Amorphous MOFs layer boosts the performance of metal anodes

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Abstract

Employing metal anodes can greatly increase volumetric/gravimetric energy density versus a conventional ion-insertion anode. However, metal anodes are plagued by dendrites, corrosion, and interfacial side reactions issues. Herein, a compact and flexible amorphous MOF layer was successfully synthesized and used as protective layer on metal anode aqueous zinc-ion battery (AZIB). Compared with the crystalline MOF layer, the unique amorphous MOF layer can inhibit dendrite growth at the grain boundary and eliminate ions migration near the grain boundary, showing high interfacial adhesion and large ion migration number ($t_{\text{Zn}^2+} = 0.82$). Besides, the amorphous MOF layer can effectively depress unfavored behaviors, e.g., corrosion of zinc anode, hydrogen evolution reaction, and dendrite growth on zinc surface. The prepared Zn anode with the amorphous MOF layer exhibited an ultra-long cycle life (ten months, 7000 h) and a low voltage (< 40 mV) at 1 mA cm$^{-2}$ in a symmetrical cell. Even at 10 mA cm$^{-2}$, it still showed a high stability for more than 5500 cycles (1200 h). The enhanced performance is realized for full cells paired with a MnO2 cathode. Besides, a flexible symmetrical battery with the Zn@A-ZIF-8 anode exhibited a good cyclability under different bending angle (0°, 90°, and 180°). Moreover, various metal substrates were successfully coated with compact A-ZIF-8. The A-ZIF-8 layer can obviously improve the stability metal anodes, including Zn, Mg and Al. The results not only demonstrate the high potential of amorphous MOFs decorated Zn anodes for AZIBs, but also propose a new family of protective layers for metal anodes.

Introduction

Metal anode have drawn considerable attention in various types of batteries due to their high energy densities. However, the propensity of metals to form nonuniform anodeposits and interfacial side reactions with electrolytes, leading to the loss of active materials and formation of the metal dendrite, seriously restrict their practical applications$^1$-$^6$, especially for safety concerns caused by dendrite growth.$^7$ To solve these problems, various strategies have been proposed (including structure design$^8$, composition control$^9$, electrolytes optimization$^{10}$, surface modification [e.g., insulating layer$^{11}$, electron-oriented layer$^{12}$, and ion-oriented layer$^{13}$] have been proposed to achieve high performance metal anodes, among which introducing a surface protective layer is considered as one of the most promising approaches$^{14,15}$, such as carbon materials, metal oxide, polymer, etc.$^{13,16,17}$

Recently, metal organic frameworks (MOFs) based protective layers have attracted considerable attention thanks to their large specific surface area, tailorable pore structure and insulating feature. Zhang et al.$^{18}$ constructed a ZIF-8 MOF film on Mg metal anode by an electrochemical deposition method, which can eliminate nonselective inter-crystalline diffusion of electrolyte and realize selective Mg$^{2+}$ transport. Similarly, Wang et al.$^{19}$ prepared a $\text{Zn}_3(\text{BTC})_2$ coating layer on Zn anode by doctor blade method with binder, and found the structural grids of Zn-BTC hindered the two-dimensional diffusion of Zn$^{2+}$ and regulated the electric field on Zn anode, resulting in a uniform Zn$^{2+}$ flux, stable stripping/plating, and a long lifespan of 800 h at 1 mA cm$^{-2}$. Even though good outcomes have been obtained by using MOF layer
on metal anode, some serious challenges are still awaiting solutions: (1) The introduced polymer binder blocks MOF channels, that severely impedes metal ion transport.\textsuperscript{20} (2) The rigid lattice structures of crystalline MOFs usually have poor mechanical properties, leading to structural failure caused by the volume change of metal anode during cycling. (3) Polycrystalline MOFs possess a multitude of grain boundaries where dendrites grow favorably causing irreversible damage to the MOF protective layer.\textsuperscript{21} This can be attributed to the combination of electrons with metal ions at the grain boundary, which shows relatively high electron conductivity, and then reduces the metal ions, resulting in a short circuit,\textsuperscript{22} which is key issue for ceramic solid electrolytes as well. For example, Shen et al.\textsuperscript{23} suggested that in the samples with more obvious grains and grain boundaries by X-ray tomography, lithium metal dendrites can penetrate solid Li\textsubscript{7}La\textsubscript{3}Zr\textsubscript{2}O\textsubscript{12} (LLZO) along the grain boundaries and cause short circuits. Similarly, Wu et al.\textsuperscript{24} studied the origin and evolution of Li dendrite growth and found Li dendrite growth along the phase boundaries or defective sites of garnet LLZO. So far, how to eliminate the local high electric field caused by grain boundaries of crystalline MOF protective layer and to build a MOF protective layer with high interfacial adhesion is still a huge challenge. Hence, developing a MOF layer that can overcome these demerits becomes imperative, yet still remains a very challenging task.

