In order to meet the growing demand of energy storage for the power grid, aqueous NH₄⁺ batteries are attracting increasing attention as a promising alternative due to their environmental significance, abundant resources, and fast diffusion ability. In this work, FeFe(CN)₆ (FeHCF) is synthesized as a cathode material for aqueous NH₄⁺ batteries and Fe₂(SO₄)₃ is utilized as a kind of functional additive in the electrolyte based on the “common ion effect” to enhance its electrochemical performance. The results indicate that the initial capacity of FeHCF is about 80 mA h g⁻¹ with a coulombic efficiency of 97.8%. The retention rate can attain 96.3% within nearly 1000 cycles. Multivariate analysis methods are carried out to characterize the mechanism of FeHCF in aqueous NH₄⁺ batteries. From the practical standpoint, FeHCF has outstanding cycling stability and rate capability, making it feasible to be applied in the power grid.

1. Introduction

Gaseous emissions from the burning of fossil fuels are constantly polluting the air, further contributing to global warming and causing serious consequences, which has received increasing attention. Meanwhile, the dependence on foreign sources can cause weakness in international relations which may endanger social stability. These concerns have enabled us to focus our attention on the employment of alternative energy sources.¹,² Among them, developing energy storage devices especially rechargeable batteries is a considerable strategy to provide stable energy.³–⁸ Now they have become an indispensable part in our lives on account of their extensive utilization in many fields such as electronic portable devices.⁹ In recent decades, as a representative of rechargeable batteries, Li⁺ batteries with high energy density have satisfied a wide spectrum of needs.¹⁰–¹⁷ However, in consideration of inflammable and volatile organic electrolytes, their safety cannot be ignored.¹⁸,¹⁹ In this situation, high-safety aqueous batteries, based on a simpler electrolyte environment, can substantially address the security problem and can be used as potential alternatives.²⁰–²³

When it comes to aqueous batteries, aqueous Li⁺ batteries are undoubtedly the first system to be considered. The first aqueous Li⁺ battery was designed by Dahn et al. as early as 1994.²⁴ Later, other alkali metal ions have also been extensively studied.²⁵–³² In stark contrast, nonmetallic cations like NH₄⁺, H⁺ and H₂O⁺ have attracted less attention. The historical disregard for them seems unreasonable and has narrowed the scope of battery research. In fact, exclusive properties may be exhibited by nonmetallic cations that need to be explored.³³ Among these nonmetallic cations, NH₄⁺ has lower corrosion and a less degree of hydrogen evolution. Under these conditions, aqueous NH₄⁺ batteries [AIBs] can be regarded as a good choice. Recently, Ji et al. have reported some successful works of using NH₄⁺ as the charge carrier, which exhibits excellent electrochemical properties especially in ultra-fast kinetics.³⁴,³⁵ It is because NH₄⁺ has a lower molar mass, smaller size of hydrated ions and faster diffusion rate in aqueous electrolytes.³⁶,³⁷ Therefore, the intrinsic safety of AIBs and the sustainability of NH₄⁺ in the Earth can make AIBs competitive candidates in the energy storage field to meet the requirements of safety and cheapness.

As for electrode materials in aqueous batteries, two factors are mainly considered. The first is the chemical stability of electrode materials in aqueous electrolytes. The second is that the working voltage of the materials is between water decomposition voltages. Beyond this range, hydrogen evolution and oxygen evolution reactions will occur constantly, making them fail to work. Based on these, Prussian blue and its analogues (PBAs) are regarded as promising cathode materials due to their stability in water and the large insertion sites in their cubic structure.³⁸,³⁹ To our knowledge, the use of Prussian blue in aqueous electrolytes was first reported by Neff in 1978.⁴⁰ Then, Itaya et al. revealed a phenomenon that Prussian blue shows high reversibility during the ion inser-
tion/extraction process, further indicating the feasibility of using PBAs in aqueous electrolytes. Since then, PBAs have become a major category of electrode materials in the aqueous battery field. Herein, we point out that AIBs using FeFe(CN)$_6$ (a kind of PBA) as the electrode material can show great electrochemical performance, resulting from its large open structure. The working voltage range of FeHCF we used is 0.2–0.8 V, which is less than the decomposition voltage of water (0.18–1.05 V vs. standard hydrogen electrode). Meanwhile, FeHCF has the advantages of low cost, environmental friendliness, and easy synthesis. Moreover, based on the “common ion effect”, Fe$_2$(SO$_4$)$_3$ is added as a functional additive into the NH$_4$(SO$_4$)$_2$ electrolyte in this work mainly to improve the cycling stability of AIBs. More details will be discussed below.

