Preparation of Pt-based Nanoparticles by Electrodeposition Techniques and Their Applications to Catalysts for Fuel Cells

（電析法を用いた白金系ナノ粒子の作製および燃料電池用触媒への応用）

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Preparation of Pt-based Nanoparticles by Electrodeposition Techniques and Their Applications to Catalysts for Fuel Cells

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Chapter 1 General Introduction

1.1 Introduction

Fuel cells attract attention as clean energy devices because they generate electricity with chemical energy which is produced by the reaction of hydrogen and oxygen to water without CO₂ evolution. In addition, fuel cells have high power generation efficiency because they are not influenced by the second law of thermodynamics. Besides, fuel cells are also expected to be utilized for Smart Energy System in which they are combined with information technology and solar power generations.

Fuel cells have been developed for over forty years since they were installed in Gemini 5 in the Gemini programs. In recent years, several policies have been administered to assist market introduction of fuel cells. In Europe in 2008, European Fuel Cell and Hydrogen Joint Technology Initiative formulated a system for supporting technology development and verification test. In United States in 2009, the government supported 42 million dollars to facilitate commercialization and installation of fuel cells. On the other hand, in Japan demonstration run tests of fuel cell vehicles have been held in various regions due to their spread. Road maps on fuel cells and hydrogen energy formulated by New Energy and Industrial Technology Development Organization (NEDO) describe that household fuel cells and fuel cell vehicles begin to be practically used in around 2015, and become wide-spread in around 2030.

Fuel cells are often classified in terms of their electrolyte as shown in Table 1. There are four typical fuel cells, polymer electrolyte fuel cells (PEFCs), phosphoric acid fuel cells (PAFCs), molten carbonate fuel cells (MCFCs), and solid oxide fuel cells (SOFCs) whose electrolyte was different. PEFCs are composed of a conductive polymer
<table>
<thead>
<tr>
<th></th>
<th>PEFC</th>
<th>PAFC</th>
<th>MCFC</th>
<th>SOFC</th>
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</thead>
<tbody>
<tr>
<td>Electrolyte</td>
<td>Conductive polymer membrane</td>
<td>Phosphoric acid</td>
<td>Molten carbonate</td>
<td>Ion conducting ceramics</td>
</tr>
<tr>
<td>Working Temperature</td>
<td>RT～100℃</td>
<td>150～200℃</td>
<td>600～700℃</td>
<td>700～1000℃</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Pt catalyst</td>
<td>Pt catalyst</td>
<td>Anode : Ni-Cr, NiAl</td>
<td>Anode : Ni/YSZ</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cathode : NiO</td>
<td>Cathode : (La, Sr)MnO₃, (La, Ca)MnO₃</td>
</tr>
<tr>
<td>Feature</td>
<td>• Light weight</td>
<td>• Practical use</td>
<td>• High power generation</td>
<td>• High power generation</td>
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<td></td>
<td>• Low temperature operation</td>
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<td>efficiency</td>
<td>efficiency</td>
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<td></td>
<td>• High energy density</td>
<td></td>
<td>• Internal reforming</td>
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<tr>
<td>Application</td>
<td>• Electric vehicle</td>
<td>• On-site power generation</td>
<td>• Large scale power generation</td>
<td>• Large scale power generation</td>
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<td></td>
<td>• Household fuel cell</td>
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<td></td>
<td>• Portable device</td>
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electrolyte membrane and two electrodes with Pt nanoparticle electrocatalysts. PEFCs have characteristics of lightweight, low-temperature operation, high energy density etc. In PAFCs, phosphoric acid is an electrolyte, and electrocatalysts are the same as those in PEFC. PAFCs were put into practical use as on-site power generation. MCFCs also have a molten carbonate electrolyte. Ni-Cr or Ni-Al and NiO are used as the anode and cathode, respectively. MCFCs showed high power generation efficiency, so that they were expected to be applied for large scale power generation. But now, only a few large scale tests were carried out. The electrolyte of SOFCs is ion conducting ceramics. Ni-YSZ and (La, Sr)MnO$_3$ or (La, Ca)MnO$_3$ are used as the anode and cathode, respectively. SOFCs work at high temperatures of 700 - 1000 °C, so impurities in fuel gas such as CO can also be used as fuel. Moreover, SOFCs have high power generation efficiency like MCFCs, so that they are being developed for large-scale power generation.

PEFCs are better candidates as power sources of the household fuel cells and fuel cell vehicles. However, there are some serious problems to be resolved. The high price of PEFCs must be the most important urgent problem. At present, the prices of a household fuel cell system costs and a fuel cell vehicle are around 2.5 million yen and 10 million yen, respectively. Such high price PEFCs are ascribed to the use of a large amount of Pt used as catalysts. So reducing the consumption of Pt is a high priority issue for practical use.

1.2 Background

1.2.1 Catalysts for fuel cells

Pt-based nanoparticles are commonly used as electrocatalysts for PEFCs because of
their high catalytic activity. Hydrogen oxidation and oxygen reduction reactions readily proceed on their surface. In addition, the Pt-based nanoparticles exhibit higher corrosion resistance and stability than other transition metals. The Pt-based nanoparticles are loaded on carbon black (CB) powders with high surface area and distribute with high dispersity.

Pt is a well-known noble metal whose price was about 4,800 yen per gram in April 2013. So Pt is 2,700 times and twice as expensive as Ni (about 1.8 yen per gram) and Pd (about 2,300 yen per gram), respectively. The reserves of Pt are poor, so that reducing the consumption of Pt is an urgent issue.

There have been many researches on the reduction of Pt consumption. For example, in order to enlarge surface area, increasing the dispersity of Pt nanoparticles and decreasing their size [1-5] have been investigated. In addition, alloying with foreign metals [6-14] and shape controlling [15-19] of Pt nanoparticles are also ways to improve the catalytic activity. There are so many reports on Pt-Ru and Pt-transition metal alloys as electrocatalysts for fuel cells. The Pt-Ru alloy is the best anode catalyst because it promotes the oxidation of CO to CO₂ via bifunctional mechanism [7], leading to high CO-tolerance. The Pt-transition metal alloys also exhibit high catalytic activity for oxygen reduction reaction, and recently Pt-Co alloy has been studied as for a new ORR catalyst [8, 9, 13, 14]. When it comes to the shape-controlled Pt nanoparticles, several types of nanoparticles such as a cubic structure enclosed by the (100) plane and a tetrahedral one enclosed by the (111) plane were prepared [14-18]. The shape-controlled Pt nanoparticles are exemplified in Table 2.

1.2.2 Preparation methods of Pt nanoparticles

The preparation method of Pt-based nanoparticles was usually classified into two. One is the preparation of Pt colloids in solutions and their loading on CB powders.
<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Contents</th>
<th>Paper</th>
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<tr>
<td><strong>Alloying</strong></td>
<td></td>
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<td><strong>Shape controlling</strong></td>
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For example, a Pt-sulfite complex prepared from H$_2$PtCl$_6$ and NaHSO$_3$ is mixed with H$_2$O$_2$ to form a Pt oxide colloid, and then the resultant colloid is reduced by H$_2$ bubbling [20]. Another is thermal decomposition of catalyst precursors loaded on CB powders in an H$_2$ atmosphere. For example, Pt(NO$_3$)$_2$(NH$_4$)$_2$ loaded on CB was reduced in an H$_2$ atmosphere [21]. In each case active catalysts were obtained.

However, there are some problems with these methods. First, a lot of reagents such as Pt salts, H$_2$ gas or other reductants, stabilizers etc., are required for preparing Pt nanoparticles. Consequently, they will raise the preparation cost, and complex treatments of various wastes are needed. Second, the loss of Pt during the preparation of catalysts seems to become serious. Third, controlling the rate for Pt deposition is not so easy that mean particle size and size distribution of the resultant Pt nanoparticles are hard to control.

1.2.3 Electrodeposition technique

So far electrodeposition techniques have developed in plating, in other words, film-forming. The plating technique is used for many applications such as corrosion control, abrasion resistance, printed-wiring, decoration and so on. For corrosion control, Zn plating is most commonly used. The base Fe metal is covered with a Zn film which is less noble than Fe, and protected by the sacrificial dissolution of the Zn film. In addition, Ni plating has also been used for the corrosion control. In this case, the base Fe metal is protected by the nobler Ni metal, leading to the improvement of the corrosion resistance of the base metal. Cr plating is used for abrasion resistance because of its high hardness, and Cu plating is used for printed-wiring because of its low resistance. Au plating or Ag plating is used for decoration because of its splendid appearance. Type of plating and their application examples are shown in Table 3.
Table 3 Various platings and their applications.

<table>
<thead>
<tr>
<th>Plating</th>
<th>Application</th>
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<tr>
<td>Zinc (alloy) plating</td>
<td>Bolt, Nut, Hinge, Stapler, Roof (zinc roof), and etc</td>
</tr>
<tr>
<td>Nickel (alloy) plating</td>
<td>Magnetic disc, Clip, Pachinko ball, Substrate for decorative plating, and etc</td>
</tr>
<tr>
<td>Cupper (alloy) plating</td>
<td>Printed wiring, Car body, Substrate for decorative plating, and etc</td>
</tr>
<tr>
<td>Chrome (alloy) plating</td>
<td>Faucet, Piston, Shaft, and etc</td>
</tr>
<tr>
<td>Tin (alloy) plating</td>
<td>Solder, Terminal pin, Roof (tin roof), Tank of gasoline, and etc</td>
</tr>
<tr>
<td>Gold plating</td>
<td>Terminal pin, Accessory, Watch, Glasses, and etc</td>
</tr>
<tr>
<td>Silver plating</td>
<td>Dish, Mirror, Accessory, and etc</td>
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</tbody>
</table>
Usually, thicker films are desirable for plating. So plating techniques to form thick films have developed. The preparation of catalysts is expected as a new application of the electrodeposition technique. Comparing with current preparation methods of Pt-based nanoparticles, the electrodeposition is a low-cost process because reagents and working process for preparation are reduced. Moreover, the electrochemical control of Pt deposition is so easy that mass-production of Pt nanoparticles is possible.

1.3 Objectives of this study

Main objective of this study is to prepare Pt-based nanoparticle catalysts, Pt-transition metal alloy nanoparticles and shape-controlled Pt nanoparticles, for PEFCs by electrodeposition techniques. So far, there have been many researches on plating techniques such as alloy plating and noble metal plating and electrodeposition mechanism, but there are only a few reports on the preparation of Pt-based nanoparticles by electrodeposition. In this study, two electrodeposition techniques were employed to prepare Pt-based nanoparticles. One is double potential step electrolysis (DPSE) in which potential is successively stepped to two potentials and at each potential different redox reactions occur to control the composition of Pt alloy nanoparticles. Potential step techniques are often used in electrochemical measurements, but they have never been used for controlling the composition of nanoparticles. The DPSE was applied to the preparation of Pt-Ni and Pt-Co nanoparticles with a Pt surface layer. Moreover, it was also found that the alloy nanoparticles exhibited higher corrosion resistance and higher activity for oxygen reduction reaction (ORR) than the Pt nanoparticles.

Another is a galvanostatic electrolysis (GE). This is not a special technique, but in this study it was used for the preparation of shape-controlled Pt nanoparticles by
utilizing a small amount of platinum ions which were produced by the electrochemical
dissolution of a Pt anode. In this method the concentration of dissolving platinum ions
was extremely low, which can reduce the consumption of Pt.

1.4 Outline of this thesis

This thesis consists of 6 chapters.

In Chapter 1, background on electrocatalysts for fuel cell applications, general
preparation methods of Pt nanoparticles, and electrodeposition techniques were
described, and objectives of this study and outline of this thesis were also written.

In Chapter 2, Pt-Ni nanoparticles were prepared by DPSE in which Pt-Ni alloy was
deposited during the first potential step and the Ni constituent was dissolved during the
second potential step. A cycle of the DPSE in a nickel plating bath containing PtCl$_6^{2-}$ led
to the formation of the Pt-Ni nanoparticles with about 5.4±1.5 nm in size. The Pt-Ni
nanoparticles gradually grew up with repeating the DPSE process, and surface Ni
content of the particles was controllable by some parameters of the DPSE. The Pt-Ni
nanoparticles deposited by this technique were covered with a Pt skin surface layer.

