Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Alkyl-substituted poly(arylene piperidinium) membranes enhancing the performance of high-temperature polymer electrolyte membrane fuel cells

Jinyuan Li,[abc] *Congrong Yang,*[ab] *Xiaoming Zhang,*[ab] *Zhangxun Xia,*[ab] *Suli Wang,**[ab] *Shansheng Yu,*[d] *and Gongquan Sun**[ab]

[a] *Division of Fuel Cells and Battery, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China.*

[b] *Key Laboratory of Fuel Cells & Hybrid Power Sources, Chinese Academy of Sciences, Dalian 116023, China.*

[c] *University of Chinese Academy of Sciences, Beijing 100039, China.*

[d] *Key Laboratory of Automobile Materials of MOE and Department of Materials Science, Jilin University, Changchun 130012, P. R. China*

E-mail: suliwang@dicp.ac.cn; gqsun@dicp.ac.cn

Supporting Figures

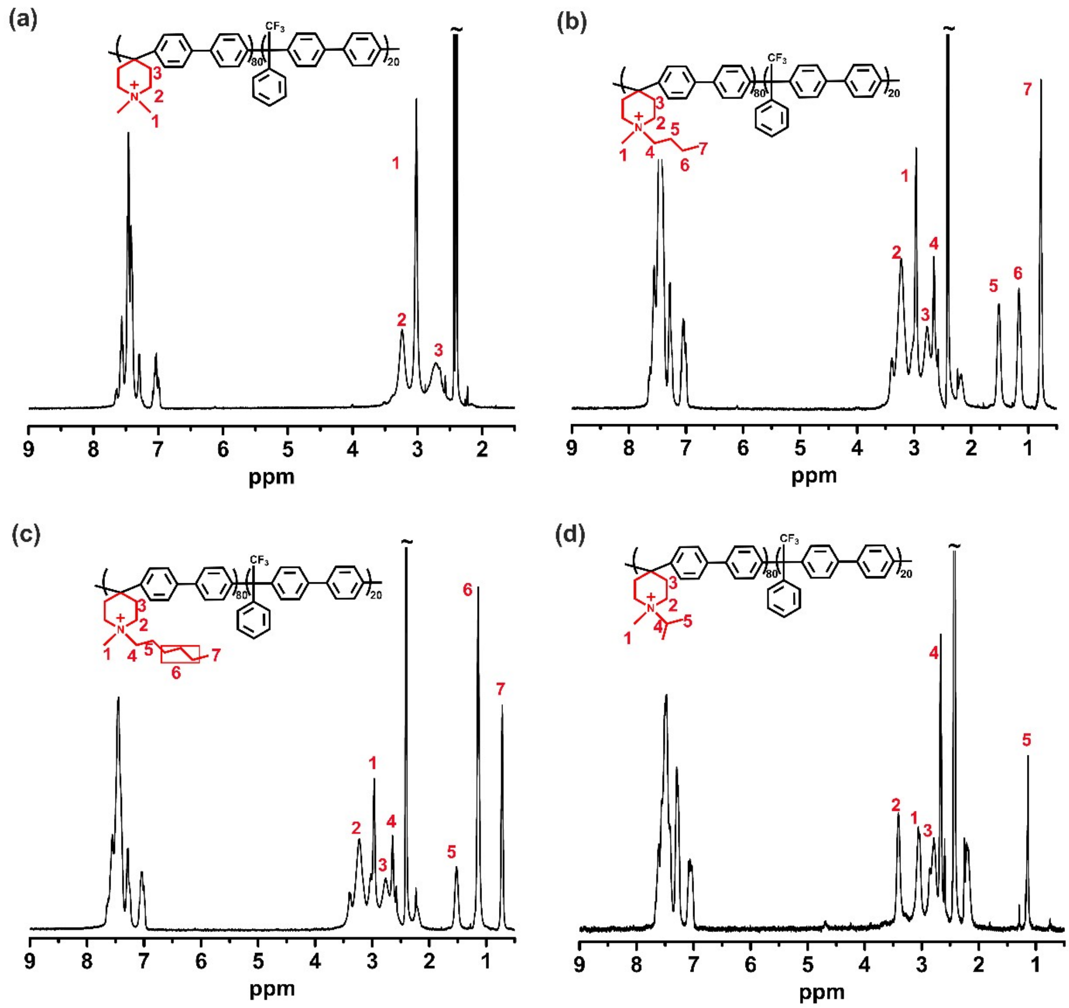

Fig. S1 ^{1}H NMR spectra of (a) PAP-BP-80-Me, (b) PAP-BP-80-Bu, (c) PAP-BP-80-He, and (d) PAP-BP-80-iPr. The spectra were recorded with DMSO-d_6 solution containing 10 vol% of Trifluoroacetic acid (TFA). The anion is omitted for clarity.

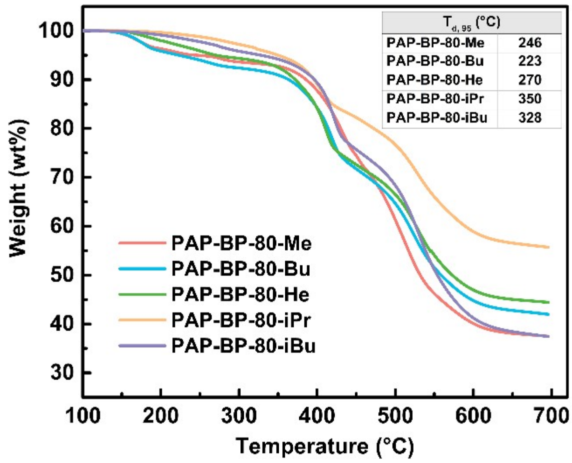

Fig. S2 TGA traces of PAP-BP-80-R membranes measured at 10 °C min^{-1} under Argon atmosphere.

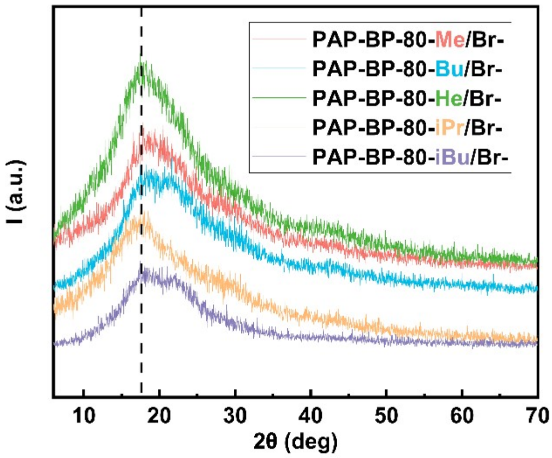

Fig. S3 X-Ray diffraction spectra of PAP-BP-80-R. The dashed line denotes the peak for PAP-BP-80-He, -iPr, and -iBu, which corresponds to lower 2θ values and higher d-spacing.

