ABSTRACT: The interfacial structure and activity for the oxygen reduction reaction (ORR) were investigated on a PtNi surface alloy on a Pt(111) electrode (PtNi/Pt(111)). The PtNi surface alloy was prepared by thermal annealing of Ni2+ modified on Pt(111) at 573–803 K. After optimizing the alloying temperature and the amount of added Ni, the ORR current density of PtNi/Pt(111) at 0.9 V (reversible hydrogen electrode) increases 9.5 times compared with that of Pt(111), and the activity is decreased by 24% after 1000 potential cycles. The atomic composition and subsurface structure of PtNi/Pt(111) were determined by in situ infrared reflection-absorption spectroscopy and X-ray diffraction. The surface contains a (111)-oriented Pt-skin and the subsurface of the 2nd–5th layers of the PtNi alloy contains less than 11% Ni atoms. The layer spacings of the surface alloy layers are slightly expanded compared with those of bare Pt(111). Homogeneous alloying with a small amount of Ni in the subsurface layers achieves the high ORR activity and durability.

INTRODUCTION

The enhancement of the activity of cathode catalysts for the oxygen reduction reaction (ORR) is essential for the widespread use of polymer electrolyte fuel cells at low cost. Bimetallic alloys comprising Pt and base metals have been widely studied as ORR catalysts. In particular, Pt alloyed with iron group elements, such as PtNi, PtCo, and PtFe, show high mass activity for ORR compared with that of commercial Pt/C catalysts. The perturbation of electronic structure induced by the heterometal activates the ORR. Stamenkovic et al. have reported a volcano-type relationship between the ORR activity and the d-band center of Pt alloys; PtNi, Pt5Co, and Pt3Fe show high ORR activities. The surface compositions of Pt-base metal alloys affect their electronic structures. On Pt-base polycrystalline alloys, the ORR activity and the durability are enhanced by the Pt-skin structure. As for the surface composition of the Pt-ally particles, most of the alloys have a Pt-skin shell and an alloyed core.

Single crystal electrodes are useful for understanding the relationship between ORR activity and surface structure. The atomic arrangement of the Pt surface significantly affects the electrocatalytic reactions; the ORR current density at 0.9 V (reversible hydrogen electrode (RHE)) increases in the order of Pt(100) < Pt(110)-(1 × 1) < Pt(111) < Pt(110)-(1 × 2). The active site for ORR has been studied using the high index planes of the Pt single crystal; the ORR activity on the (111) terrace with (111) and (100) step structures was higher than that on the (100) terrace with step structures. The dependence of ORR activity on the surface structure also appears on Pt3Ni and Pt3Co alloy single crystal electrodes. The ORR current density at 0.9 V (RHE) for Pt3Ni(111) was 10 times higher than that for Pt(111), and the compositions of the Pt-skin surface and alloyed subsurface have been revealed.

Recently, the ORR activity has been widely investigated on various surface alloys formed on single crystal electrodes. The surface composition and structure of the surface alloy can be easily controlled by the preparation conditions. Wadayama et al. have evaluated the ORR activity of the PtNi/Pt(111) electrode prepared by molecular beam epitaxy (MBE) and revealed the dependence of the surface structure and the ORR activity on the alloying temperature. Attard et al. have prepared Ru quasi single crystal surfaces and PtNi alloys on Pt(111) modified by wet and annealing processes and revealed that the PtNi alloys on Pt(111) show the repeating effects of the modification and annealing process. These PtNi surface alloys on Pt(111) activate the ORR as much as Pt3Ni(111).
However, there are no reports on the detailed subsurface structure of the PtNi surface alloy electrode. Because the activity of the Pt alloy electrode is mostly governed by the subsurface composition and lattice strain, understanding the relationship between activity and interfacial structure is important for the development of highly active catalysts.

The surface and subsurface structures of PtSn surface alloy on Pt(111) have been reported for the ethanol oxidation reaction. In situ surface X-ray diffraction (SXRD) measurement revealed detailed structures of the surface and subsurface layers of the PtSn surface alloy. Although the Sn atoms were located in the surface layer, the elution of surface Sn atoms was restrained by the formation of the PtSn alloy layer.

In this study, the PtNi surface alloy on Pt(111) (PtNi/Pt(111)) was prepared by thermal annealing of Ni$^{2+}$ modified on Pt(111) under a reductive atmosphere. The annealing temperature and the amount of added Ni$^{2+}$ were optimized for the ORR. Although the scanning transmission electron microscopy and X-ray photoelectron spectroscopy provide quantitative information on the alloy layer, their application to in situ measurements is difficult. Therefore, the surface and subsurface structures were determined by in situ SXRD measurement. The vibrational frequency of adsorbed carbon monoxide (CO), which is sensitive to the surface structure, was compared in the PtNi alloy and Pt(111) surfaces using in situ infrared reflection–absorption spectroscopy (IRAS).

