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Structural effects on the oxygen reduction reaction on the high index planes of Pt_3Ni: $n(111)$–(111) and $n(111)$–(100) surfaces

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ABSTRACT

Active sites for the oxygen reduction reaction (ORR) have been studied on $n(111)$–(111) and $n(111)$–(100) surfaces of Pt_3Ni in 0.1 M $HClO_4$ using rotating disk electrode (RDE). The activity for the ORR is decreased with the increase of the step atom density on $n(111)$–(111) surfaces. This fact is completely opposite to that of the same series of Pt on which the activity is enhanced at higher step atom density. The ORR gives the highest activity on $n(111)$–(100) surfaces of Pt_3Ni with terrace atomic rows $n = 3$ and $n = 5$. These results show that the activity for the ORR of (100) step is superior to that of (111) step on Pt_3Ni electrodes.

1. Introduction

Pt is used as electrocatalysts of fuel cells. Reduction of Pt loading in the electrocatalysts is one of the most important subjects for widespread of fuel cells, because the amount of natural resources of Pt is limited. The oxygen reduction reaction (ORR) is the reaction at the cathodes of fuel cells. The high overpotential of the ORR results in the high consumption of Pt in the cathodes. Development of electrocatalysts with high activity for the oxygen reduction (ORR) is necessary for the reduction of Pt loading in fuel cells.

It is well known that reaction rate and selectivity of an electrochemical reaction depend on the surface structure of the electrode remarkably [1–4]. One of the strategies for the enhancement of the ORR activity is the control of the surface structures of the electrode. Activity for the ORR depends on the crystal orientation on the low index planes of Pt: $Pt(100) < Pt(111) < Pt(110)$ in 0.1 M $HClO_4$ [5]. On the other hand, the activity series on the low index planes of Pd is opposite to that on Pt: $Pd(110) < Pd(111) < Pd(100)$ in 0.1 M $HClO_4$ [6]. However, studies using the low index planes are not adequate to elucidate the active site for electrochemical reactions precisely. Structure of surfaces vicinal to the low index planes (high index planes) can be modified systematically. The high index planes can determine the structure of the active site for the ORR in atomic scale.

The study on the ORR was extended to the high index planes of Pt [7–10] and Pd [6,11]. A high index plane is notated as $n(hkl)$–$(h'k'l')$, in which n, (hkl) and $(h'k'l')$ show the number of terrace atomic rows, terrace and step structures, respectively. On $n(111)$–(111) and $n(111)$–(100) surfaces of Pt, the activity for the ORR increases with the increase of the step atom density d_S except $Pt(110) = 2(111)$–(111) and $Pt(311) = 2(111)$–(100) in 0.1 M $HClO_4$ [9,10]. On $n(100)$–(111) and $n(100)$–(110) surfaces of Pt, however, the activity does not depend on the surface structures [10]. The activity on the surfaces with (111) terrace is higher than that with (100) terrace. The structural analysis supports that the active site of the ORR is located between the (111) terrace edge and the (111) terrace atomic rows neighboring to the edge on Pt electrodes [10]. On Pd electrodes, however, the active site for the ORR is (100) terrace [6,11]. Difference of the step structure does not affect the ORR activity on Pd electrodes at all.

An alloy catalyst has higher activity than a pure metal. Pt alloys including transition metals such as Fe, Ni, and Co enhance the carbon monoxide tolerance at the anode [12,13] as well as the ORR activity at the cathode [14–16]. Stamenkovic et al. evaluated the activity for the ORR on the low index planes of Pt_3Ni, and found that the activity on $Pt_3Ni(111)$ electrode is 10 times as high as that of $Pt(111)$ [16]. Monolayer of Pt skin is formed on the low index planes of Pt_3Ni. Wadayama et al. prepared Pt enriched Ni/Pt(111) [17] and Co/Pt(111) [18] surfaces using molecular beam epitaxy (MBE) method. The topmost layers of these surfaces are also composed of monolayer of Pt. The ORR activities of Pt enriched Ni/Pt(111) and Co/Pt(111) are 8 and 10 times higher than that of clean Pt(111), respectively. The activity for the ORR is enhanced as $(100) < (110) < (111)$ on $Pt_3Ni(hkl)$ alloy and Pt enriched $Co/Pt(hkl)$.

