

Catalytic Activities of Directly Synthesized Nitrogen Doped Carbon Nanofibers

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Introduction

Carbon nanofibers (CNF) were widely used as the material of functional composites, semiconductor device, sensors and carrier for various catalysts. The functions of carbon material were determined by the surface activities. To enhance the surface activities of carbon material, the effects of imported functional groups onto the carbon surface have been reported. However, most of activation methods adopt very harsh treatment and corrosive conditions in the strong acid and high temperature. This treatment can be a cause of deformation of the carbon's originality and surface activity

To avoid the damages of the carbon, it is introduced to enhance the activities that doping hetero-atoms such as nitrogen, sulfur and boron in the carbon structure. The hetero-atoms that remain in the carbon structure provide polarity on the surface and new surface functions. In the case of nitrogen doped carbon materials, one method is post doping on the surface of prepared carbon. Another is directly carbonization using precursor with carbon and nitrogen.

In this study, N-doped CNFs were directly synthesized from the acetonitrile (CH_3CN) by catalytic chemical vapor deposition over MgO supported nickel-iron catalysts at the various temperatures. The structural and chemical properties of N-doped CNFs were investigated by SEM, FE-TEM, EA, XPS, XRD. The electro-catalytic activities of N-doped CNFs were evaluated and applied to cathode electro-catalyst of fuel cell.

Experimental

Previous study, thin CNFs were successfully synthesized over a MgO supported nickel-iron catalyst, which was used in this study. The catalyst was prepared following the procedure used by Chen et al. and Pang et al.

CNFs were synthesized on the fixed alumina plate in the quart tube placed on the electronic furnace. After the prepared catalysts about 0.1g were placed on the reactor, the reactor was heated and purged with nitrogen and hydrogen gas. When the temperature approach to desired point ($300^\circ\text{C}\sim 680^\circ\text{C}$), the pre-vaporized acetonitrile as nitrogen and carbon source were supplied and reacted for a 1hour. The reactor was cool down

to the room temperature with nitrogen purge. Then, synthesized N-doped CNFs were collected.

The structure of CNFs was examined using SEM, FE-TEM and the CNFs growth rate and synthetic yield were calculated as the created weight and TG (air) analysis. After the catalysts were removed by 10% HCl solution for 48hours treating, nitrogen adsorption isotherm, XRD were conducted. The contents and chemical states of doping nitrogen were evaluated by element analysis and XPS.

The N-doped CNFs were evaluated electrochemically by cyclic voltammetry (CV) and linear sweep voltammetry for ORR activity using the conventional 3-electrode apparatus. Finally, the performance with ORR activity as the cathode materials of direct methanol fuel cell was compared with the commercial carbon black.

Results and Discussion

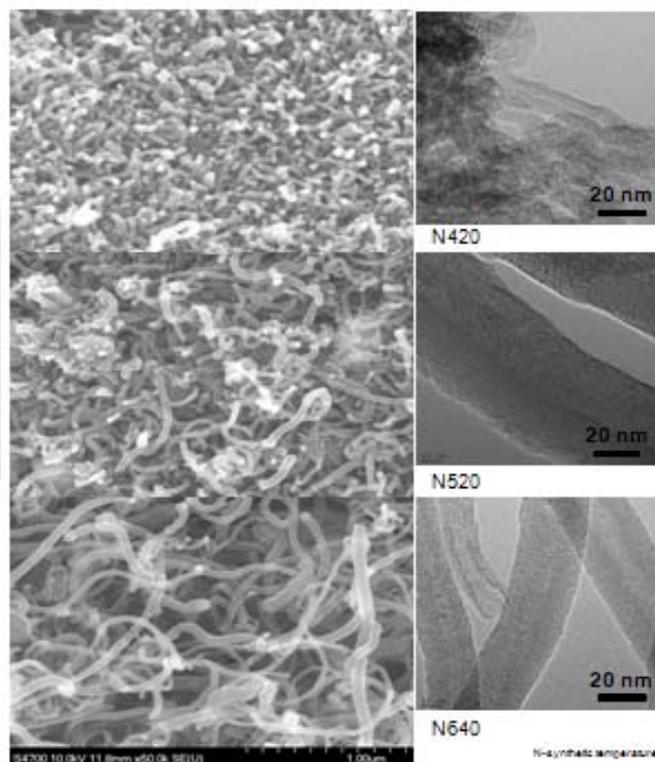


Fig. 1 Temperature dependency of N-doped CNF's structures with SEM, FE-TEM

Fig.1 shows SEM and FE-TEM image of N-doped CNFs according to synthesis temperature. The diameter of N-doped CNFs tends to be grow thick as increase synthesis temperature. In contrast, the diameter's uniformity tends to be increase according to reduce the synthesis temperature. The N-doped CNFs seems herringbone type structure through FE-TEM images. At the high temperature, some N-doped CNFs has the appearance of bamboo structure.

