

이종 원자 도핑 탄소 나노재료를 이용한 PEMFC Cathode용 촉매 합성 및 평가

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Heteroatom-doped carbon nanostructures as non-precious cathode catalysts for PEMFC

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Abstract

Recently, enormous research efforts have been focused on the development of non-precious catalysts to replace Pt for electrocatalytic oxygen reduction reaction (ORR), and to reduce the cost of proton exchange membrane fuel cells (PEMFCs). In recent years, heteroatom (N, B, and P) doped carbon nanostructures have been received enormous importance as a non-precious electrode materials for oxygen reduction. Doping of foreign atom into carbon is able to modify electronic properties of carbon materials. In this study, nitrogen and boron doped carbon nanostructures were synthesized by using a facile and cost-effective thermal annealing route and prepared nanostructures were used as a non-precious electrocatalysts for the ORR in alkaline electrolyte. The nitrogen doped carbon nanocapsules (NCNCs) exhibited higher activity than that of a commercial Pt/C catalyst, excellent stability and resistance to methanol oxidation. The boron-doped carbon nanostructure (BC) prepared at 900 °C showed higher ORR activity than BCs prepared lower temperature (800, 700 °C). The heteroatom doped carbon nanomaterials could be promising candidates as a metal-free catalysts for ORR in the PEMFCs.

Keywords: Heteroatom-doped carbon, boron-doped, nitrogen-doped, non-precious catalyst, cathode, fuel cell, proton exchange membrane fuel cell (PEMFC)

1. Introduction

Recently, non-precious catalysts have attracted huge research interests to substitute conventional Pt based catalysts for oxygen reduction reaction (ORR), and to reduce overall cost of proton exchange membrane fuel cell (PEMFCs). In particular, doping heteroatom into carbon network is one of the promising technology to modify electronic and physical properties of the carbon, the doped nitrogen and boron act as electron donor and acceptor at the trigonal and hexagonal sites of the carbon, respectively.

Present study describes a simple and cost-effective route for the preparation of nitrogen and boron doped carbon nanostructures. The developed route is a solvent-, catalyst-, and template-free thermal annealing process. In this paper, morphology and electrocatalytic properties of heteroatom doped carbon nanostructures is presented.

2. Experimental

The NCNCs were synthesized by solid state pyrolysis of gadolinium(III) diethylene triaminepentaacetate at 700 and 900 °C under autogenic atmosphere resulted in $Gd_2O_2CO_3$ and Gd_2O_3 filled carbon, respectively. The products were treated with concentrated HCl to remove oxide, and the carbons

derived from $Gd_2O_2CO_3@C$ and $Gd_2O_3@C$ were named as NCNC₇₀₀ and NCNC₉₀₀, respectively. The BCs were also synthesized by using same technique as the NCNCs. Tetraphenylboron sodium was thermally decomposed under autogenic atmosphere at 700, 800 and 900 °C are denoted as BC₇₀₀, BC₈₀₀ and BC₉₀₀, respectively. As-prepared BCs were treated with concentrated HCl to dissolve any metal oxide, and HCl treated samples were additionally purified by using distilled water of 80 °C to remove impurities including sodium borate.

3. Results and discussion

FE-SEM image of NCNC₇₀₀ exhibits the presence of rod and capsule-like morphology with uniform carbon coating and the diameter of the rod is in the range of 80 to 100 nm (Fig. 1a). Fig. 1b shows, SEM image of BCs, indicates the presence of porous rod stack and a few carbon layers. The TEM image of the NCNCs show that the capsule consists of an outer diameter of 80 to 120 nm and an inner diameter of 25 to 50 nm (Fig. 1c).

Fig. 2a depicts the Raman spectra of NCNCs, which shows two peaks at 1358 cm^{-1} of D bands and 1594 cm^{-1} of G bands of carbon. The peak at 1358 cm^{-1} is due to presence of defects in the hexagonal graphitic layers; the peak at 1594 cm^{-1} is due to the sp^2 -bonded carbon atoms in a two-dimensional hexagonal graphitic layer.

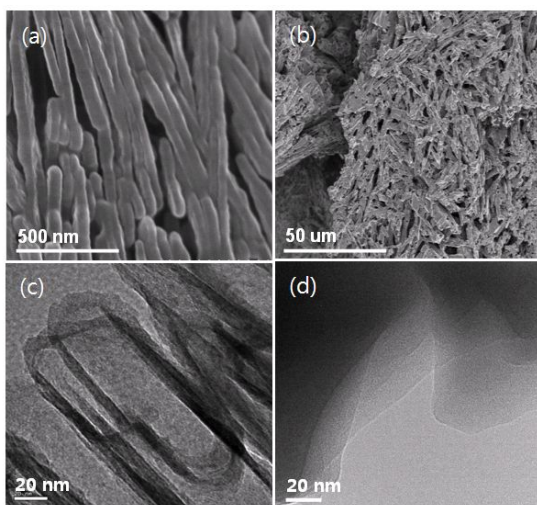


Fig. 1. FE-SEM images of (a) NCNC₇₀₀, (b) BC₉₀₀ and TEM images of (c) NCNC₇₀₀, (d) BC₉₀₀.

