Manipulating electrocatalytic reaction and ion intercalation to improve aqueous batteries

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Abstract

Widening the electrochemical stability window of aqueous electrolytes through suppressing water decomposition represents a basic principle for aqueous batteries. However, we report that electrocatalytic water decomposition can be leveraged to enhance the performance of aqueous batteries. Using the $\text{Na}_x\text{Fe}[\text{Fe}(\text{CN})_6]\|\text{NaTi}_2(\text{PO}_4)_3$ aqueous battery as a platform, we demonstrate that electrocatalytic water oxidation can serve as an electrochemical activation approach to achieving higher full cell capacity. Upon overcharging the cell, the desodiated $\text{Na}_x\text{Fe}[\text{Fe}(\text{CN})_6]$ becomes active to catalyze water oxidation and $\text{NaTi}_2(\text{PO}_4)_3$ with Na-vacant sites allows for extensive Na-ion intercalation from electrolyte, leading to significantly increased cyclable Na ions. Through synchrotron analyses, we observe considerable structural evolutions and charge-compensating reactions in both electrodes during electrochemical activation. The high structural and chemical reversibility empowers a major increase in discharge capacity (i.e., from 56 mAh/g-cathode to 124 mAh/g-cathode), specific power, and lifespan. This study offers fundamental insights into manipulating electrocatalytic reactions for improving aqueous batteries.

Introduction

While Na-ion batteries have been considered as a potential alternative to Li-ion batteries for some applications such as grid storage¹⁻³. However, similar to Li-ion batteries, flammable Na-ion organic electrolytes also pose considerable safety concerns over Na-ion batteries. Na-ion aqueous batteries, which utilize water-based electrolytes, can eliminate the potential hazard of cell explosion, and reduce electrolyte toxicity^{4,5}. However, constructing a sustainable, high-energy aqueous Na-ion battery with a two-electrode, rocking-chair cell configuration has been challenging arising from technical barriers in identifying a compatible electrode-electrolyte system.

Owing to its narrow electrochemical stability window (1.23 V vs. SHE)⁶, water in aqueous electrolytes can be readily oxidized through oxygen evolution reaction (OER) on the positive electrode when the applied voltage exceeds the water oxidation potential. As a result, the regions near the electrode surface becomes more acidic, which can chemically degrade electrode materials. Furthermore, oxygen molecules can react with the reduced anode (Na-ion intercalated), thus reducing energy efficiency and causing irreversible capacity loss⁷. Many efforts have been devoted to expanding the voltage window of aqueous electrolytes to enhance the output energy without introducing OER^{4,8,9}. For example, the development of “water-in-salt” Na-ion electrolytes, through reducing free water molecules and enhancing cation-anion associations, enables an enlarged voltage stability window of 2.14 V for the 9.26 m sodium triflate (NaTOf) aqueous electrolyte and achieves a stable output specific energy of 31 Wh/kg at 0.2C for a $\text{Na}_{0.66}[\text{Mn}_{0.66}\text{Ti}_{0.34}]\text{O}_2\|\text{NaTi}_2(\text{PO}_4)_3$ battery⁴. Similarly, other Na salts with high solubility in water, such as sodium perchlorate (NaClO_4)^{6,8,10}, sodium trifluoromethanesulfonimide (NaTFSI) and sodium bis(fluorosulfonyl)imide (NaFSI)^{5,11,12}, have also been used to formulate “water-in-salt” Na-ion electrolytes to improve the performance of aqueous Na-ion batteries. Therefore, avoiding

reaching the OER potential has been a norm for determining the upper cutoff voltage and obtaining stable performance in aqueous batteries.

Managing the cathode-anode crosstalk is another technical challenge in developing aqueous Na-ion batteries with a two-electrode, rocking-chair cell configuration. The Prussian blue ($\text{Na}_x\text{TM}[\text{Fe}(\text{CN})_6]_y$, PB) cathode and Na super ionic conductor $\text{NaTi}_2(\text{PO}_4)_3$ (NTP) anode are promising electrode couples for aqueous Na-ion batteries due to their excellent stability against water and rapid ion transport kinetics^{10,13–15}. A successful integration of these electrodes would lead to full cells with excellent power density and cycle life^{14,16}. However, such a promising full cell system is handicapped by some fundamental challenges. First, the specific capacity, or the cyclable Na ions, of this system is solely dependent on the Na-ion content in the PB cathode. As-synthesized PB materials usually have a high $[\text{Fe}(\text{CN})_6]^{4-}$ vacancy concentration and tend to have Fe in its Fe^{3+} form, which inevitably leads to Na-ion deficiency due to the charge compensation need^{13,17}. Several groups have reported the synthesis of Na-rich PB cathodes by controlling reaction temperature and modulating precursors in the PB synthesis^{13,18,19}. Nevertheless, some of these Na-rich cathodes either lack the measurement in the full cell system or exhibit unsatisfactory full cell performance^{17,20}. Second, PB materials can serve as OER catalysts and induce water oxidation^{21,22}. Depending on the type and concentration of vacancy defects in PB materials, the OER overpotential can range from 258 mV to 334 mV at 10 mA/cm^2 ^{22–24}. Therefore, the conventional wisdom has called for designing Na-rich PB cathodes with poor OER reactivity for constructing aqueous Na-ion full cells. Counterintuitively, can we leverage these fundamental challenges to allow the use of PB cathodes with any Na-ion stoichiometry and still achieve high-capacity full cell performance? Can we take advantage of water oxidation reaction on the positive electrode and Na-ion intercalation into the negative electrode during the formation cycle to

increase cyclable Na ions in the full cell? If successful, our study will allow us to perform two distinct reactions on positive and negative electrodes, namely, surface-mediated electrocatalytic reaction and ion intercalation reaction, respectively. Practically, this study will lead to a new approach to increasing Na-ion inventory for stable, high-capacity batteries.

