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Stable Zn-Ion Hybrid Supercapacitor Zinc Anode Achieved by Artificial Protective Layer of Nitrogen-Sulfur Co-Doping Activated Carbon

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Zinc metal anodes are one of the promising aqueous anodes due to their low redox potential and high capacity. However, the growth of dendrites severely destabilizes the electrode/electrolyte interface and accelerates the generation of side reactions that ultimately degrade the electrochemical performance. Here, we used a simple and effective interface engineering strategy to construct nitrogen and sulfur double-doped orange peel-based biomass activated carbon (NS-OPC) artificial protective layer on zinc foil. Among them, nitrogen-containing functional groups and S heteroatoms can regulate the transport and deposition of Zn^{2+} , and the hierarchical porous structure of activated carbon not only provides a large number of active sites for Zn^{2+} , but also provides enough space for the growth of Zn^{2+} dendrites. The symmetric cell with NS-OPC artificial protective layer showed excellent cycle stability (1200 h) at the current density of 1 mA cm⁻². Finally, the YP50llNS-OPC/Zn full cell was constructed to validate the performance of the NS-OPC/Zn. The capacity retention rate was 92.6% after 3000 cycles at 10 A g⁻¹. This work provides a feasible strategy for accelerating the industrial application of aqueous zinc-ion hybrid supercapacitors. (DOI: 10.1149/1945-7111/ acb66e]

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The growing demand for renewable energy drives the development of electrochemical energy storage systems with high safety, high stability, low cost, and environmental protection.¹⁻⁴ Due to the high theoretical capacity (820 mAh g^{-1}), low redox potential (-0.765 V (compared to standard hydrogen electrode)), low cost, and abundant reserves of metallic zinc, aqueous zinc-based batteries (AZIBs) are ideal candidates for next-generation energy storage devices.⁵⁻¹⁰ However, the unstable interface due to severe dendrite growth and the occurrence of side reactions severely hinders the application of aqueous Zn-based batteries.^{11–13} First, large dendrites appear at the anode during Zn deposition/stripping due to the nonuniform electric field distribution and unconstrained 2D diffusion of Zn^{2+} . The excessive growth of these dendrites can pierce the separator and cause an internal short circuit, which seriously affects the cycling performance of the battery.^{14–16} Second, since the standard electrode potential of Zn/Zn^{2+} is lower than that of H₂/H⁺, the reduction of bare Zn metal during cycling is accompanied by water splitting (through the hydrogen evolution reaction HER). This phenomenon generates H₂ and destabilizes the zinc metal surface. At the same time, HER can generate by-product OHions on the surface of zinc metal to form inert $Zn(OH)_4^{2-}$, which consumes the zinc anode and electrolyte.^{17–19}

In order to solve these problems and realize zinc metal anodes with long cycle life, the main solutions currently adopted include constructing artificial protective layers,^{20–22} constructing 3D framework structures,^{23–25} and electrolyte modification.^{26,27} Among them, constructing an artificial protective layer is an effective measure to regulate the growth of dendrites while preventing side reactions. Reasonable artificial protective layer design can induce the uniform deposition of Zn^{2+} on the Zn-electrolyte interface, which ensures the cycling stability of the Zn anode. Coatings commonly used to improve zinc anodes include carbon materials,²⁸ polymers,²⁹ inorganic compounds,² metal nano-ions,³⁰ and hybrid coatings.³¹ Among them, carbon materials are widely used in artificial protective layers due to their advantages such as chemical stability, high electrical conductivity, adjustable morphology, and low cost. In addition, the introduction of heteroatoms into carbon materials also contributes to the performance improvement. For example, Wu et al. used nitrogen-doped carbon to modify the zinc anode. The high porosity and nitrogen-containing functional groups of the coating are conducive to a uniform electric field and accelerated ion diffusion, so the cycle stability of both symmetric cells and full cells has been improved.³² Zhou et al. adjusted the transport of Zn^{2+} by introducing O-containing functional groups on the carbon cloth, thereby improving the cycling stability of the battery.³³

