Electronic Supplementary Information

## Synthesis of small-sized intermetallic PtCo fuel cell catalysts by promoting inner surface utilization of carbon supports

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**Synthesis of MC support.** In a typical synthesis,<sup>1</sup> 1.0 g of benzene-1,2,4,5- tetracarboxylic acid (marked as BTAA) was first dispersed in 100 mL of deionized water containing Mg(OH)<sub>2</sub>. The mole ratio of Mg(OH)<sub>2</sub> to BTAA was 2:1. The solution was stirred for 1 h at 100 °C before rotary evaporation to obtain the powder. Then the collected powder was transferred into a corundum crucible and the furnace was ramped from room temperature to 800 °C at a heating rate of 10 °C min<sup>-1</sup> and held for 2 h under flowing N<sub>2</sub>. After cooling to room temperature, the carbonized product was washed with 1 M HCl solution and deionized water several times to remove metal species. The wet carbon products were finally dried at 60 °C overnight, marked as MC.



**Figure S1.** Limiting current as a function of dry mole fraction of oxygen for five different total pressures in a cell with the cathode catalysts of PtCo-IW/KJ300 (a) or PtCo-OAm/KJ300 (b). Total  $O_2$  transport resistance ( $R_{Total-O2}$ ) as a function of total reactant gas pressure for MEAs made with the cathode catalysts of PtCo-IW/KJ300 (c) or PtCo-OAm/KJ300 (d).



**Figure S2.** XRD pattern (a) and TEM image (b) of PtCo colloids prepared from OAm method. The inserted histogram is the corresponding statistics of PtCo NPs size distributions.



**Figure S3.** Nitrogen sorption isotherms of KJ300(a), PtCo-IW/KJ300 (b), PtCo-OAm/KJ300 (c), MC (d), and YP-50F (e).



Figure S4. XRD patterns of treated PtCo-IW/KJ300 and PtCo-OAm/KJ300

<b>T</b> (00)	Outlet pressure	Relative	Dry mole
Temperature (°C)	(kPa)	humidity (%)	) fraction $O_2$
80	100		0.010
	150		0.015
	200	70	0.020
	250		0.025
	300		

**Table S1.** Test stand protocol for limiting current measurements. Every mole fraction of oxygenwas run at each pressure.

Table S2. Size and metal content of prepared catalysts.

Catalysts	Particle size <sup>1</sup> (nm)	Particle size <sup>2</sup> (nm)	Pt(wt%) <sup>3</sup>	Co(wt%) <sup>3</sup>
PtCo-IW/KJ300	4.5	4.6	14.6	4.3
PtCo-OAm/KJ300	13.1	11.0	14.1	4.0
PtCo-IW/MC	11.9	10.6	14.5	4.1
PtCo-IW/YP-50F	8.7	8.0	14.0	4.1

<sup>1</sup> Estimation of the main peak at 41.6° by the Debye-Scherer equation based on XRD data

<sup>2</sup> Statistics analysis from HADDF-STEM images

<sup>3</sup> ICP-AES measurement

Table S3. ICP-AES results for metal content of treated catalysts

Catalysts	Pt(wt%)	Co(wt%)	Pt/Co
treated PtCo-IW/KJ300	13.4	2.5	1.6
treated PtCo-OAm/KJ300	13.9	2.7	1.5

## References

 L. Tong, Q. Q. Yang, S. Li, L. Le Zhang, W. J. Zeng, Y. W. Ding, L. Fan and H. W. Liang, Building the Bridge of Small Organic Molecules to Porous Carbons via Ionic Solid Principle, *Nano Res.*, 2022, 16, 80–87.