Herein, we proposed an amorphous MOFs as a new type of protective layer for the metal anode. Compared to crystalline MOFs, the amorphous MOFs showed unique properties (including the absence of grain boundaries and defects, enhanced flexibility, and better interfacial bonding force), while keeping the advantage of crystalline MOFs. As the demonstration, aqueous zinc-ion batteries (AZIBs) with Zn anode were studied owing to their high theoretical capacity (820mAh g\textsuperscript{-1}), low redox potential (-0.762 V \textit{vs} the standard hydrogen anode), low-cost and high safety.\textsuperscript{5,25-28} These properties are attractive for large-scale energy storage and wearable devices. The problem of Zn dendrite formation, continuous parasitic hydrogen evolution reaction (HER), and irreversible by-products are barriers to practical AZIBs.\textsuperscript{29} A continuous and compact A-ZIF-8 MOF layer was successfully prepared on zinc anode by a facile strategy. With the protection of the A-ZIF-8 layer, the corrosion of zinc, the side reaction of hydrogen evolution, and the growth of dendrites on the zinc surface were suppressed, according to in situ optical electron microscopy and various characterizations. The symmetric cell, fabricated with the amorphous MOF layer modified Zn foil anode, achieves a long lifetime of more than 7000 hours at a current density of 1 mA cm\textsuperscript{-2} with a low overpotential (<40 mV), and is still running as of this writing. Even at 10 mA cm\textsuperscript{-2}, the symmetric cell still exhibits a stable plating/stripping performance for more than 5500 cycles (1200 h). These properties were further studied by Zn@A-ZIF-8//MnO\textsubscript{2} full cell with 98.9% capacity retention after 2000 cycles at the current density of 1 A g\textsuperscript{-1}. Besides, various metal substrates could be successfully coated with compact A-ZIF-8-MOF by the same route and the corresponding metal anode exhibits enhanced stability performance.

\textbf{Results}

\textbf{Structural characterization of A-ZIF-8 layer}
A facile spray method was used to prepare the A-ZIF-8 (A-ZIF-8) protective layer (Supplementary Fig. 1). ZIF-8 crystals are known to be structurally similar to zeolites, in which 2-methylimidazole (Hmim) donates a proton and couples with the Zn$^{2+}$ node to form a ZnN$_4$ tetrahedron\(^\text{30}\) (Fig. 1a). However, in the presence of CH$_3$COO$^-$, the copolymerization of Zn$^{2+}$ with Hmim ligand was partially prevented by the steric hindrance due to the relatively large anion size of CH$_3$COO$^-$.\(^\text{31}\) As a result, the nucleation of orderly linked ZnN$_4$ tetrahedra was disrupted, resulting in A-ZIF-8 structure (Fig. 1b). As seen in Fig. 1c, a continuous and compact A-ZIF-8 layer with no grain boundary was successfully coated on zinc foil. After increasing the heating time to 8 h, ZIF-8 grains with clear boundaries appeared on the zinc foil surface according to the field emission scanning electron microscopy (FESEM, Fig. 1d, Supplementary Fig. 2) and atomic force microscopy (AFM, Supplementary Fig. 3), suggesting that a longer heating time facilitates the generation of crystalline structure of ZIF-8. The thickness of the A-ZIF-8 layer was observed to be approximately 2.2 $\mu$m (Fig. 1e). Based on elemental mappings (Fig. 1f), all the elements were evenly distributed in the layer. The amounts of the C and N elements on Zn@A-ZIF-8 origin from the presence of the A-ZIF-8. The diffraction peaks of the C-ZIF-8 were consistent with those of the simulated ZIF-8 (Fig. 1g), indicating that the C-ZIF-8 had a crystalline structure. However, the loss of long-distance order as indicated by XRD patterns makes it difficult to characterize the amorphous structures.\(^\text{32}\) As shown in Fig. 1g and Supplementary Fig. 4, the A-ZIF-8 exhibits an absence of bragg peaks due to amorphous structure. The flat surface of the Zn@A-ZIF-8 anode is also confirmed by atomic force microscopy (AFM) (Fig. 1h, Supplementary Fig. 5).

Figure 1i showed that contact angles are 93.5°, 47.5°, and 45.5° for the zinc foil, Zn@C-ZIF-8, and Zn@A-ZIF-8, respectively, indicating that the hydrophilicity of the anode can be enhanced by the C/A-ZIF-8 modification. It was reported that enhancing the hydrophilicity of the metal anode facilitates contact between electrolyte ions and the metal anode, contributing to the Zn$^{2+}$ flux regulation and uniform zinc deposition.\(^\text{33,34}\) As seen in Fig. 1j and Supplementary Fig. 6, the Zn@A-ZIF-8 has the largest ion transference number (i.e., 0.82) because of the absence of grain boundary. Brunauer-Emmett-Teller (BET) measurement indicates the surface area of A-ZIF-8 is as high as 1265 m$^2$ g$^{-1}$, and the main pore size distribution is 2–4 nm in diameter (Supplementary Fig. 7). Raman spectroscopy measurements were used to characterize the bond between Zn ions and the Hmim ligand. As shown in Supplementary Fig. 8, both Zn@C-ZIF-8 and Zn@A-ZIF-8 showed distinct peaks at 168 and 205 cm$^{-1}$, corresponding to the Zn = N bond. Besides, Fourier transform infrared spectroscopy (FTIR) spectra (Supplementary Fig. 9) revealed that the N-H...H stretch between 2400–3100 cm$^{-1}$ disappears completely for both A-ZIF-8 layer and C-ZIF-8 layer (compared to Hmim powders), suggesting that Hmim was deprotonated and incorporated into the ZIF-8 framework.\(^\text{31}\) The XPS spectra of samples (Supplementary Fig. 10) also verify the existence of C, N in both of the Zn@ZIF-8 and Zn@A-ZIF-8 sample. Moreover, the Zn 2p XPS spectra of the Zn foil, Zn@C-ZIF-8 and Zn@A-ZIF-8 samples (Fig. 1k) can be split into two peaks, corresponding to Zn 2p$_{1/2}$ and Zn 2p$_{3/2}$ of Zn$^0$. Compared with Zn foil, both peaks for Zn@A-ZIF-8 sample shifted to higher binding energies, which might be ascribed to the fact that the metal Zn center is Zn$^{2+}$ in the A-ZIF-8. High-resolution C 1s and N 1s spectra of the fabricated anodes are provided in the Supplementary Fig. 11,
which indicate the chemical state of A-ZIF-8. The amorphous structure was further confirmed by extended X-ray adsorption fine structure (EXAFS) analysis (Fig. 1l). A-ZIF-8 exhibited a strong peak at ca. 1.6 Å for Zn-N coordination, which was similar to ZIF-8 powder (via chemical coprecipitation process in methanol, Supplementary Fig. 12). However, the number of N coordinated with Zn was decreased in the A-ZIF-8 structure compared with that in ZIF-8 powder (Supplementary Fig. 13, Supplementary Table 1), which lead to coordination defects between metal ions and organic ligands caused by the relatively large anion size of CH$_3$COO$^-$. Thus forming a disordered amorphous structure.

