Morphological Control of Carbon-Supported Pt-Based Nanoparticles via One-Step Synthesis

Tatsuichiro Nakamoto ^a, Ryohei Seki ^b, Ken-ichi Motomiya ^a, Shun Yokoyama ^a, Kazuyuki Tohji ^a, and Hideyuki Takahashi ^a

^a Graduate School of Environmental Studies, Tohoku University, Sendai, Miyagi 980-8579, Japan

^b Manufacturing Innovation Division, Panasonic Corporation, Kadoma, Osaka 571-8502, Japan

The morphology of Pt-based nanoparticles supported on carbon is controlled to enhance the oxygen reduction reaction (ORR) catalytic performance. Herein a simple one-step method without a polymer surfactant is demonstrated to synthesize Pt-Cu nanoclusters, Pt-Cu nanospheres, and Cu-doped Pt nanoplates. Metal precursors are reduced in a NaCl or NH₄Cl aqueous solution containing carbon supports, and nanoparticles are directly deposited on carbon. Cl⁻ ions generated from NaCl or NH₄Cl behave as oxidative etchants when O₂ is dissolved in the synthesis solution, delaying the reduction of metal ions and leading to larger particles. Nanoclusters are obtained in the absence of Cl⁻ ions. In addition, NH₄⁺ guides the growth direction of Pt in the presence of oxidative etchants, forming a plate-like morphology that exposes the {111} facets. Half-cell measurements are performed in acidic media to evaluate the electrochemical properties. Cu-doped Pt nanoplates exhibit a 3.67-times higher ORR catalytic activity than the commercial Pt catalysts thanks to the synergistic effect with a small amount of Cu and selective exposure of the {111} facets. The result suggests that transition metals in Pt-based electrocatalysts may be unnecessary to form intermetallic alloyed crystals for the enhanced ORR performance.

1. Introduction

Proton-exchange membrane (PEM) fuel cells, which can provide clean, highly efficient electricity, are essential to improve the sustainability of our society. Since the sluggish kinetics of the oxygen reduction reaction (ORR) determine the performance of PEM fuel cells, precious Pt catalysts are crucial in the cathode electrode (1, 2). To date, great efforts have been undertaken to reduce the Pt loading by enhancing the ORR catalytic performance. The most widely accepted and successful strategy is to combine Pt with inexpensive transition metals such as Fe, Co, Ni, or Cu to form Pt-based alloys (3-10). The formation of Pt-based alloys modifies the electronic structure on the surface of catalytic particles and improves the ORR catalytic performance (11-14). The difference in the atomic radius induces surface strain, which can also contribute to the electrochemical properties (11, 15). Among the various transition metals, Cu is regarded as one of the best candidates due to its abundance, low cost, and good catalytic properties (5, 7, 8, 10). Another promising strategy is to control the shape of the catalytic particles. Previous studies have shown that the catalytic activities depend on the crystal facets, which can be manipulated by the shape of catalytic particles (16-19). In addition, shape-controlled catalytic particles with a higher density of steps and edges on the surface are more active than spherical ones (20, 21).

During the past few decades, a variety of Pt-based nanoparticles with different shapes (plates, polyhedrons, multipods, etc.) have been synthesized to enhance the ORR catalytic performance (16-19). However, the reported methods for the shape control postulate polymer surfactants and complicated processes, which are undesirable for practical use. To control the growth direction and to obtain anisotropic shapes, which are thermodynamically unfavored, polymer capping agents are widely used with oxidative etchant (22, 23), but they often inhibit the ORR by remaining on the surface (24). Moreover, most of the shape-controlled nanoparticles are synthesized through plural or seed-mediated reactions to introduce stacking faults or twin defects into the nuclei of the nanoparticles (22). After the synthesis of catalytic nanoparticles, additional deposition process is also required because nanoparticles need to be deposited on carbon supports for the use as electrocatalysts (25, 26). Therefore, a simple method that alleviates the need for polymer surfactants and complicated processes to prepare carbon-support nanoparticles with controlled shapes is highly desired.

Herein we propose a facile and simple aqueous phase method for morphological control of Pt-based nanoparticles supported on carbon. The present method provides a true one-step synthesis of Pt-based electrocatalysts with controlled shapes. Pt and Cu precursors are simply reduced together in the presence of a carbon support in an aqueous solution NH_4Cl or NaCl but without adding a polymer capping agent or a dispersing agent. This method successfully synthesized Pt-Cu nanoclusters, Pt-Cu nanospheres, and Cu-doped Pt nanoplates supported on carbon. The Cu-doped Pt nanoplates exhibit the highest ORR performance among the synthetic and the commercial catalysts thanks to a synergistic effect with the small amount of Cu and selective exposure of $\{111\}$ facets.

2. Experimental

2.1 Chemicals and materials

Hexachloroplatinic(IV) acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$; 98.5%), copper(II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$; 99.0%), ammonium chloride (NH_4Cl ; 99.5%), sodium chloride (NaCl ; 99.5%), sodium tetrahydroborate (NaBH_4 ; 95.0%), isopropyl alcohol (99.7%), Nafion[®] dispersion solution (DE521; 5%), and perchloric acid (HClO_4 ; 60%) were purchased from FUJIFILM Wako Pure Chemical. Carbon black (Ketjenblack EC) and Pt/C (TEC10E50E; 46.4 wt%Pt) were purchased from Tanaka Kikinzoku Kogyo. The above chemicals and materials were used as received.

Ammonium hexachloroplatinate(IV) ($(\text{NH}_4)_2\text{PtCl}_6$) was prepared in-house as follows. One gram of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ was dissolved into 50 mL of deionized water and the same volume of 3 mol L^{-1} of NH_4Cl aqueous solution was subsequently added. The mixture was kept at 30 °C for a day, which gave a yellow precipitate. Before experimental use, the purity and yield were confirmed to be acceptable (see Supplementary).