Inspired by the above artificial protective layers, NS-OPC is proposed as an artificial protective layer for Zn anodes to suppress dendrite growth by adjusting Zn^{2+} deposition and interfacial electric field distribution. The NS-OPC coating has a hierarchical porous structure, resulting in a larger specific surface area, which provides abundant nucleation sites for Zn^{2+} and sufficient growth space for Zn dendrites. The introduction of S heteroatoms can effectively uniformize the electric field distribution and reduce the local current density, so that Zn^{2+} can be uniformly deposited. The abundant N-doped functional groups can also effectively induce uniform nucleation and deposition of Zn²⁺. More importantly, the conductive NS-OPC/Zn artificial protective layer helps to balance the electric field near the Zn anode and suppress the tip growth of Zn dendrites. At the same time, a reasonable thickness can reduce the transport resistance of zinc ions and effectively control the deposition morphology. Due to the presence of graphitic nitrogen and S heteroatoms, the NS-OPC/Zn coating exhibits excellent rate capability, which mainly improves the electrical conductivity of the electrode material. Therefore, the NS-OPC/ZnIINS-OPC/Zn symmetric cell can be cycled for 1200 h. Full cell YP50||NS-OPC/Zn to further evaluate its performance. At a current density of 10 Ag^{-1} , its initial discharge specific capacity is 57.2 mAh g^{-1} , and it maintains a Coulombic efficiency of around 100% for 3000 cycles, better than YP50||Bare Zn (YP50||Bare Zn initial discharge specific capacity of 41.7 mAh g⁻¹, And the capacity began to decay significantly after 900 cycles). Considering the simplicity of the preparation process, this NS-OPC protective layer may be valuable for practical application of aqueous zinc-ion hybrid supercapacitors.

Material and Methods

Materials.—KOH (AR) was purchased from Tianjin Damao Chemical Reagent Factory, thiourea (CH₄N₂S, AR, \geq 99%) was

purchased from Shanghai Macklin Biochemical Co., Ltd., and HCl (AR, 36.0%) was purchased from Sinopharm Chemical Reagent Co., Ltd.

Sample preparation.—Rinse the fresh orange peel with a large amount of deionized water, put the washed orange peel into a blast dryer at 100 °C to dry for 24 h, and then put it in a wall breaker and grind it into powder. The orange peel powder was carbonized at 600 °C for 2 h under nitrogen atmosphere, and the heating rate was 5 °C \min^{-1} . Then, the carbonized carbon and KOH were activated at a ratio of 1:4 at 850 °C for 2 h in a nitrogen atmosphere, and the heating rate was 5 °C min⁻¹. The activated carbon was then treated with thiourea, and thiourea and OPC were dispersed in 60 ml of deionized water in an optimized ratio (1:4), mechanically stirred for 12 h, heated at 80 °C to remove moisture, and heated at 850 °C to remove water. Nitrogen-sulfur-doped orange peel-derived porous carbon (NS-OPC) was synthesized by calcination in Ar atmosphere for 3 h at a heating rate of 5 $^{\circ}$ C min⁻¹. Then the synthesized NS-OPC was put into HCl for cleaning, then the NS-OPC was cleaned with a circulating water-type multi-purpose vacuum pump, and finally put into a blast drying oven for drying.

Characterizations.—The morphologies and microstructures of the sample were observed using scanning electron microscopy (SEM, Gemini SEM 300) and transmission electron microscopy (TEM, JEOL JEM-2100). Raman spectra were obtained with a horiba evolution microscope Raman spectrophotometer (sem = 532 nm). The N, S functional groups were characterized by Fourier transform infrared spectroscopy (FTIR, Thermo Scientific Nicolet iS20). X-ray diffractometer (XRD) data were obtained using a powder X-ray diffractometer (D8 ADVANCE A25) with a scan range from 5° to 90°. The pore structures of all samples were determined according to nitrogen adsorption-desorption isotherms using a JW-BK222 automatic volumetric adsorption analyzer (Micromeritics sorption analyzer). The specific surface area and pore size distribution were calculated by the Brunauer-Emmett-Teller (BET) method. X-ray photoelectron spectroscopy (XPS) adopts ESCALAB 250Xi X-ray photoelectron spectrometer from ThermoFischer Company of the United States. Electrochemical impedance spectroscopy (EIS) was performed on the Modulab XM DSSC at an amplitude of 5 mV in the frequency range from 0.01 Hz to 100 kHz.

