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Abstract: Prussian blue analogs are promising cathode materials in aqueous ion batteries that have attracted increasing attention, but their low specific capacity and limited cycling stability remain to be further improved. Effective strategies to optimize the electrochemical performance of Prussian blue cathode materials are the aspects of electrolyte and structure modification. In this work, Na₂MnFe(CN)₆@PPy nanocubes were prepared by a simple co-precipitation method with PPy coating. Compared with the uncoated electrode material, the discharged capacity of the Na₂MnFe(CN)₆@PPy cathode material is raised from 25.2 to 55.0 mAh g⁻¹ after 10 cycles in the Na-Zn hybrid electrolyte, while the capacity retention is improved from 63.5% to 86.5% after 150 cycles, indicating higher capacity and better stability. This work also investigates the electrochemical performances of Na₂MnFe(CN)₆@PPy cathode material in hybrid electrolyte of Li-Zn and K-Zn adjusted via different mixed ion solutions. The relevant results provide an innovative way to optimize advanced aqueous hybrid batteries from the perspective of cycling stability.

Keywords: Prussian blue analogues; cathode materials; aqueous zinc-ion batteries; hybrid ion electrolyte

1. Introduction

As a new type of secondary energy storage battery, aqueous zinc-ion battery (AZIB) has the advantages of environmental friendliness, high safety, non-toxicity, etc., which suggests rather broad application prospects. AZIBs can be assembled in air, which is convenient and efficient compared to lithium-ion batteries, which must be assembled in a glove box [1–3]; thus, it is considered to be a promising alternative to lithium-ion batteries, which have been incorporated widely in portable electronic devices. Zinc metal anode has low redox potential (-0.76 V vs. standard hydrogen electrode), high-quality specific capacity (820 mAh g⁻¹) [4,5], etc. Combined with high electrical conductivity (5.91 $\mu\Omega$ cm) and fast reaction kinetics of aqueous electrolyte, AZIBs exhibit advantages such as high specific capacity, high safety, low cost, and long cycle life, making them gradually become a hot research point in aqueous battery systems [6,7]. However, AZIBs still face great challenges, especially the cathode materials in AZIBs which show irresistible fading of capacity in long-cycle tests, and the study of ion storage mechanisms still remains to be further investigated. The current research on the cathode materials of AZIBs can be broadly classified as the following: vanadium-based cathode materials, manganese-based cathode materials, organics cathode materials, and Prussian blue analogue (PBA) cathode materials [8-13].

Compared with other cathode materials of rechargeable AZIBs, the biggest advantage of PBA material lies in its high working voltage platform, even up to 1.7 V [14,15]. However, PBA materials are prone to suffer complex phase transformation in the reaction process, and unstable structure will lead to collapse of the framework, leading to low



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). specific capacity and poor cycling performance. For example, Svensso et al. found that CuHCF electrode material is prone to irregular structural damage during battery cycle. The specific capacities of CuFe(CN)₆ electrode materials is only 53 mAh g^{-1} at 60 mA g^{-1} [16]. Munseok et al. demonstrated nickel hexacyanoferrate $K_{0.86}$ Ni[Fe(CN)₆]_{0.954}(H₂O)_{0.766} as the cathode material which shows a rather low capacity of 55.6 mAh g^{-1} at 11.2 mA g^{-1} , and the coulombic efficiency exhibits a rapid decay in 20 cycles in aqueous zinc ion electrolyte [17], which is lower than vanadium and manganese cathode materials in AZIBs [4]. Therefore, it is of prime importance to improve the electrochemical performance of PBA cathode material; strategies of coating polymer materials on the surface of PBA have been reported [18,19], indicating that improvement in the electrochemical properties of PBA cathode materials can be achieved by coating or mixed methods. Conductive polymer materials have attracted attention due to their excellent electrical conductivity, for example, polypyrrole (PPy), polyamide (PI), polyethylene glycol (PEG), etc., which have been proved to be conductive skeletons of electrode materials [20]. The electronic conductivity of PPy is relatively high (up to $102 \,\mathrm{S \, cm^{-1}}$) among all conductive polymers because of the alternating conjugation of single and double bonds in the macromolecular structure, and the extra electrons in the double bond can move freely across the polymer chain. Furthermore, to eliminate the effect of the vacancies in the PBA material, researchers have used approaches of surface modification and composition optimization to reduce the lattice defects, which suggests that by coating with PPy the [Fe(CN)₆] vacancies in PBA material can be reduced and the electrochemical performance of the electrode is improved [21,22]. By coating with PPy, the damage to the structure can also be alleviated due to the mitigation of Mn^{2+} emissions of Mn^{II}-Fe^{III}-based PBA material, resulting in better stability of electrochemical performance [23]. Therefore, intensive research studies have been carried out to promote the electrochemical properties of PBA cathode materials by coating with PPy. Xue et al. proposed a polypyrrole-modified KHCF@PPy cathode material for potassium-ion batteries via an in situ polymerization coating method which shows better electronic conductivity and electrochemical properties [21]. Chen et al. synthesized $K_2Mn[Fe(CN)_6]$ cathode material for aqueous zinc batteries which can achieve superior rate capability and prolonged cycle life due to the better electronic conductivity enhanced by coating with PPy [24]. Previous reports have been focusing on the effect of PPy in PBA materials in various types of ion batteries. However, the PBA cathode materials coated with PPy in aqueous hybrid batteries have not received much attention, which needs to be further investigated.

