and NTP@Zn symmetric cells cycled at 0.5 mA cm−2 after 100 stripping/plating cycles were disassembled for SEM analysis. The SEM image of NTP@Zn foil remained highly flat and dense without any detectable protrusions (Figure 5f). Meanwhile, the mobile phone camera with NTP@Zn foil indicates that zinc ions are deposited under the coating of NTP and the NTP coating is stable and undamaged (Figure 5f, inset). However, the SEM image of the bare Zn foil showed alarming sags and crests, which represented a very uneven Zn stripping/plating process (Figure 5d). The surface of bare Zn foil also had lots of macroscopic sharp protuberances (Figure 5d, inset).

2.3. CNT/MnO2 Cathode

【】In order to study the electrochemical properties of the coated Zn foil in full batteries, we prepared the CNT/MnO2 cathode material by a coprecipitation method.[8] Its XRD pattern shows the main peaks indexed to PDF#744-0141 (Figure S18, Supporting Information). The carbon content of CNT/MnO2 composite cathode material was 18% in the TGA curve (Figure S19, Supporting Information). The appearance and the elements distribution of CNT/MnO2 was shown in Figure S20, Supporting Information.

2.4. Full Cell

【CV、EIS分析】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】Figure 6c displays the rate property of NTP@Zn/MnO2 battery at a series of current densities. The NTP@Zn/MnO2 battery can be seen to exhibit an average discharge capacity of 207, 196, 170, 155, 130, and 128 mA h g−1 at the current density of 1, 2, 5, 10, 20, and 30 C, respectively. With the increase of the current densities, the discharge capacity hadn’t decreased substantially even in 30 C. When the currentdensity returns back to 1 C after 60 cycles, NTP@Zn/MnO2 battery still retains a capacity of 275 mA h g−1. The rate capability of bare Zn/MnO2 in Figure 6c indicates that the performance is inferior in high rate due to the limit of high charge-transfer resistance. The long-term stability of NTP@Zn/MnO2 battery was superior to that of bare Zn/MnO2 (Figure 6d). After 600 cycles at 5 C, a reversible capacity of 128 mA h g−1 on NTP@Zn/MnO2 battery can still be achieved. Both Zn/MnO2 batteries deliver high CE of nearly 100%, indicative of favorable cycling reversibility. The long cycling performance and corresponding CE of the cells are plotted in Figure 6e. NTP@Zn/MnO2 battery retains a considerable capacity of 105 mA h g−1 with a CE nearly 100% after 10 000 charge/discharge cycles at 10 C. Each cycle capacity attenuation rate is only 0.004%. The long cycling performance of NTP@Zn/MnO2 battery represents the best level compared with Zn/MnO2 battery to date (Table 1). In addition, the cycle performance of TPO@Zn/MnO2 and ZPO@Zn/MnO2 are also provided in Figure S24, Supporting Information, which remains 126.1 and 123.5 mA h g−1 after 300 cycles at 10 C, respectively.

3. Conclusion

【固态保护层结论概括】In summary, we designed a NTP solid-state electrolyte protection layer to stabilize Zn metal anode. Due to the high ionic conductivity and low electrochemical activity of NTP, the “ion passable fence” of NTP coating enables uniform zinc-ion flux and suppresses zinc dendrites growth. Meanwhile, the NTP coating can successfully prevent side reactions on the Zn metal anode/electrolyte interface. Therefore, stabilized Zn anode with high rate performance and super long cycling has been achieved in symmetrical cells and Zn/MnO2 battery.

## [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).

2. Results and Discussion

2.1. Synthesis and Characterization

【制备过程阐述】The synthesis process of Zn@ZnSe is illustrated in Figure 1c. Briefly, selenium (Se) powder and Zn foil were placed in a tube furnace in an atmosphere of Ar/H2. When heated to 350 °C for 2 h, Se powder melted and reacted with H2 to form H2Se, which could react with the surface of Zn foil to form a ZnSe protective layer in situ.[28,29] 【制备过程颜色变化】Figure 1d shows that the surface of Zn changes from silver-gray to brown after selenization. As presented in Figure 1e, there are many scratches on the bare polished Zn metal surface. However, when covered with the protective layer, the surface becomes smoother, and the scratches basically disappear (Figure 1f). The elemental mapping images are shown in Figure S1 in the Supporting Information. 【形貌分析】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】Figure 1i shows that the X-ray diffraction (XRD) pattern of Zn foil matches well with hexagonal Zn (JCPDS No. 04-0831). Three new characteristic diffraction peaks appear at 27.3°, 45.3°, and 53.7° after in situ selenization (inset of Figure 1i), which coincide with the (111), (220), and (311) crystal planes of cubic ZnSe (JCPDS No. 65-9603), respectively. 【实验最佳温度确定】Additionally, we investigated the optimal temperature for constructing the ZnSe protective layer. As displayed in Figure S2 in the Supporting Information, the intensity of the characteristic peaks of ZnSe gradually increases with temperature (from 300 to 400 °C). As shown in Figure S3 in the Supporting Information, a uniform ZnSe layer cannot be formed on the Zn surface at 300 °C, while at 400 °C, the surface is deformed and damaged due to its proximity to the melting point of Zn. Therefore, 350 °C is the optimal temperature to construct a uniform ZnSe protective layer on a Zn surface. 【最佳厚度确定】The optimal thickness of the ZnSe protective layer was also investigated. The results in Figure S4 in the Supporting Information reveal that a thickness of 800 nm, which is obtained after 2 h of reacting at 350 °C, is optimal.【亲水性分析】 In addition, Zn@ZnSe exhibits a better hydrophilicity than bare Zn (Figure S5, Supporting Information), indicating that the electrolyte can penetrate the ZnSe layer to facilitate Zn2+ transport toward the anode surface.[14] 【XPS实验分析】X-ray photoelectron spectroscopy (XPS) was employed to investigate the chemical state of Zn@ZnSe. In the high-resolution Zn 2p spectrum (Figure S6, Supporting Information), two peaks at 1021.64 and 1044.71 eV are ascribed to Zn 2p3/2 and Zn 2p1/2, respectively. Similarly, in the high-resolution Se 3d spectrum (Figure 1j), the fitting peaks centered at 53.84 and 54.71 eV arise from Se 3d5/2 and Se 3d3/2, respectively.[30] In addition, there is a weak, broad peak at 59.17 eV attributed to the presence of small amounts of SeOx on the surface.[31]

2.2. Electrochemical Properties of Symmetric Cells

【电化学性能分析】To explore whether such a ZnSe protective layer is effective in aqueous Zn-ion batteries, the electrochemical performances of the bare Zn and Zn@ZnSe symmetric cells were systematically investigated. As shown in Figure 2a, the rate performances of the Zn and Zn@ZnSe symmetric cells were evaluated at current densities ranging from 0.5 to 10 mA cm−2 with a fixed capacity of 1.0 mAh cm−2. The bare Zn cell always delivers a higher overpotential, which stems from its increased interfacial resistance due to continuous corrosion and the accumulation of byproducts. 【过电位分析】In particular, after the current density increases to 10 mA cm−2, the overpotential increases sharply and fluctuates greatly (up to 2.5 V; Figure S7, Supporting Information), mainly due to internal short circuits stemming from the growth of Zn dendrites.[32] In contrast, the Zn@ZnSe cell exhibits ultrastable voltage profiles with low overpotential and excellent reversibility. Even at a high current density of 10 mA cm−2, the Zn@ZnSe cell can still maintain a very low average overpotential of 95 mV (Figure 2b). Upon returning to 0.5 mA cm−2, this cell can still operate stably for more than 450 h with an extremely low average overpotential of 25 mV during Zn stripping/plating cycles (Figure S8, Supporting Information). 【对称电池性能分析】The cycling performances of the bare Zn and Zn@ZnSe symmetric cells were investigated at 1 mA cm−2 with a capacity of 1 mAh cm−2 (Figure 2c). During the first cycle, the bare cell shows a large Zn nucleation overpotential of 58.1 mV, which is far higher than the 15.5 mV of the Zn@ZnSe cell, signifying that the presence of a ZnSe protective layer can significantly reduce the energy barrier of Zn deposition (Figure 2d).[33] In the subsequent cycles, the Zn cell still delivers a higher overpotential until an abnormal fluctuation occurs ≈110 h later. After 200 h, the polarization voltage increases dramatically and fluctuates violently (the inset of Figure 2c; Figure S9, Supporting Information), and the cell gradually fails. In contrast, the Zn@ZnSe symmetric cell can run steadily for more than 1500 h with a smaller overpotential (≈28 mV) and without any sign of fluctuations or short circuits.

【！！！扩散过程受限和临界电流密度效应分析】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】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】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】The long-term cycling stabilities of these full cells were investigated at a high current density of 2C. As shown in Figure 3c, the capacities of these two cells quickly decay in the initial 200 cycles, which is related to the dissolution of Mn2+ from the cathode.[37] After 200 cycles, the capacity of the bare Zn||MnO2 still fades rapidly until it decays sharply to almost no capacity after cycling for ≈900 cycles (Figure S13a, Supporting Information). This behavior is attributed to the short-circuit failure of the cell due to continuous corrosion and side reactions and the severe Zn dendrite growth during Zn stripping/ plating cycles. In contrast, Zn@ZnSe||MnO2 can still operate steadily after 900 cycles (Figure S13b, Supporting Information). Zn@ZnSe||MnO2 possesses a lifespan twice that of Zn||MnO2 (up to 1800 stable cycles) and still holds a capacity of ≈100 mAh g−1 with a high CE near 100%, thereby showing extremely high stability. The test results of these full cells further confirm the effectiveness of the ZnSe protective layer in inhibiting the growth of Zn dendrites and occurrence of side reactions. The rate performance test results also verify this point (Figure S14, Supporting Information).

2.4. Elimination of Interfacial Side Reactions by the ZnSe Protective Layer

【实验分析与理论计算结合】We combined various experiments and systematic theoretical calculations to explore how the ZnSe protective layer improves the electrochemical performance of Zn metal anodes and deeply understand its internal mechanism.【！！！腐蚀、界面副反应测试XRD、SEM】 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】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】The corrosion reactions of Zn are accompanied by H2 evolution, so the ability of the ZnSe protective layer to inhibit H2 evolution was further investigated. We inspected symmetric coin cells that had been operating for 300 h at 10 mA cm−2 with a capacity of 1 mAh cm−2 and found that the bare Zn cell partially detaches due to the increase in pressure by the continuous generation of H2; thus, electrolyte leakage occurs (it became a white powder after drying). In contrast, the Zn@ZnSe cell is still well preserved, indicating that H2 evolution has been effectively suppressed (Figure S17, Supporting Information). To observe H2 evolution more intuitively, we used homemade transparent cells to run for 50 cycles at 10 mA cm−2 with 1 mAh cm−2 and then observed the generation of H2 bubbles. As shown in Figure S18 in the Supporting Information, the bare Zn surface exhibits many H2 bubbles, while no H2 bubbles appear on the Zn@ZnSe surface, further demonstrating the effective inhibition of H2 evolution by the ZnSe protective layer. 【静置-循环测试】We further adopted a more stringent method to evaluate the electrochemical performance of the Zn@ZnSe symmetric cell over its full lifecycle, that is, alternate cycling (48 h) and resting (24 h) at high rates (10 mA cm−2 with 1 mAh cm−2). Figure 4e shows that after resuming operation from the rest period, the Zn@ZnSe cell always runs stably with a low polarization voltage (<100 mV) and without any fluctuations or short circuits, thereby exhibiting excellent electrochemical stability. The above experimental results show that the ZnSe protective layer can effectively eliminate the impact of interfacial side reactions, ensuring that the Zn anode is not corroded in either storage or working periods.

2.5. Inhibition and Regulation of Dendrite Growth by the ZnSe Protective Layer

【！！！原位光学显微镜变化过程分析】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】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】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】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】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】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】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】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】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】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】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】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.

