

## SURFACE TREATMENT OF NANOSHELL CARBON WITH IRON CATION

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### Introduction

Nanoshell is a nanocarbon material that is characterized by its unique hollow shell like structure, whose diameter ranged between 20 nm and 50 nm, and by its catalytic activity for electrochemical oxygen reduction reaction (the cathode reaction of PEMFC) [1,2]. Our study revealed that the electrocatalytic behaviors of the nanoshell, such as the activity for oxygen reduction reactions (ORR) and the selectivity (%H<sub>2</sub>O) to 4-electron reduction of oxygen ( $O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$ ) depended on the transition metals used for the preparation. For example, the nanoshells prepared with Co (CoNS) usually showed higher ORR activity than the ones with Fe (FeNS), while FeNS showed higher 4-electron selectivity than CoNS did.

The objective of the present study is to observe the influences of the Fe-treatment on the electrocatalytic behaviors of a CoNS, with an expectation of realization of a high performance cathode catalyst possessing both higher ORR activity and higher 4-electron selectivity.

### Experimental

Nanoshell was prepared by the following method. A phenol-formaldehyde resin was mixed with cobalt phthalocyanines in acetone, and then the mixture was carbonized at 1000°C in a nitrogen stream for 1 h. The obtained carbons was pulverized by using a planetary ball mill followed by acid treatment with conc. HCl in order to remove the metal species appeared on the surface of the carbons. The carbon thus prepared is referred to as CoNS.

The Fe-treatment was done by impregnation - heat-treatment - acid-washing operations. The prepared CoNS was impregnated in FeCl<sub>2</sub>·6H<sub>2</sub>O aqueous solutions with different Fe contents (1~8 wt%) and the solvent was removed by a rotary evaporator. The Fe-loaded CoNs was heat-treated at 700°C where the temperature is just above the decomposition of FeCl<sub>2</sub>·6H<sub>2</sub>O for 1 h. Then, the sample was acid-washed with conc. HCl followed by rinsing with distilled water. The samples thus prepared are referred to as xFe-CoNS, where x stands for the Fe loading.

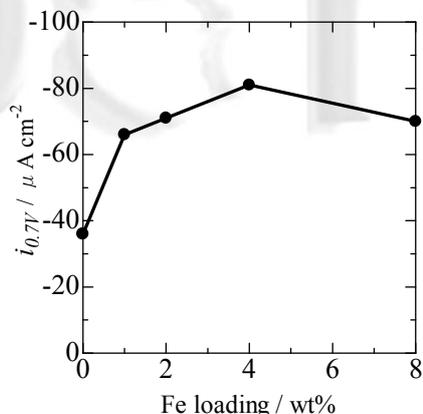
The ORR activities of the obtained carbons were examined by a rotating disk electrode voltammetry at room temperature, where oxygen saturated 0.5M H<sub>2</sub>SO<sub>4</sub> solution was used as the electrolyte. Five milligrams of the ground carbon were mixed with Nafion® solution (50 μl) (Aldrich), ethanol (Wako Pure Chemicals), and ion-exchanged water (150 μl each) under ultrasonication to make a catalyst ink. Four micro liters of the catalyst ink was applied on a glass-like carbon disk electrode (6 mmφ). After evaporating the

solvents, the ORR voltammograms were recorded by sweeping the potential from 0.8 V to -0.1 V vs. Ag/AgCl at 0.5 mVs<sup>-1</sup>, with rotating the electrode at 1500 rpm. The rotating ring disk electrode apparatus was RRDE-1 (Nikko Keisoku Co. Ltd.) connected to a dual potentiostat, Electrochemical Analyzer Model 700A (ALS Co. Ltd.). Transmission electron microscopic (TEM) observation was carried out for the ground sample placed on a copper grid coated with amorphous carbon film. The transmission electron microscope (JEM2010, JEOL) was operated at an acceleration voltage of 200 kV

### Results and Discussion

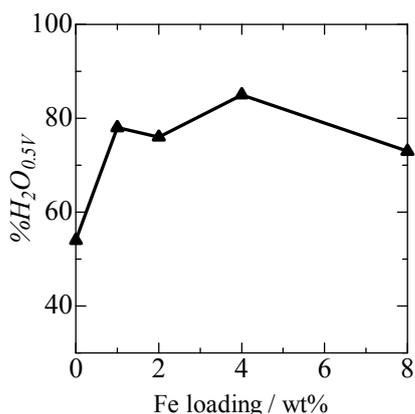
XRD studies revealed that no remaining Fe species were on the surfaces of the CoNS after the acid washing; only the cobalt species were detected at  $2\theta = 44.1^\circ$  in the X-ray diffractograms, which is due to the cobalt species located in the positions such as encapsulated or embedded in the carbon matrix. Further, no Fe species were detected by XPS measurements.

