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Influence of the temperature of heat treatment on phosphoric acid fuel cell cathodes

KENRO MITSUDA, HISASHI SHIOTA, HIROSHI KIMURA, TOSHIAKI MURAHASHI
Central Research Laboratory Mitsubishi Electric Corporation 1-1, Tsukaguchi-honmachi 8-Chome, Amagasaki, Hyogo, 661, Japan

The thermal behaviour of electrode materials during heat treatment from 250–400 °C was studied. The cathode performance changed by two steps depending on temperature of the heat treatment. At the first step (300–320 °C), polytetrafluoroethylene (PTFE) melted unexpectedly, giving hydrophobic character to the catalyst layer. This change drastically improved the cathode performance. At the second step (340–400 °C), support carbon was oxidized by catalytic action of platinum, increasing the PTFE content from 45 to 83 wt %. This caused a gradual decline in the cathode performance. The poor cell performance of the electrode treated below 300 °C is due to the fact that PTFE is not melted at that temperature. Triton X-100 used as a surfactant in the PTFE dispersion disappeared completely from the electrode at these temperatures by oxidation, catalysed by platinum.

1. Introduction

The electrodes of phosphoric acid fuel cell (PAFC) essentially comprise an admixture of catalyst particles (platinum supported on carbon) and polytetrafluoroethylene (PTFE) particles deposited on a substrate material such as porous carbon. To obtain good cell performance, a homogeneous dispersion of the catalyst and PTFE particles is necessary throughout the electrode structure. Gas diffusion channel networks in the electrode also have to be maintained; the performance of cathode is sensitive to this.

Several methods have been used for the electrode fabrication. Flocculate, which is made by floccing a co-suspension of catalyst particles and PTFE particles, has mainly been used [1–3]. The flocculate is fabricated on a substrate by the filtering method [1] or screen printing method [2]. Recently, dry method [3] has been used for fabrication, wherein the flocculate is dried and reduced to a powder. We have used a reverse roll coating method (RRC method) to fabricate the catalyst paste on a substrate [4]. Most of these methods have used Triton X-100 as the dispersing agent of the PTFE particles. In some cases, Triton X-100 is also used to disperse the catalyst powder. By using the surfactant, we can obtain, without great effort, a good dispersion of catalyst particles and PTFE particles. However, the surfactant should be removed completely from the electrode before operation of the electrode. If the surfactant remains, it will have a bad effect on the wetproofing of the electrode.

One of the purposes of heat treatment is to remove the surfactant. Breault *et al.* [1] selected 280 °C to remove the surfactant, and Watanabe *et al.* [5] also selected the same temperature in an inert gas. Mori *et al.* [6] studied the influence of temperature from 320–370 °C in air, and observed the increase of the acid absorption capability of the catalyst layer below 350 °C. They concluded that the residues of Triton X-100 enhanced acid absorption. Holtz *et al.* [7] also gave warnings on surfactant remaining. They decomposed Triton X-100 absorbed on various carbon powders at higher temperatures, observed exothermic heat during Triton X-100 decomposition from 300–500 °C, and concluded that the surfactant remains up to 400 °C. We also studied the thermal behaviour of Triton X-100 with differential scanning calorimetry (DSC) and infrared (i.r.) spectrophotometry [8]. Under nitrogen, Triton X-100 evaporates with only slight decomposition, and it evaporates completely above 350 °C, and nothing is left. In an oxygen containing gas, Triton X-100 was thermally oxidized above 230 °C, leaving a slowly decomposing material, but it also evaporates completely above 350 °C. So, we concluded that one can remove it completely from the electrode whether in air or in nitrogen by heating above 350 °C. However, we could not deny the probability of the remaining of the surfactant below 350 °C. This probability is repudiated in this report.

Another purpose of the heat treatment is to bind catalyst powder with PTFE particles by melting. However, the reported conditions of the heat treatment, namely, temperature, atmosphere and length of time were diverse. For example, Breaut *et al.* [1] heat treated at 310–335 °C for 15 min, while Goller and Salonia [3] treated at 338 °C for 20 min in air. Christner and George [9] heat treated their cathode at 350 °C for 20 min, while Baker and Klein [10] treated at 325 °C for 15 min. Honji *et al.* [11] fabricated their cathode at 320 °C for 30 min in air, while Maoka [12] treated at 340 °C for 20 min in nitrogen. Namely, the

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treatment temperature is selected generally from 310–350 °C and the heat treatment time from 15–30 min. Maoka [12] reported the influence of heat treatment temperature on electrochemical properties of a cathode by means of half-cell apparatus, and concluded that the inferiority of the low temperature treatment is caused by the fact that PTFE remains unmelted. He and several other investigators believe that the melting point of PTFE particle is about 327 °C, and this temperature is the beginning point of melting [6, 12]. However, the melting point of virgin PTFE particle is 342 °C [13, 14] and not 327 °C. Once the polymer melts and is solidified, then upon remelting, it melts at the previously reported and widely accepted lower temperature of about 327 °C [14]. Moreover, these temperatures are not the beginning points of melting but the peak temperatures [14]. The melting or unmelting phenomena are discussed fully in this paper.

