Nitrogen-doped Carbon Coated Zinc as Powder-based Anode with PVA-Gel Electrolyte Enhancing Cycling Performance for Zinc-ion Batteries

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Abstract

Zn-powder based anodes are considered as candidates for Zn-based batteries in practical industrial applications in terms of cost, large-scale processing, versatility and tunability. However, Zn-P-based anodes suffer from even more severe side effects including corrosion, passivation, and uncontrolled dendrite growth. Herein, we successfully fabricated nitrogen-doped carbon coating layer on Zn particles (Zn-NC) as anode material for more homogeneous Zn deposition by inducing more zincophilic site on N-doped carbon layers and enhanced electrical connection with carbon networks on Zn-NC particle surface. Nevertheless, metallic Zn deposited on Zn-NC surface still suffers from unavoidable side effects with continuous cycling, even though the dendrite growth was suppressed. It is worth mentioned that PVA-gel electrolyte greatly improves the cycling performance of Zn-NC with limited water content, which can alleviate side reactions. Experiments and simulations address the importance of NC layers with higher electricity, chemical stability, and zincophilic property, as well as the role that PVA-gel electrolyte plays for the further improved cycling performance. Zn-NC with PVA-gel electrolyte achieves ultra-long cycling hours with over 3500 h at 1 mA cm\(^{-2}\) and 850 h at 5 mA cm\(^{-2}\) in symmetrical cells. This study provides a promising pathway and in-depth mechanistic analysis for Zn-powder based anode in versatile applications especially for flexible energy-storage devices.

Key Words
Zn anode, Carbon-coating surface modification, Gel-based electrolyte, Free-standing anode, Aqueous zinc-ion batteries.
1. Introduction

Owing to the admirable energy density and high cycling stability, lithium-ion batteries (LIBs) has become dominant rechargeable energy supply in many fields from consumer devices and electric vehicles to power grids in recent years [1-4]. However, the price of lithium resources keeps increasing and safety issues are frequently reported [5-7]. Seeking for an alternative electrochemical energy storage become necessary. Rechargeable aqueous batteries especially zinc ion batteries (AZIBs) are regarded as promising batteries systems for grid-scale storage and flexible wearable devices attributed to its safety, easy assembly, low cost, rich Zn resources, and environmentally friendly properties [8-10]. Metallic zinc with high theoretical capacity (820 mAh g⁻¹) and low electrochemical potential (−0.76 V vs. SHE) could be a desirable anode material for AZIBs. However, Zn anode is unstable in aqueous electrolyte with heterogeneous dissolution/deposition process on Zn surface during cycling resulting into zinc dendrite and side reaction associated including hydrogen evolution, corrosion, and passivation [11-13].

Currently, commercial zinc foil has been most widely employed as anode materials in recent studies owing to its low cost and convenience. Many efforts have been done for homogeneous zinc plating achieving dendrite free zinc anode including various surface modification protection [14-16] and electrolyte modifications [17-20]. Despite the enhancement of electrochemical performance for zinc foil, the low utilization of thick zinc foil (usually >80μm) lowers cell-level energy density with large N/P ratio (> 50) and low depth of discharge (DOD <3%) [21-23]. By contrast, zinc powder, known as the anode materials for dry batteries, exhibits prominent advantages in terms of cost, large-scale processing, versatility and tunability in practical industrial applications [6, 24-26]. Especially, granular zinc powders are easier to be adjusted regarding to the particle size and balance the N/P ratio for the high utilization of zinc anode. However, more challenges appearing on zinc powders are entirely different from that of the planner zinc foil. Firstly, the Zn ions preferentially plating on convex of the Zn powders resulting dendrite like Zn foil [27]. More seriously, high contact area of zinc powders in aqueous electrolyte deteriorates the intrinsic instability of metal zinc.
with more severe corrosion and hydrogen evolution, and eventually leads to cell failure by increasing internal pressure and triggering seal failure of cells [10, 28, 29]. In addition, continuous repeating Zn dissolution/deposition process results in loose connection between Zn particles and conductive skeleton leading to dead Zn formation during the cycling [30, 31]. So far there are various approaches concerning the modification of Zn-P as anode materials, such as wet spinning method [32], 3D printing approach [33], slurry anode [27], construction of mixed ionic-electronic conducting scaffolds [34], and graphene hybridization [25]. Nevertheless, compared with the work of surface modifications of Zn foil, the research on Zn-P is limited.

