Quantitative TEM Analysis for the Pt Morphology in the Catalyst Layers of Polymer Electrolyte Membrane Fuel Cells

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We carried out quantitative transmission electron microscopy (TEM) analysis for the Pt morphology in the cathode catalyst layer of polymer electrolyte fuel cells (PEFCs) for investigating the transportation of Pt species during the cell operation. The specimens for the TEM observation were cut off from the catalyst layer with approximately 100nm thickness without embedding it in a resin. The size and number of the Pt particles contained in the same volume of the catalyst layer were accumulated to obtain their size distributions. The distributions of Pt surface areas and volumes were also estimated from the size distributions, assuming that the Pt particles are sphere. The total volumes of the Pt particles estimated by the analysis corresponded to 65-86% of those calculated from the Pt loadings at the MEA preparations. The change in the Pt morphology before and after a potential cycling test without power generation was investigated. For the cycled MEA, the Pt surface area per weight (the specific Pt surface area) calculated from the TEM observation was nearly identical to the electrochemically active surface area (ECSA) by cyclic voltammetry(CV). This novel method for the TEM analysis provides the distributions of the Pt concentration in the whole catalyst layer as well as the Pt surface distribution and the Pt volume distribution in a given area of the catalyst layer without chemical analysis or spectroscopy. Those data can be used to understand the dependence of the microstructures of the catalyst layer on the cell performances.

Key Words: PEFC, TEM, Size Distribution, Durability

1 Introduction

Polymer electrolyte fuel cells (PEFCs) are expected as a key technology to solve the global environmental problems. However, PEFCs have several issues to overcome for their commercialization. The degradation of the cathode catalyst layer under low Pt loading is perhaps the most serious issue. In long term cell operations, it is mainly caused by the decrease in the electrochemically active surface area (ECSA) of supported Pt nanoparticles.\(^2\) To improve the durability, it is important to establish an analytical method to understand the degradation mechanism.\(^3,5\)

It is generally believed that the following two mechanisms are involved in the decrease of Pt surface areas. One is the Ostwald-ripening process which is caused by reduction of the surface energy of Pt particles. It dissolves the Pt particles with less than 4 nm in diameter to form Pt ions in an ionomer. The Pt ions are deposited on neighboring larger Pt particles to increase the Pt particle size. The other is the Pt diffusion process at a micrometer scale. The Pt ions dissolved in the ionomer are transported within the ionomer phase by the diffusion, by the water flux, and by the electrical field. It eventually leads to the Pt precipitation when the concentrations of Pt ions exceed its solubility in the ionomer. As a result, the ECSA gradually decreases during the cell operation.

Ferreira et al.\(^6\) utilized TEM to investigate the change in the Pt morphology and the particle size distributions across the cathode layer after a potential cycling test. They quantitatively analyzed the Pt transportation phenomena in the catalyst layer. Their depth profiles of Pt volume (weight) and ECSA are questionable in reliability since the Pt particle size histograms to obtain all the data were derived from only 100 measurements of the Pt particle size in every TEM view area. In addition to arbitrariness to choose those Pt particles, fixing the number of particles in a given view area brings an inaccuracy in the estimation of the Pt volumes and surface areas per unit volume of the catalyst layer. For a view area near the cathode/membrane interface, agglomerated Pt particles with larger diameters had to be accumulated in a larger volume of the catalyst layer. On the contrary, for a view area containing well dispersed smaller Pt particles, the smaller volume of the catalyst layer was considered. Thus, their Pt density (weight/surface area) profiles may not necessarily represent the true catalyst layer.

In this work, we wanted to clarify how the Pt species move in the catalyst layer during the cell operation in order to understand the degradation mechanism of the cathode catalyst. The second priority is to understand the change in the depth profile of the Pt surface area density across the cathode catalyst layer and total Pt surface area in a unit volume of the cathode after potential cycle tests. Comparing those data with \(I/V\) and ECSA
measurements, we make it easier to understand the degradation phenomena of the cathode and to design a new fine structure of the catalyst layer with improved performance and durability.

We made the Pt particle size distributions contained in the same volume of the catalyst layers by cross sectional TEM analysis of the catalyst layer for acquiring the true depth profile of Pt volume (weight) density and surface area density. For accurate investigations, we prepared specimens to minimize overlapping Pt particles and to keep their same thickness as much as we can. We also tried to elucidate the surface area and the volume distributions quantitatively by normalizing the Pt amount.

