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Article / Book Information

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Title(English)	Study of the Oxygen Reduction Reaction Activity on Multi-Walled Carbon Nanotubes with Defects Formed by Rapid Thermal Annealing
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論 文 要 旨

THESIS SUMMARY

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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

To reach the goal of the carbon neutrality, building a sustainable green energy system is desirable. Proton exchange membrane fuel cell (PEMFC), which directly converts hydrogen energy into electricity and only produces water as the reaction product, is considered as a promising device to satisfy the energy requirements, especially in vehicles and other portable facilities, without polluting the environment.

However, the efficiency of PEMFC is largely limited by the sluggish kinetics of the oxygen reduction reaction (ORR) at the cathode. Thus, improving the ORR activity is a critical issue for the development of PEMFC. Platinum (Pt)-based catalysts have outstanding catalytic activity and are already applied in commercial products. However, a relatively high cost has restricted their widespread applications. Thus, many efforts have been devoted to finding alternative catalysts for the conventional costly Pt-based electrocatalysts.

Carbon-based catalysts are among the most promising alternatives and have attracted increasing interest. Defect engineering is generally used to add the ORR activity to the pure carbon with perfect hexagonal carbon structure. There are three main technologies for defect engineering in carbon materials: metal-free heteroatom doping, metal-containing heteroatom doping and creating intrinsic defects (defects formed by solely carbon atoms), with different catalytic mechanism and active sites.

Nitrogen is one of the most studied doping heteroatoms for carbon-based materials. The understanding of the factors that affect nitrogen doping is important as nitrogen atoms have a direct relationship with the active sites. This understanding is still insufficient. On the other hand, the optimization of intrinsic defects is expected to improve the ORR performance of defective carbon materials. Thus, this study mainly focuses on two issues for improving the ORR performance of carbon-based electrocatalysts: one is the investigation on the factors affecting nitrogen-related ORR active sites, another is the optimization of defective carbon with intrinsic defects.

Nitrogen doping and defect generation are employed using rapid thermal annealing (RTA) as a vital technology to avoid the severe weight loss and structural change in the carbon during annealing, in contrast to the traditional long-time annealing. It also helps clarify the factors that affect the formation of ORR active sites. For the nitrogen-doped carbon, the RTA enables getting insight into the relationship between oxygen functional groups (OFGs), intrinsic defects and nitrogen doping. For defective carbon, the RTA can help form highly active intrinsic defect sites without severe structure

change in the carbon.

In Chapter III, multi-walled carbon nanotubes (MWCNTs) were oxidized and chemically drilled by using cobalt oxide as the oxidation catalyst in an O_2/Ar atmosphere. A series of defective MWCNTs with different oxidation temperatures and time were prepared, characterized, and used as the ORR electrocatalysts. It is suggested that short-time heating helps make highly active defects and the heating conditions (such as heating time and temperature) affect the formation of defects. The sample annealed at 400 °C for 5s exhibits the highest degree of defectiveness and the best ORR electrochemical activity.

In Chapter IV, OFGs are suggested to be essential to the formation of nitrogen doping. To further glean the relationship between the active sites and OFGs, the controlled experiments were carried out by performing Ar annealing at different temperatures (300°C, 500°C, 700°C, 900 °C) on defective MWCNT before nitrogen-doping to remove particular OFGs. The results show that the ORR activity decreased with the increase of the annealing temperature and a huge activity drop occurs between the 300°C and 500 °C annealed samples. This trend is related to the concentration of FeNx structures which are detected with X-ray photoelectron spectroscopy. This suggests that the removed OFGs are the active sites for nitrogen doping and the paired carboxyl group (-COOH) which decomposed between 300 °C and 500 °C has the most important relationship with the formation of the FeNx structure.

In Chapter V, intrinsic defects are considered as another critical parameter for affecting the nitrogen-doping level. Based on the results in Chapter III, different kinds of MWCNT with intrinsic defects were employed as the substrate for nitrogen doping. The results show that the intrinsic defects can facilitate the nitrogen doping and the formation of the FeNx structure. The nitrogen doped defective MWCNTs with the intrinsic defects prepared by the RTA have the highest ORR performance.

In conclusion, the carboxyl group promotes nitrogen doping while the paired carboxyl groups facilitate the formation of FeNx. The intrinsic defects can also promote nitrogen doping and active site formation. The defective carbon produced by rapid oxidation exhibits showed high ORR activity. This study provides an essential insight into the design of defective carbon-based ORR catalysts to improve electrocatalytic activity. It is also interesting to consider whether there exists a synergistic effect between intrinsic defects and OFGs in the formation of FeNx structures and the ORR performance of nitrogen-doped carbon catalysts.