In this work, we aim to answer these questions by investigating the electrocatalytic and ion intercalation processes in the platform $\text{Na}_x\text{Fe}[\text{Fe}(\text{CN})_6]\|\text{NaTi}_2(\text{PO}_4)_3$ full cell operated in a 17 m NaClO_4 electrolyte. We discover that the electrochemical activation through performing electrocatalytic and ion intercalation reactions during the formation cycle significantly increases cyclable Na ions, leading to a specific discharge capacity improvement from 56 mAh/g to 124 mAh/g. During electrochemical activation, the desodiated PB cathode catalyzes water oxidation and Na ions in the electrolyte intercalate into the Na-vacant sites of NTP anode. Our in-depth synchrotron spectroscopic and imaging studies not only reveal the chemical and structural changes of these electrodes during electrochemical activation but also pinpoint the cathode-electrolyte interfacial reaction initiated by the pH gradient near the cathode surface. This electrochemically activated full cell exhibits an energy density of 57 Wh/kg at 1C and a capacity retention of 63% at 20C after 1000 cycles. This study provides insights into leveraging electrocatalytic reactions in aqueous Na-ion batteries and offers an electrochemical approach to managing ion inventory in rechargeable batteries.

Results and Discussion

Structural and electrochemical characterization of as-synthesized electrodes

The as-synthesized Na-deficient $\text{Na}_x\text{Fe}[\text{Fe}(\text{CN})_6]$ (NaFeHCF) exhibits a typical face-centered cubic crystal structure with an open frame structure comprising N-coordinated high spin Fe and

C-coordinated low spin Fe (**Fig. S1 (a)**). The NaFeHCF particles have a cubic morphology with 500 – 700 nm in size (**Fig. S1 (b)**). The chemical formula of the as-synthesized NaFeHCF is determined to be $\text{Na}_{0.94}\text{Fe}[\text{Fe}(\text{CN})_6]\cdot 2.8\text{H}_2\text{O}$ through the inductively coupled plasma mass spectrometry (ICP-MS) measurement and thermogravimetric analysis (TGA) (**Table S1** and **Fig. S2**). We choose a “water-in-salt” electrolyte (i.e., 17 m NaClO_4) due to its expanded electrochemical stability window allowing for high-voltage charging/discharging of NaFeHCF cathodes. As shown in **Fig. S3**, the electrochemical window of the 17 m NaClO_4 electrolyte reaches ~2.8 V, which is much larger than the theoretical stability window of pure water (~1.23 V). The cyclic voltammetry (CV) profile of NaFeHCF exhibits characteristic peaks for high-spin and low-spin Fe redox couples (**Fig. S1 (c)**), and the galvanostatic charging/discharging shows a specific discharge capacity of 110 mAh/g for the NaFeHCF cathode at 1C (**Fig. S1(d)**). Based on the charge capacity in the first cycle, the cyclable Na ions stoichiometry in the as-synthesized NaFeHCF is calculated to be ~0.75 per chemical formula. The OER starting potential is decreased from 1.75 V of bare current collector (**Fig. S4**) to 1.56 V of as-prepared NaFeHCF electrode, suggesting that NaFeHCF can serve as a catalyst to facilitate water decomposition. Similar measurements conducted on the carbon-coated NTP anode confirm the successful synthesis of $\text{NaTi}_2(\text{PO}_4)_3$, which exhibits a spherical morphology with a diameter of 100-200 nm and delivers a specific charge capacity of 122 mAh/g at 1C (**Fig. S5**).

Electrochemical activation of Na-ion aqueous batteries

In aqueous batteries composed of Na-deficient NaFeHCF cathodes and NTP anodes, the amount of cyclable Na ions is intrinsically limited by the Na-ion stoichiometry in as-synthesized PB cathodes, resulting in inferior specific capacity. We hypothesize that performing electrochemical activation through electrocatalytic OER on the NaFeHCF cathode and ion intercalation reactions

in the NTP anode can increase cyclable Na ions in aqueous batteries. Increasing the cell voltage will thermodynamically enable oxidation on the NaFeHCF cathode and reduction on the NTP anode. The oxidation will start with Na deintercalation from the NaFeHCF lattice, followed by electrocatalytic OER on the cathode. When the negative potential is above the H₂ evolution potential, the reduction will be exclusively limited to Na-ion intercalation in the NTP lattice since there are many Na-ion vacant sites in the as-synthesized NTP. **Fig. 1a** schematically shows such electrocatalytic and ion intercalation processes. The electrochemical reactions in **Table 1** illustrate how such an electrochemical activation method can create more cyclable Na ions to participate in the subsequent traditional cell operation (**Fig. 1b**). In other words, the Na-deficient NaFeHCF cathode can be electrochemically activated through overcharging and later converted to a Na-rich electrode. Therefore, if successful, the electrochemical activation method can increase capacity and energy density of aqueous Na-ion batteries.

Table 1. The hypothesized electrochemical reactions during electrochemical activation This table shows that the Na-ion storage in the full cell is increased from x to $x+2z$ by comparing the pristine cathode and fully discharged cathode, where x represents the original content of Na ions in the pristine NaFeHCF electrode, $2z$ represents the content of introduced Na ions from the electrolyte, and $x+2z$ is smaller than 2.

