

RESEARCH ARTICLE

Zincophilic Nanowire Array With Hydrophobic Iodine Elimination Layer for Ultrastable Zinc-Iodine Battery

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ABSTRACT

Among the ultrafast rechargeable batteries, aqueous zinc-iodine (Zn-I₂) batteries receive renewed interest for their cost-effectiveness, environmental friendliness and efficient double electron transfer mechanism. However, the shuttle corrosion of polyiodide and the dendrite problem of zinc metal anodes lead to rapid battery failure. Here, we first introduced a zincophilic nanowire array with hydrophobic iodine elimination effect to stabilize the zinc anode for a stable dendrite-free and corrosion-free zinc-iodine battery. The in situ constructed composite nanowire array provides an ordered and continuous zincophilic channel to induce stable non dendritic zinc deposition and possesses a hydrophobic iodine elimination effect, preventing simultaneous electrolyte and polyiodide corrosion. As a result, the zinc-iodine full cell has achieved the ultralong 350000 cycles at a high specific current of 50C, with a minimal capacity attenuation of 0.00011% per cycle. Our work offers a reference strategy for achieving ultrafast-charging Zn-I₂ batteries with maximum chemical stability.

1 | Introduction

The intermittence and timeliness of renewable energy (such as hydropower, solar energy and wind power) put forward higher requirements for grid scale energy storage [1–3]. If the grid cannot withstand all the energy inflows in the peak period in a short time, it will lead to huge energy consumption and serious security risks. In addition to flywheel storage, compressed air storage and pumped storage, ultrafast rechargeable batteries with powerful long-term cycling stability provide a sustainable and cost-effective grid level energy storage mode [4–7]. Compared to Li-based and Na-based batteries, aqueous zinc ion batteries (AZIBs) have drawn significant focus in rapid-charging battery

research owing to the superior ionic conductivity (up to 1 S cm^{−1}) of aqueous electrolytes, high energy density, cost-effectiveness and nonflammability [8–14]. However, most of the cathode materials of traditional AZIBs are of intercalation structure [15, 16], where metal ions are difficult to diffuse inside the active material [17]. In particular, Zn²⁺ ions face significant diffusion challenges in solid materials due to its strong interaction with the solid matrix, resulting in the large energy barrier of ion transition. In the process of fast charging, it is inescapable to lead to the structural collapse and volume change (expansion and contraction) of the cathode material, facing rapid capacity attenuation, which represents a critical challenge to the sustainability of rechargeable batteries. With the use of same aqueous electrolyte,

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the zinc iodine (Zn-I_2) battery has an efficient double electron transfer mechanism ($\text{I}^- \leftrightarrow \text{I}_3^-/\text{I}_5^- \leftrightarrow \text{I}_2$) [18], in which the cathode iodine has redox mediating effect [19], and is expected to achieve sustainable energy conversion and storage under rapid charging [20–22].

Nevertheless, it is well established that iodine-based cathode chemistries face significant practical challenges due to the highly corrosive nature of iodine and polyiodide species. This corrosivity complicates battery packaging as well as current collector stability, potentially offsetting the cost and performance benefits offered by the electrode and electrolyte materials. Especially, iodine will be converted into I^- during discharging process. Due to the hydrophilic solubilization phenomenon [23], I^- and non-polar iodine (I_2) (weak interaction with H_2O) form intermolecular soluble complex polyiodide ($\text{I}_3^-/\text{I}_5^-$) (strong interaction with H_2O) (Figure S1), which increases the solubility by about 500 times. The shuttle effect of violently dissolved I_3^- results in rapid capacity decay and poor cycle life. To address these issues, many researchers focus on the optimization of cathode host material [24–27], membrane modification [28, 29] and new electrolyte [30–32], and have made some progress in zinc-iodine batteries. Pang et al. prepared a metal nitrogen carbon material (Fe-N-C) as an iodine host material to enhance the physical and chemical adsorption of iodine species [33]. In another example, Yang et al. engineered a Janus separator incorporating cation-exchange resin and single-walled carbon nanotubes to repress the shuttle of polyiodides [34]. Meanwhile, developing sustainable Zn-I_2 batteries still faces critical challenges, including zinc anode dendrite formation and parasitic side reactions (hydrogen evolution, passivation, and corrosion) [35, 36]. In addition, the dissolution of polyiodide intermediate and reaction with zinc anode will further intensify the corrosion of zinc anode and the decay of active substance. Under adverse conditions of polyiodides corrosion, hydrogen evolution reaction, and uneven deposition of zinc ions, the comprehensive improvement of zinc anode performance has been neglected, which can lead to a mismatch between performance and sustainability of Zn-I_2 batteries, seriously hindering their practical application.

More than the exploration of cathode materials, most efforts have focused on building high-performance zinc anodes, committing to developing advanced fast charging AZIBs and pursue batteries with fast zinc conduction ability [37]. The construction of 3D structure is a promising method to obtain stable working zinc anode under high current density/capacity [38, 39]. The 3D structure efficiently increases the specific surface area to provide abundant nucleation reaction sites, and reduces the local charge density of uniform zinc deposition to inhibit dendrite growth [40, 41]. Among them, 3D nanowire arrays provide highly ordered and fully exposed active surfaces of individual nanostructures, which can better modulate uniform distribution, rapid migration of Zn^{2+} ions and effective charge transfer at the zinc anode/electrolyte interface. Meanwhile, 3D nanowire arrays with abundant spatial gaps will also alleviate the strong volume expansion stress generated during repeated zinc plating/stripping processes. Also, the highly exposed and continuous channel nanoarray structure extremely optimizes the zinc deposition behavior, thus avoiding the emergence of “hot spots” near the prominent zinc core [42]. The 3D nanoarray shows the potential to work sustainably under extreme conditions of fast

charging. Moreover, the dendrite growth and side reactions can be effectively inhibited by surface modification with inorganic and organic coatings [43, 44]. Metal inorganic coating materials such as ZnF_2 [45], Sn [46], and ZnS [37] regulate the diffusion of Zn^{2+} to inhibit dendrites, and act as a physical barrier to effectively inhibit side reactions. However, in zinc-iodine batteries, the metal coatings inevitably react violently with the polyiodides in the electrolyte. And under high current/capacity, the local electric field becomes larger and the charge still accumulates under high Zn^{2+} ion concentration. The brittle metal coating produces violent volume expansion, which leads to cracking and peeling, and cannot achieve long-term protection and repeated circulation under fast charging conditions [47]. In addition, recycling and environmental pollution of inorganic metal coatings is also a complex dilemma [48]. Therefore, selecting appropriate organic polymer coating materials that can effectively repel polyiodides and have certain physical and mechanical properties may be a green and sustainable strategy.

Herein, we design a sustainable dendrite-free and corrosion-free stable zinc anode (polyvinylidene difluoride- ZnOHf@Zn , noted as PVDF- ZnOHf@Zn) with a two-way synergistic effect of zinc affinity and hydrophobicity, involving the 3D zincophilic ZnOHf nanowire arrays and the hydrophobic iodine removal layer of PVDF. The in situ constructed nanowire arrays have continuous, highly ordered, and fully exposed active surfaces of individual nanostructures. The electric field distribution, zinc ion flux and local current density were optimized to induce uniform deposition of zinc at the bottom of the nanowire array. PVDF provides a hydrophobic iodine elimination effect, which has hydrophobicity, making $\text{I}_3^-/\text{I}_5^-$ by-products insoluble in PVDF polymer and repelled by multiple functions. It can effectively prevent capacity degradation and a short cycle life caused by simultaneous electrolyte and polyiodide corrosion toward zinc anode. Besides, the synergism of the two effects forms a uniform hybrid solid-electrolyte interphase (SEI) on the surface of zinc anode, inducing stable non-dendritic zinc deposition. This collaborative design not only optimizes fast zinc conduction to enhance the fast charging capacity of the battery, but also effectively inhibits the adverse reactions between electrolyte/polyiodide and zinc anode, showing excellent electrochemical performance even at high current density/capacity. As a result, the synergistic zinc anode exhibits a stable cycle for 600 h at a current density of $10 \text{ mA cm}^{-2}/1 \text{ mAh cm}^{-2}$, which is much better than the anode without collaborative design and bare zinc. And the assembled large-area pouch symmetrical cell has stably cycled for 1100 h at a high current density/capacity of 2 mA cm^{-2} (40 mA)/ 1 mAh cm^{-2} (20 mAh). More importantly, the fabricated zinc-iodine full cell has achieved the longest cycle of 350000 cycles reported so far, and the capacity attenuation is the minimum of 0.00011% each cycle. Our work provides a reference strategy for the sustainable high-performance zinc anode, and opens up a possible way to promote the practical application of zinc-iodine battery.

2 | Results and Discussion

2.1 | Synergistic Zinc Anode Design

In general, the bare zinc has serious corrosion and side reactions in the electrolyte, and the deposited zinc is uneven, which easily

forms zinc dendrites with poor cycling performance. For Zn-I₂ batteries, it is also important that the anode effectively resist the presence of polyiodide to prevent corrosion [49]. However, there are few reports on zinc anodes that combine rapid zinc conduction, inhibition of side reactions, and especially the rejection of polyiodide corrosion. Therefore, a long-term dendrite-free and corrosion-free stable zinc anode with a two-way synergistic effect of zinc affinity and hydrophobic iodine elimination is proposed. This collaborative design has the following advantages: First, the in situ constructed 3D nanowire zinc conductive layer provides continuous and highly ordered zinc affinity channels, which optimize electric field dispersion, zinc ion flux, and local current density, achieving uniform zinc deposition under high Zn²⁺ ion concentration. It shows great potential in achieving highly reversible and high current galvanizing/stripping behavior under the ultrafast charging condition. Second, large size I₃⁻/I₅⁻ ions form hydrated ion groups with thick solvation layer in aqueous electrolyte. PVDF hydrophobic alkyl long chain effectively repels hydrated I₃⁻/I₅⁻ ions due to the steric hindrance effect, which makes I₃⁻/I₅⁻ insoluble and unstable in PVDF polymer, causes them to aggregate, and prevents them from contacting with Zn matrix and causing corrosion. Meanwhile, the F atoms with strong electronegativity on the C—F bond repel each other with polyiodide which are the halogen compounds, due to the strong electrostatic interaction. The molecular electrostatic potential (ESP) analysis of PVDF and I₃⁻/I₅⁻ shows that the F group shows the most negative potential (Figure S2), reflecting its electrostatic repulsion with I₃⁻/I₅⁻. PVDF has strong hydrophobic properties, further protecting the zinc anode by effectively inhibiting the corrosion of polyiodide and electrolyte. In addition, a uniform hybrid SEI was formed on the surface of the zinc anode under the synergistic effect of zincophilic nanowire array for rapid zinc conduction and PVDF for hydrophobic iodine elimination, which cooperatively induced non-dendritic zinc deposition. Therefore, it would illustrate good electrochemical performance even in repeated cycles at high current density/capacity.