### RESULTS AND DISCUSSION

Figure 1 shows the alloying temperature dependence of cyclic voltammograms (CVs) and ORR voltammograms on Pt(111) modified with 300 pmol Ni$^{2+}$ (equivalent to 2 ML) in 0.1 M HClO$_4$. The CV shows the hydrogen adsorption/desorption regions between 0.05 and 0.35 V, the double layer region between 0.35 and 0.6 V, and the OH adsorption/desorption regions above 0.6 V, indicating that the Pt layer is exposed on the surface. In acidic media, Ni is oxidized or dissolved above 0.3 V. As there are no oxidation peaks at the first cycle, the oxidation and dissolution of Ni do not occur. The onset potentials of H$\text{upd}$ and OH$\text{ad}$ shift negatively and positively, respectively. Similar potential shifts are also observed on Pt$_3$Ni(111), which result from the change of the electronic structure of the surface Pt atoms due to alloying with Ni atoms.

![Figure 1](image-url)
PtNi/Pt(111) annealed at 723 K shows the highest ORR activity. Figure 1c shows the potential dependence of the charge density of the oxide species above 0.6 V. The total charge density of oxide formation at 0.9 V is remarkably reduced by the alloying, and the ORR current density increases with the decreasing oxide species. OHad is one of the blocking factors for the ORR on Pt electrodes, and the IR band intensity of OHad is related to the ORR activity. The d-band center shift of Pt modified with Ni weakens the adsorption energy of OHad, which enhances the ORR activity. The alloying at 803 K decreases the ORR activity, indicating that Ni sublimates or migrates to the bulk.

Figure 1b shows the Ni concentration dependence of CVs and ORR voltammograms of PtNi/Pt(111) at 723 K in 0.1 M HClO4. The amount of added Ni also affects the OH adsorption/desorption peaks. The ORR activity of PtNi/Pt(111) modified with 450 pmol of Ni (equivalent of 3 ML) and annealed at 723 K is 9.5 times higher than that of Pt(111), as shown in Figure 1d.

The durability of PtNi/Pt(111) modified with the Ni equivalent of 3 ML was evaluated by potential cycles. Figure 2a shows CVs of PtNi/Pt(111) after 100 and 1000 cycles between 0.6 and 1.0 V. After 100 cycles, the charge densities of hydrogen adsorption/desorption and OH adsorption/desorption increase dramatically. The potential cycle including the oxidation/reduction of Pt promotes dissolution of surface Pt atoms and results in the defective surface. The peaks at 0.13 and 0.3 V are assigned to the hydrogen adsorption/desorption on the (110) and (100) step sites, respectively. In the case of the Cu/Pt(111) surface alloy, the potential cycle causes dealloying due to Cu dissolution and similar CV peaks of hydrogen adsorption/desorption appear. Figure 2b shows the potential cycle dependence of ORR voltammograms of PtNi/Pt(111). The ORR activity at 0.9 V decreases by 24% after 500 cycles, and the activity is maintained after 1000 cycles as shown in Figure 2c. Similar activity reduction was reported on Pt(111) after 1000 potential cycles. The initial activity loss is due to the dissolution of subsurface Ni and/or surface Pt atoms, and a stable surface alloy layer is formed after 500 cycles. The (100) step on the Pt3Ni(111) surface activates the ORR; the ORR activities of Pt3Ni(322) and (211), which have three and five terrace atomic rows, respectively, are higher than that of Pt3Ni(111). For PtNi/Pt(111) prepared by MBE, the durability depends on the coverage of Ni. Although the degradation after 1000 cycles of PtNi/Pt(111) below 2 ML-thick Ni is more than 50% of the initial activity, the durability is improved above 3 ML-thick Ni.