Electrochemical measurements.—All synthesized materials were electrochemically evaluated using a CR2025 type coin cell. The active material, carbon black (Super-P) and polyvinylidene fluoride (PVDF) binder (weight ratio 8:1:1) were mixed in N-methyl-2-pyrrolidone (NMP) solvent, and then the slurry was the NS-OPC/Zn electrode was prepared by coating the material on the metal zinc foil (the treatment method of the zinc foil in this paper is to rinse with an appropriate amount of deionized water, hydrochloric acid and ethanol in turn and dry it in the air). Commercial YP50, carbon black (Super-P), and polyvinylidene fluoride (PVDF) binder (8:1:1 by weight) were mixed in N-methyl-2-pyrrolidone (NMP) solvent, and the slurry was the YP50 cathode was prepared by coating the material on stainless steel foil.

Using bare Zn and NS-OPC/Zn as electrodes, filter paper as separator, and 1 M ZnSO₄ aqueous solution as electrolyte, CR2025 symmetrical cells were assembled. Using bare Zn and NS-OPC/Zn as anode, YP50 as cathode, filter paper as separator, and 1 M ZnSO₄ aqueous solution as electrolyte, CR2025 full cells were assembled. The galvanostatic charge and discharge test (GCD) test was carried out using the LAND-CT2001A battery test system. EIS and cyclic voltammetry (CV) tests were performed using a Parstat model 4000 A single-channel electrochemical workstation. The sweep interval for CV was 0.01–1.8 V, and the sweep rates were 10, 20, 30, 50, and 100 mV S⁻¹, respectively. The test frequency for EIS was 0.01 Hz to 100 kHz, and the amplitude was 5 mV. The scanning interval of CV was -0.2-0.2 V, and the scanning rate was 0.1 mV s⁻¹, which is used to test the Tafel testing. The hydrogen

evolution capacity of the Zn foil with and without NS-OPC coating was investigated by linear sweep voltammetry (LSV) with a scan rate 5 mV s⁻¹ in 1 M ZnSO₄ electrolyte.

Results and Discussion

An artificial protective layer was constructed by coating NS-OPC on 0.03 mm zinc foil by a simple doctor blade coating process (Fig. 1a). The appearance of zinc foil before and after modification was examined by SEM. Figure 1b shows the zinc foil before modification. The exposed zinc foil has a rough surface with many uneven depressions, which may be caused during the production process. As shown in the inset in Fig. 1c, NS-OPC was uniformly coated on the surface of the Zn foil, and the NS-OPC sample exhibited a large number of pore structures (Fig. S1), which provided a larger ratio of the surface area provides abundant nucleation sites for $Zn^{2+.6}$ The EDS results in Fig. 1d also show that elements such as C, S, and N are uniformly distributed on the surface of the zinc foil. To determine the composition of the prepared electrodes, XRD, XPS, FTIR and Raman tests were performed. As shown in Fig. 1e, the peak around 22° represents the (002) plane, indicating that NS-OPC belongs to typical amorphous carbon. The XRD pattern of the NS-OPC/Zn sample has small peaks from NS-OPC and a series of strong peaks from metallic Zn, indicating its composition and high purity.^{28,34} XPS and FTIR indicated the chemical valence states and functional group species in NS-OPC/Zn. The presence of N1s and S2p peaks indicates the successful doping of N/S elements, as shown in the full XPS spectrum of Fig. S1a. The C1s spectra (Fig. S1b) correspond to five C-C/C=C (284.8 eV), C-S (285.44 eV), C-O (286.72 eV), C=O (288.96 eV) and $\pi - \pi^*$ (290.93 eV), respectively functional group. In the O1s spectrum (Fig. S1c), two peaks can be fitted, which are S-O/ C=O at 531.54 eV and C-OH at 532.89 eV. Figure 1f is the XPS fine spectrum of N1s, which can be fitted to four peaks at 397.4 eV, 399.13 eV, 400.34 eV and 402.46 eV, which are pyridine-N (33.9%), pyrrole-N (14.5%), graphite-N (43.35%) and oxide-N (8.25%). Abundant N-doped functional groups can effectively induce the nucleation of $Zn^{2+,20}$ Figure 1g is the XPS fine spectrum of S2p, the existence of C-S-C S2p 3/2 (163.47 eV) peak and C-S-C S2p 1/2 (164.7 eV) peak and C-SO_x-C (168.28 eV) peak is further confirmed S was successfully doped into the carbon matrix. In addition, S doping facilitates the penetration of the electrolyte on the surface of the Zn anode.³⁵ The wetting Angle test of bare Zn and NS-OPC/Zn is shown in Fig. S4. The decrease of wetting Angle from 133.1° to 94.2° indicates the enhanced wettability of the material, which is conducive to the diffusion of Zn^{2+} and the transfer of electrolyte. Figure 1h shows the infrared spectrum of NS-OPC/Zn. The presence of polar groups such as C=O and N-H can simultaneously adjust the interfacial electric field and ion distribution, resulting in directional migration of Zn^{2+} .³⁶ Fig. 1i is the Raman spectrum of NS-OPC/Zn, the two main peaks at 1338.7 cm^{-1} and 1594.3 cm^{-1} can be attributed to the D and G peaks, respectively. The D peak represents the disordered structure of graphite,³⁷ and the G peak represents the ordered structure of sp2 hybridized carbon atoms in the graphite layer.³⁸ The intensity ratio of I_D/I_G can effectively evaluate the degree of graphitization and structural defects of carbon materials.³⁹ The I_D/I_G value of NS-OPC/Zn was 1.176. This result indicates that NS-OPC/Zn has a low degree of graphitization and has obvious amorphous features, possibly with a large number of surface defects.⁴⁰⁻⁴² In addition, the nitrogen adsorption/desorption of NS-OPC/Zn is shown in Fig. 1j, showing a typical type IV isotherm, showing a sharp rise at a relatively low pressure with $P/P_0 < 0.1$, which Indicates the presence of a large number of micropores. A hysteresis loop appears at $0.4 < P/P_0 < 1.0$, indicating the coexistence of micropores and mesopores. The specific surface area of NS-OPC is 2203.56 m^2g^{-1} , which is sufficient for the growth of zinc dendrites space.⁴³ Figure S3 shows the pore size distribution of NS-OPC, it can be seen that the pores of NS-OPC are mainly concentrated at 1.5 nm and 3.0 nm. TEM further confirmed



