Synthesis of cobalt nanoparticle embedded carbon nanofiber catalysts with high oxygen reduction reaction activity

MinJoong Kim[a], DoHwan Nam[a], HeeYoung Park[b], KwangSup Eom[c], EunAe Cho[b], ChoRong Kwon[b], SungJong Yoo[b], and HyukSang Kwon[a,*]

[a]Dept. of Materials Science and Engineering, KAIST
Daejeon Guseong-dong 373-1, Republic of Korea
[b]Fuel cell Research Center, KIST
Seoul 136-791, Republic of Korea
[c]School of Chemical & Bimolecular Engineering
Center for Innovative Fuel Cell and Battery Technologies
Georgia Institute of Technology, Atlanta, Georgia 30332, USA.

The development of non-precious metal catalysts (NMPCs) to replace high-cost Pt catalysts is mainly focused on oxygen reduction reaction (ORR) because of its sluggish reaction kinetics. Previous reports examined that the heat treatment at 400 ~ 1000 °C derived transition metal-nitrogen bond coordinated with carbon structure (Me-N-C) exhibits ORR activity in various pH conditions [1-5]. However, the current developed NMPCs have poor ORR activity than Pt catalysts.

Nanofiber structure has a great potential to improve the catalytic activity due to its large surface area to volume ratio. It has also high porous structure for efficient diffusion of gaseous reactants. So, electrospun PAN based carbon nanofiber (CNF) catalysts containing transition metal have attracted attentions in recent dates [6-11]. Electrospun PAN nanofiber has been commonly used as a precursor for commercial CNF. When transition metal is added to PAN nanofiber, transition metal and nitrogen species of PAN make an ORR active Me-N-C complex within graphitic carbon structure after heat treatment at high temperature above 700 ° C.

The contents and chemical state of transtion metal and nitrogen species are very significant factors in enhancing ORR activity of Me-N-C complex type catalysts. It is predicted that the ORR activity would be improved by increasing the contents of them. The beneficial effects of nitrogen contents on ORR activity were verified by conducting heat-treatment under nitrogen containing gas condition, such as NH_3 [9,10]. However, effects of transition metal contents in CNF on ORR activity are somewhat unclear.

In this study, nanoporous Co-CNF catalysts for ORR were synthesized by electrospinning and following heat treatment technique using PAN and cobalt as precursors. And then, we investigated effects of cobalt contents and chemical state of nitrogen in CNF on structural characteristics and ORR activity in alkaline media.

After heat treatment, PAN was transformed to graphitic carbon structure, and Co nanopatricles of 20~50 nm embedded in graphitic carbon shell were observed. As higher the Co contents, the amount of Co nanoparticles in graphitic carbon structure increased. CNF without Co have a little catalytic activity in 0.1 M KOH solution. And, it catalyzed 2-electron involved oxygen reduction reaction. However, Co nanoparticles embedded CNF exhibited surprising high ORR activity comparable with commercial 20 wt.% Pt./C catalyst. Their ORR activity increased with Co contents in the graphitic CNF. And, they catalyzed almost 4-eletron involved oxygen reduction. It is predicted that Co-N bond and Co nanoparticles neighboring with graphitic carbon structure increase the kinetic property by catalyzing the 2x2 serial oxygen reduction reactions in alkaline media. Co addition in CNF has beneficial effects on ORR activity by formation of active sites 1) Co-N_x site, and 2) Co/Co_xO_y phase particles according to dual site mechanism in alkaline media [12].

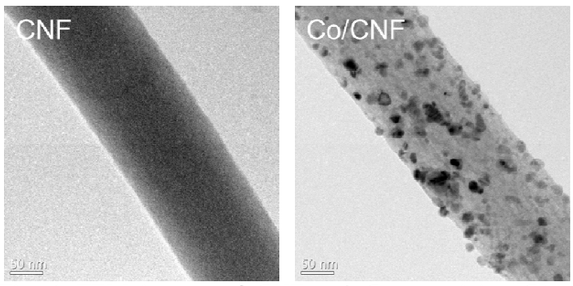

Fig. 1 TEM images of CNF and Co containing CNF catalysts

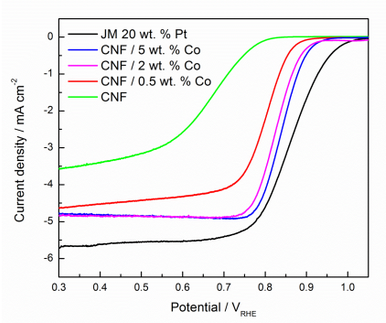

Fig. 2 Measured ORR activity of CNF and Co containing CNF catalysts in 0.1 M KOH solution.

References

1. M. Lefèvre, E. Proietti, F. Jaouen, J.P. Dodelet, Science, **324** (2009) 71-74.
2. R. Bashyam, P. Zelenay, Nature, **443** (2006) 63-66.
3. F. Jaouen, E. Proietti, M. Lefèvre, R. Chenitz, J.P. Dodelet, G. Wu, H.T. Chung, C.M. Johnston, P. Zelenay, Energy and Environmental Science, **4** (2011) 114-130.
4. G. Wu, K. Artyushkova, M. Ferrandon, J. Kropf, D. Myers, P. Zelenay, in, Vienna, 2009, pp. 1299-1311.
5. G. Wu, K.L. More, C.M. Johnston, P. Zelenay, Science, **332** (2011) 443-447
6. S. Gupta, D. Tryk, I. Bae, W. Aldred, E. Yeager, J Appl Electrochem, 19 (1989) 19-27.
7. N. Nakagawa, M. Ali Abdelkareem, D. Takino, T. Ishikawa, T. Tsujiguchi, ECS Transactions, 41 (2011) 2219-2229.
8. J. Wu, H.W. Park, A. Yu, D. Higgins, Z. Chen, The Journal of Physical Chemistry C, 116 (2012) 9427-9432.
9. J. Yin, Y. Qiu, J. Yu, Electrochemistry Communications, 30 (2013) 1-4.
10. J. Yin, Y. Qiu, J. Yu, ECS Solid State Letters, 2 (2013) M37-M39.
11. S. Uhm, B. Jeong, J. Lee, Electrochimica Acta, 56 (2011) 9186-9190.
12. T.S. Olson, S. Pylypenko, P. Atanassov, K. Asazawa, K. Yamada, H. Tanaka, The Journal of Physical Chemistry C, 114 (2010) 5049-5059.