

Investigation of platinum utilization and morphology in catalyst layer of polymer electrolyte fuel cells

Xiaoliang Cheng^{*}, Baolian Yi, Ming Han, Jingxin Zhang, Yaguang Qiao, Jingrong Yu

Fuel Cell R&D Center, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

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Abstract

Platinum utilization in the gas-diffusion catalyst layer and thin-film catalyst layer is investigated. The morphology of PTFE and Nafion in a simulated catalyst layer is examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The results show that the platinum utilization of the thin-film catalyst layer containing only Pt/C and Nafion is 45.4%. The low utilization is attributed to the fact that the electron conduction of many catalyst particles is impaired by some thick Nafion layers or clumps. For the gas-diffusion (E-TEK) electrode, the platinum utilization is mainly affected by the proton conduction provided by Nafion. The blocking effect of PTFE on the active sites is not serious. When the electrode is sufficiently impregnated with Nafion by an immersion method, the platinum utilization can reach 77.8%. Transmission electron micrographs reveal that although some thick Nafion layers and clumps are observed in the Pt/C + Nafion layer, the distribution of Nafion in the catalyst layer is basically uniform. The melted PTFE disperses in the catalyst layer very uniformly. No large PTFE clumps or wide net-like structure is observed. The reactant gas may have to diffuse evenly in the catalyst layer. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: PTFE; Nafion; PEMFC; Platinum utilization; Morphology

1. Introduction

Proton-exchange membrane fuel cells (PEMFCs) have been receiving attention on account of their highly attractive properties as a power source for both stationary and mobile applications [1–12] [13–15]. As these fuel cells require platinum or platinum alloy catalyst particles to provide sufficient catalytic activity, however, the high cost and scarce resources of the catalyst has restricted the development of PEMFCs [1–4]. To lower the platinum loading and to improve further the performance of the electrode, it is necessary to prepare an electrode with high platinum utilization. Unfortunately, for a gas-diffusion catalyst layer (such as the E-TEK electrode) impregnated with Nafion solution by brushing or spraying, the platinum utilization is only about 20% [1,5]. Wilson and Gottesfeld [2] suggested that the impregnation of Nafion into the catalyst layer was not very uniform. In other work [1], part of the whole thickness of the catalyst layer was impregnated with Nafion. Further addition of Nafion resulted in the formation of a film on the external surface of the

electrode [6]. To circumvent these problems with the gas diffusion electrode, a thin-film catalyst layer was prepared by mixing Nafion solution with Pt/C catalyst [2,7]. Nevertheless, platinum utilization in the thin-film catalyst layer is still unknown. As Nafion is an electron insulator, it is considered possible for the Nafion solid to cover the carbon surface and blocked the conduction of electrons by the carbon particles supported with platinum and cause the decrease of platinum utilization.

The low platinum utilization in the electrodes not only causes a waste of platinum but also restricts the further improvement of the electrode performance. To make electrode with high platinum utilization and better performance, it is necessary to investigate platinum utilization in present electrodes and determine how it is influenced by other factors. To date, these objectives have not received much attention. No investigation has been carried out on the influence of PTFE and Nafion on the platinum in the gas-diffusion or thin-film catalyst layers.

As PTFE and Nafion provide hydrophobicity and proton conduction in the catalyst layer [1,2], their morphology will influence the gas diffusion and proton conduction properties of the catalyst layer. For gas diffusion in the