Herein we proposed nitrogen-doped-carbon-coated Zn powders (Zn-NC) as anode materials for Zn ion batteries. The coated carbon layers improve the electric connection of active particles. Moreover, induced N in carbon layer increases zincophilic site on particle surface for more homogeneous plating of Zn. The symmetric cell of Zn-NC anode shows 450h long cycling time in ZnSO$_4$ aqueous electrolyte, much higher than that of Zn-P anode. It is noteworthy that extremely long span life more than 3500 h in PVA-gel electrolyte has been achieved. As schematic illustration shows in Figure 1, the surface modification of conductive nitrogen-doped-carbon layers enhances the electrical conductivity and zincophilic property for much better homogenous deposition and prevention of “death Zn” formation. In addition, gel-based electrolyte that reduces the free water molecules and side reactions facilitates high zinc reversible capacity and cycling stability in Zn-NC electrode. As far as we know, this is the first time to propose a strategy of combining surface modification of Zn-powder-based anode and gel-based electrolyte to achieve extremely long cycling span life for Zinc ion batteries.
2. Experimental Section

2.1 Fabrication of Zn_NC electrode

The Zn powders (Shanghai Xiangtian Nano Materials Co., Ltd.) were washed with acetone, 0.05 M HCl solution, water, deionized water, and ethanol respectively by sonication for 10 minutes each step. Then Zn powders were dried in over (60 ℃) and collected for use throughout all experiment.

Firstly, 0.5g polyvinyl pyrrolidone (PVP) (OKA, China) powders were dissolved in 150 mL ethanol. Then, 3g Zn powders were added into the PVP solution, followed by stirring for 2 hours and drying 60 ℃ in oven overnight to obtain the PVP-wrapped Zn powders (PVP@Zn). Subsequently, the PVP@Zn powders were heat in tube furnace 400 ℃ 4 hours in Ar atmosphere for carbonization. The Nitrogen-doped carbon coating Zinc powders (Zn-NC) were obtained after cooling down. The anode was prepared by mixing the Zn-NC powders, carbon blacks and Poly (vinylidene fluoride) (PVDF) with mass ratio 8:1:1 with N-methylpyrrolidone (NMP) as solvent for grinding to electrode slurry. Then, the slurry was dried on 80 ℃ for about 6 hours and grinded into powders. Finally, the prepared powders were pressed into free-standing film (30 mg) for 1.1cm diameter of circle shape with 20 MPa. Zinc powders (Zn-P) electrode was prepared by the same method mentioned above by replacing Zn-NC with Zn-P.

Figure 1. Schematic illustration of synergies of N-doped carbon layers and PVA gel electrolyte for deposition on Zn powder surface.
2.2 Fabrication of Gel electrolyte

14.54g trifluoromethanesulfonate Zn(OTF)$_2$ (Bidepharm, China) was dissolved into water fixing to 20 mL to prepare 2M Zn(OTF)$_2$ solution. Subsequently, 1.6g Poly(vinyl alcohol) (PVA) (Aladdin) was added into Zn(OTF)$_2$ solution with continuous stirring on 80 ℃ until the solution turning to transparent. The gel electrolyte Zn(OTF)$_2$/PVA was obtained after cooling down. Followed the steps above, Zn(OTF)$_2$/Mn(OTF)$_2$/PVA gel electrolyte was prepared by dissolving 0.71g Mn(OTF)$_2$ and 14.54g Zn(OTF)$_2$ into water to prepared 20mL to prepare 2M Zn(OTF)$_2$ and 0.1M Mn(OTF)$_2$ (Bidepharm, China) solution. Then, 1.6g PVA was added and heated to prepare Zn(OTF)$_2$/Mn(OTF)$_2$/PVA gel electrolyte as mentioned.

2.3 Fabrication of MnO$_2$@CNT electrode

The MnO$_2$@CNT was used as cathode in this work [35]. 0.1g MWCNT (XFNANO, China) was added to 30mL 0.6M MnSO$_4$ (Sigma-Aldrich) solution, followed by sonication for 1 hour to disperse the CNTs. Subsequently, 30mL 0.1M KMnO$_4$ (ChengDu Chron Chemicals Co., Ltd) was added to the mixture dropwise under continuous stirring with color turning to dark brown. The mixture containing CNTs, MnSO$_4$, and KMnO$_4$ was keep stirring for 2 hours and transferred into autoclave for hydrothermal treatment 140 ℃ for 10 hours. After cooling down, the powders were collected by filtration, and continuously washed with deionized water several times to remove impurities. The MnO$_2$@CNT powders was dried at 80℃ overnight and ready for use. The cathode was prepared by mixing the MnO$_2$@CNT powders, carbon blacks and Poly(vinylidene fluoride) (PVDF) with mass ratio 7:2:1 with N-methylpyrrolidone (NMP) as solvent grinding to into slurry. The slurry was coated on Ti foil evenly and dried on 80 ℃ overnight. Finally, 1.2cm diameter round piece was cut as the electrode for coin cell with ~1.3mg cm$^{-2}$ mass loading.

2.4 Materials Characterizations

The microscopic morphologies of all samples were observed through scanning electron microscope (SEM) (FEI Inspect F50) and the transmission electron microscopy (TEM, Tecnai G2 F20). The elements distribution analysis was performed
by Energy Dispersive Spectroscopy (EDS) (EDAX OCTANE SUPER). The surface chemical composition and elemental valence of the sample were analyzed by X-ray photoelectron spectroscopy (XPS) with Al Kα radiation (1486.6 eV) (Thermo Fisher K-Alpha 250xi). The crystalline structure was measured by DX-2700BH X-ray diffraction (XRD) (Cu Ka radiation: k = 1.5406 Å). The FTIR spectra was performed by Nicolet Is10.

