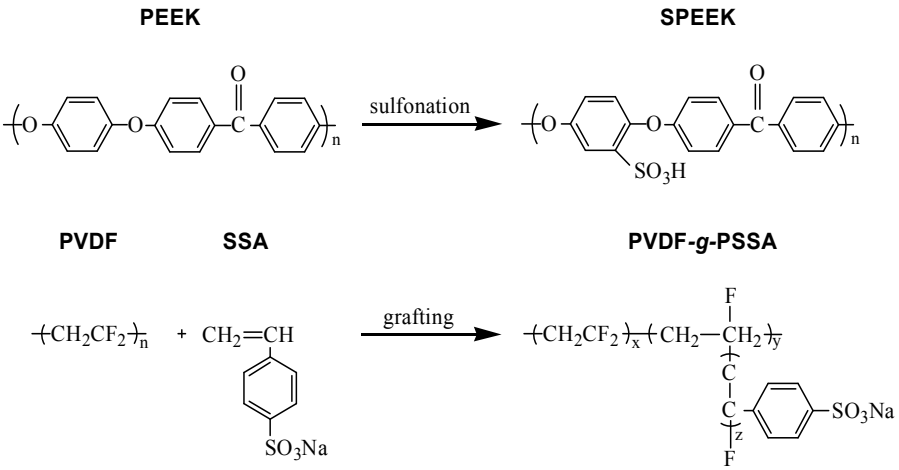
Electronic Supplementary Material (ESI) for RSC Advances.


# Supplementary Information

## 1. Synthesis and characterization of the SPEEK and PVDF-*g*-PSSA




Scheme S1. Synthetic procedures of the SPEEK and PVDF-*g*-PSSA graft copolymer.

Scheme S1 shows the synthetic procedures of the SPEEK and PVDF-*g*-PSSA. The PVDF-*g*-PSSA was synthesized by one-step ATRP reaction with details described in literature.[1] The grafting reaction was confirmed by Fourier-transform infrared (FTIR) spectroscopy. The FTIR spectra were recorded on a Nicolet-560 IR spectrometer. Fig. S1 shows the FTIR spectra of the pristine PVDF and PVDF-*g*-PSSA. Compared to pristine PVDF, the PVDF-*g*-PSSA copolymer exhibits a stronger absorption band at 1160 $cm^{-1}$, which results from the stretching vibration of sulfonic acid groups. The absorbance at 1006 $cm^{-1}$ is assigned to the in-plane bending vibrations of a phenyl ring substituted with a sulfonic acid group, and the 1128 $cm^{-1}$ peak results from a sulfonic acid anion attached to phenyl ring. The absorbance at 1036 $cm^{-1}$ is due to the asymmetric stretching vibration of sulfonic acid groups. [2] The FTIR results indicate that the styrene sulfonic acid (SSA) side chains were successfully grafted onto the PVDF backbone.

The IEC of the PVDF-*g*-PSSA and SPEEK membrane were determined by the classical back-titration method and the results were listed in Table S1. The dry membrane in acid form was soaked in 100 ml of 1 M NaCl solution for 24 h to replace the $H^+$ ions to $Na^+$ ions. The exchanged $H^+$ ions were titrated with 0.01 M NaOH solution using phenolphthalein as an indicator. The IEC value of membrane was calculated from the following equation:

$$\mathrm{IEC} = (V_{\mathrm{NaOH}} \times C_{\mathrm{NaOH}}) / W_{\mathrm{dry}}$$

where $V_{\mathrm{NaOH}}$ is the titrated volume of NaOH solution, $C_{\mathrm{NaOH}}$ is the concentration of the NaOH solution and $W_{\mathrm{dry}}$ is the weight of the dry membrane.

