



Simulation experiments on the effect of freezing of carbon substrate catalyst

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ABSTRACT

By adiabatic expansion due to the introduction of an evacuation process, the water drop of about 2 mm diameter were cooled to 243 K by forming ice drops at the triple point of water. The sublimation temperature of ice rapidly decreased 243 K within 60 s and remained constant for 80 s. Subsequently, it became room temperature in about 60 s and the water drop disappeared owing to sublimation. By repeating this process, carbon and catalyst were markedly altered. Transmission electron microscopy (TEM) based on in situ observation elucidated the freezing problem in polymer electrolyte fuel cell (PEFC). Structural alterations of carbon due to freezing were observed and discussed as the oxidation phenomenon of carbon.

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1. Introduction

One of the major costs in polymer electrolyte fuel cell (PEFC), particularly for automotive applications, is the use of platinum-based electrodes on carbon substrates to catalyze both the anodic oxidation of hydrogen and the cathodic reduction of oxygen. Recent studies have reached an important milestone toward automotive PEFC applications by envisioning a feasible technical roadmap toward meeting the stringent automotive target [1,2]. In addition to the sort encountered in automotive stop-go, acceleration, and shut-down/starting operations, the behavior of water drops below the freezing point in the catalyst and gas diffusion layer (GDL) is an increasing problem [3,4]. In previous studies, we demonstrated the alteration of carbon particle without Pt particles, Pt particles on a carbon particle (Pt-on-C), and Pt particles in a carbon particle (Pt-in-C) due to the various simulated conditions of the catalyst during electric power generation [5–7]. The impact of H₂ molecules on Pt clusters accelerated the movement of Pt clusters [6]. Carbon particle alterations were induced by the chemical energy associated with the oxidation of carbon: $C + O_2 \rightarrow CO_2 + 0.22 \text{ eV}$. The energy of the reaction on the surface diffused into the inner part of the particle faster than the dissipation caused by radiation, which has been theoretically proposed to be involved in the crystallization of amorphous cosmic dust [8,9].

During the PEFC operation, an oxygen reduction reaction in the catalyst layer produces water. At a normal operation temperature (353 K), the water produced can be removed either in vapor or liq-

uid drops via vapor phase diffusion or capillary-driven liquid flow. In this study, the freezing of a water drop containing catalyst was performed by the adiabatic expansion of the water with the drop by introduction of a vacuum-evacuating system based on in situ observation by transmission electron microscopy (TEM) as well as the techniques cited in the previous papers [5,6]. The sublimation of the ice drop resulted in a rapid temperature decrease until 243 K and was suggested to be one of the degeneration factors of the catalyst [10]. In this study, the fundamental effect of freezing on the catalyst was also clarified by high-resolution transmission electron microscopy (HRTEM).

2. Experimental procedure

A water drop of 2 mm diameter was used in this study. The water drop on a glass plate was evacuated by a vacuum system as shown in Fig. 1b. The pumping speed of vacuum and the temperature alteration of the water drop on a chromel–alumel thermocouple of 0.1 mm diameter are measured as schematically shown in Fig. 1c. The water drop set at room temperature at 1 atmosphere was cooled by adiabatic expansion. The water drop froze near the triple point of water (273.01 K, 609.14 Pa) after about 40 s. The temperature of the frozen drop abruptly decreased at 243 K within 10 s, as shown in Fig. 1a. The obtained curves agreed with the vapor pressure alteration of ice, as indicated in Fig. 2, i.e., the sublimation of ice occurred [10]. The sublimation of ice was fast until 243 K. The ice drop became smaller by this sublimation. The temperature of the ice drop was kept at about 243 K for 80 s. The evaporation of ice occurred and the temperature of ice became room temperature. In this process, the water drop disappeared through the sublimation of ice. Water drops smaller than 1 mm in diameter disappeared before 243 K. Therefore