Herein, Na₂MnFe(CN)₆ (NMHFC) nanocube material was synthesized by simple co-precipitation method. Then, NMHFC sample was coated with PPy under ice bath condition and is referred to as NMHFC@PPy. The specific capacity and cyclic stability of the electrode material were improved by the coating of Ppy, of which the capacity retention after 150 cycles was enhanced in the Na-Zn hybrid battery. Electrochemical performances were further conducted via different types of electrolyte, which gives the proof of considerable promotion of cycle capacity in hybrid electrolyte. We also investigated the kinetic properties of NMHFC@PPy in the Na-Zn hybrid electrolyte using multiple scan rates of CV (Cyclic Voltammetry) tests, while the mechanism of zinc storage in the reaction was revealed by means of ex situ XRD (X-Ray Diffraction) and XPS (X-ray Photoelectron Spectroscopy). This work shares the insight into the research of enhancing the electrochemical performance of the Ppy-coated PBA cathode materials, which provides a new approach to the design of cathode materials in aqueous hybrid batteries.

2. Materials and Methods

2.1. Material Synthesis

 $Na_2MnFe(CN)_6$ nanocubes were synthesized by a simple co-precipitation method. Typically, 2 mmol MnSO₄, 4 mmol K₄Fe(CN)₆, and 15 g NaCl were dissolved in 50 mL of water, respectively, denoted as solutions A, B, and C, respectively. Then, solution A and solution B were added dropwise to solution C simultaneously under magnetic stirring for 10 min. The white suspension solution obtained was maintained at room temperature for 12 h, and then the resulting precipitates were filtered and wash with deionized water and dried at 60 $^{\circ}$ C overnight. Finally, a dark gray powder was obtained and recorded as Na₂MnFe(CN)₆, marked as NMHFC.

Synthesis of Na₂MnFe(CN)₆@PPy was performed as follows: 0.0345 g NMHFC powder prepared above, 0.5 mL pyrrole, and 0.1 mmol FeCl₃ (applied as the initiator) were dispersed in 40 mL deionized water and stirred for 6 h at 0–5 °C to complete the reaction. The final composites obtained were washed three times with deionized water and ethanol, respectively, then dried in a vacuum oven at 60 °C for 6 h. The black powder obtained was noted as NMHFC@PPy.

2.2. Material Characterization

The crystal structure of the samples was characterized by X-ray diffraction (XRD, Bruker, MA, USA) with a D8 Advance X-ray diffractometer equipped with Cu K α X-ray source. Field-emission scanning electron microscopy (SEM, JEOL-7100F microscope, Tokyo, Japan) was employed to analyze the morphology and elemental composition of the samples. Transmission electron microscopy (TEM, JEM-1400Plus, Tokyo, Japan) was conducted to adopt further studies on morphologies of the prepared materials. Raman spectra were obtained using a micro-Raman spectroscopy system (Raman, Renishaw INVIA, London, UK), while Fourier transform infrared spectroscopy (FTIR, Nicolet 6700, Thermo Fisher Scientific, Waltham, MA, USA) was performed to obtain the unique functional groups and molecular bonds in compound molecules. The surface elemental valence and molecular structure were analyzed by X-ray photoelectron spectroscopy (XPS, AXIS SUPRA, Kratos, Tokyo, Japan). STA449F3 (NETZSCH F3, Selb, Germany) was used to conduct the thermo-gravimetric analysis at a heating rate of 10 °C/min from room temperature to 800 °C under a N₂ atmosphere.