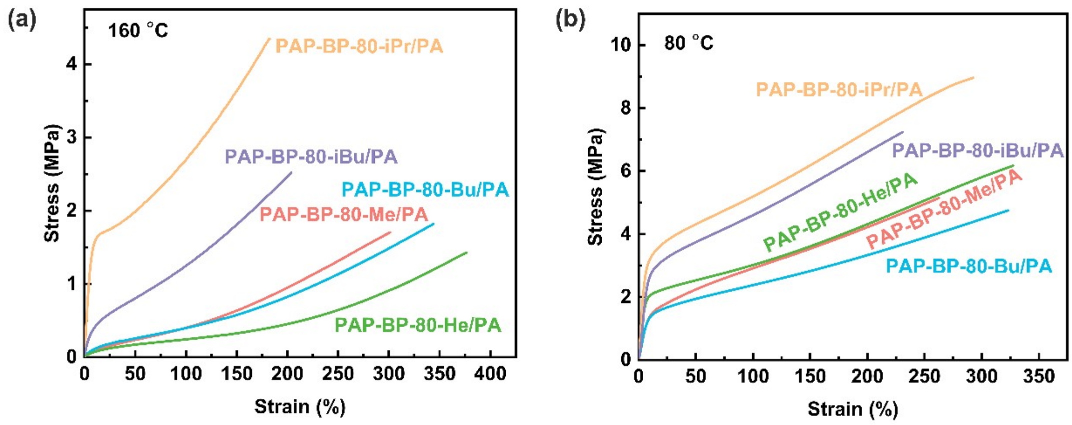

Fig. S4 Stress-strain curves of PA-doped PAP membranes at 160 ℃ (a) and 80 ℃ (b).

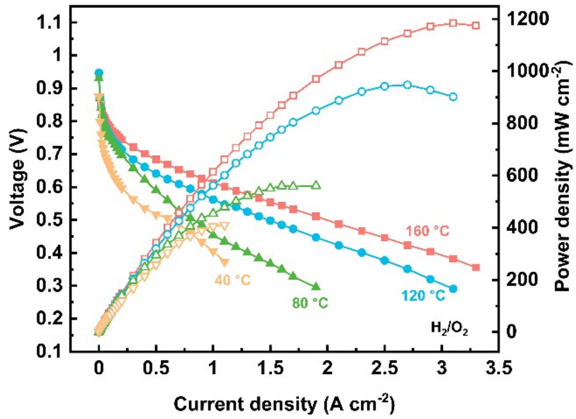

Fig. S5 H_2/O_2 Fuel cell performance of PAP-BP-80-iBu/PA. Testing conditions: cathode: PtCo/C (1.5 mg_{Pt} cm^{-2}), anode: Pt/C (0.5 mg_{Pt} cm^{-2}), PTFE binder. The thickness of the PA-doped PEMs was approximately 60 μm.

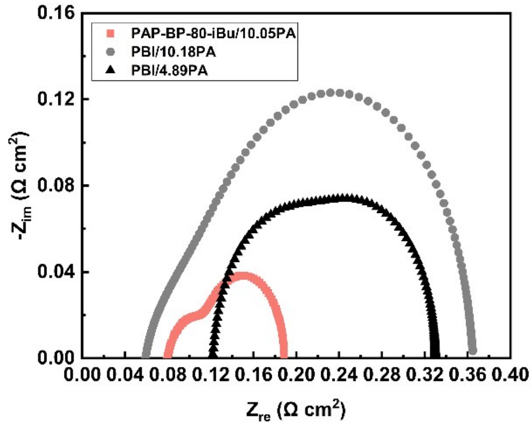

Fig. S6 EIS analysis of PAP-BP-80-iBu/10.05PA, PBI/10.18PA and PBI/4.89PA MEA at 120 °C, H_2/O_2 (0.1/0.2 slpm) and at 0.8 A cm^{-2}.

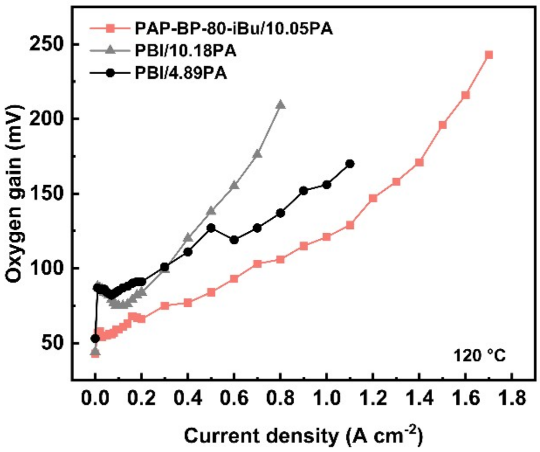

Fig. S7 Oxygen gain of fuel cells based on PA-doped PAP-BP-80-iBu and PBI membranes.

