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Investigation of the Carbon Corrosion Process for Polymer Electrolyte Fuel Cells Using a Rotating Disk Electrode Technique

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The carbon corrosion process of low surface area Pt/XC72 and high surface area Pt/BP2000 was investigated using an accelerated durability testing method under simulated fuel cell conditions (a rotating disk electrode approach). A steam etching experiment was also carried out for further understanding of the carbon corrosion process for XC72 and BP2000. It was observed that different carbon corrosion processes resulted in different performance (electrochemical active surface area, mass activity, and double layer capacity) decals of catalysts. The corrosion process was studied using transmission electron microscopy. In Pt/XC72, major corrosion occurred at the center of the Pt/XC72 particle, with some minor corrosion on the surface of the carbon particle removing some amorphously structured carbon black filaments, whereas in Pt/BP2000, the corrosion started on the surface.

Polymer electrolyte fuel cells (PEFCs) have been considered one of the best candidates for future automobile propulsion due to their zero emissions, high energy efficiency, and use of carbon neutral fuels, i.e., hydrogen.1 As PEFCs are being driven toward commercialization, the focus of PEFC research and development has shifted to reducing cost and improving durability while increasing performance, because improving PEFC components can effectively reduce the cost of implementing PEFC systems, making widespread commercialization more realistic due to a reduced stack replacement frequency. In addition, enhanced durability performance of PEFCs is essential for PEFC application in automotive propulsion. PEFC performance loss during long-term operations under steady and dynamic conditions has been attributed to the degradation of Pt and Pt alloy catalyst nanoparticles,2-5 the corrosion of catalyst carbon supports, and the degradation of the Nafion ionomer network inside the catalyst layer and the Nafion membrane.6-14

Carbon corrosion results in the degradation of the catalyst layer, which not only causes a decrease in the electrochemically active surface area (ECSA)15 and an increase in the total resistance because of the loss of structural integrity,6 but also has an effect on the Pt particle growth6 and causes an increased mass-transfer loss due to the increased hydrophilicity within the catalyst layer.7-19 On a commercial carbon support surface (Vulcan XC72 carbon black), carbon oxidation occurs at 65°C, and a potential of >0.8 V (vs reversible hydrogen electrode) was reported by Dowlapalli et al.20 and Kangasniemi et al.21 In the work of Borup et al.22 and Mathias et al.,23 it was observed that at 1.2 V, a commercial Pt/C catalyst lost 15% of its weight after 20 h testing. Carbon support is stable at steady-state conditions; however, severe carbon corrosion occurs during startup/shutdown cycles and fuel starvation because a high potential spike (~1.2 to 1.5 V) is established during the startup/shutdown period as well as in the fuel starvation regions.24-26 PEFCs in automotive applications undergo an estimated 30,000 startup/shutdown cycles over the lifetime of a vehicle,27 which negatively cause carbon corrosion to affect durability and lifespan. Borup et al. indicated that carbon corrosion during start–stop cycles worsened in low humidity,28 Dowlapalli et al.29 and Roen et al.24 showed that the existence of Pt nanoparticles on the surface of carbon accelerated the corrosion of the carbon support. The corrosion of carbon supports in PEFCs has been investigated by several groups,30-34 in membrane electrode assembly (MEA) configurations, the most common methods for carbon corrosion testing include load on–load off cycles,35 simulated drive cycles,36 open-circuit voltage (OCV) conditions,37 and high voltage cycles38 [0.9–1.5 V vs rotating disk electrode (RDE)] under H2/N2 and H2/air. It was found by Ferreira et al.39 that a 46% loss of ECSA was measured at 0.2 A cm−2 (0.75 V) after 2000 h, while in OCV (0.95 V) conditions, a 75% loss was observed over the same period. However, after 10,000 cycles between 0.87 and 1.2 V in just 100 h, 69% of the ECSA was lost. Carbon corrosion in the catalyst layer of the PEFC can be monitored by determining the amount of CO2 gas emitted from a running cell by glassy carbon (GC) and NMR.35-37 A scanning electron microscope (SEM) can also be employed to observe the carbon corrosion of the catalyst layer.24, 38 Hyun et al.39 employed low angle annular-dark-field scanning transmission electron microscopy to examine the three-dimensional morphology and structure of corroded carbon/Pt systems. Some researchers observed that the catalyst layer becomes thinner after carbon corrosion.40 Li et al.41 observed a 50% cathode catalyst layer thickness loss in a highly corroded region after 220 potential cycles (0.6–1.0 V). Shi et al.42 showed the carbon corrosion from the CF atomic ratio by energy-dispersive X-ray analysis. However, it is very difficult to decouple the carbon corrosion in MEAs from the experimental data due to the complexity of the PEFC degradation, because in fuel cells, there are different degradation processes occurring at the same time (degradation of Pt and alloy catalyst nanoparticles, ionomer degradation, membrane degradation, and carbon corrosion). In addition, the study of carbon corrosion using an MEA configuration takes a long period of time to complete. Colón-Mercado et al. developed an accelerated degradation test in a simulated fuel cell system to investigate carbon corrosion in a three-electrode system using an RDE. However, little work has been reported on the corrosion process or on the fine structure of carbon black support corrosion in PEFCs. In a previous paper, it was shown that a higher degradation of the carbon support was observed at higher potentials.42 For this reason, in this study, we concentrated our efforts on studying the durability of the carbon support from 0.85 to 1.4 V [vs normal hydrogen electrode (NHE)], where the major damage is expected to occur during fuel cell operations. This paper presents an investigation of carbon corrosion using an accelerated degradation test (ADT) under conditions similar to those in fuel cells using an RDE. A steam etching method was also employed to confirm the carbon corrosion processes of the two carbon supports (VXC72 CB and BP2000).
Experimental