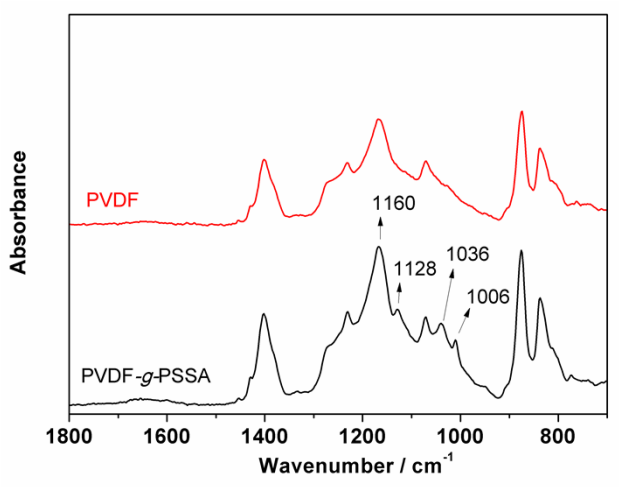



Fig. S1. The FT-IR ATR spectra of pristine PVDF and PVDF-*g*-PSSA

Table S1 IEC of the SPEEK and PVDF-*g*-PSSA

| Sample | IEC (mmol $g^{-1}$) |
|---|---|
| PVDF-*g*-PSSA | 0.04 |
| SPEEK | 1.45 |

## 2. Morphology of the blend membranes with different amounts of fluoropolymer

As can be seen from the SEM images of the SPEEK/PVDF-*g*-PSSA membranes (Fig. S2a-d), the PVDF-*g*-PSSA particles evenly disperse in SPEEK matrix at the PVDF-*g*-PSSA content of 5 wt. % up to 20 wt. % and their size increases gradually with increasing PVDF-*g*-PSSA content. In contrast, the SEM images of the SPEEK/PVDF membranes (Fig. S2e-h) exhibit an obvious non-uniform phase separation when the PVDF content higher than 10 wt. %. From the high-magnification SEM images of the SPEEK/PVDF-*g*-PSSA (20 wt. %) membrane (Fig. S2i and S2j), it is found that the PVDF-*g*-PSSA particles exhibit rough surfaces with hierarchical microstructure, and are broken in the cryo-fracture process instead of being extracted from the matrix. As a comparison, the high-magnification SEM images of the SPEEK/PVDF (20 wt. %) membrane (Fig. S2k and S2l) display that the PVDF particles exhibit smooth surfaces, and obvious voids can be observed between the particle and SPEEK matrix. They leave smooth empty cavities when detached from the matrix.

