Electronic Supplementary Information

Mesoporous Carbon Confined Intermetallic

Nanoparticles as Highly Durable Electrocatalysts for

Oxygen Reduction Reaction

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Experimental details

1. Material synthesis

1.1. Preparation of ZIF-8 DMC supports

Typically, 3606 mg of zinc (II) nitrate hexahydrate were dissolved in a methanol solution and the other methanol solution contained 4021 mg 2-methylimidazole. After 30 min of magnetic stirring, mixed the two solutions and continuous stirred at room temperature for 24 hours. Then the precipitate were collected by centrifugation, washed at least three times with methanol, then dried at 40°C in a vacuum oven for 10 hours. The precursors are designated as ZIF-8, subsequently ZIF-8 were heated at a temperature of 950 °C in a tube furnace under Ar flow for 3 hours to remove Zinc and obtain the ZIF-8 DMC, and then the products were treated in 0.5 M H₂SO₄ at 80 °C to further remove residual zinc. (when the MOF was UIO-66, use HF replace H₂SO₄, other conditions remain unchanged) Subsequently washed until PH is neutral, collected by centrifugation and dried, the pretreated ZIF-8 DMC support can be obtained.

1.2. Preparation of Pt₃Co/DMC-F

At first, 20 mg pretreated ZIF-8 DMC was impregnated by dropwise addition of 100 μ l 0.256 M H₂PtCl₆ and 0.086 M CoCl₂ mixed solution. Then ultrasound for an hour and freeze-dried the Pt and Co impregnated ZIF-8 DMC immediately. subsequently heated at a temperature of 750 °C in a tube furnace under H₂/Ar (92%) flow for 2 hours, the heat rate is 3 °C per minutes. The assynthesized catalyst is denoted as Pt₃Co/DMC-F.

1.3. Preparation of Pt₃Co/DMC

Use room temperature drying replace freeze-drying and other conditions are consistent with Pt₃Co/DMC-F, the as-synthesized catalyst is denoted as Pt₃Co/DMC.

1.4. Preparation of Pt₃Co/C-F

Use XC-72 replace ZIF-8 DC and other conditions are consistent with Pt_3Co/DMC -F, the assynthesized catalyst is denoted as Pt_3Co/C -F.

1.5. Preparation of Pt₃Co/C

Use room temperature drying replace freeze-drying and other conditions are consistent with Pt₃Co/C-F, the as-synthesized catalyst is denoted as Pt₃Co/C.

2. Physical characterizations

X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker D8 Advance diffractometer with Cu K α radiation (λ =1.5418 Å) with graphite monochromator (40 KV, 40 mA). SEM was performed with a Hitachi S5500 SEM/STEM. TEM and EDS analysis were carried out using a JEOL 2010F microscope operated at 200 kV. HRTEM imaging was carried out on a FEI-Titan ST electron microscope operated at 300 kV. STEM and elemental mapping images were obtained by a JEOL ARM200F (JEOL, Tokyo, Japan) operated at 200 kV with cold field emission gun and double hexapole Cs correctors (CEOS GmbH, Heidelberg, Germany). XPS was performed on an Axis Ultra DLD X-ray photoelectron spectrometer employing monochromated Al-Ka X-ray sources (*hv*=1486.6 eV). The inductively coupled plasma atomic emission spectrometry (ICP-AES) analysis of samples was performed on IRIS Intrepid II XSP (ThermoFisher).

3. Electrocatalytic Testing

Electrochemical measurements were carried out by using an electrochemical workstation ((Ivium, Netherlands) coupled with a rotating disc electrode (RDE, Pine, AFMSRCE 3005) in a three-electrode cell. A Pt wire and Ag/AgCl (3 M KCl) were used as the counter and reference electrodes, respectively. The potential of the Ag/AgCl (3 M KCl) was calibrated with a RHE reference electrode: in 0.1 M HClO₄ at room temperature, E (RHE) = E (Ag/AgCl) + 0.288 V. A

glassy carbon electrode (GC, 0.196 cm²) was using as the working electrode. 4 mg assynthesized catalysts were dispersed in the mixture containing 975 μ L ethanol and 25 μ L of 5 wt.% Nafion solution to form the homogeneous catalyst ink by sonicating for 40 min. Then 5 μ L of the dispersion were drop-casted on the disk electrode respectively and dried at room temperature to yield a thin-film electrode. The loading mount of metal Pt for the three assynthesized catalyst was 20.4 μ g cm⁻². The potential scan rate was 50 mV/s for the CV measurement. ORR measurements were conducted in a 0.1 M HClO₄ solution purged with oxygen during the measurement. The scan rate and rotation rate for ORR measurement were 10 mV/s and 1600 rpm. The accelerated durability tests (ADTs) were performed at room temperature in O₂-saturated 0.1 M HClO₄ solutions by applying the cyclic potential sweeps between 0.6 and 1.1 Versus RHE at a sweep rate of 50 mV/s for 5000 cycles. For comparison, the commercial Pt/C (JM, 20 wt% Pt) was used as the benchmark catalyst with a loading amount of 25.5 µg cm⁻².