2. Experimental

2.1 Materials synthesis

The FeFe(CN)$_6$ (FeHCF) sample was synthesized using a co-precipitation method. Specifically, a solution of K$_2$Fe(CN)$_6$ (50 mL, 0.1 mol L$^{-1}$) was gradually added to the FeCl$_3$ solution (100 mL, 0.1 mol L$^{-1}$) under magnetic stirring. The mixed green solution was kept stirring for about 6 hours before centrifugation. Then the final sample was dried at 80 °C overnight in an oven.

2.2 Materials characterization

The X-ray diffraction (XRD) of FeHCF was performed using a Bruker D2 Phaser diffractometer. Its morphology was observed through scanning electron microscopy (SEM, Zeiss Gemini 300) and transmission electron microscopy (TEM, JEOL JEM 2100F). Thermogravimetry analysis (TGA, Netzsch STA 449 F3) was performed in a N$_2$ atmosphere at 20–550 °C. Fourier transformed infrared spectroscopy (FTIR) was performed by using a Vertex 80 FTIR system. The chemical composition of FeHCF was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES, PerkinElmer 8300) on Fe and K elements. X-ray photoelectron spectroscopy (XPS) was carried out using a physical electronics quantra scanning ESCA microprobe to analyse the surface chemistry.

2.3 Electrochemical measurements

The electrochemical performance was examined using a three-electrode cell, with FeHCF, Pt and Ag/AgCl as the working, counter and reference electrodes, respectively. The working electrode was fabricated by smearing a mixture of active materials (80 wt%), acetylene black (10 wt%) and polytetrafluoroethylene (PTFE, 10 wt%) on carbon paper and dried in air at 80 °C. Cyclic voltammetry (CV) was performed on the CHI 660D workstation and galvanostatic charge/discharge (GCD) tests were conducted using a LAND-CT2001A system.

3. Results and discussion

The XRD pattern of FeHCF and its Rietveld refinement are shown in Fig. 1a, in which the experimental XRD data are consistent with the simulated XRD pattern, signifying that pure and well-crystallized FeHCF is successfully synthesized. Besides, all the XRD peaks well reveal its face-centered cubic structure with a spatial basis of Fm$ar{3}$m in FeHCF. The corresponding structure is displayed in Fig. 1b, where the Fe ions are coordinated by turns with the C and N atoms of the C≡N ligands. Therefore, it forms a large stereoscopic framework for the insertion of NH$_4^+$. From the TGA result of FeHCF (Fig. 1c), the weight loss at around 200 °C is 20.93%, which is caused by the removal of crystal water. In addition, Fig. 1d shows the FTIR spectrum, where the sharp peak at 2095 cm$^{-1}$ can be ascribed to the vibration of the Fe–C≡N bonds. The peaks at 3424 and 1608 cm$^{-1}$ correspond to the stretching and bending vibrations of O–H in H$_2$O. To further confirm the chemical composition of FeHCF, the ICP-AES test was performed. The result in Table S1† shows that the content of the Fe element is much larger than that of K (Fe: 4.56% and K: 0.02%), thus the K element can be negligible. Combined with the above analysis, it can be determined that the chemical formula of the synthetic FeHCF sample is FeFe(CN)$_6$·4H$_2$O in this work.

To explore the NH$_4^+$ storage capacity of the FeHCF nanoparticles, cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) measurements were implemented. Fig. 3a shows the CV curves of FeHCF at 0–0.8 V, which overlap very well, suggesting the high reversibility of NH$_4^+$ insertion/extraction in FeHCF. As can be seen, the anodic/cathodic peaks at 0.34/0.18 V versus the standard hydrogen electrode (SHE) are consistent with the SEM results, further displaying the sphere-like nanostructure of FeHCF. Moreover, the uniform distribution of C, Fe and N elements in FeHCF can be confirmed by the energy dispersive spectroscopy (EDS) elemental mappings (Fig. 2g).

