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Study of the Oxygen Reduction Reaction Activity on Multi-Walled Carbon Nanotubes with Defects Formed by Rapid Thermal Annealing

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In the last two decades of the 21st century, there has been growing concern about the sever pollution in the major cities, and the significant contribution has been caused by the vehicles to this problem, which consumed almost 25% of the total energy. The rapid increase of CO_2 emission after the industrial revolution has raised the risk and the trend of the global warming, which not only leads to the climate and ecosystem change, but also affects all aspects in the society including economics and health. 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. Much research has been conducted on the development of highly active ORR catalysts to reduce the overpotential. Platinum (Pt)-based catalysts have outstanding catalytic activity and are already applied in commercial products. However, a ~~relatively~~ high cost of platinum has restricted their widespread applications. Thus, many efforts have been devoted to finding alternative catalysts to the conventional costly Pt-based electrocatalysts. Among them, carbon-based materials are one of the most promising candidates.

Among the carbon-based catalysts, despite significant efforts to improve the ORR activity of non-doped carbon electrocatalysts, the ORR activity of carbon catalysts with merely intrinsic defects is still largely inferior to that of Pt-based catalysts in acidic media due to the inertness of pure carbon. 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

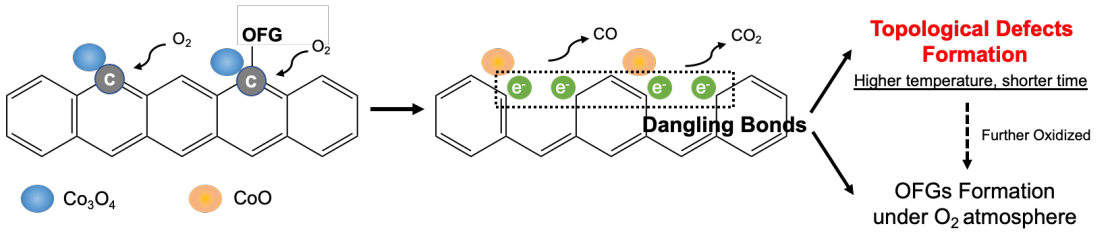
doping and creating intrinsic defects (defects formed by solely carbon atoms), with different catalytic mechanism and active sites.

Among various kinds of heteroatoms (for example N, B) for the carbon doping, nitrogen atoms have the similar radius with carbon atoms, which can decrease the lattice mismatch after doping comparing with other elements, such as S and P with significant size mismatches. Nitrogen doping is among the most extensively studied heteroatoms because the N-doped carbon material has excellent ORR activity but also that the material is easy to be modified. Generally, nitrogen doping can be typically grouped into three kinds. (1) Nitrogen doping by annealing the carbon materials with the N-containing precursors and Fe-containing agents at high temperatures in the N_2 or NH_3-containing atmosphere. This leads to the N-doped materials with high N content and high ORR activity, although it is expected that many N components are embedded in the graphene sheets. (2) Nitrogen doping by annealing the nanocarbon materials such as carbon nanotubes (CNTs) in N-containing gas. This can also lead to highly active ORR catalysts with the N mainly in the form of pyridinic and pyrrolic N. But this kind of material is generally less active than the catalysts rich in FeNx sites. (3) Nitrogen doping by post-annealing the defective carbon materials in NH_3-containing gas. The ORR activity of the material prepared by this method can occasionally be high, although it depends on both their original defective structure and Fe impurity contained the carbon precursor. Although the nature of the nitrogen doping-induced active sites is still controversial, the understanding of the factors that affect nitrogen doping is important as nitrogen atoms have a direct relationship with the active sites. On the other hand, the optimization of intrinsic defects is expected to improve the ORR performance of the 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.

However, although extensive efforts have been done to prepare highly active nitrogen doped carbon material, it is still hard to say that the nitrogen doping level or the active site formation is under controlled because the catalysts are just the residue after the pyrolysis process and a large weight loss generally happens in the annealing process. The weight loss can reach 50% or more in a few ten seconds of typical NH3 annealing, therefore the insight on the nitrogen

