Supporting Information for

Generating H^+ in Catholyte and OH^- in Anolyte: An Approach to Improve Stability of Aqueous Zinc-Ion Batteries

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Experimental Section

Synthesis of VO_2 nanosheets@rGO composite and the corresponding film electrode

In a typical synthesis, 222 mg of NH_4VO_3 was dissolved in 96 mL deionized water at 80 ℃ under stirring. Afterwards, 570 uL HCOOH was dropped into the solution and stirred to a uniform state. Then, the solution was transferred to a 100 mL Teflon-lined autoclave and heated at 180 ℃ for 12 h. After hydrothermal process, the autoclave was naturally cooled to room temperature. The resultant precipitates were washed with deionized water and ethanol for three times, respectively. Next, the precipitates were added into a uniform rGO solution which is prepared through a modified Hummer's method[1], with the mass fraction of rGO is controlled to 15 wt.% in VO_2/rGO composite. Afterwards, 30 wt.% CNTs were added into the mixture solution and were uniformly distributed by ultrasonic cell disruptor. Then the suspension was vacuum filtrated with a polyether sulfone filter paper (pore size 0.45 μm), followed by washing with DI-water for three times. Ultimately, a flat film with a mass loading of ~2 mg cm^{-2} was obtained.

Materials Characterization

The morphologies, crystallographic and microstructural characteristics of the samples were measured using FE-SEM (JEOL-7100F), XRD (D8 Advance X-ray diffractometer with a Cu Kα radiation source), transmission electron microscopy with a scanning voltage of 200 kV (TEM, JEM-2100F) and Raman spectrum (DXR, Thermo-Fisher Scientific, with 532 nm excitation from an argon ion laser). The chemical states and atomic structure information were investigated by XPS (Thermo Fisher Scientific- ESCALAB 250Xi).

Electrochemical Characterization

The prepared binder-free films were directly used for electrodes. Electrochemical experiments were conducted based on coin cells (CR2016-type), with the film being punched into 8 mm round disk as the cathode and Zn metal as the anode. 3 M $Zn(OTf)_2$ aqueous solution was served as the electrolyte. The bipolar membrane and glass fiber were used as separators. Galvanostatic charge/discharge measurements were performed by a multichannel battery testing system (LAND CT2001A) in the voltage range of 0.3 V to 1.5 V for all the batteries without any resting process. The current densities are calculated based on the whole mass of VO_2 and rGO for both the batteries assembled with bipolar membrane separator and glass fiber, respectively. The rate performance was collected after one cycle of activation at 0.1 A g^{-1}. The cyclic voltammetry (CV) was conducted with EC-LAB. All the tests were carried under room temperature.