2.5 Electrochemical Measurements

This work was using CR-2025-type coin cells for electrochemical performance test. Symmetrical cells were assembled with two Zn_NC, Zn_P or Zn foil electrodes, 2M ZnSO₄ aqueous solution or Zn(OTF)₂/PVA gel as electrolyte separated by glass fiber filter (GF-D, Whatman). For the full cells Zn||MnO₂ assembly, MnO₂@CNT electrode was used as the cathode, and 2M ZnSO₄+0.1M MnSO₄ or Zn(OTF)₂/ Mn(OTF)₂/PVA gel as electrolyte. Cycling performance and rate capacity were evaluated by Newark workstation. Cyclic Voltammetry (CV), Linear scan voltammetry (LSV), Chromoamperogram (CA) and Electrochemical impedance spectroscopy (EIS) tests were conducted by using CHI 600E electrochemical workstation. As to three-electrode system, platinum (Pt) foil and Ag/AgCl serves as counter electrode and reference electrode with scan rate 1 mVs⁻¹. Linear polarization with different electrolytes was carried out by three-electrode system with scan rate 1 mVs⁻¹. The A. C. impedance spectra are record on electrochemical workstation with a frequency range from 0.1 Hz to 100000Hz with a voltage of 5 mV.

2.6 Simulation Method

The electrostatic field at the interface was conducted by COSMOL Multiphysics. The simulation model is constructed to stand for the grinded Zn particles 250 nm with and without carbon coating. According to TEM images, the size of Zn or Zn-NC particles were set as 250 nm, both width and length were 3 μm.

The calculation was performed by density functional theory (DFT) by Materials Studio with DMol3 code. Perdew-Burke-Ernzerhof (PBE) function within the generalized gradient approximation (GGA) was employer for exchange-correlation effects. The projector augmented wave (PAW) method was used as model of the core electrons. The convergences of energy maximum force, and maximum displacement was set as 10⁻⁵ Ha, 0.004 HaÅ⁻¹, and 0.005Å. The adsorption energy
(E_{ads}) was defined as:

\[ E_{ads} = E_{total} - E_{surface} - E_a, \]

where \( E_{total} \) was the total energy of the adsorbate, \( E_{surface} \) was the bare surface energy obtained from DFT calculation, and \( E_a \) was the energy of the Zn atom.

3. Results and Discussion

Carbon coating has already been a common and effective strategy to enhance the electrochemical performance of Si-based anode for lithium-ion batteries by improving the electrical conductivity and stability of the SEI film [36-38]. However, there is few works about the carbon coating method in the Zn-powder based anode study. Here, we firstly fabricate the N-doped carbon coating method for Zn particles to enhance its electrochemical performance. The schematic illustration in Figure 2a displays the fabrication process of Zn-NC, in which polyvinyl pyrrolidone (PVP) acts as N-doped carbon resource to encapsulate Zn particles. Generally, Zn powders (Zn-P) are coated with PVP layer by dispersing into PVP/ethanol solution. Then the N-doped carbon coated Zn powders (Zn-NC) are obtained by calcination of Zn powders with PVP layer owing to the presents of nitrogen N in the PVP. The final obtained Zn-NC shows black color as Figure 2b shows. The presence of N-doped carbon (NC) layers was confirmed by the X-ray Photoelectron spectroscopy (XPS) of Zn-NC in Figure S1a. Comparing to the Zn-P, the wide pattern of Zn-NC shows typical peaks of Zn 2p, O 1s, N1s and C 1s. The presents of N1s and much higher proportion of C 1s peak in Zn-NC indicates the successful introduction of N-doped carbon coating. There is almost no differences of Zn 2p pattern for Zn-P and Zn-NC (Figure 2c), suggesting the surface modification without any crystal structure change of Zn metal. In Figure 2e, the N1s spectra for Zn-NC illustrates that the main type of peak at 398.5 eV attributes to pyridinic N that is the basis of the model set in following simulation. The small amount of C 1s peak of Zn-P could be explained by the polluted carbon adsorbed on the sample surface, which could be approved by relative peak of C-O and C=O in Figure S1b. FT-IR spectra of Zn-NC and PVP confirms the carbonization process of PVP layer, with more CH\textsubscript{2} eliminates (Figure 2f). Specifically, the characteristic peaks of Zn-NC were located at 3420 cm\textsuperscript{-1}. 

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indicating O-H stretching from adsorbed moisture, 2942 and 2852 cm\(^{-1}\) indicating asymmetric \(\nu(CH_2)\) of pyrrole ring and symmetric \(\nu(CH_2)\) of chain, 1633 cm\(^{-1}\) corresponding C=O and 815 assigned to C-N [26, 39]. The XRD patterns of Zn-NC and Zn-P in Figure 2g indicate the stable phase of Zn in Zn-NC which agrees to the result of XPS Zn 2p pattern. TEM images of Zn-NC in Figure 2h and Figure S2 display that the carbon layers were successfully coated on Zn particles with network structure entangling to the Zn-P particles. In the elemental mappings of Zn-NC (Figure 2i), the evenly distributed C and N signals of Zn-NC further confirms the N-doped carbon successfully coated on the surface of Zn powders.

