Electronic Supplementary Information (ESI)

A Zwitterionic Composite Membrane for High-Performance Zinc/Bromine Flowless Battery

Dabin Han, Edzordzi Kwame Gikunoo and Sangaraju Shanmugam*

Department of Energy Science & Engineering,
Daegu Gyeongbuk Institute of Science & Technology (DGIST),
Daegu 42988, The Republic of Korea.

*E-mail: sangarajus@dgist.ac.kr

* Corresponding authors. Tel.:+82 53 785 6413; fax: +82 53 785 6402.

Experiment

Synthesis of Zwitterionic SiO_2 (Z-SiO_2)

The zwitterionic SiO_2 (Z-SiO_2) was prepared through hydrolysis and condensation reaction between the zwitterionic silane and silica obtained from tetraethyl orthosilicate (TEOS, Sigma-Aldrich). The zwitterionic silane was first synthesized using 1,3-Propane sultone (Sigma-Aldrich) with (3-aminopropyl)triethoxysilane (APTS, Sigma-Aldrich). Briefly, 0.5 g of APTS was added to 15 mL of tetrahydrofuran (THF, Sigma-Aldrich). Next, 0.5 g of propane sultone with 10 mL of THF was added through a dropwise method in the APTS solution. The mixture was stirred with refluxing under the N_2 atmosphere at 50 ℃ for 3 hours and then dried the solvent in a vacuum oven at 40 ℃ for 24 hours. A yellowish solid product was obtained. The molecular structure was analyzed through the ^{1}H NMR and FT-IR spectra, as shown in (Figure). The chemical shifts (δ) of the amphoteric chain were assigned in the ^{1}H NMR result in (Figure) as follows; ^{1}H NMR (400 MHz, D_2O), δ (ppm): 0.60-0.78 (-$SiCH_2$-), 1.10 (-CH_3), 1.72 (-$SiCH_2CH_2$-), 2.07 (-$N^+CH_2CH_2CH_2SO_3^-$), 2.93-3.13 (-$SiCH_2CH_2CH_2N^+$-), 3.56 (-$CH_2SO_3^-$), 3.82 (-CH_2O-). Table. S1† lists the amount of C, H, N, and S in zwitterionic silane measured by the CHNS element analysis.

Before synthesizing the Z-SiO_2, the SiO_2 surface was activated at 150 ℃ for 2 hours. The zwitterionic silane and SiO_2 in a weight ratio of 1:1 was reacted. It was refluxed under the N_2 condition in a round flask using toluene as a solvent at 110 ℃ for 5 hours. The yellow-colored Z-SiO_2 was obtained through a centrifuge by repeated washing with toluene and acetone several times to remove unreacted residues. The scheme of the Am-SiO_2 structure is shown in Fig. S1†.

Membrane preparation

The Z-SiO_2-X powders were each introduced into perfluorosulfonic acid (PFSA) ionomer (Nafion®, 1100 EW, 15 wt%) and prepared Nafion/Z-SiO_2 composite membranes. 15.6 mg of Z-SiO_2-X and 5mL of Nafion were mixed using 15 mL pf ethanol as a solvent and stirred until a homogeneous solution was overserved. The solution was cast on the glass petri dish and evaporated at 50, 60, 70, and 80 ℃ for 1 hour each, and then heat-treated at 100 ℃ for 4 hours. The dried membrane was peeled off from the petri dish and soaked in 2.5 M $ZnBr_2$ (Junsei) electrolyte overnight before use. For comparison, a Nafion composite membrane with bare SiO_2 (PFSA/SiO_2) was prepared the same way as the PFSA/Z-SiO_2-X composite membranes.

Materials Characterization

SiO_2, Z-SiO_2, and membrane morphology were analyzed using Transmission electron microscopy (TEM, FEI-Tecnai G2 F20). Zwitterionic silane structure was characterized by Fourier transform infrared spectroscopy (FT-IR, Fernto-Cary 660) and ^1H Nuclear Magnetic Resonance Spectrometry (NMR, Bruker-Avance Ⅲ 400). The surface composition of Z-SiO_2 was analyzed through an X-ray photoelectron spectrometer (XPS, Thermo Scientific-ESCALAB 250xi) with CHNS elemental analysis.