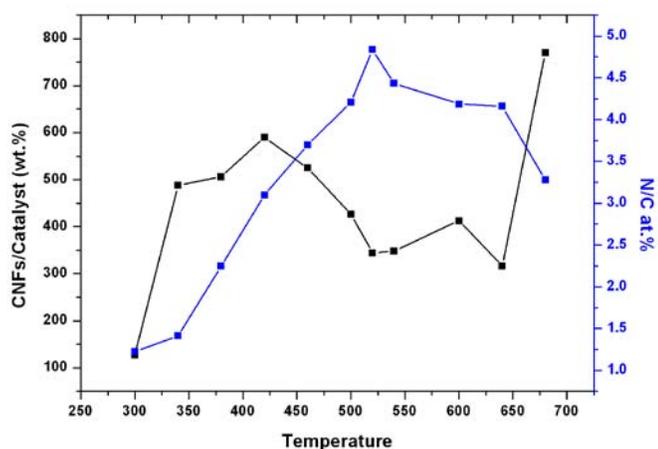


Fig. 2 The synthetic quantities of N-doped CNFs and nitrogen contents from element analysis.

The synthetic yields and atomic percents of doped nitrogen are compared as synthetic temperatures in fig. 2. The CNFs can synthesize at low temperature 300°C, percentage of nitrogen is 1.3 wt%. Up to 450°C, the synthetic quantity increase significantly with temperature. The synthesis amount is decrease up to 520°C and not changes as far as 620°C, but after 650°C synthetic quantity increase rapidly again. On the contrary, the nitrogen contents in N-doped CNFs increase gradually at 520°C. The nitrogen contents show a peak at 520°C and decrease down higher temperature. Therefore, probably there exist three types of synthesis mechanism according to synthetic temperature. At low temperature below 450°C, synthetic quantity and nitrogen contents are increased together. This results indicate that the diffusion of dissolved carbon and nitrogen through the catalyst elevate with risen temperature. A section of 450~520°C, the diffusion of nitrogen is increased but the formation of carbon conflicts with nitrogen, sometimes disturbed. From 520°C to 650°C, the conflicts get to the region of trade-off and over 650°C, the element of carbon secure the dominance position.

Fig. 3 shows the specific current of the ORR activity normalized by BET surface area, and here we able to confirm the enhanced activity for ORR of N-doped CNFs compared with nitrogen non-doped carbons. The N-doped CNFs are found to have significant catalytic activity for ORR, although the overpotentials are larger by 0.2~0.3V than Pt catalysts. The activity dependency on the contents and chemical states of doped nitrogen will be discussed based on the experimental result.

Also, N-doped CNFs are adopted cathode materials into the single cell of direct methanol fuel cell. Further detailed study and applications using its catalytic activities will be commented

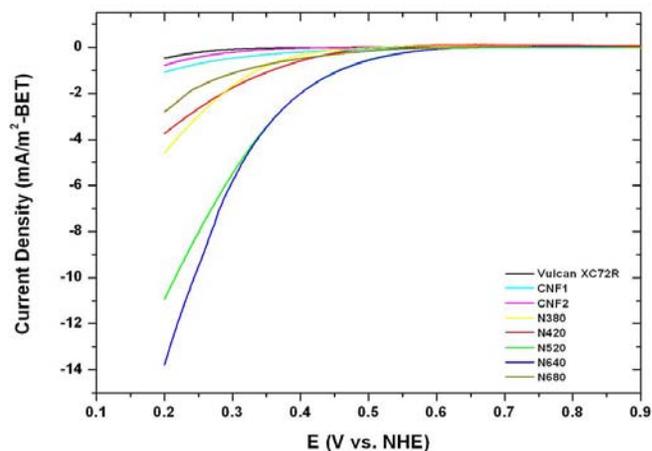


Fig. 3 Hydrodynamic voltammograms of the carbons for ORR at 3600 rpm

Conclusions

N-doped CNFs were successfully synthesized by CVD method directly from the acetonitrile as various reaction temperatures, and the structural and chemical properties of N-doped CNFs were examined. Electrochemical techniques were conducted in order to understand the dominant factor of catalytic activities of the N-doped CNFs for ORR. The present N-doped CNFs were expected to be cathode catalysts and catalytic supports, and need to be more studies.

References

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