2.2 Synthesis

$(\text{NH}_4)_2\text{PtCl}_6$ (0.013 mmol), CuCl_2 (0.013 mmol), and carbon black (7.5 mg) were added to an aqueous solution containing 30 mmol of NH_4Cl or NaCl . The solution pH and volume were adjusted to 9.2–9.3 and 90 mL, respectively. NaBH_4 (30 mg) dissolved in 10 mL of deionized water was injected to start the synthesis reaction. The solution was kept at 30 °C for 4 h while stirring. It was subsequently filtered, rinsed, and dried. The samples synthesized with NH_4Cl , NaCl , or neither were labeled as Amm/C, Sod/C, and None/C, respectively.

2.3 Characterizations

The crystal structure was analyzed by powder X-ray diffraction (XRD; Smart-Lab, Rigaku) measurements performed with Cu $\text{K}\alpha$ radiation. Nano-sized metal precipitates on carbon supports were observed by a transmission electron microscope (TEM; EM-002B, Topcon) or a scanning transmission electron microscope (STEM; HD-2700, Hitachi High-Technologies) operated at 200 kV. The elemental composition was measured by an energy dispersive X-ray spectrometer (EDS; TEAM EDS system, AMETEK) equipped on the STEM and induced coupled plasma-atomic emission spectrometer (ICP-AES; Optima 3300XL, Perkin Elmer). Ultraviolet-visible absorption spectra (UV-vis; U-3900, Hitachi High-Technologies) were recorded to confirm the complex state of Pt ions in an aqueous solution. The reduction behavior of the metal species was evaluated by ICP-AES measurements against the reaction time.

2.4 Electrochemical measurements

All electrochemical measurements were performed in a conventional three-electrode system consisting of a polished glassy carbon electrode (GCE; 0.283 cm^2), reversible hydrogen electrode (RHE), and platinum coil as the working, reference, and counter electrodes, respectively. Typically,

catalyst ink was prepared by dispersing 3.7 mg of the catalyst powder in a mixture of ultrapure water (3.8 mL), isopropyl alcohol (1.2 mL), and Nafion[®] solution (14 μ L) followed by ultrasonication. Afterwards, 14.4 μ L of the catalyst ink was dropped onto the GCE and dried at ambient conditions. Cyclic voltammetry (CV) was conducted in a N₂-saturated HClO₄ solution (0.1 mol L⁻¹) at a scanning rate of 50 mV s⁻¹. The electrochemical active surface area (ECSA) was determined by integrating the electric charge associated with adsorption/desorption of hydrogen atoms in the CV, assuming the charge for monolayer hydrogen adsorption on the Pt surface is 210 μ C cm⁻². Thereafter, the linear sweep voltammogram (LSV) was recorded with a rotating disk electrode (RDE) in O₂-saturated HClO₄ solution (0.1 mol L⁻¹) at a scanning rate of 10 mV s⁻¹. The rotation speed of the working electrode was controlled at 1000, 1250, 1500, 2000, or 2750 rpm.

3. Results and discussion

3.1 Synthesis and characterizations

The catalytic samples were synthesized with NH₄Cl (Amm/C), NaCl (Sod/C), or neither (None/C). The crystal structure and composition of bimetallic electrocatalysts significantly affect the ORR catalytic activity (6, 7, 21, 27-32). The synthetic samples in this study should contain Pt₁Cu₁ alloy crystals since they were obtained via a chemical reduction of Pt and Cu ions at a 1:1 ratio. Figure 1 shows the XRD profiles of the synthetic samples along with the commercial Pt/C. The diffraction peaks of the commercial Pt/C appearing at 39.8, 46.2, 67.5, and 81.3° are indexed to the (111), (200), (220), and (311) planes of face-centered cubic (fcc) Pt, respectively. All profiles of the synthetic samples exhibit a typical pattern for metallic fcc crystal structures. The diffraction peaks of None/C and Sod/C are located between those of Pt and Cu, indicating the formation of Pt-Cu alloy crystals. Although Amm/C includes Cu salt in the synthesis solution, the diffraction peaks appear at almost the same position as the commercial Pt/C except for an additional minor peak at 85.7° of the (222) plane. Therefore, Cu ions are not reduced completely or redissolved immediately after precipitation during the synthesis of Amm/C. An explanation of the different Cu contents is discussed later to reveal the synthesis mechanism.

The composition ratio of Pt and Cu in each sample was estimated by Vegard's law, which predicts a linear variation in the lattice constant with the composition, and it was compared to the measurement results by EDS and ICP-AES (Table I). Note that the value obtained by Vegard's law indicates the composition ratio in alloyed crystals, whereas EDS and ICP-AES counterparts reflect the elemental ratio of whole states. Although the lattice constant of Amm/C corresponds to that of pure Pt, a non-negligible amount of Cu is detected by EDS and ICP-AES, indicating Cu atoms are doped in the fcc Pt crystals. The EDS and ICP-AES results of None/C and Sod/C suggest that Pt and Cu are contained at the same ratio, which coincides with the initial additive amount of metal precursors. On the other hand, the content of Cu atoms in the fcc crystal decreases from the additive ratio in the following order: the additive (50 at%) > Sod/C (33 at%) > None/C (23 at%). Therefore, part of Cu atoms in Sod/C and None/C does not exist as alloyed fcc crystals but does exist in other crystal phases, amorphous states, or atomic clusters.

