Electronic Supporting Information (ESI)

Sulfonated poly(arylene ether ketone)/polyoxometalate-graphene oxide composite:

High ion selective membrane for all vanadium redox flow battery

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Experimental

Preparation of SPAEK / PW-mGO composite membrane: SPAEK (0.3 g) and PW-mGO (3 mg) were completely dissolved in DMAc. The resulting mixture was ultra-sonicated for 1 h and then stirring for 6h. Solvent casting method was used to fabricate the membrane. The prepared solution poured on a flat glass plate and dried vacuum oven at 60 °C for 6 h. Finally, the membrane was peeled off from the glass plate using DI water and again dried at 80 °C. The prepared composite membrane was pre-treated in 1 M H_2SO_4 solution and washed with DI water for 5 times. The membrane thickness was evaluated at 5 random points and the average thickness was found to be 50 ± 5 μm.

Materials characterization: Membrane morphology was checked by field-emission scanning electron microscope (FE-SEM, Hitachi, S-4800II) with setting up the voltage of 3 kV. The membrane sample was sputtered with Osmium before SEM observation.

Water uptake (WU) and swelling degree of membranes were determined by comparison of weight and dimensions of dry and wet samples according to Eq. (1) and (2). Membrane samples were heated at 90 ˚C for 12 h using vacuum oven and then soaked in DI water (24 h) at room atmosphere.

$$\text{Water uptake } (\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \tag{1}$$

$$\text{Swelling degree} (\%) = \frac{L_{wet} - L_{dry}}{L_{dry}} \times 100 \tag{2}$$

where, W_{wet} is the wet membrane and W_{dry} is the dry membrane weight. Similarly, L_{wet} is the wet membrane and L_{dry} is the dry membrane length.

Ion exchange capacity (IEC) was obtained by a titration method. The membrane sample was dried overnight using vacuum oven at 90 ˚C and then shocked in 3M NaCl solution for 12 h. Finally, titration was conducted in 0.01 M NaOH using phenolphthalein indicator. The IEC value was determined according to Eq. (3)

$$IEC = \frac{V_{NaOH} \times C_{NaOH}}{W_{dry}} \tag{3}$$

where, V_{NaOH} is the volume of NaOH used at the neutralized point, C_{NaOH} is the concentration of NaOH and W_{dry} was the dry membrane weight.

Proton conductivity was measured using membrane conductivity cell (Bekktech) with the gas accessory. Specific voltages were applied to Pt electrodes using potentiostat and corresponding currents were obtained. The resistance (R) is calculated using the angle of the line, which joints the data points. During measurement, 100% relative humidity (RH) was fixed with different temperature. The membrane conductivity was determined according to the Eq. (4)

$$\sigma = \frac{L}{R \times W \times T} \tag{4}$$

where, L = 0.425 cm is the constant length among Pt electrodes; R is the resistance of membrane in Ω; W is the sample width in cm and T is the membrane thickness in cm.

Measurements of VO²⁺ permeability and ion selectivity: The permeation rate of vanadium ion across the membranes was analyzed using a membrane diffusion cell at ambient temperature. Sample membrane with specific area 9 cm² that act as a barrier of electrolyte transformation between the two reservoirs. Equal volume (150 mL) of two reservoir, where the left reservoir was loaded with 1.5 mol L⁻¹ VOSO₄ in 3 mol L⁻¹ H₂SO₄, and the right reservoir was loaded with 150 mL of 1.5 mol L⁻¹ MgSO₄ in 3 mol L⁻¹ H₂SO₄ solution to limit the effects of osmotic pressure as well as stability of ionic strengths. The solutions in the both reservoir were continuously stirred by magnetic stirrers throughout the entire measurement to avoid the concentration polarization. The aliquot sample was taken at regular time intervals from the right reservoir and the concentration of vanadium ion was determined using an ultraviolet and visible (UV-Vis) spectrometer. The crossover of vanadium ion was obtained by the following equation [S1].

$$V_R \frac{d\,C_R(t)}{dt} = A \frac{P}{L} \left[C_L - C_R(t) \right] \tag{5}$$

where, $C_R(t)$ is the vanadium ion concentration measured by UV–vis spectrometer in the right reservoir with respect to time, and C_L is the vanadium ion concentration in the left reservoir. A is the active area and L is the thickness of the membrane. P is the crossover of vanadium ion and V_R is the volume of the right reservoir. It was assumed that the concentration change of the vanadium ion in the left reservoir should always be negligible and applied for a pseudo-steady-state order across the membrane.