In Chapter 3, the Pt-Co nanoparticles covered with a Pt skin layer were prepared by
the DPSE. Both Pt-Ni and Pt-Co nanoparticles exhibited higher corrosion resistance and
ORR activity than the Pt nanoparticles even after deterioration tests. Especially, when
the surface contents of Co and Ni were around 4 and 8 at.%, respectively, the leaching
of transition metal did not occur. Moreover, at 2 at.% Co surface content for Pt-Co
nanoparticles their relative surface area was kept more than 90 % even after
deterioration tests.

In Chapter 4, Pt nanoparticles with a cubic structure were prepared by the GE. In
this method low concentration of platinum ions, which were produced by oxidative
dissolution of the Pt anode, were reduced at the graphite cathode to form cubic
nanoparticles. This could be ascribed to slow Pt deposition which was dominated by the
diffusion of the platinum ions.

In Chapter 5, the nucleation and nucleus growth processes of the cubic Pt
nanoparticles during the GE were examined in detail and a mechanism for the formation
of cubic Pt nanoparticles was proposed. It was suggested that the balance between
growth rate of Pt nanoparticles on the graphite cathode and dissolution rate of the Pt
anode was important to form the cubic structure.

In Chapter 6, general conclusions of the results obtained in this study were
described.
References


2. 1 Introduction

Various Pt-based binary or ternary alloy nanoparticles with low Pt content and superior electrochemical properties have been developed as electrocatalysts for use in solid polymer electrolyte fuel cells [1-19]. Recently, there has been considerable interest in the preparation of structure-controlled Pt-based nanoparticles [9-11].

The Pt-based nanoparticles are almost prepared by chemical reduction methods such as gas phase reduction [7, 12-16], liquid phase reduction [17-19], and so on. However, the chemical reduction methods are unsuitable for preparing the structure-controlled nanoparticles. In these cases, additional reductants and hydrogen gas are introduced to produce metal colloids, and a series of complicated processes are needed. Furthermore, it is hard to control the reaction, so that advanced techniques are required to obtain desired catalysts.

In contrast, electrochemical methods are suitable for preparing the structure-controlled nanoparticles. For example, in the potentiostatic method, the amount and composition of the deposits and deposition rate can be easily controlled by electrode potential, charge passed, and plating bath composition.

So far, there have been some papers on the electrodeposition of Pt-based catalysts by the potentiostatic [20-23] and galvanostatic [24, 25] methods. Several groups controlled the composition of Pt-Ru catalyst by changing the plating bath composition, and proposed the optimum composition of Pt-Ru catalyst for methanol [20] or ethanol [21, 22] oxidation. And, Bauer et al. [25] introduced the surfactant into the plating bath
to control the composition of Pt-Ru catalyst, and electrodeposited on the carbon felt with the potentiostatic method. The composition control using electrodeposition methods are often done, but to our knowledge the structure control has not been examined yet.

In the potentiostatic methods, electrode reaction can be controlled by applied electrode potential. Therefore the electrode potential is a key factor for preparing the structure-controlled alloy or binary particles. However, there are no reports on the preparation of structure-controlled Pt-based alloy nanoparticles by potentiostatic methods. While, there are interesting statements on the effect of electrochemical operation on the performances of Pt-alloy nanoparticles. Coutanceau et al. [24] prepared Pt-Ru nanoparticles with improved DMFC performance using a galvanostatic pulse technique. They described the current off time (relaxation time) of the pulse significantly influenced the electrode performance. And Lima et al. [23] electrochemically prepared Pt-Ru-M (M= Au, Co, Cu, Fe, Mo, Ni, Sn or W) ternary alloy catalysts to improve the methanol oxidation. And they described that the catalysts must be submitted to voltammetric cycles between 0 and 0.35 V in order to stabilize the catalytic activity.

In this chapter, a novel preparation method for the structure-controlled Pt-Ni nanoparticles by means of double potential step electrolysis (DPSE) in a nickel plating bath containing low concentration of PtCl$_6^{2-}$ is shown. The DPSE is composed of potential steps for the electrodeposition of Pt-Ni alloy and the following selective dissolution of the Ni component, which makes it possible to prepare alloys with different surface compositions. The Pt-Ni nanoparticles prepared by the DPSE were characterized spectroscopically and electrochemically, and their compositions and structure were discussed. Furthermore, catalytic activity for oxygen reduction reactions (ORR) of the Pt-Ni nanoparticles was evaluated.
2.2 Experimental

The working electrode for the DPSE was a glassy carbon (GC) disc of 5.6 mm in diameter. The counter and reference electrodes were a Pt wire and the Ag/AgCl electrodes, respectively. Electrode potentials against the Ag/AgCl electrode were transformed into those against the reversible hydrogen electrode (RHE). A plating bath for the Pt-Ni deposition was a modified Watts nickel bath composed of 0.91 M NiSO$_4$·6H$_2$O, 0.19 M NiCl$_2$·6H$_2$O, 0.49 M H$_3$BO$_4$, and 2.5 mM H$_2$PtCl$_6$·6H$_2$O. For the Pt deposition, 2.5 mM H$_2$PtCl$_6$ aqueous solution was used. The plating baths are named the Pt-Ni plating bath and Pt plating bath hereafter.

A typical potential step pattern of the DPSE is shown in Fig. 2.1. In the first step an electrode potential for the codeposition of Pt and Ni was applied on the GC electrode for 5 s. After 5 s, the electrode potential was stepped to a potential for the Ni dissolution and kept for 0 to 30 s, which is the second step. In the present study, the potential for the codeposition of Pt and Ni was set in the range from -0.34 to -0.64 V because Ni deposited on not GC but Pt, and hydrogen evolution was suppressed. In contrast, the potential for the Ni dissolution was set in the range of 0.16 to 0.36 V because only Ni dissolved. After given cycles of the DPSE, the GC electrode with deposits were quickly lifted up from the solution, rinsed with ultrapure water and used for various experiments.

For evaluating catalytic activity of the Pt-Ni deposits on the GC disc for ORR, hydrodynamic voltammograms were measured with a rotating disc electrode system at rotation speeds from 400 to 2500 rpm in an O$_2$-saturated 0.1 M sulfuric acid solution at 30 °C. Voltammograms were measured in the potential range from 0.26 to 1.26 V at a scan rate of 1 mV s$^{-1}$, and kinetically controlled current ($i_k$) was evaluated from Koutecky-Levich plots.
Fig. 2.1 A typical potential step pattern of DPSE.
The surface composition of the Pt-Ni deposits was evaluated by X-ray photoelectron spectroscopy (XPS). The data were collected with a monochromatic Al Kα radiation. A gold wire was fixed on each sample and Au 4f spectra were measured together with Pt 4f and Ni 2p spectra for calibration of binding energy. The bulk composition of the Pt-Ni deposits was evaluated by inductively coupled plasma emission spectroscopy (ICPS). For ICPS analysis, the deposits were dissolved in aqua regia, followed by being diluted with ultrapure water. Particle size and surface morphology of the Pt-Ni deposits were observed by transmission electron microscopy (TEM). The crystal structure of the Pt-Ni deposits was examined by X-ray diffractometry (XRD) using Cu Kα radiation.

2.3 Results and discussion

2.3.1. Preparation of Pt-Ni alloy nanoparticles prepared by DPSE

Figure 2.2 shows typical TEM photographs and particle size distributions of the deposits after the 1st, 2nd, 4th and 10th cycles of DPSE. Potentials applied at the 1st and 2nd steps of the DPSE were -0.44 and 0.26 V, respectively, and the duration of the 2nd step was 10 s. The deposits after the 1st cycle were spherical particles with size of about 5.4±1.5 nm, while after the 2nd, 4th and 10th cycles aggregates of nanoparticles were formed, and their average sizes increased to 13.9±5.6, 47.5±16.5, and 73.6±15.2 nm, respectively. The TEM images show that Pt-Ni nanoparticles gradually grow up with repeating the DPSE process.

The time course of apparent current density during the first two cycles of the DPSE is shown in Fig. 2.3. The surface Ni content of the Pt-Ni particles after each step in various cycles was evaluated by XPS and summarized in Fig. 2.4.

In the 1st cycle, when a potential of -0.44 V was applied, the reduction current due
Fig. 2.2 Typical TEM photographs and particle size distributions of the Pt-Ni deposits (a) after the 1st, (b) 2nd, (c) 4th, and (d) 10th cycles of the DPSE. Potentials applied at the 1st and 2nd steps of each cycle were -0.44 V and 0.26 V, respectively, and the duration of the 2nd step was 10 s.
Fig. 2.3 Time course of current density during the first two cycles of the DPSE. Potentials applied at the 1st and 2nd steps of each cycle was -0.44 and 0.26 V, respectively, and the duration of the 2nd step was 10 s. Current density was estimated with apparent surface area.
Fig. 2.4 Ni content of the Pt-Ni particles after each step in various cycles evaluated by XPS. Potentials applied at the 1st and 2nd steps of each cycle were -0.44 V and 0.26 V, respectively, and the duration of the 2nd step was 10 s. White and black bars show the surface Ni content of particles measured after the 1st and 2nd steps, respectively.
to the codeposition of Pt and Ni, that is formation of the Pt-Ni particles, was observed as shown in Fig. 2.3. The surface Ni and Pt contents of the particles after this step were 41 and 59 %, respectively. Ni is preferentially deposited on Pt at -0.44 V, while Pt is deposited on Pt and GC. So, Pt nuclei are formed on the GC and then the electrochemical codeposition of Ni and Pt occurs on the Pt nuclei accompanied with the formation of new Pt nuclei for the first 5 s. Because of the large difference in deposition potential between Ni and Pt on the GC (Pt and Ni were deposited on the GC at 0.46 and -0.74 V, respectively.), Pt was deposited on not the Ni but the GC, resulting in higher Pt content than Ni.

When the potential was stepped from -0.44 V to 0.26 V, a spike of oxidation current was observed, followed by a monotonous decrease in the current down to zero within 10 s. This suggests that the surface Ni component of the Pt-Ni nanoparticles predominantly dissolved out and the Pt component remained, leading to the formation of a Pt skin layer. However, the surface Ni content after the 2nd step appeared to be still 27 % because the photoelectrons from the Ni component in the underneath layer of the Pt skin layer within the escape depth of photoelectrons were detected.

In the 2nd cycle, both the reduction current at the 1st step and the oxidation current at the 2nd step were much higher than those in the 1st cycle. This indicates that the Pt skin layer formed on the Pt-Ni nanoparticles surface in the 1st DPSE process worked as a substrate for the codeposition of Pt and Ni and the following dissolution of the surface Ni component. As Fig. 2.4 shows, the surface Ni content after the 1st step of the 2nd cycle increased up to 82 %, which was ca. two times higher than that of the 1st cycle. As mentioned above, Ni preferentially deposits on Pt, not on GC. Moreover, in the Pt-Ni plating bath Ni\(^{2+}\) concentration is ca. 110 times higher than the PtCl\(_6^{2-}\) concentration. Therefore, in the 2nd cycle the Ni deposition on the Pt skin layer of the Pt-Ni nanoparticles is likely to occur much more than the Pt deposition, leading to the
significant increase in the Ni content.

The surface Ni content after the 2nd step was nearly constant irrespective of cycle number, as seen from Fig. 2.4, suggesting that the surface Ni completely dissolved out and the Pt skin layer was formed again. In addition, the surface Ni content after the 1st step in the subsequent cycles was also approximately constant. Therefore, the codeposition of Pt and Ni in the 2nd cycle seems to occur on the Pt skin layer of the Pt-Ni nanoparticles, leading to the growth of the Pt-Ni nanoparticles.

In order to confirm the deposition mode of the Pt-Ni nanoparticles on a GC electrode as deduced above, Pt nanoparticles were deposited on a GC electrode by a cycle of the DPSE in the Pt plating bath in advance, and then the Pt-deposited GC was used for the DPSE in the Pt-Ni plating bath. In this case the surface Ni content after the 1st step in the 1st cycle jumped up to 77 %, while that after the 2nd step were 26 %. These values were closely equivalent to those after two cycles of the DPSE processes for the GC substrate. Therefore Ni preferentially deposits on Pt whenever GC is used as a substrate.

