

# PREPARATION OF FINELY DISPERSED NANOSHELL CARBONS BY USING PENDANT-TYPE COBALT PHTHALOCYANINE

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## Abstract

A number of studies have been conducted to look for non-platinum catalysts for cathode in proton exchange membrane fuel cell (PEMFC). Our stance in dealing with this issue is to establish methodology to prepare carbons with activity for oxygen reduction reaction (ORR), which is based on modification of the carbonization processes by the actions of additives. The most promising result of ours is the introduction of a type of nanostructure to carbon materials, i.e. nanoshell. Nanoshell is formed by carbonization of polymers in the presence of metal complexes such as cobalt phthalocyanine, and has a unique structure such as hollow nanosphere made of graphene. Smaller sizes were preferable for higher ORR activity since such small nanoshells tended to possess surface defects acting as active sites. Hence the requirement for the preparation of nanoshells is to reduce the size by suppressing the aggregation of the metal complexes in the carbon precursor polymer matrix. Pendant-type cobalt phthalocyanine complexes were synthesized and used as catalysts for carbonization of a phenol-formaldehyde resin. The sizes of the nanoshells were approximately 20 nm of diameters, which led to the enhanced activity for ORR of the carbons.

## Introduction

Development of a non-platinum cathode catalyst is a key point for the development of practical uses of proton exchange membrane fuel cells (PEMFC). The present authors have been interested in the preparation of carbon-based catalysts by modifying their preparations. We have revealed that two types of modifications were promising for that purpose; one is to introduce nanoshell carbons by the catalytic action of transition metals in carbonization, and another is to dope nitrogen and/or boron atoms into carbon.

Previously, we have realized that the formation of the nanoshell is essentially important for showing catalytic activity, however we have also revealed that excess formation of the nanoshell resulted in a decrease in the activity. The active nanoshells usually appeared with diameters as small as 30-50 nm, of which the surfaces were surrounded by defective graphene patches. On the other hand, the nanoshells with lower activity commonly have large diameters (>50nm), of which surfaces were surrounded by well-aligned graphenes. We consider that the defective sites act as active sites for oxygen reduction reaction (ORR), which would be introduced by reducing the diameters of the nanoshells.

In the present paper we employed pendant-type cobalt phthalocyanine complexes as the reagent for the preparation of nanoshell with smaller diameter. The use of the pendant-type cobalt phthalocyanine complexes instead of using a cobalt phthalocyanine monomer were expected to achieve the formation of smaller nanoshells by suppressing the crystal growth the cobalt particles, since the present method can provide spatially dispersed phthalocyanine moieties.

## Experimental

### *Sample Preparation*

The pendant type cobalt phthalocyanines were prepared by condensation of tetraaminophthalocyaninato cobalt (II) (Wako Pure Chemicals Co. Ltd.) and poly (acrylic acid) (Wako Pure Chemicals Co. Ltd, MW 25,000). They were reacted in water by heating in oil bath at 120 °C for 12 h. After the reaction, the solvent was removed by using a rotary evaporator. Two types of polymers were prepared, of which the differences were in the numbers of the vinyl unit. The ratios of the phthalocyanine unit to the vinyl unit were selected as two and five, which were referred to as p-CoPc2 and p-CoPc5, respectively.

The obtained cobalt complexes were mixed to a novolac type phenol-formaldehyde resin by a laboratory kneader operated in Ar atmosphere at 130°C and at 300rpm for 10min. The mixing ratio was fixed at 3wt% Co based on the weight of the phenol-formaldehyde resin.

Carbonization of the mixtures was performed by heating them at a predetermined temperature, 800~1200°C in a nitrogen flow. The heating rate and the carbonization duration were chosen as 10°C/min and 1h, respectively. After carbonization, the samples were pulverized by using a planetary ball mill (P-7, Fritsch). In order to remove the metal impurities, the samples were washed by HCl. The carbons were thoroughly rinsed with distilled water until the supernatant solution became neutral. The samples were dried under vacuum overnight, and then they were supplied to further measurements such as X-ray diffraction, transmission electron microscopy, N<sub>2</sub>-adsorption.

