Structure control of a carbon-based noble-metal-free fuel cell cathode catalyst leading to high power output

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A carbon-based noble-metal-free O_2 reduction catalyst for a polymer electrolyte fuel cell (PEFC) cathode was produced from commonplace, safe and inexpensive compounds (glucose, adenine, Fe gluconate) and the catalyst structure was controlled between a graphene-layered structure and a highly porous amorphous structure for the activity enhancement, which led to the power density of the highest level among the noble-metal-free cathode type PEFCs.

Swift and widespread substitution of fuel cells for conventional energy systems would help to improve the global environment and the most promising fuel cell is one using a polymer electrolyte (PEFC).[1–3] The PEFC generates electricity by electron emission from H_2 producing H^+ (H_2 oxidation) at the anode, electron introduction into O_2 forming bonds to H^+ transported through the polymer electrolyte (O_2 reduction) at the cathode, and emitting water in principle. Due to the fast ionic conduction in the perfluorosulfonate ion-exchange membrane used as the polymer electrolyte, the PEFC is able to efficiently generate a high power around 80 °C when active heterogeneous catalysts are used in the electrodes. This is within a reasonable temperature range for start-up of the PEFC from room temperature and makes the PEFC advantageous for use as a power source in electric vehicles and for cogeneration systems for domestic electricity and heating.[3] Nanoparticles of Pt or Pt alloys supported on electron-conductive carbon black have hitherto been used as the catalyst since it has been generally recognized that only these metals are active for the reactions and stable in the highly acidic atmosphere of the polymer electrolyte. However, limited Pt reserves and supply will prohibit widespread use of the PEFC. There is therefore an increased demand for a catalyst that functions with far less or no Pt, especially for the cathode due to the slow reaction rate of O_2 reduction, which requires a sufficient amount of Pt.[4] It would be more desirable to use catalysts free from noble metals because the price of these metals rises under high-demand circumstances.

There have been many studies reported on PEFCs using noble-metal-free cathode catalysts, which aim to improve their insufficient power output compared to Pt-based PEFCs.[5–9] The most extensively studied noble-metal-free catalyst might be pyrolyzed Fe porphyrin on a carbon material. A PEFC using such a catalyst generated 0.20 W cm^{-2} at an O_2 partial pressure, $p(O_2)$, of 4.0×10^2 kPa.[5,6] A PEFC using pyrolyzed Fe(II) acetate on N-enriched carbon generated 0.22 W cm^{-2} at a $p(O_2)$ of 2.6×10^2 kPa.[7] It was reported quite recently that a PEFC using a noble-metal-free cathode catalyst with Co–N coordination in the form of a Co–polypyrrole–carbon composite generated 0.15 W cm^{-2} at a $p(O_2)$ of 2.6×10^2 kPa with excellent durability.[8]

We recently produced a noble-metal-free cathode catalyst with heme-like structure using an alternative production method which involved pyrolyzing a mixture of glucose, glycine, and Fe(II) lactate.[9] Although the durability of this carbon-based catalyst was significantly improved by the changed composition of the mixture, the power output of the PEFC using the catalyst (0.014 W cm^{-2} at a $p(O_2)$ of 54 kPa) was much lower than the PEFCs referred to above. This first study was prompted by the fact that porphyrin macrocycles are biosynthesised from glycine and that Fe^{2+} is introduced into the centre of the porphyrin to form heme. Heme is involved, for example, in cytochrome c oxidase as the active site for oxygen reduction in aerobic organisms. We were then further prompted by the fact that the enzyme has Cu at its active site to produce a carbon-based noble-metal-free cathode catalyst containing Cu.[10]

