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主 論 文 の 要 旨

論文題目 The Oxygen Reduction Catalytic Activity of Hetero-atom Doped Carbon Materials by Solution Plasma （ソリューションプラズマを用いた異種原子ドープカーボン材料の酸素還元触媒性能）

氏 名 金 大旭

論 文 内 容 の 要 旨

The oxygen reduction reaction (ORR) is one of the most important factors in the performance of an energy conversion device, in particular, the cathode reaction of fuel cell and metal-air battery. Effective ORR catalysts are essential for desirable current density and stability. Commercially, Pt-based materials with good electrochemical properties have been widely used as ORR catalysts. However, the main drawbacks of Pt catalyst include high manufacturing cost, short-term durability, methanol tolerance and easily polluted by carbon monoxide (CO).

Chapter 1 begins with a general introduction to the ORR that fundamentals and potential catalysts and formation of materials, and application. The purpose of this study is to invent non-noble metal catalyst as alternative to Pt-based catalyst. Therefore, in this study, we synthesized and progress three different types of ORR catalyst: metal nanoparticle based, metal compound based and metal-free based. In chapter 2, our study focused on applying non-noble metal carbide (WC) as ORR catalyst without any noble metals. The nanocomposite of tungsten carbide on two different carbon matrices, pure carbon matrix (WC/C) and N-doped carbon matrix (WC/N-C) were compared. The nitrogen was doped within the carbon matrix for the synergetic effect between N-doped and WC to improve the ORR activity. Although the ORR activity of WC/N & # 8211;C was still incompatible to that of Pt, the material presented a 40 % higher durability compared to that of Pt/C catalyst. In order to further improve the ORR catalytic activity, Chapter 3 researches to the effect of metal-nitrogen compounds on ORR. The Fe-N4-macrocycle catalysts were compared to N4-macrocycle catalysts. The introduction of Fe into N4 macrocyclic structure demonstrated not only superior in terms of ORR activity, but also higher electron transfer process and electrocatalytic stability. It was observed that the transition metal in N4-macrocycle catalyst can act as a stabilizer and an enhancer for a better catalytic activity and stability as ORR catalyst. In fact the results were highly related to the chemical bonding and the

band gap energy difference in Fe-N4 site. Also, FP-MCSs are shown the fast four-electron process, as on Pt.

On the other hands, hetero-atom doped carbon matrix has been attracting numerous attentions due to superior electrochemical stability, light weight and low cost. Hence, in chapter 4, various type of hetero-atom, including N, B and P with carbon matrix was synthesized by SPP. Detailed chemical structure and electrochemical performance of each catalyst was performed. Due to different electronic structure and chemical properties in boron and phosphorus, it was supposed that N with B or P multiple doping can change electron structure of carbon matrix. Therefore, the binary hetero-atom carbon matrix was expected to possess new active site corresponding to the ratio and position of dopants. The effect of each dopants on ORR was as follows; N $>$ P $>$ B. However, the multiple doped carbon such as B-N-doped and P-N-doped were enhanced ORR activity and stability. In comparison with N-doped, the ORR potential was positively shifted to - 0.27 V and - 0.24 V.

Finally, chapter 5 summarized the effect of each type of catalysts and it might be a promising and efficient catalytic material for ORR in energy conversion devices. In this study, we have successfully synthesized three different types of ORR catalysts: metal nanoparticle based, metal compound based and metal-free based by a single process, solution plasma process. The results observed that (1) The activity of metal nanoparticle based ORR catalyst increased with doping of nitrogen within the carbon matrix, (2) The addition of transition metal Fe further enhanced the ORR catalytic activity in N-doped based catalyst and (3) the binary non-metal hero-atom catalysts exhibited superior ORR catalytic activity than single hetero-atom N, B or P based carbon matrix.