Studies on the structural effects on the ORR have been limited to the low index planes of Pt alloy electrodes. In this paper, we extend the study to the high index planes of Pt_3Ni to elucidate the active site for the ORR. Our previous study shows that the surfaces

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with (1 1 1) terrace have higher activity for the ORR in the high index planes of Pt. Therefore, we first study the orientation dependence of the ORR on n(1 1 1)–(1 1 1) and n(1 1 1)–(1 0 0) series of Pt_3Ni (n = 2, 3, 5, 9 and ∞). The hard sphere models of the surfaces examined are shown in Fig. 1.

2. Experimental

A single crystal bead of Pt_3Ni (about 3 mm in diameter) was prepared according to the following procedure. A Pt_3Ni wire (Tanaka Kikinzoku, 1 mmφ) was set in a quartz tube. The end of the wire was melted in Ar atmosphere (99.9999%) using induction furnace (HOTSHOT 3.5, Alonics) for prevention of the oxidation of the doped Ni.

No (1 1 1) and (1 0 0) facets appeared on the surface of the bead. The single crystal bead was oriented with the use of X-ray Laue back reflection method, and then mechanically polished with diamond slurries.

The polished crystal was annealed in Ar(95%)/H_2(5%) atmosphere about 1300 K using induction furnace for the removal of the distortions due to the mechanical polishing, and then cooled down to room temperature. The annealed surface was protected with ultrapure water saturated with Ar(95%)/H_2(5%), and transferred to an electrochemical cell.

Electrolytic solutions were prepared from ultrapure water treated with Milli-Q Advantage A10 (Millipore) and suprapure grade chemicals (Merck). Voltammograms of the ORR were measured in the hanging meniscus RDE configuration [7,8,19,20] using electrochemical analyzer (ALS 701C) and rotating ring disk electrode apparatus (BAS:RRDE-3).

Potential was scanned from 0.05 V (RHE) to the positive direction up to 1.0 V (RHE) at scanning rate 0.010 V s^{-1} and rotation rate 1600 rpm. Current was divided by geometric surface area to obtain current density, because a single crystal surfaces is atomically flat, and Pt skin is expected to be formed on the high index planes of Pt_3Ni as is the case of the low index planes [16]. The specific activity for the ORR is estimated using the kinetic current density at 0.90 V (RHE) $j_{k,0.90V}$ according to the following equation [21,22]:

$$\frac{1}{j}=\frac{1}{j_k}+\frac{1}{j_L},$$

where j and j_L are total current density and limiting current density, respectively.

3. Results and discussion

Fig. 2 shows Laue back reflection pattern of Pt_3Ni(1 1 1) prepared by the method mentioned above. The Laue patter has hexagonal symmetry characteristic of a (1 1 1) surface of fcc structure. This result indicates the high quality of the single crystal electrode.

Fig. 3 shows voltammograms of n(1 1 1)–(1 1 1) and n(1 1 1)–(1 0 0) surfaces of Pt_3Ni in 0.1 M $HClO_4$ saturated with Ar. On n(1 1 1)–(1 1 1) surfaces, the redox peaks at 0.17 V (RHE) increase with the decrease of the terrace width n (namely the increase of d_S), reaching maximum on Pt_3Ni(1 1 0). The notation of n(1 1 1)–(1 1 1) can be also written as (n – 1)(1 1 1)–(1 1 0); the redox peaks at 0.17 V (RHE) are due to the adsorption and the desorption of hydrogen at (1 1 0) structure. However, structural effects on the voltammogram are less remarkable than those on the high index planes of Pt [10,23,24].