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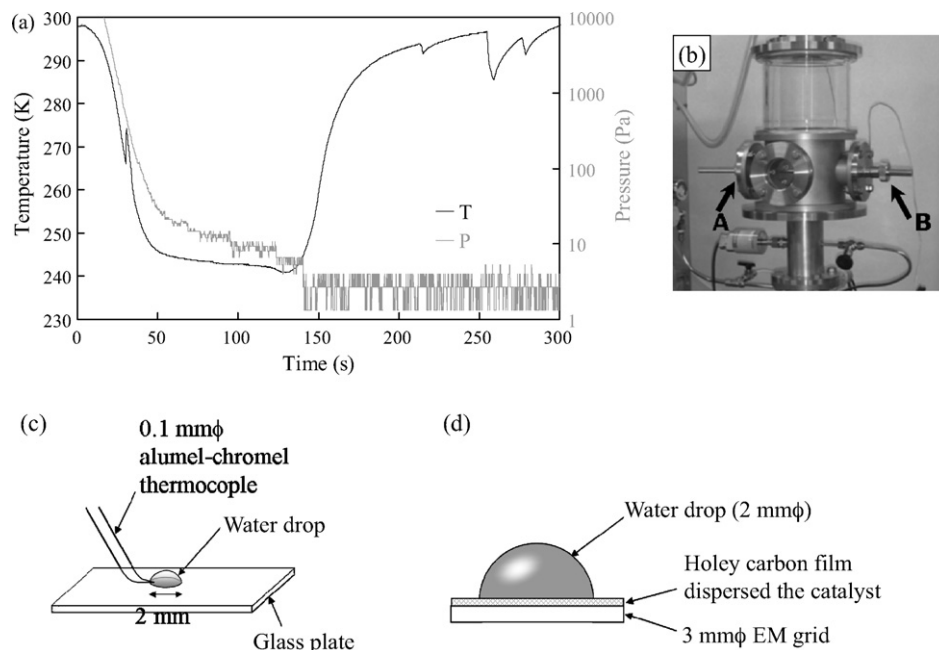


Fig. 1. (a) Simultaneous measurement of vacuum (P) and temperature of water drop (T) of about 2 mm diameter. The ice drop was produced nearly at the triple point of water. An abrupt temperature decrement of ice due to sublimation, as shown in Fig. 2, occurred. The ice drop became smaller with sublimation and its temperature increased with radiation from the vacuum chamber. The water drop of 2 mm ϕ disappeared within 200 s. The alteration indicated by an arrow shows the formation of ice. The decrement of pressure was measured by capacitance manometer (ULVAC, GM-1000). The temperature alteration was measured by chromel–alumel thermocouple as shown in (c). (b) shows the vacuum system. TEM specimen holder for carrying the water drop was set at the position A or B. The water drop on the electron microscopic grid was shown schematically in (d).

the sublimation occurred up to 243 K. To determine the effect of freezing at 243 K, an ice drop of order of 2 mm diameter was used.

The Pt-on-C (commercial catalyst) used: Vulcan carbon and/or Pt-in-C (Ritsumei catalyst) [12] system was dispersed on an amorphous holey carbon film supported by a standard grid for TEM observation. Before the freezing experiment, the specimens were observed using a Hitachi H-9000 NAR TEM and the observation position was determined. The holder carrying the Pt/C specimen dispersed on the electron microscopic grid as indicated in Fig. 1d was placed in a special gas reaction chamber with a diameter of 170 mm and a height of 300 mm. Since the 150 mm height glass

cylinder was used, we can see the freezing of water drop on the TEM holder inserted at the position A in Fig. 1b. The water drop was directly put on the specimen on the holder and evacuated. After the ice drop disappeared, the specimen was transferred again to the TEM. This process was repeated and observed at the same position. Fine structure alteration was performed by HRTEM. The diffraction pattern analyzed was hardly altered during the experiment, i.e., the Pt clusters and amorphous carbon structure can be identified.

Typical structures of the Vulcan carbon, amorphous and turbostratic structure particles are shown in Fig. 3. All the structures are based on the graphite. The HRTEM image clearly shows the structure differences. Graphite (0002) lattice spacing of 0.34 nm was mainly seen in Vulcan carbon particle. In the case of turbostratic structure (0002) lattice spacing was larger than 0.34 nm [13].

3. Results and discussion

3.1. Pt-on-C

Fig. 4 shows a typical alteration of the Pt-on-C catalyst on a holey carbon film. A marked alteration of the dispersed catalyst on holey carbon film was observed by the third cycle, i.e., a portion of the catalyst disappeared in Fig. 4d.

