Electronic supplementary information

The hollandite-type β-FeOOH(Cl) as a new cathode material for chloride ion batteries

Guoqing Zhao, Gengping Wan, Yulin Tang, Xuefei Xu, Xuechun Zhou, Maofan Zhou, Zhen Deng, Shiwei Lin, Guizhen Wang*

Key Laboratory of Advanced Materials of Tropical Island Resources (Hainan University), Ministry of Education, Haikou 570228, China

**Corresponding authors.*

Tel: +86-137 0040 8893. E-mail: wangguizhen0@hotmail.com (Guizhen Wang).

Experimental section

β-FeOOH NRs was synthesized by a simple hydrothermal method. 0.2 mol $FeCl_3$ and 0.2 mol urea were added to 60 ml distilled water, stirring until clear. The mixed solution was transferred to a Teflon-lined autoclave and heated to 80 ℃ for 24 h and the obtained product was washed by ethanol and distilled water and dried at 60 ℃ in the oven overnight.

The β-FeOOH electrode was prepared by a slurry coating method. The active material β-FeOOH, carbon black and polyvinylidene fluoride (PVDF) binder were mixed with N-methyl-2-pyrrolidone (NMP) in the weight ratio 6:3:1. The slurry was coated on a stainless steel as current collector and vacuum dried at 80 ℃ for 24 h. 0.5 m 1-butyl-1-methylpyrrolidinium chloride (BpyCl) in propylene carbonate (PC) and 1-butyl-1-methylpiperidinium bis(trifluoromethylsulfonyl)imide (PP14TFSI) was used as electrolyte and Li metal as the anode electrode. The galvanostatic charge-discharge cycling and cyclic voltammograms (CV) curves were collected in the range 1.2–3.0 V.

Size distribution was tested by Zetasizer Nano S90 (4mW He-Ne,633nm) with the sample of β-FeOOH dispersed in water 0.001%–40% (w/w). X-ray diffraction (XRD) was used to analyze the structure and morphology of samples on a Rigaku SmartLab 3kW with Cu Kα radiation using 40 kV working voltage and 30 mA working current. Scanning electron microscopy (SEM) images were taken by using a field emission scanning electron microscopy (FESEM, Verios G4). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were captured by a JEOL JEM-2100 microscope instrument at an acceleration voltage of 200 kV. Mass contents were measured by thermal gravimetric analysis system (Q600, TA, America). The IR spectra were measured with a Bruker TENSOR27 FT-IR spectrometer with scanning 32 times and the spectral resolution was 4 cm^{-1} for each spectrum. X-ray Photoelectron Spectrometer (XPS) were conducted by using a PHI5000 Versaprobe-II spectrometer with a monochromatic Al Kα (1486.6 eV) source and the spectra were calibrated using carbon spectrum as a reference. The specific surface area, pore size distribution and pore volume were measured using the nitrogen adsorption-desorption technique (ASAP2460 Physisorption instrument).

