Short communication

Stability of platinum particles on a carbon substrate investigated by atomic force microscopy and scanning electron microscopy

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Abstract

To investigate the stability of platinum particles, a flat carbon substrate coated with platinum nano-particles was made as a model of PEMFC cathode catalyst. Changes of the platinum particles caused by potential retention in acid solution were observed by FE-SEM. Stability of the carbon substrate without platinum was also observed by AFM. The position of the AFM and FE-SEM observation before and after each potential retention was identical so that morphological change could be traced like *in situ* experiments. Behaviors of each particle, i.e. disappearance, migration and aggregation, was observed after potential retentions. Statistical analysis of the images revealed that small platinum particles on the model electrode decreased in number, especially at high potentials and under an oxygen atmosphere.
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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have been considered to be some of the most attractive candidates for power sources in transportation and stationary applications because of their high-energy conversion efficiency, high-energy density and low emissions of noxious gases. However, before they can be commercialized, the short lifetime of the membrane electrode assembly (MEA) must be overcome [1–13]. To improve the durability of the MEA, degradation mechanisms should be clarified. Among the various aspects of MEA degradation, a decrease in the electrochemical surface area (ESA) of the cathode catalyst has attracted attention as a criterion for the degree of degradation [7–10]. Although a decrease in the ESA is not always accompanied by a significant deterioration of the I–V performance of a cell, structural changes in the catalyst particles may have occurred. There have been several suggestions regarding what determines the decrease in the ESA [4,7,8,10], such as coarsening of the catalyst particles by aggregation or electrochemical

Ostwald-ripening, or a loss of the contact between the catalyst particles and the catalyst support by carbon corrosion. Recently, several studies have investigated the mechanisms of degradation by TEM observation of degraded MEAs [8,10–13]. In addition to coarsening of the platinum particles on the carbon support, many particles were found in the electrolyte phase. This phenomenon indicates that a significant amount of ionic species was produced in the cathode catalyst layer and diffused over a long distance in the electrolyte.

Although TEM enables inspection of the degradation phenomena visually, it is destructive method and not suitable for following changes with time. Furthermore, because the catalyst particles of a PEMFC are covered by polymer electrolyte, it is difficult to observe them even with a non-destructive method. Therefore, a combination of a model electrode system and a non-destructive observation to avoid these limitations should be an effective approach to pursue degradation processes. In this work, an electrode made by the deposition of platinum nanoparticles on a flat carbon substrate was used as a model of the cathode catalyst to investigate the stability. The model electrode was observed by FE-SEM before and after potential retention in acid solution, and changes in the particles were examined. There are differences in the electrolyte and substrate between

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model experiment and MEA in PEMFC. As will be discussed later, these differences may affect phenomena quantitatively. However, qualitative findings can be drawn from the trends of the results, such as the effects of the retention potential and atmosphere.

Our previous work using atomic force microscopy (AFM) revealed that the morphology of a carbon substrate is not always stable even at a potential within the range of the PEMFC conditions [14]. Therefore, prior to examining the stability of a platinum-deposited electrode as a model electrode, morphological changes of carbon electrodes without platinum particles were observed by AFM to ensure the stability of the substrate.

2. Experimental

For the examination of the stability of carbon substrates without platinum, a glassy carbon plate (GC, Tokai Carbon) was used for the substrates. As a stability test, the substrate was kept at 1.0 V versus RHE in an oxygen saturated $1.0 \, mol \, dm^{-3}$ $HClO_4$ solution at $80 \, °C$. The geometric area of the electrode was fixed at $0.264 \, cm^2$ using an O-ring. Before and after the stability test, the surface of the substrate was observed by AFM (SPA300 unit + SPI3800 controller, Seiko Instruments). At the end of the stability test, the electrolyte in the cell was replaced by distilled water completely.