^{*} Corresponding author

catalyst layer, it would be easier to diffuse along a passageway provided by continuous or net-like PTFE than to diffuse evenly through a catalyst layer in which there are discrete and dense clumps of PTFE. No particular advantage can be expected when PTFE exists in the immediate vicinity of the catalyst sites [2]. In the preparation process of the thin-film catalyst layer, although Pt/C is blended with Nafion solution ultrasonically, it is still unknown whether Nafion will spread uniformly on the carbon surface or form clumps in the catalyst layer after the solvent is evaporated. This kind of structural difference will greatly influence proton conduction in the catalyst layer. Up to now, however, although many efforts have attempted to investigate the morphology of the catalyst layer by observing the cross-section surface of the electrode using scanning electron micrographs [5,8,9,16], the practical morphology of PTFE and Nafion in the catalyst layer is still unclear. This may be due to the fact that the cross-section surface of an electrode cold fractured or split by knife is uneven and the resolution of scanning electron microscopy (SEM) is not very high, such that it is very difficult to distinguish clearly the Pt/C catalyst, PTFE and Nafion on the uneven cross-section surface and to research the morphology of PTFE and Nafion in the catalyst layer. Although transmission electron microscopy (TEM) has higher resolution than SEM, it cannot be used to observe directly the cross-section surface of an electrode. Ticianelli et al. [9] have searched for PTFE in the catalyst layer through TEM micrographs, but as PTFE melts through electron-beam heating in the TEM, no evidence of PTFE in any of the fields analyzed was found.

In this paper, the influence of PTFE and Nafion on platinum utilization in the two commonly used catalyst layers—the E-TEK electrode impregnated with Nafion and the thin-film catalyst layer—is investigated by means of SEM and TEM. The morphology of PTFE and Nafion blended with Pt/C catalyst is investigated. The influence of these two materials on gas diffusion and proton conduction is discussed. As it is quite difficult to observe clearly the morphology of PTFE in the catalyst layer by observing the cross-section of the electrode directly, a simulated catalyst layer was prepared on a smooth and flat glass plate, which can be observed with SEM of high resolution.

2. Experimental

The catalyst was a 20% E-TEK Pt/C catalyst with the average Pt diameter of about 2 nm. The E-TEK electrode contained 40 wt.% PTFE in the catalyst layer. Its platinum loading was 0.4 mg cm^{-2} (20% E-TEK Pt/C). The Nafion membrane was a Nafion 117 membrane supplied by Du Pont. All the chemical reagents were AR grade. The experimental instrument was a DPGS-1 potenti/galvanostat (NIKKO KEISOKU) and a HB-104 function generator.

The E-TEK electrode impregnated sufficiently with Nafion solution for the measurement of cyclic voltammograms (c–v curves) was prepared as follows. The gas-diffusion layer on the other side of the catalyst layer was scraped away so that Nafion solution could impregnate more easily into the catalyst layer of the E-TEK electrode. The electrode was then immersed in 2.5 wt.% Nafion solution for 30 min and treated ultrasonically every 5 min for 20 s so that Nafion impregnated completely into the catalyst layer of the electrode and made contact with the catalyst itself. The 2.5 wt.% Nafion solution was obtained by diluting 5 wt.% Nafion with isopropyl alcohol. After the solvent was evaporated, the electrode was hot-pressed on to a Nafion membrane. For the E-TEK electrode brushed with 5% Nafion, the Nafion loading was 1 mg cm^{-2} .

The thin-film catalyst layer for the measurement of c–v curves was prepared by means of the method proposed by Wilson and Gottesfeld [2]. The content of Nafion in the catalyst layer was 30 wt.%. At this content, the thin-film catalyst layer had the highest performance [4].

In the measurement of c–v curves, humidified argon was passed through the test electrode compartment and humidified hydrogen through the counter electrode compartment. Because of the negligible overpotential at the counter electrode for the hydrogen oxidation or evolution reaction, the counter electrode also served as a reference electrode. The sweep rate in the c–v measurement was 50 mV s^{-1} .

The specimens for SEM photographs were prepared by spreading a very thin layer of 5 wt.% pure PTFE emulsion or the ink-like mixture of Pt/C + PTFE emulsion + water on a smooth glass plate, the specimens were then heated to 240°C to remove the surfactant. Some specimens were further heated to 340°C to melt the PTFE.