2.3. Electrochemical Measurements

The three different hybrid electrolytes were prepared by dissolving LiCF₃SO₃ and $Zn(CF_3SO_3)_2$; NaCF₃SO₃ and $Zn(CF_3SO_3)_2$; and KCF₃SO₃ and $Zn(CF_3SO_3)_2$ in distilled water, then marked as Li-Zn, Na-Zn, and K-Zn, respectively, and the concentration of all electrolytes was 1 mol L⁻¹. Electrochemical performance tests were carried out with coin batteries (CR2016) assembled in the air. The cathode consisted of active material, acetylene black, and binder (PTFE) in a weight ratio of 6:3:1. High-purity zinc foil with a thickness of 0.1 mm was directly used as anode after cutting and polishing. Glass fiber film (GF/A, Whatman) was applied as separator of the cathode and anode. Galvanostatic discharge–charge tests were conducted with the LAND battery testing system (CT2001A, Wuhan, China). Cyclic voltammetry (CV) tests were performed using a VMP3 multichannel electrochemical workstation (Bio-Logic, Grenoble, France).

3. Results and Discussion

The XRD test results of NMHFC and NMHFC@PPy nanocubes are shown in the Figure 1a. All diffraction peaks can be attributed to the cubic phase space group (FM-3m) with good crystallinity (JCPDS: 73-0687) [25,26]. The XRD patterns of coated NMHFC@PPy nanocubes are rather close to those of the uncoated ones. All of the diffraction peaks exhibit sharp shapes, while the intensity of the diffraction peaks was only weakened after coating with PPy. Compared with bare NMHFC, the PPy-modified nanocubes show no peak of other phases, since PPy on the surface is amorphous, revealing that the coating process of PPy does not change the crystal structure of the material [27]. With the intention of confirming the coating of PPy, FTIR tests of the samples before and after coating were performed (Figure 1b); according to previous literature, the characteristic peaks belonging to PPy appear at about 1559 and 1650 cm⁻¹, which can be attributed to the =C-H vibration of the pyrrole in the benzene ring and the C-N stretching vibration, respectively [20,28,29], indicating the appearance of specific vibrational IR peaks of PPy in the material, while the peaks at ~597, 1617, 2066, and 3418 cm⁻¹ can be ascribed to

the PBAs [30]. Therefore, NMHFC@PPy nanocubes have been successfully obtained by a chemical polymerization method. Figure S1 shows the Raman spectra of NMHFC@PPy ranging from 100 to 2000 cm⁻¹. Four peaks were observed around 110.1, 460.5, 519.5, and 582.6 cm⁻¹. These peaks reflect the bonding of the ($C\equiv N$)⁻ ions with metal ions in different valence transition. Two peaks were observed at 110.1 cm⁻¹ and 460.5 cm⁻¹, which can be attributed to the bonding vibrations of both Fe^{II}-CN-Mn^{II} and Fe^{III}-CN-Mn^{III}, respectively, since the cyanogen coordination with the lower valence Fe^{II} and Mn^{III} is higher than that with the higher valence Fe^{III} and Mn^{III} at lower wave positions [26]. From the TG profile (Figure S2), the mass loss before 200 °C is caused by the evaporation of interstitial water [31]. The water content in NMHFC@PPy is about 8.7%. Owing to the fact that the temperature of decomposition of PPy is close to the evaporation temperature of the coordinating water [32], the PPy content can only be roughly calculated to be 7.3 wt. % for NMHFC@PPy.



Figure 1. Characterization of as-synthesized NMHFC and NMHFC@PPy. (a) XRD patterns, (b) FTIR spectra.