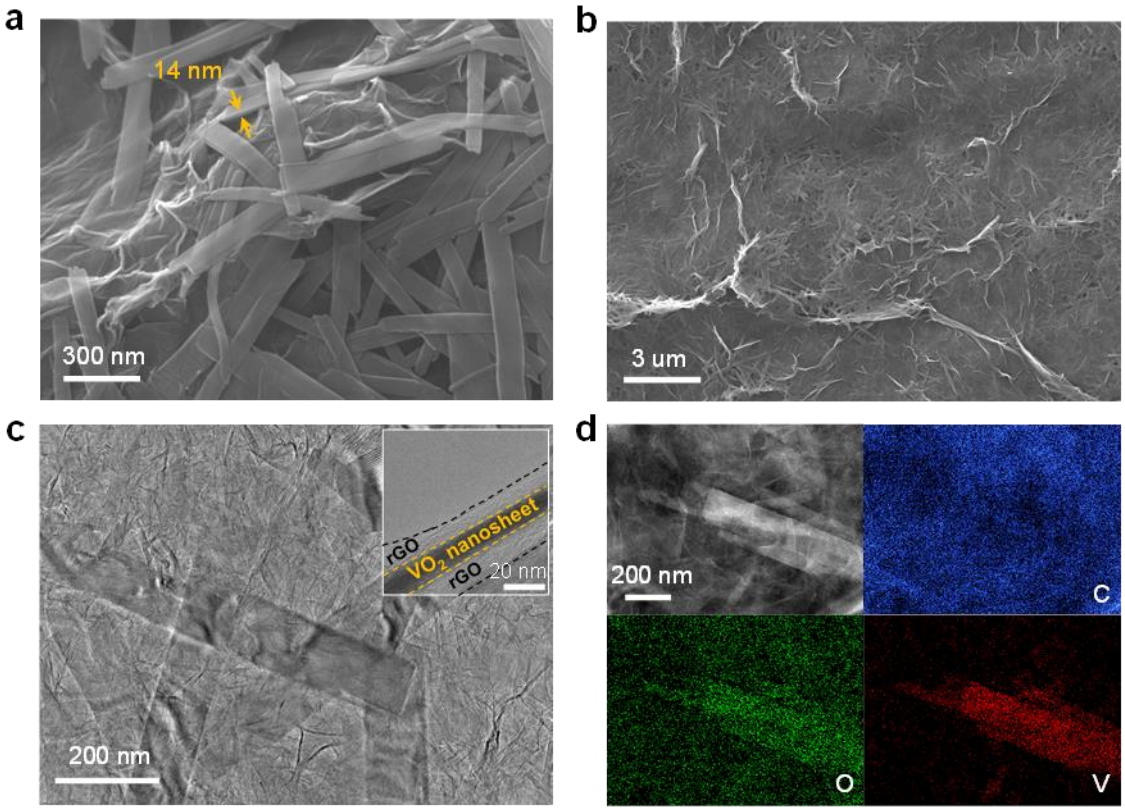

Figure S1. (a,b) SEM images of the VO_2/rGO composite. The thickness of the VO_2 nanosheet is about 14 nm. (c) TEM image of the VO_2/rGO composite. The inset also exhibits that the thickness of the VO_2 nanosheet is about 14 nm. (d) EDS mapping of the VO_2/rGO composite.

