Enhanced Activity for Oxygen Reduction Reactions by Carbon-supported High-index-facet Pt-Ti Nanoparticles

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ABSTRACT
Pt-Ti alloy nanoparticles (NPs) were synthesized over carbon-black supports via a wet-chemistry route. The prepared Pt-Ti NPs were atomically disordered and surrounded by high-index facets to have a spherical form. Controlled vacuum-annealing yielded atomically ordered Pt0.75Ti0.25 NPs, which were surrounded by the low-index {111} facets. The spherical Pt-Ti NPs exhibited enhanced activity than pure Pt NPs or even faceted Pt0.75Ti0.25 NPs toward the electrochemical oxygen-reduction reaction (ORR).

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Keywords : Oxygen Reduction Reaction, Pt-Ti Alloy, High-index Surface

1. Introduction

Polymer-electrolyte membrane fuel cells (PEMFCs) are attracting increasing interest as an energy source for electric vehicles and mobile electronics.1 However, PEMFCs have been precluded from wide applications because state-of-the-art PEMFCs use a large amount of platinum (Pt) catalysts especially at the cathode to promote the oxygen-reduction reaction (ORR).2 Alloying Pt and late-d-transition metals such as cobalt (Co) improves the ORR activity because of the optimized surface d-band structure, but poses a problem of segregation and/or leaching which degrades the catalytic performance.3 Alloy phases of Pt and early-d-transition metals (Pt–T) atoms significantly stabilize the surface by forming low-index facets (the formation enthalpy \(\Delta H_f\) of PtTi: \(\Delta H_f = -298 \text{kJ mol}^{-1}\) of Ti; \(\Delta H_f = -12 \text{kJ mol}^{-1}\) of Co). However, the ORR over Pt-T is usually sluggish because the surface energy of the low-index Pt-T facets is too low to efficiently promote decomposition or desorption of hydroxyl admolecules (OH).4–8

Herein, we report that intermetallic Pt-T can, when rationally synthesized in spherical nanoparticles (NPs, particle size \(\sim 3 \text{nm}\)) bearing high-index facets, exhibit an enhanced ORR activity. Room-temperature reduction of Pt and Ti precursors in an apotic solvent dispersing carbon black (CB) successfully yielded spherical Pt-Ti alloy NPs over the CB support (Pt-Ti NPs/CB, Pt:Ti = 0.75:0.25). The Pt-Ti NPs were then annealed in vacuum at different temperatures up to 900°C to promote faceting of the NPs, retaining the chemical composition and particle size. Polyhedral Pt-Ti NPs, which were predominantly surrounded by the low-index \{111\} facets, were obtained at temperatures higher than 600°C. The Pt-Ti NPs/CB showed higher activity than CB-supported Pt NPs (Pt NPs/CB) or even polyhedral Pt-Ti NPs toward the ORR because the high-index surface of Pt-Ti NPs weakly adsorbs the OH groups at active sites on kinks and/or edges.