Figure 2.5 shows current-potential (i-E) curves in an N$_2$-saturated 0.1 M sulfuric acid solution for the Pt-Ni nanoparticles-deposited GC electrodes obtained after the 1st and 2nd steps in the 4th cycle of the DPSE. For comparison, the i-E curve of the Pt nanoparticles-deposited GC electrode prepared by 4 cycles of the DPSE is also shown in Fig. 2.5 (c). The i-E curve in Fig. 2.5 (c) has typical waves due to adsorption and desorption of atomic hydrogen on Pt in the potential range below 0.3 V vs. RHE, while the i-E curve after the 1st step in Fig. 2.5 (a) shows that a large oxidation current is observed in this potential range at the initial cycle. In the 2nd sweep, typical redox waves due to the adsorption and desorption of atomic hydrogen on Pt were observed, suggesting that the Ni component near the surface of the Pt-Ni nanoparticles dissolved out during the 1st sweep to form a Pt skin layer on which the adsorption and desorption
Fig. 2.5 Current density-potential (i-E) curves, in an N₂-saturated 0.1 M sulfuric acid solution, of the Pt-Ni nanoparticles-deposited GC electrodes (a) after the 1st step, (b) the 2nd step in the 4th cycle of the DPSE, and (c) the Pt particles. Solid line: the 1st sweep. Dotted line: the 2nd sweep. Sweep rate: 20 mV s⁻¹. Current density was estimated with apparent surface area.
of atomic hydrogen occurred. The i-E curve after the 2nd step (Fig. 2.5 (b)) did not show the oxidation current at all in the initial positive sweep, suggesting that the surface Ni component of the Pt-Ni nanoparticles had completely dissolved out to form the Pt skin layer during the 2nd step.

The bulk Ni content of the Pt-Ni nanoparticles was determined by ICPS. The bulk Ni contents of the Pt-Ni nanoparticles after the 1st, 2nd, 4th, and 10th cycles were 32, 31, 26, and 23 %, respectively. These values were slightly higher than those determined by XPS, ascribing to the Pt skin layer formed on the surface of Pt-Ni nanoparticles.

2.3.2. Control of composition of Pt-Ni alloy nanoparticles

The Ni content of the Pt-Ni nanoparticles can be controlled by some parameters such as applied potential at the first step of the DPSE (E$_1$) and the H$_2$PtCl$_6$ concentration of the Pt-Ni plating bath. At first, the E$_1$ value was changed from -0.34 V to -0.64 V, and the holding time of the potential applied at the second step, -0.26 V, was also changed from 0 to 30 s. The results are summarized in Fig. 2.6. The lower the E$_1$ value was, the higher the surface Ni content was, suggesting that the E$_1$ value significantly influenced the Ni deposition rate because the Ni$^{2+}$ concentration was much higher than the PtCl$_6^{2-}$ concentration in the Pt-Ni plating bath.

When the E$_1$ value was -0.44 V or less, the surface Ni content significantly decreased for the initial 5 s of the 2nd step and was almost constant in 10 s, suggesting that the Ni dissolution has finished within the initial 10 s. On the other hand, when the potential applied at the 1st step was -0.34 V, the Ni surface content kept constant even after 30 s, indicating that the Ni dissolution hardly occurs in this case. Considering that the Ni deposition on Pt started at ca. -0.24 V, the overpotential for the Ni deposition is too small to deposit at faster speed than Pt, leading to the preferential Pt deposition on the Pt-Ni nanoparticles, that is the Pt coating of the surface Ni component.
Fig. 2.6 Changes in Ni content of the Pt-Ni particles over time. Potentials applied at the 1st step were -0.34 (●), -0.44 (○), -0.54 (▲), and -0.64 V (△) for 5 s, respectively, and the 2nd step, 0.26 V for 10 s. Ni contents were evaluated by XPS.
For the structural characterization of the Pt-Ni nanoparticles by XRD and XPS, a Pt-Ni film prepared on a gold plate by 4000 cycles of the DPSE was used. The potentials applied at the 1st and 2nd steps in each cycle of the DPSE were -0.44 and 0.26 V, respectively, and the duration of the 2nd step was 10 s. The surface Ni and Pt contents of the resultant Pt-Ni nanoparticles were 20 and 80 %, respectively. Figure 2.7 (a) shows an XRD spectrum of the Pt-Ni nanoparticles on Au. The diffraction peak of Pt-Ni (111) was observed at 2θ = 38.2 °, which was between Ni (111) and Pt (111) peaks. The spectrum shows that Pt and Ni codeposited on GC were practically alloyed and the Pt skin layer was too thin to be detected by XRD.

Figures 2.7 (b) and (c) show the Pt 4f and Ni 2p spectra of the Pt-Ni nanoparticles on Au, which has been subjected to XRD analysis. Both the Pt 4f7/2 and Pt 4f5/2 peaks shifted slightly toward higher binding energy, as reported previously [26], suggesting that the electronic structure of the Pt skin layer is influenced by the Ni component in the underneath layer. In contrast, the shift of the Ni peaks was not distinctly observed. Hillebrecht et al. has reported that many Ni alloys had a Ni satellite peak shift, but Ni alloys with noble metals, which had electronegativity higher than Ni, significantly did not show such the peak shift [27].

2.3.3. ORR activity of Pt-Ni alloy nanoparticles

Typical hydrodynamic voltammograms for ORR on the Pt-Ni nanoparticles- and Pt nanoparticles-deposited GC in an O2-saturated 0.1 M sulfuric acid solution are shown in Fig. 2.8 (a). Both Pt-Ni and Pt nanoparticles were prepared by 10 cycles of the DPSE in which the potentials applied at the 1st and 2nd steps were -0.44 and 0.26 V, respectively, and the duration of the 2nd step was 10 s. Before the hydrodynamic voltammogram measurement, real surface area of the Pt-Ni and Pt nanoparticles was evaluated from their cyclic voltammograms in an N2-saturated 0.1 M sulfuric acid solution. The real
Fig. 2.7 (a) XRD spectrum, (b) XPS Pt 4f spectrum, and (c) XPS Ni 2p spectrum of the Pt-Ni particles prepared by 4000 cycles of the DPSE. Potentials applied at the 1st and 2nd steps of each cycle were -0.44 and 0.26 V, respectively, and the duration of the 2nd step was 10 s.
surface area was equivalent to each other. As Fig. 2.8 (a) shows, the Pt-Ni nanoparticles-deposited GC had lower overpotential for ORR than the Pt nanoparticles-deposited GC. Hydrodynamic voltammograms for ORR on the Pt-Ni nanoparticles-deposited GC were measured at different rotation speeds, and Koutecky-Levich plots were drawn, as shown in Fig. 2.8 (b). All plots had a linear relationship between $i^{-1}$ and $\omega^{-1/2}$. The number of electrons for ORR was determined to be 4 from the slope of each plot, which means that $O_2$ was reduced to water on the Pt skin layer of the Pt-Ni nanoparticles. Kinetic current ($i_k$) was evaluated from the inverse of the intercept at $\omega^{-1/2} = 0$ for each plot, and was independent of rotation speed. Specific activity (SA) was defined as $i_k$ per real surface area and was evaluated at different potentials. These results are summarized in Table 2.1. The SA values of the Pt nanoparticles-deposited GC at various potentials were approximately in agreement with those reported previously [26, 28]. At any potential, the SA values of the Pt-Ni nanoparticles-deposited GC are ca. two times higher than those of the Pt nanoparticles/GC, indicating that the Pt-Ni particles on GC have high electrocatalytic activity for ORR.

In general, using diffusion-limited current ($i_L$) and $i_k$, the measured current ($i$) is represented as follows.

$$i^{-1} = i_k^{-1} + i_L^{-1}$$  \hspace{1cm} (1)

Since $i_L$ is determined from Fig. 2.8 (a), the $i_k$ can be evaluated from the following equation.

$$i_k = i_L \frac{i}{(i_L - i)}$$  \hspace{1cm} (2)

By inserting the data of Fig. 2.8 (a) into eq. (2), a log $|i_k| - E$ plot or Tafel plot for each electrode is made, as shown in Fig. 2.9. Tafel slopes for both electrodes were ca. -120 mV decade$^{-1}$ in the high current region and ca. -70 mV decade$^{-1}$ in the low current region. These suggest that ORR on the Pt and Pt-Ni nanoparticles proceeded via the
Fig. 2.8 (a) Typical hydrodynamic voltammograms for ORR on the Pt-Ni nanoparticles- and Pt nanoparticles-deposited GC electrodes at a rotation speed of 2500 rpm in an O$_2$-saturated 0.1 M sulfuric acid solution. Sweep rate: 1 mV s$^{-1}$. Current density was estimated with apparent surface area. (b) Koutechy-Levich plots for the Pt-Ni nanoparticles-deposited GC electrode.
Table 2.1 Specific activity (SA) at 0.85, 0.75, and 0.65 V for Pt-Ni or Pt nanoparticles modified GC electrodes

<table>
<thead>
<tr>
<th>Potential</th>
<th>Specific activity (mA cm⁻²)</th>
<th>Pt-Ni alloy</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.85 V</td>
<td>0.034</td>
<td>0.014</td>
<td></td>
</tr>
<tr>
<td>0.75 V</td>
<td>1.99</td>
<td>1.08</td>
<td></td>
</tr>
<tr>
<td>0.65 V</td>
<td>18.28</td>
<td>8.80</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 2.9 Tafel plots for ORR on the Pt-Ni and Pt nanoparticles-deposited GC electrodes in 0.1 M sulfuric acid solution at room temperature.
same rate-determining step. It has been inferred that the former corresponded to ORR on Pt surface covered with oxides and the latter corresponded to that on clean Pt surface [26, 29, 30]. The transition of the Tafel slope is probably related to the adsorption of oxygen-containing species such as OH$_{ad}$ [31].

2.4 Summary

The Pt-Ni nanoparticles with a Pt skin layer were prepared by the DPSE with Ni plating bath containing low concentration of PtCl$_4^{2-}$. In the first step of the DPSE, the codeposition of Pt and Ni occurred and Ni dissolved in the second step, the Pt skin layer was formed on the Pt-Ni nanoparticles. A cycle of the DPSE in a nickel plating bath containing PtCl$_6^{2-}$ led to the formation of the Pt-Ni nanoparticles with size of about 5.4±1.5 nm, which gradually grew up with repeating the DPSE process, and surface Ni content of the particles by XPS was controllable by changing some parameters of the DPSE. The Pt skin layer was effective for the improvement of catalytic activity. The electrocatalytic activity of the Pt-Ni nanoparticles for ORR was ca. two times higher than that of Pt nanoparticles. This was attributed to the Pt skin layer hindering of Ni dissolution from the deeper site of the Pt-Ni nanoparticles.
References


3. 1 Introduction

The alloying of Pt with transition metals such as Co, Ni, Fe etc. gives higher electrocatalytic activity for ORR than pure Pt [1-8, 10-14]. The ORR activity of the Pt-based alloys can be influenced by the shortening of Pt-Pt interatomic distance [7], and the increase in the d-electron vacancy of Pt [8] etc. With an increase in d-electron vacancy of Pt, electron donation from the adsorbed oxygen molecules to Pt atoms increases, leading to weaker O-O bonding and stronger Pt-O bonding. But, too much d-electron vacancy of Pt lowers ORR activity because of too strong Pt-O bonding. Therefore, Pt-based alloys with appropriate d-electron vacancy of Pt have the maximum ORR activity.

It is well-known that transition metal components in Pt-based alloys preferentially dissolve out in acidic solutions during electrochemical operations. So, the durability of Pt-based alloys should be also discussed as a function of the content of transition metal components and surface structure of the alloys. Bonakdarpour et al. [9] studied the dissolution of Fe and Ni components in Pt$_{1-x}$M$_x$ (M=Fe, Ni; 0<x<1) catalysts, which were prepared by sputtering, in 0.3 or 1 M H$_2$SO$_4$ and 0.3 or 1 M HClO$_4$. They demonstrated with energy dispersive spectrometer and X-ray diffraction data that at x<0.6 the surface Fe and Ni components preferentially dissolved out, while at x>0.6 both components dissolved on the whole. In addition, X-ray photoelectron spectroscopic data demonstrated that both components were not detected at the catalyst surface after the acid treatment. Other researchers also reported the surface transition
metal components of Pt-based alloys completely disappeared in almost cases [8, 10]. The preferential dissolution of transition metals from Pt-based alloys caused negative effects such as the lowering of ORR activity [11], the decrease in electrochemical surface area [12] and so on. Hector et al. found that there was a close correlation between the amount of the dissolved metal components and the ORR activity for the Pt-based alloy catalysts [11]. Travitsky et al. concluded that the corrosion of the transition metal components caused the increase in grain size of Pt and the decrease in electrochemical surface area (ECSA) [12]. In proton exchange membrane (PEM) fuel cell systems, transition metal ions dissolved out from Pt alloy catalysts would redeposit somewhere else in the cell, leading to the degradation of cell performances.

