

PREPARATION OF PN-DOPED CARBONS FROM PHOSPHORIC ACID MODIFIED FOLIC ACID AND THEIR CATALYTIC ACTIVITY FOR OXYGEN REDUCTION REACTION

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Introduction

Catalytic ORR activity of carbon-based materials is one of the most interesting and exciting subject of carbon material science, because it gives us an expectation of large cost-down of the polymer electrolyte fuel cell (PEFC) by replacing the current expensive platinum-based catalyst. Doping of non-metallic hetero-atoms to carbon materials is fascinating to realize the catalysts. Nitrogen is the oldest element recognized as an effective dopant. Doping of multiple elements, co-doping, enhances the possibility of catalyst designing¹. PN-doping is one of the examples of co-doping.

Herein, to establish a more generalized PN-doping method allowing the use of more common compounds, we developed the technique of controlled phosphoric acid treatment (CPAT) that is potentially applicable to non-special N-containing organic compounds and applied it to folic acid (FA) as a commonly occurring N-containing organic compound. During CPAT, phosphoric acid (PA) acts as both a P-doping agent and a chemical activator to introduce pores. The CPAT method, we used here, includes pretreatment with phosphoric acid at various temperatures to alter the properties of the precursors of carbons. In the present study, PN-doped precursors synthesized at CPAT temperatures of 400–800 °C were carbonized at 1000 °C to prepare PN-doped carbons, and factors influencing the ORR catalytic activity of these carbons were investigated in detail.

Materials and Methods

N- and P-containing precursors were prepared by heating FA in the presence of PA. Typically, FA (1 g; Wako, Wako Special Grade) was ground with ethanolic PA (85 wt%, 1 g; Wako, Wako Special Grade) using a mortar and pestle, and the obtained mixture was placed in a furnace, heated to 400–800 °C in a flow of N₂ at a rate of 50 °C min⁻¹, and then held at this temperature for 1 h. The carbonized samples were then pulverized at 650 rpm for 50 min using a planetary ball mill (P-7, Fritsch), sieved to retrieve particles smaller than 106 μm in diameter, vigorously stirred in deionized water at 80 °C for 1 h, and dried to obtain P-T specimens (T = CPAT temperature). Controls were prepared in the same manner without the addition of PA and were referred to as H-T (T = pretreatment temperature). The doped and control precursors were carbonized at 1000 °C for 1 h in a stream of N₂ to afford PH-T and HH-T specimens, respectively (T = treatment temperature).

The ORR activity of carbons was probed by rotating disk electrode voltammetry. The reversible hydrogen electrode (RHE) and a glassy carbon plate were employed as reference and counter

electrodes, respectively. The electrolyte corresponded to a 0.5 M solution of H₂SO₄ in de-ionized water. Net ORR voltammograms were obtained as the difference between linear sweep voltammograms recorded at 1500 rpm in O₂-saturated and N₂-saturated electrolytes.

N₂-adsorption, XPS, work function measurements were employed to characterize the prepared materials.

Results and Discussion

CPAT had two roles when applied to FA. One was to dope phosphorus in the precursors and another was to develop the BET specific surface area. The P-doping effect was dominant up to the CPAT temperature of 700 °C, which was switched to activation above the temperature

The P-doping levels in the carbonized samples were influenced by the P-content in the CPAT precursors as shown in Figure 1.

Consequently, the carbon with the highest doping level (PH-700) was obtained by the carbonization of P-700, the FA treated with PA at 700 °C.

The ORR activity of the carbons prepared in the present study was evaluated by linear sweep voltammetry using the rotating electrode technique.

The ORR voltammograms are presented in Figure 2 (a). The HH-series samples showed ORR activities but their magnitudes were not so large compared to the PH-series samples. The highest ORR activity was observed for PH-700. Fig. 2(b) shows the dependence of the ORR activity, represented by the current density at 0.5 V vs. RHE, on the CPAT temperature. This figure clearly shows the ORR activity increased with the CPAT temperature up to 700 °C