As for the morphological analysis of Pt particles on a carbon support, Ito et al.21 proposed 3-D visualization analysis using TEMT (transmission electron microtomography) as an effective new method. They pointed out that 2-D TEM observations were difficult to distinguish whether or not the particles observed was overlapped, and that the mean Pt diameters determined from the 2-D images tend to be larger than those from the 3-D images. 3-D TEM is a powerful method to investigate the Pt morphologies at a nanometer-scale in the catalyst layer. Although accurate information on such fine portions of the catalyst layer is desired to obtain, the information about the whole catalyst layer is also required for examining the degradation mechanism of the cathodes. In this study, we used conventional 2-D TEM to investigate the Pt morphologies by measuring the sizes of overlapping Pt particles using an image processing software. Our analysis also supported that there are two kinds of the transportation mechanism for the Pt particles during the cell operation, as Ferreira et al. concluded. One is the long-range transportation which leads to the change in the Pt concentration distribution and the other is the short-range transportation which results in the particle growth named Ostwald-ripening. However, our analysis can quantitatively provide the Pt volumes and surface areas in a unit volume of the catalyst layer, which are important to reveal Pt transportation mechanisms.

2 Experimental

Membrane Electrode Assemblies (MEAs) were prepared by the Decal method.2 A Nafion 112 with 50 μm thickness was used as a membrane, a catalyst slurry consisting of the Pt/C catalyst (TEC10E50E, Tanaka Corp. (Japan)) and Nafion solution was deposited on a substrate film with a Pt loading of 0.3±0.05 mg cm−2 and the ionomer/carbon ratio was 0.8 for the anode and cathode. The catalyst on the film was hot-pressed against the Naftion membrane at 0.6 MPa and 150°C for 5 min. A gas diffusion layer (GDL) with micro porous layers (MPL) supplied by SGL Carbon AG (Germany) was used. The thicknesses of the catalyst layer and the GDL were approximately 10 μm and 200 μm, respectively. The electrode area was 36 cm². Carbon separators with a serpentine-type flow field were utilized.

In the catalyst layer after the potential cycling test by Ferreira et al., there existed many Pt particles with large non-spherical shapes apart from the carbon support. The existence of such particles brings much discrepancy between the data obtained by the spherical approximation and the actual values. In this study, relatively moderate conditions for durability tests of MEAs were employed to avoid the excess appearance of nonspherical Pt particles. After the initial conditioning of the MEA, the square-wave potential cycles between an open circuit voltage (OCV) and 0.6 V with each pulse width of 3 s were applied on the cathode under fully humidified gas flows of hydrogen and nitrogen for the anode and cathode, respectively. CV and IV measurements were carried out every 1000 cycles to determine the ECSA and to evaluate the performance degradation.

The morphological analysis of Pt nanoparticles in the cathode was performed for the two MEAs, i.e., pristine and 6000 potential cycled MEAs, by a field-emission transmission electron microscope (FE-TEM, NihonDenshi, JEM-2010F) at an acceleration voltage of 200 kV. The specimens for the TEM observation were prepared as follows: i) The MEA was fed with dried nitrogen for 5 hrs for drying and the catalyst coated membrane (CCM) was carefully removed from the test cell. ii) A rectangular piece with a dimension of 30 μm (length)×20 μm (height)×10 μm (thickness) was cut off from the CCM by focused Ga ion beam (FIB) without embedding it in a resin. iii) The piece was held between two tungsten rods on a sample holder. iv) The membrane side of the piece was reinforced with tungsten by thermal decomposition. iv) The specimen for TEM observation was sliced by FIB in such a way that the thickness reaches approximately 100 nm with observing it with the scanning ion microscope (SIM).

The analysis was performed for view areas containing well dispersed Pt particles without excess existence of voids, or abnormal agglomeration of Pt particles which are originally contained in the purchased catalyst, to examine the size distribution. The analysis areas were several microns apart from the membrane/catalyst layer interface and the GDL/catalyst layer interface. The analysis areas were 200 nm × 150 nm, 400 nm × 300 nm, and 800 nm × 600 nm before and after the potential cycling test. The Pt nanoparticles were counted up to 42 nm in diameter with an interval of 1 nm by visually examining TEM images which were enlarged 600,000 times. The spatial resolution of the TEM images was 0.5 nm.

For the large and non spherical Pt particles, we assumed spherical particles mimicking them and measured their diameters to calculate their volumes and surface areas. We separated the overlapped multi-particles into individual particles with our best efforts to measure their diameters. The averaged diameter was assumed for each of the individual particles consisting of the multi-particles.