To measure the ion conductivity (δ) of a membrane according to Br_2 capture, the ion conductivity was checked while replacing the 0.2 M Br_2 with 2.25 M $ZnBr_2$ electrolyte every 24 h. The ion conductivity was calculated by dividing the area resistance of the membrane thickness from the area resistance results. The area resistance was measured without carbon

felt electrodes in the flowless cell. The membrane is divided into two compartments with an effective area of 3.92 cm^2. The two compartments were fully filled out 0.2 M Br_2 with 2.5 M $ZnBr_2$ through each electrolyte inlet hole. The area resistance was evaluated with an electrochemical impedance analyzer (biologic potentiostat analyzer) at an amplitude of 10 mV in the frequency range of 1 Hz to 100 kHz. The area resistance was calculated by the formula below:

$$ASR = A \times (r_1 - r_2)$$

where A is the effective area, r_1 is the ohmic resistance of the cell with the membrane, and r_2 is solution resistance without the membrane.

Bromine capture ability of the PFSA/Z-SiO_2 was confirmed by immersion in 0.2 M Br_2 solution with 2.5 M $ZnBr_2$ electrolyte for 24 h through a Raman spectroscopy (Renishaw-invia Qontor) with a laser wavelength of 514 nm, spectral range of 100-500 $cm^{-1,}$ and power illumination of 100 mW.

Zinc/Bromine Flowless battery (ZBFLB) performance evaluation

Before assembling the Zinc/Bromine flowless battery (ZBFLB), the membrane was immersed in 2.5 M $ZnBr_2$ electrolyte overnight.

The ZBFLB performance of the membrane was evaluated by assembling a single cell. The effective area of the membrane was 3.92 cm^2, which was sandwiched between two carbon felt electrodes (12T), two graphite bipolar plates, two current collectors, and two end-plates. The carbon felts were thermally treated at 530 ℃ for 8 hours under an air atmosphere. An 8

mL of 2.5 M $ZnBr_2$ electrolyte was injected using a syringe into the hole at the top of each chamber. The state of charge (SOC) was calculated according to the volume and concentration of the electrolyte. SOCs of 10% (107.2 mAh) and 40% (421.0 mAh) were charged at 10 mA cm^{-2} and discharged with a cut-off at 0.01 V at 10 mA cm^{-2}. Using a battery analyzer (BST8-3, MTI Corp.), all measurements were performed at room temperature.

