

Synthesis of Facet-controlled PtNi Nanoparticles and Evaluation of Performance in PEM Fuel Cell

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ABSTRACT

The research discussed in this paper set out to reduce the amount of Pt used in automotive polymer electrolyte fuel cells. Octahedral PtNi nanoparticles supported by carbon black (octahedral PtNi/C), which displays a high level of oxygen reduction reaction activity, was synthesized, and its effect in reducing the amount of Pt employed in an actual fuel cell was evaluated.

Performance tests of a fuel cell using the octahedral PtNi/C as a cathode material showed that Pt mass activity at 0.9 V was 3.4 times that of a market Pt catalyst. These results demonstrate that the octahedral PtNi/C is well suited as a catalyst material, displaying a high level of oxygen reduction reaction activity even in an actual fuel cell, and reducing the amount of Pt used in the cathodes by approximately 70%. The octahedral PtNi/C also displays good durability performance, with a rate of decline in mass activity of 19% after 10,000 0.6-0.9 V potential cycles, against 29% for the market Pt catalyst.

1. Introduction

Fuel cells are electrochemical devices that use hydrogen as fuel and generate electricity through the reaction of hydrogen and oxygen. Because they do not produce CO₂, expectations are high for fuel cells as a power source with minimal environmental impact. Among the numerous characteristics that make polymer electrolyte fuel cells (PEFC) well suited as an automotive power source are their high power conversion efficiency, their high power density, their compactness and low weight, their low operating temperature of approximately 80°C, and their degree of freedom in design. A significant amount of research is therefore being focused on their practical realization.

One of the major issues to be addressed in order to realize the widespread use of fuel cell vehicles (FCV) fitted with PEFC is the reduction of cost. Current PEFC electrode catalysts employ high-cost platinum (Pt) due to its high level of hydrogen oxidation activity and comparative chemical and electrochemical stability. However, Pt displays insufficient activity in relation to the oxygen reduction reaction (ORR), and large amounts of Pt are therefore used in FCV in order to compensate for this, becoming a factor in increased cost. Cathode catalyst materials that display a high level of ORR activity while using minimal Pt are being developed throughout the world in order to address this issue. The use of Pt and transition metal alloys is a

representative approach⁽¹⁾⁻⁽³⁾, but this method only increases ORR activity by around twofold against pure Pt, and therefore has little effect in reducing the amount of Pt. The use of Pt-shell/transition metal-core nanoparticles has been investigated as another approach, and it has been reported that this realizes a higher level of ORR activity than the use of Pt alloy nanoparticles⁽⁴⁾⁻⁽⁷⁾. However, the transition metals employed in the cores of these Pt-shell/transition metal-core nanoparticles elute in the high-oxidation environment of the cathode, and it is believed that this presents issues of durability.

Catalyst activity is known to generally change in response to crystal face orientation, and it is expected that this effect will also characterize Pt catalysts for PEFC. Markovic et al. report that the ORR activity of single-crystal Pt increases in the order {100}<{111}<{110}⁽⁸⁾. Stamenkovic et al. report that the ORR activity of single-crystal Pt₃Ni alloy increases in the order {100}<{110}<{111}, demonstrating a different tendency to Pt⁽⁹⁾. In addition, the ORR activity of Pt₃Ni{111} per specific surface area is the highest, at approximately 10 times that of Pt{111}, indicating that the ORR activity of Pt catalysts is increased through the combination of alloying and the effect of crystal face orientation.

The activity of a catalyst per unit mass is generally expressed as the product of activity per specific surface area and unit area⁽¹⁰⁾. In other words, in order to effectively increase catalyst activity, it is important to increase

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the specific surface area, or to select a material with an inherently high level of activity. Because the use of nanoparticles would make it possible to increase the specific surface area of the catalyst, if a material such as Pt₃Ni{111}, which has an inherently high level of ORR activity, could be produced as nanoparticles, activity per unit of Pt mass would increase, which could be expected to reduce the volume of Pt used in FCV.

Using the liquid-phase chemical reduction method to synthesize nanoparticles, the research team selected poly (diallyldimethylammoniumchloride) (PDDA) as an additive and polyol as a reducing agent and obtained octahedral PtNi nanoparticles supported by carbon black (octahedral PtNi/C) with {111} exposed on the particle surfaces by growing the particles slowly. Reports published by other researchers have indicated that rotating disk electrode (RDE) evaluation of the ORR activity of octahedral PtNi/C shows an high level of mass activity, four to 10 times that of a conventional Pt electrode⁽¹¹⁾⁻⁽¹³⁾. However, there are still no reports concerning the generation performance or durability of octahedral PtNi/C when employed in actual PEFC cells.