The Fe-treatment onto the CoNS resulted in the increase of the ORR activity as well as the 4-electron selectivity as shown in Fig. 1. The ORR activity showed the maximum increase at 4 wt% where the activity was doubled compared to the pristine CoNS (Fig. 1). The 4-electron selectivity increased from 54% for the pristine CoNS to 80% for the 4%Fe treated CoNS (Fig. 2). The dependences of the ORR activity and the 4-electron selectivity resembled to each other, indicating strong correlation between the ORR activity and the 4-electron selectivity.



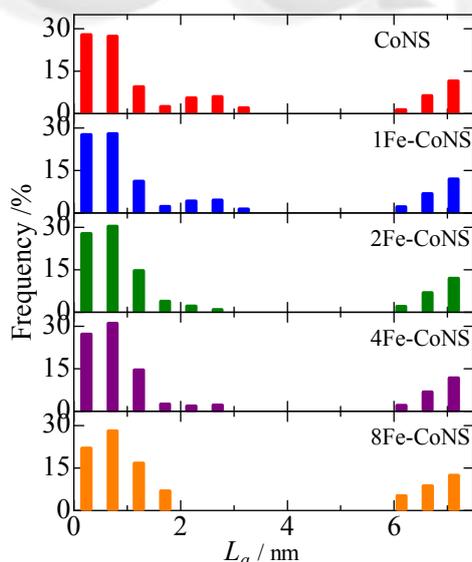
**Fig. 1** Dependence of the ORR activity represented by the current density at 0.7 V vs. NHE on the amounts of Fe used for the surface treatments. The activity and the selectivity were obtained from the hydrodynamic voltammograms.

Since no remaining Fe species on the Fe-treated CoNS were detected, the abovementioned changes in the electrochemical properties of the CoNS cannot be attributed to the direct catalytic modification by the Fe species loaded on CoNS. Hence, the changes should be attributed to the changes in the surface properties of the CoNS itself.



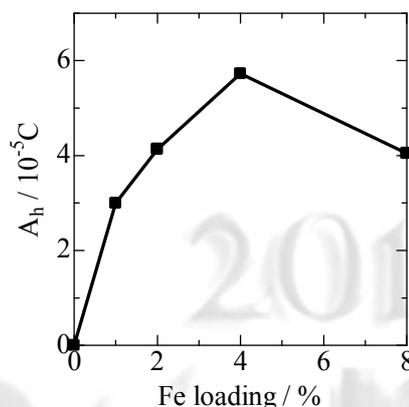
**Fig. 2** Dependence of the 4-electron selectivity on the amounts of Fe used for the surface treatments. The activity and the selectivity were obtained from the hydrodynamic voltammograms.

Interesting features were observed in the crystallite size ( $L_a$ ) distribution ( $L_a$ SD) calculated from (10) diffraction of carbon by applying the Diamond analysis coded by Fujimoto et al (Carbon Analyzer DiHiGa). **Fig. 3** shows the  $L_a$ SD of the Fe-treated CoPc and the pristine CoPc. The  $L_a$ SD of the pristine CoPc consisted of three major contributions; i.e. 0~2 nm (contribution A), 2~4 nm (B), 6 nm~ (C). The integrated frequencies of the contribution A increased by the Fe-treatment, which became obvious with the increase in the amount of Fe used for the treatment at the expenses of the contribution B. The decreases in the  $L_a$  by the Fe-treatment meant the formation of the edge sites in the graphitic structures, which was also observed for the N and/or B-doped carbons with enhanced ORR activities [3].



**Fig. 3**  $L_a$  size distribution histograms of the pristine (CoNS) and the Fe-treated CoNS (xFe-CoNS).

The Fe-treatment of CoNS was also revealed to introduce quinone groups on the CoNS, which were detected by cyclic voltammetry of the carbons. It was shown that the reversible quinone peaks at  $\sim 0.6$  V vs Ag/AgCl were developed with the increase in the amounts of Fe used for the treatment. The electric charges consumed in the redox reaction of the quinone groups were calculated by integrating the area surrounded by the peak and the baseline due to the residual currents. **Fig. 4** shows the relation between the charge consumed in the redox process including quinones and the amount of the Fe used for the treatments. Treatment with only 1 % of Fe induced a large increase in the electric charge due to the redox reaction of quinones. The charge increase up to 4 wt% and then decreased; this feature is similar to the ones shown in Figs. 1 and 2; indicating these three factors have intimate relationship.



**Fig. 4** Dependence of the electric charge consumed in the redox reaction of the quinone groups formed on Fe-treated CoNSs.

### Conclusions

The ORR activity and the 4-electron selectivity of the nanoshell prepared with Co (CoNS) were revealed to be improved by the Fe-treatment. However, the Fe species did not directly caused such improvements, since no remaining species were detected by XPS. The reduction in  $L_a$  leading to the increase in the numbers of the edge sites as well as the introduction of quinone surface groups formed by the treatment should be responsible for these improvements.

### References

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- [3] Ozaki J, Anahara T, Kimura N, Oya A. Simultaneous doping of boron and nitrogen into carbon to enhance its oxygen reduction activity in proton exchange membrane fuel cells. *Carbon*2006;44: 3358-3361.