Durability of Pt/Graphitized Carbon Catalyst Prepared by the Nanocapsule Method for the Start/Stop Operating Condition of Polymer Electrolyte Fuel Cells

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The objective of this research was to assess the feasibility of the use of highly corrosion resistant graphitized carbon (GC) as a support for Pt nanoparticles in polymer electrolyte fuel cells and to assess the role of the state of Pt dispersion in the maintenance of performance. Three types of 50 wt % Pt-loaded catalysts (commercial Pt/ CB, Pt/GC and an in-house-prepared nanocapsule Pt/GC) were subjected to durability testing by means of a standard voltage step protocol (0.9 V ↔ 1.3 V vs. RHE, holding 30 s at each voltage, 1 min for one cycle) at 65 °C with H₂ (anode) and N₂ (cathode), and ambient pressure (0.1 MPa). The durability was estimated on the basis of either 3000 potential cycles (commercial Pt/CB) or 10000 cycles (commercial Pt/GC and nanocapsule Pt/GC). The current-voltage curves were measured initially and after certain numbers of cycles N at 65 °C, 100 % RH with H₂ and air. The electrochemically active surface area (ECA) decreased with increasing N, particularly the commercial Pt/CB, which underwent severe degradation in the cathode. In contrast, commercial Pt/GC and nanocapsule Pt/GC showed slow ECA degradation, due to the high corrosion resistance of GC. Furthermore, it was found that the decrease in cell performance was smaller for the nanocapsule Pt/GC compared to that for the commercial Pt/GC by 10 to 50 mV, because the Pt nanoparticles of the nanocapsule Pt/GC were well dispersed over the whole GC surface. We also examined the changes in the state of dispersion of the Pt nanoparticles by use of transmission electron microscopy (TEM).

Key Words: PEFC, Durability, Start/Stop Cycle, Nanocapsule Method

1 Introduction

Polymer electrolyte fuel cells (PEFCs) directly convert chemical energy to electrical energy with high efficiency and thus constitute a highly promising technology for portable devices, automobile power systems and stationary power supply systems. Nevertheless, the high system cost, including that of platinum, has impeded the widespread commercialization. Thus, one of the obvious ways to reduce the cost is to reduce the amount of Pt used in the catalyst layer (CL) in the PEFC, both by improving the true activity of the Pt-based electrocatalysts for the oxygen reduction reaction (ORR) and, as has been recognized more recently, by improving their durability. To maximize the electrochemically active area (ECA) for the ORR, the cathode catalysts employed thus far have consisted of Pt nanoparticles ranging from 2 to 3 nm in size dispersed on high surface area (S) carbon black (CB) supports (e.g., Sₐ = 800 m² g⁻¹). However, it has been found that Pt/CB cathode catalysts are degraded under PEFC operating conditions due to a combination of processes, which include (1) loss of active surface area due to agglomeration or dissolution of Pt nanoparticles, and (2) corrosion of CB. and thus carbon is thermodynamically unstable at the typical operating potentials of the oxygen cathode, which can range between 0.5 and 0.9 V vs. the reversible hydrogen electrode (RHE). It is well known that the corrosion rate of pure, uncatalyzed carbon black is slow, even under PEFC operating conditions, but is accelerated with increasing Pt concentration, particularly at high temperatures and high potentials. In our previous work, we have proposed a new method to evaluate the degradation of Pt catalysts and CB supports separately and to clarify the accelerating factors for their degradation. One of the main results was that the corrosion of the CB support was accelerated mainly by raising the operating potential to 0.90 V (vs. RHE) under a test simulating a daily start and stop operation mode for residential PEFCs. During the start-stop cycles of fuel cell vehicles (FCVs), the cathode potential can momentarily climb to more than 1.2 V due to the so-called "reverse-current mechanism" which significantly accelerates the carbon corrosion.