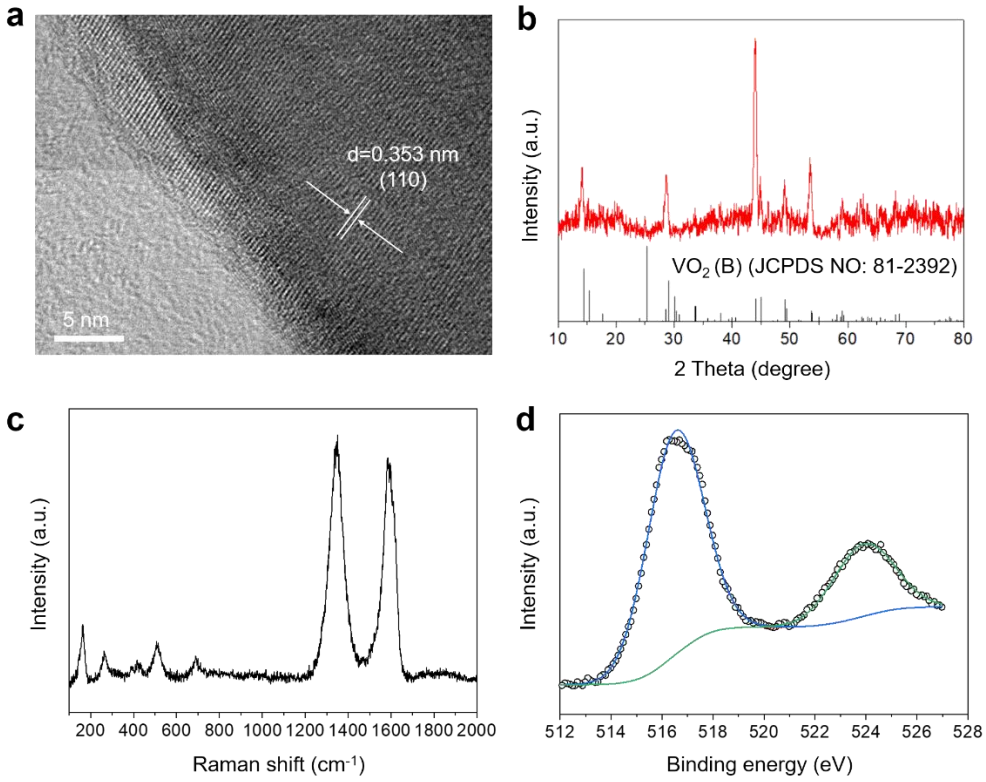

Figure S2. Characterization of the VO_2/rGO composite. (a) High-resolution TEM image. (b) XRD pattern. (c) Raman spectra. (d) XPS spectra of V 2p core level. The results indicate a pure phase of VO_2(B).

Figure S3. Optical image of the front and back of the bipolar membrane.

Table S1. Parameters of the bipolar membrane

Transmembrane voltage	1.6 V① (inorganic salt solution)
	1.25 V② (acids and bases)
Hydrolysis efficiency	≥95%
Burst strength	0.25 MPa
Thickness	0.20 mm

① 1 mol/L NaCl/$\frac{1}{2}Na_2SO_4$, 100 mA/cm^2, room temperature
② 1 mol/L NaOH/HCl, 100 mA/cm^2, room temperature

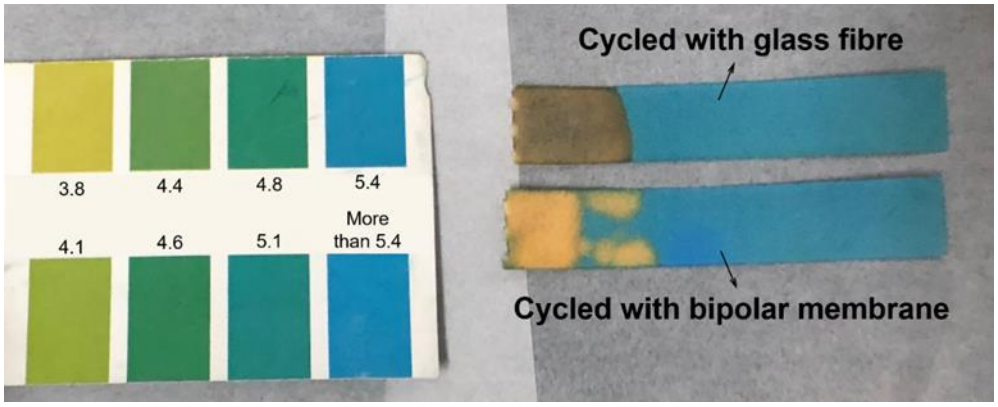

Figure S4. Batteries are assembled with glass fiber and bipolar membrane, respectively. After cycling for three times, the batteries are disassembled and the pH of the respective catholyte are tested using pH indicator paper.