	Cathode	Anode
Charge	$\text{Na}_x\text{Fe}[\text{Fe}(\text{CN})_6] \longrightarrow \text{Fe}[\text{Fe}(\text{CN})_6] + x \text{Na}^+ + x \text{e}^-$	$\text{NaTi}_2\text{PO}_4 + x \text{e}^- + x \text{Na}^+ \longrightarrow \text{Na}_{1+x}\text{Ti}_2(\text{PO}_4)_3$
Overcharge	$z \text{H}_2\text{O} \longrightarrow 2z \text{H}^+ + z/2 \text{O}_2 + 2z \text{e}^-$	$\text{Na}_{1+x}\text{Ti}_2(\text{PO}_4)_3 + 2z \text{Na}^+ + 2z \text{e}^- \longrightarrow \text{Na}_{1+x+2z}\text{Ti}_2(\text{PO}_4)_3$
Discharge	$\text{Fe}[\text{Fe}(\text{CN})_6] + (x+2z) \text{Na}^+ + (x+2z) \text{e}^- \longrightarrow \text{Na}_{x+2z}\text{Fe}[\text{Fe}(\text{CN})_6]$	$\text{Na}_{1+x+2z}\text{Ti}_2(\text{PO}_4)_3 \longrightarrow \text{NaTi}_2(\text{PO}_4)_3 + (x+2z) \text{Na}^+ + (x+2z) \text{e}^-$

To test our hypothesis, the NaFeHCF||NTP full cell is charged with and without electrochemical activation during the first cycle. **Fig. 1c** displays the first charge-discharge curve of the full cell at 1C from 0.2 V to 2 V in the 17 m NaClO₄ electrolyte, delivering a discharge capacity of 56 mAh/g mainly contributed by the low spin Fe redox couple above 1.0 V. In comparison, the first discharge capacity can reach 124 mAh/g when the full cell is charged to 250 mAh/g in the first charge (i.e., electrochemical activation), where a plateau appears at 2.05 V likely due to water oxidation (**Fig. 1d**). Meanwhile, the unique discharge plateau around 0.8 V suggests that the high spin Fe has become redox active after electrochemical activation. The electrochemically activated full cell shows negligible capacity decay within 100 cycles at 1C after the voltage window is switched to 0.2 V to 2 V (discussed in Battery performance section).

Figure 1. The reaction scheme and performance of NaFeHCF||NTP full cell with electrochemical activation (a) The scheme of redox reactions on both electrodes upon electrochemical activation. Light blue arrow suggests the direction of Na-ion transport. The content in the blue dashed frame indicates that water oxidation occurs on the NaFeHCF cathode surface while the yellow dashed frame shows that Na ions in the electrolyte intercalate into NTP anode; (b) The scheme of redox reactions on both electrodes upon discharging. The excess Na ions induced by electrochemical activation in the NTP anode are extracted and inserted into cathode during discharging, resulting in the enriched Na-ion storage in the fully discharged NaFeHCF cathode compared to the pristine material; (c) The first charge-discharge curve of NaFeHCF||NTP

full cell without electrochemical activation in the first charge. The voltage window is 0.2 V – 2 V and the current rate applied to the cell is 1C (170 mA/g-cathode). Such cell exhibits inferior specific capacity of 56 mAh/g; (d) The first charge-discharge curve of NaFeHCF|NTP full cell with electrochemical activation in the first charge. The cell is overcharged to 250 mAh/g upon first cycle and normal charging protocol (0.2 V – 2V) is applied to the following cycles. Such cell exhibits superior specific capacity of 124 mAh/g. The specific capacity is calculated based on the mass of active cathode.

Na-ion stoichiometry and structural changes of electrodes during electrochemical activation

To understand the mechanism underlying the improved performance of NaFeHCF|NTP full cell after electrochemical activation, we first use X-ray diffraction (XRD) to measure the structural evolution of both electrodes during the first cycle. As shown in **Fig. 2a**, the cubic phase of the as-synthesized NaFeHCF cathode is converted to a monoclinic phase at the end of discharge, which implies that the crystal lattice can accommodate more Na ions, resulting in a low symmetry structure. The X-ray absorption near-edge structure (XANES) in **Fig. 2c** demonstrates that, the Fe in NaFeHCF is oxidized during normal charging while exhibits negligible change in terms of oxidation states upon electrochemical activation process. After the first complete cycle, the Fe K-edge of the discharged NaFeHCF (“0.2 V DC”) shifts to an even lower energy compared to that of the as-synthesized NaFeHCF (**Fig. 2d**), showing that Fe oxidation state is lowered, and the Na-ion stoichiometry is increased in the NaFeHCF cathode in the discharged state. Moreover, the newly appeared shoulder peak at about 7118 eV for the discharged NaFeHCF can be attributed to the 1s to 4p transition followed by ligand-to-metal charge transfer (LMCT), which suggests a strong covalent bonding between Fe ions and CN ligands. Since this pre-edge feature is mostly

observed in Na-rich PB materials with low Fe oxidation states²⁵, we can confirm that the discharged NaFeHCF cathode has become Na-rich.

The NTP anode experiences solid-solution reactions in the first cycle. The lattice structure exhibits a typical expansion-contraction behavior upon sodiation-desodiation (**Fig. 2b**), suggesting a reversible redox reaction in the anode. Meanwhile, the Ti K-edge XANES reveals that Ti is continuously reduced during electrochemical charging (from pristine to 250 mAh/g) (**Fig. 2f**), which suggests that Na-ion intercalation takes place in the NTP anode throughout the process. The Ti reduction also leads to longer Ti-O bond lengths, which is quantified by the EXAFS analysis (**Fig. 2h**) and is in good agreement with the XRD results (**Fig. 2b**). Furthermore, energy-dispersive X-ray spectroscopy (EDS) measurements reveal the Na/Ti atomic ratio of NTP anodes at different states of charge and discharge. Four regions are measured for each electrode using SEM-EDS and the averaged results are summarized in **Fig. 2g**. The Na/Ti atomic ratio continuously increases upon cell normal charging and electrochemical activation, which directly shows that, as we have hypothesized, the Na-ion is intercalated to the NTP anode to complete the full cell reaction. The higher Na/Ti atomic ratio at the cell discharged state compared to the as-synthesized NTP shows that there are still excess Na ions stored in the NTP anode. The NaFeHCF cathode has run out of cyclable Na ions after 70 mAh/g in the first charging of the NaFeHCF||NTP full cell, thus additional Na ions can only be acquired from the aqueous electrolyte. The Na-ion concentration in the electrolyte is 17 m, which is well beyond the critical “WIS” criterion (8.19 m). Therefore, such an additional Na-ion intercalation would show negligible impact on the electrolyte concentration and the electrolyte voltage stability window.

