Novel N-Doped Carbon Cathode Catalyst for Polymer Electrolyte Membrane Fuel Cells Formed on Carbon Black

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Carbonization of Co–[poly(4-vinylpyridine)] (Co–PVP) complex on carbon black gave rise to oxygen reduction reaction (ORR) activity. Surface analysis revealed that the activity was caused by the introduction of nitrogen on to the surface of the carbon black but not by the presence of residual cobalt.

Development of a non-platinum catalyst is required for the practical utilization of polymer electrolyte membrane fuel cells (PEMFC). Metal carbides,[1] metal oxynitrides,[2] and macrocyclic N₄-complexes and their pyropolymers[3–5] have been considered as candidates. We have clarified that the introduction of nano-shells[6] and doping with nitrogen and/or boron[7,8] are the crucial factors in activating oxygen reduction reaction (ORR) activity on carbons. In addition, the combination of these two factors provides more active catalysts.[9,10] Ikeda et al. conducted first-principles simulations suggesting that the graphite-like nitrogen located on the three-coordinated sites in a zig-zag edge was responsible for catalyzing ORR.[11] Niwa et al. confirmed the above theoretical study by using synchrotron radiation spectroscopy.[12]

We have prepared carbon catalysts by pyrolyzing starting polymers. The introduction of carbon materials such as carbon black with fractal surface morphology is highly expected to modify the carbonization process. Indeed Kanno et al. claimed a suppressive effect on thermal expansion from the addition of carbon black during the carbonization process, clearly indicating that modification had occurred during the initial carbonization process of the pitch.[13] If we mix a metal complex polymer with thermoplasticity with carbon black, some crucial effects takes place. In this letter, we would like to report the formation of a new type of N-doped carbon catalyst for ORR together with our preliminary characterization results.

Preparation of the Co-complex polymer was performed by stirring poly(4-vinylpyridine) (PVP) (1 g, 9.51 mmol) and anhydrous cobalt(II) chloride (0.62 g, 4.76 mmol) in ethanol at room temperature for 12 h, followed by Soxhlet extraction to retrieve the pure Co-complex polymer (PVP–CoCl₂) as a solid residue in a thimble. The obtained Co-complex polymer was mixed with carbon black (KB, EC600JD, LION) at a mass ratio of 30/70 in an agate mortar (Co–PVP/KB). The mixture was subjected to carbonization at 1000 °C for 1 h. in a nitrogen stream, where the heating rate was 10 °C min⁻¹. The obtained carbonized samples were pulverized by agate mortar and pestle into particles under 106-μm diameter. Finally the sample was acid-washed with concentrated HCl in order to remove the possibility of cobalt species participating in the catalytic action of the carbon (Co–PVP/KB1000). The above-mentioned procedure from carbonization to acid washing was also applied to the KB and the Co-complex polymer individually to prepare the control samples, which are referred to as KB1000 and Co–PVP1000, respectively.
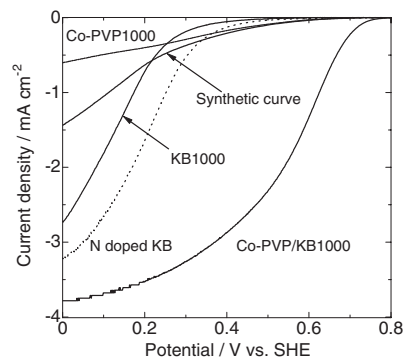

Figure 1. Polarization curves for prepared sample and the synthetic curve (arithmetic curve of KB1000 and Co–PVP1000) which is the theoretical curve of Co–PVP/KB1000, N-doped KB (prepared by the ammo-oxidation method, N/C = 0.012). The mass of catalyst is 57 μg.

The introduction of Co–PVP to the carbon black resulted in a remarkable improvement in the ORR activity. Figure 1 shows the linear sweep voltammogram of the carbons prepared in this study, which was obtained by rotating electrode voltammetry under the following electrolytic conditions: rotating speed was 1500 rpm, the electrolyte was 0.5 M H₂SO₄ saturated with O₂ gas at room temperature, the potential sweep rate was 1 mV s⁻¹. As shown in Figure 1, Co–PVP/KB1000 exhibited the highest E_{O_2} of 0.77 V vs. SHE, where E_{O_2} was defined as the potential giving a current density of −10 μA cm⁻². This was higher than the E_{O_2}'s of the carbon black (0.50 V) and Co–PVP1000 (0.69 V). Although the E_{O_2}'s of Co–PVP1000 and Co–PVP/KB1000 are quite similar to each other, the current density of Co–PVP1000 was obviously smaller than that of Co–PVP/KB1000. The voltammogram for Co–PVP/KB1000 exceeded the synthetic curve obtained by arithmetic summation of the constituents (i.e., KB1000 and Co–PVP1000), which clearly indicated a synergetic effect caused by the combination of KB and Co–PVP1000.

Figure 2 shows the mixing state of Co–PVP/KB, where the constituents are roughly dispersed but not in intimate contact. When the mixture was heat-treated at 390 °C, the melting point of the polymer, most of the carbon black particles were embedded in the melted polymer. Thermogravimetry of Co–PVP/KB showed a large weight loss at 400 °C. At this temperature, Co–PVP spread over the KB surface, which guaranteed an intimate contact between Co–PVP and KB. The large BET surface area of the carbon black (1260 m² g⁻¹) was halved by the incorporation with Co–PVP, even after carbonization (670 m² g⁻¹). This is another piece of evidence of the intimate contact between Co–PVP and KB.

