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ORR Activity and Durability of MBE-prepared Pt monolayers on Au(hkl) Single Crystal Substrates

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Background

Relation between oxygen reduction reaction (ORR) activities and topmost surface structures of Pt-based alloy nano-particles (NPs) is a key for developing highly-active, low-Pt-content cathode-electrode catalysts for PEMFC. However, disscussion of ORR is complicated because of uncertainties in outermost surface structures of the alloy NPs. Although Adzic and co-workers showed the Pt monolayer on Au(111) is less ORR active than clean Pt(111),$^{1)}$ Pt-shell-Au-core (Pt@Au) NPs show higher ORR activity than that of pure Pt NPs.$^{2)}$ The published results clearly indicate atomic-level surface structures determine ORR proceeding on the real nano-sized catalysts. In this study, we prepared Pt/Au(111), (100), and (110) (Pt/Au(hkl)) bimetallic surfaces by molecular beam epitaxy (MBE) and performed EC measurements in an inert atomosphere.

Experimental

MBE apparatus and UHV-EC sample transfer system have been described.$^{3)}$ $Pt_{0.3nm}$/Au(hkl) samples were prepared through 0.3-nm-thick-Pt depositions onto UHV-cleaned Au(hkl) surfaces by an electron-beam evaporation method. The resulting surface structures were verified with reflection high-energy electron diffraction (RHEED) and STM in UHV. EC measurements were conducted by a conventional glass-made electrochemical cell and rotating disk electrode (RDE) apparatus set in a N_2-purged glove box: RHE is used as a reference. CV (LSV) curves for the $Pt_{0.3nm}$/Au(hkl) samples are recorded in N_2-purged (O_2-saturated) 0.1 M $HClO_4$.

Results and discussion

Because standard electrode potentials for Pt and Au are 1.18 and 1.5 V, respectively, the potential sweep beyond 1.5 V should cause EC oxidation and reduction of not only the epitaxial Pt layers but also the Au atoms present at subsurface regions. Fig.1 presents the CV curves of the $Pt_{0.3nm}$/Au(hkl) recorded before and after the potential sweeps of 1.7V. The CV curves of as-prepared samples clearly depend on the surface symmetries of the Au substrates. After the 1.7V-potential-sweep, EC charges of the hydrogen adsorption (Q_{Had}) for the $Pt_{0.3nm}$/Au(hkl) are increased irrespective of the Au surface symmetries. For example, the 1.7V-potential-sweep of the $Pt_{0.3nm}$/Au(111) (blue) increases redox currents at 0.13 V that might stem from 110 step generation into the Pt(111) epitaxial surface. An LSV curve of the 1.7V-potential-swept $Pt_{0.3nm}$/Au(111) exhibited more positive shift than the as-prepared sample. The results clearly indicate that surface defects such as 110 steps at the topmost Pt(111) lattice might contribute to the ORR activity enhancement. Also, increase in Q_{Had} for the $Pt_{0.3nm}$/Au(100) (green) and the positive shift of the LSV curve (not shown) suggest that extension of the topmost Pt(100) lattice correlate with ORR enhancement. As for the $Pt_{0.3nm}$/Au(110) (orange), the 1.7V potential-sweep increases the Q_{Had}. However, the LSV curve remained unchanged (not shown), indicating that extension of Pt(110) facets on Au(110) seems to be independent of the activity enhancement.

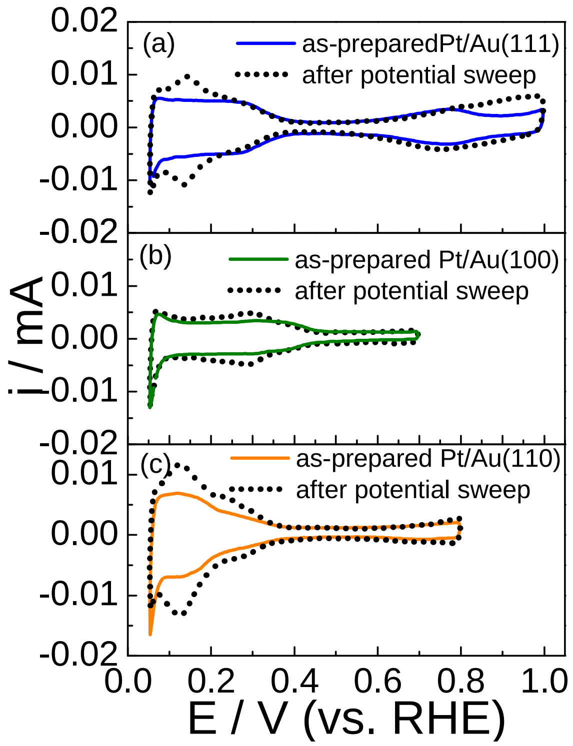

Fig. 1 Change in CV curves for $Pt_{0.3nm}$/Au(hkl) before (as-prepared) and after 1.7V potential sweep.

To evaluate electrochemical stability of the $Pt_{0.3nm}$/Au(111), potential cycles between 0.6V to 1.0V are applied in O_2 saturated 0.1M $HClO_4$. Fig. 2 shows ORR activity changes during the potential cycles. The ORR activities decrease with increase the cycles: the j_k value at 0.9 V is estimated to be ca. 60 % after 1000 cycles. The Q_{Had} value estimated for the CV curve recorded after 1000 cycles slightly increased.

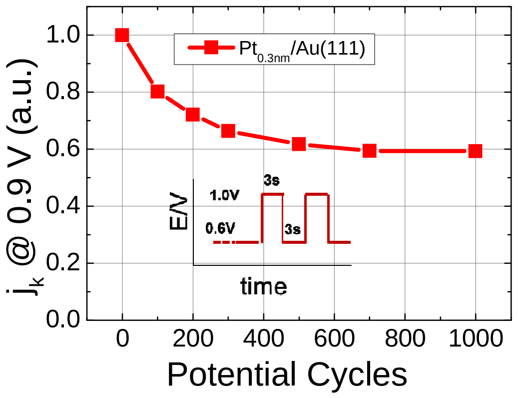

Fig. 2 ORR activity dependence on the potential cycling of the $Pt_{0.3nm}$/Au(111).

The results obtained in this study suggest that the topmost surface structures of Pt@Au NPs determine the electrocatalysis mechanism and that the morphologies of the most dense plane of Pt(111) correlate with the degree of the ORR activity enhancement.

Acknowledgement

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