The membrane ion selectivity (S) was evaluated via proton conductivity (δ) with vanadium ion crossover of (P), by the following Eq. (6),

$$S = \frac{\delta}{P} \tag{6}$$

Measurements of vanadium flow battery performance: The VRB for the charge-discharge test was assembled by loading the membrane among two pieces of carbon felt electrodes with an active area 9 cm^2. The membrane-electrode assembly (MEA) was compressed and clasped through two graphite plates, which act as current collectors. Two copper sheets were attached in the outer positions of two graphite plates that're worked for battery terminal connectors. This assembly was sealed by two poly vinyl chloride (PVC) end plates. The carbon fleece (5 mm uncompressed thickness) was activated before using in VRBB by thermal treatment at 500 ˚C for 30 min. The VRB charge–discharge curves was evaluated for SPAEK/PW-mGO composite membranes and the commercial Nafion-212 membrane were determined by an ambient temperature at 40 mA cm^{-2}.

Vanadium electrolyte solution for both anolyte and catholyte (30 mL in each) with a composition of 1.7M V (± 3%), V^{3+} / V^{4+} 1:1 (±3%), 4.5M SO$_4^-$ (±5%) was employed for VRB operation. The electrolyte solution was circulated with a peristaltic pump (Reglo ICC 2ch Pump) at a flow rate of 10 mL min^{-1}. Electrolyte vessels were de-aerated using continuous N$_2$ flow to avoid the chemical oxidation of the vanadium redox couples.

A multi-channel battery analyzer (BST8-3, MTI Corp.) was fabricated to check performances of the battery. VRB operation during charge-discharge same conditions was applied for each membrane sample, such as Nafion-212 and SPAEK/PW-mGO composite membrane. The maximum and minimum limit of the charge-discharge voltage was applied 1.6 and 1 V, respectively that prevent from corrosion of the electrodes and graphite plates. The self-discharge rate of the battery was conducted by time tracking of the open circuit voltage (OCV) decrease of a fully charged battery. The data for all membranes were collected until the open circuit voltage dropped below 0.8 V. Corresponding data for coulombic efficiency (CE), voltage efficiency (VE),

and energy efficiency (EE) of the VRB fabricated with different membranes were evaluated by the following equations.

$$CE = \frac{\text{discharge capacity}}{\text{charge capacity}} \times 100 \tag{7}$$

$$VE = \frac{\text{middle point of discharge voltage}}{\text{middle point of charge voltage}} \times 100 \tag{8}$$

$$EE = CE \times VE \tag{9}$$

Table S1. Physicochemical characteristics of Nafion-212, SPAEK, SPAEK/PW-mGO (1%) and

SPAEK/PW-mGO (2%) membranes.

Membrane	Water uptake (%)	Swelling degree (%)	IEC (meq g^{-1})	Proton conductivity (mS cm^{-1}) @100%RH at room temperature	VO^{2+} permeability (10^{-7}cm^2 min^{-1})	Ion selectivity (10^6 S min cm^{-3})
NRE-212	24	10.10	0.94	54	3.3	0.16
SPAEK	74	9.27	1.72	61	1.0	0.61
SPAEK/PW -mGO (1%)	96	8.74	2.12	71	0.28	2.5
SPAEK/PW -mGO (2%)	90	7.49	1.94	65	0.16	4.0

Table S2. VRB performance assembled with Nafion-212, SPAEK, SPAEK/PW-mGO (1%) and SPAEK/PW-mGO (2%) membranes under charge-discharge current density of 40 mA cm^{-2}.