2. Experimental

An organometallic Pt precursor, Pt(1,5-cyclooctadiene)Cl2 (99%) was purchased from STREM Chemicals. TiCl4 (99%) was purchased from Kishida Chemicals to prepare a Ti precursor, Ti(tetrahydrofuran)4Cl4. Sodium metal and naphthalene were gotten to prepare a reducing agent sodium naphthalide from NIPPON SODA CO. LTD. and JEF Chemical Corporation. Tetrahydrofuran (THF, anhydrous, 95%) was also used as purchased from Sigma-Aldrich. The chemicals and solvents were always treated in a dry Ar atmosphere. The precursor for Ti, Ti(tetrahydrofuran)4Cl4, was synthesized from TiCl4 and distilled THF according to literature procedures.9–11 Precursor solutions were prepared by dissolving 0.04 mmol (14.89 mg) of Pt(1,5-cyclooctadiene)Cl2, 0.16 mmol of Ti(tetrahydrofuran)4Cl4 (53.42 mg) and 250 mg of CB (Vulcan XC-72R (E-TEK)) in 20 mL of distilled THF under a dry Ar atmosphere. The precursor solutions were then transferred into a syringe. Again under a dry Ar atmosphere, 0.72 mmol of sodium metal and 0.72 mmol of naphthalene were added into a two-neck flask containing 20 mL of distilled THF. One of the two necks of the flask was capped with a rubber septum. A darkgreen solution of sodium naphthalide was obtained by stirring the solution overnight at room temperature under a dry Ar atmosphere. The precursor solution was injected through the septum into the two-neck flask.
containing the stirred sodium naphthalide solution. The sodium naphthalide solution turned dark brown immediately upon injection. After stirring overnight, the solution was distilled off at a reduced pressure to leave a dark-brown precipitate. The precipitate was washed with hexanes and methanol in sequence to remove byproducts, such as naphthalene and NaCl, again under a dry Ar atmosphere. After each washing step, the precipitate was separated from the washing solvent by centrifugation without air exposure. The final precipitates were dried by evacuation at room temperature. The products were air-stable, black powders.8–11 The Pt-Ti NPs/CB was annealed in vacuum at different temperatures for 1 hour. Pt NPs/CB was also prepared by a wet-chemical approach using lithium triethylborohydride as a reducing agent. 0.04 mmol (14.89 mg) of Pt(1,5-cyclooctadiene)Cl2 and 250 mg of CB were dissolved in an anhydrous THF solution in Ar atmosphere. These suspensions were stirred for 0.5 h. Then 2 mmol of lithium triethylborohydride was transferred in the precursor solutions by a Schlenk line. The solutions were stirred for 15 h to complete the reaction under Ar-atmosphere. The suspension were centrifuged for 10 min at 6000 rpm, and then subsequently washed with 20 mL of anhydrous methanol for three times, finally dried under vacuum. Powder X-ray diffractometry (pXRD) was performed using CuKα radiation (Panalytical X’Pert PRO; λ = 0.1548 nm) with an increment of 0.02 degrees in a range of diffraction angles from 20 to 80 degrees. An obliquely finished Si crystal (non-diffraction Si plate) was used as a sample holder to minimize the background. Hard X-ray photoemission spectroscopy (HX-PES) was performed using an X-ray with photon energy of 5.95 keV at BL15XU of SPring-8, Japan. Sample powders were first dispersed in ethanol or and dropped onto carbon substrates. The sample was thoroughly dried in air and transferred into an ultra-high-vacuum (UHV) chamber equipped with an electron spectrometer (Vacuum Generator, Scienta R4000). The binding energy of photoelectrons was referenced to the Fermi energy of an Au film that was electrically connected to the sample. All the starting materials for bulk Pt0.75Ti0.25 alloy were purchased from Furuya Kinzoku Co. Stoichiometric amounts of Pt (99.9%) and Ti (99.999%) were melted together in a pure Ar (99.9999%) atmosphere and cooled to room temperature. A 200 kV transmission electron microscope (TEM and/or STEM, JEM-2100F, JEOL) equipped with two aberration correctors (CEOS GmbH) for the image- and probe-forming lens systems and an X-ray energy-dispersive spectrometer (JED-2300T, JEOL) for compositional analysis was used. Both the aberration correctors were optimized to realize the point-to-point resolutions of TEM and scanning transmission electron microscopy (STEM) as 1.3 and 1.1 Å, respectively. A probe convergence angle of 29 mrad and a high-angle annular-dark-field (HAADF) detector with an inner angle greater than 100 mrad were used for HAADF-STEM observation. The chemical composition of the CB-supported Pt-Ti NPs was determined using inductively coupled plasma-mass spectrometry (ICP-MS, PE-3300 DV).