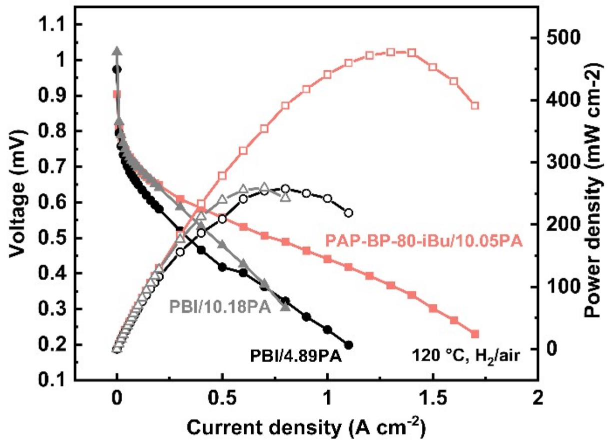

Fig. S8 i-V curve and power density of HT-PEMFCs using PA-doped PAP-BP-80-iBu and *m*-PBI membranes at 120 °C and H_2/air condition without external humidification or backpressure. Testing conditions: anode: Pt/C (0.5 mg_{Pt} cm^{-2}), cathode: PtCo/C (1.5 mg_{Pt} cm^{-2}), PTFE binder. The thickness of the PA-doped PEMs was approximately 60 μm.

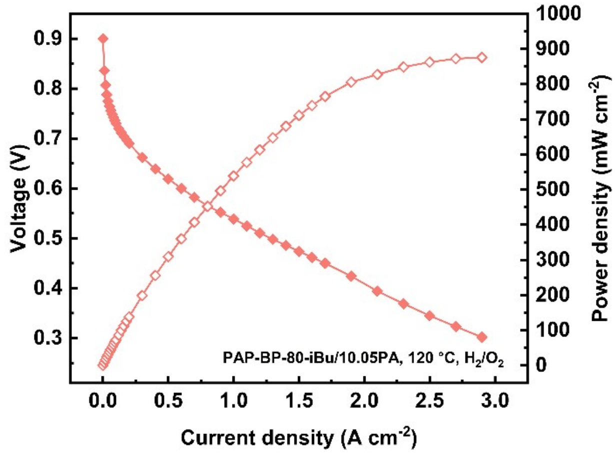

Fig. S9 i-V curve and power density of HT-PEMFCs using PA-doped PAP-BP-80-iBu at 120 °C without external humidification or backpressure. Testing conditions: anode: Pt/C (0.5 mg_{Pt} cm^{-2}), cathode: PtCo/C (0.5 mg_{Pt} cm^{-2}), PTFE binder. The thickness of the PA-doped membrane was 36 μm.

Supporting Tables

Table S1 PA uptake and ADL of PA-doped membranes.

PA-doped membrane	72% PA			85% PA		
	PA uptake/%	ω (PA)	ADL	PA uptake	ω (PA)	ADL
PAP-BP-80-Me	302.8	66.3	10.96	421.4	77.8	16.61
PAP-BP-80-Bu	270.3	59.1	9.35	385.2	77.8	16.14
PAP-BP-80-He	207.8	57.3	7.72	345.9	65.0	12.71
PAP-BP-80-iPr	246	55.4	7.02	323	69.1	10.72
PAP-BP-80-iBu	300.9	65.5	10.05	405.8	63.6	12.28
PBI	205	51	4.89	427.5	61.5	10.18

Table S2 Comparison of proton conductivity and mechanical strength of ion-pair membranes.

