Electronic Supporting Information (ESI)

Ultra-high proton/vanadium selectivity of modified sulfonated poly(arylene ether ketone) composite membrane for all vanadium redox flow batteries

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Materials characterization

The ZrO_2 nanotube and membrane morphology were observed by field-emission scanning electron microscope (FE-SEM, Hitachi, S-4800II) with driving voltage 3 KV. The membrane was coated with osmium before the FE-SEM observation. The microstructure of the ZrO_2 nanotube was analyzed by field-emission transmission electron microscope (FE-TEM, Hitachi, HF-3300) with a setup voltage of 300 kV. The samples were dispersed ultrasonically in ethanol and finally deposited sample on copper grid dried under UV lamp for TEM analysis. The crystal structure of different samples was determined by powder X-ray diffraction (XRD, Panalytical, Empyrean) with CuKα radiation at a setup voltage of 40 KV and current 30 mA. The thermal stability of filler material and membranes was analyzed by the thermal gravimetric analyzer (Thermo plus EVO, TG 8120). The small part of the sample was kept inside the crucible and then continue thermally heating from 30 to 900 ˚C under an air atmosphere with heating rate was of 10 ˚C min^{-1}.

Water uptake (WU) of the membrane was obtained by comparison of initial and final weights in water absorption test as shown in Eq. (S1). Membranes were heated in the vacuum oven at 90 ˚C for 12 h. The dry sample weight was measured and then placed in DI water at room temperature for 24 h. Similarly, the swelling degree of the membrane was determined by comparison of dimensions of dry and wet samples according to Eq. (S2).

$$\text{Water uptake } (\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \quad \text{(S1)}$$

$$\text{Swelling degree } (\%) = \frac{L_{wet} - L_{dry}}{L_{dry}} \times 100 \quad \text{(S2)}$$

where, W_{wet} is the weight of the sample after 24 h and W_{dry} is the weight of the dry sample. Similarly, L_{wet} is the length of the sample after 24 h and L_{dry} is the length of the dry sample.

Ion exchange capacity (IEC) was determined by a titration method using phenolphthalein as an indicator. The membrane samples were heated in the vacuum oven at 90˚C for 12 h, and then the sample was then shocked in 3M NaCl solution for 12 h to exchange the H^+ in the membrane with Na^+. The solution was then finally titrated using 0.01 M NaOH and calculated according to Eq. (S3).

$$IEC = \frac{V_{NaOH} \times C_{NaOH}}{W_{dry}} \quad \text{(S3)}$$

where, V_{NaOH} is the NaOH volume (mL) at the equivalent point, C_{NaOH} is the NaOH concentration (M), and W_{dry} is the dry membrane weight.

The oxidative stability of Nafion-212, SPAEK and SPAEK/ZrNT membranes were investigated using Fenton's reagent (3% H_2O_2 containing 2 ppm $FeSO_4$) at 80 ˚C [S1]. A small part of membrane sample was immersed in Fenton's reagent and calculated the residual weight of membrane sample after 1 h.

The mechanical stability of the membrane samples were investigated using the tensile test instrument (SFM-100kN, United Testing Systems, Inc. USA). The membrane sample with dry condition whose area of 36×18 mm was inserted in the tensile instrument and measurement conducted with a speed of 5 mm min^{-1}.

The proton conductivity of the membrane samples was determined by using a membrane conductivity cell (Bekktech) at 100% relative humidity (RH) under ambient temperature, where hydrogen gas was passing during operation. Membrane samples were fixed in the cell in between two platinum electrodes. The potentiostat was used to apply specific voltages in Pt electrodes, and corresponding currents were detected. The cell resistance (R) is calculated from the slope of the line that interconnects the data points. The conductivity of the membrane was measured according to the Eq. (S4).

$$\sigma = \frac{L}{R \times W \times T} \quad \text{(S4)}$$

where, L = 0.425 cm is a constant distance between two Pt electrodes in the cell, R is the ohmic resistance in Ω, W and T are the sample width (cm) and thickness (cm), respectively.

Table S1 Membrane thickness and cyclic performance of the VRB assembled with Nafion-212, SPAEK, SPAEK/ZrNT (0.5%), SPAEK/ZrNT (1%) and SPAEK/ZrNT (1.5%) membranes at current density of 40 mA cm^{-2}.

