

Retraction for *Chemical Communications*:

Pt-free cathode catalysts prepared *via* multi-step pyrolysis of Fe phthalocyanine and phenolic resin for fuel cells

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We, the named authors, hereby wholly retract this *Chemical Communications* article, due to the fact that we have discovered that data relating to figure 2 and figure 3 presented in the communication were fabricated.

Signed: Libin Wu, Yuta Nabae, Shogo Moriya, Katsuyuki Matsubayashi, Nazrul M. Islam, Shigeki Kuroki, Masa-aki Kakimoto, Jun-ichi Ozaki and Seizo Miyata, Tokyo Institute of Technology, Japan, 17 April 2013

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Pt-free cathode catalysts prepared *via* multi-step pyrolysis of Fe phthalocyanine and phenolic resin for fuel cells†

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Pt-free cathode catalysts for polymer electrolyte membrane fuel cells have been prepared by multi-step pyrolysis of FePc and PhRs, in the best of which show extensively high initial cell performance and good durability compared to other present precious-metal-free cathode catalysts to date.

Polymer electrolyte membrane fuel cells (PEMFCs) have received a great deal of attention in terms of applications in transportation, portable devices and combined heat and power systems based on their high energy conversion efficiency and scalability. One major problem for PEMFCs in commercial applications is the cost and scarcity of platinum, which is used as the cathode catalyst. It is extremely important to develop precious-metal-free cathode catalysts.

Since Jasinski discovered the catalytic property of Co phthalocyanine¹ and Jahnke reported heat-treatment of Co TAA (Co dibenzotetraazaannulene),² numerous attempts have been made to develop precious-metal-free cathode catalysts by pyrolyzing precursors containing transition metals (mainly Fe or Co), a nitrogen source and a carbon source.^{3–13} The nature of the catalytically active site of these materials has remained obscure. One convincing model for the active sites is the catalytic center based on metal–N coordination. Fe cations coordinated to two or four pyridinic nitrogens incorporated into graphene sheets are considered to be catalytically active for oxygen reduction reaction (ORR).³ Another group of models for the active sites claim that nitrogen-doped carbon materials themselves are catalytically active.^{13–16} ORR active catalysts prepared without any transition metals have also been reported.^{17,18} While some of these precious-metal-free cathode catalysts show quite promising fuel cell performances,^{8,9,12} the durability needs to be much improved if they are to be considered for commercial applications.¹⁹ Increasing the pyrolysis temperature to around 1000 °C is a reasonable approach to improve the durability of carbon based materials, but treatments at such high temperatures generally result in deactivation of the catalysts, which is due to the decomposition of the active sites.²¹

Our research group has been developing nitrogen-containing carbon materials that are electrocatalytically active.²⁰ Our carbon catalyst materials are prepared by pyrolyzing mixtures of polymers and metal complexes, rather than metal complexes loaded onto a carbon support surface. This approach could result in high density of active sites and high durability of the resulting catalysts, since the chemical structure of the active sites can be produced both in the bulk and on the surface of the carbon. One of the most active ORR catalysts in our research group is prepared by pyrolyzing a mixture of Fe phthalocyanine and phenolic resin.²¹ No matter whether the actual catalytically active sites for ORR contain Fe species or not, we assume that edge-plane exposure and sufficient nitrogen content are essential to obtain highly active carbon-based ORR catalysts, and that Fe species are important (a) to increase the nitrogen content of the resulting carbon due to Fe–nitrile coordination, and (b) to increase the edge-plane exposure of the resulting carbon due to catalysis by Fe nano-particles.²¹ If the temperature for the single step pyrolysis is too high in the presence of Fe species, the nitrogen content of the resulting carbon largely decreases because Fe nano-particles enhance nitrogen elimination.

This study focuses on how the durability of carbon-based ORR catalysts can be improved without losing catalytically active sites. We hereby report a multi-step pyrolysis of Fe phthalocyanine (FePc) and phenolic resin (PhRs) to prepare highly active and highly stable ORR catalysts. The hypothesis is based on the conclusion of our previous work: Fe species are important at up to 600 °C to increase the catalytically active sites, but Fe nano-particles kill the active sites at over 700 °C.²¹ If one assumes that the chemical structure of the active sites has been formed at around 600 °C, post-treatment of the catalysts prepared at 600 °C could be effective to improve the stability after removing the Fe species that kill active sites.