Figure 1 XRD profiles for None/C, Sod/C, Amm/C, and the commercial Pt/C. Black and white bars at the bottom indicate the reference patterns by the International Center for Diffraction Data (ICDD) of fcc Pt (No. 04-0802) and fcc Cu (No. 04-0836), respectively.

Table I Metal compositions of the synthetic samples measured by various methods.

	XRD		EDS		ICP	
	Pt (at%)	Cu (at%)	Pt (at%)	Cu (at%)	Pt (at%)	Cu (at%)
None/C	77	23	48	52	46	54
Sod/C	67	33	49	51	47	53
Amm/C	100	0	95	5	94	6

TEM observations were performed to reveal the morphological features of the synthetic samples. Nano-sized metal precipitates are uniformly deposited on carbon supports without noticeable aggregation, although carbon black agglomerates in the aqueous solution during the synthesis due to the surfactant-free conditions. Figures 2a to 2f show typical images and the corresponding distribution histograms of the particle diameters. None/C contains small nanoparticles, which are 2.4 nm on average and can be expressed as nanoclusters (Figures 2a and 2d). In contrast, larger particles are synthesized in the presence of NaCl (Figures 2b and 2e) or NH₄Cl (Figures 2c

and 2f). The mean particle sizes of Sod/C and Amm/C are 5.0 and 7.6 nm, respectively. The size distribution broadens as the particles grow, which agrees with the general trend.

Figure 2 TEM images and particle size distributions of (a)(d) None/C, (b)(e) Sod/C, and (c)(f) Amm/C.

In addition to particle size, particle shape and/or exposed crystal facets drastically affect the catalytic activities (21, 27-29, 32). Although the particle sizes differ, both None/C and Sod/C have spherical particle shapes (Figures 2a and 2b). In contrast, Amm/C has triangular, bar-like, and distorted shapes (Figure 2c). STEM experiments were conducted to fully understand the morphological features of Amm/C. Figure 3a shows a high-angle annular dark field (HAADF) image displaying two metallic particles. Figure 3b shows a secondary electron (SE) image of the same area. The HAADF and SE images mutually compensate the location of metallic elements and the surface profile. Comparing Figures 3a and 3b reveals the triangular plate-like morphology. The illustration located over Figures 3a and 3b indicates the estimated shape of particles in the STEM images. Consequently, the various shapes in Figure 2c are nanoplates observed from different directions.

Figure 3c shows a high-resolution TEM (HRTEM) image observed from an edge of the nanoplate. The 0.23-nm spacing of lattice fringes corresponds with the (111) plane of fcc Pt, indicating the top and bottom surfaces of the nanoplates are enclosed by the {111} facets. The minor diffraction peak of the (222) plane in Figure 1 also supports the growth orientation. Note that

thermodynamically favored shape for fcc crystals is cuboctahedron enclosed by $\{100\}$ and $\{110\}$ facets (33), which is nearly spherical such as None/C and Sod/C. This indicates that kinetic control should form the thermodynamically unfavored plate-like morphology. In conclusion of the above characterizations, Pt-Cu nanoclusters (None/C), Pt-Cu nanospheres (Sod/C), and Cu-doped Pt nanoplates (Amm/C) supported on carbon are synthesized.

Figure 3 (a) HAADF- and (b) SE-STEM images of the same area and (c) a HRTEM image of Amm/C. Illustration shows triangular nanoplates estimated from (a) and (b).

3.2 Synthesis mechanism

Fully understanding the synthesis conditions for each sample is the most important clue to reveal the synthesis mechanism. The complex species of the Pt precursors before the reaction was estimated from the UV-vis spectra (Figure 4a). All solution samples were prepared without carbon black or Cu salt, and diluted by water to obtain reliable absorbance. The UV-vis spectrum of Sod/C shows a peak around 260 nm, which corresponds to $[\text{PtCl}_6]^{2-}$ in previous reports (34-37). Although Pt(IV) complex ions tend to hydrolyze in an alkaline solution, an excess concentration of Cl^- can prevent it (38), and Sod/C maintains the initial complex structure of $[\text{PtCl}_6]^{2-}$ by adding NaCl.

For None/C, which does not include additive Cl^- in the solution, the absorption spectrum broadens toward the shorter wavelength region compared to Sod/C counterpart. The absorption peak of $[\text{PtCl}_6]^{2-}$ at 260 nm undergoes a blue shift when part of Cl^- is exchanged by OH^- . For example, the absorption peak appears at 240 nm for $[\text{PtCl}_4(\text{OH})_2]^{2-}$ and 210 nm for $[\text{PtCl}(\text{OH})_5]^{2-}$ (34, 35). Therefore, the peak broadening suggests that $[\text{PtCl}_{6-x}(\text{OH})_x]^{2-}$ ($0 \leq x \leq 6$) is mixed in the synthesis solution of None/C.

Despite including NH_4Cl , which can supply Cl^- to prevent hydrolysis, Amm/C does not show absorbance except for that ascribed to the matrix. In other words, neither chloride nor hydroxide complexes are in the solution of Amm/C. Another possible species is $[\text{Pt}(\text{NH}_3)_6]^{4+}$ (39). Although NH_4Cl may provide NH_4^+ but not NH_3 , half of the provided NH_4^+ changes into NH_3 because the pH of the synthesis solution corresponds to the acid dissociation constant of NH_4^+ (40). The amine complex absorbs light at a shorter wavelength than the hydroxide and chloride counterparts according to the spectrochemical series, which predicts the strength order of the ligand field splitting as $\text{NH}_3 >$

$\text{OH}^- > \text{Cl}^-$ (41, 42). Thus, the absorption band of $[\text{Pt}(\text{NH}_3)_6]^{4+}$ should be located at a shorter wavelength region than those of $[\text{PtCl}_{6-x}(\text{OH})_x]^{2-}$ and be hidden in that of the matrix.