**Mechanical Properties Of A-ZIF-8 Layer**

Due to the unique structure of amorphous MOFs, they could have better mechanical properties than crystalline MOFs. As shown in Supplementary Fig. 14, even though the prepared Zn@A-ZIF-8 was folded into various shapes, the integrity of the protect layer was still retained. No exfoliation or cracks could be observed on the A-ZIF-8 layer, which indicates a strong bonding between zinc substrate and the A-ZIF-8 protective layer. This strong bonding can be attributed to the formation of HMIM hydrogen bond (N-H...N) chains on Zn foil, resulting in a strong interfacial interaction. The binding energies of pristine and A-ZIF-8 on Zn (002) surface were calculated to evaluate the interaction strength between ZIF-8 and Zn using the forcite module with universal force field of Materials Studio 2017. First, bulk Zn (Supplementary Fig. 15a) and C-ZIF-8 units cells (Fig. 2a) were fully optimized. A-ZIF-8 (Fig. 2b) was obtained by Heating and annealing process based on pristine ZIF-8 supercell. All the partial atomic charges were defined by the QEQ methods. The Zn (002) surface structure (Supplementary Fig. S15b) was obtained by cleaving the optimized Zn, which contained five Zn layers. Then, one 12×7 supercell of Zn (002) surface (Supplementary Fig. S15c) was constructed serving as ZIF-8 adsorption substrates. One 2×2×2 supercell of ZIF-8 was placed on the Zn (002) surface to build ZIF-8/Zn (002) system (Fig. 2c). The lattice mismatch between ZIF-8 and Zn (002) surface was less than 2%. Placing the A-ZIF-8 on the Zn (002) surface, we built the A-ZIF-8/Zn (002) system (Fig. 2d). There is one vacuum layer of larger than 20 Å perpendicular to the surface.

After geometry optimization, the molecular dynamic simulations under NVT (T = 298 K) ensemble were carried out to fully relax the two binding systems, during which the bottom layer of Zn substructure was fixed. The Ewald scheme and atom-based cutoff method were applied to treat electrostatic and van der Waals (vdW) interactions with a cut-off value of 12.5 Å, respectively. Equations of motion were integrated with a time step of 1 fs. After obtaining stable adsorption configuration, the binding energy $\Delta E$ was calculated according to the following Eq. 3$^6$:

$$\Delta E = E_{total} - E_{Zn} - E_{ZIF-8}$$

Where $E_{total}$ is the total energy of binding system, $E_{Zn}$ and $E_{ZIF-8}$ are the energies of the isolated Zn substrate and ZIF-8, respectively. Specifically, a weak interaction between crystalline ZIF-8 and Zn (002)
with binding energy $-67.86$ kcal/mol (Fig. 2e) was obtained, while the A-ZIF-8 shows a higher binding energy of $-266.96$ kcal/mol with abundant HMIM hydrogen bond (N-H...N) chains, suggesting the strong interaction between A-ZIF-8 layer and Zn substrate. Besides, nano-scratch tests were performed to quantitatively study the bonding force between zinc substrate and protective layer. In each scratch test, there are three stages: (I) a very small load was applied to the surface to trace and map the original topography of the sample surface; (II) Following the same path, but the specified normal load is applied; (III) a very small load is again applied to track and measure the residual surface deformation along the scratch path after tip unloading (elastic recovery). In the following results, these three stages are represented by blue, green, and orange curves, respectively, the area between green and orange curves corresponds to the degree of elastic recovery (the possibility of coating peeling). The results (Figs. 2f and 2g) showed that the A-ZIF-8 layer has a larger elastic recovery area than the C-ZIF-8 layer, which means the former has a stronger binding between zinc substrate and protective layer. The corresponding 3D optical image of a 100 mN ramp load nano-scratch test on Zn@A-ZIF-8 and Zn@C-ZIF-8 is shown in Supplementary Fig. 16.