Four different samples were studied in the present work. 600-I-N₂ was prepared by single step pyrolysis of FePc and PhRs at 600 °C under nitrogen atmosphere. The other three samples were prepared by post-treatment of 600-I-N₂. 800-II-N₂ and 800-II-NH₃ were prepared by pyrolyzing 600-I-N₂ at 800 °C under nitrogen and ammonia atmospheres, respectively. 1000-III-NH₃ was prepared by pyrolyzing 800-II-NH₃ at 1000 °C under an ammonia atmosphere. Acid washing was carried out after each pyrolysis step. Table 1 shows the results of elemental analysis and specific surface area of the four samples. 600-I-N₂ has the highest Fe content. Our previous work suggests that the majority of FePc has decomposed and formed Fe nano-particles by around 600 °C.²¹ The residual Fe in 600-I-N₂ is in the form of nano-particles

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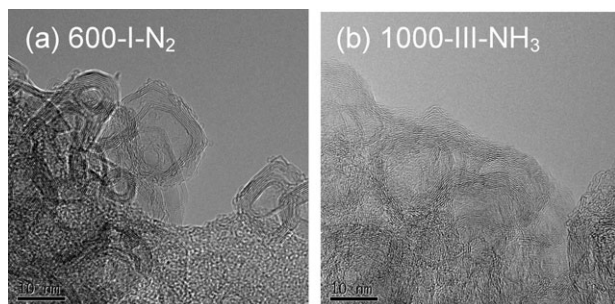
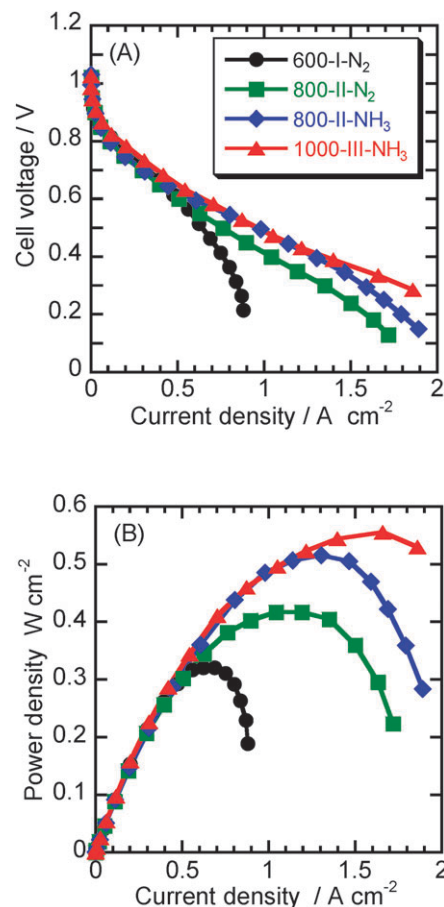
Table 1 Results of elemental analysis and N₂ gas adsorption

Sample name	Elemental analysis (wt%)			EPMA results Fe (wt%)	Specific surface area/m ² g ⁻¹	
	C	H	N		A _{BET}	A _{meso}
600-I-N ₂	84.0	2.0	3.0	2.18	384	86
800-II-N ₂	92.3	1.1	1.6	0.77	432	112
800-II-NH ₃	87.9	1.3	2.9	0.73	533	88
1000-III-NH ₃	95.8	0.9	0.9	0.59	849	392

fully encapsulated by carbon layers, and therefore inaccessible to acid washing. By treating 600-I-N₂ at higher temperature such as 800 °C, some of this Fe residue can be removed, as reflected in the lower Fe contents in 800-II-N₂ and 800-II-NH₃. This is because Fe nano-particles sinter at high temperature and the opportunity for Fe particles to become exposed to acid increases during the washing procedure. As for the nitrogen content, it tends to decrease as the final treatment temperature increases. Ammonia atmosphere is effective to retain higher nitrogen content, as 800-II-NH₃ contains more nitrogen than 800-II-N₂. Another effect of ammonia treatment is etching of the carbon materials.¹² The BET surface area (A_{BET}) and mesopore surface area (A_{meso}) of 800-II-NH₃ are higher than that of 800-II-N₂. The etching effect is more significant when an extra step of ammonia treatment is applied, as seen in 1000-III-NH₃, especially for A_{meso}, which is thought to be important for mass transport in catalyst layers of fuel cells.

Fig. 1 shows transmission electron microscopy (TEM) images for 600-I-N₂ and 1000-III-NH₃. A nanoshell-like structure is observed in both samples. This suggests that the morphology of the prepared carbon does not change drastically during the post-treatment of 600-I-N₂, probably because the Fe nano-particles have been largely removed. This type of nano-structure is probably relevant to the degree of edge exposure and meso-porosity of the carbon materials.²⁰

Electro-catalytic activity for ORR of these four samples has been investigated by fuel cell testing using a small scale single cell. Fig. 2 shows H₂-O₂ polarization curves at 0.2 MPa absolute pressure and 80 °C. Our carbon-based catalysts show good open-circuit voltages (OCV) of 1.01–1.03 V, and good current densities. The current densities measured at 0.5 V are 0.62, 0.76, 0.96 and 0.96 A cm⁻² for 600-I-N₂, 800-II-N₂, 800-II-NH₃ and 1000-III-NH₃, respectively. The maximum power output for 1000-III-NH₃ is 0.56 W cm⁻². It should be noted that the catalytic activity did not decrease after treatment at such high temperature. To our knowledge, this fuel cell performance is better than other state-of-art