There have been some attempts [10-12] to prepare Pt-based alloy catalysts with a Pt skin layer which was formed in advance to prevent transition metals from leaching. The Pt-based alloys as a core can be protected from acid solutions by the stable Pt skin layer as a shell. The Pt skin layer had higher stability than the pure Pt due to the electronic effect of underlying alloys [15, 16]. The Pt skin layer is formed by annealing of the Pt-based alloy nanoparticles [17, 18], replacement of a Cu monolayer deposited on a core particle by underpotential deposition (UPD) with Pt [19], and the electrochemical stabilization treatment [10]. However, all these methods are two-step processes which are composed of the preparation of Pt-based alloy particles and the following treatment for the Pt skin layer formation. Therefore, simpler technique for the Pt skin layer formation is desirable.

The DPSE introduced in Chapter 2 is a novel preparation method of Pt-Ni nanoparticles covered with a Pt skin layer [20]. With this method, Pt-Ni alloy nanoparticles with desired composition and size could be easily obtained in one process by selecting appropriate electrode potential for the DPSE and plating bath composition. And the resultant Pt-Ni nanoparticles exhibited higher ORR activity than Pt
nanoparticles in acid solution. Recent studies on fuel cell cathode catalysts mostly focused on Pt-Co nanoparticles. So it is significant to apply the DPSE to the preparation of Pt-Co nanoparticles.

In this chapter Pt-Co nanoparticles with a Pt skin layer were prepared by the DPSE. And the electrochemical stability and the corrosion resistance of the resultant Pt-Co nanoparticles were investigated as a function of the alloy composition by cyclic voltammetry (CV) and XPS, and compared with those of the Pt-Ni nanoparticles.

3.2 Experimental

The Pt-Ni and Pt-Co nanoparticles with different compositions were prepared on a glassy carbon (GC) disc or plate by the DPSE. All deposits in this chapter were prepared by a cycle of the DPSE. The counter and reference electrodes were Pt wire and the Ag/AgCl electrodes, respectively. Electrode potentials measured against the Ag/AgCl electrode were transformed into those against the reversible hydrogen electrode (RHE). Plating baths for Pt-Ni and Pt-Co depositions were based on Watt’s nickel bath, composed of 0.91 M MSO₄⋅6H₂O, 0.19 M MCl₂⋅6H₂O, 0.49 M H₃BO₄, and 1.25, 2.5, 5.0, 10 or 20 mM H₂PtCl₆⋅6H₂O (M = Ni or Co). Each plating bath was called a Pt-Ni bath and Pt-Co bath, respectively. For the Pt deposition, 2.5 mM H₂PtCl₆ aqueous solution was used. Detailed information on the DPSE was described in Chapter 2.

For evaluating ORR activities of Pt-Ni and Pt-Co nanoparticles-deposited GC discs, hydrodynamic voltammograms were recorded with a rotating disc electrode system at rotation speeds from 400 to 2500 rpm in an O₂-saturated 0.1 M sulfuric acid solution at 30 °C. Each voltammogram was measured in the potential range between 0 and 1.0 V at
a scan rate of 1mV s\(^{-1}\). Kinetically controlled current (\(i_k\)) was evaluated from Koutecky-Levich plots.

The stability of Pt-Ni and Pt-Co nanoparticles catalysts was evaluated from the change in real surface area with potential cycling. The real surface area was evaluated by integrating the oxidation peaks due to atomic hydrogen desorption. Corrosion resistance was evaluated from the change in surface Ni or Co content with potential cycling in an N\(_2\)-saturated 0.1 M sulfuric acid solution at 30 °C. Potential cycling was performed over the potential range between 0.05 V and 1.2 V at a scan rate of 100 mV s\(^{-1}\).

The surface compositions of Pt-Ni and Pt-Co nanoparticles were evaluated by XPS. The data were collected with a monochromatic Al K\(\alpha\) radiation. A gold wire was fixed on each sample and Au 4f spectra were measured together with Pt 4f and Ni or Co 2p spectra for calibration of binding energy. The values indicated by a subscript, such as Pt\(_{93}\)Ni\(_7\) or Pt\(_{94}\)Co\(_6\), represent mole percent of Pt, Ni and Co components at the surface. The bulk compositions of the Pt-Ni and Pt-Co nanoparticles were evaluated by XPS after Ar\(^+\) sputtering for 0.3 min. The sputtering rate was about 2 nm / min for oxide layer of SiO\(_2\). In the chapter 2, the bulk compositions were determined by ICPS. The bulk compositions evaluated by XPS after 0.3 min sputtering were almost agreement with those evaluated by ICPS. So in this chapter, the bulk compositions were determined by XPS after 0.3 min sputtering. Particle size and surface morphology of the Pt-Ni and Pt-Co nanoparticles were observed by transmission electron microscopy (TEM). The Pt-Ni and Pt-Co nanoparticles were fixed on Cu mesh with collodion membrane for TEM specimens. The nanoparticles were transferred to the Cu mesh by directly wiping the surface of the nanoparticles-deposited GC with the Cu mesh.
3. 3 Results and Discussion

3.3.1 Composition and structure of the Pt-Ni and Pt-Co nanoparticles prepared by DPSE

TEM images and size distributions of the Pt$_{93}$Ni$_{7}$ and Pt$_{94}$Co$_{6}$ nanoparticles are shown in Fig. 3.1. In both cases spherical particles are observed. The average size and standard deviation of the Pt$_{93}$Ni$_{7}$ and Pt$_{94}$Co$_{6}$ nanoparticles were 4.4 ± 1.0 nm and 4.0 ± 1.0 nm, respectively.

The Ni or Co content of Pt-Ni or Pt-Co nanoparticles can be controlled by a potential applied at the 1st step of the DPSE and PtCl$_{6}^{2-}$ concentration of the Pt-Ni or Pt-Co baths. Surface and bulk Ni or Co content in the Pt-Ni or Pt-Co nanoparticles prepared at different potentials at the 1st step in DPSE or PtCl$_{6}^{2-}$ concentrations was evaluated by XPS and summarized in Table 3.1. As the 1st step potential was set at more negative potentials or the PtCl$_{6}^{2-}$ concentration decreased, the surface Ni and Co contents distinctly increased.

Figure 3.2 shows change in Ni or Co content with Ar$^{+}$ sputtering time for Pt-Ni and Pt-Co nanoparticles prepared by a cycle of DPSE. In any composition, the Ni or Co content in the Pt-based alloy nanoparticles was increased with sputtering time, and reached a constant value at a sputtering time of 0.3 min.

Figure 3.3 shows current-potential (i-E) curves of the Pt$_{93}$Ni$_{7}$ and Pt$_{94}$Co$_{6}$ nanoparticles-deposited GC electrodes after each step of the 1st cycle of DPSE in an N$_2$-saturated 0.1 M sulfuric acid solution. The i-E curves in Fig. 3.3 (a) and (b) are measured with the Pt$_{93}$Ni$_{7}$ nanoparticles-deposited GC obtained after the 1st and 2nd steps of DPSE, respectively, and those in Fig. 3.3 (c) and (d) are measured with the Pt$_{94}$Co$_{6}$ nanoparticles-deposited GC obtained after the 1st and 2nd steps of the DPSE,
Fig. 3.1 TEM photographs and size distributions of (a) Pt$_{93}$Ni$_{7}$ nanoparticles and (b) Pt$_{94}$Co$_{6}$ nanoparticles prepared by a cycle of DPSE. Potentials applied at the 1st and 2nd steps were -0.39 V and 0.26 V for the Pt$_{93}$Ni$_{7}$ nanoparticles, and -0.44 V and 0.16 V for the Pt$_{94}$Co$_{6}$ nanoparticles. The durations of the 2nd step were 10 s in both nanoparticles.
Table 3.1 The preparation conditions and transition metal contents of the Pt and Pt alloy nanoparticles measured by XPS.

<table>
<thead>
<tr>
<th>Solutions</th>
<th>PtCl$_6^-$ concentration</th>
<th>1st step Potential (vs. RHE)</th>
<th>2nd step Potential (vs. RHE)</th>
<th>measured by XPS (surface)</th>
<th>measured by XPS (after 0.3 min sputtering)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-Ni</td>
<td>20 mM</td>
<td>-0.39 V</td>
<td>10</td>
<td>7</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>2.5 mM</td>
<td>-0.44 V 5</td>
<td>10</td>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>1.25 mM</td>
<td>-0.59 V 30</td>
<td>30</td>
<td>32</td>
<td>44</td>
</tr>
<tr>
<td>Pt-Co</td>
<td>20 mM</td>
<td>-0.44 V</td>
<td>10</td>
<td>6</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>5.0 mM</td>
<td>-0.44 V 5 0.16 V</td>
<td>10</td>
<td>19</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>2.5 mM</td>
<td>-0.54 V 30</td>
<td>30</td>
<td>28</td>
<td>43</td>
</tr>
<tr>
<td>Pt</td>
<td>2.5 mM</td>
<td>-0.44 V 5 0.26 V</td>
<td>10</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Fig. 3.2 Change in Ni or Co content of the Pt alloy nanoparticles prepared by a cycle of DPSE with Ar\(^+\) sputtering time. Sputtering rate was about 2 nm min\(^{-1}\) for oxide layer of SiO\(_2\).
Fig. 3.3 Current density-potential (i-E) curves of the Pt alloy and Pt nanoparticles-deposited GC electrodes in an N\textsubscript{2}-saturated 0.1 M sulfuric acid solution. Solid and dotted curves show curves at the 1st and 2nd sweeps, respectively. Sweep rate was 20 mV s\textsuperscript{-1}.

(a) Pt\textsubscript{93}Ni\textsubscript{7} nanoparticles-deposited GC electrode after the 1st step of DPSE
(b) Pt\textsubscript{93}Ni\textsubscript{7} nanoparticles-deposited GC electrode after the 2nd step of DPSE
(c) Pt\textsubscript{94}Co\textsubscript{6} nanoparticles-deposited GC electrode after the 1st step of DPSE
(d) Pt\textsubscript{94}Co\textsubscript{6} nanoparticles-deposited GC electrode after the 2nd step of DPSE
(e) Pt nanoparticles-deposited GC electrode.
respectively. For comparison, an i-E curve of the Pt nanoparticles-deposited GC is shown in Fig. 3.3 (e). The i-E curve has typical redox waves due to adsorption and desorption of atomic hydrogen on Pt in the potential range below 0.3 V vs. RHE.

In Fig. 3.3 (a) and (c), at the 1st sweep a large oxidation peak was observed in the potential range below 0.3 V, while at the 2nd sweep it decreased, suggesting that the surface Ni of Pt$_{93}$Ni$_{7}$ nanoparticles or surface Co of Pt$_{94}$Co$_{6}$ nanoparticles dissolved out during the 1st sweep. On the other hand, in Fig. 3.3 (b) and (d) such a decrease in oxidation peak was not observed. This indicates that the surface Ni or Co component of the Pt$_{93}$Ni$_{7}$ or Pt$_{94}$Co$_{6}$ nanoparticles has completely dissolved out during the 2nd step of the DPSE.

As Fig. 3.2 demonstrates, in any composition, the surface Ni or Co content in the Pt-based alloy nanoparticles is increased with sputtering time, and reaches a constant value at a sputtering time of 0.3 min which is broadly estimated to be thickness of 0.6 nm. Considering that the escape depth of photoelectrons from the surface is about 1 nm [21], the Ni or Co content of the thin surface layer of Pt$_{93}$Ni$_{7}$ or Pt$_{94}$Co$_{6}$ nanoparticles with the particle size of 4.4 or 4.0 nm should be much less than their bulk content.