**Anti-corrosion And Dendrite Suppression Properties Of A-ZIF-8 Layer**

To explore the anti-corrosion behavior of the A-ZIF-8 layer, Zn foil and Zn@A-ZIF-8 were soaked in a 2 M ZnSO$_4$ solution for 3 days. As shown in Fig. 3a, the bright Zn foil turned dark grey, suggesting that corrosion reaction took place. In contrast, the Zn@A-ZIF-8 changed slightly, indicating that the A-ZIF-8 as a protective layer took effect. By examining their micromorphology, it was observed that Zn@A-ZIF-8 retains a flat surface, while Zn foil has a large number of regular hexagonal by-products deposited on surface (Fig. 3a). In order to identify the by-products, XRD analysis was conducted, showing some new peaks appearing at 8–25$^\circ$ that are consistent with the characteristic peaks of (Zn(OH)$_2$)$_3$(ZnSO$_4$)(H$_2$O)$_3$ (PDF#78–0247) (Fig. 3b). With the protection of amorphous MOFs, no obvious peaks can be identified in basic zinc sulfate. The anti-corrosion properties were further examined through the linear polarization curves (Fig. 3c). Compared with the Zn foil (-1.02 V), the lower corrosion potential ($V_{corr}$) of the Zn@A-ZIF-8 (-1.003 V) and Zn@C-ZIF-8 (-1.007 V) can be achieved.

The corrosion current density ($I_{corr}$) of the Zn@A-ZIF-8 and Zn@C-ZIF-8 anodes are 3.8 mA cm$^{-2}$ and 4.1 mA cm$^{-2}$ respectively, which are much lower than the Zn foil (7.5 mA cm$^{-2}$). The higher corrosion positive potential and lower corrosion current of the Zn@A-ZIF-8 anode indicate the less tendency of corrosion reaction (dissolved O$_2$-induced passivation). The deposition and growth of Zn are studied by chronoamperometry (CA) at an overpotential of -150 mV using three-anode system (Fig. 3d). The current variation at a constant overpotential can reflect nucleation, process, and surface changes of anode surface. At the overpotential of -150 mV, the current density keeps increasing over 200 s for the Zn foil, suggesting a long and rampant 2D diffusion process and rough deposition propagation. The absorbed ions laterally diffuse along the surface to find the most energetically favorable sites for charge transfer. Additionally, compared with zinc foil, the diffusion mode for the Zn@A-ZIF-8 anode evolves to
initial 2D diffusion in the first 30 s, followed by a continuous and stable 3D diffusion, suggesting the restricted zinc ions tend to nucleate in the vicinity of initial nucleation sites rather than thermodynamically favorable adsorption sites with a low energy barrier on the anode. In addition, hydrogen evolution reaction (HER) was studied by the linear sweep voltammetry (LSV) test on different anode. As shown in Fig. 3e, the lowest onset potential (i.e., -1.79 V) was noted for the Zn@A-ZIF-8, indicating the best suppression effect on HER. As shown in Fig. 3f, the symmetric cells based on the Zn@A-ZIF-8 anode exhibit a lower nucleation overpotential (NOP) (32 mV) at a current density of 1 mA cm$^{-2}$ during the initial process, which is much smaller than Zn foil anode (65 mV). The lower NOP means a lower nucleation barrier, beneficial for a relatively uniform metal plating process.

Moreover, the microscopic morphologies of the Zn foil anode and Zn@A-ZIF-8 anode after 50 cycles at 1 mA cm$^{-2}$ are probed by SEM. As shown in the surface and cross-sectional SEM images (Fig. 3g) showed that the Zn@A-ZIF-8 anode maintains a smooth surface, while irregularly shaped and disordered Zn dendrites are observed on the surface of Zn foil. Furthermore, the in-situ optical visualization of 40 minutes Zn deposition at a current density of 5 mA cm$^{-2}$ is recorded in Fig. 3h. After an initial 5 min of deposition, nonuniform protuberances appeared on the Zn foil surfaces, and grew into needle-like dendrites afterwards. After 40 min electroplating, the dendrites on the Zn foil evolved into a mossy and rough surface, which would enhance the local electric field on dendrite area, therefore, accelerating dendrite growth and increasing the risk of short circuit. During the electroplating process a large number of bubbles were generated on the Zn foil surface due to hydrogen evolution. By contrast, a uniform Zn deposition layer formed and grew on the Zn@A-ZIF-8 anode through the whole electroplating process. Piecing together all the learned information, the functional mechanism of the A-ZIF-8 as protective layer was proposed, as shown in Fig. 4, the hydrogen evolution, corrosion, and dendrites of zinc anode can be perfectly solved by our ultra strong binding and grain boundary free A-ZIF-8 coating.

**Electrochemical performances of Zn@A-ZIF-8 anode.**

The electrochemical behavior of Zn foil anode and Zn@A-ZIF-8 anode based symmetric cells were evaluated at different current density (Figs. 5a, 5c, Supplementary Fig. 17). At a current density of 1 mA cm$^{-2}$ (Fig. 5a), the Zn foil symmetric cell showed abrupt failure after 120 h. Impressively, benefiting from the A-ZIF-8 layer, the Zn@A-ZIF-8 symmetric cell achieved an ultra-long cycle life, about ten months (7000 h), which is 12 times higher than the cycle life of crystalline MOF protective layer (Fig. 5b). At a high current density of 10 mA cm$^{-2}$, the Zn@A-ZIF-8 symmetric cells still exhibit high stability with a prolonged cycling life of over 5500 cycles (1200 h, Fig. 5c). While the Zn foil symmetric cell suffers severe polarization after 105 h at 10 mA cm$^{-2}$. The performance of Zn@A-ZIF-8 anode is compared with that of other surface-modified Zn anodes reported in recent studies (Fig. 5d). The rate performance of symmetric cells using the Zn foil anode and Zn@A-ZIF-8 anode are shown in Fig. 5e. Compared with the Zn foil anode, the Zn@A-ZIF-8 anode displays a stable voltage profile with a lower voltage hysteresis. When the current density increases from 1 to 10 mA cm$^{-2}$, the cells using the Zn@A-ZIF-8 anode exhibit a steadily increasing hysteresis of 36, 43, 45, 46, and 52 mV, respectively (Fig. 5f).
Besides, when the current densities increased to 20 mA cm\(^{-2}\) (51% Zn utilization, Fig. 5g), the Zn@A-ZIF-8 symmetric cells can keep cycling for over 150 h, indicating that A-ZIF-8 layer has excellent tolerance to volume change of the Zn anodes. Electrochemical impedance spectroscopy (EIS) tests were performed before and after 50 cycles (Fig. 5h). The charge transfer resistance (R\(_{\text{CT}}\)) of the Zn@A-ZIF-8 anode was slightly lower than that of the Zn foil anode before cycling. After 50 cycles, the R\(_{\text{CT}}\) was significantly reduced due to the infiltration of electrolytes during the cycling process, indicating the fast charge transfer and Zn plating/stripping kinetics.

