Phenanthroline Covalent Organic Framework Electrodes for High-Performance Zinc-Ion Supercapattery

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ABSTRACT: Aqueous zinc-ion batteries and capacitors are potentially competitive grid-scale energy storage devices because of their great features such as safety, environmental friendliness, and low cost. Herein, a completely new phenanthroline covalent organic framework (PA-COF) was synthesized and introduced in zinc-ion supercapacitors (ZISs) for the first time. Our as-synthesized PA-COF shows a high capacity of 247 mAh g⁻¹ at a current density of 0.1 A g⁻¹ with only 0.38% capacity decay per cycle during 10 000 cycles at a current density of 1.0 A g⁻¹. Although covalent organic frameworks (COFs) are attracting great attention in many fields, our PA-COF has been synthesized using a new strategy involving the condensation reaction of hexaketocyclohexanone and 2,3,7,8-phenazinetetramine. Detailed mechanistic investigations, through experimental and theoretical methods, reveal that the phenanthroline functional groups in PA-COF are the active zinc ion storage sites. Furthermore, we provide evidence for the cointercalation of Zn²⁺ (60%) and H⁺ (40%) into PA-COF using inductively coupled plasma atomic emission spectroscopy and deuterium solid-state nuclear magnetic resonance (NMR). We believe that this study opens a new avenue for COF material design for zinc-ion storage in aqueous ZISs.

Zinc-ion supercapacitors (ZISs) are promising energy storage devices among the monovalent (Li⁺, Na⁺, and K⁺) and multivalent metal-ion (Mg²⁺, Ca²⁺, and Al³⁺) batteries because of their high safety, nontoxicity, and relatively low cost. More efforts are being exerted to develop diverse cathode materials for aqueous ZISs such as manganese-based and vanadium-based oxides as well as Prussian blue analogues (PBAs). Herein, we report a completely new phenanthroline covalent organic framework (PA-COF), which was synthesized and used as a ZIS cathode. As we know, COFs are an emerging class of organic polymers with periodic skeletons constructed by spatially stitching organic building blocks via strong covalent linkage. COFs not only have a reticular π-conjugated backbone but also possess a permanent porosity and crystallinity due to their topological architecture. The highly crystalline π-conjugated backbone of COF provides a stable chemical and physical reaction environment, which is particularly useful for the long-term operation at variable cathodic and anodic polarizations. In fact, although many COFs with different topological skeletons have been synthesized for application in energy storage, catalysis, sensors, gas storage, etc., detailed studies of the electrochemical behavior of COF as cathodes in aqueous ZIS has seldom been mentioned to date. Moreover, it has been reported that there still remains a great challenge to design a chemically and thermally stable polymeric electrode material, with rich nucleophilic centers for electrophilic Zn²⁺ ion acceptor.

The design of PA-COF we report here was inspired by the modular nature of COFs, which can be adjusted by tailoring an electron-rich backbone with heteroatoms at the molecular level. For example, it has been reported that nitrogen substitution in 1,4,5,8-naphthalenetetraacarboxylic dianhydride (NTCDA) can improve the specific capacity and cycling...
stability of NTCDI electrode in zinc-ion batteries (ZIBs). It has also been reported that nitrogen-doping in hierarchical porous carbon can promote the chemical adsorption of Zn\textsuperscript{2+} ions. Thus, we anticipated that PA-COF with electron-rich backbone and rich nitrogen active sites, as well as the medium pore size of 2–5 nm, might facilitate the reversible mobile ion intercalation. As a result, we have developed and tested this new PA-COF as cathode in ZISs. We demonstrate a high capacity of 247 mAh g\textsuperscript{−1} at a current density of 0.1 A g\textsuperscript{−1}, with only 0.38% capacity decay per cycle during 10,000 cycles at a current density of 1.0 A g\textsuperscript{−1}. We further extensively studied the intercalation mechanism of PA-COF in aqueous zinc ion supercapattery by experimental and theoretical methods and found it to involve cointercalation of Zn\textsuperscript{2+} (60%) and H\textsuperscript{+} (40%). We believe that this study opens a new avenue for COF material design and application in zinc-ion storage in aqueous electrolytes.

