

Supporting information

Novel Solvent-Template Method to Manufacture Nano-scale Porous Membranes for Vanadium Flow Battery Application

Hongzhang Zhang, Cong Ding, Jingyu Cao and Wanxing Xu, Xianfeng Li* and Huamin Zhang*

To find a couple of non-volatile template solvent and volatile solvent is essential for exactly controlling the amount of template solvent and the ions transport channel size. In this article, sulfolane and dimethylacetamide (DMAC) with boiling point of 285 °C and 166 °C were chosen as the non-volatile template and volatile solvent, respectively

The volatile feature of the solvents is test as follows: firstly, adding the solvents in three bottles with the same shape and size; secondly, heating the bottles under constant temperature; thirdly, record the weight of the bottles at interval time. One bottle was filled with 4 g DMAC, one was filled with 2 g DMAC and 2 g sulfolane (mutually soluble), and one was filled with 4g sulfolane. As shown in Figure S1, the DMAC was evaporated quickly in 30 hours, but the sulfolane did not evaporate at 30 °C. However, the sulfolane evaporated slightly at 60 °C. Compared with sulfolane, the DMAC evaporated more quickly. So the sulfolane is perfect as the solvent template, and the evaporating temperature should better be set as 30°C.

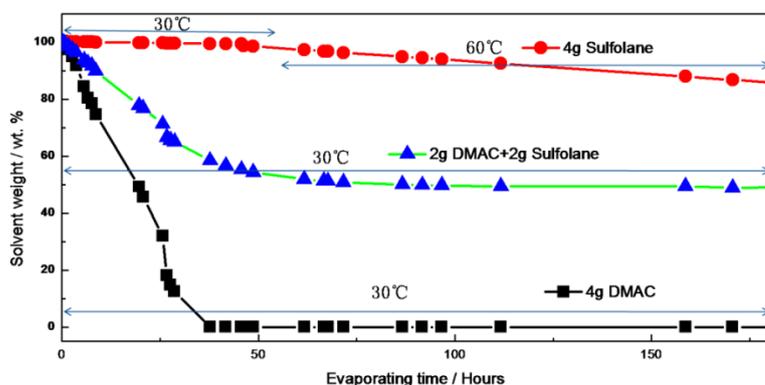


Figure S1. The solvent evaporating speed of the sulfolane and DMAC

The PES/SPEEK polymer was dissolved in sulfolane and DMAC (binary solvent) by weight ratio 1:2:1, and casted on to the glass plate with the thickness of 250 μm , heating at 30 °C. The concentration of the polymer was calculated at interval time and shown in Figure S2. As could be seen, the PES/SPEEK polymer concentration increased to 50 wt. % in 5 hours and kept stable afterwards. It could be deemed that there is no DMAC left in the membrane after 5 hours evaporation at 30 °C.