The oxidation of carbon support by heat treatment is another problem, though it has not been reported in any detail up to date. This problem has also been made clear in this report.

The physical and chemical changes of electrode materials during the heat treatment from 250–400 °C have been reported in this paper with the purpose of clarifying the relationship between the cathode performance and its material properties during the heat treatment.

2. Experimental procedure

Electrodes were fabricated using the RRC method [4]. Fibrous carbon paper (Kureha Chemical Industry Ltd) was used as the substrate for cathodes. Wet-proofed substrate was prepared by treating it with a polytetrafluoroethylene (PTFE) dispersion, followed by heating at 360 °C, and coating with a catalyst layer. The catalyst layer was made of a carbon-supported platinum catalyst and PTFE. PTFE fine particles (0.2–0.3 μm diameter) was used which was dispersed in water (TFE-30J, Mitsuifluorochemical). Triton X-100 is added to stabilize hydrophobic polymer particles. The carbon support was a graphitized furnace black with the platinum content of 10 wt %. The nominal PTFE content of the catalyst layer was selected to be 45 wt % relative to the total weight of catalyst powder and PTFE in the catalyst layer. The cathodes were all previously heat treated at 250 °C for 40 min under nitrogen, then they were sintered at a fixed temperature range from 250–400 °C for 20 min. The heat treatment and sintering were done using serial furnace with a fixed oxygen concentration (2, 10 or 21% O_2), controlled by mixing air with nitrogen, and the oxygen concentration in the furnace was monitored by an oxygen gas detector (oxygen analyser model LC-700 Toray Industries Inc.). The temperature was kept within 4 °C with six PID controllers (Chino Works LTD).

Single cell test was conducted at 190 °C under 1.013×10^5 Pa. Air or pure oxygen was used as the oxidant, and pure hydrogen was used as the fuel. The air, oxygen and hydrogen utilization were set at 70, 20 and 20%, respectively. The arrangement of the single cell was the same as those reported in the previous paper [15, 16]. Acid absorption of catalyst layer was measured using an apparatus similar to that of Mori *et al.* [6]. The electrode (9 cm^2) contacting with phosphoric acid was maintained at 120 °C for a week in air. From the weight gain of the electrode, the acid absorption per unit area was calculated.

Pore volume and distribution of the catalyst layer was analysed using a porosimeter (Autopore 9200 of Shimadzu, Limited). The residue of Triton X-100 in the catalyst layer (before and after heat treatment) was extracted with acetone, and analysed using an i.r. spectrometer (Shimadzu IR27G) and ultra violet (u.v.) spectrometer (Shimadzu MPS-2000). The thermal properties of PTFE in the catalyst layer were studied using a differential scanning calorimeter (Perkin-Elmer DSC-2). The size of platinum catalyst particles was determined from the halfwidth of a Pt (2 2 0) peak using an X-ray diffractometer (Shimadzu XD-3A); the Scherrer equation [17] was used to calculate platinum particle size.

3. Results

3.1 Cell performance

Fig. 1 shows the cell performance versus heat treatment temperature. The oxygen concentration in the heat treatment atmosphere was 10%. The cell performance data was obtained with hydrogen/oxygen and hydrogen/air after 100 (the broken lines) and 600 h (the solid lines). This figure has the following three characteristics concerning heat treatment temperature.

(i) From 280–300 °C, the cell performance was poor especially with hydrogen/air.