To evaluate the total Ni or Co content of the Pt-based alloy nanoparticles, it was measured by ICPS. For example, the total Ni and Co contents of Pt$_{93}$Ni$_{7}$ and Pt$_{94}$Co$_{6}$ were evaluated to be 30 and 26 %, respectively. Meanwhile the Ni and Co contents of Pt$_{93}$Ni$_{7}$ and Pt$_{94}$Co$_{6}$ evaluated by XPS were 7 and 6 %, respectively. The total Ni and Co contents are much higher than those determined by XPS, clearly indicating that Pt is enriched near the surface of the nanoparticles. This also means that XPS is available for evaluating the Ni and Co contents near the surface in this study. In addition, as shown in Fig. 3.3 (b) and (d), both Pt-Ni and Pt-Co nanoparticles after the 2nd step of DPSE electrochemically behaved just like the Pt nanoparticles (Fig. 3.3 (e)). Therefore, it is likely that a very thin Pt layer, that is, a Pt skin layer is formed on the surface of Pt-Ni
or Pt-Co nanoparticles during a cycle of DPSE.

3.3.2 ORR activity of the Pt-Ni and Pt-Co nanoparticles

Hydrodynamic voltammograms at a rotation speed of 1600 rpm of the Pt-Ni and Pt-Co nanoparticles-deposited GC electrodes in O$_2$-saturated 0.1M H$_2$SO$_4$ are shown in Fig. 3.4. The Koutecky-Levich plots obtained at different rotation speeds were drawn, and each plot had linear relationship between measured current ($i$) and $\omega^{-1/2}$, and kinetically controlled current ($i_k$) was evaluated from the inverse of the intercept at $\omega^{-1/2} = 0$ for each plot. The SA for ORR is defined as $i_k$ per real surface area of Pt at 0.8 V (vs. RHE). The SA values of the Pt-Ni and Pt-Co nanoparticles with various compositions are summarized in Table 3.2. The Pt-Ni and Pt-Co nanoparticles almost had higher SA than the Pt nanoparticles. The lower the Ni or Co content was, the higher the SA value was. This result seems to contradict to the result by Toda et al. [8], who described that the maximum activity was obtained at ca. 30 and 40 % bulk contents of Ni and Co, respectively. However, even though the surface contents were very low in our research, the bulk contents of Pt-Ni and Pt-Co nanoparticles were also ca. 30 ~40 %, as shown in Table 3.1. Therefore, if the bulk content of Ni and Co is used, our result is in agreement with Toda’s result.

The improvement in ORR activity of the Pt-based alloy is ascribable to the increased d-electron vacancy of Pt atoms at the surface layer caused by underlying alloy [8]. In principle, the increase in d-electron vacancy shifts the Pt 4f$_{7/2}$ and Pt 4f$_{5/2}$ peaks in the XPS spectra toward higher binding energies, while the Pt 4f peaks of the present Pt-Ni and Pt-Co nanoparticles showed a slight shift (0.1~0.3 eV) toward higher binding energies, implying that the d-electron vacancy of the surface Pt atoms was increased. So far, there have been some papers on the relationship between d-orbital vacancy or composition and ORR activity [8, 22], and the volcano type correlation has
Fig. 3.4 Hydrodynamic voltammograms for ORR on Pt$_{93}$Ni$_7$, Pt$_{94}$Co$_6$, and Pt nanoparticles-deposited GC electrodes at a rotation speed of 1600 rpm in an O$_2$ saturated 0.1M sulfuric acid solution. Each nanoparticle was prepared by a cycle of DPSE. Sweep rate was 1 mV s$^{-1}$. 
Table 3.2 Specific Activity (SA) at 0.8 V on Pt-Ni, Pt-Co, and Pt nanoparticles-deposited GC.

<table>
<thead>
<tr>
<th>Specific Activity (SA)</th>
<th>mA cm$^{-2}$ at 0.8V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt$<em>{93}$Ni$</em>{17}$</td>
<td>0.79</td>
</tr>
<tr>
<td>Pt$<em>{80}$Ni$</em>{20}$</td>
<td>0.56</td>
</tr>
<tr>
<td>Pt$<em>{68}$Ni$</em>{32}$</td>
<td>0.47</td>
</tr>
<tr>
<td>Pt$<em>{94}$Co$</em>{6}$</td>
<td>0.71</td>
</tr>
<tr>
<td>Pt$<em>{81}$Co$</em>{19}$</td>
<td>0.53</td>
</tr>
<tr>
<td>Pt$<em>{72}$Co$</em>{28}$</td>
<td>0.65</td>
</tr>
<tr>
<td>Pt</td>
<td>0.49</td>
</tr>
</tbody>
</table>
been proposed. However, the direct relationship between the XPS peak shift and the ORR activity is unclear. Each XPS spectrum is the average of about 1 nm depth from the surface and does not reflect only the electronic structure at the outermost surface of nanoparticles on which oxygen reduction occurs. Therefore the XPS peak shift may not be closely connected to the ORR activity. Other factors may be needed to explain the high ORR activity of the Pt-Ni and Pt-Co alloy nanoparticles.

3.3.3 Corrosion resistance and stability of the Pt-Ni and Pt-Co nanoparticles

For evaluating the stability and corrosion resistance of the Pt-Ni and Pt-Co nanoparticles-deposited GC electrodes, the repetitive potential cycling was conducted in the potential range from 0.05 to 1.2 V in an N₂-saturated 0.1M sulfuric acid solution. It should be noted that Ni or Co dissolves in the potential range below 0.45V and Pt dissolves in the potential range above 0.8 V [23, 24], and in addition, the aggregation of Pt particles occurs in the potential range below 0.75 V [25]. Therefore, the repetitive potential cycling should be a severe condition to metamorphose the Pt-Ni and Pt-Co alloy nanoparticles.

Figure 3.5 (a), (b), and (c) show CVs measured at the 10th, 100th, 700th, and 1000th cycles of potential cycling with Pt, Pt₉₃Ni₇, and Pt₉₄Co₆ nanoparticles-deposited GC electrodes, respectively. All the nanoparticles were prepared by the DPSE in which the potential applied at the 1st and 2nd steps were -0.44 and 0.26 V for the Pt nanoparticles, -0.39 and 0.26 V for the Pt-Ni nanoparticles, and -0.44 and 0.16 V for the Pt-Co nanoparticles, respectively. In Fig. 3.5 (a), the peaks at potentials more negative than 0.3 V due to the adsorption and desorption of atomic hydrogen on Pt got smaller with an increase in the number of potential cycling, indicating clearly the loss of the surface area. The surface area loss has been ascribed to the dissolution / redeposition of Pt nanoparticles [22-24]. Even in case of the Pt₉₃Ni₇ and Pt₉₄Co₆ nanoparticles as shown
Fig. 3.5 Cyclic voltammograms of (a) Pt, (b) Pt_{93}Ni_{7}, and (c) Pt_{94}Co_{6} nanoparticles-deposited GC electrodes in an N_{2}-saturated 0.1 M sulfuric acid solution. Each nanoparticle was prepared by a cycle of DPSE. Sweep rate was 100 mV s^{-1}.
in Fig. 3.5 (b) and (c), the surface area loss was observed with an increase in the number of potential cycling, but it looked smaller than that for the Pt nanoparticles.

Relative surface areas of the Pt-Ni and Pt-Co nanoparticles with different compositions at various cycle numbers were measured and summarized in Fig. 3.6 (a) and (b), respectively. Each relative surface area was defined as a ratio of Pt real surface area at each cycle to that at 10th cycle.

For any Pt-based alloy nanoparticles, the relative surface area was decreased within initial several hundred potential cycles and then became constant. The lower the surface Ni or Co content was, the slower the decrease of relative surface area was. In addition, the decrease rate of relative surface area for the Pt-Co nanoparticles was lower than that for the Pt-Ni nanoparticles. Especially in case of 2 % Co content, the decrease rate was so low and its relative surface area was kept more than 90% even after 1000 potential cycles.

Figure 3.7 shows the surface Ni or Co content in the Pt-based alloy nanoparticles after the 1000 potential cycles (vertical axis) plotted against that before the potential cycling (horizontal axis). When the surface Ni or Co content before potential cycling was less than about 8 % Ni for the Pt-Ni nanoparticles or less than about 4 % Co for the Pt-Co nanoparticles, the plots were on the straight line with gradient = 1, indicating that the surface Ni or Co content was unchanged even after the 1000 potential cycling.

When the surface Ni or Co content before the potential cycling was higher than 8 % Ni or 4 % Co, the plots deviated from the straight line and reached a constant value, indicating that the Ni or Co dissolves out from the Pt-alloy nanoparticles depending on its content.

In many researches on the deterioration of Pt-transition metal alloy catalysts, surface transition metals were not detected by XPS after deterioration tests [8, 9]. However, in the present case, the surface Ni or Co component was detected even after the potential
Fig. 3.6 Relative surface areas as a function of the cycle number for the (a) Pt-Ni and (b) Pt-Co nanoparticles-deposited GC. Each nanoparticles were prepared by a cycle of DPSE. The relative surface area is determined with the reference to the real surface area at the 10th cycle. The heavy line in each graph shows the curve for the Pt nanoparticles-deposited GC. The durations of the 2nd step for preparing Pt72Ni28, Pt68Ni32, Pt72Co28, and Pt68Co32 were 30 s, and the rest, 10 s.
Fig. 3.7 Changes in transition metal contents of Pt-Ni and Pt-Co nanoparticles by 1000 potential cycles as a function of (○) the surface Ni contents of the Pt-Ni nanoparticles and (●) the surface Co contents of Pt-Co nanoparticles. Each nanoparticle was prepared by a cycle of DPSE.
cycling test. This clearly indicates that the Ni or Co components of nanoparticles prepared by DPSE are tightly held in the skin layer, in case that the Ni or Co content was less than about 8 % Ni for the Pt-Ni nanoparticles or less than about 4 % Co for the Pt-Co nanoparticles.

It is generally believed that Pt is stabilized, that is the dissolution of Pt is suppressed, by alloying with transition metals [12, 16]. Greeley et al. [15] reported that a Pt skin layer on Pt-based alloys is more stable than pure Pt by density functional theory calculation. In this research, on the Pt alloy nanoparticles with low surface transition metal contents such as Pt0.96Ni0.04 and Pt0.98Co0.02, the decrease rate of the relative surface area was slower than that for Pt. These nanoparticles exhibited no leaching of transition metal even after potential cycling (Fig. 3.7). Therefore, the surface area losses in Fig. 3.5 (b) and (c) were not ascribed to the leaching of Ni and Co components. These results also confirm the existence of the stable Pt skin layer on the Pt-based alloy nanoparticles.

In addition, after the 1000 potential cycles, hydrodynamic voltammograms of the Pt0.93Ni0.07 and Pt0.94Co0.06 nanoparticles-deposited GC electrodes were measured in O2-saturated 0.1 M sulfuric acid solution and their SA values for ORR at 0.8 V were evaluated. The SA values after the 1000 potential cycles were 0.64 mA cm\(^{-2}\) for Pt0.93Ni0.07 and 0.57 mA cm\(^{-2}\) for Pt0.94Co0.06, and decreased by ca. 80 % compared to the initial SA (Table 3.2). But both alloy nanoparticles maintained higher performance than the Pt nanoparticles. The Pt 4f peaks of the Pt0.93Ni0.07 and Pt0.94Co0.06 nanoparticles after 1000 potential cycles also shifted slightly toward higher binding energies than those of Pt nanoparticles (Fig.3.8). The degree of peak shift after 1000 potential cycles was also the same as that before potential cycling. As mentioned above, the degree of Pt 4f shift does not always depend on the degree of d-electron vacancy. However, the peak shift was actually observed, suggesting the electronic structure of surface Pt was changed, and
Fig. 3.8 XPS Pt 4f spectrums of (a) Pt\textsubscript{93}Ni\textsubscript{7} nanoparticles before 1000 potential cycles, (b) Pt\textsubscript{93}Ni\textsubscript{7} nanoparticles after 1000 potential cycles, (c) Pt\textsubscript{94}Co\textsubscript{6} nanoparticles before 1000 potential cycles, and (d) Pt\textsubscript{94}Co\textsubscript{6} nanoparticles after 1000 potential cycles.
therefore the nanoparticles maintained higher ORR performance even after 1000 potential cycles.

