Enhanced electrocatalytic performance due to anomalous compressive strain and superior electron retention properties of highly porous Pt nanoparticles

Dae-Suk Kim, Cheonghee Kim, Jung-Kon Kim, Jun-Hyuk Kim, Ho-Hwan Chun, Hyunjoo Lee, Yong-Tae Kim

School of Mechanical Engineering, Pusan National University, Busan 609-735, Republic of Korea
Department of Chemical and Biomolecular Engineering, Yonsei University, Seoul 120-749, Republic of Korea
School of Mechanical Engineering, Pusan National University, Busan 609-735, Republic of Korea

Abstract
The shape and structure of electrocatalysts at the nanoscale level have a decisive effect on their activity and durability in low-temperature fuel cells. Herein, we report the discovery of unexpected structural phenomena in exotic nanostructures: the anomalous compressive strain and superior electron retention properties of highly porous Pt (HP-Pt) nanoparticles synthesized using a weakly interacting organic capping agent, tetradecyl trimethyl ammonium bromide. Even though the particle size of the HP-Pt nanoparticles was much larger than those of commercial electrocatalysts, bond length shortening occurred anomalously, and the downshifted d-band center eventually led to increased oxygen reduction reaction activity. This is because the HP-Pt nanoparticles had a highly porous urchin-like dendritic structure, interestingly in the single-crystalline phase, despite the large particle size. In addition, their electron retention properties were superior to those of commercial samples, which led to drastically enhanced stability against Pt dissolution at high potentials.

1. Introduction
One of the most serious hurdles to be overcome in the commercialization of proton exchange membrane fuel cells (PEMFCs) is the considerable activation loss in the cathode because of the slow kinetics of the oxygen reduction reaction (ORR), which in turn results in a large amount of Pt usage for cathode electrocatalysts and thereby increases the production cost of such fuel cells [1,2]. Furthermore, the rather fast deterioration of the cathode electrocatalysts, mainly due to both Pt dissolution and coalescence, makes it difficult to meet the US Department of Energy targets for durability: 5000 h for transportation and 40,000 h for stationary applications [3,4]. For these reasons, considerable effort has been devoted toward enhancing the ORR activity and durability of Pt-based cathode electrocatalysts for PEMFCs.

The most widely considered idea is alloy formation (with either solid-solution or phase-segregated structures) with various transition metals. Representative alloys reported to date include a Pt3Co solid solution [5], Pt3Ni [6], Pt modified with Au clusters [4], a PtCu phase-segregated structure [7], and Pt-on-Pd nanodendrite systems [8]. Although these alloys have shown enhanced ORR activity (due to the compressive strain effect caused by alloying with transition metals having small atomic radii and the ligand effect caused by the overlapping of electronic structures), leaching of the transition metals, which is considered to be one of the most serious problems in terms of durability, is inevitable in most alloy electrocatalysts (except for some phase-segregated alloys).

Another challenge in improving the ORR activity and durability is controlling the shape of the electrocatalyst particles, which can exist as spheres [9], cubes [10], tetrahedra [11], cages [12], wires [13], and sheets [14]. In particular, dendritic nanoparticles have been synthesized intensively [15] and evaluated for various electrocatalytic reactions, including oxygen reduction [8] and small-molecule oxidation [16], because these nanoparticles have a highly porous structure, which leads to a large surface area per unit mass.

Lim et al. reported that Pd–Pt bimetallic nanodendrites synthesized by the seed-growth technique demonstrated an activity 2.5 times higher than that of commercial Pt/C [8]. They concluded that
the enhanced ORR activity was attributable to an increase in the surface area caused by the dendritic shape and the facets like Pt(1 1 1) preferred for the ORR. The degree of durability enhancement was relatively less remarkable than the activity increase, and the authors did not discuss in detail the mechanism of such an improvement. Similarly, Peng and Yang demonstrated the enhanced ORR activity and durability of Pt-on-Pd dendritic nanoparticles formed through a sequential synthetic method [15]. They elucidated that the origin of the ORR activity enhancement was the improved tolerance against OH poisoning, which was indicated by the positive shift of the onset and peak potentials for hydroxyl ion adsorption during the forward sweep in cyclic voltammetry (CV). They also suggested that the durability enhancement could be explained by the favored interfacial structures between the Pt and Pd supports and the larger particle size of the Pt-on-Pd nanoparticles. However, in most papers on dendritic nanoparticles, little discussion has been provided on the most essential origin of performance enhancement, such as the compressive strain effect for ORR activity [7] and the electron retention property identified by the d-band vacancy change at high potentials for durability [4,17].

