

Supporting Information

A triflate porous layer stabilizing Zn anodes for high-performance Zn-ion batteries

Ruijun Rao,^a Jingtao Chen,^a Mengxi Bai,^a Qiufen Li,^a Xiang Wang,^a Jiashuai Li,^a
Dongze Li,^a Xiaoyan Lin,^a Siyuan Shao,^a Ziqi Wang^{*a}

^a: Department of Materials Science and Engineering, College of Chemistry and Materials Science, Jinan University, Guangzhou 511443, P. R. China.

E-mail: wangzq@jnu.edu.cn.

Experimental Section

Synthesis of MOF-OTf

MOF-808 was prepared in the following steps. In a 100-mL beaker, 0.34 g $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, 0.22 g benzene-1,3,5-tricarboxylic acid (BTC), 20 mL N, N-dimethylformamide (DMF), and 20 mL formic acid were added sequentially and agitated for 30 min at room temperature to make a homogeneous solution. Then, the solution was transferred into a Teflon-lined stainless-steel autoclave and heated at 100 °C for 48 h. After naturally cooling down, the precipitate, referred to as MOF-808, was collected by centrifuging, washed with ethanol, and dried in a vacuum oven at 150 °C for 24 h. To make the MOF-OTf, 0.6 g MOF-808 was soaked in 25 mL of 0.5 M HOTf for 48 h, with the HOTf solution refreshed every 12 h. The MOF-OTf was obtained by centrifuging, washed with ethanol, and dried in an oven at 150 °C for 24 h.

Preparation of the MOF-OTf@Zn

The commercial Zn foil was wiped using alcohol and dried before use. 90 wt.% MOF was mixed with 10 wt.% poly (vinylidene fluoride) (PVDF). Then, an appropriate

amount of N-methyl-2pyrrolidone (NMP) was dropped into the above mixture to form a slurry, which was coated to the surface of the pristine Zn foil using a doctor blade and dried naturally for 30 min to obtain the MOF-OTf@Zn. The preparation of MOF-808@Zn, MOF-OTf@Cu, and MOF-808@Cu used the similar coating process.

Preparation of NVO cathode material

1.5 g of NH_4VO_3 was dissolved in 90 ml of deionized water, and then the pH was adjusted to 2.0 by the dropwise addition of 1 M of concentrated hydrochloric acid with continuous stirring. The mixture was then placed in a Teflon-lined stainless steel autoclave and heated at 180 °C for 48 h. After cooling to room temperature, the precipitate was collected by filtration and washed with deionized water to obtain $(\text{NH}_4)\text{V}_3\text{O}_8$ cathode material.

Battery assembly

The NVO cathode material, conductive carbon (Super P), and PVDF binder in a mass ratio of 7:2:1 were dispersed in N-methyl-2pyrrolidone (NMP) to form a homogeneous slurry. The NVO cathode was obtained by coating the slurry on a piece of stainless steel current collector and drying at 60 °C. The active material loaded on each cathode is about 2.0 mg cm^{-2} . A set of CR2032 coin MOF-OTf@Zn|NVO full cells were assembled with the NVO cathodes, MOF-OTf@Zn anodes, and 2 M ZnSO_4 aqueous electrolyte.

Characterization

A PerkinElmer Spectrum Two spectrometer collects the data for the FTIR. XRD patterns were captured using a Rigaku Miniflex 600 X-ray diffractometer with $\text{Cu K}\alpha$ radiation in the reflection mode. SEM tests were performed with a Hitachi TM3030 Tabletop Microscope. The XPS data was obtained through a Thermo Scientific K-Alpha+ apparatus. TEM was tested using a JEOL F200 Thermal Field Emission Transmission Electron Microscope. The contact angle was obtained with a DSA-100 contact angle meter. In-situ observations of Zn deposition behaviors were conducted on

an optical microscopy (G1200, Sheng Chuang). The plating/stripping tests and battery cycling with LANHE CT3002A cell test systems. CA, CV, LSV, EIS and Tafel plots were tested with an Admiral Squidstat Plus electrochemical working station.

