

## Electrochemical Construction of Ni and Co core - Pt Shell Nanoparticles As Catalysts for Oxygen Reduction Reaction

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### 1. Introduction

Because of modern social problems such as an environmental pollution and energy crisis, polymer electrolyte fuel cell (PEFC) has been expected as one of the clean and high power sources for next generation [1]. PEFC should require platinum (Pt) as a cathode material for oxygen reduction reaction (ORR). However, Pt is one of the most expensive and precious metals, and moreover, electrocatalytic activity of polycrystalline Pt for ORR is not enough to actual operation. Thus, many studies, such as construction of Pt nanoparticles, Pt ultra-thin layers, and alloys with/without Pt, have been carried out in order to increase the electrocatalytic activity for ORR and reduce the cost of Pt electrocatalyst for PEFC.

There are two methods to prepare Pt nanoparticles, such as chemical and electrochemical methods. Chemical reduction method needs many reagents, not only Pt complex ion, but also reduced reagent and surfactant, and also heat treatments to remove the biproducts and to deposit them onto the electrode surface. These treatments should cause a contamination and/or aggregation of Pt nanoparticles, leading that it is difficult to control the size and size distribution. On the other hand, electrochemical method is so simple and we can control the size and size distribution of Pt nanoparticles by optimizing of the deposition condition such as concentration of Pt complex ion, deposition potential, and deposition period. Recently, Rios-Reyes et al. succeeded to electrochemically prepare Co nanoparticles with narrow size distribution on the carbon electrode surface by using  $\text{Na}_2\text{SO}_4$  electrolyte solution [2].

In order to increase electrocatalytic activity and to reduce the cost of the Pt electrocatalyst, in this study, we electrochemically prepared the Ni and Co nanoparticles on the glassy carbon electrode (GCE) with several deposition conditions, and then the nanoparticle surface was covered with Pt monoatomic layer by galvanic replacement [3,4]. These nanoparticles were so-called to core-shell nanoparticles and abbreviated here as Pt@Ni and Pt@Co, respectively.

### 2. Experimental

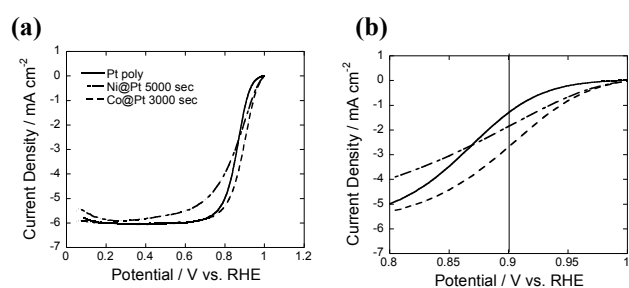
Potential of the GCE was stepped from open circuit potential (OCP) to electrodeposition potentials as -1.68 V (vs. MSE) for Ni and as -1.57 V (vs. MSE) for Co in a deaerated 10 mM  $\text{NiSO}_4$  or  $\text{CoSO}_4$  solution containing 1 M  $\text{Na}_2\text{SO}_4$  [2,5]. After several periods, the potential was stepped back to OCP. In order to convert the surface layer of Ni or Co particles with Pt, a few drops of concentrated  $\text{K}_2\text{PtCl}_6$  solution was added.

The linear sweep voltammograms (LSVs) of the prepared GCEs modified with Pt@Ni and Pt@Co nanoparticles were measured in an oxygen saturated 0.1 M  $\text{HClO}_4$ . Characterization of Pt@Co and Pt@Ni nanoparticles was performed by atomic force microscopy

(AFM) and X-ray photoelectron spectroscopy (XPS).

### 3. Results and Discussion

Figure 1 shows LSVs of the GCEs modified with Pt@Ni or Pt@Co nanoparticles, which were prepared for deposition periods of 5000 s and 3000 s, respectively, measured in the oxygen saturated 0.1 M  $\text{HClO}_4$ . Result of polycrystalline Pt was also shown in Fig. 1. Cathodic current in Fig. 1 can be assigned to ORR. The more positive the LSV curve is, the higher the electro motive force of PEFC is (the less overpotential is). The higher cathodic current at a certain potential, the higher the reaction rate. Kinetic current density,  $J_k$ , which was obtained from Koutecky-Levich plot, at 0.9 V and half-wave potential,  $E_{1/2}$ , were listed in Table 1. As clearly seen in Fig. 1 and Table 1, the electrocatalytic activities of both Pt@Ni and Pt@Co nanoparticles are higher than that of polycrystalline Pt. These results suggested that surface energy of the monoatomic layer of Pt was modified with the core nanoparticles of Ni or Co. We are now going to investigate the relationship between the size of Pt@Ni and Pt@Co nanoparticles and electrocatalytic activity for ORR.



**Figure 1.** LSVs of the prepared GCEs modified with Pt@Ni and Pt@Co nanoparticles and the polycrystalline Pt electrode measured in the oxygen-saturated 0.1 M  $\text{HClO}_4$ . Potential scan was positively started from 0.05 V. Pt@Ni and Pt@Co were prepared by the deposition period of 5000 s and 3000 s, respectively. Rotation rate: 1600 rpm, scan rate: 10  $\text{mV s}^{-1}$ . (b) Expanded one of (a) between 0.8 V and 1.0 V.

**Table 1.** Analysis data of the half-wave potential,  $E_{1/2}$ , and the kinetic current density,  $J_k$ , at 0.90 V.

|         | $E_{1/2}$ / V<br>(vs. RHE) | $J_k$<br>mA cm <sup>-2</sup> |
|---------|----------------------------|------------------------------|
| Pt@Ni   | 0.87                       | 3.10                         |
| Pt@Co   | 0.86                       | 4.85                         |
| poly Pt | 0.86                       | 1.62                         |

### References.

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