Since these experiments confirmed that GC is stable at 1.0 V, a model electrode of the cathode catalyst was made by the electrodeposition of platinum nano-particles on a GC substrate in a plating bath containing H_2PtCl_6 according to the method described by Zoval et al. [15] The model electrode was kept at a fixed potential in the range of 0.6–1.2 V versus RHE in a $1.0 \, mol \, dm^{-3}$ $HClO_4$ solution at $80 \, °C$ for 50 h as a degradation process. The solution was saturated with oxygen or nitrogen gas by bubbling during potential retention to control the atmosphere. Before and after the degradation process, the sample was observed by a field-emission scanning electron microscope (FE-SEM, JSM-6700FA, JEOL). The size distribution of the particles in the FE-SEM images was analyzed using an image analyzer (Luzex-FS, Nireco). The positions of the AFM or FE-SEM observations on the sample before and after each degradation process were identical, which makes it possible to discuss not only changes in the particle size distribution but also the behavior of each particle individually as *in situ* experiments. Reproducible adjustment of the observation position had become possible by a specially designed sample holder which can be used commonly for AFM, FE-SEM, and electrochemical treatment. In addition, comparison of inherent structure or topography with the images obtained at the former observation helps us to identify the position during observation at higher magnitudes. *In situ* SEM observation is impossible for experiments with liquid electrolyte, so this technique, i.e. identical position observation, should extend the application of SEM observation also in other fields. As for AFM, *in situ* observation could be basically applied in our experiments. However, technical difficulties should be overcome in our experimental condition (in a strong acid solution at a high temperature). In general, adopting of the identical position observation technique in scanning probe microscopy

(SPM), including AFM and STM, relieves restriction of technical difficulties.

3. Results and discussion

3.1. AFM observation of carbon substrates without platinum particles

Fig. 1 shows the stability of GC substrate kept at 1.0 V in an acid solution at $80 \, °C$. Generally, among carbon materials, graphitized carbon is highly resistant to corrosion. However, a highly oriented pyrolytic graphite (HOPG) plate with platinum particles was corroded during a potential retention at room temperature [14]. We also observed roughening over the entire surface of an HOPG substrate without platinum particles during a potential retention at $80 \, °C$ (not shown). It is likely that the fragileness (easy to be exfoliated) of the HOPG substrate facilitates these morphological changes by the corrosion. On the other hand, the GC substrate showed little change in morphology as shown in Fig. 1. Based on these results, we decided to use the GC substrate to observe the stability of platinum particles. However, the surface of GC is extremely rough, which prevents us from distinguishing platinum particles from the substrate in AFM images. Therefore, we hereafter adopted FE-SEM, which tends to produce images of platinum particles clearly, instead of AFM to observe the GC substrate with platinum particles.

