Cobalt-carbon nanofibers as an efficient support-free catalyst for oxygen reduction reaction with a systematic study of active site formation†

MinJoong Kim, a Do-Hwan Nam, a Hee-Young Park, b ChoRong Kwon, b KwangSup Eom, c SungJong Yoo, b JongHyun Jang, b Hyoung-JuHn Kim, b EunAe Cho a and HyukSan Kwon a

Recently, major efforts have been devoted to exploring cheap and active non-precious metal catalysts for the oxygen reduction reaction (ORR) in fuel cells for large-scale applications. Herein, we report electrospun cobalt–carbon nanofibers (Co–CNFs) as an efficient catalyst for the ORR, together with a systematic study of the active site formation. The ORR activity of the Co–CNFs increases with increasing Co content up to approximately 30 wt%, at which high ORR activity is exhibited, comparable with a commercial Pt/C catalyst in alkaline media. XPS and structural analysis reveals a Co–pyridinic N x bond at the edge plane, and more Co nanoparticles were found in the Co–CNFs as the Co content was increased. These sites can behave as the primary and the secondary active sites for the ORR, according to a dual-site mechanism. The ORR activity of the Co–CNFs may deteriorate even if only one of these sites is limited. The high ORR activity of the Co–CNF catalysts results from the synergetic effect of dual site formation for the ORR.

Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are one of the most promising energy conversion devices because of their advantages such as high efficiency, high power density and low air-pollutant emission. Despite the remarkable progress in PEMFC technology, large-scale commercialization has still faced some challenges in terms of cost and durability. Cost reduction is the most crucial issue for the commercialization of PEMFCs. Among various components, an expensive platinum (Pt) catalyst and its application account for almost half of the stack cost (DOE Annual Merit Review, 2014). Therefore, various strategies have been proposed to reduce Pt usage in the electrode, especially in the cathode due to the sluggish oxygen reduction reaction (ORR) kinetics. 1,2 The most common approach in the past has been to enhance the Pt mass activity for the ORR via alloying with a transition metal, 3 core–shell structuring, 4 or the use of nano-structured thin films (NSTFs). 5

These approaches enable high performance even with a small amount of Pt. However, there is an ultimate limit to cost reduction because these catalysts are still precious-metal-based materials.

A recent major effort has been the development of non-precious-metal catalysts (NPMCs) without sacrificing performance. Since Jasinski reported macrocyclic Co-phthalocyanine as an ORR electrocatalyst, 6 NPMCs containing transition metal-N x moieties (M–N–C) have attracted continuing interest. 7–9 These catalysts ensure a negligible cost compared with Pt because they consist of earth-abundant substances: transition metals, nitrogen and carbon. Although early findings were not appropriate for use in a practical electrode, follow-up studies revealed the potential for a high ORR activity, comparable with that of Pt. 10–13 M–N–C catalysts can be synthesized by subsequent pyrolysis of a precursor mixture under inert or ammonia gas conditions. Work on M–N–C catalysts has mainly focused on optimization of the synthesis process, considering various precursor mixtures. 14–15 Thus, macrocyclic M-N x organics (phthalocyanine, 16 porphyrin 17,18), N-containing reactive polymers (polypyrrole, 19 polyaniline, 20,21 polyaclaylonitride 22), and highly porous supports (carbon, zeolite 23) with transition metals (Fe, Co) have been considered as promising materials to make efficient ORR active sites.

Although the ORR activity of the M–N–C catalyst strongly depends on the precursor selection, a large surface area is always a prerequisite for a high reaction volume. From this perspective, a nanostructure is a very attractive morphology to

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attain a high surface area. Various nanostructures may create a synergetic effect to enhance the catalytic activity with optimized precursors. Conventional synthesis has been limited in modifying the nanostructure of the M–N–C catalyst. The precursors are mechanically mixed and then pyrolyzed on the support material. The final morphology, such as the porosity, mainly depends on only the structure of the support material, and has not been uniform. Structural control of the support material requires additional processes, which makes the synthesis process too complicated and hampers the reproducibility of the performance of catalysts. Facile synthesis is necessary to yield various uniform nanostructures, regardless of the support material.