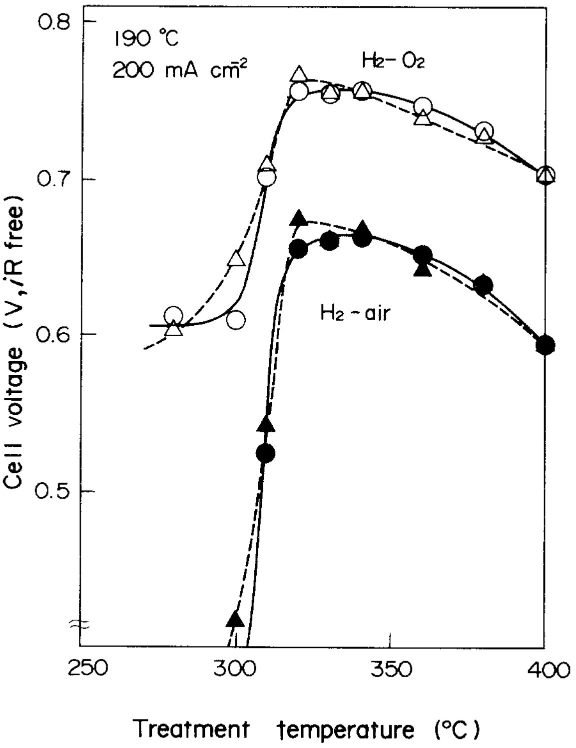

Figure 1 Variation of single cell performance with heat treatment temperature: (——) 600 h and (– – –) 100 h.

(ii) From 300–320 °C, the cell performance increased rapidly.

(iii) From 340–400 °C, the cell performance declined gradually.

3.2 Acid absorption of catalyst layer

The change in the acid absorption of the electrode left at 120 °C was measured by weight increase. Fig. 2 shows the acid absorption after 160 h versus the temperature of the heat treatment, in which the amount of the absorped acid was saturated. The characteristics of the results are summarized as follows:

1. From 250–300 °C, the acid absorption was high normalized.
2. From 300–320 °C, the acid absorption decreased rapidly to one half.
3. From 340–400 °C, the acid absorption decreased gradually furthermore.
4. The influence of oxygen content was relatively small.

From our measurements of pore volume and distribution of the pore diameter of the catalyst layers, it was found that the total volume of pores in the catalyst layer was equal to the volume of the maximum acid absorption. Accordingly, for samples from 250–300 °C, almost all pores in the catalyst layer were filled with the acid. On the other hand, for samples from 300–400 °C, about half of the volume of pores was filled with the acid.

3.3 Evaporation and decomposition of Triton X-100

In this section, the thermal behaviour of Triton X-100 coexisted with platinum catalyst is examined.

We reported the thermal behaviour of Triton X-100 alone under various gases with differential scanning calorimetry (DSC) and i.r. spectrophotometry below 350 °C [8]. In nitrogen gas, Triton X-100 evaporated without decomposition. However, in air or gas containing oxygen, thermal oxidation occurred, where a strong ν_{co} band appeared in the i.r. spectra. Oxygen increased the evaporation rate of Triton X-100 remarkably.

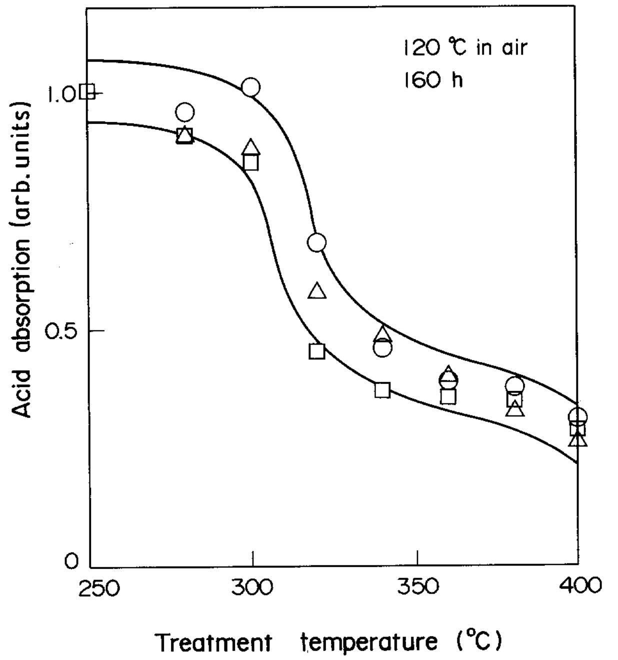

Figure 2 Variation of the quantity of acid absorption with heat treatment temperature: (□) 2%; (△) 10% and (○) 21% O_2.

First, we confirmed that Triton X-100 and the thermally oxidized products are both soluble in acetone, and made an acetone solution of them. After acetone was evaporated from the solution, i.r. spectra were measured for each sample. u.v. spectra were also measured after adding distilled water. Triton X-100 itself had a strong u.v. absorption band in the 200–220 nm region and a weak one in the 270–280 nm region. The thermally oxidized sample also had absorption band in a similar region. As for i.r. spectra, Triton X-100 itself and the thermal oxidation products (residue and evaporated deposit) have distinctive absorption bands in the IR region [8]. Especially, the latter has a new strong absorption band (1700 cm^{-1}) which is assigned to ν_{co}.

