



Short communication

## Enhancement of oxygen reduction activity with addition of carbon support for non-precious metal nitrogen doped carbon catalyst

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## ABSTRACT

An improved synthesis scheme of non-precious metal N-doped carbon catalysts for oxygen reduction reaction is reported. The non-precious metal N-doped carbon catalysts were prepared by pyrolysis of the mixture (phenol resin, Ketjen black carbon support and cobalt phenanthroline complex). The drastic improvement of distribution state of Ketjen black supported non-precious metal N-doped carbon catalysts was observed by means of transmission electron microscopy (TEM). In addition, the non-precious metal N-doped carbon catalyst synthesized with Ketjen black carbon support showed much higher oxygen reduction reaction (ORR) activity relative to unsupported non-precious metal N-doped carbon catalyst in O<sub>2</sub>-saturated 0.5 mol l<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> at 35 °C. Moreover, the highest ORR activity was obtained with addition of optimum amount of Ketjen black carbon support was thirtyfold compared to unsupported non-precious metal N-doped carbon catalyst at 0.7 V. Similarly, the performance of a polymer electrolyte fuel cell (PEFC) using the non-precious metal N-doped carbon catalyst as the cathode electrode catalyst was obviously better than that of the non-precious metal N-doped carbon catalyst before optimization. Microstructure, specific surface area and surface composition of the non-precious metal N-doped carbon catalysts were analyzed by XRD, XPS and BET measurement with nitrogen physisorption, respectively.

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### 1. Introduction

A fuel cell technology is expected as a next generation's clean energy source. The reason for the motivation of fuel cell research is the feature of high thermal efficiency. Thermodynamic cell voltage of PEFC is about 1.2 V. However, the cell voltage is below thermodynamic value primarily due to over-potential of cathode reaction in PEFC. Therefore, more platinum catalyst is used in cathode electrode to stimulate the cathode reaction. Great many researchers have presented the reports on improvement of catalytic activity and durability to reduce the usage of platinum such as alloying [1–6], core-shell structure [7–10], control of shape and size [11–14], and support effect [15,16].

On another front, a study of non-platinum catalyst is highly significant from the perspective of platinum resource depletion and has been studied [17–19]. There has been a considerable research on non-platinum catalysts and the research is divided into two major groups such as (i) cobalt and iron compound

catalysts (Co–N–C, Fe–N–C) [20–37] and (ii) N-doped carbon catalysts [38–42].

It is well known that carbon has a catalytic ability and N-doped carbon was shown with higher catalytic ability [43,44]. Moreover, a zigzag edge in carbon exhibits the higher density of state (DOS) in the vicinity of Fermi level [45,46] and exhibits the higher ORR activity by doping nitrogen in the vicinity of the zigzag edge plane [47,48]. However, the carbon catalyst activity is low relative to that of platinum catalyst. In addition, decrease in fuel cell performance using the carbon catalyst as a cathode electrode catalyst is caused by a deficiency of catalytic active site.

In this communication, the non-precious metal N-doped carbon catalysts were evenly formed on Ketjen black carbon support in order to increase the catalytic active site by preventing further agglomeration in the pyrolysis and were illustrated in Fig. 1. The morphology of the non-precious metal N-doped carbon catalysts was observed by TEM and the ORR activity was evaluated using rotational disk electrode (RDE) technique. An improved synthesis scheme for non-precious metal N-doped carbon catalyst in which N-doped carbon is uniformly distributed on Ketjen black carbon support is demonstrated. The effectivity of the addition with Ketjen black carbon support for the improvement in the ORR activity is presented.

