

1 **Supporting Online Material**

2 **Efficient Oxygen Reduction by a Fe/Co/C/N**

3 **Nano-Porous Catalyst in Neutral Media**

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13  
14 **Experimental section**

15  
16 **Synthesis procedure of FeCo-MFR-1 (FeCo-MFR used for MFC)**

17 A schematic diagram for the MFR synthesis is shown in Fig. S1. In the initial step, 6.45 g of  
18 melamine, 12 ml formaldehyde (37%) and 1g sodium hydroxide are dissolved in 200 ml of distilled  
19 water under 80°C. The mixture was agitated for four hours for the hydroxylation reaction, and then 1  
20 g carbon particle (Ketjenblack EC 300J, Mistubishi Chemical) was ultrasonically dispersed into the  
21 above solution using an ultrasonic probe. Next 3.36 g Fe(NO<sub>3</sub>)·9H<sub>2</sub>O and 1.12g Co(acetate)<sub>2</sub>·4H<sub>2</sub>O  
22 were dissolved into 20 ml hydrochloric acid (HCl) solution (pH 1). The mixed salt/acid solution was  
23 added into the melamine/formaldehyde solution, and the pH value was quickly tuned to 2 using a  
24 HCl solution (5M) for polymerization. After polymerization for 3 hours, the polymer gel paste was  
25 put into the furnace at 150°C for 5 hours for cross-linking the melamine-formaldehyde resin  
26 (solidification).

27 To synthesize FeCo-MFR catalysts, the solidified sample was grinded to powder using a quartz  
28 mortar. Then, it was put into a tubular furnace (Koyo) and pyrolyzed at 700°C in the presence of  
29 ammonia gas for 1.5 h. Heat-treated products were ultrasonically leached in concentrated HCl solution  
30 for 8 h to remove non-coordinated metal species from the catalysts. The leached sample was washed  
31 in water three times. Finally, the catalysts were collected by filtration and dried at 80°C.  
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1     **Synthesis procedure of FeCo-MFR-2**

2     A procedure to synthesise FeCo-MFR-2 was the same with that for FeCo-MFR-1 except for a pH  
3     value during the polymerization (pH 3 to 4); previous studies have used similar pH values for  
4     polymerization.

5  
6     **Synthesis procedure of FeCo-Melamine (not solidified)**

7     For synthesizing a FeCo-melamine catalysts, 6.45 g of melamine, 3.36 g  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and 1.12g  
8      $\text{Co}(\text{acetate})_2 \cdot 4\text{H}_2\text{O}$  are dissolved in 200 ml of distilled water under  $80^\circ\text{C}$ . The mixed solution was  
9     vacuum-dried using a rotary evaporator. The powder sample was grinded to powder, and it was put  
10    into a tubular furnace to be pyrolyzed at  $700^\circ\text{C}$ , similar to heat treatment of FeCo-MFR catalyst. The  
11    products were leached in concentrated HCl solution to remove unbound metal species from the  
12    catalysts. The leached sample was washed in water three times and dried at  $80^\circ\text{C}$ .

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14    **Preparation of the FeCo-PANI catalyst**

15    The FeCo-PANI catalyst was prepared according to ref. 20. Carbon supports (Ketjenblack EC 300J,  
16    Mistubishi Chemical) were pretreated in  $\text{HNO}_3$  solution for 24 hours. Aniline (2.0 ml) and 0.4 g of  
17    the acid-treated carbon support was added into a 0.5 M HCl solution. The suspension was kept  
18    below  $10^\circ\text{C}$ , and APS and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{Co}(\text{acetate})_2 \cdot 4\text{H}_2\text{O}$  were added. After polymerizing  
19    PANI for 24 h, the suspension was vacuum-dried using a rotary evaporator. The subsequent  
20    heat-treatment was performed at  $700^\circ\text{C}$  in ammonia gas for 1.5 h. The heat-treated sample was  
21    leached in HCl for 8 h to remove unbound metal species from the catalyst, washed in water and  
22    dried at  $80^\circ\text{C}$ .

