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# PtNi Alloy Nanoparticles Prepared by Nanocapsule Method for ORR Catalysts in Alkaline Media

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#### Abstract

PtNi alloy nanoparticles prepared by unique nanocapsule method exhibited high oxygen reduction reaction activity in alkaline media. The catalytic activity was dependent much on the alloy composition. At the optimum composition (ca. 50 atom% of Ni), the mass activity was more than twice as high as that of pure Pt nanoparticles.

Keywords: oxygen reduction reaction, PtNi alloys, nanoparticles, alkaline solution

#### 1. Introduction

Polymer electrolyte fuel cells (PEFCs) have attracted much attention because of their high energy conversion efficiency and low emission levels.<sup>1,2</sup> Currently, most PEFCs utilize acidic polymer membranes (such as Nafion from DuPont), however, replacing acidic (proton-conductive) polymers with alkaline (anion-conductive) polymers provides significant advantages including possible use of non-precious metals as electrocatalysts.<sup>3-6</sup> A number of researches have been reported in the literature for developing high performance electrocatalysts in alkaline media.<sup>7-9</sup> These researches include PtM (M: transition metals such as Co, Ni, and Fe) nanoparticles deposited on carbon support. Some are claimed to exhibit much higher ORR activity than that of pure Pt.<sup>10</sup>

Nanocapsule method could effectively provide metal and alloy nanoparticles with well-controlled particle size and size metal complexes by reducing distribution in reverse-micelles.<sup>11-13</sup> We have recently reported that PtCo alloy nanoparticles deposited on carbon prepared by nanocapsule method exhibited high oxygen reduction reaction (ORR) activity in alkaline solution.<sup>14</sup> The alloy nanoparticles showed volcano-type dependence of the ORR activity on the alloy composition, where the highest activity was obtained for Pt<sub>60</sub>Co<sub>40</sub>. The results prompted us to investigate different alloy nanoparticles to find whether similar composition dependence on ORR would be observed since the nanocapsule method is applicable to a number of transition metals. In fact, PtNi alloy nanoparticles were claimed to exhibit better ORR activity than PtCo in acidic media.<sup>15</sup> In this paper, we report characterization and ORR activity in alkaline media of PtNi alloy nanoparticles.

# 2. Experimental

Preparation of carbon-supported PtNi nanoparticle (PtNi/C). A typical procedure is as follows. Pt(acac)<sub>2</sub> (0.13 mmol), Ni(acac)<sub>2</sub> (0.13 mmol), and 1,2-hexadecanediol (260 mg) were dissolved in 12.5 mL of diphenyl ether under nitrogen flow in a 100 mL round-bottom flask equipped with a magnetic stirrer bar. The mixture was heated at 110 °C for 30 min followed by the addition of oleic acid (0.27 mmol) and oleyl amine (0.24 mmol). The mixture was heated at 220 °C for 30 min. LiBEt<sub>3</sub>H (1.0 mL) was added dropwise into the mixture. The mixture was slowly added into a suspension of acetylene black (AB800, 129.6 mg) in 12.5 mL of diphenyl ether. The mixture was then heated at 270 °C for 1 h and cooled to 20 °C. The mixture was heated again at 270 °C for 1 h and then, cooled to 50 °C. The product was recovered by filtration and heated at 400  $^{\circ}C$  in 5% H\_2/N\_2 atmosphere for 4 h. Then, the product was washed with 50% ethanol for 5 min. The washing procedure was repeated four times. The black powders thus obtained were heated at 400  $^\circ C$  for 4 h in 5% H\_2/N\_2 atmosphere.

Electrochemical measurements. Rotating ring disk electrode equipment (Nikko Keisoku RRDE-1) with a gas-tight Pyrex glass cell was used to measure the ORR activity of the PtNi/C. A ring-shaped platinum wire and a reversible hydrogen electrode (RHE) were used as the counter electrode and the reference electrode, respectively. The electrode potentials are stated relative to RHE. The electrolyte solution (0.1 M KOH) was prepared from 3 M KOH and Milli-Q water. Prior to the ORR measurements, the working disk electrode was cleaned by cycling the potential between 0.05 and 1.0 V at a sweep rate of 0.5 V s<sup>-1</sup> in deaerated 0.1 M KOH until steady voltammograms were obtained. The electrochemically active surface area (ECSA) of Pt was calculated from the electric charge of the hydrogen adsorption in the negative-going potential scan from 0.05 to 0.40 V in cyclic voltammetry at 25 °C. After bubbling air in 0.1 M KOH for at least 30 min, hydrodynamic voltammograms for the ORR at the working disk electrodes were recorded by sweeping the potential from 0.2 to 1.0 V at a rate of 5 mV s<sup>-1</sup> and at rotation rates of 1000, 1250, 1500, 1750, 2000, 2250, 2250, and 2750 rpm. The Pt ring collection electrode was potentiostatted at 1.1 V, where the anodic oxidation of hydrogen peroxide is diffusion-limited.