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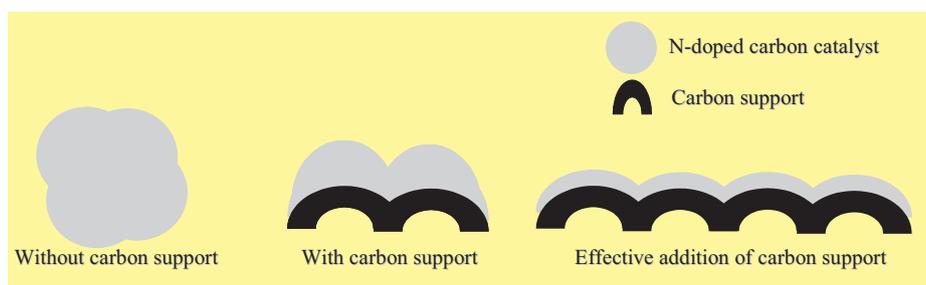


Fig. 1. Catalytic illustration of N-doped carbon catalyst on carbon support.

## 2. Experimental

### 2.1. Catalysts preparation

The preparation of non-precious metal N-doped carbon catalysts was as follows. 0.002 mol of cobalt(II) nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , Wako Pure Chemicals) was dissolved into 20 ml of EtOH, and was stirred for 10 min. The solution was added 0.006 mol of 1,10 phenanthroline ( $\text{C}_{12}\text{H}_8\text{N}_2$ , Wako Pure Chemicals) as a nitrogen source and was brought about the color of yellow precipitation derived from cobalt phenanthroline complex shortly after addition of 1,10 phenanthroline, followed by the addition of 1.0 g of phenol resin (PR-51794, Sumitomo Bakelite) as a carbon precursor. After that, this solvent was eliminated from the mixture by drying in a vacuum. The solvent-eliminated mixture was added 0–2.0 g of Ketjen black carbon support (KB, specific surface area:  $800 \text{ m}^2 \text{ g}^{-1}$ , Lion Ltd.) and was mixed homogeneously. The mixture was carbonized for 3 h by raising the temperature up to  $900^\circ\text{C}$  at  $10^\circ\text{C min}^{-1}$  in a nitrogen atmosphere. In order to remove unwanted metal elements deposited in the non-precious metal N-doped carbon catalyst, the sample was treated with 3.0 M HCl solution by boiling for 6 h, and washed thoroughly with deionized water. In this study, non-precious metal N-doped carbon catalysts were synthesized by changing a ratio of KB:phenol resin = 0–2.0:1.0, in weight were denoted as NC, NC + KB0.2, NC + KB0.4, NC + KB0.6, NC + KB1.0, NC + KB2.0, respectively.

### 2.2. Characterization

The surface area and pore size distribution of the non-precious metal N-doped carbon catalysts were determined by the Brunauer–Emmett–Teller (BET) method with nitrogen physisorption. The properties of the non-precious metal N-doped carbon catalysts were evaluated using an X-ray diffractometer with  $\text{Cu K}\alpha$  radiation (XRD, Rigaku RINT-1500), transmission electron microscopy with an acceleration voltage of 200 kV (TEM, Hitachi HF-2200) and X-ray photoelectron spectroscopy (XPS, ULVAC•PHI ESCA5500 MC, with  $\text{Mg K}\alpha$  radiation; the shift correction was made by setting the  $\text{C1s}$  at  $284.5 \text{ eV}$ ). The electric resistivity of the catalysts was measured using a column-shaped equipment at room temperature.

Table 1  
Characteristics of KB, NC and NC + KB catalysts.

| Catalyst   | Specific surface area ( $\text{m}^2 \text{ g}^{-1}$ ) | Electric resistivity ( $\Omega \text{ cm}^{-1}$ ) | Surface composition (at.%) |     |     |       |        |       |
|------------|---|---|----------------------------|-----|-----|-------|--------|-------|
|            |   |   | C1s                        | N1s | O1s | Co2p3 | N/C    | O/C   |
| KB         | 800   | 0.055   | 97.8                       | 0.1 | 2.1 | 0     | 0.0010 | 0.021 |
| NC         | 207   | 0.022   | 95.8                       | 0.7 | 3.4 | 0.1   | 0.0073 | 0.035 |
| NC + KB0.2 | 151   | 0.010   | 96.4                       | 1.2 | 2.3 | 0.1   | 0.0128 | 0.023 |
| NC + KB1.0 | 228   | 0.081   | 96.1                       | 1.0 | 2.8 | 0.1   | 0.0104 | 0.029 |
| NC + KB2.0 | 419   | 0.042   | 96.3                       | 0.6 | 3.1 | 0     | 0.0062 | 0.032 |