The vibrational frequency of adsorbed CO is sensitive to the surface structure and the electronic state of the substrate. Figure 3 shows the IRAS spectra for adsorbed CO on Pt(111) and PtNi/Pt(111) modified with the Ni equivalent of 3 ML in 0.1 M HClO4 at 0.1 V. The reference spectra were obtained at 0.9 V whereas the oxidation of CO ad on the Pt electrode is completed. The spectra for adsorbed CO on Pt(111) have two stretching bands around 2065 and 1780 cm⁻¹, which are attributed to linear-bonded and multibonded CO, respectively, forming the (2 × 2)-3CO structure. The spectra of CO adsorbed on PtNi/Pt(111) also show two stretching bands similar to those of CO adsorbed on Pt(111). There is no specific band of CO adsorbed on the Ni surface. The spectra for adsorbed CO on Ni(111) show two stretching bands around 2040 and 1900 cm⁻¹, which are attributed to linear-bonded and bridge-bonded CO, respectively. This result indicates that the structural and electronic properties of the PtNi/Pt(111) surface are similar to those of Pt(111). In the case of PtNi/Pt(111) prepared by MBE, the frequency shift...
of the Pt–CO band is caused by modification with Ni resulting in change of its electronic structure. On the alloying surface, the band shift of Pt–CO depends on the subsurface composition as well as surface structure; the band shift increases in proportion to the amount of heteroatoms in the surface or subsurface layers. The band frequencies on PtNi/Pt(111) are similar to those on Pt(111), which suggests that the amount of Ni in the subsurface layer is very low. Therefore, we determined the surface and subsurface structures of PtNi/Pt(111) using SXRD.

Figure 4 shows the specular and (0 1) CTR profiles of the PtNi/Pt(111) alloyed with 450 pmol Ni at 723 K in 0.1 M HClO₄ at 0.5 V. The dots with error bars are the data points, and the solid lines are the structure factor calculated using the optimized model. (b) Schematic model of the side view of the PtNi/Pt(111) after optimization. (c) The surface and subsurface composition ratios of Pt and Ni in the PtNi/Pt(111).

Table 1. Structural Parameters of the PtNi/Pt(111) Alloyed with 450 pmol Ni at 723 K and Pt(111) in 0.1 M HClO₄ at 0.5 and 0.39 V, Respectively

|                  | PtNi/Pt(111) | Pt(111)³⁹ |
|------------------|--------------|-----------|
| occupancy of first layer | 0.76 ± 0.01  | 0.90 ± 0.05 |
| occupancy of second layer | 0.93 ± 0.01  | 0.97 ± 0.03  |
| occupancy of third layer  | 0.97 ± 0.01  | 0.99 ± 0.03  |
| occupancy of fourth layer | 0.98 ± 0.01  |           |
| occupancy of fifth layer  | 0.99 ± 0.01  |           |
| distance of first–second/nm | 0.235 ± 0.002 | 0.230 ± 0.003 |
| distance of second–third/nm | 0.229 ± 0.001 | 0.228 ± 0.002 |
| distance of third–fourth/nm | 0.227 ± 0.001 | 0.227 ± 0.002 |
| distance of fourth–fifth/nm | 0.226 ± 0.001 |           |
| distance of fifth–bulk/nm | 0.227 ± 0.001 |           |

where Zₐ is the atomic number.

The X-ray diffraction method cannot directly determine the atomic composition of the surface or subsurface layers because the spatial electron density contributes to the structural factor. Therefore, we estimated the compositions of Pt (θₚ) and Ni (θₙi) in each layer using the following equations

\[
\begin{align*}
\theta_{Pt} & = \frac{Z_{Pt} \theta_{Pt} + Z_{Ni} \theta_{Ni}}{Z_{Pt}} \quad \text{for PtNi/Pt(111)}
\end{align*}
\]

\[
\theta_{Pt} + \theta_{Ni} = 1
\]

Figure 4b,c shows the optimized model of the PtNi/Pt(111) and the composition ratio of Pt and Ni. The layer spacings of PtNi/Pt(111) are slightly expanded compared with those of bare Pt(111). The composition of Ni below the second layer is 1–11%. Although the amount of Ni corresponding to 3 ML is modified, Ni in the 5 surface layers is less than 0.2 ML, and residual Ni will sublimate or migrate to the bulk during thermal annealing.

The high ORR activity of the PtNi/Pt(111) is achieved by the electronic perturbation between the surface Pt atoms and the subsurface Ni atoms, similar to the case of Pt₃Ni(111). However, the composition ratio of Ni atoms in the second layer is much lower than the 52% of Pt₃Ni(111). This result indicates that a small amount of subsurface Ni contributes to the activation of the ORR. The in-plane structure of the PtNi/Pt(111) is similar to those on Pt(111), indicating that the surface has a flat (111) domain. The band assigned to multibonded CO appears on high index surfaces wider than 7 and 16 atomic rows on (111)-(110) and (111)-(100), respectively. Because no Ni–CO band is observed, Ni atoms are not exposed on the topmost layer. Therefore, the Pt-skin structure with the (111) domain is formed, and the low occupancy factor below the second layer indicates the reduction of electron density due to the incorporation of Ni. The topmost surface layer may be due to the excess Pt atoms resulting from the formation of the subsurface PtNi alloy. A similar excess Pt island layer was observed on the PtSn surface alloy.

