Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Materials

Investigation on the performance decay of proton exchange membrane basing on sulfonated heterocyclic poly(aryl ether ketone)s in Fenton's reagent

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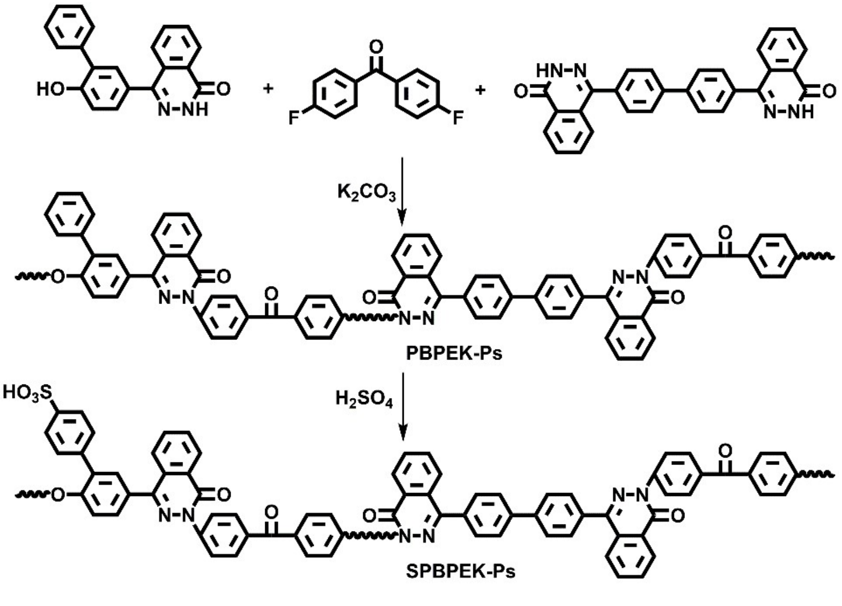
Polymer preparation

The poly(bis-phthalazinone ether ketone)s with pendant phenyl moieties (PBPEK-P-8) was prepared via a nucleophilic polycondensation reaction[1, 2], as depicted in Scheme S1. PBPEK-P-8, 5 meaning the DHPZ-P molar content, was synthesized with DHPZ-P (4.5265 g, 0.0144 mol), BPBN (1.5929 g, 0.036 mol), DFK (3.9276 g, 0.018 mol), anhydrous potassium carbonate (3.2292 g, 0.0234 mol), sulfolane (10 mL), and toluene (15 mL) in a three-necked, round-bottomed flask equipped with a Dean-Stark trap and a condenser, a mechanical stirrer, and a gas inlet and outlet. After removing the water and toluene, the reaction was conducted at 195 °C until the solution viscosity not improving further. The solution was precipitated in a dilute acetic acid aqueous solution. Dissolved 5 g PBPEK-P-8 in 15 mL concentrated sulfuric acid at room temperature for 24 h. After that, the polymer solution was precipitated in deionized water. The sediments were washed to neutral and dried in the atmosphere at 60 °C to achieved SPBPEK-P-8[3].



Scheme S1. Synthesis of sulfonated poly(bis-phthalazinone ether ketone)s with pendant phenyl moieties (SPBPEK-Ps).

The ion exchange capacity (*IEC*) of sulfonated polymers was in the range of 1.35-1.46 mmol g^{-1}, in Table S1.

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The measured *IEC* (IEC_M) was close to the theory *IEC* (IEC_T) for SPPEKK-P and SPBPEK-P-8, which indicated the sulfonated groups were quantitatively introduced into polymers. The intrinsic viscosity (η) of polymers ranged in 3.4-6.5 dL g^{-1}, the number-average molecular weight (M_n) was in the range of 20.0-79.6×10 kDa, and the polymer dispersity index (*PDI*) was in the range of 1.3-3.8.

Table S1. The ion exchange capacity, sulfonation degree, intrinsic viscosity, molecular weight, and distribution of SPEEK, SPPEK, SPPEKK-P, and SPBPEK-P-8.

