# Supporting Information for

# Self-Supporting Oxygen Reduction Electrocatalysts Made from a Nitrogen-Rich Network Polymer

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This file includes:

Experimental section Tables S1 to S4 Figures S1 to S16 References.

# **1. Experimental Section**

### **Preparation of the M-PDAP Catalysts**

A schematic diagram for the M-PDAP catalyst synthesis is shown in Fig. 1 and described in detail below. As the initial step, 5.45 g of DAP and 1 g of sodium hydroxide (APS) are dissolved in 400 ml of distilled water, followed by the addition of 17.1 g of APS and 100 ml of distilled water. The resultant mixture was agitated for several minutes, and the polymerization reaction was carried out without agitation at 10°C for 12 h. Black solids were collected by centrifugation, and rinsed with distilled water three times to obtained PDAP particles. They were vacuum-dried at 70°C.

To synthesize Co-PDAP catalysts, PDAP and cobalt (II) nitrate hexahydrate (CoNO<sub>3</sub>•6H<sub>2</sub>O) were mixed in a solution of ethanol and water to form a precursor composite. Typically, 5.45 g PDAP and 3.62 g CoNO<sub>3</sub>•6H<sub>2</sub>O were suspended in 150 ml of water/ethanol (1/1 v/v). After mixing them for 1 h in an ultrasonic probe system (Misonic) and agitating the solution for additional 2 h at 60°C, the solution was evaporated under vacuum at 60°C. The remaining dry powder was grinded using a quartz mortar. To synthesize CoFe-PDAP, a mixture of 3.36 g of Fe<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>•9H<sub>2</sub>O and 1.21 g of CoNO<sub>3</sub>•6H<sub>2</sub>O (mole ratio: 2:1) was used as metal salts.

M-PDAP powders were put into a tubular furnace (Koyo) and pyrolyzed in the presence of ammonia gas for 1 or 1.5 h. A quartz tube (5 cm in diameter and 120 cm in length) with a 80 cm heating zone and a heat controller were used for pyrolysis under a temperature program (0-200°C, 1 h; 200°C, 1 h, 200-700°C, 0.75 h; 700°C, 1.5 h; 700-0°C, 2 h). Heat-treated products were ultrasonicly leached in concentrated hydrochloride (HCl) acid for 8 h to remove unstable and inactive metal species from the catalysts. The leached sample was washed in water three times. Finally, the catalysts were collected by filtration and dried at 60°C. (Note: All the M-PDAP catalysts were pyrolyzed in the presence of ammonia, while the ammonia-untreated Co-PDAP catalyst was analyzed only in Figure S2.)

# Preparation of the Co-TMPP/C catalytst

Co-TMPP/C was prepared according to ref. 1. Carbon black Vulcan XC-72R (BET surface area of 240 m<sup>2</sup> g<sup>-1</sup>) was a gift from the Cabot Corporation. It was firstly treated by sonication in a concentrated HNO<sub>3</sub> solution (6 M) for 1 h and further treated at 100°C for 6 h. The suspension was centrifuged at 3000 rpm, and a pellet was washed with deionized water three times, followed by drying under vacuum. The carbon particles (0.9 g) and tetramethoxyphenyl porphyrin cobalt (II) (Co-TMPP) (0.1 g) were dispersed in 200 ml acetone and refluxed at 60°C for 12 h, followed by drying under vacuum. The hybrid powder of Co-TMPP/C was grinded and pyrolyzed in the ammonia atmosphere at 700°C or 750°C for 1.5 h. The post-treatment of Co-TMPP/C was the same as that for the Co-PDAP catalyst.

#### **Preparation of the Co-PPY/C catalyst**

The Co-PPY/C catalyst was prepared according to ref. 2.  $HNO_3$ -treated Vulcan XC-72R was ultrasonically dispersed in 100 ml of acetone, and the suspension was added with 3 mmol of freshly distilled pyrrole and 100 ml of double distilled water. After the resulting mixture was stirred for 30 min, 100 ml of 60 mM APS solution and 0.19 g of 4-toluenesulfinic acid (TsOH) were added, and the mixture was stirred at room temperature for 4 h. The mixture was filtrated, washed 3 times with double distilled water and dried at 60°C under vacuum for 2 h. The resultant powder (PPY/C) was grinded with a quartz mortar and mixed with 0.25 g of

 $Co(CH_3COO)_2 \cdot 4H_2O$  in 200 ml of distilled water. After ultra-sonication for 1 h and vigorous stirring at 80°C for 2 h, the solvent is evaporated under vacuum. The remaining powders are pyrolyzed in an ammonia atmosphere at 700°C or 800°C for 1.5 h. The heat-treated sample is pre-leached ultrasonicly in HCl solution for 8 hours, and then washed in de-ionized water. The Co-PPY/C sample was finally dried at 60°C.