Next, we tried to extract the residue of Triton X-100 in the catalyst layer with acetone. The electrodes before and after heat treatment were immersed individually in acetone for about 1 week. Then, it was analysed by u.v. and i.r. absorptions. The u.v. and i.r. spectra of the samples before heat treatment were the same as those of Triton X-100 itself. However, for samples heat treated from 250–400 °C, almost no absorption was observed in u.v. and i.r. spectra in the same regions. It is therefore concluded that there was no residue of Triton X-100 in the electrodes sintered from 250–400 °C.

The thermal behaviour of Triton X-100 coexisting with platinum catalyst was also examined by the weight loss of the surfactant in an oven (DK-21, Yamato Science Co.). Fig. 3 shows the residue of Triton X-100 under nitrogen (containing below 1% O_2) or air after 30 min heat treatment with and without platinum black. The white triangles and white circles are for the cases without platinum, while the black triangles and black circles are for cases with platinum. In the case of Triton X-100 alone, the

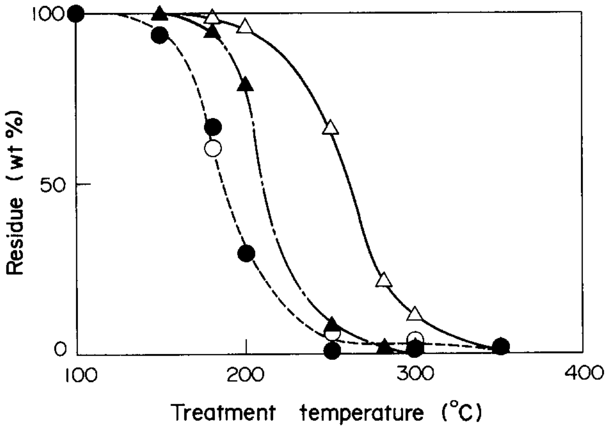

Figure 3 Variation of residue of Triton X-100 with heat treatment temperature; (△, ○) sheet without platinum, (▲, ●) sheet with platinum. Triangles are in N_2 and circles are in air.

residue decreased sharply between 150–200 °C in air, while a gradual decrease was observed under nitrogen in the same range. In the case of Triton X-100 coexisting with platinum black, a sharp decrease occurred between 200–250 °C even under nitrogen. These results indicate that the platinum black catalysed the thermal oxidation of Triton X-100 even in a gas containing little oxygen. Accordingly, almost all of Triton X-100 in the catalyst layer is removed when heat treated at 250 °C even in a gas containing little oxygen.

To summarize, two facts were clarified regarding the disappearance of Triton X-100 in the catalyst layer.

5. There is no residue of Triton X-100 in the heat treated electrodes from 250–400 °C.

6. Platinum effectively catalyses the thermal oxidation of Triton X-100 even in a gas containing little oxygen.

3.4 Melting of PTFE particles

In this section, thermal properties of PTFE in the catalyst layers are examined. The melting point (peak temperature) of virgin PTFE (initial melting point) is 342 °C [13, 14], and once the polymer has been melted, upon remelting, it melts at the lower temperature of about 327 °C (second and subsequent melting point). Accordingly, one can judge whether the PTFE in a catalyst layer has been melted or not from the peak temperature of its thermogram of DSC measurement.

Fig. 4 shows some endothermic curves of the catalyst layers baked at from 250–400 °C in 10% O_2. For a sample heat treated at temperatures below 320 °C, the endothermic peak was observed at about 339 °C (DSC temp). This temperature is close to the initial melting point of PTFE, indicating that a major part of the PTFE in the catalyst layer has not been melted. For a sample heat treated at temperature above 330 °C, an endothermic peak was observed at about 324 °C (DSC temp). This temperature is close to the second and subsequent melting point of PTFE, indicating that the PTFE in the catalyst layer has been melted previously and completely.

One can estimate the ratio of melted and unmelted PTFE from the endothermic heat of melting. Fig. 5 shows the relationship between endothermic heat of melting at about 339 °C (DSC temp) and heat treatment temperature. The ordinate was normalized by the weight of PTFE. The endothermic heat of melting at about 339 °C (DSC temp) began to decrease at 280 °C and went to zero at 330 °C, indicating that PTFE in the catalyst layer melts partly or completely at temperatures above 280 °C.

To summarize, three facts were clarified from the DSC measurements.