## [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).

【钝化膜引出】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】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】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】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】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】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】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】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】Digital images of the bare and polished Zn metal electrodes reveal that the two kinds of Zn electrodes suffered from serious surface corrosion with an obvious color change during cycling (Figure S7, Supporting Information). 【SEM分析】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】Before cycling, only the characteristic peaks of Zn metal located at 36.4°, 39.1°, and 43.3° can be found for the bare Zn electrode (Figure 1g), which suggests that the Zn5(CO3)2(OH)6 layer is hard to identify.[16] After one cycle, a small peak at 8.5° can be detected, corresponding to the (002) planes of Zn4SO4(OH)6·xH2O by-product, and the intensity increases with further cycling (50 cycles), indicating the aggravated side reactions during battery operation, which is similar to the XRD patterns of the polished Zn after different numbers of cycles (Figure S9, Supporting Information). Although removal of the Zn5(CO3)2(OH)6 reduces the energy barrier for Zn stripping/plating and prolongs the cycling lifespan from ≈100 h to ≈250 h at 2 mA cm−2 (Figure S10, Supporting Information), the performance of the polished Zn cell is still far from satisfactory due to the notorious Zn dendrite growth and side reactions. 【构建SEI的重要性】Building a dense and homogeneous SEI layer is an effective strategy to enhance the Zn reversibility.[17] 【制备方法的引入】Based on the phase diagram of sulfur (Figure S11, Supporting Information), we have elaborately grown an artificial ZnS film on the Zn metal surface by an in situ vapor–solid reaction, as illustrated in Figure 2a. Specifically, sulfur can be vaporized at ≈200 °C under the pressure of ≈1 × 10−3 atm, and the sulfur vapor will react with Zn metal by generating ZnS at high temperatures. Accordingly, Zn foil was put in a specially designed tube with 100 g sulfur powder below it. Then, the tube was evacuated and ealed. At high temperature, the gaseous sulfur vapor spread to the Zn metal surface and reacted with Zn metal to generate a dense and uniform ZnS layer. 【保护层增强可逆性分析】As aforementioned, Zn electrode, whether with/without a Zn5(CO3)2(OH)6 layer, is highly unstable, and suffers from side reactions and dendrite growth during battery operation (Figure 2b), which not only fades the CE and reversible capacity, but also shortens the cycling lifespan of Zn batteries. In striking contrast, the ZnS protective layer on the Zn surface not only effectively inhibits the corrosion reactions by blocking the electrolyte, but also suppresses the Zn dendrite growth by guiding the Zn2+ stripping/plating underneath, enhancing the reversibility of Zn metal (Figure 2b). 【XRD分析处理温度影响】To study the influence of the treatment temperature on the ZnS film, different operating temperatures of 300 °C, 350 °C, and 400 °C were conducted. From the XRD patterns of ZnS@ Zn electrodes (Figure 3a), the sample obtained at 300 °C (ZnS@ Zn-300) only shows the characteristic peaks of Zn metal, indicating no obvious formation of ZnS film at this temperature, as further confirmed by EDS mapping (Figure S12, Supporting Information). No clear S element layer can be found on the Zn metal surface, suggesting that this is an improper operating temperature. When the temperature was increased to 350 °C, the XRD pattern displayed new peaks at 28.6°, 47.5°, and 56.3°, corresponding to the (111), (220), and (311) planes of ZnS (PDF # 00-005-0566), respectively.[18] The intensity of these peaks increased when the temperature was increased to 400 °C. Figure S13 (Supporting Information) presents digital images of ZnS@Zn electrodes obtained at different temperatures, with the ZnS@Zn-300 foil showing almost no change in colors or luminosity. 【SEM分析】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】The cross-sectional image (Figure 3c) reveals a homogeneous ZnS coating layer with a thickness of ≈0.5 µm, as further confirmed by the high-resolution image (Figure S14, Supporting Information) and EDS mapping (Figure 3d). 【XPS分析】X-ray photoelectron spectroscopy (XPS) spectra of bare Zn and ZnS@Zn-350 were collected (Figure 3e,f), and the bare Zn electrode only shows the binding energies of Zn 2p1/2 and Zn 2p3/2 at 1045.1 and 1021.9 eV, respectively. Whereas the ZnS@Zn-350 displays the S signals of S 2p3/2 and S2p1/2 located at 161.9 and 163.2 eV, respectively.[19] Importantly, a small binding energy shift in the Zn 2p3/2 region was mainly due to the formation of Zn–S polar bonds at the interphase of ZnS and Zn metal,

which enhances the adhesion of the ZnS film to the Zn metal.【！！！DFT分析成键作用】 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】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】In order to study the stability of the ZnS layer, ZnS@Zn-350 foil was soaked in 1 m ZnSO4 electrolyte for 10 d. The digital images of the ZnS@Zn-350 foil show similar surfaces before and after soaking in electrolyte for 10 d (Figure S16, Supporting Information), demonstrating that this layer is highly stable. The XRD pattern was collected after the soaking in electrolyte (Figure S17, Supporting Information), which is similar to that for ZnS@Zn-350 foil before soaking and without any peaks for the Zn4SO4(OH)6·xH2O by-product, indicating that the side reactions between the Zn metal and the electrolyte were disrupted. 【线性极化实验】The impact of the ZnS layer on Zn metal corrosion was investigated by linear polarization experiments in 1 m ZnSO4 electrolyte (Figure S18, Supporting Information). Compared to the bare Zn, the corrosion potential of the ZnS@Zn-350 increased from −1.052 to −1.048 V, suggesting that it has less tendency towards corrosion reactions.[22] Notably, this ZnS layer also reduces the corrosion current by 368.5 µA cm−2. 【！ZnS层具有较差的电子导电性，但具有较高的离子导电性和较高的Zn2 t膜，因此ZnS层还具有抑制Zn枝晶生长的强大的人工SEI作用】In addition to inhibiting the side reactions, the ZnS layer also functions as a robust artificial SEI to suppress Zn dendrite growth because it has poor electronic conductivity, but high ionic conductivity and high Zn2

t film. Furthermore, the Zn2+ was further calculated to quantitat

tively describe the Zn2+ conducting ability of the ZnS protective layer. In a bare Zn symmetric cell, a rather low Zn2

t + of 0.33

was obtained (Figure S21a, Supporting Information), which is mainly due to the strong preferential solvation of Zn2+ over the anions, leading to a bulky solvation shell around Zn2+. SO4

+. 【半导体材料性质】It is well known that cubic ZnS has

been widely used as a semiconductor due to its wide-bandgap properties.[23] The electrical resistivity (ρ) of the ZnS protective film was also evaluated (Figure S19, Supporting Information). According to the following formula

ρ =

RS L

∗ =

US IL

∗ ∗

, in which

R is the resistance, I is the applied current, L is the thickness of the ZnS, U is the corresponding voltage, and S is the contact area, ρ was estimated as ≈1.5 × 105 Ω cm (σ ≈ 6.5 × 10−6 S cm−1). 【！！！优异离子导电性的作用】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】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】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】Figure 4c shows a cross-sectional image of the bare Zn metal after Zn plating (1 mA h cm−2). Remarkably, uneven deposition occurred on the Zn surface with serious agglomeration, which easily triggers dendrite growth. After deposition of 2 mA h cm−2, the agglomeration was aggravated, raising a potential safety issue after further Zn plating (Figure 4d). In contrast, no obvious Zn plates or protrusions were generated on the ZnS@Zn-350 surface after 1 mA h cm−2 of plating (Figure 4e), indicating that the ZnS protective layer helps to guide homogeneous Zn deposition underneath the film. Moreover, the thickness of the deposited Zn was ≈1.5 µm, similar to its theoretical value (≈1.7 µm under 1 mA h cm−2). Even after 2 mA h cm−2 of plating, uniform deposition under the ZnS layer was still observed, as shown in Figure 4f, resulting in dendrite-free Zn plating. 【循环结合SEM分析】The CE is one of the most important parameters used to evaluate the reversibility of Zn plating and stripping.[26] In a Cu–Zn cell, the CEs were calculated from the ratio of Zn removed from the Cu substrate to that deposited during the same cycle. The ZnS protective layer on Cu foil was obtained by the doctor blading method. First, the morphology of Zn deposition on the bare Cu and ZnS@Cu was studied at current density of 2 mA cm−2 with a capacity of 1 mA h cm−2. Clearly, the bare Cu substrate was covered by mossy Zn plates with obvious protrusions. In comparison, no obvious protrusions were generated on the ZnS@Cu surface, further indicating that the ZnS protective layer guides the Zn deposition (Figure S22, Supporting Information). In the Cu–Zn cell, the initial CE was only ≈77.6% and gradually increased to ≈97.6% after the first 20 cycles (Figure 4g). 【！！！电化学性能分析】Such a CE is still low, however, due to the poor reversibility of Zn metal caused by the side reactions and dendrite formation. Notably, the CEs fluctuate greatly after ≈120 cycles, which is mainly due to short-circuiting of the battery. The ZnS@Cu–Zn cell, however, displayed a much higher initial CE of ≈88.5% compared to the Cu–Zn cell, and it increased to 99.2% in the following 10 cycles. Even after 200 cycles, the CE remained stable, mainly benefiting from the suppression of side reactions and dendrite growth. The charge– discharge voltage profiles for different cycles of the Cu–Zn cell are shown in Figure 4h. The initial voltage hysteresis is ≈141 mV for the Cu–Zn cell, much higher than that for the ZnS@Cu–Zn cell (≈105 mV, Figure 4i), indicating a higher energy barrier for Zn nucleation/dissolution in the phase transition between Zn2+ ions and Zn metal.[27]

【对称电池分析】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

Adv. Mater. 2020, 32, 2003021

block the conduction of ions.[28] 【倍率性能分析】The rate performance of Zn cells was investigated at various current densities from 0.2 to 10 mA cm−2, as shown in Figure 5c, in which the bare Zn cell always exhibits substantially higher voltage hysteresis than the ZnS@Zn-350 cell, suggesting low polarization and favorable stability in the ZnS@Zn-350 cell. 【倍率性能循环后SEM分析】After the rate tests, the morphology of the Zn and the ZnS@Zn-350 electrodes was studied by SEM. The bare Zn electrode had an uneven surface with many agglomerated Zn plates, as shown in Figure S24 (Supporting Information), which is mainly caused by the Zn corrosion and dendrite growth. The ZnS@Zn-350 electrode displays a clean surface, however, resulting from its corrosionfree and dendrite-free stripping/plating behavior (Figure S25, Supporting Information). 【全电池性能分析】To further prove the suitability for application of ZnS@Zn-350 electrode, a MnO2/Zn full-cell was assembled by choosing MnO2 electrode as the cathode, since it is one of the most promising candidates for aqueous Zn batteries.[29] Figure S26 (Supporting Information) presents representative SEM images of electrodeposited MnO2 on carbon cloth. The surface of the carbon cloth is covered by MnO2 clusters featuring a petal-like nanostructure. The full-cell was tested in electrolyte consisting of 1 m ZnSO4 + 0.1 m MnSO4, in which MnSO4 was used as an additive to inhibit the dissolution of Mn2+ from the MnO2 cathode.[30] Typical stepwise charge–discharge curves of the MnO2/ZnS@Zn-350 battery were observed at 1 C (Figure S27, Supporting Information), suggesting the Zn2+ and H+ cointercalation mechanism.[31] 【CV分析】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】The long-term cycling stability curves of both batteries at the high rate of 5 C are plotted in Figure 5e. The cell with bare Zn foil presents an initial capacity of ≈115.6 mA h g−1. The capacity dramatically drops after 1000 cycles, however, mainly because the separator was pierced by Zn dendrites, leading to the short-circuiting of the battery. In contrast, the MnO2/ZnS@Zn-350 battery delivers a higher initial capacity (125.8 mA h g−1) compared to the MnO2/Zn battery. After 2500 cycles, a high capacity of 110.2 mA h g−1 with a high CE of 99.3% was retained, corresponding to capacity retention of 87.6%, which is mainly due to the inhibition of Zn corrosion and dendrite growth during the battery operation.

【钝化膜分析】The protective function of Zn5(CO3)2(OH)6 passive film on

Zn metal was explored in 1 m ZnSO4 electrolyte. Although this dense passivation layer could passivate Zn metal in the air by blocking oxygen and moisture, it cannot protect Zn metal in mild electrolyte. Accordingly, a homogeneous and dense ZnS protective film was introduced in situ on the Zn metal surface by a high-temperature vapor–solid strategy. 【保护膜作用分析】This film was found to be highly stable in mild electrolyte, which contributes to improving the reversibility of Zn metal by avoiding the electrolyte-induced side reactions. Moreover, this robust ZnS film shows strong adhesion, good mechanical strength, and high ionic conductivity, which enables even Zn plating/stripping, as confirmed by in situ optical microscopy. 【电池性能阐述】The ZnS@Zn-350 symmetrical cell delivered a smaller voltage polarization and longer lifespan of >1100 h at 2 mA h cm−1 compared to the bare Zn cells. Benefiting from the side-reaction-free and dendritefree ZnS@Zn-350 electrode, the MnO2/ZnS@Zn-350 full-cell displayed excellent cycling stability, with 87.6% capacity retention after 2500 cycles. Our fundamental findings offer a better understanding of Zn metal surface chemistry and pave the way to developing practical Zn metal batteries with mild electrolyte.

## [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).

【XRD分析】The X-ray diffraction (XRD) patterns confirm the successful fabrication of Zn@ZnF2

composite. The peaks at 20.76°,29.33°, 32.56°, and 51.93° are well-indexed to (111), (110), (101), and (211) planes of ZnF2, respectively (Figure 2a). 【AFM分析】The atomic force microscopy (AFM) image displays that the Zn surface is evenly and homogeneously covered by ZnF2 (Figure 2b). 【XPS分析】The high-resolution X-ray photoelectron spectroscopy (XPS) Zn 2p spectra of both Zn@ZnF2 and bare Zn foil exhibit two distinct peaks, ascribed to Zn 2p1/2 and Zn 2p3/2, respectively (Figure 2c,d). 【！！！结合能键的分析】Compared with bare Zn foil, the formation of ZnF2 layer leads to the appearance of components with slightly different binding energies, which can be resolved into minimum two signals. This can be explained by Zn-F polar bonds at the interphase of ZnF2 and Zn metal, exhibiting dissimilar coordination environments.[14,20] The F signal of F 1s at 683.99 eV further confirms the formation of Zn-F polar bonds, which can enhance the adhesion of the ZnF2 layer to the Zn metal (Figure 2e). 【DFT分析】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】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】This analysis indicates that the surface of ZnF2 could be highly conductive if the surfaces of Zn2+ ions are not pinned to any position on the ZnF2 lattice. Moreover, the lower energy barrier of Zn2+ inserted into Zn@ZnF2 can be validated by the decrease in insertion energy barrier, where the Zn insertion barrier on Zn@ZnF2 is 0.52 eV, lower than that of bulk ZnF2 (4.08 eV) and metallic Zn surface (0.67 eV) (Figure 2i). Accordingly, the Zn@ZnF2 preferentially provides electrostatic attraction toward Zn2+, accelerating the kinetics “through” reducing the deposition barrier. 【！！！界面性能影响因素】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】As expected, the ZnF2 layer shows significant higher ionic conductivity of 80.2 mS cm–1 than that of a routine glass fiber (GF) separator (9.8 mS cm–1), and even all reported Zn foil coating layers (Figure 3a; Table S1, Supporting Information), calculated from AC impedance spectra (Figure S2, Supporting Information). In comparison, the electronic conductivity of the ZnF2 layer is only 0.11 mS cm–1, tested by four-point probe, which is near four orders of magnitude lower than that of the pure Zn metal foil, 970.87 mS cm–1 (Figure 3b). 【！！！电沉积过程分析】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】Moreover, the Zn@ZnF2 electrode shows a very low charge-transfer resistance of 39.99 Ω, a tenth lower than that of the bare Zn electrode (412.62 Ω) (Figure S3, Supporting Information). The Zn2+ transfer number of the ZnF2 reaches to 0.65, which is much larger than that of the GF separator coupled with 2 m ZnSO4 aqueous electrolyte (0.28; Figure S4, Supporting Information). The above results suggest outstanding Zn2+ transportation capability of the ZnF2 layer. 【对称电池分析】To prove the efficacy of Zn@ZnF2 in suppressing dendrite formation during different rate cycling in liquid electrolytes, we choose the widely used 2 m ZnSO4 aqueous electrolyte to test. We perform a series of plating/stripping measurements in symmetric Zn//Zn and Zn@ZnF2//Zn@ZnF2 cells under galvanostatic condition. The cells are cycled at 1, 2, and 5 mA cm–2 with 1 mAh cm–2 of the Zn reversibly cycled. The Zn@ZnF2// Zn@ZnF2 cells show superior performance with a cycle life of >2500 h, where 6250 mAh cm–2 cumulative capacity is cycled (Figure 3c). Cycling at elevated current densities (from 0.5 to

