

Fuel Cell Performance of Anion Exchange Membranes with Enhanced OH⁻ Conductivity, Based on Modified Terpolymer Polyketone and Surface Functionalized Silica

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Section S1. Modification of silica (Si-N)

Amine functionalized silica (Si-N) has been synthesized by co-condensation of 3-aminopropyltriethoxysilane (APTES) through the sol-gel method. In this procedure silica (100 mg) was suspended in APTES (1.5 mL) and ethanol (1.5 mL) in the ultrasonic bath for 10 min. Then, distilled water (0.1 mL) was dropped into the reaction medium to facilitate APTES hydrolysis. After 1.5 h, NH₄OH (60 µL) catalyst was fed into the reaction mixture. Sonication was continued for 3 h, then gelation was allowed for 1 h, and finally, the gel was centrifuged (3 × 5 min, 4000 rpm) and washed with ethanol and distilled water. The final material was dried at 70 °C for 24 h.

Section S2. Modification of polyketones (MPK)

In the preparation of modified polyketone (MPK), 1 gram of terpolymer polyketone (ethylene, propylene, and carbon monoxide) was mixed with 50 mL of methanol inside a sealed 250 mL round-bottom glass reactor equipped with a mechanical stirrer and a reflux condenser. The reactor was heated to a temperature of 100°C, then 1,2-diaminopropane (1.53 mL, 0.018 mol) and triethylamine (6.97 mL, 0.05 mol) were added to the suspension. The reaction was allowed to proceed for 20 more days at 100°C. The product was then filtered and washed with methanol to remove the residual solvent and unreacted amine. Then it was dried in a vacuum for 5 hours at 102 mbar and ambient temperature. The final product (MPK) was a light brown powder.

The chemical compositions of PK before and after modification were obtained by elemental analysis and are summarized in Table S1.

Table S1. Chemical compositions of PK (terpolymer) and amino-functionalized polyketone (MPK) samples determined by elemental analysis (CHNS).

Sample	%C*	%H*	%N*	%O*
PK terpolymer	64.4	7.1	...	28.5
MPK	56.7	7.8	12.1	23.4

*Determined by elemental analyses; %O+ is obtained as difference to 100.

Section S3

The carbonyl conversion of the 1,4-dicarbonyl unit was calculated by the following formula [24, 25]:

$$N = \frac{M_N \cdot x \cdot n}{M_{W1} \cdot x + M_{W2} \cdot (1 - x)} \quad (1)$$

where N is the nitrogen content per gram obtained by elemental analysis, M_N is the atomic mass of nitrogen (14 g.mol⁻¹), n is the number of nitrogen atoms in the repetitive unit of the reacted PK ($n=2$), M_{w1} is the molecular weight of a converted 1,4-dicarbonyl unit (150 g mol⁻¹), M_{w2} is the molecular weight of the non-converted 1,4-dicarbonyl unit of PK (114 g.mol⁻¹) and x can be calculated by:

$$x = \frac{N.Mw_2}{M_N.n + N.(Mw_2 - Mw_1)} \quad (2)$$

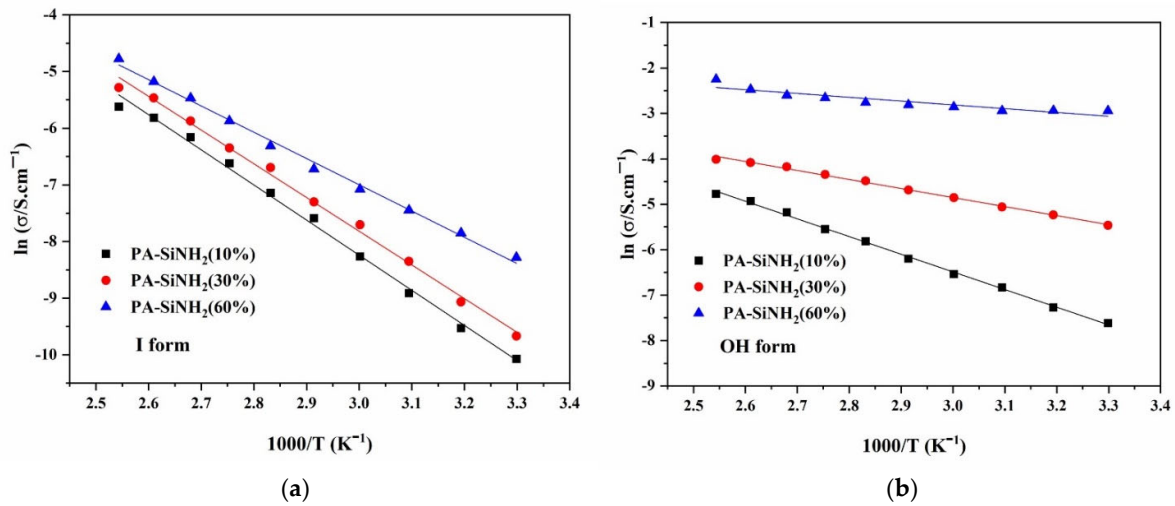


Figure S1. Arrhenius plots of conductivities for the MPK-SiN membranes with different amount of modified silica (10-60%) in (a) I form, (b) OH form.