

## **Supporting Information**

### **Mechanistic Insights into the Interplay between Ion Intercalation and Water Electrolysis in Aqueous Batteries**

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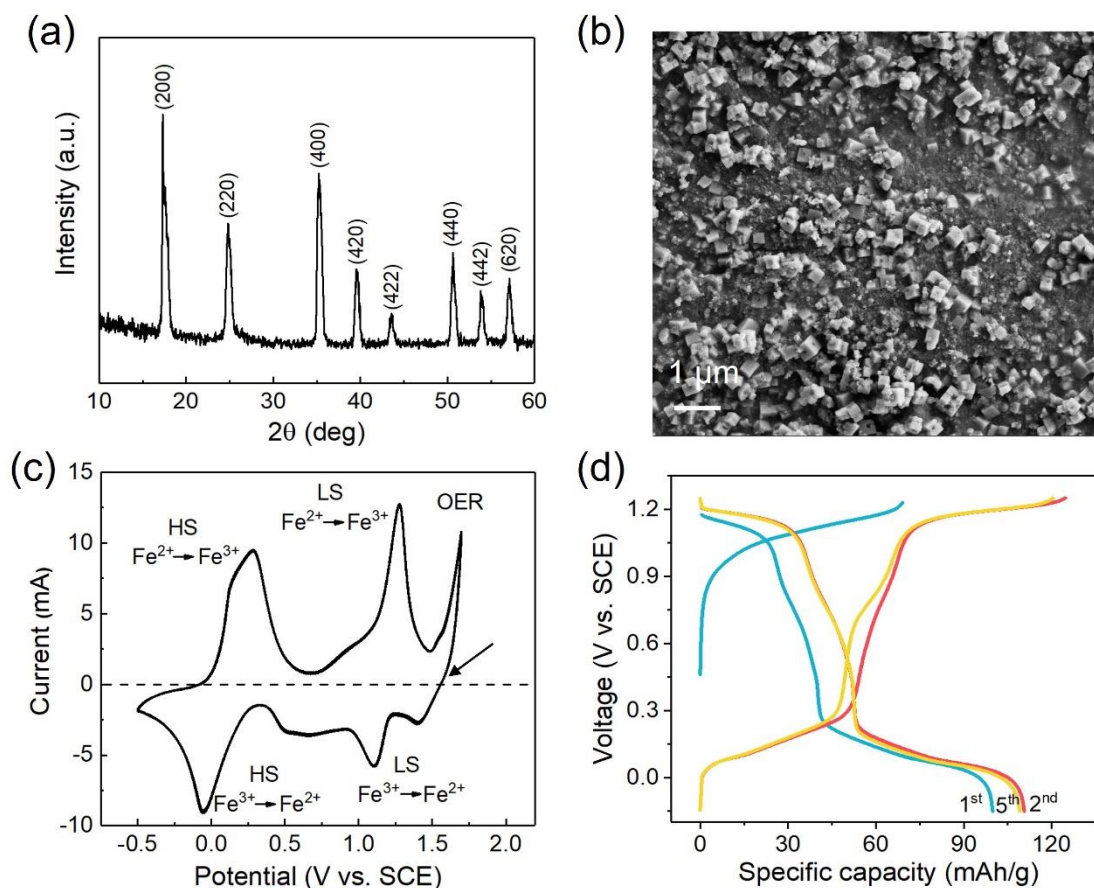
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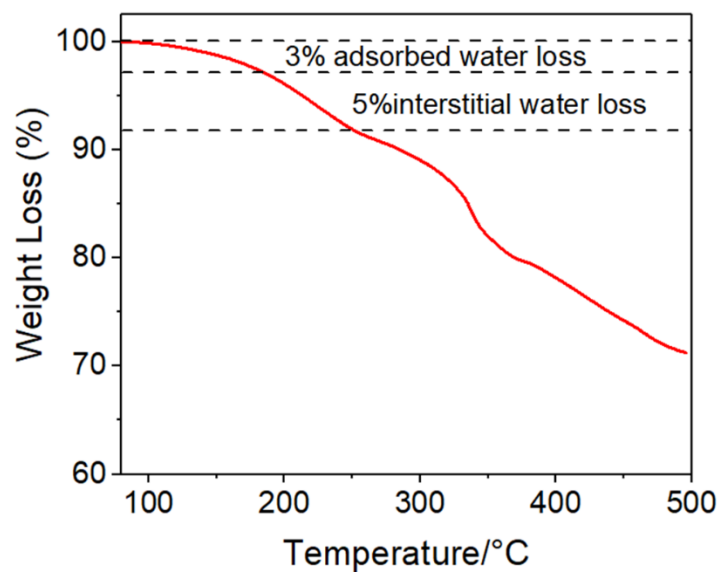
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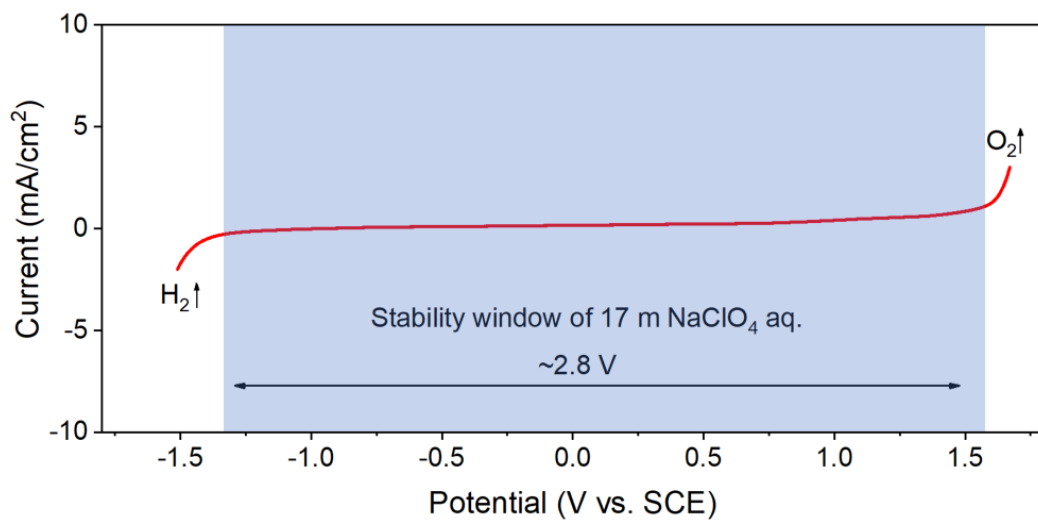
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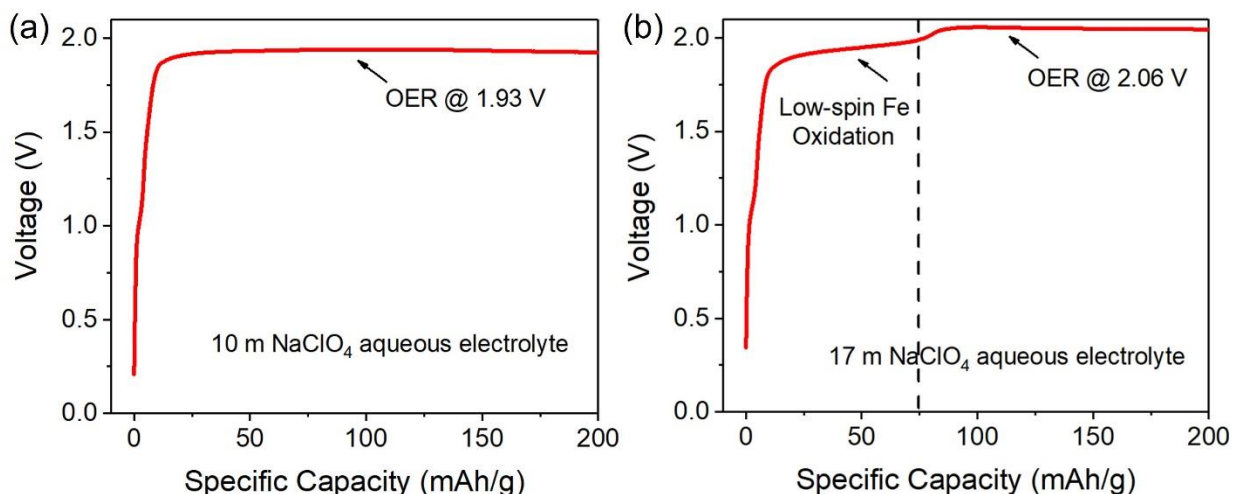
**Figure S1.** (a) XRD pattern and (b) SEM image of the as-synthesized NaFeHCF material, which exhibits cubic crystal structure and cube-like morphology. The NaFeHCF was synthesized with the presence of carbon black; (c) Cyclic voltammetry profile of NaFeHCF at a scan rate of 10 mV/s in 17 m NaClO<sub>4</sub> electrolyte. OER started from where the arrow indicated (1.56 V vs. SCE). The N<sub>2</sub> is purged into the electrolyte for 2 hours before measurement. Then the CV profile is tested under ambient condition. The scan initiates from positive direction; (d) The first, second and fifth charge-discharge curves of the NaFeHCF electrode at 1C from -0.15 V to 1.25 V (vs. SCE) in 17 m NaClO<sub>4</sub> electrolyte using a three-electrode cell configuration.