In this report, we discover the unexpected structural phenomena in exotic nanostructures, that is, the anomalous compressive strain and superior electron retention properties of highly porous Pt (HP-Pt) nanoparticles synthesized using a weakly interacting organic capping agent, tetradecl trimethyl ammonium bromide (TTAB). To date, most studies on the formation of highly porous or dendritic nanoparticles have employed surfactants or polymers with strong interactions with metal surfaces, which were difficult to remove and may have acted as surface poisons [18,19]. However, since TTAB can be removed readily from the nanoparticle surfaces, it was expected that enhanced electrocatalytic performance could be demonstrated. In order to elucidate the origin of the enhanced ORR activity and durability for HP-Pt nanoparticles, we performed a precise analysis of their fine structures and electronic energy states. From various synchrotron studies, it was found that compressive strain was exerted on the lattice, influencing the d-band center position; the d-band vacancy, which affects the oxidation potential, hardly changed at high potentials. For an in-depth analysis of the ORR activity enhancement resulting from the small compressive strain-induced change in the lattice constant, we employed fine-structure analysis techniques like high-resolution powder diffraction (HRPD) with Rietveld refinement and extended X-ray absorption fine structure (EXAFS) measurements with FEFF analysis using a synchrotron beam. Furthermore, in order to understand the origin of the stability against Pt dissolution through examination of the d-band vacancy change, we investigated the change in the white line in the Pt L3 absorption edge in detail by applying potential steps using the in situ X-ray absorption near-edge structure (XANES) technique; we used a specially designed homemade measurement cell for this analysis. In the study, the electrocatalytic properties of HP-Pt nanoparticles are compared with those of several commercial samples, such as Pt/C E-TEK, Pt/C E-TEK (300) (samples of Pt/C E-TEK heat-treated at 300 °C in a hydrogen atmosphere in order to maximize the durability), and Pt/C Premetek.

2. Experimental section

2.1. Catalyst synthesis

In a typical synthesis, aqueous solutions of 20 mM K2PtCl4 (98%, Aldrich) solution 1 mL, 400 mM tetradecltrimethylammonium bromide (TTAB; 99%, Aldrich) solution 1.25 mL and 7.25 mL of DI water were mixed in a 20-mL vial at room temperature. The mixture was heated at 90 °C for about 5 min until the solution became clear. When the solution became clear, 120 mM L-ascorbic acid (99%, Aldrich) solution 0.5 mL as the reducing agent was injected, and the solution was maintained at 90 °C for 7 hrs. The total volume of the solution was maintained at 10 mL, and final concentrations were 2 mM for K2PtCl4, 50 mM for TTAB, and 6 mM for L-ascorbic acid. The product was centrifuged at 3000 rpm for 30 min. The supernatant solution was separated and centrifuged again at 12,000 rpm for 10 min. The precipitate was collected and redispersed in 5 mL of deionized (DI) water by sonication. For the preparation of carbon-supported 20 wt.% HP-Pt nanoparticles, carbon supports (Vulcan XC-72R) were dispersed in DI water by sonication at a frequency of 70 kHz for 10 min. After sonication, the prepared HP-Pt nanoparticles, equivalent to 20% weight ratio of carbon, were dispersed in the above solution by stirring for 5 h. The precipitate was filtered and washed several times with DI water and ethanol and dried overnight in a vacuum oven at 50 °C. Commercial Pt/C E-TEK, Pt/C E-TEK annealed at 300 °C for 1 h (called Pt/C E-TEK (300)), and Pt/C Premetek with a metal loading of 20 wt.% were employed for comparison with the HP-Pt nanoparticles.

2.2. Catalyst characterization

The morphologies of the electrocatalyst samples were investigated using transmission electron microscopy (TEM, JEOL JEM-2100). Specimens for TEM observation were prepared by placing a drop of the particle-dispersed solution onto a copper grid. The microscope system was operated at an accelerating voltage of 200 keV. Two hundred nanoparticles randomly selected from the TEM images were used to measure the average size of each sample. The indexes of the surface facets and lattice fringes of the Pt nanoparticles were determined from high-resolution transmission electron microscopy (HRTEM) and Fourier transform data. All the images were recorded with a charge-coupled device (CCD) camera.

X-ray diffraction (XRD) experiments on the synthesized powders were carried out using the synchrotron radiation of the 8C2 HRPD beamline at Pohang Light Source (PLS). The incident X-rays were monochromatized to a wavelength of 1.5495 Å by a double-bounce Si(1 1 1) monochromator. The diffraction pattern was scanned in the 2θ range of 10–151°, with a counting time of 4 s per 0.02°. Scherrer's equation was used to estimate the particle size from the XRD results. For this purpose, the (1 1 1) peak of the Pt face-centered cubic (FCC) structure at 2θ = 40° was selected. The XRD patterns were analyzed by the Rietveld refinement program Fullprof [20] to determine the lattice parameters of the synthesized powders. From all the profiles in the Fullprof program, a pseudo-Voigt function was selected as the profile function.