Figure 2 (a) Schematic illustration of Zn-NC fabrication process. (b) Digital photos of Zn-P and Zn-NC. The XPS patterns of Zn-NC and Zn-P for (c) Zn 2p, (d) C1s 2P, and
(e) N1s of Zn-NC. (f) FT-IR spectra of Zn-NC and PVP. (g) XRD pattern of Zn-NC and Zn-P. (h) TEM images of Zn-NC, and (i) SEM image and elemental mappings of Zn-NC.

The hydrophobic of anode was investigated via the contact angles for Zn-NC, Zn-P and Zinc foil (Zn-F) with aqueous ZnSO$_4$ electrolyte in Figure S3. The minimum angle 53.7° of Zn-NC indicates the good best hydrophobic property of Zn-NC benefited from the hydrophilic element N and 3D-powder structure. The following is Zn-P with contact angle of 66.3°. Zn-F shows the biggest contact angles 93.1°, suggesting the hydrophobic property of electrolyte. To demonstrate the effectiveness of the N-doped carbon coating layer, Zn||Zn symmetric cells and Zn||Ti asymmetric cells for both Zn-P and Zn-NC were assembled in different electrolytes: 2M ZnSO$_4$ aqueous solution and Zn(OTF)$_2$/PVA gel electrolytes. Figure 3 compares the anode behavior of Zn-NC and Zn-P in aqueous ZnSO$_4$ electrolyte. The electrochemical impedance spectroscopy (EIS) measurements of symmetric cell of Zn-NC and Zn-P were performed in Figure S4, which could be clearly seen that the cell of Zn-NC presents lower $R_{ct}$ values than that of Zn-P, indicating that the N-doped carbon layers facilitate interface charge transport. Figure 3a compares overpotential of symmetric cells of Zn-NC and Zn-P at different current density from 0.5 to 10 mA cm$^{-2}$ with fixed charge/discharge time 1 h. Zn-NC with lower and more stable potential profile suggests better stability at wide range of current density and capacity than that of Zn-P. The Zn-P anode begins to fail when current density was increased to 5 mA cm$^{-2}$ with large continuously overpotention values, which might arise from the corrosive side reactions. Selecting 1 mA cm$^{-2}$ and 1 mAh cm$^{-2}$ for long-cycling test in Figure 3b, it is noteworthy that the symmetric cell of Zn-NC runs around 450 h, while the cycle time of Zn-P is around 80 h, even less than that of Zn foil (Zn-F) ~160 h (Figure S5). It is known that Zn-P with high surface area suffers serious side reaction including hydrogen evolution resulted from corrosive of metallic Zn and passivation leading to invalid isolated Zn [40]. Unlike the Zn-F usually failing from dendrite growth, Zn-P shows obvious bulging with failed sealing.
and leakage of electrolyte after cycling as Figure S6 shows.

To investigate the morphology changes of Zn-NC during cycling, the electrodes of 5\textsuperscript{th} and 30\textsuperscript{th} cycle at current density 1mA cm\textsuperscript{-2} were studied by SEM (Figure 3c-d). Different from the isotropic 2D Zn foil, there exit longer Zn\textsuperscript{2+} redistribution pathways coupled with more extensive nucleation and disjointed electron transition on monodispersed 3D Zn powders [24]. Zn-P displays obviously random deposition with large vertical flakes growth on its surface, resulting from the irregular current distributed on the Zn-P particles. By comparison, there is more homogeneous deposition of Zn metal on Zn-NC surface, benefited from the N-doped carbon coating layers which balances current distribution and increases more zinophilic sites by the induced N doping. At 30\textsuperscript{th} cycle, Zn-NC presents uniform dense small burrs, while more irregular large flacks grow on the surface of Zn-P. As to the Zn foil (Figure S7), the dendrite starts from a small circle rings (5\textsuperscript{th} cycle) and continue growing to bumpy hillocks-like form (30\textsuperscript{th} cycle). The plating/stripping efficiency of Zn-P and Zn-nc was studied by asymmetric cell Zn||Ti. The coulombic efficiency of Zn-NC was stabilized at around 96\% for around 180 cycles, while the Zn-P could be slightly higher that was around 96.5\%, but less cycling stability that fails after 50\textsuperscript{th} cycle (Figure 3e). Interestingly, the powder-based Zn anode shows higher coulombic efficiency than that of Zn foil. Zn-F presents worse coumlombic efficiency with fluctuation around 85\% for 150 cycles in Figure S8, demonstrating the higher reversibility of Zn-powder based anode during plating/stripping cycles. Moreover, lower resistance of Zn-NC was shown in Figure 3f in asymmetric cell than that of Zn-P, which again describes faster charge transport of Zn-NC.
Figure 3. In 2M ZnSO$_4$ aqueous electrolyte: (a) rate performance for symmetric cell of Zn-NC and Zn-P. (b) long-life cycle performance for symmetric cell of Zn-NC and Zn-P with current density of 1 mA cm$^{-2}$ and capacity 1 mAh cm$^{-2}$, insets are the detailed voltage profiles at 0-4h and 80-84h. SEM images of (c) Zn-NC and (d) Zn-P in symmetric Zn cells after 5 cycles and 30 cycles at current density of 1mA cm$^{-2}$. (e) Coulombic efficiency of Zn-NC and Zn-P in asymmetric Zn$\|\!$Ti cells with current
density 1mA cm-2 and 0.5 h discharging time. (f) AC impedance plots of Zn||Ti asymmetric cells after standing 6 hours. (g) Voltage profile for cycling performance of Zn||Ti asymmetric.