The research discussed in this paper applied octahedral PtNi/C in PEFC cells in order to evaluate its effect in reducing the volume of Pt used and its durability. PEFC cells using synthesized octahedral PtNi/C were subjected to generation tests and durability tests using electrical potential cycles. The results showed that the use of octahedral PtNi/C made it possible to reduce the amount of Pt used in the cathodes by approximately 70% against a market Pt catalyst. In addition, electrical potential cycle durability tests showed that the material demonstrated greater durability than a market Pt catalyst. This paper will provide details of this research.

2. Experiments

2.1. Synthesis of Octahedral PtNi Nanoparticles Supported by Carbon Black

The research discussed in this paper employed a simpler method than previously reported to synthesize octahedral PtNi/C⁽¹¹⁾⁻⁽¹³⁾. First, 513 mg of carbon black (Ketjen black ECP-600JD; Lion Corporation), 588 mg of platinum acetylacetonate (Sigma-Aldrich Co. LLC.), 372 mg of nickel acetate tetrahydrate (Sigma-Aldrich Co. LLC.), and 760 μ L of a 35 wt.% PDDA aqueous solution (Sigma-Aldrich Co. LLC.) were added to 50 ml of ethylene glycol (KANTO CHEMICAL CO. INC.). This mixed solution was subjected to argon gas reflux for two hours at 190°C. The products were separated from the solution by filtration, and washed multiple times in hot ethanol, acetone, and hot water. The products were dried adequately at 50°C, producing octahedral PtNi/C.

2.2. Material Characteristics

The synthesized octahedral PtNi/C was subjected to scanning electron microscope (SEM) and transmission

electron microscope (TEM) observation in order to determine the shape and size of octahedral PtNi nanoparticles. The SEM was an HD-2000 (Hitachi High-Technologies corporation), and the TEM was an H-9000 UHR (Hitachi High-Technologies corporation). Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was employed in order to study the atomic composition and the weight concentration of metal of the octahedral PtNi/C. Energy dispersion X-ray spectroscopy (EDX) with particles as the subjects of analysis was applied at the same time as SEM observation in order to study the local atomic composition ratio of the octahedral PtNi nanoparticles.

2.3. Evaluation of ORR Activity Using RDE

A catalyst film for RDE was produced using the following method. Octahedral PtNi/C was added to a mixed solution of a 35 wt.% aqueous solution of ethanol and a 5 wt.% Nafion^(R) solution (Sigma-Aldrich Co. LLC.) and dispersed using ultrasound. 10 μ L of this dispersed fluid was dripped onto a glassy carbon (GC) electrode for RDE use (surface area: 0.196 cm²) and dried slowly at room temperature, forming a catalyst film for RDE. 1.4 μ g of Pt was used for the electrode. A three-neck electrochemical cell, an RDE apparatus (Pine Research Instrumentation), and an SI1287 potentiostat (Solartron analytical) were employed in electrochemical measurements. A saturated-calomel electrode was employed as the reference electrode, with a platinum-black electrode as the counter electrode. However, all the potentials indicated in this paper are based on a reversible hydrogen electrode as the benchmark. The electrochemistry surface area (ECSA) of the octahedral PtNi/C was determined prior to RDE measurements using cyclic voltammetry (CV). A 0.1 M aqueous solution of perchloric acid was employed as the electrolyte following sufficient removal of dissolved oxygen. The range of electrical potentials was set at 0.05-1.05 V. Following 100 cycles at a potential scan rate of 400 mV/s for electrochemical cleaning of the electrodes, CV curves were obtained at a potential scan rate of 100 mV/s. Using the obtained CV curves, the range of electrical potential in which hydrogen desorption occurs (0.05-0.4 V) was integrated in order to determine the electric charge Q_H [C], and ECSA[m²/g-Pt] was found using Eq. (1)⁽¹⁴⁾.

$$ECSA = \frac{Q_H}{2.1 M_{Pt}} \quad (1)$$

Here, M_{Pt} [g] is the amount of Pt employed in the GC electrode.