### Electrochemical measurement

The activity for oxygen reduction reaction (ORR) was evaluated by rotating disk electrode voltammetry by using the prepared carbons as the working electrodes. Fabrication of the working electrode was done by pasting a carbon onto a glass-like carbon disk electrode (6mm $\phi$ ) with a binder, Nafion®, where the formulation of the carbon-Nafion® mixture - catalyst ink - was as follows; 5 mg of carbon was mixed with 50  $\mu$ l Nafion® solution (5% soln., Aldrich), 150  $\mu$ l ethanol and 150  $\mu$ l water in a plastic vial under ultra-sonication. Four micro liters of the ink was pasted evenly onto the glass-like disk electrode followed by drying in a water-vapor saturated vessel. The nominal surface density of the carbon catalyst on the electrode was 0.2 mg/cm<sup>2</sup>.

The electrolyte was 0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous solution, and the counter and the reference electrodes were a platinum plate and an Ag/AgCl electrode, respectively. The potential of the electrodes was controlled by a potentiostat (ALS700, BAS Japan Inc.) through a Luggin capillary that was positioned in the vicinity of the working electrode. All electrochemical measurements were performed at room temperature.

Oxygen reduction voltammogram was obtained with rotating the electrode by using a RRDE unit (RRDE-1, Nikko Keisoku Ltd.). First, a blank voltammogram was obtained in de-aerated 0.5M H<sub>2</sub>SO<sub>4</sub> solution by sweeping the potential at 1 mVs<sup>-1</sup> with a rotation rate of 1500 rpm. After sweeping the potential, the electrolyte solution was saturated by way of oxygen bubbling for 20 min, and was used for recording an oxygen reduction voltammogram. Finally, the net voltammogram for oxygen reduction was obtained by subtracting the voltammogram obtained in the nitrogen saturated electrolyte from the one obtained in the oxygen saturated electrolyte.

## Results and Discussion

### Pendant-type Complexes

The FTIR spectra of the obtained samples clearly showed the disappearance of COOH group on poly(acrylic acid) and the formation of CONH group, which confirmed the formation of amide bonds due to the reaction between COOH on the poly (acrylic acid) and NH<sub>2</sub>Cl on the phthalocyanine derivative.

### Structure of Carbons

The X-ray profiles of the carbons were mainly composed with (002) and (10) diffraction lines. With the increase in the carbonization temperature, the development of the (002) lines were obvious while the development of the (10) lines were stable. Such development in (002) lines continued up to 1000°C, however it conversely decreased when the carbonization was performed at 1200°C. This indicated abrupt changes in the crystalline structure of the carbons during the carbonization between 1000 and 1200°C.

For further comparison of the crystalline structure, the interlayer spacing,  $d_{002}$ , and the dimension of the stacking,  $L_c$ , are listed in Table 1. The interlayer spacing,  $d_{002}$ , was 0.34 nm for all of the samples, indicating the presence of turbostratic structure. The abrupt increases between 1000 and 1200°C are clearly expressed in terms of  $L_c$ ; i.e. the stacking thickness increased up to 1000°C and showed sudden decreases at 1200°C.