Besides the uncontrolled dendrite growth, Zn-powder-based anode also suffers from extremely serious side reactions including corrosion and passivation due to its highly exposed surface area. More homogenous deposition was achieved by N-doped carbon coating of Zn-P, since the introducing nitrogen sites boosts zincophilicity, and better cycling stability has achieved compared to the Zn-P. However, the site reaction was unavoidable since more metallic Zn deposited on the anode surface that continuously contact with water molecules resulting to corrosion and hydrogen evolution. In Figure 2b, the voltage gradually increases, and the cell shows obvious bulging of the cell after cycling 400 h (Figure 3b). The generated gas results in poor contact between Zn anode and collectors and unstable interface of anode surface and electrolytes. To further improve the cycling stability, we proposed the utilization of gel-based electrolyte that can effectively eliminate the side effect of Zn-NC during cycling. Gel electrolyte has been intensively explored for Zn ion batteries especially towards multi-functionalities [41], which can reduce the water activity by limiting the free water molecules, thereby minimizing the side effect of metallic Zn and electrolyte [42]. Moreover, the interaction between Zn\(^{2+}\) and negatively charged groups in gel system helps regulate Zn\(^{2+}\) flux and diffusion at interface and suppress dendrite growth [43]. In this work, the gel-based electrolyte was prepared from the mixture of Zn(OFT)\(_2\) and PVA.

The performance of Zn-NC in gel-based electrolyte was examined by symmetric cell Zn||Zn and asymmetric cell Zn||Ti. Ultra-long cycling life of Zn-NC was achieved for more than 3500 h at 1 mA cm\(^{-2}\) and 1 mAh cm\(^{-2}\) with voltage profile around 0.06-0.07V. In comparison, the quick failure of Zn-P was observed for only around 58 h, even worse than that in aqueous electrolyte (Figure 4a). Large and fluctuated voltage profile appears on Zn-P because then non-conductive gel polymers increase the resistance inside Zn-P anode. Accompanied by uneven current on the particles, irregular
SEI formation on the Zn-P surface and aggregation of Zn-P particles during cycling finally leads to large amount of “insulating Zn” and poor cycling stability. Remarkably, even at higher current density of 5 mA cm$^{-2}$, Zn-NC still enabled durable Zn plating/stripping for more than 900 h with stable voltage profile around 0.18V as Figure 4b shows. Figure 4c presents the rate performance of different current density and consistent charge/discharge time. Generally, the voltage profile in gel electrolytes were larger than that in aqueous electrolyte due to the high viscosity and lower conductivity [44]. Dual measures of gel electrolyte and N-doped coated layer on Zn powders simultaneously achieves super stable behavior of Zn-NC as metallic Zn anode. Figure 4d and 4e illustrates the results of asymmetric cell Zn||Ti of Zn-NC and Zn-P. The coulombic efficiency of Zn-NC maintains 97-98% over 250 cycles, while Zn-P drops quickly after 130 cycles. Compared to the aqueous electrolyte that Zn-NC maintains 94-95% for 180 cycles, the gel electrolyte significantly improves the stability of plating/stripping behavior for Zn-NC. The detail of charge/discharge curve at 50$^{th}$ cycle is presented on Figure 3e, that the nucleation overpotential of 0.1V, lower than Zn-P (0.12V), indicating better conductivity of Zn-NC than that of Zn-P. The uneven deposition on Zn-P particles in gel electrolytes turn to agglomeration and isolation of particles coated by PVA polymers leading to poor cycling stabilities. The N-doped carbon layer on Zn-NC can enhance the connections of Zn particles and more uniform deposition of Zn metals, avoiding the issues of Zn-P during cycling.