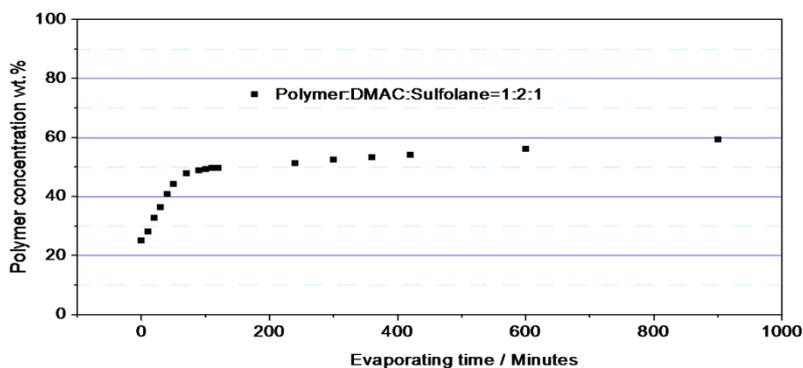


Figure S2. The polymer concentration of the liquid membrane on the glass plate

The polymer composition of the SPEEK and PES was detected via FTIR, ¹H-NMR and TGA. Figure S3 shows the FTIR spectra of PES, SPEEK and the PES/SPEEK membranes. The absorption bands at 1027 and 1079 cm⁻¹ are attributed to the symmetric and asymmetric O=S=O stretching vibrations of PES and SPEEK respectively. The absorption bands at 1650 are attributed to the Ar-C(=O)-Ar vibration of SPEEK, The absorption band at 1252 cm⁻¹ is attributed to the stretch asymmetric vibration of O=S=O. These characteristic bands illustrated the existance of sulfonic acid group in SPEEK. As for the IR absorbtion peaks of sulfone, 1323 cm⁻¹ and 1299 cm⁻¹ are attributed to the antisymmetric stretch vibration of Ar-(O=S=O)-Ar, 1240 cm⁻¹ is attributed to the antisymmetry stretch vibration of Ar-O-Ar, 1578 cm⁻¹ and 1486 cm⁻¹ are attributed to the stretch of C=C on the benzene ring. These charateristic bands illustrated the existance of PES. As for the SPEEK/PES composite membrane, the FTIR absorption curve also shows the typical peaks of both kind of chemical materials

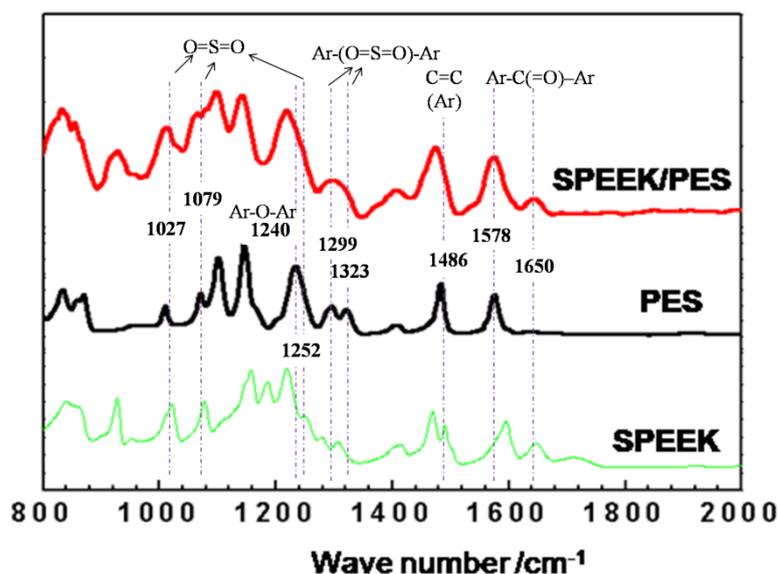


Figure S3. The FTIR absorb spectra of SPEEK, PES and SPEEK/PES membranes

FigureS4 shows the peaks of ¹H NMR spectra of PES, SPEEK and the PES/SPEEK membranes with chemical shift ranging from 6.0 to 8.0 ppm, corresponding to the chemical shift of protons attaching to the aromatic rings.

The NMR spectra information confirmed the chemical structure of the PES and SPEEK resin. The signal at 7.5 ppm is assigned to the aromatic hydrogen (H₁) ortho to the sulfonated groups. Based on this information, the degree of sulfonation (DS) and ions exchange capacity (IEC) of the SPEEK polymer could be calculated by Eq. (S1,S2) according to the ¹H-NMR data.

$$\frac{DS}{12-DS} = \frac{A_{H_1}}{\sum A_H} \quad (S1)$$

$$IEC = \frac{DS}{288.3+80 \times DS} \quad (S2)$$

Where AH₁ is the peak area of H₁, \sum AH is the integral peak area of all aromatic hydrogen, 288.3 is the molecular weight of PEEK unit, and 80 is the molecular weight of sulfonate group.