Polymer	$IEC_T{}^a$ (mmol g^{-1})	$IEC_M{}^b$ (mmol g^{-1})	*DS* (%)	η (dL g^{-1})	M_n (×10 kDa)	*PDI*
SPEEK	-	1.40	40	5.3	79.6	1.3
SPPEK	-	1.42	50	3.8	18.3	3.8
SPPEKK-P	1.48	1.46	100	6.4	20.0	3.2
SPBPEK-P-8	1.37	1.35	80	6.5	33.2	2.1

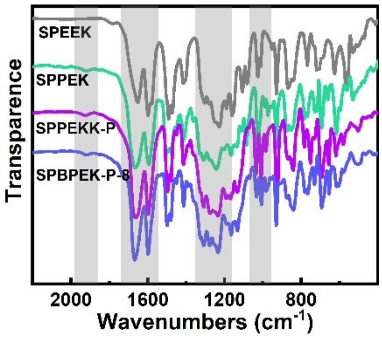


Figure S1. The FT-IR spectra of SPEEK, SPPEK, SPPEKK-P, and SPBPEK-P-8.

The molecular structure of SPEEK, SPPEK, SPPEKK-P, and SPBPEK-P-8 was characterized on FT-IR spectroscopy and nuclear magnetic resonance (NMR) spectroscopy, shown in Figure S1, S2, and S3. After sulfonated modification, the characteristic absorbed bands of sulfonic acid groups for SPPEKK-P and SPBPEK-P-8 appeared in 3492, 1030, and 1010 cm^{-1}[3, 4], the absorption intensity of which was enhanced along with the increase of DHPZ-P units in chains. And the characteristic absorbed band for $C=N-H^+$ appeared at 1920 cm^{-1}[5]. And the polymer component of sulfonated polymers was identified with ^{1}H-NMR, which further suggested the sulfonic acid groups were quantitatively introduced into polymers.

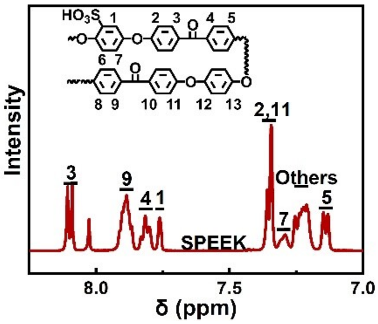


Figure S2. The ^{1}H-NMR spectra for SPEEK.

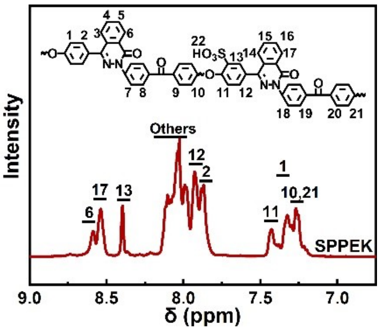


Figure S3. The ^{1}H-NMR spectra for SPPEK.

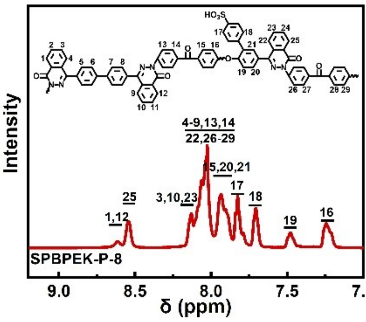


Figure S4. The ^{1}H-NMR characterization of SPBPEK-P-8.

Membrane preparation and performance

Membranes were prepared by a solution casting method. The sulfonated polymer was dissolved in NMP to form a 10 wt% homogeneous solution[6]. The solution was cast on the horizontal glass plate, under 60 °C for 12 h to remove the solvent. Finally, the membranes were stripped from the plate by soaking the glass panels in water and dried under 60 °C in cases for other uses. Membranes were cut in 3×3 cm^2 and soaked in the water at 25, 50, 75, and 95 °C for 24 h, respectively. The tensile test was carried out on Instron 5567 instrument with a 2 mm min^{-1} stretching rate. And the proton conductivity of the membranes was measured through a four-probe electrochemical impedance spectroscopy technique on Zennium E4 electrochemical workstation (Germany, ZAHNER).