# **Preparation of the Co-PANI/C catalysts**

The Co-PANI/C catalyst was prepared according to ref. 3. Carbon supports (Ketjenblack EC 300J, Mistubishi Chemical) were pretreated in HNO<sub>3</sub> 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  $Co(NO_3)_2 \cdot 6H_2O$  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 12 h to remove unbound metal species from the catalyst, washed in water and dried at 80°C.

# Pt/C catalyst

Pt/C (20% Pt [w/w]) was purchased from the fuel cell company (TEC10E20A, Tanaka kikinzuko Kogyo).

# **Physical characterization**

Scanning electron microscopy (SEM) was performed using a JSM-6700 machine (JEOL). Distribution of elements in a catalyst was characterized using SEM-EDX (JOEL). A Brunauer-Emmett-Teller (BET) surface area and pore distribution in a catalyst were analyzed using a Micromeritics Tristar 3000 machine (Shimadzu). X-ray photoelectron spectroscopy (XPS) of a catalyst was performed to determine an elemental composition at surface, in which a Kratos Ultra AXIS Spectrometer system equipped with a monochromatic Al-K $\alpha$  source was operated at 15 kV. A sample was palletized and placed on a stainless steel disk for the analysis. Five sweeps are carried out for each element concurrently, with C 1s, N 1s, Co 2p, Fe 2p and O 1s regions being scanned.

#### Rotating ring disk-electrode (RRDE) assay

An oxygen reduction reaction (ORR) activity and four-electron selectivity of a catalyst were investigated using a bipotentiostat (Pine Instrument) equipped with a rotating ring-disk electrode (RRDE). Glassy carbon disk (0.198 cm<sup>-2</sup>) and Pt ring electrodes were used as working and counter electrodes, respectively. A saturated calomel electrode (SCE, 0.244 V+0.0591\*pH vs. reversible hydrogen electrode [RHE] at 25°C) was used as a reference electrode. The disk electrode was uniformly covered with a catalyst ink (a mixture of 2 mg of a catalyst, 20  $\mu$ l of a nafion® solution [5 wt%, DuPont] and 1 ml of ethanol). RRDE polarization performance was measured in an oxygen-saturated K<sub>2</sub>H<sub>2</sub>PO<sub>4</sub>/KH<sub>2</sub>PO<sub>4</sub> solution (PBS, pH 7) at 25 °C and a scan rate of 5 mV s<sup>-1</sup>. The Pt ring electrode was poised at 0.6 V vs SCE. The rotation speed of RRDE was set at 1500 rpm using a speed controller (Pine Instrument Co.). The RDE tests were done similarly to the RRDE tests, while the ring electrode was not used. Before RRDE and RDE experiments, the Pt ring was activated by potential cycling between 0.1 and 1.4 V for several minutes in a 0.05 M H<sub>2</sub>SO<sub>4</sub> solution.

#### Calculation of an electron-transfer number

A number of electrons (*n*) transferred to oxygen during ORR was calculated according to the following equations:  $n = 4i_D/(i_D+i_R/N)$ , where  $i_D$  is a Faradic current at the disk,  $i_R$  is a Faradic current at the ring, and *N* is a collection efficiency (0.19) as determined by the dimension of the electrode (ref. 4). The collection efficiency was also checked using 5 mM ferricyanide in 0.1 M KCl solution, which was close to the manufacture's value. The potential was scanned from 0.8 to -0.3 V vs. SCE at pH 1.

# Stability test

The stability of the CoFe-PDAP catalyst was evaluated by continuously measuring its ORR activity in cyclic voltammogram (CV) and rotating disk electrode (RDE) tests. CV was carried out in a three-electrode electrochemical reactor connected to a potentiostat (HV100, Hokuto Denko). A Co-PDAP loaded carbon plate (0.5 mg cm<sup>-2</sup>), a platinum wire and an Ag/AgCl/sat.KCl electrode (0.197 V+0.0591\*pH vs. RHE at 25°C) were used as working, counter and reference electrodes, respectively. Pure nitrogen or oxygen gas was bubbled in the electrochemical reactor at a rate of 30 ml min<sup>-1</sup>. The scan rate of CVs was 5 mV s<sup>-1</sup>. The RDE stability test was performed in an O<sub>2</sub>-saturated H<sub>2</sub>SO<sub>4</sub> solution (pH2) at a rotation speed of 500 rpm and a scan rate of 5 mV s<sup>-1</sup>.

