A Metal Coordination Polymer for Fuel Cell Applications: Nanostructure Control Toward High Performance Electro catalysis*

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Metal coordination polymers, such as cobalt-coordinated polypyrrole (CoPPy), have attracted much attention, because they are promising alternatives to oxygen reduction electrocatalysts for fuel cell applications, owing to their high oxygen reduction activity as well as corrosion protection performance. In this catalyst, incorporated cobalt acts as the catalytic active site for the catalytic reaction. Thus, if we can increase the number of active cobalt sites, the catalytic activity should increase. We demonstrated the improvement of catalytic activity of CoPPy, i.e., increase of cobalt sites, by the nano-scale structure control using appropriate counter-ion doping. We found that the inter-chain distance of PPy with dodecylbenzensulfonic acid (DBS) was significantly increased, up to 4.8 Å, while inter-chain distance of PPy with chloride ion was 3.4 Å. Also, the amount of cobalt on CoPPy-DBS was five times larger than that of CoPPy-Cl. This result indicates that the amount of the cobalt sites increase and consequently the catalytic activity is enhanced when the inter-chain distance increased by counter-ion doping.

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I. INTRODUCTION

Fuel cells, which directly convert the chemical energy of a chemical reaction between hydrogen and oxygen into electricity by electrochemical reactions, are expected to be a highly efficient and environmentally friendly next generation energy source. The critical technological hurdle for wide spread use of fuel cells is improvement of catalysts that promote the electrochemical reactions of fuel cells. Although platinum and platinum-based materials are the best fuel-cell catalysts, they have a durability problem, i.e., they dissolve and agglomerate at high potentials in acidic electrolytes (under the fuel-cell operating conditions), and their cost is very high. Thus, development of low cost, preferably non-platinum, oxygen reduction catalysts having higher catalytic activities and higher durability is the main research interest in this field.

While considerable amount of work has been carried out in order to find effective non-platinum catalysts, such as non-noble metal alloys and chalcogenides, no effective catalyst has been found yet: the catalytic activity of these metal based catalysts is still insufficient, and they are less stable than platinum-based catalysts. Metal coordination complexes, such as metallophthalocyanines and other macrocyclic transition metal complexes, have also been extensively investigated since low cost transition metal can be used [1]. In these catalysts, the metal-nitrogen centers are considered as the active oxygen reduction reaction (ORR) sites. The electronic state of metal in the metal-nitrogen center is tuned to a suitable one for ORR, showing very high open circuit potential [2]. Overall catalytic activities of such metallo-organic complexes are, however, still insufficient because the density of active sites is low due to their large macrocyclic structure. Besides, durability is also insufficient: such a complex is unstable in acidic conditions at high potential.

Newly developed metal coordination polymers, such as cobalt coordinated polypyrrole, are potentially better catalysts than metal coordinated complexes. Like metallo-complexes, they have tunable transition metal-nitrogen centers effective for oxygen reduction, but, unlike metallo-complexes, periodically arranged nitrogen of polypyrrole enables high-density arrangement of metal-nitrogen centers. Moreover, the polymers are much more stable in acidic solutions even at high potentials. Indeed, Yuasa et al. and Bashyam and Zelenay showed cobalt coordinated polypyrrole (CoPPy) has relatively high activity and high durability in acidic electrolytes [3, 4]. The performance, however, seems to be able to be improved more since the amount of cobalt sites is not enough, less than 20 % of full nitrogen sites, in their polymers.

In this paper, we report our novel approach to increasing the amount of incorporated cobalt for improving the catalytic activity, controlling the nanostructure of PPy using appropriate counter ion doping. We succeeded in increasing the number of incorporated cobalt atoms, more than five times larger, and increased open circuit potential as well as the oxygen reduction current.