### 2.3. Electrochemical measurements

Electrochemical measurements of the non-precious metal N-doped carbon catalysts were carried out using the conventional three-electrode method using a rotational disk electrode (RDE) as working electrode, a grassy carbon bar as counter electrode and Ag/AgCl as reference electrode, respectively. The non-precious metal N-doped carbon catalyst was ultrasonically dispersed in deionized water ( $2.0 \text{ mg ml}^{-1}$ ) and  $20 \mu\text{l}$  of the dispersed solution was pipetted onto the glassy carbon surface of the RDE (surface area:  $0.2 \text{ cm}^2$ ), yielding a catalyst loading of  $0.2 \text{ mg cm}^{-2}$ . After drying,  $5 \mu\text{l}$  of 0.1 wt.% Nafion solution (Aldrich, isopropyl alcohol:DI water = 1:1, in wt.%) was dropped to adhere the non-precious metal N-doped carbon catalyst on the glassy carbon electrode, followed by drying the catalyst in air. All potentials in this study are given vs. normal hydrogen electrode (NHE). ORR activity of the non-precious metal N-doped carbon catalysts was evaluated with linear sweep voltammetry (LSV), rotation rates of 400, 625, 900, 1600, 2500 rpm in  $\text{O}_2$ -saturated  $0.5 \text{ mol l}^{-1}$   $\text{H}_2\text{SO}_4$  aqueous solution at  $35^\circ\text{C}$ .

The performance test of membrane-electrode assemblies (MEAs) of the non-precious metal N-doped carbon cathode catalysts (loading:  $2.5 \text{ mg cm}^{-2}$ ) was carried out in a single cell. The anode catalyst was 70 wt.% Pt/C catalyst and the Pt loading was  $0.4 \text{ mg cm}^{-2}$ , the hydrocarbon membrane was used as a proton-conducting membrane, respectively. Pressureless humidified pure  $\text{H}_2$  gas and humidified pure  $\text{O}_2$  gas at  $79^\circ\text{C}$  were supplied to the divided anode and cathode electrode, respectively. Flow rate of each gas was controlled to keep ratio of the gases utilization constant:  $\text{H}_2$  and  $\text{O}_2$  utilization rates are 70% and 8%, respectively.

## 3. Results and discussion

### 3.1. Catalyst characterization

The fundamental property of the major samples is summarized in Table 1, and electric resistivity of these samples does not make much difference in general view. Pore size distribution of these samples is showed in Fig. 2. Like KB, NC was synthesized without KB has a distinctive pore of 3 nm, and the pore size distribution of NC + KB types were synthesized with KB approaches that of KB with increasing the additive amount of KB. This result implies that

