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Sulfonated graphene oxide decorated block copolymer as proton exchange membrane: improving the ion selectivity for all vanadium redox flow batteries

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Experimental

Materials

4,4′-Difluorobenzophenone (DFBP), 4,4′-biphenol (BP) and Bis(4-fluorophenyl) sulfone (FPS) were purchased from TCI Inc, Tokyo, Japan. N,N-dimethylacetamide (DMAc), Dimethyl sulfoxide (DMSO), N-methyl-2-pyrrolidone (NMP), toluene, 20% Oleum, graphite (average particle size less than 20 μm), and H_2SO_4 were procured from Sigma-Aldrich, Korea. Sulfanilic acid and $NaNO_2$ were purchased from Daejung Chemicals, Korea and used as received. The Nafion-212 membrane (50 μm thickness) was purchased from Aldrich, Korea and the pretreatment of the Nafion-212 membrane was carried out by boiling with 5% H_2O_2 and 1M H_2SO_4 solution for 1 h each and finally washed with DI water at several times before use.

Synthesis of oligomer for hydrophilic block

A round-bottomed flask (100 mL) was integrated with DFBP (5 g) and 20% Oleum, and the sulfonation was sustained at 113 °C for 9 h with reflux. The obtained solution has been discharged into ice and neutralized using a solution of 3 M NaOH. The NaCl was then added slowly into the hybrid mixture results precipitation of the yellow product, which was mixed with DI water and subsequently purified using dialysis. The solution was dehydrated in a vacuum oven at 100 °C to get sulfonated DFBP (SDFBP). Using of SDFBP (6.6 g, 15.7 mmol), BP (2.3 g, 12.6 mmol), potassium carbonate (2.9 g, 21 mmol), DMSO (32 mL), and toluene (16 mL), the process was continued at heating of 145 °C for 2 h and then 170 °C for 2 h in a Dean-Stark trap under N_2 flow. Finally, the solution was added into IPA (500 mL) to get precipitation of oligomer for the hydrophilic block with 77% yield.

Synthesis of oligomer for hydrophobic block

A round-bottomed flask (100 mL) was charged with BP (3.2 g, 16.7 mmol), FPS (4.0 g, 15.7 mmol), potassium carbonate (4.6 g, 33.4 mmol), DMAc (32 mL), and toluene (16 mL). The process was continued at a heating temperature of 145 °C for 1 h and then 170 °C for 1 h in a Dean-Stark trap under N_2 flow. The resulting viscous mixture was dropped wise added into DI water (1 L), and resulting white precipitate was purified by methanol washing and subsequently drying in a vacuum oven for the oligomer of the hydrophilic block with 82% yield.

Synthesis of SPEKS block copolymer

A round-bottomed flask (100 mL) was charged with hydrophilic oligomer (0.24 g, 0.07 mmol) and hydrophobic (0.46 g, 0.07 mmol), calcium carbonate (0.0701 g, 0.7 mmol), potassium carbonate (0.029 g, 0.21 mmol), 4 mL of DMSO and 1 mL of toluene. The polymerization was carried out at 145 °C for 30 h with vigorous stirring using the magnetic bar, and then, at ambient atmosphere 1 mL of DMSO was dissolve into the polymer mixture for reducing viscosity and poured dropwise into 1 M HCl solution. The light yellow fiber was treated with 3 M NaCl solution to transfer sodium form and finally, the product was dried using vacuum oven for SPEKS with 76% yield.

Preparation of graphene oxide

Modified Hummers method was used to synthesize graphene oxide from natural graphite powder [S1]. Graphite powder (1 g) was blended with NaCl (50 g), and the resulting mixture was treated with DI water and ethanol at several times to remove NaCl completely. Once evaporation was finished, H_2SO_4 (4 mL) was charged and the dissolve with $K_2S_2O_8$ (0.84 g) and P_2O_5 at 80 °C for

4.5 h. The corresponding solution was then stirred using DI water (167 mL) in ambient atmosphere. Subsequently, the dispersion was filtered, washed with DI water and evaporated. Then, it was mixed with H_2SO_4 (40 mL) with $KMnO_4$ (5 g) in a two-neck flask and stirred up to completely dissolved. Afterward, DI water (84 mL) was mixed with the hybrid solution and stirred slowly at 35 °C for 2 h. Finally, DI water (167 mL), H_2O_2 (10 mL) were charged and continue stirring for certain time. The obtained solution was centrifuged before achieve pH 7 and dried using vacuum oven to get brown powder.

Preparation of sulfonated graphene oxide

Graphene oxide (5 mg) was charged with 0.06 M sulfanilic acid (8 mL), and the mixture was heated at 70 °C under continuous stirring. Then, $NaNO_2$ (2 mL, 0.006 M) solution was mixed dropwise and continued reaction for 12 h. Finally, the mixture was centrifuged and washed with DI water until the pH becomes neutral.

Table S1 The performance of VRBs with SPEKS and SPEKS/sGO (0.5%) membranes in comparison with previous work.

Membrane	Thickness (μm)	Proton conductivity (mS cm^{-1})	VO^{2+} Permeability (10^{-7} cm^2 min^{-1})	Coulombic efficiency (%)	Energy efficiency (%)	Current density (mA cm^{-2})	Open circuit voltage (h)	Ref.
SPEKS/sGO (0.5%)	50	51	0.50	99.0	82.5	40	438	This work
SPEKS	50	19	0.24	97.2	74.7	40	271	This work
S-PAEK-40	50	53	11.15	89.5	82.6	20	NA	S2
SPEEK/g-C_3N_4-1.5	80	7.9	3.70	97.5	83.6	30	68	S3
S/GO-NH_2-2	60	38	2.04	97.2	89.5	50	160	S4
SPEEK/PPD-GO-1	80	16.4	13.50	96.5	82.5	30	56	S5
PBI-10%	45	NA	1.17	99.4	78.2	40	140	S6
S/Q-15	60	47	1.30	96.1	88.4	50	53	S7
S/GO2@PTFE	67	14.6	7.6	98.4	81.2	80	NA	S8
sPEEK	50	52.0	3.5	96.1	79.5	40	NA	S9
TMA-5	45	NA	NA	97.0	92.0	40	100	S10
S@CCP	35	NA	2.2	95.0	90.0	40	91.7	S11
S/CNT@PDA	60	97.7	8.7	97.2	91.9	40	NA	S12
SE3/P	70	42.6	7.1	98.5	88.1	40	NA	S13
s-FSPI	60	22.8	0.74	99.6	77.0	60	NA	S14
Nafion-212	51	56	3.3	90	78	60	53	S15

Table S2 Tensile stress, areal resistance, retained vanadium ion species after ion selectivity measurement and VRB discharge capacity at 40 mA cm^{-2} for different membranes.