Coulombic efficiency (CE) is an important parameter to evaluate the reversibility of a cell anode during electrochemical process. In this work, the prepared Zn//Ti and Zn//Ti@A-ZIF-8 cells were studied during the galvanizing/stripping process. As shown in Fig. 6a, at a current density of 3 mA cm\(^{-2}\), the average CE of Zn//Ti@A-ZIF-8 cells reached 99.5% after running over 1000 cycles. By contrast, the Zn//Ti cell obtained an average CE of 79.2% and showed dramatic fluctuations after running 80 cycles, suggesting that the galvanizing/stripping process on Ti foil encounters instability issue. The initial voltage gap of Zn//Ti@A-ZIF-8 cells is 51mV, much smaller than that of Zn//Ti cells (i.e., 115mV) as exhibited in Fig. 6b and Supplementary Fig. 18. It indicates that the A-ZIF-8 layer can effectively reduce the energy barrier for Zn nucleation/dissolution and suppress dendrite growth on Ti foil. The Zn@A-ZIF-8 anode was further investigated in full cell, where homemade α-MnO\(_2\) was used as cathode. Before the test, the structure and morphology of the cathode material were observed by X-ray diffractometer and scanning electron microscope as shown in Supplementary Fig. 20. Zn//MnO\(_2\) full cells were tested in an electrolyte consisting of 2 M ZnSO\(_4\) and 0.2 M MnSO\(_4\). The cyclic voltammetry (CV) curves of ZIBs based on the Zn foil anode and the Zn@A-ZIF-8 anode are exhibited in Fig. 6c. The typical redox peaks with high reversibility can be observed for different anodes, suggesting the presence of A-ZIF-8 layer does not affect the electrochemical kinetics of Zn plating/stripping. The AC impedance spectrum of AZIBs is shown in Fig. 6e. The R\(_{\text{CT}}\) value of the Zn@A-ZIF-8//MnO\(_2\) cell (167.8 Ω) is lower than that of the Zn foil //MnO\(_2\) cell (557.7 Ω), suggesting a fast charge transfer of Zn@A-ZIF-8 //MnO\(_2\) cell, which is in good agreement with the results from a symmetric cell. In addition, the long-term cycling stability of full cell was tested at a current density of 1 A g\(^{-1}\). The Zn@A-ZIF-8//MnO\(_2\) cell exhibits much better cycling stability with a capacity retention rate of 98.9% over 2000 cycles than the MnO\(_2\)//Zn cell (30.8%) as shown in Fig. 6f, which agrees well with the galvanostatic charge/discharge curves (Fig. 6d and Supplementary Fig. 21). The elevated electrochemical properties of the Zn@A-ZIF-8//MnO\(_2\) cell could be attributed to the high reversible properties of the Zn@A-ZIF-8 anode, which possesses a stable cyclic life without Zn dendrites. Furthermore, the morphology changes of the Zn foil anode and Zn@A-ZIF-8 anode after 1000 cycles in the full cell were investigated by SEM (Supplementary Fig. 22). The Zn@A-ZIF-8 anode shows a flat and dense surface after 1000 cycles, while a rough surface with lots of protrusions on Zn foil was observed.

Flexible symmetrical batteries based on Zn foil and Zn@A-ZIF-8 anode were assembled, and their cycle performances were tested at different bending angle (Fig. 7a). The lifespan of the Zn foil symmetric cell
varies with various bending angles (Supplementary Fig. 23). A 400 h survival time was achieved for unfolded; a 150 h survival time was stabilized for folded 90 degrees, and only a 50 h survival time was retained for folded 180 degrees. Locally high electric field intensity promotes the migration of zinc ions towards the folded area, resulting in an uneven zinc deposition. The SEM images (Supplementary Fig. 24b) are also consistent with the optical image (Supplementary Fig. 23b). Because more Zn is deposited onto the folded area. For the Zn symmetric cells based on Zn@A-ZIF-8 anode, the Zn symmetric cells demonstrate extraordinary cyclability for more than 800 h regardless of the bending angles (Fig. 7a).