Membrane	Thickness (μm)	CE (%)	VE (%)	EE (%)
Nafion-212	55	89.65	84.24	75.53
SPAEK	50±5	97.76	83.41	81.56
SPAEK/PW-mGO (1%)	50±5	98.70	84.57	83.53
SPAEK/PW-mGO (2%)	50±5	98.73	82.75	81.72
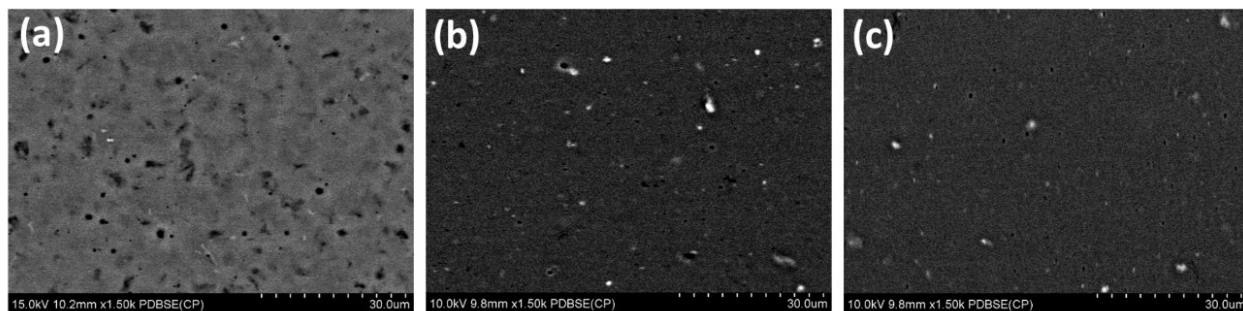
Fig. S1 SEM images (back scattering mode) of (a) pure SPAEK, (b) SPAEK/PW-mGO (1%), and (c) SPAEK/PW-mGO (2%) membranes surface.
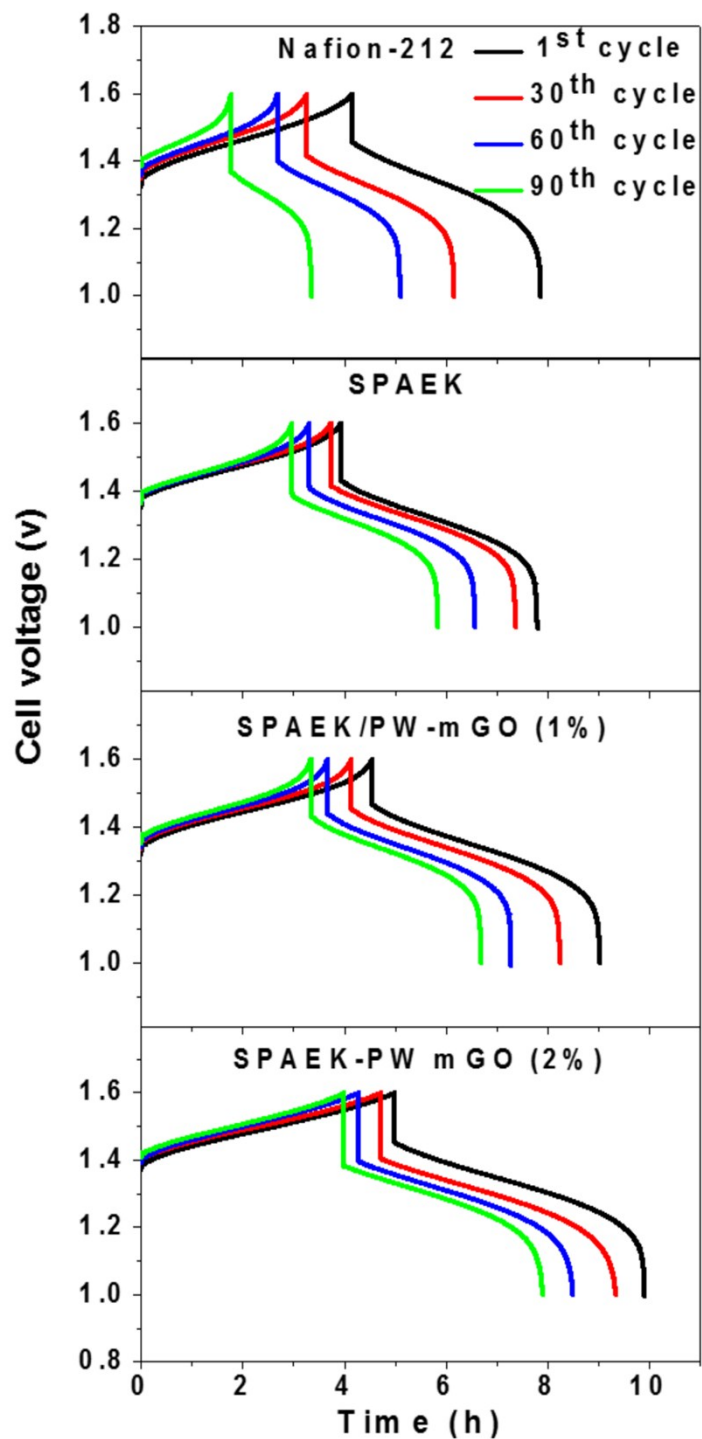
Fig. S2 Charge-discharge curves of the VRB assembled with Nafion-212, SPAEK, SPAEK/PW-mGO (1%) and SPAEK/PW-mGO (2%) membranes at 40 mA cm^{-2}.