Pathways of redox reactions during electrochemical activation

Redox reactions during electrochemical activation are complicated due to the presence of electrocatalysis, ion intercalation, and interfacial side reactions. Understanding the pathways of redox reactions can inform the improvement of electrochemical activation. For the NaFeHCF cathode, the XRD and XANES results show that, during the electrochemical activation (from 70 mAh/g to 250 mAh/g in the first charge), although the oxidation state of Fe is unchanged (**Fig. 2d**), crystal lattice exhibits expansion behavior (**Fig. 2a**). Considering that OER generates protons near the electrode surface (**Fig. 1a** and **Table 1**) and builds up a pH gradient across the cathode-electrolyte interface, we conjecture that lattice variation is mediated by OER. The EXAFS results of Fe K-edge show three major peaks around 1.34, 2.42 and 4.60 Å, corresponding to scattering path of shorter Fe-C (N), longer Fe-N(C) and Fe-Fe shells, respectively (**Fig. 2e**). The peak located at 1.9 Å, which has been observed in other PB materials^{25,26}, is likely associated with the twisted local structure surrounding the central Fe atom owing to some residual Na ions in NaFeHCF. Further comparison regarding the Fe oxidation state between charged NaFeHCF and as-prepared Na-free FeHCF reference supports our speculation (**Fig. S6**). After electrochemical activation process (250 mAh/g), the intensity of Fe-C and Fe-N peaks decreases. This result implies that, as previously reported^{23,24}, the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ group in PB materials is sensitive to the pH value in the solution and can potentially dissolve into electrolytes during OER, leading to the variation of chemical and structural environment surrounding Fe atoms.

Therefore, we further perform synchrotron X-ray fluorescence microscopy (XFM) on battery separators to quantify transition metal dissolution from the electrodes. We collect separators from battery cells at different states of charge (SOCs) to investigate Fe and Ti dissolution. Upon charging the cell to 70 mAh/g, both cathode and anode show no discernable TM dissolution (**Fig. S7**). However, upon electrochemical activation, Fe in the NaFeHCF cathode undergoes more

severe dissolution, whereas Ti in the NTP anode is more stable. The areal concentration of dissolved Fe species is determined to be $3.78 \pm 1.52 \mu\text{g}/\text{cm}^2$ after the complete electrochemical activation to 250 mAh/g. Moreover, transmission electron microscopy (TEM) images show the evolution of the NaFeHCF particle morphology after electrochemical activation (**Fig. S8**). The particles transform from cubic-shaped crystals in the as-synthesized state to irregular-shaped crystal after electrochemical activation, which is associated with the Fe dissolution behavior. The EXAFS results together with XFM and TEM analyses confirm the occurrence of Fe leaching and accompanied structural and morphological variation.

Figure 2. Structural evolution and charge compensation mechanism upon electrochemical activation (a) Ex-situ synchrotron XRD patterns of the NaFeHCF cathode. Normal charging

indicates the capacity increasing from pristine to 70 mAh/g, while electrochemical activation indicates the capacity increasing from 70 mAh/g to 250 mAh/g. DC denotes state of discharge to different voltages. (b) Ex-situ synchrotron XRD patterns of the NTP anode. Reversible lattice expansion and contraction is observed during electrochemical cycling. (c) Fe K-edge XANES spectra of the NaFeHCF cathode at different charging and discharging states; (d) Zoom-in of Fe K-edge XANES spectra; (e) Fourier-transformed magnitude of Fe K-edge EXAFS spectra of the NaFeHCF cathode at pristine and different charging states; (f) Ti K-edge XANES spectra of NTP anode at different charging and discharging states. The result of 150 mAh/g is close to the result of 0.2 V DC, which suggests that the Ti^{3+} is not completely oxidized to Ti^{4+} and there are some residual Na ions in NTP anode; (g) Na/Ti atomic ratio of the NTP anode during cycling determined by SEM-EDS measurements. The error bars show the standard deviation of four independent measurements; (h) Fourier-transformed magnitude of Ti K-edge EXAFS spectra of the NTP anode at pristine and different charging states.

We employ a transparent two-electrode cell to directly visualize OER (**Fig. S9**) and investigate the electron pathways on both electrodes during electrochemical activation using synchrotron X-ray spectroscopy. Here we apply Na-free FeHCF (see Experimental Methods for synthesis details) as the cathode to eliminate Fe oxidation so that the charge capacity is solely contributed by OER in the first charge of the FeHCF||NTP cell. We use the same NTP electrode and 17m NaClO_4 as the counter/reference electrode and electrolyte, respectively. After we apply the electrochemical activation protocol to this cell, the charging voltage profile exhibits a plateau feature at 2.3 V (**Fig. S10**), which is higher than the plateau we observe in the coin cell platform (~ 2.05 V). The larger overpotential can be attributed to the kinetic barrier caused by the larger electrolyte resistance (thicker electrolyte) in the two-electrode platform. The bubble evolution on the electrodes can be

tracked using the glassware platform (**Supplemental Movie 1 and 2**). **Fig. 3a – 3d** show the snapshots of the pristine and electrochemically activated cells, with regions of interest labeled in the photos. Gas bubbles appear on the front and back sides of FeHCF cathode upon electrochemical activation (**Fig. 3b and 3d**), confirming the generation of oxygen gas. In contrast, no gas bubble was observed on either side of the NTP anode upon electrochemical activation, indicating that hydrogen evolution reaction (HER) does not occur on the NTP surface. Therefore, these results further confirm that the reduction on the NTP anode takes place through Na-ion intercalation.

We further perform hard XAS measurements on pristine electrodes and electrodes collected from the electrochemically activated cell. **Fig. 3e-3f** reveal that the Fe K-edge energy in the Na-free FeHCF cathode has negligible change whereas the peak intensity of Fe-C(N) shell declines after electrochemical activation, which is consistent with those measured using the NaFeHCF||NTP cell platform. Furthermore, we observe Ti reduction in the NTP anode (**Fig. 3g and 3h**), which further confirms that Na-ion intercalation in the anode is accessible when the Na-free FeHCF cathode is used during electrochemical activation. In summary, electrons released by OER on the cathode enable complete reduction reaction of NTP anode through Na-ion intercalation at the expense of partial structural distortion of FeHCF cathode.