The electrospinning technique is a facile and cost-effective synthesis method used to prepare uniform 1-dimensional (1-D) polymer nanofibers. Nanofiber structures have received much attention in various research areas, such as catalysis, as electrode materials and in sensor development, because these structures have a high surface-area-to-volume ratio. Moreover, various nanostructures, such as core–shell and hollow-fiber structures, can be produced via a simple process using the electrospinning technique. Electrospinning is a powerful method that can be used to easily prepare a uniform nanostructured catalyst without a support material.

Electrospun polyacrylonitrile (PAN)-based M–N–C catalysts have been already studied by a few research groups. After the pyrolysis, the PAN nanofiber is transformed into a carbon nanofiber (CNF), and the transition metal with CNFs (M-CNFs) exhibits ORR activity. However, their ORR activities were low in alkaline and acidic media because of the lack of understanding of the ORR active sites and mechanism. This issue is not only confined to CNF-type catalysts, but to all M–N–C catalysts. The nature of the ORR on M–N–C catalysts remains a controversial subject, which hinders the design of a highly active M–N–C catalyst. To overcome this problem, it is necessary to clarify the ORR active sites of M–N–C catalysts by detailed structural analysis.

Herein, we report an electrospun Co-CNF catalyst as an efficient catalyst for the ORR, together with a systematic study of the ORR active sites, in order to make highly active nanostructured NPMCs using a facile method. To accomplish this goal, we focused on structural characteristics associated with the ORR active sites, such as doped N, graphitic carbon structure and the Co phase, as a function of Co contents. Nanofibrous Co-CNF catalysts with various Co contents were easily prepared using an electrospinning technique with low-cost precursors. By investigating the correlation between the structural variation and the ORR activity, we aim to elucidate the ORR active sites of the Co-CNF catalyst, for designing highly active NPMCs to replace Pt catalyst.

Experimental
Preparation of Co-CNF catalyst

The Co-PAN nanofibers were fabricated using the electrospinning technique. To prepare the electrospinning solution, 2 g of PAN (Mw = 150 000) and various amounts of cobalt(II) acetate were added to 18 g of dimethylformamide (DMF). The cobalt(II) acetate content in the electrospinning solution was varied from 0 to 0.5, 2, and 5 wt%. The precursor solutions were mechanically stirred for 24 h and then electrospun with an applied potential of 15 kV. The distance between the needle and bottom plate was maintained at 13 cm. The as-spun Co-PAN nanofibers were dried for 24 h in a vacuum oven at 40 °C.

The Co-CNF catalysts were synthesized via carbonization of the Co-PAN nanofibers at high temperature. The dried Co-PAN nanofibers were first stabilized at 220 °C for 3 h in air and then carbonized at 900 °C for 1 h under a N2 atmosphere. After the carbonization, the Co-PAN nanofibers were transformed into black Co-CNFs. The synthesized Co-CNF catalysts were used for the ORR activity measurements.

Physical characterization

The nanofiber structure was examined by scanning electron microscopy (SEM). Transmission electron microscopy (TEM) was used to examine the morphology of the Co-CNF catalysts. The cross-section sample for TEM observation was prepared using the focused ion beam (FIB) technique. Phase analysis of Co-CNF catalysts was performed using X-ray diffraction (XRD) and Raman spectroscopy. Raman spectroscopy was conducted using a 514 nm laser beam and a charge-coupled device detector with 4 cm−2 resolutions to characterize the properties of the CNF and metallic phases. The chemical state of Co and N in the CNFs was analyzed using X-ray photoelectron spectroscopy (XPS).