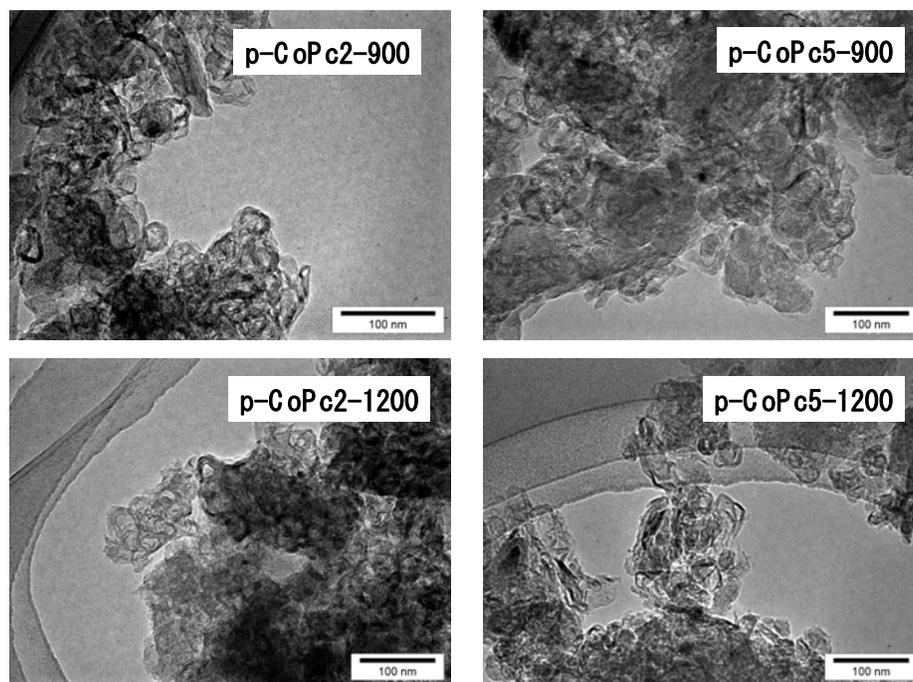
The results of the N<sub>2</sub>-adsorption are also presented in Table 1. Except for p-CoPc2-800, the carbons showed similar BET surface areas of about 300m<sup>2</sup>/g. The mesopore volumes,  $V_{meso}$ , were also similar for all of the samples. So, the porosity of the carbons was not affected by the kinds of the pendant-type complexes nor by the carbonization temperature.

**Table 1.** Structural Parameters of the Prepared Samples.

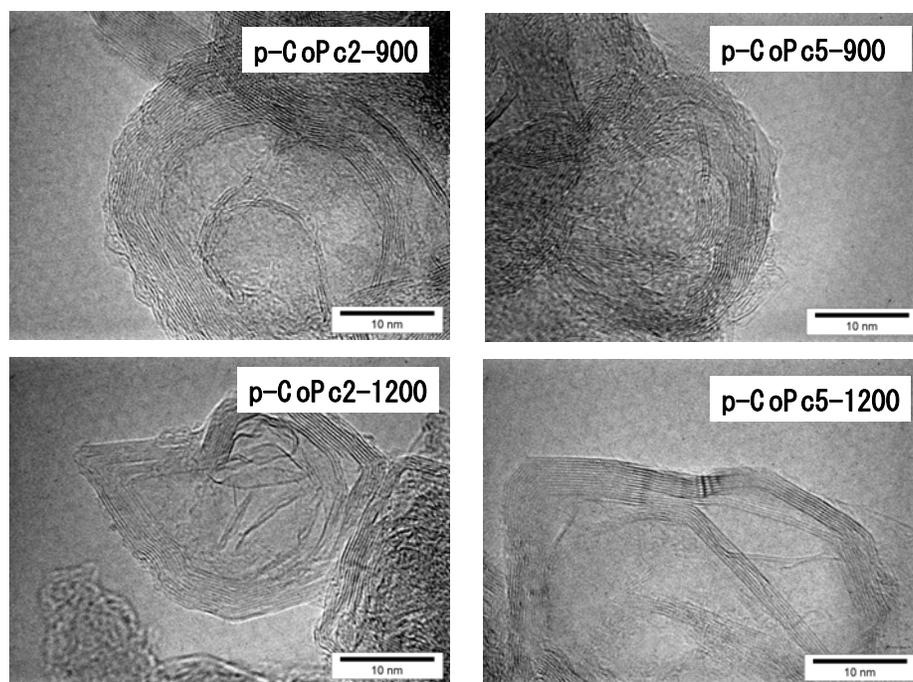
	HTT (°C)	XRD		N <sub>2</sub> -adsorption	
		$d_{002}$ (nm)	$L_c$ (nm)	$S_{BET}$ (m <sup>2</sup> /g)	$V_{meso}$ (cc/g)
p-CoPc2	800	0.34	2.6	231	0.22
	900	0.34	2.7	333	0.21
	1000	0.34	3	354	0.23
	1200	0.34	2.3	301	0.31
p-CoPc5	800	0.34	1.2	349	0.19
	900	0.34	2.3	315	0.2
	1000	0.35	3.2	300	0.23
	1200	0.35	2.5	329	0.27