The morphology change of Zn-NC in PVA-gel electrolyte after cycling were displayed in Figure 4f and 4g for front and cross section of Zn-NC anode. At early deposition stage 5$^{th}$ cycle, large and thin flakes covered on the Zn-NC powders forms porous 3D structure which is different from stretching up vertically of Zn-NC in the aqueous electrolyte (Figure 2c). With continuous cycling, flakes turn to be ticker and the denser package observed from the cross view after 30 cycles, suggesting that PVA helps regulate the deposition inside the porous structure of Zn-NP particles rather than vertical orientation, achieving relative smoothy flaky surface.
Figure 4. In Zn(CF$_3$SO$_3$)$_2$ /PVA gel electrolyte: long-life cycle performance for symmetric cell of Zn-NC and Zn-P with (a) current density 1 mA cm$^{-2}$, 1 mAh cm$^{-2}$, and (b) 5 mA cm$^{-2}$, 2.5 mAh cm$^{-2}$. (c) rate performance for symmetric cell of Zn-NC and Zn-P. (d) Coulombic efficiency of Zn-NC and Zn-P in asymmetric Zn||Ti cells with current density 1 mA cm$^{-2}$ and 0.5 h discharging time. (e) Voltage profile of Zn-NC and Zn-P in asymmetric Zn||Ti cells at 50$^{th}$ cycle. (f, g) SEM images of Zn-NC for front and cross section in symmetric cells after 5 cycles and 30 cycles at current density of 1 mA cm$^{-2}$ with gel electrolyte.
Concerning about that the side reaction of Zn-powder based anode is a dominant factor of cell failure, more comprehensive analyses regarding H\textsubscript{2} evolution and passivation were carried out to investigate the inhibitive effect of PVA-based gel electrolyte on HER and passivation of Zn-NC anode. Density functional theory (DFT) was employed to investigate the effects of N-doped carbon coating and PVA molecules in electrolyte. According to the XPS, the main N-doping is pyridinic N which is set as the model of NC layer. Figure 5a calculates the adsorption energy of Zn atom to crystal plane Zn (002) -0.21 eV and Zn atom to N-doped carbon coating (NC) layers -2.86 eV, suggesting better zincophilic property of Zn-NC surface, in agreement with SEM image of Figure 3c. As metallic Zn deposits on NC surface layer, Figure 5b displays the adsorption energy of PVA molecules on the Zn plane (002) -0.68 eV, higher than that of H\textsubscript{2}O -0.42 eV, indicating that the PVA molecules in electrolyte could be adsorbed on the electrode surface to protect the anode from the side reaction of active H\textsubscript{2}O. It has been widely reported that the organic polymers homogenize interfacial reactions and regulate Zn deposition behavior helping more uniform SEI formation [45-47]. Hence, the PVA-gel electrolyte contributes to regulation of Zn\textsuperscript{2+} solvation structure and formation of the protective SEI layers, which is beneficial for elimination of the side reaction and homogenous deposition during cycling. To better understand the role of PVA in corrosion resisting theoretically, the binding energy and adsorption energy were calculated. Figure 5c calculates the binding energy of Zn\textsuperscript{2+}-H\textsubscript{2}O and Zn\textsuperscript{2+}-PVA, in which Zn\textsuperscript{2+} and PVA exhibit extremely strong binding force -121.1 kcal mol\textsuperscript{-1}, higher than the Zn\textsuperscript{2+} and H\textsubscript{2}O -70.5 kcal mol\textsuperscript{-1}, suggesting that Zn\textsuperscript{2+} has good solvation effect with PVA that tends to replace the H\textsubscript{2}O molecules in the solvation structure of Zn\textsuperscript{2+} [48]. The charge difference between NC model with and without Zn atom are shown in Figure 5d, in which the charge transfers when Zn on N-doping sites, improving capability to capture Zn atoms. The interfacial charge-density models of NC layer with Zn atom reveals that more electrons of the N-doping sites on carbon layer create the active sites for preferential Zn deposition. The simplified COMSOL simulation of electric field distributions for bare Zn powders and Zn-NC powders in Figure 5e
indicates more evenly surface distributed electric field on Zn-NC interface, which facilitates high flux conduction of Zn\(^{2+}\) and more homogenous Zn deposition.

