Supporting information:

Construct proton transport highway induced by polarity-driving in proton exchange membrane to enhance the performance of fuel cells[†]

Jialin Li^a, Xuzhou Tian^b, Chunlei Xia^b, Yuting Duan^a, Yi-nan Sun^a, Binghui Liu^a, Liming Wu^a, Chunyu Ru^d, Shi-Tong Zhang^b, and Chengji Zhao^{*a, c}

^a Alan G. MacDiarmid Institute, College of Chemistry, Jilin University, Changchun 130012, P. R. China. Email: zhaochengji@jlu.edu.cn

^b. State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun, 130012, P. R. China.

^c Key Laboratory of Advanced Batteries Physics and Technology (Ministry of Education), Jilin University, Changchun 130012, P. R. China

^{d.} Powertrain Dept, General Institute of FAW, Changchun 130012, P. R. China

*Corresponding author: Chengji Zhao (Prof. Zhao)

Tel: +86-(0)431-85168870

Fax: +86-(0)431-85168870

Email address: zhaochengji@jlu.edu.cn

Electronic supplementary information for:

- 1. The synthesis procedures of polymers and monomers. (Fig. S1, Fig. S2)
- 2. ¹H NMR spectrum of polymers and monomers. (Fig. S3, Fig. S4)
- 3. The summary of test results. (Table S1)
- 4. The contrast of aggregation sizes. (Fig. S5)
- 5. The BDE images of the model compounds. (Fig. S6)
- 6. Imagines of frontier orbital electron density distributions. (Fig. S7)
- 7. The results of DFT. (Table S2, Table S3, and Table S4)
- Possible sites for HO• radical attack on different model compounds without carbonyl groups. (Fig. S8)
- 9. Redox reactions in the Fenton test. (Formula. S1-7)
- 10. The whole oxidation process in Fenton reagent. (Fig. S9)
- 11. AFM images. (Fig. S10)
- 12. Summary of electrochemical performances. (Table S5)



Figure S1. The synthesis procedure of DMNF.

In a beaker, 12 g 2, 6-dimethoxynaphthalene and 30 g 4-fluorobenzoyl chloride were dissolved in chloroform (100 mL). Then, anhydrous ferric chloride (0.8125 g) was added into the system at 5 °C. At 10 °C, the reaction mixture was stirred for 24 h. After that, chloroform was distilled to remove the solvent. The residue was washed by deionized water. The crude product was recrystallized twice from N, N dimethylformamide (DMF) to afford DMNF.



Figure S2. The synthesis procedures of (a) SBHP-SC, (b) SMHP-SC.

In a beaker, 3,5-di(trifluoromethyl) aniline (10 g) and concentrated hydrochloric acid (80 mL) were stirred until they were dissolved in 100 mL water at 80 °C. 6 g sodium nitrite was then

added dropwise into the solution. After stirring for 3 hour, the solution underwent filtration and the filtrate was then slowly added from a dropping funnel to a 1000 mL beaker containing 1,4benzoquinone (4 g) and sodium bicarbonate (15 g) at 0-3 °C. After a 8 hour stirring process, the product was thoroughly washed with deionized water and allowed to dry out naturally. Afterward, the product (15 g), zinc powder (6 g), deionized water (80 mL) and toluene (80 mL) were added into a four-necked flask equipped with a mechanical stirrer, a thermometer, a nitrogen inlet and a Dean–Stark apparatus with a reflux condenser. After refluxing for 3 hours at 80 °C, the hot mixture was then filtered. And the crude was dried and recrystallized from methanol to give grey needles of DFBP. Finally, the powder was purified by column chromatography.



Figure S3. ¹H NMR spectra of (a) SBHP-SC, (b) SBLP-SC, (c) SMHP-SC, and (d) ORIGIN-

SC.



Figure S4. ¹H NMR spectra of (a) DFBP and (b) DMNF.

3. The assemblage of test results.

Table S1. The values of the values of proton-conductive activation energy (Ea) of Fig. 3a and Fig. 3i; and the performance summary of oxidative stability (τ), methanol permeability (P) and selectivity (Φ) of membranes with the same IEC.

	Ea	τ	Р	Ф (104 S·s·cm-3)	
	(kJ∙mol-1)	(minute)	(10-6 cm2·s-1)		
ORIGIN-SC	13.47				
SMHP-SC	11.31				
SBHP-SC	11.06				
SBLP-SC	12.97				
ORIGIN-PE	14.05	15	3.65	4.05	
SMHP-PE	11.14	54	3.19	5.78	
SBHP-PE	10.89	69	2.93 6.72		
SBLP-PE	13.22	33	3.49	4.78	

* Ea is calculated from an Arrhenius plot for proton conductivity.