X-ray photoelectron spectroscopy (XPS) experiments were performed at the PLS 8A1 undulator (U7) beamline equipped with a variable-included angle plane-grating monochromator. The incident photon energy was 630 eV, and photoelectrons emitted from the surface of the Pt/C electrocatalysts, which were adhered to the carbon tape, were collected, and their energies were analyzed by an electron analyzer (Physical Electronics: Model PHI 3057 with an Omega lens and a 16-channel detector). Although Ar-ion bombardment cleans the sample surface, it also produces some negative effects, such as variation of the surface topography and preferential sputtering; hence, we did not clean the sample surface by Ar-ion bombardment. The binding energies of the photoemission spectra were calibrated using the peak position of the Au 4f line at 84.0 eV from a standard Au sample located next to the sample of interest. The XPS binding energies were analyzed using the XPS spectral data processing software XPS International to process the distribution of the Pt species and the relative intensities of the synthesized powder. Details of fitting analysis are provided in Fig. S2 of Supporting information.
Pt L₃ edge (11,564 eV) X-ray absorption spectroscopy (XAS) spectra were recorded at the BL7C1 beam line of PLS with a ring current of 120–170 mA at 2.5 GeV. A Si(1 1 1) double-crystal monochromator was employed to monochromatize the X-ray photon energy. The data were collected in the transmission mode with He and N₂ gas-filled ionization chambers as detectors. Higher-order harmonic contamination was eliminated by using detuning to reduce the incident X-ray intensity by ca. 40%. Energy calibration was completed using standard Pt foil. Every experiment on the Pt/C electrocatalysts was conducted using a homemade measurement cell with an aluminum holder for the XAS powder experiments. The in situ XANES data were recorded using a potentiostat (Biologic VSP) via chronoamperometry measurements with potential steps in N₂-saturated 0.1 M HClO₄ solutions. All the spectra were recorded at room temperature. The spectra were processed using the program IFEFFIT [21] (IFEFFIT version 1.2.11, Copyright 2008, Matthew Newville, University of Chicago, http://cars9.uchicago.edu/ifeffit/) with background subtraction (AUTOBK) [22] and normalization. The phase shift and back-scattering amplitude were calculated theoretically using the FEFF 9.03 code [23]. Fourier transform for the EXAFS spectra was performed in the range of approximately 2.5–16 Å⁻¹ in k-space and 1–3 Å in the R window. From these analyses, structural parameters such as the coordination number (N), bond distance (R), Debye–Waller factor (Δσ²), and inner potential shift (∆Eo) were calculated.

2.3. Electrochemical measurements

All electrochemical measurements were performed in a three-electrode electrochemical cell connected to a potentiostat (Biologic VSP) at room temperature. A glassy carbon electrode (5 mm in diameter) was used as the working electrode; it was polished with diamond solution and Al₂O₃ slurries and then washed in DI water with sonication before the experiments. HP-Pt/C powder (2 mg) was dispersed well in DI water (2 mL) using an ultrasonicator, and 20 μL of the dispersion was dropped onto the glassy carbon electrode with a micropipette to afford a Pt loading of 20 μg/cm² on the electrode. Uniform, thin HP-Pt/C films were prepared by evaporating the water at room temperature. Nafion solution (0.025 wt.%, 20 L) was dispersed well in DI water (2 mL) using an ultrasonicator, and 20 μL of the dispersion was dropped onto a suspension-dried glassy carbon electrode and dried in a vacuum oven at 70 °C for 30 min. A Pt wire and a silver chloride electrode (Ag/AgCl sat. 3.5 M KCl) were used as the counter and reference electrodes, respectively. The Ag/AgCl reference electrode was calibrated on a daily basis for the two samples. This indicated that a compressive lattice strain was exerted on the lattice, which could lead to a change in the electronic structure and thereby in the electrocatalytic activity [7].

3. Results and discussion

3.1. Basic morphology and structure of HP-Pt nanoparticles

The morphology and lattice structure of the HP-Pt nanoparticles were identified from the bright-field and dark-field TEM images. As shown in Figs. 1a–c, the commercial samples are spherical with a size of about 3–4 nm. On the other hand, the HP-Pt nanoparticles shown in Fig. 1d have urchin-like dendritic shapes and are highly porous, with an average diameter of about 13 nm. Fourier transformation of the dark-field image obtained by TEM allows us to image the reciprocal lattice points for the hkl planes and thereby enables us to analyze the lattice structure and check the morphology simultaneously. It is interesting to note that the reciprocal lattice points, rather than the Ewald circle, are clearly shown in the Fourier-transformed dark-field image, as seen in the inset of Fig. 1e. This implies that the HP-Pt nanoparticles are not polycrystalline secondary particles but primary particles with lattice structures in the single-crystalline phase. Furthermore, the facets of the HP-Pt nanoparticles are identified to consist of Pt(1 1 1) and (1 1 0) rather than (10 0) or high-index planes, as observed in Fig. 1f.

This understanding is also supported by the HRPD patterns obtained using a synchrotron beam followed by Rietveld refinement. Fig. 2a shows the HRPD patterns and the reflection peaks, indexed as (1 1 1), (2 0 0), (3 1 1), (2 2 2), (3 3 1), and (4 2 0), corresponding to face-centered cubic Pt with a lattice constant a = 3.930 Å (PDF standard cards, JCPDS 10-1311, space group Fm3m[225]). The average particle size of the electrocatalysts was calculated from the full-width at half-maximum of the Pt(1 1 1) peak using Scherrer’s equation:

\[ d = \frac{k \lambda}{β \cos θ} \]  

where \( d \) is the average particle size (Å); \( k \), the shape-sensitive coefficient (0.9); \( λ \), the wavelength of the radiation used (1.5490 Å); \( β \), the full-width at half-maximum (in radians) of the peak; and \( θ \), the angle at the position of the peak maximum (in radians). The peak corresponding to Pt(1 1 1) at around 2θ = 40° was used in the calculation of the Lorentzian function. The calculated crystallite sizes were 12.9 nm for HP-Pt nanoparticles, 3.3 nm for Pt/C E-TEK, 6.2 nm for Pt/C E-TEK (300), and 3.8 nm for Pt/C Premetek, which are in good agreement (within the margin of error) with the values evaluated from the TEM images (Table 1). In the Rietveld refinement results, it is interesting to note that the lattice parameter of the HP-Pt nanoparticles is the smallest among those of the four kinds of electrocatalysts studied. In addition, as shown Fig. 2b, the peak position corresponding to hkl (1 1 1) for Pt/Pt/C was shifted to a higher angle in comparison with that for the other commercial samples. This indicates that a compressive lattice strain was exerted on the lattice, which could lead to a change in the electronic structure and thereby in the electrocatalytic activity [7].