Figure 1. (a) Schematic diagram of NS-OPC/Zn synthesis. (b) SEM images of bare Zn. (c) SEM image of NS-OPC/Zn. (d) EDS image of NS-OPC/Zn electrode. (e) XRD patterns of NS-OPC, bare Zn and NS-OPC/Zn. (f), (g) N1s and S2p spectra of NS-OPC/Zn. (h) FT-IR spectrum of NS-OPC/Zn. (i) Raman spectra of NS-OPC/Zn. (j) N₂ adsorption-desorption isotherms of NS-OPC/Zn.

that NS-OPC is a hierarchical porous structure composed of micropores/mesopores/macropores (Fig. S1b), these abundant pores provide abundant sites for the nucleation of Zn^{2+} , and have Contributes to fast reaction kinetics.^{44,45} Furthermore, NS-OPC/Zn exhibited excellent adhesion and flexibility after repeated bending, showing the potential to effectively accommodate the volume change of the Zn anode surface during cycling (Fig. S5).

To explore the effect of NS-OPC coating modification on Zn plating/stripping behavior, the cycling stability at different current densities was evaluated by assembling Zn|Zn symmetric cells with and without NS-OPC coating. Figure 2a compares the voltage

distributions of NS-OPC/Zn symmetric cells and bare Zn symmetric cells at a current density of 1 mA cm^{-2} and an areal capacity of 0.5 mAh cm^{-2} . The voltage fluctuation of the bare zinc anode is obvious, indicating that the zinc/electrolyte interface is unstable. Furthermore, starting from 50 h, the voltage started to increase gradually, which is indicated by the growth of Zn dendrites. The voltage dropped sharply by 170 h, which indicated that the cell failed due to the accumulation of zinc dendrites to a certain extent piercing the separator and causing a short circuit. However, the NS-OPC/Zn anode exhibited drastically different performance, which maintained a stable voltage plateau throughout the 1200 h cycling. In addition,