PEM (PA-doped)	σ^b (mS cm^{-1})	TS^d (MPa)	Reference
PAP-BP-80-iBu	107.7 (160 °C)	2.53 (160 °C) 5.15 (120 °C) 7.13 (80 °C)	This work
QAPOH	131 (160 °C)	1.6-3 (80 °C)	1,2
PPO–BIm-65-15	54 (140 °C)	2.8 (80 °C)	3
Methyl-QPEEK	50 (200 °C)	6 (130 °C)	4
PVC-42%7#	48 (160 °C)	14.2 (rt)	5
PVC-19%APIm	257 (180 °C)	2.2 (120 °C)	6
PTP-BeIm	88 (180 °C)	3.3 (rt)	7

Table S3 Membranes used for fuel cell performance evaluation.

Membrane (PA-doped)	Thickness (μm)	Acid uptake (%)	ADL	σ (mS cm^{-1})	
				160 °C	rt
PAP-BP-80-iBu	58	300.9	10.05	109	23.2
PBI	57	427.5	10.18	98.3	6.2
PBI	60	204.8	4.89	50.6	46.1

Table S4 Summary and Comparison of the representative PEMFCs performances under H_2/O_2 condition in current research.

PEM (PA-doped)	Pt (mg cm-^{2}) cathode (-), anode (+)	Temp (°C)	Power density (mW cm^{-2})	Ref.
PAP-BP-80-iBu	1.5 (-), 0.5 (+)	160 120 80 40	1228 947 560 410	This work
PAP-BP-80-iBu	1.5 (-), 0.5 (+)	160 120 80	1651 1539 875	This work
QAPOH (QASOH binder)	0.75 (-), 1.0 (+)	180	800	1
QAPOH (PWN70 binder)	0.6 (-), 0.5 (+)	160 120	1130 680	2
QAPOH (Nafion-PWN70 binder)	0.7 (-), 0.5 (+)	160 120 80	1673 960 525	8
DMBP-TB	0.5	160 80 40	815 354 216	9
TDAP-PSU-88	0.5	150	453	10
P/CN-0.5 (CN-doped PES/PVP)	0.4	160	512	11
PPW-5 (PWA-doped PES/PVP)	0.35	160	416	12
PES/PVP	0.35	160	637	13
Asymmetrical porous PBI	1.0	160	835	14
p-OPBI-ATMP	1.2 (total)	160 80	980 268.1	15
ABPBI/5IL@SNR (ABPBI with silicon nanorods and ionic liquid)	0.4	180 120 80	280 210 150	16
PTP-41%BeIm	1.13	180 120	995 593	7
P-BPSH60	0.5	100	1121	17
M-BT	0.5 (-, Pt/C), 0.5 (+, Pt/C)	80	696	18
Nafion HP	0.1 (-, Pt/C), 0.1 (+, Pt/C)	80	1370	19

NRE 211	0.2 (-, sub-Pt_3Co-MC), 0.2 (+, Pt/C)	80	1770	20
	0.5	120	350	21
Pt−SiO_2/NP	0.5 (-), 0.3 (+)	60	1400	22
SPP-QP-f	0.5	120	390	21