3.2. Investigation of ORR activity

In order to investigate the ORR activity of the HP-Pt nanoparticles, we conducted thin-film rotating disk electrode (TF-RDE) measurements [24]. Fig. 3 shows the results of electrochemical measurements for the HP-Pt nanoparticles and several commercial samples. The specific and mass activities of the samples were determined by calculating \( j_k \), the mass-transport-corrected kinetic current. For this calculation, the surface area employed was the electrochemical surface area (ECSA) calculated from the hydrogen adsorption/desorption region in CV, as follows [25]:

\[ \text{ECSA} = \frac{Q_H}{I × q_H} \]
where \( L \) is the catalyst loading (\( \text{µg/cm}^2 \)) on the working electrode; \( Q_o \), the charge for the hydrogen adsorption (mC/cm²), calculated as the mean value of the amounts of charge exchanged during the electroadsorption and electrodesorption of \( \text{H}_2 \) on the catalyst sites after double-layer correction [24]; and \( q_h \), the charge required to oxidize a monolayer of \( \text{H}_2 \) on Pt (0.210 mC/cm²) [26].

As seen in Table 2, both the specific and mass activities of the HP-Pt nanoparticles were higher than those of the commercial samples. At 0.9 V (versus RHE), the specific activity obtained for the HP-Pt nanoparticles was 680.22 A/cm², whereas those for Pt/C E-TEK, Pt/C E-TEK (300), and Pt/C Premetek were 213.13, 84.08, and 223.35 A/cm², respectively. While the trend for the mass activity was almost same as that for the specific activity, the degree of activity enhancement was less appreciable. It should be noted that in the case of the Pt/C E-TEK (300) samples (heat-treated at 300 °C in a hydrogen atmosphere), the limiting current could not reach the theoretical value based on the Levich equation at 1600 rpm. In fact, for Pt/C E-TEK (300) homogeneous thin-film deposition of catalysts on the glassy carbon (working) electrode could not be effected by the aqueous catalyst solution dropping method; this was because unlike in the case of the other samples, the surface of the carbon support after annealing was too inert for the formation of a homogeneous catalyst solution in water. Therefore, the geometric area of the glassy carbon electrode was incompletely filled with the catalyst particles, so that the limiting current could not reach the theoretical value calculated from the Levich equation. Detailed results for the ORR activity evaluation at various rotation speeds are provided in Fig. S1 of Supporting information.

As shown in Fig. 3c, the electrode current densities measured at constant potentials were used to produce a Koutecky–Levich plot [27], which represents the inverse current density (J⁻¹) as a function of the inverse square root of the rotation rate (\( \omega^{-1/2} \)) and indicates the first-order kinetics with respect to molecular oxygen. The Koutecky–Levich equation is written as

\[
\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} = \frac{1}{j_k} + \frac{1}{B \omega^{1/2}}
\]

\[
B = \frac{0.62nFAC_0D_0^{2/3}}{\eta^{1/6}}
\]

where \( j \) is the experimentally obtained current; \( j_k \), the kinetic current; \( j_d \), the diffusion-limited current; \( n \), the number of electrons transferred; \( F \), the Faraday constant (\( F = 96485.3399 \text{ C/mol} \)); \( A \), the geometric area of the electrode (\( A = 0.19625 \text{ cm}^2 \)); \( C_0 \), the \( \text{O}_2 \) concentration in the electrolyte (\( C_0 = 1.26 \times 10^{-3} \text{ mol/L} \)); \( D_0 \), the diffusion coefficient of \( \text{O}_2 \) in HClO₄ solution (\( D_0 = 1.93 \times 10^{-5} \text{ cm}^2/\text{s} \)); and \( \eta \), the viscosity of the electrolyte (\( \eta = 1.009 \times 10^{-2} \text{ cm}^2/\text{s} \)) [28]. The slope of the lines (\( j^{-1} \) versus \( \omega^{-1/2} \)) is \( 1/B \). The calculated value of \( B \) was 0.0915 mA s⁻¹/² for the four Pt/C catalysts, and the number of transferred electrons was calculated to be four for these four kinds of Pt electrocatalysts.