Electrochemical measurement

All the electrochemical measurements were conducted in a standard three-compartment electrochemical cell using a glassy carbon electrode of a rotating disk electrode (RDE), Pt wire and a saturated calomel electrode (SCE) filled with saturated KCl solution, as the working, counter and reference electrodes, respectively. All the potentials were measured in 20 °C 0.1 M KOH and referenced against the reversible hydrogen electrode (RHE). The potential difference between the SCE and the RHE was obtained from a cyclic voltammetry (CV) curve measured in the hydrogen-saturated 0.1 M KOH solution, using a Pt disc as the working electrode. The sweep rate was 0.1 mV s−1. The Co-CNF catalyst ink slurry was prepared by mixing the catalysts with 2 mL of DI water and 50 μL of 5 wt% Nafion solution as a binding material. The 20 wt% Pt/C catalyst ink slurry was prepared by mixing the catalysts with 460 μL of 2-propanol and 40 μL of 5 wt% Nafion solution as the binding material. After mixing and ultrasonication, a drop of the ink slurry was loaded onto a glassy carbon substrate. The dried electrode was then transferred to the electrochemical cell. Catalyst loadings of the Co-CNF and Pt/C catalysts were 498 mg cm−2 and 20 μgPt cm−2, respectively.

The ORR experiments were performed in oxygen-saturated 0.1 M KOH solution at room temperature. The RDE rotating rate was 1600 rpm and the sweep rate was 5 mV s−1. In a rotating ring-disc electrode (RRDE) experiment, the ring potential was set to 1.5 V and the rotating rate and the sweep rate were the
same as in an ORR experiment. The electron transfer number (n) and the H$_2$O$_2$ yield of catalysts were evaluated based on equations in the ESI [eqn (S1) and (S2)]. As an accelerated stress test (AST), CV was conducted with cycling potentials from 0.6 to 1.1 V in an Ar-purged 0.1 M KOH solution at a scan rate of 50 mV s$^{-1}$. The ORR activity was compared before and after 10,000 cycles.

Results and discussion

Structural and electrochemical properties of Co-CNF catalysts

We first investigated the morphological characteristics of the Co-CNF catalysts as a function of the Co content. Fig. 1a and b present SEM images of the as-spun (a) PAN and (b) Co-PAN nanofibers. These nanofibers exhibit uniform 1-D structures with a diameter of approximately 500 nm. The Co addition to PAN does not affect the electrospray nanofiber structure, and also the chemical bonding of the PAN, from the IR spectrum in Fig. S1.$^\dagger$ After the pyrolysis, PAN is transformed into a carbon structure via a carbonization process involving the decomposition of hydrogen and nitrogen. As a result, the diameter decreased from 500 to 200 nm whilst maintaining the well-defined 1-D structures, as observed in Fig. 1c and d. The quantitative amounts of Co in the CNFs are summarized in Table 1. After the pyrolysis, the Brunauer–Emmett–Teller (BET) surface area of the 32.2 wt% Co-CNFs was measured to be 350.18 m$^2$ g$^{-1}$, which is slightly higher than those of previously-reported carbon-based catalysts.$^{26,34}$ These results demonstrate that the 1-D structures of the CNFs synthesized in this study can provide a high surface area without additional supports.

Fig. 2a–d present TEM images of the Co-CNFs with various amount of Co. As illustrated in Fig. 2a–d, metallic nanoparticles of 20–30 nm size were formed in the Co-CNFs after the pyrolysis. More metallic nanoparticles were formed upon increasing the amount of Co in the CNFs. Therefore, these metallic nanoparticles could be Co nanoparticles that are formed during the pyrolysis process. These nanoparticles were densely segregated on the outside of the CNFs and partially embedded in a few carbon layers, as illustrated in Fig. 2e and f. These graphite-like carbon layers are well known in pyrolyzed M–N–C catalysts.$^{35}$ The presence of the graphitic carbon phase in pyrolyzed M–N–C catalysts may play a role in hosting stable ORR active sites by enhancing the electronic conductivity and corrosion resistance of carbon.$^{35}$ From that viewpoint, it may be important to analyze the structural characteristics of the ‘metallic nanoparticles’ and the ‘graphitic carbon layer’ to understand the nature of the ORR active sites in the Co-CNFs.