The ratio of D to G bands intensity, I_D/I_G , indicates the quality of the carbon and degree of disorder in the graphitic carbon. The I_D/I_G of the NCNC₇₀₀ and NCNC₉₀₀ are 0.86 and 0.78, respectively, which means the NCNC₇₀₀ possesses more defect sites than the NCNC₉₀₀.

The XPS wide spectra of NCNCs exhibits the presence of C, N and O (Fig. 2b) as elucidating composition of N in NCNC₇₀₀ and NCNC₉₀₀ is 7.1% and 3.2%, respectively.

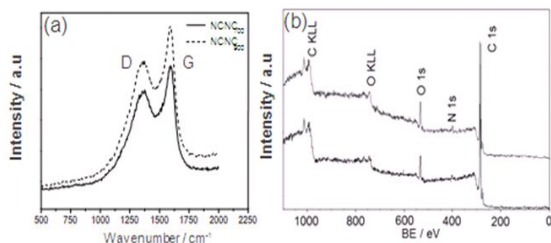


Fig. 2. (a) Raman and (b) XPS survey spectra of NCNCs

The linear sweep voltammograms (LSVs) in Fig. 3a show a significant oxygen reduction current as compared with a commercial Pt/C (10%, E-TEK). The ORR activities of NCNC₇₀₀, NCNC₉₀₀ and Pt/C are 7.9 mA/cm², 10.6 mA/cm² and 6.8 mA/cm² at -0.4 V, respectively. Fig. 3b depicts rotating-disk voltammograms of the ORR at the NCNC₇₀₀ electrode at different rotation rates, in which the current density increases with increasing rotation rates. K-L plots (not shown) derived from Fig. 3b at various potentials indicate constant slope over the potential range of -0.35 to -0.50 V, which means consistent electron transfer at different potentials and first-order reaction kinetic of the ORR. Electron transfer numbers calculated from Koutecky-Levich equations are 3.96, 2.46 and 3.92 at NCNC₇₀₀, NCNC₉₀₀ and Pt/C, respectively. The difference in ORR activities between NCNC₇₀₀ and NCNC₉₀₀ can be attributed to existence of high amount of pyridinic-nitrogen in NCNC₇₀₀(27.6%) than NCNC₉₀₀(19.8%).

The selectivity for the ORR of the NCNC₇₀₀ is also significantly better than that of Pt/C as shown in Fig. 3c. It suggests that NCNC₇₀₀ can prevent the occurrence of mixed potential during operation of the fuel cell, and electrode stability for ORR is outstanding as compared with the commercial Pt/C catalyst. The ORR activity of BCs with increasing thermal annealing temperature. The current density of BC₇₀₀, BC₈₀₀ and

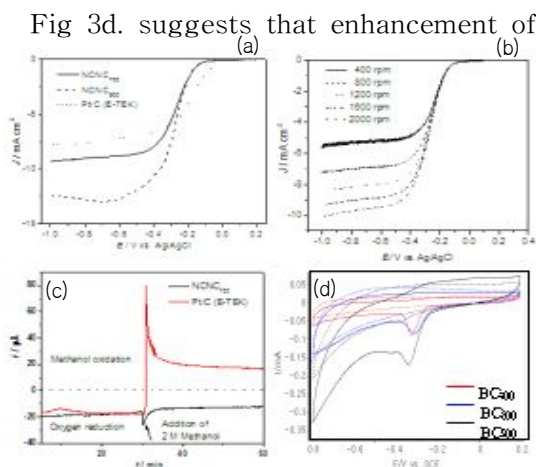


Fig. 3. (a) LSVs of NCNCs and Pt/C (E-TEK) at 1600 rpm, (b) RDE voltammograms of NCNC₇₀₀ electrode (c) Chronoamperometric response at -0.4 V of NCNC₇₀₀ and Pt/C followed by addition of 2 M methanol, (d) CVs of BCs in O₂ saturated 0.1 M KOH at a scan rate of 10 mV/s⁻¹

BC900 is 104.5 $\mu\text{A}/\text{cm}^2$, 182.6 $\mu\text{A}/\text{cm}^2$ and 478.8 $\mu\text{A}/\text{cm}^2$, respectively. The onset potential of BC700, BC800 and BC900 is -0.26 V, -0.22 V and -0.20 V, respectively. The difference of the ORR activities can be attributed to the existence of graphitic carbon in BCs. A detailed investigation of the effect of temperature and boron doping levels on ORR activities is in progress.

4. Conclusion

The NCNCs and BCs as a non-precious catalysts for the ORR have been prepared by a facile and cost-effective thermal annealing route, which is free of catalyst, solvent and template. Moreover, these catalysts displayed the outstanding ORR performance in alkaline medium. The electrode stability and selectivity for ORR

of the NCNCs was better than the conventional Pt/C catalysts. The results suggest that the heteroatom-doped carbon could be an ideal choice for replacing conventional Pt based catalysts for ORR in alkaline medium.

Acknowledgements

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