The rate-determining step (RDS) in the ORR is the one-electron-transfer reaction shown below in reaction (5), for which the theoretical Tafel slope is estimated to be -118 mV/decade on the basis of the assumptions that the onset potential is independent of the coverage of surface oxygen species and that the cathodic transfer coefficient is 0.5 [29].

\[
\text{S} + \text{O}_2 + \text{H}^+ + e^- \rightarrow \text{S} - \text{O}_2\text{H}
\]  

The Tafel slope under acidic conditions, in particular in an aqueous HClO₄ solution, in which the anion is hardly adsorbed on the electrode surface, is generally divided into two regions: -59 mV/decade at higher potentials (about 1.0–0.8 V versus RHE) and -118 mV/decade at potentials low enough for the formation of an oxide-free surface. It is well known that such a deviation in the Tafel slope at high potentials in aqueous HClO₄ solution arises from the Temkin condition, where the potential is dependent on the surface coverage of
OH produced by water dissociation [30]. Density functional calculations have shown that the ORR activation energy at the neighboring sites of an adsorbate molecule increases because the identical directions of the induced dipole moments for the oxygen molecules and the adsorbate (OH) species give rise to repulsive forces between them [31]. Therefore, the potential varies with surface coverage in this range, and the Tafel slope is not \(-118\, \text{mV/decade}\) (the value obtained for the one-electron-transfer reaction (RDS), wherein there is no dependence of the potential on surface coverage) but \(-59\, \text{mV/decade}\). The surface oxide is gradually reduced with the cathodic scan, and eventually, the transition occurs at the point where the surface OH coverage cannot have any effect on the shift of the potential. In other words, it occurs at the potential of the transition from the adsorbate (OH) species to face-centered cubic Pt (PDF standard cards, JCPDS 10-1311, space group \(Fm\overline{3}m\)). Therefore, the potential varies with surface coverage in this range, and the Tafel slope is not \(59\, \text{mV/decade}\).

Fig. 2. (a) HRPD patterns for Pt peaks with Rietveld refinement. The reflection peaks, indexed as \((111), (200), (220), (311), (222), (331),\) and \((420)\), correspond to face-centered cubic Pt (PDF standard cards, JCPDS 10-1311, space group \(Fm\overline{3}m\)). (b) Comparison of magnified peak of hkl\((111)\).

### 3.3. Discussion of enhanced ORR activity

It is well known that the catalytic activity is significantly affected by the surface strain that results from changes in the size or shape of catalyst particles or from alloy formation with a base metal that has a different bulk Wigner–Seitz radius [32–34]. This is because the adsorption strength of the adsorbate in the transition state, the key factor determining the catalytic activity, can be tuned with the d-band structure of the catalyst particles, which in turn varies markedly with surface strain. On the basis of the surface strain effect, we found a clue to the origin of the enhanced ORR activity of the HP-Pt nanoparticles in the EXAFS measurements. As seen in Fig. 4a, the peak at around 2.6 Å, corresponding to the Pt–Pt first nearest neighbor (1NN) of the radial distribution function (RDF) for the HP-Pt nanoparticles, was clearly shifted to a lower \(r\) value as compared to that of the commercial samples, indicating that compressive strain was exerted on the lattice of these HP-Pt nanoparticles. Indeed, the \(r\) value for the peak position in the EXAFS RDF is incorrect because of the phase shift for the absorber–neighbor pair, and the exact bond length for the Pt–Pt 1NN should be determined by fitting to the theoretical model using the widely available FEFF code. The obtained bond length was 2.754 Å for the HP-Pt nanoparticles, which was about 0.013 Å shorter than that for the Pt/C E-TEK commercial sample. The detailed EXAFS parameters, such as coordination number, energy shift, and Debye–Waller (DW) factor, can be found in Table 3. In general, it is widely recognized that a smaller particle has a shorter bond distance owing to the increased surface tension [35,36]. Hence, there is a clear inconsistency between our data and this general phenomenon. We believe that this discrepancy is attributable to three factors: the highly porous urchin-like morphology, the single-crystalline phase, and the lower degree of surface oxidation for HP-Pt nanoparticles. Even though the HP-Pt nanoparticle size is about 13 nm, the surface-to-volume ratio is quite higher than that of a spherical particle because of the highly porous urchin-like morphology. It has been reported that a porous structure can lead to compressive strain in the lattice and thereby result in shorter bond lengths [37]. In addition, in spite of their somewhat complicated and porous shapes, which can readily lead to high structural disorder and can be formed from the agglomeration of several primary particles, the HP-Pt nanoparticles are in the single-crystalline phase rather than a polycrystalline phase composed of primary particles. Even though the HP-Pt nanoparticle size is about 13 nm, the surface-to-volume ratio is quite higher than that of a spherical particle because of the highly porous urchin-like morphology. It has been reported that a porous structure can lead to compressive strain in the lattice and thereby result in shorter bond lengths [37]. In addition, in spite of their somewhat complicated and porous shapes, which can readily lead to high structural disorder and can be formed from the agglomeration of several primary particles, the HP-Pt nanoparticles are in the single-crystalline phase rather than a polycrystalline phase composed of primary particles. 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### Table 1

