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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 cells (PEFCs), which consume hydrogen to generate electricity, and proton exchange membrane water electrolyzers (PEMWEs), which produce hydrogen, have attracted much attention as the two ends of the hydrogen energy industry. The 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 H₂ production, and plays an important role in the development of hydrogen energy. However, both PEFCs and PEMWEs 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 thesis is to control both metal composition and shape, aiming the enhancement of the activity and durability of oxygen reduction reaction (ORR) catalysts for the PEFC and oxygen evolution reaction (OER) catalysts for PEMWE. Thus, I investigated (i) PtNi bi-alloyed nanowire ORR catalysts; (ii) PtNiCo multi-alloyed nanowire ORR catalyst, and (iii) PtNiIr multi-alloyed nanowire OER catalyst, 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 Chapters 3, I synthesized PtNi NWs as the ORR electrocatalyst at three different heating temperatures of 433, 493 and 553 K, which are denoted as NW_{433K}, NW_{493K} and NW_{553K} respectively, 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 decrease as the heating temperature increases. I found a structural transformation for NW_{493K} from PtNi NWs contain PtNi NPs into beads-on nanowires (**Figure 1b,e**) with the Pt-skin and PtNi-alloy-core during potential cycles. Because such structural transformation was not observed on NW_{433K} and NW_{553K} (**Figure 1**), 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 as high as the mass activity of commercial Pt/C, and high durability with low metal dissolution during 2000 potential cycles even at 353 K. The linear sweep voltammograms (LSVs) before and after potential cycling (**Figure 2**) show that the half-wave potential difference ($\Delta E_{1/2}$) was not observed for NW_{493K}. This high durability originates from a change of the electronic structure of the surface Pt brought 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.

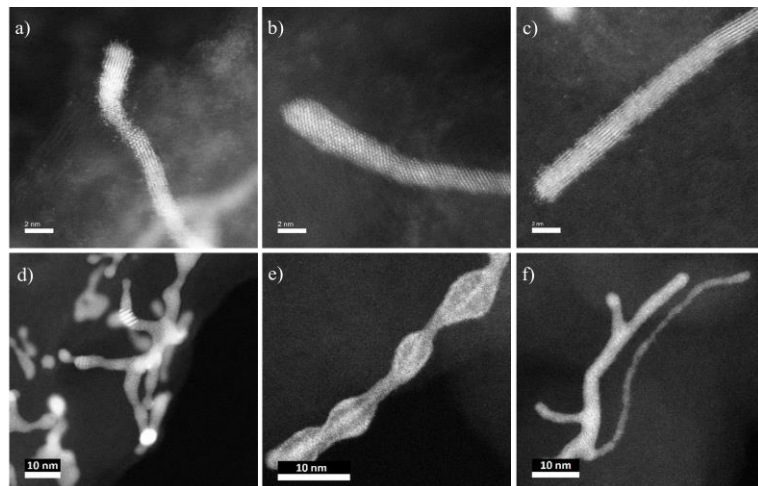


Figure 1. HAADF-STEM images of PtNi (a) NW_{433K}, (b) NW_{493K}, and (c) NW_{553K} before potential cycles, and (d) NW_{433K}, (e) NW_{493K}, and (f) NW_{553K} after potential cycles.

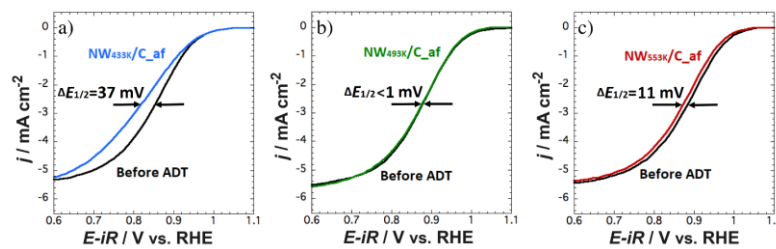


Figure 2. LSVs of carbon loaded PtNi (a) NW_{433K}/C before (in black) and after potential cycles (in blue), (b) NW_{493K} before (in black) and after potential cycles (in green), (c) LSVs of NW_{553K}/C before (in black) and after potential cycles (in red). LSVs were recorded at 1600 rpm and 10 mV s⁻¹ in a 0.1 M HClO₄ aqueous solution under oxygen. The arrows indicate the $\Delta E_{1/2}$.

In Chapters 4, I incorporated Co into PtNi NWs to optimize the *d*-band center position for multi-alloy catalysts to enhance ORR activity. I synthesized PtNiCo multi-alloy NWs (PtNiCo NWs) at three different synthesis temperatures of 493, 533 and 573 K in the presence of PtNiCo NPs (**Figure 3**). The PtNiCo NWs were also loaded on Vulcan XC-72R and characterized. I found that the length of PtNiCo NWs and the number of co-present PtNiCo NPs decrease as synthesis temperatures increase. All the PtNiCo NWs show 2.5 times higher ORR mass activity than PtNi NW_{493K} in Chapters 3, in agreement with the theory that the addition of Co

changes the position of the *d*-band center to an optimized position. After 2000 potential cycles at 353 K, PtNiCo NWs synthesized at 493 K, which coexists with NPs and has a high CoNi alloy composition, also transformed into beads-on nanowires similar to Chapter 3, keeping ORR activity. The structural transformation induced by Ostwald ripening assisted by the co-existing NPs can enhance the durability even for multi-alloy catalysts.

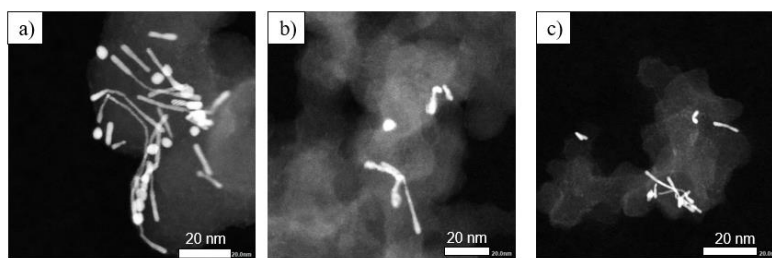


Figure 3. HAADF-STEM images of PtNiCo (a) NW_{493K}, (b) NW_{533K}, and (c) NW_{573K}.

In Chapters 5, I synthesized PtNiIr NWs at the heating temperature of 493 K, then loaded them on boron doped nanodiamond (BDND) or a carbon black of Vulcan XC-72R. BDND has excellent stability over a wide potential window due to its diamond characteristics. This time I obtain PtNiIr NWs in the absence of NPs. Both BDND and carbon supported PtNiIr NWs exhibited high initial OER catalytic activity, which is 15 times higher mass activity than commercial IrO₂ catalysts. The results of CO stripping voltammetry of the PtNiIr NWs showed that many Ir active sites were exposed on the surface. After potential cycles, effects of the different supports were manifested. The carbon support showed severe degradation, leading to agglomeration, dissolution and redeposition of PtNiIr NWs, and drastically reducing the catalytic activity. On the other hand, BDND remained virtually unchanged, and PtNiIr NWs kept the structural and OER activity well. PtNiIr NWs/BDND will initiate the development of OER catalysts with high durability for PEMWEs.

In conclusions, I successfully synthesized highly active and durable alloy NW catalysts with different compositions for the ORR and OER. I also reveal the occurrence conditions and evolution process of bead-on nanowires 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.