3.4 Summary

The Pt-Ni and Pt-Co nanoparticles covered with a Pt skin layer were prepared by the DPSE. The composition and size of the resultant nanoparticles were controlled by two step-potentials, a holding time of the 2nd step-potential and the number of cycles. The Pt-Ni and Pt-Co nanoparticles prepared by the DPSE exhibited higher ORR activity, corrosion resistance, and stability than Pt nanoparticles, suggesting that Pt-skin layer was effective for the improvements of them.

The corrosion resistance and stability varied with the surface composition of the Pt-Ni and Pt-Co nanoparticles, and the nanoparticles with lower surface Ni or Co contents showed better performances. Especially in case of 2 % surface Co content in the Pt-Co nanoparticles, surface area was more than 90 % even after 1000 cycles and the loss of Co was not occurred. That is, there has a strong correlation between the corrosion resistance and stability.

A Pt-skin layer on the Pt-Ni or Pt-Co nanoparticles by the DPSE was stabilized because the Pt-skin layer was alloyed with underneath Ni or Co. Comparing the Pt-Ni and Pt-Co, the Pt-Co was more stable, that is, the Pt-Co was formed more stable Pt skin layer.
References


Chapter 4 Preparation and Characterization of Cubic Pt Nanoparticles by Galvanostatic Electrolysis

4.1 Introduction

Pt-based nanoparticles are known to have high activity as anode and cathode catalysts for polymer electrolyte fuel cells. However, there are some serious problems such as poor Pt reserves and high price. Since the consumption of Pt is on the increase, its reduction is an urgent issue. So far there have been many researches on this issue [1-21]. The preparation of Pt nanoparticles with higher dispersion and smaller sizes [1-6], which caused the increase in specific surface area, and alloying of Pt with other metals, which caused electronic modification [7-21], has been investigated for improving the catalytic activity.

It is known that catalytic activity is closely related to surface atomic arrangement which influences a distance between neighboring two atoms and their electron densities etc. So the control of surface structure which consists of specific crystal plane with high catalytic activity must be an ultimate technique to prepare active catalysts with low Pt contents. Recently, Pt nanoparticles with a cubic or a tetrahedral structure which was composed of only the (100) plane or the (111) plane, respectively, have been prepared [22-27].

In general, the growth rate of metal deposits strongly depends on crystal plane [22, 24-29]. So if the supply of metal ions is very slow, they would be preferentially deposited on the crystal plane which has the fastest growth rate. Thus the shape-controlled metal nanoparticles may be realized without any stabilizer. In this chapter, this idea will be proved with the preparation of shape-controlled Pt
nanoparticles. For this purpose, an electrolytic cell which is composed of the graphite cathode, the Pt anode and a diluted acidic electrolyte solution was used, and during galvanostatic electrolysis (GE) Pt ions which oxidatively dissolved out of the Pt anode were deposited on the graphite cathode after diffusing through the electrolyte solution. The deposited Pt nanoparticles were characterized by spectroscopic and electrochemical measurements.

4.2 Experimental

The cathode and anode were a graphite plate (10 mm × 30 mm × 3 mm) and a Pt sheet (99.95 %, 20 mm × 30 mm × 0.1 mm), respectively. The distance between both electrodes was fixed to be 2 cm. An Ag/AgCl/sat. KCl electrode was used as the reference electrode. The 0.5 M HNO₃ and H₂SO₄ solution were used as electrolyte. The galvanostatic electrolysis (GE) was performed at a cathodic current density of 100 mA cm⁻² and 50 °C. Before the electrolysis, the Pt anode was polished by potential cycling between -0.21 and 0.94 V. To characterize surface structure of Pt nanoparticles deposited on the graphite cathode, cyclic voltammograms (CVs) in an N₂-saturated 0.1 M (= mol L⁻¹) H₂SO₄ solution at 30 °C. Cu-stripping voltammograms in an N₂-saturated (0.1 M H₂SO₄ + 0.2 mM CuSO₄) solution were recorded in a potential range between -0.21 and 0.29 V at a scan rate of 50 mV s⁻¹ at 30 °C. In the Cu-stripping voltammograms, the working electrode was held at 0.06 V for 2 min to deposit Cu adatoms on the Pt surface, and then the electrode potential was scanned from 0.06 to 0.64 V at a scan rate of 100 mV s⁻¹ at 30 °C. For evaluating activity for formaldehyde oxidation reaction of Pt nanoparticles, chronoamperometric measurements were carried out in an N₂-saturated (0.5 M H₂SO₄ + 0.5M HCOOH) solution. In the
chronoamperometric measurements, electrode potential was held at 0.14 V for 20 min. The surface morphology of deposited Pt nanoparticles was observed by a Field-Emission Scanning Electron Microscope (FE-SEM). The elemental analysis of the Pt nanoparticles was conducted by Energy Dispersive X-ray spectroscopy (EDX). The concentration of Pt ions anodically dissolved in the electrolyte solution was analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

4.3 Results and discussion

4.3.1 Preparation of the cubic Pt nanoparticles by GE

Figure 4.1 shows time course of the potential of the graphite cathode during GE at a cathodic current density of 100 mA cm$^{-2}$ (anode: 50 mA cm$^{-2}$) in a 0.5 M HNO$_3$ or 0.5 M H$_2$SO$_4$ solution (50 °C) for 12 h when the Pt sheet or graphite plate was used as the anode. In each case, the cathode potential was around -1.0 V at the beginning of the electrolysis, and hydrogen evolved on the graphite cathode surface. And then the cathodic potential shifted in the positive direction with time and finally reached a constant value. With the graphite anode, the steady potential of the graphite cathode was around -0.65 V in nitric acid and around -0.75 V in sulfuric acid. The electroreduction of NO$_3^-$ with hydrogen evolution occur in the HNO$_3$ solution because the electrode potential was enough negative to reduce NO$_3^-$ to NO$_2^-$ (the standard electrode potential: 0.636 V vs. Ag/AgCl), while in the H$_2$SO$_4$ solution only hydrogen evolution occurs, leading to more positive steady cathode potential for the former.

With the Pt anode, the steady cathode potential was shifted to around -0.28 V which was more positive than that with the graphite anode. The difference of around 0.37 V in cathode potential between the Pt and graphite anodes suggests that additional reactions
Fig. 4.1 Time courses of the potential of the graphite cathode during GE in 0.5 M HNO$_3$ at 50 °C when (a) the Pt sheet or (b) the graphite plate was used as the anode, and in 0.5 M H$_2$SO$_4$ at 50 °C when (c) the graphite plate was used as the anode. Cathodic current density: 100 mA cm$^{-2}$. 
occurred at the graphite cathode. Platinum ions which are produced by the oxidative dissolution of the Pt anode during the GE can move to the graphite cathode and be reduced to deposit metallic Pt. The concentration of platinum ions dissolved in the HNO₃ solution for GE for 24 h was evaluated to be 156 ppb by ICP analysis. Moreover, the potential of the Pt anode during the electrolysis was around 1.9 V at which Pt could be oxidatively dissolved together with oxygen evolution [30, 31]. These results clearly indicate that platinum ions are produced by the dissolution of the Pt anode during the GE.

When the volume of the electrolyte solution was changed to 100 or 300 mL with keeping the distance between the cathode and anode constant, time courses of the potential of the graphite cathode are shown in Fig. 4.2. In each case, the cathode potential consequently reached the same value (around -0.28 V), but potential change became slower with increasing the solution volume. The ICP analysis for each volume of electrolyte solution exhibited that the amount of dissolved platinum ions was almost equal irrespective of the solution volume, indicating that the larger the solution volume was, the lower the concentration of dissolved platinum ions was. If the concentration of platinum ions is low, the supply of platinum ions to the graphite cathode will be slow, leading to the slow Pt deposition at the cathode. Therefore, the larger solution volume causes the slow cathodic potential change, which means the potential change is closely related to the concentration of dissolved platinum ions.

Figure 4.3 shows SEM image of the graphite cathode surface after the GE in 0.5 M HNO₃ solution for 8 h. The Pt nanoparticles formed cubes with sizes of ca. 5~20 nm. Before the electrolysis, there were not any Pt nanoparticles on the graphite cathode surface. These results clearly exhibit that the Pt nanoparticles were formed on the graphite cathode surface during the GE. Since Pt²⁺ ions were not added into the electrolyte solution in advance, they must have been supplied from the Pt anode.
Fig. 4.2 Time courses of the potential of the graphite cathode during the GE at 50 °C in (a) 50, (b) 100, and (c) 300 ml of 0.5 M HNO₃. Cathodic current density: 100 mA cm⁻². Anode: Pt sheet.
Fig. 4.3 SEM images of the graphite cathode surface after the GE for 8 h in 0.5 M HNO$_3$ solution at 50 $^\circ$C. Current density: 100 mA cm$^{-2}$. 
4.3.2 Characterization of the cubic Pt nanoparticles by GE

CVs of the Pt nanoparticles-deposited graphite electrodes prepared in the GE in 0.5 M HNO₃ solutions with and without 0.6 μM Pt(NO₂)₂(NH₃)₂ for 8 h were recorded in an N₂-saturated 0.1 M H₂SO₄ solution at 30 °C. In the former, graphite electrode was used as anode, and separated with a glass filter to avoid dissolution of Pt. The concentration of Pt(NO₂)₂(NH₃)₂, 0.6 μM, was determined on the basis of the total amount of Pt²⁺ ions deposited on the graphite cathode in a 0.5 M HNO₃ solution without Pt(NO₂)₂(NH₃)₂ during the GE at 100 mA cm⁻² for 8 h. The results are shown in Fig. 4.4. The CV of the Pt nanoparticles formed in the electrolyte solution containing Pt(NO₂)₂(NH₃)₂ agreed with that of polycrystalline Pt, as shown in Fig. 4.4 (b). On the other hand, in the CV of the Pt nanoparticles prepared in the electrolyte solution without Pt(NO₂)₂(NH₃)₂, as shown in Fig. 4.4 (a), a couple of distinct redox peaks at ca. 0 V and shoulders at ca. 0.1 V were observed. The redox peaks are assigned to hydrogen adsorption/desorption on the terrace of the Pt (100) plane, while the shoulders are assigned to that on the edge and corner sites, respectively [25, 31], which was characteristic of a cubic structure.

In addition, Cu-stripping voltammograms were measured to characterize the structure of the deposited Pt nanoparticles. It is known that the surface structure of Pt influences the deposition/dissolution of Cu atoms like hydrogen adsorption/desorption. Cu-stripping voltammograms for the Pt nanoparticles-deposited graphite electrodes prepared in the GE in 0.5 M HNO₃ solutions with and without 0.6 μM Pt(NO₂)₂(NH₃)₂ for 8 h are shown in Fig. 4.5 (a) and Fig. 4.5 (b), respectively. In Fig. 4.5 (a), two oxidation peaks were observed at around 0.2 and 0.55 V, which were assigned to the desorption of upd-Cu on the Pt (110) and (100) plane, respectively [32]. That is, Pt nanoparticles were composed of (100) and (110) planes, which was characteristic of the cubic structure. In contrast, the curve in Fig. 4.5 (b) was similar to that of
Fig. 4.4 Cyclic voltammograms of Pt nanoparticles-deposited graphite cathodes prepared in the GE at 100 mA cm$^{-2}$ in (a) 0.5 M HNO$_3$ solution for 8 h, and (b) 0.5 M HNO$_3$ solution with 0.6 μM Pt(NO$_2$)$_2$Cl(NH$_3$)$_2$ for 8h. Each voltammogram was recorded in N$_2$-saturated 0.1 M H$_2$SO$_4$ solution at 30 °C. Sweep rate was 50 mV s$^{-1}$. 
Fig. 4.5 Cu-stripping voltammograms of Pt nanoparticles-deposited graphite cathodes prepared in the GE at 100 mA cm\(^{-2}\) in (a) 0.5 M HNO\(_3\) solution for 8 h, and (b) 0.5 M HNO\(_3\) solution with 0.6 \(\mu\)M Pt(NO\(_2\))\(_2\)(NH\(_3\))\(_2\) for 8h. Each voltammogram was performed in an N\(_2\)-saturated (0.1 M H\(_2\)SO\(_4\) + 0.2 mM CuSO\(_4\)) solution at 30 °C. Sweep rate was 100 mV s\(^{-1}\).
polycrystalline Pt, suggesting the formation of polycrystalline nanoparticles.