10 mAh cm–2) reveals a much more stable voltage profile with a smaller voltage hysteresis (Figure 3d). Even at a high rate of 10 mA cm–2 with 10 mAh cm–2 of the Zn reversibly cycled, Zn@ZnF2//Zn@ZnF2 cells can be operated steadily for ≈590 h without apparent irreversible voltage observed (Figure 3e). In contrast, Zn//Zn cells last only 600 h at a low current of 1 mA cm–2 and <250 h at 2 and 5 mA cm–2, meanwhile succumbing to substantial voltage fluctuation just after a few cycles. The difference in cycling stability is pronounced at high current

densities. 【过电位分析】The plating/stripping overpotential

for Zn@ZnF2 is only 56.4 mV, significantly lower than that of bare Zn (238.9 mV). The excellent reversibility and cyclic lifespan remarkably outperform all of its counterparts with dendrite precaution-oriented and hydrogen evolution suppression designs (Figure 3f). 【低过电位分析：高离子导电性和快速离子扩散，以及ZnF2层在水环境中的良好稳定性】The outstanding reversibility of Zn deposition/dissolution low overpotential originates from high ionic conductivity and fast ion diffusion of ZnF2 solid in Zn2+ion conductor as well as good stability of ZnF2 layer in aqueous environment (Figure S5a,b, Supporting Information). Surprisingly, the Zn@ZnF2//Zn@ZnF2 cell can cycle over 400 h at 2 mA cm–2 and 140 h at 5 mA cm–2 with 1 mAh cm–2 of Zn reversibly cycled in an alkaline electrolyte of (6 m KOH + 0.2 m Zn(AC)2). In sharp contrast, after only <10 h plating/stripping cycles with Zn//Zn cell in the same condition, a sudden polarization occurs due to intensified Zn-dendrite formation (Figure S6, Supporting Information). It demonstrates that this design achieves superior reversible cycling performance at both mild and alkaline electrolytes. 【保护层优点】It should be mentioned that the ZnF2 protective layer should be uniform in terms of composition and thickness, which dominates the cation transport. As a result, it can homogenize the transport of Zn2+ cations toward the electrode surface. In contrast, lumpy coating layer will accelerate the dendrite growth. As shown in Figure S7 (Supporting Information), Zn@ZnF2 electrode with commercial ZnF2 pow-ders being coated induces fast dendrite formation and growth, leading to only ≈290 h cycling stability of symmetric cells in mild electrolyte, much lower than bare Zn electrode-based cells (600 h, purple line in Figure 3c). The morphologies of Zn@ZnF2 and bare Zn electrodes are analyzed after 50 cycles of stripping/plating in symmetric cells at 2 mA cm–2 with 1 mAh cm–2 of the Zn reversibly cycled.【循环后SEM分析】 The scanning electron microscopy (SEM) image confirms that the smooth and dense surface of the Zn deposition with the ZnF2 layer remains essentially flat with no obvious dendrites (Figure 3g). Inversely, for bare Zn electrode, the deposited Zn is highly porous and consists of thin platelets (Figure 3h). From the cross-sectional SEM image, a clear gap is observed beneath the ZnF2 layer for the Zn@ZnF2 electrode at the stripped state (Figure 3i). 【！！锌倾向于较低能量处生长】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】 Consequently, it prefers to bring Zn2+ ions back into the empty region beneath the ZnF2 layer and the Zn plating reaction can be well confined under ZnF2 layer, in which uneven Zn layer can be deposited on Zn anode and thus dendrite growth is suppressed.

【不对称电池分析】The Zn plating/stripping Coulombic efficiencies are quantified using asymmetric Zn//Cu, Zn@ZnF2//Cu, and Zn// ZnF2@Cu cells with 1 mAh cm–2 of the Zn reversibly cycled. The Coulombic efficiency of Zn plating/stripping is calculated from the ratio of charge passed in each segment (Figure 3k; Figure S8, Supporting Information). The discharge/charge Coulombic efficiency of Zn@ZnF2//Cu electrodes reaches 99% within only 40 cycles, increases to 99.5% within 90 cycles, and stably maintains for 1000 cycles without any decay. Likewise, the discharge/charge Coulombic efficiency of Zn//ZnF2@Cu electrodes reaches to 99.3% within 50 cycles, and stably maintains for 440 cycles without any decay. With regard to bare Zn, the Coulombic efficiency is lower in the same condition and the cell quickly fails after only ≈100 plating/stripping cycles (Figure S9a, Supporting Information). 【局部短路分析】The observed Coulombic efficiency’s fluctuations are consistent with failure either as a result of

localized short-circuiting or by reconnection of fragmentary Zn deposits that broke away from the electrode (“dead” Zn). Figure 3l exhibits the corresponding voltage profiles for Zn@ZnF2//Cu cell, which consists of the typical plateau for Zn plating/stripping on the Cu surface at a very low overpotential of ≈52.7 mV, revealed by the voltage hysteresis between Zn plating and stripping curves (155.5 mV; Figure S9b, Supporting Information). Encouragingly, the voltage profiles remain stable over 1000 cycles, suggesting exceptional reversibility of Zn@ZnF2 electrode.

【成核过电位低的分析】The nucleation overpotential of Zn//Cu and Zn@ZnF2// Cu asymmetric cells is investigated for insight into the effect of ZnF2 layer on the Zn deposition. The Zn@ZnF2 displays only 42.5 mV nucleation overpotential at 1 mA cm–2, much lower than that of bare Zn (79.4 mV), which propones a dramatically reduced Zn deposition barrier (Figure S10a, Supporting Information). Likewise, the same rules are appropriate for the current densities of 2 and 5 mA cm–2 on Cu foil (Figure S10b–d, Supporting Information). The reduced nucleation overpotential is attributed to the lower local current density that forces Zn2+ migration on the surface of Zn metal enabled by the ZnF2 matrix. The ZnF2 layer establishes a solid-state diffusion barrier to homogenize the interfacial Zn2+ flux and mediate the migration of Zn2+ special to Cu substrate surface. 【计时电流法分析】The chronoamperometry (CA) is further conducted to reveal the nucleation procedure and surface fashion. The current curve of Zn@ZnF2 dictates an stable and constant 3D diffusion procedure at ≈9.3 mA cm–2 after short 2D diffusion (4 s) under an overpotential of −150 mV, revealing that adhered underlying Zn2+ ions move laterally and are reduced to Zn0 locally in very close proximity to a place where the initial adsorption occurs (Figure S11, Supporting Information). 【二维扩散过程和粗糙的沉积传播过程】The deposition ultimately evolves into a smooth and compact Zn layer. In sharp contrast, the current density continuously elevates beyond 100 s, depicting a long and fast 2D diffusion process and rough deposition propagation. The Zn2+ tends aggregate and uneven dendrite growth to minimize surface energy and exposed area (“tip” effect).[35,36] The exchange current density is utilized to precisely evaluate the kinetics of Zn deposition, which reflects the direct interaction of ZnF2 layer with the Zn metal surface, by the following equation[37,38]

ii FRT tot 0 = (/ )(η /2) (1)

where η depicts the deposition overpotential, and i0 represents the exchange current density. 【交换电流分析】Generally, lower values of the exchange current density give information that the surface of the Zn metal is inhibited or passivated, representing the degree to which additive Zn2+ is absorbed to the active metal surface and suppresses the reduction reaction. The Zn@ZnF2 electrode offers a low exchange current of 8.9 mA cm–2, much lower than that of bare Zn (16.7 mA cm–2), suggesting reduced redox reaction liveness of Zn@ZnF2 electrode under equilibrium potential (Figure S12, Supporting Information). 【！！！保护层的作用】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】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】We further achieve the hydrogen evolution polarization curves of both electrodes in sodium acid phthalate buffer solution with a pH value of 5.0, close to that for 2 m ZnSO4 electrolyte (pH = 4.6), which can separate hydrogen evolution reaction with Zn precipitation procedure. The Zn@ZnF2 electrode shows much lower hydrogen evolution current density in a wide voltage range from −0.72 to −1.31 V versus standard hydrogen electrode (SHE) in compared to that of bare Zn electrode (e.g., 0.024 mAh cm–2 for Zn@ZnF2 electrode and 5.85 mAh cm–2 (almost 139 time higher than Zn@ZnF2) for bare Zn electrode at −1 V vs Zn/Zn2+) (Figure S15a, Supporting Information). 【tafel曲线分析】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】The Zn corrosion is another side reaction of oxygen-induced passivation on the interface of Zn metal and electrolyte with oxygen dissolved. With regard to the bare Zn, the corrosion potential of the coated Zn@ZnF2 increases from −0.665 to −0.650 V versus Zn/Zn2+ (Figure S16, Supporting Information). Meanwhile, the ZnF2 protective layer also reduces the corrosion current by 105.3 mA cm–2. The results elucidate less tendency of corrosion reactions and a lower corrosion of Zn@ZnF2 electrode. 【】To accurately quantitate gas production, we set up a battery–gas chromatography–mass spectrometry (GC-MS) appliance to in situ monitor hydrogen flux by measuring the evolved hydrogen utilizing GC during the Zn charging/discharging process in routine 2 m ZnSO4 aqueous electrolyte at 10 mA cm–2 with 5 mAh cm–2 of Zn reversibly cycled. 【产气分析】As shown in Figure 4c, the hydrogen evolution rate during symmetric Zn//Zn cell operation is conducted to 3.18 mmol h–1 cm–2 and increases to 3.76 mmol h–1 cm–2. The anabatic side hydrogen evolution originates from the increase of contact area between Zn metal and electrolyte due to uneven distribution of Zn deposition. Prior to the electrochemical test, the cell rests for 1 h to obtain adsorption/desorption balance and sufficient wetting. The hydrogen evolved during the resting process (0.56 mmol h–1 cm–2) is attributed to chemical oxidation due to the unstable thermodynamic properties in aqueous solution. Inversely, there was almost no H2 (0.02 mmol h–1 cm–2) detected in symmetric Zn@ZnF2//Zn@ZnF2 cell (Figure 4d). To study rechargeable batteries in practical application, we construct electrochemical cells using a conventional α-MnO2 as cathode and bare Zn or Zn@ZnF2 as anode. During the process of charging, hydrogen evolution increases and reaches a maximum value of 7.7 mmol h–1 cm–2, which is attributed to the decomposition of water in Zn anode surface (Figure 4e). Assisted by the ZnF2 protective layer, the hydrogen evolution on Zn anode surface is almost completely suppressed during the whole charge period (maximum 0.06 mmol h–1 cm–2) (Figure 4f). 【理论计算分析】In theory, to investigate the mechanism of suppressing side

of hydrogen evolution reaction, we calculate hydrogen adsorption Gibbs free energy of ΔGH for Zn (002) and Zn@ZnF2 (ZnF2 side). Theoretically, the optimized hydrogen evolution reaction activity can be achieved when ΔGH is close to zero, and if ΔGH is larger (smaller) than zero, hydrogen binding is too weak (strong), accordingly adsorption (desorption) is suppressed.[39] As shown in Figure 4g, Zn@ZnF2 interface exhibits a much higher ΔGH value of 1.31 eV compared with Zn (1.00 eV) and Pt(111) benchmarks (−0.04 eV), confirming that hydrogen evolution reaction can be greatly suppressed with the interface structure.

【全电池性能分析】The fully prototype pouch-type cells with high areal capacity

are assembled to prove the practical application of our strategy. We choose full-fledged and promising α-MnO2 as cathodes coupled with bare Zn and Zn@ZnF2 anodes for aqueous Zn batteries, and the cell configuration consists of a single whole set of anode–separator–cathode. The cells possess a high areal capacity of ≈3.2 mAh cm–2 and are cycled at a current rate of 1 C. As expected, both cells of Zn//MnO2 and Zn@ZnF2//MnO2 display similar galvanostatic charge/discharge profiles at the first cycle (Figure 5a,b). The Zn@ZnF2//MnO2 cell can well maintain their voltage profiles and 93.63% capacity even after 1000 cycles with 3.31 mAh cm–2 of Zn reversibly cycled in each segment. In contrast, the Zn//MnO2 cell presents a similar initial areal capacity of 3.20 mAh cm–2. However, the capacity dramatically decays to 2.15 mAh cm–2 only after 100 cycles (with 67.15% initial capacity retained) and to 1.18 mAh cm–2 (with 36.88% initial capacity retained) (Figure 5c). To the best of our knowledge, currently, there are barely Zn anodes at depth of discharge (DOD) higher than 1 mAh cm–2 reported. The high areal capacity of ≈3.2 mAh cm–2 Zn reversibly cycled at each cycle demonstrates a superhigh cycling stability of Zn@ZnF2 anodes for 1000 charge/discharge cycles. 【循环后SEM分析】To investigate the essence of attenuation, the surface appearance of Zn anode after the full cell test is studied. Not surprisingly, the Zn@ZnF2 anode remains smooth and intact after 1000 cycles test (Figure 5d). Inversely, the bare Zn anode becomes porous and consists of thin platelets after only 300 cycles (Figure 5e). In order to accurately quantify the gas production of Zn//MnO2 and Zn@ZnF2//MnO2 full battery, the 4 × 4 cm2 pouch-type cells are fabricated and used to measure the volume of pouch cell before and after the cycling test. As depicted in Figure 5f,g, the Zn//MnO2 pouch cell is remarkably swollen while there is no change of Zn@ZnF2//MnO2 cell. 【产气分析】Detailed measurement of the produced gas volume reveals that the Zn// MnO2 cell produces about 126.4 times higher gas volume than that of Zn@ZnF2//MnO2 cell (≈0.5 cm3 for Zn@ZnF2//MnO2 cell vs ≈63.2 cm3 for Zn//MnO2 cell) after 15 cycles’ test. The hydrogen evolution rate for Zn//MnO2 is about ≈0.016 cm3 (mAh)–1, which is 133.3 times higher than that of Zn@ZnF2// MnO2 cell (0.00012 cm3 (mAh)–1). The dramatically suppressed hydrogen evolution during cycling suggests the successful inhibition of side reaction by ZnF2 layer, which thus elevates the reversibility of electrochemical plating/stripping of metallic Zn. 【多层袋型电池】The exceptional performance of single-layer Zn@ZnF2// MnO2 pouch cell inspires us to construct high-energy multilayer pouch-type batteries. The battery configuration consists of ten whole sets of anode–separator–cathode stacks with a size of 4 × 6 cm2, which is fabricated in ambient air environment without any complicated procedures and protections. As shown in Figure 5h, the 850 mAh Zn@ZnF2//MnO2 battery presents excellent cycling performance with a 93.17% initial capacity retained after 160 cycles at 0.2 C. In comparison, the Zn// MnO2 battery rapidly decays to 49.78% and fails (short-circuit) only after 15 cycles. The results demonstrate excellent largescale and practical use of our strategies.