The highly adhesive A-ZIF-8 layer can eliminate local high electric field during folding and prohibit Zn dendrite piecing in the curve area (Fig. 7b). The SEM images of 800 h cycled Zn@A-ZIF-8 anode shows uniform and flat zinc deposition even in the folded area (Supplementary Fig. 24d). Besides, the A-ZIF-8 layer could be deposited on other metal substrates such as Al, Cu, and Mg by the same procedure (Fig. 7c). Cross-sectional SEM images suggest good adhesion of the A-ZIF-8 layer to these substrates (Fig. 7d), indicating a broad potential application as protection layers for metal anodes. The Mg@A-ZIF-8/Mg@A-ZIF-8 and Al@A-ZIF-8/Al@A-ZIF-8 symmetric batteries were assembled to explore the application of A-ZIF-8 layers in other battery systems. Compared with that of bare Mg anode (2.1V, 25 h), the Mg@A-ZIF-8 anode achieved a lower stripping overpotential of 1.05 V and a higher cycle life (250 h, Fig. 7e). This is because the A-ZIF-8 layer eliminates nonselective intercrystalline diffusion of electrolyte and realize selective Mg$^{2+}$ transport. Different from the rough and loose surface layer on the Mg foil anode (Supplementary Fig. 25), the Mg@A-ZIF-8 anode displayed a flat surface after 50 cycles (Fig. 7f, Supplementary Fig. 26), suggesting that the MOF membrane can stabilize the Mg metal anode during the plating/stripping cycles, possibly attributed to the MOF channels. Similarly, as shown in Supplementary Fig. 27, the Al@A-ZIF-8/Al@A-ZIF-8 symmetrical battery exhibits 300 h cycle life, which is higher than the Al foil/Al foil symmetrical battery (120 h).

**Discussion**

In conclusion, a compact and continuous A-ZIF-8 protective layer were realized to stable Zn anode via a facile method. Benefiting from the advantages of MOFs structure and amorphous structure, the A-ZIF-8 as protective layer is able to accelerate Zn$^{2+}$ transport, suppress side reactions, reduce overpotential for Zn deposition, and stabilize zinc stripping/plating process. The symmetric Zn cells based on the amorphous A-ZIF-8 coated anode exhibited a superior lifespan (about 60 times higher) to that of the Zn foil anode (7000 h vs. 120 h) at a current density of 1 mA cm$^{-2}$. Besides, the A-ZIF-8 coated anode exhibits a high average CE of 99.5% with a low voltage gap of 51 mV over 1000 cycles. The good cyclic stability was also achieved in the MnO$_2$/Zn@A-ZIF-8 full cells, with 98.9% capacity retention after 2000 cycles at a current density of 1 A g$^{-1}$. Meanwhile, for a flexible symmetrical battery, the uneven zinc deposition caused by local high electric field intensity in the folded area with different bending angles (0°, 90° and 180°) can be successfully suppressed. Moreover, the enhanced mechanical properties of the A-ZIF-8 protective layer and versatile method are appealing to practical applications. All these results prove that the amorphous MOFs could be a promising protective layer for metal anodes.
Methods

Preparation of A-ZIF-8 precursor solutions

All chemicals are of analytical grade and used in this experiment without further purification. Different with the conventional synthesis of ZIF-8, 0.548 g zinc acetate (Zn (CH$_3$COO)$_2$·2H$_2$O) instead of zinc nitrate was added to 25 mL methanol, and then kept static for 10 mins until a transparent solution was observed. Subsequently, 0.821g 2-methylimidazole was added into the solution, followed by 12 h stirring at room temperatures. The final precursor solution was collected for further use.

Preparation Of Zinc Anodes

Firstly, the zinc foil (80 µm, purity ≥ 99.9%) was polished with 600#, 800#, and 2000# metallographic sandpaper sequentially. Secondly, the polished zinc foil was rinsed with ethanol and deionized water, and then dried in a vacuum oven. After that, the zinc foil was pressed into zinc discs with a diameter of 12 mm. After cleaning the zinc discs with ultrasonic method in a mixed solution of 50 wt% alcohol and 50 wt% acetone (50wt% each) for 30 min, they were dried in a vacuum oven for further use.

Preparation Of Zn@A-ZIF-8, Zn@C-ZIF-8 Anodes

The A-ZIF-8 layer was prepared by the in-situ spray method. To prevent colloid aggregation during spraying, the Zn foil was heated to 150°C by using a hot plate. The spray gun (HD-130), that has a 0.3 mm nozzle, a 5 mL container, a 4 bar air pressure supplied by a compressor, was adopted for the spray. The distance from the nozzle tip to the zinc foil was about 10 cm. The flow rate of the sol sprayed was about 1 mL min$^{-1}$, and the spraying time was set to 2 min to obtain a uniform thickness. The coated zinc foil was transferred into a tube furnace at 150°C with a ramp of 5°C min$^{-1}$ for 0.5 h or 8 h under nitrogen flow to obtain Zn@A-ZIF-8, Zn@C-ZIF-8, respectively. Finally, the obtained anode materials were cut into 12 mm discs by a tablet press and transferred into a drying oven for use.

Preparation Of α-MnO$_2$ Cathode Material

In a typical synthesis process, 3 mmol MnSO$_4$·H$_2$O and 2 mL 0.5 mol L$^{-1}$ H$_2$SO$_4$ were magnetically stirred in 60 mL distilled water for 10 min, and then 20 mL 0.1 mol L$^{-1}$ KMnO$_4$ was slowly added to the above solution. The mixture was stirred for 1 h, and then sonicated for 1 h. Afterwards, the mixture was transferred to a Teflon-lined autoclave, being heated at 120°C for 12 h. The obtained product was collected by vacuum filtration, washed with deionized water at least three times, and then dried in a vacuum at 60°C for 12 h$^{44}$.