7. By the heat treatment at temperatures from 250–280 °C, PTFE in the catalyst layer does not melt at all.

8. By treatment below 330 °C, PTFE in the catalyst layer melts partly.

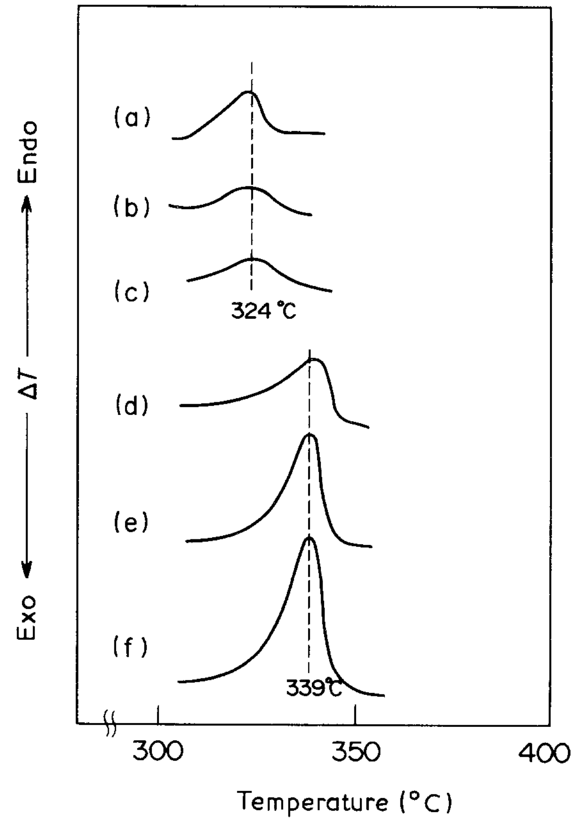

Figure 4 Endothermic curve of heat treated catalyst layer by DSC; heat treatment temperatures are: (a) 400; (b) 340; (c) 330; (d) 320; (e) 310 and (f) 250 °C.

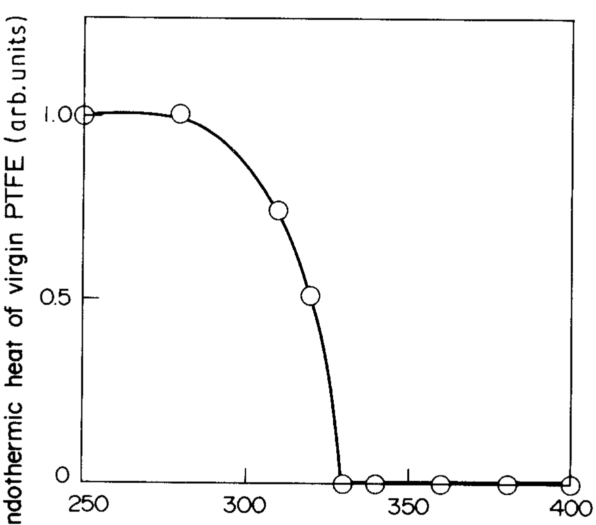

Figure 5 Variation of endothermic heat of virgin PTFE with heat treatment temperature.

9. By treatment above 330 °C, PTFE in the catalyst layer melts completely.

3.5 Oxidation of support carbon

Fig. 6 shows the decrease in electrode weight with treatment temperature. The weights of the electrodes are normalized with respect to that baked at 250 °C. The ratio of the weight of PTFE and that of the

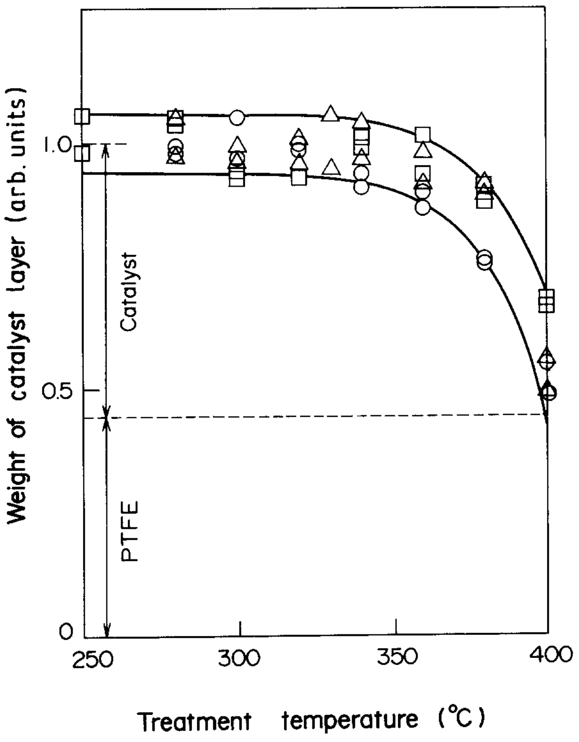

Figure 6 Variation of the weight of catalyst layer with heat treatment temperature: (□) 2%; (△) 10% and (○) 21% O_2.