2.2 | Preparation and Characterization

Based on the above analysis, the stable zinc anode with the bidirectional synergistic zincophilic and hydrophobic effect would show excellent side reaction resistance and enhanced electrochemical performance. As shown in Figure 1a, first, highly ordered ZnOHF NWs were grown in situ on the surface of zinc matrix in NH₄F aqueous solution by a hydrothermal synthesis method. This is a hydrothermal reaction involving dissolution-reprecipitation and in situ conversion. The hydrolysis of NH₄F creates an alkaline solution environment. Under hydrothermal high temperature and high pressure, the surface of zinc sheet will have a slight corrosion reaction with the weak alkaline solution, slowly releasing Zn²⁺ ions. In the solution near the surface of the zinc sheet, there are high concentrations of Zn²⁺, F⁻ provided by NH₄F hydrolysis, and OH⁻ produced by zinc corrosion and hydrolysis. When these three ions reach supersaturation, they will react to form ZnOHF nuclei and continue to grow. Because F⁻ and OH⁻ will selectively adsorb on the specific crystal surface and inhibit its lateral growth, the crystal will be guided to preferentially elongate along the 1D direction to form a highly ordered ZnOHF nanowire structure. Subsequently, PVDF was uniformly coated on ZnOHF@Zn. After vacuum drying to remove any

possible solvent, the PVDF-ZnOHF@Zn electrode was finally obtained. Due to the well-known lotus effect [50], high surface roughness and micro-nano scale array structure lead to low surface energy, which can effectively enhance the hydrophobic performance and make the PVDF-ZnOHF@Zn electrode exhibit very low water adhesion, which will be discussed in detail in a later section. PDVF with different thickness may have potential impacts on the PVDF-ZnOHF@Zn electrode. Higher content will lead to the accumulation and coverage of polymer in ZnOHF NWs. Lower content will weaken the protective effect of PVDF polymer coating. Subsequent comparative studies show that the optimal content of PVDF is about 0.1 mg cm⁻². Notably, benefiting from the convenient, environmental and low-cost fabrication process, the PVDF-ZnOHF@Zn electrode can also be easily scaled-up with a large size of 5cm² × 15cm² (Figure S3).

First, the microstructure of the PVDF-ZnOHF@Zn electrode was characterized by scanning electron microscope (SEM). Needle-like ZnOHF nanowires formed with ordered alignment on the zinc electrode surface (Figure S4). Energy dispersive spectroscopy (EDS) mapping confirmed the uniform spatial distribution of F, O, and Zn within the nanowire arrays (Figure S5), which proves that their composition is uniform. Compared with the SEM image of ZnOHF@Zn grown only with ZnOHF NWs (Figure S6), PVDF polymer traces on the surface of the PVDF-ZnOHF@Zn electrode could be observed. Besides, the cross-sectional SEM image and the corresponding EDS mapping also confirmed this point (the element mapping of C coincided with the position of the PVDF-ZnOHF layer), and showed that the thickness of the layer was about 3–5 μm (Figures S7 and S8). In addition, different contents of PVDF were coated on zinc foils to determine their approximate thickness (Figure S9). The well-defined crystallinity of ZnOHF NWs was verified by high-resolution transmission electron microscopy (HRTEM), as shown in Figure 1b. The corresponding selected area electron diffraction (SAED) patterns reveal distinct concentric rings indexed to the (310), (230), and (221) planes of the nanowire arrays, confirming high crystallinity. The measured lattice spacing of 0.270 nm corresponds to the (310) plane in ZnOHF nanowires (Figures 1c,d). As shown in Figure 1e,f, the HADDF-STEM and element mapping images further confirm that the ZnOHF nanowires were successfully synthesized. Through the element mapping overlay of C and Zn (Figure 1g), notably, compared to Zn and O elements, which are largely distributed in the central part of the nanorods, the element mapping of C is mainly uniformly distributed around the periphery of individual nanorod, indicating that PVDF polymer is excellently coated on the nanorods. The crystal structure and chemical composition of PVDF-ZnOHF@Zn were investigated by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Compared with bare Zn, the new diffraction peaks at 20.6°, 32.4°, 33.6°, 35.5°, 51.5°, 57.5° and 59.2° correspond to (110), (310), (201), (400), (221), (511) and (002) crystal planes of ZnOHF, respectively (Figure S10), which aligns with HRTEM analysis, confirming the crystalline ZnOHF nanowires' presence. XPS results further support the successful growth of the nanowire arrays, as depicted in Figure S11. A distinct F 1s peak at 687.2 eV confirms Zn—F bond formation (Figure S12). In addition, a minor binding energy shift is also detected in the Zn 2p spectral region, which is attributed to the existence of polar bonds between nanowire arrays and zinc matrix, leading to the improvement of interface adhesion and binding force. In the O 1s spectrum, the

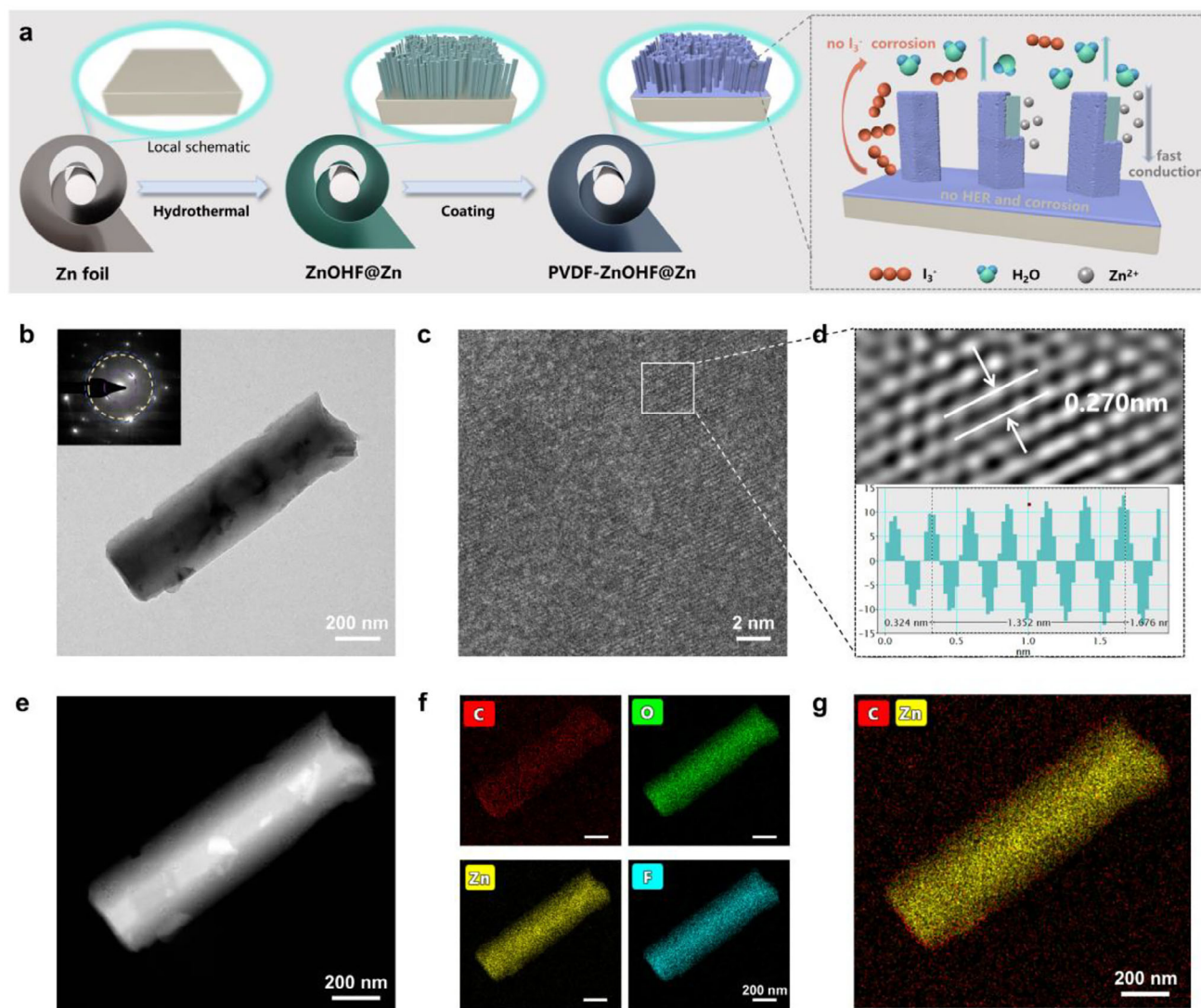


FIGURE 1 | Preparation and characterization of PVDF-ZnOHF@Zn electrode. (a) Schematic diagram of the preparation of PVDF-ZnOHF@Zn electrode and its effect mechanism. (b) High-resolution TEM images and the corresponding selected area electron diffraction (SAED) images of the ZnOHF nanowires. (c) HRTEM image and (d) the interplanar spacing measurement image. (e-f) STEM image and the corresponding elemental mapping images of PVDF-ZnOHF@Zn electrode.

characteristic peak at 530.5 eV disappears, corresponding to the Zn–O bond, which means that the formation of the nanowire arrays layer can effectively prevent the formation of ZnO, thereby improving the stability of the zinc electrode in air. Meanwhile, in the high-resolution C 1s spectrum, the existence of C–F bond indicates the existence of PVDF.