Figure 2 shows the comparison of the TEM images of the selected samples with different carbonization temperatures. Obviously, the nanoshell, represented by the foam-like structure, was observed for all of the samples prepared in the present

study. The formation of the nanoshell started at 800°C, and the fringes of the nanoshell became clearer. The magnified images of the nanoshell are presented in Figure 3. In the cases of the samples prepared at lower temperatures than 1000°C, the shapes of the nanoshells are convex. The nanoshells prepared at 1200°C showed clearer alignments of graphene with linear shape, and sometimes concave structures were also observed. In this sense, the crystalline structure of the nanoshell changed abruptly by the increase of the carbonization temperature from 1000°C to 1200°C.



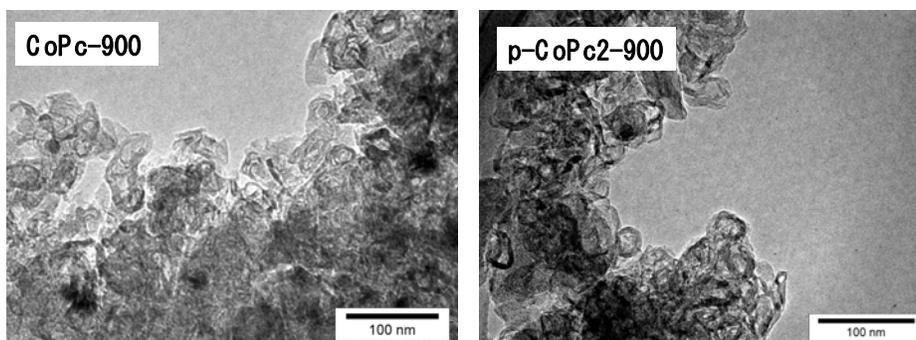
**Figure 1.** Selected TEM Images of the Nanoshells Prepared.



**Figure 2.** Magnified TEM Images of the Nanoshells Shown in Fig. 1.

A comparison of the nanoshell structure was made in Fig. 3 between the present carbons and the carbons prepared by the conventional method, i.e. using non-polymerized cobalt phthalocyanine (designated by CoPc900). The most striking difference was the size of the nanoshells; 20 nm of diameter was obtained by employing the present method, which was smaller than the nanoshells prepared by the conventional method, 30-50 nm. The present method also provided the uniform

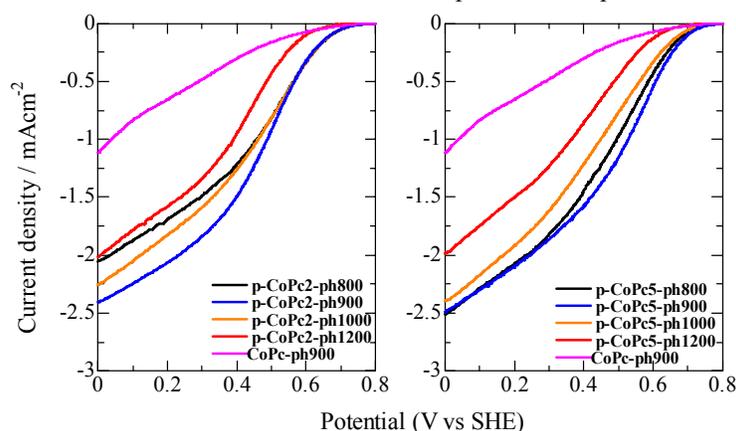
distribution of the nanoshell, however the conventional method produced amorphous region and the aggregated metal particles in the material. Detailed studies on the surface structures of the nanoshells prepared by the two different ways revealed the following features; in the case of the nanoshell prepared by the present method, the surface defects were observed, while the nanoshell prepared by the conventional method showed less defective feature with more developed and aligned graphenes. According to our previous study, such surface defects on the nanoshell would act as the active sites for the electrochemical reduction of oxygen.