Membrane	Thickness	CE (%)	VE (%)	EE (%)
Nafion-212	51	89.65	84.25	75.53
SPAEK	55±5	97.76	83.43	81.56
SPAEK/ZrNT (0.5%)	55±5	99.63	84.13	83.82
SPAEK/ZrNT (1%)	55±5	99.81	83.17	83.00
SPAEK/ZrNT (1.5%)	55±5	99.86	82.42	82.31

Table S2 The performance of VRBs with SPAEK/ZrNT composite membranes in comparison with previous work.

Membrane	Thick-ness (μm)	Proton conductivity (mS cm^{-1})	Permeability (cm^2 min^{-1})	Coulombic Efficiency (%)	Energy efficiency (%)	Current density (mA cm^{-2})	Open circuit voltage (h)	Ref.
SPAEK/ZrNT (0.5%)	**55**	**65**	**0.25×10^{-7}**	**99.6**	**83.8**	**40**	**518**	**This work**
SPAEK-PWmGO (1%)	50	71.0	0.28×10^{-7}	98.7	83.5	40	458	S2
SPEEK/g-C_3N_4-1.5	80	7.9	3.7×10^{-7}	97.5	83.6	30	68	S3
PVA/OMS-7	60	69.1	NA	97.3	81.5	30	68	S4
SPEEK/PAN/-20	55	15.0	11.3×10^{-7}	96.2	83.5	80	62	S5
AIEM-II	45	48.0	2.9×10^{-9}	95.6	75.1	40	300	S6
sPEEK	50	52.0	3.5×10^{-7}	96.1	79.5	40	NA	S7
Nafion-212	51	56	3.3×10^{-7}	90	78	60	53	S8

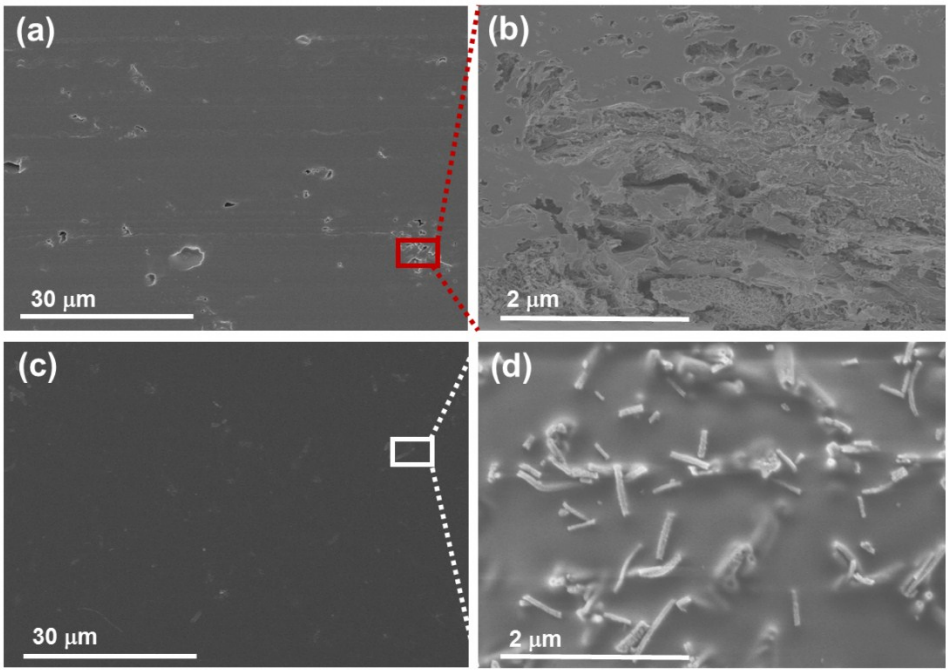

Fig. S1 FE-SEM images of (a) and (b) SPAEK. (c) and (d) SPAEK/ZrNT (1%) membranes at different magnification.