* No error bars of the diagrams of the values were given as their values were computed with the

corresponding mean of different parameters.

* τ is the elapsed time for membranes to start to break into pieces in Fenton's reagent at 80 °C.

Arrhenius equation:

$$\ln(\sigma) = \ln(\sigma_0) - \frac{E_a}{R \cdot T}$$

where R is the gas constant (8.314 J·mol⁻¹·K⁻¹), and T is the absolute temperature (K).

In the methanol permeability test, samples are normally clamped between diffusion chambers containing different concentrates of solution. Thereinto, the same volume of a certain concentration methanol solution and deionized water are injected respectively on both sides. After several hours, a portion of the solution in the water compartment will be taken out, and the methanol concentration can then be ready for calculation. However, such results are deviant with real values. In addition, the results calculated from this method are usually lower than the real values. However, the methanol permeability test in this paper was still chosen in the way of plotting LSV curves to reduce more experimental errors. Generally, WU expresses the water molecule's mass ratio in wet membranes at a specific temperature; thus, the overall states of membranes in water can be presented intuitively. However, for studying the influence of the volume, IEC, and molecule structure of the PEMs on the proton transport channels, λ shows the moles of water molecule per mole of acid group, which is vital for guiding the regulation of molecule synthesis and the degree of sulfonation. At the same time, in terms of industrial production of PEMs or scientific research on the synthesis of PEMs, apparent ion mobility should be shed light on as a crucial indicator of modifying and optimizing proton transport channel structures.¹ In addition to the fact that incomplete proton transport channels and remote ion clusters cause the high-energy barrier of proton transport, the different cluster structures formed by acid groups in diverse aggregation states are also non-negligible. While the exact structure remains controversial, the transport channels are thought to be nominally cylindrical.^{2,3} Both the theoretical IEC and the actual IEC titrated represent the numbers of sulfonic acid groups associating-dissociating protons rather than the actual number of the protons transporting in the wet membranes under different conditions. In an extreme case, the apparent ion mobility would be nought if all sulfonic acid groups in the membranes remain non-ionizing.^{4,5} Therefore, it is very difficult to improve the comprehensive performance of the membrane by simply improving the IEC of the membrane without adjusting the microphase structure in the membrane. High IEC stands for the potential for high conductivity, but due to the hydrophilicity of cations, the lack of suitable microstructure would usually result in higher water absorption and swelling ratio. The molecule with sulfonated units of 90% (m=0.9) was also successfully synthesized. However, when immersed in water for less than 12 hours at 80 °C, the membranes swelled extremely and dissolved at last. In contrast, the dissolution did not occur on SMHP-PAEK or SBHP-PAEK.

4. The contrast of aggregation sizes.



Figure S5. DLS diagram of ORIGIN-SC (a), SMHP-SC (b), SBHP-SC (c) and SBLP-SC (d) at

room temperature in dimethyl sulfoxide solution with the concentration of 0.02 mg mL⁻¹.



Figure S6. The bond dissociation energy (BDE) of different molecules after the attack by HO• radical from various attack sites (SBHP-m, SBLP-m, SMHP-m and SMLP-m represented

relevant model compounds): (a) the model compounds with carbonyl groups; (b) the model

compounds with without carbonyl groups.



Figure S7. According to the results of DFT, the LUMO frontier orbital electron density distributions of different model compounds: (a) SBHP-m, (c) SMHP-m, (e) SBLP-m, (g) ORIGIN-m; the HOMO frontier orbital electron density distributions of different model compounds: (b) SBHP-m, (d) SMHP-m, (f) SBLP-m, (h) ORIGIN-m.

7. The results of thermal enthalpy changes based on DFT.

Table S2. The values of bond dissociation energy (BDE) of different model compounds (containing carbonyl groups) between reactants and products. There are seven kinds of possible sites for HO• radical attack on SBHP-m and SBLP-m; four possible sites on SMHP-m and ORIGIN-m.

	SBHP-m	SBLP-m	SMHP-m	ORIGIN-m
1	47630.60124	47620.95893	47625.54414	47549.58406
2	47629.08894	47620.86292	47627.16688	47551.19801
3	47629.03686	47620.01515	47628.85300	47552.63689
4	47630.42617	47620.23792	47626.88199	47550.85100
5	47628.53862	47622.30117		
6	47630.14191	47621.97675		
7	47628.49595	47620.72361		

Table S3. The values of bond dissociation energy (BDE) of different model compounds (without

	SBHP-m	SBLP-m SMHP-m		ORIGIN-m	
1	47627.10350	47607.49131	47625.26678	47566.54126	
2	47625.55857	47610.86543	47625.25047	47566.63915	
3	47628.55619	47603.71495	47625.35401	47568.18345	
4	47629.08330	47607.09723	47625.25047	47567.23152	
5	47628.82414	47604.36693			
6	47630.61756	47607.24720			
7	47628.97474	47605.67592			

carbonyl groups) between reactants and products.