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Average particle size (nm)</th>
<th>Lattice parameter (Å)</th>
<th>Reliability factors</th>
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<tr>
<td>Pt/C E-TEK</td>
<td>3.3</td>
<td>3.91</td>
<td>(R_p = 45.20%, R_{exp} = 40.10%, R_{exp} = 35.10%, S = 1.14)</td>
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<td>Pt/C E-TEK (300)</td>
<td>6.2</td>
<td>3.92</td>
<td>(R_p = 24.80%, R_{exp} = 24.40%, R_{exp} = 15.67%, S = 1.56)</td>
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<tr>
<td>Pt/C Premetek</td>
<td>3.8</td>
<td>3.93</td>
<td>(R_p = 27.20%, R_{exp} = 25.70%, R_{exp} = 16.21%, S = 1.59)</td>
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<tr>
<td>HP-Pt/C</td>
<td>12.9</td>
<td>3.91</td>
<td>(R_p = 24.60%, R_{exp} = 23.20%, R_{exp} = 14.88%, S = 1.56)</td>
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effect caused by the high surface-to-volume ratio, which in turn is due to the exotic urchin-like morphology and the well-ordered single-crystalline phase. Another possible reason for the anomalous short bond length of the HP-Pt nanoparticles is the low degree of surface oxidation resulting from the relatively larger particle size. It has been reported that a high oxidation state of Pt has the effect of increasing the Pt–Pt bond length [41]. Therefore, the high oxidation state of the Pt surface compared to that of the HP-Pt nanoparticles can result in a relatively longer Pt–Pt bond. A lower oxidation state for the HP-Pt nanoparticles can also help in lowering the bond length, although this effect is not so critical. The compressive strain exerted on the lattice of these HP-Pt nanoparticles is consequently thought to be the main origin of the enhanced ORR activity. The increased overlap of the d-band electrons between the metal atoms, brought about by the compressive strain, results in bandwidth broadening, and in order to keep the d-band occupancy fixed, the energy of the d-band electron moves down from the Fermi level. The downshifted d-band center position weakens the adsorption of atomic oxygen, and the ORR activity is enhanced by the decreased overpotential [32–34]. In summary, the origin of the enhanced ORR activity of the HP-Pt nanoparticles is their unique, highly porous and urchin-like dendritic structure, which can give rise to compressive strain owing to the high surface-to-volume atomic ratio.

In addition to the compressive strain effect, the high proportion of advantageous facets for the ORR, such as Pt(111), in the HP-Pt nanoparticles can be considered another reason for the enhanced ORR activity. It is interesting to note that while the mass activity for the HP-Pt nanoparticles was only about 1.4 times higher than those of the commercial samples, the specific activity was over four times higher, as shown in Table 2. This result can be attributed to the fact that the surface of the HP-Pt nanoparticles consists mainly of facets that are advantageous for ORR, like Pt(111) or Pt(110), even though the large particle size leads to a small ECSA. As shown in Fig. 3a, the shape of the CV curve in the hydrogen adsorption/desorption potential region is more rectangular for the HP-Pt nanoparticles than for the commercial samples. This is characteristic of the Pt(111) facet showing the best ORR activity in an acid medium containing non-adsorbing anions [42]. The high proportion of Pt(111) can be also identified from the HRTEM image, as shown in Fig. 1f. Accordingly, while the increase in activity per Pt mass unit was not so high, a massive increase appeared in

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Half-wave potential (V versus RHE)</th>
<th>T (µg/cm²)</th>
<th>ECSA (m²/gPt)</th>
<th>Mass activity (µA/µgPt)</th>
<th>Specific activity (µA/cm²Pt)</th>
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<td>Pt/C E-TEK</td>
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<td>34.63</td>
<td>84.08</td>
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<tr>
<td>Pt/C Premetek</td>
<td>0.85</td>
<td>20</td>
<td>51.08</td>
<td>119.52</td>
<td>223.35</td>
</tr>
<tr>
<td>HP-Pt/C</td>
<td>0.88</td>
<td>20</td>
<td>27.89</td>
<td>204.05</td>
<td>680.22</td>
</tr>
</tbody>
</table>

Fig. 3. (a) CV curves for Pt/C E-TEK and HP-Pt/C nanoparticle catalysts in N₂-saturated 0.1 M HClO₄ solution with a scan rate of 20 mV/s. (b) ORR polarization curves for Pt/C E-TEK, Pt/C E-TEK (300), Pt/C Premetek, and HP-Pt/C in O₂-saturated 0.1 M HClO₄ solution with sweep rate of 5 mV/s and rotation of 1600 rpm. (c) Koutecky–Levich plots for ORR at 0.8 V (versus RHE). (d) Tafel plots for ORR (dashed lines indicate transition potentials from low Tafel slope to high Tafel slope).
the activity per Pt surface area unit. This is in good agreement with a previous report, which stated that the specific activity for ORR increases with the proportion of low-index planes and particle size [43]. Furthermore, Markovic et al. showed that the order of ORR activity of the three low-index facets was Pt[111] ≫ (1 1 0) ≫ (1 0 0) in perchloric acid [42]. Therefore, we can conclude that the high proportion of advantageous facets like Pt[1 1 1] in the HP-Pt nanoparticles is another clear reason for their enhanced ORR activity.