The morphology of NMHFC and NMHFC@PPy nanocubes were characterized by SEM, of which the results are shown in Figure 2a,b. The edges of the nanocubes after coating are blurred. The presence of Na, Mn, and Fe in the material was confirmed by EDS-mapping analysis (Figures 2e and S3); the obvious increase in C and N was evident in the EDS-mapping pattern after coating, which, combined with the previous IR results, further indicates that PPy had been obtained on the NMHFC nanocubes. TEM characterizations of NMHFC and NMHFC@PPy nanocubes were shown in Figure 2c,d, which reveals that the samples are nano-cubic particles. After PPy coating, the morphology and size of NMHFC@PPy remain unchanged; the edges of the nanocubes turn into a rough and irregular state, indicating the existence of PPy.

In order to analyze the electrochemical performance of the as-synthesized PBA cathode material, in this work the CR2016 coin-type cells with different electrolytes and polished zinc as anode were assembled. Since the rechargeable aqueous hybrid ion batteries (RAHBs) system has been proved to be an efficient way to improve the electrochemical properties [33–38], we applied a Na-Zn hybrid battery in the following tests (1 mol L^{-1} NaCF₃SO₃ and Zn(CF₃SO₃)₂ mixed ion solution as the Na-Zn hybrid electrolyte). Figure 3a shows the charge and discharge curves of NMHFC@PPy in the first 10 cycles at 200 mA g^{-1} ; similar discharging plateaus near 1.4 V were observed. The capacity of NMHFC@PPy reaches about 55.0 mAh g^{-1} after the first 10 cycles, while the uncoated NMHFC shows only about 25.2 mAh g^{-1} (Figure S5a). This result proves that the coating of PPy can significantly improve the electrochemical performance of the material, mainly on the grounds that the PPy coating on the material surface increases the electrical conductivity and improves the kinetics of ion intercalation in the structure, and the PPy on surface also protects the integrity of the electrode material during charging and discharging, thus improving the cycling performance of the electrode material. During the cycles, compared with the uncoated electrode material (Figure S5a), the charge and discharge curves of NMHFC@PPy do not show any obvious shape change, which proves that the electrochemical properties

of this material are more stable after coating. In addition, the CV diagram shows that the PPy-coated material (Figure 3b) has a smaller change in reaction capacity from the first to the tenth cycle compared with the uncoated one (Figure S5b), which further indicates that the PPy-coated electrode material has a better capacity retention. Long-cycle performance tests were conducted at a current density of 200 mA g^{-1} . As shown in Figure 3d, the PPy-coated electrode materials exhibited higher cycling capacity and cycling stability. The discharged capacity of NMHFC@PPy is 50.1 mAh g^{-1} after 150 cycles with a retention of 86.5%, while the uncoated electrode material showed a significant decrease in the first 30 cycles, and the capacity was only 25.1 mAh g^{-1} after 150 cycles with a retention of 63.5%, indicating that the ionic conductivity of the material was enhanced after coating of PPy, thus improving the kinetics of ion deintercalation in the framework of cathode material and demonstrating a higher reaction of capacity. The XRD patterns of the electrode materials after 100 cycles in the Na-Zn hybrid electrolyte (Figure S6) show that the NMHFC@PPy cathode retains a better crystal structure after 100 cycles compared with the electrode material without coating with PPy, indicating better preservation of the structure improved by PPy. Furthermore, PPy exhibits higher tensile strength, good flexibility, and corrosion resistance, which can buffer the volume change of the cathode material during the charging and discharging process, resulting in the improved cycling stability of the material.



Figure 2. SEM and TEM images of NMHFC (**a**,**c**) and NMHFC@PPy (**b**,**d**) and (**e**) EDS-mapping elemental analyses of NMHFC@PPy.



Figure 3. (a) Charge and discharge curves of NMHFC@PPy from first to tenth cycle at a current density of 200 mA g^{-1} ; (b) CV curves of NMHFC@PPy at a scan rate of 0.1 mV s^{-1} ; (c) long-cycle performance at 200 mA g^{-1} of NMHFC@PPy and NMHFC; (d) rate performance; (e) EIS tests of NMHFC@PPy and NMHFC; (f) charge and discharge curves in different electrolytes at a current density of 50 mA g^{-1} .