Figure 3. Reaction pathways during electrochemical activation (a) The appearance of the front side of the FeHCF cathode and the back side of the NTP anode in the pristine state; (b) The appearance of the front side of the FeHCF cathode and the back side of the NTP anode in the electrochemically activated state; (c) The appearance of the back side of the FeHCF cathode and

the front side of the NTP anode in the pristine state; (d) The appearance of the back side of the FeHCF cathode and the front side of the NTP anode in the electrochemically activated state. The bubble formation on the cathode confirms the occurrence of OER while HER is not observed on the NTP anode; The Fe K-edge (e) XANES spectra and (f) EXAFS spectra of pristine and electrochemically activated FeHCF cathode; The Ti K-edge (g) XANES spectra and (h) EXAFS spectra of pristine and electrochemically activated NTP anode.

Battery performance of electrochemically activated NaFeHCF||NTP full cells

To understand the practical impact of the electrochemical activation protocol, we measure battery performance at different C rates. We expect that at low C rates electrode-electrolyte side reactions are kinetically favored thus leading to lower Coloumbic efficiency, whereas at high C rates these reactions are kinetically limited. Hence, high current rate is usually preferred in aqueous batteries because of not only the excellent ionic conductivity of aqueous electrolyte but also suppressed side reactions. Here we investigate how the electrochemically activated cell may respond differently to various C rates in terms of capacity, Coulombic efficiency, and cycle life.

Fig. 4a and **4b** exhibit the battery performance of NaFeHCF||NTP full cells with normal charging protocol and with electrochemical activation in the first charge, respectively. The cell without electrochemical activation delivers inferior discharge capacity but retains good Coulombic efficiency (~97%) during the first 100 cycles at 1C. In comparison, the cell with electrochemical activation shows significantly improved discharge capacity (110 mAh/g @ 2nd cycle) and a 98% capacity retention within 100 cycles at 1C. Note that the electrochemical activation process introduces excess Na ions into NTP anode, it can potentially serve as a Na-ion reservoir to compensate the Na loss during electrochemical cycling, which promotes a more stable performance. However, the Coulombic efficiency drops to ~90% in the electrochemically

activated cell, indicating that, as we expected, oxygen molecules accompanied by Fe dissolution on the cathode leads to the energy inefficiency.

The electrochemically activated NaFeHCF||NTP full cell displays an excellent rate capability (**Fig. 4c**). Specifically, the cell delivers a discharge capacity of ~ 120 mAh/g-cathode at 1C from 0.2 V to 2 V and still retains 101 mAh/g at 10C, with high Coulombic efficiency of $\sim 99\%$. At high C rates, side reactions are inhibited, and thus Coulombic efficiency is improved. The battery testing results at different C rates demonstrate the electrochemical activation method can be applied to fast charging, high power batteries. The Ragone plots show that the electrochemically activated NaFeHCF||NTP cell is superior to or on par with the performance that the literature has demonstrated for Na-rich PB/NTP systems^{13,14,16}. Our NaFeHCF||NTP full cell delivers a specific energy of 57 Wh/kg at a specific power of 64 W/kg and still maintain a specific energy of 48 Wh/kg at a specific power of 626 W/kg (**Fig. 4d**). Furthermore, the electrochemically activated NaFeHCF||NTP full cell demonstrates good cycle life, with a high discharge capacity of 102 mAh/g at 20C and a capacity retention of 63% after 1000 cycles (**Fig. 4e**). In summary, the electrochemically activated NaFeHCF||NTP cell exhibits significantly improved discharge capacity and energy compared to the baseline cell. The performance improvement becomes more meaningful in fast-charging, high-power applications.

Figure 4. The performance of electrochemically activated NaFeHCF/NTP full cell. First 100 cycles of full cell at 1C (a) without and (b) with electrochemical activation; (c) Typical charge-discharge curves of the full cell at 1C, 2C, 5C and 10C rates, where the inset shows the variation of Coulombic efficiency at different C rates; (d) Ragone plot shows the comparison of output specific power and energy for the full cell with reported Na-rich PB/NTP aqueous full cells, the energy and power densities of full cells are calculated based on the total mass of the active cathode and anode; (e) Long-term cycling performance of the electrochemically activated NaFeHCF/NTP

full cell at 20°C. Beyond electrochemical activation in the first cycle, all of the batteries were measured at 0.2-2 V. 1C is defined as 170 mA/g.

Conclusion

Understanding and tailoring electrocatalytic reactions is a long-standing scientific challenge in the development of advanced aqueous batteries. At the single electrode level, electrocatalytic reactions compete with ion intercalation reactions, which negatively impacts battery performance such as capacity and cycle life. In this study, we perform OER electrocatalytic reaction and Na-ion intercalation simultaneously in full cell aqueous Na-ion batteries, as an electrochemical activation approach to improving battery performance. Through systematic chemical, structural, and electrochemical analyses, we conclude that such an electrochemical activation method can effectively mitigate the ion inventory issue in full cell batteries, especially those based on high-concentration electrolytes, such as “water-in-salt” electrolytes. Specifically, in our Na-deficient NaFeHCF||NTP platform, charging NaFeHCF beyond the Na-ion deintercalation potential leads to catalytic water oxidation on the desodiated NaFeHCF electrode. Meanwhile, Na-ion intercalation takes place in the NTP anode, with Na ions desolvated from the electrolyte. This electrochemical activation significantly increases cyclable Na ions in the full cell, resulting in a significant boost of initial specific discharge capacity from 56 mAh/g to 124 mAh/g. Due to the favorable structural and chemical reversibility of electrode materials, the electrochemically activated cell offers a higher specific energy and power, and better cycle life. We expect that in alkali battery cells where slight decomposition of electrolyte is not a concern, such as “water-in-salt” electrolyte studied herein, the electrochemical activation protocol can be applied to resolve the challenges surrounding ion loss in alkali ion batteries. One may be able to perform intermittent electrochemical activation to compensate ion loss during the long-term operation of batteries. We

also recognize that the interfacial electrocatalytic process may compromise the stability of electrode materials. For example, the pH gradient created at the cathode-electrolyte interface during electrocatalytic reactions may distort the lattice structure of cathode and promote Fe dissolution. Nevertheless, this interfacial side reaction is mitigated at high current densities, shedding light on using the electrochemical activation approach for fast-charging, high-power batteries. For practical batteries, the generated oxygen gas may be vented after electrochemical activation in the first cycle or captured by oxygen scavengers in the cell. In summary, this study creates fundamental insights into the impact of electrocatalytic reaction on intercalation chemistry and provides a strategy to manipulate ion inventory and storage in aqueous batteries.