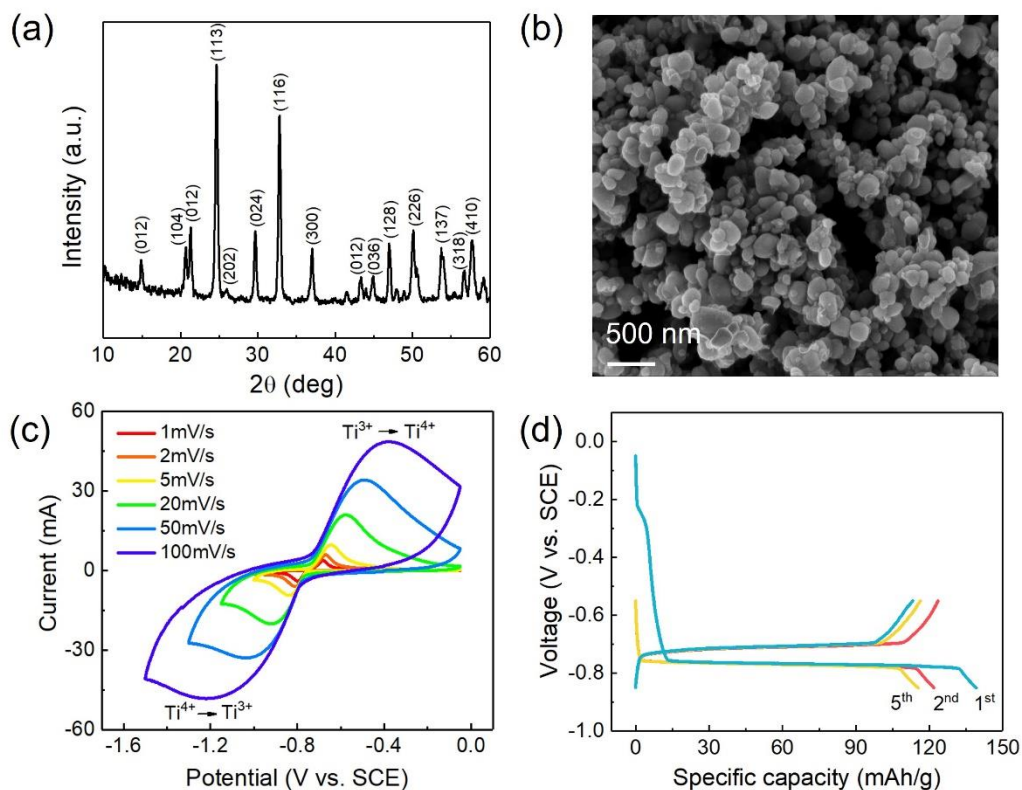
**Figure S2.** Thermogravimetric analysis (TGA) for the NaFeHCF sample. The TGA was performed at a heating rate of 10°C/min under N<sub>2</sub> gas flow. The NaFeHCF sample shows two different slopes from room temperature to 250°C, which corresponds to 3% adsorbed water and 5% interstitial water.