The small proportion of low-coordinated sites can be considered the third origin of the enhanced ORR activity of the HP-Pt nanoparticles; this is because a small proportion of these sites can result in decreased surface oxidation by OH adsorption as identified from the XANES and EXAFS results depicted in Fig. 4. It is widely recognized that for small particle sizes, the proportion of low-coordinated sites increases on the surface, and such sites can hinder the ORR activity by acting as blocking sites with very strong OH adsorption. Mayrhofer et al. reported that the ORR specific activity decreases for small particles with high oxophilicity, because the active sites for oxygen adsorption or O–O splitting are effectively blocked by the strong OH adsorption at these low-coordinated sites [43]. As shown in Fig. 4b, the white line for the commercial samples is much higher and the edge energy ($E_0$) is shifted to the higher side as compared to that for the HP-Pt nanoparticles. Furthermore, there is a strong peak at around $R = 1.6$ Å in the RDF (without consideration of the phase shift in the EXAFS model), corresponding to the Pt–O 1NN peak, for two types of commercial samples (Pt/C E-TEK and Premetek), as seen in Fig. 4a. These results imply that the commercial samples with sizes of 3–4 nm have a high proportion of low-coordinated sites at which OH is prone to be adsorbed by the dissociation of water in the air. However, after the samples were annealed in a reductive atmosphere, the strong peak corresponding to surface oxidation in the EXAFS RDF decreased in size because of the reduction of both the amount of surface hydroxide and the number of unstable low-coordinated sites. In the case of the HP-Pt nanoparticles, the number of low-coordinated sites is small because of the lowest-intensity white line and the lowest absorption energy ($E_0$) in the XANES spectra and the absence of the oxidation peak in the EXAFS RDF. Hence, in summary, the origins of the enhanced ORR activity for HP-Pt nanoparticles are the compressive surface strain leading to a downshift of the d-band center position, the high proportion of advantageous facets like Pt[1 1 1], and the small proportion of low-coordinated sites acting as ORR blocking sites.

### 3.4. Investigation of stability against Pt dissolution

Apart from electrocatalytic activity, the durability problem for electrocatalysts is one of the most significant hurdles to be overcome in the commercialization of fuel cells. It is widely recognized that the degradation mechanisms of Pt-based cathode electrocatalysts can be categorized into four types: Pt dissolution, Pt agglomeration (sintering), carbon corrosion, and base-metal leaching for alloy electrocatalysts [44]. Among these, the issues most closely related to this study are Pt dissolution and sintering, because the electrocatalysts adopted for this investigation are Pt-only nanoparticles on the same carbon black support (Vulcan XC-72). Notably, many works have indicated that the growth of the catalyst particle size after fuel cell operation is due to the Ostwald ripening caused by dissolution and redeposition, rather than coarsening through migration [45,46]. Because of this, we investigated in detail the stability of the nanoparticles against Pt dissolution by accelerated potential cycling between 0.6 and 1.1 V (versus RHE). The stability was determined by comparing the ECSA before and after cycling. As seen in Fig. 5, for the HP-Pt nanoparticles, 27.3% of the ECSA is lost because of Pt dissolution after 4000 cycles, while the losses for E-TEK, E-TEK (300), and Premetek are 47.8%, 35.7%, and 53.1%, respectively. This result indicates that the HP-Pt nanoparticles have better durability as well as higher activity for the ORR than do the commercial samples tested.

### 3.5. Discussion of enhanced stability against Pt dissolution

It is well known that Pt dissolution is the most serious degradation factor at intermediate or high ($\approx 0.8$ V versus RHE) potentials for Pt/C electrocatalysts [47]. The following three reactions can be considered as the origin of Pt dissolution [48]:

$$\text{Pt} \rightarrow \text{Pt}^{2+} + 2e^- \quad (\text{Pt dissolution}) \quad (6)$$

$$\text{Pt} + \text{H}_2\text{O} \rightarrow \text{PtO} + 2\text{H}^+ + 2e^- \quad (\text{Pt oxide formation}) \quad (7)$$

$$\text{PtO} + 2\text{H}^+ \rightarrow \text{Pt}^{2+} + \text{H}_2\text{O} \quad (\text{Pt oxide dissolution}) \quad (8)$$

### Table 3

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>N (Å)</th>
<th>$R_0$ (Å)</th>
<th>$\sigma^2 \times 10^{-6}$ (Å$^2$)</th>
<th>r-Factor ($\times 10^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/C E-TEK</td>
<td>9.1</td>
<td>2.76 (3)</td>
<td>5.1</td>
<td>1.89</td>
</tr>
<tr>
<td>Pt/C E-TEK (300)</td>
<td>10.5</td>
<td>2.77 (3)</td>
<td>4.6</td>
<td>1.67</td>
</tr>
<tr>
<td>Pt/C Premetek</td>
<td>9.2</td>
<td>2.76 (3)</td>
<td>4.9</td>
<td>1.95</td>
</tr>
<tr>
<td>HP-Pt/C</td>
<td>10.8</td>
<td>2.75 (4)</td>
<td>4.1</td>
<td>1.75</td>
</tr>
</tbody>
</table>

Fig. 4. (a) Fourier transforms and (b) XANES data of the Pt L3-edge for Pt/C E-TEK, Pt/C E-TEK (300), Pt/C Premetek, and HP-Pt/C.
Fig. 5. CV Curves for (a) Pt/C E-TEK catalyst, (b) Pt/C E-TEK (300), (c) Pt/C Premetek, and (d) HP-Pt/C before and after 4000 cycles of accelerated durability tests.