Figure 4 (a) UV-vis spectra of the synthesis solutions and (b) the simulated result of Cu complex species in the synthesis solution of Amm/C.

$\text{Cu}(\text{II})$ ions preferentially form amine complexes in the presence of ammonia, whereas hydroxides are stable in the high pH region without ammonium species. Complex species of Cu at different pH values were simulated by solving equations for the equilibrium constants (40, 43, 44). Figure 4b shows the result for Amm/C, which contains ammonia in the synthesis solution, suggesting that the Cu complex species around the pH of the synthesis solution is $[\text{Cu}(\text{NH}_3)_4]^{2+}$ with a small ratio of $[\text{Cu}(\text{NH}_3)_3]^{2+}$, and the Cu precursor of Amm/C is determined to be an amine complex. The other simulations for None/C and Sod/C are shown in Figure S4, suggesting that their Cu precursors are both Cu hydroxide as expected. In regard to the synthesis conditions, it should also be noted that Cl^- contained in the solution of Sod/C and Amm/C can behave as an oxidative etchant when O_2 is present in the reaction field (45), which is often denoted as Cl^-/O_2 .

To evaluate the kinetic features for each synthesis condition, the concentrations of metal species in the synthesis solutions were tracked by ICP-AES measurements with various reaction times. Figure 5 plots the metal ion concentrations as a function of reaction time normalized by the initial

value. When focusing on the early stage of Pt reduction (i.e., the first 30 minutes) in Figure 5a, the reduction rates clearly differ. Reduction of Pt ions during the synthesis of None/C is relatively fast and is completed within 5 minutes, while Sod/C takes 30 minutes. Moreover, comparing Sod/C and Amm/C, although the gradients of the section between 1–30 minutes are almost the same, the reduction rate is smaller for Amm/C than Sod/C because they reach different values. Hence, the reduction rate of Pt decreases in the following order: None/C >> Sod/C > Amm/C. In the chemical reduction synthesis of nanoparticles, a reduction leads to smaller particle sizes, which may be responsible for the smaller nanoparticles of None/C.

The variations in the reduction rates among the present synthesis conditions should be a consequence of the difference in the complex species of precursors (46) and/or oxidative etching by Cl^-/O_2 (45, 47-49). The reduction rate for None/C without Cl^- is much faster than those for Sod/C and Amm/C with Cl^- . This suggests that Cl^-/O_2 plays a key role in delaying the reaction of Pt reduction (18). It should be noted that the reducing power during the synthesis of Amm/C expires before the completion of precipitation reaction, and Pt ions remain in the solution even after stirring for 4 h.

Figure 5 (a) Pt and (b) Cu concentrations in the synthesis solutions as a function of reaction time. Error bars indicate standard deviations (N = 3).

Figure 5b shows precipitation behavior of Cu in the synthesis solutions. The most noticeable feature is that Cu ions are immediately reduced and subsequently redissolved during the synthesis of Amm/C, which is the reason for the low Cu loading in Amm/C. Therefore, the Cu-amine complex ion simulated as the main species in Figure 4b is extremely stable under the present conditions and is formed preferentially when the reducing power is expired. Despite the result that reduction rate of Pt for Amm/C is the slowest, its Cu counterpart at the early stage is comparable or slightly faster. The standard electrode potential of the Cu complex ions into metallic Cu is -0.054 V vs. normal hydrogen electrode (NHE) for $[\text{Cu}(\text{NH}_3)_4]^{2+}$ and -0.222 V vs. NHE for $\text{Cu}(\text{OH})_2$ (50, 51). Note that the potential for $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is derived from the standard Gibbs energies of formation. The Cu-amine complex ion, namely, the Cu precursor for Amm/C is reduced easier and faster although the precipitated metal Cu starts to redissolve simultaneously with the expiration of the reducing power.

The synthesis of metal nanoparticles with anisotropic morphologies, including nanoplates like Amm/C, generally requires capping agents with long chains to select the growth direction and/or seeds of a second metal to introduce defects in their crystals at the nucleation step. Because molecules containing N atoms strongly adsorb on a Pt surface, they are often chosen as capping agents (22), however, ammonia or ammonium ions are too small to exhibit a capping effect. Besides, in some cases, a trace amount of second metal ions behaves as seeds and assists in forming anisotropic Pt nanoparticles (52, 53).

To reveal the synthesis mechanism and to reach the origin of the morphological features, further experiments were conducted. Two additional conditions based on the procedure to synthesize Amm/C were undertaken. One was without a Cu salt in solution, and the other was while purging by N_2 gas to expel dissolved O_2 . Figure 6 shows the typical TEM images of them. As shown in Figure 6a, Amm/C synthesized without Cu salt exhibits non-spherical nanoparticles similar to that synthesized with Cu salt in Figure 2c. The nanoplates synthesized without Cu clearly suggest that the formation of the plate-like morphology is not assisted by Cu seeds in the present study. On the other hand, purging with N_2 during the synthesis forms spherical nanoparticles without plate-like nanoparticles (Figure 6b), indicating that dissolved O_2 in the solution with the ammonium species plays a key role in forming the plate-like morphology.

Figure 6 TEM images of Amm/C synthesized (a) without Cu salt and (b) under a N_2 atmosphere.