In this study, adenine and Fe(II) gluconate were used instead of glycine and Fe(II) lactate, respectively, all of which are commonplace, inexpensive compounds. Glucose, adenine, Fe(II) gluconate dihydrate, and Cu(II) gluconate were simply mixed and finely ground. No other complex mixing techniques were used in this study. The molar ratio of glucose to adenine and that of Fe(II) to Cu(II) were both preliminary set at 1 and the sum of the metal contents in the mixture was 1 wt%. The mixture was heated at 150 °C in air for 24 h for dehydration of glucose, which is often carried out before carbonisation of glucose. After grinding this dehydrated mixture, the powder was heated in 100 cm^3 min^{-1} of flowing Ar at 1000 °C for 2 h after raising the temperature at 5 °C min^{-1}. The obtained carbon material was finely ground again and a treatment with an acid solution was carried out to remove soluble metallic species. The treatment was performed in 0.5 mol dm^{-3} H_2SO_4 at boiling temperature for 1 h, followed by filtering, washing with high-purity water, and drying in vacuum at room temperature. Further carbon materials were formed similarly using only one type of gluconate, with the metal content in the starting mixture again 1 wt%. The resulting carbon materials which contained both Fe and Cu, only Fe, or only Cu are hereafter called GAdFeCu, GAdFe, and GAdCu, respectively. The yields, the metal contents, the results of the elemental analysis, and the specific surface areas are shown in Table 1.

Fig. 1 shows the transmission electron micrographs and the X-ray diffraction (XRD) spectra of the carbon materials. A tangled ribbon-like structure was mainly observed in GAdFe. The

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Table 1 Yields, contents of elements, and specific surface areas of the carbon materials

		GAdFeCu	GAdFe	GAdCu
Yield (%)		8.3	12.7	18.0
Contents of elements (wt%)[a]	H	1.0	0.6	1.2
	C	85.2	92.7	83.5
	N	2.2	1.2	2.8
	O	10.5	4.6	19.2
	Fe	0.34	0.21	—
	Cu	0.11	—	0.26
Specific surface area (m^2 g^{-1})[b]		515	251	1010

[a] Analysis was carried out for the elements: H, C, N, and O. The metal contents were measured after combustion of the carbon matrix and dissolution of the residue by 0.5 mol dm^{-3} H_2SO_4. The deviations in the sum of the contents of the elements from 100% were attributed to the experimental error, the reason of which is unknown at present. [b] Specific surface area was determined by the Brunauer–Emmet–Teller (BET) plot of the N_2 adsorption isotherm at −196 °C.

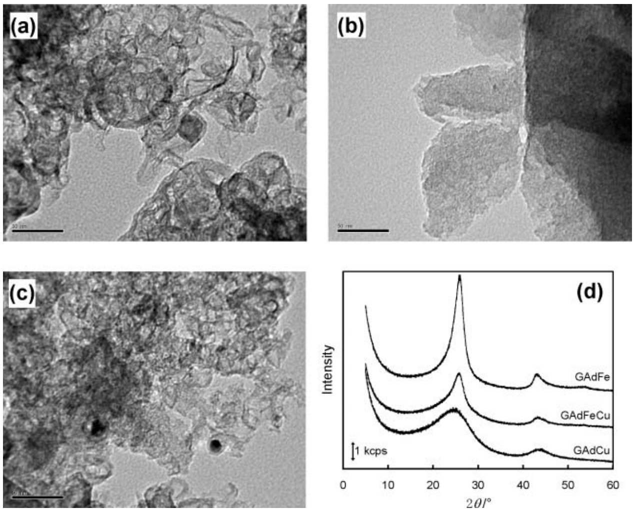

Fig. 1 Transmission electron micrographs (TEMs) of (a) GAdFe, (b) GAdCu, and (c) GAdFeCu and (d) their X-ray diffraction spectra. Acceleration voltage for obtaining the TEM was 200.0 kV. The scale bars in the micrographs correspond to 50 nm. Cu-Kα radiation was used in the X-ray diffraction. Each spectrum was shifted by 2 kcps for easier comparison.

formation of graphite crystals has been reported in the pyrolysis of mixtures of vinyl polymers and Fe powder or Fe oxides.[11] Based on that report and the XRD spectrum of GAdFe showing development of the (002) diffraction peak, the ribbon was attributed to graphene layers. In contrast, GAdCu showed amorphous structure with much higher specific surface area than GAdFe. GAdFeCu showed the intermediate structure between GAdFe and GAdCu as well as the specific surface area. The Cu inclusion converted the graphene-layered structure to the partially amorphous structure with the micropore development, implying that the carbon structure was controlled by the Cu inclusion. The round dark gray particles observed in GAdFe and GAdFeCu might be metallic species surrounded by graphene layers or carbon matrix which have avoided dissolution in the acid treatment.