An aliquot of 1 mg of Pt-Ti NPs/CB was suspended in a solution of 995 µL distilled water and 250 µL isopropanol alcohol. Additionally, 5 µL of a 5% w/w Naflon® solution (EW: 1,100, Aldrich) in alcohols was added to this suspension. The resulting suspension was sonicated for 1 hour. The suspension was coated onto a 5-mm-diameter glassy carbon (GC) electrode. Prior to performing electrochemical measurements, the electrodes were pre-treated by cycling the potential between −0.2 and +1.2 V twenty times at 10 mV s⁻¹ in 0.1 M H2SO4. The ORR activities of Pt-Ti NPs/CB and Pt NPs/CB were subsequently examined in O2-saturated 0.1 M H2SO4 using a three-electrode cell with a NaCl-3 M Ag/AgCl reference electrode. The electrochemical tests were performed at room temperature (23 ± 1°C), at a sweep rate of 10 mV s⁻¹ and a rotation speed of 2000 rpm.

Figure 1. pXRD patterns of as-prepared Pt-Ti NPs/CB, the materials annealed at 100–900°C and CB. The solid bars at the bottom are simulated pXRD peaks for the FCC-type structure of Pt0.75Ti0.25 alloys.

Figure 2. HX-PES spectra in the Pt 3d region for (a) Pt NPs/CB, (b) FCC-type Pt0.75Ti0.25 bulk, (c) as-prepared Pt-Ti NPs/CB and (d) annealed 900°C Pt-Ti NPs/CB.

3. Results and Discussion

Figure 1 shows the powder X-ray diffraction (pXRD) profiles for Pt-Ti NPs/CB, the materials annealed at 100–900°C and CB. A simulated pXRD pattern for the FCC-type Pt0.75Ti0.25 alloy phase (Fm3m, a = 0.390 nm) is indicated by solid bars.12 The pXRD profile for CB shows two intense peaks at 25.0° and 43.5° in 2θ corresponding to the 002- and 101 diffractions of carbon. With increasing the annealing temperature, in addition to these two major peaks, two shoulders became intense at 40° and 47°, which were assigned to the 111- and 200 diffractions of the FCC-type Pt0.75Ti0.25 alloy phase. The enhanced pXRD diffractions of the annealed Pt-Ti NPs/CB may be ascribed to either development of atomic ordering or particle growth.

Figure 2 shows the hard X-ray photoemission spectroscopy (HX-PES)13 profiles in the Pt 3d region for the reference Pt NPs/CB (a), bulk Pt0.75Ti0.25 alloy (b) and the as-prepared (c) and annealed (d, 900°C) Pt-Ti NPs/CB, respectively. It was confirmed by pXRD that the bulk Pt0.75Ti0.25 has a pure phase of FCC type structure.10,11 The Pt 3d5/2 peak for the bulk Pt0.75Ti0.25 was +0.3 eV lower in binding
energy in comparison with that of Pt NPs. The Pt 3d$_{3/2}$ peaks for the as-prepared and annealed Pt-Ti NPs/CB were consistent with the bulk Pt$_{0.75}$Ti$_{0.25}$, indicating that the chemical composition and average atomic environment of both the as-prepared and annealed Pt-Ti NPs/CB were the same as those of the bulk Pt$_{0.75}$Ti$_{0.25}$.

Figure 3 presents transmission electron microscope (TEM) images of the (A, C) Pt-Ti NPs/CB and (B, D) of the material annealed at 900°C. The Pt-Ti NPs in Pt-Ti NPs/CB appear as dark spots, which are uniformly dispersed over the CB support (Fig. 3A). The average particle size of the Pt-Ti NPs was evaluated to be 2.15 nm (inset) with a hundred of the particles in the TEM image. The high-resolution TEM image and the corresponding fast-Fourier transformation (FFT) pattern (Fig. 3C and its inset) demonstrate that the Pt-Ti NPs had an FCC-type structure, as expected from XRD, and a spherical form that was surrounded by high-index facets. After annealing at 900°C, the Pt-Ti NPs were almost similar in the degree of dispersity over the CB support although the average particle slightly increased to 2.65 nm by thermal agglomeration of small number of the NPs (Fig. 3B and its inset). The CB support inhibited thermal agglomeration. However, the Pt-Ti NPs on the sample annealed at 900°C were, unlike the as-prepared Pt-Ti NPs, exhibited clear lattice fringes as the result of improved crystallinity although a small amount of Pt NPs are immobilized, block the diffusion of ORR even if high active Pt electrocatalysts were coated on GC electrode as Markovic showed.14 In this study, Pt NPs/CB having high-index and low-index facets, and the as-prepared Pt-Ti NPs/CB sample having high-index facets were compared in the ORR activity.

