論文 / 著書情報
Article / Book Information

題目(和文)	カーボンナノチューブ電極の酸素還元反応特性に関する研究
Title(English)	Study on the Oxygen Reduction Reaction Characteristics of Multi-Walled Carbon Nanotube Based Electrocatalysts
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出典(和文)	学位:博士(工学), 学位授与機関:東京工業大学, 報告番号:甲第11307号, 授与年月日:2019年9月20日, 学位の種別:課程博士, 審査員:脇 慶子,北本 仁孝,和田 裕之,田巻 孝敬,本倉 健
Citation(English)	Degree:Doctor (Engineering), Conferring organization: Tokyo Institute of Technology, Report number:甲第11307号, Conferred date:2019/9/20, Degree Type:Course doctor, Examiner:,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

（博士課程）
Doctoral Program

論 文 要 旨

THESIS SUMMARY

系・コース： Department of, Graduate major in	応用化学 エネルギー	系 コース	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of	（工学）
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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

The objective of this dissertation is to systemically understand the annealing effect, degradation behavior and the active site clarification of different Multi-walled Carbon Nanotube (MWCNT)-based electrocatalysts.

Nowadays, the world faces two intertwined challenges: producing sustainable energy and protecting the environment. In order to solve both energy and environmental problems, proton-exchange membrane fuel cells (PEMFC) have been extensively studied because of their high efficiency and zero greenhouse gas emissions. To popularize the use of PEMFCs, the expensive Pt/C catalyst must be replaced with active, low-cost electrocatalysts. With their competitively high activity and controllable structure, carbon based electrocatalysts are expected as alternative catalysts for the oxygen reduction reaction (ORR).

In general, there are three main types of carbon-based electrocatalysts: transition metal-nitrogen-carbon complexes (MNC), nitrogen-containing carbon (CNx), and defective carbon (DC) catalysts. The development history of these three kinds of carbon based electrocatalysts were reviewed. Interestingly, for most electrocatalysts, a high-temperature heat treatment was required to form the active sites. Basically, the high-temperature annealing was applied to construct the nitrogen coordinated metal carbon sites (MNC), carbonize the nitrogen-containing precursors (CNx), and remove the surface O-functionalities to facilitate the restructuring of carbon to form topological defects (DC).

Nevertheless, the understanding of the effect of the annealing process is still insufficient. To further elucidate the ORR mechanism, a detailed study on the heat treatments of the carbon itself is required. To date, the annealing process for the activation of the carbon nanotubes has been performed on the time scale of hours. In this type of long-time annealing process, not only the removal of surface O-functionalities but also the healing of defective structure may occur. Such healing is highly unfavorable for the high ORR performance.

Hence, in this study we adopted the rapid thermal annealing (RTA) method for catalyst processing. RTA is a novel technique in the preparation of ORR catalysts where a heat treatment of several tens of seconds can suppress the defect healing and metal impurity diffusion at a certain annealing temperature. For DC, through investigating the effect of annealing temperature and annealing holding time, it can be concluded that 1. Relative high temperature (900^{o}C) is necessary to remove CO releasing functionalities, and result in

the formation of topological defect active site. 2. Long time annealing at high temperature will result in the carbon reconstruction and result in the deactivation. For CNx and MNC, RTA could also successfully introduce nitrogen into the electrocatalysts and result in high activity.

In Chapter III, for non-nitrogen doped MWCNTs, the annealing process conducted for 32 s to reach the temperature up to 900°C has features including the inhibition of high-temperature carbon structure defect healing and contributed to the best ORR activity. The complete recovery of ORR activity after repeated degradation and re-annealing suggested that the formation of topological defects during the removal of CO desorbing O-functionalities are the key structural features that give rise to the observed ORR activity.

In Chapter IV, for nitrogen-doped MWCNTs, the RTA could also successfully improve the onset potential of multi-walled carbon nanotube electrocatalysts doped with nitrogen by rapid thermal annealing to 900 °C in 32s (HA-N900) reaching up to 0.84V vs RHE. However, due to the existence of trace metal impurities in the carbon nanotubes, the real active site in the nitrogen doped carbon based electrocatalyst is still not well understood. In degradation and re-doping experiments, we probed the active sites in HA-N900. To directly observe the surface property changes accompanying the activity change, we characterized the samples coated on the glassy carbon after cyclic voltammetry measurements and applied different types of re-doping process. Based on the electrochemical measurements and X-ray photoelectron spectroscopy, the active site of the oxygen reduction reaction in HA-N900 is unlikely to be the pyridinic nitrogen or the carbon atom neighboring the pyridinic nitrogen. Instead, the active site appears to be the Nx-Fe site established by Fe impurities in the carbon nanotubes.

In Chapter V, after probing the active site in the nitrogen doped MWCNTs, the degradation behavior difference in acid and alkaline solutions were studied through detailed characterization of CV, XPS and Raman Spectroscopy. The durability test in acid solution will introduce O-functionalities and remove the active nitrogen species simultaneously, which resulted in a serious activity degradation. However, the durability test in alkaline solution will result in a serious carbon corrosion that still maintain a high ORR activity in alkaline solutions.

In conclusion, the RTA was successfully applied in processing the MWCNT based electrocatalysts and result in high activity. Through the degradation and reheating method, the topological defects may play an important role in the enhancement of ORR activity in DC catalysts, while the Nx-Fe appeared to be the high active active-site in the Fe impurities containing acid washed MWCNTs. The active sites were successfully probed, but for the final application, further investigation is necessary to improve the active site density in the MWCNTs.