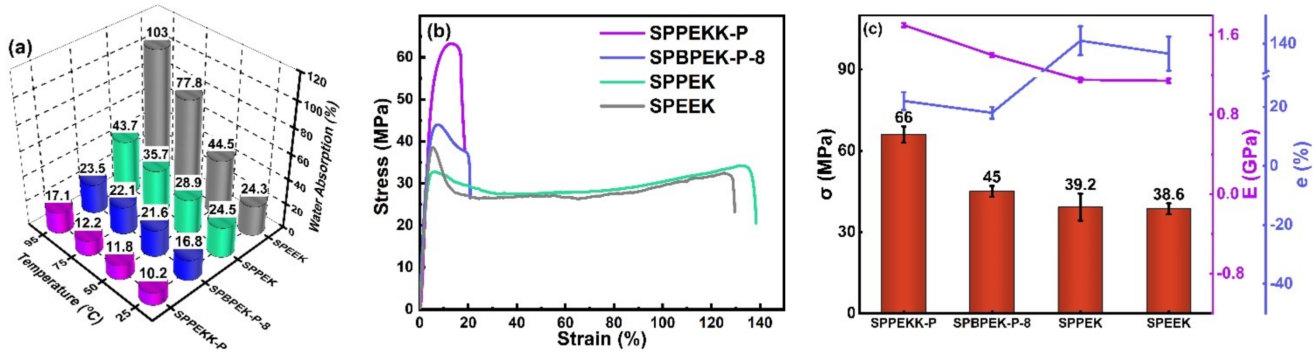


Figure S5. The (a) water absorption, (b) stress-stain curves, (c) mechanical performance of SPEEK, SPPEK, SPPEKK-P, and SPBPEK-P-8 membranes.

The water absorption and mechanical performance of the membranes were shown in Figure S5. SPEEK and SPPEK membranes performed excessive water absorption due to the positive contribution between the water absorption of sulfonated main chains and the plasticization effect of water molecules to sulfonated main chains. SPPEKK-P and SPBPEK-P-8 were the sulfonated side chains polymer. Water molecules mainly concentrated around the sulfonated phenyl groups, so the plasticization effects of water molecules to main chains were lower than SPEEK and SPPEK membranes.

The proton conduction performance of the membranes was shown in Figure S6. SPEEK exhibited the highest proton conductivity among all sulfonated poly(aryl ether ketone)s membranes due to the excessive water absorption. SPPEK performed favorable proton conductivity for the same reason as SPEEK membrane. SPPEKK-P and SPBPEK-P-8 had side groups in molecular chains, which had a more complete proton conduction network than SPEEK and SPPEK membranes. Compared with SPEEK and SPPEK membranes, the BPBN unit reinforced the tight stacking of molecular chains, and the water absorption became low and the proton conduction channel became narrow, so the proton conductivity was slightly inferior to that of SPEEK and SPPEK membranes. As the IEC decreased, the proton conduction channel became less connected and narrow, and the water absorption of the membrane decreased, so the proton conductivity declined.

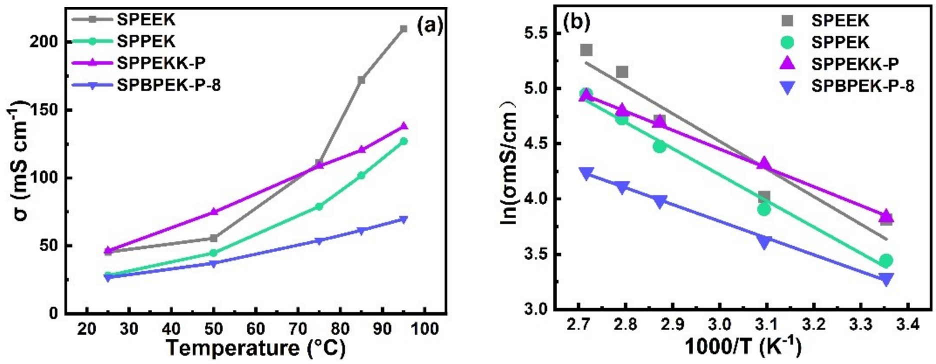
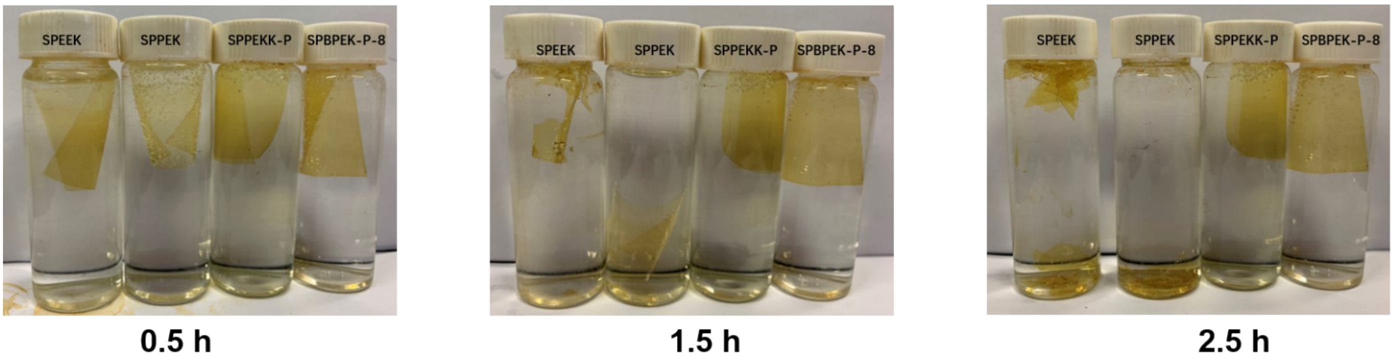


Figure S6. The (a) proton conductivity and (b) fitting active energy of SPEEK, SPPEK, SPPEKK-P, and SPBPEK-P-8 membranes.