**Fig. 1** TEM image of (a) 600-I-N₂ and (b) 1000-III-NH₃ catalysts.**Fig. 2** (A) *I*-*V* polarization curves and (B) power density curves with (●) 600-I-N₂, (green squares) 800-II-N₂, (blue diamonds) 800-II-NH₃ and (red triangles) 1000-III-NH₃ cathode catalysts. Cathode: the catalysts 4 mg cm⁻², O₂ 0.2 MPa. Anode: Pt/C catalyst 0.5 mg cm⁻², H₂ 0.2 MPa. Electrolyte: Nafion-115. *T*: 80 °C.

precious-metal-free cathode catalysts. For example, Lefèvre *et al.* recently reported a Fe-based catalyst with an initial current density at 0.5 V of approximately 0.8 A cm⁻² at equivalent temperature and higher absolute pressure, 0.3 MPa.¹² It is concluded that the combination of multi-step pyrolysis and multi-step acid treatment for FePc/PhRs results in significantly active ORR catalysts.

The difference in the current densities among these four catalysts is mainly observed at the higher current density region, where the mass transport effect is assumed to be the rate limiting process. In other words, the activation overpotentials for these four catalysts seem quite similar, indicating that high temperature treatment does not destroy the catalytically active sites if Fe species are removed at each stage of the

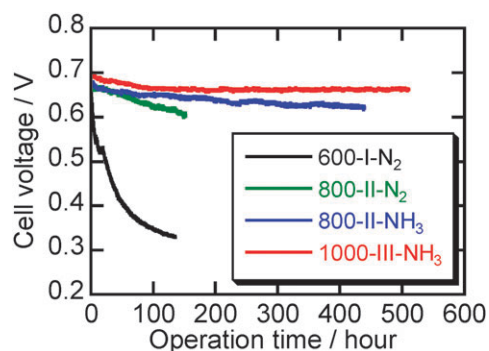


Fig. 3 Time courses for cell voltages measured at 0.1 A cm^{-2} with (black) 600-I-N₂, (green) 800-II-N₂, (blue) 800-II-NH₃ and (red) 1000-III-NH₃ cathode catalysts. Cathode: Air 0.1 MPa. Anode: H₂ 0.1 MPa. *T*: 80 °C.

preparation protocol. Higher current densities from ammonia-treated catalysts presumably derive from the porosity of the catalyst, which is improved by ammonia etching. This effect is most significant for 1000-III-NH₃, which shows quite high mesopore surface area.

The durability of these cathode catalysts was investigated by operating the fuel cells at 0.1 A cm^{-2} current density, in flowing atmospheric pressure H₂ and air at 80 °C, as shown in Fig. 3. For all cells, potential drops at the initial stage were observed. After this initial potential drop, the degradation properties significantly depend on the cathode catalyst. 600-I-N₂ shows poor durability. The current density of this catalyst decreased drastically within 100 hours. It can be concluded that single-step pyrolysis at intermediate temperature can provide catalytically active species but any practical durability cannot be expected. The durability of 800-II-N₂ and 800-II-NH₃ is much better than that of 600-I-N₂. Furthermore, 1000-III-NH₃ shows excellent durability. The cell voltage remains steady for hundreds of hours. The durability of these catalysts depends on the operation current. If the cells are operated at 0.4 A cm^{-2} , the cell voltages degrade more quickly (see Fig. S1, ESI[†]). However, the catalysts prepared *via* multi-step pyrolysis (800-II-N₂, 800-II-NH₃ and 1000-III-NH₃) are still much more durable than 600-I-N₂. The high durability resulting from multi-step pyrolysis probably derives from a higher degree of graphitization due to treating the samples at high temperature.

It is concluded that our new catalyst, 1000-III-NH₃, shows excellent catalytic activity and durability in real fuel cell conditions. The maximum output in this study (0.56 W cm^{-2} at 80 °C and 0.2 MPa, H₂-O₂ gas) is better than other state-of-art precious-metal-free cathode catalysts.^{8,9,12} It is difficult to conclude with the present data whether transition metal species are involved as catalytically active sites for ORR. However, this study provides a breakthrough in terms of methodology for preparation of highly active and highly stable ORR catalysts. The general understanding of this class of materials is that there is a trade-off between catalytic activity and durability.³ The present results clearly suggest that the combination of multi-step pyrolysis and multi-step acid treatment is effective to overcome this trade-off. Further research is required to improve catalytic activity and durability, and

clarify the catalytically active center for precious-metal-free ORR catalysts.

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