As explained in the introduction, it was necessary to introduce a way to avoid miscounting of the overlapping particles along the optical axis as much as possible. For the case in which two or more Pt particles were over-
lapped, they were separated to each other by changing a focus depth for a TEM image using the image processing software (Digital Micrograph, Gatan Inc.), as shown in Fig. 1. The particles which are still difficult to separate each other were excluded from the counting, though that was rare.

**Fig. 1** The procedure to determine the particle sizes of overlapping Pt particles. In the figures, (1) means defocusing, and (2) means removing the noise using the image processing software.

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**3 Results and Discussion**

The TEM observation revealed that most of the Pt particles were spherical, although several large particles were distorted. Therefore, we estimated the distributions of the Pt volume and the ECSA in the same volume of the catalyst layer under the spherical approximation using the following expressions

\[
s(\phi_m) = \pi \phi_m^2 n(\phi_m) \\
\nu(\phi_m) = \pi \phi_m^2 n(\phi_m)/6 \\
S_{PT} = 2\pi \Sigma(\phi_m) \\
V_{PT} = \Sigma \nu(\phi_m) \\
S_{SPT} = S_{PT} \times 10^{2}/(V_{PT} \times 21.45)
\]

where \(\Sigma\) means summation from 1 to \(M\) regarding to \(m\).

- \(\phi_m\): \([\phi_1=1.0, \phi_2=2.0, \phi_3=3.0, \ldots, \phi_M=42.0]\) [nm];
- \(n(\phi_m)\): The number of Pt particles with diameter \(\phi\), \((\phi_{m-1.0}) < \phi \leq \phi_m\) representing the size distributions;
- \(s(\phi_m)\): The surface area of Pt particles with diameter \(\phi\) [nm\(^2\)]; \((\phi_{m-1.0}) < \phi \leq \phi_m\) representing the size distributions;
- \(\nu(\phi_m)\): The volume of Pt particles with diameter \(\phi\) [nm\(^3\)]; \((\phi_{m-1.0}) < \phi \leq \phi_m\) representing the size distributions;
- \(S_{PT}\): Total Pt surface area in an analyzing view area [nm\(^2\)];
- \(V_{PT}\): Total Pt volume in an analyzing view area [nm\(^3\)];
- \(S_{SPT}\): Specific Pt surface area in an analysis area [m\(^2\) g\(^{-1}\)].

The error margin of the results becomes large if an analytical view area is too small. This is because the Pt

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**Fig. 2** Positions and dimensions of TEM view areas for the pristine cathode. The total numbers of Pt particles and accumulated volumes of Pt contained are shown in each view area. (A3) contains the analyzing areas of (a1) to (a4).
particles are not distributed uniformly in the actual catalyst layer. On the other hand, the total number of the Pt particle to analyze becomes enormous if the view area is too large. We investigated the relationship between the error margin and the view area size. As for the smaller view area, seven areas of 200 nm × 150 nm shown in Fig. 2 (a1)-a7 were chosen for the analysis. These areas are approximately 1.5 μm apart from the membrane/catalyst interface. As for the larger area, two areas of 400 nm × 300 nm shown in Fig. 2 (A1)-(A2) were selected. The volume in the larger view area is four times larger than that in the smaller view area.

Figure 3 plots the Pt volumes calculated with the spherical approximation in the view areas as a function of the number of Pt particles visually counted in the corresponding view areas. The variance of the data became considerably small for the large view areas (400 nm × 300 nm) whereas it is larger for the small view areas (200 nm × 150 nm). Therefore, the values estimated from the larger view areas (400 nm × 300 nm) were adapted for the discussion below. The inclination of the fitting line for those data in Fig. 3 corresponds to the average diameter of the Pt particles. The average diameter was estimated to be 2.6 nm. For the potential cycled sample, the large view areas (800 nm × 600 nm) were adapted for discussion because the number of the Pt particles became much less than that of the pristine sample. The total volumes of Pt included in the analysis areas estimated from the size distribution using formula (4) were compared with those calculated from the Pt loading and the catalyst layer thickness. For the pristine sample, the Pt loading and the catalyst layer thickness were 0.266 mg/cm² and 11.5 μm, respectively. Table 1 summarizes the Pt volumes. It seems that 65-86% of Pt calculated from the Pt loadings can be recognized by the TEM observation. The small value of Pt volume corresponding to (A3) attribute to the view area, (a1) or (a3), in which the Pt particles contained are considerably fewer than the others. If calculated only from the view areas, (A1) and (A2), in which the Pt particles are distributed in average, the ratio of Pt volume recognized reaches 83–86%. The unrecognized Pt volume of 14–17% may be caused by i) the existence of uncountable Pt particles (φ < 1 nm), especially for the pristine sample, ii) the partial dropout of Pt during the thickness adjustment of the specimen, and iii) the inaccuracy derived from the spherical approximation and the overlapping of particles.