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accordance with the previous literature. The insertion reaction of FeHCF in this work can be concluded as follows:

$$\text{Fe}^{3+} [\text{Fe}^{3+} (\text{CN})_6] + \text{NH}_4^+ + e^- \rightarrow \text{NH}_4^+ [\text{Fe}^{3+} (\text{CN})_6]$$

Moreover, it is worth mentioning that compared with the CV curves of FeHCF using the pure (NH$_4$)$_2$SO$_4$ solution, the addition of Fe$_2$(SO$_4$)$_3$ to the electrolyte has no effect on the redox peaks, as shown in Fig. S1,† which indicates that Fe$^{3+}$ would not affect the NH$_4^+$ insertion/extraction process. At the same time, it can be seen that both the hydrogen evolution reaction and the irreversible capacity of the first cycle are restricted after the addition of additives.

In order to determine the appropriate concentration of the Fe$_2$(SO$_4$)$_3$ additive, a series of electrolyte additives at different concentrations (0.05 M, 0.1 M, and 0.2 M Fe$_2$(SO$_4$)$_3$) were used to test the cycling performance of AIBs. As shown in Fig. S2,† comparing the performance of the 0.05 M and 0.1 M additives, the latter performs better. However, when the Fe$_2$(SO$_4$)$_3$ additive concentration is increased to 0.2 M, the cycling performance does not improve significantly, which is similar to that of the 0.1 M additive. Therefore, in consideration of performance and cost, 0.1 M Fe$_2$(SO$_4$)$_3$ is finally selected as the electrolyte additive. Fig. 3b shows the first three GCD profiles of FeHCF in the saturated (NH$_4$)$_2$SO$_4$ electrolyte containing 0.1 M Fe$_2$(SO$_4$)$_3$ at 30 mA g$^{-1}$. Consistent with the CV results, there is a gentle slope area from around 0.45 to 0.25 V during the discharge process and a similar plateau range during the charge process. Fig. 3c shows the comparison of the reversible capacity and cycling stability of FeHCF in the (NH$_4$)$_2$SO$_4$ electrolyte with and without the Fe$_2$(SO$_4$)$_3$ additive. The initial discharge capacity in the electrolyte without the additive is 76.1 mA h g$^{-1}$ at 30 mA g$^{-1}$, outperforming the previously reported PBAs for NH$_4^+$ storage, such as (NH$_4$)$_{1.47}$Ni[Fe(CN)$_6$]$_{0.88}$ (51 mA h g$^{-1}$), K$_{0.6}$Ni$_{1.2}$Fe(CN)$_6$ (51 mA h g$^{-1}$), and NaFeFe(CN)$_6$ (62 mA h g$^{-1}$). However, the cycling stability in the pure (NH$_4$)$_2$SO$_4$ electrolyte is not very good, dropping from 76.1 to 71.4 mA h g$^{-1}$ during 300 cycles. Notably, a better cycling performance is achieved after adding the Fe$_2$(SO$_4$)$_3$ additive to the electrolyte, and the capacity retention rate is almost 100% within the same cycles. Besides, the specific capacity is stable at 81.4 mA h g$^{-1}$, increasing by about 5 mA h g$^{-1}$ compared with that in the pure (NH$_4$)$_2$SO$_4$ electrolyte. The rate performance of FeHCF with and without the Fe$_2$(SO$_4$)$_3$ additive is further characterized in Fig. 3d. As shown, the discharge capacity with the additive is about 79, 76, 74, 72 mA h g$^{-1}$ at 50, 200, 400, 800 mA g$^{-1}$, respectively. There is no significant reduction in the specific capacity during the return from 800 to 200 mA g$^{-1}$. Moreover, the electrochemical polarization shown in Fig. 3f does not increase much at higher current density. The second half of Fig. 3d shows the quite stable cycling performance of FeHCF at 200 mA g$^{-1}$, which still maintains about 75 mA h g$^{-1}$ after nearly 1000 cycles, delivering a high capacity retention of

Fig. 1 Characterization of FeHCF. (a) XRD pattern. (b) Crystal structure. (c) TGA curve. (d) FTIR curve.
96.3%. However, the rate performance without the Fe$_2$(SO$_4$)$_3$ additive is notably worse and the capacity decreases quickly, further confirming the effectiveness of the additive. Fig. 3e shows the multifaceted performance comparison between FeHCF and other representative PBA electrodes.\textsuperscript{34,49,51} As can be seen, our material shows the highest capacity, the lowest polarization and better cycling stability, demonstrating a better comprehensive performance.