# MFC

CoFe-PDAP was used as a cathode catalyst in a single-chamber MFC equipped with a graphite-felt anode and a cathode membrane (called air cathode) as reported previously (ref. 5). An air cathode had four layers of polytetrafluoroethylene at the outer surface of a base carbon paper, while a cathode catalyst was loaded at the inner surface at a density of 4 mg (total weight) cm<sup>-2</sup> using nafion as a binder. Geometric sizes of anode and cathode were 4 cm<sup>2</sup> and 1 cm<sup>2</sup>, respectively. Rice paddy-field soil was used as a source of microbes, while a mixture of starch, peptone, and fish extract was used as the fuel. An MFC with a Pt/C cathode catalyst was also operated as a reference, and their performances were compared by measuring polarization and power curves as described elsewhere (ref. 6). In order to prevent the anode and cathode from short-circuiting, a separator (paper towel) was inserted between them. The anode and cathode were connected via an external circuit and a resister (10 k $\Omega$ ). The anode solution was gently agitated at 50 rpm.

# 2. Effects of pyrolysis temperature

In order to determine an optimum pyrolysis temperature, polarization curves of ORR under neutral conditions (in PBS, pH 7) were drawn for Co-PDAP catalysts pyrolyzed at different temperatures (Figure S1). This figure shows that Co-PDAP prepared at 700°C exhibited the highest activity for ORR with onset potentials of 0.82 V (vs RHE). For a nitrogen-containing catalyst, a low pyrolysis temperature is preferable, since incubation at a high temperature may release nitrogen atoms from carbon backbones. On the other hand, for an electrode catalyst, a high pyrolysis temperature is preferable, since it can increase electric conductivity of a carbon material. In case of a conductive polymer as a starting material of an electrode catalyst, however, a relatively low temperature is also possible for its intrinsic conductivity. This should be a reason why the electrode catalysts can be synthesized from PDAP and PANI at a relatively low pyrolysis temperature (700°C) compared to those (750°C and 800°C) for Co-PPY/C and Co-TMPP/C (see below). As shown in Table S1, the XPS analysis indicated

that nitrogen and cobalt atoms were gradually lost according to the increase in pyrolysis temperature. Accordingly, the Co-PDAP catalyst prepared at 700°C exhibited the best ORR activity.

Figure S1



Figure S1. a) Polarization curves of Co-PDAP catalysts in RDE tests (rotating speed, 1500 rpm, pH7, catalyst: 1 mg/cm<sup>-2</sup>), showing influences of pyrolysis temperature on its ORR activity. b) A SEM image of Co-PDAP catalyst pyrolyzed at  $700^{\circ}$ C.

Table S1. Elemental compositions of Co-PDAP samples pyrolyzed at different temperatures. Variations in these values in repeated experiments were less than 5%.

Temp.	C mol%	N mol%	O mol%	Co mol%	
600 °C	71.74	19.45	4.99	3.81	
700 °C	88.07	10.30	0.99	0.64	
750 °C	91.4	6.73	1.37	0.5	
800 °C	95.53	3.36	0.73	0.41	
900 °C	96.63	2.67	0.41	0.29	

#### **3.** Effects of ammonia treatment

Effects of ammonia treatment during the pyrolysis process on the BET surface area and ORR activity were also studied (Figure S2). It was found that the ammonia treatment was beneficial for the catalyst; the BET surface area of ammonia-treated Co-PDAP was much larger than that without ammonia treatment (299 m<sup>2</sup> g<sup>-1</sup> vs. 568 m<sup>2</sup> g<sup>-1</sup>). This is likely because carbon atoms can effectively be etched by ammonia gas during the pyrolysis process, resulting in the formation of a large amount of mesopores in catalysts, as has already been reported by another group (ref. 7). The RDE test showed that, although the onset potential was not changed, the limiting current density was improved, reaching close to 6 mA cm<sup>-1</sup>.



Figure S2. BET surface-area (a) and ORR-activity (b) analyses of Co-PDAP with and without ammonia treatment (catalyst: 1 mg/cm<sup>-2</sup>).