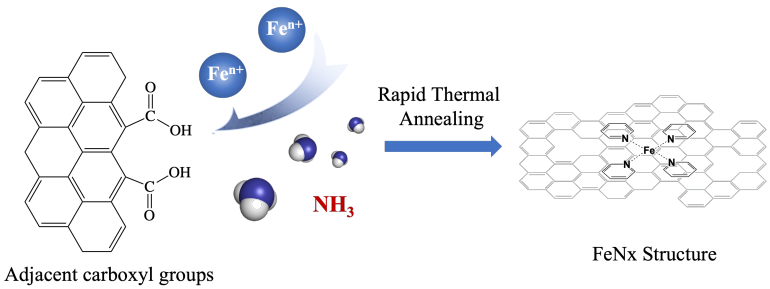
doping process related to the structure of the carbon precursor is hardly to be examined. Especially, in case the carbon precursor contains a large amount of oxygen, the carbon oxidation will be serious, resulting in a large weight loss at high temperature annealing. Nitrogen doping and defect generation 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 preparing the defective carbon, the RTA can help form highly active intrinsic defect sites without severe structure change in the carbon.

In Chapter III, a simple and economical method was developed to prepare highly active dopant-free ORR catalysts. Multi-walled carbon nanotubes (MWCNTs) were oxidized and chemically drilled by using cobalt oxide as the oxidation catalyst in an O_2/Ar atmosphere. Rapid oxidation can help create highly active defect sites with improved ORR activity without fully damaging the MWCNT structure. The oxidation condition (annealing temperature and time) for chemically drilling MWCNTs was optimized and the effect of the defectiveness of MWCNTs on ORR performance was studied. 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 oxidation conditions affect the formation of defects. The highest I_D/I_G ratio of 1.63 and the most positive onset potential 0.76 V vs RHE are shown on DMWNT-400-5s (the defective carbon produced by rapid oxidation of 400 °C and 5s). On the other hand, intrinsic topological defect formation and OFG formation as the competing reaction, occur during the rapid oxidation process, which results in 400 °C and 5s annealing as the optimal oxidation condition, as shown in Scheme 1-1. The high activity of defective MWCNTs produced by rapid oxidization is not only on account of the creation of highly active defect sites, but also owing to the fewer detrimental OFGs around the carbon edges in rapidly oxidized defective MWCNTs. The electron transfer number obtained from the rotating ring-disk electrode measurement is in a range of 2.3-2.7, indicating a dominant 2-electron reaction pathway of ORR of the non-doped defective MWCNTs and the non-doped defective MWCNTs as the ORR active sites.



Scheme 1-1 The possible process of the oxidation by CoO_x on HA CNT.

In Chapter IV, a simple method is proposed for removing a part of the OFGs from DMWNTs by performing Ar annealing at various temperatures (300°C, 500°C, 700°C, and 900°C) prior to nitrogen doping. Raman and XPS characterization of Ar annealed DMWNTs revealed that different types of OFGs decomposed on DMWNTs surface at different temperatures. The electrochemical performance of nitrogen doped DMWNTs was investigated, and the ORR onset potential decreased with increasing annealing temperature, with a noticeable drop found on samples doped with nitrogen without the assistance of carboxyl groups. According to X-ray photoemission spectroscopy results, the removal of paired carboxyl groups reduced the amount of nitrogen atoms doped into the DWMNTs and the formation of the FeNx structure while the carboxyl group affect the nitrogen doping level. The onset potential increased by increasing the carboxyl group concentration via HNO_3 washing. All the data for surface oxygen concentration, overall nitrogen content, electron transfer number, and onset potential demonstrated that the carboxyl groups were critical for nitrogen doping of DMWNTs and aiding in the formation of FeNx structure. Considering all of these findings, it can be concluded that the removed OFGs at 500°C played an essential role in nitrogen doping. That is, the paired carboxyl group (-COOH) aids nitrogen doping on the defective CNTs, which contributes to the FeNx structure formation. This work establishes a framework for improving electrocatalytic activity and designing nitrogen-doped carbon-based ORR catalysts.



Scheme 1-2 Illustration of possible mechanism of the FeNx formation

In Chapter V, the intrinsic defects are considered as another critical parameter for affecting the nitrogen-doping level because nitrogen doping is hard to be performed in the pristine MWCNTs with little defects. 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 with the highest nitrogen content of 1.8 at. %. The Temperature programmed desorption (TPD) result shows that there is almost no carboxyl group existed on the defective CNT produced by the rapid oxidation. Even without the help of OFGs, the nitrogen doping ~~still~~ can be proceeded by the intrinsic defects produced by the rapid oxidation. These findings give a guidance on improving nitrogen doped carbon materials by the optimizing intrinsic defects.

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 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.