**Figure 3.** Comparison of the Nanoshell of This Work with the one by Conventional Method.

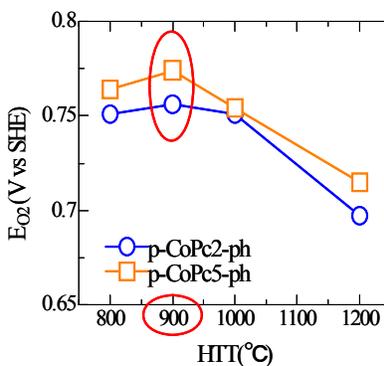
### Electrochemical Reduction of Oxygen

The linear sweep voltammograms of the carbons prepared by using the pendant-type complexes are presented in Figure 4. Since the oxygen reduction reaction is the cathode reaction of PEMFC, the carbons that showed reduction current at higher potentials are active catalysts for the reaction. The electrocatalytic activity of the carbons prepared at 800-1000°C showed the reduction currents at  $> 0.7$  V vs. SHE, and the activity of the carbons prepared at 1200°C showed decreases in the onset potentials of the reduction reaction. This trend was common both for p-CoPc2 and p-CoPc5 series.



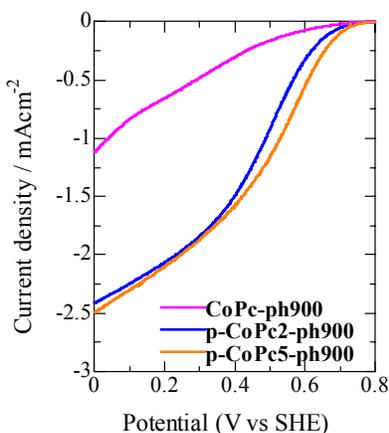
**Figure 4.** Oxygen Reduction Voltammograms of the Nanoshells with Different Pendant-type Phthalocyanine Complexes.

In order to observe the differences in the activity with the carbonization temperature, we took the potential where the current density was  $-10\mu\text{A}/\text{cm}^2$  as an indicator of the activity. The obtained potentials are plotted against the carbonization temperature in Figure 5. Although very small potential differences were observed among the carbons prepared at 800-1000°C, the carbons prepared at 900°C gave the best results.



**Figure 5.** Changes in ORR Activity of Nanoshells with their Carbonization Temperature.

The carbons prepared at 900°C were compared in Figure 6, where the voltammogram of the nanoshell carbon prepared by the conventional method is also included. Obviously, extremely large increases in the electrocatalytic activities were obtained for the present carbons. The largely enhanced electrocatalytic activities are inferred to be caused by the formation of smaller nanoshells, of which the surfaces are covered by defective graphenes patches.



**Figure 6.** Comparison of the ORR Activity of the Present Nanoshells with the one by Conventional Method.

## Conclusion

In this study, we intended to form nanoshell carbons with smaller diameters by employing pendant-type cobalt complexes to be mixed with phenol-formaldehyde resin. Successfully, the diameters of the nanoshells were reduced to 20 nm. Simultaneously, the distribution of the nanoshells in the bodies of the materials was uniform. Particularly, the carbons prepared at 800-1000°C were revealed to possess defective patches of graphene. Electrocatalytic activities of the carbons were examined for electrochemical reduction of oxygen. The electrocatalytic activities were compared with the nanoshell prepared by the conventional method, and large enhancement was observed. In conclusion, the use of pendant-type complexes was an effective way to introduce ORR activity to carbon materials.

## References

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