Compositional mapping with a scanning transmission electron microscope (STEM) demonstrated the uniform distribution of Pt and Ti in the Pt-Ti NPs. STEM-energy dispersive spectroscopy (EDS) mappings have also demonstrated that the average mole ratios of Pt to Ti for both the as-prepared and annealed Pt-Ti NPs/CB were consistent with the desired value for Pt$_{0.75}$Ti$_{0.25}$. Pt:Ti = 73.7:26.3 for as-prepared Pt-Ti NPs, and = 74.4:25.6 for annealed 900°C Pt-Ti NPs (Fig. 4). ICP-MS showed that the weight percentages of Pt in Pt-Ti NPs/CB and Pt NPs/CB were 1.9 wt%.

Figure 5 shows linear-sweep voltammograms for (a) the Pt-Ti NPs/CB and those annealed Pt-Ti NPs/CB at (b) 300, (c) 500 and (d) 900°C in an oxygen-saturated 0.1 M H$_2$SO$_4$ solution. Here, CB-supported Pt NPs (Fig. 5e) were used as a control. The ORR curves obtained with CB-supported Pt- and Pt-Ti NPs have relative broad shapes when compared with the curves reported in other paper with the same sulphuric acid concentration. Therefore, the strange shapes will give some doubt that Pt NPs (or Pt-Ti NPs) used in this study do not exhibit the reliable data for ORR. However, we would like to stress that the broad shapes for ORR in this study come from much lower loading of Pt atoms (0.95 µg cm$^{-2}$) on GC electrodes with 1.9 wt% Pt NPs/CB or 1.9 wt% Pt-Ti NPs/CB. Low loading of electrocatalysts on the electrodes cause apparent sluggish kinetics of ORR even if high active Pt electrocatalysts were coated on GC electrode as Markovic showed. In this study, Pt NPs/CB and Pt-Ti NPs/CB having much lower loading of Pt on CB should be synthesized to prevent these NPs on CB from agglomerating by heat-treatment for changing the degree of crystallinity of Pt-Ti NPs. When the samples having much lower Pt loading on CB were fixed with high Pt loading on the GC electrode to increase the sharpness of voltammogram curve, in reverse, the shape of ORR curves degenerates into broad shapes because a deal of CB particles, on which small amount of Pt NPs are immobilized, block the diffusion