Membrane	Tensile stress (N)	Areal resistance (Ω cm^2)	Vanadium ions (%)	Discharge capacity (mAh)
Nafion-212	16.77	1.05	1.25	1339.6
SPEKS	13.22	2.67	0.84	1508.7
SPEKS/GO	16.56	2.15	0.89	1747.1
SPEKS/sGO (0.5%)	17.88	1.23	0.93	1977.1
SPEKS/sGO (1%)	18.11	1.14	1.55	1775.3
SPEKS/sGO (1.5%)	18.27	1.31	1.29	1792.1

Table S3 Cyclic performance of the VRB assembled with Nafion-212, SPEKS, SPEKS/GO, SPEKS/sGO (0.5%), SPEKS/sGO (1%) and SPEKS/sGO (1.5%), R-SPEKS, R-SPEKS/sGO (0.5%) membranes at current density of 40 mA cm^{-2}.

Membrane	CE (%)	VE (%)	EE (%)
Nafion-212	89.6	84.2	75.5
SPEKS	97.2	76.9	74.7
SPEKS/GO	97.5	79.7	77.7
SPEKS/sGO (0.5%)	99.0	83.3	82.5
SPEKS/sGO (1%)	98.8	83.8	82.8
SPEKS/sGO (1.5%)	99.4	82.4	81.9
R-SPEKS	95.6	76.0	72.7
R-SPEKS/sGO (0.5%)	97.7	76.9	75.1

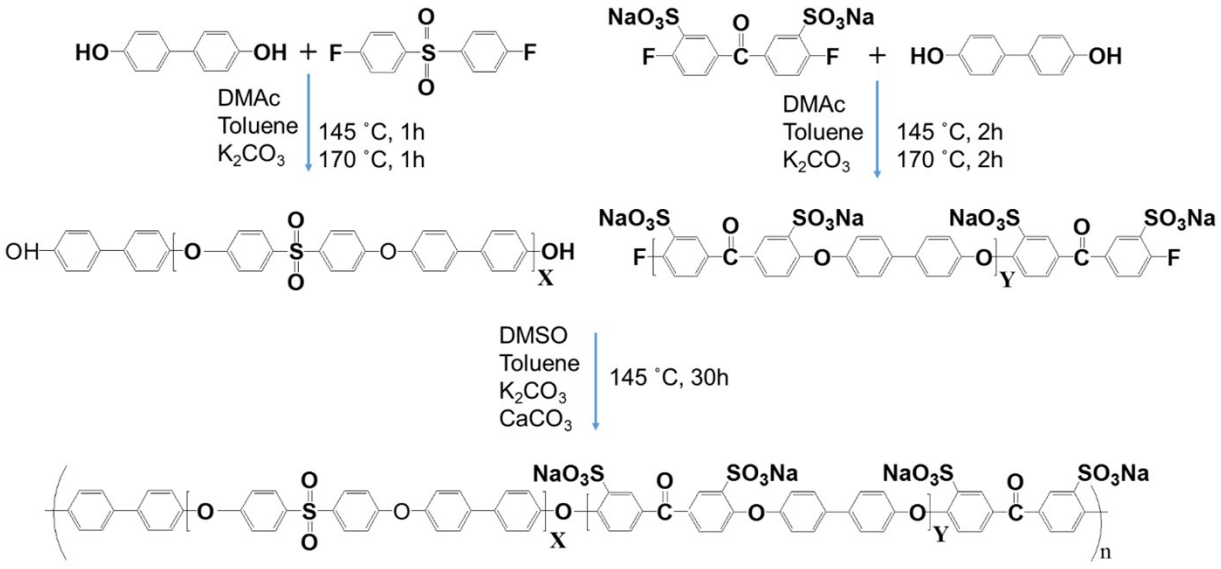

Fig. S1 Schematic description of synthesis of hydrophobic, hydrophilic and block copolymers.

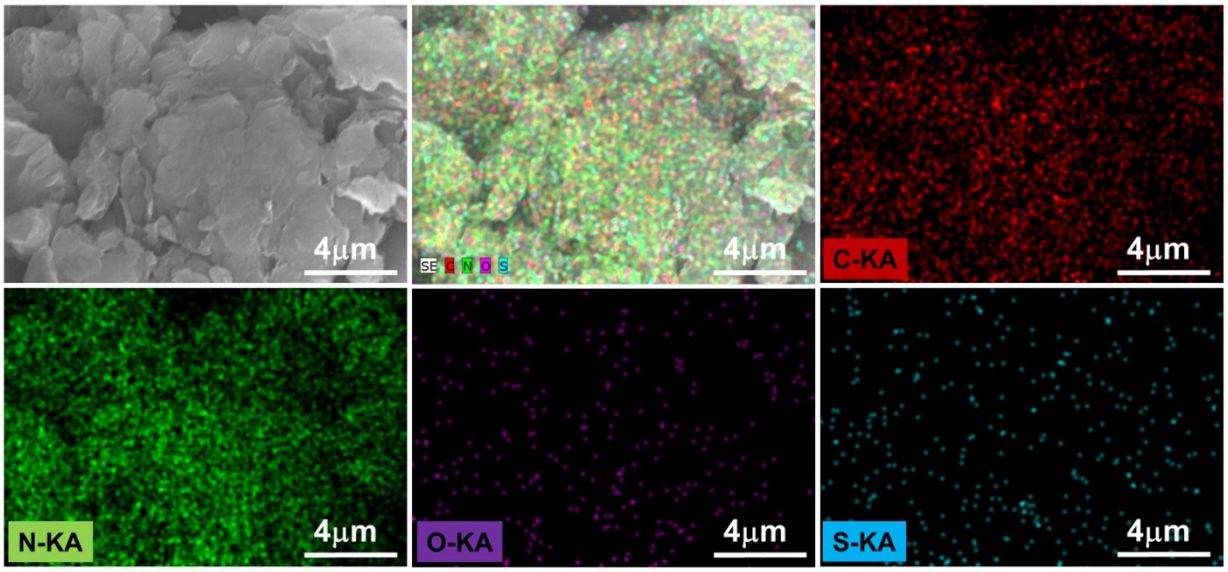

Fig. S2. FE-SEM elemental mapping of sample graphene oxide (GO).