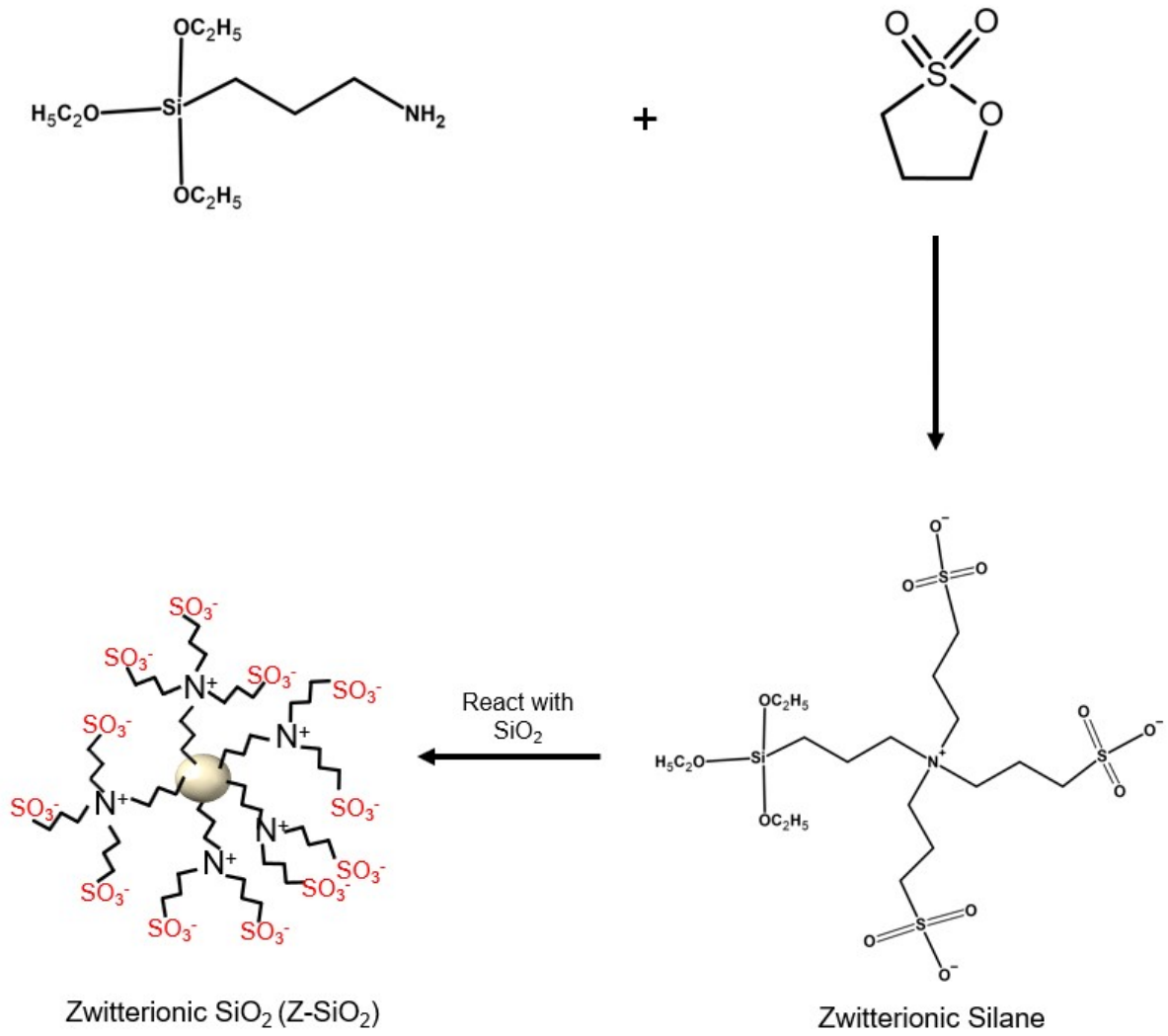

Fig. S1. The synthesis process of zwitterionic silane and zwitterionic SiO_2 (Z-SiO_2).

Table S1. The CHNS elemental analysis of zwitterionic silane and Z-SiO_2.

Compounds	C (%)	H (%)	N (%)	S (%)	S/N (atomic ratio)
Zwitterionic silane	33.10	5.91	2.51	13.40	2.33
Z-SiO_2	12.46	3.94	1.63	7.51	-

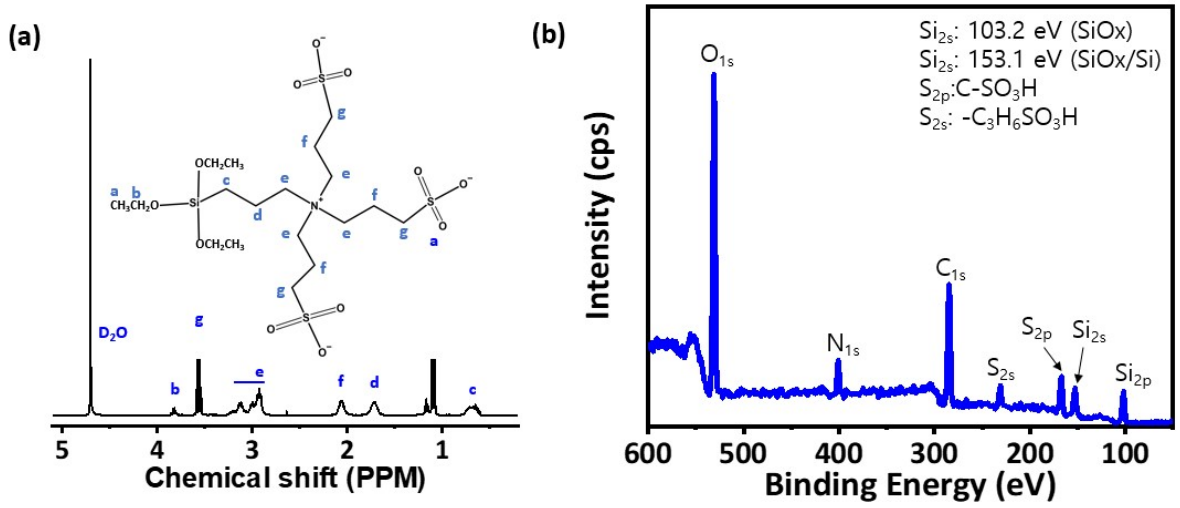

Fig. S2. (a) ^{1}H NMR result of zwitterionic silane and (b) XPS survey result of Z-SiO_2.