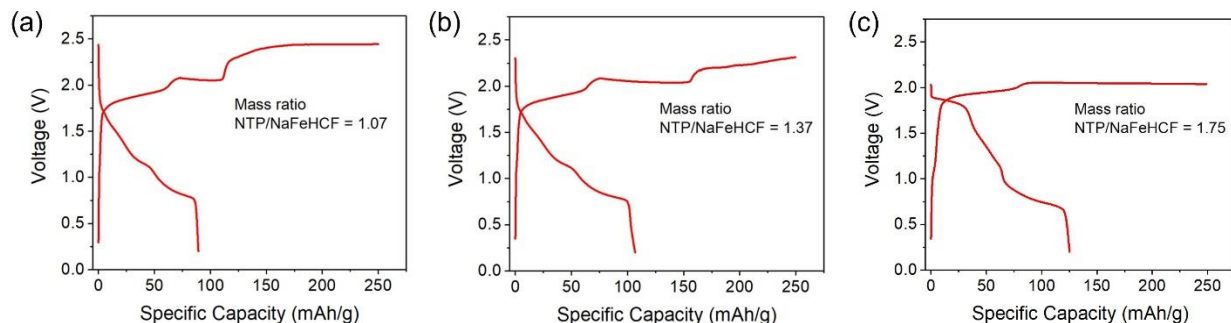
**Figure S3.** The electrochemical stability window for 17 m NaClO<sub>4</sub> electrolyte determined by CV measurements on carbon rod at a scan rate of 10 mV/s. The electrochemical window is expanded to 2.8 V (vs. SCE).