Preparation of the catalyst.— Two catalyst supports were used: a low surface area (254 m²/g) carbon black Vulcan XC72 and a high surface area (1500 m²/g) Black Pearl BP2000, both from Cabot (Billingera, MA). Both of the carbon blacks were immersed in a 10 g L⁻¹ platinum precursor [Pt(NH₃)₂(OH)₂Cl₂] salt solution. The mixture of the carbon blacks and the platinum precursor was dried in an oven at 110°C. Reduction of the adsorbed platinum precursor to a metallic form was carried out by treatment with hydrogen gas at elevated temperatures. Generally, the preferable temperature of the reducing reaction is in the approximate range of <200°C. For the exact temperature, thermographic analysis was used to determine the Pt loading for 20% Pt/XC72 and 20% Pt/BP2000.

ADT.— Materials.— All chemicals were used as received: a 5 wt % Naion solution (Ion Power, Inc., New Castle, DE), 60% perchloric acid (99.999% purity, Fisher Scientific), 70% isopropyl alcohol (IPA, Fisher Scientific), and high purity water (resistance ~18.2 MΩ). Oxygen (research grade, 99.999% purity) and nitrogen gases (research grade, 99.999% purity) were obtained from Praxair.

Electrochemical apparatus.— A glassy carbon rotating disk electrode (GCRDE) was used as the working electrode (0.196 cm², Pine Instruments, Inc., Raleigh, NC). The GCRDE was polished with a 0.3 μm followed by a 0.05 μm alumina suspension to give it a mirrored finish. Sonication was used to suspend 35 mg of Pt/VXC72 (or Pt/BP2000) catalyst in a solution of 200 μL 5 wt % Naion, 3 mL IPA, and 2 mL distilled water for 5 min. A total of 10 μL of the suspension (loading: 0.35 mg Pt/cm²) was pipetted onto the GC and was dried at room temperature overnight. Electrochemical measurements were carried out using three compartments: a catalyst/GC as a working electrode, a Pt wire as a counter electrode, and Ag/AgCl as a reference electrode. Electrochemical measurements were recorded using a PARSTAT 2273 advanced electrochemical system (Princeton Applied Research, Oak Ridge, TN). All potentials cited in this paper were normalized with respect to the NHE potential.