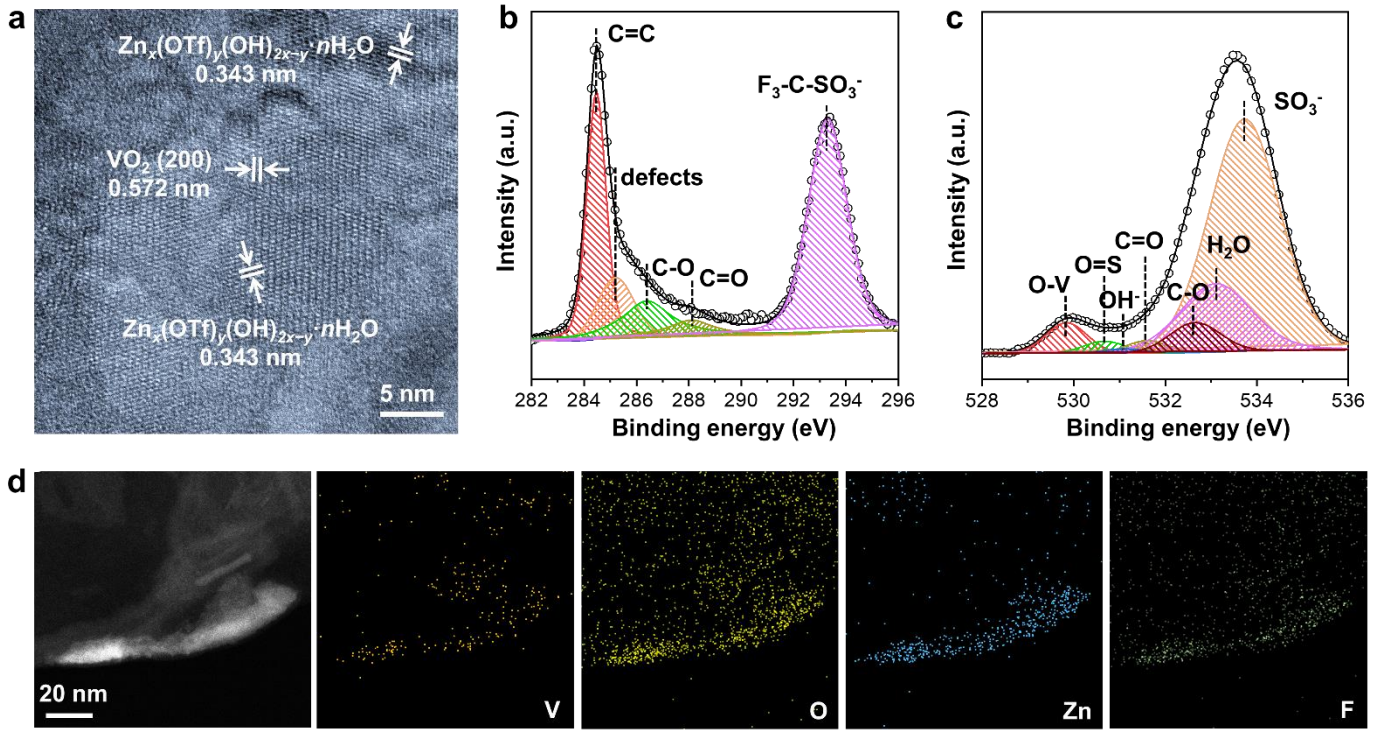

Figure S5. Characterizations of the VO_2/rGO composite in bipolar membraned-based cell (BMC) at discharged state. (a) HRTEM. (b) XPS spectrum of C 1s spectra and (c) XPS spectrum of O 1s spectra. (d) EDS mapping.