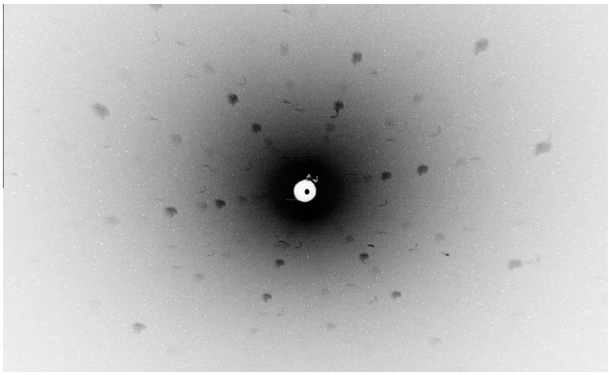
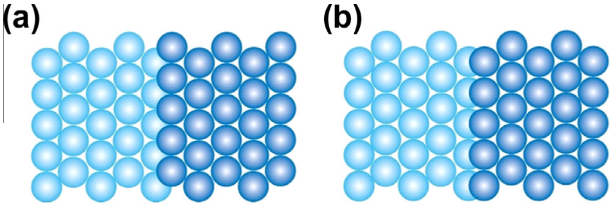


Fig. 2. Laue back reflection pattern of prepared Pt_3Ni(1 1 1).



n(111)-(111) n(111)-(100)

Fig. 1. Hard sphere models of the high index planes of Pt_3Ni examined (top view): (a) n(1 1 1)–(1 1 1) and (b) n(1 1 1)–(1 0 0) surfaces.

On n(1 1 1)–(1 0 0) surfaces, redox shoulders are found at 0.27 V. These shoulders can be due to the desorption and the adsorption of hydrogen at (1 0 0) step according to the voltammograms of Pt [10,23,25]. However, the peak intensities show smaller structural effects than those on n(1 1 1)–(1 1 1) surfaces of Pt_3Ni. We prepared several high index planes of Pt_3Ni with the same orientation, and all the voltammograms gave the same tendency. These facts may indicate that perfect Pt skin may not be formed on the high index planes of Pt_3Ni.

Table 1 shows anodic charges of the adsorbed hydrogen between 0.05 and 0.40 V (RHE) of Pt_3Ni and Pt electrodes after the correction of the double layer charges. Theoretical charges of pure Pt electrodes are also shown in the table on the assumption that one hydrogen atom is adsorbed to one Pt atom of the topmost layer. The charges of pure Pt electrodes are lower than those of theoretical values in 0.1 M $HClO_4$. This tendency is general on Pt electrodes in 0.1 M $HClO_4$, for example, the charge of the hydrogen desorption is only 2/3 of the theoretical value on Pt(1 1 1). The observed charge on Pt_3Ni(1 1 1) is less than that on Pt(1 1 1) as reported before [16], although perfect Pt skin is formed on Pt_3Ni(1 1 1). The difference between Pt_3Ni and Pt gets smaller with the decrease of n (namely increase of d_S) on n(1 1 1)–(1 1 1) surfaces. On n(1 1 1)–(1 0 0) surfaces, the difference between Pt_3Ni and Pt is smaller on the surfaces with larger terrace (n = 5 and 9), but the difference gets larger on the surfaces with narrower terrace (n = 2 and 3).

Fig. 4 shows ORR voltammograms on n(1 1 1)–(1 1 1) and n(1 1 1)–(1 0 0) surfaces of Pt_3Ni. The ORR currents depend on the surface structure between 0.7 and 1.0 V, at which the ORR is kinetically controlled. The ORR currents show no structural effect between 0.3 and 0.7 V, because the reaction is diffusion controlled at this potential range. The ORR currents shows smaller structural effects on n(1 1 1)–(1 1 1) surfaces of Pt_3Ni in the kinetically controlled region. The currents depend on surface structure remarkably on n(1 1 1)–(1 0 0) surfaces in the kinetically controlled region, although the voltammograms show little structural effects in Ar saturated solution (Fig. 3(b)).

The limiting currents drop in the adsorbed hydrogen region on the high index planes of Pt as shown in Fig. 4(c) and (d). The adsorbed hydrogen atoms hinder the 4 electron reduction of O_2, producing H_2O_2 via 2 electron reduction [26]. The hindrance of the 4