3.2. FE-SEM observation of the model electrode

A SEM image of the model electrode prepared by the electrodeposition of platinum particles on the GC substrate is shown in Fig. 2. The size distribution of the platinum particles obtained by an analysis of SEM images of a $4.4 \, \mu m^2$ area (a connection of four images including Fig. 2(a)) is also shown. Although the average size (4.9 nm) is not small enough, the mode value of the size distribution (about 3 nm) is almost the same as that in the practical catalyst of PEMFCs. Therefore, we considered this electrode to be appropriate for investigating the behaviors of small particles on support materials. Figs. 3 and 4 show a comparison of SEM images obtained before and after degradation processes at 1.2 V and 1.0 V in an oxygen atmosphere, respectively. By inspecting the changes in each particle in detail, disappearance, migration and aggregation following migration can be determined, as shown by the arrows in the images. While potential retention at lower potentials (0.8 V and 0.6 V) also induced migration and disappearance, there were only a few such examples. Figs. 5 and 6 show the dependence of the changes in the size distribution of the platinum particles on the potential of the degradation process under oxygen and nitrogen atmosphere, respectively. Since these histograms were made by analyzing SEM images obtained within the same $4.4 \, \mu m^2$ area using the identical position observation, not only the size distribution but also the absolute number of the particles can be discussed. In an oxygen atmosphere, small particles decreased in number when the retention potential was high (1.2 V and 1.0 V). Retention at a lower potential (0.8 V and 0.6 V) did not
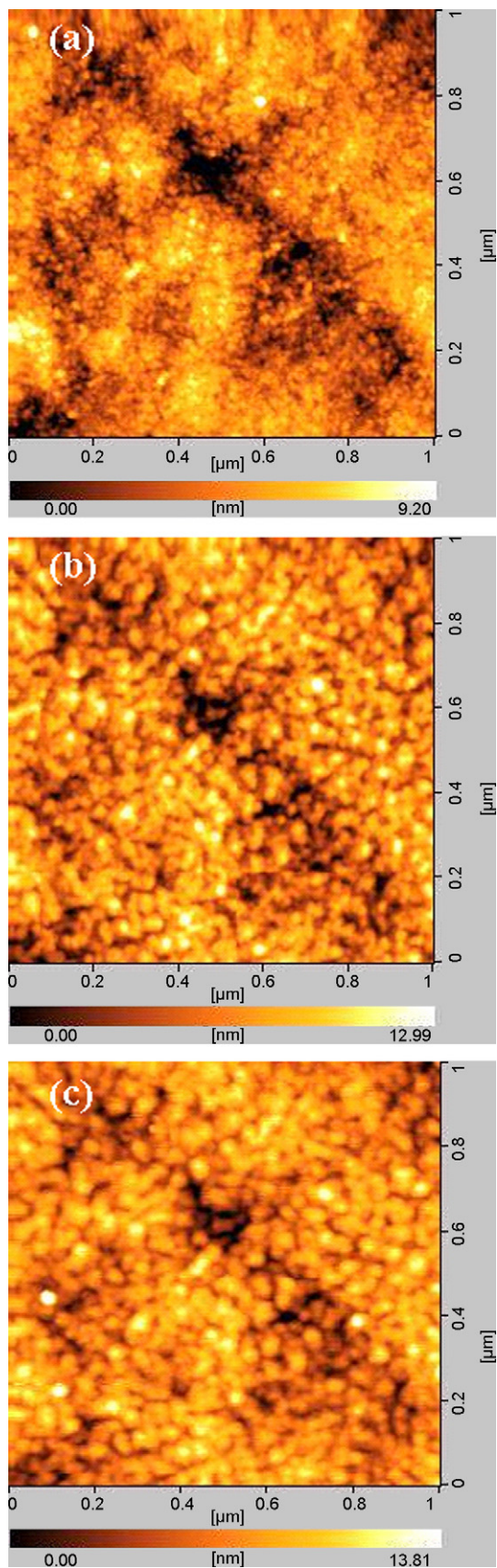
Fig. 1. AFM images (1 μm × 1 μm) of a polished GC surface (a) before and after potential retention at 1.0 V for (b) 50 h and (c) 100 h in an O$_2$-saturated HClO$_4$ solution at 80 °C.
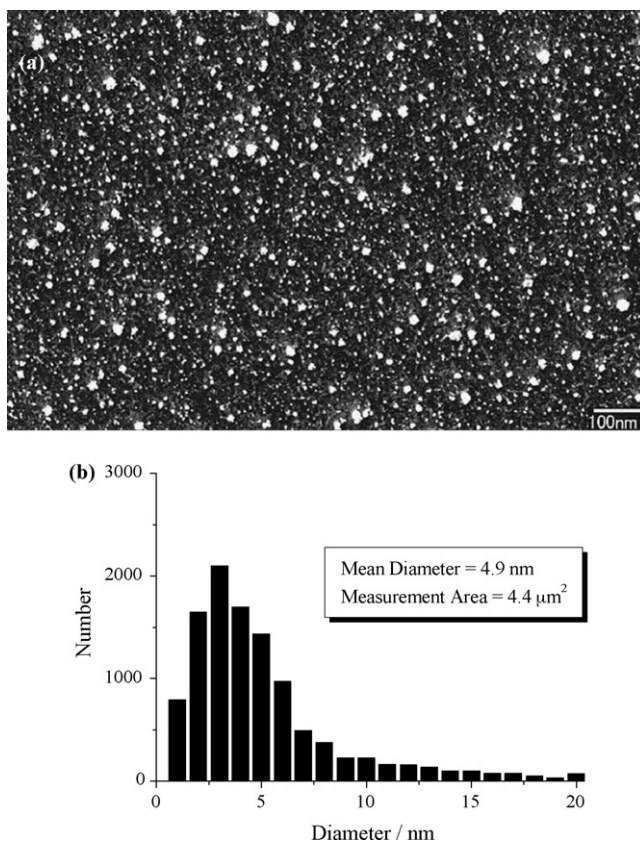