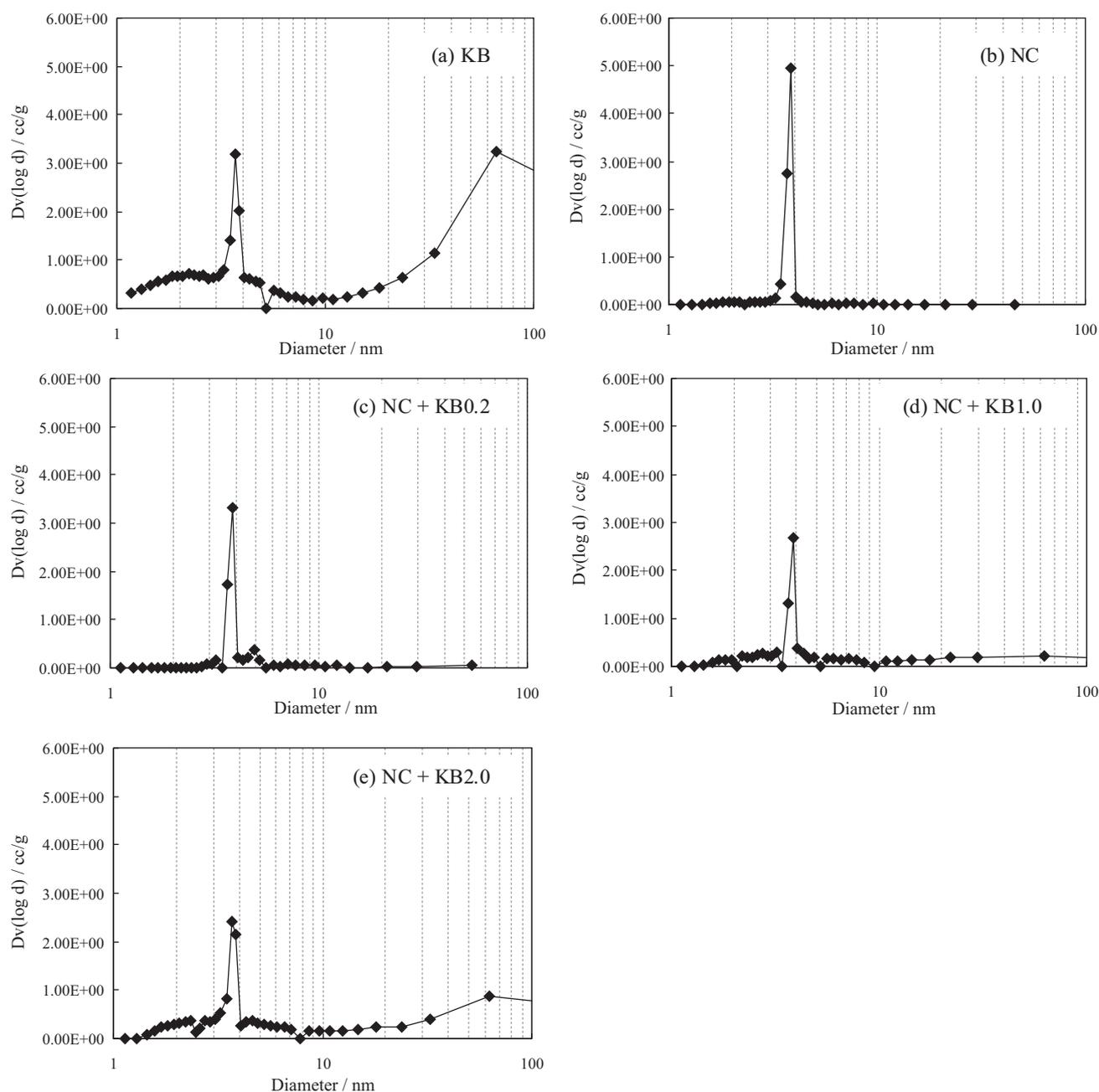


Fig. 2. Pore size distributions of KB, NC and NC+KB catalysts: (a) KB, (b) NC, (c) NC+KB0.2, (d) NC+KB1.0 and (e) NC+KB2.0.

non-precious metal N-doped carbon catalysts were formed on KB surface.

XRD patterns of the samples indicate that graphitization degree of NC and NC+KB types decreased with the increasing additive amount of KB which is amorphous carbon (Fig. 3). That is, the diffraction peak of NC and NC+KB types from C (002) plane is  $26^\circ$  in  $2\theta$  became significantly broader with increasing the additive amount of KB, and the shape of the diffraction peak approached that of KB. In addition, the sharp diffraction peak corresponding to Co (111) plane ( $2\theta = 44^\circ$ ) was obviously confirmed in NC, NC+KB0.2 and NC+KB1.0. These residual cobalt compositions, which were not removed in HCl treatment, are in carbon interlayer because cobalt surface composition was hardly detected in the samples by XPS analysis, as shown in Table 1.

