Electronic Supplementary Information

Ultra-high ion selectivity hybrid proton exchange membrane incorporated zwitterion-decorated graphene oxide for vanadium redox flow batteries

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Experimental

Materials

Natural graphite powders (NGP) (325 mesh) were purchased from Qingdao Laixi graphite Co., Ltd. Ethylenediamine was supplied by Tianjin Fengchuan Chemical Reagent Technology Co., Ltd. 1-(3-Dimethylaminopropy)-3-ethylcarbodiimide hydrochloride (EDC), N-Hydroxysuccinimide (NHS) and 1, 3-propane sultone were obtained from Sigma-Aldrich. Tetrahydrofuran (THF), N, N-dimethyl formamide (DMF) and concentrated sulfuric acid (H_2SO_4, 98%) were provide by Tianjin Guangfu fine Chemical Research Institute. Sulfonated poly(ether ether ketone) (SPEEK, Mn=38018) with 59% sulfonated degree was prepared in our lab.

Characterization

AFM imaging

AFM imaging measurements were recorded with Dimension Icon (Bruker) under the

tapping mode. For tapping-mode AFM, a commercial Si cantilever (TESP) of about 300 kHz resonant frequency was used.

Sulfonic acid uptake

First, the membrane (W_1) is immersed into 3 mol L^{-1} H_2SO_4 solution for 24 h at room temperature, and then it is dried till constant (W_2). SU is calculated by equation (1). Subsequently, the SU membrane is blow-washed by water to remove the outside sulfuric acid, and then it is dried to constant (W3). The SU inside membrane (SUI) is calculated by equation (2).

$$\mathrm{SU} = \frac{(W_2 - W_1)/M_{H2SO4}}{W_1} \qquad (1)$$

$$\mathrm{SUI} = \frac{(W_3 - W_1)/M_{H2SO4}}{W_1} \qquad (2)$$

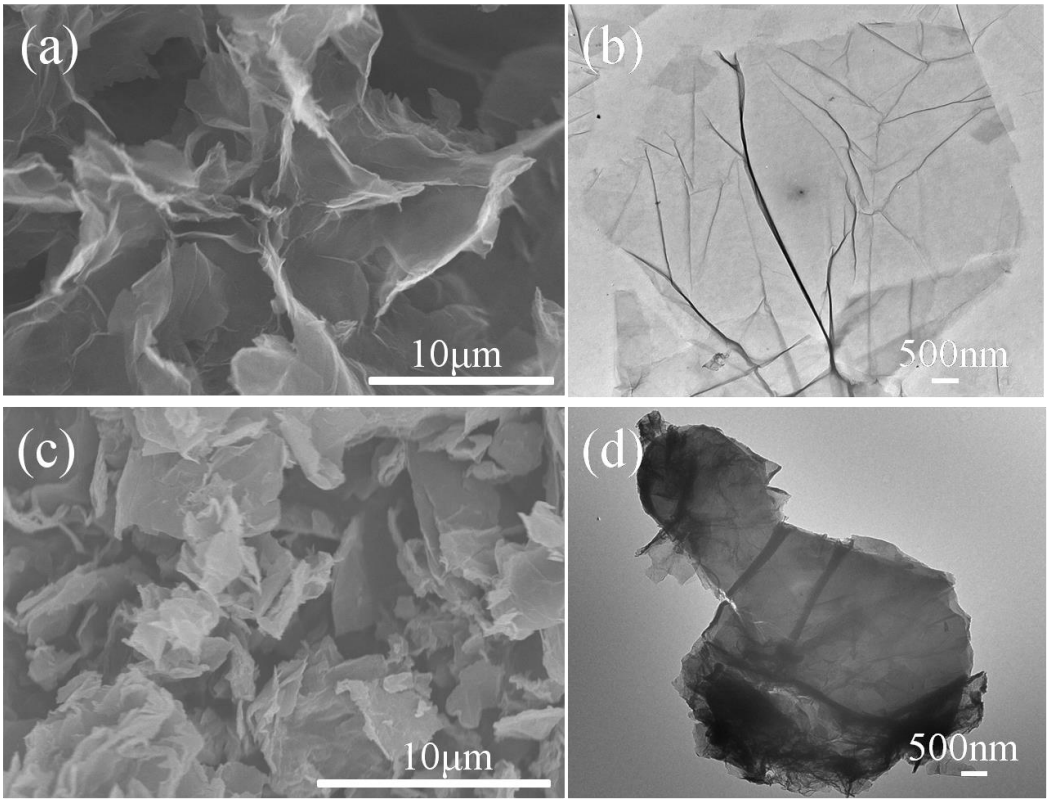

Fig. S1 SEM and TEM images of GO (a, b) and ZC-GO (c, d).