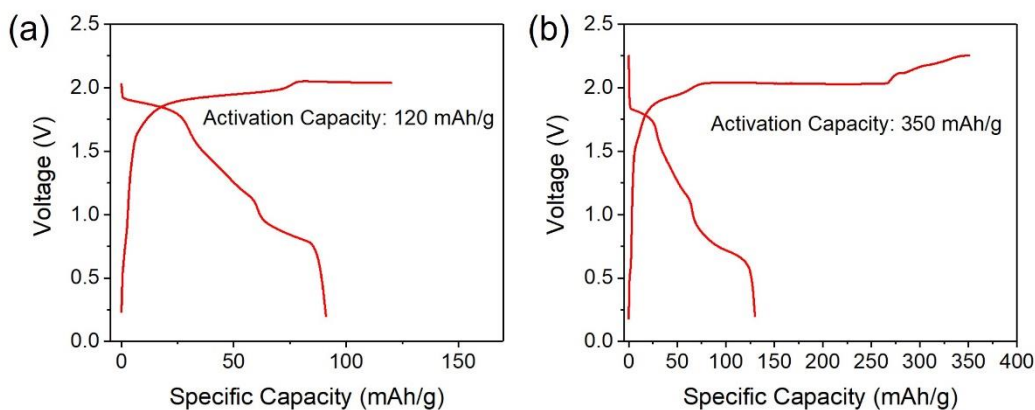
**Figure S4.** The first charging curve of NaFeHCF||NTP full cell with (a) 10 m NaClO<sub>4</sub> and (b) 17 m NaClO<sub>4</sub>. Considering the narrow voltage window of dilute electrolytes (“salt-in-water” electrolyte), we tested the NaFeHCF||NTP full cell performance with two different concentrations of NaClO<sub>4</sub> electrolytes (10 m and 17 m, “water-in-salt” electrolytes) before making the final selection. The test results are shown in **Figure S4**, which demonstrate that the OER potential (~1.93 V) lies within the working potential of NaFeHCF||NTP full cell and the Na-ion cannot be fully extracted from NaFeHCF when the concentration is equal to 10 m. When the electrolyte concentration reaches 17 m, the charge curve exhibits two distinct plateaus, where the first plateau can be assigned to the low-spin oxidation and the second plateau can be assigned to OER (~2.06 V), therefore satisfying the prerequisite for the typical charging process as well as further activation process.



**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  $\text{NaClO}_4$  electrolyte, showing reversible redox reaction of  $\text{Ti}^{3+}/\text{Ti}^{4+}$ . The  $\text{N}_2$  is purged into the electrolyte for 2 hours before measurement. Then the CV profile is tested under ambient condition. The scan initiates from positive direction; (d) The first, second and fifth charge-discharge curves of the NTP electrode at 1C from -0.85 V to -0.55 V (vs. SCE) in 17 m  $\text{NaClO}_4$  electrolyte using a three-electrode cell configuration.

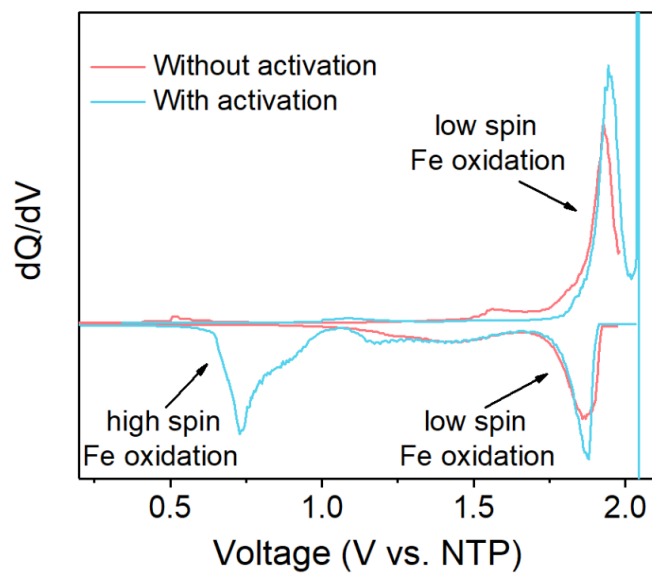


**Figure S6.** The electrochemically activated full cell performance with different mass ratio of NTP/NaFeHCF (a) 1.07; (b) 1.37 and (c) 1.75. The activation capacity is set to 250 mAh/g. The results show that as the mass ratio increases, the specific capacity is also gradually elevated to ~125 mAh/g. The second plateau feature in (a) and (b) can be potentially assigned to the hydrogen evolution reaction on the NTP anode since all of the available sites have been occupied by Na ions at the end of the first plateau. The mass ratio of 1.75 is equal to a specific capacity ratio of 1.9, which is higher than the typical value of 1.2~1.3. We attribute the reason to the fact that the initial coulombic efficiency (discharge/charge) of NTP is only ~80% (**Figure S5 (d)**), which indicates that some of the inserted Na ions cannot be extracted during the first cycle. Hence, during the activation process, we need to have extra NTP materials to get more Na ions inserted to compensate the capacity loss caused by “dead Na-ion” in the full-cell configuration.