To mitigate the corrosion of the carbon support, the use of graphitized carbon blacks, for which the de-
gree of graphitization of the initial carbon support is essentially complete, and carbon nanotubes was found to be effective. Graphitized carbon black-supported Pt catalysts (Pt/CB) are already commercially available. However, for GC supports, the mass activities of Pt have been found to be lower than those for conventional Pt/CB catalysts, because it is difficult to disperse Pt nanoparticles uniformly on the GC support, which usually has a smaller specific surface area (e.g., $S_{\text{sc}} = 150 \text{ m}^2 \text{ g}^{-1}$) via conventional preparation methods. To solve this problem, we have developed an improved Pt/GC catalyst preparation approach, known as the nanocapsule method. With the conventional nanocapsule method, the catalyst easily becomes aggregated on the support, because there is a required step in which the organic moieties that make up the capsule are removed prior to dispersing them on the carbon black. Without the protection of the organic moieties of the capsules, the naked Pt particles aggregate easily on the support. However, our modified nanocapsule method can be used to prepare highly dispersed catalysts, because the organic moieties are removed only after the filled nanocapsules are dispersed on the high area support. We have succeeded in measuring enhanced ORR activities and durability, using the rotating ring-disk electrode (RRDE) technique, for well dispersed Pt nanoparticles on the GC support, which were prepared via the nanocapsule method. In that work, it was found that one of the most important factors leading to the high durability is the highly dispersed state of Pt particles on the GC.

In the present work, we have examined the state of dispersion of Pt particles on GC, using transmission electron microscopy (TEM), before and after a durability test with a membrane-electrode assembly (MEA). We have also examined cell performance changes during start-stop cycles, which were estimated using current-voltage (I-V) measurements, and compared these results with ECA measurements. The durability tests of three types of catalysts (commercial Pt/CB, c-Pt/CB, commercial Pt/GC (c-Pt/GC), and nanocapsule Pt/GC (n-Pt/GC)) were performed by a standard voltage step protocol (0.9 V to 1.3 V at the cathode vs. the hydrogen anode, holding 30 s at each voltage, i.e., 1 min for one complete cycle) recommended by the Fuel Cell Commercialization Conference of Japan (FCCJ).

2 Experimental

2.1 Preparation of Pt nanoparticles supported on graphitized carbon

The n-Pt/GC was prepared by the nanocapsule method. First, 0.25 mmol of platinum acetylacetonate, Pt(acac)$_3$, was dissolved in a mixed solvent of 1.2-hexadecanediol (260 mg) and diphenyl ether (125 mL). The projected platinum loading on GC was 50 wt.%. The mixture was heated at 110°C for 20 min in N$_2$ atmosphere with magnetic stirring. Then, oleic acid (85 µl) and oleylamine (80 µl) were added, followed by addition of GC. The temperature was elevated to 220°C, and was maintained constant for 30 min. Then, LiBEt$_3$H (1.0 ml) was added dropwise into the mixture, followed by re-fluxing at 270°C for 30 min. The mixture was cooled to room temperature and filtered. The powder thus obtained was dried at 60°C in vacuum and was heat-treated at 400°C for 4 h in flowing N$_2$ in order to remove the organic moieties completely. The catalyst powder thus obtained is denoted as n-Pt/GC.

2.2 Preparation of membrane electrode assembly (MEA)

The catalyst pastes were prepared with a planetary ball mill from the three types of catalysts (commercial Pt/CB and Pt/GC, supplied by Tanaka Kikinzoku Kogyo K.K., and the in-house-prepared nanocapsule Pt/GC) with Nafion binder (DE521, E.I. Du Pont de Nemours & Co., Inc.) for 30 min. The mass ratio of Nafion binder (dry basis) to carbon black (Nafion binder/carbon) was adjusted to 0.7.

To prepare a uniformly coated catalyst-coated membrane (CCM), the catalyst paste was directly sprayed onto the electrolyte membrane, which was maintained at 55°C, by use of a pulse-swirl-spray apparatus (PSS, Nordson Corp.), and then dried at 60°C in an electric oven. The electrolyte membrane used was a commercial Nafion membrane (NRE 212, Dupont, 50 µm thickness). The active geometric area of the electrode was 29.2 cm$^2$, and the Pt loading on both cathode and anode sides was 0.5 ± 0.1 mg Pt cm$^{-2}$.