The cross sections of the catalyst layer before and after the potential cycling test for the size distribution

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**Table 1** Comparison of Pt volumes in a unit volume of a cathode catalyst layer, estimated from TEM observations and Pt loadings.

<table>
<thead>
<tr>
<th>Sample and view area</th>
<th>Pt volume [× 10⁷ nm³/μm²]</th>
<th>Ratio [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(A) TEM based</td>
<td>(B) Loading based</td>
</tr>
<tr>
<td><strong>Pristine MEA</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200 nm × 150 nm</td>
<td>(a1) 6.97</td>
<td>10.8</td>
</tr>
<tr>
<td></td>
<td>(a2) 9.57</td>
<td>10.8</td>
</tr>
<tr>
<td></td>
<td>(a3) 4.24</td>
<td>10.8</td>
</tr>
<tr>
<td></td>
<td>(a4) 7.18</td>
<td>10.8</td>
</tr>
<tr>
<td></td>
<td>(a5) 9.75</td>
<td>10.8</td>
</tr>
<tr>
<td></td>
<td>(a6) 7.37</td>
<td>10.8</td>
</tr>
<tr>
<td></td>
<td>(a7) 6.34</td>
<td>10.8</td>
</tr>
<tr>
<td>400 nm × 300 nm</td>
<td>(A1) 8.93</td>
<td>10.8</td>
</tr>
<tr>
<td></td>
<td>(A2) 9.22</td>
<td>10.8</td>
</tr>
<tr>
<td></td>
<td>(A3)† 6.99</td>
<td>10.8</td>
</tr>
<tr>
<td><strong>Cycled MEA</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>800 nm × 600 nm</td>
<td>(B1) 15.38</td>
<td>19.9</td>
</tr>
<tr>
<td></td>
<td>(B2) 19.54</td>
<td>19.9</td>
</tr>
</tbody>
</table>

*a* Pt volume contained in unit volume of catalyst layer estimated from TEM image

*b* Pt volume contained in unit volume of catalyst layer based on Pt loading. 11.5 μm and 7.5 μm were adopted as thickness and 0.266 mg cm⁻² and 0.320 mg cm⁻² were adopted as the amount of Pt loading for pristine MEA and for cycled MEA respectively.

† (A3) consists of (a1), (a2), (a3) and (a4)
analysis were summarized in Fig. 4. Square solid lines indicate the analysis areas for counting the Pt particles. The distribution of the Pt volume at a given position in the catalytic layer can be obtained for the cycled MEA. The Pt volume densities were also shown in Table 1. The Pt density in the view area of (B1) near the membrane decreased faster than that in (B2) near the GDL. Our results indicate the long-range transportation of the Pt species, leading to the uneven distribution of the Pt volume densities through the catalyst layer for the cycled MEA.

Figure 5 shows the Pt size distributions at the view areas of (A2) and (B2) near GDL. The distributions are normalized with the total number of the particles, which is conventionally used to obtain the Pt size distributions. In this study, the number of Pt particles with a given diameter can be compared absolutely before and after the cycling tests, as shown in Fig. 6. It shows the size distributions in the same volume of the catalyst layer which is 800 nm (width) × 600 nm (height) × 100 nm (thickness). In this sense, these distributions may be rather called the Pt size variations. It revealed that the total number of Pt particles substantially decreased after the potential cycles. It should be concluded that the total number of Pt particles decreased, especially for the particles with less than 4 nm in diameter, and that larger particles with more than 10 nm in diameter increased after the potential cycling test. In spite of those drastic changes of Pt morphology, the average diameter of Pt particles changed only from 2.55 nm to 4.38 nm after the potential cycling test, which is probably caused by Ostwald-Ripening.