To clarify the phases of the metallic nanoparticles and carbon of the Co-CNFs, XRD analysis was performed. Fig. 3a presents the XRD patterns of the as-spun PAN nanofibers and Co-CNFs. The pattern of the Co-PAN nanofibers does not exhibit any obvious diffraction peaks, whereas all of the patterns of the Co-CNFs exhibit a broad peak at low angle and some sharp peaks. The broad peak at approximately 25.8° is consistent with graphite. Its broad nature means that the CNFs consist of disordered graphitic structures with low crystallinity.

The main three sharp diffraction peaks at approximately 44.2°, 51.5° and 75.9° are consistent with Co, and the other small peaks except those for Co are consistent with Co$_3$O$_4$ and CoO. For higher Co contents, the diffraction peaks for Co and Co oxides sharpen, which results from the increase in the amount of crystalline nanoparticles, as observed in the TEM images (Fig. 2).

The Raman spectra also demonstrate the structural variation in the Co-CNFs based on the Co content. As observed in Fig. 3b, the Raman spectra of the Co-CNFs exhibit small peaks at low wavenumbers below 800 cm$^{-1}$ and two major peaks at approximately 1360 and 1583 cm$^{-1}$. The small peaks are assigned to the general four Raman-active phonon modes of the Co$_3$O$_4$ phase ($A_{1g}$, $E_{2g}$, $2F_{2g}$).$^{36}$ These metallic phase peaks sharpen with increasing Co content. These results are consistent with the XRD patterns and TEM images.

The two major peaks corresponding to the D (1360 cm$^{-1}$) and G (1583 cm$^{-1}$) bands reflect the carbon structures in the CNFs. The D band is assigned to the $A_{1g}$ mode and is associated with the breakage of symmetry that occurs at the defect sites on the walls and edges of the carbon sheets. The G band corresponds to the $E_{2g}$ active mode of graphite, which consists of two adjacent carbon atoms in a graphene-like structure. The relative intensity ratio of the D and G band peaks ($I_D/I_G$) is used to measure the amount of disorder in the carbon structure. As the defect density in the carbon structure increases, the $I_D/I_G$ value also increases. In the case of highly ordered carbon, the $I_D/I_G$ value is almost close to 0.$^{37}$ The $I_D/I_G$ values of the Co-CNFs were calculated to be approximately 1 regardless of the Co content, which indicates that a large quantity of defects exist in all of the Co-CNFs. The pyrolyzed Co-CNFs have a somewhat disordered carbon structure with defects rather than being ideally graphitic.

To investigate the effects of the Co content on the ORR activities of the Co-CNFs, the RDE currents were measured. Fig. 4a shows the measured ORR activities, of the commercial Pt/C and Co-CNFs catalysts containing various amounts of Co, in an O$_2$-saturated 0.1 M KOH solution at a rotating speed of 1600 rpm. The CNF without Co exhibits very poor ORR activity.

![SEM images of electrospun (a) PAN, (b) Co-PAN nanofibers (5 wt% Co acetate) and (c) CNF, (d) 32.2 wt% Co-CNF after pyrolysis at 900 °C for 1 h under a N$_2$ gas environment.](image-url)
The on-set potential and limiting current density are very low, and the half-wave potential is below 0.7 V. However, Co addition in the CNFs led to a drastic increase in the ORR activity. As the Co content was increased from 0 to 3.1, 15.8 and 32.2 wt%, the half-wave potential increased from 0.664 to 0.791, 0.817 and 0.832 V, respectively, due to an enhancement of the kinetic properties. The 32.2 wt% Co-CNF catalyst exhibited high ORR activity, comparable with that of a commercial 20 wt% Pt/C catalyst. The half-wave potential difference between these two catalysts was only 44 mV. The on-set potential was also high, at near 1.0 V.