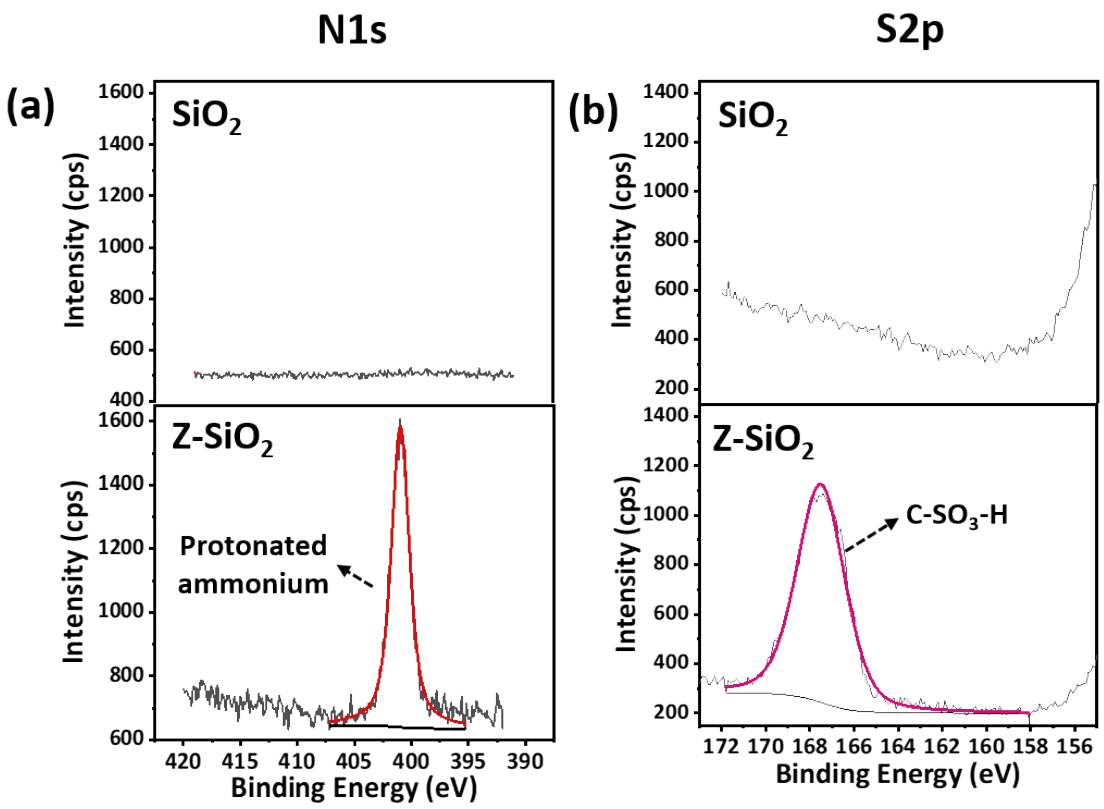

Fig. S3. XPS spectra. (a) N1s of bare SiO_2 and Z-SiO_2; (b) S2p of bare SiO_2 and Z-SiO_2.