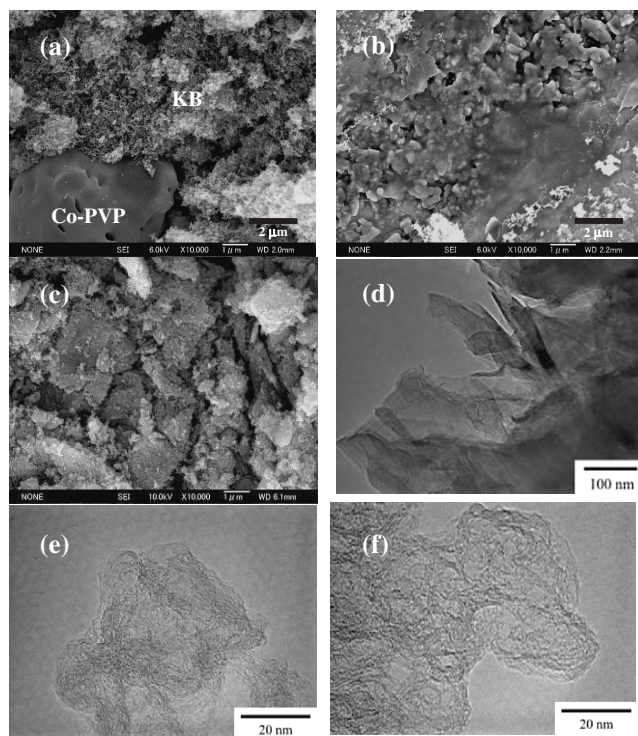The surface chemical compositions obtained by X-ray pho-

Figure 2. SEM images of (a) Co–PVP/KB1000 before heat treatment, (b) Co–PVP/KB heat-treated at 390 °C and (c) Co–PVP/KB1000, and TEM images of (d) Co–PVP1000, (e) Co–PVP/KB1000, and (f) KB1000.

Table 1. XPS surface composition of the prepared samples

Sample	XPS analysis/atom %			
	C	N	O	Co
Co–PVP/KB1000	98.0	0.2	1.7	ND[a]
KB1000	97.8	0.0	2.2	—
Co–PVP1000	96.3	0.4	3.3	ND

[a]Not detected.

toelectron spectroscopy (XPS) are tabulated in Table 1. Obviously the acid washing was completed since no cobalt was observed. The most important finding is the introduction of nitrogen atoms to Co–PVP/KB1000 at the expense of the oxygen atoms. Similar N1s XPS spectra observed for Co–PVP1000 and Co–PVP/KB1000 as shown in Figure 3, indicate the formation of no additional nitrogen species in the latter sample.

The TEM images of the carbonized samples are shown in Figures 2c–2e. Co–PVP1000 exhibited the formation of flaky carbon. Rarely, the formation of nanoshells with diameters larger than 50 nm was observed. The Co–PVP/KB1000 included a structure that was different from the original stacking structure observed for KB1000 (Figure 2f). However, the complicated and diverse structure of the KB did not allow the newly introduced structure to be distinguished from the original structure.

Two characteristic features were observed for Co–PVP/KB1000: the formation of the carbon structure originated from the Co–PVP polymer complex and the introduction of nitrogen atoms to the product carbon. These features could be responsible for the synergetic enhancement of ORR in Co–PVP/KB1000. Although the structure formed was far from being a nanoshell structure and still needs to be investigated, the introduction of
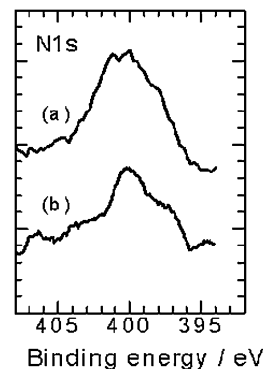

Figure 3. XPS spectra of the N1s peaks of (a) Co–PVP1000 and (b) Co–PVP/KB1000.

nitrogen must be taken into account as an explanation for the ORR activity. Ammo-oxidation has previously been employed to introduce nitrogen atoms into carbon black, and this turned out to enhance the ORR activity.[12] However, the increase in the ORR activity was less than that in the present study of Co–PVP/KB1000 (N/C = 0.002), in which even the nitrogen content was higher. We have claimed that the formation of nanoshells and the introduction of nitrogen atoms are critical requirements for ORR catalytic activity of carbons. Co–PVP/KB1000 showed excellent ORR activity, though it has neither a nanoshell structure nor a surface metal species. Yuasa et al. prepared a similar cobalt complex catalyst supported on carbon black (CoPPy/CB) and reported that the maximum ORR activity was obtained when the catalyst was heat-treated at 700 °C.[14] Whilst, our catalyst gained the highest activity upon heat treatment at 1000 °C and contained detectable amount of cobalt by XPS. Hence, our catalyst works on different activation mechanisms from Yuasa's catalyst. These facts indicate that the present catalyst could be a new class of carbon catalysts for ORR. Further structural studies are being conducted in our laboratory.

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