Relationship between electronic property and catalytic activity for oxygen reduction reaction of nitrogen-doped and non-doped structurally defected single-walled carbon nanotube electrocatalysts

Koji Yokoyama[1], Yoshinori Sato[2], Masashi Yamamoto[2], Tetsuo Nishida[2], Kenichi Motomiya[1], Kazuyuki Tohji[1], and Yoshinori Sato[1,3]

[1]*Graduate School of Environmental Studies, Tohoku University, Aoba 6-6-20, Aramaki, Aoba-ku, Sendai 980-8579, Japan*
[2]*Stella Chemifa Corporation, 1-41, Rinkai-cho, Izumiotsu, Osaka 595-0075, Japan*
[3]*Institute for Biomedical Sciences, Interdisciplinary Cluster for Cutting Edge Research, Shinshu University, Asahi 3-1-1, Matsumoto 390-8621, Japan*

kyokoyama@dc.tohoku.ac.jp

Carbon nanomaterials are emerging as metal-free, cheap, and long-life electrocatalysts for oxygen reduction reaction (ORR) at the cathode of polymer electrolyte fuel cells. Nitrogen doping into carbon nanomaterials has been a common approach to improve their ORR catalytic activities [1]. On the other hand, structural defect introduction without nitrogen doping has also been reported to improve the ORR catalytic activity [2]. However, the roles of nitrogen species and structural defects in carbon-based electrocatalysts have not been understood comprehensively. Here, we report on the synthesis of both nitrogen-doped and non-doped structurally defected single-walled carbon nanotubes (SWCNTs) by a combination of defluorination-assisted nanotube-substitution reaction [3,4] and high-temperature annealing treatment. We evaluated the ORR catalytic activities of the prepared samples in an acid electrolyte to investigate the roles of nitrogen species and structural defects. In addition, the electronic properties including the work function, carrier type, and conductivity were measured and correlated with their ORR catalytic activities.

Highly crystalline SWCNTs (hc-SWCNTs) were synthesized by the arc-discharge method. The hc-SWCNTs were fluorinated at 250 °C using 20% F_2/N_2 gas for 4 h to prepare fluorinated SWCNTs. Then they were reacted with ammonia at 500 °C for 30 min in a gas flow of 1% NH_3/N_2. The resulting sample (N-SWCNTs) was further annealed at 1000 °C for 3 h in a N_2 flow to synthesize AN-SWCNTs. To prepare structurally defected SWCNTs without nitrogen doping (AF-SWCNTs), the F-SWCNTs were annealed at 500 °C for 30 min and subsequently at 1000 °C for 3 h in a N_2 flow.

The AN-SWCNTs contained 0.8 at% nitrogen, and the ratio of graphitic-type nitrogen (Gr-N) to the total nitrogen species reached up to 50% by the annealing treatment. The onset potential and numbers of electrons transferred per oxygen molecule in ORR of the AN-SWCNTs were +0.65 V (vs. Ag/AgCl) and 4.00, respectively (Fig. 1), indicating that the AN-SWCNTs exhibited the best ORR catalytic activity. The work function of the AN-SWCNTs was lower than those of the hc-, N-, and AF-SWCNTs, and their carrier type was *n*-type even in air, compared to *p*-type for the hc-, N-, and AF-SWCNTs. The conductivity of the AN-SWCNTs was higher than those of the N- and AF-SWCNTs. These results indicate that low work function and high conductivity of Gr-N enriched AN-SWCNTs can contribute to excellent ORR catalytic activity.

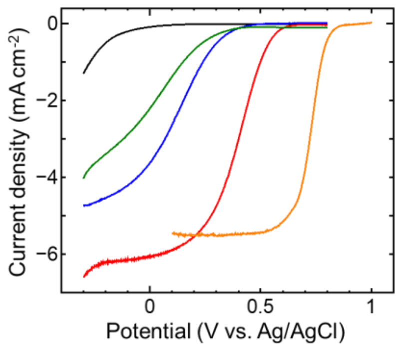

Fig. 1 Linear sweep voltammograms of the hc- (black), N- (blue), AN- (red), AF-SWCNTs (green), and Pt-C (orange) on GC electrodes in O_2-saturated 0.5 M H_2SO_4 electrolyte (scan rate: 10 mVs^{-1}, rotation rate: 1600 rpm).

References:
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