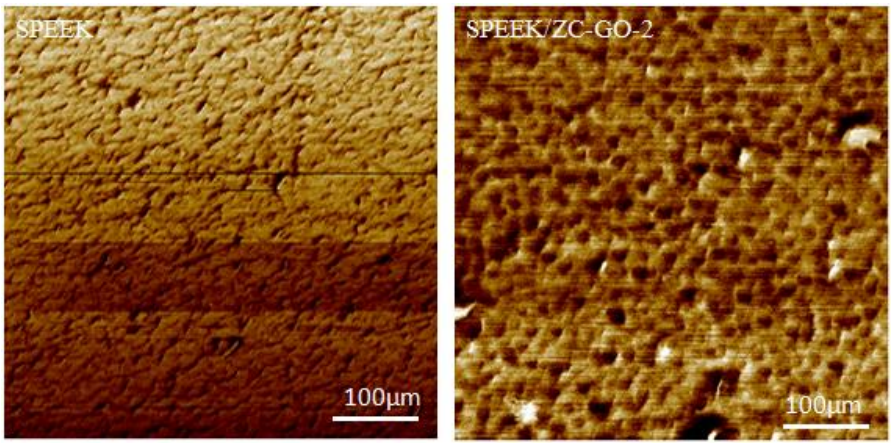

Fig. S2 AFM phase image of SPEEK and SPEEK/ZC-GO-2 membranes.

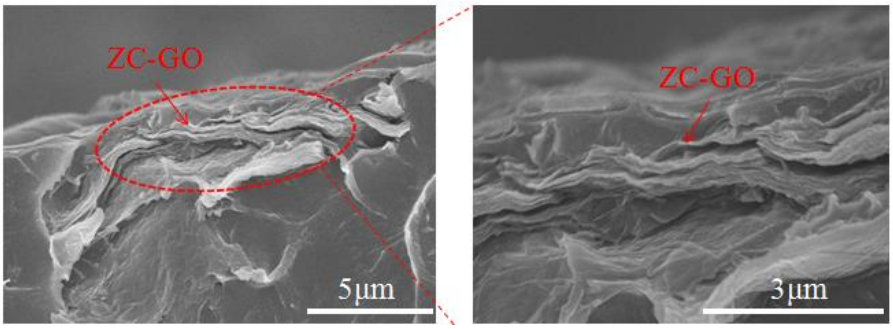

Fig. S3 Cross-section SEM images of SPEEK/ZC-GO-2 hybrid membrane after DMF vapor corrosion.

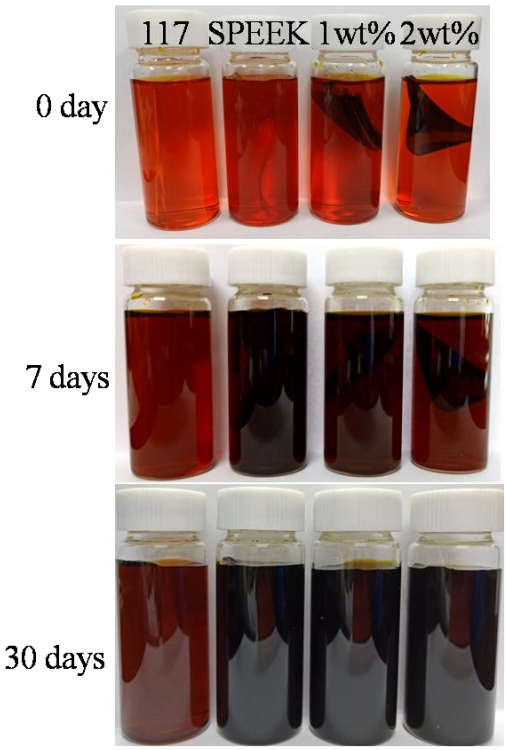

Fig. S4 Photographs of Nafion 117, SPEEK, SPEEK/ZC-GO-1 and SPEEK/ZC-GO-2 membranes soaked into the solution of 1.5 mol L^{-1} VO_2^+ in 3 mol L^{-1} H_2SO_4 in the chemical stability test process.

Table S1. The *in-plane* and *through-plane* swelling ratio of SPEEK/ZC-GO hybrid membranes.

Membranes	ZC-GO (wt%)	$SR_{in\text{-}plane}$ (%)	$SR_{through\text{-}plane}$ (%)
SPEEK/ZC-GO	1	13.2 ±0.1	14.9 ±0.1
	2	12.7 ±0.2	14.6 ±0.1
	3	12.2 ±0.1	14.4 ±0.1

Table S2. Sulfuric acid uptake of SPEEK and SPEEK/ZC-GO membranes.

Membranes	ZC-GO (wt%)	SU (mmol g^{-1})	SUI (mmol g^{-1})
SPEEK	-	0.59 ±0.01	0.09 ±0.02
SPEEK/ZC-GO	0.5	0.77 ±0.02	0.11 ±0.01
	1	0.96 ±0.02	0.13 ±0.02
	2	1.07 ±0.03	0.14 ±0.03
	3	1.28 ±0.01	0.18 ±0.03