The oxygen-reduction current obtained by RDE was affected by the activation-controlled current and the diffusion-limited current. It was necessary to remove the effect of the diffusion-limited current from the oxygen-reduction current and focus on the activation-controlled

current only in order to more accurately evaluate catalyst activity. In the present research, a Koutecky-Levich plot was obtained, and the activation-controlled current was isolated. An oxygen-saturated 0.1 M aqueous solution of perchloric acid was used as the electrolyte for RDE measurements. Electrode rotation speeds of 400, 800, 1200, 1600 and 2000 rpm were employed. Electrical potentials from 1.05 to 0.05 were scanned at a scan rate of 10 mV/s. A TEC10E50E catalyst (TANAKA KIKINZOKU KOGYO) was evaluated under the same conditions in order to compare ORR activity with a market Pt nanoparticle catalyst supported by carbon black (Pt/C). The amount of Pt in the electrodes of the market Pt/C at the time of evaluation was 3.9 μg .

2.4. Evaluation of Cell Generation Performance

The membrane-electrode assembly (MEA) used in cell generation tests was produced using the decal method. Octahedral PtNi/C was added to a mixed solution of ion-exchanged water and a 5 wt.% Nafion^(R) solution (Sigma-Aldrich Co. LLC.) and dispersed using ultrasound. This dispersed fluid was sprayed uniformly onto a 30 mm-square PTFE sheet of 100 μm in thickness and dried at 80°C to produce cathode decal sheets. Market Pt/C was employed to form anode decal sheets using the same method. A proton exchange membrane (NR-212; Dupont) was sandwiched between the cathode and anode decal sheets and hot-pressed. The amount of Pt in each electrode was determined by measurement of the difference in the weight of the PTFE sheets before and after the decals were formed. The amount of Pt in the anode and cathode was 0.50 mg/cm^2 and 0.14 mg/cm^2 , respectively. To provide a comparison, an MEA using a market Pt/C for the cathode was produced using the same method. In this case, the amount of Pt was 0.50 mg/cm^2 in both the anode and the cathode.

The MEA were fitted in fuel cells (Japan Automobile Research Institute standard cells) together with gas diffusion layers (GDL25BCH; SGL Carbon), and the cells were connected to a fuel cell test system (NF Corporation). Table 1 shows the test results. Cell resistance was measured using the current interruption method, and the values for voltage shown in the current-voltage (I-V) curve have had cell resistance subtracted.

2.5. Evaluation of Durability Using Potential Cycles

Table 2 shows the conditions for durability evaluation tests using potential cycles. Cell potential was varied using a potentiostat (HD-3000; Hokuto Denko corporation). The ECSA and the I-V curve for the cathode were compared before and after the potential cycle in order to study changes in catalyst surface area and cell performance. CV measurements for the calculation of ECSA were conducted with hydrogen flowing to the anode and nitrogen flowing to the cathode, and the anode as a pseudo reference electrode. ECSA was calculated using Eq. (1). Table 1 shows the conditions used for the tests.

Table 1 Conditions for fuel cell test with octahedral PtNi/C as cathode material.

	Anode	Cathode
Cell temperature [°C]	70	
Gas	H ₂	Air
Gas stoichiometric ratio	1.4	1.8
Relative humidity [%]	50	73
Back pressure [kPa]	130	100

Table 2 Conditions for durability test of octahedral PtNi/C by potential cycling.

	Anode	Cathode
Cell temperature [°C]	70	
Gas	H ₂	Air
Gas stoichiometric ratio	1.4	1.8
Relative humidity [%]	100	100
Back pressure [kPa]	130	100
Potential [V]	0.6 - 0.9	
Shape of potential wave	Square	
Potential retention time [sec.]	20	
Cycle number [times]	10,000	

3. Results and Consideration

3.1. Material Characteristics

Figure 1 shows electron micrographs of the synthesized octahedral PtNi/C. The low-magnification SEM image shown in Fig. 1(a) indicates a good dispersion of 10-15 nm octahedral nanoparticles on the carbon black. The high-magnification SEM image shown in Fig. 1(b) indicates that the nanoparticles are not completely octahedral, but are actually truncated octahedrons with their vertices cut off. Figure 1(c) shows a high-resolution TEM image of the octahedral PtNi nanoparticles. In order to examine the orientation of the exposed faces, they were photographed perpendicular to the plane of the page. Figure 1(d) shows a pseudo electron diffraction pattern image obtained by applying fast Fourier transformation to the area enclosed by the square in Fig. 1(c). The diffraction spots from A to F correspond to the exposed faces from A to F in Fig. 1(c). As a result of applying exponents to the diffraction spots, the faces with cut vertices (B and E) were identified as {100} and the other faces (A, C, D and F) were identified as {111}.

