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## 学位論文内容の要旨/Dissertation Abstract

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### 学位論文題名/Title of Dissertation

Enhancement of the activity and durability of platinum alloy nanowire electrocatalysts for oxygen reduction and evolution reactions

(白金合金ナノワイヤー触媒における酸素還元および酸素発生反応に対する活性と耐久性の向上)

In recent years, the development of hydrogen energy has seen tremendous growth as the demand for clean energy development has increased. Polymer electrolyte fuel cell (PEFC), which consume hydrogen to generate electricity, and proton exchange membrane water electrolyzer (PEMWE), which produce hydrogen, have attracted much attention as the two ends of the hydrogen energy industry. PEFC is a promising device to supply electricity and heat, which promises to rewrite the existing energy supply mode. PEMWE also has many advantages as an environmentally friendly electrolyzer for H<sub>2</sub> production, and plays an important role in the development of hydrogen energy. However, both PEFC and PEMWE face the activity decrease problem due to catalyst degradation in the strong acidity and high potential of the working conditions. Therefore, development of more active and durable electrocatalysts is urgently required. The objective of this paper is to challenge the control of both metal composition and shape, aiming on enhance the activity and durability of oxygen reduction reaction (ORR) catalysts for PEFC and oxygen evolution reaction (OER) catalysts for PEMWE. Thus, I investigated the performance of (i) PtNi bi-alloyed nanowire ORR catalysts; (ii) PtNiCo multi-alloyed nanowire ORR catalysts, and (iii) PtNiIr multi-alloyed nanowire OER catalysts, respectively. This thesis consists of six chapters. Chapters 3 and 4 present the study of ORR catalysts for PEFC, Chapter 5 presents the study of OER catalysts for PEMWE, and the others are general statements.

In Chapter 3, I synthesized PtNi NWs as the ORR electrocatalyst at three different heating temperatures of 433, 493 and 553 K to obtain PtNi NWs in the presence and absence of PtNi nanoparticles (NPs). The three types of PtNi NWs were loaded on Vulcan XC-72R and characterized. The Ni contents in the PtNi NWs increases from <5 to 15 at% and the number of nanoparticles decreases as the heating temperature increases. I found a structural transformation from PtNi NWs prepared at 493 K contain PtNi NPs into beads-on nanowires with the Pt-skin and PtNi-alloy-core during potential cycles. Because such structural transformation was not observed on the other two types of PtNi NWs prepared at 433 K and 493 K, the Ostwald ripening of co-present NPs to NWs with the 15 at% Ni content results in the formation of the beads-on nanowires. This beads-on nanowire had high ORR activity, which is two times two times as high as that of commercial Pt/C, and high durability that tolerant to metal dissolution during 2000 potential cycles even at 353

K. The high durability originates from a change of the electronic structure of the surface Pt brought about by the structural transformation, revealed by using CO stripping voltammetry and *in situ* X-ray absorption spectroscopy: the down-shift of the *d*-band center suppresses the surface oxide formation, thereby inhibiting the chemical dissolution of metals via M-O species.

In Chapter 4, I tried to incorporate Co into PtNi NWs to get higher ORR activity. I synthesized PtNiCo multi-alloy NWs (PtNiCo NWs) in the presence of PtNiCo NPs at a heating temperature of 493 K for comparison with PtNi NWs which also synthesized at 493 K in the previous chapter. The PtNiCo NWs were also loaded on Vulcan XC-72R and characterized. I found that the length of PtNiCo NWs was shorter than that of PtNi NWs even at the same synthesis temperature. The PtNiCo NWs show higher ORR activity, in agreement with the theory that the addition of Co changes the position of the *d*-band center to an optimized position. Due to the PtNiCo NWs also have co-existing NPs, they also transformed into beads-on nanowires after 2000 potential cycles at 353 K. Although the activity of PtNiCo NWs slightly decreased, it maintained activity 2.5 times than the commercial Pt/C. I am confirming again that the structural transformation induced by Ostwald ripening assisted by the co-existing NPs can enhance the durability.

In Chapter 5, I synthesized PtNiIr NWs at the heating temperature of 493K, then loaded them on boron-doped nanodiamond (BDND) or Vulcan XC-72R and characterized. BDND has excellent stability over a wide potential window due to its diamond characteristics. This time I obtain pure PtNiIr NWs without any presence of NPs. Both BDND and Vulcan supported PtNiIr NWs exhibited robust initial OER catalytic activity, with MA up to 15 times higher than commercial IrO<sub>2</sub> catalysts. The results of CO stripping voltammetry of the PtNiIr NWs showed that a large number of Ir active sites were exposed on the surface, indicating the source of OER activity. After potential cycles, effects of the different supports were manifested. The Vulcan XC-72R support showed severe degradation, leading to agglomeration, dissolution and redeposition of the PtNiIr NWs, and drastically reducing the catalytic activity. On the other hand, BDND remained virtually unchanged, and PtNiIr NWs undergoing no structural changes, so that kept OER activity well. The performance of PtNiIr NWs/BDND is a great advance for nanostructured metal OER catalysts with carbon-based support, and can dramatically accelerate the development of OER catalysts with high efficiency for PEMWE.

In conclusion, I successfully synthesized highly active and durable alloy NWs catalysts with the different compositions for ORR and OER. I also reveal the occurrence conditions and evolution process of structural transformation from nanowires to bead-on NWs during potential cycling. This structural transformation changes the electronic state of the catalyst surface and prevents the etching of the metal contents, thus improving the activity and durability of the catalyst. This self-optimization phenomenon during the reaction provides a new direction for research in the development of high-performance catalysts.