

Oxidation of Methanol on Pt-Ni Alloy Nanoparticles

Prepared by Spontaneous Deposition

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Introduction

Spontaneous deposition is a simple and unique method that is based on a redox reaction with an aid of a driving force of a potential gap. There have been many researches using various binary electrocatalysts with mono- and multi- layers prepared by this method, but they were composed of only precious metals. We have applied the method to the deposition of Pt on Ni that was not a precious metal. We found that Pt-Ni alloy nanoparticles were produced on a Ni substrate, resulting in the improved electrocatalytic activity for methanol oxidation. In this work, the effect of additives or substrates on the electrocatalytic activity for methanol oxidation was investigated.

Experimental

A Ni disk with the diameter of 5 mm and height of 5 mm was annealed at 500 °C in H₂ atmosphere for 1 h to remove surface oxide. After cooling the Ni disk down to ambient temperature, 10 mM H₂PtCl₆ aqueous solutions containing 0-100 mM NiSO₄ as an additive were cast on the Ni disk, respectively. After 5 min, the prepared electrocatalysts were washed with Millipore water (18.3 M Ω) and then used for various measurements. Ni₃Mo and Ni₃W alloys as a substrate were prepared by arc melting.

Results and Discussion

Figure 1 shows SEM images of the prepared deposits. The deposits were nanoparticles with apparent sizes of 250-300 nm. When higher concentrations of Ni²⁺ were involved in 10 mM H₂PtCl₆ aqueous solution, the particle size of the deposits became small. The (1 1 1) diffraction peak for each deposit caused line-broadening, suggesting the production of nanoparticles, and shifted in higher diffraction angles, suggesting alloying between Pt and Ni.

Assuming that each deposit is a homogeneous Pt-Ni alloy, its composition was estimated according to Vegard's law (Fig. 2). AES also showed that each deposit was composed of only Pt and Ni. XPS spectra for the Pt-Ni alloy nanoparticles showed that Pt 4f_{7/2} peak shifted in higher binding energies than Pt and Ni 2p_{3/2} peak shifted in lower binding energies than Ni. The positions of the Pt 4f_{7/2} and Ni 2p_{3/2} peaks kept constant irrespective of the Ni²⁺

concentration. The onset potential for methanol electrooxidation was evaluated by cyclic voltammetry. The onset potential for Pt-Ni electrodes was somewhat more negative than that for Pt. Potentiostatic measurement for methanol oxidation showed that current decay for the Pt-Ni electrodes was slower than that for a Pt electrode. Ni²⁺ in H₂PtCl₆ aqueous solution made no difference on the onset potential and current decay in the potentiostatic measurement for methanol electrooxidation compared with Pt-Ni.

In case of Pt-Ni₃Mo and Pt-Ni₃W electrodes, the onset potential for methanol electrooxidation was more negative than Pt-Ni electrodes. Current decay in the potentiostatic measurement also effectively suppressed.

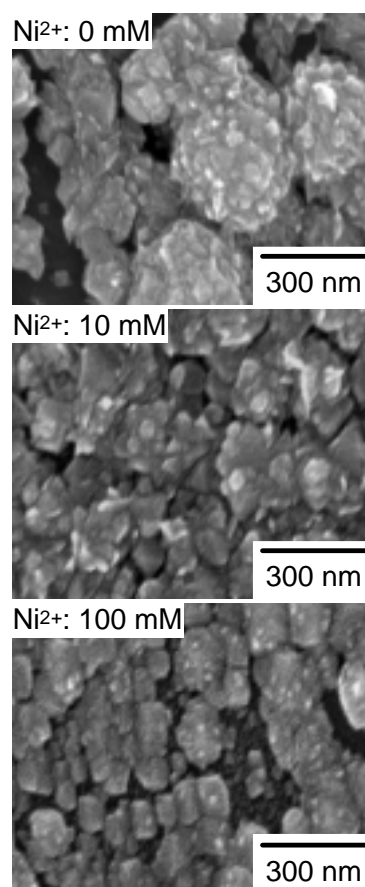


Fig. 1 SEM images of the prepared deposits

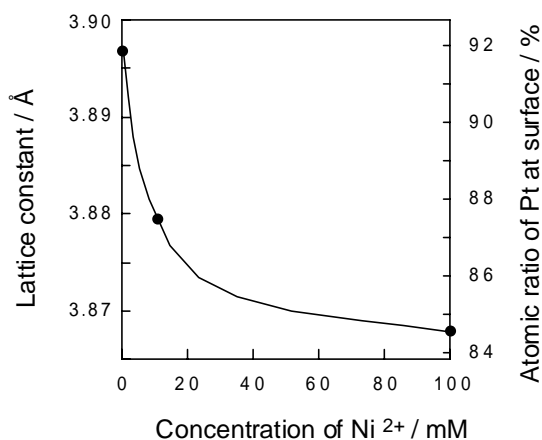


Fig. 2 Content of Pt in deposits