The catalytic activity of the carbon materials for cathodic O_2 reduction was examined by fixing the carbon material with the polymer electrolyte as a binder to form a catalyst layer on a rotating glassy carbon disk electrode (GC RDE) and immersing it in O_2-saturated 0.1 mol dm^{-3} $HClO_4$ at 25 °C.[9] Fig. 2 shows the relationships between the electrode potential and currents at the catalyst layers measured by rotating the electrodes at 2000 rpm. The sign of the cathodic current was taken as negative. The current at the GAdFe layer was comparable to those for the carbon materials formed from glucose, glycine, and Fe lactate in the preceding study.[9] The lower current at the GAdCu layer than the GAdFe layer might be due to the intrinsic low activity of Cu-involving species as the active site for O_2 reduction,[12] suggesting O_2 reduction occurred mainly on the active site involving Fe.

The current increased by the inclusion of Cu in the carbon material, although the current was still smaller than that at the catalyst layer formed from Pt-loaded carbon black, Pt/C (Fig. 2). The larger specific surface area of GAdFeCu than GAdFe was one factor for the increase. Another factor might be the change in the valence state of Fe on the surface of the carbon material. The increase in Fe(II) in GAdFeCu compared to GAdFe was suggested by X-ray photoelectron spectra (Fig. 3) based on the peak position that reported for Fe(III), 710.8–711.8 eV, and Fe(II), 707.1–708.7 eV,[13,14] although the peak intensity, and consequently, the atomic ratio of Fe on the surface (below 0.1 atom%) was low. According to the O_2 reduction mechanism proposed by Bouwkamp-Wijnoltz *et al.* for pyrolysed Fe porphyrin adsorbed on carbon, Fe(II) on the catalyst surface is required for the first step of the multi-step reaction.[15] Assuming the mechanism is also valid for the carbon materials produced in this study containing Fe on the surface, the activity increase could be explained by the increase in Fe(II) on the surface. It would be necessary to analyse the active site structure in future studies by overcoming possible obstacles due to the low surface atomic ratio.

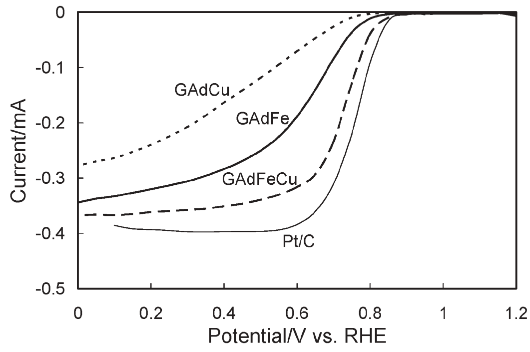

Fig. 2 Relationships between electrode potential and oxygen reduction current of negative scans at catalyst layers formed from GAdFe (solid line), GAdCu (dotted line), GAdFeCu (dashed line), and Pt/C (thin line) in O_2-saturated 0.1 mol dm^{-3} $HClO_4$ at 25 °C. Scan rate: 10 mV s^{-1}. Electrode rotation speed: 2000 rpm. The reference electrode was a reversible hydrogen electrode (RHE). The current was determined by subtracting the background current from the measured current. The background current was obtained in an Ar atmosphere without rotation. The catalyst layers of GAdFe, GAdCu, and GAdFeCu were formed on a GC RDE (diameter 3 mm) by pipetting and drying 2 μl of a catalyst paste prepared from 50 mg of the carbon material, 5 mg of carbon black, 0.5 ml of 5 wt% solution of a polymer electrolyte (Nafion), and 0.5 ml of high-purity water. The catalyst layer of Pt/C (Johnson Matthey, Pt content of 10 wt%, Vulcan XC-72R as carbon black) was formed by pipetting and drying 1 μl of a catalyst paste prepared from 10 mg of Pt/C, 0.1 ml of 5 wt% Nafion solution, and 0.9 ml of high-purity water.

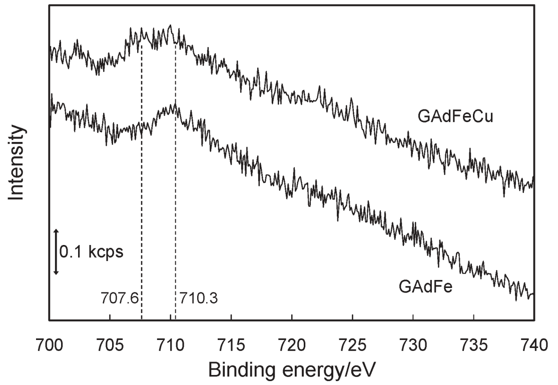

Fig. 3 X-Ray photoelectron spectra of Fe 2p in GAdFe and GAdFeCu. Al-Kα radiation was used. The carbon materials were fixed on an Al adhesive tape. Each spectrum was arbitrary shifted in the y-axis direction for easier comparison.