This indicated that the exposed faces of the synthesized octahedral PtNi nanoparticles were almost all {111}.

It was considered that two synthesis conditions were essential to obtaining octahedral PtNi/C. One of these was the addition of PDDA. PDDA is a polymer, and because it has a high density of quaternary ammonium cations, which are considered to be adsorption points, it displays strong adsorptivity in relation to metal ions and metal particle surfaces^{(15), (16)}. This property has the following two effects on the particles:

- (1) By increasing the size of the particles, it increases the {111} exposure ratio; and
- (2) By controlling the speed of particle growth, it planarizes the exposed crystal faces.

With regard to (1), by coordinating Pt^{2+} and Ni^{2+} during the formation of particle nuclei in the initial stages of the reaction, the PDDA inhibits reduction to Pt and Ni, minimizing the number of nuclei formed. It is conjectured that as a result, the majority of the precursors are consumed in the growth of the particles, which grow to the comparatively large size of 10–15 nm. Figure 2 shows the relationship between the ratio of each section of the octahedral particle surfaces (the ratio of the number of atoms composing a specific section to the total number of atoms in the exposed surfaces) and the size of the particles, as determined by calculations. As particle size increases, the ratio of {111} becomes higher than corners and edges, until it is approximately 90% at 11 nm. In other words, to help ensure that the majority of octahedral particle surfaces are {111}, it is necessary to increase the size of the particles, and it is considered that PDDA contributes to increasing their size.

With regard to (2), it is conjectured that when the nuclei grow into particles, the PDDA is strongly absorbed into the particle surfaces, and continuous metal precipitation reactions occur slowly and uniformly on the particle surfaces. As a result, {111} with few steps or kinks and planar at the atomic level are exposed, producing octahedral particles with the regular shape shown in Fig. 1.

The second essential synthesis condition is that the surface energy of the {111}PtNi is lower than that of other faces. The exposure ratio of the crystal faces is determined by the speed of growth of the faces, and this is dependent on the magnitude of surface energy. In other words, the

Table 3 Atomic ratio and weight concentration of octahedral PtNi/C as determined by ICP-AES.

	Pt	Ni	C
Atomic ratio [at.%]	62.2	37.8	
Weight concentration [wt.%]	27.5	5.0	67.5

higher the surface energy of the crystal face, the faster its growth, and the exposed area of the face decreases as the particle grows, until it finally disappears. In the case of PtNi alloys, which have a face-centered cubic lattice crystal structure, it has been reported that {111}Pt₃Ni has a lower surface energy and its growth is slower than other crystal faces^{(11), (17), (18)}. In addition, PDDA is selectively adsorbed by {111}PtNi, and this is thought to further reduce the surface energy of {111}PtNi. It is considered that the multiple effects of PDDA discussed above made it possible to obtain octahedral PtNi nanoparticles with large numbers of planar {111} exposed at their surfaces.

Table 3 shows the composition ratio of octahedral PtNi/C measured using ICP-AES. The atomic composition ratio of Pt and Ni in the octahedral PtNi/C was Pt:Ni = 62.2:37.8. The starting atomic composition ratio at the time of synthesis was Pt:Ni = 50:50, meaning that the ratio of Pt was higher in the obtained octahedral PtNi/C than in the

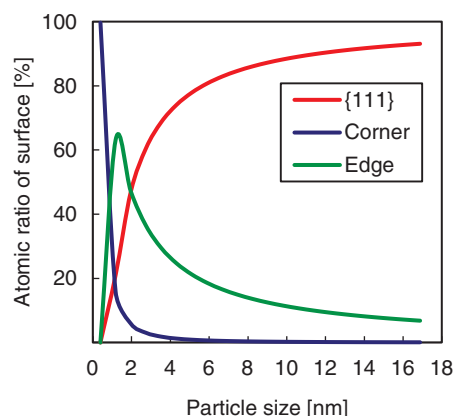


Fig. 2 Calculated relationship of particle size and atomic ratio of {111}, corner, and edge on octahedral nanoparticle surface.