Electrochemical measurements.— All experiments were performed at room temperature. After preparation of the catalyst on the GC, the catalyst was electrochemically cleaned by potential cycling between 0.05 and 1.2 V at 10 mV/s for 200 cycles in a N₂ saturated, 0.1 M HClO₄ solution. The area under the desorption peak of underpotentially deposited hydrogen in a CV (scan rate of 20 mV/s between 0.05 and 1.2 V) was used to evaluate the ECSA of the Pt catalyst on the electrode. Polarization curves for the oxygen reduction reaction (ORR) on the RDE were recorded by scanning the potential from 0.05 to 1.2 V at 20 mV/s in oxygen saturated, 0.1 M HClO₄ electrolyte. To perform the ADT, a cyclic voltammogram (CV) was used with a scan rate of 20 mV/s between 0.85 and 1.4 V. The area under the desorption peak of underpotentially deposited hydrogen in a CV (scan rate of 20 mV/s between 0.05 and 1.2 V) was used to evaluate the ECSA of the Pt catalyst on the electrode. The degradation of catalyst Pt nanoparticles during the ADT cycling was followed by monitoring the Tafel slopes of the catalysts before and after 1800 ADT cycles for both Pt/XC72 and Pt/BP2000.

Steam etching experiment.— XC72 and BP2000 were employed. A tube furnace (with gas inlet and exit) was designed to be used for the steam etching process. The aggregates of these carbon black powders were milled before etching experiments. The milled carbon black powders were placed into the tube furnace and then were purged with nitrogen while the temperature was increased through programmed heating at a heating rate of 5°C/min. The steam was introduced into the furnace when the furnace reached the desired temperatures, and the steam continued flowing through the furnace for a certain length of time. The flow rate of the steam (vapor) was 0.5 cm³/min, and the flow rate was the same in all experiments. The steam etching experiments lasted for 3 h at 800°C.

Characterization of steam etched carbon blacks.— After 1800 consecutive ADT and steam etching experiments, the catalyst was collected for the morphology examination to be done using a Hitachi S-4800 SEM and a Philip Tecnai 20 transmission electron microscope (TEM). Image J 1.42 software was used to determine the average particle size and the size distribution; about 200 particles were analyzed.

Results and Discussion

Electrochemical measurement on the activity degradation for the ORR.— The principal objective of this study was to investigate the carbon black corrosion process for PEFCs using an RDE approach under simulated PEFC conditions and to provide a model system for studying the catalyst support corrosion mechanism for PEFCs.

The typical CV and polarization curve results, before and after consecutive ADT (1800 cycles), respectively, are shown in Fig. 1a and b for Pt/XC72 and in Fig. 1c and d for Pt/BP2000. Assuming the hydrogen adsorption–desorption process was on a polycrystalline Pt surface, the ECSA was determined by integrating the Η₂ peak. The pair of peaks observed between 0.05 and 0.30 V (vs NHE) corresponded to the desorption–adsorption of hydrogen on the Pt surface. With ADT cycling, a reduction on the Η₂ peak was observed for both catalysts, indicating an increase in Pt particle size due to Pt nanoparticle agglomeration. After 1800 consecutive cycles, the ECSA loss of Pt/XC72 was 64.2%, which was less than that of Pt/BP2000, 80.4% (Table I). An interesting phenomenon can be seen in Fig. 1c. A redox couple appeared at 0.55 V in the voltammogram of the Pt/BP2000 catalyst after 1800 cycles. This redox couple corresponds to the redox couple of quinone/ hydroquinone, a carbon corrosion product, C₁₅Ο₂ → quinone. However, as seen in Fig. 1a, such a redox couple was not obvious in the voltammogram of Pt/XC72 after cycling. It seems that this redox couple was hidden in the broad peaks between 0.40 and 0.80 V, which may suggest a different carbon corrosion mechanism for XC72 than for BP2000.