When Pt ions are reduced in the presence of Cl^-/O_2 , Pt nanoparticles gradually grow while oscillating between precipitation and dissolution. Then capping agents restrict the precipitation or dissolution sites, resulting in selective growth (22, 23). Selective adsorption of capping agents is an important factor for anisotropic growth of nanoparticles. For ammonia molecules and ammonium ions in the synthesis solution of Amm/C, adsorption on the (111) facet of Pt is weaker than other facets (54, 55). Although ammonium species have no long chain to express the capping effect, an explanation for synthesis mechanism of nanoplates can be deduced by focusing on the electrical charges of the precursor and surface. During the synthesis of Amm/C, etched Pt ions are stabilized into negatively charged $[\text{PtCl}_6]^{2-}$ by coordinating with Cl^- (23, 45), while the Pt precursor of Amm/C is positively charged $[\text{Pt}(\text{NH}_3)_6]^{4+}$. Since negatively charged $[\text{PtCl}_6]^{2-}$ prefers to precipitate on positively charged facets covered by NH_4^+ , $\langle 111 \rangle$ growth is inhibited and a plate-like morphology, which exposes the $\{111\}$ facets, is formed.

3.3 Electrochemical measurements

For Pt-Cu bimetallic electrocatalysts, it has been reported that exposed Cu atoms dissolve during pretreatment in an acidic atmosphere and a Pt thin layer forms on the surface (13, 56). To stabilize the electrode and obtain reproducible data, the electrochemical properties were evaluated after applying potential for 200 cycles. ECSA, which was determined from the CV in Figure S5, is 35.5, 19.7, and 21.0 $\text{m}^2 \text{g}^{-1}$ for None/C, Sod/C, and Amm/C, respectively. Since ECSA highly depends on the specific surface area of the catalytic particles, None/C, which carries the tiny nanoclusters on the surface, shows comparable value to the commercial Pt/C (36.4 $\text{m}^2 \text{g}^{-1}$), whereas those of Sod/C and Amm/C are smaller. It is difficult to unconditionally predict ECSAs of Sod/C and Amm/C from their particle sizes due to their differences in shape. However, considering the size of plate-like materials is often overestimated against the spherical counterpart, the result that Amm/C with larger plate-like particles shows a slightly larger ECSA than Sod/C with smaller spherical particles is reasonable.

The ORR catalytic performance was investigated on RDE at various rotation speeds. The polarization curve was corrected for the non-Faradaic background current by subtracting the current in CV recorded in N_2 -saturated electrolyte. The kinetic current for the ORR was derived from the segment of the Koutecky-Levich plot, and normalized by the Pt loading or ECSA. Figures 7a and 7b present the half-cell potentials as a function of mass activity and specific activity, respectively. The gradients coincide with that of Tafel slope due to the linear normalization. For all curves in Figures 7a and 7b, the slope gradually changes from -60 to $-120 \text{ mV decade}^{-1}$ as the current density increases, indicating the same ORR mechanism for all of the synthetic samples and the commercial Pt/C (57, 58). It should be noted that the rate-limiting step in the ORR for Pt-based catalysts is electron transferring to adsorbed O_2 regardless of the current density region. Consequently, the change in Tafel slope does not imply a change in the rate-limiting step but is related to the onset potential of adsorption of oxygenated species (11-15, 57, 58).

Figure 7 Half-cell potentials as a function of (a) mass activity (MA) and (b) specific activity (SA). (c) The ORR catalytic properties at 0.9 V vs. RHE normalized by those of the commercial Pt/C.

Table II The ORR catalytic properties at 0.9 V vs. RHE and relative values against the commercial Pt/C.

	ECSA (m ² g ⁻¹ _{Pt})	vs. Pt/C	Mass activity (mA mg ⁻¹ _{Pt})	vs. Pt/C	Specific activity (mA cm ⁻² _{Pt})	vs. Pt/C
Pt/C	36.4	1	166	1	0.46	1
None/C	35.5	0.98	323	1.95	0.91	1.98
Sod/C	19.7	0.54	194	1.17	0.99	2.15
Amm/C	21.0	0.58	354	2.13	1.69	3.67

Table II summarizes the mass and specific activities at 0.9 V vs. RHE along with ECSA, and Figure 7c exhibits the relative ORR catalytic properties against the commercial Pt/C. The mass activities for None/C, Sod/C, and Amm/C are 323, 194 and 354 mA mg⁻¹, respectively. Amm/C is 2.13-times greater than that for the commercial Pt/C. While mass activity is the most important factor based on the perspective of industry and commerce (1, 59), it is determined by the product of ECSA and specific activity, thus itself is basically uncontrollable.

Compared to the specific activity of the commercial Pt/C (0.46 mA cm⁻²), those for None/C and Sod/C, which have spherical nanoparticles with different sizes, are twice as high. The enhanced activity is explained by the synergistic effect between Pt and Cu. It has been theoretically and experimentally demonstrated that alloying of Pt atoms with a transition metal changes the surface electronic structure, modifies the bonding energy with oxygenated species, and leads to the high activity (12-14). Particle size and/or distance (20, 28, 60-62), and the atomic composition ratio in the alloy crystal (5-7, 10, 30-32) might also affect the activity. However, their impact is not significant in the present system or the comprehensive value results in the same level. Although further experiments are required for a full understanding, the difference in mass activity between None/C and Sod/C is dominantly ascribed to the difference in ECSA.

Amm/C exhibits the highest specific activity (1.69 mA cm⁻²) in this study, and is superior to the commercial Pt/C by 3.67 times. As discussed above, the catalytic particles in Amm/C are Cu-doped Pt nanoplates selectively exposing the {111} facets. According to previous studies on a model electrode for the ORR in aqueous perchloric acid solution, the Pt (111) facet is more active than the polycrystalline Pt surface. However, neither is remarkable nor the best even among low index facets (21, 27-29, 32). Therefore, the perspective of the exposed crystal facet is insufficient to interpret the high activity. The small amount of doped Cu atoms no doubt plays an important role for the ORR. Compared to the pure Pt crystal and alloy, a different trend of the ORR performance against crystal facet has been reported (29, 32). Stamenkovic and his co-workers have suggested that an alloyed Pt (111) facet shows a much higher activity than other low index facets by using well-defined electrode of Pt₃Ni with Pt skin, while Pt (111) is less active than Pt (110) in the pure crystal system (29). The enhanced specific activity of Amm/C arises from both the selective exposure of (111) facet and the existence of Cu atoms in Pt crystal.