The DS and IEC of the SPEEK polymer determined by ¹H-NMR is calculated as 0.61 and 1.8 mmol g⁻¹. Then the IEC of PES /SPEEK membrane is caculated as:

$$\frac{1.8 \text{ mmol/g} \times 2\text{g}}{2\text{g}+3\text{g}} = 0.72 \text{ mmol/g}$$

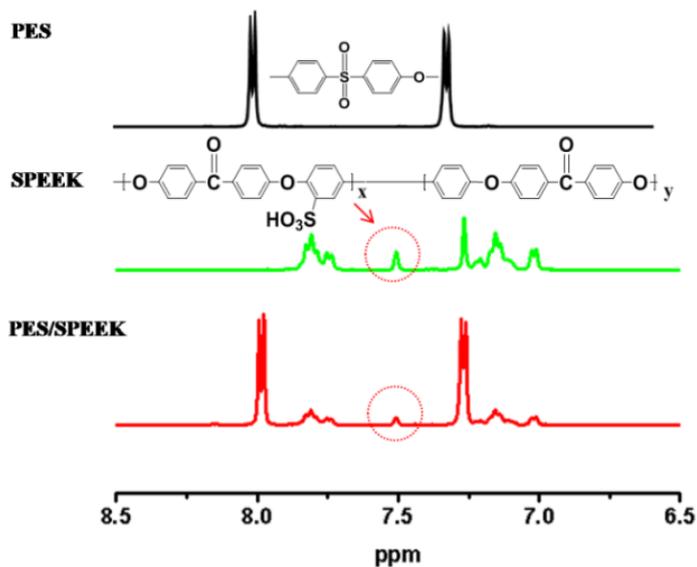


Figure S4. The NMR spectra of the PES, SPEEK and PES/SPEEK membranes

Figure S5 shows the TG of PES, SPEEK and PES/SPEEK membranes by heating from 120 °C to 800 °C under nitrogen atmosphere. The weight loss stage occurring at around 250 °C is attributed to the splitting-off of the sulfuric acid groups of SPEEK membranes. However, this degradation step is deferred to around 350 °C for the blend material of PES/SPEEK, which might due to the decreased concentration of sulfonation group. The TGA curve clearly indicates the excellent thermal stability of prepared membranes.

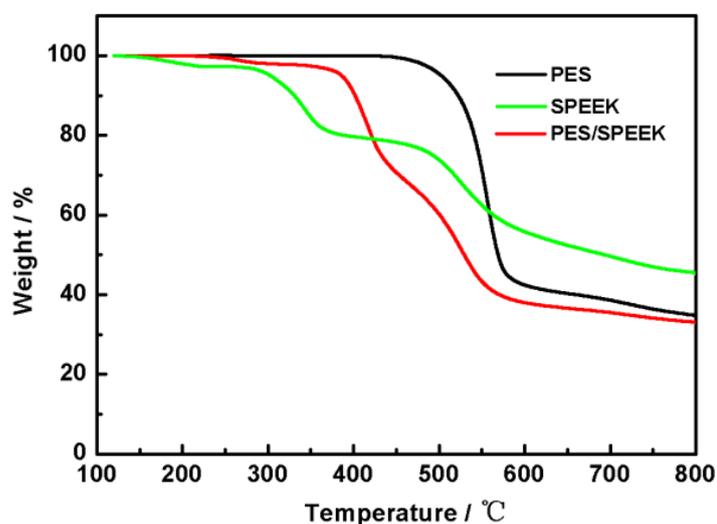


Figure S5. The TG spectra of the PES, SPEEK and PES/SPEEK membranes

Figure S6 shows the lower surface of M2~M3 under TEM after dying with Pb²⁺. As for the M3 prepared by solvent template method, the pores (ions transport channels) are form via the free volume left by washing out the sulfolane template, which is considered to be highly connected as a result of the strong salvation effect between the solvent and the polymers

However for the M4 prepared by traditional immersion phase inversion method, the template distribution will rearrange during the phase separation process, leading to the formation of sponge like pores. Although the sponge pore size is quite large, the pores are almost non-connected among each other. So most ions

