Supporting Information

for

Electrocatalytic Activity of Electrochemically Dealloyed

PdCu₃ Intermetallic Compound towards Oxygen Reduction

Reaction in Acidic Media

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Figure S1 The simulated FFT profiles of (A) fcc (pure Pd) and (B) Cu₃Au (ordered intermetallic phase) type structures from 121 zone. (C) High resolution-TEM image of ordered intermetallic PdCu₃ NP and (D) the FFT pattern obtained from (C).



Figure S2 EDS profiles of ordered intermetallic PdCu₃ NPs/CB.



Figure S3 STEM-EDS line profiles of intermetallic PdCu₃ NP (A) before and (B) after the electrochemical dealloying in which 50 times' potential cycling was carried out as shown in Figure 4. Insets: HAADF-STEM images of intermetallic PdCu₃ NP. Scale bars are 10 nm.



Structural stability: PdCu₃ ordered structure > PdCu_{3 Pd_seg} > PdCu_{3 Cu_seg}

Figure S4 Segregation tendency of A) PdCu₃ ordered structure to B) PdCu₃ (Pd_seg) and C) PdCu₃ (Cu_seg).

The bulk structure of PdCu₃ consists of Pd:Cu (1:3) as a L1₂ structure belonging to face centered cubic (FCC) structure. On the other hand, the surface structure can be different from the bulk one in the atom array by the surface energy or the difference in atomic radii of Pd and Cu [1]. For instance, Ma et al. reported that the metal species which has lower surface energy and larger atomic size could be segregated to the alloy surface. The energy (1.790 J m⁻²) of Cu(111) is lower than that (2.003 J m⁻²) of Pd(111) [2], implying the segregation of sublayer Cu atoms to the outermost surface as shown in Figure S3(C). On the other hand, from the viewpoint of the difference in atomic sizes of Pd and Cu, sub-layer Pd atoms are apt to surface segregation because Pd is larger in atomic size than Cu. Eventually, however, PdCu₃ catalyst does not, show any segregation phenomena for both Cu and Pd, as can be seen from positive segregation energies of Cu (439 meV) and Pd (173 meV) in Figure S3. It could be correlated to the composition-dependent property of alloy. In general, the Pd skin structure can be favorable in Pd₃Cu, but not PdCu₃, which means that the Cu-dominant PdCu₃ alloy has the shrunk lattice constant (3.74 Å) compared to that of pure Pd structure (3.93 Å). The surface segregation of larger Pd atom in PdCu₃ with narrow lattice constant may make its structure unstable due to a relatively strong compression of the Pd-Pd surface.



Figure S5 Top view of oxygen adsorption sites on PdCu3 (order) surface. Oxygen is

adsorbed on the site 5 strongly.



Figure S6 Comparison of the ORR performance before (dotted line) and after (solid line) the electrochemical dealloying.



Figure S7 ORR on PdCu₃ NPs/CB electrocatalyst for (solid line) cathodic and (dashed line) anodic going scan at 5 mV s⁻¹ in the potential range between 0.05 and 1.1 V (vs. RHE) in O_2 -saturated 0.1 M HClO₄.



Figure S8 Comparison of the ORR performance at (A) Pd NPs/CB, (B) Pd-Cu NPs/CB and (C) PdCu₃ NPs/CB electrocatalysts before and after 1000 potential cycles at 100 mV s⁻¹ in the potential range of 0.05 - 0.9 V (vs. RHE) in N₂-saturated 0.1 M HClO₄.



Figure S9 (A) Typical TEM image and (B) its particle size distribution of $PdCu_3$ NPs/CB after after 1000 potential cycles at 100 mV s⁻¹ in the potential range of 0.05 - 0.9 V.



Figure S10 Koutecky–Levich plots for the ORR at PdCu₃ NPs/CB.

The number of electrons transferred (n) and kinetic current (i_k) can be calculated using Koutecky-Levich equation.

$$i^{-1} = i_{\rm k}^{-1} + (0.62 {\rm nFAD}^{2/3} \omega^{1/2} \nu^{-1/6} {\rm Co}_2)^{-1}$$
(1)

where n is the number of electrons transferred, F is Faraday's constant, A is the area of the electrode, D is the diffusion coefficient of O_2 in 0.1 M HClO₄ solution, ω is the angular frequency of rotation, v is the kinematic viscosity of the electrolyte, and Co_2 is the concentration of O_2 in 0.1M HClO₄ solution.



Figure S11. Ab-initio molecular dynamics of oxygen adsorption on PdCu₃ skeleton, Pd, Pt (111). The relative energy was normalized by the ground state structure. PdCu skeleton configuration was calculated at 298 and 353 K.

References

- [1] Y. Ma and P. B. Balbuena Surf. Sci., 2008, 602, 107-113.
- [2] L. Vitos, A. Ruban, H. L. Skriver and J. Kollar Surf. Sci. 1998, 411, 186-202.