The following equation was used to get the average CE of the Zn|Cu cells during the first 20 cycles.

$$ACE = \frac{20Q_c + Q_s}{20Q_c + Q_r}$$

where Q_r is the initial plating capacity. Q_c is the capacity for the 20 plating/stripping cycles. Q_s is the final stripping capacity.

Supplementary Figures

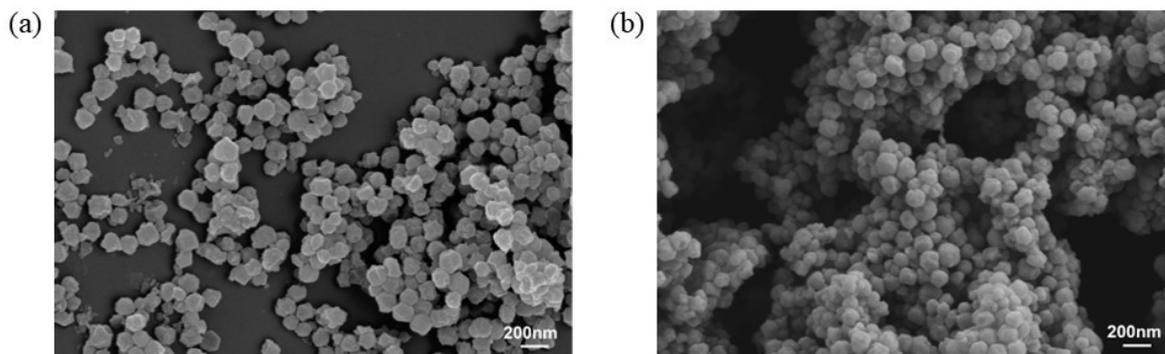


Fig. S1. SEM images of the as-prepared (a) MOF-808 and (b) MOF-OTf.

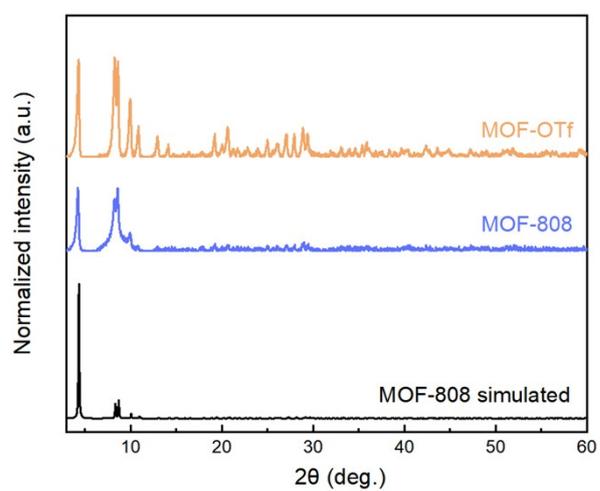


Fig. S2. XRD patterns of the simulated and synthesized MOF-OTf and MOF-808.

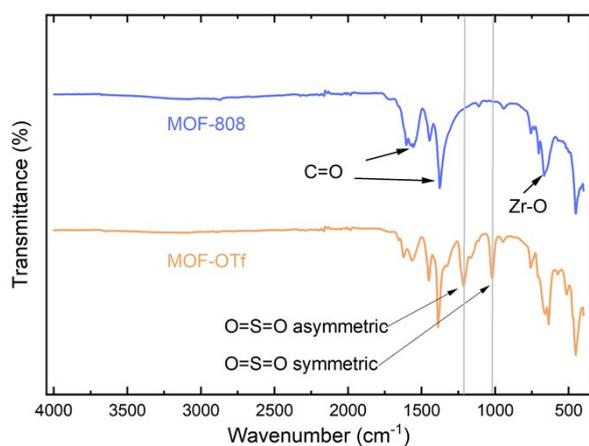


Fig. S3. FTIR of the MOF-OTf and MOF-808.