2.3 | Side Reaction Resistance

Long-term exposure of Zn foil to electrolyte will cause serious side reactions and by-products accumulation ($\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot x\text{H}_2\text{O}$, etc.), leading to the decomposition of electrolyte and loss of active zinc. The high surface roughness and low surface energy make the PVDF-ZnOHF modified layer have outstanding hydrophobic performance. From the contact angle test (Figure 2a), the contact angle of bare Zn is 95.9° , showing hydrophobicity. After the modification of ZnOHF NWs, the contact angle is 51.3° , which

is infiltrated with aqueous electrolyte. After the PVDF coating, the contact angle of 115.3° is large, which confirms the strong hydrophobic characteristics of the PVDF-ZnOHF@Zn electrode. To study the corrosion resistance of the anode, the bare Zn, ZnOHF@Zn and PVDF-ZnOHF@Zn were soaked in 2 M ZnSO_4 electrolyte to evaluate the chemical stability. Figure S13 exhibits the digital images of three electrodes before and after soaking in the electrolyte for 7 days. After immersion for 7 days, the bare Zn surface became uneven, indicating that severe side reactions had taken place. In contrast, the appearance of the ZnOHF@Zn and PVDF-ZnOHF@Zn electrodes is basically unchanged under the protection of the modified layer, which proves that both ZnOHF physical barrier and PVDF coating can effectively enhance the resistance to side reactions. XRD results also show that obvious diffraction peaks appeared at 9.5° , 16.1° and 25.2° after immersion in bare Zn (Figures 2b,c), corresponding to the by-products of $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot x\text{H}_2\text{O}$, showing poor resistance to side reactions. The XRD results of the ZnOHF@Zn and PVDF-ZnOHF@Zn

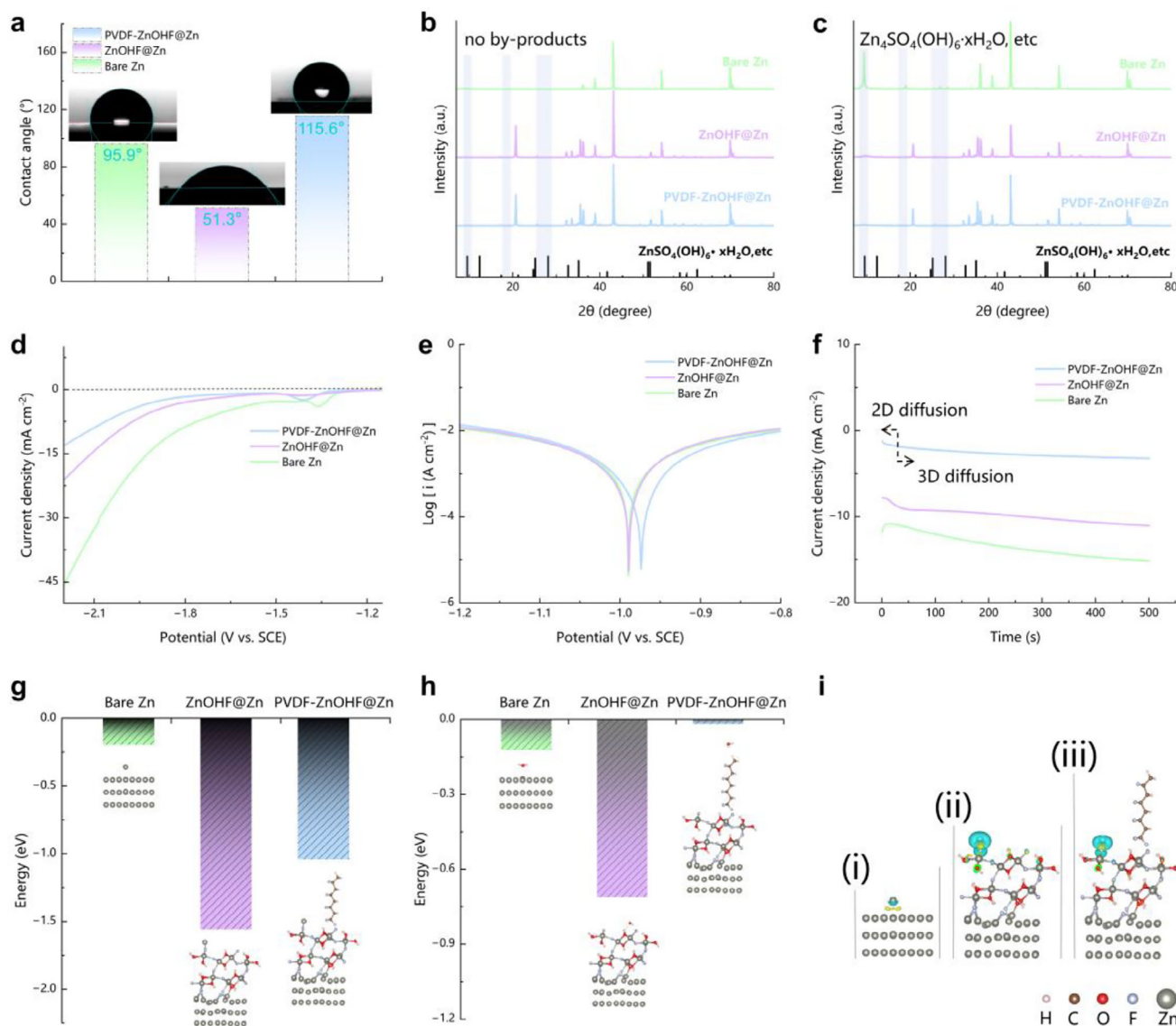


FIGURE 2 | Side reaction stability of PVDF-ZnOHF@Zn electrode. (a) Contact angles of 2 M ZnSO_4 electrolyte on the different electrodes. XRD patterns of different electrodes (b) before and (c) after soaking in 2 M ZnSO_4 aqueous solution for 7 days. (d) LSV curves and (e) LP curves of different electrodes with a scan rate of 1 mV s^{-1} . (f) Chronoamperograms (CAs) of different electrodes at a -150 mV overpotential. Adsorption energy for (g) Zn atom and (h) H_2O molecule adsorbed on the different electrodes surface. The insets in (g, h) are the optimized models for DFT calculations. (i) The charge density difference of (i) bare Zn, (ii) ZnOHF@Zn and (iii) PVDF-ZnOHF@Zn induced by Zn adsorption.

electrodes only show the diffraction peaks of ZnOHF NWs after immersion treatment, and the detected by-products are not obvious, showing excellent stability. In situ XRD was conducted to further study the corrosion reaction on the zinc anode surface during the cycling process of the battery. As the discharge voltage reached 1.2 V , in situ XRD of the bare Zn battery showed obvious diffraction peaks at 24.5° , 36.1° and 41.3° , assigned to basic zinc salt ($\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot x\text{H}_2\text{O}$, ZHS), iodine and ZnI_2 species, respectively (Figure S14a), which was attributed that the polyiodides moved to the Zn anode surface under the electric field, triggering a parasitic reaction and leaving iodide (such as ZnI_2) residues on the electrode. At the same time, the zinc salts ($\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot x\text{H}_2\text{O}$, etc) produced by the side reaction between the electrolyte and the zinc cathode also remained on the electrode. The ZnOHF@Zn battery was also detected the significant diffraction peaks assigned to iodine and ZnI_2 species

(Figure S14b). In contrast, only weak peaks were observed in the PVDF-ZnOHF@Zn cell (Figure S14c), demonstrating its effective resistance to corrosion reactions.

From the results of linear sweep voltammetry (LSV) (Figure 2d), the PVDF-ZnOHF@Zn electrode needs a maximum overvoltage of -2.12 V (vs. SCE) to achieve a current density of 10 mA cm^{-2} , which confirms its optimal side reactions resistance. As shown in Figure 2e, the corrosion potential of the ZnOHF@Zn and PVDF-ZnOHF@Zn electrodes was higher than that of the bare Zn, which effectively reinforced the corrosion resistance of the electrode. The PVDF-ZnOHF@Zn electrode exhibited the optimum corrosion resistance with the highest value of -0.97 V (vs. SCE). In addition, the Chronoamperometry curves (Figure 2f) display that the response current in the bare Zn cell continues to increase during the testing under constant overpotential 150 mV , showing