Concerning that Zn-powders suffer more serious side effects of corrosion, the corrosion accompanied by hydrogen evolution can also be observed from the thickness change of cells before and after 100 h cycling (Figure 5f). The thickness of Zn-P increases 1.24 mm in aqueous electrolyte with serious swelling of cell. Even Zn-NC also suffers from cell swelling with 0.5 mm increase of thickness. PVA-based gel electrolyte displays minimum difference 0.14 mm between before and after cycling, indicating that PVA-based gel electrolyte inhibits the hydrogen evolution reaction efficiently, which agrees on the results of theoretical calculation. From the Tafel curve in Figure 5g, Zn-NC exhibited a corrosion potential of 0.98 V in aqueous electrolyte slightly lower than Zn-P with 0.985 V corrosion potential, indicating the N-doped carbon layer on Zn-NP slightly reduces the corrosion rate. Zn-F shows less corrosion potential 0.973 V in aqueous electrolyte, illustrating the less tendency to corrosion owing to the less surface area compared to the powder-based Zn metal (Figure S9). Significantly lower corrosion potential of Zn-NC in gel electrolyte with 0.893 V suggests that the PVA played a prominent part in corrosion resisting. This result agrees to the experiment of thickness change and simulation calculation. Chronoamperometry (CA) was conducted to investigate the nucleation and surface change of Zn deposition in symmetric cell under constant overpotential -150 mV for 200 s in Figure S10. The current of Zn-F continuous increase for 60 s, while the currents of Zn-NC and Zn-P increase within 15 s, demonstrating the relatively placid diffusion and smooth Zn deposition to avoid charge accumulation of anode. As inserted schematics diagrams shows, 2D diffusion process of Zn\(^{2+}\) is the lateral movement of Zn\(^{2+}\) on anode surface resulting in Zn aggregation and dendrite growth eventually [49]. In addition to the cyclability in cell system, the calendar life is also important for Zn-ion batteries, especially for Zn-powder based anode. The XRD analysis in Figure 5h compares the Zn-P in aqueous electrolytes, and Zn-NC in both aqueous and gel electrolytes for aging 200 h. Interestingly, there is not much difference between Zn-NC in aqueous and serious side reaction occurs for both aqueous and gel electrolytes compared to the initial
state in Figure 2g, which is credited to the carbon coating layer that isolates the metallic Zn off the water molecules, enhancing the calendar life when it assembled into cell. Conversely Zn-P presents clear peak of ZnO phase, indicating the instability of ZnO in aqueous electrolyte for the serious side reaction of the exposed Zn particles occurring with the byproduct of ZnO detected.