To our knowledge, such excellent rate and cycling performances can be contributed to two factors. Firstly, it can be contributed to the large open channels of the FeHCF framework, which allows NH\textsuperscript{+} to be transported quickly from the lattice to the central sites of the cubic framework without much obstruction.\textsuperscript{50,52} Secondly, the capacity fading is alleviated due to the electrolyte optimization based on the common ion effect. As is known to all, the common ion effect usually exists at the acid–base equilibrium and the precipitation–dissolution equilibrium. The common ion effect means that the addition of the corresponding metallic cation can affect the dissolution equilibrium of the metallic cation and impede its dissolution.\textsuperscript{42} Based on the common ion effect, much attention has been paid to the electrolyte optimization by adding some functional additives to enhance the cycling stability of the battery. Meanwhile, it is pointed out that the choice of additives mainly rests with the cathode materials.\textsuperscript{44} Considering the common ion effect and Fe-based cathode material used in this work,\textsuperscript{45} Fe$_2$(SO$_4$)$_3$ is chosen to be added into the (NH$_4$)$_2$SO$_4$ electrolyte. The addition of Fe\textsuperscript{3+} can impact the precipitation–dissolution equilibrium of Fe\textsuperscript{3+} from the FeHCF cathode, and guarantee the stability of Fe\textsuperscript{3+} in the FeHCF framework, further impeding the dissolution of FeHCF. The capacity fading is attributed to the structural collapse and the
dissolution of the FeHCF nanoparticles. Since the destruction of FeHCF is lessened, the cycling performance of the AIBs can be significantly improved.

To prove this, some experiments were performed on the electrode and electrolyte before and after cycles, including ICP, XRD and SEM analyses. As shown in Table S2,† when using the pure (NH₄)₂SO₄ solution without the additive, the content of the Fe element in the electrolyte increases from 0 to 0.062 M after being cycled, which can be attributed to the dissolution of Fe in the FeHCF material during the charge/discharge process. However, when using the electrolyte with the 0.1 M Fe₂(SO₄)₃ additive, the content of the Fe element remains almost unchanged, resulting from the “common ion effect”. In other words, Fe³⁺ from the additive can affect the dissolution equilibrium of FeHCF in the electrolyte and guarantee the stability of Fe²⁺ in the FeHCF framework, thus impeding the dissolution of FeHCF. The ICP results directly show that the addition of additives reduces the structural collapse and the dissolution of the FeHCF nanoparticles. Besides, the results of the XRD and SEM analyses can be seen in Fig. S3 and S4.† As shown, there is no obvious change in the XRD and SEM results of the FeHCF electrode using the electrolyte with the additive before and after being cycled, which means that the structure of FeHCF is not destroyed after 500 cycles, further indicating the positive effect of the additive.

The NH₄⁺ storage kinetics of FeHCF in AIBs at different scan rates was investigated through CV tests. As shown in Fig. 3g, there was no change in the shape of the redox peaks with an increase of the scan rate. The corresponding peak voltages remain close, indicating the low polarization and the fast kinetics. According to the equation given below, the linear log (ν) vs. log(Iₚ) plots at anodic and cathodic peaks are fitted.

\[
\log(I_p) = \log(a) + b \log(\nu)
\]

In the equation, the slope b = 0.5 suggests that the current is controlled by semi-infinite diffusion, while b = 1 indicates a pseudo-capacitive process. The slopes of the two curves are 0.79 and 0.78, respectively, revealing that the storage of NH₄⁺ in FeHCF is dominated by both capacitive contribution and diffusion control.53

To further confirm the insertion mechanism of NH₄⁺ into FeHCF, the ex situ XRD patterns at selected voltages were