Fig. 2. (a) FE-SEM image and (b) size distribution of Pt particles deposited on a GC substrate.

cause significant changes in the size distribution. This tendency agrees with findings based on an inspection of each particle in the images described above. In contrast, potential retention in a nitrogen atmosphere showed almost no significant changes at any potential (Fig. 6). Statistical analyses of the results shown in Figs. 5 and 6 are summarized in Table 1. Mean diameter increased after the potential retention at 1.2 V in O$_2$ atmosphere because small particles decreased significantly as shown in Fig. 5(a).

The degradation of MEAs observed by TEM [10–13], including observation after a potential retentions in a nitrogen atmosphere [12], led to dissolution and changes in the size distribution of platinum particles. However, contrary to the expectation based on these results, few changes were observed on the model electrode after the corresponding degradation processes, as shown in Fig. 6. This discrepancy may be due to the differences in the electrolyte and substrate between model experiment and MEA in PEMFC. With regard to the electrolyte, while sufficient aqueous acid solution surrounds the catalyst particles in the model experiment, only a small amount of ionomer resin surrounds the particles in the catalyst layer of the MEAs. If particle growth in the catalyst layer occurs by an Ostwald-ripening mechanism, particles on the model substrate may tend to become thin without the growth of other larger particles, since the ionic species produced by dissolution should be easily removed. However, neither growth nor thinning was observed on the model
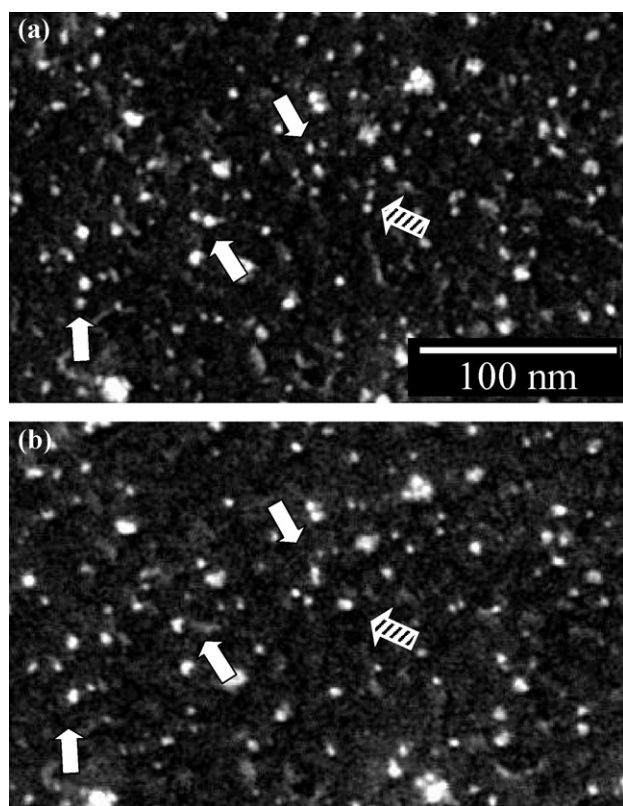
Fig. 3. FE-SEM images of a Pt/GC electrode (a) before and (b) after a potential retention at 1.2 V (vs. RHE) for 50 h in an O_2-saturated 1.0 M $HClO_4$ solution at 80 °C. White and striped arrows show the disappearance and aggregation, respectively, of the particles during potential retention.
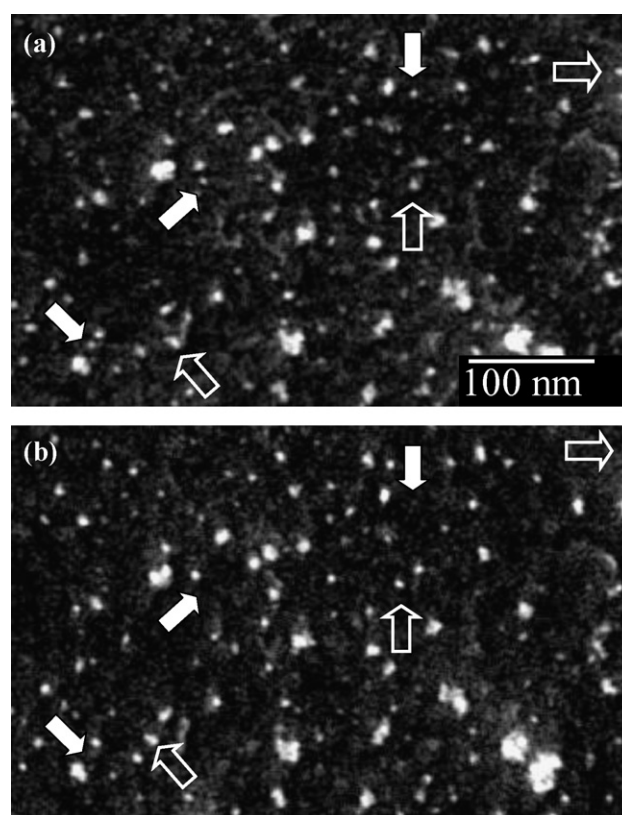