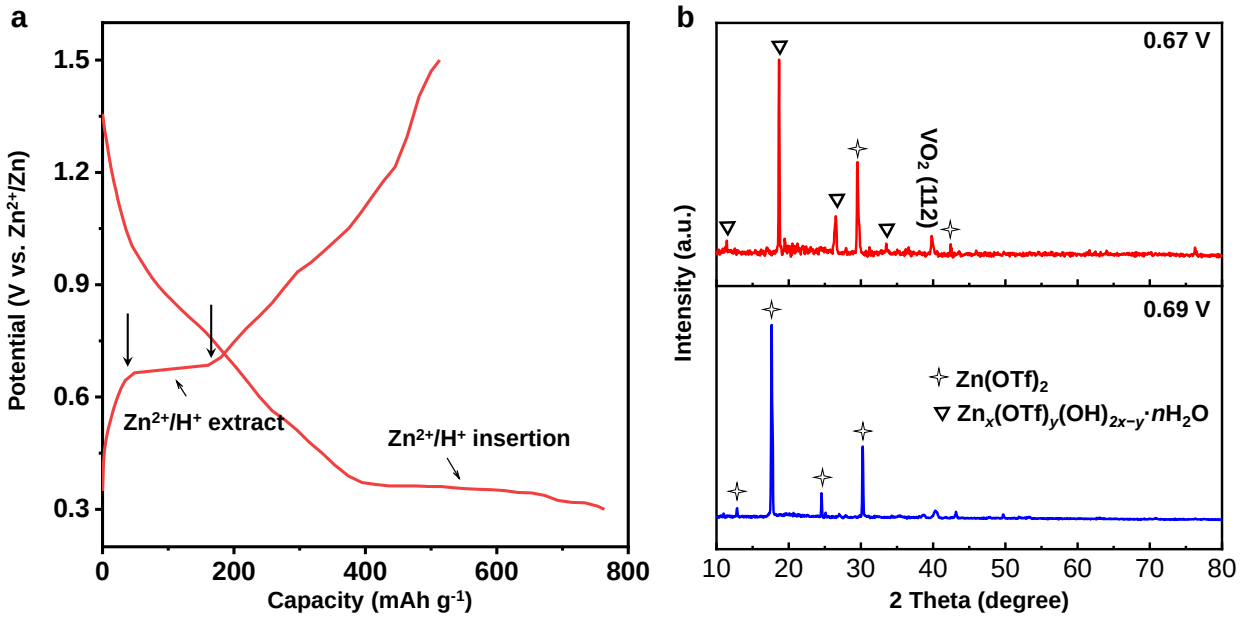

Figure S6. (a) Galvanostatic charge-discharge curves of BMC at 100 mA g^{-1} during the first cycle. (b) XRD patterns of the VO_2/rGO composite in BMC at 0.67 V and 0.69 V during the first charge.

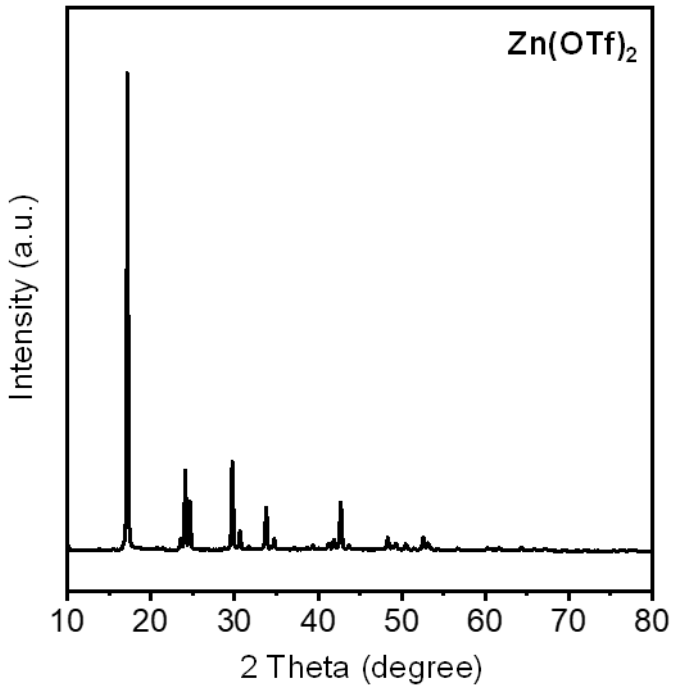

Figure S7. XRD pattern of $Zn(OTf)_2$ powder. This pattern supplements Figure S6.