Preparation Of ZIF-8 Powder
Typically, 0.734 g of Zn(NO$_3$)$_2$·6H$_2$O and 0.810 g of 2-methylimidazole were dissolved separately in 50 mL methanol, respectively. Then, the methanol solution of 2-methylimidazole was added into the methanol solution of Zn(NO$_3$)$_2$·6H$_2$O, and the corresponding mixture was stood at room temperature for 24 h. The ZIF-8 powders were collected from solution by centrifugation at 8000 r.p.m for 5 min, which were further washed three times by methanol. The resultant products were dried at 60 °C in a vacuum oven overnight.

**Assembly Of Zn//Zn Symmetric Cells And Zn //MnO$_2$ Cells**

The CR2025-type coin symmetric cell was assembled by the anodes obtained in the previous steps (Zn foil or Zn@A-ZIF-8, Zn@C-ZIF-8; diameter: 12 mm, thickness: 80 µm), 2 M ZnSO$_4$ electrolyte, and a glass fiber separator. The cathode of the Zn//MnO$_2$ full cell was prepared by mixing $\alpha$-MnO$_2$ powder, carbon black and Polyvinylidene fluoride with 1-methyl-2-pyrrolidone (NMP) in a mass ratio of 7:2:1. The obtained slurry was coated on Ti foil, and then dried at 80°C for 10 h in a vacuum oven. Based on such cathodes (MnO$_2$ mass loading: 1 mg cm$^{-2}$), Zn//MnO$_2$ full cells were assembled with the anode (Zn foil or Zn@A-ZIF-8), electrolyte (2 M ZnSO$_4$ and 0.2 M MnSO$_4$) and glass fiber separators. All cells were assembled under open-air condition and aged for 10 h before performing electrochemical measurements.

**Assembly Of Al//Al Symmetric Cells And Mg //Mg Cells**

The Al//Al symmetric cell was assembled with the Al foil anode or Al@A-ZIF-8 anode (diameter:12 mm, thickness:100 µm), 2 M Al(NO$_3$)$_3$ electrolyte, and glass fiber separator. The Mg//Mg symmetric cell was assembled from the Mg foil anode or Mg@A-ZIF-8 anode (diameter:12 mm, thickness:100 µm), 0.5 M Mg (TFSI)$_2$ in DME electrolyte, and glass fiber separator.

**Design Of Flexible Zn //Zn Symmetric Cells**

Zn foils were tailed into the size of 3cm x 5 cm. Three-layer configurations including Zn foil or Zn@A-ZIF-8, separator (two layers of non-woven papers), and Zn foil or Zn@A-ZIF-8 were used to do initial tests with liquid electrolytes. The three-layer symmetrical battery was assembled with a plastic mold, sealed with hot melt adhesive, and folded at different angles and fixed with clamps for testing.

**Characterizations**

The morphologies and structures of the materials and anodes were observed by FESEM (JEOL JSM-7800F), X-ray diffractometer (Bruker), Raman (HORIBA Science Lab RAM HR Evolution), and Fourier transform infrared (FTIR) spectra (Thermo Fisher/Nicolet 6700). N2 adsorption-desorption isotherms are measured at 77 K on a Micromeritics TriStar II 3020 volumetric adsorption analyzer after degassing in a vacuum at 120°C overnight. Atomic force microscope (AFM) is performed on a NT-MDT NTEGRA Spectra
The morphology of the symmetric battery containing Zn foil and Zn@A-ZIF-8 anodes during the galvanizing process was observed with an Olympus BX43 optical microscope. A zinc foil with a length of 1 cm, a width of 1 cm, and a thickness of 80 µm were fixed on a transparent glass plate, a domestic optical battery was constructed, and galvanostatic deposition was performed using an electrochemical workstation (CHI 660E) at a current density of 5 mA cm\(^{-2}\). The surface wettability of the anodes was measured with the OCA25 contact angle measurement system (Data Metaphysics, Germany).

**Electrochemical Measurements**

Galvanostatic charge/discharge curves (GCD) curves were obtained by a battery test system (LAND CT2001A, China). Cyclic voltammetry (CV), linear sweep voltammetry (LSV), and linear polarization (LP) curves were measured on a CHI 760E electrochemical workstation. Meanwhile, electrochemical impedance spectroscopy (EIS) was measured in the frequency range from 100 k Hz to 0.1 M Hz under the condition of an AC voltage of 5 mV.

**Declarations**

**Data availability**

Source data are provided with this paper. Data supporting the findings of this study are available within the article and the associated Supplementary Information. Additional data are available from the corresponding authors upon reasonable request.

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**Author contributions**

Xuan Zhang., Maowen Xu., Yinzhu Jiang., Yingying Lu., and Shujuan Bao., conceived and designed the experiment. Yang Xiang., Xuan Zhang., Yannan Wang., Shuai Dai., participated in writing and revising the paper. Yang Xiang. performed the electrochemical tests, analyzed the data, and wrote the manuscript. Liyuan Zhou., Pingping Tang., synthesized the samples, performed the characterizations of A-ZIF-8. All authors have read and approved the final paper.

**Declaration of Competing Interests**

The authors declare that they have no competing interests.