Fig. 4. FE-SEM images of a Pt/GC electrode (a) before and (b) after potential retention at 1.0 V (vs. RHE) for 50 h in an O_2-saturated 1.0 M $HClO_4$ solution at 80 °C. White and black arrows show the disappearance and migration, respectively, of the particles during potential retention.

electrodes, which indicates that dissolution of the platinum particles did not occur on our model electrode. On the other hand, if aggregation of the particles occurs mainly by migration in the catalyst layer of MEAs, the same phenomenon should be observed on the model electrode. In fact, migration and aggregation were observed, as shown in Figs. 3 and 4, but were not dominant behaviors in these experiments. This may be due to the difference in the substrate material, which should affect the mobility of the particles on the substrate. In the case of phosphoric acid fuel cells (PAFCs), surface oxidation of the graphite support inhibits the migration of the catalyst particles [16]. The

difference in the nature of the electrolyte may also cause the difference in the amount of dissolved platinum. If the 'solubility' of the ionic species produced by dissolution in an ionomer resin is higher than that in an aqueous solution, the Ostwald-ripening mechanism might be accelerated. At any rate, our experiments using a model electrode did not show any phenomena related to Ostwald-ripening, while aggregation and disappearance were observed. It is likely that the driving force of the ripening of particles is not large, at least under a potentiostatic condition. In an actual catalyst layer of a PEMFC, fluctuation of the operation voltage or potential distribution in the electrolyte along

Table 1
Mean diameter, total number and its relative change of the platinum particles shown in Figs. 5 and 6

