Surface structure and the oxygen reduction reaction of Pt-based catalysts

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Introduction Enhancement of the activity for the oxygen reduction reaction (ORR) is one of the most important subjects for the reduction of Pt loading in fuel cells. The activity for the ORR strongly depends on the surface structure of Pt [1-5], Pd [6,7], Pt_3Ni [8] and Co/Pt [9] electrodes. High index planes play a key role for the determination of the active sites for the ORR. We summarize structural effects on the ORR on the high index planes of Pt, Pt_3Ni and Pt_3Co in this paper. The hard sphere models of the surfaces are shown in **Fig. 1**.

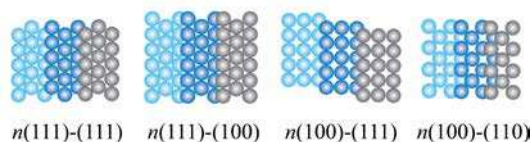$n(111)$-(111) $n(111)$-(100) $n(100)$-(111) $n(100)$-(110)

Fig. 1 Hard sphere models of the high index planes examined. In the notation of $n(hkl)$-$(h'k'l')$, n, (hkl) and $(h'k'l')$ show the number of terrace atomic rows, terrace and step structures, respectively.

Experimental A single crystal bead of Pt was prepared according to the Clavilier's method. The beads of Pt_3Ni and Pt_3Co were obtained using induction furnace in Ar atmosphere [10] and the method reported by Wakisaka et al. [11], respectively.

ORR was measured using hanging meniscus rotating disk electrode with rotation and scanning rates 2000 rpm and 0.010 V s^{-1}, respectively. Potential was scanned from 0.050 V (RHE) to the positive direction. All the potentials were referred to RHE. The ORR activity is estimated using a cathodic current density at 0.90 V(RHE) $j_{ORR,0.90\,V}$ in 0.1 M $HClO_4$.

Results and Discussion

Pt Electrodes Real structures of the low and the high index planes of Pt were determined using surface X-ray scattering in electrochemical environments [12,13]. The surfaces with $n=2$, such as Pt(110) = 2(111)-(111) and Pt(311) = 2(111)-(100) are reconstructed to (1×2) structures, whereas those with $3{\leq}n$ have unreconstructed (1×1) structures at 0.1 and 0.5 V(RHE).

The values of $j_{ORR,0.90\,V}$ are plotted against the step atom density d_S in **Fig. 2**. The ORR activity increases with the increase of d_S on the surfaces with (111) terrace up to $n=5$, showing the active sites are located around the step. The surfaces with $n=2$ give minima of the activity. On the surfaces with (100) terrace, the activity is independent of surface structures. The activity of the surfaces with (111) terrace is higher than that with (100) terrace remarkably.

The plots of $n(111)$-(111) and $n(111)$-(100) are located on the same line between $n=5$ and $n=\infty$ in **Fig. 2**. This fact supports that the active sites are common on these series. Although step structure of $n(111)$-(111) differs from that of $n(111)$-(100), (111) terrace edge is common to these series. Thus (111) terrace edge can be assigned to the active site for the ORR. However, Pt oxide is preferentially formed at the terrace edge, preventing the ORR according to theoretical studies. Thus, another candidate for the active site is (111) terrace atomic row neighboring to the terrace edge. **Fig. 2(c)** shows possible active sites for the ORR on Pt electrodes.

Pt_3Ni and Pt_3Co Electrodes On Pt_3Ni, the ORR activity decreased with the increase of d_S on $n(111)$-(111),

whereas the activity gave maxima on the surfaces with $n=3$ and $n=5$ on $n(111)$-(100). On Pt_3Co, however, the activity increased with the increase of d_S on $n(111)$-(111). No minimum was found on $Pt_3Co(110)$ $n=2$. The structural effects on the Pt alloy electrodes differ from those on Pt electrodes remarkably. Detailed structural effects will be discussed in the presentation.
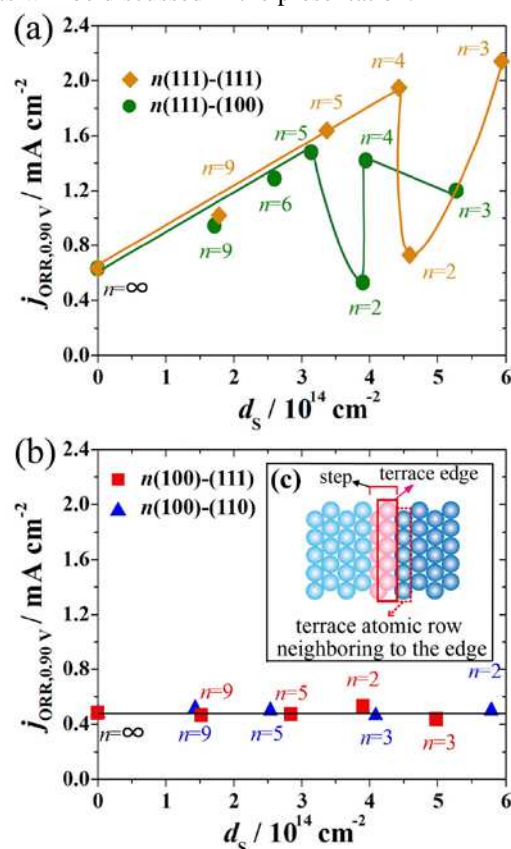

Fig. 2 (a) (b) The ORR activity at 0.90 V(RHE) $j_{ORR,0.90\,V}$ plotted against the step atom density d_S on the high index planes of Pt [5]. **(c)** Active sites for the ORR on Pt electrodes

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