Electrochemical Evaluation of Oxygen Reduction Reaction Activity of Pt-surfaced PtNi Dodecahedral Nanoframes

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Abstract

Pt-based bimetallic nanoframes have been demonstrated to have high activity for a number of electrocatalytic reactions. Their morphology, crystal facets and compositions are important factors that regulate their catalytic activities. In this research we demonstrate electrochemical performance of Pt surfaced PtNi dodecahedral nanoframes with variable Pt/Ni ratios for applications such as renewable fuel for automotive industry. We demonstrate that combining Pt with first-row transition metals such as Ni increases oxygen reduction reaction (ORR) kinetics that is usually hindered on Pt by the relatively strong bonding of oxygen species near the thermodynamic potential for ORR and that results in a significant overpotential. Cyclic voltammetry was employed to evaluate the electrochemical properties of the PtNi nanoframes as a function of oxidative etching time. Etching time affects the Pt percentage in the PtNi skeleton and that has an impact on the ORR activity of the nanoframes. The ORR activity of the nanoframes increases and then decreases with increasing acetic acid etching time and reaches the top of activity volcano at 6 hrs of etching, with a specific activity of 1.9 mA_{cm}⁻². This study reveals the significance of the composition of the sublayer and also provides guidance for further tuning to improve the performance of Pt-based alloy nanocatalysts.

Synthesis and Characterization of PtNi Nanoframes

To understand the effect of composition and crystal facets on the ORR activity of PtNi nanoframes, we synthesized a series of PtNi rhombic dodecahedral nanoframes via a two-step solution-based process, wherein solid PtNi rhombic dodecahedra undergo oxidative etching to form dodecahedral PtNi nanoframes as seen in Fig. 1.

Figure 1. Illustration of the synthetic routes of PtNi rhombic dodecahedral nanoframes.

XPS Spectroscopy: This method was used to investigate surface composition of the PtNi NFs (Fig. 2 and Fig 3). Our survey scans revealed relatively small but still detectable Ni peaks for samples with Pt content less than 60%. These results suggest that for samples with Pt content of 28.0% and 46.6% Ni is present at the surface of the particles. It was found that the Pt 4f_{7/2}, 4f_{5/2}, 4d_{5/2}, and 4d_{3/2} peaks of the PtNi NFs were located at 70.4, 73.7, 314, and 331.3 eV, respectively. The Pt 4f peaks for commercial Pt NP/C samples were shifted to 74.7 eV (1eV higher binding energy level compared to PtNi NFs) which suggests that the PtNi alloy at the core of the material influences the electronic properties of the Pt surface sites.

Figure 2. XPS survey spectra of catalyst ranges from 28.0% Pt to 65.4% Pt.

Figure 3. XPS spectra of Pt 4f (A) and 4d (B) of PtNi NF catalysts with compositions ranging from 28.0% Pt to 65.4% Pt.

Electrochemical Evaluation

Cyclic Voltammetry: The CVs of PtNi NFs (Fig. 4) display the hydrogen adsorption/desorption (0 – 0.4 V) and surface oxide regions (0.6 – 1.0 V) and are consistent with presence of Pt-rich, nanostructured surface. The fact that the hydrogen adsorption region is relatively independent from the etching time suggests formation of a Pt skin during the etching process. This phenomenon also suggest that the capping agents used in the synthesis have consistent effect on various samples. Since Ni is readily leached from the surface, the density of Ni sites was expected to be very low regardless of the overall concentration of Ni in the particle. The oxide reduction peaks potentials show a volcano-type dependence on Pt content. The maximum reduction potential of 868 mV was observed in 57.3% Pt sample. Peak potentials for the PtNi NFs were shifted by +40 to +70 mV compared to peaks observed in the CV for commercial Pt NP/C electrode. Because of that PtNi NFs were expected to have increased ORR performance due to weaker interaction with oxygen adsorbates.

Figure 4. Cyclic voltammograms (A) of PtNi nanoframes as a function of Pt content. The cathodic oxide reduction peaks (B) and the trend in oxide reduction peak potential with respect to composition (C) are also shown.

ORR Performance: Catalytic activity of the PtNi NFs displayed a volcano-type dependence as a function of etching time (Fig. 5) with the peak performance (1.9 mA_{cm}⁻²) for the 6-hour etching time corresponding to 46.6% Pt content. That trend was similar to the position of the oxidation reduction peak. Over the entire composition regime, the mass activity of the PtNi NFs samples are approximately 2-fold higher than the U.S. Department of Energy mass activity target of 0.44 A mg⁻¹ projected for 2020.

Figure 5. ORR polarization curves of PtNi nanoframes (A) collected in oxygen-saturated 0.1 M HClO₄ at a rotation rate of 1600 rpm. The onset region of the polarization curve is highlighted as an inset. The specific and Pt mass activities as a function of nanoframe composition (B) are shown in comparison with Pt NP/C.

Catalyst Durability

A 5000-cycle extended durability test for ORR catalysts was performed. The experiment consisted of taking polarization curves before and after durability testing and comparing it to commercial Pt NP/C under identical conditions. This test resulted in a relatively small 10 mV shift in the half-wave potential of the polarization curve for PtNi NFs compared to 16 mV shift for the Pt NP/C. In addition to that, there was a 14% decrease in the ECSA observed when comparing CVs before and after the durability test compared to 38.7% decrease for the Pt NP/C. All the above indicated that the PtNi NFs have better durability compared to an analogous Pt NP/C catalyst.

Figure 6. Cyclic voltammogram and ORR polarization curves of the PtNi nanoframe catalyst.