In summary, we quantitatively assessed the parasitic hydrogen evolution flux during Zn deposition process including a Zn//Zn asymmetric cell and Zn//MnO2 full cell by in situ battery–gas chromatography–mass spectrometry analysis. The hydrogen evolution flux reaches 3.76 mmol h–1 cm–2 in each segment of the Zn//Zn cell, and maximum 7.70 mmol h–1 cm–2 in Zn//MnO2 (≈3.2 mAh cm–2) full cell at full charged state. The Zn deposition is loose and causes dendrite growth due to undesirable side reaction in aqueous system. 【！！！离子导体的作用】 To overcome these challenges, we create a solid Zn2+-ion conductor of ZnF2 to inhibit side reaction and enhance electrochemical reversibility of Zn metal electrode. The designed Zn@ZnF2 electrode shows remarkably suppressed hydrogen evolution in comparison to the based Zn electrode (3.76 vs 0.02 mmol h–1 cm–2 in symmetric cell and 7.70 vs 0.06 mmol h–1 cm–2 in full cell). Meanwhile, the Zn@ZnF2 architecture can regulate Zn electrodeposition and promote the Zn2+ diffusion. 【对称电池分析】Accordingly, the Zn@ZnF2// Zn@ZnF2 symmetry exhibits highly reversible Zn cycling over 2500 h at 5 mA cm–2 and deep cycling at a high current density of 10 mA cm–2 and a high areal capacity of 10 mAh cm–2 with an low total over potential of 56.4 mV. As a result, the Zn@ZnF2//MnO2 full cell with a high areal capacity of ≈3.2 mAh cm–2 can operate over 1000 cycles with 93.63% initial capacity retained at ≈100% Coulombic efficiency. 【全电池分析】Finally, an 850 mAh large-capacity Zn@ZnF2//MnO2 full cell with a size of 4 × 6 cm2 can reversibly work over 160 cycles (800 h) with 93.17% initial capacity being retained. This strategy of advanced Zn metal anode with high reversibility and significantly suppressed side reaction opens a way to achieve highareal-capacity aqueous Zn metal batteries.

## [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.

Results and Discussion Texture Formation ofZn via Electrodeposition

【XRD分析各向异性】We first investigated the effects of electrolytes on the texture control of deposited metallic Zn. X-ray diffraction (XRD) spectra in Figure 1a shows the dominant intensity of Zn (002) diffraction is over the highly depressed (100) and even far over (101) diffractions,indicating clearly the anisotropy of the synthesized metallic Zn. 【！！！择优取向分析】Hence,electrodeposition using zinc sulfonate salt, zinc trifluoromethanesulfonate (Zn(OTf)2)(Figure 1b), leads to the preferred orientation of (002) in the synthesized Zn (Figure 1c and d). On the contrary,a governing (101) is obtained by using ZnSO4 with the largely depressed (100) and (002). With reference to the commercial zinc foil, it indicates that the preferred orientations in the metallic structure of Zn can be tuned via changing the types of electrolyte in the electrodeposition. From the perspective of material growth, it is not only critical to form the preferred orientation, but also equally important to align the oriented crystalline domains.Concerning Zn, an out-of-plane alignment of (002) to substrate exposes (100) plane but favors the dendrite growth.[6b]

【衍射分析择优取向】In order to explore the relative orientation of surface normal of the deposited Zn (002) basal plane with respect to the substrate,pole figures were extracted from the diffraction information as afunction of sample rotation and titling. Figure 1e clearly confirms the parallel alignment of the surface normal of (002) and the substrate normal, and meanwhile rules out the isotropic arrangement of the oriented domains.【SEM分析生长结构】Scanning electron microscopy (SEM) images further confirm the proposed growth structure,showing uniform domains (Figure 1f and Figure S1) consisting of hexagonal-like plates on the surface (Figure 1g). Acolumnar structure is then proposed for the synthesized Zn with the parallel alignment between its basal plane and the Cu substrate (Figure 1d), with reference to the ridge structure by ZnSO4

(Figure 1h,i and Figure S1).[15] 【添加剂对生长晶面的影响】Based on the above,the OTf-induced Zn (002) texture can be achieved, benchmarking against the (101) texture by the conventional sulphate electrolyte. To verify the essence of possessing OTf

-Zn2+ in the

electrolyte,a distinct case was considered when deposition proceeds with Zinc di[bis(trifluoromethylsulfonyl)imide] (Zn(TFSI)2

), where Zn2+ is bonded to the -N(CF3 instead of the sulfonate group.[13f] SO3)2 group 【DFT分析】Though (100) growth can be depressed, the synthesized metal still has amore intense (101), whose morphology consists of randomly oriented flakes (Figure S2). This motivates adetailed look at the zinc coordination in the electrolyte towards the deposited structure.DFT calculations were then performed to study the zinc coordination with OTf in the aqueous environment (Figure 1b)[16] (Please refer to Supporting Information, Experimental Section for calculation details). Specifically,two OTf groups replace the positions of two water molecules (n=5, 6) in the original Zn(H2

O)6 2+ octahedral complex. This substitution process is energetically favorable with aGibbs free energy of 11.5 eV.Inthis newly formed Zn(OTf)2 complex, the average bond length of Zn-O between Zn2+ OTf (2.075 )iseven shorter than that between Zn2+ H2O(2.125 ). Meanwhile,the OTf

(H2 -Zn2+ O-Zn2+

O)4 and

and coordination

has astrong interaction energy of 6.71 eV,substantially larger than that of H2

(0.53 eV). This provides

strong evidence on the reconstruction of the zinc coordination by OTf

in the salt-in-water regime.Also,the reconstructed .[3b]

zinc coordination is supported by the significant altered water network with the presence of OTf

in the sulfonate-containing group is replaced by -CH3 Angew.Chem. Int.Ed. 2021, 60,7213 –7219

When the headgroup ,i.e.,

Figure 2. The effects of sulfonate anions on the texture formation. a) XRD spectra of the deposited Zn in aseries of sulfonate-based electrolytes of2M zinc methanesulfonate (Zn(MS)2 sulfonate (Zn(ES)2

(DBS)2), respectively.b)DFT optimized structures of Zn(OTf)2 VESTA.[17] \*adion (right), visualized with ), 2M zinc ethane), and 0.5 Mzinc dodecyl benzene sulfonate (Zn(H2O)4

complex suspending on Cu (200) surface (left), and further attaching on the surface with the Zn(OTf)2

SEM images showing the Zn deposited at times of c) 1min and d) 10 min;and e) the formation of Zn (002) facets by Zn(OTf)2 an overpotential of 0.15 V. f) Scheme of the proposed OTf

-induced

growth of the Zn (002) texture. g) Cyclic voltammetry (CV) curves of Zn plating/stripping in 2M Zn(OTf)2

at ascan rate of1mVs1 .

h) Chronocoulometry curves of Zn plating/striping in 2M Zn(OTf)2 based on the CV curves in (g). i) Long-term coulombic efficiencies of 2M Zn(OTf)2

aconstant capacity of1mAhcm2 0.5 mAcm2

2020 Wiley-VCH GmbH .Scale bar:2 mmfor (c);5 mmfor (d), (e). www.angewandte.org 7215

and 2M ZnSO4 evaluated by Ti j Zn asymmetric cells at and acurrent density of

at Zn(CH3 SO3)2 (Zn(MS)2 ), the (002) texture can also be

achieved, with nearly the same intensity ratio of (002)/(101) and parallelly exposed basal plane (Figure 2a and Figure S3). Theachieved texture by Zn(MS)2

suggests the possibility of

reducing the cost of electrolyte and attempts towards environmental friendliness by using non-fluorine components.Onthe other hand, increasing the chain length between two head groups leads to amore favorite (101) growth (Figure S3). 【！空间位阻和负电荷沿分子链的重新分布削弱了与锌的配位】It can be attributed to the steric hindrance and redistribution of the negative charge along the molecule chain that weakens the coordination to zinc.Supporting the role of sulfonate group,itprovides auseful guideline to the design of the sulfonate-based electrolytes for the texture control of zinc deposition. Meanwhile,weoptimized the concentration of Zn(OTf)2

to achieve agood quality of the deposited film

(Figure S4). 【！外延生长材料和衬底之间晶格不匹配的要求(通常在10%以内】Further,the interfacial interplay of the deposited zinc,

anion group,and substrate was deliberated. Note that though the Zn (002) texture is formed, Cu substrate shows nearly isotropic arrangement on its (111) and (002) planes (Figure S5). Also,considering the requirement on lattice mismatch between growing material and substrate towards an epitaxial growth (typically within 10%), Zn (101) is likely to be favored by Cu (111) (D1.25%) or Fe (111) (D0.38%), comparing to (002). This implies that more than lattice mismatch, there is large room for interfacial design and engineering towards the control of texture growth. 【！研究电解质和衬底之间界面上的锌配位】To envision more details on the interface,westudied the zinc coordination at the interface between the electrolyte and substrate to understand the deposition process.DFT calculations were carried out between different zinc coordinations and Cu surfaces.Itshows clearly that OTf

facilitates the

stabilization of zinc ion on the Cu surface at the complete dehydrated state (Figure 2b). On the Cu surface,the predicted binding energy of the Zn(OTf)2

\*adion is 13.90 to

13.36 eV based on different exposed planes,which is one order of magnitude higher than that of the zinc adion ( 1.25 to 1.00 eV) (Table S1). Thestronger adsorption energy may receive contribution from the interaction between oxygen from OTf Zn(OTf)2

\*adions facilitates their diffusion to the flat surface

sites,which are generally less energetically favorable than the sites at steps and kinks.[18]

【负离子的形成和扩散影响Zn的成核和生长】Consequently,the formation and

diffusion of adions influence the nucleation and growth of Zn. Ahigh density of planar nucleation sites can subsequently form and distribute across the surface,comparing to the attachment of adions to steps or kinks.Normal growth of the material can advance,despite proceeding in alayer-by-layer mode.Tostudy the growth aspect, time-dependent study shows aparallel alignment of hexagonal plates to the Cu surface observed at the early growth stage (1 min) (Figure 2c and Figure S6 for the large scale image). In 10 mins,the individual growth sites start to merge to form afilm (Figure 2d and Figure S6 for the large scale image). The continuous metallic film can be eventually formed after acertain deposition time,e.g., 60 min as in Figure 1c and f. This confirms the normal growth mode of the columnar Zn film. Recognizing the competitive relation between overpotential (i.e., h,the applied deposition potential with reference to the bulk zinc deposition potential) and surface energy on nucleation and growth,[18, 19]

we then investigated

the effects of h. At h of 0.15 V, the dominance of (002) is evident (Figure S7), with well-defined hexagonal Zn (002) plane aligned parallel to the surface normal (Figure 2e). However,further increase h to 0.25 Vleads to more significant (101). This is attributed to the more dominant power from h overcoming the effects of OTf

receiving the impact form hydrogen evolution reaction (Figure S7).[20] Hence,weproposed an anion-induced model for the Zn (002) texture deposition (Figure 2f). OTf

Chemie

Theabove finding reveals the key role of the sulfonate-Zn2+

based electrolytes in electrochemical deposition through the strong OTf

interaction. Hence,the exploration of novel

electrolytes with both high zincophilicity and stripping/plating reversibility is ongoing for precise control on the selective deposition of textured Zn. Thereversibility of stripped and plated Zn in acertain electrolyte system is quantified primarily through coulombic efficiency (CE). TheCEs were investigated using cyclic voltammetry in athree-electrode cell. 【CV分析库伦效率】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】Electrochemical Performance ofthe Zn (002) Texture in ZIB