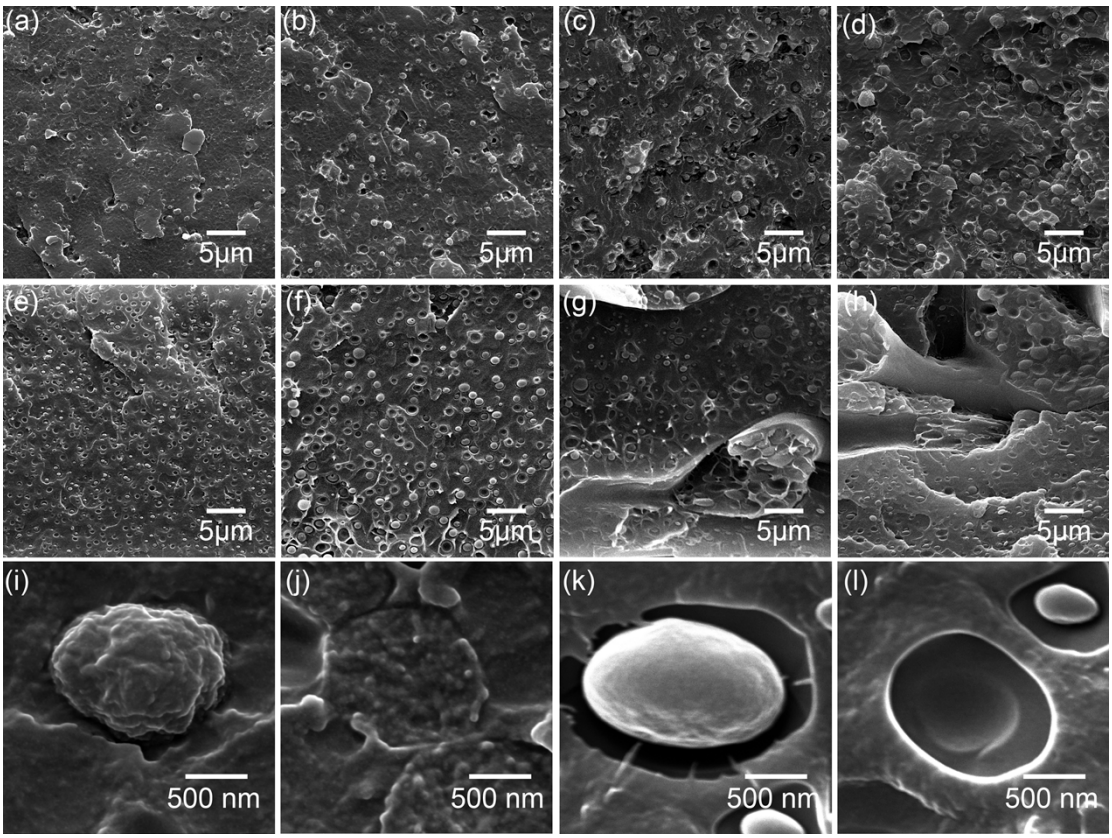



Fig. S2. The SEM images of the SPEEK/PVDF-*g*-PSSA blend membranes at the PVDF-*g*-PSSA content of (a) 5 wt. %, (b) 10 wt. %, (c) 15 wt. %, and (d) 20 wt. %; the SEM images of the SPEEK/PVDF blend membranes at the PVDF content of (e) 5 wt. %, (f) 10 wt. %, (g) 15 wt. %, and (h) 20 wt. %; (i) and (j) high-magnification SEM images of the SPEEK/PVDF-*g*-PSSA (20 wt. %) membrane; (k) and (l) high-magnification SEM images of the SPEEK/PVDF (20 wt. %) membrane

## 3. Electrochemical impedance spectroscopy analysis of the SPEEK/PVDF-*g*-PSSA (5 wt. %) membrane.

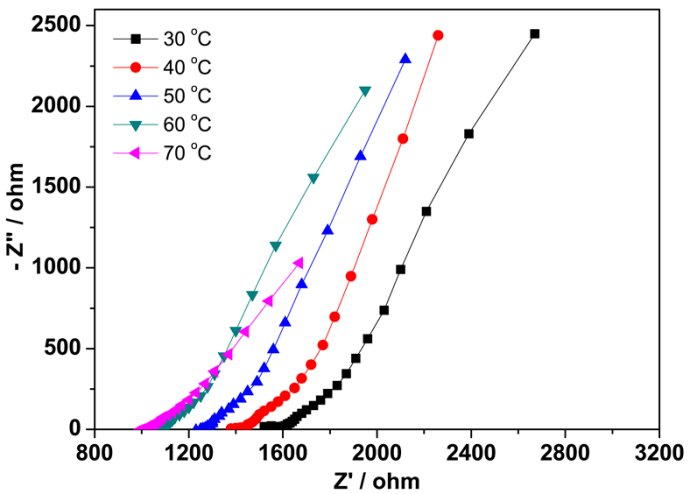



Fig. S3. Nyquist plots of the SPEEK/PVDF-*g*-PSSA (5 wt. %) membrane at various temperatures.

The typical AC impedance spectra of the SPEEK/PVDF-*g*-PSSA (5 wt. %) membrane at various temperatures are shown in Fig. S3. The bulk resistance of the membrane, $R_b$, was determined from the intercept of the impedance arc in the high frequency region with real axis. The

$R_b$ values of the SPEEK/PVDF-*g*-PSSA (5 wt. %) membrane range from 1000 to 1600 ohm, and decrease with increasing temperature form 30 to 70 $^oC$. The linear response of the system in the low frequency region of the Nyquist plots is dominated by the electrode blocking effects of the electrode/membrane interface. When the alternating current is applied to the membrane, a large number of ions reach the electrode before reversal of polarity and result in the charge buildup, which leads to the electrode blocking effects.

## References


1. Y. W. Kim, D. K. Lee, K. J. Lee and J. H. Kim, *European Polymer Journal*, 2008, **44**, 932-939.

2. R. A. Weiss, A. Sen, C. L. Willis and L. A. Pottick, *Polymer*, 1991, **32**, 1867-1874.