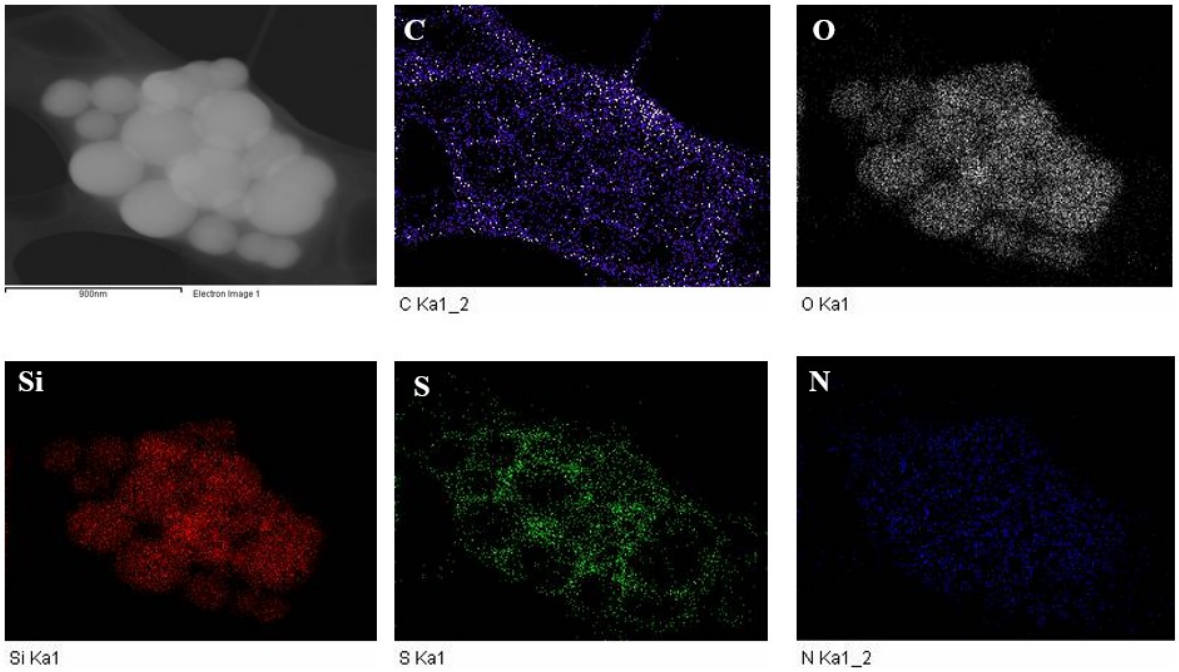

Fig. S4. EDS elemental mapping of Z-SiO_2.

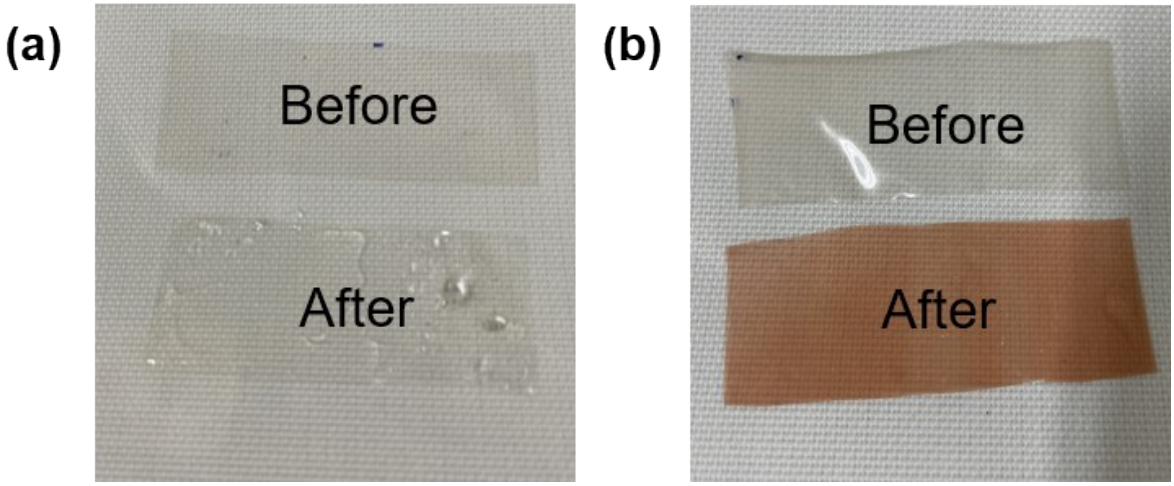

Fig. S5. Before and after immersing in 0.2 M Br_2 with 2.5 M $ZnBr_2$ electrolyte for 24 h; (a) NRE-212 and (b) PFSA/Z-SiO_2.