the uncontrolled spontaneous 2D diffusion of Zn^{2+} , which may result in the rapid growth of dendrites. Yet the response current in the PVDF-ZnOHF@Zn battery is rapidly stable and transits to a constant 3D diffusion condition, proving its favourable dendrite inhibition ability, which is attributed to the synergy between PVDF coating with good physical barrier effect and ZnOHF NWs with rich zinc affinity sites. To verify the synergistic effect of zinc affinity and hydrophobicity on the PVDF-ZnOHF@Zn electrode, the adsorption energies of Zn atoms and H_2O molecules on the bare Zn, ZnOHF@Zn and PVDF-ZnOHF@Zn surface were simulated and calculated based on density functional theory (DFT) (Figures 2g,h). It is noted that the DFT relies on idealized, static surface models and does not account for the dynamic evolution of the electrode-electrolyte interface under real electrochemical environments. We will simulate electric-field distribution, Zn^{2+} ion flux, and current density to elucidate the kinetics of ion transport in the following sections. Through crystal structure analysis, Zn (001) and ZnOHF (110) are their stable surfaces. The PVDF-ZnOHF@Zn (110) surface exhibits an H_2O adsorption energy of -0.02 eV, contrasting with -0.12 eV for bare Zn (001) and -0.71 eV for ZnOHF@Zn (110), demonstrating significantly weaker H_2O adsorption on PVDF-ZnOHF@Zn compared to bare Zn and ZnOHF@Zn. The PVDF-ZnOHF modified layer provides hydrophobicity interaction, weakening the adsorption of H_2O on the PVDF-ZnOHF@Zn surface, thereby inhibiting the side reactions at the anode/electrolyte interface. In addition, the calculated adsorption energy of Zn atoms on PVDF-ZnOHF@Zn (110) is remarkably higher than that of bare Zn (-1.04 eV vs. -0.20 eV), demonstrating that the PVDF-ZnOHF@Zn electrode has better zinc affinity than bare Zn. Compared with bare Zn, the charge distribution at the interface between the PVDF-ZnOHF@Zn electrode and Zn^{2+} ions is balanced (Figure 2i), which accelerates the diffusion of Zn^{2+} ions, alleviates the interface concentration gradient, avoids the formation of “tip effect” on the Zn anode, and promotes uniform zinc deposition. On the other hand, the difference in the strength of the interactions can be further revealed by comparing the charge density difference of H_2O adsorbed on the different electrodes (Figure S15). The yellow and blue regions in the charge density results indicate the accumulation and depletion of electrons, respectively, and H_2O molecule has a lighter connection with the PVDF-ZnOHF@Zn electrode, indicating a strong repulsive interaction between them, which further demonstrates the hydrophobic property of the PVDF-ZnOHF@Zn electrode.

2.4 | Polyiodine Ions Tolerance

For Zn- I_2 batteries, apart from the major challenges related to the formation of zinc dendrites and many side reactions (hydrogen evolution reaction, passivation, etc.), the inevitable “shuttle effect” leads to the diffusion of polyiodide to the anode, and the violent reaction on the zinc anode side, leading to the rapid failure of the batteries, which poses a huge challenge to the sustainability of batteries. Effective isolation of polyiodides from the zinc anode is therefore critical to suppress corrosion. To comprehensively evaluate the resistance of the modified synergetic electrode to polyiodide ions, visualization experiments, Raman, UV-vis spectra, DFT simulation, etching XPS and TOF-SIMS techniques were applied. First, the bare Zn, ZnOHF@Zn and PVDF-ZnOHF@Zn were immersed in $2 \text{ mmol L}^{-1} \text{ I}_3^-$ solution (The concentration of

iodine solution refers to the previous report. The concentration of polyiodide under specific working conditions of the battery can be simulated by estimating the content of iodine dissolved in the electrolyte). After soaking for 24 h, the color of the solution around the bare Zn electrode gradually became lighter until it was completely transparent after 48 h (Figure S16). And the solution around the ZnOHF@Zn and PVDF-ZnOHF@Zn electrodes has no obvious color change in the whole process, which strongly indicates that the PVDF-ZnOHF layer can avert the corrosion of the anode caused by polyiodide ions.

The UV-vis spectrum of the polyiodide solution after immersing the electrodes reveals the two peaks of about $\sim 290 \text{ nm}$ and $\sim 350 \text{ nm}$ attributed to I_3^- species, and there is a more obvious concentration difference among the polyiodide solution of the three electrodes (Figure 3a), which confirms the isolation ability of the PVDF-ZnOHF@Zn electrode to I_3^- . The difference of the polyiodide solution of the three electrodes before and after immersion was further analyzed by Raman testing. Raman spectroscopy shows two peaks $\sim 110 \text{ cm}^{-1}$ and $\sim 160 \text{ cm}^{-1}$ (Figure 3b), corresponding to I_3^- and I_5^- species respectively. After immersion, the strength of the two peaks corresponding to bare Zn was significantly weakened (Figure 3c), indicating that there was a bad corrosion reaction between the polyiodide and bare Zn, while in the solution immersed by the PVDF-ZnOHF@Zn electrode, the signals of I_3^- and I_5^- were always the strongest throughout the test process, highlighting its effective isolation effect. To visually demonstrate the isolation effect of PVDF on polyiodides, an H-type glass cell was used to visual-ize the polyiodide diffusion experiment (Figure S17): the left chamber was filled with brown-yellow 0.5 M I_3^- and 1.5 M ZnSO_4 solution, and the right chamber was filled with transparent 2 M ZnSO_4 solution. The GF separator coated with 0.1 mg cm^{-2} of PVDF was prepared, which is used to construct the pure GF separator for comparison. After the duration of 15 mins, the GF-based H-type cell already showed polyiodide permeation. By 5 h, most of the polyiodide had diffused in the right chamber on the right side, and by 12 h the entire chamber was saturated with polyiodide solution. In contrast, the color of the GF@PVDF-based H-type cells exhibited virtually no color change within the first hour. After 12 h, the right chamber showed a more obvious faint yellow color, and the left and right chambers still maintained a significant color difference after about 24 h, which indicated that there was a significant difference in polyiodide concentration on both sides. The results demonstrate that PVDF effectively inhibits the diffusion of polyiodide.

The polyiodide is unstable in the PVDF matrix. Density functional theory (DFT) was applied to study the interaction mechanism at atomic scale to further understand the solvation potential and stability of polyiodide in zinc anode. When dissolution occurs, I_3^- and I_5^- species leave their aggregates, followed by simultaneous solvation. Therefore, the dissolution of I_3^- and I_5^- species is highly correlated with two interactions: first, the cohesion strength (ΔE_{CE}) between I_3^- and I_5^- species, which determines the molecular dissolution of I_3^- and I_5^- species from aggregates; second, adsorption energy (ΔE_{SE}) of I_3^- and I_5^- species in bare zinc and the PVDF-ZnOHF@Zn electrode. These two attractions compete with each other, which determines whether dissolution occurs. We used the competitive solvation potential ($\Delta P = \Delta E_{\text{SE}} - \Delta E_{\text{CE}}$) to directly compare the cohesive

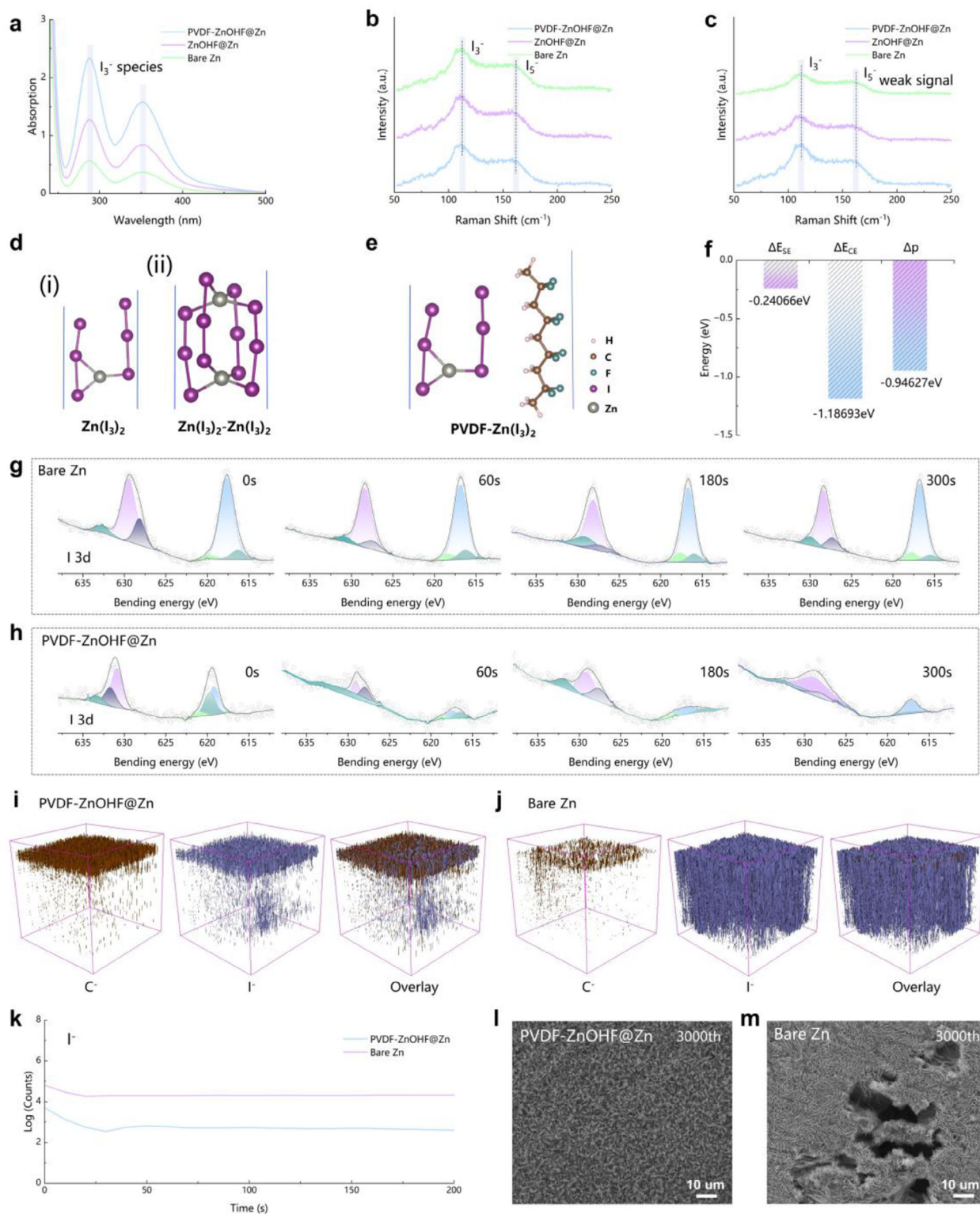


FIGURE 3 | Polyiodine ions resistance and mechanism analysis of PVDF-ZnOHF@Zn electrode. (a) UV-vis absorption spectra of adsorption test in 2 mmol L⁻¹ I₃⁻ solution. Raman spectra for the polyiodide solution of the three electrodes. (b) before and (c) after immersion. (d) Optimized configurations of (i) Zn(I₃)₂ and (ii) Zn(I₃)₂-Zn(I₃)₂. (e) The optimized adsorption configurations of Zn(I₃)₂ on PVDF. (f) Energy comparison of ΔE_{CE}, ΔE_{SE} and ΔP for I₃⁻. I 3d XPS spectra of (g) bare Zn and (h) PVDF-ZnOHF@Zn after etching. The 3D visualization of C⁻ and I⁻ in the TOF-SIMS sputtered volumes of (i) PVDF-ZnOHF@Zn and (j) bare Zn. (k) The corresponding TOF-SIMS depth profiles for I⁻. SEM images of (l) PVDF-ZnOHF@Zn and (m) bare Zn after 3000 cycles. Scale bar, 10 μm for (l,m).