II. EXPERIMENTAL

Our synthesis method of cobalt coordinated polypyrrole (CoPPy) consists of two parts: the polymerization of pyrrole and the incorporation of cobalt ions into the obtained PPy particles. Polypyrrole was prepared by the chemi-

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chemical polymerization using ferric salt as the oxidizer. Pyrrole monomer was mixed and stirred with a ferric salt in methanol solution, and then the PPy black particles were obtained. During this process, the anion of ferric salt was incorporated into PPy particles as a counter ion. In the same way, we can choose counter ions incorporated into PPy particles by changing the anion of ferric salts. We chose three counter ions, chloride, dodecylsulfonic acid (DS), and dodecylbenzensulfonic acid (DBS), that have different sizes and structures, as shown in Fig. 1. Cobalt ions were incorporated by immersing PPy particles in a solution of acetate tetrahydrate in methanol. The suspension involving PPy and Cobalt ion was refluxed under nitrogen atmosphere. After cooling down to room temperature, the product was collected by filtration, washed with ethanol and water, and finally dried to obtain CoPPy.

The structure, i.e., the inter-chain distance of obtained PPys with three different counter-ions, was characterized by x-ray diffraction (XRD) with Cu Kα radiation (λ = 1.54 Å). The fraction of cobalt in the pyrrole rings (Cobalt/Nitrogen of Pyrrole ring) was estimated by x-ray photoelectron spectroscopy (XPS). Then we investigated the relationship between the amount of incorporated cobalt and the inter-chain distance. The electrochemical behaviors and the oxygen reduction reaction of CoPPy were characterized by standard three-electrode electrochemical measurement in 1M perchloric acid solution. Scan rate was 5 mV/s. The sample was mounted on highly oriented pyrolytic graphite (HOPG) electrode with Nafion ionomer. The reference electrode was Ag/AgCl. In this article, the potential is described with respect to normal hydrogen electrode (NHE).

III. RESULTS AND DISCUSSION

Figure 2 shows XRD profiles of three PPys, i.e., PPy-Cl, PPy-DS, and PPy-DBS. The diffraction intensity is plotted against d-spacing calculated by Bragg’s law (d = \( \frac{\lambda}{2 \sin \theta} \), 2θ : diffraction angle). Broad peaks, which correspond with the nearest neighbor inter-chain distance are observed in all profiles. We can see that the inter-chain distance varies with counter-ions. While the inter-chain distance of PPy-Cl is 3.4 Å the inter-chain distances of PPy-DS and PPy-DBS become wider, 3.6 Å and 4.8 Å respectively. This result indicates that the nano-structure of PPys, such as the inter-chain distance is controllable by choosing desirable counter-ions.

Then the amount of incorporated cobalt in our CoPPy was measured by using XPS. The relationship between the fraction of incorporated cobalt ions to the number of pyrrole rings (nitrogen) and the d-spacing value (inter-chain distance) of the polymers is summarized in Fig. 3. The fraction of incorporated cobalt in CoPPy-DBS was five times larger than that of CoPPy-Cl. The detail mechanism of this phenomena is not currently clear, but we might speculate that a wide inter-chain structure is appropriate for incorporating cobalt ions with radii 0.74 Å i.e., nearly 1.5 Å in diameter [6]. The amount of cobalt involved in CoPPy with toluenesulfonic acid (TS) reported by Yuasa was estimated to be at most 20 atm% of overall...
The peaks observed at 781.7 and 797.5 eV are assigned to shows the cobalt 2p XPS spectrum for our CoPPy-DBS.

FIG. 6: Cyclic voltammogram of PPy-DBS. The black and red curves correspond to CVs at nitrogen purged electrolyte and oxygen saturated electrolyte, respectively.

pyrrole in the polymers [3]. The amount of cobalt in our CoPPy-DBS was two times larger than that of CoPPy-TS.