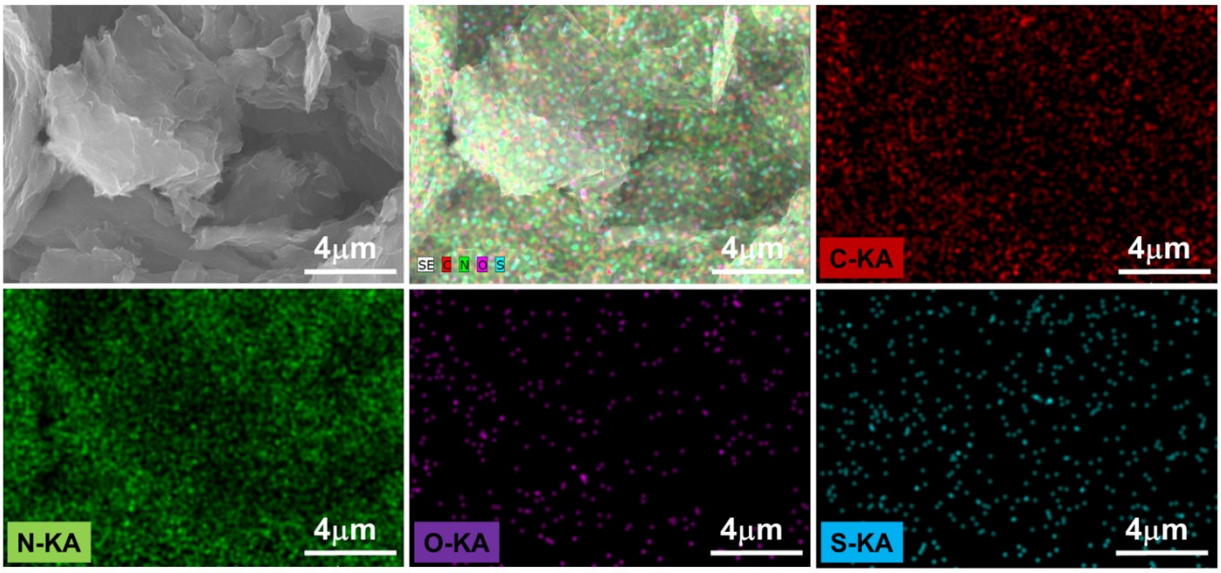

Fig. S3 FE-SEM elemental mapping of sample sulfonated graphene oxide (sGO).

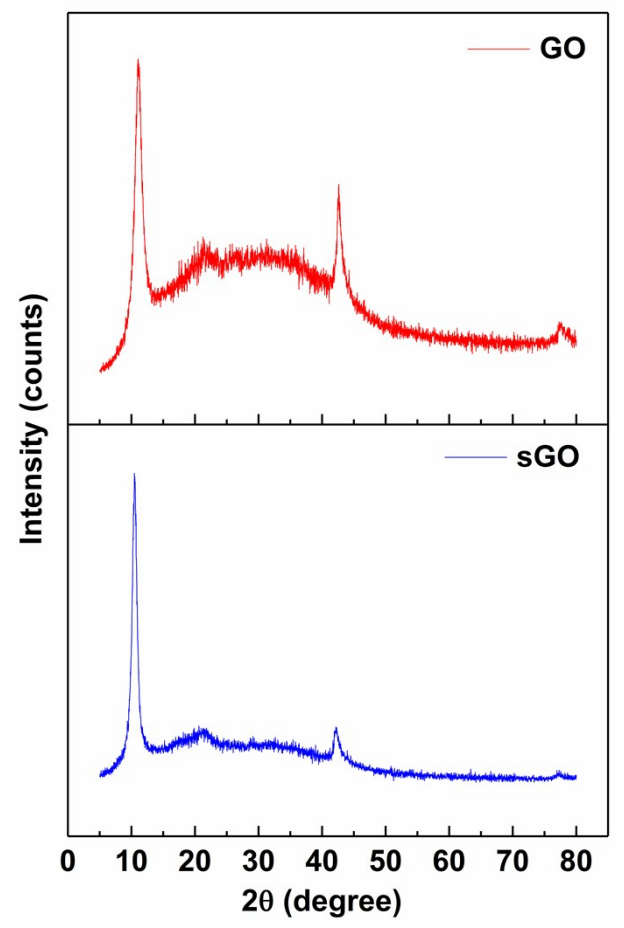

Fig. S4 Powder X-ray diffraction pattern of GO and sGO.

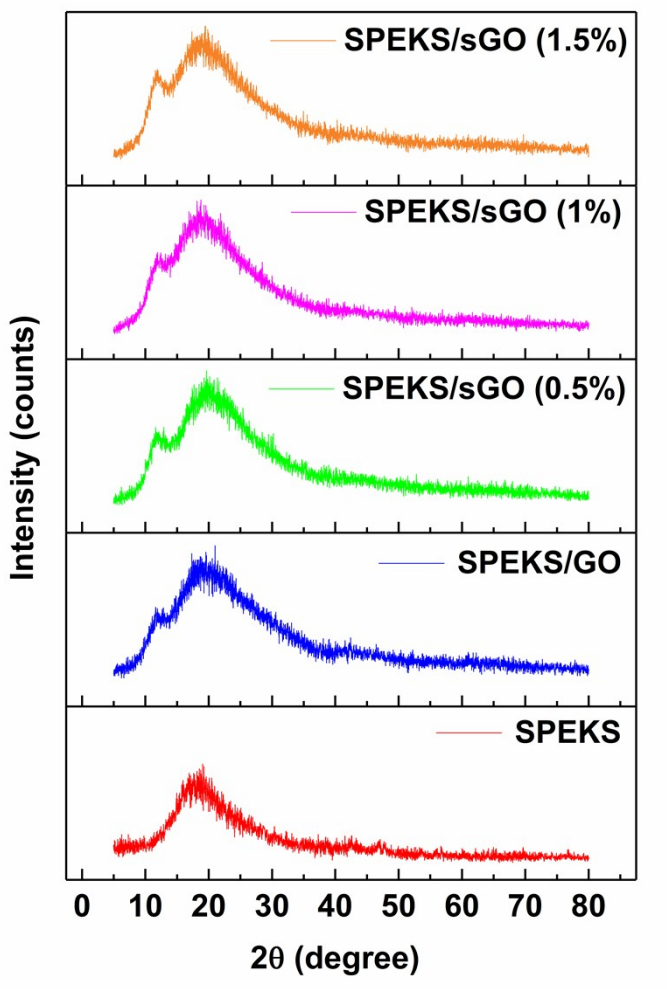

Fig. S5 Powder X-ray diffraction pattern of samples SPEKS, SPEKS/GO, SPEKS/sGO (0.5%), SPEKS/sGO (1%) and SPEKS/sGO (1.5%) membranes.