When applied in a rechargeable battery, it is critical toassess the lifespan of metal anode during stripping/ plating.The control on the Zn texture with preferred orientationenables rationalizing its electrochemical behaviors. To elim-inate any detrimental effects from deposition substrate (e.g.,Cu due to its relatively low oxidation potential, Figure S11), the deposited metallic zinc“paper"s were peeled off from thesubstrate and denoted with their textures for further inves-tigation, respectively. At a current density of 1 mAcm 2, thestripping/plating curve shows that the (101) zinc paper can beshort-circuited in 2 M ZnSO4 within only≈105 h (Figure 3a).The lifetime can be improved to≈243h by using thecommercial Zn foil, while resulting in larger polarization(Figure S12). In sharp contrast, the (002) zinc paper is able toproceed a stable stripping/plating of 800 h in 2 M Zn(OTf)2 at1 mAcm-2 (Figure 3a). Also, the (002) zinc paper showsa lower initial polarization of 98.5 mV compared with114.1 mV for its (101) counterpart, where the polarizationretains well at 84.0 mV after 800h cycling (Figure 3b).Importantly, the advantage of the (002) zinc paper is morepronounced at a high current density of 10 mAcm 2. The(101) counterpart shorts at ≈20h in ZnSO4 (Figure 3c), which is due to the fast dendrite growth under high currentdensity. The fast deterioration is not significantly improved byusing the Zn foil, but can be mediated when applying the(002) Zn paper in ZnSO4, where the lifetime elongates to≈75 h (Figure S13). However, the (002) zinc paper canpresent a stable stripping/plating of 200 h in Zn(OTf)2, whichis an ≈10-fold increase compared with its counterpart (Figure 3c), exhibiting its extraordinary stability.Meantime, the polarization is well retained, i.e., 114.9 mVat the 1st compared with 97.2 mV at the 200th

cycle, cycle (Figure 3d). To

investigate the deposition overpotential in the symmetric cells,the curves were decoupled from the information collected on acustomized three-electrode setup.Zn(002) presents asignificantly lower deposition overpotential of 0.012 Vthan 0.036 Vfor the Zn foil (Figure S14), showing its merits in the kinetics of deposition. Further,exsitu XRD spectra indicate that after stripping/ ,the (002) texture of the zinc paper is

plating at 1mAcm2

identical to that of the pristine sample (Figure 3e). SEM clearly presents the (002) hexagons laying parallelly on the surface,without protrusion (Figure 3f and Figure S15). Even after stripping/plating at 10 mAcm2

,the hexagonal basal

planes can be unambiguously viewed (Figure 3f and Figure S15). 【！！！002晶面的优点】Interestingly,the dominance of (002) over (101) appears to be enhanced from the XRD pattern (Figure 3e), where (101) can be hardly detected. This may further support the templating role of the exposed (002) planes during plating,which promotes the (002) growth with adendrite-freefeature (Figure 3g and Figure S15, please refer to Figure S16 for the detailed surface analysis). Consequently,itcontributes to the significant increase of the lifetime of the Zn anode.On the contrary,protrusions are widely observed for the (101) zinc papers (Figure 3h and Figure S17). This can be understood from the growth of the kink/step-driven ridge structure. Such an uneven and protruding plating can be the main cause of short-circuit during stripping/plating in ZnSO4

. 【！！！电化学性能评价电解液】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】 In summary, we have demonstrated the electrodeposition of the Zn (002) texture via the sulfonate-based electrolytes. A columnar growth model is proposed based on the co-align ment of the Zn (002) plane normal and the substrate normal as verified by the pole figures. To understand the formation mechanism of the (002) texture, interaction at the interface of Zn, OTf@ , and Cu substrate has been investigated by DFT calculations, correlated with the empirical study on the synthesis. Based on the above, an anion-induced growth of the Zn (002) texture is revealed, where the strong coordina tion of OTf@ with Zn2+ plays the key role. With the texture control on metallic Zn, we have rationalized the electro chemical behaviors of the Zn (002) and (101) textures. Highly reversible Zn stripping/plating has been achieved with the (002) zinc paper. Especially at a high current density of10 mAcm@2 , the lifetime of the (002) zinc paper can be & 10- fold longer than its (101) counterpart. The dendrite-free characteristic and templating role during plating has been revealed for the (002) plane. The assembled V2O5 /(002) zinc paper full cell presents a high cycling stability (64.1% capacity retention for 2000 cycles at 1 Ag@1 , with a CE of & 100%). The developed anion texturing strategy opens a route to the design of zincophilicity electrolytes for achieving desirable stable Zn texture and further high performance ZIBs, which can be prospering by exploring a wide range of electrolytes. To demonstrate the practicability of the strategy, we verify the feasibility of achieving (002) texture by non-fluorine sulfonate-based electrolyte and on a wide range of conducting substrates. Besides the general adaptability for materials processing, we anticipate that it serves as a platform for rationalizing the electrochemical performance in energy storage devices towards exploring zinc chemistry

## [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.

【！！！锌板的缺点】Aqueous zinc-ion batteries (ZIBs) are attracting great interest owing to the distinctive merits of Zn anodes.[1] Metallic zinc is the most common anodes of ZIBs. Although commercial Zn foil is low-cost and can be produced on a large scale, its intrinsic surface roughness will lead to dramatic enhancement of local electric field near tips.[2] charging process, Zn2+

During prefers to continuously deposit on

the tips with the enhanced electric field, which gradually evolves into Zn dendrite.[3]

The continuous growth of the

dendrite can lead to an internal shorting failure after piercing the separators of batteries. Moreover, during Zn stripping, Zn dendrite could be prone to break from its root and convert into dead zinc, resulting in poor Coulombic efficiency (CE) and severe capacity fading.[4]

develop strategies to protect Zn anodes against undesired dendrite.

【！！！保护层的好处】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】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】Therefore, the in situ growth methods have to be further considered to fabricate highly uniform artificial layer on Zn anodes of ZIBs. Inspired by this, we developed an in situ spontaneously reducing/ assembling strategy to directly assemble ultrathin and uniform MXene layers onto the surface of Zn anodes, where the thickness of MXene layers can be well controlled. Ultrathin thickness will be beneficial to the fast transport of electrolyte ions. Furthermore, the MXene layer can effectively inhibit the formation of Zn dendrite and side reactions on Zn anodes. Therefore, ZIBs based on Zn anodes with MXene layers exhibit enhanced electrochemical performance.

【制备过程阐述】Figure 1a illustrates the growth of MXene layer on Zn

anode by a synchronously reducing and self-assembling process. Since Ti3

in our case. In a typical experiment, Ti3 As a result, it is highly desired to HCl/LiF.[9]

first prepared by selective etching of the aluminum atomic layers in the MAX (Ti3

C2Tx is most widely studied, it is selected C2Tx dispersion was

AlC2) phase with a mild etchant of During this process, a large amount of negatively

charged oxygen-containing groups will generate on the surface of MXene sheets. Since the reduction potential of removing the oxygencontaining groups is higher than that of Zn/Zn2+

(0.76 V vs.

SHE), the MXene sheets can be reduced by Zn foil. Therefore, Zn foil was placed on the surface of above well-dispersed MXene solution. At the interface between Zn foil and MXene dispersion, the surface of Zn foil is ionized and the electrons from Zn foil are readily transferred to the MXene sheets (Figure 1a).【！！！正负电荷的相互作用】 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】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】Furthermore, in the C1s

XPS spectra (Figure 2 f and g), the peak intensity of CO (286.3 eV) is weakened and the peak intensity of OC=O (288.8 eV) almost disappears, further indicating the removal of oxygen-containing groups. Moreover, the peak of CC (285.0 eV) is also weakened due to the consumption of COH groups on the carbon layers.[11] to Ti3

Such conversion from Ti3 C2 Tx

C2Txy can be also reflected in the O 1s XPS spectra, where the peak intensity of CTi(OH)x

(532.2 eV) is

decreased and the peak intensity of TiO (529.6 eV) is increased (Supporting Information, Figure S3), demonstrating the conversion of CTi(OH)x

bonds to TiO bonds.

【润湿性分析】Furthermore, the thickness of the MXene layer can be adjusted by controlling the assembly time (Supporting Information, Figure S4). The MXene-coated Zn foil with different assembly time are denoted as MZnx (x=10, 30, 60, and 90 min, respectively). Impressively, compared with pure Zn foil, the wettability between MXene layer and electrolyte is enhanced (Figure 2d; Supporting Information,

high-resolution XPS spectra of C1s regions of f) Ti3C2Tx film, and film.

Figure S5), which will be beneficial to the permeability of electrolyte. 【对称电池分析】To understand the feasibility of MXene layer in protecting

C2Tx and Zn can take place spontaneously

Zn anode, the electrochemical behaviors of MZnx were measured in a symmetric cell at 0.2 mAcm2

(Figure 3a). The

voltage profiles of symmetric cells with MZnx present smaller voltage fluctuation in comparison with that of pure Zn, indicating the more reversible Zn plating/stripping process owing to the existence of MXene layer. 【循环性能分析】Impressively, among MZnx, MZn-60 displays a more stable voltage profile with a lower voltage hysteresis of 47 mV for 800 h of 400 cycles (Figure 3a; Supporting Information, Figure S6). In contrast, an increased voltage hysteresis and a sudden voltage drop were detected after 167 h in the pure Zn-based cell, ultimately resulting in the cell failure due to the dendriteinduced internal short circuit. Furthermore, the enhanced cycling stability with lower voltage hysteresis of MZn-60 against pure Zn can be also achieved at 0.5, 1, 3, and 5mAcm2

(Supporting Information, Figure S7). Different

from MZn-60, the corresponding symmetrical cells based on MZn-10 and MZn-30 begin to appear larger voltage fluctuation after 165 and 260 h, respectively (Figure 3a). 【！！！厚度对电解液运输能力的影响】It may be ascribed to that these relatively thin MXene layers easily suffer from the unfavorable mechanical stability due to volume changes during Zn plating/stripping process (Supporting Information, Figure S8). Furthermore, it is noted that larger voltage fluctuation will appear again and the polarization is also increased in the case of MZn-90. It is ascribed to the degraded ion transportation capacity between Zn foil and electrolyte due to the increase of MXene layer thickness.[12] 【倍率性能和对称电池性能分析】Hence, MZn-60 would be the optimal protective layer. Figure 3b displays the rate performance of the symmetric

cells with MZn-60. It displays the stable voltage profiles with a lower voltage hysteresis at high rate states in comparison with the case of pure Zn-based cells. When the current density is increased from 0.5 to 5 mAcm2

, the cells with MZn-60

exhibit a steadily increasing hysteresis of 48, 54, 80, and 112 mV, respectively (Figure 3c; Supporting Information, Figure S9). However, the cell with pure Zn breaks down at 5mAcm2 0.5 mAcm2

. Furthermore, when the current density returns to after 50 cycles, the voltage hysteresis can be

recovered to 46 mV, suggesting a high stability of MZn-60. Impressively, such voltage hysteresis is also superior to most of previously reported anodes of ZIBs with different coating layers due to ultrathin thickness and unique structure of MXene layer (Figure 3 f).[2, 12,13]

【CV分析】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】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】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】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】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】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

2864 www.angewandte.org

, 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】In summary, a uniform MXene layer was assembled on

the surface of Zn anode by developing a facile in situ spontaneously reducing/assembling strategy. The MXene layer endows the anode with distinct merits including low nucleation energy barrier and uniformly distributed electric field, resulting in uniform Zn deposition. As a result, the MZn anode exhibits long-term cycling stability, lower voltage hysteresis as well as smooth dendrite-free surface, suggesting its potential to serve as stable anodes of ZIBs. As a proof of concept, MZn-60/MnO2

batteries were assembled. Impressively, they deliver an excellent cycling stability with 81% capacity retention after 500 cycles. Undoubtedly, such MXene-integrated Zn anodes with enhanced electrochemical performance and dendrite-free behaviors sheds fresh insights for a highly stable Zn-based battery system.

