Oxygen reduction reaction activity of MBE-prepared Ni/Pt(111) : dependence of surface Pt-layer thickness

N.Todoroki, Y. Asakimori, T. Wadayama

Graduate School of Environmental Studies
Tohoku University
Sendai 980-8579, JAPAN

Pt-based bimetallic alloy nanoparticles have been widely studied as for oxygen reduction reaction (ORR) catalysts for polymer electrolyte fuel cells (PEFCs). Recent studies demonstrated that the topmost surface structures and alloy compositions strongly affect the ORR activity and durability [1]. Particularly, thickness of Pt-enriched surface layers (Pt-skin) is an important factor to determine the activity [2]. In this study, we fabricated well-defined Ni/Pt(111) surface alloys having various-thick Pt-skin layers and investigated the layer-thickness-dependence on the ORR activity.

Pt-skin layers were fabricated by molecular beam epitaxy (MBE). Pt(111) single crystal substrate was cleaned by repeated Ar^+ sputtering and annealing in UHV. Then, 1ML-thick Ni was deposited onto clean Pt(111) by an electron-beam evaporation method at 823K to generate Pt-enriched topmost surface. Subsequently, various-thick Pt(111) epitaxial layers were deposited onto the Pt-enriched surface at room temperature, and, then, were annealed at 573K for 5 min. The resulting topmost surface structures were observed by scanning tunnelling microscopy (STM) in UHV. Then, the MBE-prepared surfaces were transferred without being exposed to air to an electrochemical system set in an N_2-purged glove box. Cyclic voltammogramas (CVs) were recorded in N_2-purged 0.1M $HClO_4$, and, then, linear sweep voltammograms (LSVs) were recorded by a rotating electrode (RDE) method at 1600 rpm after saturating the solution with O_2. ORR activity was estimated by kinetic-controlled current density (j_k) at 0.9V vs. RHE by using Koutecky-Levich equation.

We have previously deduced that 823K-, 1ML-thick-Ni deposition onto clean Pt(111) generates ca. 1ML-thick Pt-enriched surface layer (Pt-skin(111)) [3]. Fig. 1 shows STM images of (a) the Pt-skin(111) and (b) 1-, (c)2-, (d) 3-ML-thick Pt epitaxially grown on the Pt-skin(111) (m ML-Pt/Pt-skin(111), m:1~3) surfaces. The Pt-skin(111) shows wide terraces with sub-atomic-scale corrugations (height of ca. 0.05 nm). In contrast, the m ML-Pt/Pt-skin(111) clearly exhibit island-like hexagonal shape Pt(111) epitaxial layers.

Fig. 2 summarizes CVs of the Pt-skin(111) and the m ML-Pt/Pt-skin(111). The onset potentials of H and OH adsorption for the Pt-skin(111) shift to lower and higher potentials, respectively, relative to that of clean Pt(111). CVs of the m ML-Pt/Pt-skin(111) show increase of H and OH adsorption currents relative to the Pt-skin(111). In addition, anodic peaks of OH adsorption shift to lower potentials with increasing additionally-grown Pt(111) epitaxial layer thickness, suggesting that reduction in electronic and/or strain effects of the subsurface Ni atoms.

Fig. 3 presents kinetic current density (j_k) and specific ORR activities of the corresponding surfaces. The Pt-skin(111) and 1ML-Pt/Pt-skin(111) showed ca. 9 and 12 times higher ORR activities than Pt(111). In contrast, the activity enhancement factors for the 2ML- and 3ML-Pt/Pt-skin(111) can be estimated to be 8 and 6,

respectively. These results suggest that outermost surface structures and thickness of the topmost Pt-skin layers strongly affect the ORR activity.
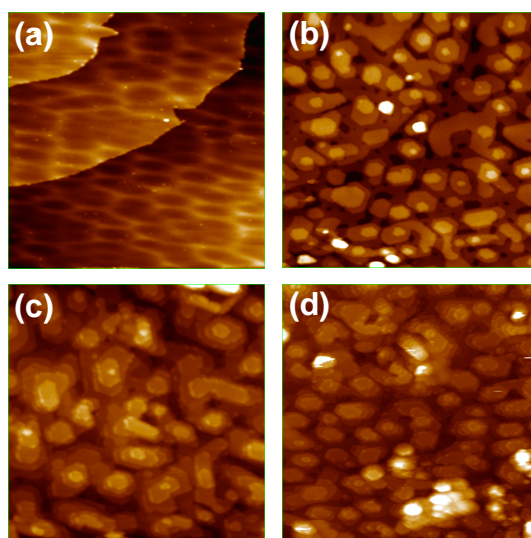

Fig. 1 STM images (100 nm × 100 nm) of (a) the Pt-skin(111) and (b) 1- , (c) 2-, (d) 3-ML Pt/Pt-skin(111).
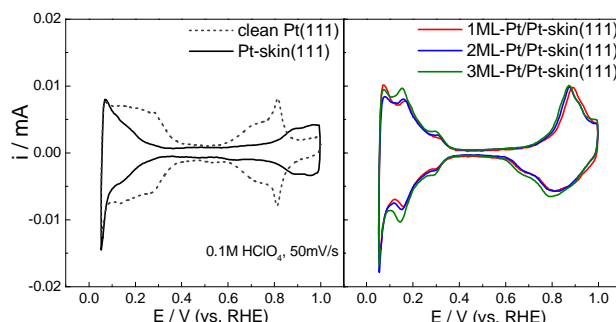

Fig. 2 cyclic voltammograms of (a) the Pt-skin(111) and (b) 1-3 ML Pt/Pt-skin(111).
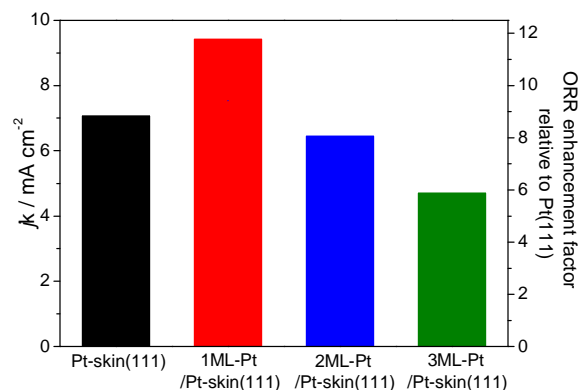

Fig. 3 ORR activities of the Pt-skin(111) and 1-3 ML/Pt-skin(111).

References

[1] V.R. Stamenkovic, et. al., Nat. Mater. **6** (2007) 241.; L. Gan, et. al., Nano Lett. **12** (2012) 5423.
[2] C. Wang, et. al., J. Am. Chem. Soc., **133** (2011) 14396.
[3] T. Wadayama, et. al., Electrochem. Commun. **12** (2010) 1112.

Acknowledgements