TEM images of the samples are shown in Fig. 4. Compared with NC synthesized without KB, a higher dispersion state was obtained in NC+KB types synthesized with KB. NC forms a carbon aggregate

(Fig. 4(a)). In contrast, NC+KB types were uniformly supported on KB and a graphite-like structure along with verge of KB was formed (Fig. 4(b), (f) and (h)). Moreover, The dispersivity of NC+KB1.0 and NC+KB2.0 is clearly improved relative to that of NC+KB0.2 (Fig. 4(e)–(g)).

### 3.2. Catalytic activity and cell performance

The NC weight ratio, additive KB amount and ORR activities of the samples evaluated catalytic activity are listed in Table 2. Here NC content ratio was calculated by the supposition, which is that the amount of KB hardly changes before and after pyrolysis, as shown in Eq. (1):

$$\text{NC (wt.\%)} = \frac{AP_{\text{WT}} - KB_{\text{WT}} - Co_{\text{WT}}}{AP_{\text{WT}}} \times 100 \quad (1)$$

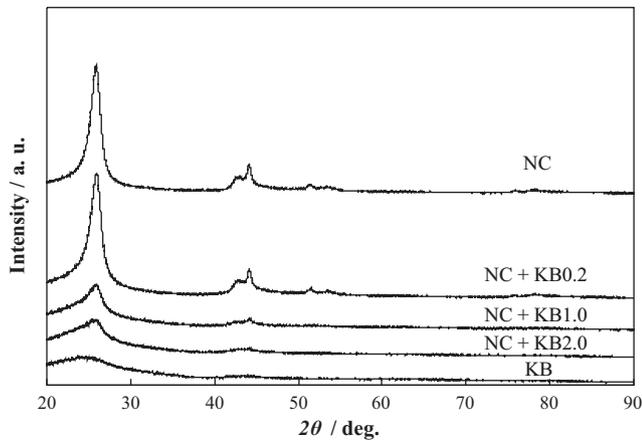


Fig. 3. X-ray diffraction patterns of KB, NC and NC + KB catalysts.

**Table 2**  
NC weight ratio and ORR activities of NC and NC + KB catalysts.

| Catalyst | Ketjen black carbon support (g) | NC (wt.%) | $I$ ( $A g^{-1}$ ) (NC) @ 0.7 V | $I$ ( $A g^{-1}$ ) (NC+KB) @ 0.7 V |
|----------|---------------------------------|-----------|---------------------------------|------------------------------------|
| NC       | 0                               | 100.0     | -0.15                           | -0.15                              |
| NC+KB0.2 | 0.2                             | 72.9      | -0.74                           | -0.61                              |
| NC+KB0.4 | 0.4                             | 63.4      | -0.74                           | -0.53                              |
| NC+KB0.6 | 0.6                             | 57.9      | -1.46                           | -0.95                              |
| NC+KB1.0 | 1.0                             | 36.4      | -4.13                           | -1.50                              |
| NC+KB2.0 | 2.0                             | 36.1      | -2.17                           | -0.78                              |

where  $AP_{WT}$  is the weight of the catalyst after pyrolysis,  $KB_{WT}$  is the weight of KB and  $Co_{WT}$  is the weight of additive cobalt metal. NC content ratio decreased gradually with increasing the additive amount of KB. Linear sweep voltammograms of NC and NC + KB types for ORR are shown in Fig. 5. ORR activities in Fig. 5(i) and (ii) are compared based on the amount of N-doped catalytic carbon and total amount of non-precious metal N-doped carbon catalyst, respectively. NC + KB types synthesized with KB have clearly higher activities than NC synthesized without KB in  $O_2$ -saturated