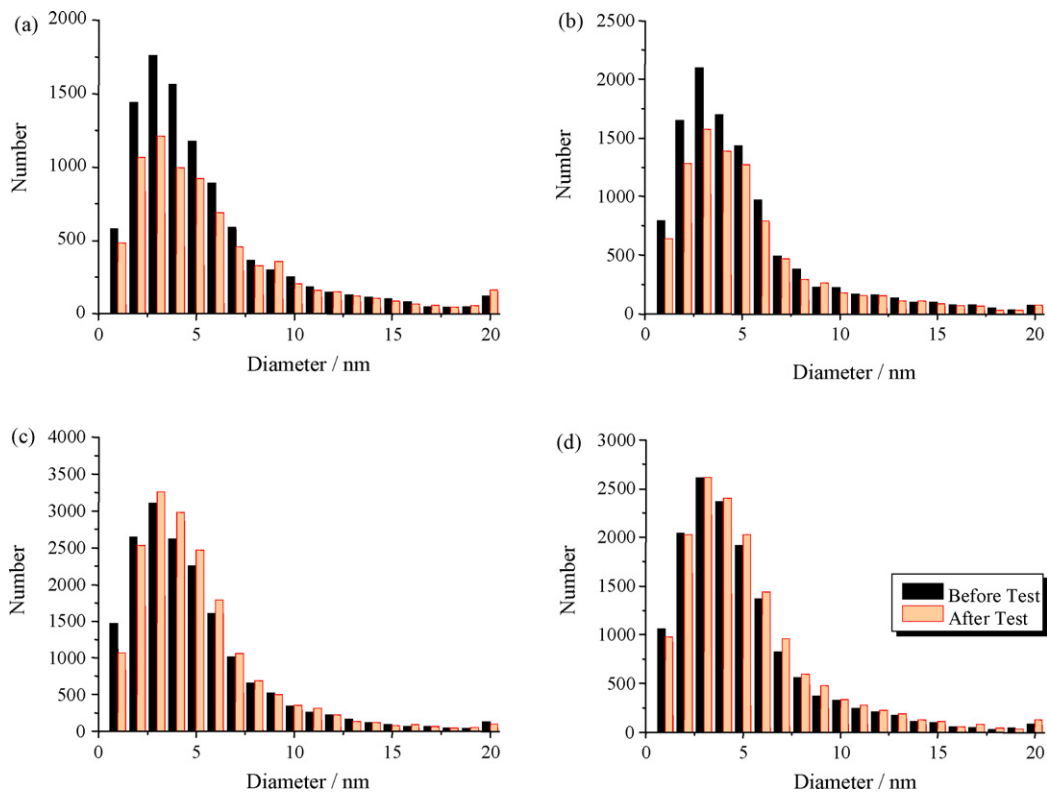| Atmosphere	Retention potential (V)	Before test		After test	
		Mean diameter (nm)	Total (number)	Mean diameter (nm)	Total number (change)
O_2	1.2	5.3	9910	5.8	7640 (77%)
	1.0	5.0	10900	5.1	8960 (82%)
	0.8	4.9	17420	4.9	17850 (102%)
	0.6	4.9	14490	5.1	14980 (103%)
N_2	1.2	5.4	7910	5.3	7420 (94%)
	1.0	5.6	7900	5.6	6970 (88%)
	0.8	6.7	5580	6.3	5600 (100%)
	0.6	5.3	8680	5.5	8860 (102%)