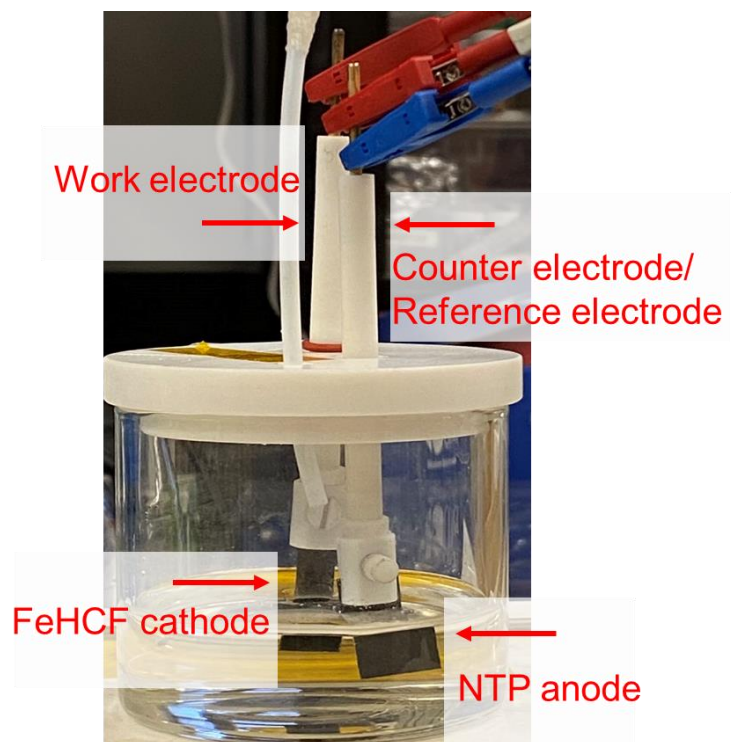


**Figure S7.** The electrochemically activated full cell performance with different activation capacities. (a) 120 mAh/g and (b) 350 mAh/g. The mass ratio of NTP/NaFeHCF is set to 1.75. The results suggest that higher activation capacity can lead to higher specific discharge capacity. However, if the activation capacity is too large, extra parasitic side reactions that have been previously observed in **Figure S6** can be introduced at high voltage region ( $>2.1$  V). Combining the results from **Figure S6** and **S7**, we decide to use a mass ratio of 1.75 and an activation capacity of 250 mAh/g to realize the electrochemical activation process.

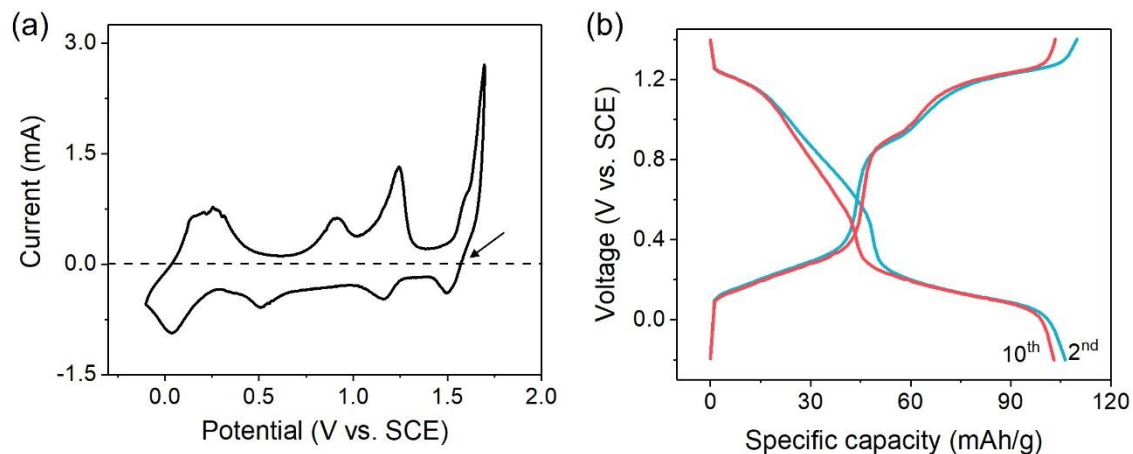




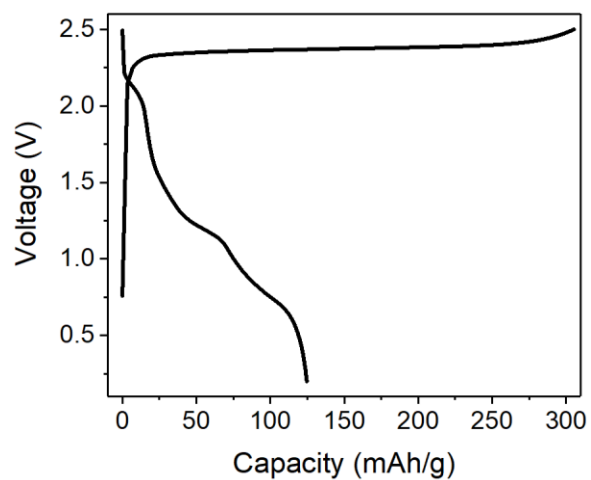
**Figure S8.**  $dQ/dV$  analysis of NaFeHCF||NTP full cell system during the first cycle.