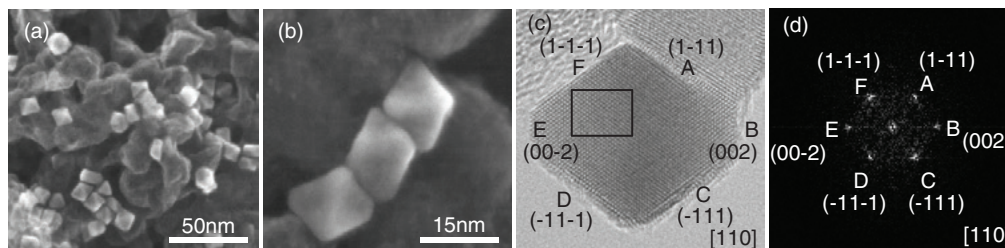
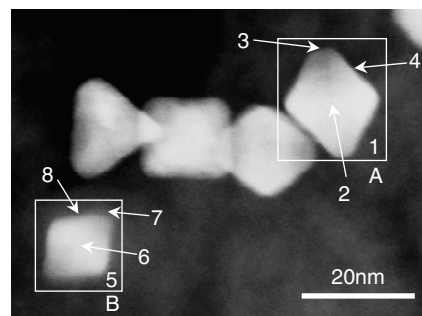


Fig. 1 SEM (a) and (b) and high-resolution TEM (c) images of octahedral PtNi/C. Square shows area image-processed by inverse Fourier transformation to obtain pseudo-electron diffraction pattern. Pseudo-electron diffraction pattern (d) of octahedral PtNi nanoparticles.

starting atomic composition. The mass concentration of the metals in the octahedral PtNi/C was Pt: 27.5 wt.% and Ni: 5.0 wt.%, making a total of 32.5 wt.%.

SEM-EDX particle analysis was applied to the octahedral PtNi nanoparticles in order to determine their local atomic composition ratio. **Figure 3** shows the results. For Particle A, the composition ratio of the entire particle (Measurement Area 1) was Pt:Ni = 63.8:36.2. This result corresponds well with the ICP-AES results. The composition ratio in Measurement Area 2, in the center of Particle A, was Pt:Ni = 57.3:42.7. The composition ratio in Measurement Area 3, at a corner, was Pt:Ni = 80.7:19.3, and the composition ratio in Measurement Area 4, at an edge, was Pt:Ni = 72.3:27.7. These results indicate that there is variation between composition ratios depending on the area. The composition distribution of Particle B demonstrated the same tendency as that of Particle A. These results indicate that the atomic composition ratio of the octahedral PtNi nanoparticles is not uniform, but that they display a characteristic composition distribution, in which the ratio of Ni is greater in the centers of the particles and the ratio of Pt is greater at the corners and edges of the particles.



Analysis points		Atomic ratio [at.%]	
		Pt	Ni
1	Particle	63.8	36.2
2	Center	57.3	42.7
3	Corner	80.7	19.3
4	Edge	72.3	27.7
5	Particle	67.2	32.8
6	Center	58.1	41.9
7	Corner	80.8	19.2
8	Edge	73.6	26.4

3.2. Evaluation of ORR Activity Using RDE Method

Figure 4(a) shows the CV curves for the octahedral PtNi/C and the market Pt/C. The CV curves of Pt nanoparticles generally show currents associated with

Fig. 3 Dark-field SEM image of octahedral PtNi/C including EDX analysis areas (squares) and points (arrows). Table shows atomic ratio at each analysis point.

