Supplementary Information

Framework Ensemble Facilities High Pt Utilization in Low Pt Loading Fuel Cell

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Experimental

Synthesis of PVP-Pt

2.5 nm PVP-stabilized Pt nano-particles (NPs) were prepared by refluxing a mixture of PVP (533 mg, Mw=30,000), methanol (180 ml), and aqueous solution of H_2PtCl_6 (6.0 mM, 20 ml) in a flask (500 ml) for 3 hours under air. Methanol was removed by rotary evaporator. The NPs in the remaining solution were precipitated by acetone and then collected by centrifugation at 6,000 rpm for 5 minutes. The sample was cleaned with methanol and acetone to remove excess free PVP. Finally the obtained Pt NPs were dispersed in methanol (90 ml) to give a Pt content of 0.26 mg/ml according to the amount of H_2PtCl_6.

Synthesis of Pt@ZIF-8

Typically, methanolic solutions of zinc acetate (5 mM, 100 ml), 2-methylimidazole (20 mM, 100 ml) and 0.26 mg/ml PVP-Pt nanoparticles (1ml) were mixed briefly and then kept at room temperature for 24 hours without stirring. The product was collected by centrifugation, washed several times with methanol, and vacuum dried overnight.

Synthesis of PtZn@3DF and 3DF

The obtained Pt@ZIF-8 powders were put into quartz tube and then pyrolyzed under N_2+H_2 (9:1) atmosphere at 900 °C for 1h.

Synthesis of PtZn@3DF-E and JM-Pt/C-E

The PtZn@N-MCF and JM-Pt/C were immersed into the sulfonated tetrafluoroethylene based fluoropolymer-copolymer (Nafion) solution for 24h and then dried it under vacuum condition (<0.1 Torr) at 60 °C for 6h.

Characterization

X-ray diffraction (XRD) patterns were recorded on a XRD-6000 using Cu Kr radiation (λ=1.5418 Å) at a step rate of 2° s^{-1}. Low-resolution transmission electron microscopy (TEM) was carried out on a FEI Tecnai G220S-TWIN instrument operating at 120 kV. High-resolution transmission electron microscopy (HRTEM) was carried out on a Zeiss LIBRA 200 FETEM instrument operating at 200 kV. XPS was acquired using a Kratos XSAM800 spectrometer equipped with monochromatic Al X-ray source (Al KR, 1.4866 keV), the vacuum in the analysis chamber was maintained at 10^{-7} Pa, and the binding energy was calibrated by using 284.5 eV as the C 1s peak energy.

Electrochemical measurements

The catalysts were evaluated electrochemically in three-electrode one-compartment cell, in which 0.1M $HClO_4$ was used as the electrolyte, a saturated Ag/AgCl electrode and a Pt wire were used as reference and counter electrodes, respectively.

The electrocatalytic activity of catalysts for oxygen reduction was determined by cyclic voltammetry (CV) at a sweep rate of 50mVs^{-1} followed by liner sweep voltammetry (LSV) at a sweep rate of 10mVs^{-1} with a rotational disk electrode (RDE). The measurements were performed at 25 °C after purging O_2 or N_2 for 30 min. RDE measurements were conducted with a varying rotating speed of 1600 rpm. A glassy carbon disk of 5 mm diameter coated with a film of catalyst was used as working electrode. To prepare the working electrode, 2mg of PtZn@3DF catalyst and a drop of 0.1wt% Nafion solution were ultrasonically dispersed in 400μL of a water-ethanol (1:1 v/v) mixed solvent to form a homogeneous ink. As a comparison, 2 mg of Pt/C was ultrasonically dispersed in 1000μL of EtOH with a drop of a 0.1wt % Nafion solution. Then 10μL and 5μL of the catalyst ink were loaded onto a RDE, respectively. After evaporation of ethanol in air, the catalyst layer was covered with a thin film of Nafion by adding a drop of 0.01wt % Nafion solution. Finally, the RDE was

dried at air temperature. All potentials in this study are given relative to the potential of the reversible hydrogen electrode (RHE).