Figure 1 presents the polarization curves for Pt/XC72 (Fig. 1b) and Pt/BP2000 (Fig. 1d), at room temperature in 0.1 M HClO₄ saturated with O₂ using a GCRDE at 1600 rpm. At high potentials (between 0.96 and 0.80 V vs NHE), the ORR was under kinetic control. This region was followed by a mixing control region of charge transfer and mass transfer. As can be seen in Fig. 1, the difference between the Tafel slopes before and after 1800 ADT cycles for both Pt/XC72 and Pt/BP2000 is very small, suggesting that the change in catalytic activity of both catalysts was minimal. The degradation of catalyst Pt nanoparticles during the ADT cycling was not the dominating process. As found in Table I, the mass activity of the catalysts after cycling became worse. The mass activity (current density at 0.75 V vs NHE) loss of Pt/XC72 and Pt/BP2000 was 75.6% and 84.6%, respectively, which is very similar to the losses in ECSA for both catalysts (mainly attributed to Pt nanoparticle agglomeration). Therefore, it can be concluded that Pt/BP2000 is less stable than Pt/XC72 under equivalent conditions, which might be due to the higher surface area of BP2000 (1450 vs 250 m²/g of XC72). Figure 1b and d shows that the polarization curves of each catalyst before and after cycling were parallel to each other, suggesting that the Tafel slopes of the catalysts do not change much and, hence, the catalytic activity is similar. However, each other, suggesting that the Tafel slopes of the catalysts do not change much and, hence, the catalytic activity is similar.
philic groups (i.e., ketone and phenyl groups) from the carbon corrosion; hence, these pores are filled with water, gas reactant transport is severely hindered, and the steep decrease in the current density is seen as cell voltage goes down (i.e., <0.60 V), namely “flooding.” However, in the RDE configuration, the thin catalyst layer on the GC electrode is completely immersed in the liquid electrolyte. Hence, there is no gaseous reactant transport issue and, consequently, no flooding should be observed. Therefore, the huge voltage drop for each catalyst after cycling must have been caused mainly by carbon corrosion.

To measure the performance of the catalyst during the ADT cycling, the Pt nanoparticles were exposed to extremely corrosive conditions. The Pt nanoparticles on the carbon surface experienced an extensive particle agglomeration process through the surface migration of catalyst nanoparticles under the potential cycling in the solution. Carbon corrosion facilitated the surface particle migration by weakening or even breaking the interaction/bonds between the Pt nanoparticles and the carbon supports. Carbon corrosion also caused the detachment of the Pt nanoparticles from the carbon support, which may have formed agglomerates or been washed away in the water, particularly when the current density was high. Thus, carbon corrosion contributed a great deal to the catalyst performance loss. By cycling the catalyst in acidic media, the corrosion of the carbon support could have also resulted in a significant loss of catalyst performance. For the platinum catalyst, Pt nanoparticles on different carbon supports (XC72 and BP2000) were oxidized into ions and migrated/dissolved into the electrolytes under high potentials (i.e., >0.85 V). Then the dissolved Pt ions were redeposited on the surface of the larger particles, a phenomenon known as Ostwald ripening. As for carbon corrosion, it could have not only increased the resistance of the catalyst layer but also could have partly enhanced the aggregation of the Pt particles and thus caused the migration and dissolution of the Pt particles. Therefore, the ECSA and mass activity loss can be attributed to the increase in the Pt particle size and carbon support corrosion.

![Figure 1](https://www.elsolucion.com/images/chemicals/Pt.png)

**Figure 1.** (Color online) Voltammograms and polarization curve (on an RDE) for different Pt-based carbon supports before and after 1800 ADT cyclings in 0.1 M HClO₄ purged with N₂ at room temperature at a sweep rate of 20 mV s⁻¹. The catalyst layer consisted of a total metal loading of 70 μg and 3 μL of a mixture of Nafion solution (5 wt % from Ion Power, U.S.) and IPA (1:20). [(a) and (b)] Pt/XC72 and [(c) and (d)] Pt/BP2000.