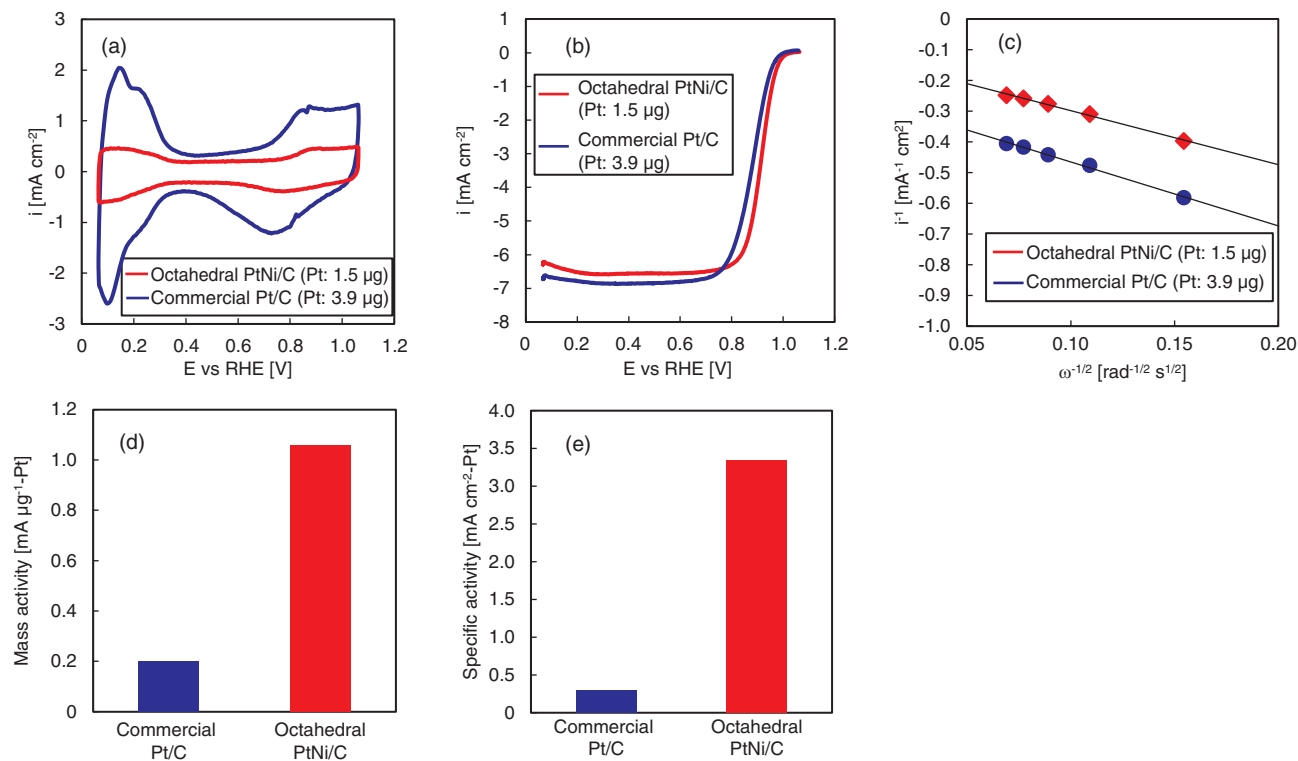


Fig. 4 (a) CV curves, (b) polarization curves and (c) Koutecky-Levich plot for octahedral PtNi/C (Pt: 1.5 μg) and commercial Pt/C (Pt: 3.9 μg) as determined by RDE measurements. Comparison of (d) mass activity and (e) specific activity at 0.90 V between octahedral PtNi/C and commercial Pt/C.

hydrogen adsorption and desorption from 0.05-0.4 V and the formation and reduction of oxides on the surface from 0.7 V onwards. The CV curve for the market Pt/C showed conspicuous peaks at 0.13 V and 0.20 V, but these were not observed for the octahedral PtNi/C. A CV curve with no peaks in the potential range for adsorption and desorption of hydrogen matches well with the reported CV curve for Pt{111} single crystals in 0.1 M perchloric acid⁽¹⁹⁾, suggesting significant exposure of Pt{111} on the surfaces of the octahedral PtNi nanoparticles. In addition, the current flow associated with the formation of oxides on the surfaces from approximately 0.69 V in the market Pt/C has shifted to the higher potential side, from approximately 0.75 V, in the octahedral PtNi/C. This is thought to indicate that the overpotential of the octahedral PtNi/C is high in relation to the formation of oxides on the nanoparticle surfaces, impeding oxide formation, demonstrating that the substance displays a different surface characteristic to conventional Pt catalysts. The ECSA of the octahedral PtNi/C, as determined from hydrogen desorption peaks, was 32 m²/g-Pt, less than half of the figure of 68 m²/g-Pt for the market Pt/C. The average particle diameter for the market Pt/C is 2.3 nm, smaller than that of the octahedral PtNi nanoparticles, and this difference is reflected in the figure for ECSA.

Figures 4(b) and 4(c) respectively show the ORR polarization curve obtained using RDE and a Koutecky-Levich plot for 0.90 V. The intercept current values in the Koutecky-Levich plot are values for oxidation-reduction current with the effect of the diffusion-limited current removed. Figure 4(d) shows these as figures for mass activity specified by the amount of Pt in the electrodes. The mass activity of the octahedral PtNi/C is 5.3 times that of the market Pt/C. These results indicate that by using the octahedral PtNi/C, it is possible to obtain a specific current volume using approximately 81% less Pt as a conventional Pt catalyst. Figure 4(e) shows oxidation-reduction current values specified by ECSA as specific activity. The specific activity of the octahedral PtNi/C was 11.5 times that of

the market Pt/C. This shows that the octahedral PtNi nanoparticles are a catalyst material essentially well suited to ORR.