For ORR test, the Koutecky-Levich equation can be used as follows:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{Bw^{1/2}} + \frac{1}{J_K}$$

$$B = 0.2nFC_0 \left(D_0\right)^{2/3} u^{-1/6}$$

Where J is the measured current density, J_K and J_L are the kinetic- and diffusion-limiting current densities, ω is the electrode rotating speed in rpm, n is the electron transfer number in oxygen reduction, F is the Faraday constant, C_0 is the bulk concentration of O_2, D_0 is the diffusion coefficient of O_2, ν is the kinematic viscosity of the electrolyte, The constant 0.2 is adopted when the rotating speed is in rpm.

The specific kinetic current densities (J_k) associated with the intrinsic activity of the catalysts can be obtained by the following relation:

$$J_k = \frac{J_L * J}{J_L - J}$$

Rattle drum test: the LSV curves were recorded in O_2-purged 0.1 M $HClO_4$ solutions at a different pH (1, 3, 7), particularly using a self-made working electrode. Firstly, a viscous suspension consisting of catalyst, nafion solution, and ethanol (with mass ratio of nafion to catalyst = 0.35:1) was pipetted onto the carbon paper to reach Pt loading of 0.06 mg cm^{-2} (effective area = 0.785 cm^2). The catalyst was naturally dried at room temperature and loaded into the ring groove of the working electrode. Specially, the side loaded with catalyst faces outside, allowing that O_2 molecules enter into the catalyst layer through carbon paper. When testing, the head of the "rattle-drum" was sealed with Vaseline and totally soaked in the HClO4 solution as working electrode. And the three-electrode systems also include a carbon rob counter electrode and an Ag/AgCl (in 3.0 M KCl) reference electrode. Flowing rate of O_2 is maintained at 100 mL/min during the test.

Single Fuel cell testing.

The PtZn@3DF catalyst "ink" was prepared by ultrasonically mixing the catalyst powder with 5wt% Nafion solution (DuPont) and anhydrous alcohol for approximately 15 min. The Nafion content in the dry catalyst layer was 33wt%. The suspension was pipetted onto the gas diffusion layer and finally heated at 80ºC for 3 hours. The weight difference was measured and used to calculate the loading of the catalysts on carbon paper. The Pt loading was 0.06mg cm^{-2} when the PtZn@3DF catalyst and Pt/C (Johnson-Matthey In. UK) used as cathode. For the catalyst layer with vacuum inspirited treatment, 200ul 0.1% Nafion solution was sprayed on the cathodes, after that, put the cathodes in vacuum oven to dry under vacuum condition (<0.1 Torr) at 60 °C for 6h. A suspension consisting of 60wt% PtRu/C catalysts, 5 wt% Nafion solution (DuPont) (33wt% in the catalyst layer), and anhydrous alcohol was used to prepare the opposite catalyst layer. The Pt loading was controlled at 0.06 mg cm^{-2} on the anodic side. The MEA (5cm^2) was prepared by hot-pressing the cathode, Nafion HP membrane, and the anode at 135ºC and 5 MPa for 150s. The Nafion HP membrane (DuPont) was pretreated with 3 vol. % H_2O_2 and 0.5M H_2SO_4 for 1h to remove impurities. The membrane was then washed several times with hot ultrapure water. Pure hydrogen and oxygen were supplied to the anode and cathode at a flow rate of 150 and 200mL min^{-1}, respectively.