#### 4. Comparison in ORR activities of the four Co-coordinating catalysts

ORR activities of Co-PDAP, Co-PPY/C, Co-PANI/C, and Co-TMPP/C were evaluated by the RRDE tests, and results are shown in Fig. S3. In addition, numbers of electrons transferred to oxygen in the RRDE tests were calculated (Table S2). As shown in Fig. S3, the highest activities were obtained with Co-PDAP catalyst. Electron transfer numbers (*n*) of Co-PDAP were 3.96, indicating that the product of ORR was mostly water.



Figure S3. Comparisons in polarization curves of four Co-coordinating catalysts (1, Co-PPY/C; 2, Co-PANI/C; 3, Co-TMPP/C; 4, Co-PDAP) pyrolyzed at temperatures reported in the respective reference papers (a and b) and all pyrolyzed at 700°C in the presence ammonia gas, analyzed by the RRDE test at pH 7 (a and c, disk currents; b and d, ring currents). Catalysts were loaded at  $1 \text{ mg/cm}^{-2}$ .

Table S2. Calculated electron transfer numbers for the four Co-coordinating catalysts as analyzed by the RRDE experiments (at 0.6V vs RHE).

	Co-PPY/C	Co-PANI/C	Co-TMPP/C	Co-PDAP
n (at 0.6 V) /pH7	2.91	3.02	3.65	3.96

#### 5. Surface physical properties of the four Co-coordinating catalysts

BET surface areas of the catalysts were determined by the low-temperature nitrogen absorption method. The BET surface area of Co-PDAP catalyst estimated from the data in Fig. S4 was 568 m<sup>2</sup> g<sup>-1</sup>, that was substantially larger than those of the other catalysts (Co-TMPP/C, 150 m<sup>2</sup> g<sup>-1</sup>; Co-PANI/C, 317 m<sup>2</sup> g<sup>-1</sup>; Co-PPY/C, 196 m<sup>2</sup> g<sup>-1</sup>).

Figure S4



Figure S4. BET surface areas of the four Co-coordinating catalysts.

#### 6. Surface elemental contents of the four Co-coordinating catalysts

XPS analyses were carried out to estimate surface elemental compositions of the four Co-coordinating catalysts (Co-PDAP, Co-TMPP/C, Co-PPY/C, and Co-PANI/C). Fig. S5 presents N 1s and Co  $2p^{3/2}$  spectra of the four catalysts, showing that Co-PDAP exhibited the highest peaks of N 1s and Co  $2p^{3/2}$  in the XPS spectra. Based on the N 1s spectra, the majority (approx. 90%) of nitrogen units in the Co-PDAP catalyst is attributed to pyridinic-N and quaternary-N, whose peaks are centered at 398.3 and 400.5 eV, respectively. In the Co  $2p^{3/2}$  spectrum of Co-PDAP, a clear peak is seen around 780 eV, indicating that Co is mostly coordinated to nitrogen (ref. 7). Table S3 summarizes the surface elemental compositions of the four Co-coordinating catalysts estimated from the XPS spectra. This table shows that the surface N and Co contents of Co-PDAP (10.30 mol.% and 0.64 mol.%, respectively) are much higher than those of the other catalysts.



Figure S5. XPS spectra of N 1s (a) and Co  $2p^{3/2}$  (b) for the four Co-coordinating catalysts.

Table S3. Surface elemental compositions in the four Co-coordinating catalysts.

	C (mol%)	N (mol%)	Co (mol%)	O (mol%)	
Co-PPY/C	93.27	5.39	0.21	0.63	
Co-PANI/C	91.17	3.14	0.35	5.34	
Co-MTTP/C	98.31	1.08	0.24	0.36	
Co-PDAP	88.07	10.30	0.64	0.99	

# 7. Influences of coordinated metals on the ORR activity of M-PDAP

Since iron impregnated  $CN_x$  has been reported to exhibit high ORR activities (ref. 8), we compared ORR activities of iron-, cobalt- and iron/cobalt-coordinating PDAP catalysts (Fig. S6). This figure shows that CoFe-PDAP performed the best among them. Nitrogen adsorption/desorption isotherms of CoFe-PDAP and Pt/C catalysts are shown in Fig. S7, while elemental composition of CoFe-PDAP was analyzed by XPS (Figure S8).



Figure S6. RDE polarization curves for (1) Co-PDAP, (2) Fe-PDAP, (3) CoFe-PDAP and (4) PDAP at pH7. (loaded catalyst: 1 mg cm<sup>-2</sup>) It is presented that the ORR activity of pyrolysed pure PDAP can be largely improved after introducing the cobalt and/or iron. The differences of ORR onset potential and half-wave potential should be due to the introduction of new active centers in the catalysts.

Table S4 Surface elemental compositions of Co-PDAP, Fe-PDAP, CoFe-PDAP and PDAP materials.