Fig. 6. XANES spectra obtained with (a) Pt/C E-TEK and (b) HP-Pt/C nanoparticles at the Pt L3 edge at different potentials. (c) Comparison of the change of the absorption edge peaks of the XANES spectra for Pt/C E-TEK and HP-Pt/C as a function of potential, obtained with electrocatalysts at different potentials in 0.1 M HClO₄. (d) Homemade measurement cell used for the in situ XANES experiments.
Dissolved Pt is redeposited onto a larger neighboring particle by Ostwald ripening or precipitated on the proton exchange membrane by the hydrogen molecules permeating from the anode. Pt loss occurs through these processes, and thus the performance of the fuel cell gradually deteriorates.

The highly improved stability against Pt dissolution in the case of the HP-Pt nanoparticles can be explained from two viewpoints: the electronic energy state of the surface and the unique morphology with large primary particle size. First, strong evidence for the electronic energy state was obtained from the XANES experiments performed with potential steps applied using a specially designed homemade cell (the details are shown in Fig. 6d). The white line in the XANES is a strong peak due to the dipole-allowed transition of the HP-Pt nanoparticles can be explained from two viewpoints: the electronic energy state of the surface and the unique morphology with large primary particle size.

The highly improved stability against Pt dissolution in the case of the HP-Pt nanoparticles can be explained from two viewpoints: the electronic energy state of the surface and the unique morphology with large primary particle size. First, strong evidence for the electronic energy state was obtained from the XANES experiments performed with potential steps applied using a specially designed homemade cell (the details are shown in Fig. 6d). The white line in the XANES is a strong peak due to the dipole-allowed transition of the core electron to the continuum state. Hence, the white line would increase remarkably for a catalyst that is prone to ionization, or, in other words, is easily dissolved upon applying a potential. Fig. 6 shows the change in the white line at the Pt L-3 absorption edge; this change is induced upon applying a potential to cause electronic excitation from the Pt 2p3/2 core orbital formed through spin–orbit coupling to the Pt d-band vacancy. It is interesting to note that the degree of white-line increase at high potentials for the HP-Pt nanoparticles is the lowest among that for all the samples, implying that these nanoparticles are the most stable catalysts against Pt dissolution. That is to say, the HP-Pt nanoparticles require a much higher oxidation potential for dissolution, and therefore, this is the decisive origin of their increased durability.

Such improved electron retention properties at high potentials can be attributed to the surface conditions of the HP-Pt nanoparticles. As shown in Fig. 7 and Table 4, the proportion of fully reduced Pt is much higher in the HP-Pt nanoparticles, which have fewer low-coordinated sites on the surface, than in the other samples. This is in good agreement with the results found in the literature [44]; the surfaces with a high proportion of low-coordinated sites show a high oxidation state owing to an increase in the number of initially adsorbed oxygen species. This phenomenon can readily be identified in the Pt/C E-TEK (300) heat-treated sample, for which the EXAFS RDF peak corresponding to the Pt-O 1NN disappeared after heat treatment. Hence, the low proportion of low-coordinated sites for HP-Pt nanoparticles can be considered to be the main origin of their enhanced electron retention properties and the electron-rich phase on their surface.

The above conclusion can be further supported by the fact that the shape change in the CV curve in the region of OH formation (around 0.6 V) is more distinct in the commercial samples, which have a higher proportion of low-coordinated sites such as step-edge, kink, and corner sites because of their smaller particle size, as indicated by the arrows in Fig. 5. This is because such low-coordinated sites are more prone to be dissolved during potential cycling than high-coordinated sites such as terrace sites. Hence, the potential for OH formation is greatly shifted to the positive side. In contrast, the current profile change of OH formation for the HP-Pt nanoparticles is relatively smaller after cycling, demonstrating that the nanoparticle surface is originally composed of high-coordinated sites and can therefore be more tolerant to dissolution.

The final state effect may be another significant reason for the enhanced electron retention characteristics observed at small proportions of low-coordinated sites. It is widely recognized that it is much more difficult for small particles to make up for the holes generated by photoelectron emission because of their discrete electronic structure; therefore, the binding energy is shifted to a higher value in X-ray photoemission spectra [49]. In the case of the HP-Pt nanoparticles, since the primary particle size is large, the final state effect can be minimized because of the absence of such a discrete electronic structure; consequently, a high proportion of the electron-rich phase is obtained, as indicated by the Pt 4f core peak.

### 4. Conclusions

The HP-Pt nanoparticles synthesized using a weakly interacting organic capping agent, TTAB, showed enhanced ORR activity and stability against Pt dissolution. The origins of their enhanced ORR activity and stability were identified by performing EXAFS measurements and in situ XANES studies. The high proportion of surface atoms (due to the urchin-like morphology) in the single-crystalline phase, despite the large primary particle size, led to the generation of compressive strain through the high surface tension; therefore, the ORR activity was enhanced by the downshifted d-band center position. The unique urchin-like morphology also provided a high proportion of facets advantageous for the ORR, such as Pt[1 1 1] and [1 1 0]. In terms of durability, the stability against Pt dissolution was markedly enhanced because of the improved electron retention property and the decreased proportion of low-coordinated sites, which played key roles in the upshift of the oxidation potential in comparison with that of the spherically shaped commercial samples. From the above discussion, we can conclude that the highly porous urchin-like morphology is a promising structure for ORR electrocatalysts used in PEMFCs.
Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.jcat.2012.04.004.

References