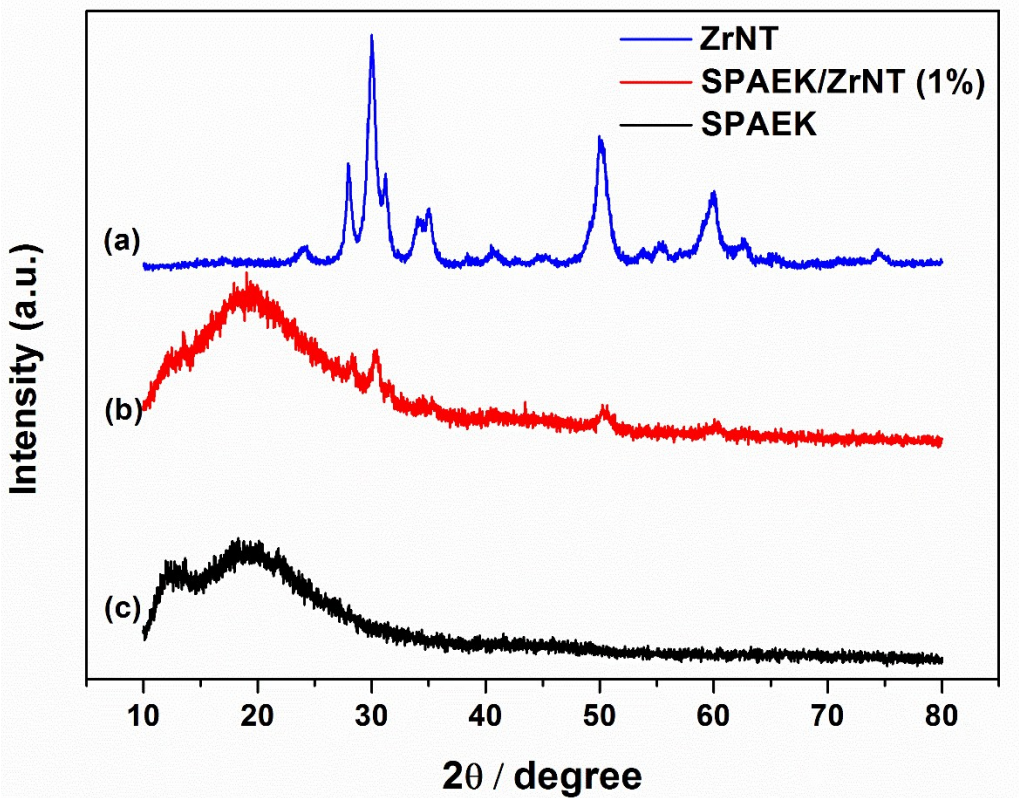

Fig. S2 Powder X-ray diffraction pattern of samples (a) ZrNT. (b) SPAEK/ZrNT (1%) membrane. (c) SPAEK membrane.