Fig. 5 shows the magnified images of one part at the point indicated by the arrow A, which is completely lost by the third cycle. The macroscopic feature of the catalyst was hardly altered. However, the fine structure of carbon and the arrangement of the Pt catalyst were altered, as indicated by enlarged images by the arrows A to D. The arrangement of the Pt catalyst and structure of carbon films were altered by the treatments. The alteration of the configuration in Fig. 4d hardly changed by more cycle. Fig. 6 shows the enlarged image at the remained position in Fig. 4d just after the 5 cycle. As indicated by arrow A, carbon in this region disappeared rapidly. Then, the Pt clusters with small black dots coagulated. As indicated by arrows B, the structure of the Vulcan carbon particles altered

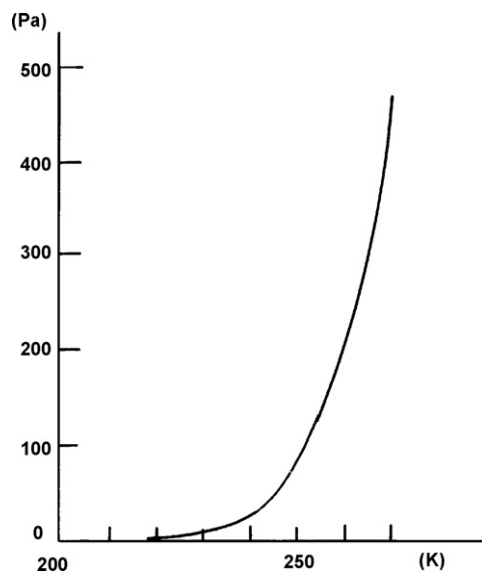


Fig. 2. Vapor pressure of ice with the temperature plotted using the scientific table, as indicated in a previous paper [10]. The temperature decrement due to the sublimation of ice is faster between 273 and 243 K.

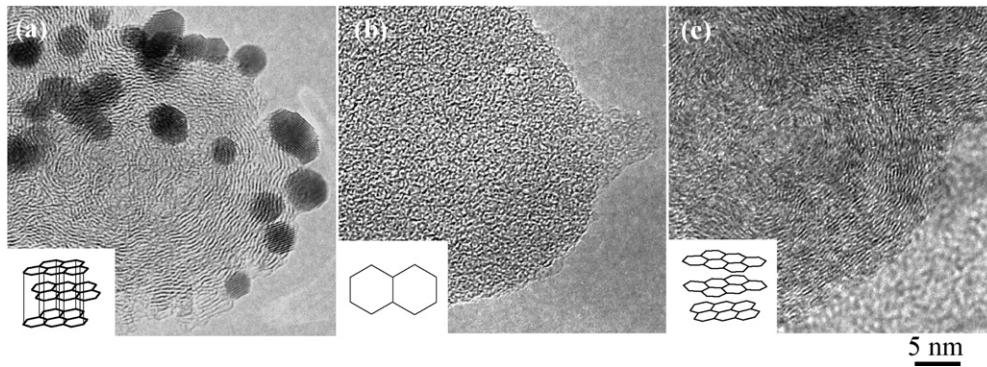


Fig. 3. (a) Typical examples of Vulcan carbon particle (distorted onion structure) covering Pt catalyst. The lattice image of (111) of Pt clusters can be seen. (b) Typical amorphous particles (no long large ordering of graphite structure). (c) Turbostrucitc structure particles. Short range ordering of graphite structure can be seen.

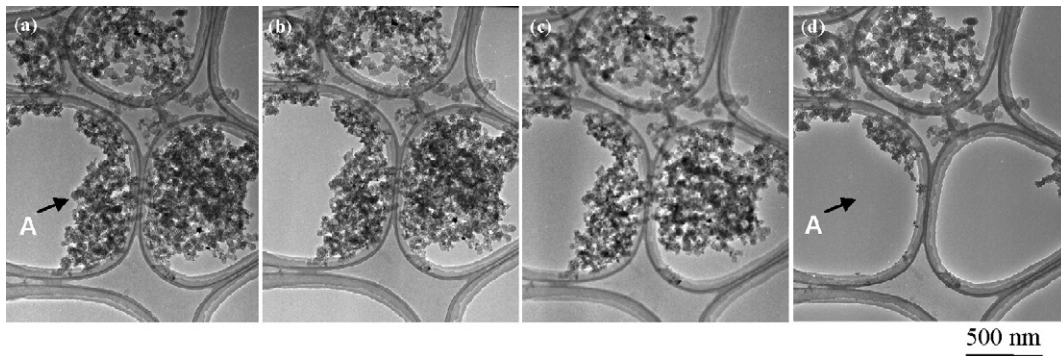


Fig. 4. Alteration of Pt-on-C. Dispersion of the catalyst on holey carbon film shown in (a) was put in the water drop of about 2 mm diameter. By the third cycle of the process shown in Fig. 1a, a part of catalyst indicated by arrow A in (a) disappeared by third cycle as indicated by an arrow A in (d).