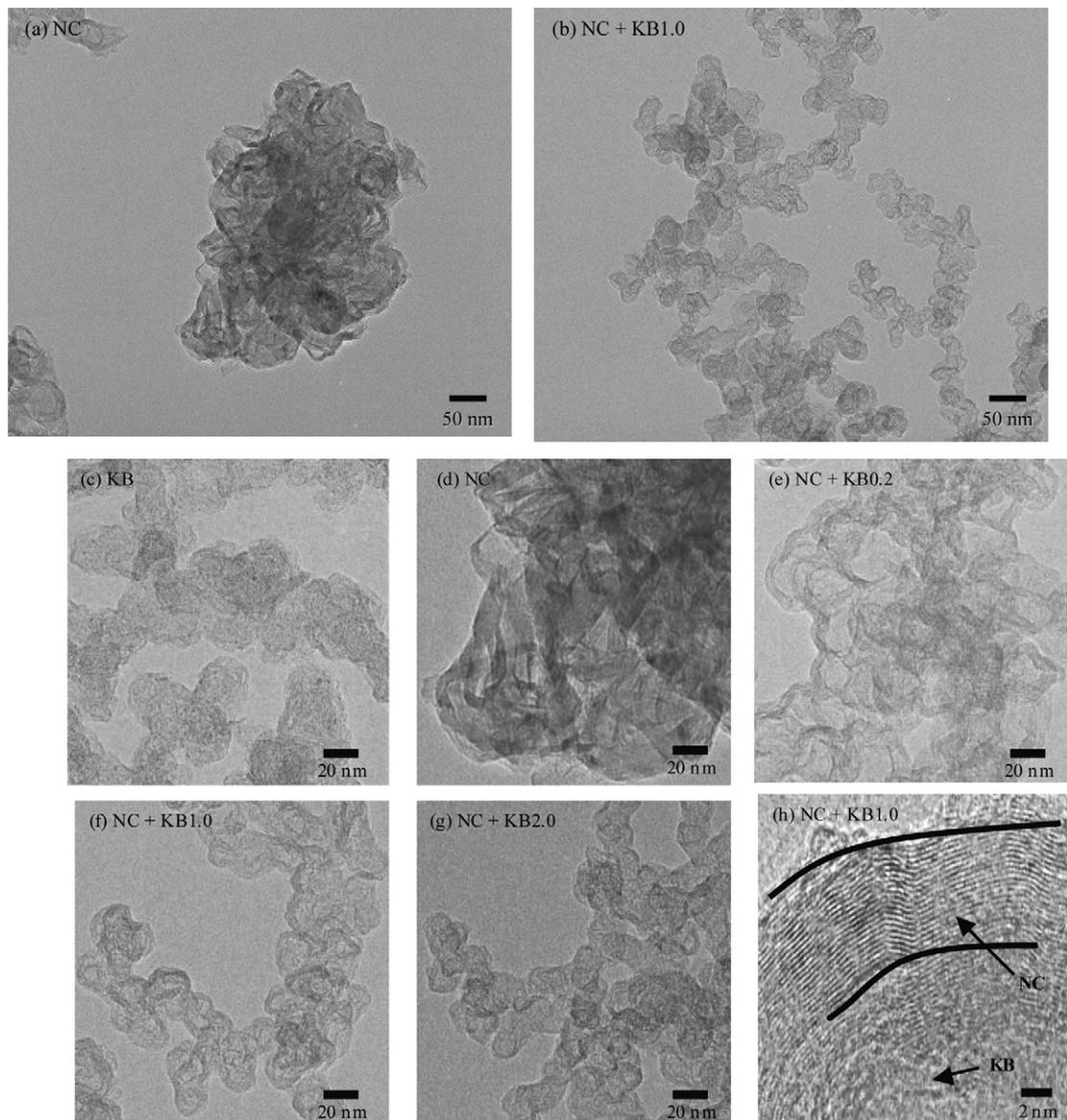
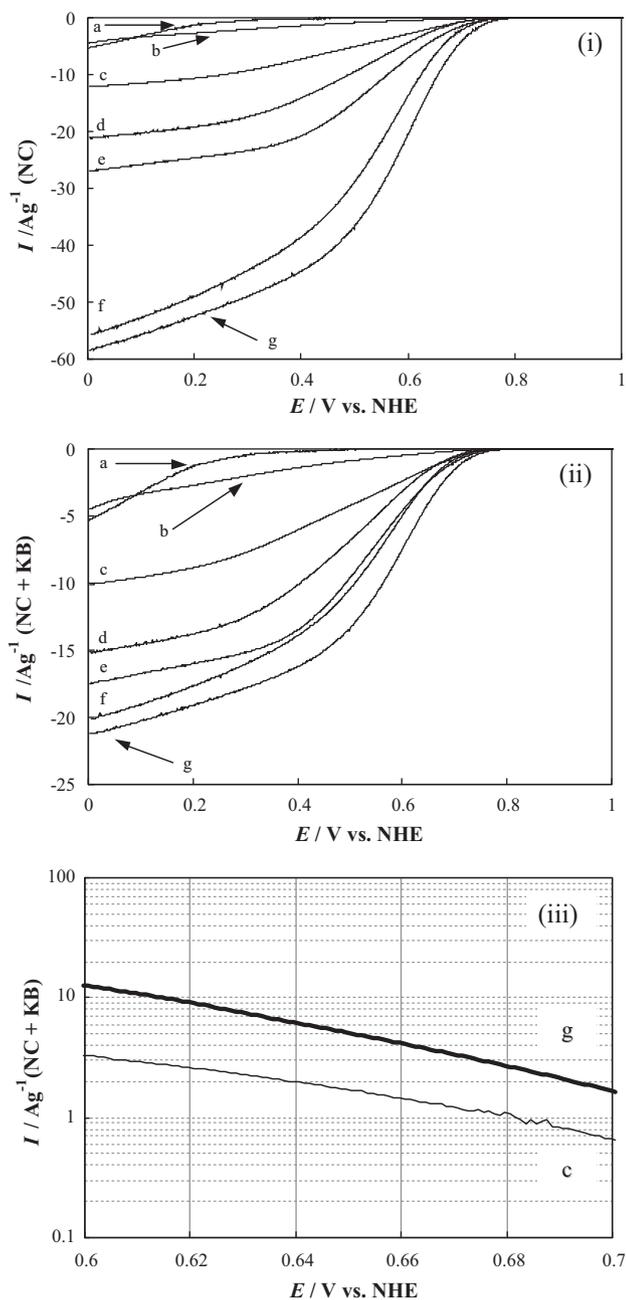
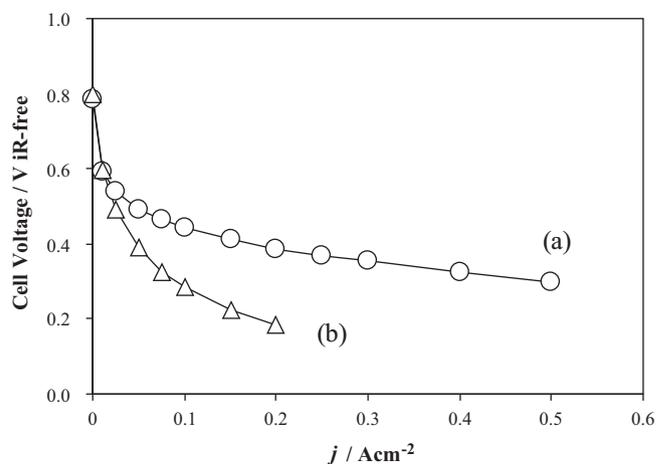