0.5 h

1.5 h

2.5 h

Figure S7. The state of SPEEK, SPPEK, SPPEKK-P, and SPBPEK-P-8 membranes with different treated time in Fenton's reagent at 80 °C.

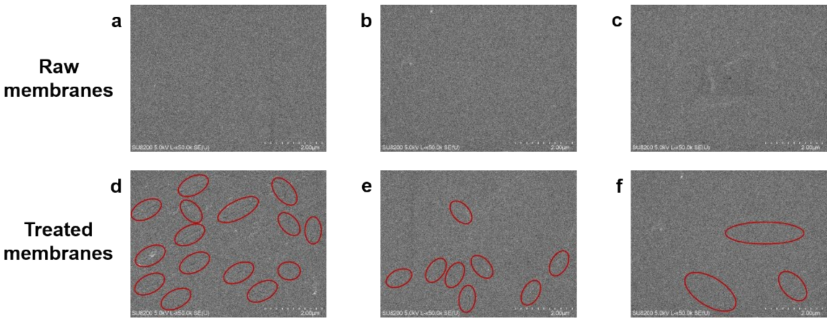


Figure S8. The (a and d) SPPEK and (b and e) SPPEKK-P, and (e and f) SPBPEK-P-8 membranes.

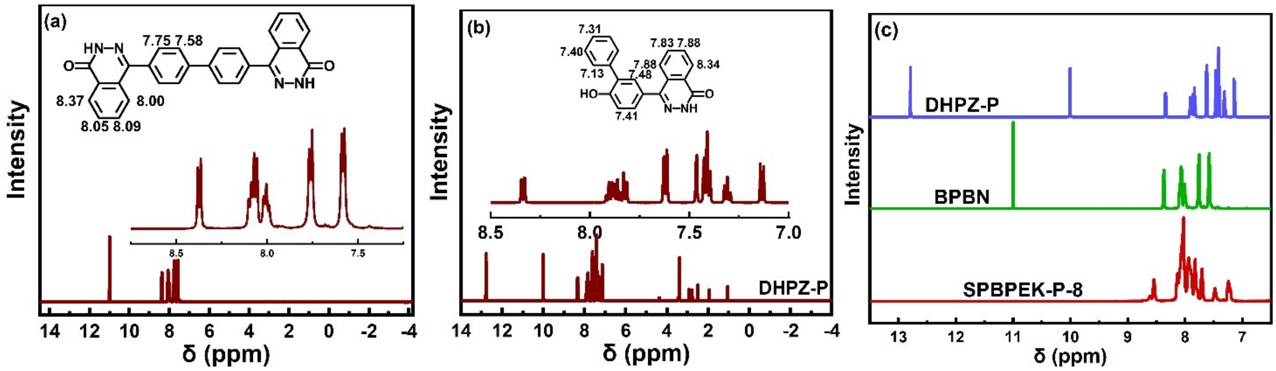


Figure S9. The (a) ^{1}H-NMR spectra of (a) BPBN, (b) DHPZ-P and (c) SPBPEK-P-8.