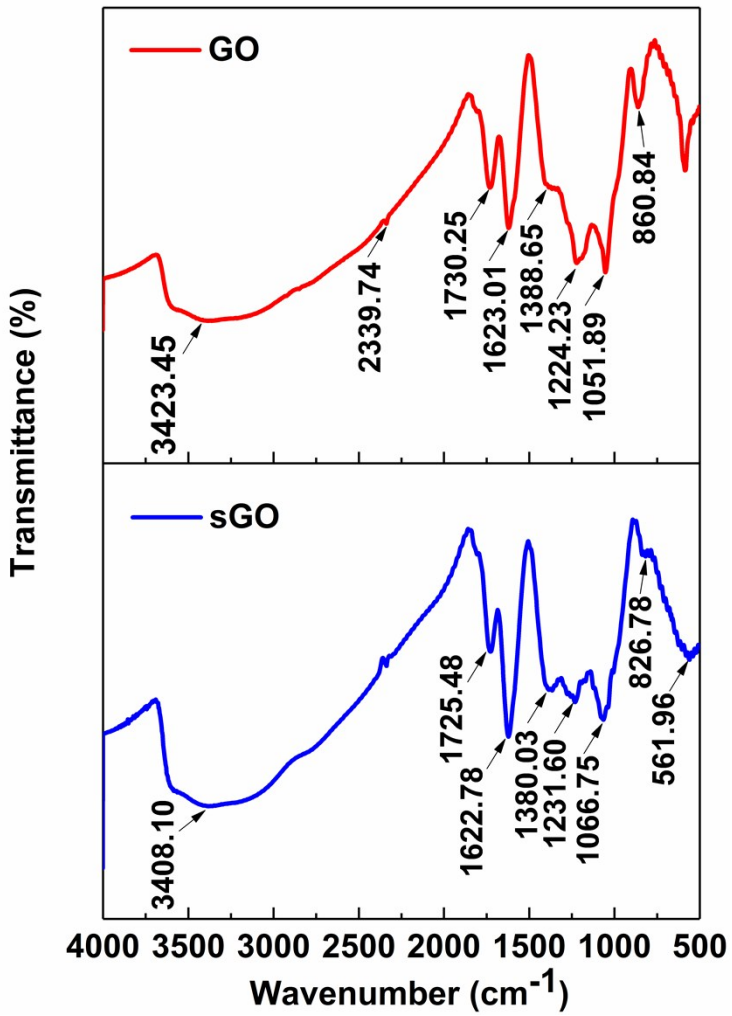

Fig. S6 FT-IR spectra of GO and sGO.

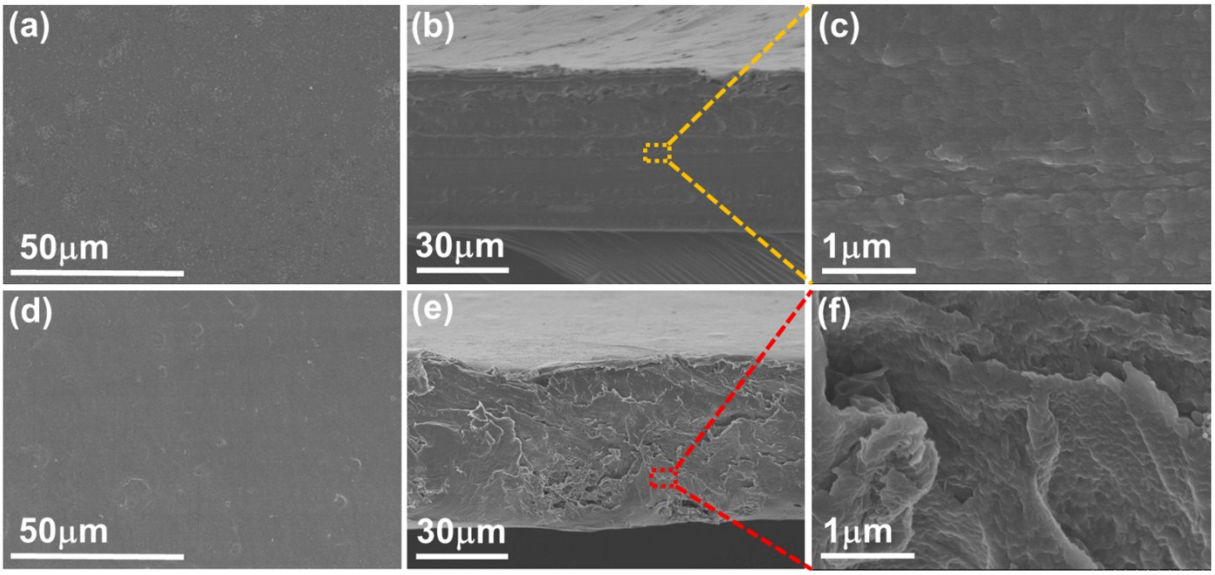

Fig. S7 FE-SEM image of SPEKS membrane (a) Surface, (b) and (c) Cross-section; SPEKS/sGO (0.5%) membrane (d) Surface, (e) and (f) Cross-section.