Experimental Section

Material synthesis:

The $\text{Na}_x\text{Fe}[\text{Fe}(\text{CN})_6]$ (NaFeHCF) was synthesized through a co-precipitation method. First, 0.75 g carbon black power was added to 100 mL deionized water and sonicated for 2 hours to obtain homogenous solution. Then, 10 mmol $\text{Na}_4[\text{Fe}(\text{CN})_6]$ and 1 mL concentrated hydrochloric acid were dissolved in the as-prepared solution. The mixture was continuously stirred at 60°C for 8 hours. Finally, the composite was washed with deionized water three times, filtered, and dried in the vacuum oven at 100°C for 12 hours. The Na-free FeHCF was synthesized by using $\text{K}_3[\text{Fe}(\text{CN})_6]$ as a single ion source. Typically, 10 mmol $\text{K}_3[\text{Fe}(\text{CN})_6]$ and 1 mL concentrated hydrochloric acid were added to 100 mL deionized water. Then the mixture was heated at 60°C for 8 hours under vigorous stirring. The precipitates were washed with deionized water three times, filtered, and dried at 120°C for 12 hours to obtain the FeHCF product. NTP material was synthesized through the solid-state method. First, stoichiometric amounts of $\text{NH}_4\text{H}_2\text{PO}_4$, Na_2CO_3 and TiO_2 were ball-milled with acetone at a rate of 500 rpm for 8 hours. The mixed precursors were dried in the vacuum oven at 60°C for 12 hours and heated at 900°C for 24 hours in a box furnace. The product was mixed with sucrose, ball-milled at a rate of 500 rpm for 2 hours and calcined in the tube furnace at 850°C for 2 hours to obtain the final $\text{NaTi}_2(\text{PO}_4)_3/\text{C}$ product.

Electrochemical measurements:

To prepare the composite electrodes for three-electrode measurements, poly(vinylidene difluoride, as the binder) (PVDF) was first dissolved into N-methyl-2-pyrrolidone, then the active material (NaFeHCF or NTP) and acetylene carbon were added into the solution and thoroughly mixed, following the weight ratio of active material: PVDF: acetylene carbon = 8:1:1. The electrode slurry

was drop casted onto the carbon paper (Toray Carbon Paper 090, The Fuel Cell Store) and dried in air. The aqueous electrolytes used here was 17 m NaClO₄, which was prepared by dissolving 17 mol NaClO₄ salt in 1 L water. The three-electrode cell was constructed using NaFeHCF composite (3.2 mg/cm²) or NTP composite (3.6 mg/cm²) electrode as the working electrode, Pt foil as the counter electrode, and standard calomel electrode (SCE) as the reference electrode. The transparent two-electrode cell contains FeHCF as the working electrode (3.2 mg/cm²), and NTP (3.6 mg/cm²) as the counter/reference electrode. The mass ratio of FeHCF/NTP is 1/2.2 by controlling the area of electrodes. Both cyclic voltammetry (CV) and galvanostatic cycling with potential limitation (GCPL) measurements were conducted on a potentiostat (SP-150, Biologic, France). To prepare composite electrodes for full cell testing, polytetrafluoroethylene (PTFE) was thoroughly mixed with active materials (NaFeHCF or NTP) and acetylene black, following the weight ratio of active material: PTFE: acetylene black = 8: 1: 1. The mixture was compressed on a stainless-steel grid. The fabricated electrodes were used as cathodes and anodes, separately, with the Whatman glass fiber (1827-047934-AH) as the separator. The full aqueous Na-ion cells were assembled in CR2032-type coin cells and galvanostatically charged/discharged on electrochemical workstations (Wuhan Land Company). The mass ratio of NaFeHCF/NTP is 1/1.8, the mass loading of NaFeHCF is 3.2 mg/cm² and the mass loading of NTP is 4.5 mg/cm². 1C corresponds to the specific current rate of 170 mA/g.

Materials characterization:

The morphology of the materials was characterized on a LEO 1550 field-emission scanning electron microscopy (SEM) with an accelerating voltage of 6 kV. EDS measurements were carried out with the SEM with an accelerating voltage of 20 kV. The lab X-ray diffraction (XRD) results were obtained on a Rigaku Miniflex II diffractometer with a Cu K α X-ray radiation ($\lambda = 1.54 \text{ \AA}$)

in a scan range of 10-60°. ICP-MS measurements were performed on a Thermo Electron ICAP-RQ spectrometer (Thermo Fisher). TEM images were acquired from a JOEL 2100 Cryo transmission electron microscope at an acceleration voltage of 200 kV. The synchrotron XRD patterns were collected at the beamline 11-3 of SSRL at SLAC National Accelerator Laboratory with the X-ray wavelength of 0.9762 Å. A LaB₆ sample was used to calibrate the diffraction configuration. The XRD patterns were converted to the Cu K α -based XRD with the wavelength of 1.5406 Å. The hard XAS measurements were carried out at beamline 7-BM (QAS) of the NSLS-II at Brookhaven National Laboratory, except for the data collected for ex-situ NaFeHCF in Figure 2b-2d, which were collected at beamline 20-ID at the Advanced Photon Source, Argonne National Laboratory. Both the Fe and Ti K-edge spectra were collected in the fluorescence mode, with the samples aligned at an angle of ~45° with respect to the incident beam and the Lytle detector. The XANES and EXAFS data were analyzed with the ATHENA software. The energy calibration was carried out using the first inflection point of the Ti or Fe K-edge spectra of the transition metal foil as a reference. The samples for hard XAS and synchrotron XRD were sealed with Kapton tapes and stored in Ar-filled glove box before measurements. XFM measurements were conducted at the 2-ID-E beamline at the Advanced Photon Source, Argonne National Laboratory. The samples were raster-scanned by a sub-micrometer focused 10-keV X-ray beam with a step size of 10 μ m. The fluorescent X-rays were detected with a four-element silicon-drift Vortex detector and the raw data were processed and quantified with MAPS.