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24    **Price evaluation for the FeCo- MFR catalyst**

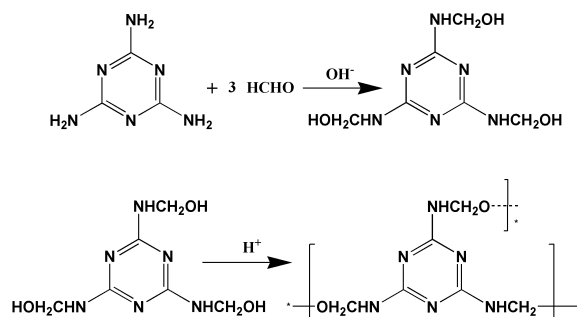
25    Prices (per gram) for melamine, sodium hydroxide,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Co}(\text{acetate})_2 \cdot 4\text{H}_2\text{O}$  (reagent  
26    grade; Wako Pure Chemicals, Japan) and carbon particles are \$0.08, \$0.03, \$0.17, \$0.17, and \$0.02,  
27    respectively, and those (per milliliter) for formaldehyde and concentrated hydrochloride solutions  
28    are \$0.02 and \$0.02, respectively. On the the hand, based on these prices and the yield (30%), a cost  
29    (per gram) for FeCo-MFR was estimated to be approximately \$6.6. The conventional Pt/C is  
30    prepared from dihydrogen hexachloroplatinate hexahydrate and carbon supports. The price of  
31    dihydrogen hexachloroplatinate hexahydrate with a Pt content of 37.5% is \$154/g (Wako Pure  
32    Chemicals), and the cost for 1 g Pt/C (20 wt%) containing 0.2 g of Pt is therefore approx. \$82.

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34    **Pt/C catalyst**

35    Pt/C (20% Pt [w/w]) was bought from the fuel cell company (Tanaka Kikinzoku).

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1 Figure S1

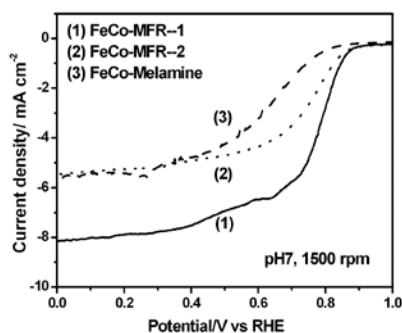


10 Figure S1 The schematic diagram of the synthesized process of melamine-formaldehyde resin.

11 **Note:** Figure S1 shows the schematic diagram for the MFR polymer synthesis. Crucial step for our  
12 synthesis is the MFR network formation catalyzed by acid and heat solidification. In previous reports,  
13 MFR syntheses were always performed in pH 3 to 4 solution without further solidification treatment,  
14 resulting in weak polymer backbones. In such cases, nitrogen atoms in precursors may easily be  
15 escaped from carbon matrix during the pyrolysis, resulting in loss of active sites comprised of metals  
16 and nitrogen atoms. Here, the pH value was quickly adjusted to 2.0, and the hybrid resin was further  
17 cross-linked and solidified at 150°C to form the rigid polymer with branched networks. After the  
18 heat-treatment, FeCo-MFR maintains a high content of nitrogen and a complex porous structure.

19

20 Figure S2



29 Figure S2 Effects of polymerization and solidification procedures. Steady-state polarization  
30 curves for ORR of the (1) FeCo-MFR-1 (2) FeCo-MFR-2 and (2) FeCo-Melamine catalysts at a  
31 rotation rate of 1500 rpm in a pH 7 solution. (catalysts loaded at 1 mg cm<sup>-2</sup>)

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1 Table S1

	C	N	O	Fe	Co
2 FeCo-melamine	97.2%	1.7%	0.6%	0.3%	0.2%
3 FeCo-MFR-1	81.9%	7.7%	3.9%	2.6%	3.9%
4 FeCo-MFR-2	88.2%	5.3%	4.3%	1.0%	0.6%

5  
6 **Table S1** The comparison of surface elemental contents for FeCo-melamine and FeCo-MFR  
7 catalyst analyzed from XPS

8 **Note:** We compared ORR activities of FeCo-melamine and FeCo-MFR catalysts with (1) and  
9 without (2) the solidification treatment. Fig. S2 shows polarization curves for ORR in the RRDE  
10 experiments. The figure shows that, compared to FeCo-MFR-2 and FeCo-melamine, FeCo-MFR-1  
11 shows a high ORR half-wave potential and diffusion current. Table S1 summarizes the surface  
12 element contents of the three catalysts. It is shown that the surface nitrogen/metal contents in  
13 FeCo-MFR-1 were substantially higher than those in FeCo-melamine and the FeCo-MFR-2. These  
14 results suggest that the formation of rigid polymer precursor in FeCo-MFR-1 reduces losses of  
15 nitrogen and metals during the pyrolysis, resulting in the high ORR activity.