To further investigate the electrochemical properties in different electrolytes, this work continues with an in-depth analysis of electrochemical measurements. In the following work, different RAHBs will be taken into electrochemical tests, and their special advantages will be analyzed. Three more types of electrolyte include: $Zn(CF_3SO_3)_2$ at a concentration of 1 mol L⁻¹, mixed ionic solution of Li-Zn (LiCF₃SO₃ and Zn(CF₃SO₃)₂), and K-Zn (KCF₃SO₃ and Zn(CF₃SO₃)₂); all concentrations were specified as 1 mol L⁻¹. Figure 3f shows the charging and discharging curves of NMHFC@PPy cathode material in four different electrolytes of plain Zn, Li-Zn, Na-Zn, and K-Zn at a current density of 50 mA g^{-1} all in the third cycle to reduce the effect of polarization. The pure Zn electrolyte shows the lowest discharged capacity of 37.1 mAh g^{-1} , while Li-Zn, Na-Zn, and K-Zn hybrid electrolytes exhibit discharged capacities of 57.3, 84.7, and 59.6 mAh g^{-1} , respectively, indicating the highest discharged capacity in the Na-Zn hybrid electrolyte. Meanwhile, the Na-Zn hybrid electrolyte shows the longest platform of midpoint voltage. As shown in Figure S4, the cycling performance tests of the Li-Zn, Na-Zn, and K-Zn samples were conducted at a current density of 50 mA g^{-1} , which corresponded to the charge–discharge curves in Figure 3f. The discharge capacities of the Li-Zn and K-Zn hybrid electrolytes were both lower than 50 mAh g^{-1} after 100 cycles, with the coulombic efficiencies less than 80%, while the discharged capacity in the Na-Zn hybrid electrolyte reaches 99.3 mAh g⁻¹ after 100 cycles with coulombic efficiency up to 93.3%, indicating higher capacity and stability. It is presumed that irreversible side reactions may appear during the charging process, which may lead to damage to the material structure resulting in electrochemical degradation. The capacity in K-Zn hybrid electrolyte is close to that in Li-Zn; both suffer from rapid capacity decays due to the fact that the framework of the material collapses in the continuous reaction. The Li-Zn hybrid electrolyte exhibits capacity decay after the first few cycles, relating to the solventization reaction of Zn^{2+} in the electrolyte, which could affect the pH of the solution and, thus, the cation-solvent interaction. It has been reported that the pH of Li-Zn hybrid electrolyte ranges from pH = 3 at 1 mol L^{-1} , which leads to hydrolysis side reactions, all the way to pH \approx 7 at high concentrations of Li-Zn hybrid solution; hydrolysis could be effectively inhibited by neutral pH, implying that

Li-Zn hybrid electrolyte requires higher concentrations of the mixed solution to inhibit the occurrence of hydrolysis side reactions for better cycling stability [39].

In view of the electrochemical performance of NMHFC@PPy cathode materials in different hybrid electrolytes, it was found that NMHFC@PPy showed the best cycling efficiency and stability in the Na-Zn hybrid electrolyte among the four comparison samples. To further investigate the zinc storage performance by coating with PPy, Na-Zn mixed solution was used as the electrolyte for the following tests, with NMHFC@PPy as the cathode material.

In order to further investigate the kinetic properties of NMHFC@PPy cathode material, CV tests with different scan rates of the electrode reaction was conducted. In CV testing, it is possible to distinguish whether the cell behaves diffusively or pseudocapacitively during charging and discharging by mathematically analyzing the scan rate (v, mV s⁻¹) with the resulting peak current response (i, A). With the increase of scan rate, the peak current of redox increases gradually, and the peak potential difference between oxidation peak and reduction peak also rises. The oxidation peak shifts to high potential and reduction peak shifts to low potential, indicating that the electrochemical polarization increases with the increase of scan rate. The following formula exists between the i and the v, which is discussed [40]:

$$=av^b$$
 (1)

For the cathode electrode material, the electrochemical reaction process generally contains both battery properties and pseudocapacitance properties. Therefore, the current response at a specific voltage consists of two components: the diffusion contribution ($k_2v^{1/2}$) and the capacitance contribution (k_1v), which can be shown as:

i

$$i = k_1 v^{\frac{1}{2}} + k_2 v \tag{2}$$

where k_1 and k_2 are constants whose value magnitude can reflect the percentage of different property response contributions at a specific voltage. The current magnitudes at different sweep speeds and specific voltages can be obtained by multi-sweep speed cyclic voltammetry tests. Therefore, the corresponding k_1 and k_2 values can be gained by linearly fitting the current response at different sweep speeds using the above equations, and the diffusion contribution and capacitance contribution at specific sweep speeds can be obtained by integrating the k_1 and k_2 values obtained at each voltage.