<table>
<thead>
<tr>
<th>Voltage (V)</th>
<th>Current Density (mA/cm²)</th>
<th>Log iₑ (A/mgPt)</th>
<th>ECSA (m²/gPt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>0.0 0.2 0.4 0.6 0.8 1.0</td>
<td>0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.8 1.0</td>
<td>-3.0 -2.5 -2 -1.5 -1 -0.5 0 0.5 1.0</td>
</tr>
<tr>
<td>0.60</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.65</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.80</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.85</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.90</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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**Table I.** ECSA and kinetically controlled ORR currents at 0.75 V vs NHE for the Pt-based different carbon supports before and after 1800 consecutive ADT cyclings.

<table>
<thead>
<tr>
<th>At 0.75 V</th>
<th>iₑ (A/gPt)</th>
<th>ECSA (m²/gPt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/XC72</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0</td>
<td>98.7</td>
<td>89.7</td>
</tr>
<tr>
<td>1800h</td>
<td>24.1</td>
<td>32.1</td>
</tr>
<tr>
<td>Loss (%)</td>
<td>75.6</td>
<td>64.2</td>
</tr>
<tr>
<td>Pt/BP2000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0</td>
<td>68.7</td>
<td>54</td>
</tr>
<tr>
<td>1800h</td>
<td>10.58</td>
<td>10.6</td>
</tr>
<tr>
<td>Loss (%)</td>
<td>84.6</td>
<td>80.4</td>
</tr>
</tbody>
</table>
BP2000 as compared to XC72 but also indicates that the corrosion resistance of Pt/XC72 is higher than that of Pt/BP2000, especially in the initial period.

Double layer capacity (DLC) was also obtained by integrating the CV curve from 0.32 to 0.85 V (vs NHE) for both Pt/XC72 and Pt/BP2000. DLC is directly proportional to the carbon surface area. To compare the exact change in the DLC of the catalyst layer and the electrolyte, the CV curve was also measured on a fresh GC electrode (without any catalysts) after it went through the exact same ADT process. All the values shown in the right axis of Fig. 2b (Pt/XC72) and Fig. 2d (Pt/BP2000) have had the DLC values subtracted from those of the fresh GC electrode, which served as the background. In Pt/XC72, the DLC initially increased, maintained the same level from the 300th to the 900th cycle, and then decreased after the 900th cycle. However, in Pt/BP2000, the DLC showed a different trend with an increase in the number of cycles; it decreased at a much higher rate (0.23 mC/cm² cycle) compared to that of the Pt/XC72 (0.15 mC/cm² cycle), especially between the 300th and 900th cycles (0.05 mC/cm² cycle for Pt/XC72 and 0.26 mC/cm² cycle for Pt/BP2000). The increase in DLC in Pt/XC72 suggests that carbon corrosion may take place starting from the center of the carbon particles, which results in more surface area; further corrosion causes the loss of the carbon particles from the catalyst layer, which results in the loss of electric contact with the bulk, indicated by the decrease in the DLC after 1200 cycles. However, the decrease in the DLC for Pt/BP2000 shows a linear relationship with the cycle number, suggesting a continuous loss of surface area for the BP2000 carbon particles during cycling. The different trends of the DLC of Pt/XC72 and Pt/BP2000 with regard to cycle number indicate the different carbon surface area changes during the carbon corrosion process and, in turn, different carbon corrosion mechanisms.