Table S2. Transference number and ion conductivity of membranes.

Membrane	Transference number (t_-)	Ion conductivity (mS cm^{-1})
NRE-212	0.28	2.60
PFSA/SiO_2	0.30	4.12
PFSA/Z-SiO_2	0.55	7.71

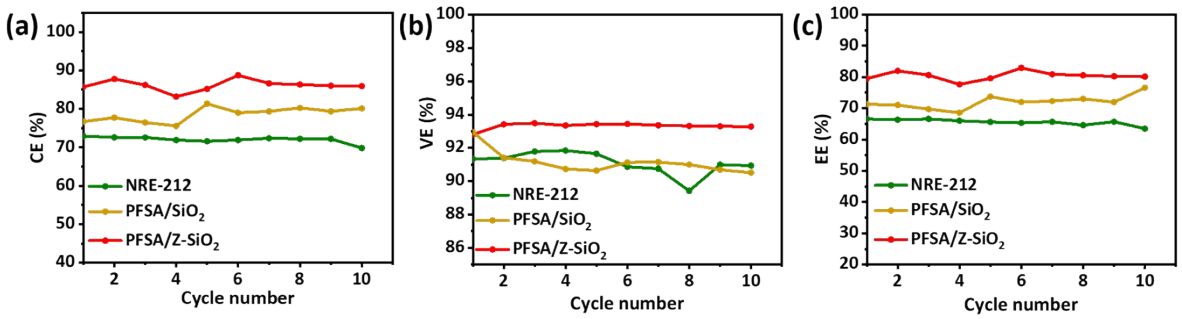

Fig. S6. The ZBFLB performance at 10% SOC; (a) CE, (b) VE and (C) EE.

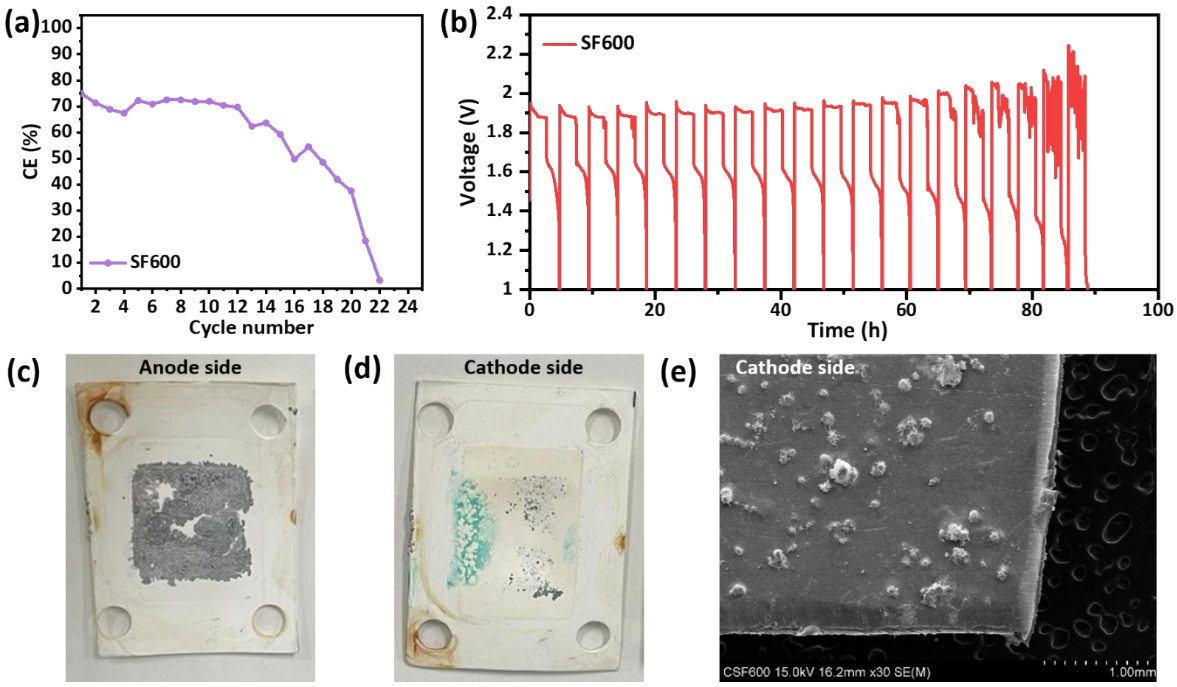

Fig. S7. (a) The ZBFLB performance at 10% SOC for CE, (b) polarization curve of charge-discharge for SF600 at 10% SOC, (c) after cycling test for anode side, (d) after cycling test for cathode side and (d) SEM image of after cycling test of cathode side.