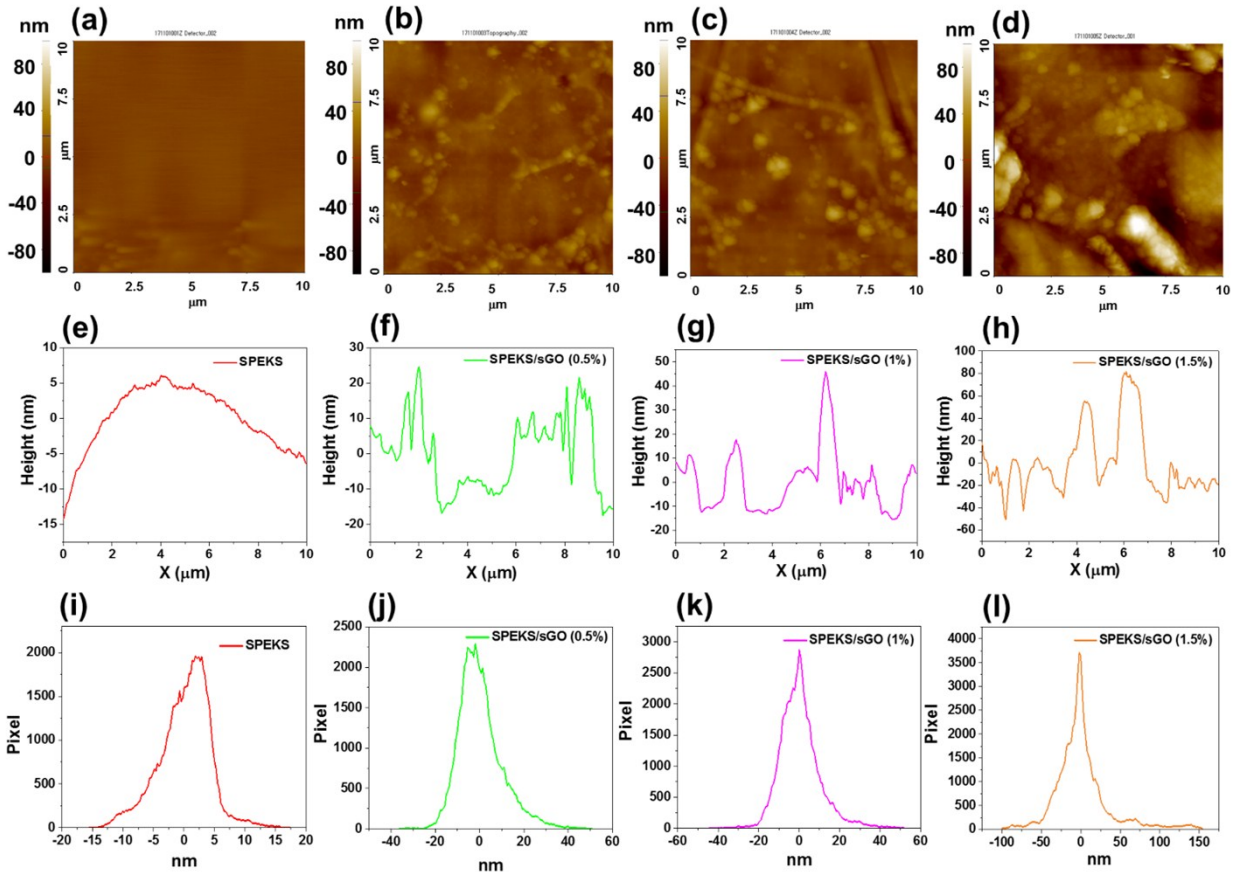

Fig. S8 Topography: (a) SPEKS, (b) SPEKS/sGO (0.5%), (c) SPEKS/sGO (1%) and (d) SPEKS/sGO (1.5%) membranes. Line profile: (e) SPEKS, (f) SPEKS/sGO (0.5%), (g) SPEKS/sGO (1%) and (h) SPEKS/sGO (1.5%) membranes. Histogram: (i) SPEKS, (j) SPEKS/sGO (0.5%), (k) SPEKS/sGO (1%) and (l) SPEKS/sGO (1.5%) membranes.

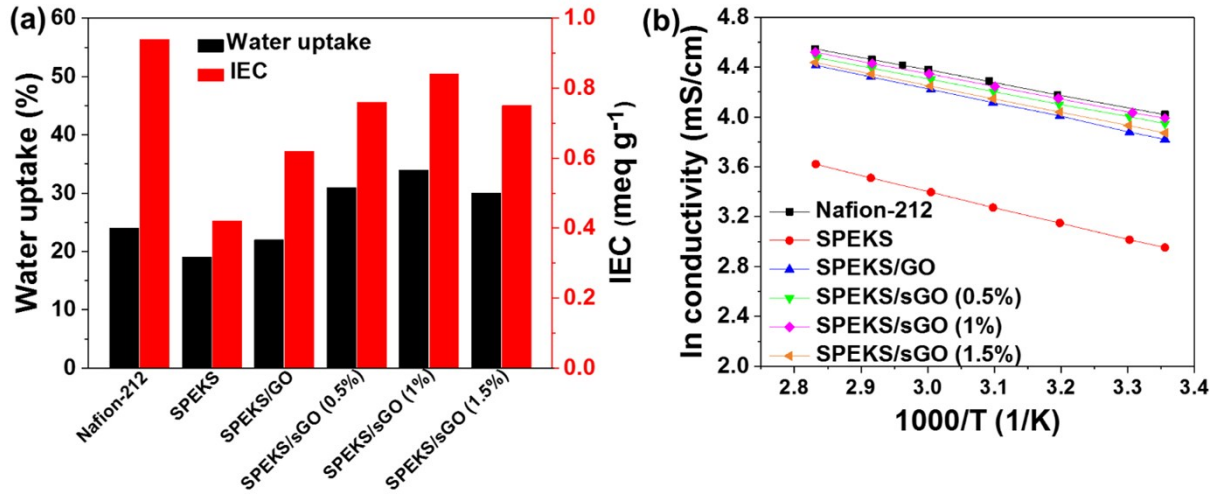

Fig. S9 (a) Water uptake and IEC value of Nafion-212, SPEKS, SPEKS/GO, SPEKS/sGO (0.5%), SPEKS/sGO (1%) and SPEKS/sGO (1.5%) membranes. (b) Regression curve of proton conductivity with T^{-1} for Nafion-212, SPEKS, SPEKS/GO, SPEKS/sGO (0.5%), SPEKS/sGO (1%) and SPEKS/sGO (1.5%) membranes measured at 25 to 80 °C under 100% RH.

