

SURFACE MICROSTRUCTURE CONTROL OF NITROGEN-DOPED CARBON DERIVED FROM CHITOSAN

Ryunosuke Okuda^{1*}, Koichi Suematsu², Ken Watanabe², Kengo Shimano²

¹*Department of Molecular and Material Sciences, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka, 816-8580, Japan*

²*Department of Advanced Materials Science and Engineering, Faculty of Engineering Science, Kyushu University, Kasuga, Fukuoka, 816-8580, Japan*

*Presenting author's e-mail: okuda.ryunosuke.977@s.kyushu-u.ac.jp

Introduction

Carbon materials with high specific surface area and high conductivity are very suitable for the cathode for metal-air batteries. Among the numerous carbon materials, nitrogen-doped carbon is one of the promising candidates for cathode material, because of its high oxygen reduction activity¹. We previously proposed the nitrogen-doped carbon derived from chitosan, which contains the amino group as the nitrogen source, and demonstrated the remarkable high oxygen reduction activity as compared with that of Ketjen black. In order to further improve the oxygen reduction activity, it is important to design the surface microstructure of carbon. The specific surface area is one of the critical factors to be controlled, because it is directly related to the number of reaction sites. In general, the activation treatment for the carbon is often used for modifying the surface structure. In our method, zinc chloride is used as a chemical activator. Recently, we found that the existence of unintentional water vapor during the activation at elevated temperature enhanced the activation. However, the mechanism of the activation with zinc chloride and water vapor is still not clear. Here, in this research, we aimed to clarify the concerted activation mechanism of zinc chloride and water vapor. We also investigated the dependence of amount of zinc chloride on the microstructure, nitrogen functional group, and oxygen reduction activity of nitrogen-doped carbon.

Materials and Methods

Zinc chloride was mixed with chitosan dissolved in dilute hydrochloric acid. The resulting precursor solution was kept stirring with a magnetic stirrer for 1 h, and evaporated to dryness at 300°C. The obtained powder was calcined in tubular furnace for 5 h under wet nitrogen flow prepared by bubbling water at 30°C. The obtained nitrogen-doped carbon powder was ground in a mortar and washed with hydrochloric acid to remove zinc. Subsequently, it was washed with an aqueous solution of sodium carbonate to remove chlorine and then washed with distilled water. The pore structure of nitrogen-doped carbon was evaluated by nitrogen gas adsorption and desorption method, and the surface nitrogen group was quantified by XPS. To evaluate the oxygen reduction activity, the gas diffusion electrode was fabricated by the method reported elsewhere². The oxygen reduction activity of the obtained gas diffusion electrode was evaluated by galvanostatic polarization method in 8M KOH aqueous solution at 80°C.

Results and Discussion

In order to reveal the effect of the activator on the specific surface area, we synthesized the nitrogen-doped carbon under different activation condition. Figure 1 shows the calcination temperature dependence of the specific surface area for the obtained nitrogen-doped carbon with different activation condition. In the case of the calcination with the activator, the specific surface area increased as the calcination temperature increases. In addition, among three activation conditions, the activation with both zinc chloride and water vapour exhibits the highest specific surface area. It is noted that zinc chloride may evaporate at such elevated temperature because the boiling point of zinc chloride is 732°C. On the other hand, however, the specific surface area was increased even though the calcination temperature was above the boiling point. From the result of XPS, no chlorine remained after heat treatment at 1000°C and only zinc was detected. This indicates that zinc chloride may react with water vapour, resulting the formation of zinc oxide. In addition, according to the thermodynamic calculation, zinc oxide can act as the activator ($\text{ZnO} + \text{C} \rightarrow \text{Zn} + \text{CO}$). Thus, the activation with the ZnO formed by the reaction of zinc chloride and water vapor seems to be the cause of high activation efficiency with zinc chloride and water vapour. Moreover, the nitrogen-doped carbon fabricated under the optimized activation condition exhibited excellent oxygen reduction activity and higher oxygen reduction activity than that of commercially available 27.7 wt.%Pt-loaded carbon (TEC10A30E).

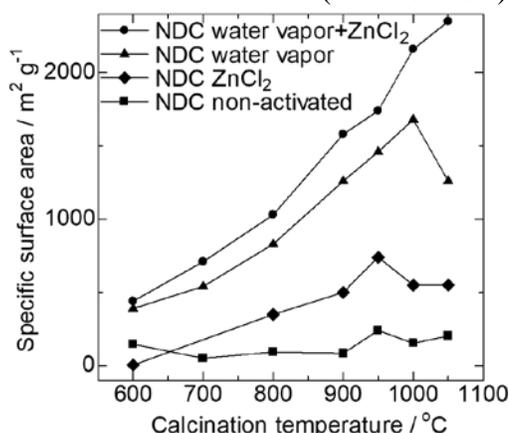


Figure 1. Calcination temperatures dependence of specific surface area for nitrogen-doped carbon (NDC) fabricated with different combinations of activators

Conclusions

The concerted activation in which zinc chloride and water vapor coexisted showed the highest specific surface area at 1050°C, probably due to the activation with ZnO that formed by the reaction between zinc chloride and water vapor at elevated temperature. In addition, the fabricated nitrogen-doped carbon showed higher oxygen reduction activity than that of 27.7 wt.%Pt-loaded carbon. Thus, we believed that the nitrogen-doped carbon with well-designed surface structure is the promising candidate for cathode of metal-air batteries.

References

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