The synthetic process of PA-COF is presented in Figure 1a, which involves a solvothermal condensation reaction of hexaketocyclohexane and 2, 3, 7, 8-phenazinetetramine. The as-synthesized PA-COF is a novel 1,4,5,8,9,12-hexaazatriphenylene (HAT) derivative\textsuperscript{27} that introduces nitrogen-rich phenanthroline units into the conjugated and rigid aromatic framework. The incorporation of the phenanthroline structure was confirmed by the emergence of Fourier transform infrared spectroscopy (FT-IR) peaks at 1236 and 1460 cm\textsuperscript{−1} (Figure 1b), which corresponds to the stretching of C\textsuperscript{−}C=N\textsuperscript{−}C and C=C\textsuperscript{−}N, respectively (Figure S1, peaks a and c, Supporting Information). This difference in FT-IR and \textsuperscript{13}C solid-state NMR results confirms the successful preparation of PA-COF and the formation of its rigid conjugated frameworks. Additionally, the thermal stability of as-synthesized PA-COF material was confirmed by the thermogravimetric analysis (TGA) in argon gas (Figure S2, Supporting Information). We find that the weight loss in PA-COF is only 10% when the temperature was increased to 600 °C. In contrast, the hexaketocyclohexane and phenazinetetramine precursors show a weight loss of 85% and 30% at 600 °C, respectively. The higher thermostability of PA-COF compared with its precursors confirms the formation of rigid conjugated frameworks. In addition, two broad peaks at 3.4° and 26.7° can be observed in the powder X-ray diffraction (PXRD) profile of as-synthesized PA-COF (Figure 1c), which can be assigned to (100) and (001) planes. The PXRD result demonstrates the periodic structure of PA-COF. Particularly, the broad peak around 26.7° is mainly due to π−π stacking construction, revealing the existence of a multilayered COF structure with an interlayer distance of 3.34 Å. The simulated PXRD patterns of the inset model with an eclipsed orientation (inset in Figure 1c: AA eclipsed model) match well with the experimental results (another two simulated results are shown in Figure S3, and the corresponding crystallographic parameters are shown in Table S1, Supporting Information).

The morphology variation of scanning electron microscopy (SEM) images from precursor to as-synthesized COF further verifies the reaction product is PA-COF. The as-synthesized PA-COF is made up of globular particles with diameters around 300 nm (Figure 1d), which is totally different from the irregular morphologies of the precursors and confirms its
formation (Figure S4a,b, Supporting Information). The uniform elemental distribution of C and N in transmission electron microscopy (TEM) images also demonstrates the homogeneous nature of PA-COF (Figure 1e). In addition, the specific surface area is 19.6 m$^2$/g and the mesoporous nature with a pore size of 2–5 nm in PA-COF was calculated from the IV-type isotherms (Figure 1f). Such a low surface area and mesoporous nature account for the chemical interaction of ions with host COF material, instead of a simple physical adsorption, as will be discussed later.

The structure of the aqueous ZIS using PA-COF cathode and Zn anode in 1.0 M ZnSO$_4$|Zn metal ZIS. Electrochemical behavior of PA-COF in 1.0 M ZnSO$_4$ electrolyte within a potential window of 0.2–1.6 V. (b) Cyclic voltammetry (CV) curves at a scan rate of 0.05 mV s$^{-1}$. (c) (Dis-)charge profiles and (d) Galvanostatic cycling performance at a current density of 0.1 A g$^{-1}$. (e) Rate performance measured in the current range of 0.05–10 A g$^{-1}$. (f) Long-term cycling stability at a current density of 1.0 A g$^{-1}$.

Figure 2. Schematic illustration of zinc ion supercapattery (ZIS) and electrochemical performance. (a) Schematic configuration of PA-COF|1.0 M ZnSO$_4$|Zn metal ZIS. Electrochemical behavior of PA-COF in 1.0 M ZnSO$_4$ electrolyte within a potential window of 0.2–1.6 V. (b) Cyclic voltammetry (CV) curves at a scan rate of 0.05 mV s$^{-1}$. (c) (Dis-)charge profiles and (d) Galvanostatic cycling performance at a current density of 0.1 A g$^{-1}$. (e) Rate performance measured in the current range of 0.05–10 A g$^{-1}$. (f) Long-term cycling stability at a current density of 1.0 A g$^{-1}$.
common phenomenon in aqueous zinc-ion batteries (ZIBs). However, such a high capacity in our devices is due to the chemical intercalation of ions coupled with electron transfer on the active sites of PA-COF, rather than the capacity from an electric double layer. This is because PA-COF shows a specific area of only 19.6 m² g⁻¹, whereas the specific capacity stored through physical absorption–desorption (electric double layer) should be proportional to the specific area (Table S2). Further, we will present a detailed analysis of the storage mechanism of Zn²⁺ and H⁺ in the PA-COF which is dominated by the intercalation process in the subsequent section.