Figure 2. Cycling performance of Zn plating/stripping behavior and corresponding nucleation overpotential at the condition of (a), (b) 1 mA cm⁻² and 0.5 mAh cm⁻², and (c), (d) 2 mA cm⁻² and 0.5 mAh cm⁻². (e) Rate performance of bare Zn and NS-OPC/Zn at 0.25–4 mA cm⁻², 0.5 mAh cm⁻². (f) Nyquist plots of bare Zn before and after cycling. (g) Nyquist plots of NS-OPC/Zn before and after cycling. Time-dependence response of potentiostatic DC polarization for Znl Zn cell (h)Bare Zn. (i) NS-OPC/Zn. (j) The calculated transference number of Zn²⁺.

the NS-OPC/Zn cell shows only a low nucleation overpotential of 14.6 mV (Fig. 2b), which is much lower than that of bare Zn of 44.3 mV, indicating a significantly lower Zn deposition barrier. Similarly, at a high current density of 2 mA cm⁻², the NS-OPC/Zn anode still exhibited excellent cycling stability up to 700 h (Fig. 2c) and a low nucleation overpotential of 16.8 mV (Fig. 2d). Table SI shows the comparison between the results of this work and those of others in recent years. As shown in Fig. 2e, the rate performance of symmetric cells using bare Zn and NS-OPC/Zn at different current densities and areal capacities of 0.5 mAh cm⁻² was also tested. The voltage of the symmetric cell with bare zinc was higher at current

densities of 0.25, 0.5, 1, 2 and 4 mA cm⁻², while the voltage of the symmetric cell with NS-OPC/Zn was lower at current densities of 0.25, 0.5, 1, 2 and 4 mA cm⁻², and remained stable with the increase of current density. Meanwhile, the voltage plateau remains stable even at high current densities, which indicates the superior rate capability of NS-OPC/Zn compared to bare Zn. The linear polarization of bare Zn and NS-OPC/Zn electrodes was measured in the open circuit potential range of -0.2 to 0.2 V with a scan rate of 0.1 mV s to study the corrosion performance (Fig. S6). The corrosion current of the NS-OPC/Zn electrode is 0.419 mA cm⁻², which is smaller than that of the bare Zn electrode, which is 2.32 mA cm⁻²,



Figure 3. (a) Cycling performance and (b) corresponding coulombic efficiency of Zn plating/stripping behavior in CulZn asymmetric cell at the current density of 1 mA cm⁻². Charge -discharge curves of CulZn cells after different cycle number (c) Bare Zn and (d) NS-OPC/Zn.

which reduces the corrosion tendency and has better corrosion resistance, which is beneficial to suppress the occurrence of side reactions.⁴⁶ As shown in Fig. S7, the NS-OPC/Zn clearly lowers the current density of hydrogen reaction at the voltage of $0 \sim -1 V$, which indicates that the NS-OPC coating is beneficial to suppress the hydrogen evolution reaction. Figures 2f and 2fg are the Nyquist plots of bare Zn and NS-OPC/Zn before and after cycling, and they show similar curves. The semicircle in the curve represents the charge transfer resistance, and the larger the diameter of the semicircle, the more the higher the electrode resistance is. The impedance of bare Zn before cycling is 713 Ω , which is much larger than that of NS-OPC/Zn (12 Ω), and the impedance increases to 4170 Ω after cycling for 100 h, while the impedance of NS-OPC/Zn increases to 111 Ω after cycling for 100 h. Much smaller than the impedance of bare Zn. The lower charge transfer resistance of NS-OPC/Zn is due to the electronegativity of the N and O atoms in NS-OPC that repel SO₄² thus limiting anion migration and promoting cationic migration.⁴⁷ The reason for the reduced impedance of NS-OPC/Zn is that the doping of N and S functional groups improves the electrolyte wettability and ion transport rate of the material.

Normally, the formation of Zn dendrites is caused by the uneven distribution of Zn ions and concentration polarization, and a higher Zn ion migration number (t_{Zn}^{2+}) can reduce the effect of concentration polarization, thus reducing the space charge near the electrode surface. In this case, in order to explore the effect of NS-OPC coating on the kinetics of interfacial electrodeposition, the t_{Zn}^{2+} before and after modification of NS-OPC coating was measured on the assembled ZnlZn symmetric cell (The calculation of zinc ion migration number is in the Electrical Measurements section of Supporting Information). The corresponding results are given in Figs. 2h and 2i, respectively, the t_{Zn}^{2+} of bare Zn was calculated to

be 0.44, however, after coating the NS-OPC protective layer, this value can be increased to 0.67. As shown in Fig. 2j, this improvement is due to the N, S co-doping structural defects as well as the porous structure of the NS-OPC coating, which can provide more zinc-philic active sites, effectively promoting Zn^{2+} transport, trapping Zn^{2+} on the surface of NS-OPC alleviate the uneven distribution of local charge density near the surface of Zn metal anode.^{48,49}

