Electronic Supporting Information (ESI)

# Fabrication of SPAEK-Cerium zirconium oxide nanotube composite membrane with outstanding performance and durability for vanadium redox flow batteries

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### **Experimental details**

## Materials

Zirconium (IV) acetylacetonate (Zracac), cerium (IV) acetylacetonate (Ceacac), polyacrylonitrile (PAN,  $M_w = 150,000 \text{ g/mol}$ ), *N*, *N*-dimethylacetamide (DMAc), and NRE-212 were purchased from Sigma-Aldrich, Korea. Ethanol, H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>, were bought from Daejung Chemicals, Korea. Vanadium electrolyte 1.7 M V (±3%), V<sup>3+</sup>/V<sup>4+</sup> 1:1 (±3%), 4.5 M SO<sub>4</sub><sup>--</sup> (±5%) was purchased from FC International, South Korea and were utilized as received.

#### Material characterization

<sup>1</sup>H-NMR spectroscopy (Bruker AV 400 spectrometer at 400 MHz) was performed in DMSO-d<sub>6</sub> ( $\delta$  = 2.50 ppm) as a solvent to confirm the structures of the SPAEK/Ce<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> (2%) composite membrane. Structure of Ce<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> nanotube and surface morphology were investigated by field-emission scanning electron microscope (FE-SEM, Hitachi, S-4800II) with 3 kV setup. The membrane was coated with osmium for FE-SEM investigation. The microstructure of the Ce<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> nanotube was analyzed by transmission electron microscope (Bio-TEM, with a setup voltage of 200 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 samples was analyzed by powder X-ray diffraction (XRD, Panalytical, Empyrean), CuK $\alpha$  radiation with setting up 40 kV and 30 mA. O1s and V2p signal of SPAEK/Ce<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> (2%) composite membrane examined by the X-ray photoelectron spectroscopy (Thermo Scientific ESCALAB 250Xi).

Thermogravimetric analysis (Thermo plus EVO, TG8120) was investigated to evaluate the thermal stability of the membranes. The sample was kept in a crucible then it was heated from ambient temperature to 600 °C at a heating rate of 10 °C min<sup>-1</sup> under an oxygen atmosphere. The mechanical stability of the membranes was observed by the tensile test machine (SFM-100kN, united testing system, Inc. the USA) at room temperature with a crosshead speed of 5 mm min<sup>-1</sup>. The size of each membrane sample in the dry state was  $36 \times 18 \text{ mm}^2$ .

Water uptake and swelling degree were acquired by measuring the weight of membranes and the change in the membrane length, respectively in dry and wet conditions. The water uptake and swelling ratio were acquired according to the following equations [S1].

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

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

The ion exchange capacity (IEC, mmol  $g^{-1}$ ) of the membranes was checked by acid-base titration by using phenolphthalein as an indicator. In this method, the sample was soaked in 50 mL of a 3 M NaCl aqueous solution for 24 h to exchange H<sup>+</sup> ions with Na<sup>+</sup> ions. After that, the solution was titrated using 0.01 M NaOH solution. The IEC was calculated based on the equation (3) [S1].

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

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

The theoretical IEC can be calculated according to the DS by the equation (4) [S2].

$$IEC = \frac{DS}{2(500.5 - 38.1 DS)}$$
(4)

The proton conductivity of the samples was obtained by fixing it in between two platinum electrodes of a membrane conductivity cell (Bekktech), at 100% relative humidity (RH); 25 °C temperature; by operating conductivity cell (Bekktech), hydrogen gas was being passed during measurement. The conductivity of the membranes were determined according to the reference [S1].

## The measurement of vanadium flow battery performance

The battery was assembled by sandwiching the membrane with the geometric area of 9 cm<sup>2</sup> between two carbon felt electrodes, and no electrocatalyst was used, in turn assembled between two graphite plates act as current collectors. As a terminal connector for battery, two copper sheets were attached with two graphite plates. After that, the cell assemblage was fastened by two polyvinyl chlorides (PVC) end plates. Eventually, the carbon electrode (5 mm uncompressed thickness) was activated by being thermally treatment at 500 °C for 30 min with 5°C/min heating rate. At 40 mA cm<sup>-2</sup> current density in ambient temperature, the cyclic charge–discharge curves of the battery was constructed with the NRE-212, SPAEK, SPAEK/Ce<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> (1%),

SPAEK/Ce<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> (2%), SPAEK/Ce<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> (3%). A 25 mL of vanadium electrolyte with a composition of 1.7 M V ( $\pm$ 3%), V<sup>3+</sup>/V<sup>4+</sup> 1:1 ( $\pm$ 3%), 4.5 M SO<sub>4</sub><sup>-</sup> ( $\pm$ 5%) was applied in each anolyte and catholyte. The electrolyte flow rate of 12 mL min<sup>-1</sup> was maintained by a peristaltic pump (Reglo ICC 2ch Pump). Anolyte and catholyte reservoirs were de-aerated by continual nitrogen flow to abstain oxidation of vanadium solution.