Table 1. Characterization and ORR properties of Pt100-xNix/C

| Tuble 1: Characterization and Okty properties of 1 tion-xi the |          |               |                  |               |                    |                             |                             |                                 |
|--|----------|---------------|------------------|---------------|--------------------|-----------------------------|-----------------------------|---------------------------------|
| x (atom%)  |          | Metal         | Diameter (nm)    |               | ECSA <sup>a)</sup> | Mass activity <sup>b)</sup> | Mass activity <sup>b)</sup> | P <sub>H2O2</sub> <sup>c)</sup> |
| Feed   | Obtained | loading (wt%) | $d_{\text{TEM}}$ | $d_{\rm XRD}$ | $(m^2 g^{-1})$     | $(A g_{metal}^{-1})$        | $(A g_{Pt}^{-1})$           | (%)                             |
| 25   | 28       | 22            | 3.1              | 2.2           | 55                 | 373                         | 416                         | 0.2                             |
| 40   | 43       | 20            | 3.1              | 1.9           | 22                 | 323                         | 396                         | 0.2                             |
| 50   | 51       | 21            | 3.1              | 2.2           | 20                 | 634                         | 832                         | 0.1                             |
| 75   | 62       | 17            | 3.2              | 2.5           | 16                 | 146                         | 218                         | 0.4                             |

a) Electrochemically active surface areas obtained from the CVs in Figure 1. b) At 0.85 V versus RHE. c) Percentage of hydrogen peroxide production with regard to the total ORR at 0.76 V vs RHE.

# 3. Results and Discussion 3-1. Preparation and characterization of PtNi/C

A series of  $Pt_{100-x}Ni_x$  (x = molar composition of Ni, atom%) alloy nanoparticles deposited on carbon support were prepared from Pt(acac)<sub>2</sub> and Ni(acac)<sub>2</sub> as metal precursors via nanocapsule method. Diphenyl ether, and oleic acid and oleylamine were used as solvent and surfactants, respectively, to encapsulate the metal precursors in reverse-micelles. The targeted alloy (or feed precursor) compositions were x = 25, 40, 50, and 75, respectively. Similar to the PtCo alloy nanoparticles,14 acetylene black was used as a carbon support because of its high specific surface area (779 m<sup>2</sup> g<sup>-1</sup>) and relatively small number of interior pores. In all cases, PtNi nanoparticles deposited on acetylene black were obtained. Table 1 summarizes the composition, loading amount of the total metals, diameter of the resulting  $Pt_{100-x}Ni_x/C$ . The average alloy compositions measured by X-ray fluorescence (XRF) analyses were x = 28, 43, 51, and 62, nearly comparable (or somewhat lower for x = 62) compared to the targeted values, while loading amounts of the total metals measured by thermogravimetric analyses (TGA) were 17-22 wt% close to the targeted value (20 wt%) within acceptable errors. The transmission electron microscopic (TEM) images revealed that the PtNi particles were highly dispersed on the carbon support (Figure S1). The average particle sizes (dimeters) were  $d_{\text{TEM}} =$ ca. 3.1-3.2 (±0.4-0.6) nm. There were no serious aggregations of the nanoparticles observed throughout the sight of the view. The X-ray diffraction (XRD) patterns exhibited characteristic peaks assignable to fcc phase of PtNi alloy and carbon support (a large and broad peak at  $2\theta = ca. 25^{\circ}$ ) (Figure S2). No peaks assignable to Ni metal and oxides were observed. The peaks of PtNi shifted toward larger angle as increasing Ni content because of the smaller lattice constant of Ni (352 pm) compared to that of Pt (392 pm). The average crystallite sizes were calculated with Scherrer's equation using the peak at  $2\theta =$ 67-70° (220 plane) to be  $d_{XRD} = 1.9-2.5$  nm, slightly smaller than the particle sizes obtained from the TEM images.

# 3-2. Electrochemical properties and ORR activity of PtNi/C

The Pt<sub>100-x</sub>Ni<sub>x</sub>/C catalysts were mounted on a glassy carbon disk electrode and covered with a thin ionomer layer (Tokuyama AS-4 anion exchange polymer containing quaternary ammonium groups) to measure the electrochemical properties. Figure 1 shows cyclic voltammograms (CVs) of the catalysts in N2-saturated 0.1 M KOH aqueous solution. The potential cycles were carried out between 0.05 and 1.0 V vs RHE for at least 80 cycles to confirm a stable surface structure. The redox waves above ca. 0.8 V vs RHE were for oxidation/reduction of the surface Pt. Another redox waves below 0.3 V vs. RHE were for hydrogen desorption/adsorption at polycrystalline Pt on the surface. The electrochemically active surface areas (ECSAs) calculated from the electric charge of the hydrogen desorption waves assuming 0.21 mC  $cm^{-2}$  for smooth polycrystalline Pt, were 55 m<sup>2</sup> g<sup>-1</sup> for x = 25 and decreased as increasing x as shown in Figure 2, due to the decreased content of Pt atoms on the surface. The ECSAs were much smaller than the specific surface areas expected from the diameters ( $d_{\text{TEM}}$ ). Similar results were obtained for PtCo/C catalysts.<sup>14</sup> It is suggested that Ni atoms were present on the surface in alkaline media even after potential cycles, while in acidic media transition metals tend to dissolve resulting in the formation of Pt shell structure.