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Pt(111) determined by the (0 1) rod is identical to that of Pt(111). A small amount of Ni is incorporated uniformly in the second layer without segregation. The ORR activity depends on the alloying temperature and the amount of the modified Ni, as described above. The appropriate diffusion state of the Ni atoms is necessary in the second layer, and the alloying at higher temperatures (>800 K) causes migration of Ni in the deeper layers. The initial Ni dose of more than 600 pmol deactivates the ORR. The increase of the initial Ni dose increases the surface segregation of Pt due to subsurface PtNi formation, which may cause a decrease of the interaction with subsurface Ni.

A small amount of Ni in the subsurface improves the durability, as shown in Figure 2c. In the Pt base metal alloy, the dissolution of the subsurface base metal gives rise to the restructuring of the surface structure. The reduction of base metal content will inhibit the dissolution and destruction of the surface layer. The distribution of the Ni atoms in the subsurface layers of the PtNi/Pt(111) contributes to the ORR activity and durability.

**CONCLUSIONS**

PtNi/Pt(111) was prepared by thermal annealing of 150–600 pmol NiCl₂ modified on Pt(111) at 573–803 K. The ORR activity of Pt(111) modified with 450 pmol NiCl₂ at 723 K is 9.5 times higher than that of Pt(111), and the activity is decreased by 24% after 1000 potential cycles. The surface and subsurface structures of PtNi/Pt(111) were determined by IRAS and X-ray diffraction. The surface and subsurface comprise the Pt-skinn PtNi alloy containing a small amount of Ni (<11%), respectively. The highly uniform distribution of Ni atoms enhances the ORR activity and the durability.

**EXPERIMENTAL SECTION**

A Pt single crystal bead for voltammogram and IRAS measurements was prepared by Clavilier’s method. A Pt crystal bead was oriented using the reflection of a He–Ne laser and then mechanically polished with diamond slurries. A Pt(111) disk (8 mm in diameter, MaTech, Germany) was used for the SXRD measurement. The Pt(111) surface was annealed in an H₂ + O₂ flame and then cooled to room temperature under an Ar atmosphere. The annealed surface was protected with ultrapure water (Milli-Q Advantage A10; Millipore). All of the solutions were prepared using ultrapure water. PtNi surface alloys were prepared according to the following procedure. A solution of 75–300 μM NiCl₂·6H₂O that corresponds to 1–4 monolayers (ML) (2 μL) was dropped on the Pt(111) surface protected with ultrapure water. The surface was dried and then annealed using an induction furnace at 573–803 K for 10 min under an Ar (95%) + H₂ (5%) atmosphere. The potential is referred to a RHE.

The ORR activity was estimated from the kinetic current density, where the Koutecky–Levich equation: \( j = j_k + J_0 \), was derived to measure the current density and the limiting current density, respectively. The current densities are normalized to the geometrical surface area of the Pt surface. The durability test was performed by applying the square potential wave between 0.6 and 1.0 V at 0.17 Hz in 0.1 M HClO₄ saturated with Ar.

For the IR measurement of adsorbed CO, the sample was immersed in 0.1 M HClO₄ saturated with CO at 0.1 V for 20 min and then pressed onto a CaF₂ prism. The IRAS electrochemical cell was attached to a Fourier-transform IR spectrometer (FT-IR 6600; JASCO). The 32 spectra were accumulated with 4 cm⁻¹ resolution.

SXRD measurement was performed with a multiaxis diffractometer at BL13XU (SPring-8). The X-ray energy used was 20 keV. Integrated intensities were measured by rocking scans and then corrected for Lorentz and area factors. A hexagonal surface coordinate system was used for the Pt(111) crystal in which the reciprocal wave vector is \( Q = H a^* + K b^* + L c^* \), where \( a^* = b^* = 4\pi/\sqrt{3}a \), \( c^* = 2\pi/\sqrt{6}a \), \( a = 0.2775 \) nm, and \( L \) is along the direction normal to the surface. Structure refinement was conducted using the least-squares method with the ANA-ROD program.

**AUTHOR INFORMATION**

Corresponding Author

E-mail: mmakamura@faculty.chiba-u.jp.

**ORCID**

Nagahiro Hoshi: 0000-0001-5808-580X
Masashi Nakamura: 0000-0002-2986-1133

**Notes**

The authors declare no competing financial interest.

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