strength and solvation energy of I_3^- and I_5^- species. The positive ΔP indicates that I_3^- and I_5^- species can be dissolved and adsorbed, while the negative ΔP indicates that I_3^- and I_5^- species tend to aggregate themselves. First, the possible structures of polyiodide intermediate were optimized (Figure S18), and it is calculated that type1 has the lowest energy and the most stable structure. Second, we optimized the adsorption configurations of I_3^- and I_5^- species on autogenous aggregation and PVDF molecular configuration respectively (Figure 3d,e; Figure S19). The results reveal that the cohesion strength (ΔE_{CE}) of I_3^- and I_5^- species is far less than the adsorption energy (ΔE_{SE}) of that in PVDF molecular, different from the strong redox reaction tendency of polyiodide with bare Zn directly. In addition, the calculated Δp value is shown in Figure 3f and Figure S20. I_3^- and I_5^- species show the negative “ Δp ” values, confirming that polyiodide is insoluble in PVDF-ZnOHF@Zn, which effectively prevents the corrosion of polyiodide ions on zinc anode. Etching XPS was carried out to plumb the surface of the PVDF-ZnOHF@Zn anode after cycling in the zinc iodine full battery, and the in-depth test was carried out with increasing time of Ar^+ etching. The high-resolution spectra of I 3d region fits three pairs of coupling peaks 617.2/628.7, 618.0/629.5 and 619.0/630.9 eV, which are attributed to I_3^- , I_2^- and I_5^- species, respectively. On the surface of bare Zn, the reduction of polyiodide species was not observed with the increase of Ar^+ sputtering depth (Figure 3g), indicating that the bare Zn surface was seriously corroded by excessive iodine. In contrast, upon further sputtering for 300s, the content of iodine on the surface of the PVDF-ZnOHF@Zn anode weakened from 0.4% to nearly 0% (Figure 3h), indicating that polyiodide mainly exists on the outer surface of the electrode, which is effectively isolated from the zinc anode. In addition, in the F 1s spectrum, the content of C–F decreased (Figure S21), which was attributed to the decrease of PVDF content after etching part of the electrode surface. Subsequently, time-of-flight secondary ion mass spectrometry (TOF-SIMS) equipped with Ga^+ ion beam was further carried out to characterize the material composition of the zinc anode surface after cycling. For the PVDF-ZnOHF@Zn anode after cycling, 3D visualization shows that the content of polyiodide gradually decreases with the etching depth for 200 s (Figure 3i; Figure S22), which firmly verifies that polyiodide is only distributed on the outside of the PVDF-ZnOHF@Zn electrode and the content is very low, which is consistent with the XPS analysis results. The content of C^- species representing PVDF polymer decreased (Figure S23), and the 3D visualization mapping of C^- and I^- overlapped, which further explained the isolation effect of PVDF on polyiodide ions. While the 3D visualization of bare Zn shows that the signal intensity of polyiodide has been high throughout the etching process, while the signal intensity of C^- is very small (Figure 3j and Figure S24), implying the deep reaction between the surface of bare zinc anode and polyiodide ions. The corresponding TOF-SIMS depth profiles for I^- also explains this result (Figure 3k). Besides, SEM images shows that obvious pits and cracks appeared on the surface of the bare zinc electrode after cycling (Figure 3m). The PVDF-ZnOHF@Zn electrode surface is smooth and complete (Figure 3l), without obvious protrusions or indentations, indicating that it has excellent corrosion resistance and the ability to inhibit dendritic growth. In situ Raman testing was conducted to further study the role of PVDF in blocking polyiodides. The in situ Raman spectroscopy of the PVDF-ZnOHF@Zn batteries did not reveal the characteristic peaks

corresponding to the I_3^- and I_5^- species, respectively (Figure S25a,b). By contrast, the peaks of polyiodides were detected during the electrochemical reaction processes in the batteries with ZnOHF@Zn (Figure S25c,d). Especially in the bare Zn battery, the peak intensity of the I_3^- and I_5^- species is obviously higher (Figure S25e,f). As the discharge proceeds, polyiodide species at the cathode shuttle to the Zn anode surface under the electric field, inducing parasitic side reactions between the polyiodides and Zn anode and leaving iodide residues on the anode. No discernible polyiodide signatures were observed in the PVDF-ZnOHF@Zn cell, demonstrating the effective blocking ability to polyiodide of the PVDF layer.

2.5 | Zn Deposition Behavior

The synergistic electrode design simultaneously regulates Zn deposition behavior. The electrode after cycling was characterized in detail, and the SEM and physical images of Zn foil and PVDF-ZnOHF@Zn with deposition capacity of 1, 2, 5 and 10 mAh cm^{-2} were displayed (Figure 4a–d; Figures S26 and S27). Even after zinc deposition with capacities of 1 mAh cm^{-2} , a large number of schistose dendrites and some hexagonal byproducts appeared on the Zn foil. When the capacity was increased to 5 mAh cm^{-2} , the flaky zinc dendrite with larger size was formed.

In contrast, the PVDF-ZnOHF@Zn electrode maintained a 3D nanowire array structure without obvious flake-like dendrites at all deposition capacities. At the same time, the SEM images after zinc deposition with capacities of 10 mAh cm^{-2} show that the nanowire arrays make contact tightly with the Zn matrix after zinc deposition, indicating that the zinc deposition occurs where Zn^{2+} meets charges, and the galvanizing reaction can be well limited to the lower end of the nanowire layer, which is credited to the synergistic effect of the PVDF-ZnOHF modified layer to generate uniform hybrid SEI on the Zn anode surface, inducing stable non-dendritic zinc deposition. The electric field dispersion, Zn^{2+} ion flux and current density of the zinc anode were further simulated. For bare Zn, the rough surface would lead to the concentration of electric field, electric charge and local current on the bulges, resulting in serious polarization (Figures 4e–g). Combined with the non-uniform Zn^{2+} ion flow, Zn will actively deposit on the bulge and form dendrites. On the contrary, the electric field distribution as depicted in Figures 4h–j, PVDF-ZnOHF@Zn electrode can effectively optimize the Zn^{2+} ion flux and the uniformity of the electric field distribution on the zinc anode surface, averting the “hot spot” near the prominent zinc core, so as to optimize the zinc deposition process. It shows a great role in achieving highly reversible and high current galvanizing/stripping behavior under the ultrafast charging condition. Further analyzing the morphology and structure of SEI film, a representative layer of uniform ultra-thin film on the surface of Zn anode can be observed from the high angle annular dark-field (HAADF) image (Figure S28). In addition, energy dispersive X-ray spectroscopy (EDX) mapping images showed uniform element distribution (C, O, F, Zn) (Figure S29). The elements of C, O, F and Zn are uniformly distributed on the whole particle surface, and the existence of Zn, F and O is observed on the outer edge of the particle (in the white dotted line). The obvious difference of Zn deposition morphology indicates that the PVDF-ZnOHF modified layer has outstanding ability