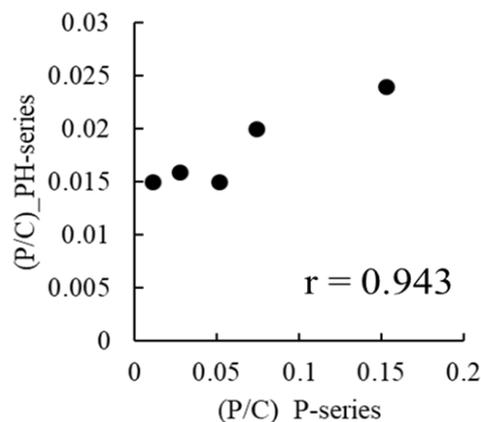


Figure 1. Correlation between the P content in P-series and PH-series samples

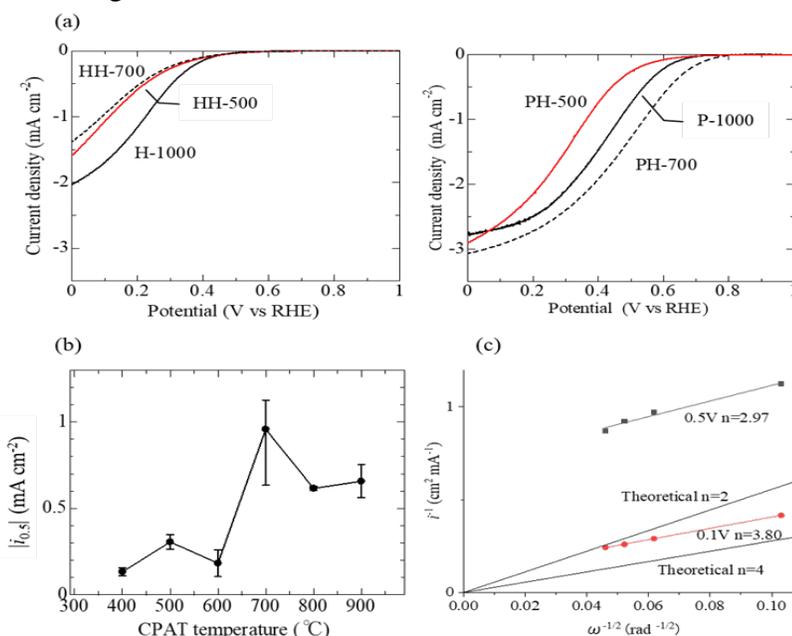


Figure 2. ORR activity of the carbons. (a) HH-series and PH-series, (b) dependence of ORR activity on the CPAT temperature, (c) Koutecky-Levich plot of PH-700.

and decreased by CPAT at higher temperatures than 700 °C. Koutecky-Levich plot gives a way to calculate the number of electrons in the reaction (n). Figure 2(c) shows a K-L plot of PH-700. The number n varied with the potential, with which the plot was made; $n=2.98$ at 0.5 V vs. RHE and $n=3.80$ at 0.1 V vs. RHE. This result concluded that PH-700 included both four-electron process and two electron process for ORR.

A comparison of the ORR activity with the BET-SSA revealed that the development of the surface area was not the predominantly influential factor of the ORR activity. So far, the purpose of introduction of phosphorus to nitrogen-doped carbons was to form pyridinic nitrogen species. In the present case, we found no correlation between the ORR activity and the pyridinic nitrogen species

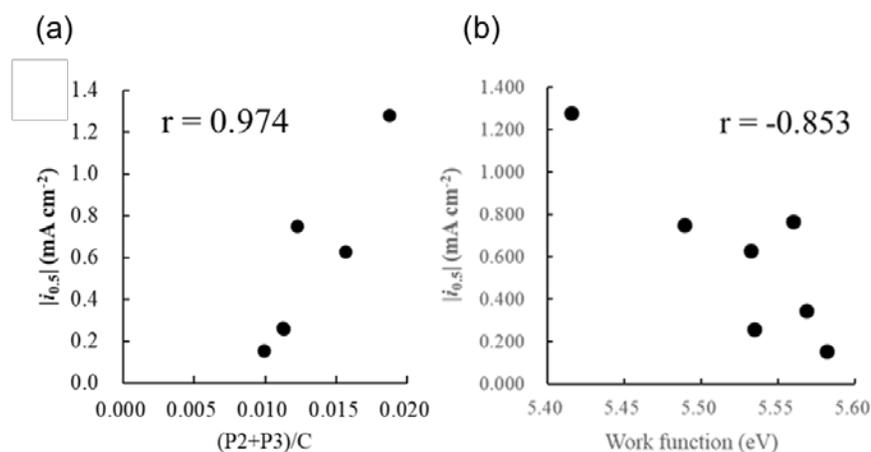


Figure 3. Dependences of ORR activity on the phosphoric surface groups (a) and the work function (b).

detected by N 1s XPS; however, strong correlations were observed when comparing the ORR activity with some specific P-species, $-C-PO_2$ and $-C-PO_3$. Figure 3 (a) presents the relation between the ORR activity and the summed surface concentrations of these P-species, giving a good correlation coefficient of 0.974. Work function determines the position of Fermi level in the material, of which great relevance to the ORR activity has been reported. The work functions of the present carbons were measured by Kelvin method in an inert atmosphere. Figure 3 (b) shows the relation between the ORR activity and the work function with a correlation coefficient $r=-0.853$. These two correlations shown in Figure 3 probably meant that the formation of $-C-PO_2$ and $-C-PO_3$ led to reduce the increase the Fermi levels of the carbons. Higher Fermi energy is advantageous for ORR.

Conclusions

In this study, we developed the technique of controlled phosphoric acid treatment (CPAT) to prepare precursors of ORR active carbons from folic acid. The CPAT temperature of 700 °C successfully produced the carbon with the highest activity, of which the origin was the formation of specific P-containing surface species resulting in raising the Fermi level of the carbon.

References

1. Ozaki, J., Kimura, N., Anahara, T, Oya, A. (2007). Preparation and oxygen reduction activity of BN-doped carbons. *Carbon* 45, 1847-1853.