Based on the theory discussed above, CV tests at different scan rates were performed for NMHFC@PPy cathode material (voltage ranging from 0.4 to 1.9 V) with scan rates of 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, and 2.0 mV s⁻¹, and the results are shown in Figure 4, where it can be seen that as the scan speed increases, the corresponding redox peaks shift toward the anode and cathode, respectively. This can be attributed to the polarization effect at high currents, which will lead to poor cycling performance at high currents if the polarization is too large. In addition, it can be clearly observed that the end current changes significantly during the test from 0.4 to 1.9 V. The electrochemical analysis of the NMHFC@PPy electrode material was carried out using the above equation. Based on Figure 4c, we can find the proportions of pseudocapacitive and diffusion-controlled contributions from the total capacity at various scan rates of 0.1 to 2.0 mV s⁻¹. The contribution of the pseudocapacitance process (red shaded region) is 58.04% at a scan rate of 0.8 mV s⁻¹ (Figure 4d), due to good rate performance of the NMHFC@PPy material.



Figure 4. (a) CV curves at different scan rates; (b) logarithmic relationship between peak current and scan rate; (c) the diffusion and capacitance contributions at different a scan rates; (d) the contribution proportion of pseudocapacitance at 0.8 mV s^{-1} .

To investigate the changes of the crystal structure during the charging and discharging process of the aqueous hybrid Na-Zn battery, we conducted ex situ XRD tests of NMHFC@PPy during the first cycle in Figure 5a. As can be seen from the ex situ XRD patterns in the Na-Zn hybrid electrolyte, the diffraction peaks during the charge and discharge process indicates that no phase transition occurred during the electrochemical redox process, and the results show similar patterns of the initial and fully charged state, which indicates good reversibility of NMHFC@PPy electrode material. Moreover, the peak at 18.1° belongs to PTFE, which acts as the binder in the electrode material, while the peaks at 16.8°, 34.0°, and 38.2° are attributed to the NMHFC@PPy cathode; they all exhibited weakened intensities when discharged to 0.4 V, indicating the intercalation of Zn²⁺ according to previous reports [41]. Besides, the peak at 23.8° shows a slight shift to a larger angle when the electrode was fully discharged and charged, which gives further proof of the intercalation and deintercalation of Zn^{2+} [21,24]. Figure S7 shows the ex situ XRD and XPS patterns of NMHFC electrode material. As can be seen from the ex situ XRD results, the cathode without coating with PPy exhibits alike peaks compared with the coated one, while the peaks at fully discharged state maintained worse crystal structure when discharged to 0.4 V in comparison to NMHFC@PPy, suggesting that the coating of PPy can improve the reversibility of the electrode material during the cycle [21]. In addition, the ex situ Fe 2p XPS results of NMHFC demonstrate that the changes of peaks are relatively small (0.3 eV), indicating that the volume change during the charge–discharge process can be reduced via PPy coating [24]. To further characterize the situation of the material before and after the charging and discharging process, EDS-mapping analysis was performed on the elemental distribution of the material before and after discharge. As shown in Figure S8, the results show that when the electrode material is discharged to 0.4 V, after the Zn²⁺ intercalation occurs in the corresponding charge–discharge curve, the presence of Zn element can be clearly detected in the elemental spectrum. At the same time, the morphology of the material does not change significantly after discharge, and the material

still maintains the morphology of nanocubes, indicating that the morphology of the clad material is well preserved after the discharge, which demonstrates the excellent stability of the material. The ex situ XPS Zn 2p spectra of NMHFC@PPy electrode material in different states were also collected in Figure 5b (initial, full discharge at 0.4 V, and full charge at 1.9 V states). There exists no signal for Zn in the XPS spectrum of the initial NMHFC@PPy electrode. When discharged to 0.4 V, an obvious Zn $2p_{3/2}$ - $2p_{1/2}$ spin–orbit doublet was detected, indicating the successful intercalation of Zn²⁺ into the structure of the cathode material, while the signal of Zn exhibits a weakened state when the cathode is fully charged to 1.9 V. The XPS results indicate the successful insertion/extraction of Zn²⁺ ions into/from the NMHFC@PPy electrode during discharge/charge processes.