To examine whether the shape of the Pt nanoparticles is influenced by the nature of electrolyte solutions, the GE was carried out in 0.5 M H₂SO₄ solution. The rate of Pt deposition in the H₂SO₄ solution was slower than that in the HNO₃ solution, and only a few Pt nanoparticles were deposited even after 200 h. The concentration of Pt²⁺ ions dissolved in 0.5 M H₂SO₄ solution after the GE for 211 h was 36 ppb which was less than a quarter of that in 0.5 M HNO₃ solution. This suggests that both the rate of Pt dissolution at the anode and that of Pt deposition at the cathode in 0.5 M H₂SO₄ solution were slower than those in 0.5 M HNO₃ solution. The Pt nanoparticles-deposited graphite electrode prepared in 0.5 M H₂SO₄ solution showed the similar CV to that prepared in 0.5 M HNO₃ solution (Fig. 4.6), suggesting that irrespective of electrolyte solution the Pt nanoparticles with the cubic structure were prepared in the present electrolysis technique. From these results, Pt nanoparticles with the cubic structure were obtained when Pt²⁺ ions in the solution were extremely low.

4.3.3 Oxidation of formaldehyde of the cubic Pt nanoparticles by GE

To evaluate the formaldehyde oxidation reaction (FOR) activity of the cubic Pt nanoparticles, chronoamperometric measurements were carried out in an N₂-saturated (0.5 M H₂SO₄ + 0.5M HCOOH) solution. Figure 4.7 shows time courses of oxidation current density per real surface area of Pt for the cubic and polycrystalline Pt nanoparticles. The oxidation current density for cubic nanoparticles was higher than that for polycrystalline nanoparticles, showing cubic nanoparticles exhibit high FOR activity. The similar result has been obtained by Solla-Gullon et al [33].
Fig. 4.6 Cyclic voltammograms of Pt nanoparticles-deposited graphite cathodes prepared in the GE at 100 mA cm$^{-2}$ in 0.5 M H$_2$SO$_4$ solution for 200 h. The voltammogram was recorded in N$_2$-saturated 0.1 M H$_2$SO$_4$ solution at 30 °C. Sweep rate was 50 mV s$^{-1}$. 
Fig. 4.7 Chronoamperograms at 0.14 V for (a) cubic Pt nanoparticles and (b) polycrystalline Pt nanoparticles in an N$_2$-saturated 0.5 M H$_2$SO$_4$ + 0.5M formaldehyde solution at 30 °C.
4.4 Summary

Cubic Pt nanoparticles were prepared on the graphite cathode by using Pt$^{2+}$ ions dissolving out of the Pt anode during GE. The concentration of Pt$^{2+}$ ions in the electrolyte solution was so low that the deposition of Pt was extremely slow, leading to the formation of nanoparticles with the cubic structure. The cubic Pt nanoparticles exhibited higher electrocatalytic activity than polycrystalline Pt nanoparticles for FOR.
References

Chapter 5  
**Effect of Current Density on Shape of Pt Nanoparticles by Galvanostatic Electrolysis**

5.1 Introduction

The shape control of Pt nanoparticles is an attractive method to obtain high catalytic activities. The surface of shape-controlled nanoparticles often consists of a specific plane. For example, Pt nanoparticles with the cubic and tetrahedral structures were enclosed by the (100) and (111) planes, respectively. It has been reported that catalytic activity was strongly dependent upon crystal plane [1-6]. Markovic et al. found exchange current density for hydrogen evolution reaction (HER) and hydrogen oxidation reaction (HOR) on Pt single crystals in a sulfuric acid solution was increased in the order of (111) < (100) < (110) [4]. In contrast, Housmans et al. reported that the maximum reactivity of methanol oxidation reaction in sulfuric and perchloric acid solutions was increased in the order of (111) < (110) < (100) [6]. In this way the catalytic activity of Pt nanoparticles can be enhanced by appropriate control of their crystal plane or shape.

Recently, many studies on the preparation of the shape-controlled Pt nanoparticles have been reported [7-16]. For this purpose, chemical reduction methods with some stabilizers which adsorb on a specific plane to suppress crystal growth are often applied. For example, poly (N-vinyl-2-pyrrolidone) (PVP) is preferentially adsorbed on the Pt(111) plane to form tetrahedral nanoparticles, while sodium polyacrylate is adsorbed on the Pt(100) plane to form cubic nanoparticles [8]. Long et al. synthesized cubic, octahedral, tetrahedral and polyhedral Pt nanoparticles using PVP as a stabilizer, Ethylene glycol as a reductant, and AgNO₃ as an additive [16]. However, these methods
cannot control the deposition rate and always require a reductant and a stabilizer. In addition, it is hard to remove the stabilizers because of their strong adsorption, leading to the degradation of catalytic activity [17]. While, in electrodeposition technique, any reductant is not needed because the deposition can be controlled by an electricity [18, 19].

In chapter 4, I succeeded in preparing shape-controlled Pt nanoparticles at a graphite cathode by galvanostatic electrolysis (GE) in a one-compartment cell which was composed of the graphite cathode and Pt anode in acidic solutions. In this system platinum ions were produced by oxidative dissolution of the Pt anode and then used for the deposition of shape-controlled Pt nanoparticles at the graphite cathode. The concentration of dissolved platinum ions was so low that the deposition of Pt was extremely slow, which seemed to cause the formation of nanoparticles with the cubic structure. In this chapter, the effect of current density on the shape of Pt nanoparticles deposited during GE was examined in detail and the key factors to the formation of cubic nanoparticles were proposed.

5.2 Experimental

Pt nanoparticles were prepared on a graphite plate by the GE in a 0.5 M HNO₃ solution at 50 ℃, according to chapter 4. In addition, in order to simultaneously control both cathodic and anodic current densities, two galvanostats were used, and each galvanostat separately controlled cathodic and anodic current densities. For this purpose, a two-compartment cell which was separated by an anion-exchange membrane (Selemion (AHO), AGC Engineering) was used. In one compartment the graphite electrode as a cathode, the Pt electrode as an anode, and reference electrode were placed,
while in another compartment a Pt electrode as a counter electrode to the graphite cathode and Pt anode was placed.

Surface structure of Pt nanoparticles deposited on graphite cathodes was characterized by cyclic voltammetry and Cu-stripping voltammetry. Specific procedure is shown in chapter 4.

The surface morphology of deposited Pt nanoparticles was observed with a Field-Emission Scanning Electron Microscope (FE-SEM). The elemental analysis of the Pt nanoparticles was conducted by Energy Dispersive X-ray spectroscopy (EDX). The concentration of Pt ions anodically dissolved in the electrolyte solution was analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

5.3 Results and Discussion

5.3.1 Growth of the cubic Pt nanoparticles by GE

Figure 5.1 shows SEM images of the graphite cathode surface after the GE at a cathodic current density of 100 mA cm$^{-2}$ (anodic current density: 50 mA cm$^{-2}$) with the one-component cell containing a 0.5 M HNO$_3$ solution (50 °C). The nanoparticles were observed in each photograph and identified as Pt by EDX analysis. After the electrolysis for 4 h, shapeless Pt nanoparticles with 3~5 nm in size deposited, and they grew up with time to form polygons after 6 h (Fig. 5.1 (b)) and cubes after 8 h (Fig. 5.1 (c)).

The surface structure of the Pt nanoparticles deposited at the graphite cathode for different periods of time was characterized by CVs in an N$_2$-saturated 0.1 M H$_2$SO$_4$ solution (30 °C) and Cu-stripping voltammograms in an N$_2$-saturated (0.1 M H$_2$SO$_4$ + 0.2 mM CuSO$_4$) solution (30 °C). Fig. 5.2 shows CVs of the Pt nanoparticles-deposited graphite cathodes after GE at a cathodic current density of 100 mA cm$^{-2}$ (anodic current
Fig. 5.1 SEM images of the graphite cathode surface after the GE at a cathodic current density of 100 mA cm\(^{-2}\) (anodic current density: 50 mA cm\(^{-2}\)) with the one-compartment cell containing a 0.5 M HNO\(_3\) 0.5 M HNO\(_3\) (50 °C) for (a) 4, (b) 6, and (c) 8 h.
Fig. 5.2 Cyclic voltammograms in an N\textsubscript{2}-saturated 0.1 M H\textsubscript{2}SO\textsubscript{4} at 30 ° C for Pt nanoparticles-deposited graphite cathodes after the GE at a cathodic current density of 100 mA cm\textsuperscript{-2} (anodic current density: 50 mA cm\textsuperscript{-2}) with the one-compartment cell containing a 0.5 M HNO\textsubscript{3} (50 °C) for 4, 6 and 8 h. Sweep rate: 50mV s\textsuperscript{-1}. 
density: 50 mA cm\(^{-2}\)) in 0.5 M HNO\(_3\) solution (50 °C) for 4, 6 and 8 h. After the electrolysis for 8 h, a couple of distinct redox peaks at around 0 V and shoulders at around 0.1 V were observed. The peaks at around 0 V are characteristic of hydrogen adsorption/desorption on terraces of the Pt (100) plane [10, 20], suggesting that many Pt nanoparticles with a cubic structure were produced at the graphite cathode, which confirmed the SEM images in Fig. 5.1 (c). On the other hand, the shoulders at around 0.1 V are assigned to hydrogen adsorption/desorption on edges and corners of a cubic structure [10, 20].

Stripping behaviors of a Cu monolayer formed by underpotential deposition (upd-Cu) have been studied by many researchers [21-26]. A typical CV of a polycrystalline Pt electrode in a (0.1 M H\(_2\)SO\(_4\) + 0.2 mM CuSO\(_4\)) solution is shown in Fig. 5.3 (a). The Peak 1 and Peak 2 in Fig. 5.3 (a) are assigned to the oxidative dissolution of bulk Cu and upd-Cu, respectively [24]. Fig. 5.3 (b) shows Cu-stripping voltammograms from 0.06 to 0.64 V for the Pt nanoparticles-deposited graphite cathode after the GE at a cathodic current density of 100 mA cm\(^{-2}\) (anodic current density: 50 mA cm\(^{-2}\)) with the one-compartment cell containing a 0.5 M HNO\(_3\) solution (50 °C) for 4, 6 and 8 h. It is known that the upd-Cu on Pt surface is sensitive to its surface structure [21-26]. So in the present experiment surface structure of the Pt electrode is characterized by the peak 2. The desorption peaks of upd-Cu on the Pt (110), (111), and (100) planes are observed at around 0.20, 0.45, and 0.55 V, respectively [21]. As can be seen from Fig. 5.3 (b), the large peak at 0.2 V and the small peak at around 0.45 V scarcely changed with electrolysis time, while the peak at 0.55 V was greatly increased with time, suggesting the growth of the (100) plane. This is in good agreement with the results of SEM images (Fig. 5.1) and CVs (Fig. 5.2).

Why were the cubic Pt nanoparticles formed during the GE using the Pt anode? What is the most important factor in the formation of the cubic Pt nanoparticles?
Fig. 5.3 (a) A cyclic voltammogram of a polycrystalline Pt electrode in an N$_2$-saturated (0.1 M H$_2$SO$_4$ + 0.2 mM CuSO$_4$) solution (30 °C). Sweep rate: 100mV s$^{-1}$. (b) Cu-stripping voltammograms for the Pt nanoparticles-deposited graphite cathode after the GE at a cathodic current density of 100 mA cm$^{-2}$ (anodic current density: 50 mA cm$^{-2}$) with the one-compartment cell containing a 0.5 M HNO$_3$ solution (50 °C) for 4, 6 and 8 h, and typical polycrystalline Pt electrode. Sweep rate: 100mV s$^{-1}$. 
shape of nanoparticles is closely related to their surface energy. For example, the (111), (110) and (100) planes of the face-centered cubic (fcc) structure have different surface energy, and the (111) plane has the lowest surface energy among them [27], suggesting that the tetrahedral structure enclosed by the (111) plane is the most stable. In addition, final configuration of nanocrystals is dependent upon the R value, which is defined as the ratio of the growth rate along the (100) plane to that along the (111) plane [27]. If the R value of a nanoparticle is low or the relative growth rate of (111) is fast, it grows into the cubic structure. On the other hand, if the R value of a nanoparticle is high, it grows into the tetrahedral structure. In the present study, it is deduced that the growth rate along the (111) plane is faster than that along the (100) plane [28, 29]. Wang et al also reported that at room temperature the shape of nanoparticles was determined by the kinetics of their formation, not by thermodynamics [30]. In this way the growth rate of Pt nanoparticles and the diffusion rate of platinum ions can become key factors for forming the cubic structure.