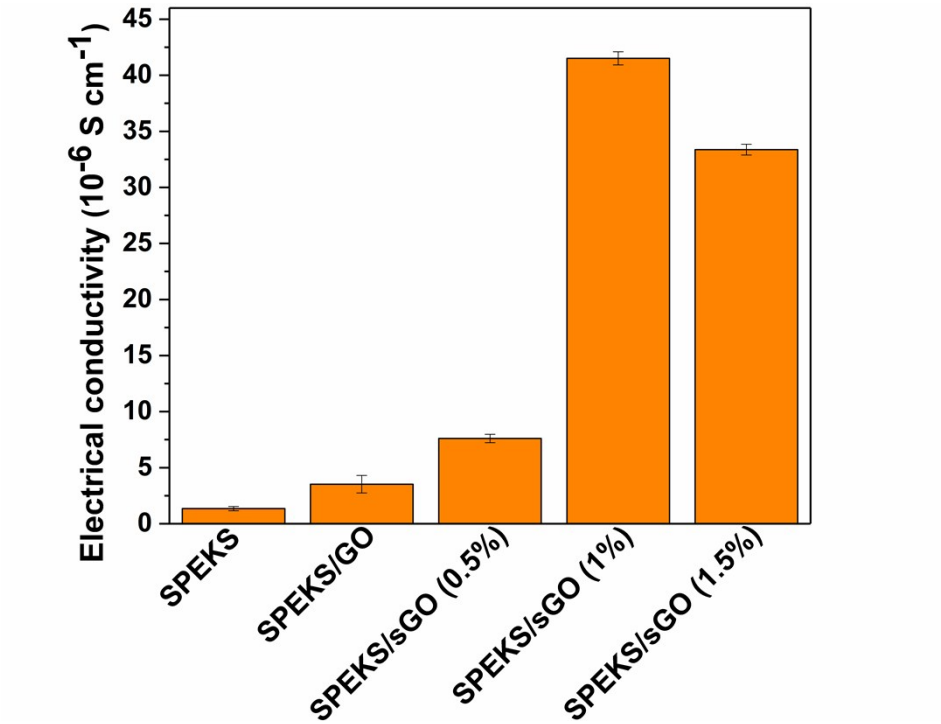

Fig. S10 The electrical conductivity measurement of SPEKS, SPEKS/GO, SPEKS/sGO (0.5%), SPEKS/sGO (1%) and SPEKS/sGO (1.5%) membranes.

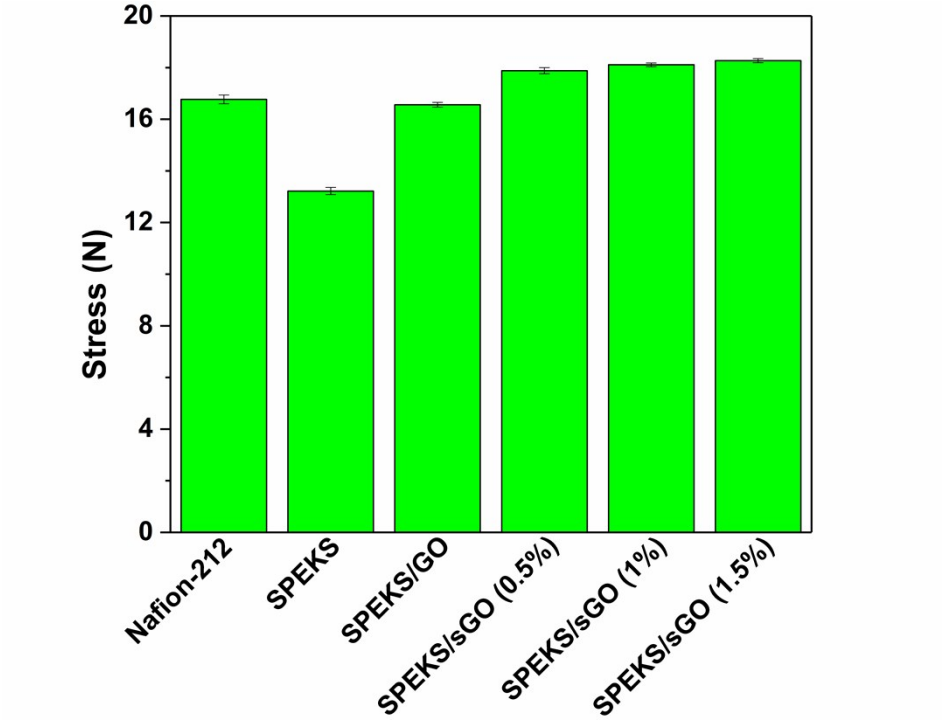

Fig. S11 The tensile stress of Nafion-212, SPEKS, SPEKS/GO, SPEKS/sGO (0.5%), SPEKS/sGO (1%) and SPEKS/sGO (1.5%) membranes.

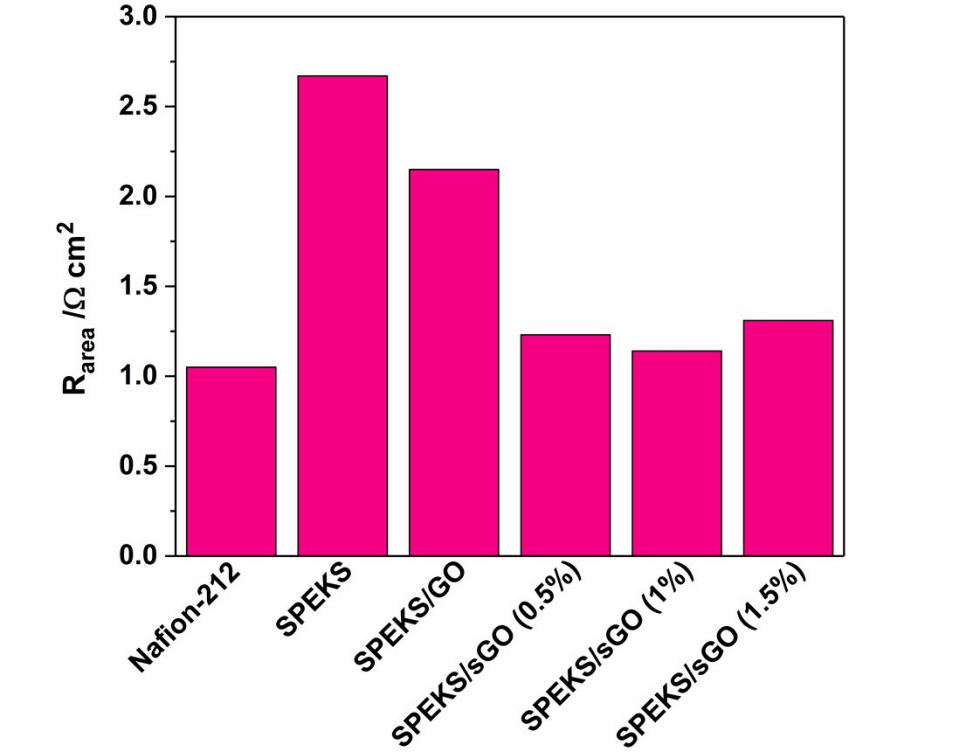

Fig. S12 Areal resistance of the samples of Nafion-212, SPEKS, SPEKS/GO, SPEKS/sGO (0.5%), SPEKS/sGO (1%) and SPEKS/sGO (1.5%) membranes.