Figure 7 shows the Pt volume distributions in the same volume of the catalyst layer derived from the size distributions using formula (2). Figure 8 represents the change in the Pt volume which is the difference of the Pt volumes obtained before and after the potential cycle test. The graph represents the quantity of the distributive transportation of Pt. It reveals that the Pt particles with less than 4 nm in diameter were extremely unsta-
ble and easily transported to the surfaces of the larger particles. We found that the volume change occurs not only for the smaller Pt particles with less than 20 nm in diameter but also for the larger Pt particles up to 40 nm in diameter.

Figure 9 compares the surface area distributions before and after the potential cycling test. Almost all the surface areas contributed from the smaller Pt particles with less than 4 nm in diameter were diminished. The ECSA change with the potential cycles is shown in Fig. 10. The specific surface areas of Pt, which means surface areas per unit Pt weight, represented by $S_{p,w}$ in formula (5), considerably decreased during the potential cycles as summarized in Table 2.

It is tentatively concluded that the particle coarsening occurred at (B2) in Fig. 2 more rapidly than at (B1), although it might be contradiction with the fact that the density of Pt volume in (B2) was higher than that in (B1), as shown in Table 1. These results are slightly different from those reported by Ferreira. This may due to the fact that the total time for the durability test in our experiments was shorter than that in theirs. In addition, the number of the potential cycles we applied was fewer than theirs. It is suggested that the particle growth by Ostwald-ripening occurred in the catalyst layer proceeded with different rates, which is probably caused by the local density distributions of Pt species in the ionomer.

The specific surface area ($S_{p,w}$) of the pristine sample estimated from our TEM observations was 1.5 times larger than the ECSA obtained by the electrochemical measurement. It is suggested that the inactive Pt surface areas, which are not contacted to the ionomer or the electrode system, is counted in our method.

On the other hand, the specific surface areas calculated from the TEM observation were the same level as the ECSA for the catalyst layer after 6000 potential cycles. Figure 11 shows the potential cycle dependence of $I$-$V$ characteristics in the Tafel region. The current densities at a voltage of 0.9 V highly depends the ECSAs

![Fig. 8](image_url) Change in the Pt volume distributions obtained by subtracting the volume after the potential cycling test from that before.

![Fig. 9](image_url) Pt surface area distributions in the same volume of the catalyst layer ($800 \times 600 \times 100$ nm$^3$) derived from the size distributions using formula (1).

![Fig. 10](image_url) The decrease in ECSA with potential cycles at 65℃ under fully humidified conditions.

![Fig. 11](image_url) Potential cycled $I$-$V$ characteristics in the Tafel region.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{p,w}$ [m$^2$/g] (Near Membrane)</th>
<th>$S_{p,w}$ [m$^2$/g] (Near GDL)</th>
<th>ECSA [m$^2$/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine MEA</td>
<td>(A1) 93</td>
<td>(A2) 98</td>
<td>65</td>
</tr>
<tr>
<td>Cyclced MEA</td>
<td>(B1) 39</td>
<td>(B2) 23</td>
<td>40</td>
</tr>
<tr>
<td>Ratio</td>
<td>(Cycled/Pristine) 42%</td>
<td>(Cycled/Pristine) 23%</td>
<td>62%</td>
</tr>
</tbody>
</table>
except for the initial state because no conditioning was performed to form stable triple-phase boundaries. The current density ratio (10.7/18.5) for 500 cycled and 6000 cycled MEAs was comparable to the ECSA ratio (40/64). It means that the Pt particles electrochemically isolated in the pristine state are connected to the ionomer phase and re-deposited as electrochemically active Pt particles during the durability test. The ECSA would slightly increase by the re-deposited Pt and the stabilization of the triple-phase boundary for the initial several hundred hours, whereas the decrease in the ECSA by coarsening the Pt particles would become significant thereafter as shown in Fig. 10.

4 Conclusions

Both the spatial densities and the size distributions of the Pt particles at a given of the catalyst layer of a PEFC can be examined using the novel TEM analysis without chemical analysis or spectroscopy. The surface area/volume distributions of the Pt particles were also elucidated from the size distributions using the spherical particle approximation. For the pristine catalyst layer, more than 65% of the Pt calculated from the Pt loading was recognized by this analysis. It revealed that the Pt particles with less than 4 nm in diameter were extremely unstable during a cell operation, easily dissolved, and finally deposited on the surface of larger particles. These phenomena occur on large Pt particles with even more than 20 nm in diameter. The specific surface areas calculated from this TEM analysis were the same level as the ECSAs for the catalyst layer after 6000 potential cycles. These change in the ECSAs the change in the current densities at the cell voltage of 0.9 V in the I-V characteristics.

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References