A charge-discharge voltage of 1.6 to 1 V was applied to minimize the corrosion between electrodes and graphite plates. The self-discharge rate of the battery was evaluated at ambient temperature by time tracking the open circuit voltage (OCV), which dropped below 0.8 V. The cyclic efficiencies of the VRFB were ascertained at different current densities using the equation in reference [S1].

## The measurement of oxidative and chemical stability

The oxidative stability of membranes was observed by immersion of a small part of the membrane in Fenton's reagent (2 ppm FeSO<sub>4</sub> in 3% H<sub>2</sub>O<sub>2</sub>) at 80 °C and calculated the residual weight of the sample after 1 h. In the meantime, the membranes were observed every 15 min to record any changes in appearance until they began to disintegrate. On the other hand, the chemical stability of the membranes was investigated by immersion in 1.5M VO<sup>2+</sup> in 3.0M H<sub>2</sub>SO<sub>4</sub> solution up to 4 weeks. The weight losses of membranes were investigated using the equation in reference [S3].

Membrane	Thickness (µm)	Proton conductivity (mS cm <sup>-1</sup> )	Vanadium permeability (cm <sup>2</sup> min <sup>-1</sup> )	Ion selectivity (S min cm <sup>-3</sup> )	Coulombic efficiency (%)	Current density (mA cm <sup>-2</sup> )	OCV (h)	Ref.
SPAEK/Ce <sub>2</sub> Zr <sub>2</sub> O <sub>7</sub> (2%)	45	87	0.0129× 10 <sup>-7</sup>	67.4× 10 <sup>6</sup>	99.4	40	441	Present work
SPAEK	45	67	0.1566× 10 <sup>-7</sup>	4.3×10 <sup>6</sup>	97.7	40	172	Present work
SPAEK/PW- mGO(1%)	50	71	$0.28 \times 10^{-7}$	2.5× 10 <sup>6</sup>	98.7	40	458	S1
SPES/PVA	170	76	$2.80 \times 10^{-7}$	0.25× 10 <sup>6</sup>	92.6	36	158	S4
SE3/P	70	42.6	$7.1 \times 10^{-7}$	0.06× 10 <sup>6</sup>	N/A	N/A	N/A	S5
SPFEK-[PDDA/PSS] <sub>2</sub>	130	23.8	1.16× 10 <sup>-7</sup>	0.20× 10 <sup>6</sup>	82.1	30	80	<b>S</b> 6
SPEEK/GO2@PTFE	67	14.6	$7.6 \times 10^{-7}$	$0.02 \times 10^{6}$	98.4	80	N/A	S7
SPEEK/PAN/-20	55	15.0	11.3× 10 <sup>-7</sup>	0.013×10 <sup>6</sup>	96.2	80	62	<b>S</b> 8
SPEEK	50	52.0	$3.5  imes 10^{-7}$	N/A	96.1	40	N/A	S9
SPEEK/gC <sub>3</sub> N <sub>4</sub> -1.5	80	7.9	$3.7  imes 10^{-7}$	N/A	97.5	30	68	S10
AIEM-II	45	48	$2.9 \times 10^{-7}$	N/A	95.6	40	300	S11
NRE-212	51	56	$3.3 \times 10^{-7}$	1.4 ×10 <sup>6</sup>	90	60	53	S12

**Table S1** The performance of VRFB operated with SPAEK/Ce2Zr2O7 composite membrane in comparison with previous work.



**Fig. S1** The molecular structure of the sulfonated poly(arylene ether ketone) (SPAEK) block copolymer.



Fig. S2 FE-SEM images of cross-section morphology of (a) and (b) SPAEK, (c) and (d)  $SPAEK/Ce_2Zr_2O_7$  (2%).



Fig. S3 Powder X-ray diffraction pattern of samples (a) SPAEK, (b) SPAEK/Ce<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> (2%) composite membrane, and (c) Ce<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>NT.



Fig. S4 FE-SEM images of surface morphology of (a) SPAEK, (b) SPAEK/Ce<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> (1%), (c) SPAEK/Ce<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> (2%), and (d) SPAEK/Ce<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> (3%).



Fig. S5 Thermograms of the NRE-212, SPAEK,  $Ce_2Zr_2O_7NT$ , SPAEK/ $Ce_2Zr_2O_7$  (1%), SPAEK/ $Ce_2Zr_2O_7$  (2%), and SPAEK/ $Ce_2Zr_2O_7$  (3%) membranes measured at room temperature to 600 °C with a heating rate of 10 °C min<sup>-1</sup> in an air atmosphere.



Fig. S6 Tensile test of the dried SPAEK/Ce<sub>2</sub> $Zr_2O_7$  composite membranes in comparison with NRE-212 and pristrine SPAEK membrane under an ambient condition.



**Fig. S7** <sup>1</sup>H NMR spectra of (a) SPAEK/Ce<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> (2%) before chemical stability check and (b) SPAEK/Ce<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> (2%) after chemical stability check in 1.5 M VO<sub>2</sub><sup>+</sup> in 3.0 M H<sub>2</sub>SO<sub>4</sub>



Fig. S8 FE-SEM images of (a) Surface and (b) cross section of SPAEK/Ce<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> (2%) composite membrane after 100 cycles in VRFB.

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