To further illustrate the carbon corrosion of the two catalysts, the polarization curves after different cycle numbers are shown in Fig. 3. The different potential ranges of the polarization curves correspond to different control steps: OCV to 0.85 V is the kinetic control.
range. 0.85–0.65 V is the ohmic control range (i.e., mixing control of both kinetic and mass transport), and a potential below 0.65 V is in the mass transport control range. To observe the effects of potential cycling on the performance, the ORR mass activity current density at 0.85 V (kinetic performance), 0.75 V (ohmic performance), and 0.65 V (mass transport performance) (vs NHE) as a function of cycle number, respectively, is presented in Fig. 3. The mass activity loss with the cycle number for Pt/XC72 (a and b) and Pt/BP2000 (c and d), obtained at room temperature in 0.1 M HClO4 saturated with O2 using a GCRDE at 1600 rpm is presented in Fig. 3. The current density decay rates at 0.85, 0.75, and 0.6 V were 0.02, 0.08, and 0.13 A g⁻¹ cycle⁻¹, respectively, for Pt/XC72 and 0.018, 0.07, and 0.125 A g⁻¹ cycle⁻¹, respectively, for Pt/BP2000. These values indicate a strong correlation between Pt particle agglomeration, carbon corrosion, and the value of the mass activity current density decay. For both Pt/XC72 and Pt/BP2000, the kinetic performance degradation (due to the catalytic activity change) indicated by the mass activity current density at 0.85 V (vs NHE) was much smaller than the mass transport performance degradation, indicated by the mass activity current density at 0.65 V (vs NHE) (0.02 and 0.018 vs 0.13 and 0.125 A g⁻¹ cycle⁻¹). The mass transport performance is determined by the morphology and hydrophilicity of the carbon particle surface and, consequently, by carbon corrosion during the ADT cycle. The higher degradations of the mass transport performance in Fig. 3b and d suggest that carbon corrosion plays a much bigger role than catalyst degradation in affecting the performance during the ADT cycling. The trends of mass activity loss are very similar to those of the ECSA shown in Fig. 2b and d. As can also be seen in Fig. 3b and d, the initial decay was much faster for the Pt/BP2000 catalyst than for Pt/XC72 (at the 900th cycle, a 62% mass activity loss for Pt/XC72 and a 97.6% loss for Pt/BP2000), which confirms the conclusion, again, that Pt/BP2000 corrodes more easily than Pt/XC72.

From the study of the TEM images of the two catalysts (Fig. 4 and 5), different corrosion processes for different carbon supports were suggested. The TEM images and the Pt particle size distribution of Pt/XC72 before and after 1800 consecutive cyclings are shown in Fig. 4a-c. As can be seen in Fig. 4a and b, the micrograph of the homemade Pt/XC72 sample before and after 1800 consecutive ADT cycles shows that the change in morphology and size of the XC72 sphere was almost negligible, comparing the fresh Pt/XC72 (Fig. 4a) with the cycled Pt/XC72 (Fig. 4b). However, the center of the carbon black particle became brighter (as shown by the arrows pointing in Fig. 4b) than the rest of the particle. Comparing that with the micrograph of a fresh Pt/XC72 in Fig. 4a, apparently, a hole began to emerge after 1800 consecutive cycles, indicating that the center of Pt/XC72 corrodes more easily. This corrosion process resulted in the slow decrease in the ECSA and the mass activity before 900 cycles because the corrosion in the center may have had little effect on the Pt nanoparticles, which sat on the carbon surface at the very beginning.

The particle size distribution of the platinum nanoparticles is shown in Fig. 4c and is based on more than 200 particles analyzed using the software Image J. The mean particle size was obtained by using a weighted average based on the distribution data. The Pt particle size increased from 3.32 to 4.27 nm (mean particle size) after 1800 continuous ADT cycles in the RDE system, accounting for a 28% loss in Pt surface area. The observed increase in the Pt particle size is probably due to the particle migration mechanism,[25] which is explained by the migration and aggregation of platinum particles to form larger particles. Colón-Mercado et al.[26] reported that the Pt catalyze average particle size after 1100 continuous ADT cycles (from −0.03 to 1.24 V vs NHE in 0.3 M H₂SO₄ purged with N₂ at room temperature at a sweep rate of 5 mV s⁻¹) increased from 2.86 to 6.92 nm.