Figure 5. (a) Ex situ XRD and (b) ex situ XPS patterns of NMHFC@PPy cathode material during the first cycle in different states.

To explore the chemical composition of NMHFC@PPy cathode material, XPS spectra of NMHFC@PPy in different states are shown in Figure S9; the elements of C, N, O, and Fe are found in the initial state of NMHFC@PPy. XPS spectra of Fe 2p and C 1s in different states are shown in Figure 6. After coating with PPy, the initial Fe $2p_{3/2}$ XPS peak (Figures 6a and S10a) of NMHFC@PPy cathode material can be fitted by the peak related to Fe^{II} (705.4 eV) and the peak attributed to Fe^{III} (708.8 eV) [42], and the C 1s XPS peak (Figure 6d) can be fitted by the peaks related to C-C/C=C (281.4 eV) and C-N(289.9 eV) [41,43]. When the electrode is fully discharged to 0.4 V (Figure S10b), the peak changes attributed to Fe 2p (0.6 eV) are larger than that of NMHFC (0.3 eV, Figure S7b), indicating that the coating of PPy can reduce the volume change in the charge and discharge process, while the strength of the peak fitted to Fe^{III} increases. The C 1s shows a new peak of C-H in 285.5 eV (Figure 6c) in fully discharged state. However, after the cathode material has been fully charged in the Na-Zn hybrid electrolyte, the peak of Fe^{II} shows a slight change (705.5 eV) compared with the initial one (Figure S10c), while C 1s is almost the same as the initial one (Figure 6b), and Fe 2p shows weak Fe^{III} peaks in initial and charged states, mainly due to the oxidation of Fe in the synthetic process. This indicates that the intercalated Zn²⁺ in the PPy-coated cathode material mainly interacts with the redox reactions of Fe ions of both Fe^{II} and Fe^{III} when the electrode material is fully discharged, and C–H bonds of PPy also contribute to the ionic conductivity of the cathode material during the discharge process, which is similar to the previous reports [30,44].



Figure 6. XPS spectra of NMHFC@PPy in different states; (a) Fe 2p and (b-d) C 1s.

4. Conclusions

In this paper, NMHFC nanocubes were synthesized by a simple co-precipitation method and modified by PPy coating to obtain NMHFC@PPy nanocubes. Compared with bare NMHFC, the as-prepared NMHFC@PPy cathode material exhibited an enhanced cycling stability and rate performance due to the better electronic conductivity provided by PPy. The capacity retention was improved from 63.5% to 86.5% by coating with PPy after 150 cycles in a Na-Zn hybrid battery, while the rate performance of NMHFC@PPy cathode material in high current densities is also superior to that of the uncoated one. These advances provide new research views for development of modified PBA cathode materials for cycling-stable aqueous hybrid batteries in the future.

Supplementary Materials: The following supporting information can be downloaded at: https:// www.mdpi.com/article/10.3390/coatings12060779/s1, Figure S1: Raman spectra of NMHFC@PPy; Figure S2: TG curve of NMHFC@PPy; Figure S3: EDS-mapping elemental analysis of NMHFC; Figure S4: Cycling performance curves of NMHFC@PPy in Li-Zn, Na-Zn, and K-Zn mixed ionic electrolytes at current density of 50 mA g⁻¹; Figure S5: Charge and discharge curves of NMHFC from first to tenth cycle at a current density of 200 mA g⁻¹, CV curves of NMHFC at a scan rate of 0.1 mV s⁻¹; Figure S6: XRD patterns of NMHFC@PPy and NMHFC electrode material after 100 cycles; Figure S7: (a) Ex situ XRD and (b) ex situ Fe 2p XPS patterns of NMHFC cathode material during the first cycle in different states; Figure S8: SEM and EDS-mapping analyses of NMHFC@PPy electrode material before discharge and after discharge to 0.4 V; Figure S9: XPS spectra of NMHFC@PPy in different states; Figure S10: Fe 2p XPS spectra of NMHFC@PPy in different states.

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