

Supporting Information

Supporting 1 (S1)

The electrochemically active area (S_{ECA}) of the PtFe_x/OMC samples is calculated by Eq (1).

$$S_{\text{ECA}} = \frac{S}{m c \nu} \quad (1)$$

Where S is the area by integrating the total charge corresponding to the desorption peak of hydrogen in CV curve (shown in Table S1), m is the mass of PtFe_x/OMC catalyst (0.049 mg based on the 25 μL ink used), c is the Pt single crystallite hydrogen adsorption constant: 0.21 mC/cm², and ν is the scan rate of 50 mV/s.

Table S1. The integrating area of the desorption peak of hydrogen of PtFe_x/OMC samples.

	Pt/OMC	PtFe/OMC	PtFe ₂ /OMC	PtFe ₃ /OMC
$S / \text{mA V}$	0.11	0.17	0.19	0.39

Supporting 2 (S2)

To further describe ORR activity of PtFe_x/OMC in acid solution in the presence and absence of methanol in acid, we carried out the study on the activity of PtFe_x/OMC catalysts in the presence of methanol in acid, the mass activity (MA) represents for the current per unit mass of catalyst in 0.5 M H₂SO₄, and the specific activity (SA) for the current per unit surface area of catalyst in 0.5 M H₂SO₄. The MA' and SA' represent the corresponding activity in 0.5 M H₂SO₄+1 M CH₃OH, respectively.

The mass activity (MA), which is the current per unit mass of the PtFe_x/OMC samples, is the corresponding i_{kin} (shown in Eq.2) at the potential of 660mV (SCE = 0.9V·RHE), and the mass of PtFe_x/OMC samples can be calculated. The net kinetic current of ORR was obtained by using the following formula: [27, 38, 47]

$$i_{kin} = \frac{i_{lim} \cdot i_{obv}}{i_{lim} - i_{obv}} \quad (2)$$

where i_{kin} is the current derived from diffusion coupled kinetics in the porous reaction layer, i_{lim} is the limited current, i_{obv} is the observed current. The values of i_{kin} and MA are shown in Table S2. From Fig. 8a and 8b, it can be seen that i_{kin} increases with the Fe loading content increasing. This proves that PtFe_x/OMC catalysts have a high kinetic current of ORR, as compared with Pt/OMC catalyst.

The other is specific activity (SA) for the current per unit surface area of catalyst, the SA was obtained by the following formula:

$$SA = \frac{MA}{S_{ECA}} \quad (3)$$

where S_{ECA} is electrochemical surface area obtained from hydrogen desorption peaks in CV. The SA is shown in Table S2.

It should be noted that in the presence of 0.5 M H₂SO₄+1 M CH₃OH, it is difficult to calculate the MA' and SA' of Pt/OMC at the potential of 660mV (SCE = 0.9V·RHE), because of some of the catalytically active sites Pt and OMC channels blocked or covered by adsorbed intermediates from methanol. The catalytically active sites are decreased, the MA' and SA' for the ORR can be ignored.

Table S2. Electrochemical characterizations for the PtFe_x/OMC catalysts in 0.5 M H₂SO₄ or 0.5 M H₂SO₄+1 M CH₃OH. (MA, SA: in 0.5 M H₂SO₄; MA', SA': in 0.5 M H₂SO₄+1 M CH₃OH)

	At 660 mV (vs SCE)					
	i_{kin}	MA	SA	i_{kin}	MA'	SA'
	/mA cm ⁻²	/mA mg ⁻¹	/mA m ⁻²	/mA cm ⁻²	/mA mg ⁻¹	/mA m ⁻²
Pt/OMC	-0.45065	2.8	129.6	0.46257	-	-
PtFe/OMC	-1.23617	7.6	228.2	-0.15012	0.9	27.0
PtFe ₂ /OMC	-1.4819	9.1	244.0	-0.40954	2.5	67.0
PtFe ₃ /OMC	-3.54977	21.7	283.7	-1.2596	7.8	100.6

27 A. N. Golikand, L. Irannejad, *Electroanal.*, 2008, 20, 1121.

38 W. Z. Li, W. J. Zhou, H. Q. Li, Z. H. Zhou, B. Zhou, G. Q. Sun and Q. Xin, *Electrochim. Acta*, 2004, 49, 1045.

47 X. Li, L. An, X. Y. Wang, F. Li, R. Q. Zou, and D. G. Xia, , *J. Mater. Chem.*, 2012, **22**, 6047.

Supporting 3 (S3)

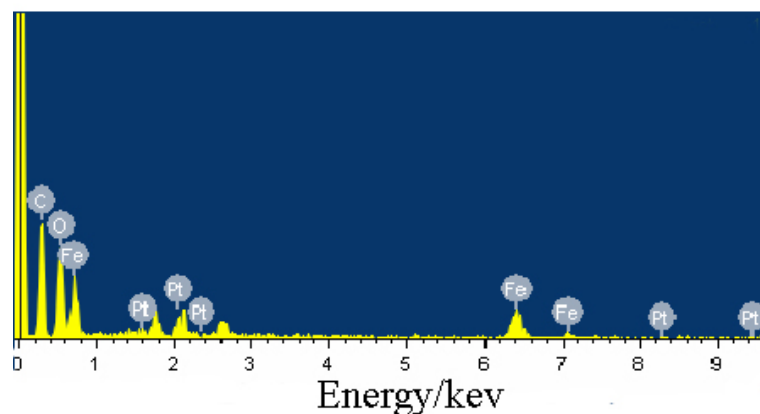


Figure S1 depicts a typical EDS spectrum for the PtFe₃/OMC catalysts, showing that the sample is composed of C, Fe and Pt elements, and no other impurity could be observed. The presence of oxygen mainly comes from atmospheric O₂, or CO₂ adsorbed on the surface of the sample.