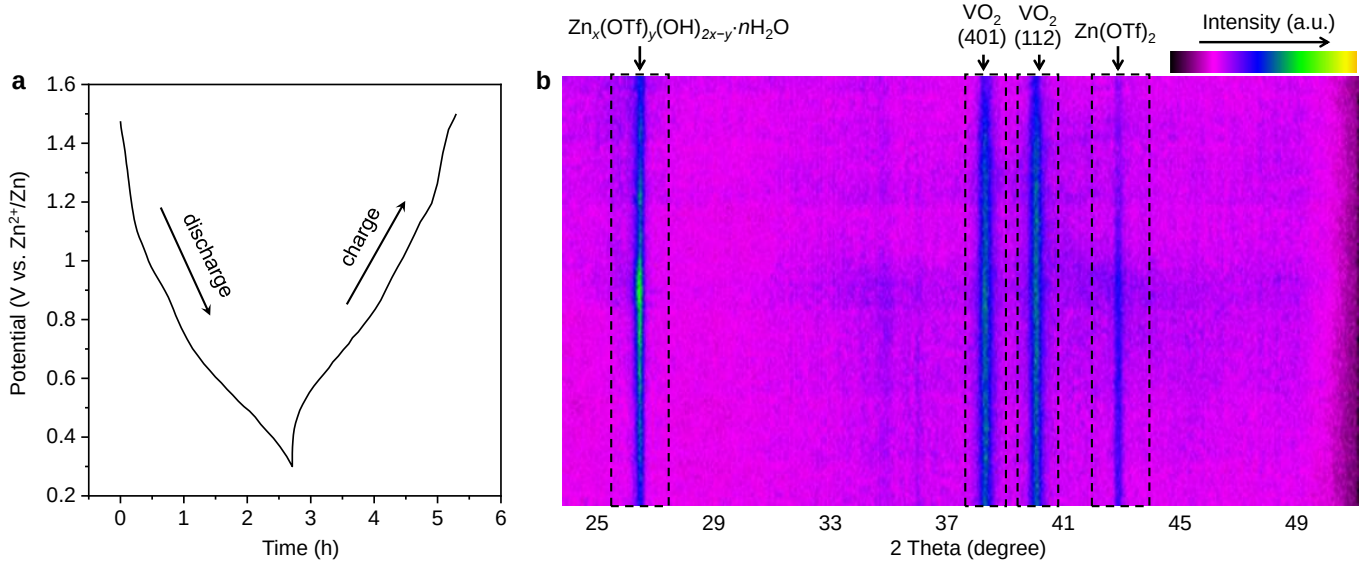

Figure S8. *In situ* XRD investigation of (a) charge-discharge curves at 100 mA g^{-1} and (b) two-dimensional *in situ* XRD patterns.

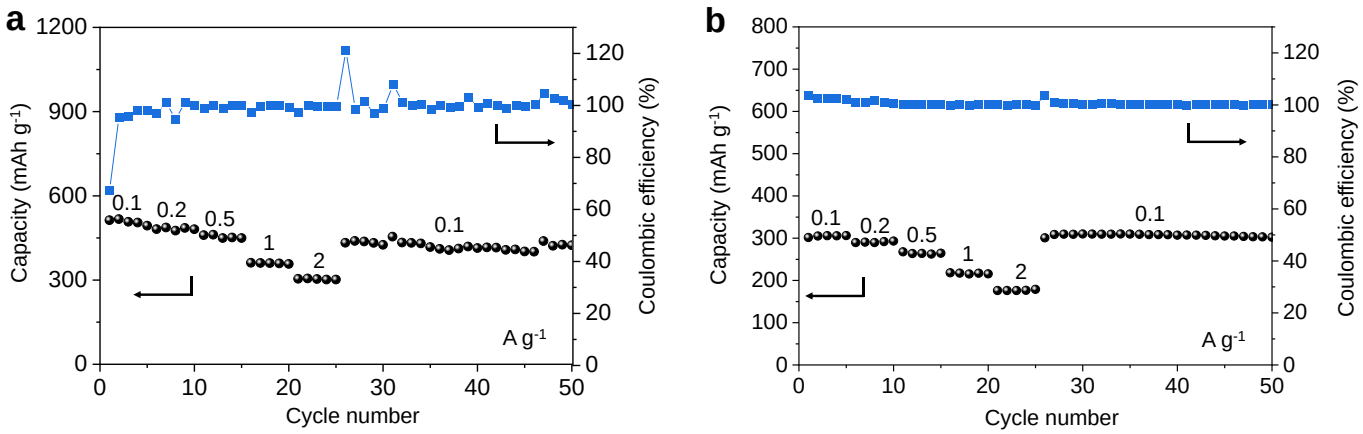

Figure S9. Rate performances of (a) BMC and (b) GFC.