3.3. Evaluation of Cell Performance

Figure 5(a) shows I-V curves for an MEA using cathodes employing octahedral PtNi/C with 0.14 mg/cm² of Pt and an MEA using cathodes employing a market Pt/C with 0.50 mg/cm² of Pt. The I-V curves are virtually identical, despite the fact that the amount of Pt used in the octahedral PtNi/C is less than 1/3 the amount used in the market Pt/C. Figures 5(b) and 5(c) respectively show a Tafel-plot with mass activity on the horizontal axis and a comparison of mass activity at 0.9 V. Mass activity in the MEA using cathodes employing octahedral PtNi/C is 3.4 times that in the MEA using cathodes employing the market Pt/C. These results indicate that the replacement of the market Pt catalyst by the octahedral PtNi/C in PEFC cathodes makes it possible to reduce the amount of Pt used in the cathodes by 71%, and demonstrate that this significant reduction in the amount of Pt used in the cathodes will also be realized in actual fuel cells.

The 5.3-fold increase in mass activity realized through the use of octahedral PtNi/C as determined by RDE is smaller in actual fuel cells at 3.4-fold. It is considered that one reason for this is the fact that residual PDDA is present on the surfaces of the octahedral PtNi nanoparticles in the MEA, and this impedes the ORR. It is conjectured that the immersion of the electrodes in an aqueous solution for electrochemical cleaning in the RDE method causes the water-soluble PDDA in the electrolyte to elute or decompose, and the octahedral PtNi nanoparticles are evaluated with no PDDA present on their surfaces. In the case of the fuel cell performance tests, it is considered that while the MEA was subjected to a sufficient number of polarization cycles prior to the measurements in order to help enable the highest level of performance, because the environment around the electrode layers is almost exclusively gaseous, the effect in reducing PDDA is minimal, and the cells were measured with a higher quantity

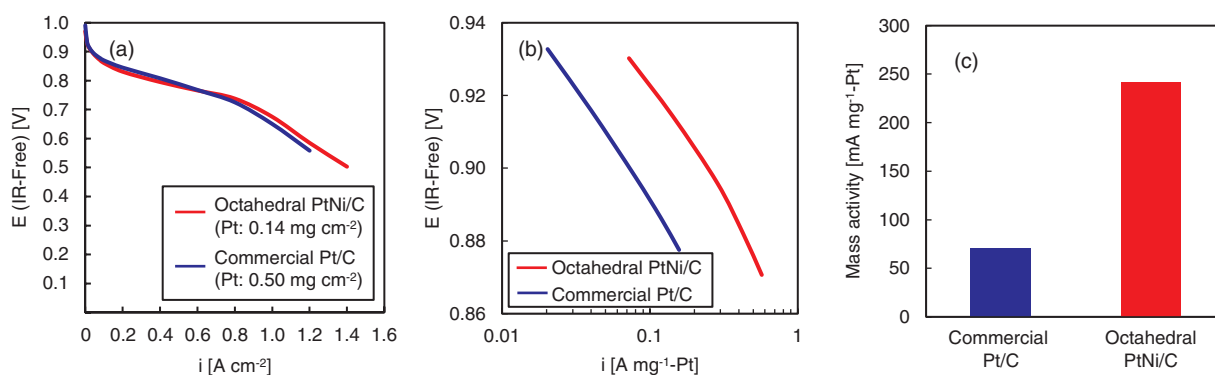


Fig. 5 (a) Polarization curves of PEFC using octahedral PtNi/C and commercial Pt/C for cathodes. (b) Tafel plots for octahedral PtNi/C and commercial Pt/C in fuel cell tests. (c) Comparison of mass activity at 0.9 V for the octahedral PtNi/C and commercial Pt/C.

of PDDA adsorbed into the surfaces of the octahedral PtNi nanoparticles than was the case for RDE evaluation.

3.4. Evaluation of Durability Using Potential Cycles

Figure 6(a) compares I-V curves for a fuel cell with octahedral PtNi/C in the cathodes before and after 10,000 0.6-0.9 V potential cycles. The potential cycles produce no major changes in the I-V curves in any of the current ranges. Figure 6(b) shows changes in mass activity with potential cycles. The rate of decline in mass activity for the octahedral PtNi/C is 19%, lower than the figure of 29% for the market Pt/C. Even after 10,000 0.6-0.9 V potential cycles, the octahedral PtNi/C retains its good performance, displaying 4.1 times the mass activity of the market Pt/C. The results discussed above demonstrate that the octahedral PtNi/C displays a higher level of durability in relation to 0.6-0.9 V potential cycles than the market Pt catalyst.