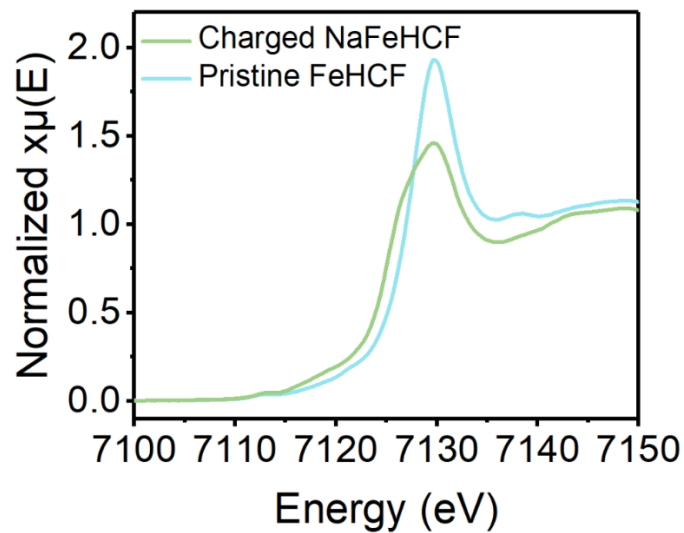
**Figure S9.** Optical graph of the transparent two-electrode glassware cell



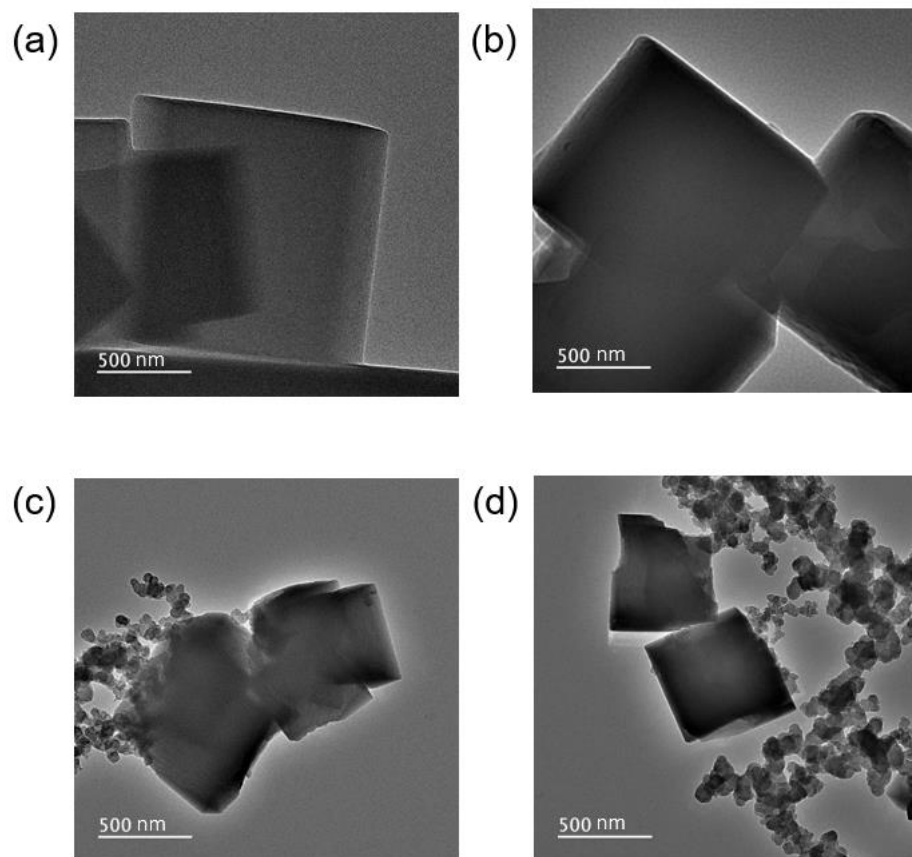
**Figure S10.** (a) Cyclic voltammetry profile of FeHCF at a scan rate of 1 mV/s in 17 m NaClO<sub>4</sub> electrolyte. OER started from where the arrow indicated (1.57 V vs. SCE). The N<sub>2</sub> is purged into the electrolyte for 2 hours before measurement. Then the CV profile is tested under ambient condition. The scan initiates from positive direction.; (b) The second and tenth charge-discharge curves of the FeHCF electrode at 5C from -0.2 V to 1.4 V (vs. SCE) in 17 m NaClO<sub>4</sub> electrolyte using a three-electrode cell configuration.