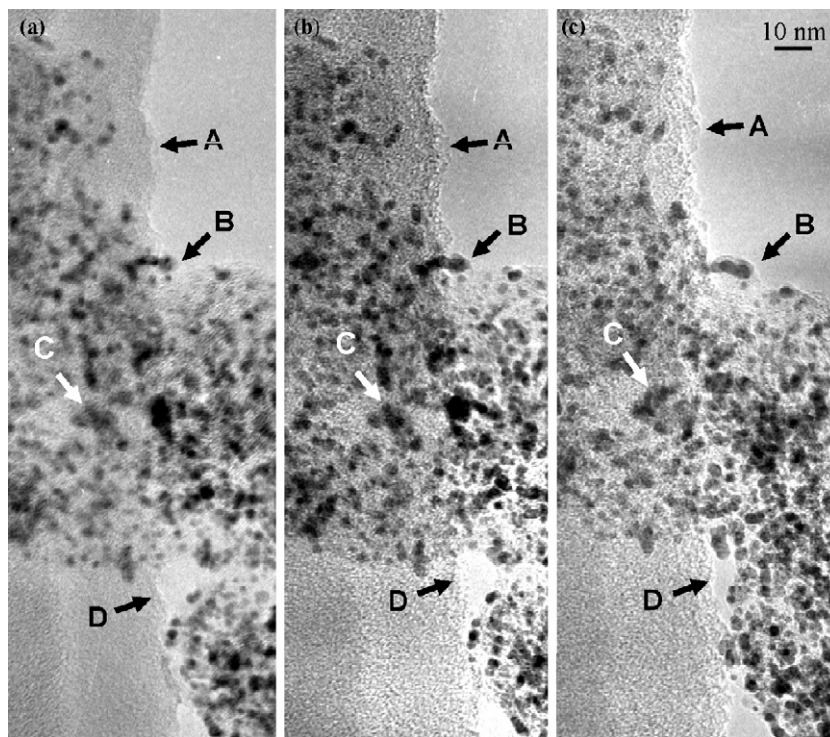


Fig. 5. Magnified TEM images of part indicated by arrow A in Fig. 3. (a), (b) and (c) correspond to (a), (b) and (c) in Fig. 3. Same positions before the disappearance of the catalyst by third cycle are shown. As indicated by the arrow A, periphery of the holey carbon film altered. The catalyst indicated by the arrows B drastically altered in (c), i.e., the surface is covered with carbon layer and rearranged from the start. The state of the coagulated catalyst also altered as indicated by arrow C for the example. The new catalyst appeared at the position indicated by the arrow D.

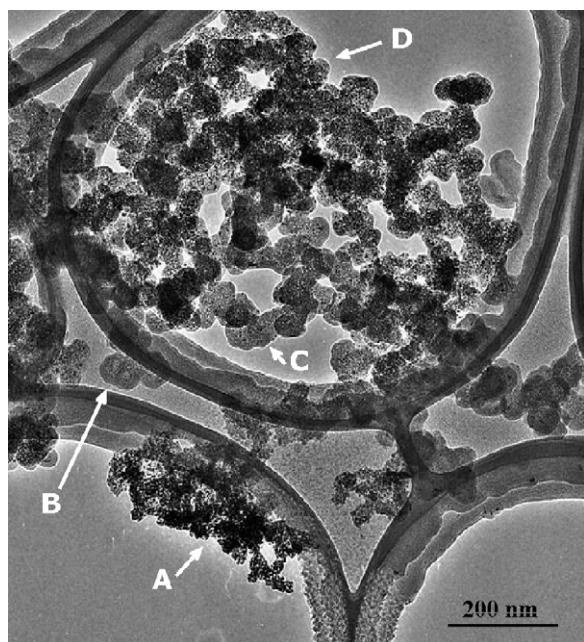


Fig. 6. TEM image of Fig. 4d after two more cycles in Fig. 4d (five cycles). The macroscopic alteration as indicated by arrow A in Fig. 1 was hardly observed after three cycles. The enlarged image corresponds as indicated by arrow A, carbon was rapidly lost and the Pt catalysts coagulated. As indicated by arrows B, the carbon particle structure altered, i.e., central part changed to the void cluster as well as the ketjen carbon particle. This suggests that the crystallization took place for Vulcan carbon particles in the position in Fig. (d). As indicated by arrow C and D, the distribution of Pt clusters on carbon particle drastically altered.

