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Supporting Information

Enhanced Proton Conductivity of Multiblock Poly(phenylene ether ketone)s via Pendant Sulfoalkoxyl Side Chain with Excellent H_2/Air Fuel Cell Performance

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MesoDyn simulation details

In mesoscale simulation, topology of polymer chain is defined as a Gaussian chain composed of coarse-grained beads. Each bead represents the group or cluster of molecules. Originally, the number (or length) of each bead in Gaussian chain was calculated by Equation (1):

$$N_{bead} = M_{polymer} / (M_{monomer}C_n) \quad (1)$$

Here, N_{bead} is the number of beads, $M_{polymer}$ is the molecular weight of the polymer (an approximate value of 50,000 was used), $M_{monomer}$ is the molecular weight of the monomer and C_n is the characteristic ratio of the polymer. The Flory-Huggins χ parameters as interaction parameters between two beads for simulation in MesoDyn were calculated by Equation (2):

$$\chi_{AB} = V_{ref}(\delta_A - \delta_B)^2 / RT \quad (2)$$

Here, V_{ref} is a reference volume, which was the mean molar volume of two beads in this study. δ is a solubility parameter of each bead, R is the gas constant and T is absolute temperature. We calculated χ parameters with the solubility parameters obtained by van Krevelen prediction in Synthia module (see Table S1 and S2). Finally, the input parameter for MesoDyn module was calculated from Eqn (3):

$$\nu^{-1}\varepsilon_{AB} = \chi_{AB}RT \quad (3)$$

Other parameters used in this simulation are the followings: the time step of 50 ns, the noise parameter of 75.002, the compressibility parameter of 10 kT, the grid spacing of 1.0 nm, the total grid size of 32 nm x 32 nm x 32 nm, temperature of 298 K, and the total number of steps of 10000.

Gas permeability. The experiment was carried out by the similar approach as reported elsewhere.[1] In brief, H_2 and O_2 permeability was measured in an in-house fuel cell station (HTS-125, Shanghai Hephas Energy Co. Ltd), equipped with a gas chromatography (Agilent 7890A GC, United States) with thermal conductivity detector. Ar and He were used as a carrier for the measurement of H_2 and O_2, respectively. Membranes were placed in the center of the cell, and the test gas was introduced onto one side of the membrane at a flow rate of 20 mL/min. Carrier gas was introduced onto the other side of the membrane at the same flow rate and was analyzed by the GC. The same humidity conditions were applied to both test and carrier gases to ensure homogeneous wetting of the membrane samples. Each test was equilibrated over 4 h, and then 15 mL of flow gas was sampled and subjected to the GC to quantify the test gas permeated through the membrane. The measurement was repeated until stable permeation data were obtained. The gas permeability coefficient, Q (barrer = 1×10^{-10} cm^3 (STD) cm/cm^2 cm mmHg), was calculated by Equ (4):

$$Q = \frac{273}{T} \times \frac{1}{A} \times B \times \frac{1}{t} \times l \times \frac{1}{76 - Pwater} \quad (4)$$

where T (K) is the absolute temperature, A (cm^2) is the permeation area, B (cm^3) is the volume of the test gas permeated through the membrane, t (s) is the sampling time, l (cm) is the thickness of the membrane, and P_{water} (cmHg) is the water vapor pressure.

Table S1. Parameters of mesoscale simulation.

Polymer structure	Bead	Molar Volume	Solubility parameter van Krevelen at 298 K (Synthia)	Characteristic ratio at 298 K (Synthia)
DFBP	D	149.78	21.51	3.64
MHQS	MS	183.50	23.27	3.40
6FBPA	F	217.99	18.65	3.42

Table S2. Calculated χ parameters of mesoscale simulation.

Bead Pair	δ_1	V_1	δ_2	V_2	V_{ref}	χ parameter
D-MS	21.51	149.78	23.27	183.50	166.64	0.21
D-F	21.51	149.78	18.65	217.99	183.89	0.61
MS-F	23.27	183.50	18.65	217.99	200.74	1.74