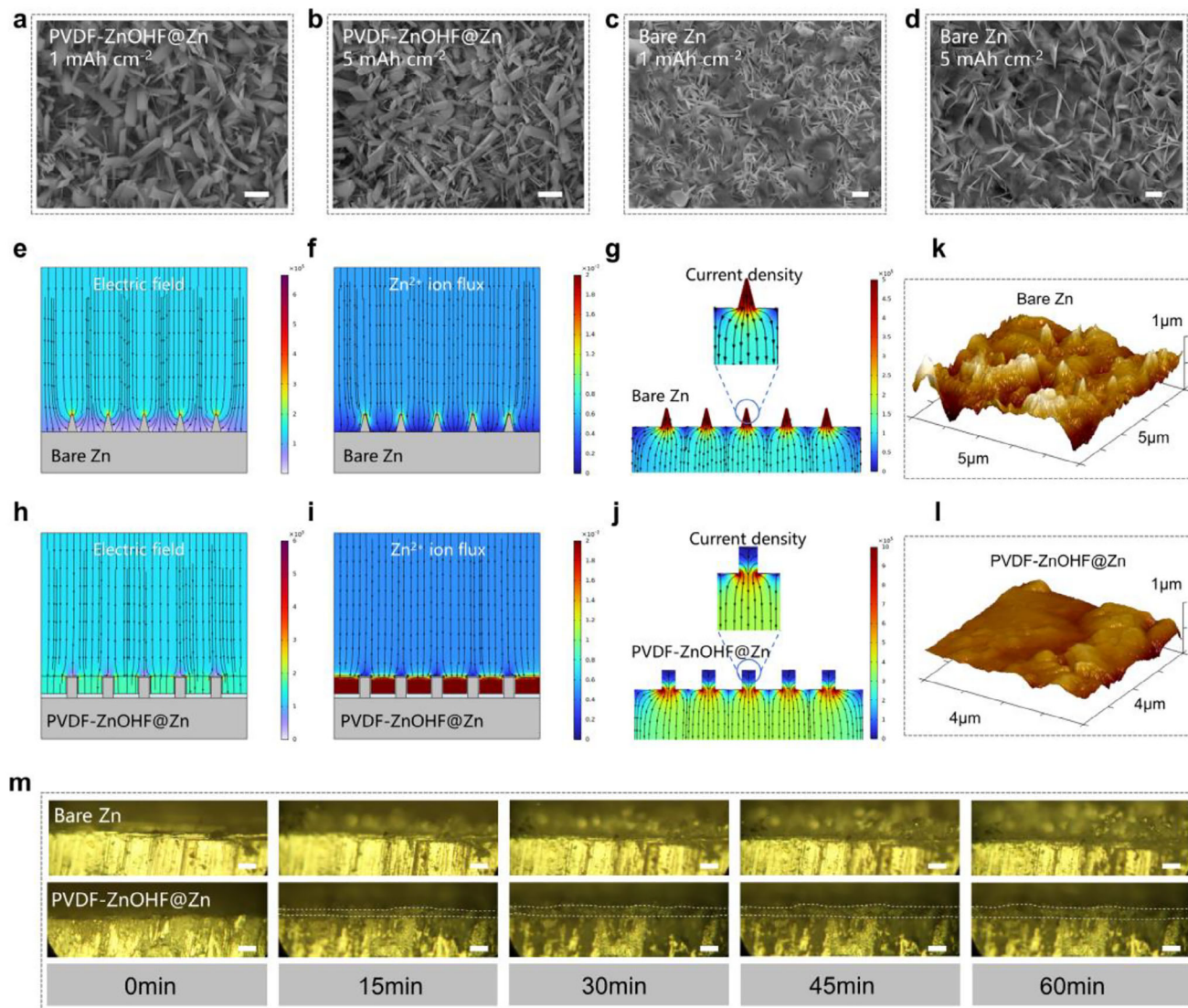


FIGURE 4 | Zn deposition morphology of PVDF-ZnOHF@Zn electrode. SEM images of (a), (b) PVDF-ZnOHF@Zn and (c), (d) bare Zn electrode after zinc deposition at 1 mA cm^{-2} current density with capacities of 1 mAh cm^{-2} and 5 mAh cm^{-2} . Scale bar, $10 \mu\text{m}$ for (a–d). The finite element simulations of bare Zn and PVDF-ZnOHF@Zn electrodes. Simulations of electric field distribution, Zn^{2+} ion flux, and current density of (e–g) bare Zn and (h–j) PVDF-ZnOHF@Zn electrodes. The AFM images of (k) bare Zn and (l) PVDF-ZnOHF@Zn electrode after 100 cycles at a current density/capacity of $1 \text{ mA cm}^{-2}/1 \text{ mAh cm}^{-2}$. (m) In situ optical microscopic images of the zinc plating on bare Zn and PVDF-ZnOHF@Zn, respectively. Scale bar, $20 \mu\text{m}$.

to assist the uniform zinc deposition and restrain the formation of dendrites. AFM images also support this analysis. Different from the rough and uneven surface of bare Zn (Figure 4k; Figure S30), the surface of the PVDF-ZnOHF@Zn electrode (Figure 4l; Figure S31) is more even and flat, with lower roughness, and the electrode height remains basically unchanged. In addition, the in situ optical microscope provides a visual viewpoint to observe the electroplating process more vividly. As shown in Figure 4m, a large number of zinc dendrite clusters and bulges appeared on the bare Zn electrode surface during the 60 min electroplating process. By contrast, the PVDF-ZnOHF@Zn electrode exhibited a flat and smooth surface, with few dendrites and no bulges, and resulted in a compact and flat surface, which confirmed that there were no excessive side reactions during the cycle, effectively inhibiting the dendritic growth and prolonging the life of the battery.

2.6 | Electrochemical Performance

The sustainability and reversibility of Zn^{2+} deposition/exfoliation were further investigated by assembling symmetrical cells (Zn/Zn , $\text{ZnOHF@Zn}/\text{ZnOHF@Zn}$ and $\text{PVDF-ZnOHF@Zn}/\text{PVDF-ZnOHF@Zn}$). The PVDF-ZnOHF@Zn displays a long-term cyclic stability of 2000 h compared with the bare Zn (cycling lifetime of 180 h) and the ZnOHF@Zn (cycling lifetime of 350 h) in the symmetrical batteries under a current density/capacity of $1 \text{ mA cm}^{-2}/1 \text{ mAh cm}^{-2}$ (Figure 5a). Even at high current densities of 5 mA cm^{-2} and 10 mA cm^{-2} , the batteries with the PVDF-ZnOHF@Zn electrode still have stable cycles of 1500 h and 600 h respectively (Figure S32; Figure 5b), which is much better than other controlled batteries, due to the excellent Zn^{2+} reversibility and stability of the PVDF-ZnOHF layer. The PVDF-ZnOHF@Zn electrode is easily amplified,

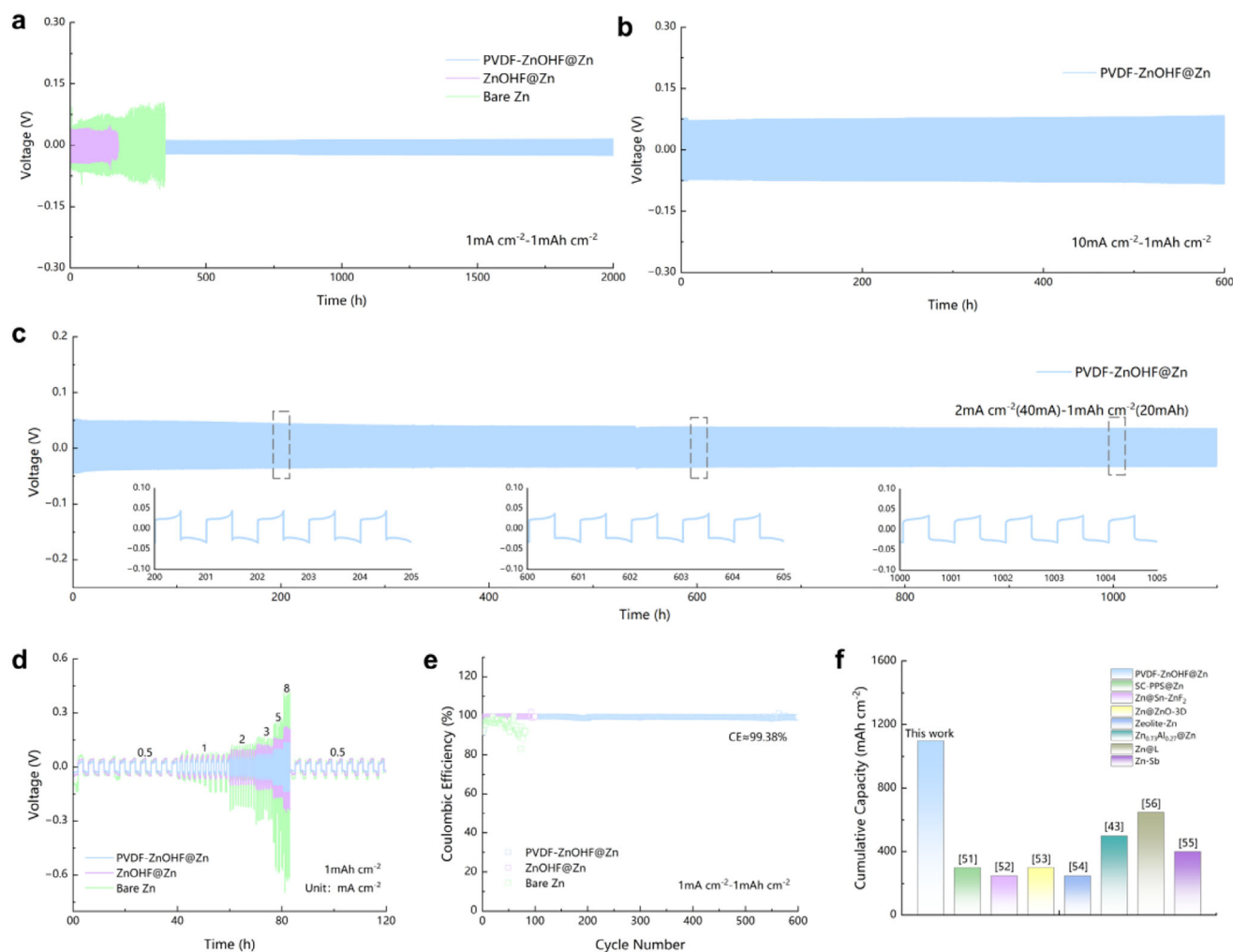


FIGURE 5 | The electrochemical performance of PVDF-ZnOHF@Zn electrode. Voltage profiles of symmetrical cells at current densities/capacities of (a) 1 mA cm⁻²/1 mAh cm⁻² and (b) 10 mA cm⁻²/1 mAh cm⁻². (c) Voltage profiles of symmetric pouch cells at a current density/capacity of 2 mA cm⁻² (40 mA)/1 mAh cm⁻² (20 mAh). (d) Rate performance of bare Zn, ZnOHF@Zn and PVDF-ZnOHF@Zn electrodes. (e) Coulombic efficiency (CE) profiles of the three electrodes. (f) Comparison of the PVDF-ZnOHF@Zn electrode with previously reported studies on zinc anodes.