Table S4. The values of thermal enthalpy changes of different model compounds (with carbonyl
groups) between reactants and products after the attacks from hydroxyl radicals on ether bonds.

	SBHP-m	SBLP-m	SMHP-m	ORIGIN-m
1	-23.43812601	-42.14231658	-34.68687027	-112.1247418
2	-22.76543529	-38.56927464	-34.36370262	-109.2645512
3	-23.03902965	-38.28564012		
4	-25.89671019	-45.33383244		



Figure S8. Possible sites for HO• radical attack on different model compounds without carbonyl

groups.

9. Chain redox reactions in Fenton reagent:

Chain initiation reaction:

$$F_e^{2+} + H_2 O_2 \rightarrow F_e^{3+} + OH^- + HO \bullet (1)$$

Chain transfer reaction:

$$F_e^{2+} + HO \bullet \to F_e^{3+} + OH^- (2)$$

$$F_e^{3+} + H_2O_2 \to F_e^{2+} + H^+ + HO \bullet + H_2O (3)$$

$$HO \bullet + R - C - O - C - R' \to R - C - O - C^{\bullet} - R' + H^+ + H^{\bullet} (3)$$

Chain terminal reaction:

$$2H0 \bullet \rightarrow H_2O_2 (4)$$

$$F_e^{3+} + O^{2-} \rightarrow F_e^{2+} + H^+ + O_2 (5)$$

$$F_e^{3+} + HO_2 \bullet \rightarrow F_e^{2+} + H^+ + O_2 (6)$$

$$F_e^{3+} + O^{2-} + H^+ \rightarrow H_2O_2 + O_2 (7)$$

10. The whole oxidation process in Fenton reagent.



Figure S9. The whole oxidation process in the Fenton reagent, including the reduction reaction

of H_2O_2 catalyzed by Fe^{2+} and the oxidation reaction of polymers.

11. AFM images:



Figure S10. AFM imagines of the height images: (a) ORIGIN-PE, (d) SBLP-PE, (g) SMHP-PE; the phase images: (b) ORIGIN-PE, (e) SBLP-PE, (h) SMHP-PE; the 3D height images: (c) ORIGIN-PE, (f) SBLP-PE, (i) SMHP-PE.

Table S5. The values of power density (PD_{max}) and open-circuit voltage (OCV) of DMFC and H_2/air

single cells.

	methanol/O ₂		methanol/O ₂		H ₂ /air		H ₂ /air (RH	
	(1 M)		(2 M)		(75RH %/100%)		100%/100%)	
	PD _{max}	OCV						
	(mW·cm ⁻²)	(V)						
ORIGIN-PE	48.78	0.718	58.38	0.685	210.07	0.907	325.37	0.924
SMHP-PE	70.10	0.756	83.68	0.705	320.01	0.931	416.08	0.938
SBLP-PE	60.74	0.721	74.82	0.695	279.53	0.921	382.87	0.921
SBHP-PE	77.80	0.773	94.71	0.712	370.30	0.939	485.09	0.940



Figure S11. The power density and polarisation curves of DMFC single-cell based on PEMs with the same IEC at 25 °C: (a) SMBJP-PE, (b) SMHP-PE, (c) SBLP-PE, (d) ORIGIN-PE.



Figure S12. The power density and polarisation curves of H_2 /air single-cell based on PEMs with the same IEC at 80 °C, 50%/100% relative humidity of anode side/cathode side: (a) SMBJP-PE,

(b) SMHP-PE, (c) SBLP-PE, (d) ORIGIN-PE.

References

- 1 K. D. Kreuer, J. Membrane Sci., 2001, 185, 29-39.
- 2 L. Rubatat, A. L. Rollet, G. Gebel and O. Diat, *Macromolecules*, 2002, 35, 4050-4055.
- 3 K. Schmidt-Rohr and Q. Chen, Nat. Mater., 2008, 7, 75-83.
- 4 H. Lapid, N. Agmon, M. K. Petersen and G. A. Voth, *The Journal of Chemical Physics*, 2005, **122**, 14506.
- 5 T. J. Peckham, J. Schmeisser, M. Rodgers and S. Holdcroft, *Journal of Material Chemistry*, 2007, 17, 3255-3268.