The MEA was prepared by hot-pressing a CCM sandwiched between two gas diffusion layers (GDLs, 25BCH, SGL Carbon Group Co., Ltd.) at 140°C and 1.0 MPa for 3 min. The MEA was placed into a single serpentine pattern cell (Japan Automotive Research Institute (JARI) standard cell) consisting of two carbon separator plates.

2.3 Test procedure

The durability test was performed according to the procedure shown in Fig. 1. All of the cells were operated.

![Fig. 1 Durability test procedure to evaluate the degradation of c-Pt/CB, c-Pt/GC, and n-Pt/GC catalysts. Inset: standard voltage step protocol recommended by FCCJ.](image-url)
under ambient pressure at every step. The first step in the durability test was the measurement of the initial performance. The initial performance test included the measurement of both I-V curves and cyclic voltammetry. The I-V curves were measured at a cell temperature $T_{\text{cell}}$ of 65°C with hydrogen (H$_2$) and air at ambient pressure (0.1 MPa). Humidified H$_2$ gas was supplied to the anode, and air to the cathode, respectively. The gas utilizations of H$_2$ and air were 70% and 40%, respectively. All of the gases were humidified identically at 100% RH by bubbling through a water reservoir maintained at 65°C. In order to measure the ECA of Pt in the initial state, cyclic voltammetry was carried out at 65°C by use of a potentiostat (HZ-5000 Automatic Polarization System, Hokuto Denko). The cathode compartment was purged with nitrogen (N$_2$) (100 mL min$^{-1}$, 100% RH), while H$_2$ gas (100 mL min$^{-1}$, 100% RH) was supplied to the anode. The anode was used as both reference electrode and counter electrode. Prior to the potential sweep, the potential was maintained at 0.085 V for 3 s. Then, the N$_2$ flow was stopped, and the potential was swept from 0.085 V to 1.000 V at 20 mV s$^{-1}$. The value of ECA was determined from the hydrogen adsorption charge, referred to as $\Delta Q_{\text{ads}} = 0.21 \, \text{mC cm}^{-2}$, adopted conventionally for clean polycrystalline platinum. Then, the durability test of each catalyst was performed by the standard voltage step protocol recommended by the FFCJ$^{37}$ at 65°C with H$_2$ and N$_2$, and ambient pressure (0.1 MPa). Humidified H$_2$ gas was supplied to the anode and N$_2$ to the cathode, respectively. The flow rate of all gases was controlled at 100 mL min$^{-1}$ by a mass flow controller. These gases were humidified identically at 100% RH. As shown in the inset in Fig. 1, the voltage at the cathode was stepped between 0.9 V and 1.3 V, with a holding period of 30 s at each voltage. After given number of potential step cycles (N), step 3 was performed to examine the changes in ECA. The last step for the durability test was to re-measure the I-V curves at the same cell temperature as in step 4.

2.4 Transmission electron microscopy (TEM)

TEM examination was carried out with a Hitachi H-9500 microscope at an acceleration voltage of 100 kV. Particle size distribution histograms were obtained from the image analysis of 500 randomly selected Pt particles in the TEM images. In addition, particle length distributions were obtained.

3 Results and Discussion

3.1 Characterization of each catalyst using TEM

Figure 2 shows the TEM images (low and high magnification) of c-Pt/CB, c-Pt/GC, and n-Pt/GC with the particle size distribution histograms. For the n-Pt/GC, Pt particles were well dispersed over the whole surface of the GC support, and their size distribution was fairly narrow, as shown in Fig. 2 (c). In contrast (Fig. 2 (b)) for c-Pt/GC, many Pt particles were segregated on the edges or grain boundaries of the GC support. Also, the particle size distribution for c-Pt/GC was wider than that for n-Pt/GC. The average particle sizes of each catalyst, which were obtained by TEM, the metal loading amounts, and ECA values based on the cyclic voltammograms (CVs) are shown in Table 1.

