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Supplementary information

In-situ construction of interconnected ion transfer channels in anion-exchange membranes for fuel cells application

Jiangju Si,[b] Haining Wang,[a] Shanfu Lu,[a,*] Xin Xu,[a] Sikan Peng[a] and Yan Xiang[a,*]

Computational calculation details: The geometry optimizations were carried out using the density functional theory (DFT) method at the B3LYP/6-31G (d,p) level. All calculations were performed using the Gaussian 09 program .[S1]

Mechanical strength: A tensile tester (CMT6503, Shengzhen SANS Test Machine Co. Ltd, China) was used to analyse the tensile stress–strain behaviour of the fully hydrated MQ-PEEK and SQ-PEEK membranes in OH^- forms at room temperature. A constant crosshead speed of 5 mm/min was used for samples of 1 cm width and 3 cm length.

The ion exchange capacity (IEC): the IEC_m of membranes were determined by titration. 0.2-0.5 g of membranes in OH^- form was immersed in a standard hydrochloric acid solution (0.1 mol/L, 25 mL) for 48 h. The solution was then titrated with a standard solution of potassium hydroxide (0.1mol/L) with phenolphthalein as an indicator. The membrane was washed and immersed in deionized water for 24 h to remove any residual HCl, and then dried under vacuum at 45 ºC for 24 h and weighed to determine the dry mass (in Cl^- form). The IEC_m of the membrane is calculated with equation S1.

$$IEC_m = \left[n_{i(H^+)} - n_{f(H^+)} \right] / m_{dry(Cl^-)} \qquad \text{(S1)}$$

where $n_{i(H^+)}$ is the initial amount of proton in the HCl solution, $n_{f(H^+)}$ is the final amount of proton in the HCl solution determined by titration, and $m_{dry(Cl^-)}$ is the mass of the dry membrane in Cl^- form. The IEC_m were obtained by the average of three different measurements. The theoretical IEC were calculated from the quaternization degree (QD) of membranes.

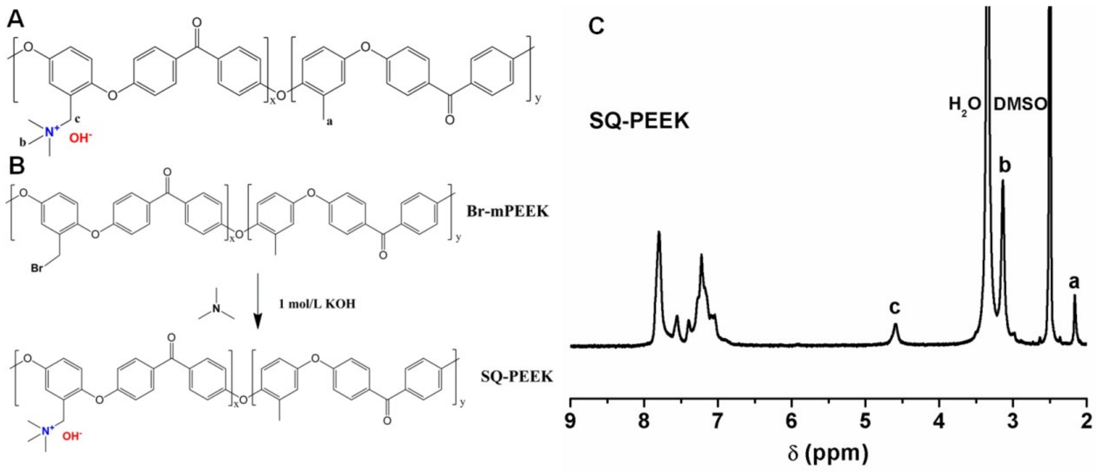

Fig. S1 The chemical structure (A), synthesis route (B) and ^{1}HNMR spectroscopy (C) of single quaternary ammonium PEEK (using trimethylamine as quaternization agent, SQ-PEEK).

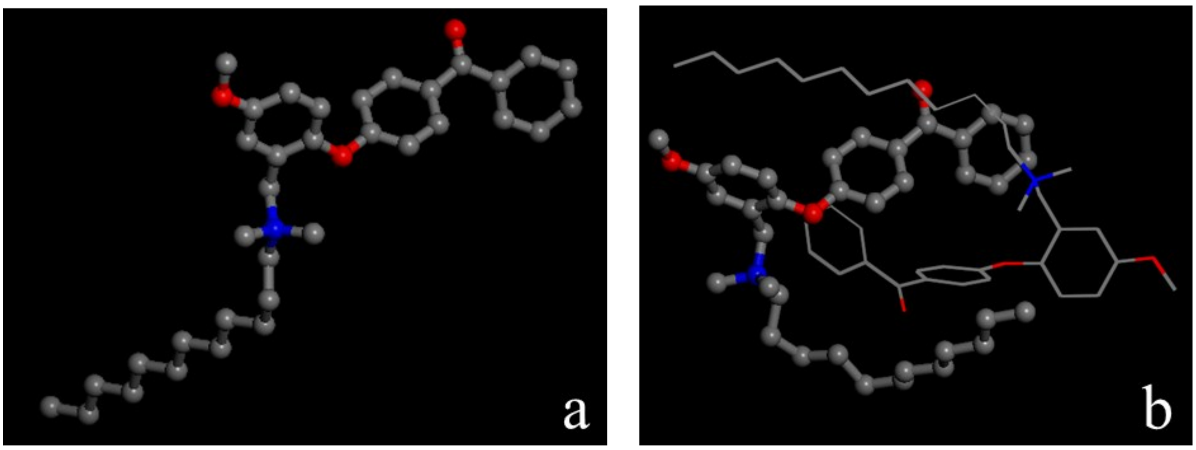

Fig. S2 Optimized (a) monomer and (b) dimer geometries of MQ-PEEK structural units obtained from density functional theory (DFT) calculations. The hydrogen atoms are not shown for a better illustration.