Figure 2e shows that the rate capability of the PA-COF electrode, where capacities of 265, 234, 202, 176, 153, 125, 93, and 68 mAh g⁻¹ were obtained at a current densities of 0.05, 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, and 10 A g⁻¹, respectively. The capacity recovers to 240 and 210 mAh g⁻¹ when the current was switched back to 0.05 and 0.1 A g⁻¹, respectively. More importantly, a remarkable cycling stability was achieved with only 0.38% capacity decay per cycle within 10 000 cycles at a current density of 1.0 A g⁻¹ (Figure 2f). Additionally, the particle morphology of the PA-COF electrode after 100 cycles at a current density of 1.0 A g⁻¹ shows only minor changes compared to the pristine sample, indicating a stable framework of the PA-COF material (Figure S6a,b). This cycling stability is the best that has been reported for the COF material in zinc ion batteries or capacitors.

Herein, the charge storage mechanism of PA-COF in aqueous ZIS was analyzed through the various physicochemical techniques. The electrochemical behaviors of PA-COF electrode in 1.0 M Na₂SO₄ (pH=7), 1.0 M Na₂SO₄ (pH=5), and 1.0 M ZnSO₄ (pH=7) electrolytes were tested, separately. Three different discharged curves were observed. We find that the specific capacity of the PA-COF electrode in 1.0 M ZnSO₄ electrolyte is much greater (i.e., 270 mAh g⁻¹) than that in 1.0 M Na₂SO₄ (pH=7) and 1.0 M Na₂SO₄ (pH=5) electrolytes (Figure 3a). These comparative results demonstrate that the Zn²⁺ intercalation is dominant, even though the radius of hydrated Zn²⁺ (i.e., 0.43 nm) is larger than that of hydrated Na⁺ (0.358 nm) and H⁺ (0.1 nm) ions. The intercalation of Zn²⁺ is further confirmed by the cyclic voltammogram (CV) measurement in the different electrolytes (Figure 3b). We find that the CV curve in 1.0 M ZnSO₄ electrolyte shows the largest integral area, implying the highest specific capacity among the three electrolytes. This is consistent with the highest discharge capacity seen in Figure 3a. In addition, two pairs of reduction–oxidation broad peaks can be observed within a potential window of −0.8−0.6 V (vs Hg₂Cl₂/Hg). The profiles and number of redox peaks are apparently different from those in 1.0 M Na₂SO₄ (pH=7) and 1.0 M Na₂SO₄ (pH=5) electrolytes. In addition, strong evidence for Zn²⁺ intercalation into PA-COF can be observed from the comparative TEM and SEM mapping images after discharge and charge processes. The Zn signal can be clearly observed in the electrode after the second discharge (Figure 3c), whereas the Zn signal is not easy to observe in the electrode after the second recharge (Figure S7, Supporting Information). The same variation can be observed in the SEM mapping images (Figure S8a-b, Supporting Information). These results show that reversible Zn²⁺ (de)intercalation within the PA-COF electrode does indeed take place.

Solid-state NMR was used to further analyze the possible proton intercalation in PA-COF electrodes that were discharged to 0.2 V in deuterium oxide electrolyte. We find that only one D₂O peak around 8.6 ppm can be observed in the pristine electrode, whereas an additional chemical peak around 3 ppm appears in the electrode after the second discharge.
Figure 4. (a) Comparative $^{13}$C solid-state NMR spectra of pristine and discharged PA-COF electrodes. (b) N 1s X-ray photoelectron spectroscopy (XPS) of PA-COF electrode in the pristine and discharge–recharge states and the corresponding Zn 2p XPS. (c) Electronegativity simulation of PA-COF. (d) Simulation of binding energies with different numbers of Zn$^{2+}$ in PA-COF.