Although some reports have focused on the relationship between the metal compositions of

electrocatalyst and the ORR properties, controlling the range of the second metal loading is limited to form intermetallic alloy with Pt (5-7, 10, 30-32). It is noteworthy that composition ratio of the second metal in catalytic particles is generally higher than 20 at%, whereas the Cu ratio for Amm/C is less than 10 at% as written in Table I. The improved specific activity of Amm/C suggests that the small amount of doped Cu atoms can induce a synergistic effect with the Pt surface to enhance the ORR performance on (111) facet. These results provide motivation to investigate the lower region of the second metal loadings in Pt-based electrocatalysts.

4. Conclusions

Carbon-supported Pt-Cu nanoclusters (None/C), Pt-Cu nanospheres (Sod/C), and Cu-doped Pt nanoplates (Amm/C) were successfully synthesized by a simple one-step method without a polymer surfactant. During the synthesis of Sod/C and Amm/C, Cl^- ions with dissolved O_2 work as an oxidative etchant (Cl^-/O_2) to delay the reduction rate, resulting in larger particles. Cl^-/O_2 and NH_4^+ are triggers to form the plate-like morphology of Amm/C. The Cu-doped Pt nanoplates exhibit a 3.67-times higher ORR catalytic activity than the commercial Pt catalysts due to a synergistic effect with a small amount of Cu and selective exposure of the {111} facets. The result suggests that a large amount of Cu to form intermetallic alloys is unnecessary for the enhanced ORR performance.

In addition, $(\text{NH}_4)_2\text{PtCl}_6$ which was used as the Pt salt, is the known intermediate product in the recycling process of Pt (63, 64). Therefore, the present study shows a possibility to combine the material synthesis and resource recovery into one process. However, the Pt yield in the synthesis of Amm/C is insufficient for practical use due to the expiration of reducing power. Other reducing agents with a continuous effect will enhance the Pt yield. Moreover, the ORR catalytic performance should be further enhanced because a wider plate will be obtained.

Acknowledgement

This work was partially supported by JSPS KAKENHI Grant Number JP18H03416.

References

1. M. Debe, Electrocatalyst approaches and challenges for automotive fuel cells. *Nature* **486**, 43-51 (2012).
2. *Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan* (2017).
3. T. Toda, H. Igarashi, H. Uchida, M. Watanabe, Enhancement of the electroreduction of oxygen on Pt alloys with Fe, Ni, and Co. *Journal of the Electrochemical Society* **146**, 3750-3756 (1999).
4. R. Srivastava, P. Mani, N. Hahn, P. Strasser, Efficient oxygen reduction fuel cell electrocatalysis on voltammetrically dealloyed Pt-Cu-Co nanoparticles. *Angewandte Chemie-International Edition* **46**, 8988-8991 (2007).
5. P. Mani, R. Srivastava, P. Strasser, Dealloyed Pt-Cu core-shell nanoparticle electrocatalysts for use in PEM fuel cell cathodes. *Journal of Physical Chemistry C* **112**, 2770-2778 (2008).
6. M. Oezaslan, F. Hasche, P. Strasser, Oxygen Electroreduction on PtCo_3 , PtCo and Pt_3Co Alloy Nanoparticles for Alkaline and Acidic PEM Fuel Cells. *Journal of the Electrochemical Society* **159**, B394-B405 (2012).