1	C (mol%)	N	0	Co	Fe
	(1101%)	(mol%)	(mol%)	(mol%)	(mol%)
Co-PDAP	88.1	10.3	1.0	0.6	0
Fe-PDAP	88.4	9.9	0.7	0	1.0
CoFe-PDAP	88.7	9.5	0.6	0.3	0.9
PDAP	88.0	10.2	1.8	0	0

Figure S7



Figure S7. Tafel plot derived from RRDE polarization curves of Figure 2.

Figure S8



Figure S8. RRDE polarization curve (disk currents) of CoFe-PDAP and Pt/C (20% Pt) loaded on disks at 0.5 mg (total weight) cm<sup>-1</sup> in a H<sub>2</sub>SO<sub>4</sub> solution (pH 2).



Figure S9. EDS-SEM elemental mapping (C, N, Co, Fe) of CoFe-PDAP catalyst.

Figure S10



Figure S10. a) Nitrogen adsorption/desorption isotherms of CoFe-PDAP and Pt/C catalysts and b) pore distribution in CoFe-PDAP catalyst.





Figure S11. XPS analysis of N 1s (a), Fe  $2p^{3/2}$  (b) and Co  $2p^{3/2}$  (c) for the CoFe-PDAP catalyst. N1, pyridinic-N; N2, quaternary-N; N3, quaternary-N<sup>+</sup>-O<sup>-</sup>; N4, pyrrolic-N.

#### 8. Stability of the CoFe-PDAP catalyst in CV and RRDE tests

Stability of CoFe-PDAP in acidic solutions was tested by continuously measuring its ORR activities in CV and RRDE experiments. As shown in Figure S9, CoFe-PDAP was stable, and no decrease in the ORR activity was detected during these experiments. Before and after the CV stability test, XPS was performed to check changes in elemental composition (Figure S10). In this analysis, no changes in surface elemental composition were detected.





Figure S12. Stability of the CoFe-PDAP catalyst. a), CVs drawn in the electrochemical reactor with nitrogen or oxygen bubbled at 30 ml min<sup>-1</sup> (a catalyst loaded at 1 mg cm<sup>-2</sup>; electrolyte, a  $H_2SO_4$  solution at pH 2; a scan rate, 5 mV s<sup>-1</sup>). b) a RRDE test (a catalyst loaded 1 mg cm<sup>-2</sup>; electrolyte, an oxygen-saturated  $H_2SO_4$  solution at pH 2; a scan rate, 5 mV s<sup>-1</sup>). b) a rate, 5 mV s<sup>-1</sup>; a rotation speed, 500 rpm).



Figure S13. XPS spectra (a, full spectra; b, N 1s; c, Fe 2p; d, Co 2p) for the CoFe-PDAP catalyst before (black line) and after (red line) the CV stability test.

#### 9. Crossover effects of methanol on ORR activities of CoFe-PDAP and Pt/C

Pt-based ORR catalysts are known to suffer from crossover effects of organics (ref. 9). We performed RRDE polarization analyses of the CoFe-PDAP and Pt/C catalysts in the presence and absence of methanol to evaluate organics crossover effects (Figure S14). As shown in this graph, the ORR catalytic current was largely affected by methanol, and anodic (methanol oxidation) current was larger than ORR current above 0.6 V (vs. RHE). On the contrary, no effect of methanol was observed for CoFe-PDAP, indicating that CoFe-PDAP is superior to Pt in ORR in the presence of organics.



Figure S14. Polarization curves in the RRDE tests for CoFe-PDAP (1, 2) and Pt/C (3, 4) in oxygen-saturated PBS (pH7), in the absence (1, 3) and presence (2, 4) of 1M methanol (rotation speed, 1500rpm). Curve 2 totally overlaps with curve 1.

Figure S15



Figure S15. Anode and cathode polarization curves for MFCs equipped with the Pt/C or CoFe-PDAP cathode. Either of these catalysts was loaded at 4 mg cm<sup>-2</sup>.

#### 10. Power-output stabilities of MFCs equipped with the Pt/C and CoFe-PDAP catalysts

The performance of the CoFe-PDAP-cathode MFC as assessed by  $P_{\text{max}}$  (ref. 6) was stable during the one-month continuous operation, while that of the Pt/C-cathode MFC was gradually decreased (Figure S16).

Figure S16



Figure S16. Stabilities of MFCs with either of the two cathode catalysts; (1) Pt/C, (2) CoFe-PDAP.

#### **11. References**

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