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**Figure 3.** TEM images of (A, C) the as-prepared Pt-Ti NPs/CB and (B, D) the Pt-Ti NPs/CB annealed at 900°C. (C, D) are the magnified images of individual Pt-Ti NPs in (A, B). The insets in (A, B) provide the histograms of size distribution for the as-prepared and annealed Pt-Ti NPs. The insets in (C, D) show the FFT pattern obtained from (C, D). The weight percentages of Pt atom in as-prepared and annealed Pt-Ti NPs/CB were 1.9 wt%.
of molecular oxygen to the catalyst surfaces. Therefore, we have no choice but to set experimental conditions with Pt loading of 0.95 µg cm$^{-2}$ on the GC electrodes. Our experimental conditions and evaluation basis deviates from the standard protocol for analyzing the ORR activity. Naturally, we confirmed that 20 wt% Pt NPs/CB could exhibit the reliable data for ORR when 20 wt% Pt NPs/CB was synthesized with our procedure for Pt NPs/CB. Our 1.9 wt% Pt NPs/CB are a reliable sample for ORR activity tests. The Pt loading, NP average size and degree of dispersion of NPs on CB in the 1.9 wt% Pt NPs/CB sample was strictly controlled with the similar particle conditions to that of Pt-Ti NPs/CB to strictly compare the ORR activity between Pt-Ti NPs/CB and Pt NPs/CB. We think that not so much the high loading condition as the low loading condition of catalysts will lead to clear difference of electrocatalytic activity. The two facts that the sample annealed at 900°C is the mixture of NPs having high-index and low-index facets and that NPs size of the sample annealed at 900°C slightly increases should be considered in the comparison with the voltammograms obtained with the annealed and as-prepared samples. The surface area of NPs increased 1.5 times after annealing at 900°C. The balance between positive factor of the incorporation of NPs having high-index facets in the annealed samples and negative factor of the increase in the surface area of the NP catalyst for the enhancement of ORR determines the sharpness of voltammogram curve for ORR of Fig.5(d). The difference in the surface area of NPs is thought to have little effect on the sharpness of the voltammograms because the O$_2$ diffusion layers formed adjacent to the NP surfaces grow and then three-dimensional diffusion occurs around the NPs even in the lower overpotential. Therefore, the curve d obtained with the 900°C-annealed sample should be shifted to the negative potential direction if the sample were composed of only NPs having low-index facets. The onset potential of the Pt-Ti NPs/CB, 0.880 V (Fig. 5a), was $+35$ mV higher than that of the Pt NPs, 0.845 V (Fig. 5e). The Pt-Ti NPs exhibited higher ORR activity than the Pt NPs and 900°C-annealed Pt-Ti NPs based on the lower onset potential and sharpness of ORR curves. The onset potential for the 900°C-annealed Pt-Ti NPs, 0.866 V, was higher than the corresponding value for the Pt NPs. Although identical to the 900°C-annealed Pt-Ti NPs in particle
size, chemical state, Pt loading weight and dispersity on the CB, the Pt-Ti NPs were superior in their ORR activity to all the other NPs. Our results clearly indicate that the disordered atomic arrangement in the Pt-Ti NPs, which is accessible only through low-temperature routes, significantly enhances the ORR activity. The same results for ORR with Pt-Ti and Pt NPs could be obtained with 0.1 M HClO₄ aqueous solutions.

Jennings et al. computationally evaluated the adsorption energy of OH groups to the surface, \( |E_{\text{ads}}| > 0 \), of a truncated-octahedron cluster, Pt₃₂Ti₆, whose composition is close to that of the Pt-Ti NPs. The authors have demonstrated that \( |E_{\text{ads}}| \) for the Pt₃₂Ti₆ cluster is always lower than that for pure Pt clusters, excluding the case in which OH groups are located at the intersection of the \{100\} and \{111\} surfaces. According to the theoretical results, the Pt-Ti NPs had lower \( |E_{\text{ads}}| \) than pure Pt NPs because they were ellipsoidal in shape and had neither clear facets nor intersections of facets (Fig. 3C). It is known that the sluggish ORR over Pt catalysts is due to strong OH adsorption to the surface. The lowe \( |E_{\text{ads}}| \) for the Pt-Ti NPs was most likely the most important factor in the enhanced ORR activity of the material (Fig. 5a). The 900°C-annealed Pt-Ti NPs were highly atomically ordered and surrounded by the \{111\} and \{100\} facets (Fig. 3D). Again according to the theoretical results, \( |E_{\text{ads}}| \) for the bridge/hollow sites of the 900°C-annealed Pt-Ti NPs can be very high at the \{100\}\{111\} intersection. Therefore, we conclude that the catalytic degradation observed in the 900°C-annealed Pt-Ti NPs is attributed to strong OH adsorption onto the bridge/hollow-sites at the \{100\}\{111\} intersection, which can inhibit smooth migration or desorption of OH on the surface.

4. Conclusions

Pt₀.₇₅Ti₀.₂₅ alloy catalysts, differing only in atomic ordering, were successfully prepared on CB supports through a wet chemistry approach. The room-temperature-synthesized, atomically disordered Pt₀.₇₅Ti₀.₂₅ NPs (Pt atom loading on GC: 0.95 µg cm⁻²) exhibited a +60 mV shift in the onset potential for ORR compared with the control Pt NPs. The ORR specific activity of the Pt₀.₇₅Ti₀.₂₅ NPs was significantly higher than that of either the Pt NPs or the post-900°C-annealed Pt₀.₇₅Ti₀.₂₅ NPs with an enhanced atomic order.

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