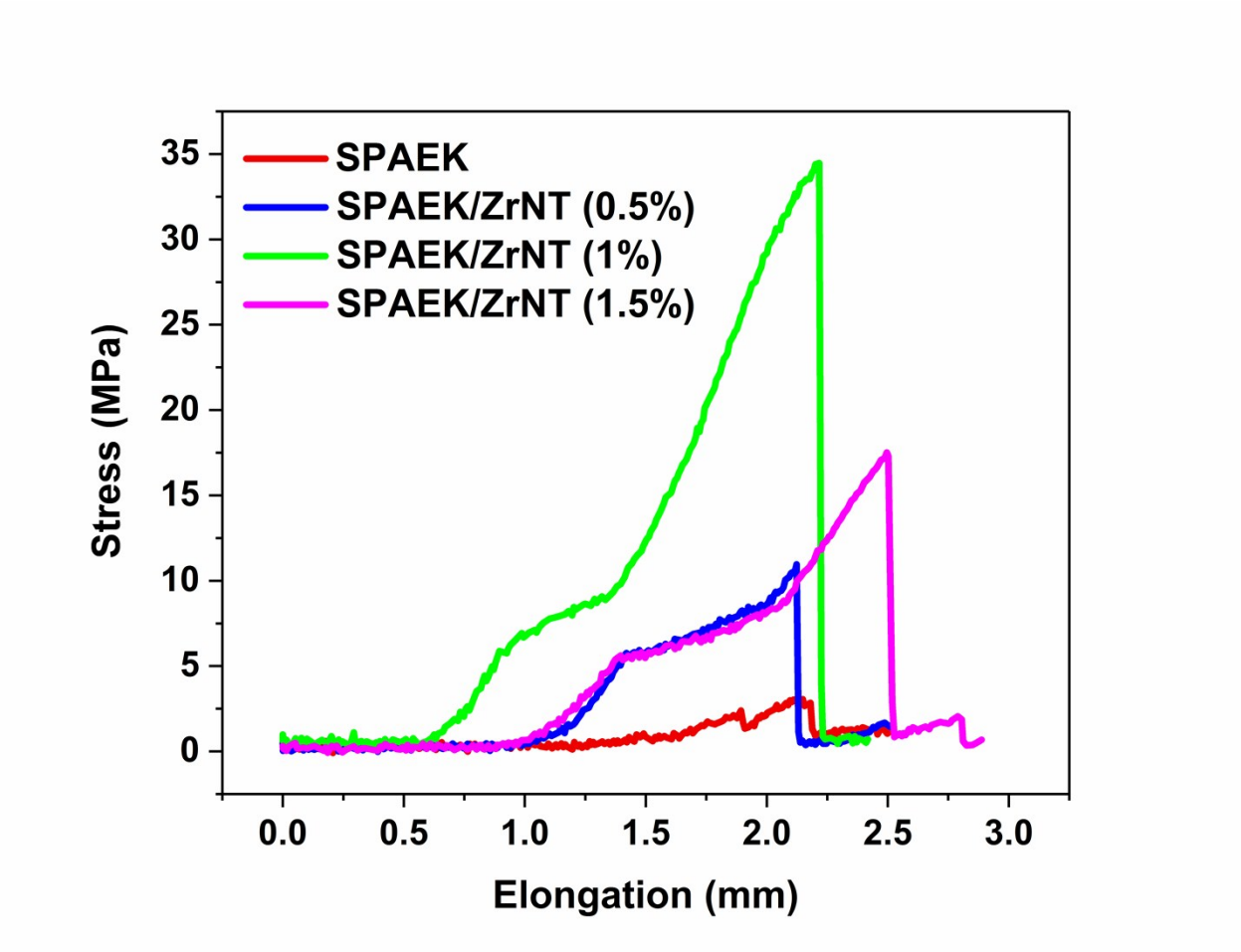

Fig. S3 Tensile test of the dried SPAEK/ZrNT composite membranes in comparison with pristine SPAEK membrane under an ambient condition.

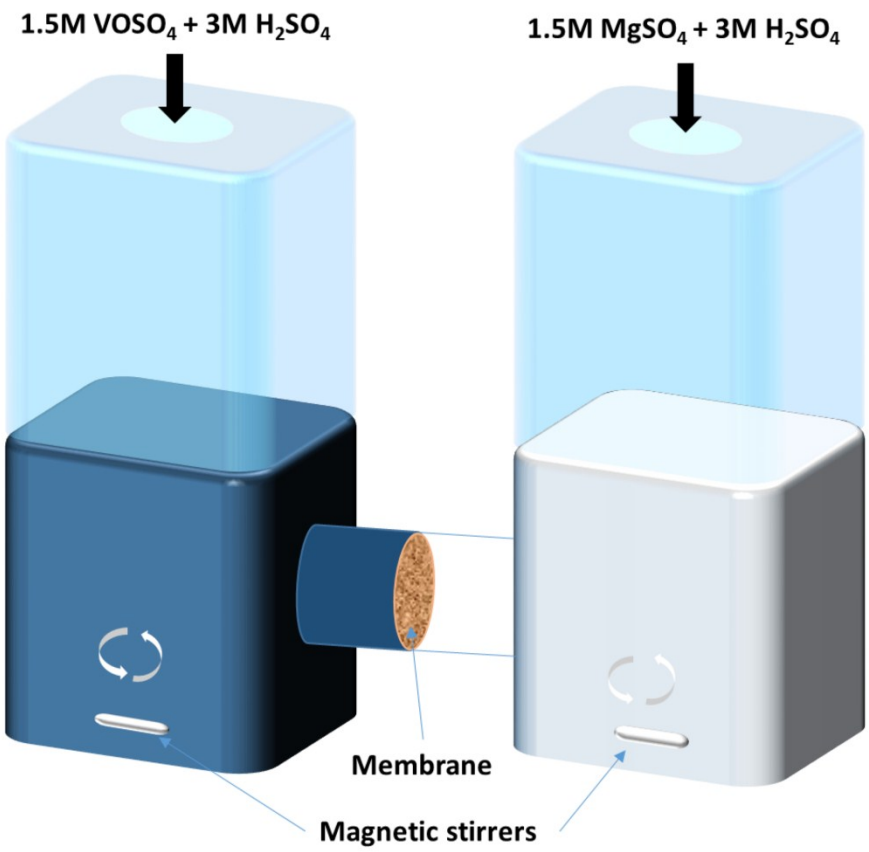

Fig. S4 Schematic diagram of the cell used for the measurement of vanadium ion permeability of SPAEK/ZrNT composite membrane.