![Fig. 3](image-url)
recorded to clarify its crystal structural variations. As shown in Fig. 4a, all XRD patterns show a consistent face-centered cubic structure at selected voltages (Fig. 4b), indicating that the NH$_4^+$ insertion/extraction in FeHCF is a solid solution reaction. Fig. 4c and d are the partial enlarged versions of Fig. 4a, in which the (1 0 0) peak slightly shifts from 17.50° to 17.61° with the lattice contraction during the discharge process (NH$_4^+$ insertion), while it returns to its original state after charging (NH$_4^+$ extraction), which is consistent with the existing reports. Moreover, it is suggested that the bulky size of NH$_4^+$ can lead to complete dehydration, in other words, it expels a certain amount of lattice water from the structure, which may be the reason for the lattice shrinkage upon NH$_4^+$ insertion. This shrinkage in the unit-cell volume can explain why the discharge capacity of FeHCF is a little smaller than the charge capacity, reflected in Fig. 3b.

The changes in the chemical valence were analysed by ex situ XPS. As can be seen in Fig. 4e-g, the redox reactions are mainly embodied in the Fe 2p area. Resulting from the spin–orbit coupling, they are divided into Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$, with the former being stronger and having a larger area than the latter. Fig. 4e shows that both the Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$ peaks can be fitted into three sectors, corresponding to the peaks of Fe$^{2+}$, Fe$^{3+}$ and the satellite. The appearance of Fe$^{2+}$ in Fig. 4e can be attributed to the incomplete extraction of K$^+$ from K$_3$Fe(CN)$_6$ in the sample preparation process, which has been reported in the previous literature. The binding energy of Fe$^{2+}$ is a little lower than that of Fe$^{3+}$ (the peaks at 708.3 eV and 722.3 eV belong to Fe$^{2+}$ 2p$_{3/2}$ and Fe$^{2+}$ 2p$_{1/2}$, while the peaks at 710.0 eV and 723.3 eV are specified as Fe$^{3+}$ 2p$_{3/2}$ and Fe$^{3+}$ 2p$_{1/2}$ in FeHCF, respectively). During the discharge process (Fig. 4f), the area ratio of the Fe$^{3+}$ peaks decreases significantly. This phenomenon well exemplifies the reduction from Fe$^{3+}$ to Fe$^{2+}$, testifying the insertion of NH$_4^+$ into FeHCF. Then during the charge process, the Fe$^{3+}$ peaks obviously strengthen along with the weakening of the Fe$^{2+}$ peaks, which could be explained by the oxidation of Fe$^{2+}$ to Fe$^{3+}$, suggesting the extraction of NH$_4^+$ from FeHCF. Overall, both the ex situ XRD and the XPS results show the reversible NH$_4^+$ insertion/extraction process in FeHCF.

4. Conclusion

In conclusion, the AIBs consisting of low-cost FeHCF with the (NH$_4$)$_2$SO$_4$ electrolyte show good electrochemical performance in a suitable voltage range. Moreover, based on the “common ion effect”, the cycling stability is further improved by adding...
Fe₃(PO₄)₂ as a functional additive into the electrolyte. Attributed to the positive effects of electrolyte optimization, the AIBs in this work show a high specific capacity of 81.4 mA h g⁻¹ in the first cycle, and the coulombic efficiency reaches 97.8%. Besides, the AIBs demonstrate an outstanding rate capability (72 mA h g⁻¹ at 800 mA g⁻¹) and capacity retention (96.3% within nearly 1000 cycles at 200 mA g⁻¹). In a word, FeHCF is a promising electrode material to be applied in large-scale NH₄⁺ storage, which is of great significance in both essential studies and industrial production.

Author contributions
Siyun Li: investigation, data curation, software, formal analysis, methodology, writing—original draft. Maoting Xia: data curation, methodology, validation, writing—review & editing. Chengxiang Xiao: data curation, methodology. Xikun Zhang: writing—review & editing. Haoxiang Yu: methodology. Liyuan Zhang: formal analysis. Jie Shu: conceptualization, supervision, funding acquisition, project administration, writing—review & editing.

Conflicts of interest
The authors declared that they have no conflicts of interest in this work.

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