**References**


**Figures**
Figure 1

The morphology and structure characterization of the A-ZIF-8 layer. a Structural illustration of crystalline ZIF-8 and Zn ions conduction. b Structural illustration of A-ZIF-8 and Zn ions conduction. Field emission scanning electron microscopy (FESEM) image of (c) Zn@A-ZIF-8, and (d) Zn@C-ZIF-8. e Cross-sectional SEM image of Zn@A-ZIF-8. f Energy dispersive spectroscopy (EDS) mappings of (e). g X-ray diffraction (XRD) patterns of simulated ZIF-8, Zn foil, Zn@A-ZIF-8, and Zn@C-ZIF-8. h Atomic force microscopy (AFM) image of Zn@A-ZIF-8 anode. i Optical photos of the contact angle between electrolyte and different zinc anode. j Zn$^{2+}$ transference number of the symmetric cells. k Zn 2p X-ray photoelectron
spectroscopy (XPS) spectra of Zn foil, Zn@A-ZIF-8, and Zn@C-ZIF-8. Pseudoradial distribution functions of zinc foil, ZIF-8 powder and A-ZIF-8 from experiment and corresponding fitting data. (Data were extracted through Fourier transformation of the X-ray adsorption spectra (inset) obtained at the K edge of zinc.)

Figure 2

**Binding interaction characterization.** Top view of (a) optimized C-ZIF-8 unit cell and (b) amorphous ZIF-8 structure with same scales as 2×2×2 supercell crystal structure of A-ZIF-8. Side view of (c) optimized ZIF-8 supercell crystal structure and (d) amorphous ZIF-8 structure on Zn (0 0 2) surface. e Binding energy of Zn@ZIF-8/A-ZIF-8. f, g Load vs displacement graph of a 100 mN ramp load nano-scratch test over a scratch distance of 200 μm for Zn@A-ZIF-8 and Zn@C-ZIF-8.
Figure 3

**Anti-corrosion and suppression of hydrogen evolution reaction and dendrite growth.** a Optical and SEM images of Zn foil and Zn@A-ZIF-8 anodes immersed in 2M ZnSO₄ solution for 3 days. b XRD patterns of Zn foil and Zn@A-ZIF-8 anodes after submerged in 2 M ZnSO₄ electrolyte 3 days. c Linear polarization curves of Zn foil and Zn@A-ZIF-8 anodes in 2 M ZnSO₄ electrolyte. d Chronoamperogram of different
anodes. e LSV curves of Zn foil and Zn@A-ZIF-8 anodes in 1 M Na₂SO₄ electrolyte at 5 mV s⁻¹. f Nucleation overpotential of different anodes at a current density of 1 mA cm⁻². g Surface and cross-sectional SEM images of Zn foil anode and Zn@A-ZIF-8 anode before and after 50 cycles. h Optical microscopy images of zinc deposition on zinc foil and Zn@A-ZIF-8 at 5 mA cm⁻².

Figure 4

Structure design and elucidation of suppression mechanism. a, b Schematic comparison of Zn deposition process on Zn foil surface, Zn@C-ZIF-8 surface, respectively. c Schematic presentation of Zn deposition process on Zn@A-ZIF-8 surface.
Figure 5

**Electrochemical performance of different Zn anodes.** a) Cycling performance of symmetric cells with different anodes (electrolyte: 2 M ZnSO\(_4\) solution; current density: 1 mA cm\(^{-2}\); area capacity: 1 mA h cm\(^{-2}\)). b) Comparison of the cycle life of Zn@A-ZIF-8 and Zn@C-ZIF-8 anode. c) Cycling performance of symmetric cells with different anodes in 2 M ZnSO\(_4\) electrolytes at current densities of 10 mA cm\(^{-2}\) with an area capacity of 1 mA h cm\(^{-2}\). d) Comparison of the electrochemical performance of Zn@A-ZIF-8 anode with other anodes reported in the literature (the details and references are listed in Supplementary Table S2). e) Rate performance of different cells and the corresponding voltage hysteresis at different current densities.
densities from 1 to 10 mA cm\(^{-2}\). The corresponding voltage hysteresis at different current densities from 1 to 5 mA cm\(^{-2}\). Cycling performance of symmetric cells with different anodes in 2 M ZnSO\(_4\) electrolytes at 51% DoD\(_\text{Zn}\). Nyquist plots of different symmetric cells before and after 50 cycles.

**Figure 6**

**Electrochemical performance of Zn//Ti and Zn//MnO\(_2\) cells with different anodes.**

- **a** Zn plating/stripping CE at a current density of 3 mA cm\(^{-2}\) with an area capacity of 3 mA h cm\(^{-2}\).
- **b** Discharge/charge voltage profiles of the asymmetrical cells at various cycles based on Ti@A-ZIF-8 anode.
- **c** CV curves of the Zn//MnO\(_2\) and Zn@A-ZIF-8//MnO\(_2\) cells (second cycle, 1 mV s\(^{-1}\)).
- **d** Discharge/charge curves of the Zn@A-ZIF-8//MnO\(_2\) full cell at different cycles at a current density of 1 A g\(^{-1}\).
- **e** EIS spectra before cycling.
- **f** Long-term cycling performance of different cell.
Figure 7

Application of A-ZIF-8 layers in flexible battery and other anodes. a Voltage vs time profile of Zn symmetric cell based on Zn@A-ZIF-8 anode under different angles. b Optical images of cycled Zn@A-ZIF-8 anode at bending angle of 180°. c Optical images of the prepared A-ZIF-8 layer on Cu, Mg, Al, Zn foil. d Cross-sectional SEM images of different anode. e Galvanostatic cycling of symmetric cell of Mg, Mg@A-ZIF-8 anode at a current density of 0.1 mA cm⁻². f Cross-sectional SEM image of Mg@A-ZIF-8 anode after stripping/plating cycles.

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