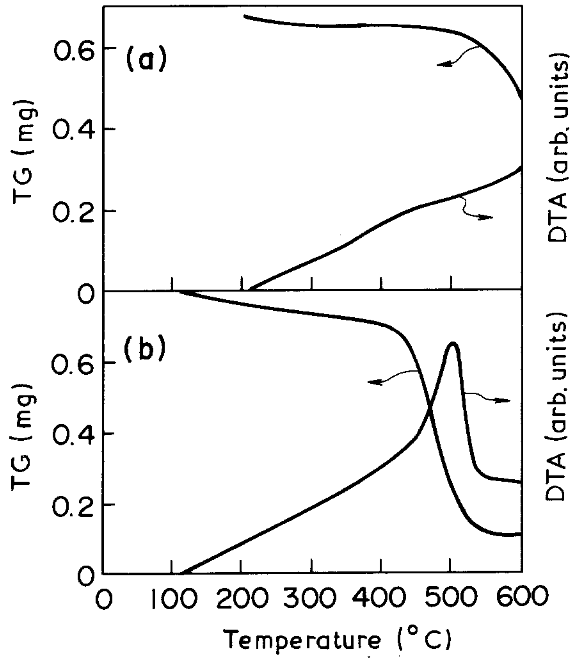

Figure 7 DTA–TG curve of: (a) graphitized carbon powder and of (b) Pt catalyst powder supported on the same graphitized carbon.

catalyst in the catalyst layer are also shown in this figure by arrows. The weight of the catalyst layer began to decrease above 350 °C, and became about 40% at 400 °C. The weight loss of PTFE at 400 °C in air was only 0.03% [18]. Platinum weight was not reduced at such low temperatures. Accordingly, the weight loss above 350 °C is due to oxidation of support carbon, and almost all of the support carbon disappeared at 400 °C. The weight loss increased with the increase of oxygen concentration in the atmospheric gas. It is clear, therefore, that oxygen accelerates the oxidation of support carbon. Because of the disappearance of support carbon, PTFE contents in the catalyst layer increases relatively.

We also studied weight loss of the catalyst powder itself using a differential thermal analysis–thermogravimetric (DTA-TG) analyser at a heating rate of 5 °C $\min^{-1}$ in stagnant air. In Fig. 7, (a) is for the support carbon (Pt free) powder and (b) is for the catalyst powder (10 wt % Pt). The weight of the naked carbon powder begins to decrease at 440 °C, and the weight of the catalyst powder begins to decrease at 340 °C. The weight of carbon decreased more vigorously in the presence of platinum, showing the catalytic effect of platinum on the oxidation of support carbon.

To summarize the results, three points can be made:

10. Above 350 °C, PTFE contents increased relatively by the oxidation of support carbon.

11. Oxygen accelerates the oxidation of support carbon.

12. Platinum has a catalytic effect on the oxidation of support carbon.

3.6 Growth of platinum particle size

Fig. 8 shows the platinum particle size of a virgin electrode versus heat treatment temperature. From 250–400 °C, the platinum particle size of a virgin electrode was hardly affected by heat treatment temperature. The platinum particle sizes of the electrodes after 600 h of operation in the single cell test are also shown in this figure by black triangles. After the cell operation, in all cases, the platinum particle size increased a little.

To summarize, the following result was obtained:

13. The platinum particle size was hardly affected by the heat treatment temperature.

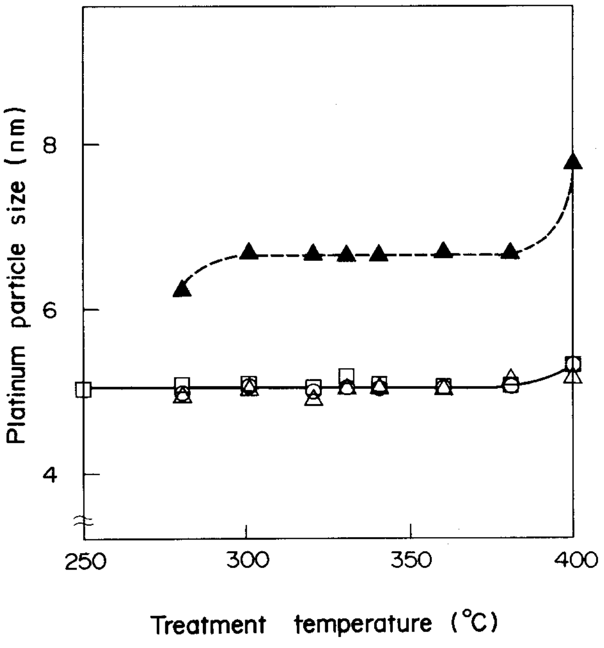

Figure 8 Variation of platinum particle size with heat treatment temperature before (solid line) and after (broken line) single cell test: (□) 2%; (△, ▲) 10% and (○) 21% O_2.