3.2 Changes in ECA during the durability test

We measured the changes in ECA for each catalyst during the durability test. The ECA value is a critical factor in analyzing the catalytic activity of electrodes. Figure 3 shows the CVs, which were recorded for each of the three cathodes in MEAs at 65°C after various N values in the durability test. The initial ECA values of these electrodes were calculated to be 62.8 m$^2$ g$^{-1}$ (c-Pt/CB), 38.6 m$^2$ g$^{-1}$ (c-Pt/GC), and 32.5 m$^2$ g$^{-1}$ (n-Pt/GC) (see Table 1). As shown in Fig. 3, the H$_2$-adsorption peak for c-Pt/CB decreased drastically. As shown below in the description of the TEM results, this was due to Pt catalyst detachment from the carbon support due to carbon support degradation. In contrast, the H$_2$-adsorption peaks for c-Pt/GC and n-Pt/GC changed only slightly compared with c-Pt/CB, because the GC carbon support used had a high degree of graphitization. To clarify the

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Metal loaded</th>
<th>Pt-loading/mg cm$^{-2}$</th>
<th>$d_{\text{TEM}}$/nm</th>
<th>ECA/m$^2$ g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>c-Pt/CB (commercial)</td>
<td>46.1</td>
<td>0.48</td>
<td>$2.5 \pm 0.6$ nm</td>
<td>62.8</td>
</tr>
<tr>
<td>c-Pt/GC (commercial)</td>
<td>46.7</td>
<td>0.54</td>
<td>$3.4 \pm 0.7$ nm</td>
<td>38.6</td>
</tr>
<tr>
<td>n-Pt/GC (nanocapsule)</td>
<td>46.1</td>
<td>0.51</td>
<td>$3.0 \pm 0.4$ nm</td>
<td>32.5</td>
</tr>
</tbody>
</table>
carbon corrosion for CB and GC, we calculated the background-corrected oxidation currents at 0.6 V for the hydroquinone-quinone (HQ-Q) redox peak, during the positive-going voltage sweep; these are shown in Fig. 4. The redox peak is assigned to the HQ-Q group formed during the corrosion of the carbon support. The amount of the background-corrected oxidation current was obtained by subtracting the double layer (DB) charging current from the HQ-Q redox peak current and normalizing to the mass of carbon. The results show that the values of specific current for the CB-supported Pt catalyst were quite high, but those for the GC-supported catalysts indicated low, relatively constant values during the durability test due to their high corrosion resistance.

Figure 5 (A) shows the progress of the ECA degradation versus $N$ up to 10000 cycles in log form. In Fig. 5 (B), the same values are shown normalized to the initial ECA values (B). The CB-supported catalyst (c-Pt/CB) clearly exhibited a much higher ECA degradation rate than that for the GC-supported catalysts (c-Pt/GC and n-Pt/GC). As shown in Figs. 5 (A) and 5 (B), we cannot sensibly discuss a Pt dispersion effect on the total reduction rate of ECA, due to the rather small ECA values for n-Pt/GC in comparison with that for c-Pt/GC. However, the initial rate of ECA decrease for n-Pt/GC was slightly smaller than that for the c-Pt/GC catalysts ($0 < N < ca. 3000$). This result suggests that the Pt particles for c-Pt/GC easily underwent agglomeration, because the Pt particles in c-Pt/GC were quite close together in the initial

![Fig. 3](image_url)  
**Fig. 3** Cyclic voltammograms to determine the ECA for (A) c-Pt/CB, (B) c-Pt/GC, and (C) n-Pt/GC. Cyclic voltammograms in humidified $N_2$ (100% RH) at $T_{\text{cell}} = 65^\circ C$ were obtained at a voltage sweep rate of 20 mV s$^{-1}$.

![Fig. 4](image_url)  
**Fig. 4** Plot of current values for each catalyst at 0.6 V corrected for double layer charging current (at 0.4 V) for c-Pt/CB (○), c-Pt/GC (▲), and n-Pt/GC (△) catalysts as a function of $N$ during the durability test.