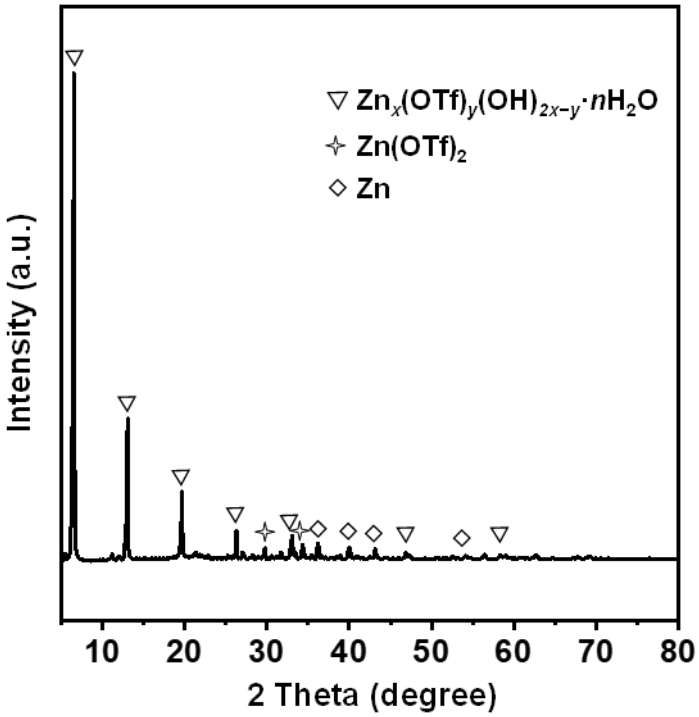

Figure S10. XRD pattern of the Zn anode after cycled in BMC for 4500 times. The $Zn(OTf)_2$ precipitation may result from electrolyte crystallization.

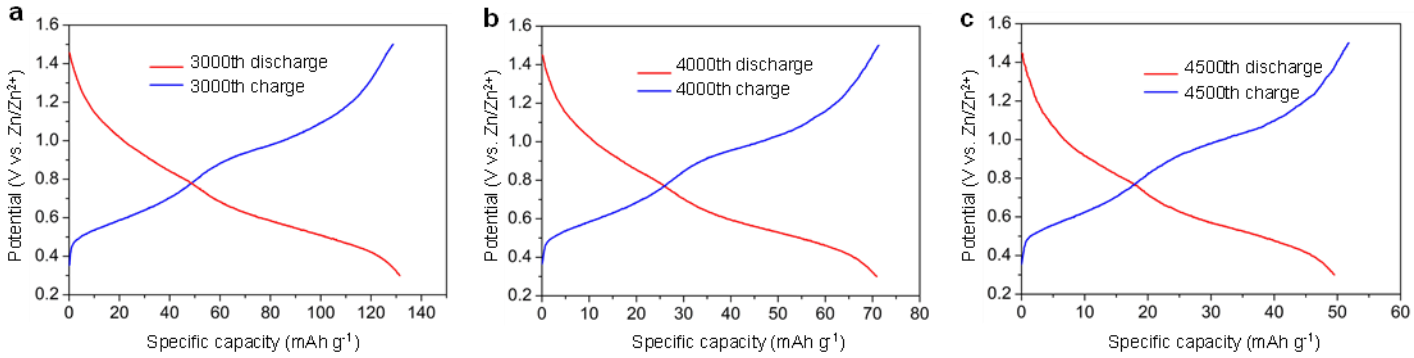

Figure S11. Charge-discharge curves of BMC at the (a) 3000th cycle, (b) 4000th cycle, and the (c) 4500th cycle.