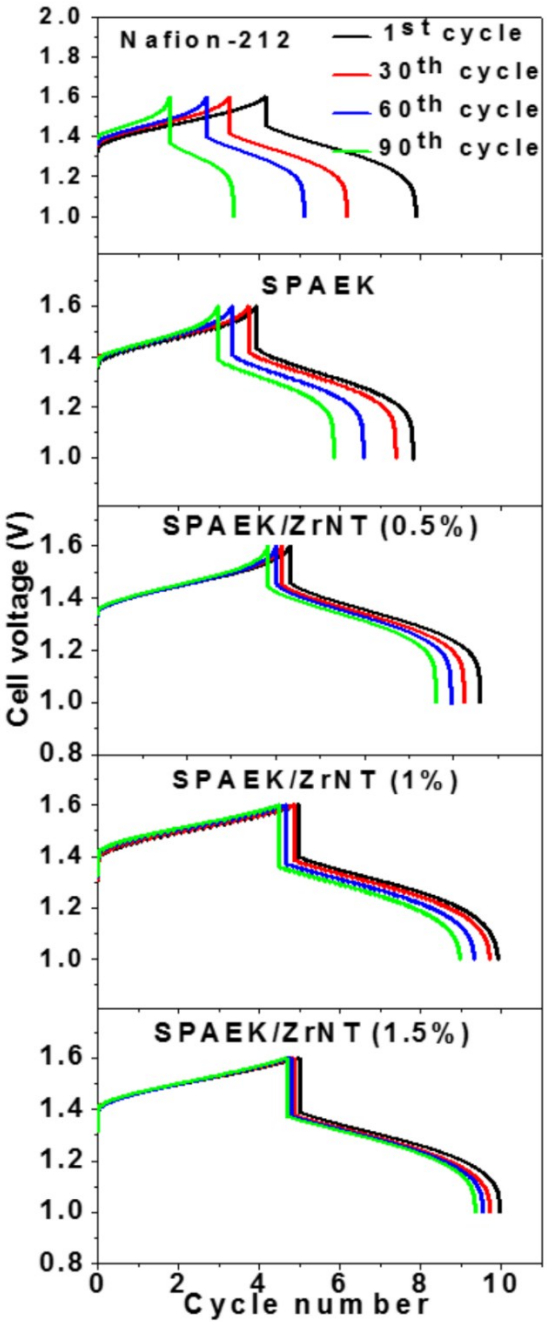

Fig. S5 Charge-discharge curves of the VRB assembled with Nafion-212, SPAEK, SPAEK/ZrNT (0.5%), SPAEK/ZrNT (1%) and SPAEK/ZrNT (1.5%) membranes at 40 mA cm^{-2} current density.