![Fig. 5](image_url)  
**Fig. 5** Plot of the progress of the ECA degradation (A) and normalized to the initial ECA values (B) for c-Pt/CB (○), c-Pt/GC (▲), and n-Pt/GC (△) catalysts as a function of log $N$. 


state. On the other hand, the Pt particles in n-Pt/GC were well-dispersed (see Fig. 2). Therefore, we propose that the Pt dispersal state on GC is one of the factors that helps to mitigate the agglomeration of Pt particles during the initial stage of degradation. Also, this effect significantly affected the time elapsed for the reduction of ECA to ca. 1/2 of its initial value, i.e., its half-life. The half life for n-Pt/GC was 2 times longer than that for c-Pt/GC and 20 times longer than that for c-Pt/CB.

3.3 Changes in cell performance resulting from the durability test

Figure 6 shows the changes in the I-V curves (A), and the differences in the voltages measured before and after the durability test for all three catalysts (c-Pt/CB, c-Pt/GC, and n-Pt/GC) (B), and finally, the differences in the voltages measured before and after the durability test for GC-supported Pt catalysts (c-Pt/GC and n-Pt/GC) on an expanded scale (C). The cell performances for all of the catalysts decreased with increasing N. In particular, c-Pt/CB showed a drastically decreased cell performance, i.e., the same trend as that for the ECA degradation. Also, the cell performances for the GC-supported catalysts degraded slightly during the test, although the N values were clearly higher than that for c-Pt/CB (CB-supported catalyst, 3000 cycles; GC-supported catalysts, 10000 cycles). These results strongly indicate that one of the reasons for decreasing cell performance is degradation of the carbon support in the high potential region.

To clarify the degradation of the cell performance, we calculated the values of voltage decrease during the test, as shown in Fig. 6 (B). This result also clearly shows that the c-Pt/CB exhibited the largest degradation rate compared with the two GC-supported catalysts, presumably due to its low corrosion resistance.

We also show the values of voltage decrease for the two GC-supported catalysts in Fig. 6 (C). The voltage decrease for n-Pt/GC was lower than that for c-Pt/GC by 10 to 50 mV in the I-V measurement, even though these two catalysts used the same GC support. Thus, we hypothesized that the decrease of cell performance was affected not only by the corrosion of the carbon support but also by the state of dispersion of the Pt particles on the carbon support.

To confirm the reason for the reduction of cell performance with the same GC support, we observed the three catalysts by TEM after the durability test. Figure 7 shows the TEM images (low and high magnification) of all of the catalysts after the durability test (N for c-Pt/CB = 3000; N for c-Pt/GC and n-Pt/GC = 10000). The average particle sizes and standard deviations were 4.4 ± 1.6 nm, 4.8 ± 1.0 nm, and 4.5 ± 1.2 nm for c-Pt/CB, c-Pt/GC,

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**Fig. 6** Cell performance I-V curves for each catalyst at 65 °C, 100% RH with H2 and air (A); differences of cell performance before and after durability testing for (B) all catalysts, and (C) the GC-supported catalysts.

**Fig. 7** TEM images (first row, low magnification; second row, high magnification) and particle length distribution histograms of (A) c-Pt/CB, (B) c-Pt/GC, and (C) n-Pt/GC powders after the durability test [N= 3000 (c-Pt/CB), 10000 (c-Pt/GC and n-Pt/GC)].
and n-Pt/GC, respectively. In order to indicate the degree of agglomeration of the Pt particles, we have measured the lengths of agglomerated Pt particles from the image analysis of 300 randomly selected Pt particles in the TEM images. The simple particle size distribution was not sufficient to show the true state of dispersion of the Pt particles. The length analysis showed that, in c-Pt/GC, there were many long Pt particles, because the initially present Pt particles underwent agglomeration, most likely due to their close proximity on the GC support. On the other hand, the particle agglomeration was suppressed for n-Pt/GC, due to the enhanced dispersion of the Pt particles on the GC, which was maintained even after the durability test. Therefore, the percentage of long connected particles (length greater than 9 nm) for n-Pt/GC (35%) was lower than that for c-Pt/GC (60%). From this result, we can understand that, for n-Pt/GC, there were a greater number of shorter agglomerates, i.e., fewer connected Pt particles, than that for c-Pt/GC. For this reason, the cell performance was well maintained during the test. Although the present voltage step protocol (0.9 V → 1.3 V) is designed primarily for the durability test of the support, the potential holding step at 0.9 V, or the similar condition in the I-V measurement, probably led to the coarsening of the Pt particles due to so-called "electrochemical Ostwald ripening," in which the Pt particle size increases via a dissolution-redeposition process.

