Supporting Online Material

Efficient Oxygen Reduction by a Fe/Co/C/N Nano-Porous Catalyst in Neutral Media

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Experimental section

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

A schematic diagram for the MFR synthesis is shown in Fig. S1. In the initial step, 6.45 g of melamine, 12 ml formaldehyde (37%) and 1g sodium hydroxide are dissolved in 200 ml of distilled water under 80°C. The mixture was agitated for four hours for the hydroxylation reaction, and then 1 g carbon particle (Ketjenblack EC 300J, Mitsubishi Chemical) was ultrasonically dispersed into the above solution using an ultrasonic probe. Next 3.36 g Fe(NO₃)·9H₂O and 1.12g Co(acetate)₂·4H₂O were dissolved into 20 ml hydrochloric acid (HCl) solution (pH 1). The mixed salt/acid solution was added into the melamine/formaldehyde solution, and the pH value was quickly tuned to 2 using a HCl solution (5M) for polymerization. After polymerization for 3 hours, the polymer gel paste was put into the furnace at 150°C for 5 hours for cross-linking the melamine-formaldehyde resin (solidification).

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

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

Synthesis procedure of FeCo-Melamine (not solidified)

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

Preparation of the FeCo-PANI catalyst

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

Price evaluation for the FeCo-MFR catalyst

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

Pt/C catalyst

Pt/C (20% Pt [w/w]) was bought from the fuel cell company (Tanaka Kikinzoku).
Figure S1

![Schematic Diagram of the Synthesized Process of Melamine-Formaldehyde Resin](image)

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

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

Figure S2

![Steady-state Polarization Curves](image)

**Figure S2** Effects of polymerization and solidification procedures. Steady-state polarization curves for ORR of the (1) FeCo-MFR-1, (2) FeCo-MFR-2, and (3) FeCo-Melamine catalysts at a rotation rate of 1500 rpm in a pH 7 solution. (catalysts loaded at 1 mg cm$^{-2}$)
Table S1  The comparison of surface elemental contents for FeCo-melamine and FeCo-MFR catalyst analyzed from XPS

<table>
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<th>Fe</th>
<th>Co</th>
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<td>FeCo-melamine</td>
<td>97.2%</td>
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<td>FeCo-MFR-1</td>
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<td>FeCo-MFR-2</td>
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<td>5.3%</td>
<td>4.3%</td>
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<td>0.6%</td>
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</table>

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

Figure S3

Figure S3 Effects of coordinated metals. Steady-state polarization curves for ORR of (1) Fe-MFR and (2) FeCo-MFR catalysts at a rotation rate of 1500 rpm in the PBS (pH 7) solution. (catalysts loaded at 1 mg cm$^{-2}$). Co-MFR showed a similar curve to that of Fe-MFR.
Figure S4

(a) Steady-state polarization curves for ORR of Fe-MFR catalysts pyrolyzed at (1) 700°C, (2) 750°C and (3) 800°C at a rotation rate of 1500 rpm in the PBS solution (pH 7). (b) Corresponding hydrogen peroxide-dependent currents from the Pt ring electrode in the RRDE system. (catalyst loaded at 1 mg cm$^{-2}$). Fe-MFR pyrolyzed below 650°C performed much worse than those at 700°C in terms of their low conductivity.

Table S2

<table>
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<th>Temp.</th>
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<th>O</th>
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<td>Fe-MFR-700°C</td>
<td>81.2%</td>
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<tr>
<td>Fe-MFR-750°C</td>
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<td>0.3%</td>
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<td>Fe-MFR-800°C</td>
<td>91.5%</td>
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Table S2 Surface elemental contents in Fe-MFR catalyst pyrolyzed at different temperatures as analyzed by XPS.

Figure S5

RRDE Stability test of the FeCo-MFR catalyst. (catalyst loading, 0.5 mg cm$^{-2}$; electrolyte, oxygen-saturated PBS solution (pH7); scan rate of 5 mV s$^{-1}$; rotation speed, 500 rpm).
Figure S6 Deconvoluted XPS N 1s spectra of FeCo-PANI.

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