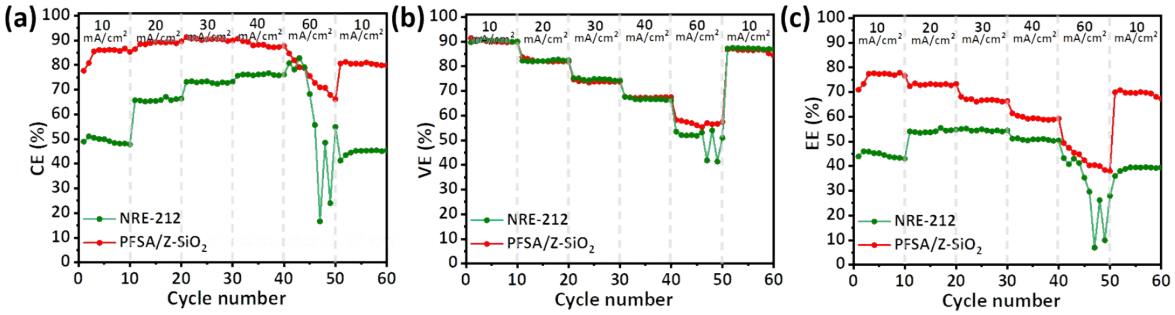

Fig. S8. Rate capability test of NRE-212 and PFSA/Z-SiO_2; (a) CE, (b) VE, and (c) EE.

Table S3. Comparison of performance with other reported results of the ZBFLB.

Modification	Current density (mA cm^{-2})	Charged capacity (mAh cm^{-2})	CE (%)	EE (%)	Capacity retention (%)	Cycle number	Cycle life (h)	Ref.
High concentration of $ZnBr_2$ electrolyte	5	1	95.0	79.0	-	2500	1666	1
N-moiety modified electrode	5	5	85.0	80.0	-	1000	1000	2
Br_2 complex additive with porous electrode	15	1	99.9	94.0	99.97	11,000	733	3
Polybromide confiner modified electrode	8	2	92.1	74.5	99.8	1200	1000	4
CCl_4 additive in electrolyte	5	0.8	96.0	81.0	-	200	67	5
SF600	10	27.3	71.5	57.5	96.1	10	42	This work
NRE-212	10	27.3	72.1	65.6	99.0	10	49	This work
PFSA/SiO_2	10	27.3	79.4	72.4	100	10	51	This work
PFSA/Z-SiO_2 (Conventional)	10	27.3	86.3	80.4	100	10	53	This work
PFSA/Z-SiO_2 (Reverse)	10	**109.4**	**89.4**	**77.5**	**99.99**	**75**	**1800**	

Reference

1 S. Liu, J. Wu, J. Huang, X. Chi, J. Yang and Y. Liu, *Sustain. Energy Fuels*, 2022, **6**, 1148–1155.

2 J. H. Lee, Y. Byun, G. H. Jeong, C. Choi, J. Kwen, R. Kim, I. H. Kim, S. O. Kim and H. T. Kim, *Adv. Mater.*, 2019, **31**, 1–10.

3 L. Gao, Z. Li, Y. Zou, S. Yin, P. Peng, Y. Shao and X. Liang, *iScience*, 2020, **23**, 101348.

4 W. Wu, S. Xu, Z. Lin, L. Lin, R. He and X. Sun, *Energy Storage Mater.*, 2022, **49**, 11–18.

5 P. Xu, C. Xie, C. Wang, Q. Lai, W. Wang, H. Zhang and X. Li, *Chem. Commun.*, 2018, **54**, 11626–11629.