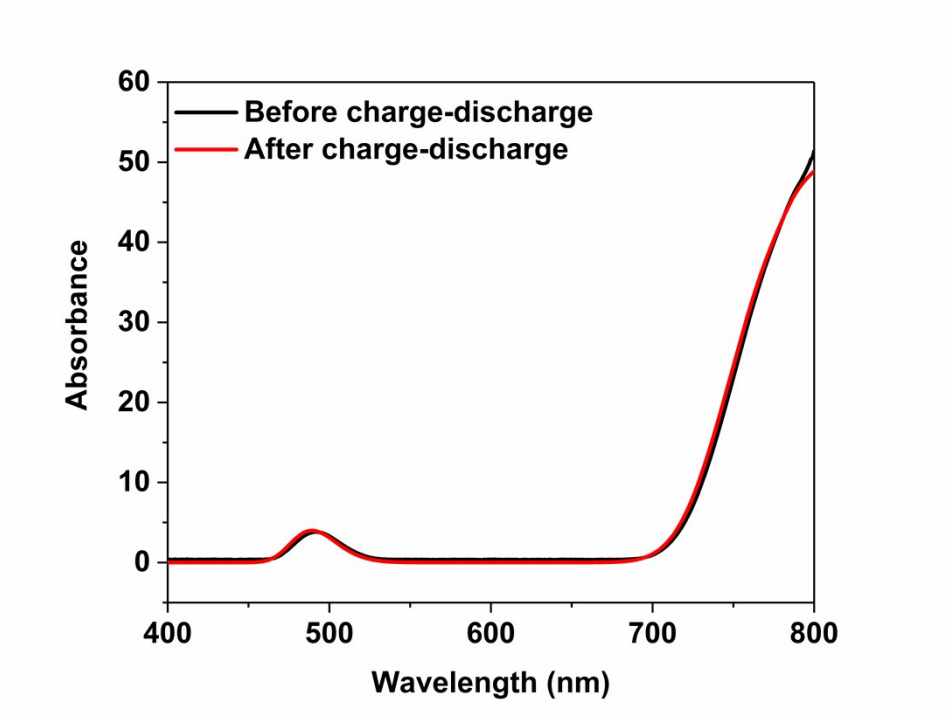

Fig. S13 UV-vis. absorption spectra of the vanadium electrolyte solution at before and after 300 charge-discharge cycles in the VRB.

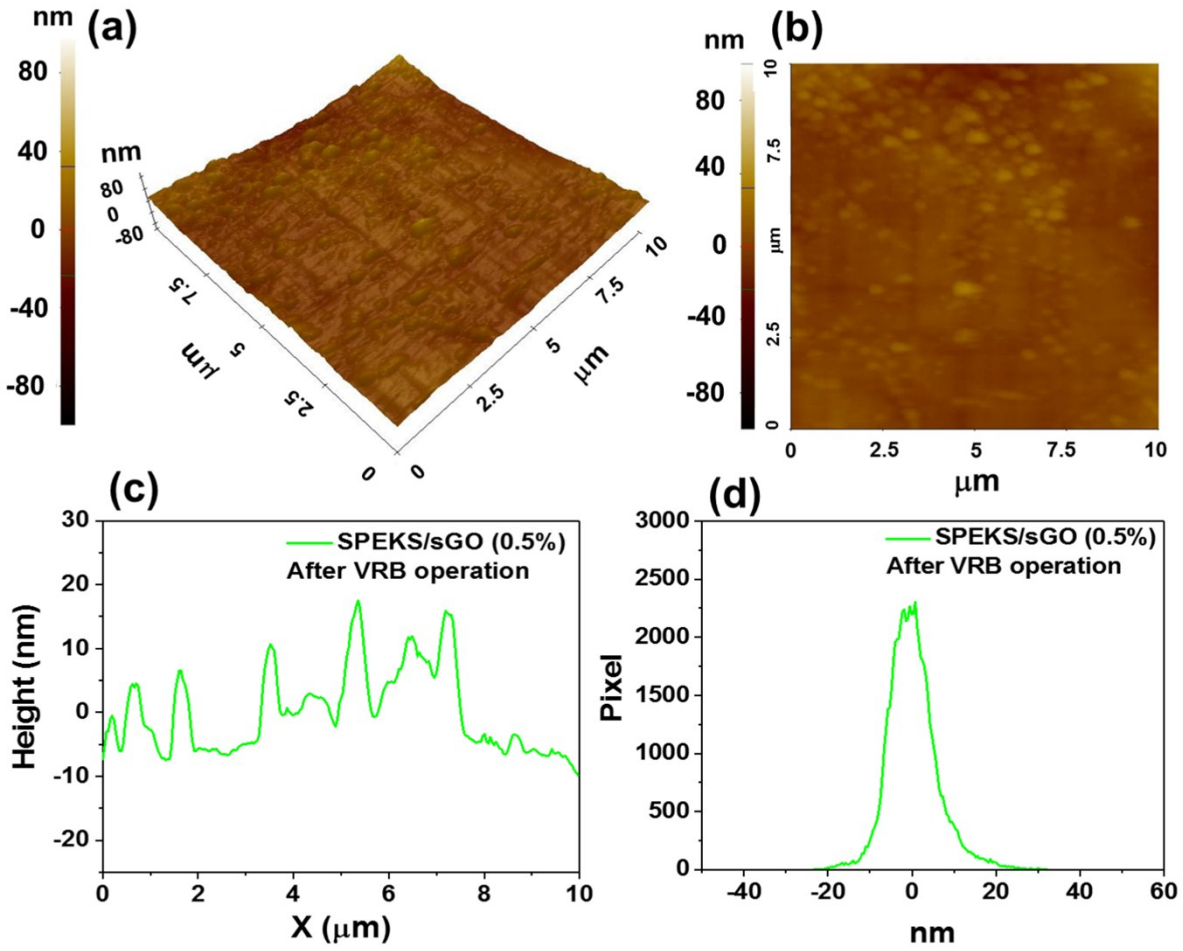

Fig. S14 AFM analysis: (a) 3D image, (b) Topography, (c) Line profile and (d) Histogram of the SPEKS/sGO (0.5%) composite membrane after 300 charge-discharge cycles in the VRB.