4. Discussion

4.1 On the poor cell performance from 280–300 °C region

As shown in Fig. 2, the acid absorption in the catalyst layer was constant from 250–300 °C (result 2). From the measurement of pore volume and distribution of pore diameter in the catalyst layer, it was found that almost all pores under 10 μm in diameter are filled with this amount of the acid. Accordingly, the catalyst layer was completely flooded with the acid, and oxygen was hard to diffuse into the catalyst layer. This is the exact reason for the poor cell performance especially with hydrogen/air.

Mori *et al.* [6] reported that the acid occupation under 350 °C is affected by the undecomposed Triton X-100. However, from our results, it is confirmed that Triton X-100 was decomposed or evaporated completely from the catalyst layer under 250 °C because of the catalytic action of platinum (results 5 and 6). Namely, there was no residue of Triton X-100 in the electrodes heat treated above 250 °C.

PTFE in the catalyst layer did not melt at all from 250–280 °C (result 7), and partly melted below 330 °C (result 8). The unmelted PTFE does not seem to give the catalyst layer hydrophobicity to the acid (results 1 and 2). Unmelted PTFE particle has small contact with the catalyst powder because the former is spherical. The PTFE particle has a fibrous structure like a cocoon [19]. Unmelted PTFE particle itself cannot give the catalyst layer any hydrophobicity to the acid, because the acid can penetrate into the gap between the particle and catalyst powder. When PTFE particle melts, these fibres get loose, spread like a maple leaf, and cover the surface. Accordingly, melted PTFE can cover the surface of the catalyst powder in the same way as Teflon® coating of a frying pan, and it must give to the catalyst layer an effective hydrophobicity to the acid. We suppose that the existence of the unmelted PTFE in the catalyst layer is the most plausible reason for flooding of the catalyst layer.

4.2 The rapid improvement of the cell performance from 300–320 °C region

Fig. 2 shows that the acid absorption decreased rapidly to one half from 300–320 °C (result 2), and a gas network could be maintained in the catalyst layer. This is the exact reason for the rapid increase of the cell performance in this region. The amount of the acid absorption is controlled by the ratio of melted to unmelted PTFE. Though the heat treatment temperature is lower than the initial melting point (342 °C) or the second and subsequent melting point (327 °C) of PTFE, these melting points are, exactly speaking, the peak temperature of the DSC endothermic curve [14], and consequently, melting of PTFE begins at a lower temperature. So, it is reasonable that a large amount of PTFE has already melted.

One can know the melted PTFE content from the endothermic heat of virgin PTFE melting in Fig. 5. Fig. 9 shows the real PTFE content in the catalyst layer. The black circles show the change of melted PTFE content, changing from 0 to 45 wt % with treatment temperature from 280–330 °C. The relationship between PTFE content and cell performance has been reported fully by Watanabe *et al.* [5]. Following their report, maximum performance was obtained at 30 wt % PTFE content for oxygen reduction. At lower PTFE content, the proportion of the main gas channels to the catalyst reaction volume was small, and the acid fills not only the reaction volume but also the gas channel. Namely, the catalyst layer is flooded at a lower PTFE content, and the gas diffusion problem occurs. As the PTFE content was increased to ca. 30 wt %, the gas channels and the gas dissolving sites increased. This phenomenon reflects the change of the Tafel slope as shown in their report. Accordingly, the rapid increase of cell performance in the 300–320 °C region is due to the change of effective PTFE content.

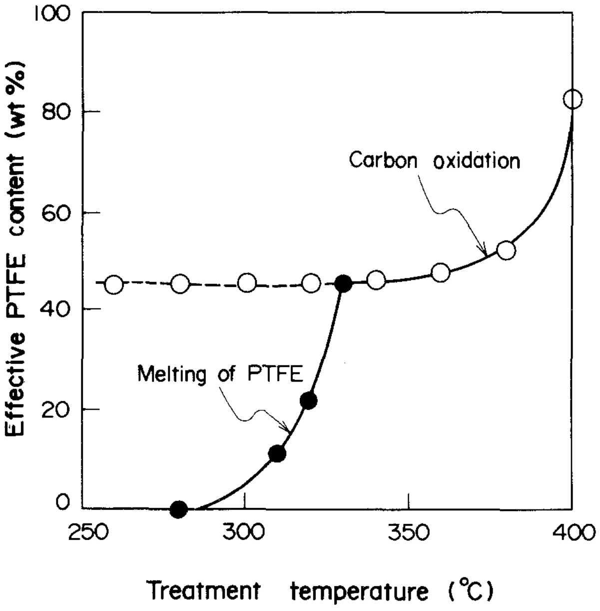

Figure 9 Variation of effective PTFE content with heat treatment temperature.