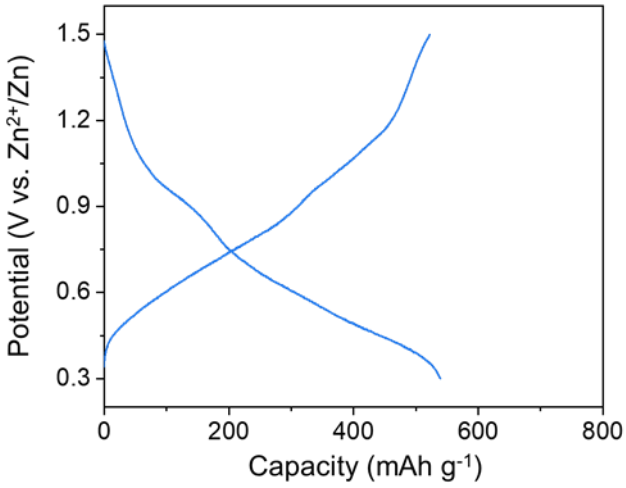

Figure S12. Charge-discharge curves at 100 mA g^{-1} of the coin cell with a bipolar membrane separator larger than the cell shells.

In this case the bipolar membrane separates the catholyte and anolyte completely and the battery shows conformal charge-discharge curve and similar capacity to the battery with normal-size bipolar membrane separator (red line in Figure 1c). Therefore, the catholyte and the anolyte would not be leaked and mixed.

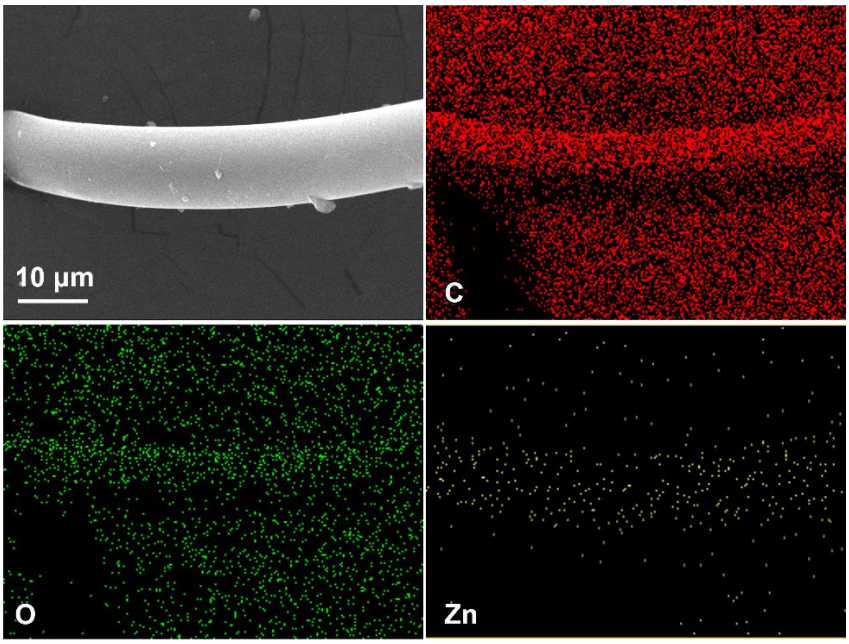

Figure S13. Study of whether the bipolar membrane allows the passage of zinc ions. We assembled a coin cell and used Zn metal as the anode, 3 M H_2SO_4 aqueous solution as the electrolyte, activated carbon cloth as the cathode, and the bipolar membrane as the separator. After 10 cycles at a galvanostatic charge-discharge current of 0.1 A g^{-1}, we disassembled the battery and obtained the SEM image and EDS mapping. We can observe that though there was no Zn^{2+} in the cathodic electrolyte, after cycling, the generated Zn^{2+} in the anodic electrolyte passed through the bipolar membrane and attached onto the activated carbon cloth.

Supporting References

(1) Li, Z.; He, Q.; Xu, X.; Zhao, Y.; Liu, X.; Zhou, C.; Ai, D.; Xia, L.; Mai, L. *Adv. Mater.* **2018**, *30*, 1804089.