the central white contrast through to the graphitization from the carbon surface [5]. Pt clusters may be lost from the carbon particle surface. As indicated by the arrows C and D, the distribution of Pt clusters clearly different. Figs. 7 and 8 show the high-resolution images of one part of the catalyst. As observed in Fig. 7, the carbon particle surface with the Vulcan structure, which shows a graphitic structure, altered the amorphous structure as observed in the pure oxygen effect at 333 K [6] and the Pt-on-C system by heating at 353 K in saturated water vapor [7].

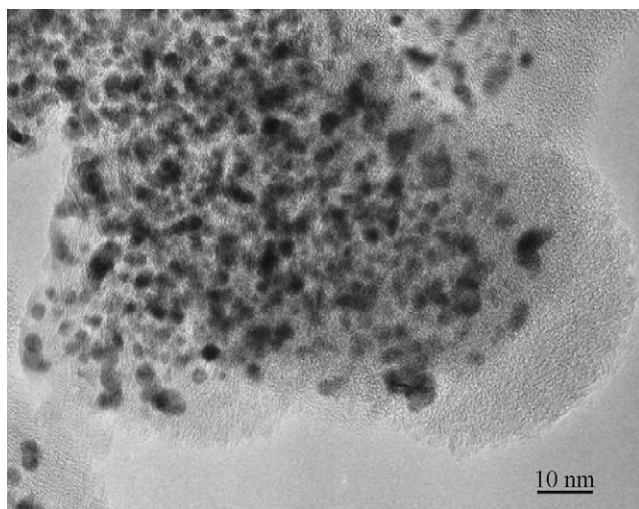


Fig. 7. The HRTEM image shows that the structure on the carbon particle surface was altered, i.e., the Vulcan structure surface indicated in Fig. 3a altered the typical amorphous structure as indicated in Fig. 3b. This structure is the part indicated by arrow D in Fig. 6. These events can be seen for a long time keeping of the catalyst in the saturated moisture condition at 353 K [7].

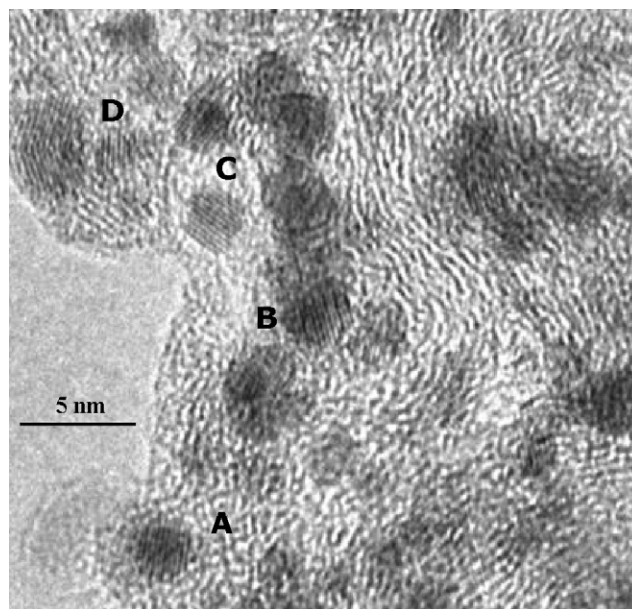


Fig. 8. HRTEM image of the Pt cluster distribution region indicated by arrow D in Fig. 6. Carbon particles coagulated with each other. The lattice image of Pt particles indicated by A to D show G. P. zone like contrasts, i.e., lattice image contrast partly strong, which have been suggested to be due to partly PtO formation as indicated in previous report for the catalyst in the electric field [13].