The TEM micrographs of Pt/BP 2000 are shown in Fig. 5a and b. The corrosion feature of Pt/BP 2000 was different from that of the Pt/XC72 samples. Compared with the fresh Pt/BP2000 (Fig. 5a), there were fewer spheres such as the carbon particles because the
boundary of BP2000 became relatively obscure after 1800 cycles. Compared with Pt/XC72, it can be concluded that the carbon corrosion on Pt/BP2000 prefers to occur on the surface; therefore, it facilitates the aggregation of Pt particles (a 1.56 nm increase for Pt/BP2000, but a 0.95 nm increase for Pt/XC72) by weakening or even breaking the interaction/bones between Pt and the carbon surface and causing the migration and dissolution of the Pt particles. This is the reason why the ECSA, the mass activity, and the DLC of Pt/BP2000 decreased more rapidly from the very beginning than those of Pt/XC72. The particle size distribution of the Pt/BP2000 catalyst (Fig. 5c) showed an increase in mean particle size from 3.7 to 5.26 nm, accounting for ~39.6% Pt loss. After 1800 cycles, the increase in the particle size of the Pt catalysts was much bigger than that of Pt/XC72, which is consistent with the decay of the ECSA and the mass activity results from both catalysts.

Figure 5. (Color online) [(a) and (b)] TEM images of Pt/BP2000 before and after consecutive ADT cycling in 0.1 M HClO₄ purged with N₂ at room temperature. (c) Pt particle size distribution before and after ADT obtained from TEM images using J image.

Figure 6. [(a) and (b)] TEM images of Pt/XC72 before and after 800°C vapor steam etching.
A 3 h, 800°C steam etching experiment of XC72 and BP2000 was carried out to help further understand different carbon support corrosion processes concluded from the simulated fuel cell experiments.

Fresh XC72 has a denser graphitic structure at the surface and a more disordered structure in the particle center, which can be seen in Fig. 6a. This feature matches the carbon black microstructure model proposed by Heckman et al. Figure 6b is the micrograph of the XC72 carbon black sample after 3 h of etching. The center of the carbon black particle became brighter as observed in Fig. 6b than the rest of particle, almost the same as observed after 1500 ADT cycles. Comparing that with the micrograph of a fresh XC72 in Fig. 6a, apparently, the center layer became much thinner after steam etching for 3 h, and the carbon layer planes were more disordered as compared with those in Fig. 6b. Through careful examination, it was found that some carbon layer planes on the outermost surface of the carbon black sphere became cracked; thus the corrosion process began from the center rather than from the surface. The particle size remained almost the same (25–30 nm), even after 3 h of etching. It is confirmed that the corrosion mainly occurred at the particle center for XC72.

The TEM micrographs of BP2000 are shown in Fig. 7. Compared with fresh XC72, the structure of fresh BP2000 (Fig. 7a) was uniform (there was no significant difference between the surface and center layers), and the crystal layer structure was as dense as that of XC72. After 3 h of steam etching at 800°C, the particle size of BP2000 significantly decreased from 20 to 10 nm, the morphology of BP2000 became more disordered than before, and there was obviously no bright spot in the center, which confirms the conclusion that the corrosion of BP2000 started on the surface.

The different structure of the graphitic carbon layers of XC72 and BP2000 resulted in the different corrosion processes. As for XC72, because of a denser graphitic structure at the surface and a more disordered structure in the particle center, the corrosion occurred mainly in the center and partly on the amorphous carbon from the surface. As for BP2000, the corrosion began on the surface due to the uniform structure of BP2000.

Conclusions

An accelerated durability test utilizing an RDE system was used to study the corrosion of XC72 and BP2000 as catalyst support. The observed corrosion processes for the different catalysts started from the center of the particle for the Pt/XC72 and on the surface of the particle for Pt/BP2000. The decay in performance of the catalysts can be explained by two key reasons: particle migration and carbon corrosion. Carbon corrosion affected the performance of the catalyst more before 900 cycles in Pt/BP2000 than in Pt/XC72. The results of the ECSA and ORR current measurement indicate a higher corrosion of Pt/BP2000 than Pt/XC72 after 1800 ADT cycles. The steam etching experiment confirmed the corrosion process observed in the RDE testing for both catalysts.

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