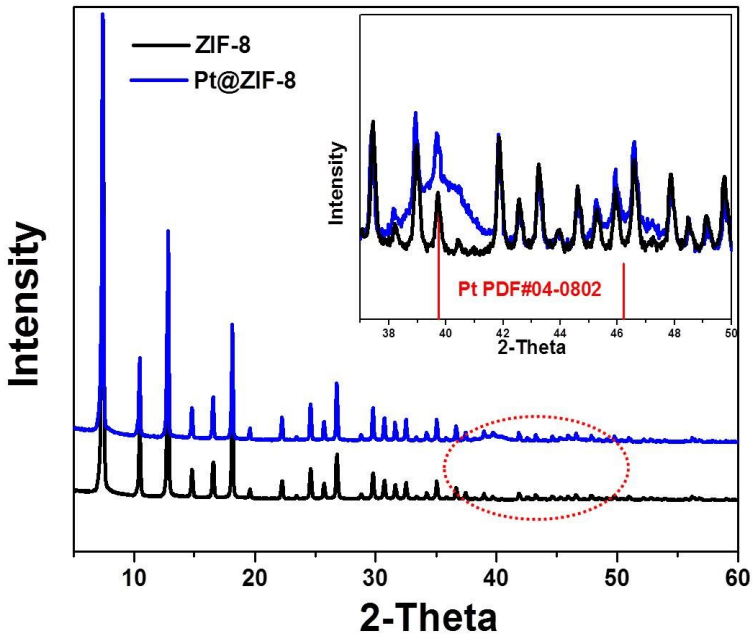

Figure S1. XRD of ZIF-8 and Pt@ZIF-8 (the inset are the enlarged peak of Pt (111) and Pt (200) planes)