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Conflict of interest:

The authors declare no conflict of interest.

Author contribution:

F.L. conceived and led the project. Y.Z. and F.L. designed experiments. Y.Z. performed material synthesis, characterization, and electrochemical experiments. L. Ma., S. T., E.H., I.H. and C.S. performed hard XAS. A.H. performed lab XRD and SEM-EDS. L. Mu. performed TEM. L.L. performed XFM. C.K. and M.M. performed synchrotron XRD. Y.Z. and F.L. wrote the manuscript with the help from all coauthors.

References

1. Jin, T. *et al.* Realizing Complete Solid-Solution Reaction in High Sodium Content P2-

- Type Cathode for High-Performance Sodium-Ion Batteries. *Angew. Chemie* **132**, 14619–14624 (2020).
2. Lee, M. *et al.* High-performance sodium–organic battery by realizing four-sodium storage in disodium rhodizonate. *Nat. Energy* **2**, 861–868 (2017).
 3. Zhu, Y. *et al.* Red phosphorus–single-walled carbon nanotube composite as a superior anode for sodium ion batteries. *ACS Nano* **9**, 3254–3264 (2015).
 4. Suo, L. *et al.* “Water-in-Salt” Electrolyte Makes Aqueous Sodium-Ion Battery Safe, Green, and Long-Lasting. *Adv. Energy Mater.* **7**, 1701189 (2017).
 5. Kühnel, R.-S., Reber, D. & Battaglia, C. A high-voltage aqueous electrolyte for sodium-ion batteries. *ACS Energy Lett.* **2**, 2005–2006 (2017).
 6. Nakamoto, K., Sakamoto, R., Ito, M., Kitajou, A. & Okada, S. Effect of concentrated electrolyte on aqueous sodium-ion battery with sodium manganese hexacyanoferrate cathode. *Electrochemistry* **85**, 179–185 (2017).
 7. Luo, J.-Y., Cui, W.-J., He, P. & Xia, Y.-Y. Raising the cycling stability of aqueous lithium-ion batteries by eliminating oxygen in the electrolyte. *Nat. Chem.* **2**, 760–765 (2010).
 8. Lee, M. H. *et al.* Toward a low-cost high-voltage sodium aqueous rechargeable battery. *Mater. Today*. **29**, 26–36 (2019).
 9. Jiang, L. *et al.* High-Voltage Aqueous Na-Ion Battery Enabled by Inert-Cation-Assisted Water-in-Salt Electrolyte. *Adv. Mater.* **32**, 1904427 (2020).
 10. Nakamoto, K., Sakamoto, R., Sawada, Y., Ito, M. & Okada, S. Over 2 V Aqueous

- Sodium-Ion Battery with Prussian Blue-Type Electrodes. *Small Methods* **3**, 1800220 (2019).
11. Zheng, Q. *et al.* Sodium-and Potassium-Hydrate Melts Containing Asymmetric Imide Anions for High-Voltage Aqueous Batteries. *Angew. Chemie Int. Ed.* **58**, 14202–14207 (2019).
 12. Reber, D., Kühnel, R.-S. & Battaglia, C. Suppressing crystallization of water-in-salt electrolytes by asymmetric anions enables low-temperature operation of high-voltage aqueous batteries. *ACS Mater. Lett.* **1**, 44–51 (2019).
 13. Wu, X. *et al.* Vacancy-Free Prussian Blue Nanocrystals with High Capacity and Superior Cyclability for Aqueous Sodium-Ion Batteries. *ChemNanoMat* **1**, 188–193 (2015).
 14. Wu, X., Cao, Y., Ai, X., Qian, J. & Yang, H. A low-cost and environmentally benign aqueous rechargeable sodium-ion battery based on $\text{NaTi}_2(\text{PO}_4)_3\text{--Na}_2\text{NiFe}(\text{CN})_6$ intercalation chemistry. *Electrochem. Commun.* **31**, 145–148 (2013).
 15. Li, Z., Young, D., Xiang, K., Carter, W. C. & Chiang, Y. Towards high power high energy aqueous sodium-ion batteries: the $\text{NaTi}_2(\text{PO}_4)_3/\text{Na}_{0.44}\text{MnO}_2$ system. *Adv. Energy Mater.* **3**, 290–294 (2013).
 16. Wu, X. *et al.* Energetic Aqueous Rechargeable Sodium-Ion Battery Based on $\text{Na}_2\text{CuFe}(\text{CN})_6\text{--NaTi}_2(\text{PO}_4)_3$ Intercalation Chemistry. *ChemSusChem* **7**, 407–411 (2014).
 17. Wu, X. *et al.* Low-defect Prussian blue nanocubes as high capacity and long life cathodes for aqueous Na-ion batteries. *Nano Energy* **13**, 117–123 (2015).
 18. You, Y., Wu, X.-L., Yin, Y.-X. & Guo, Y.-G. High-quality Prussian blue crystals as