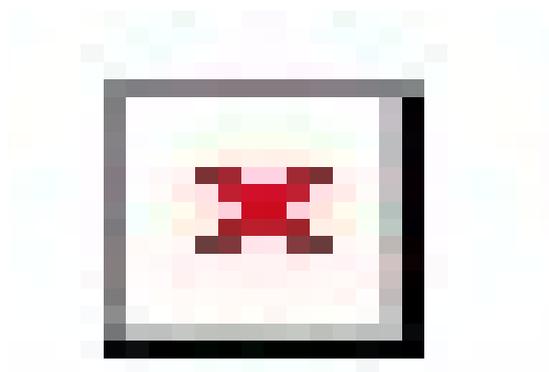


Fig. S4. ^1H NMR spectra of the MOF-OTf and MOF-808.

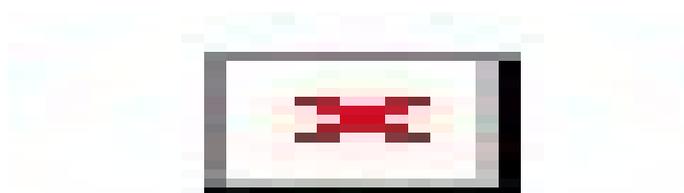


Fig. S5. Zn plating/stripping voltage curves of MOF-OTf@Zn, MOF-808@Zn, and bare Zn symmetric cells at 5 mA cm^{-2} .

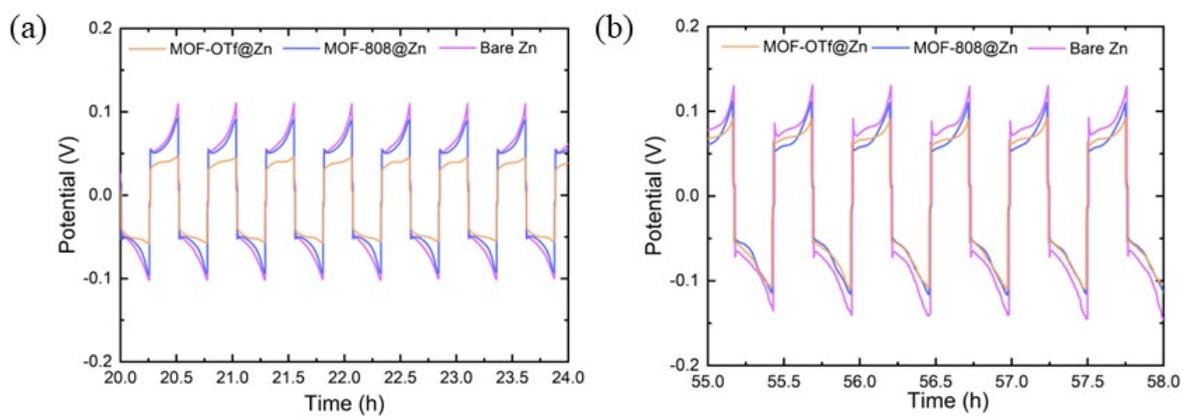


Fig. S6. The plating/stripping voltage curves at (a) 2 mA cm^{-2} and (b) 5 mA cm^{-2} of the symmetric cells.