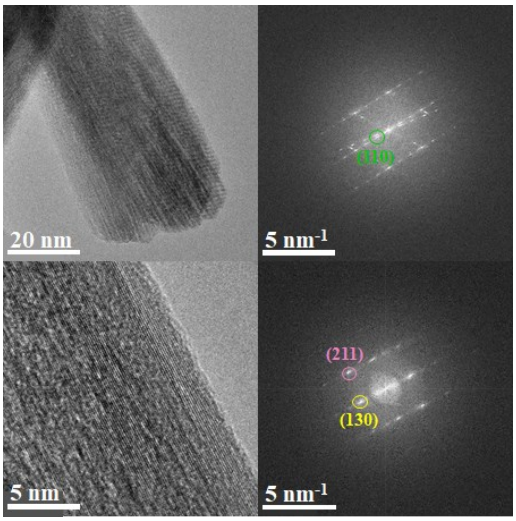
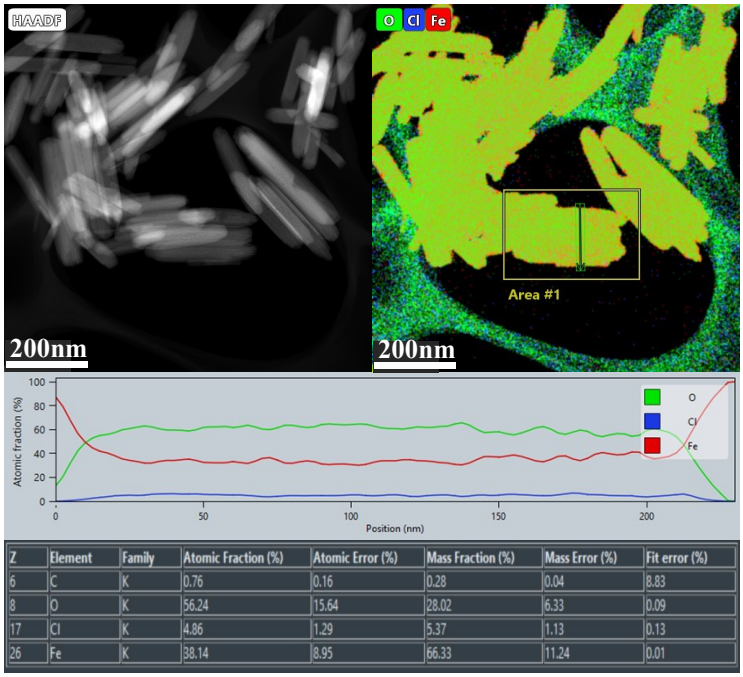


Figure S1. HRTEM and FFT images of β-FeOOH.



Z	Element	Family	Atomic Fraction (%)	Atomic Error (%)	Mass Fraction (%)	Mass Error (%)	Fit error (%)
6	C	K	0.76	0.16	0.28	0.04	8.83
8	O	K	56.24	15.64	28.02	6.33	0.09
17	Cl	K	4.86	1.29	5.37	1.13	0.13
26	Fe	K	38.14	8.95	66.33	11.24	0.01

Figure S2. The TEM and line-scan distribution in the elements of Fe, O and Cl.

Name	Mult	x	y	z	B	Occ.

Fe1	8h	0. 35579	0.15528	0.00000	0.00000	1
O1	8h	0.16000	0.20116	0.00000	0.00000	1
O2	8h	0.54648	0.16608	0.00000	0.00000	1
O3	4e	0.00000	0.00000	0.45412	0.00000	0.5
H1	8h	0.21842	0.17307	0.00000	0.00000	1
Rp = 1.63, Rwp = 2.12%, Rexp = 1.34, χ^2 = 2.49						

Table S1. Rietveld refinement results of XRD data for bare β-FeOOH.

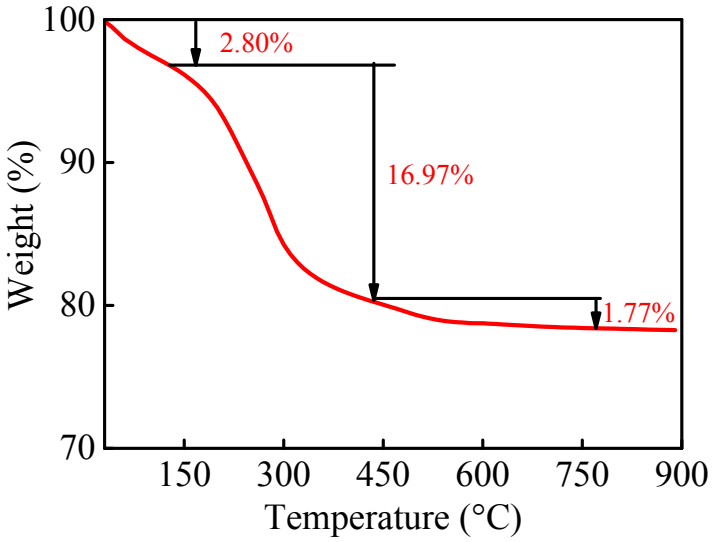


Figure S3. The TG curve of β-FeOOH.