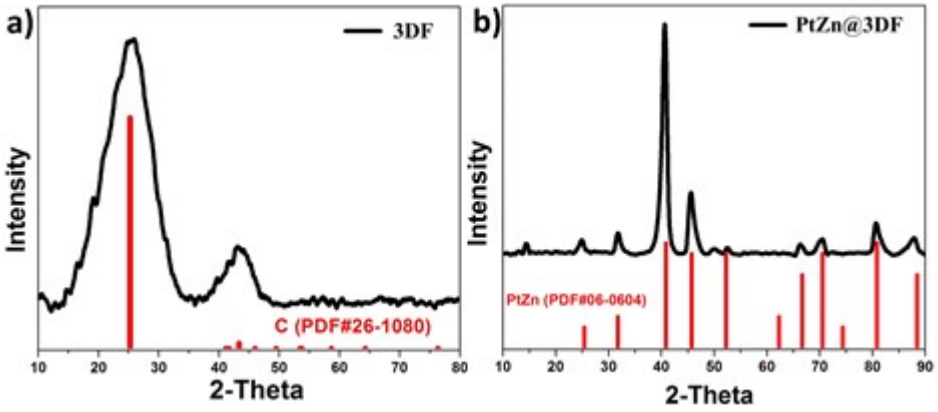

Figure S2. The XRD patterns of (a) 3DF and (b) PtZn@3DF

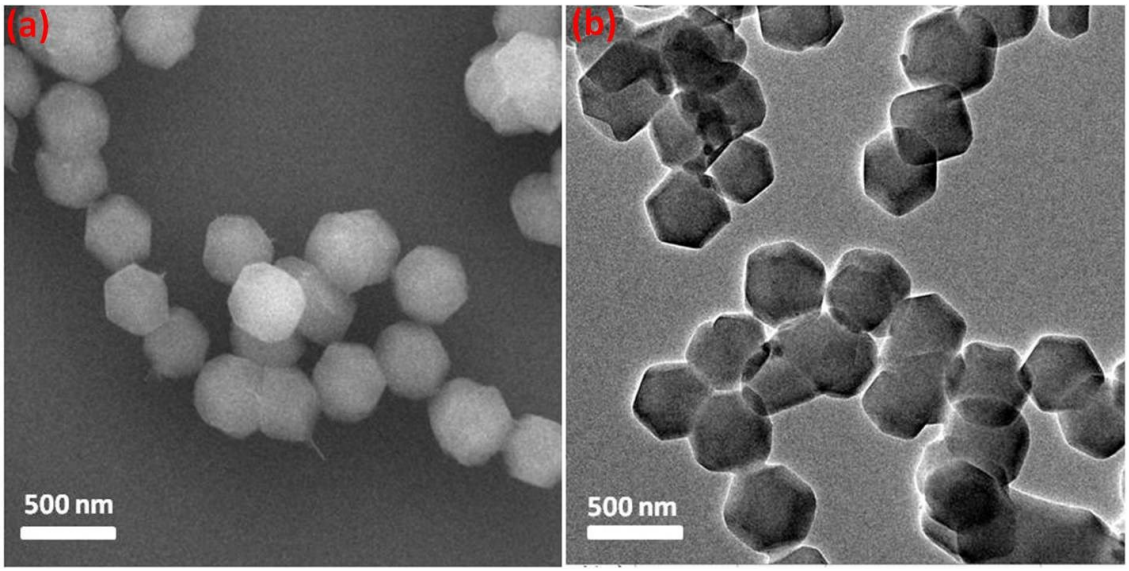

Figure S3. a) SEM and b) TEM of ZIF-8

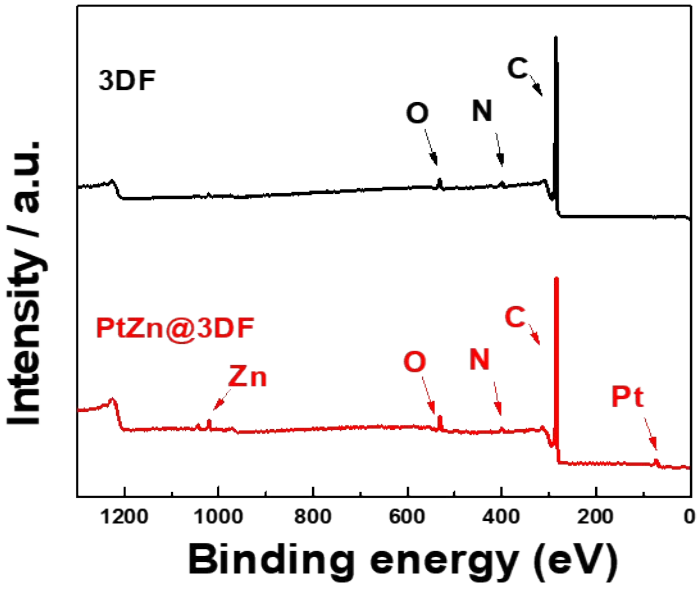

Figure S4. XPS of 3DF and PtZn@3DF

Table S1. Surface atom content of 3DF and PtZn@3DF from XPS analysis.

Sample	Elements content (atom%)				
	C	O	N	Pt	Zn
3DF	94.08	3.42	2.50	---	---
PtZn@3DF	90.84	5.03	2.97	0.40	0.76

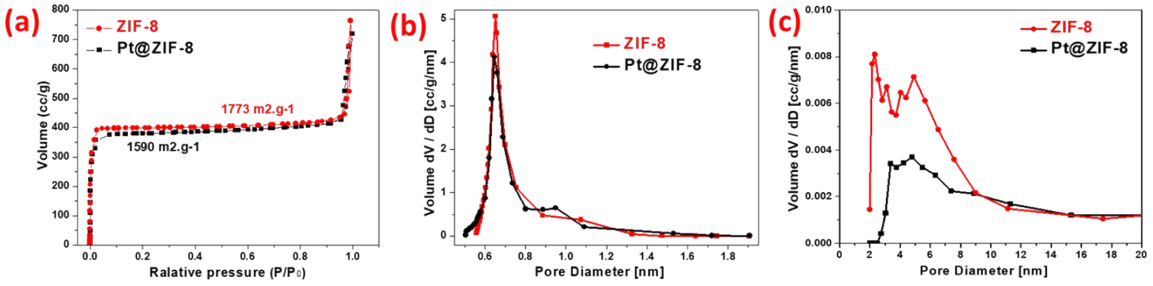

Figure S5. (a) Nitrogen sorption isotherms for ZIF-8 and Pt@ZIF-8; (b, c) Pore size distribution for ZIF-8 and Pt@ZIF-8 assessed by HK.