To clarify the reason for this result, we have proposed a "territory" concept in previous work. Watanabe et al. reported that a highly dispersed state of Pt nanoparticles on the support, with the maintenance of a sufficient interparticle distance or sufficiently large territory, is a highly critical parameter for operating Pt catalysts at a high mass activity (MA) for the ORR in 100% phosphoric acid at 190°C. A similar trend can be seen in the present results for the MEA, according to the state of dispersion of Pt before and after the durability test. On the basis of this result, we propose that when Pt particles are highly dispersed (well separated from neighboring particles) on the support, as in the case of n-Pt/GC after the durability test, the decrease of cell performance is suppressed, because O₂ molecules are supplied by spherical diffusion to the individual particles. In contrast, for Pt particles close together, as in the case of c-Pt/GC after the durability test, the cell performance was lower, because the territories (radial diffusion fields) of the catalyst particles for O₂ were overlapping. Therefore, the decrease in cell performance for n-Pt/GC was lower than that for c-Pt/GC.

In our recent work, we have proposed a new evaluation method for the effectiveness of Pt (É_0). In earlier work, we and others had considered that the fraction of the total Pt surface area that is contacted by the ionomer, which is the Pt utilization (Uₚ), can also be accessed during the ORR in the catalyst layer. However, this method was found to have some problems for measuring Pt utilization, e.g., measurement potential range, temperature effect, and anion adsorption effect. Therefore, we have proposed É_0 to evaluate its utilization under actual ORR operating conditions. The É_0 value is defined as the ratio of MA in the MEA to the ideal value, MA_{max}, which is based on channel flow double electrode (CFDE) measurements. The É_0 values (typically in the less than 10%) were found to be smaller than the Uₚ values, which are based on ECA and were in the 60% to 70% range, because the former were affected by factors such as the gas diffusion resistance and proton conductance in the catalyst layer under actual ORR operating conditions. We have thus argued that the Uₚ value, which is measured by ECA, is fundamentally different from the É_0 value, which is the effectiveness of Pt utilization, under actual ORR operating conditions. Therefore, our previous research lends dramatic support to the discussion of the differences of cell performance for both Pt/GC catalysts after the durability test. We can explain the results as follows: even though the ECA values were nearly the same after the durability test, the É_0 value for n-Pt/GC was higher than that for c-Pt/GC, because it was less affected by O₂ diffusion limitations, due to its superior Pt particle dispersion state after the durability test (see Fig. 7).

In conclusion, n-Pt/GC has an additional advantage compared with the other two catalysts: (1) compared with the conventional carbon support, there was suppression of the carbon corrosion due to the GC support’s high degree of corrosion resistance; and (2) mitigation of the coarsening of Pt particles due to the excellent separation of the Pt particles on the GC support. Hence, an essential factor for coping with both maintenance of cell performance and high durability is the highly uniform dispersion of Pt particles on the GC support.

4 Conclusions

The n-Pt/GC catalyst showed superior durability in the voltage step cycle testing between 0.9 V and 1.3 V. The amount of time elapsed for the reduction of ECA to half of the initial value at n-Pt/GC was 2 times longer than that for c-Pt/GC and 20 times longer than that for c-Pt/CB. Also, the voltage decreases for n-Pt/GC were lower than that for c-Pt/GC by 10 to 50 mV in the I-V measurement. The essential factors for maintenance of cell performance during voltage cycling are the high degree of corrosion resistance of the graphitized carbon black support and the uniform dispersion of Pt particles on the GC support, to which the nanoparticle method has contributed greatly.

Acknowledgement

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