The limiting current density also increases with increasing Co content in the CNFs. The limiting current density of NPMCs generally depends on the electron transfer number per mole $(n)$ involved in the ORR. The ORR in aqueous solutions occurs mainly via two pathways: the direct 4-electron reduction pathway from $O_2$ to $H_2O$, and the 2-electron reduction pathway from $O_2$ to hydrogen peroxide ($H_2O_2$). The 4-electron ORR pathway has a low overpotential for the ORR compared with the 2-electron ORR pathway. Therefore, the 4-electron ORR pathway is desirable to minimize voltage loss of PEMFCs.

To verify the ORR pathway of the Co-CNF catalyst, an RRDE experiment was performed. Fig. 4b presents the $H_2O_2$ yield and electron transfer number of the 32.2 wt% Co-CNF catalyst, which were evaluated using the measured disc current and ring current from the RRDE voltammogram (Fig. S2†). The $H_2O_2$ yield was below 10% over the potential range from 0.2 to 0.8 V, and the electron transfer number was about 3.8 over the same potential range. The 32.2 wt% Co-CNF catalyst can catalyze almost a 4-electron oxygen reduction reaction with a low overpotential. This result coincides well with the calculated value based on the Koutecky–Levich plot in Fig. S3.† As shown in Fig. S3,† $n$ increased from 2.26 to 3.28 and 3.81 with increasing Co content in the CNFs. Co in the CNFs has a beneficial effect in enhancing the ORR kinetics of the Co-CNF catalysts. Because the durability is an important key parameter of fuel cell catalysts,

<table>
<thead>
<tr>
<th>Co(II) acetate in the electrospinning solution</th>
<th>Co content in the Co-CNF catalysts after pyrolysis</th>
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<tr>
<td>0 wt%</td>
<td>0 wt%</td>
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<tr>
<td>0.5 wt%</td>
<td>3.1 wt%</td>
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<tr>
<td>2 wt%</td>
<td>15.8 wt%</td>
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<tr>
<td>5 wt%</td>
<td>32.2 wt%</td>
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Table 1 Co contents in the Co-CNFs based on the various Co acetate contents in the electrospinning solution

Fig. 2 TEM images of (a) CNF, (b) 3.1 wt% Co-CNF, (c) 15.8 wt% Co-CNF and (d) 32.2 wt% Co-CNF. (e) Cross-section and (f) HR-TEM images for 32.2 wt% Co-CNF.

Fig. 3 (a) XRD diffraction patterns and (b) Raman spectra of Co-PAN nanofibers (5 wt% Co acetate) and Co-CNF catalysts with various Co contents.
Before and after 10,000 voltage cycles from 0.6 to 1.0 V.

The ORR activity of (c) 32.2 wt% Co-CNF and (d) 20 wt% Pt/C, measured saturated 0.1 M KOH solution, at a rotating speed of 1600 rpm. The electron transfer number of the 32.2 wt% Co-CNF catalyst in O2- is 2 e-

Therefore, elucidation of the exact ORR active sites, which is mainly related to structural characteristics, based on a suitable mechanistic study, has been a key issue in understanding the ORR mechanism of M–N–C catalysts.

From our structural and electrochemical analysis in the above sections, we know that both the structural characteristics and catalytic activity are strongly dependent on the Co content in the CNFs. The amount of Co nanoparticles increases with increasing Co content in the CNFs. In addition, Co addition to the CNFs has beneficial effects on the ORR kinetics of the Co-CNF catalysts.

Among the various proposed mechanisms, the dual-site mechanism of Olson et al. has been widely recognized as an appropriate mechanism to evaluate the ORR mechanism in alkaline media. Among the various proposed mechanisms, the dual-site mechanism, M–N–C-type catalysts contain two distinct classes of active surface species. The primary active sites are Co-Nx bonds, and the secondary active sites are Co or Co3O4 particles, hence the ORR occurs via serial 2 × 2 electron transfer pathways as follows:

$$\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{HO}_2^- + \text{OH}^- \quad (1)$$

$$\text{HO}_2^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow + 3\text{OH}^- \quad (2)$$

$$2\text{HO}_2^- \rightarrow \text{O}_2 + 2\text{OH}^- \quad (3)$$

The Co-Nx site supports the initial adsorption of the O2 molecule and conversion of O2 to the intermediate reaction product by a 2 e- reduction reaction, as described in eqn (1). The byproducts that are formed in the first reaction step can further react at a decorating Co3O4 or Co nanoparticle phase.