Above all, the N-doped carbon coating could cover and connect the metallic Zn particles inside carbon layer to enhance the conductivity and zincophilic sites for more uniform deposition. However, the metallic Zn deposited on the Zn-NC surface with continuous cycling leads to unavoidable side effects. On the other hand, PVA in electrolytes efficiently reduces the side reaction by limiting the water activity in electrolyte. Nevertheless, nonconductive PVA in electrolyte reduces the ionic conductivity leading to large polar voltage and poor cycling stability of Zn-P in PVA-gel electrolyte. This work combines surface modification of N-doped carbon coating on anode and electrolyte optimization of PVA-gel together to real achieves ultra-long cycling hours and electrochemical stability for anode performance. The above analyses accordingly confirm the synergism of N-doped carbon layer and PVA-based gel electrolyte as illustrated in schematic diagram Figure 1a. Beneficial from NC coating and PVA-gel electrolyte, the excellent cycling performance in this work could be compared to the most recent work of Zn-powders based anode (Figure 5i, Table S1).
Figure 5. (a) Adsorption energies of Zn on Zn (002) surface and NC layer. (b) Adsorption energies of H$_2$O and PVA molecules on the Zn (002) surface. (c) Binding energies of Zn$^{2+}$ with H$_2$O and PVA. (d) models of NC layer and NC layer with Zn atom and interfacial charge-density models of NC layer with Zn atom adsorption. (e) Models of the electric field distributions for bare Zn powders (up) and Zn-NC powders (down). (f) Cell thickness before and after cycling for 100h. (g) Tafel curve of Zn-NC and Zn-P in different electrolyte. (h) XRD patterns of Zn-NC and Zn-P after aging 200 h in different electrolyte. (i) comparison of cumulative capacity of Zn-powder based anode between this work and previous works.
The full cell Zn-NC||MnO$_2$ with PVA-gel electrolyte was assembled to evaluate the electrochemical performance from potential 0.8 V to 1.8 V. The mass load of Zn-NC and Zn-P for anode was ~30 mg. The MnO$_2$@CNT was used as cathode in this work with mass load around 1.6-1.8 mg cm$^{-2}$. The structure characteristics and morphology of MnO$_2$ were summarized in Figure S13 of the Supporting Information. The cyclic voltammetry (CV) curve at scan rate of 1 mV s$^{-1}$ in Figure 6b shows the typical Mn-ion redox peaks of Zn-NC||MnO$_2$, with two cathodic peaks at 1.2 and 1.36 V illustrating the Mn$^{4+}$ reducing to Mn$^{3+}$, and anodic peak at 1.64V, reflect the oxidation process of Mn$^{3+}$ to Mn$^{4+}$ [50, 51]. Figure 6c displays galvanostatic charge–discharge (GCD) profiles with current density 0.1 A g$^{-1}$. In aqueous electrolyte, there is not much capacity difference between Zn-NC and Zn-P around to be 300 mAh g$^{-1}$. Comparing the Zn-NC in different electrolyte, PVA-gel electrolyte reduces the capacity due to the reduced ionic conductivity in gel electrolyte. The detail GCD curve for different cycles of Zn-NC in PVA-gel electrolyte at current density 0.5 A g$^{-1}$ presents 152 mAh g$^{-1}$ at 100$^{th}$ cycle, 138 mAh g$^{-1}$ at 500$^{th}$ cycle, and 125 mAh g$^{-1}$ at 1000$^{th}$ cycle (Figure 6e). Galvanostatic intermittent titration technique (GITT) measurements were carried to estimate the Zn$^{2+}$ diffusion coefficient (D$_{\text{ion}}$), with current density 0.2 A g$^{-1}$ charging for 5 minutes and relaxing 30 minutes (Figure 6d). Generally, there are two platforms in discharge curves of MnO$_2$ corresponding to two different ions insertion H$^+$ and Zn$^{2+}$. The D$_{\text{ion}}$ value at first discharge platform at around 1.4V indicating the higher diffusion rate of H$^+$ than that of the second platform at around 1.25V with lower diffusion rate of Zn$^{2+}$ [52, 53]. The ions diffusion coefficient in PVA-gel electrolyte was in the range of 10$^{-8}$ to 10$^{-10}$ cm$^2$ s$^{-1}$, higher than that in aqueous electrolyte 10$^{-8}$ to 10$^{-13}$ cm$^2$ s$^{-1}$, demonstrating the better Zn$^{2+}$ diffusion with PVA introduced in electrolyte and suggesting the fast ions intercalation/deintercalation kinetics thereby achieving better reversibility during cycling. The solvation of Zn$^{2+}$ structure in PVA-gel electrolyte was regulated which promote the intercalation/deintercalation diffusion rate and the interfacial charge storage efficiency inside cathode materials [54].
6f displays the rate performance of Zn-NC in gel electrolyte at current density increasing from 0.1 to 2 A g\(^{-1}\), and back to 0.1 A g\(^{-1}\) with reversible capacities of 228, 196, 154, 135, 114, 86 and back to 224 mAh g\(^{-1}\). Zn-NC presents better rate performance in aqueous electrolyte with 283, 221, 175, 153, 140, 122 and back to 262 mAh g\(^{-1}\) due to its high ion conductivity. Figure 6g compares cycling performance of Zn-NC and ZnP aqueous electrolyte and Zn-NC in PVA-Gel electrolyte. In aqueous electrolyte, Zn-NC improved the cycling performance compared to Zn-P in ZnSO\(_4\) benefiting from the protective NC layer. Although the aqueous electrolyte displays better initial capacity for both Zn-NC and Zn-P ~270 mAh g\(^{-1}\) than that in gel electrolyte ~150 mAh g\(^{-1}\), the capacity of Zn-NC in aqueous electrolyte drops to ~150 mAh g\(^{-1}\) at 350\(^{th}\) and fails at around 480\(^{th}\) cycle. Even worse, Zn-P shows extremely poor cycling performance with only around 170 cycles span life. It could be explained by that deposited Zn on NC layers generated from cycling still suffers side reactions with free water in electrolyte, leading to poor capacity and cell death. On the other hand, PVA-gel based electrolyte presents significantly improved cycling performance of Zn-NC with 88% retention rate after 1000 cycles, although the initial capacity was relatively low ~150 mAh g\(^{-1}\).
Figure 6: (a) Cell assembly schematic of full cell. (b) CV curve of Zn-NC||MnO$_2$ with PVA-Gel electrolyte. (c) Charge-discharge curve of full cell with Zn-NC as anode in PVA-Gel and aqueous electrolyte and Zn-P as anode in aqueous electrolyte at current density 0.1 A g$^{-1}$. (d) Rate performance of full cell of Zn-NC in gel and aqueous electrolyte and Zn-P in aqueous electrolyte. (e) GITT curve of Zn-NC||MnO$_2$ with PVA-Gel and aqueous electrolyte. (f) Charge-discharge curve of full cell with Zn-NC||MnO$_2$ with 0.5 A g$^{-1}$ at different cycle (g) Cycling performance of Zn-NC||MnO$_2$ with PVA-Gel and Aqueous electrolyte and Zn-P||MnO$_2$ in aqueous electrolyte. (g) SEM images of MnO$_2$ after cycling in PVA-gel and aqueous electrolyte.

4. Conclusion

In summary, we fabricated a N-doped carbon coated Zn powder as anode materials for Zn ion batteries, which achieves ultra-stable performance in PVA-gel electrolyte.
The covered N-doped carbon coating layers enhances the conductive connection between active anode particles. In addition, the induction of N-doping creates more zincophic sites with more uniform deposition. However, the metallic Zn deposited on the Zn-NC surface with continuous cycling leads to unavoidable side effects. Herein, utilize of PVA-gel electrolyte instead of aqueous ZnSO$_4$ electrolyte could efficiently reduce the side reaction on Zn anode surface by limiting the water activity in electrolyte, really achieving ultra-long cycling hours and electrochemical stability for anode performance. As results, Zn-NC anode exhibits outstanding cycling stability with lifespan 3500 h at 1 mA cm$^{-2}$ and 850 h at 5 mA cm$^{-2}$ in symmetric cells, which is competitive in resent work for Zn-powder based anode. When paired with MnO$_2$ cathode, the full cell delivers superior reversibly work for 1000 cycles with 88% retention. This work provides a possible strategy for designing powder-based Zn metal anode materials and might also be extended to the anode in flexible gel-based Zn-ion batteries.

Supporting Information

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