The electronic states and coordination structure were further investigated by Co 2p and N 1s XPS. The spectral features indicate that the electronic state of cobalt in CoPPy-DBS is divalent and the cobalt is connected with nitrogen atoms involved in pyrrole rings. Figure 4 shows the cobalt 2p XPS spectrum for our CoPPy-DBS. The peaks observed at 781.7 and 797.5 eV are assigned to spin-orbit doublet, i.e., excitation from 2p3/2 and 2p1/2, respectively, indicating that cobalt was in divalent state. On the other hand, we did not observe any peaks around 778 eV. This suggests that bulk metallic cobalt is not involved in our PPys.

FIG. 5: N 1s XPS spectrum obtained for CoPPy-DBS. The peak at 398.1 eV which did not appear on N 1s XPS spectrum for PPy-DBS was observed.

The electrochemical behaviors of our PPys (before Co incorporation) were characterized by cyclic voltammetry. Figure 6 shows the cyclic voltammogram of PPy-DBS taken in 1M HClO4 solution. Under inert nitrogen atmosphere, we did not observe any redox reactions, but the discharge and charge for the electric double layer occurred on the surface. In the presence of oxygen, weak oxygen reduction reaction was observed below 0.5 V. Such oxygen reduction behaviors were also observed in other conducting polymers [7].

FIG. 7: Cyclic voltammograms obtained at nitrogen-purged electrolyte. The black curve corresponds to the CV of PPy-DBS. The green, red, and blue curves correspond to the CVs of CoPPy-Cl, CoPPy-DS, and CoPPy-DBS, respectively. Broad peak incidented by arrows suggests redox reaction of incorporated cobalt.

Figure 7 shows cyclic voltammograms of CoPPy-Cl, CoPPy-DS, and CoPPy-DBS. We observed a redox reaction behavior around 0.5 V, and the current associated with the redox reaction increased as the amount of coordinate cobalt increased, namely, in the order of CoPPy-Cl, CoPPy-DS, and CoPPy-DBS. This result indicates that this redox reaction originates in incorporated cobalt. Similar behaviors are found in cobalt coordination organic complexes: for example, cobalt coordinated phthalocyanine shows redox reactions around 0.9 and −0.2 V that are ascribed for Co II/Co III and Co I/Co II valence changes, respectively [1]. Thus, the observed redox reaction of

http://www.ssj.org/ejsnt (J-Stage: http://www.jstage.jst.go.jp/browse/ejsnt/)
CoPPy could also be related with the valence change of cobalt.

Oxygen reduction behaviors of CoPPy-Cl, CoPPy-DS, and CoPPy-DBS are shown in Fig. 8. We can see that oxygen reduction reactivity significantly improves as the number of active cobalt sites increases. The open circuit potentials increase to 0.72 V and 0.76 V for CoPPy-DS and CoPPy-DBS, respectively, while that of CoPPy-Cl was as low as 0.69 V. Oxygen reduction currents at 0.6 V were also improved: the ORR current for CoPPy-Cl, CoPPy-DS, and CoPPy-DBS were 0.17 μA, 1.29 μA, and 7.65 μA: the maximum current is more than five times larger. These results indicated that increasing the amount of coordinate cobalt by the control of nano-scale structure is effective at improving oxygen reduction activity of CoPPy. This opens up the possibility of making the platinum alternative catalyst by increasing the amount of cobalt sites of CoPPy.

IV. CONCLUSION

To improve the ORR activity of CoPPy, i.e., to increase the number of active cobalt sites, we attempted to control the nanostructure of polymer that might affect metal incorporation phenomena. We synthesized three kinds of PPy with different counter-ions (Cl, DS, and DBS). We found that much cobalt can be incorporated when the inter-chain distance of PPy increases. The maximum inter-chain distance (4.8 Å) was obtained for PPy-DBS, and the amount of coordinate cobalt increased to about five times that of CoPPy-Cl. The ORR activity also improved as the amount of coordinate cobalt increased. The OCP of CoPPy-DBS was 0.76 V. Increasing active cobalt sites by controlling nano-scale structure is one effective way to improve oxygen reduction activity in CoPPy systems.

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