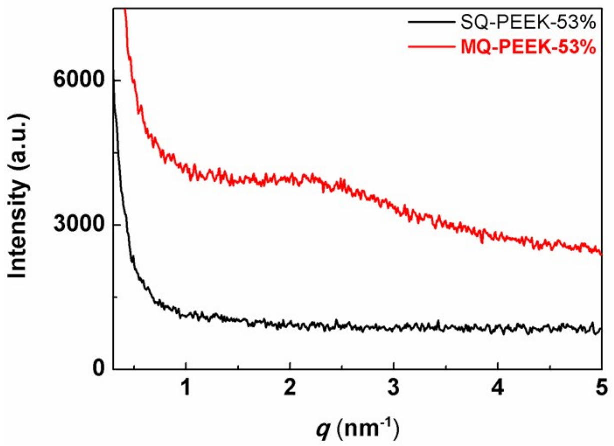

Fig. S3 SAXS profiles of SQ-PEEK 53% and MQ-PEEK 95% membranes.

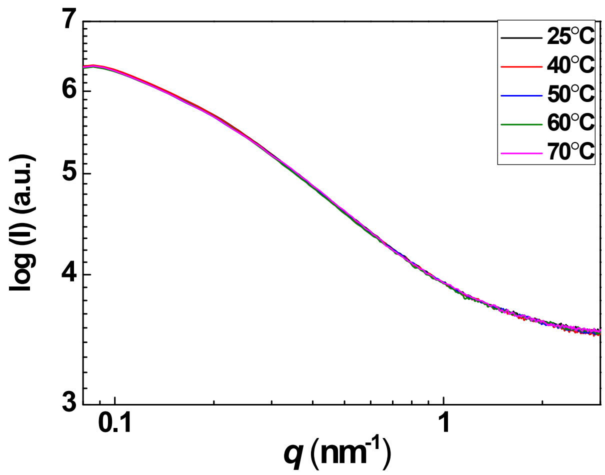

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Fig. S4 SAXS profiles of MQ-PEEK 95% membrane in OH^- form at 25–70 ºC.

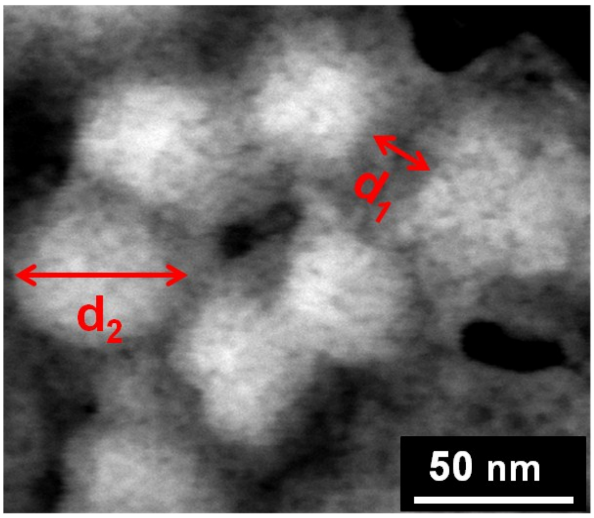

Fig. S5 Scanning transmission electron microscope (STEM) image of MQ-PEEK 95% membrane.

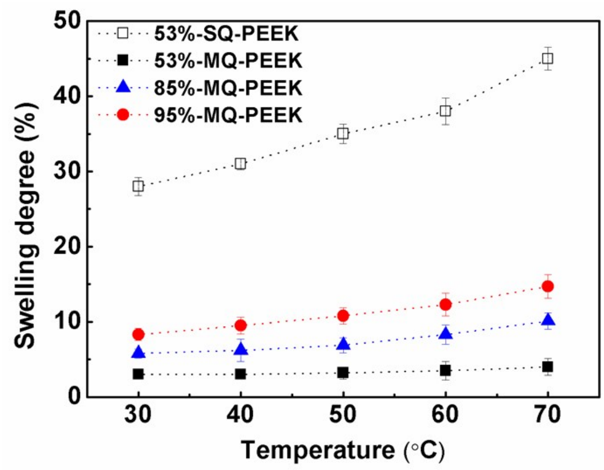

Fig. S6 Temperature-dependence of swelling degree (SD) of MQ-PEEK 53%, 85% and 95% membranes in OH^- form at 30–70 ºC. The three well-segregated MQ-PEEK membranes show extremely low SD. The SD has a lower dependence on temperature as the hydrophobicity enhances with increasing temperature, indicating that MQ-PEEK membranes possess excellent dimensional stability.

Table S1. Comparison between the theoretical IEC_t and experimental IEC_m of MQ–PEEK membranes.

Membranes	IEC (mmol g^{-1})	
	IEC_t	**IEC_m**
MQ-PEEK 53%	1.16	**1.13**
MQ-PEEK 85%	1.54	**1.49**
MQ-PEEK 95%	1.68	**1.62**

^{t}The theoretical IEC calculated from the molecular weight and the quaternization degree; ^{m}The measured IEC determined by the back titration method.

Table S2. Mechanical properties of MQ-PEEK and SQ-PEEK membranes in OH^- form at 25 ºC.

	Sample	53%	85%	95%
Tensile Strength (MPa)	SQ-PEEK-OH^-	9.6	1.1	N/A[a)]
	MQ-PEEK-OH^-	**30.9**	**23.5**	**20.7**

a) The tensile strength test is not available because the SQ-PEEK 95% membranes swell excessively.

S1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09, Gaussian, Inc., Wallingford CT.