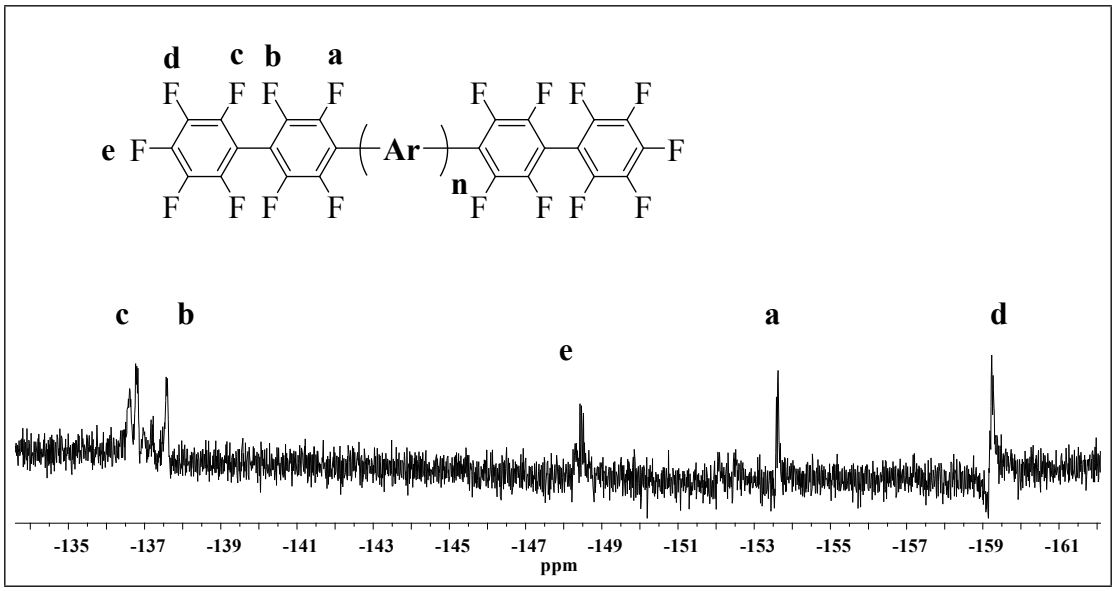

Fig. S1. ^{19}F NMR of Oligomer **1**.

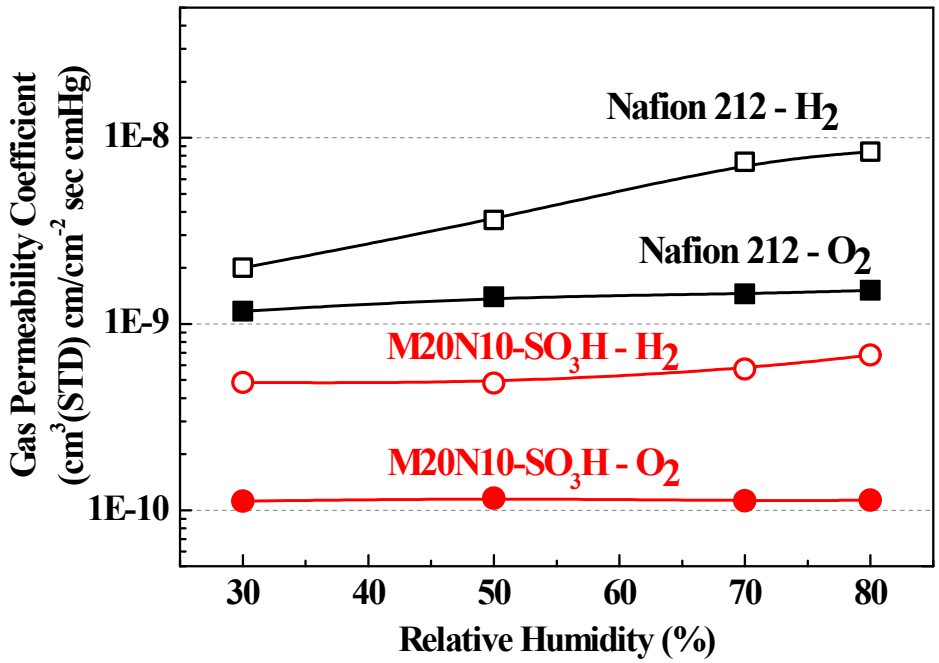

Fig. S2. Humidity dependence of H_2 and O_2 permeability coefficient of M20N10-SO_3H and Nafion 212 membranes at 70 °C.

Table S3. Oxidative stability of polymer **5**.

Membranes	*IEC*/ mequiv g^{-1}		After test
	Cal.	*Titr.*	RW [a] / %
M10N5-SO_3H	1.40	1.13	93
M20N10-SO_3H	1.41	1.41	95
M20N15-SO_3H	1.20	1.31	98

[a] Remaining weight. Measured by soaking the membrane sheets (1 cm x 4 cm) in Fenton's reagent (3% H_2O_2 containing 2 ppm $FeSO_4$) at 80 °C for 1 h.

Reference

1 T. Miyahara, T. Hayano, S. Matsuno, M. Watanabe, K. Miyatake, *ACS Appl. Mater. Interfaces*, 2012, **4**, 2881.