## [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.

3. Results and discussion

【添加剂对锌阳极沉积的影响】3.1 Effect of PEI additive on zinc anode plating

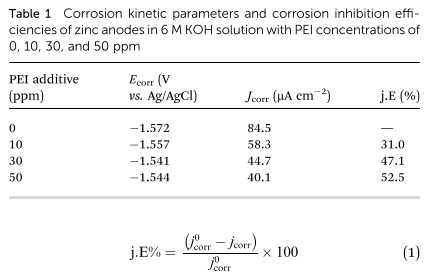
【！金属锌阳极的阴极伏安扫描曲线-PEI添加剂对锌阳极阴极反应的影响】图1显示了不同PEI浓度的碱性电解质溶液中锌金属阳极在锌还原过程中的电化学特性。(图1(a))清楚地显示了PEI添加剂对锌阳极阴极反应的影响。在没有PEI添加剂(即PEI 0ppm)的情况下，锌在-1.63 V左右出现典型的还原峰，这代表Zn2+物种在锌阳极上的还原形成金属锌矿床。Fig. 1 shows the electrochemical characteristics of zinc metal anodes during the zinc reduction process in an alkaline electrolyte solution with different PEI concentrations. The cathodic voltammetry scan curves of the zinc metal anode (Fig. 1(a)) clearly show the effects of the PEI additive on the cathodic reactions of the zinc anode. In the absence of PEI additive, i.e., PEI 0 ppm, a typical reduction peak of zinc is seen at about -1.63 V, which represents the reduction of Zn2+ species to form metallic zinc deposits on the zinc anode. 【原位光学in operando OM -阴极伏安扫描曲线锌电沉积形态演变-气泡产生HER】By in operando OM observation, the process of cathodic reactions on the zinc anode surface in additive-free electrolyte solution during the cathodic voltammetry scan is revealed. 从图S1可以看出，在锌还原峰区域(图S1(B))，从OCV到1.8 V，可以原位观察到锌沉积在成核和生长过程中的形态演变(图S1(C(a d))。当电位上升到1.8 V以上时，不仅锌层快速生长，形成粗糙的电极表面，而且气泡在电极表面膨胀，表明强烈的HER是由水分裂引起的(图S1(C(e和f))。同时，阴极伏安扫描曲线也表明，在1.9 ~ 2.0 V范围内的负电流密度随着HER强度的增大而增大。As seen in Fig. S1,† within the region of the zinc reduction peak (Fig. S1(B)),† from OCV to 1.8 V, the morphology evolution of zinc deposits during nucleation and growth can be observed in situ (Fig. S1(C(a–d))†). As the potential rises above 1.8 V, not only do the zinc deposits grow fast to form a rough electrode surface, but the bubbles also expand on the electrode surface, indicating that an intense HER is caused by water splitting (Fig. S1(C(e and f))†). Meanwhile, the cathodic voltammetry scan curve also shows that the negative current density in the range of1.9 to 2.0 V increases due to the intense HER. 【锌电沉积-原位光学-阴极伏安扫描曲线沉积过电位增大-沉积电位负移】相比之下,的情况下PEI-added电解质溶液,浓度越高的裴的开始显著增加过电压引起的电沉积锌(红色箭头在图1 (a)),和锌还原电位的显示出重大的消极转变从1.63 V至1.69 V的裴浓度增加。In contrast, in the cases of PEI-added electrolyte solution, the higher concentrations of PEI caused a notable increase of overpotential for the starting of zinc electrodeposition (red arrow in Fig. 1(a)), and the reduction potential of zinc showed a significant negative shift from 1.63 V to 1.69 V as the PEI concentration increased. 【阴极伏安扫描曲线结果分析-添加剂吸附导致成核反应优于晶体生长-极化增大；吸附导致HER增强】这些阴极扫描曲线的变化表明，在高PEI浓度下，成核反应优于锌晶体生长。这可以归因于PEI在电极表面的吸附，导致极化程度的增加。These changes of cathodic scan curves indicate the preference of nucleation reaction over zinc crystal growth at high PEI concentrations. This can be attributed to the adsorption of PEI on the electrode surface, resulting in a increase in the extent of polarization. 此外，值得注意的是，随着PEI浓度的增加，1.8 V及以上的负电流密度显著增加(图1(a)中的蓝色箭头)。这说明PEI的吸附作用导致HER的增强。Moreover, it is noticeable that the negative current density at 1.8 V and beyond is significantly raised with increasing PEI concentration (blue arrow in Fig. 1(a)). This suggests that the PEI adsorption results in the enhancement of the HER. 【计时电流-恒压锌电沉积-总述】Regarding the study of zinc plating, Fig. 1(b) shows the chronoamperogram of potentiostatic zinc plating at 1.8 V for 1800 s at various PEI concentrations. 【对比样计时电流-电流先稳定后增大-因为活性表面积增大-枝晶】In the electrolyte of PEI 0 ppm, a typical evolution tendency of dendritic zinc growth in the time–current density curve is observed. In the period of the first 500 s, a pseudo-steady-state current density of 32 mA cm2 is seen in that curve, which approximately corresponds to the limiting current density on a zinc electrode, 34 mA cm2, as confirmed by the cathodic linear sweep voltammetry scan of the zinc anode. After 500 s, the current density starts to rise noticeably, which generally indicates a rapid increase of active surface area on the electrode as a result of dendritic zinc growth. 【添加剂-计时电流-电流增大被抑制】However, the rise of current density is significantly suppressed in the presence of PEI additive. Even when only 5 ppm PEI is added, the current density increases only slightly with time. At the PEI concentrations of 10 ppm, 30 ppm, and 50 ppm, the current density remains nearly constant at about 30 mA cm2 throughout the plating process. Although the current density shows a slight decline with increasing PEI concentration, the current density curves show no measurable rise with time whatsoever. 【计时电流总结-电流密度降低-抑制锌电沉积；电流密度稳定-抑制了锌枝晶】The decline of current density with the addition of PEI indicates kinetically suppressed zinc electrodeposition. The stable current-density curves imply that dendritic zinc growth, which significantly increases the surface area, is prevented. 【计时电流初始时间电流密度变化-初始电流密度大 成核位点多；相反将导致导致锌晶化诱导时间的延长】Fig. 1(c) shows the transients of current density curves for various PEI concentrations during the initial zinc plating for 3 s. These transients of current density reveal the change of zinc nucleation behavior with an increase in PEI concentration. Within the initial 0.5 s, a high initial current density of 160 mA cm2 is observed for 0 ppm PEI, indicating that all nucleation sites on the electrode surface are activated at the beginning of zinc nucleus formation within a very short time. At 10 ppm PEI, the initial current density drops to 122 mA cm2, which indicates that the surface activation of zinc nucleation is reduced due to the PEI adsorption. However, in the cases of 30 ppm and 50 ppm PEI, in the initial 0.5 s, considerably lower initial current densities of 88 and 76 mAcm2, respectively, are found, and then the current densities rise slightly to 93 and 92 mA cm2, respectively. 初始电流密度的增加与锌核的形成和积累过程相对应，说明在较高的PEI浓度下，电极表面活性位点的减少导致锌晶化诱导时间的延长The rise of initial current density corresponds to the formation and accumulation processes of zinc nuclei, which indicate that a decrease of active sites on the electrode surface at higher PEI concentrations results in an increase of the induction time of zinc crystallization. The phenomenon of current-density rise is most prominent in the case of PEI 50 ppm. This diffusion-limited nucleation process is similar to the zinc nucleation process in ionic liquid electrolytes.23,26 【阴极极化和计时电流证明-PEI添加剂可以限制锌的成核生长行为】The results of chronoamperograms agree with the cathodic voltammetry analysis and indicate that the zinc nucleation–growth behavior can be restricted by the PEI additive. 【锌电沉积SEM-表面和截面-不同浓度不同形状-】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】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】In Fig. S2,† the effect of deposition kinetics on the morphology change and the corresponding current-density curve evolution can also be confirmed in the study of zinc anode plating at different applied potentials of 1.7 V and 1.8 V. 【电流密度变化趋势相同-形貌不同】A similar tendency of initial current-density decay and the subsequently stabilized current density curve is seen when the applied potential is changed from 1.8 V to 1.7 V (Fig. S2(a)†), which is due to the decrease of electrochemical reaction kinetics. Meanwhile, the morphology of zinc deposits changes significantly at different applied potentials (Fig. S2(b)†). The zinc deposits formed at 1.7 V feature a dense rock-shaped structure markedly distinct from the loose fern-shaped dendrite structure formed at 1.8 V, which can be attributed to the variation of deposition–growth kinetics of zinc. 【！！限制扩散改变锌电沉积形貌-好方法-动力学限制的电镀过程可以促进致密镀锌组织的形成，抑制枝晶的生长】结果表明，在温和的锌沉积过程中，采用限制扩散的电镀工艺可以改变锌晶体的生长形态。因此，PEI添加剂对锌层从松散的枝晶到致密膜的形态转变的影响主要是由于电极表面的极化导致锌扩散-沉积速率减慢This result reveals that a diffusion-limited plating protocol can dominate a mild zinc deposition process and change the growth morphology of zinc crystals. Therefore, the effect of PEI additive on the morphological transitions of zinc deposits, from loose dendrites to a dense film, is mainly attributed to the slowing down of the zinc diffusion–deposition rate caused by the polarization of the electrode surface. The kinetically restricted plating process can promote the formation of a dense zinc plating structure and suppress the dendrite growth. 【XRD-总述-包含哪些峰】Fig. 3 shows the XRD patterns of zinc deposits at various PEI concentrations obtained after 1.8 V plating for 1800 s, in comparison with that of the blank zinc foil electrode. All of the zinc deposits show the typical diffraction peaks for the (002), (100), (101), (102) and (103)/(110) planes of a hexagonal zinc crystal. 【对比样XRD-与锌箔一样101是优势晶面，100.102.103.110被抑制，002被增强-与锌枝晶的各向异性生长趋势相一致？】In the deposits obtained in the additive-free electrolyte, namely in the case of 0 ppm PEI, the preferred orientation of zinc growth is still along the (101) crystal plane, similar to the pattern of zinc foil. However, the peak intensities of the (100), (102) and (103)/(110) planes are markedly suppressed, and the rise of the (002) peak is evident. 这说明(002)面上锌矿床的生长方向也是定向的，这与锌枝晶的各向异性生长趋势相一致This indicates that the growth orientation of zinc deposits is also directed in the (002) plane, which corresponds to the anisotropic growth tendency of zinc dendrites. 【添加剂-XRD-100.102.110增强，与商业锌片一致-各向同性生长-是锌枝晶变得不太可能；002减弱110增强-说明添加剂促进晶体生长的结构变化】In the presence of PEI additive, the crystallographic pattern changes obviously. After adding 5 ppm PEI, the intensities of the (100), (102), and (110) peaks are raised, indicating a similar crystallographic surface to the commercial zinc foil. It reveals that zinc deposition returns to an isotropic growth in the presence of PEI additive, suggesting that the formation of zinc dendrites becomes much less likely. 在10ppm PEI的情况下，(002)峰被明显抑制，首选取向改变到(110)面;这些差异表明PEI添加剂促进了晶体生长的结构变化。In the case of 10 ppm PEI, the (002) peak is markedly suppressed, and the preferred orientation changes to the (110) plane; these differences indicate that the PEI additive promotes a structural change of crystal growth. 主峰(110)的强度略有下降。这可能是由于许多PEI分子在锌核的晶面上吸附，抑制了晶体的生长As the PEI concentration reaches 30 ppm and 50 ppm, although there are no obvious changes in the crystallographic pattern and preferred orientation, the intensity of the main (110) peak shows a slight decline. This is probably due to the adsorption of many PEI molecules on the crystal plane of zinc nuclei, which inhibits the crystal growth. 【XRD结果与SEM形貌变化一致】These transitions of crystallographic orientation on zinc deposits in the presence of PEI agree well with the tendency of morphological change in SEM images.

【原位观察锌沉积】3.2 In operando observation of zinc anode plating–growth

【过渡到原位形貌观察】The variation of zinc anode plating features with and without PEI additive was studied via in operando microscopy imaging at a constant potential of 1.8 V. As shown in Fig. 4, the in situ microstructure evolution during the nucleation–growth of zinc deposits is revealed by in operando TXM imaging. 【原位形貌测试装置介绍】The arrangement of the in operando TXM instrument is shown in Fig. 4(A); an in-house developed three-electrode electrochemical cell connected with a potentiostat was used for in operando measurement. The phase-contrast images of electrodeposited zinc structures are generated by the penetration of synchrotron X-rays. The X-ray penetration distance between the windows of the in situ electrochemical cell is minimized to avoid additional X-ray absorption by the electrolyte. 【原位电沉积形貌图片描述】In Fig. 4(B), the real-time evolution of TXM images for the deposition–growth of zinc nuclei in the initial period of 360 s is shown; all the images share the same scale bar of 2.5 mm. At a time of 0 s, all TXM images show good contrast between the zinc metal anode and electrolyte due to their distinct atomic numbers. 【原位电沉积形貌分析-对比样枝晶生长描述】In the absence of PEI additive (PEI 0 ppm), the continuous nucleation–growth of dendritic zinc at 1.8 V is clearly revealed in Fig. 4(B(a)). In a short time of 90 s, the nucleation of spiky zinc crystals on the electrode surface is seen as a result of the inhomogeneous diffusion–deposition and preferred axial nucleation orientation. Afterwards, fern-shaped zinc dendrites with a main stem and dense branches (shown by blue arrows) formed fast and constantly grew along the axial and radial directions in the following period of 120–360 s. 结果表明，由于电场分布的不均匀和晶体生长的择优取向的影响，锌核主导锌枝晶的垂直各向异性生长行为It reveals that the spiky zinc nuclei dominate the vertical anisotropic growth behavior of zinc dendrites due to the effects of non-uniform electric-field distribution and preferred orientation of crystal growth. 【原位电沉积形貌分析-添加剂-不同浓度】Fig. 4(B(b–d)) show that, in the presence of PEI additive, the morphology of zinc nucleus formation and growth evolution varies significantly with the PEI concentration. At a low PEI concentration of 5 ppm (Fig. 4(B(b))), the formed zinc nuclei feature a grain-shaped morphology. The morphological transition of zinc nuclei from the spiky structure to the grain-shaped structure 可以归因于PEI分子在电极表面的吸附和新形成的锌晶体通过扩散限制成核过程的特殊晶体取向can be attributed to the adsorption of PEI molecules on the electrode surface and the particular crystallographic orientation of the freshly formed zinc crystals through a diffusion-limited nucleation process. These grain-shaped zinc crystals constantly grew and then formed a dense structure with a unique nodule-shaped morphology. 结果表明，电极上吸附的PEI分子不仅在动力学上干扰了锌的沉积-生长，而且有利于形成新的晶体结构。The lower growth rate of nodule-shaped deposits in the axial direction than that of the dendrites indicates that the adsorbed PEI molecules on the electrode not only kinetically disturb the deposition–growth of zinc but also favor a new crystalline structure. In the case of 10 ppm PEI (Fig. 4(B(c))), the grain-shaped zinc nuclei formed at 90 s exhibit a denser structure due to increased PEI adsorption, which promotes the formation of dense spherical zinc deposits. These ball-shaped deposits constantly grow along the radial direction in the following period of time, resulting in a spherestacked morphology. At a PEI concentration of 30 ppm, as shown in Fig. 4(B(d)), it can be observed that the zinc nuclei evenly distribute on the electrode surface to form a dense and flat structure in the initial 90 s. The dense zinc nuclei then slowly grow laterally to form a dense coating layer afterwards. The thickness of the formed zinc coating layer is about 7.5 mmat 360 s. Obviously, the increase of electrode-adsorbed PEI molecules with concentration can promote stable and even deposition–growth of zinc crystals to form a dense coating structure, but the growth rate decreases. At a PEI concentration of 50 ppm, although the zinc nuclei on the electrode are fewer at 90 s, they constantly aggregate and thicken to form a dense coating layer structure eventually. The thickness of the zinc coating layer is about 5 mm at 360 s. The slower growth rate of zinc nuclei can be attributed to the restriction of electrodeposition kinetics with the adsorption of more PEI molecules. 【原位形貌观察总结-扩散控制影响成核进而影响形貌和结构演变】These in operando TXM observations clearly reveal that the addition of PEI at low concentrations affects the growth morphology of zinc nuclei and further dominates the structural evolution of zinc deposits via diffusion-restricted control. 【】A magnified view of the electrode surface before/after zinc plating for 360 s is shown in Fig. 5 through the mosaic acquisition mode, where single TXM frames are acquired and stitched together into one image. The total viewable region on the electrode surface is 75 mm wide and allows observation of the overall deposition morphology. Fig. 5(a) shows the electrode surface before zinc plating. 【锌电沉积-对比样-具体形貌】Fig. 5(b) shows the upright fern-shaped zinc dendrites formed after zinc plating at 1.8 V for 360 s in the PEI-free electrolyte. The height of the formed zinc dendrites is about 30 mm at 360 s, so the average growth rate is about 0.08 mms1. 【电沉积-添加剂-具体形貌-沉积厚度变小】In the presence of PEI additive, the morphological evolution of dendrite-free plating is shown in Fig. 5(c)–(f). 这表明，PEI辅助电极表面的极化促进了沉积锌的形态从5ppm PEI时的结节状结构转变为较高PEI浓度时的致密膜。锌层平均厚度随PEI浓度的增加而减小。It indicates that the PEIassisted polarization of the electrode surface promotes the change of deposited zinc morphology from a nodule-shaped structure at 5 ppm PEI to a dense film at higher PEI concentrations. The average thickness of zinc deposits decreased with increasing PEI concentration. 【电沉积形貌总结-PEI的加入可以主导锌离子在电极表面的扩散限制过程，并导致锌晶体的成核行为和生长形态的改变】Therefore, we have visualized that the addition of PEI can dominate a diffusion-limited process of zinc ions on the electrode surface, and result in the changes of nucleation behavior and growth morphology of zinc crystals. 【电沉积气泡分析-添加剂气泡多】在30ppm和50ppm PEI电解质中，沉积物表面形成了大气泡，表明HER的增强，这与阴极伏安扫描曲线的趋势很好地吻合。Moreover, it is notable that large bubbles are formed on the surface of deposits in the 30 and 50 ppm PEI electrolytes, which indicates the enhancement of the HER, which agrees well with the tendency of the cathodic voltammetry scan curve. 【电沉积形貌分析-动力学较慢的沉积过程导致致密岩石状锌矿床的生长】In Fig. S3,† a similar phenomenon in the change of growth type for zinc deposits is found in the process of zinc plating at different applied potentials (1.7 V and 1.8 V). By in operando TXM observation, compared with the dendrite growth process at 1.8 V, the kinetically slower deposition process at 1.7 V results in the growth of dense rock-shaped zinc deposits. In Fig. S4,† we can observe that the formed rock-shaped zinc deposits are closely stacked on the electrode surface, in contrast to the upright fern-shaped structure of loose zinc dendrites. 【电沉积分析总结-限制锌离子在电极表面的扩散动力学，促进稳定的无枝晶电镀过程，可以控制锌晶体的各向同性形核-生长】These results suggest that the isotropic nucleation–growth of zinc crystals can be dominated by restricting the diffusion kinetics of zinc ions on the electrode surface, promoting the process of stable dendrite-free plating. 【】To compensate for the limited viewable range of TXM images, in operando OM was utilized to continually track the evolution of morphological change and interfacial reaction on the whole electrode surface during zinc plating for 1200 s. As shown in Fig. 6, the in operando OM setup consists of an inhouse developed three-electrode visualizing reactor, a potentiostat, and a portable optical microscope. 【电沉积气泡分析-对比样-沉积枝晶-有气泡】在PEI 0 ppm中(图6(a))，由于水分裂的HER作用，在120 s的成核阶段，锌阳极表面出现许多小气泡。从360 s到1200 s，粗糙的锌枝晶在电极上快速生长。同时，气泡也在树突之间不断合并和生长The in operando OM images show the effect of PEI on zinc dendrite suppression. In PEI 0 ppm (Fig. 6(a)), many small bubbles evolve on the zinc anode surface at the nucleation step of 120 s due to the HER of water splitting. The rough zinc dendrites grow fast on the electrode from 360 s to 1200 s. Meanwhile, the bubbles also continually merge and grow between the dendrites. Hsu等报道32这些在电极表面形成的气泡会限制锌离子的局部扩散-沉积路径，促进松散的蕨类状树突的生长。As reported by Hsu et al.,32 these evolved bubbles on the electrode surface would constrict the local diffusion–deposition route of zinc ions and promote the growth of loose fern-shaped dendrites. 【电沉积气泡分析-添加剂-沉积均匀-但气泡更大】In contrast, a process of dendrite-suppressed plating during the zinc plating for 1200 s can be observed in the electrolyte with 50 ppm PEI (Fig. 6(b)), and a smooth zinc plating layer is formed. However, it is notable that the bubbles evolved more intensely on the electrode surface at 120 s in the electrolyte with 50 ppm PEI, and these bubbles were even bigger than those in the electrolyte without PEI, indicating that the addition of PEI increases the HER at the zinc surface.