Figure 1. CVs of  $Pt_{100-x}Ni_x/C$  in 0.1 M KOH saturated with  $N_2$  at 25 °C. The scan rate was set at 50 mV s<sup>-1</sup>.



**Figure 2.** Specific surface area of  $Pt_{100-x}Ni_x/C$  in 0.1 M KOH saturated with N<sub>2</sub> at 25 °C calculated from the particle size  $(d_{\text{TEM}})$  ( $\circ$ ) and CV ( $\bullet$ ).

Then, ORR activity of Pt100-xNix/C catalysts was investigated by hydrodynamic voltammetry in air-saturated 0.1 M KOH aqueous solution. Figure 3 shows a set of hydrodynamic voltammograms at a rotation rate of 1750 rpm as a typical example (see Figure S3 for the data of other rotation rates from 1000 to 2750 rpm). Data for Pt/C (x=0) were taken from the literature as a reference.<sup>14</sup> The ORR current started at above 0.97 V and reached to diffusion limit at ca. 0.4 V. The ORR current started at higher potential as increasing x up to x = 51 and then decreased for x = 62. The results were very similar to what was obtained for PtCo/C catalysts under the same conditions.<sup>14</sup> The production of hydrogen peroxide (PH2O2) with regard to the total ORR was calculated from the current detected at the ring electrode at 0.76 V. P<sub>H2O2</sub> values were very small (< 0.4%) indicating dominant four electron transfer process (Figure 4). The PH2O2 for PtNi/C was even smaller than that for PtCo/C.

From the hydrodynamic voltammograms, mass activity (MA) of the catalyst per Pt for ORR at 0.85 V was calculated and plotted as a function of x in Figure 5. PtNi/C showed similar MA value (ca. 400 A g<sub>Pt</sub><sup>-1</sup>) to that of PtCo/C when x was smaller than 30 atom%. The MA of PtNi/C also exhibited a volcano-type dependence on the Ni content and the maximum MA (832 A g<sub>Pt</sub><sup>-1</sup>) was obtained at x = 51 atom%. The highest MA per total metal (634 A g<sub>metal</sub><sup>-1</sup>) was also obtained at the same alloy composition (Table 1). It is considered that high ORR activity of PtM (M = Ni and Co) alloys is due to the weak chemical adsorption of OH species onto surface Pt atoms in the alloys to produce more available Pt sites for ORR. It is not well-understood why the optimum alloy composition differed

between PtNi/C and PtCo/C, while each transition metal should have different electronic effect on the surface Pt atoms. Compared to the acidic conditions in which the optimum content of the transition metals was ca. 20-30 atom%,<sup>16</sup> that in alkaline solution was much higher. The result may imply different ORR-enhancement mechanism of the alloys in alkaline media, where Ni and Co hydroxides would be involved.



**Figure 3.** Hydrodynamic voltammograms for ORR in air-saturated 0.1 M KOH at 25 °C at  $Pt_{100-x}Ni_x/C$ . The scan rate and the rotation rates were set at 5 mV s<sup>-1</sup> and 1750 rpm, respectively. The ring potential was set at 1.1 V vs RHE to detect hydrogen peroxide formed at the working electrode.



**Figure 4**. Hydrogen peroxide yield in ORR in air-saturated 0.1 M KOH at 25 °C at  $Pt_{100-x}Ni_x/C$  ( $\blacktriangle$ ) and  $Pt_{100-x}Co_x/C$  ( $\bullet$ ) (at 0.76 V).



Figure 5. Mass activity per platinum of  $Pt_{100-x}Ni_x/C$  ( $\blacktriangle$ ) and

Pt100-xCox/C (•) at 0.85 V.

# 4. Conclusion

A series of PtNi alloy nanoparticles deposited on acetylene black carbon support (PtNi/C) were synthesized via our original nanocapsule method so that the alloy compositions, particles sizes and their distribution were well-controlled. PtNi/C exhibited high ORR activity with volcano-type dependence on the composition, where the optimum content of Ni was ca. 50 atom%. The enhancement of the catalytic activity in alkaline solution appeared in a very narrow range of Ni content, similar to that of PtCo/C. Since the nanocapsule method is applicable to many other binary and even ternary alloy nanoparticles, more active alloy or non-precious metal catalysts may be found in the future.

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