Fig. 8 shows that carbon particles connected to each other through their surfaces altered the graphitic structure. The HRTEM images of Pt clusters indicated by A to D show the Guinier–Preston (G. P.) zone-like contrasts clearly observed in the 1 V cm^{-1} effect of the nanostructure [14]. In addition to the oxidation of carbon particles, surface of the Pt clusters was captured the oxygen at the interstitial point (100) plane of Pt. Since the oxidation energy of carbon was independent of temperature [15], the oxidation energy of carbon due to the sublimated water molecules induced the Pt cluster oxidation due to the difference between the amorphous and crystal structures of phonon velocity. The reacted energy was preferentially condensed on the surfaces of Pt clusters as discussed in previous study [7]. The exposed carbon surface altered the amorphous structure. The structure alteration of carbon occurred in the freezing of the water drop.

Since the contact potential between carbon and Pt clusters was 0.65 eV, water molecules with dipole moments were arranged on

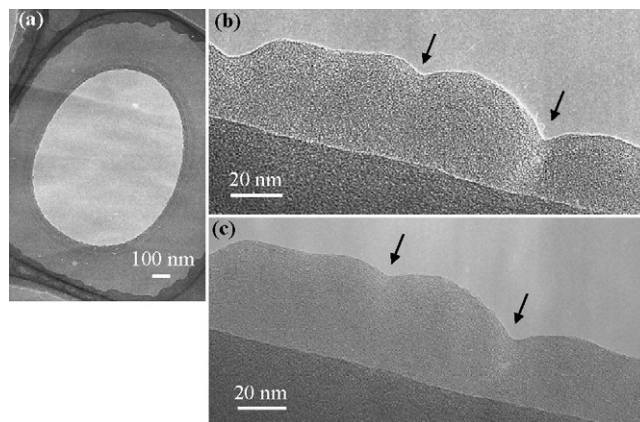


Fig. 9. (a) Holey carbon film. HRTEM images of the edge indicated by arrow in (a) after second (b) and third (c) cycle. The same position was captured. The concave regions indicated by arrow become smaller by the third cycle. The surface of the holey film became smooth.

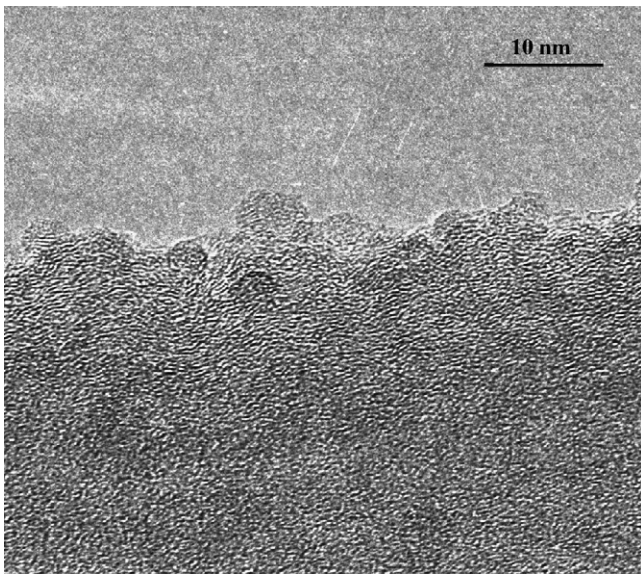


Fig. 10. HRTEM image of the carbon film. Circular carbon particles with an amorphous structure of less than 5 nm diameter appeared on the surface of the carbon film produced by more than three cycles.

the catalyst surface, as indicated in a previous report on the generation of electric power using the Pt-in-C catalyst [11]. The formation of the ice drop indicates the volume change of water to ice. This volume change caused by the destruction of the coagulated catalyst system. The sublimation of ice at 243 K was accelerated by the oxidation of carbon. Therefore freezing and sublimation process of ice markedly altered the catalyst despite of the low-temperature.

3.2. Carbon film

As shown in the previous paper, the carbon film was more stable than carbon particles at 353 K in air [5]. As shown in Fig. 4, carbon film alteration was observed in the present experimental process. The most stable holey carbon film was used and the same experiment was performed.