- superior cathode materials for room-temperature sodium-ion batteries. *Energy Environ. Sci.* **7**, 1643–1647 (2014).
19. Yang, Y. *et al.* Influence of structural imperfection on electrochemical behavior of Prussian blue cathode materials for sodium ion batteries. *J. Electrochem. Soc.* **163**, A2117–A2123 (2016).
 20. Pasta, M. *et al.* Full open-framework batteries for stationary energy storage. *Nat. Commun.* **5**, 3007 (2014).
 21. Su, X. *et al.* Operando spectroscopic identification of active sites in NiFe prussian blue analogues as electrocatalysts: activation of oxygen atoms for oxygen evolution reaction. *J. Am. Chem. Soc.* **140**, 11286–11292 (2018).
 22. Pintado, S., Goberna-Ferrón, S., Escudero-Adán, E. C. & Galán-Mascarós, J. R. Fast and persistent electrocatalytic water oxidation by Co–Fe Prussian blue coordination polymers. *J. Am. Chem. Soc.* **135**, 13270–13273 (2013).
 23. Yu, Z.-Y. *et al.* Unconventional CN vacancies suppress iron-leaching in Prussian blue analogue pre-catalyst for boosted oxygen evolution catalysis. *Nat. Commun.* **10**, 1–9 (2019).
 24. Han, L. *et al.* Enhanced activity and acid pH stability of Prussian blue-type oxygen evolution electrocatalysts processed by chemical etching. *J. Am. Chem. Soc.* **138**, 16037–16045 (2016).
 25. You, Y., Yu, X., Yin, Y., Nam, K.-W. & Guo, Y.-G. Sodium iron hexacyanoferrate with high Na content as a Na-rich cathode material for Na-ion batteries. *Nano Res.* **8**, 117–128

(2015).

26. Xie, B. *et al.* Achieving long-life Prussian blue analogue cathode for Na-ion batteries via triple-cation lattice substitution and coordinated water capture. *Nano Energy* **61**, 201–210 (2019).

Supplementary Information

Manipulating electrocatalytic reaction and ion intercalation to improve aqueous batteries

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Figure S1. (a) XRD pattern and (b) SEM image of the as-synthesized NaFeHCF material, which exhibits cubic crystal structure and cube-like morphology. The NaFeHCF was synthesized with the presence of carbon black; (c) Cyclic voltammetry profile of NaFeHCF at a scan rate of 10 mV/s in 17 m NaClO₄ electrolyte. OER started from where the arrow indicated (1.56 V); (d) The first, second and fifth charge-discharge curves of the NaFeHCF electrode at 1C from -0.15 V to 1.25 V (versus SCE) in 17 m NaClO₄ electrolyte using a three-electrode cell configuration.

Figure S2. Thermogravimetric analysis (TGA) for the NaFeHCF sample. The TGA was performed at a heating rate of 10°C/min under N₂ gas flow. The NaFeHCF sample shows two different slopes from room temperature to 250°C, which corresponds to 3% adsorbed water and 5% interstitial water.

Figure S3. The electrochemical stability window for 17 m NaClO₄ electrolyte determined by CV measurements on carbon rod at a scan rate of 10 mV/s. The electrochemical window is expanded to 2.8 V (versus SCE).

Figure S4. Cyclic voltammetry profile of bare carbon paper at a scan rate of 10 mV/s in 17 m NaClO₄ electrolyte. OER started from where the arrow indicated (1.75 V). When NaFeHCF material is casted on the carbon paper, the OER potential is lowered to 1.56 V, suggesting that NaFeHCF can catalyze water decomposition. The reduction peak located at ~1.5 V is attributed to the redox-active impurities in the pristine carbon paper.

Figure S5. (a) XRD pattern and (b) SEM image of the as-prepared NTP material, which exhibits spherical morphology and a trigonal crystal structure; (c) Cyclic voltammetry profiles of NTP at different scan rates (from 1 mV/s to 100 mV/s) in 17 m NaClO_4 electrolyte, showing reversible redox reaction of $\text{Ti}^{3+}/\text{Ti}^{4+}$; (d) The first, second and fifth charge-discharge curves of the NTP electrode at 1C from -0.85 V to -0.55 V (versus SCE) in 17 m NaClO_4 electrolyte using a three-electrode cell configuration.

Fig S6. The Fe K-edge XANES spectra of charged NaFeHCF and as-prepared Na-free FeHCF. The Fe K-edge energy of charged NaFeHCF is lower than as-prepared FeHCF, which suggests there are still some residual Na ions in the fully-charged NaFeHCF cathode.

Figure S7. The evolution of (a) Fe and (b) Ti dissolution and deposition on separators upon charging and electrochemical activation process determined by XFM measurements. The side that faces NTP was measured to investigate the Fe dissolution and deposition while the side that faces NaFeHCF was measured to investigate the Ti dissolution and deposition. These data suggest that some Fe species in the NaFeHCF is dissolved upon electrochemical activation whereas Ti species in the NTP remains stable during electrochemical cycling.

Figure S8. TEM images of (a-b) pristine and (c-d) electrochemically activated NaFeHCF particles, showing a particle morphology evolution from cubic shape to irregular shape after catalyzing OER. The morphological change implies the occurrence of Fe leaching, as discussed in the main text.

Figure S9. Optical graph of the transparent two-electrode glassware cell

Figure S10. The charging curve of two-electrode glassware cell from 0.2 V to 2.5 V in 17 m NaClO₄ electrolyte, where the plateau located at 2.3 V corresponds to the oxygen evolution reaction. The mass ratio of FeHCF/NTP is 1/2.2.

Table S1. ICP result on Fe and Na for NaFeHCF sample

Element	Na (ppb)	Fe (ppb)
Concentration	892.5	4620.4

Movie S1. Bubble evolution on the front side of FeHCF cathode (left region of the video) and back side of NTP anode (right region of the video) during electrochemical charging (activation) process. Bubble formation is observed only on the front side of FeHCF cathode.

Movie S2. Bubble evolution on the back side of FeHCF cathode (right region of the video) and front side of NTP anode (left region of the video) during electrochemical charging (activation) process. Bubble formation is observed only on the back side of FeHCF cathode.

Both videos confirm that OER occurs on the FeHCF cathode while HER does not occur on the NTP anode.