Fig. 4. TEM images of KB, NC and NC + KB catalysts: (a, d) NC, (b, f, h) NC + KB1.0, (c) KB, (d) NC, (e) NC + KB0.2, and (g) NC + KB2.0.



**Fig. 5.** Oxygen reduction activities of KB, NC and NC+KB catalysts: (i) NC based current density, (ii) NC + KB based current density and (iii) Tafel plots with applying Koutecky–Levich equation. (a) KB, (b) NC, (c) NC+KB0.2, (d) NC+KB0.4, (e) NC+KB0.6, (f) NC+KB2.0, and (g) NC+KB1.0.

$0.5 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$  at  $35^\circ\text{C}$ , rotating rate at 1600 rpm. Particularly, ORR current density of NC+KB1.0 was thirtyfold increased relative to that of NC at 0.7 V and ORR onset potential was 0.82 V at  $10 \text{ mA g}^{-1}$ . Moreover, Tafel plots of representative catalysts with applying Koutecky–Levich equation unaffected by oxygen diffusion are shown in Fig. 5(iii). NC+KB1.0 has two and a half times ORR activity relative to NC+KB0.2 at 0.7 V. Ikeda et al. reported that the catalytic active site is carbon at zigzag edge and carbon atoms bonded to graphite-like nitrogen at the zigzag edge exhibit a higher ORR activity than those bonded to pyridine-like nitrogen [48]. In addition, the improvement of the catalytic activities did not depend on the surface areas, cobalt and other atomic surface contents of non-precious metal N-doped carbon catalysts, and is due to the increase in exposed catalytic active site. Addition of carbon



**Fig. 6.** Polarization curves of NC+KB catalysts. The catalysts were prepared with different amounts of KB carbon support: (a) NC+KB1.0 and (b) NC+KB0.4.

support has an effect on increase in catalytic active site of non-precious metal N-doped carbon catalyst derived from phenol resin was demonstrated in these experiments. Though ORR activities were approximately increased with increasing addition of KB, ORR activity of NC+KB2.0 is lower than that of NC+KB1.0. Graphitization degree of N-doped catalytic carbon in NB+KB2.0 was observed in TEM image that is lower compared to that of NB+KB1.0. That is, excessive decrease of graphitization degree induces lower ORR activity.

Fig. 6 shows the polarization curves of PEFCs prepared with the different cathode electrode catalysts: (a) NC+KB1.0 and (b) NC+KB0.4. The open circuit voltages of these cells were about 0.8 V at  $80^\circ\text{C}$ . The cell with NC+KB0.4 and the cell with NC+KB1.0 showed the cell voltages of 0.22 V and 0.41 V at  $0.15 \text{ A cm}^{-2}$ , respectively. The PEFC performance with NC+KB1.0 is twice higher than that with NC+KB0.4, and this result is consistent with RDE measurements.

#### 4. Conclusions

Carbon supported non-precious metal N-doped carbon catalysts were synthesized by simple pyrolysis method. TEM images of non-precious metal N-doped carbon catalysts were synthesized with Ketjen black carbon support revealed that addition of Ketjen black carbon support had an effect on drastic improvement of catalytic carbon dispersibility. Graphitization degree of the non-precious metal N-doped carbon catalysts decreased with increasing the additive amount of Ketjen black carbon support and the shape of the diffraction peak approached that of Ketjen black carbon support. Catalytic carbon aggregate was formed by carbonization of a phenol resin without Ketjen black carbon support, which buried the catalytic active site and caused a decline of the oxygen reduction activity. Addition of Ketjen black carbon support was examined to improve the dispersibility. Oxygen reduction activities increased with increasing the additive amount of Ketjen black carbon support. Oxygen reduction current density of non-precious metal N-doped carbon catalyst with optimum amount of Ketjen black carbon support was thirtyfold increased relative to that of unsupported non-precious metal N-doped carbon catalyst at 0.7 V. Similarly, fuel cell performance was improved using the non-precious metal N-doped carbon catalyst has higher catalytic activity. These results indicate that the addition of carbon support has an effect on increase in catalytic active site of non-precious metal N-doped carbon catalyst derived from phenol resin.

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