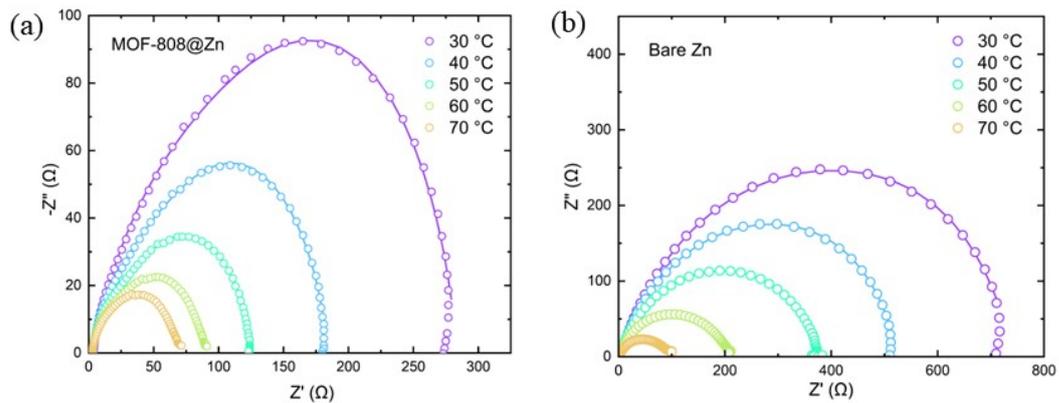


Fig. S7. EIS plots of (a) MOF-808@Zn and (b) bare Zn from 30 to 70 °C.

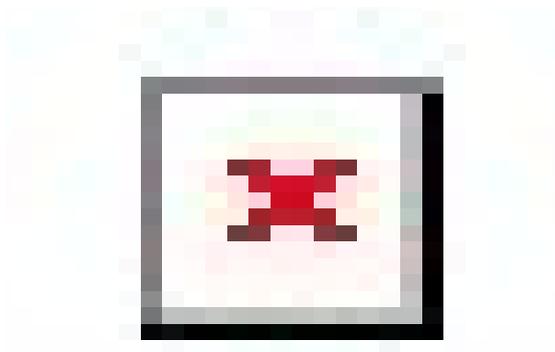


Fig. S8. Coulombic efficiency of the MOF-OTf@Zn|Cu, MOF-808@Zn|Cu and Zn|Cu asymmetric cells.

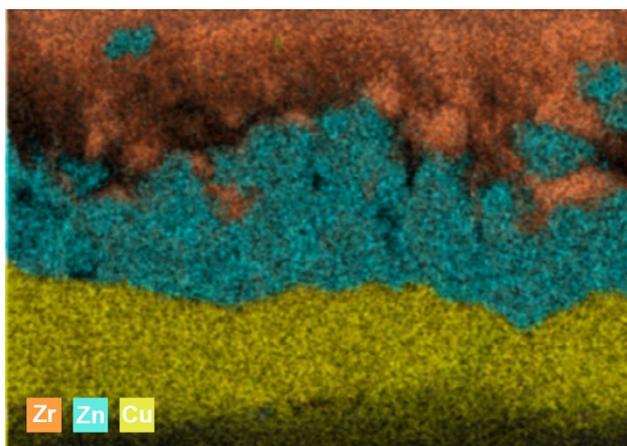


Fig. S9. EDS elemental mappings for the cross-section view of the deposited Zn on MOF-OTf@Cu.

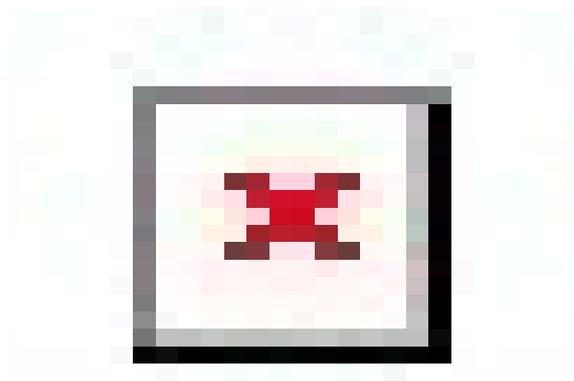


Fig. S10. XRD of the prepared NVO cathode material.