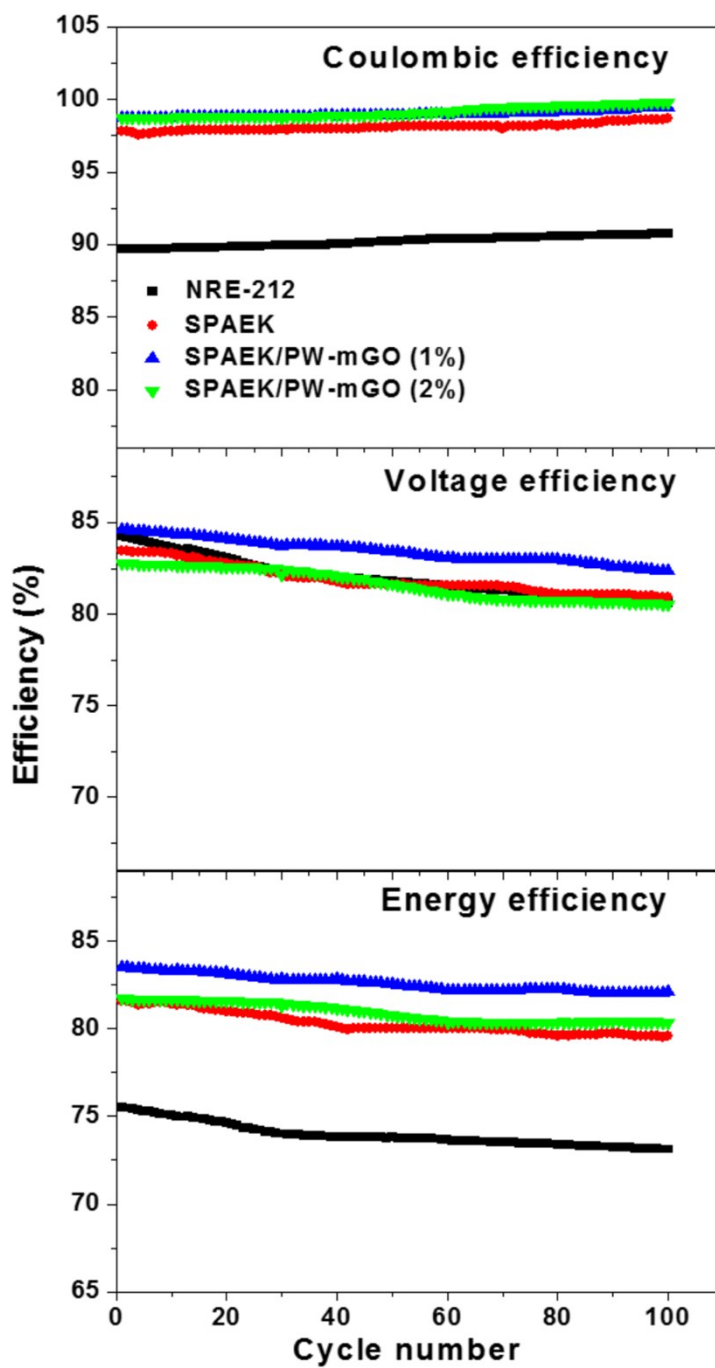
Fig. S3 Cycle performance for the VRB constructed with Nafion-212, SPAEK, SPAEK/PW-mGO (1%) and SPAEK/PW-mGO (2%) membranes as a function of cycling numbers at 40 mA cm^{-2}.
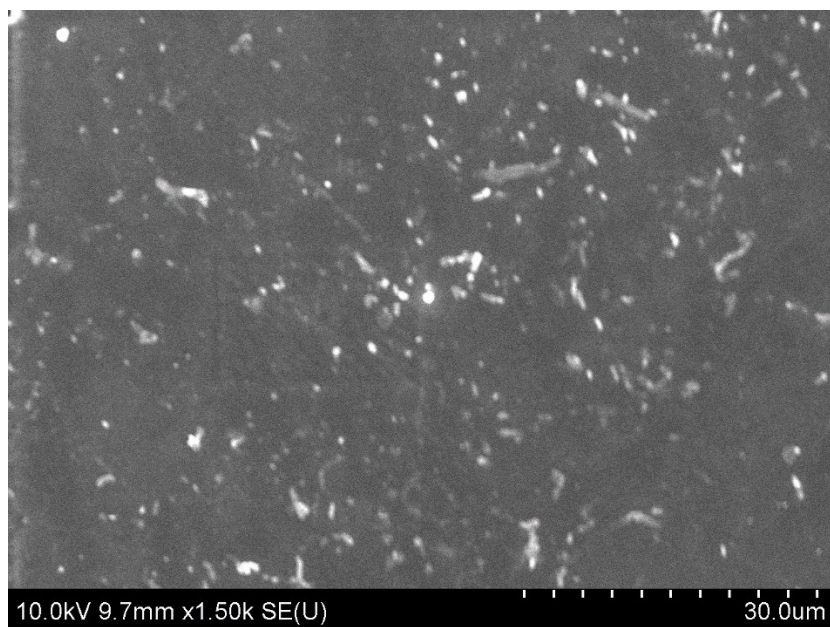
Fig. S4 FE-SEM image surface of SPAEK/PW-mGO (1%) composite membrane after 100 cycle charge-discharge operation in VRB.

References

[S1] X. L. Luo, Z. Z. Lu, J. Y. Xi, Z. H. Wu, W. T. Zhu, L. Q. Chen and X. P. Qiu, *J. Phys. Chem*.,
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