4. MEA Testing

The MEA for an H₂/air PEM fuel cell was prepared using a catalyst-sprayed membrane method reported previously by our group and conducted in an Arbin fuel cell testing system (Arbin, USA). Typically, the catalyst "ink" was sprayed on one side of a Nafion 211 membrane (DuPont, USA) in order to form the cathode catalyst Layer. Pt₃Co/DMC-F or commercial JM 20wt% Pt/C was used at the cathode (0.2 mg_{Pt} cm⁻²) and commercial JM 40wt% Pt/C was used at the anode (0.1 mg_{Pt} cm⁻²). The active area of the MEA was 5.0 cm². H₂ and air as the fuel and oxidant were fed with full humidification at 30 psi back pressure and a flow rate of 600 mL min⁻¹, and the cell testing temperature was 70 °C. AST was conducted by following the DOE/FCTT

protocol: a trapezoidal wave potential cycle between 0.6 and 0.95 V with 3 sec at 0.6 V and 3 sec at 0.95 V, and the AST temperature was 80 °C in N₂ at 0 psi back pressure.



Figure S1. SEM of pretreated ZIF-8 DMC.



Figure S2. Isothermal physisorption for ZIF-8 DMC and XC-72.



Figure S3. (a-c) Histograms of Pt_3Co/DMC -F, Pt_3Co/DMC and Pt_3Co/C -F. (d) TEM and (e) corresponding histograms of Pt_3Co/C .



Figure S4. (a-d) HAADF-STEM image and elemental mappings for Pt_3Co/DMC -F. (e) Linescans of a Pt_3Co nanoparticle. (f-i) HAADF-STEM image and elemental mappings for a Pt_3Co particle.



Figure S5. (a,b) TEM of as synthesized Pt₃Co/DMC(UIO-66)-F and (c,d) Pt₃Fe/DMC(ZIF-8)-F.



Figure S6. EDX spectra of Pt₃Co/DMC-F.



Figure S7. Specific activity Tafel plot for the different electrocatalysts.



Figure S8. (a,b) TEM images of Pt₃Co/DMC-F before and after 20000 cycles AST on MEA. (c,d) the corresponding histograms. (e,f) TEM images of Pt/C before and after 10000 cycles AST on MEA. (g,h) the corresponding histograms.



Figure S9. Raman spectra for ZIF-8 DMC and XC-72.



Figure S10. (a) Pt 4f, (b) Co 2p XPS spectra and (c) XPS wide scanning spectra of Pt₃Co/DMC-F, Pt₃Co/DMC and Pt₃Co/C-F.

composition	size (nm)	annealing temperature	reference
Pd3Pb	~6.9	600 ℃	1
PtZn	3.7 ± 0.6	800℃	2
FePt	~8	700 °C	3
Fe3Pt	5.3±0.3	600 °C	4
Fe3Pt	5.3 ± 0.3	600 °C	5
PtFe	<8	700℃	6
Pt-Fe-Cu	~5.7	700 °C	7
Pt-Fe-Au	~4.4	500℃	8
PtCo	~12.65	400°C 2h,600°C 2h,900°C 10min	9
PtCo	~5.5	800 °C	10
PtCo	~5.9	700 °C	11
PtCo	~4.8	550℃	12
Pt3Co	~5.0	900°C	13
Pt3Co	~5.6	700 °C	11
Pt3Co	~2.93	750 ℃	This Work

Table S1. Statistics of annealing temperature and particle size of ordered intermetallic nanoparticles in recent years.

Catalyst	Electrol yte	Temperat ure °C	E1/2 V vs.RHE	MA @ 0.9V (A/mgPt)	SA @0.9 V (mA/cmPt2)	Ref.
PtCo3	0.1 M HClO4	RT		0.34	0.491	14
PtCo3 800°C annealing	0.1 M HClO4	20	0.9	0.34	1.15	15
PtCo/C-700	0.1 M HClO4	RT	0.91	0.5	0.63	11
O-PtCo@Pt/C	0.1 M HClO4	25	0.9	0.0536	0.183	12
PtCo/C-900	0.5 M H2SO4	RT		0.084(@0.75 V)	2.8(@0.75V)	16
Pt-Co/C-SB	0.1 M HClO4	RT		0.151	1.445	17
PtCo@NC-10	0.1 M HClO4	RT	0.929	0.82	1.32	2
Pt3Co/C-700	0.1 M HClO4	RT	0.945	0.52	1.1	18
Acid-treated "Pt3Co"	0.1 M HClO4	RT		0.35	1.39	19
Pt3Co/C	0.1 M HClO4	25		0.217		20
Pt/40Co-NC- 900 (Pt3Co)	0.1 M HClO4	RT	0.92 (900 rpm)		1.15	13
Pt3Co-High T	0.1 M HClO4	RT	0.9		0.3	21
Pt3Co/ZIF8 DC FD	0.1 M HClO4	RT	0.93	0.83	1.44	This work

 Table S2.
 Summary of ORR performance and test conditions of PtCo ordered intermetallic catalysts.

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