This can be attributed to the presence of D$^+$ ions in the PA-COF cathodes, which was confirmed by spin relaxation studies as shown in Figure S9 (Supporting Information). The 3D spin–lattice relaxation ($T_1$) can be fitted with three components. The two short relaxations (0.423 and 0.479 s) can be assigned to component 1 (D$^+$) and 2 (OD$^-$), respectively. The very short time relaxation (0.423 s) is due to ionic charges of deuterium. In contrast, the composite 3 shows a much longer $T_1$ around 6.4 s, which can be assigned to D$_2$O. As a result, these data suggest the existence of D$^+$/OD$^-$ and D$_2$O in the electrode (inset table in Figure S9, Supporting Information), which proves that proton intercalation takes place in aqueous ZISs. In addition, the ion diffusion coefficient of the PA-COF electrode was calculated to be around $10^{-9}$ to $10^{-11}$ cm$^2$ s$^{-1}$ (Figure 3e), where the magnitude of the diffusion coefficient is similar to those in reported literature,33,34 further confirming the Zn$^{2+}$/H$^+$ intercalation mechanism within PA-COF. In addition, the charge storage kinetics of the PA-COF electrode was quantitatively analyzed to detect the capacity contribution of Zn$^{2+}$ and H$^+$ in 1.0 M ZnSO$_4$ electrolyte using a three-electrode setup. As is well-known, the charge storage commonly involves the surface capacitive effects and diffusion-controlled intercalation process.35 In this case, 70% of capacitive current is obtained at a scan rate of 2.0 mV s$^{-1}$ (Figure S10, Supporting Information). The capacitive contribution at a scan rate from 0.05 to 2.0 mV s$^{-1}$ is further identified in Figure 3f, which displays a gradual increase of capacitive current from 59% to 70%. These results imply a capacitive-like surface-controlled process of the PA-COF electrode in aqueous ZISs, which explains the high rate capabilities.

Electrochemical impedance spectroscopy (EIS) was used to differentiate the electrochemical phenomenon caused by the intercalation of different ions (Figure S11, Supporting Information). All EIS curves are mainly composed of a semicircle (charge-transfer resistance, $R_{ct}$) and slope line (ionic diffusion resistance) at the medium- and low-frequency ranges (Figure S11, Supporting Information). Initially, the fresh PA-COF electrode shows almost the same shape of semicircles in 1.0 M Na$_2$SO$_4$ (pH=7), 1.0 M Na$_2$SO$_4$ (pH=5), and 1.0 M ZnSO$_4$ electrolyte except for a slightly higher $R_{ct}$ resistance values in the 1.0 M Na$_2$SO$_4$ (pH=5) electrolyte. However, the electrode shows a noticeable difference in $R_{ct}$ after the 10th cycle in different electrolytes, indicating different Faradaic reactions in the PA-COF electrode.26 This is caused by the intercalation of different ionic species, including Na$^+$, Na$^+$/H$^+$, and Zn$^{2+}$/H$^+$ intercalation, respectively. Furthermore, a longer charge-transfer time constant was measured for the PA-COF electrode in 1.0 M ZnSO$_4$, further confirming the Zn$^{2+}$ intercalation process in the PA-COF material (Table S3, Supporting Information).

The active sites for the ion storage in PA-COF were further detected by $^{13}$C solid-state NMR, where the peak evolution of pristine and discharged sample is shown in Figures 4a and S12. Three groups of peaks can be observed, for which an obvious chemical shift occurs at the carbon in the C−C=N group (i.e., from 138.1 to 140.9 ppm). This should be ascribed to the deshielding effect,27 which is triggered by Zn$^{2+}$/H$^+$ intercalation coupled with an electron-transfer process on the covalent scaffold. This result strongly manifests the chemical reaction between the active sites and Zn$^{2+}$/H$^+$ ions during the discharge process. The reaction sites for Zn$^{2+}$/H$^+$ intercalation in PA-COF were further analyzed by X-ray photoelectron spectroscopy (XPS) as shown in Figure 4b. We find that the pristine and the charged electrodes display two well-separated N 1s peaks in Figure 4b, whereas the discharged electrode shows only a broad N 1s peak and high Zn 2p signal (Figure 4b). This variation in N 1s peak is clearly correlated with the Zn$^{2+}$/H$^+$ intercalation process that occurs during the charge cycle. The binding energy of N=C (398.9 eV) and N−C...
Figure 5. (a) In situ XRD mapping of PA-COF during the first three cycles in 1.0 M ZnSO₄ electrolyte. (b) Zinc percentage calculated from Zn²⁺ and Zn₅(OH)₆SO₄·5H₂O (ZOHS) during the first three discharge cycles. (c) Quantitative analysis of Zn²⁺ and H⁺ contributions to capacity.