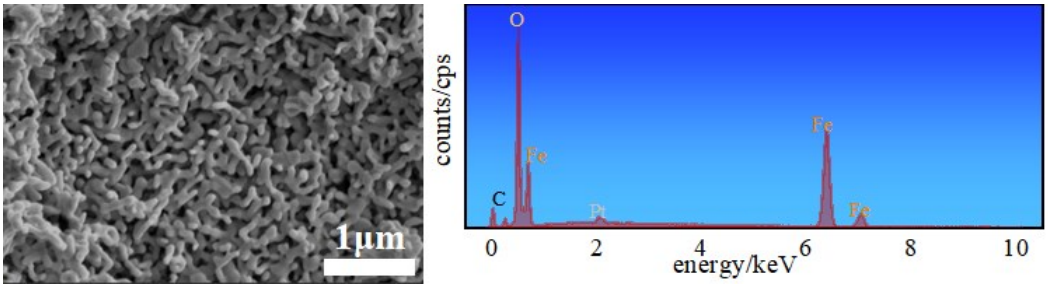


Figure S4. SEM image and the corresponding EDS result of β-FeOOH NRs after TG testing.

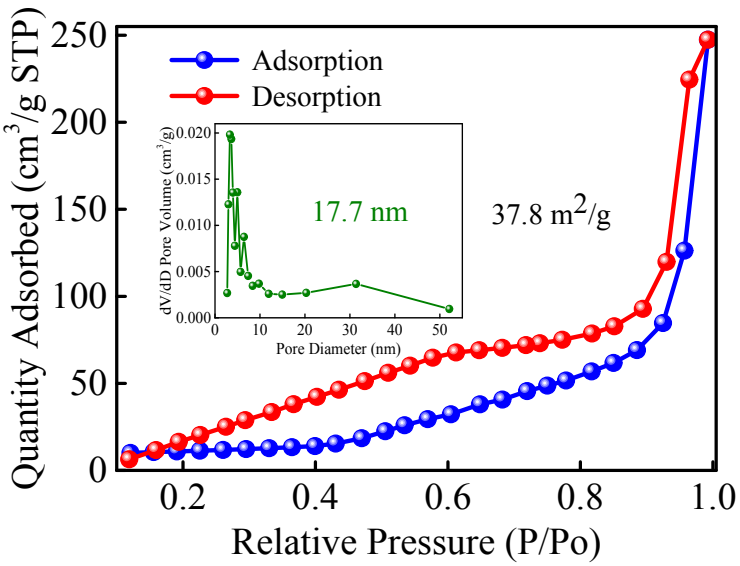


Figure S5. N2 adsorption-desorption isotherms and pore distribution of β-FeOOH.

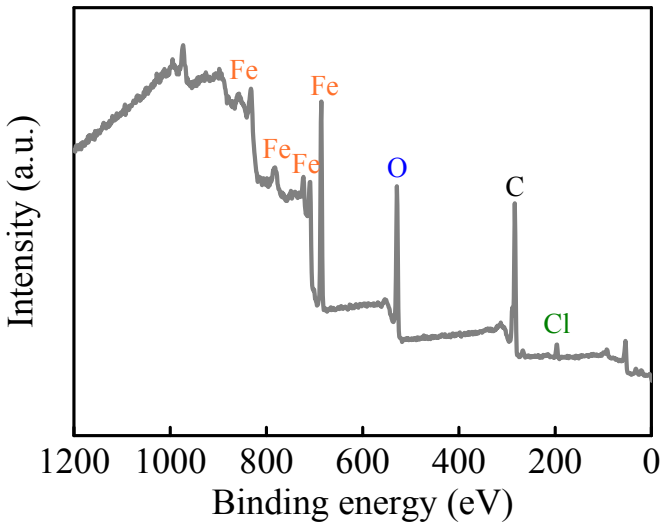


Figure S6. The survey XPS of β-FeOOH NRs.