【添加剂抑制锌腐蚀】3.3 Corrosion inhibition of zinc anodes

【tafel曲线及腐蚀动力学参数-腐蚀电流-腐蚀电压-腐蚀抑制效率】Fig. 7 shows the Tafel polarization curves of zinc anodes with different PEI concentrations. The corresponding corrosion kinetic parameters, i.e., corrosion potential (Ecorr), corrosion current density (jcorr), and corrosion inhibition efficiency (j.E%), obtained from the Tafel polarization curves are listed in Table 1. The corrosion inhibition efficiencies are defined by the following formula:34



where j0  Jcorr (mAcm2) j0corr jcorr j0 corr corr and jcorr are the values of corrosion current density in the absence and presence of PEI additive, respectively.

The smaller the jcorr, the better the corrosion inhibiting properties.35【腐蚀电流-随着PEI浓度的增加，锌阳极的腐蚀电流密度显著降低，说明PEI添加剂可以通过锌的表面吸附有效地抑制锌阳极的腐蚀。抑制腐蚀效率增大】As shown in Table 1, the corrosion current densities of zinc anodes with the addition of 0, 10, 30, and 50 ppm PEI are 84.5, 58.3, 44.7, and 40.1 mAcm2, respectively. The corrosion current density of the zinc anode decreases markedly with increasing PEI concentration, suggesting that the PEI additive can efficiently inhibit the zinc anode corrosion by the surface adsorption of zinc. The corrosion inhibition efficiency increased monotonically with the PEI concentration and reached 52.2% at 50 ppm PEI. 【腐蚀电位-添加剂正移】Meanwhile, the corrosion potential (Ecorr) with the addition of PEI shifted to more positive potential compared with that in the absence of PEI, indicating that the zinc anode self-corrosion in alkaline electrolyte solution is suppressed.36,37 【锌电极电化学性能测试-阻抗-阳极极化】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】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】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】Shown in Fig. 8(b) are the anodic polarization curves of zinc electrodes in 6 M KOH in the presence and absence of PEI. In the absence of PEI additive (0 ppm), 锌的活性溶解区约为1.35 ~ 1.1 V，电流密度随电势的增大而增大。当电位达到0.95 V时，电流密度迅速下降，表现为锌钝化过程it can be observed that the active dissolution region of zinc is about 1.35 to 1.1 V, where the current density increased with the potential. The current density rapidly dropped when the potential reached a more positive value of 0.95 V, representing the process of zinc passivation. With the PEI concentration increasing from 0 ppm to 50 ppm, the potentials of both active dissolution and passivation currents show a positive shift, which accompanies a decrease in the slope of the active dissolution current curve. It indicates that the anodic reaction of the zinc anode is polarized by the PEI adsorption. The passivation of the zinc anode is also delayed by PEI. 【锌电极电化学性能测试-阳极极化-电流无明显变化-表明锌阳极表面吸附裴分子仍然允许锌离子的迁移和扩散在阳极反应过程中,从而一定程度的电化学活性】However, the anodic dissolution currents in the presence of PEI show no significant decline, suggesting that the adsorbed PEI molecules on the zinc anode surface still allow the migration and diffusion of zinc ions during the anodic reaction process, and thus a certain level of electrochemical activity is maintained. 【浸泡SEM-对比样腐蚀严重 不均匀 深坑】Fig. 9 shows the surface morphologies of zinc anodes after immersion in 6 M KOH in the presence and absence of PEI additive for 48 h. The SEM images in Fig. 9(A) clearly reveal that the corrosion of the zinc anode in the electrolyte without PEI is so severe and nonuniform in many areas that numerous deep pits are created (Fig. 9(A(a))). 【浸泡SEM-添加剂-】However, in the presence of PEI, the non-uniform corrosion of the zinc anode is alleviated significantly. At 10 ppm PEI (Fig. 9(A(b))), the morphology of the zinc anode is flatter in spite of some large shallow pits. As the PEI concentration increases to 30 and 50 ppm (Fig. 9(A(c and d))), the surface of the corroded zinc anode becomes even smoother, indicating that the corrosion of zinc anodes is effectively inhibited by PEI adsorption. A uniform zinc anode surface without uneven corrosive pits can be observed at 50 ppm PEI. 【轮廓仪】In the 3D optical profiler images (Fig. 9(B)), the surface roughness of the corroded zinc electrode in the electrolyte of PEI 50 ppm is significantly smaller than that of the counterpart corroded in the absence of PEI (PEI 0 ppm), in good agreement with the SEM images. 【腐蚀总结】说明了PEI添加剂对锌阳极在碱性电解液中的缓蚀作用It clearly indicates the functionality of corrosion inhibition of the zinc anode in alkaline electrolyte solution by PEI additive.

【添加剂对锌阳极作用机理分析】3.4 Effects and mechanisms of PEI additive on zinc anodes

【承上启下-通过上述表征表面添加剂有什么样的作用】From the analysis of electrochemical properties and structural evolution of zinc anodes, we clearly reveal the effects of PEI additive on the zinc anode during the electrochemical processes, including the variation of zinc nucleation–growth during cathodic reaction and corrosion inhibition of zinc during anodic reaction in the alkaline electrolyte solution with different PEI concentrations. 【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】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】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】3.5 Cycling test of zinc–air full cells 【引出全电池测试】To confirm the potential of PEI additive for practical application in zinc–air batteries, the galvanostatic cycling test of zinc–air full cells with PEI concentrations of 0, 30, and 50 ppm was performed at current densities of 5 mA cm2 and 10 mA cm2. 【全电池循环分析-添加剂初始压降大-表面吸附作用】The setup of the utilized zinc–air full cell and the cycling data are shown in Fig. 11(A) and (B), respectively. In Fig. 11(B), during the cycling processes under a current density of 5 mA cm2, the cells with PEI 30 and 50 ppm show a higher charge– discharge voltage gap than that with 0 ppm at the initial cycles; this voltage polarization can be attributed to the adsorption of PEI on the electrode. 【全电池锌空循环分析-对比样后面循环极化大-锌钝化和不稳定的沉积】Despite the fact that the cell with PEI 0 ppm shows a smaller charge–discharge voltage gap at the initial cycles, it can be noticed that the polarization of the cell gradually increases, wherein the polarization mainly originated from the charging processes, which can be attributed to the zinc anode passivation and unstable electrodeposition process in cycles. 【全电池锌空循环分析-添加剂循环更稳定-充放电极化小-大电流也稳定-保持了锌电极电化学活性】In contrast, the cells with PEI additive show higher cycling stability than that with PEI 0 ppm. In particular, no obvious polarization is shown in the charge–discharge curves of the cell with PEI 30 ppm. It indicates that the moderate PEI additive is beneficial to maintain the cycling stability of the zinc–air battery. When the current density is increased up to 10 mA cm2, the cells with PEI additive still show good performance at the initial cycles, wherein the cell with PEI 30 ppm shows a narrow charge–discharge voltage gap, suggesting that the PEI additive helps maintain the electrochemical activity of the zinc anode as the current density increases and prevent the fast polarization of the cell during the cycling. 【】However, the evolving polarization in cells with PEI 30 and 50 ppm can still be seen in the extended cycles under the elevated current density of 10 mA cm2. 【全电池循环后锌电极SEM-添加剂平坦-对比样多孔多坑】Revealing the effect of PEI additive on structural evolution of the zinc anode in practical zinc–air battery cycling, Fig. 11(C) shows the morphology change of zinc anodes in zinc– air full cells with/without PEI additive after charge/discharge cycling at current densities of (a) 5 mA cm2 for 30 cycles and (b) 5 mA cm2 for 30 cycles + 10 mA cm2 for 10 cycles (40 cycles in total). In Fig. 11(C(a)), a notable difference is observed in the surface morphology of cycled zinc anodes in zinc–air cells with/ without PEI additive after the cycling at a lower current density of5mA cm2 for 30 cycles. The cycled zinc anode in the electrolyte solution with 30 ppm PEI exhibits a flatter electrode surface. In contrast, the cycled zinc anode in the PEI-free (PEI 0 ppm) electrolyte solution exhibits a porous surface morphology with numerous deep pits. 【全电池SEM结果证明添加剂作用】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】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】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】4. Conclusions

For the first time, the variation in the zinc nucleation–growth behavior and the interfacial HER in an alkaline electrolyte solution with PEI additive is revealed in operando. The effect of the PEI additive on corrosion-damage inhibition of zinc anodes in an alkaline electrolyte solution is elucidated. The in operando TXM images clearly show that the addition of PEI affects the growth morphology of zinc nuclei (from a spiky structure to a dense film) and further dominates the structural evolution of zinc deposits via adiffusion-restricted control later on in the deposition process. With the PEI concentration increasing from 5 ppm to 50 ppm, a microstructural transition of the deposited zinc morphology from a nodule-shaped structure to a dense film was observed, and the growth rate decreased considerably. From the in operando OM observation at a much larger scale, the dendrite-suppressed plating process and the formation of a smooth zinc plating layer during zinc plating for 1200 s with 50 ppm PEI are clearly monitored. However, an enhancement of bubble release on the anode surface is observed with the addition of 50 ppm PEI at the beginning of zinc plating, probably due to the PEI-induced side reaction on the electrode. Furthermore, the PEI additive also efficiently inhibits the corrosion damage of the zinc anode. The inhibition efficiency of zinc anode corrosion reached up to 52.2% with the addition of 50 ppm PEI. The SEM and 3D optical profiler images both showed significantly smaller surface roughness of the corroded zinc electrode with the addition of PEI. In the cycling test of zinc–air full cells, the cells with PEI additive show higher cycling stability than that without PEI additive at current densities of 5 mA cm2 and 10 mA cm2. Also, the structural deterioration of the zinc anode surface is effectively alleviated by the protection offered by the adsorbed PEI layer. The results show that the PEI additive maintains the electrochemical activity of electrodes in highly concentrated alkaline electrolyte solution and prevents fast deterioration during cycling. However, the cells with PEI additive show evolved polarization at higher current density, which may be due to the PEI-induced intense HER. In this work, the effects of PEI additive on both dendrite-suppressed plating and corrosion inhibition of the zinc anode as well as the related mechanisms are revealed in detail. Moreover, the beneficial effect of PEI additive on the cycling stability in practical zinc–air batteries is confirmed. A better understanding of zinc plating and the corrosion inhibition mechanism in the presence of PEI additive can shed light on the development of next-generation zinc–air rechargeable batteries with high stability and good cycling performance.