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19 Figure S3

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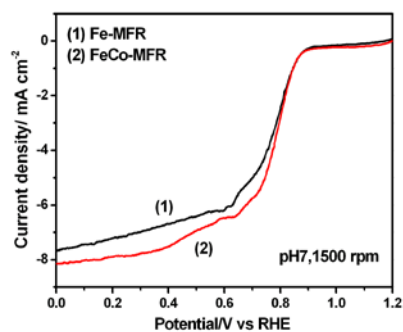
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28 Figure S3 Effects of coordinated metals. Steady-state polarization curves for ORR of (1) Fe-MFR  
29 and (2) FeCo-MFR catalysts at a rotation rate of 1500 rpm in the PBS (pH 7) solution. (catalysts  
30 loaded at 1 mg cm<sup>-2</sup>). Co-MFR showed a similar curve to that of Fe-MFR.

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1 Figure S4

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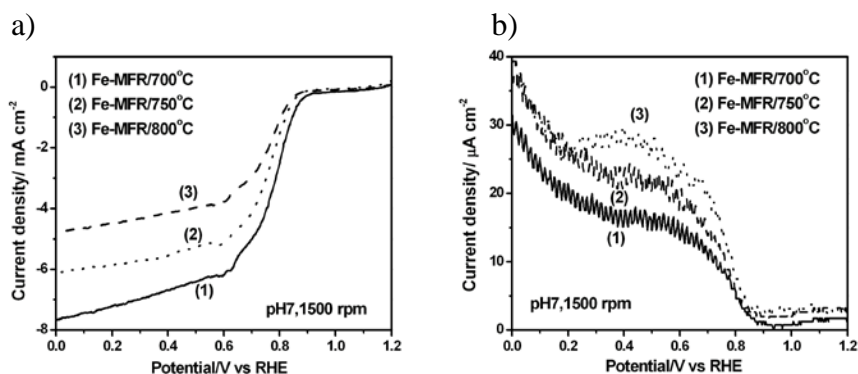
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10 Figure S4 Effects of pyrolysis temperature. (a) Steady-state polarization curves for ORR of Fe-MFR  
11 catalysts pyrolyzed at (1) 700°C, (2) 750°C and (3) 800°C at a rotation rate of 1500 rpm in the PBS  
12 solution (pH 7). (b) Corresponding hydrogen peroxide-dependent currents from the Pt ring electrode  
13 in the RRDE system. (catalysts loaded at 1 mg cm<sup>-2</sup>). Fe-MFR pyrolyzed below 650°C performed  
14 much worse than those at 700°C in terms of their low conductivity.

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16 Table S2

17

Temp.	C	N	O	Fe	Cl
Fe-MFR-700 °C	81.2%	5.6 %	8.9%	3.8%	0.5%
Fe-MFR-750 °C	88.7%	3.5%	5.7%	1.8%	0.3%
Fe-MFR-800 °C	91.5%	1.3%	5.2%	1.6%	0.4%

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21 **Table S2** Surface elemental contents in Fe-MFR catalyst pyrolyzed at different temperatures as  
22 analyzed by XPS.

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24 Figure S5

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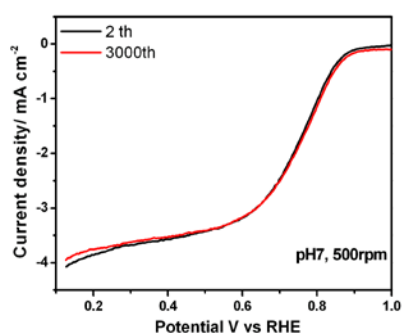
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33 Figure S5 RRDE Stability test of the FeCo-MFR catalyst. (catalyst loading, 0.5 mg cm<sup>-2</sup>; electrolyte,  
34 oxygen-saturated PBS solution (pH7); scan rate of 5 mV s<sup>-1</sup>; rotation speed, 500 rpm).

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1 Figure S6

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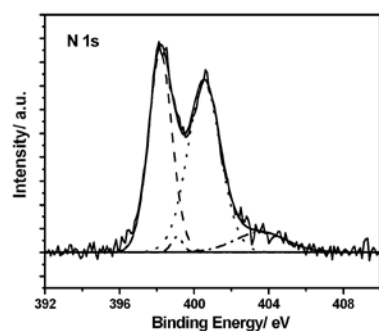
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11 Figure S6 Deconvoluted XPS N 1s spectra of FeCo-PANI.

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13 Figure S7

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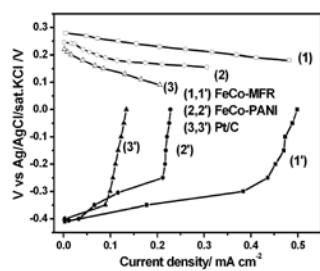
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21 Figure S7 Anode and cathode potentials of MFCs (equipped with the FeCo-MFR, FeCo-PANI and  
22 Pt/C cathodes) as a function of current density. Either of these catalysts was loaded at  $4 \text{ mg cm}^{-2}$ .

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