Reference

1. K.-S. Lee, J. S. Spendelow, Y.-K. Choe, C. Fujimoto and Y. S. Kim, *Nat Energy*, 2016, **1**, 16120.
2. V. Atanasov, A. S. Lee, E. J. Park, S. Maurya, E. D. Baca, C. Fujimoto, M. Hibbs, I. Matanovic, J. Kerres and Y. S. Kim, *Nature Materials*, 2021, **20**, 370-377.
3. Q. Li, L. Liu, S. Liang, Q. Li, B. Jin and R. Bai, *Polym. Chem.*, 2014, **5,** 2425.
4. N. Zhang, B. Wang, C. Zhao, S. Wang, Y. Zhang, F. Bu, Y. Cui, X. Li and H. Na, *J. Mater. Chem. A*, 2014, **2**, 13996-14003.
5. R. Liu, M. Liu, S. Wu, X. Che, J. Dong and J. Yang, *European Polymer Journal*, 2020, **137,** 109948.
6. R. Liu, Y. Dai, J. Li, X. Chen, C. Pan, J. Yang and Q. Li, *Journal of Membrane Science*, 2021, **620,** 118873.
7. Y. Jin, T. Wang, X. Che, J. Dong, R. Liu and J. Yang, *Journal of Membrane Science*, 2022, **641,** 119884.
8. K. H. Lim, A. S. Lee, V. Atanasov, J. Kerres, E. J. Park, S. Adhikari, S. Maurya, L. D. Manriquez, J. Jung, C. Fujimoto, I. Matanovic, J. Jankovic, Z. Hu, H. Jia and Y. S. Kim, *Nat Energy*, 2022, **7**, 248-259.
9. H. Tang, K. Geng, L. Wu, J. Liu, Z. Chen, W. You, F. Yan, M. D. Guiver and N. Li, *Nat Energy*, 2022, **7**, 153-162.
10. J. Zhang, J. Zhang, H. Bai, Q. Tan, H. Wang, B. He, Y. Xiang and S. Lu, *Journal of Membrane Science*, 2019, **572**, 496-503.
11. H. Bai, H. Wang, J. Zhang, C. Wu, J. Zhang, Y. Xiang and S. Lu, *Journal of Membrane Science*, 2018, **558**, 26-33.
12. J. Zhang, S. Chen, H. Bai, S. Lu, Y. Xiang and S. P. Jiang, *International Journal of Hydrogen Energy*, 2021, **46**, 11104-11114.
13. J. Zhang, H. Bai, W. Yan, J. Zhang, H. Wang, Y. Xiang and S. Lu, *Journal of The Electrochemical Society*, 2020, **167,** 114501.
14. L.-C. Jheng, W. J.-Y. Chang, S. L.-C. Hsu and P.-Y. Cheng, *Journal of Power Sources*, 2016, **323**, 57-66.
15. W. Li, W. Liu, J. Zhang, H. Wang, S. Lu and Y. Xiang, *Advanced Functional Materials*, 2022, **33**, 2210036.
16. X. Zhang, X. Fu, S. Yang, Y. Zhang, R. Zhang, S. Hu, X. Bao, F. Zhao, X. Li and Q. Liu, *Journal of Materials Chemistry A*, 2019, **7**, 15288-15301.
17. C. H. Park, S. Y. Lee, D. S. Hwang, D. W. Shin, D. H. Cho, K. H. Lee, T. W. Kim, T. W. Kim, M. Lee, D. S. Kim, C. M. Doherty, A. W. Thornton, A. J.

Hill, M. D. Guiver and Y. M. Lee, *Nature*, 2016, **532**, 480-483.
18. Y. Sui, Y. Du, H. Hu, J. Qian and X. Zhang, *Journal of Materials Chemistry A*, 2019, **7**, 19820-19830.
19. F. Xiao, Q. Wang, G.-L. Xu, X. Qin, I. Hwang, C.-J. Sun, M. Liu, W. Hua, H.-w. Wu, S. Zhu, J.-C. Li, J.-G. Wang, Y. Zhu, D. Wu, Z. Wei, M. Gu, K. Amine and M. Shao, *Nature Catalysis*, 2022, **5**, 503-512.
20. H. Cheng, R. Gui, H. Yu, C. Wang, S. Liu, H. Liu, T. Zhou, N. Zhang, X. Zheng, W. Chu, Y. Lin, H. Wu, C. Wu and Y. Xie, *Proc Natl Acad Sci U S A*, 2021, **118,** e2104026118.
21. Z. Long and K. Miyatake, *ACS Appl Mater Interfaces*, 2021, **13**, 15366-15372.
22. X. Zhu, H. Zhang, Y. Zhang, Y. Liang, X. Wang and B. Yi, *The Journal of Physical Chemistry B*, 2006, **110**, 14240-14248.