Supporting Information

In situ Engineered Triple Phase Boundary Enhancement in 3D Structured Carbon Supported Catalyst for High-Temperature PEMFC

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Experimental

Membrane electrode assembly (MEA) preparation, and fuel cell performance evaluation The electrodes were fabricated using a bar-coating technique. A catalyst ink was prepared by homogenizing Pt electrocatalyst, the monomer solution of HTAP-112 ionomer, and isopropyl alcohol via probe sonication. The ionomer content was adjusted to achieve the desired ionomerto-carbon (I/C) ratio. The resulting ink was uniformly applied onto a gas diffusion layer (GDL, SGL Carbon) using the bar-coating method to attain a Pt loading of 1.0 mg cm⁻² for both the cathode and anode. The coated electrodes were subsequently exposed to UV irradiation for approximately 30 min to facilitate the polymerization of the monomeric ionomer. For comparative analysis, an alternative electrode was prepared using a commercially available Nafion-20% ionomer (DuPont, USA) without UV irradiation, while maintaining identical fabrication parameters. The electrodes were then integrated with a polybenzimidazole (PBI) membrane and subjected to hot pressing at 130 °C for 1 min under a pressure of 1.0 metric ton to assemble the MEA, with an active area of 45 cm². The assembled MEA was installed in a standardized test fixture (Fuel Cell Technologies, Inc., USA), and performance evaluations were conducted using a fuel cell test station (Fuel Cell Technologies, Inc., USA). Hydrogen and oxygen/air were utilized as the fuel and oxidant, respectively. The fuel cell was operated at 160 °C without backpressure. The long-term stability test was conducted over 100 h at a constant current under H₂-air feed conditions, with flow rates of 600 and 1500 sccm, respectively, at 160 °C. The electrochemical surface area (ECSA) and impedance measurements of the MEA were performed using a Metrohm Autolab potentiostat.

Calculation of the electrochemical active surface area (ECSA)

$$ECSA\left(m^{2}g_{Pt}^{-1}\right) = \frac{Q_{H-adsorption}(mC)}{0.210(mC\ cm^{-2}) \times Pt\ loading}$$
(S1)

Calculation of the kinetic current density

The kinetic current density (J_k) can be calculated using the Koutecky-Levich equation which is expressed by,

$$\frac{1}{J} = \frac{1}{J_d} + \frac{1}{J_k} \tag{S2}$$

 $J_k = Kinetic current density$

J = Measured current density

 $J_d = Diffusion$ limited current density

$$J_d = 062 \, nFAD^{2/3} \upsilon^{-1/6} \omega^{1/2} C_{O_2} \tag{S3}$$

n = Number of electrons transferred

F = Faraday's constant (96485 C mol⁻¹)

A = Area of the electrode (0.196 cm^2)

- D = Diffusion coefficient of O₂ in 0.1M HClO₄ (1.93 x 10^{-5} cm² s⁻¹)
- v = Kinematic viscosity of the electrolyte (1.01 x 10⁻² cm² s⁻¹)
- ω = Angular frequency of rotaion ω = $2\pi f/60$
- f = RDE rotation rate in rpm
- C_{O2} = concentration of molecular oxygen in 0.1M HClO₄ (1.26 x 10⁻⁶ mol cm⁻³)

The mathematical equations used for the RRDE analysis are given below:

$$n = 4 \times \frac{Id}{Id + \frac{Ir}{N}}$$
(S4)

$$H_2 O_2 (\%) = 200 \times \frac{\frac{lr}{N}}{ld + \frac{lr}{N}}$$
(S5)

where,

- $I_r = Ring current$
- $I_d = Disc \ current$
- N = Collection efficiency of the ring electrode (0.37)

n = No of electrons



Fig. S1. ¹³C solid-state NMR spectrum of the HTPA ionomer.

Table S1. The ion exchange capacities (IECs) and phosphoric acid uptakes of the HTAP thin films (mean \pm standard deviation, n = 3).

	IEC (meq. g^{-1}) ± SD	H ₃ PO ₄ Uptake (%) ± SD
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Nafion-HP	0.95 ± 0.01	8 ± 1
HTAP-111	0.98 ± 0.2	42 ± 7
HTAP-112	1.5 ± 0.05	78 ± 3
HTAP-121	1.1 ± 0.1	45 ± 6
HTAP-113	1.2 ± 0.04	86 ± 4



Fig. S2. The steady-shear viscosity of the Nafion and HTAP-112 ionomers.



Fig. S3. (a, b) The FESEM images with the different magnifications, (c) the 2D-AFM image, and d) the 3D-AFM image of the HTAP-112 thin film depicting the porous nature.



Fig. S4. The HRTEM images of the Pt/C catalyst with (a) Nafion® ionomer, and (b) HTAP-112 ionomer.



Scheme S1. The schematic representation of the synthesis of Pt/3DPDC.



Fig. S5. The FESEM images of (a, b) the bare MS with different magnifications, and (c, d) the MS after the PDA coating and annealing at 900 °C.



Fig. S6. (a) The BET isotherm, and (b) the pore size distribution profile of the commercial Pt/C catalyst.



Fig. S7. The XPS survey spectrum of Pt/3DPDC.



Fig. S8. The comparative CV profiles of Pt/C with varying I/C ratios of (a) Nafion[®] and (b) HTAP-112 ionomers; Pt/3DPDC with varying I/C ratios of (c) Nafion[®] and (d) HTAP-112 ionomers.



Fig. S9. The RRDE ring and disk current profiles of both the HTAP-112 and Nafion ionomers with *state-of-the-art* Pt/C catalyst.



Fig. S10. The stability test of the MEA based on the HTAP-112 ionomer at constant current for about 100 h of duration.



Fig. S11. The comparative solid-state CV profiles recorded for the MEAs based on Pt/C using the HTAP-112 and PTFE-Nafion ionomers.



Fig. S12. The comparative solid-state CV profiles recorded for the MEAs based on Pt/3DPDC using the HTAP-112, ionomer-free, and Nafion-PTFE ionomers.

Table S2. The comparative performance parameters of the Pt/C-based MEAs using the different binders reported in the literature.

Binder	Pt Loading-Cathode (mg _{Pt} cm ⁻²)	Peak Power Density* (mW cm ⁻²)	Reference
PTFE	1	400	1
PVDF	0.5	464	2
PVDF and qPVB/Cl-	0.5	360	3
PTFE and PVDF	0.5	535	4
FEP	1.45	-	5
Nafion	0.5	200	6
P-PPSU-2.75	0.5	242	7
PWN70	0.6	500	8
PA-QASOH	0.6	750	8
TP-4-IM	0.5	821	9
TP-4-PZ	0.5	804	9
TP-3-PZ	0.5	756	9
PIM- Tz	0.5	828	10
Polysilsesquioxane (ph-F PSQ)	1	527 (H ₂ -air)	11
Binder less	0.1	420 (180 °C), (H ₂ - air)	12

HTAP-112	1	1190	This work
PA-SPX	0.1	730	14
QAPBI	0.5	740	13

* Unless specified, the testing conditions are 160 °C, H₂/O₂, without backpressure.

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