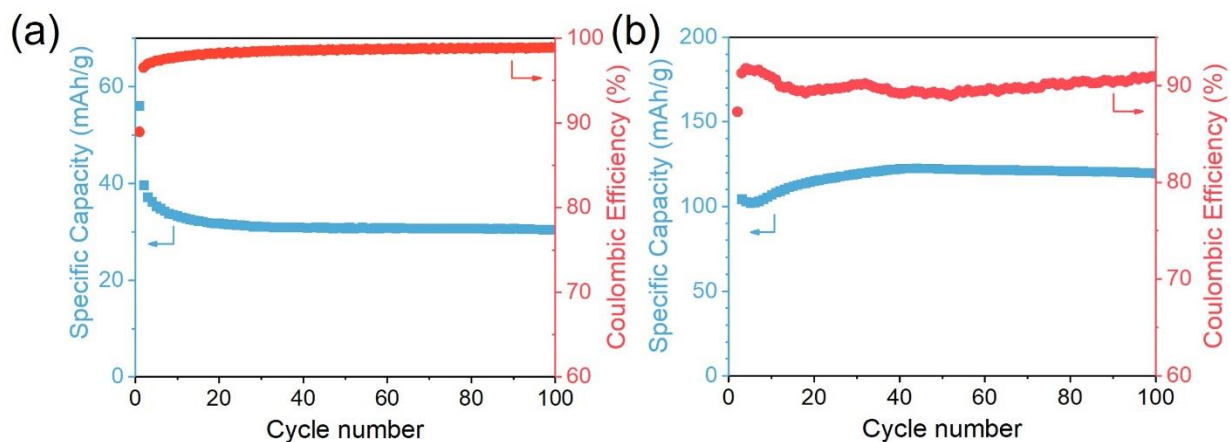
**Figure S11.** The charging curve of two-electrode glassware cell from 0.2 V to 2.5 V in 17 m NaClO<sub>4</sub> electrolyte, where the plateau located at 2.3 V corresponds to the oxygen evolution reaction. The mass ratio of NTP/NaFeHCF is 1.9.



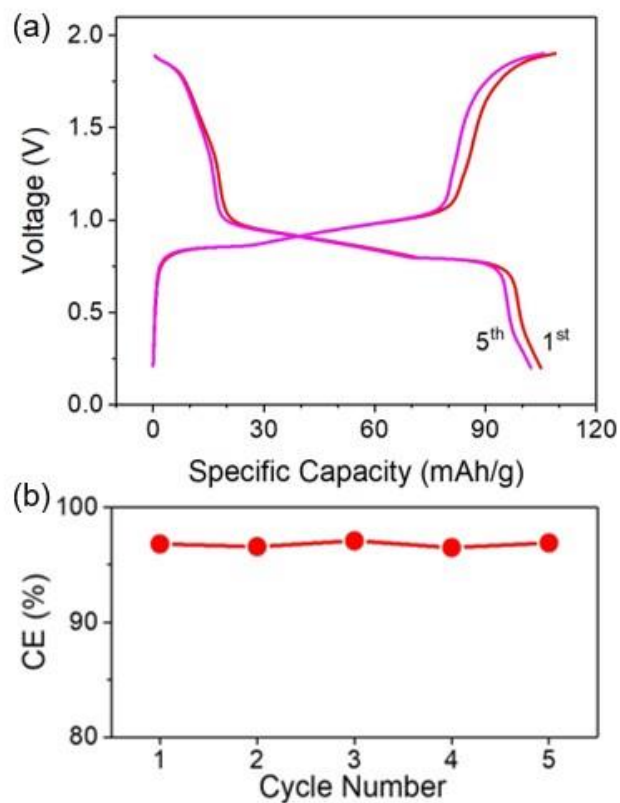
**Figure S12.** The Fe K-edge XANES spectra of charged NaFeHCF and as-prepared Na-free FeHCF. The Fe K-edge energy of charged NaFeHCF is lower than as-prepared FeHCF, which suggests there are still some residual Na ions in the fully-charged NaFeHCF cathode.



**Figure S13.** 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.

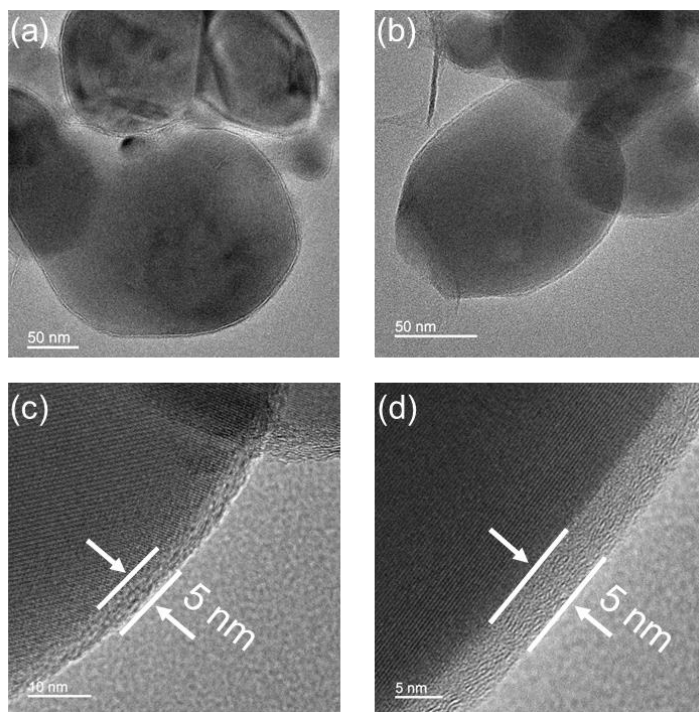


**Figure S14.** First 100 cycles of full cell at 1C (a) without and (b) with electrochemical activation. The electrochemically activated cell exhibits higher specific capacity while inferior Coulombic efficiency, which can be attributed to the generated oxygen and dissolved Fe species upon activation process.