benefiting from the cost effectiveness and expansibility of the preparation process. To further evaluate the stability and reversibility of the PVDF-ZnOHF@Zn electrode, a 4 cm² × 5 cm² large-size pouch symmetrical battery was assembled and its electrochemical performance was tested at a certain temperature. It is worth noting that compared with button battery, the dimensions of the zinc anode are expanded by nearly 20 times, so the issues caused by corrosion reactions and zinc dendrite growth will be more woeful. As depicted in Figure 5c, the PVDF-ZnOHF@Zn/PVDF-ZnOHF@Zn pouch battery keeps a minor voltage lag (52 mV) and a lasting cycle of more than 1100 h under a current density/capacity of 2 mA cm⁻² (40 mA)/1 mAh cm⁻² (20 mAh), which surpasses the Zn//Zn pouch battery with a cycling life of 230 h (Figure S33). As the symmetric cell is scaled up, the side-reactions become more pronounced. The PVDF-ZnOHF@Zn electrode still plays a significant role in mitigating these issues and sustains a stable cycle. In contrast, the rapid failure of the Zn//Zn pouch battery can be ascribed to serious parasitic reactions between the enlarged Zn anode and the electrolyte, together with swelling caused by gas evolution. Besides, the PVDF-ZnOHF@Zn/PVDF-ZnOHF@Zn battery

also has superior performance in a wide current density range of 0.5 to 8 mA cm⁻² (Figure 5d), manifesting its excellent rate performance. The better flat voltage curve and smaller voltage hysteresis of the PVDF-ZnOHF@Zn electrode than the other controlled samples can be attributed to the fact that the PVDF-ZnOHF layer optimizes the current density and Zn²⁺ ion concentration distribution through synergism, and effectively prevents the deterioration of the electrode interface (the reason why the ZnOHF@Zn/ZnOHF@Zn battery has the large voltage hysteresis in the later stage of the cycling). The PVDF polymer layer in the synergistic electrode design significantly reduces surface current density, as demonstrated by multiphysics simulations (Figure S34), thus restraining the rapid growth of dendrites on the upper surface.

Moreover, the 3D nanowire array structure can not only regulate the rapid diffusion of Zn²⁺ ions, provide a continuous and orderly zinc affinity channel, but also induce Zn²⁺ ions to migrate along the nanowires and deposit evenly on the zinc surface. Therefore, the current density and capacity of the PVDF-ZnOHF@Zn/PVDF-ZnOHF@Zn battery with stable cycle are

far higher than previously reported values of the zinc electrode based on coating protection strategy and 3D structural design (Table S1; Figure S5f) [43, 51–56]. In addition, in order to obtain the most excellent cycling sustainability, related experiments such as EIS, galvanostatic intermittent titration technique (GITT), AFM, and electrochemical performance were conducted to thoroughly investigate the effects of PVDF on ionic resistance, Zn^{2+} transport, and long-term mechanical stability. EIS result manifested that the electrode with a 0.01 mg cm^{-2} content of PVDF had the smallest charge transfer resistance (Figure S35a,b). Meanwhile, the electrodes with 0.05 mg cm^{-2} and 0.1 mg cm^{-2} PVDF showed a similar and slightly larger resistance than 0.01 mg cm^{-2} content. By contrast, the electrodes with above 0.2 mg cm^{-2} PVDF obviously exhibited elevated Zn^{2+} transfer resistance and poor ionic conductivity. In particular, the electrodes with 0.5 mg cm^{-2} and 1 mg cm^{-2} PVDF show extremely high resistance values, likely caused by interface deterioration from excessive PVDF. The Zn^{2+} transference number and GITT are subsequently performed. As presented in Figure S36, the electrodes with 0.05 mg cm^{-2} and 0.1 mg cm^{-2} PVDF conferred observably higher Zn^{2+} transference number of 0.85 and 0.75 than 0.2 mg cm^{-2} content (0.5), 0.3 mg cm^{-2} content (0.31) and 0.5 mg cm^{-2} content (0.24). The results illustrate that an appropriate amount of PVDF achieves high Zn^{2+} transference number, which does not affect the Zn^{2+} ions activity and effective migration. As shown in Figure S37, the D_{Zn} of the electrodes with 0.01 mg cm^{-2} , 0.05 mg cm^{-2} and 0.1 mg cm^{-2} PVDF is several orders of magnitude higher than that of the electrodes with above 0.2 mg cm^{-2} PVDF under discharge/charge reactions, further validating its improved interfacial kinetics and structural robustness. The SEM images of PVDF-ZnOHf@Zn electrodes with 0.1 mg cm^{-2} PVDF after cycling demonstrated mechanical structure stability without any structural damage (Figure S38). Derjaguin-Müller-Toporov (DMT) modulus was further measured by AFM to quantify the mechanical stability of PVDF (Figure S39). Before cycling, the average DMT modulus of the electrodes with 0.1 mg cm^{-2} PVDF is 3.38 GPa. After the cycle, the DMT modulus of the electrodes is an average of 2.98 GPa. The results confirmed the uniformity and mechanical stability of the electrode surface. As depicted in Figure S40, the PVDF-ZnOHf@Zn electrodes with 0.1 mg cm^{-2} PVDF have the most stable cycle performance, while the electrodes with 0.05 mg cm^{-2} PVDF show a relatively rapid capacity decay, attributed to limited corrosion resistance due to the thinner PVDF coating. Notably, as the load quantity increases, the capacity shows the obvious fluctuation, which is attributed to the larger interface resistance. Compared with other contents (Figure S41), the PVDF-ZnOHf@Zn electrodes obtained with 0.1 mg cm^{-2} PVDF have better cycling performance. Figure S42 shows that the electrode has more stable performance under the synthesis of 120°C and 2 h, which is attributed to the better crystallinity and more ordered zinc affinity channel of ZnOHf NWs under these synthetic conditions.

To further study the synergistic effect of the PVDF-ZnOHf@Zn electrode, asymmetric cells (Cu//Zn, ZnOHf@Cu//Zn and PVDF-ZnOHf@Cu//Zn) were employed to analyze zinc nucleation behavior. As depicted in Figure S43, the nucleation overvoltage of the ZnOHf@Zn (13.9 mV) is far lower than that of the bare Zn (18.7 mV), which is due to the splendid zinc conductivity and hydrophilicity of ZnOHf NWs. Notably, the synergetic PVDF-ZnOHf@Zn anode shows a small nucleation

overvoltage, which is due to the excellent electrolyte corrosion resistance of the electrode after multiple cycles, reducing the bad contact and contact resistance increase caused by corrosion. Besides, the electrochemical impedance spectroscopy (EIS) of the ZnOHf@Zn//ZnOHf@Zn battery can be seen (Figure S44), and the electron transfer resistance of the battery is significantly lower than that of the Zn//Zn battery. Meanwhile, the PVDF-ZnOHf@Zn symmetric cell exhibits comparable resistance value to the ZnOHf@Zn cell, confirming the porous PVDF layer maintains efficient electron transport without degradation. The synergistic electrode with both zinc affinity and hydrophobicity also results in high reversibility of Zn galvanizing/stripping. As depicted in Figure 5e, after 600 cycles, the Zn^{2+} deposition/stripping efficiency of the PVDF-ZnOHf@Cu//Zn battery can be increased to 99.38%. In contrast, due to short circuit, the bare Zn and ZnOHf@Zn electrodes show poor electroplating/stripping efficiency in near 80 cycles and 100 cycles, which further proves the reversibility of the synergistic promotion of Zn deposition and stripping by PVDF-ZnOHf modified layer. Besides, compared with other controls, the PVDF-ZnOHf@Cu//Zn battery has the lowest overpotential (79.8 mV) (Figure S45), indicating that the electrode enhances the electroplating/stripping kinetics of zinc.

2.7 | Electrochemical Performance of Full Cells

The previous discussion emphasized the advantages of the synergistic electrode in side reaction suppression, polyiodide ion resistance and homogenizing Zn deposition. To comprehensively study the actual enhancement effect of the PVDF-ZnOHf@Zn electrode on the battery, the zinc iodine full battery was assembled for performance testing. First, the influence of the PVDF-ZnOHf@Zn anode on the full battery under low current density of 2 C was investigated. The PVDF-ZnOHf@Zn battery has a high initial specific capacity of 206 mAh g^{-1} and a capacity retention rate of 95.2% after 200 cycles, which is significantly higher than bare Zn (186 mAh g^{-1} , 70.6%). This is because the PVDF-ZnOHf@Zn anode has superior electron-ion mixed conductive interface characteristics, which helps to reduce battery polarization, inhibit polyiodide corrosion and improve cycling stability. Besides, the voltage polarization of the PVDF-ZnOHf@Zn cell is 103 mV (Figure S46), lower than bare Zn (138 mV), illustrating this analysis. From the cyclic voltammetry (CV) curve in Figure 6a, compared with bare Zn and ZnOHf@Zn, the PVDF-ZnOHf@Zn battery has smaller voltage polarization and stronger peak current, indicating that it has superior Zn^{2+} /Zn reaction kinetics. The cyclic voltammetry (CV) analysis of PVDF-ZnOHf@Zn during the initial three cycles revealed two distinct redox peaks with excellent overlap (Figure S47), demonstrating high reaction reversibility and stability. Additional multiscan CV tests ($0.1\text{--}5 \text{ mV s}^{-1}$) showed scan-rate-dependent behavior (Figure S48), where increasing scan rates caused gradual current enhancement and minor peak shifts. Notably, well-defined redox peaks and minimal voltage polarization persisted even at elevated scan rates, confirming robust redox kinetics in the PVDF-ZnOHf@Zn full cell. And EIS result also manifests that the PVDF-ZnOHf@Zn battery has the smaller charge transfer resistance (Figure 6b), which originates from the dual functionality of the PVDF-ZnOHf layer:

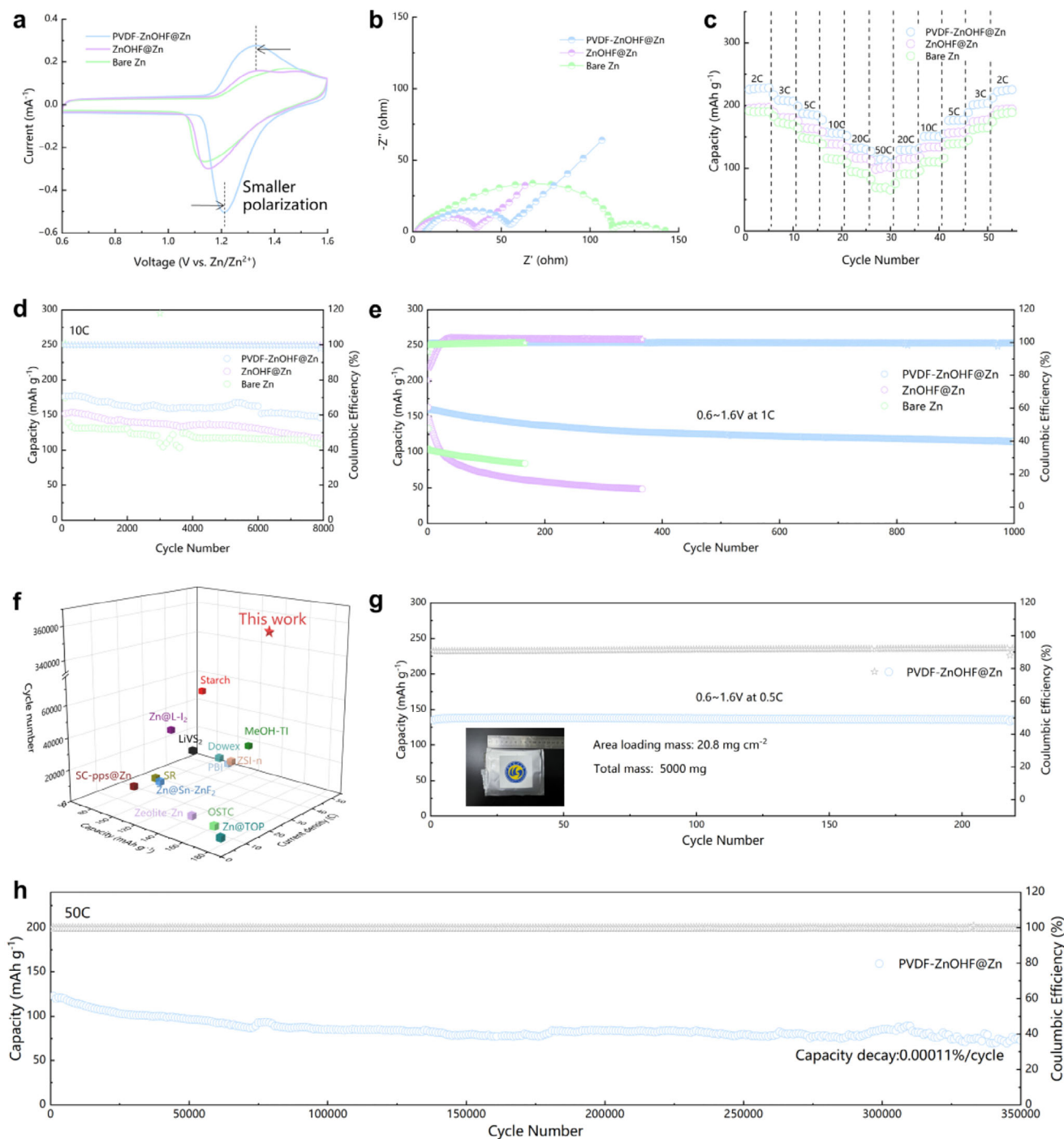


FIGURE 6 | Electrochemical performance of zinc-iodine full cells. (a) CV curves at 0.1 mV s⁻¹ and (b) EIS plots of different full cells. (c) Rate performance comparison of bare Zn, ZnOHF@Zn and PVDF-ZnOHF@Zn electrodes. (d) Cycling performances of different electrodes at current density of 10 C. (e) Cycling stability of full pouch cells at current density of 1 C. (f) Comparison of specific current, capacity and cycle number between our battery and other reported zinc-iodine batteries. (g) Cycling stability of the stacked soft pouch battery at current density of 0.5 C. (h) Long cycling performance of PVDF-ZnOHF@Zn electrode at current density of 50 C.

effectively suppressing corrosion reactions while simultaneously optimizing zinc deposition kinetics through synergistic effects.

The corrosion resistance and strong zinc affinity of the PVDF-ZnOHF@Zn electrode significantly enhanced the cycling ability, also making the improvement of the rate performance of the zinc-iodine full battery. It even provides a specific capacity

of 115 mAh g⁻¹ and a stable voltage plateau even at a high current density of 50 C (Figure 6c; Figure S49), which is higher than that of most analogous batteries reported. In addition, the PVDF-ZnOHF@Zn electrode effectively reduces the self-discharge phenomenon in the zinc iodine battery (Figure S50), highlighting the sustainability of the battery in static state and cycling process. The long cycle performance test was carried

out under a high current density to further discuss the cycle performance of the PVDF-ZnOHF@Zn electrode. As depicted in Figure 6d, the PVDF-ZnOHF@Zn cell has a high initial capacity of 177 mAh g⁻¹, and maintains a capacity of 150 mAh g⁻¹ after 8000 cycles under 10 C current density. At 20 C current density, the full cell with PVDF-ZnOHF@Zn electrode displays an initial specific capacity of 164 mAh g⁻¹ and retains 92.7% after 20000 cycles (Figures S51 and S52). The ZnOHF@Zn electrode only circulates for 14000 cycles (Figure S53), and the capacity reduction is due to the long-term continuous corrosion of electrolyte and polyiodide, resulting in low capacity retention. The capacity of bare Zn anode only with 3000 cycles decays faster (Figure S54), which is due to its more serious side reactions and corrosion, so that the active substances of anode zinc and cathode iodine are continuously consumed, and the battery eventually fails. Importantly, when the current rate increases to 50 C, the PVDF-ZnOHF@Zn battery has the longest cycle of 350000 times reported so far (Figure 6h), with a minimal capacity degradation of 0.00011% per cycle. And the stable voltage platform of the cell still exhibits highly reversible redox reaction at the first, 10000th, 100000th, 200000th and 300000th cycles (Figure S55), indicating that the PVDF-ZnOHF@Zn can also work effectively and stably at high current rate for a long time, which proves its exceptional performance in inhibiting side reactions and resisting polyiodide corrosion. To discuss the superiority of the synergistic anode in zinc iodine batteries, our study is compared with previous anode modification works (Figure 6f; Table S2) [57–66]. It has significant advantages in current density, specific capacity, cycle number and cycle stability. To verify its practical potential for high iodine loading, the button batteries can cycle stably for more than 5000 cycles with the 8.4 mg cm⁻² mass loading of I₂ (Figure S56). Meanwhile, the scalable Zn-I₂ pouch battery was assembled to further verify its practical potential. The PVDF-ZnOHF@Zn pouch battery can cycle stably for more than 1000 cycles with the 10.5 mg cm⁻² mass loading, which is far better than the ZnOHF@Zn (360 cycles) and the bare Zn (160 cycles) pouch batteries (Figure 6e). It is shown from the Figure S57 that the PVDF-ZnOHF@Zn pouch battery demonstrates the higher capacity, which is attributed to its effective inhibition of the corrosion reaction, achieving a more complete redox process. In contrast, the dissolution of polyiodide intermediate and reaction with bare Zn anode will further intensify the corrosion of zinc anode and the decay of active substance, resulting in battery capacity degradation and eventual failure. A stacked soft pouch battery with five layers of I₂@AC cathode and six layers of PVDF-ZnOHF@Zn anode alternately stacked is constructed in this work (Figure 6g), which can achieve an area load of about 20.8 mg cm⁻² with a loading mass of 5000 mg I₂, and can stably cycle for more than 200 cycles with a capacity of up to 0.7 Ah, which is superior to the similar system reported at present. A basic cost analysis of the Zn-I₂ battery alongside other battery systems was conducted in Table S3 [67–69]. The results demonstrate that the Zn-I₂ battery possesses a cost advantage in manufacturing. In addition, with the amplification of Zn-I₂ battery, the side reaction problem became more rampant. After recycling, through the SEM images, the bare Zn was seriously corroded and had large-area defects (Figure S58), while the PVDF-ZnOHF@Zn still maintains a flat appearance (Figure S59), which clearly shows its superb corrosion resistance. The superior full cell performance validates the effectiveness of our synergistic stabilization strategy for zinc anodes.

3 | Conclusion

In summary, unlike previous anode protection strategies, we report a unique zinc anode involving the zincophilic nanowire array and the hydrophobic iodine elimination protective layer. The ZnOHF nanowire zinc conductive layer provides continuous and ordered zinc affinity channels, which optimizes electric field distribution, zinc ion flux, and local current density, materializing uniform zinc deposition under the condition of rapid Zn²⁺ ion migration. Meanwhile, utilizing FTIR, Raman, XPS, TOF-SIMS and DFT calculation, the existing form and configuration of polyiodide ions at the electrode/electrolyte interface were analyzed and optimized. It was verified that polyiodide ions have multiple hydrophobic iodine removal effects in PVDF polymer, and have excellent resistance to polyiodide ion corrosion and side reactions. Therefore, the PVDF-ZnOHF@Zn electrode exhibits splendid electrochemical performance under high current density/capacity. The large-area pouch symmetric battery (4*5 cm²) produced has a stable cycling time of 1100 h at a high current density/capacity of 40 mA/20 mAh. Impressively, the full battery underwent the longest 350000 cycles and maintained an ultra-low capacity decay of 0.00011% per cycle. Our work provides a valuable strategy for a highly stable and reversible zinc anode, and opens up brand-new possibilities for achieving ultrastable and sustainable Zn-I₂ batteries.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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