5.3.2 Effect of current density on shape of Pt nanoparticles

If the deposition rate of Pt at the cathode and diffusion rate of platinum ions to the cathode or dissolution rate of the Pt anode are changed, Pt nanoparticles will grow into different shapes. The cathodic current density can control the deposition rate of Pt while the anodic current density can control the production rate of platinum ions or their diffusion rate. So the cathodic and anodic current densities were separately controlled by two galvanostats. Fig. 5.4 shows Cu-stripping voltammograms and SEM images for the Pt nanoparticles-deposited graphite cathode after GE in 0.5 M HNO₃ solution (50 °C) for 8 h. The cathodic and anodic current densities were 75 and 50, 50 and 50, and 75 and 25 mA cm⁻², respectively. In the case of an anodic current density of 50 mA cm⁻² and a cathodic current density of 100 mA cm⁻², cubic Pt nanoparticles were mainly
Fig. 5.4 Cu-stripping voltammograms (a-c) and SEM images (d-f) for the Pt nanoparticles-deposited graphite cathode after the GE in the two-compartment cell containing a 0.5 M HNO₃ solution (50 °C) for 8 h. Sweep rate: 100mV s⁻¹. Cathodic and anodic current densities were (a, d) 75 and 50, (b, e) 50 and 50, and (c, f) 75 and 25 mA cm⁻², respectively.
deposited on the graphite cathode as shown in Fig. 5.1 (c) and large oxidation peaks due to Cu-stripping at the (110) and (100) planes was observed in Fig. 5.3 (b), because terraces and edges and corners of the cubic structure were oriented in the (100) and (110) directions, respectively. When anodic current density was kept to 50 mA cm\(^{-2}\), for a cathodic current density of 75 mA cm\(^{-2}\), Cu-stripping peak at the (111) plane distinctly observed in addition to Cu-stripping peaks at the (110) and (100) planes (Fig. 5.4 (a)), and the SEM image (Fig. 5.4 (d)) exhibited that cubic nanoparticles were numerically decreased while tetragonal nanoparticles were increased, supporting the appearance of the Cu-stripping peak at the (111) plane. For a cathodic current density of 50 mA cm\(^{-2}\), a Cu-stripping peak at the (110) plane was greatly increased compared to that for 100 and 75 mA cm\(^{-2}\) while a Cu-stripping peak at the (100) plane was decreased (Fig. 5.4 (b)). In the SEM image (Fig. 5.4 (e)), there were few cubic and tetragonal nanoparticles, and polyhedron nanoparticles were mainly observed, supporting the increase in the (110) plane in the Cu-stripping voltammogram.

When cathodic current density was kept to 75 mA cm\(^{-2}\) and anodic current density was decreased to 25 mA cm\(^{-2}\) (Fig. 5.4 (c)), a pattern of Cu-stripping peaks was similar to that for the cathodic and anodic current densities of 100 and 50 mA cm\(^{-2}\), respectively, although each peak current was decreased. The SEM image (Fig. 5.4 (f)) exhibited that small cubic Pt nanoparticles were mainly observed. In this way the cathodic and anodic current densities or the rates for the deposition of Pt and diffusion of platinum ions can influence the shape of deposited Pt nanoparticles. In electrolyses for 8 h with the two-compartment cell containing a 0.5 M HNO\(_3\) solution (50 °C), the cubic nanoparticles were obtained only when cathodic and anodic current densities were 75 and 25, 100 and 50, and 110 and 75 mA cm\(^{-2}\), respectively.
Fig. 5.5 Cu-stripping voltammograms (a-c) and SEM images (d-f) for the Pt nanoparticles-deposited graphite cathode after the GE in 0.5 M HNO$_3$ + (a, d) 0.6, (b, e) 0.5, and (c, f) 0.4 μM Pt(NO$_2$)$_2$(NH$_3$)$_2$ solution at 50 ºC for 8 h. Sweep rate: 100mV s$^{-1}$. Cathodic current density: 100 mA cm$^{-2}$. Anode: Graphite plate.
5.3.3 Preparation of Pt nanoparticles by electrodeposition containing a small amount of Pt precursors

In order to examine whether shape-controlled Pt nanoparticles can be formed or not in 0.5 M HNO₃ solution (50 °C) containing platinum precursors galvanostatic electrolysis was performed with a 0.5 M HNO₃ solution (50 °C) containing 0.6, 0.5 and 0.4 μM Pt(NO₂)₂(NH₃)₂ at the cathodic current density of 100 mA cm⁻² for 8 h. In this case the graphite plate was used as the anode instead of the Pt sheet. The concentration of 0.6 μM was determined under the assumption that Pt deposited on the graphite cathode in the electrolysis in 0.5 M HNO₃ solution (50 °C) with the Pt anode at the cathodic current density of 100 mA cm⁻² for 8 h was completely dissolved. A Cu-stripping voltammograms and SEM images after each electrodeposition are shown in Fig. 5.5. For 0.6 μM Pt(NO₂)₂(NH₃)₂, Cu-stripping voltammogram (Fig. 5.5 (a)) was different from that in Fig. 5.3 (b), that is cubic nanoparticles were not obtained (Fig. 5.5 (d)). For 0.5 μM Pt(NO₂)₂(NH₃)₂, the Cu-stripping peak at the (110) and (100) planes were distinctly observed, and the SEM image (Fig. 5.5 (e)) suggested the formation of cubic Pt nanoparticles. For 0.4 μM Pt(NO₂)₂(NH₃)₂, the Cu-stripping peak at the (110) plane was greatly decreased, while that at the (100) plane was a little decreased (Fig. 5.5 (c)). The SEM image (Fig. 5.5 (f)) also exhibited the disappearance of the cubic Pt nanoparticles.

When electrolysis time is increased, the concentration of Pt(NO₂)₂(NH₃)₂ should be decreased, leading to the decrease in diffusion rate of platinum ions. In contrast, for the GE at the anodic current density of 50 mA cm⁻² with the Pt anode, the concentration of dissolved platinum ions would not be decreased because they are continuously produced at the Pt anode. So the diffusion rate of Pt²⁺ ions would not be decreased. In the GE with the Pt anode and Pt precursors, the cubic nanoparticles were prepared under specific conditions. From the SEM images in Fig. 5.4 (f) and Fig. 5.5 (e), the cubic nanoparticles
prepared in the GE with the Pt anode were bigger than those prepared in the GE with Pt precursors. In the former, nucleation and nucleus growth of Pt nanoparticles occurred very slowly due to low diffusion rate of Pt$^{2+}$ ion. As mentioned in chap. 2, since Pt preferentially deposits on Pt, not on carbon, Pt$^{2+}$ ions would be reduced on the Pt nanoparticles, leading to the increase in particle size. While, in the latter, since the initial concentration of Pt$^{2+}$ ions is higher compared to the former, nucleation can occur more frequently at the first stage of the electrolysis. But, the concentration of Pt$^{2+}$ ions or the diffusion rate of Pt$^{2+}$ ions is reduced with an increase in electrolysis time, leading to the limited growth of cubic nanoparticles.

5.4 Summary

The cubic Pt nanoparticles were obtained on the graphite electrode by GE. In this method, platinum ions slightly dissolved from the Pt anode were utilized for the deposition of Pt at the cathode. The deposition of Pt became extremely slow, leading to the formation of cubic nanoparticles. In a 0.5 M HNO$_3$ solution (50 °C) for 8 h, the cubic nanoparticles were obtained only when the cathodic and anodic current densities were 75 and 25, 100 and 50, and 110 and 75 mA cm$^{-2}$, respectively, suggesting that appropriate adjustment of growth rate of Pt nanoparticles and dissolution rate of the Pt anode is important for controlling the shape of Pt nanoparticles. This method was easily performed in acidic solutions with no extra additives such as reductants and capping reagents. Then it is expect to be a valuable method for making Pt nanoparticle catalyst.
References

Chapter 6  General Conclusions

In this thesis, the Pt-based nanoparticles were prepared by two electrodeposition techniques, Double Potential Step Electrolysis (DPSE) and Galvanostatic Electrolysis (GE). With the DPSE, Pt-Ni and Pt-Co alloy nanoparticles covered with a Pt layer could be prepared. The DPSE was composed of two-step reactions, leading to the formation of Pt-Ni and Pt-Co alloy nanoparticles covered with a Pt layer. Each alloy nanoparticle exhibited higher corrosion resistance and oxygen reduction reaction (ORR) than the Pt nanoparticles. With the GE, cubic Pt nanoparticles were obtained. During the GE, very small amount of Pt$^{2+}$ ions dissolved out of a Pt anode. The Pt$^{2+}$ ions moved to the cathode and were reduced, leading to the formation of a cubic structure.

The conclusions obtained in this study are summarized as follows.

1. A novel preparation method for Pt-based nanoparticles by means of DPSE in which Pt-Ni alloy was deposited at the first step and Ni was dissolved at the following step was developed. A cycle of the DPSE in a nickel plating bath containing PtCl$_6^{2-}$ led to the formation of the Pt-Ni nanoparticles with 5.4 ± 1.5 nm in size. The Pt-Ni nanoparticles gradually grew up with repeating the DPSE process, and the surface Ni content of the particles evaluated by XPS was controllable by changing some parameters of the DPSE. The Pt-Ni nanoparticles deposited by the DPSE were covered with a Pt skin layer, and exhibited ca. two times higher electrocatalytic activity for ORR than Pt nanoparticles.

2. The Pt-Co nanoparticles covered with a Pt skin layer were also prepared by the DPSE. Both Pt-Co and Pt-Ni nanoparticles prepared by the DPSE exhibited higher ORR activity than the Pt nanoparticles even after the deterioration test in which 1000 cycles
of potential sweep were performed between 0.05 and 1.2 V vs. RHE. And both Pt-Co
and Pt-Ni nanoparticles showed high corrosion resistance, and the surface Co and Ni
contents after 1000 cycles were kept constant around 4 % and 8 %, respectively.
Moreover, the Pt-Co nanoparticles with 2 % surface Co content had the lowest
decrement of the real surface area of Pt, and their relative surface area was kept more
than 90% even after 1000 cycles.

3. Low concentration of Pt$^{2+}$ ions, which were produced by oxidative
dissolution of the Pt anode during GE, were reduced at the graphite cathode
to form Pt nanoparticles with a cubic structure. This could be ascribed to
slow Pt deposition which would be dominated by the diffusion of Pt$^{2+}$ ions.
And the cubic nanoparticles prepared by the GE also exhibited higher
electrocatalytic activity for formaldehyde oxidation than polycrystalline Pt
nanoparticles.

4. The GE was performed in a 0.5 M HNO$_3$ solution at 50 ºC, and the cubic
nanoparticles were obtained only when the cathodic and anodic current densities were
25 and 75, 50 and 100, and 75 and 100 mA cm$^{-2}$, respectively. Moreover, in 0.5 M
HNO$_3$ solution containing Pt (NO$_2$)$_2$(NH$_3$)$_2$, the cubic Pt nanoparticles were also
obtained at a cathodic current density of 100 mA cm$^{-2}$. From these results, it was found
that the growth rate of Pt nanoparticles at the graphite cathode and the dissolution rate
of the Pt anode appropriately balanced for controlling the shape of deposited Pt
nanoparticles.
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List of Publications

1. Preparation of Novel Pt-based Nanoparticles by Double Potential Step Electrolysis and Their Electrocatalytic Activity for Oxygen Reduction Reaction
   T. Nishimura, T. Morikawa, M. Yokoi, C. Iwakura, H. Inoue

   T. Nishimura, T. Morikawa, M. Yokoi, H. Inoue

3. Preparation of Shape-Controlled Pt Nanoparticles by Galvanostatic Electrolysis
   T. Nishimura, T. Nakade, T. Morikawa, H. Inoue
   ECS Trans., Vol. 50, No. 19, pp.15-21 (2013)

4. Effect of Current Density on Electrochemical Shape Control of Pt Nanoparticles
   T. Nishimura, T. Nakade, T. Morikawa, H. Inoue