Figure 6(c) shows changes in ECSA as a result of the 0.6-0.9 V potential cycles. The rate of decline in ECSA was 4% in the octahedral PtNi/C against 28% in the market Pt/C. There are considered to be two reasons for this. One of these is the fact that the octahedral PtNi nanoparticles are large, resulting in less migration and agglomeration of the particles on the carbon black. The other is the fact that the {111} exposed on the surfaces of the nanoparticles has a comparatively high resistance to dissolution, making the particles less prone to Ostwald ripening. The facts that {111} has a higher atomic density than other crystal faces, and that its coordination number is also high, are considered to be the reason for its high resistance to dissolution.

Because the rate of decline in mass activity in the market Pt/C almost exactly corresponds to the rate of decline in ECSA, it is considered that the main factor in its decline in activity is the decline in the surface area of the catalyst. Because there was no correlation between the rate of decline in mass activity and the rate of decline in ECSA in the case of the octahedral PtNi/C, it was judged that a decline in surface area was not the main factor in the decline in activity in this case. Because the reason that octahedral PtNi/C displays a high level of ORR activity

is the large amount of {111}PtNi exposed on the surfaces of the particles, it is conjectured that the cause of the 19% decline in mass activity was the loss of {111}PtNi structures exposed on the particle surfaces due to the potential cycles.

4. Conclusion

The research discussed in this paper set out to reduce the amount of Pt used in automotive polymer electrolyte fuel cells. Octahedral PtNi/C, which displays a high level of oxygen reduction reaction activity, was synthesized, and its effect in reducing the amount of Pt employed in an actual fuel cell was evaluated.

The particles obtained were truncated octahedrons of 10-15 nm in size. TEM analysis showed that the particle surfaces were almost entirely {111}. The octahedral PtNi nanoparticles displayed a specific composition distribution, with the majority of the Pt segregated at the corners and edges.

The catalyst activity of the octahedral PtNi/C was measured using the RDE method. Pt mass activity was 5.3 times that of a market Pt catalyst, while its specific activity was 11.5 times greater. Performance tests of an MEA using the octahedral PtNi/C as a cathode material showed that Pt mass activity at 0.9 V was 3.4 times that of the market Pt catalyst. These results demonstrate that the octahedral PtNi/C is well suited as a catalyst material, displaying a high level of oxygen reduction reaction activity even in an actual fuel cell, and reducing the amount of Pt used in the cathodes by approximately 70%. The octahedral PtNi/C also displays good durability performance, with a rate of decline in mass activity of 19% after 10,000 0.6-0.9 V potential cycles, against 29% for the market Pt catalyst.

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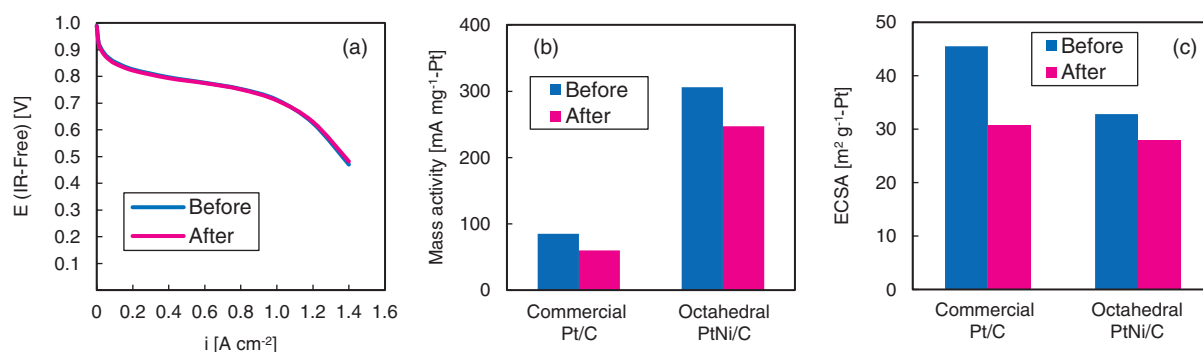


Fig. 6 (a) Polarization curves of PEFC using octahedral PtNi/C before and after 10,000 0.6 - 0.9 V potential cycles. (b) Change in mass activity and (c) ECSA for octahedral PtNi/C and commercial Pt/C as a result of 0.6 - 0.9 V potential cycling.

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