In this sense, the Co addition to the CNFs would have beneficial effects on the formation of Co-Nx and Co or Co3O4 particle-based active sites, and then the ORR activity is enhanced by the increase in the ORR active site density. Structural analysis provides sufficient evidence for increasing the secondary active sites, Co or Co3O4 particles, upon increasing the Co content in the CNF. However, the variation of the primary ORR active site, the Co-Nx bond, due to the Co addition, requires further analysis for verification.

Because Co and N play an essential role in the formation of the Co-Nx sites, XPS analysis was conducted to investigate the differences in the chemical states of Co and N due to the Co addition. The Co 2p peak analysis in Fig. S4† shows clear Co 2p3/2 and Co 2p1/2 peaks, each of which is composed of two components from CoO and Co3O4 as demonstrated by the XRD

### Table 2

| Binding energy of each N (graphitic, pyrrolic, pyridinic) in the Co-CNFs based on the Co contents |
|---------------------------------|---------------------------------|---------------------------------|
| CNFs                            | 401.0 eV                        | 400.1 eV                        | 398.0 eV                        |
| 3.1 wt% Co-CNFs                 | 401.0 eV                        | 400.1 eV                        | 398.3 eV                        |
| 15.8 wt% Co-CNFs                | 401.0 eV                        | 400.1 eV                        | 398.3 eV                        |
| 32.2 wt% Co-CNFs                | 401.0 eV                        | 400.1 eV                        | 398.3 eV                        |

as well as the activity, AST was conducted by potential cycling between 0.6 and 1.1 V in an Ar-purged 0.1 M KOH solution with a scan rate of 50 mV s-1. After 10,000 cycles, the 32.2 wt% Co-CNFs and 20 wt% Pt/C catalyst showed a negative shift of the half-wave potential by 30 and 50 mV, respectively as shown in Fig. 4c and d. These results demonstrate that the Co-CNF catalyst has better durability than the commercial Pt/C catalyst.

### Elucidation of ORR active sites in the Co-CNFs

The ORR mechanism of M–N–C catalysts is complicated and is a controversial subject. Although various mechanistic studies have been proposed, the nature of the ORR remains unknown. Therefore, elucidation of the exact ORR active sites, which is mainly related to structural characteristics, based on a suitable
patterns and Raman spectra (Fig. 3). However, the Co 2p spectroscopic signals of Co-CNF catalysts provide no information about Co-Nx sites. Most of the previous works on M–N–C catalysts also provide XPS analysis on M–Nx bonds from N 1s peaks, not from M 2p peaks.\textsuperscript{7,13} The N 1s peak analysis results are presented in Fig. 5. The CNFs and Co-CNF catalysts exhibit pyridinic N at 398.0 eV (±0.1 eV), pyrrolic N at 400.1 eV (±0.1 eV) and graphitic N at 401.1 eV (±0.1 eV). These states are the major nitrogen states in the graphene-like carbon structure.\textsuperscript{41} The CNFs contain graphitic N as the dominant nitrogen state. However, the dominant nitrogen state changes based on the Co content in the CNFs. As the Co content increases, the intensity fraction of pyridinic N increased from 38.8 to 51.5%; however, the intensity fraction of graphitic N decreased from 45.6 to 34.4%. No significant changes were observed in the pyrrolic N (from 15.6 to 14.1%) and overall N contents (from 6.6 to 7.1 at.%). The 32.2 wt% Co-CNF catalyst contains pyridinic N as the dominant nitrogen state. Pyridinic N is an edge-plane heteroatom, and graphitic N is an in-plane heteroatom of the graphene-like carbon structure. When Co is introduced in the PAN nanofibers, Co atoms may behave as an impurity phase to prevent successful carbonization. Therefore, a high amount of Co would lead to an increase in edge-plane defects such as pyridinic N, rather than graphitic N.