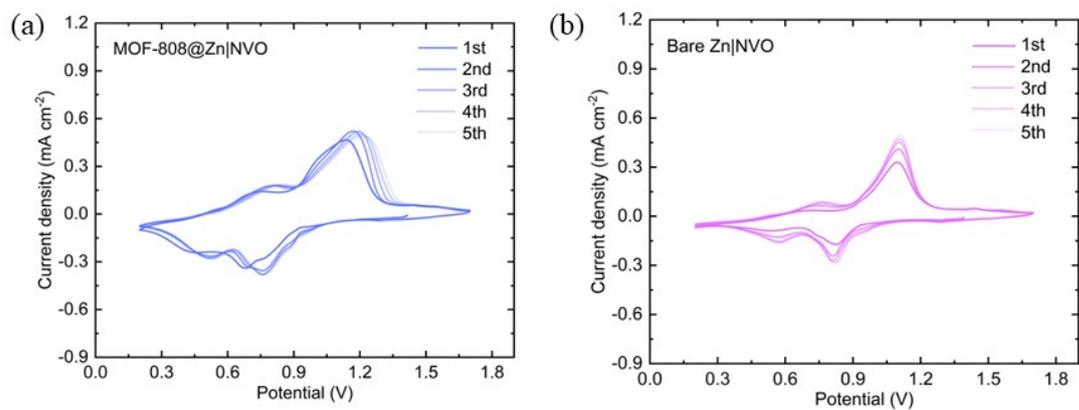


Fig. S11. CV profiles for the first five cycles at 0.5 mV s^{-1} of the full cells with (a) MOF-808@Zn and (b) bare Zn anodes.

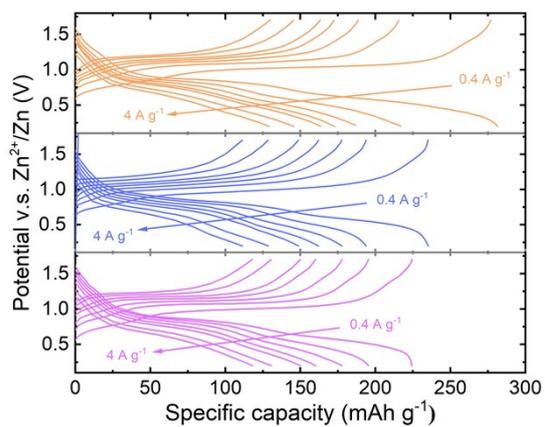


Fig. S12. The charge/discharge curves in the rate tests at corresponding current densities.

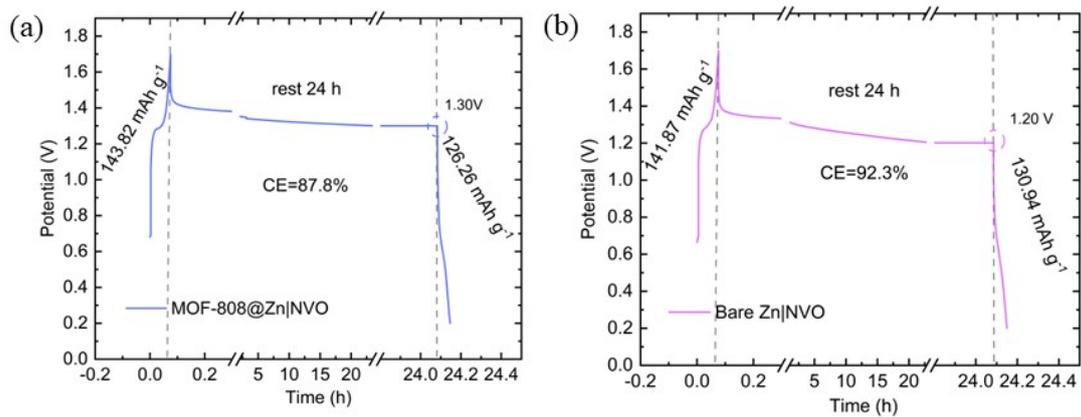


Fig. S13. Self-discharge tests of the (a) MOF@Zn|NVO, (b) bare Zn|NVO cell.