In relation to the acid wettability change of melted PTFE in the catalyst layer, Klinedinst *et al.* [20] studied the interaction between PTFE and porous metals and metal blacks [20] or between PTFE and carbon black [21]. When PTFE is heated at near the melting temperature (335–337 °C in their report) while in contact with carbon black (or metal blacks), it penetrates into the porous carbon black. The pores made of carbon black have a sucking force, and the melted PTFE must be introduced into the pores. In the same way, the melted PTFE probably penetrates into the pores of catalyst powder, and it will coat the inner walls. This phenomenon can cause a strong wetproofing effect and a binding effect by PTFE in the catalyst layer.

4.3 The gradual decrease in cell performance from 340–400 °C region

The acid absorption decreased gradually from 340–400 °C (result 3). This result is caused by the loss of carbon support (result 10). Watanabe *et al.* [5] reported that the acid occuppied mainly "primary pores" which was assigned to the space in-between the primary particles of carbon support. Accordingly, the decrease of carbon support causes the decrease of primary pores volume and the acid absorption. The decrease of total volume of the primary pores (below 0.1 μm) at a higher heat treatment temperature from 340–400 °C was ascertained by our pore distribution measurements. The decrease of carbon support also causes the increase of PTFE content. The change of PTFE content due to carbon oxidation is shown in Fig. 9 by white circles. The PTFE content increased from 45 to 83 wt % with an increase of heat treatment temperature from 340–400 °C. Watanabe *et al.* [5] reported the decline of cell performance due to an increase in the PTFE content, and attributed the lowered activity to the decrease in the utilization of platinum clusters and also to the effective conductivity of the electrolyte. On the other hand, the platinum particle size hardly changed with the increase of heat treatment temperature from 340–400 °C (result 13). Accordingly, the gradual decrease of cell performance from 340–400 °C is mainly due to the increase of the PTFE content.

Platinum catalyses the oxidation of carbon support (result 12). The surface oxide produced at such heat treatment temperature probably consists of four kinds of acidic oxide, i.e., carboxyl, phenolic hydroxyl, carbonyl and lactone [22]. These surface oxides are on the prism plane of the carbon support and not on the basal plane [23]. Platinum particles are also on the prism plane, and oxygen will be chemisorbed on the surface of the platinum particles. Then the carbon–carbon bond (C–C bond) of the surface oxides will be attacked by activated oxygen. The C–C bond will be dissociated, and forming carbon dioxide and carbon monoxide. Accompanied with the oxidation process, the platinum particles probably move around the prism plane and catalyse the oxidation of the carbon support. It is a surprising fact that the platinum particle size is hardly affected by the decay of carbon support in spite of the catalytic action or the active movement of platinum.

5. Conclusions

Three noticeable characteristics were observed for the relationship between the cathode performance and heat treatment temperature, i.e., poor performance from 280–300 °C, rapid improvement of performance from 300–320 °C and gradual decline of performance from 340–400 °C.

Triton X-100 completely disappears by heat treatment below 250 °C from the catalyst layer. Platinum catalyses the thermal oxidation of Triton X-100. The left-over of Triton X-100 is not the reason for the low performance by treatments from 280–300 °C.

Unmelted PTFE has no wetproofing effect on the catalyst. The PTFE particles in the catalyst layer do not melt at all below 280 °C and partly melt below 330 °C. Unmelted PTFE had no hydrophobic effect to the acid, and the effective PTFE content changed from 0 to 45 wt % between 280–330 °C. The poor performance from 280–300 °C and the rapid improvement from 300–320 °C must be explained by taking into account the unmelting or melting of PTFE particles.

The weight of carbon support was reduced above 350 °C by oxidation, and platinum catalyses the oxidation. Because of the loss of carbon support, real PTFE content increases, and at 400 °C, it reaches 83 wt %. This is the main reason for the gradual decline of cell performance from 340–400 °C.

Heat treatment of the electrode causes a substantial change of effective PTFE content from 0 to 83 wt % which noticeably affects the cathode performance.

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