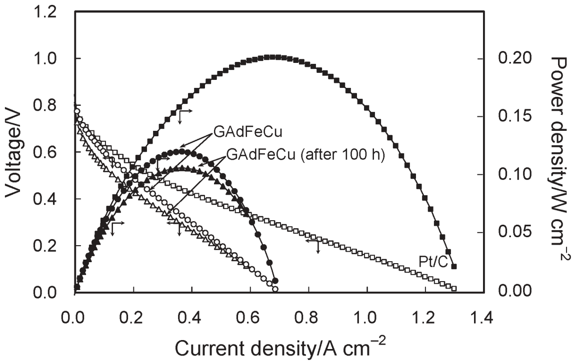

Fig. 4 Relationships between current density and cell voltage (white symbols) and relationships between current density and power density (black symbols) for PEFCs formed using GAdFeCu (circles) and Pt/C (squares) in the cathodes under atmospheric pressure (backpressure, 0 kPa). Cell temperature: 80 °C. H_2 and O_2 were supplied to the cell at 100 cm^3 min^{-1} after humidification. The partial pressures of H_2 and O_2 were 54 kPa. The composition of the cathode formed using GAdFeCu: GAdFeCu, 10 mg cm^{-2} (Fe content: 34 μg cm^{-2}); carbon black, 1 mg cm^{-2}; polymer electrolyte (Nafion), 10 mg cm^{-2}. The composition of the cathode formed using Pt/C: Pt/C, 1 mg cm^{-2} (Pt loading: 0.1 mg cm^{-2}); Nafion, 0.5 mg cm^{-2}. The composition of the anodes of both PEFCs were the same as that of the cathode formed using Pt/C. The electrode area was 5 cm^2. The current–voltage (△) and current–power (▲) relationships for the PEFC formed using GAdFeCu after continuous operation at 0.5 V under flow rates of H_2 and O_2 at 50 cm^3 min^{-1} are also shown.

The PEFC was formed using GAdFeCu in the cathode and Pt/C in the anode. The performances of the PEFC were evaluated using H_2 and O_2 under backpressures of 0, 200, and 400 kPa, corresponding to $p(O_2)$ of 54, 254, and 454 kPa (water vapour: 47 kPa). The power densities of 0.12, 0.19, and 0.24 W cm^{-2} were attained at $p(O_2)$ of 54, 254, and 454 kPa, respectively, which were comparable to the highest level of noble-metal-free-cathode type PEFC reported previously. The relationships between current density, cell voltage, and power density at the $p(O_2)$ of 54 kPa are shown in Fig. 4 as well as the relationships for a Pt-based PEFC for comparison. In addition, although the durability was lower than that reported for the Co–polypyrrole–carbon black composite catalyst,[8] the performance at the PEFCs using GAdFeCu after a 100 h continuous operation at the $p(O_2)$ of 54 kPa and 0.5 V was nearly comparable to the initial performance; the power density of 0.11 W cm^{-2} was attained.

In conclusion, the results presented here suggest that the method used for production of the carbon-based catalyst in this study could be a promising method for PEFC noble-metal-free catalyst production, due to (1) the use of the commonplace, safe, and inexpensive compounds as the starting materials, (2) the flexibility of the starting materials, and (3) procedures that were simple but allowed control of the structure of the products. The active site and the carbon matrix were simultaneously generated and closely related in the catalyst produced by the method. The control of the carbon structure between graphene-layered structure and highly porous amorphous structure was first demonstrated here and applied to the PEFC cathode catalyst, and is important from an engineering aspect. Nevertheless, the power output of the PEFC reported here is still lower than conventional Pt-based PEFCs that can generate over 0.5 W cm^{-2} at atmospheric pressure using H_2 and O_2,[16] and even the PEFC with the lowest level of Pt loading generating 0.20 W cm^{-2} (Fig. 4). Further studies are in progress to enhance the activity and improve the durability by examining various compounds as possible starting materials.

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