## [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.

2. Results and discussion 【示意图分析】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】The corresponding96 transmission electron microscopy (TEM) image further exhibits the flexible and crumpled features of the nanosheet. 【AFM分析】The thickness of the nanosheet is estimated to be ∼15nm according to the AFM measurement (Fig. S2). 【纳米片的优点】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】The interplanar distances of 0.19 and 0.18 nm observed in the high-resolution TEM (HRTEM) image corresponding to the lattice periodicities of (600) and (020) crystal planes of orthorhombic V2O5, respectively. 【FFT测试暴露晶面】The fast Fourier transform (FFT) pattern of the nanosheet is indexed to the [001] zone axis, indicating the exposure of (001) facets of E-VO nanosheets (Fig. 1c) [49,50]. The layer structure of the products is exhibited in Fig. S3. 【XRD分析】The above observation suggests that the morphology of the initial V2O5 sample is well maintained after hydrazine hydrate treatment (Fig. S4). As shown in the X-ray diffraction patterns, four peaks with gradually decreased intensity are observed at 7.6, 23.1, 31.0 and 39.0°, corresponding to (001), (003), (004) and (005) planes of layered V2O5 (JCPDS no. 40–1296), respectively (Fig. 1d) [49,50]. The (001) peak shifts to 6.3° for E-VO sample, indicating the successful enlargement of interlayer distance, thus favors the faster ions transfer and more ions storage space [27,42–45,51]. The interlayer distances are estimated to be 11.6 and 14.0 Å for V2O5 and E-VO, respectively. 【TEM分析】Such a crystal structure indicates both the two samples have preferential 2D feature with exposed (001) facets, consistent with the HRTEM observations (Fig. 1c and Figs. S3 and S4c). 【TG分析】According to the thermogravimetric analysis (TGA) results, the contents of interlayer water in per formula unit of V2O5 and E-VO are estimated to be 1.6 and 2.2, respectively (Fig. S5). 【！！！层间含水率的优点】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】XANES spectra for V2O5, E-VO and standard samples (VO2 and orthorhombic V2O5) were measured to gauge the approximate oxidation state. It is clear that the absorption K-edge energy levels of V2O5 and orthorhombic V2O5 are almost identical, indicating the oxidation states of V in V2O5 is V5+. The K-edge of E-VO locates between V4+ and V5+ standard spectra, indicating the mixed-valence state in E-VO (Fig. 1e). 【XPS分析】In the X-ray photoelectron spectroscopy (XPS) spectrum of V2O5, there are two peaks located at 517.3 and 524.8 eV, corresponding to the V2p3/2 and V2p1/2 for V5+, respectively (Fig. 1f). Besides these two strong peaks, the fitted XPS spectrum of EVO presents another two weak peaks at 516.3 and 523.4 eV, which are ascribed to the existence of V4+ (Fig. 1f). 【混合价态的优势】The formation of mixed-valence in E-VO is favorable for higher conductivity. Moreover, the oxygen vacancies will be generated to maintain the electroneutrality, which can increase the ion transfer rate and structure stability of electrode material [38–40,52]. 【制备方法的引入】Due to the formation of mixed-valence, increased interlayer water content and expanded interlayer distance, EVO is expected to exhibit higher Zn2+ storage capability than V2O5. Apart from the cathode, a unique Zn/SS mesh composite anode was

fabricated by a one-step and cost-effective strategy. Fig. 1g shows the pictures of SS mesh, Zn foil, and Zn/SS mesh. After calendaring, Zn is well embedded in the SS mesh with the interspace between adjacent parts (Fig. 1h and Fig. S6). The component of the Zn/SS mesh is evidenced by the corresponding XRD pattern (Fig. 1i). 【！！三维网状结构优势】Such a 3D network architecture can lower the local current density and provide more space for Zn deposition, thus benefit for depressing the Zn dendrites growth. To evaluate the effectiveness of Zn/SS mesh and the Zn2+ storage

capability of the cathode materials, 2032 coin cells were fabricated with 3M Zn(CF3SO3)2 aqueous solution as the electrolyte. 【GCD性能分析】Fig. 2 presents the electrochemical performances of the products. The galvanostatic charge-discharge (GCD) curves of the symmetric cells show that Zn/SS mesh cell has a lower polarization and much longer cycling stability than the bare Zn one (Fig. 2a). This is ascribed to the smooth Zn plating/stripping behavior of Zn/SS mesh caused by the uniform charge distribution and large Zn deposition space (Fig. S7). 【XRD分析】The wellmaintained XRD pattern after cycling also suggests the high stability of Zn/SS mesh (Fig. S8). The Zn/SS mesh was used as the anode to test the Zn2+ storage capability of the cathode materials. 【CV分析】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】The GCD curves of E-VO electrode at 0.1 A g−1 exhibit two sloping discharge/ charge profiles, suggesting two Zn2+ intercalation/deintercalation processes, which is consistent with the CV curves observation (Fig. S9 and Fig. 2b). From the second to fifth cycles, the GCD curves almost overlap with each other, indicating the highly reversible Zn2+ insertion/extraction process (Fig. S9). 【电化学性能分析】At the current density of 0.1 A g−1, EVO electrode delivers a much higher capacity of 450 mAh g−1 than 352 mAh g−1 for V2O5 electrode. When the current density increases to a high rate of 10 A g−1, E-VO electrode shows a high capacity retention of 49% (222 mAh g−1), superior to 36% (127 mAh g−1) of V2O5 electrode (Fig. 2c). The high Zn2+ storage capability can be further presented by

97

the Ragone plots by comparing E-VO with previously reported cathode materials for ZIBs. 【能量密度分析】A high energy density of 324Wh kg−1 is obtained at the power density of 72Wkg−1. When the power density reaches a high value of 6.9 kW kg−1, the energy density still maintains at a high value of 156 Wh kg−1. This performance is among the top tier of the reported cathode materials for ZIBs (Fig. S10). 【EIS分析空位】To better understand the higher rate capability of E-VO, we tested the electrochemical impedance spectroscopy. In the Nyquist plots, E-VO electrode shows a much smaller charge transfer resistance and Warburg diffusion resistance than those for V2O5 electrode, indicating the faster electrons and ions transfer rate in E-VO (Fig. 2d) [53]. 【循环性能分析】Upon cycling, the resistance of the electrode decreased a little bit, which is ascribed to the activation process [54]. The cycling stability of E-VO was evaluated at different current densities. After cycled at 5 A g−1 for 3000 cycles, the E-VO electrode can maintain 72% of its maximum capacity with a Coulombic efficiency of ≈100%. The initial capacity increasing is ascribed to the activation process (Fig. 2e) [28,31,54]. At the lower current densities of 0.2 and 2 A g−1, E-VO also shows quite good cycling stability (Fig. S11). The long cycling stability of E-VO electrode can also be evidenced by the well-maintained morphology and XRD pattern after cycled at 2 A g−1 for 500 cycles (Fig. S12). Such a performance is among the best for vanadium-based cathodes (Table S1). In comparison with E-VO, V2O5

.electrode only maintain 51% of its maximum capacity after 3000

cycles at 5 A g−1 (Fig. S13). The much better Zn2+ storage capability, i.e. the larger capacity, higher rate capability, and longer cycling stability, of E-VO than V2O5 is ascribed to the formation of mixed-valence, increased interlayer water content and expanded interlayer distance.【XPS、XRD、EDS分析存储机制】 To understand the Zn2+ storage mechanism in E-VO, ex situ XPS,

XRD, energy-dispersive X-ray spectroscopy (EDX) characterizations were carried out. Fig. 3 presents the ex situ XPS and XRD characterizations of E-VO at different charging/discharging states. In the XPS spectra for Zn 2p, there is no Zn signal in the original state. In contrary, two sharp peaks for Zn 2p are observed in the fully discharged state, indicating the successful insertion of Zn2+. When recharged to 1.6 V, the intensity of Zn signal decreases rapidly, indicating most of the zinc ions are extracted from the E-VO electrode (Fig. 3a and Fig. S14) [43,55–57]. In O1s spectra, the peaks located at 530 eV are assigned to the lattice oxygen in the electrodes, while the peaks at high energy region of 531–534 eV correspond to the signal of intercalated water [17,40]. In the fully discharged state, the two high energy peaks are much stronger than those for the original and fully charged states, indicating the Zn2+ insertion process is coupled with the insertion of water. The two peaks area at 531–534 eV for the fully charged state are slightly larger than those for the original state, which should be attributed to the residual Zn2+ in E-VO electrode (Fig. 3a and b). Different from the original state, the V 2p signal of fully discharged state shows obviously increased peak area of V4+ and an additional contribution from V3+, which is due to the reduction of E-VO electrode during the discharge process. After charged to 1.6 V, the slightly larger V4+ peak intensity than the original one is ascribed to the partial reduction of V5+ caused by the remained Zn2+ in the electrode [47,55]. This is consistent with the observations in Zn 2p and O 1s spectra (Fig. 3a–c). As shown in the second cycle GCD curve, more charging/ discharging states were chosen for ex situ XRD characterization (Fig. 3d). During the discharging process, the XRD peaks gradually shift to higher 2θ regions, indicating the contraction of interlayer distance. This observation is ascribed to the decreasing of interlayer electrostatic repulsion caused by the increasing of inserted Zn2+ ions amount. When the sample is discharged to 0.5 V and 0.3 V, the new peaks located at 6.8, 13.4, 19.9, 26.4 and 33.3° are observed, which is attributed to the formation of the Zn2+ interlayered new phase (ZnxE-VO) with larger interlayer distance. It is noted that the intervals between these new peaks are almost equal, suggesting the well-maintained layer structure (Fig. 3e). The above ex situ characterizations exhibit the high structure stability and reversible Zn2+ insertion/extraction process, which can be further evidenced by the EDX analysis results (Figs. S15–17).

【CV分析存储动力学】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】The higher capacitive contributions of E-VO is ascribed to its features of larger interlayer distance, mixed-valence and more interlayer water content by comparison with V2O5, which will results in the higher Zn2+ insertion/extraction rate and faster redox reaction. At a high scan rate of 0.8 mV s−1, the capacitive contribution is as high as 82% for the E-VO electrode (Fig. 4a and b). As known, the peak current (i) obeys a power-law relationship to the sweep rate (v). According to the equation of i =avb, where a and b are constants, the capacitive effects in the two electrodes were further analyzed. 【!绝对扩散控制和电容控制过程分析】For absolute diffusion-controlled and capacitive-controlled processes, the b values are 0.5 and 1, respectively [60,61]. The b values for peak 1 to peak 4 of E-VO electrode are 0.96, 0.78, 0.84 and 0.85, respectively, indicating the mainly capacitive controlled process. Moreover, these b values are all larger than the corresponding ones of V2O5 electrode, suggesting the faster charge (ions and electrons) transfer in E-VO electrode (Figs. S18c–f). 【GITT分析】In addition, the galvanostatic intermittent titration technique (GITT) was carried out to determine the diffusion coefficient of Zn2+ in the V2O5 and E-VO cathodes (Fig. 4c and d). Before the GITT measurement, the cell was first discharged/ charged at 0.1 A g−1 for 30 cycles to obtain a stable state. Subsequently, the cell was discharged or charged at 0.05 A g−1 for 20 min, and then relaxed for 2 h to make the voltage reach the equilibrium (Fig. 4c). 【扩散系数分析】The Zn2+ diffusion coefficient value during discharging process for E-VO electrode is estimated to be around 4.2×10−10−2.2×10−9 cm2 S−1, higher than 1.8×10−10−1.5×10−9 cm2 S−1 for V2O5 electrode (Fig. 4d). This is consistent with the conclusion of capacity contributions (Fig. 4a). In the charging process, E-VO also exhibits the higher Zn2+ diffusion coefficient than V2O5 (Fig. S19). 【！！水凝胶优点】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】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】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】 a facile in situ approach was developed to simultaneously introduce mixed-valence, increase the interlayer water content and expand the interlayer distance in V2O5 nanosheets. These structural modulations endow the as-obtained E-VO nanosheets with fast charge (ion and electron) transfer kinetics, sufficient Zn2+ storage space and high structural stability. Besides the cathode, a unique Zn/stainless steel mesh composite was fabricated as a high-performance anode, which demonstrates much lower polarization and uniform Zn stripping/slating behavior than bare Zn anode. As a binder-free cathode material for aqueous zinc-ion battery, E-VO electrode exhibits a superb

99

Zn2+ storage capability, i.e. the high specific capacity (450 mAh g−1 at a current density of 0.1 A g−1), good rate capability (222 mAh g−1 at 10 A g−1), and long cycling stability (72% capacity retention for 3000 cycles at 5 A g−1). Moreover, as cathode of flexible quasi-solid-state zinc-ion batteries, E-VO also shows quite good performance, i.e. high capacity under different bending states (361 mAh g−1 at 0.1 A g−1), good rate capability (115 mAh g−1 at 2 A g−1), and long cycling stability (85% capacity retention for 300 cycles at 1 A g−1). The achievements of this study can be considered as an important step toward the development of aqueous zinc-ion batteries and flexible energy storage device.