It is generally accepted that pyridinic N contains a lone electron pair in the plane of the carbon matrix to promote the ORR. The pyridinic N content is often correlated to the ORR activity of M–N–C catalysts.\textsuperscript{42,43} Recent work involving density functional theory calculations proposed that if a transition metal combines with pyridinic N in a graphene-like carbon structure, the binding energy of pyridinic N shifts in the positive direction.\textsuperscript{44}

We have calculated the binding energy of each N in the Co-CNFs, and the results are summarized in Table 2. As observed in Table 2, the binding energy of graphitic N and pyrrolic N does not change, regardless of the Co addition. Unlike other nitrogen states, the binding energy of pyridinic N shifted in the positive direction by approximately 0.3 eV when Co was added in the CNFs, which provides important evidence for the formation of Co–pyridinic N\textsubscript{x} bonds, which are the primary ORR active sites in the Co-CNFs.

Finally, we conducted two experiments to validate the ORR function of each active site. The first experiment was a CN\textsuperscript{−} poisoning experiment, to impede the ORR on the Co–N\textsubscript{x} bond by CN\textsuperscript{−} adsorption.\textsuperscript{13} The second one involved acid leaching to remove Co nanoparticles in the Co-CNFs. The aim of each experiment was to inhibit the ORR function of the primary and secondary active site, respectively. For the CN\textsuperscript{−} poisoning experiment, 10 mM KCN was added to a 0.1 M KOH solution, and the acid leaching of Co-CNFs was performed in an 80 °C 0.5 M H\textsubscript{2}SO\textsubscript{4} solution for 24 h. As shown in Fig. 6, the half-wave potential and limiting current density decreased in both experiments. The ORR activity of the Co-CNFs may deteriorate even if only one site is limited. Therefore, the high ORR activity of the 32.2 wt% Co-CNF catalyst is attributed to synergetic effects, caused by increasing both the number of Co–pyridinic N\textsubscript{x} bonds and Co nanoparticles.

**Conclusions**

Uniform and 1-D nanostructured Co-CNF catalysts, containing various amounts of Co, were synthesized using a facile electrospinning technique followed by pyrolysis. The electrospun Co-PAN contained a nanofibrous structure with a fiber diameter of 500 nm. After pyrolysis at 900 °C, the Co-PAN nanofibers were transformed into Co-CNFs, and metallic nanoparticles were formed. These metallic nanoparticles were partially embedded in the graphitic carbon layer. The carbon structure was somewhat disordered rather than being an ideal graphite structure, and the metallic nanoparticles were confirmed to be the Co and Co\textsubscript{3}O\textsubscript{4} phases from XRD and Raman analysis. The ORR activity of the Co-CNFs also increased with increasing Co content. The 32.2 wt% Co-CNF catalyst exhibited high ORR activity, comparable with that of a commercial Pt/C catalyst. The half-wave potential difference was only 44 mV. Moreover, this catalyst was capable of catalyzing almost a 4-electron ORR pathway (n = 3.81). The high ORR activity of the Co-CNF catalyst may be attributed to an increase in the number of ORR active sites. According to the dual-site mechanism, there are two active sites in M–N–C catalysts. The primary active sites are the Co–N\textsubscript{x} bonds, and the secondary active sites are the Co nanoparticles. The XPS N 1s peak analysis revealed that the Co addition leads to an increase in the number of Co-pyridinic N\textsubscript{x} bonds. In addition, the amount of Co nanoparticles also increased with increasing Co content, as observed in the TEM images. Additional CN\textsuperscript{−} poisoning and acid leaching experiments also validated the ORR function of each active site. For the highly active
CNF-based M–N–C catalysts, a strategy is needed to increase both active sites, the M-pyridinic N bonds and the metallic nanoparticles.

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Notes and references