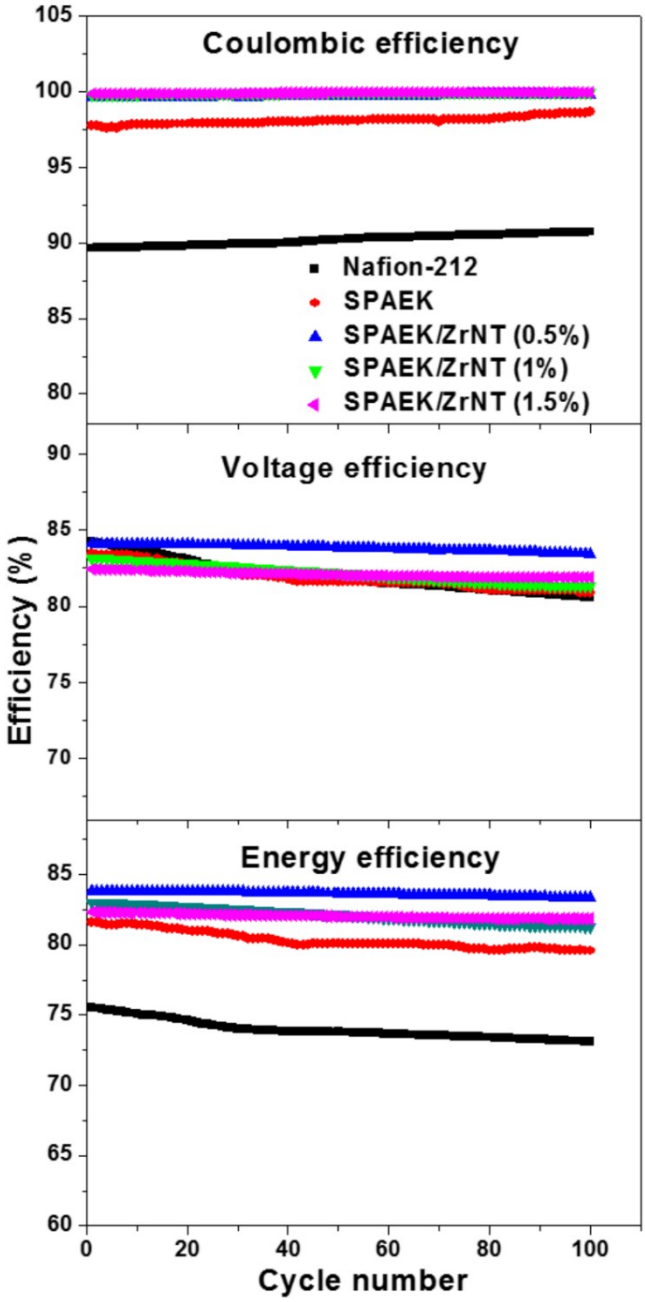

Fig. S6 Cycle performance for the VRB assembled with Nafion-212, SPAEK, SPAEK/ZrNT (0.5%), SPAEK/ZrNT (1%) and SPAEK/ZrNT (1.5%) membranes as a function of cycling numbers at 40 mA cm^{-2} current density.

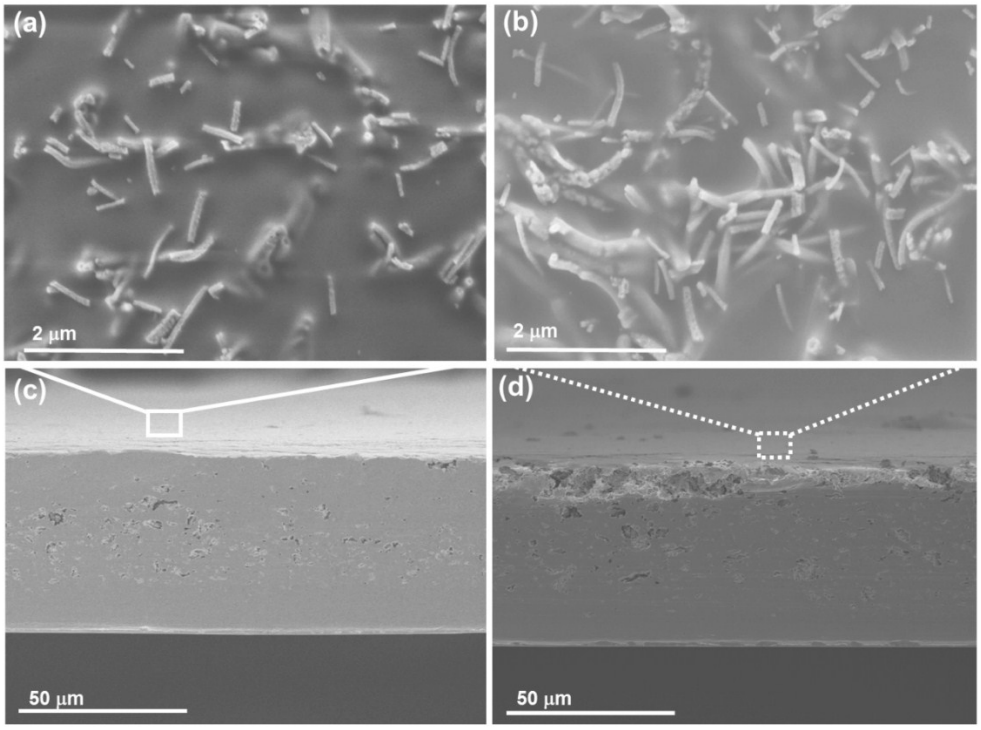

Fig. S7 FE-SEM images of the surface and cross-section morphology of SPAEK/ZrNT (1%) composite membrane (a) and (c) initial. (b) and (d) after over 100 charge-discharge cycles in VRB.

Notes and references

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