Fig. 5. Size distributions of platinum particles on a GC substrate before and after potential retention at (a) 1.2 V, (b) 1.0 V, (c) 0.8 V, and (d) 0.6 V in an O_2-saturated acid solution at 80 °C.
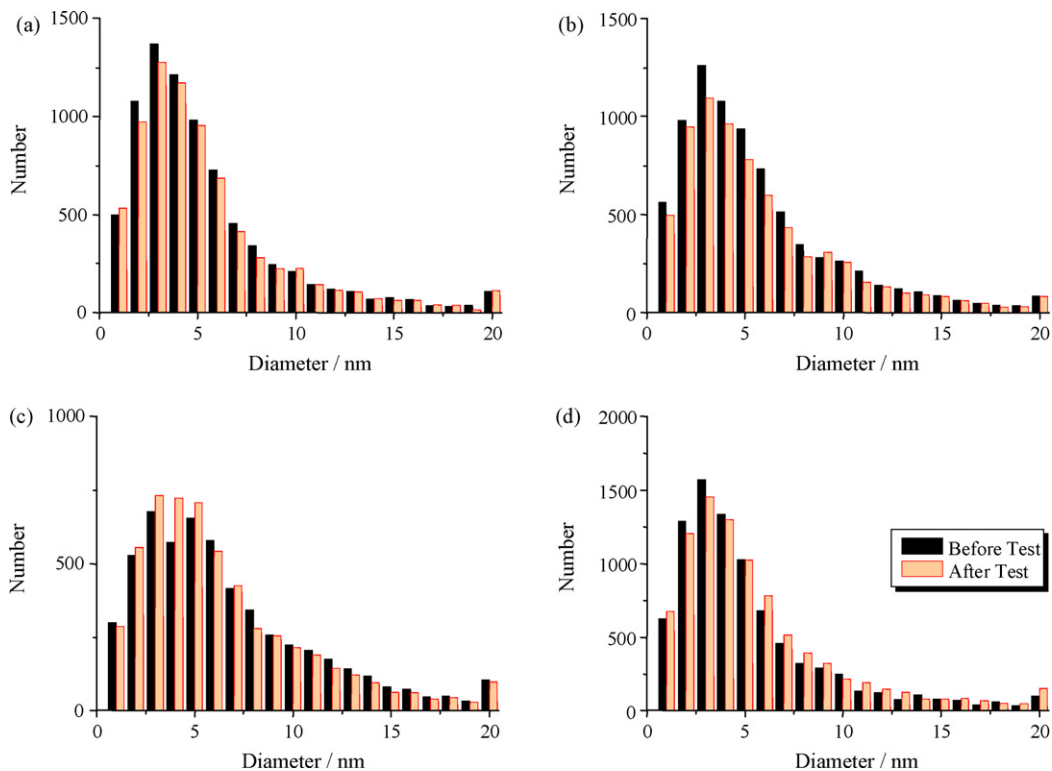
Fig. 6. Size distributions of platinum particles on a GC substrate before and after potential retention at (a) 1.2 V, (b) 1.0 V, (c) 0.8 V, and (d) 0.6 V in a N_2-saturated acid solution at 80 °C.

the cross-plane direction in the catalyst layer could promote the ripening of the particles.

The mechanism of the effects of the atmosphere on the model electrode should also be considered. There are two possible candidates for this mechanism: the effects of oxygen on the platinum particles and on the carbon substrate. Oxygen may accelerate dissolution of the platinum particles, since the oxygen pressure has been reported to affect the surface oxidation of platinum [17]. Although there were little morphological changes in the GC substrate, as shown in Fig. 1, retention at a higher potential might induce surface corrosion. Acceleration of graphite corrosion by oxygen atmosphere was reported [18]. However, it is unlikely that oxygen molecules would affect the electrochemical corrosion of carbon directly, since the oxygen source for the formation of CO_2 from carbon is assumed to be water. The effects of the atmosphere on carbon corrosion are now under investigation.

4. Conclusions

As a model electrode to investigate the stability of the platinum particles, platinum nano-particles were deposited on a GC substrate and their changes during potential retention in an acid solution were observed by FE-SEM. Observation at an identical position before and after a potential retention allowed to trace changes like *in situ* experiments. At all of the potentials examined, migration and the disappearance of platinum particles were observed by comparing images obtained before and after potential retention. This implies that aggregation following migration may induce the decrease in the ESA of MEAs in addition to the dissolution. Platinum particles on the model electrode decreased in number after retention at 1.2 V and 1.0 V in an oxygen atmosphere. This was caused by platinum dissolution or carbon corrosion. On the other hand, few changes were observed at any potential in a nitrogen atmosphere. This suggests the existence of some mechanisms by which oxygen affects the degradation.

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