7. Y. Sohn, J. Park, P. Kim, J. Joo, Dealloyed PtCu catalyst as an efficient electrocatalyst in oxygen reduction reaction. *Current Applied Physics* **15**, 993-999 (2015).
8. V. Pryadchenko *et al.*, Bimetallic PtCu core-shell nanoparticles in PtCu/C electrocatalysts: Structural and electrochemical characterization. *Applied Catalysis a-General* **525**, 226-236 (2016).
9. J. Choi *et al.*, Gram-scale synthesis of highly active and durable octahedral PtNi nanoparticle catalysts for proton exchange membrane fuel cell. *Applied Catalysis B-Environmental* **225**, 530-537 (2018).
10. Y. Liu *et al.*, Preparation and application in assembling high-performance fuel cell catalysts of colloidal PtCu alloy nanoclusters. *Journal of Power Sources* **395**, 66-76 (2018).
11. J. Kitchin, J. Norskov, M. Barteau, J. Chen, Modification of the surface electronic and chemical properties of Pt(111) by subsurface 3d transition metals. *Journal of Chemical Physics* **120**, 10240-10246 (2004).
12. V. Stamenkovic *et al.*, Changing the activity of electrocatalysts for oxygen reduction by tuning the surface electronic structure. *Angewandte Chemie-International Edition* **45**, 2897-2901 (2006).
13. V. Stamenkovic *et al.*, Trends in electrocatalysis on extended and nanoscale Pt-bimetallic alloy surfaces. *Nature Materials* **6**, 241-247 (2007).
14. H. Hansen, V. Viswanathan, J. Norskov, Unifying Kinetic and Thermodynamic Analysis of 2 e(-) and 4 e(-) Reduction of Oxygen on Metal Surfaces. *Journal of Physical Chemistry C* **118**, 6706-6718 (2014).
15. A. Nilekar, M. Mavrikakis, Improved oxygen reduction reactivity of platinum monolayers on transition metal surfaces. *Surface Science* **602**, L89-L94 (2008).
16. J. Zhang, H. Yang, J. Fang, S. Zou, Synthesis and Oxygen Reduction Activity of Shape-Controlled Pt₃Ni Nanopolyhedra. *Nano Letters* **10**, 638-644 (2010).
17. B. Larsen *et al.*, Platinum Nanoplates as Fuel Cell Electrocatalysts. *Journal of the Electrochemical Society* **159**, F622-F627 (2012).
18. L. Ma *et al.*, Control Over the Branched Structures of Platinum Nanocrystals for Electrocatalytic Applications. *Acs Nano* **6**, 9797-9806 (2012).
19. H. Liu *et al.*, Synthesis of ultrathin platinum nanoplates for enhanced oxygen reduction activity. *Chemical Science* **9**, 398-404 (2018).
20. K. KINOSHITA, PARTICLE-SIZE EFFECTS FOR OXYGEN REDUCTION ON HIGHLY DISPERSED PLATINUM IN ACID ELECTROLYTES. *Journal of the Electrochemical Society* **137**, 845-848 (1990).
21. A. Bandarenka, H. Hansen, J. Rossmeisl, I. Stephens, Elucidating the activity of stepped Pt single crystals for oxygen reduction. *Physical Chemistry Chemical Physics* **16**, 13625-13629 (2014).
22. Z. Peng, H. Yang, Designer platinum nanoparticles: Control of shape, composition in alloy, nanostructure and electrocatalytic property. *Nano Today* **4**, 143-164 (2009).
23. R. Long, S. Zhou, B. Wiley, Y. Xiong, Oxidative etching for controlled synthesis of metal nanocrystals: atomic addition and subtraction. *Chemical Society Reviews* **43**, 6288-6310 (2014).
24. D. Li *et al.*, Surfactant Removal for Colloidal Nanoparticles from Solution Synthesis: The Effect on Catalytic Performance. *Acs Catalysis* **2**, 1358-1362 (2012).
25. E. Antolini, Carbon supports for low-temperature fuel cell catalysts. *Applied Catalysis B-Environmental* **88**, 1-24 (2009).
26. Y. Wang, B. Fang, H. Li, X. Bi, H. Wang, Progress in modified carbon support materials for Pt and Pt-alloy

- cathode catalysts in polymer electrolyte membrane fuel cells. *Progress in Materials Science* **82**, 445-498 (2016).
27. N. MARKOVIC, H. GASTEIGER, P. ROSS, OXYGEN REDUCTION ON PLATINUM LOW-INDEX SINGLE-CRYSTAL SURFACES IN SULFURIC-ACID-SOLUTION - ROTATING RING-PT(HKL) DISK STUDIES. *Journal of Physical Chemistry* **99**, 3411-3415 (1995).
 28. N. Markovic, H. Gasteiger, P. Ross, Kinetics of oxygen reduction on Pt(hkl) electrodes: Implications for the crystallite size effect with supported Pt electrocatalysts. *Journal of the Electrochemical Society* **144**, 1591-1597 (1997).
 29. V. R. Stamenkovic *et al.*, Improved Oxygen Reduction Activity on Pt₃Ni(111) via Increased Surface Site Availability. *Science* **315**, 493-497 (2007).
 30. C. Wang *et al.*, Correlation Between Surface Chemistry and Electrocatalytic Properties of Monodisperse Pt_xNi_{1-x} Nanoparticles. *Advanced Functional Materials* **21**, 147-152 (2011).
 31. Y. Liu, C. Hangarter, U. Bertocci, T. Moffat, Oxygen Reduction Reaction on Electrodeposited Pt_{100-x}Ni_x: Influence of Alloy Composition and Dealloying. *Journal of Physical Chemistry C* **116**, 7848-7862 (2012).
 32. S. Kobayashi, M. Wakisaka, D. Tryk, A. Iiyama, H. Uchida, Effect of Alloy Composition and Crystal Face of Pt-Skin/Pt_{100-x}Cox [(111), (100), and (110)] Single Crystal Electrodes on the Oxygen Reduction Reaction Activity. *Journal of Physical Chemistry C* **121**, 11234-11240 (2017).
 33. Y. Xia, Y. Xiong, B. Lim, S. Skrabalak, Shape-Controlled Synthesis of Metal Nanocrystals: Simple Chemistry Meets Complex Physics? *Angewandte Chemie-International Edition* **48**, 60-103 (2009).
 34. T. Mang, B. Breitschdel, P. Polanek, H. Knözinger, Adsorption of platinum complexes on silica and alumina: Preparation of non-uniform metal distributions within support pellets. *Applied Catalysis A: General* **106**, 239 - 258 (1993).
 35. Z. Jin, Z. Chen, Q. Li, C. Xi, X. Zheng, On the conditions and mechanism of PtO₂ formation in the photoinduced conversion of H₂PtCl₆. *Journal of Photochemistry and Photobiology A: Chemistry* **81**, 177 - 182 (1994).
 36. M. Georgieva, B. Andonovski, Determination of platinum(IV) by UV spectrophotometry. *Analytical and Bioanalytical Chemistry* **375**, 836-839 (2003).
 37. Z. Tang, D. Geng, G. Lu, A simple solution-phase reduction method for the synthesis of shape-controlled platinum nanoparticles. *Materials Letters* **59**, 1567-1570 (2005).
 38. W. A. Spieker, J. Liu, J. T. Miller, A. J. Kropf, J. R. Regalbuto, An EXAFS study of the co-ordination chemistry of hydrogen hexachloroplatinate(IV). *Applied Catalysis A: General* **232**, 219-235 (2002).
 39. B. Farrell, I. Sevonkaev, D. Goia, Preparation of Dispersed Spherical Platinum Particles with Controlled Size and Internal Structure Versatile and cost-effective route to platinum powders for large scale electronic applications. *Platinum Metals Review* **57**, 161-168 (2013).
 40. R. Goldberg, N. Kishore, R. Lennen, Thermodynamic quantities for the ionization reactions of buffers. *Journal of Physical and Chemical Reference Data* **31**, 231-370 (2002).
 41. R. Tsuchida, Absorption Spectra of Co-ordination Compounds. I. *Bulletin of the Chemical Society of Japan* **13**, 388-400 (1938).
 42. T. Ishii, S. Tsuboi, G. Sakane, M. Yamashita, B. K. Y. Breedlove, - Universal spectrochemical series of six-coordinate octahedral metal complexes for modifying the ligand field splitting. - *Dalton Transactions*, - 680 (2009).