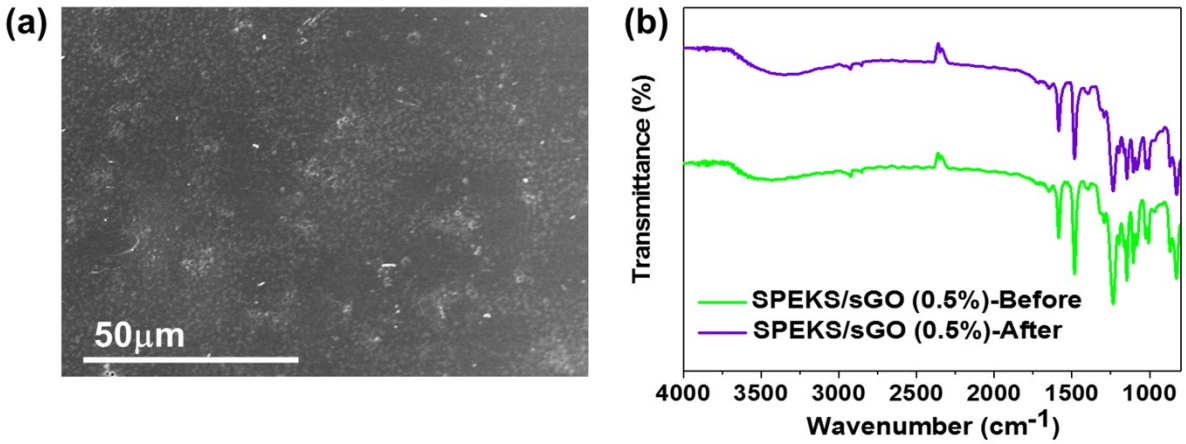

Fig. S15 (a) FE-SEM image of SPEKS/sGO (0.5%) membrane surface after 300 charge-discharge cycle of the VRB. (b) FT-IR spectra of SPEKS/sGO (0.5%) membrane before and 300 charge-discharge cycles of the VRB.

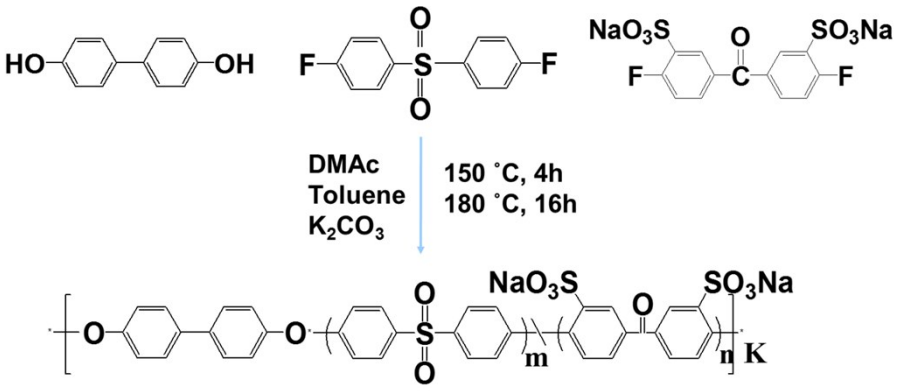

Fig. S16 Schematic description of synthesis of random sulfonated poly(ether ketone sulfone) copolymer membrane.

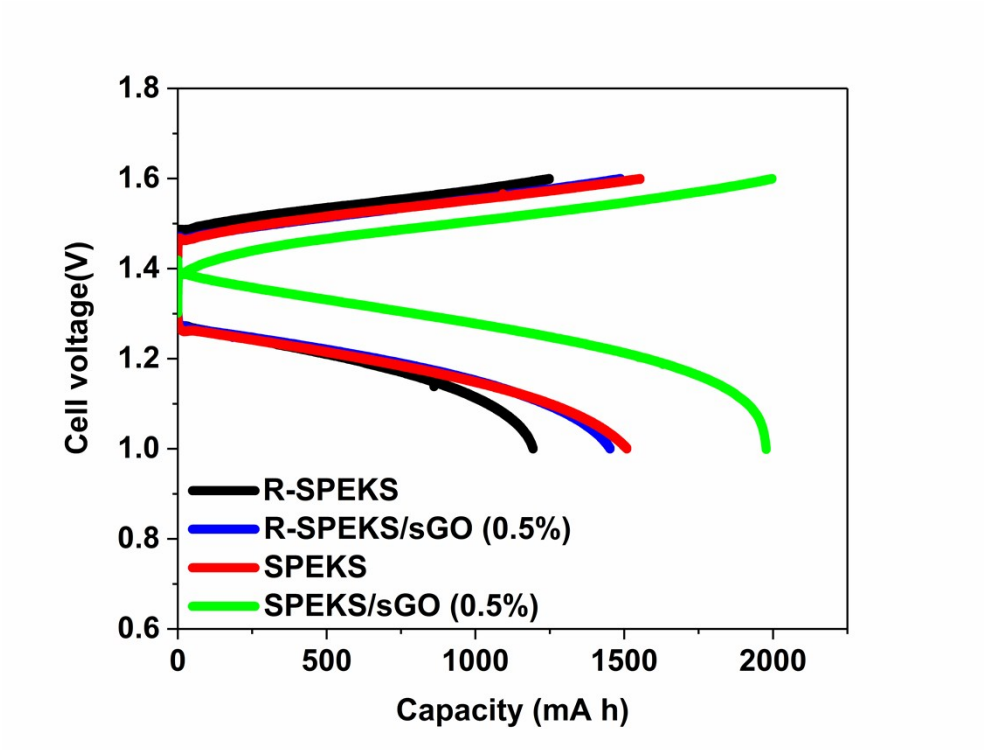

Fig. S17 VRB charge-discharge capacity of random copolymer membrane R-SPEKS, pure SPEKS block copolymer and their composite membranes.

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