In addition, at a current density of 1 mA cm^{-2} , a comparison of the coulombic efficiency tests of CulZn asymmetric cells was also performed (Fig. 3a). The cells coated with NS-OPC maintained an average coulomb efficiency of 99% after 50 cycles (Fig. 3b), which was significantly better than that of bare Zn. In addition, the comparison of charge-discharge curves with different cycle times (Figs. 3c, 3d) also showed that the battery has higher plating/ stripping stability and lower polarization effect after being modified by the NS-OPC coating.

Figure 4a is the cross-sectional SEM image of bare Zn before cycling, there are obvious uneven protrusions and depressions on the surface of bare Zn foil, which may be caused by mass production. Since the flatness of the zinc anode surface will directly affect the distribution of its local current density, the uneven surface is likely to cause uneven nucleation of Zn^{2+} , which in turn results in uneven dendrite growth. As shown in Fig. 4b, a large number of vertically grown flaky Zn dendrites appeared on the surface of the bare Zn electrode after cycling for 100 h, and these dendrites were unevenly distributed.^{50,51} In the subsequent deposition, Zn^{2+} tends to be further deposited on the basis of the original nucleation, and more Zn dendrites are gradually formed after continuous accumulation and deposition (Fig. 4c). Further, from the SEM images of the surface of the bare Zn electrode after cycling, it can be observed that these sheet-like dendrites are unevenly stacked on the surface of the Zn



Figure 4. (a) Cross-sectional SEM image of bare Zn before cycling. (b) Cross-sectional SEM image of bare Zn after cycling. (c) Local enlarged image of the cross-sectional SEM image of bare Zn after cycling. (d) Cross-sectional SEM image of bare Zn after cycling SEM images. (e) elemental mapping of bare Zn after cycling. (f) schematic diagram of bare Zn after cycling. (g) cross-sectional SEM image of NS-OPC/Zn before cycling. (h) NS-OPC/Zn after cycling SEM images of the cross-section of NS-OPC/Zn. (i) Local enlarged image of the cross-sectional SEM image of NS-OPC/Zn after cycling. (j) SEM image of NS-OPC/Zn after cycling. (k) Elements of NS-OPC/Zn after cycling Mapping diagram. (l) Schematic diagram of NS-OPC/Zn after cycling.

foil to form a pile of sharp "small peaks." The further growth of these "small peaks" will pierce the separator and cause a short circuit of the battery, which will not only reduce the cycle life of the battery, but also cause safety hazards. The EDS element map in Fig. 4e also proves that the "small peaks" formed by the accumulation of platelets are zinc dendrites. The schematic diagram of Fig. 4f visualizes the growth of Zn dendrites on bare Zn. Figure 4g is the cross-sectional SEM image of NS-OPC/Zn before cycling. The thickness of the NS-OPC/Zn coating is 23.8 μ m, and there are a

large number of pore structures, which are composed of micropores, mesopores and macropores, not only can provide enough space for the growth of Zn dendrites, but also provide active sites for the nucleation of Zn²⁺. Figure 4h is the cross-sectional SEM image of NS-OPC/Zn after cycling. Small-sized flaky Zn dendrites grow in the abundant pore structure, which can also be seen from the enlarged view of Fig. 4i. The Zn dendrites are uniformly distributed in the pores because Zn^{2+} combines with the pyridine sites in the N-doped functional groups to form Zn-N bonds.⁵² The Zn-N bond



Figure 5. CV curves of of full cells with (a) bare Zn and (b) NS-OPC/Zn anodes at different scan rates. (c) EIS spectra of the full cells with bare Zn and NS-OPC/Zn anodes. (d) the cycle performance of the full cells with bare Zn and NS-OPC/Zn anodes at 10 A /g^{-1} . (e) Rate performance of the full cells with bare Zn and NS-OPC/Zn anodes.

induces homogeneous nucleation of Zn on the carbon matrix and inhibits the formation of Zn dendrites. In addition, S doping can also effectively uniform the electric field distribution, reduce the local current density, and uniformly deposit Zn^{2+} .³⁵ From the SEM image of NS-OPC/Zn after cycling in Fig. 4j, the flaky Zn dendrites growing in the channel structure can be seen more intuitively, which can be proved by the EDS element map in Fig. 4k. The schematic diagram in Fig. 4l visualizes the growth of Zn dendrites in the NS-OPC coating, thus avoiding the cell short circuit caused by the puncture of the separator by the Zn dendrites.