43. L. Trevani, J. Roberts, P. Tremaine, Copper(II)-ammonia complexation equilibria in aqueous solutions at temperatures from 30 to 250 degrees C by visible spectroscopy. *Journal of Solution Chemistry* **30**, 585-622 (2001).
44. K. Powell *et al.*, Chemical speciation of environmentally significant metals with inorganic ligands - Part 2: The Cu²⁺-OH⁻, Cl⁻, CO₃²⁻, SO₄²⁻, and PO₄³⁻ systems - (IUPAC technical report). *Pure and Applied Chemistry* **79**, 895-950 (2007).
45. B. Wiley, T. Herricks, Y. Sun, Y. Xia, Polyol synthesis of silver nanoparticles: Use of chloride and oxygen to promote the formation of single-crystal, truncated cubes and tetrahedrons. *Nano Letters* **4**, 1733-1739 (2004).
46. T. Yang, K. Gilroy, Y. Xia, Reduction rate as a quantitative knob for achieving deterministic synthesis of colloidal metal nanocrystals. *Chemical Science* **8**, 6730-6749 (2017).
47. Y. Xiong *et al.*, Kinetically controlled synthesis of triangular and hexagonal nanoplates of palladium and their SPR/SERS properties. *Journal of the American Chemical Society* **127**, 17118-17127 (2005).
48. Y. Wang, H. Peng, J. Liu, C. Huang, Y. Xia, Use of Reduction Rate as a Quantitative Knob for Controlling the Twin Structure and Shape of Palladium Nanocrystals. *Nano Letters* **15**, 1445-1450 (2015).
49. N. Nalajala, A. Chakraborty, B. Bera, M. Neergat, Chloride (Cl⁻) ion-mediated shape control of palladium nanoparticles. *Nanotechnology* **27**, (2016).
50. G. Milazzo, S. Caroli, V. K. Sharma, C. International Union of Pure and Applied Chemistry. Electrochemistry, *Tables of standard electrode potentials*. (New York %8 c1978, Wiley, 1978).
51. A. J. Bard, R. Parsons, J. Jordan, C. International Union of Pure and Applied, *Standard potentials in aqueous solution*. (New York %8 1985, M. Dekker, 1985).
52. X. Teng, H. Yang, Synthesis of platinum multipods: An induced anisotropic growth. *Nano Letters* **5**, 885-891 (2005).
53. S. Lim *et al.*, Synthesis of Platinum Cubes, Polypods, Cuboctahedrons, and Raspberries Assisted by Cobalt Nanocrystals. *Nano Letters* **10**, 964-973 (2010).
54. J. M. Gohndrone *et al.*, Ammonia adsorption and decomposition on several faces of platinum. *Journal of Vacuum Science & Technology A* **7**, 1986-1990 (1989).
55. G. Novell-Leruth, A. Valcarcel, A. Clotet, J. Ricart, J. Perez-Ramirez, DFT characterization of adsorbed NH_x species on Pt(100) and Pt(111) surfaces. *Journal of Physical Chemistry B* **109**, 18061-18069 (2005).
56. M. Bele *et al.*, A highly active PtCu₃ intermetallic core-shell, multilayered Pt-skin, carbon embedded electrocatalyst produced by a scale-up sol-gel synthesis. *Chemical Communications* **50**, 13124-13126 (2014).
57. A. Holewinski, S. Linic, Elementary Mechanisms in Electrocatalysis: Revisiting the ORR Tafel Slope. *Journal of the Electrochemical Society* **159**, H864-H870 (2012).
58. E. Coleman, M. Chowdhury, A. Co, Insights Into the Oxygen Reduction Reaction Activity of Pt/C and PtCu/C Catalysts. *Acs Catalysis* **5**, 1245-1253 (2015).
59. *Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan* (2017).
60. S. Kumar, S. Zou, Electroreduction of O₂ on uniform arrays of Pt and PtCo nanoparticles. *Electrochemistry Communications* **8**, 1151-1157 (2006).
61. M. Nesselberger *et al.*, The effect of particle proximity on the oxygen reduction rate of size-selected platinum clusters. *Nature Materials* **12**, 919-924 (2013).

62. S. Taylor, E. Fabbri, P. Levecque, T. Schmidt, O. Conrad, The Effect of Platinum Loading and Surface Morphology on Oxygen Reduction Activity. *Electrocatalysis* **7**, 287-296 (2016).
63. M. Jha *et al.*, Hydrometallurgical recovery/recycling of platinum by the leaching of spent catalysts: A review. *Hydrometallurgy* **133**, 23-32 (2013).
64. H. Dong, J. Zhao, J. Chen, Y. Wu, B. Li, Recovery of platinum group metals from spent catalysts: A review. *International Journal of Mineral Processing* **145**, 108-113 (2015).