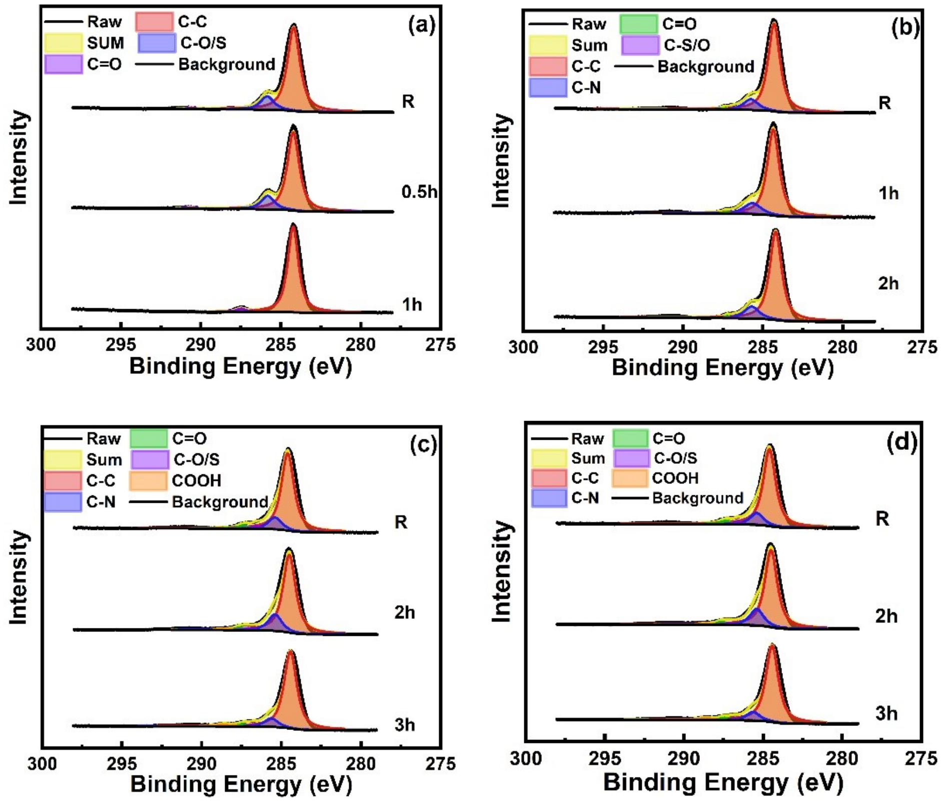
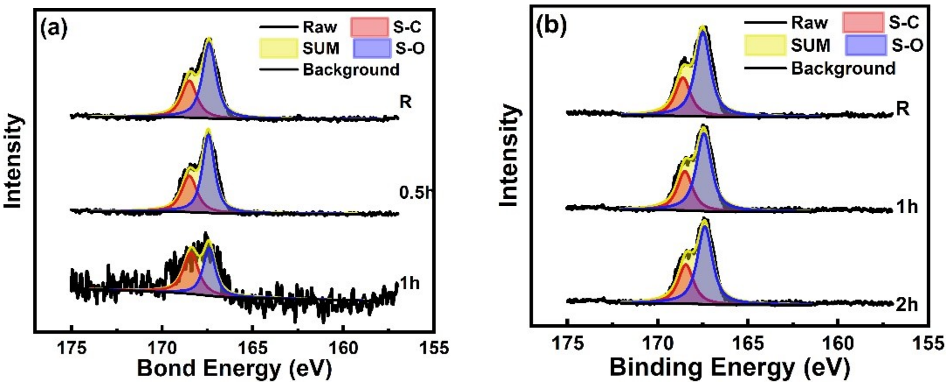


Figure S10. The comparison of XPS for C element in (a) SPEEK, (b) SPPEK, (c) SPPEKK-P, and (d) SPBPEK-P-8 membranes with different treatment time.



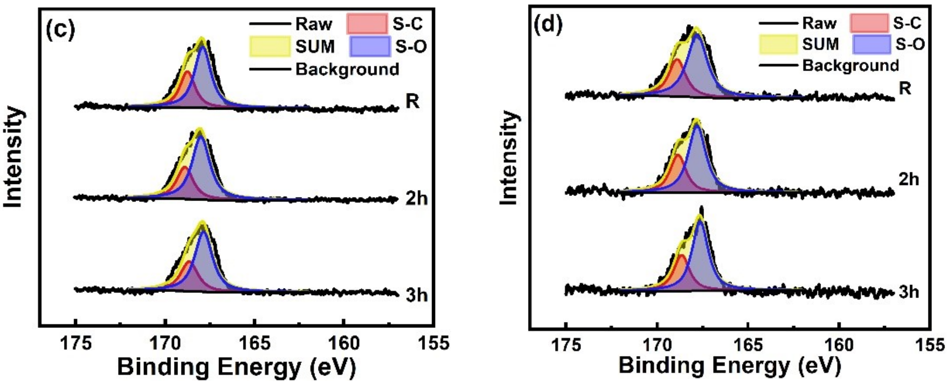


Figure S11. The comparison of XPS for S element in (a) SPEEK, (b) SPPEK, (c) SPPEKK-P, and (d) SPBPEK-P-8 membranes with different treatment time.

Reference

1. Q. Liu, S. Zhang, Z. Wang, N. Li, Y. Chen, P. Xu and X. Jian, *European Polymer Journal*, 2021, **143**, 110205.
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