To demonstrate the feasibility of NS-OPC/Zn, full-cell performance tests were performed using commercial activated carbon YP50 as the cathode of Zn-ion hybrid supercapacitors. Figures 5a and 5b are the CV of zinc-ion hybrid supercapacitors of YP50||NS-OPC/Zn and YP50||Bare Zn at 10, 20, 30, 50 and 100 mV s⁻ respectively. The CV curve profiles of the modified full cells still maintain the original shape, showing the rectangular shape of Faraday hump, which means that the NS-OPC/Zn coating has no obvious effect on the reaction mechanism of the full cell. Furthermore, as shown in Fig. S8, YP50||NS-OPC/Zn obtained higher capacity and lower polarization after adding NS-OPC coating, which is consistent with the CV results. Figure 5c shows the EIS of YP50||NS-OPC/Zn and YP50||Bare Zn. The semicircle diameter in the high frequency region is positively correlated with the charge transfer resistance (R_{ct}), while the slope in the low frequency region Inversely proportional to the diffusion resistance of Zn^{2+} in the electrolyte, compared with YP50||Bare Zn, YP50||NS-OPC/Zn has a lower charge transfer resistance, which is favorable for the migration of Zn^{2+} . The linear part of the Nyquist curve of YP50IINS-OPC/Zn in the low frequency region is closer to vertical than that of YP50||Bare Zn, which indicates that YP50||NS-OPC/Zn has lower ion diffusion resistance, these All due to the doping of N and S, the electrical conductivity, electrolyte wettability, and ion transport rate of the material are improved. Compared with the YP50||Bare Zn Zn-ion hybrid supercapacitor, the YP50||NS-OPC/Zn exhibited higher cycling stability and higher capacity at a high current density of 10 Å g⁻¹ (Fig. 5d). YP50llNS-OPC/Zn has a capacity retention rate of 92.6% and a Coulombic efficiency close to 100% after 3000 cycles, while the capacity of YP50llBare Zn begins to decay sharply after 900 cycles, and after 1500 cycles, the capacity retention rate is only 70%, and the cycle stability is far behind that of YP50llNS-OPC/Zn. As shown in Fig. 5e, the capacities of YP50llNS-OPC/Zn at current densities of 0.2, 0.5, 1, 2, 5, and 10 A g^{-1} were 92, 74.3, 70.2, 67.2, 61.5, 55.2 mAh g^{-1} , when the current density returned to 0.2 A g^{-1} , the capacity recovered to 87 mAh g^{-1} , showing a superior rate performance than YP50llBare Zn.

Conclusions

In conclusion, we prepared a novel NS-OPC coating through a simple activation and doping process and investigated its role as an artificial protective layer. The hierarchical porous structure not only provides abundant nucleation sites for the deposition of Zn^{2+} , but also provides sufficient space for the growth of Zn dendrites. The abundant nitrogen-containing functional groups and sulfur heteroatoms not only provide uniform nucleation sites for Zn deposition, but also facilitate the uniform transport of Zn^{2+} . Furthermore, through various characterization techniques, we found that these advantages effectively suppressed the growth of dendrites and the occurrence of side reactions, and ensured uniform zinc deposition/stripping with high reversibility. Therefore, the cycle life of the symmetric cells coated with NS-OPC was extended to 1200 h at a current density of 1 mA cm^{-2} . Even at a high current density of 2 mA cm^{-2} , NS-OPC/ Zn can still provide a long cycle life of 700 h. More importantly, in the full cell, the NS-OPC/Zn anode enables the cell to retain 92.6% capacity after 3000 cycles at a high current density of 10 A g⁻ Taken together, this work provides a simple and controllable method for the preparation of NS-OPC coatings, opening a new avenue for the development of zinc metal anodes towards next-generation largescale energy storage applications.

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