Fig. 9a shows the holey carbon film. The characteristic alteration was detected by HRTEM observation. Fig. 9b shows the same posi-

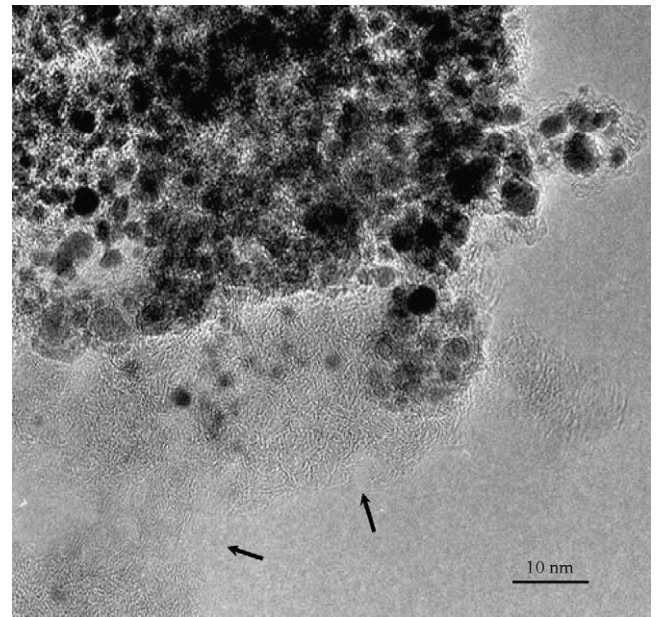


Fig. 12. HRTEM image of the catalyst in carbon particle, after the second cycle. Amorphous carbon particles were crystallized as indicated an arrow A which hardly contains Pt clusters. The carbon particle surface contained Pt clusters also graphitized.

tion of the specimen after cycles of 2 and 3. The concave regions indicated by arrows altered and surface becomes smooth. This shows that the local movement of carbon is similar to that during the sintering phenomenon. In the 3-cycled film, we can observe a more characteristic alteration of the surface structure of the carbon film, as shown in Fig. 10. Amorphous spherical carbon appeared on the surface of the carbon film. The contrast observed in the film region suggests the formation of spherical carbon of 5 nm order diameter. This spherical carbon structure is the typical amorphous structure. Spherical particles can be produced by freezing in the present experiment. This clearly shows that the oxidation of carbon occurred on the surface and the oxidation energy of 0.22 eV altered the structure of the carbon film. Since the phonon mean free path was on the order of 1 nm for the amorphous structure (microcrystallite size), the surface structure alteration occurred. The water-to-ice

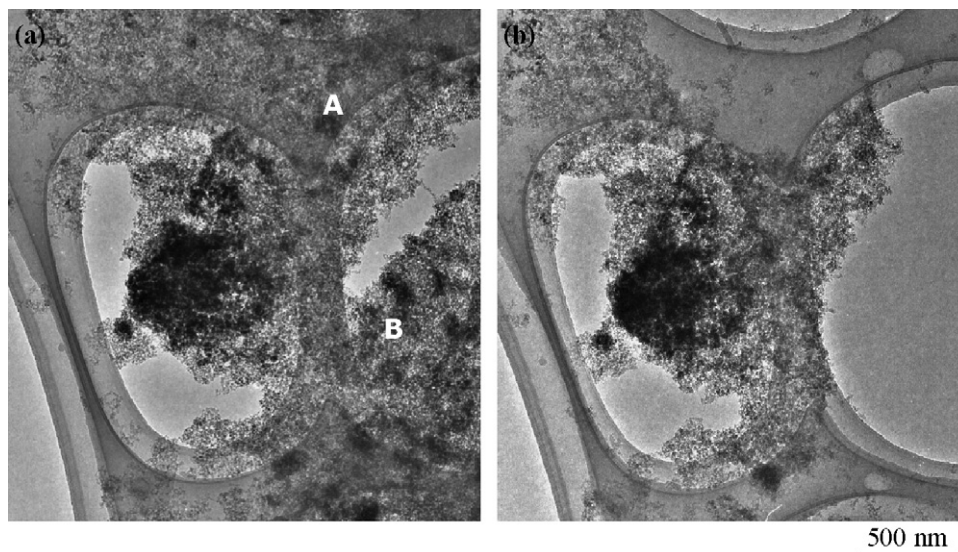


Fig. 11. Alteration of Pt-in-C catalyst. The observation position in (a) showed the dispersion on holey carbon film. The catalysts indicated by A and B in (a) disappeared by the first cycle, as shown in (b).