Figure 6. Flexible supercapattery fabricated using PA-COF cathodes. (a) Thickness and bending measurements. (b) Digital image of 1.5 V LED light powered by tandem ZISs. (c) (Dis-)charge curves at initial state and after bending. (d) Cycling performance under repeated bending conditions.
The binding energy then returns to the initial state after the electrode is discharged to 0.2 V. The binding energy then returns to the initial state after the electrode is charged to 1.6 V. Accordingly, the electrochemical active sites for Zn\(^{2+}/H^+\) binding within the PA-COF skeleton were confirmed by the electrostatic potential surface (ESP) in Figure 4c, as shown in the red region near the corner nitrogen of two nearby phenanthroline rings. The reddish ESP indicates strong chemical affinity for cation coordination. The binding energies of PA-COF bonded with 6, 12, and 18 Zn\(^{2+}\) are negative in Figure 4d, indicating the efficient utilization of the nitrogen sites and a relatively large capacity for zinc batteries. Thus, the hexagonal 2D lattice with phenanthroline unit enriched with negative ESP region can efficiently host cations, such as Zn\(^{2+}/H^+\), within the channels of the PA-COF.

The identification of the capacity contribution from Zn\(^{2+}\) and H\(^+\) in the PA-COF material is important to understand for the intercalation mechanism. We analyzed the reaction products in the first three (dis-)charge process by in situ X-ray diffraction (Figure 5a) patterns. A regular variation of the intense peaks at 16.2° (002) and 24.3° (003) can be found during the (dis-)charge process, mainly indicating the formation of the triclinic crystal phase Zn\(_4\)(OH)\(_2\)SO\(_4\)·5H\(_2\)O (ZOHS) (PDF no. 39-0688). This result is consistent with the SEM and elemental mapping images in Figure S8 (Supporting Information), where plenty of zinc hydroxide sulfate flakes can be observed. The growth of ZOHS nanoflakes primarily results from the increased OH\(^-\) concentration near the cathode, which also reflects the intercalation of H\(^+\). A quantitative analysis of zinc and sulfur elements after the (dis-)charge process was then run using inductively coupled plasma atomic emission spectroscopy (ICP-AES). We find that 38.1%, 46.6%, and 48.2% Zn\(^{2+}\) is presented in PA-COF electrode, which accounts for 54.5%, 61.3%, and 60.0% of the total capacity in the first three cycles, respectively (Figure Sb and Table S4, Supporting Information). In this case, this analysis of ICP-AES confirms that the capacity contributions from Zn\(^{2+}/H^+\) should be from H\(^+\). We further confirm the capacity contributions through capacity measurement in the pure 1 M ZnSO\(_4\) and H\(_2\)SO\(_4\) (pH 5) electrolyte, respectively (Figure 5c). The results show a Zn\(^{2+}\) intercalation of 59.3%, 63.3%, and 66%, which is consistent with the capacity contribution calculated from ICP-AES results.

A high-performance flexible supercapacitor was designed and fabricated for practical applications. The flexible supercapacitor has a thickness of 0.3 mm and can be bent to around 120° (Figure 6a), demonstrating a robust construction. The value of the open-circuit voltage (OCV) is 1.16 V, which is almost identical to that of the coin-cell type supercapacitor (Figure S13, Supporting Information). This result demonstrates the reproducibility of the COF electrodes and batteries. A tandem battery was fabricated to achieve a higher voltage for the specific applications, such as lighting the 1.5 V LED lamp (Figure 6b, Video S1, Supporting Information). The flexible devices demonstrated a high stability under the bending conditions (Figure 6c,d). We find that the (dis-)charge profiles are very similar after the bending test, excluding a slight capacity decay (Figure 6c). The cycling measurement indicates that the flexible device tends to be stable after a small capacity fluctuation in the initial 60 cycles at 1.0 A g\(^{-1}\). These features demonstrate that the PA-COF flexible supercapacitor has potential in energy storage and wearable electronics applications.

We have synthesized a new phenanthroline covalent organic framework (PA-COF) and evaluated it as a cathode material for an aqueous zinc ion supercapacitor (ZIS). The as-synthesized PA-COF delivers a high capacity of 247 mAh g\(^{-1}\) at a current density of 0.1 A g\(^{-1}\). Furthermore, the COF cathode shows an average capacity decay of only 0.38% per cycle during 10 000 cycles at a current density of 1.0 A g\(^{-1}\). We confirmed the intercalation mechanism of Zn\(^{2+}/H^+\) by electrochemical analysis and "D-solid-state NMR, in which the capacity contribution of Zn\(^{2+}\) and H\(^+\) was quantitatively analyzed. In addition, the function of the phenanthroline unit was identified to serve as the active ion-binding sites in PA-COF through the experimental analysis and theoretical simulations. We believe that our new COF design strategy opens a new direction for COF electrodes in aqueous ion batteries.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.0c00903.

Experimental section, Figures S1–S13, and Tables S1–S4 (PDF)

Video S1 (MP4)

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Notes
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