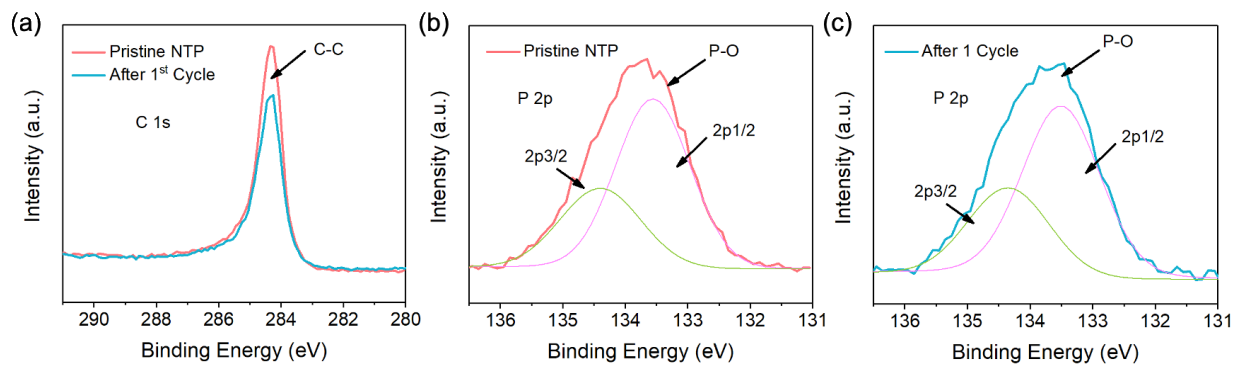


**Figure S15.** (a) The first and fifth charge-discharge curves of the re-assembled NaFeHCF/NTP full cell. The current density is 170 mAh/g and the voltage range is set to 0.2 – 1.9 V to avoid potential OER at high voltage; (b) The Coulombic efficiency of corresponding first five cycles. The Coulombic efficiency can reach up to ~97%, which indicates that the side reactions caused by generated oxygen can be mitigated by re-assembling the cell.





**Figure S16.** TEM images of NTP anode after electrochemical activation process. (a) and (b) show a uniform coating layer on the NTP surface; (c) shows the amorphous nature of coated layer and the thickness is ~5 nm; (c) and (d) suggest that there is no extra layer formed on the top of the coating layer.



**Figure S17.** (a) C 1s and (b)-(c) P 2p binding-energy spectrum of pristine NTP and NTP after the first cycle. The negligible changes in both C and P spectrum suggest that there is no pre-formed layer on the surface of NTP after the electrochemical activation process.

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

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

**Table S2.** ICP results of Fe and Na for NaFeHCF samples at different states. The calculation does not take the Fe dissolution into consideration.

<u>NaFeHCF</u>	Na (ppb)	Na (Stoichiometry)	Fe (ppb)	Fe (Stoichiometry)
1 <sup>st</sup> Charge	195.5	0.13	7025.7	2
1 <sup>st</sup> Discharge	2047.8	1.78	5591.3	2
2 <sup>nd</sup> Charge	153.4	0.20	3661.7	2

**Table S3.** ICP results of Ti and Na for NTP samples at different states

NTP	Na (ppb)	Na (Stoichiometry)	Ti (ppb)	Ti (Stoichiometry)
1 <sup>st</sup> Charge	874.6	2.89	1266.3	2
1 <sup>st</sup> Discharge	1805.1	1.93	3916.8	2
2 <sup>nd</sup> Charge	334.5	2.82	495.1	2

**Table S4.** Electrochemical cycle life of Na-rich PB-based aqueous Na-ion batteries

Samples	Full-cell configuration	Cycling stability	Refs.
$\text{Na}_{1.4}\text{Cu}_{1.3}[\text{Fe}(\text{CN})_6] \cdot 8\text{H}_2\text{O}$	<u>NaCuHCF/NTP</u>	85 mAh/g @ 10C, 87% retention after 1000 cycles	<u>ChemSusChem</u> <b>7</b> , 407–411 (2014)
$\text{Na}_{1.94}\text{Ni}_{1.03}[\text{Fe}(\text{CN})_6] \cdot 4.8\text{H}_2\text{O}$	<u>NaNiHCF/NTP</u>	89 mAh/g @ 5C, 88% retention after 250 cycles	<u>Electrochem. Commun.</u> <b>3</b> 1, 145–148 (2013)
$\text{Na}_{1.85}\text{Co}[\text{Fe}(\text{CN})_6]_{0.99} \cdot 2.5\text{H}_2\text{O}$	<u>NaCoHCF/NTP</u>	95 mAh/g @ 5C, 98% retention after 100 cycles	<u>ChemNanoMat</u> , <b>1</b> , 188–193 (2015)
$\text{Na}_{0.94}\text{Fe}[\text{Fe}(\text{CN})_6] \cdot 2.8\text{H}_2\text{O}$	<u>NaFeHCF/NTP</u>	102 mAh/g @ 5C, 86.7% retention after 500 cycles	This work

**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.