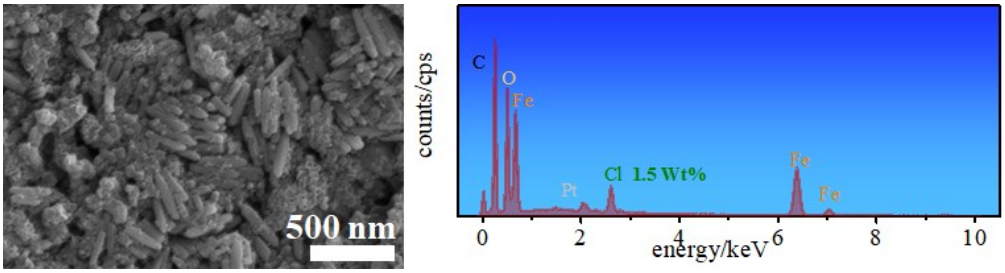


Figure S7. SEM image and the corresponding EDS result of β-FeOOH NRs after 100 cycles.

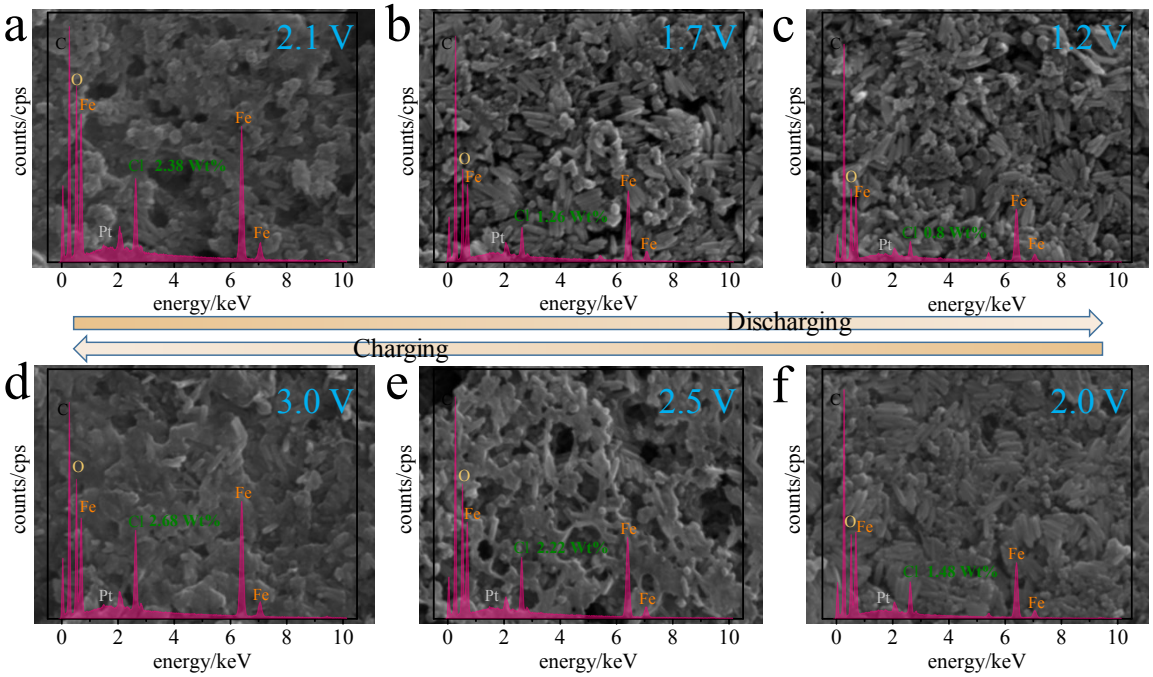


Figure S8. Ex situ SEM images (1 μm) and the corresponding EDS results of β-FeOOH cathode during discharging and charging process.