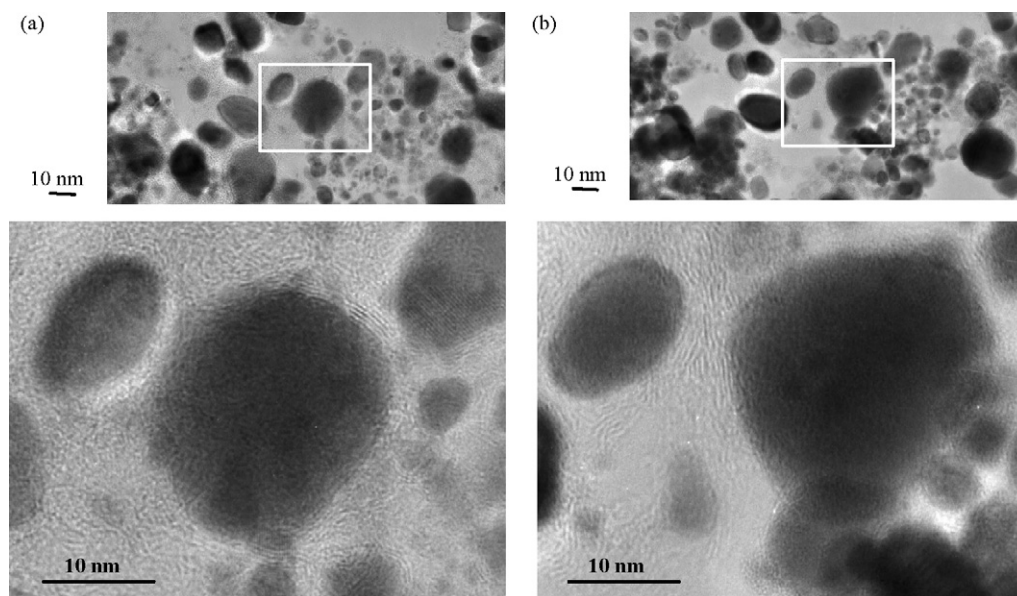


Fig. 13. HRTEM image of the catalyst in carbon particle after the second (a) and third (b) cycles. The crystallized carbon structure again transformed to the amorphous structure as elucidated in previous report. The well-crystallized carbon layer on large Pt clusters as indicated by an arrow was clearly destroyed.

volume change, freezing and sublimation of ice may also accelerate the fine structure alteration, i.e., oxidation of carbon take place.

3.3. Pt-in-C

To investigate the difference in alteration of the Pt-in-C catalyst (Ritsumei catalyst) and the fundamental phenomenon as well as previous results, the same experiment was conducted on this system. As shown in Fig. 11, the typical macroscopic lost of the catalyst was also observed by the first cycle.

Fig. 12 shows the HRTEM image of the specimen after two cycles. Black dots indicate Pt clusters covered with carbon particles. The carbon particle with the amorphous structure was graphitized, as observed in the image and indicated by arrows.

Fig. 13 also shows the alteration of the amorphous layer after two and three cycles. As in the discussion on the phonon mean free path difference between crystal and amorphous structures, the oxidation energy of carbon condensed more on the Pt cluster layer. The graphitized carbon on Pt cluster layer which is one of the stable structure, was transformed to the amorphous structure, as seen in previous experiments [5,7], i.e. the carbon structure was altered to amorphous – graphitic – amorphous processes and the lost of the of carbon was the effect on the oxidation.

4. Summary

A Pt-on-C catalyst, a carbon film, and a Pt-in-C catalyst were altered by freezing water drops in vacuum. The freezing and sublimation of ice induced marked carbon structure alteration. The volume change of water drop to the ice drop, the sublimation of the ice, and the dipole movement of water molecules arranged on a Pt or carbon surface caused marked carbon structure alterations. The

sublimation of ice decomposed H_2O molecule to the H_2 and O. The oxygen gas oxidized the carbon surface structure. From the present observations, carbon structure alterations due to oxidation were considered to be due to the lost of carbon and the Pt cluster coagulation for the Pt-on-C catalyst. Therefore, the repetition of the water drop formation on the catalyst and freezing phenomena induced in the degeneration of the catalyst. If the Nafion is contained in the catalyst, the movement of the Nafion became prominent. The result will be published elsewhere. In the present experiment, only the freezing effect of the catalyst on Vulcan carbon particle, carbon film and the catalyst in carbon particles have been presented.

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