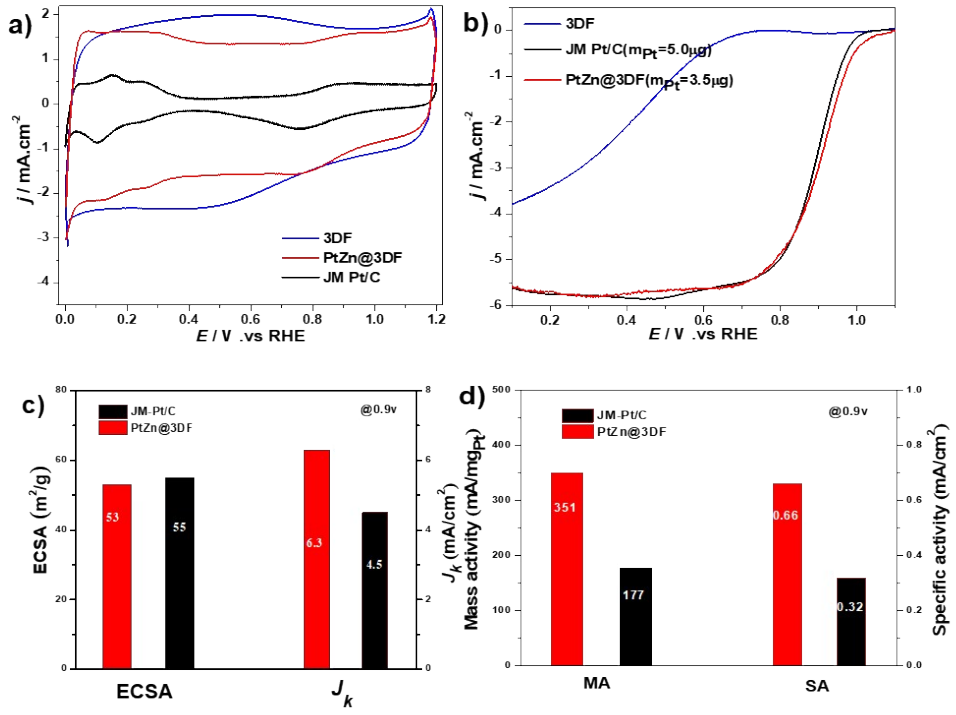

Figure S6 a) CV curves of 3DF, PtZn@3DF and Pt/C recorded in N_2-purged 0.1 M HClO4 solution at a scan rate of 50 mV s^{-1}; b) The ORR polarization curves of 3DF, PtZn@3DF and Pt/C modified electrodes recorded in an O_2-saturated 0.1 M $HClO_4$ solution at room temperature (1600 rpm, sweep rate of 10 mV s^{-1}); c) ECSA and J_k (0.90V vs.RHE) values of two catalysts; (d) Mass activity and specific activity of the PtZn@3DF and JM Pt/C at 0.90V vs.RHE. The Pt loading is 25 μg_{Pt} cm^{-2} for JM Pt/C (20%) and is 17.5 μg_{Pt} cm^{-2} for PtZn@3DF.

