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# Structural effects on the oxygen reduction reaction on single crystal electrodes Pt modified with amines

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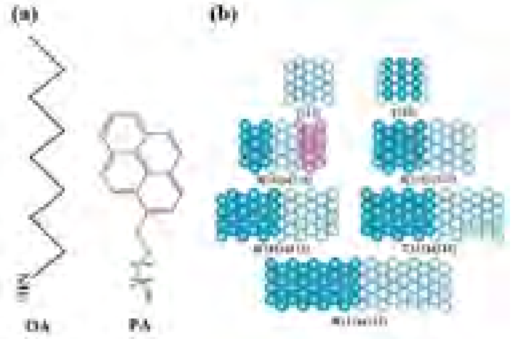
Enhancement of the activity for the oxygen reduction reaction (ORR) is important for the development of fuel cells. Structural effects on the ORR have been studied using single crystal electrodes of Pt[1-5], Pd[6], $Pt_3Ni$[7] and $Pt_3Co$[8]. Recently, Miyake *et al,* reported that Pt nanoparticles modified with amines such as OA and PA (Fig. 1(a)) give higher activity for the ORR and durability than bare Pt nanoparticles. We have studied structural effects on the enhancement of the ORR by the amines on n(111)-(111) surfaces of Pt that have the highest activity for the ORR. In the notation n(hkl)-(mno), n, (hkl) and (mno) shows number of terrace atomic rows, structure of terrace and step, respectively. Hard sphere models of the surfaces examined are shown in Fig. 1(b). The ORR voltammograms were measured in 0.1 M $HClO_4$ saturated with $O_2$ using rotating disc electrode (RDE) at room temperature. The activity for the ORR was estimated using specific activity at 0.90 V(RHE) jk. OA/PA=9/1 (molecular ratio) was adsorbed on a single crystal surface of Pt. The peaks of hydrogen adsorption/desorption and oxide formation in voltammograms shrink after the modification of OA/PA in Ar saturated solution. The value of jk of Pt(111) modified with OA/PA was 2.5 times as high as that of bare Pt(111). On Pt(331)=3(111)-(111) that has the highest activity for the ORR in n(111)-(111) surfaces, however, the value of jk after OA/PA modification is lower than that of the bare surface. Detailed study on the structural effects shows that OA/PA enhances the ORR activity on the surfaces with terrace atomic rows $n \geq 7$. On the surfaces with $n \leq 6$, OA/PA deactivates the ORR. We have also studied the OA/PA effect on Pt(100) of which surface is composed of flat terrace with 4-fold symmetry. The ORR activity on Pt(100) is deactivated after the OA/PA modification. OA/PA enhances the ORR activity of Pt electrodes with more than 7 atomic rows of (111) terrace, but deactivating the ORR on narrow (111) surfaces with terrace atomic rows less than 6 and (100) structure. The reason of the enhancement of the ORR activity by OA/PA has not been elucidated. DFT calculation attributed the higher activity on n(111)-(111) surfaces of Pt compared with Pt(111) to the destruction of well-ordered structure of adsorbed water on (111) terrace. OA/PA may also change the adsorbed water structure on wide (111) terrace. Structure of adsorbed water needs to be elucidated using vibrational spectroscopy.



## Biography

Nagahiro Hoshi is a Professor of Department of Applied Chemistry and Biotechnology, Graduate School of Engineering, Chiba University, Japan. He has his expertise in Surface Electrochemistry. The main target of the study is the elucidation of surface structures of electrocatalysts that have high activity and selectivity in electrochemical reactions. He can prepare well-defined single crystal electrodes of Pt, Pd, Ir, Rh, Au, Cu, Pt alloys, $TiO_2$, etc., in his laboratory. He can also synthesize shape controlled nanoparticles of Pt and Pt alloys. His present research projects are the reduction of Pt loading in electrocatalysts of fuel cells and enhancement of conversion efficiency of dye sensitized solar cell.

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