Table S2. Comparison of the Performance of PEMFC between PtZn@3DF-E and Other Pt-Based Catalysts in the Literature

Catalysts	Pt utilization (g/kW)（@peak power density Fuel Cell）	Operation Condition	Refs
Pt/Cu-SAC	0.238	H_2/O_2 70°C	1
$Pt_A@Fe_{SA}$-N-C	0.252	H_2/O_2 100 kPa_{abs} 65°C	2

PtCo@CNTs-MOF	0.098	H_2/O_2 200 kPa_{abs} 80°C	3
Pt_3Ni	0.633	H_2/O_2 150 kPa_{abs} 80°C	4
$Pt_{36}Co/C$	0.498	H_2/O_2 150 kPa_{abs} 65°C	5
PtCoFe/SG	0.377	H_2/O_2 75°C	6
Pt-TiO2@PANI	0.52	H_2/O_2 70°C	7
PtZn@3DF-E	0.14	H_2/O_2 200 kPa_{abs} 80°C	This work

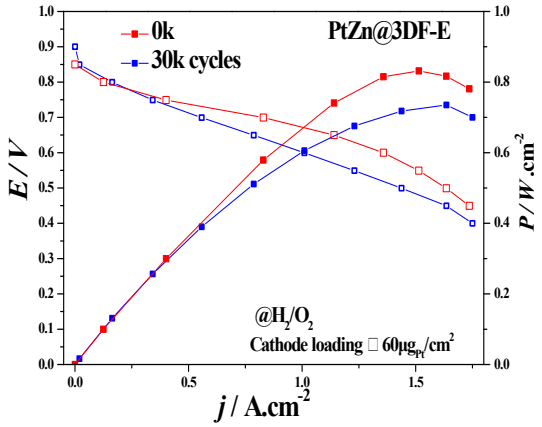

Figure S7 Comparation of PtZn@3DF-E catalyst before and after aging test.

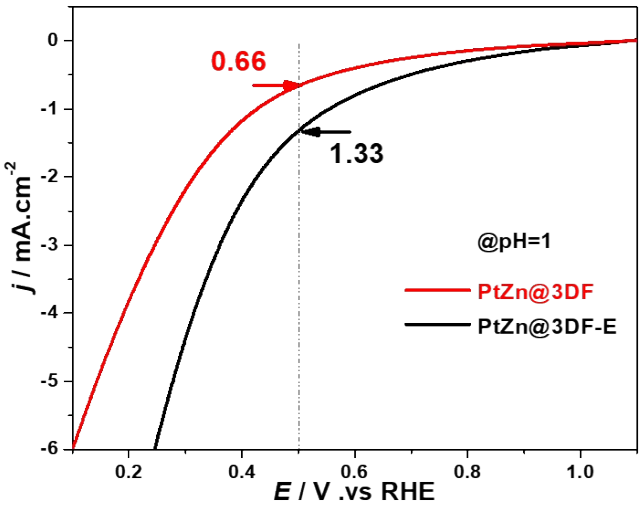

Figure S8. the self-made "rattle-drum"-like working electrode modified by PtZn@3DF and PtZn@3DF-E catalysts (0.06 mg Pt/cm^2), which was evaluated in $HClO_4$ solution.

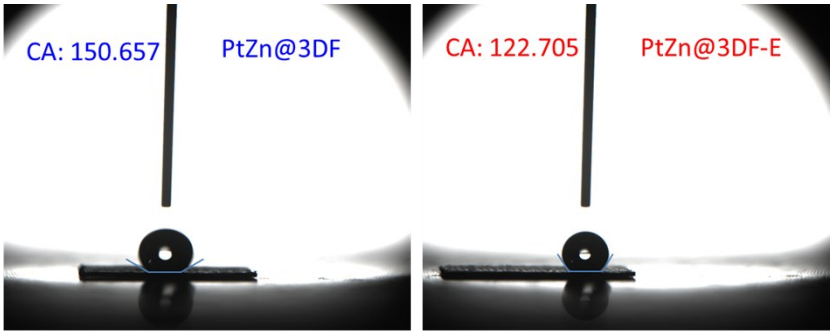

Figure S9. the contact angle of catalyst layers fabricated by PtZn@3DF and PtZn@3DF-E catalysts.

Reference:

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