The morphology of Nafion in the Pt/C layer was examined by means of TEM micrographs. First, the Nafion/catalyst/water/alcohol ink was prepared from a 5 wt.% Nafion solution combined with alcohol and water, and then thoroughly mixed by ultrasound. The ratio of Pt/C and Nafion (dry weight) was 3:1 or 1:1. After this the ink was dried completely in a vacuum oven at 80°C . The resulting solid (catalyst + Nafion) was ground and dispersed ultrasonically in ethyl acetate to obtain a suspension. The specimens for TEM were prepared with this suspension. Nafion solid cannot dissolve in ethyl acetate.

3. Results

3.1. Platinum utilization in catalyst layers

The c–v curve of the thin-film catalyst layer is shown in Fig. 1. The charge of the hydrogen desorption peak was 53.4 mC. As the average diameter of the Pt particles in 20% E-TEK catalyst is about 2 nm, and the density of platinum is 21.4 g cm^{-3} (assuming the shape of the Pt particles to be spherical), the surface area of the platinum

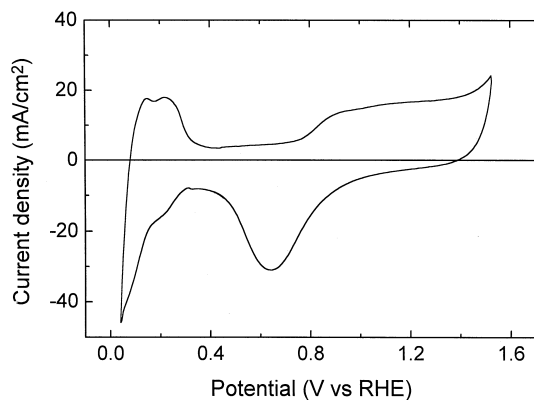


Fig. 1. Cyclic voltammogram for thin-film catalyst layer with the Pt loading of 0.4 mg cm^{-2} at a sweep rate of 50 mV s^{-1} .

is calculated to be $140 \text{ m}^2 \text{ g}^{-1}$ [1]. Assuming a charge of $210 \text{ } \mu\text{C cm}^{-2}$ for the surface of Pt [1], from the charge of the hydrogen desorption peak (53.4 mC), the electrochemical surface area is calculated to be $63.6 \text{ m}^2 \text{ g}^{-1}$. By comparison with the surface area obtained from the platinum particle size, the utilization of Pt particles in the thin-film catalyst layer can be calculated as: $(63.6/140) \times 100\% = 45.4\%$. That is, more than half of the platinum in the thin-film catalyst layer has not been utilized.

For the gas-diffusion electrode, as the proton conduction is provided by the impregnated Nafion, the platinum utilization is influenced by the degree of contact between the catalyst and the impregnated Nafion. It is difficult for the 5 wt.% Nafion to be impregnated sufficiently into all the small pores and contacted with the catalyst by using the brushing or spraying method. Therefore, in the experiments performed here, to impregnate the electrode sufficiently, the electrode was immersed in diluted Nafion solution and treated ultrasonically.

The *c-v* curves of an E-TEK electrode impregnated with Nafion by immersing in Nafion solutions or by brushing with 5 wt.% Nafion solution on the surface of the catalyst layer are shown in Fig. 2. The hydrogen peak current of the electrode immersed in Nafion solution is

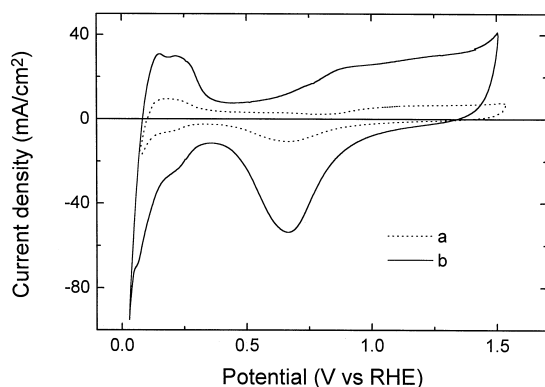


Fig. 2. Cyclic voltammograms of E-TEK electrode (Pt loading: 0.4 mg cm^{-2}): (a) brushed with Nafion solution (1 mg cm^{-2} Nafion); (b) immersed in Nafion solution. Sweep rate is 50 mV s^{-1} .

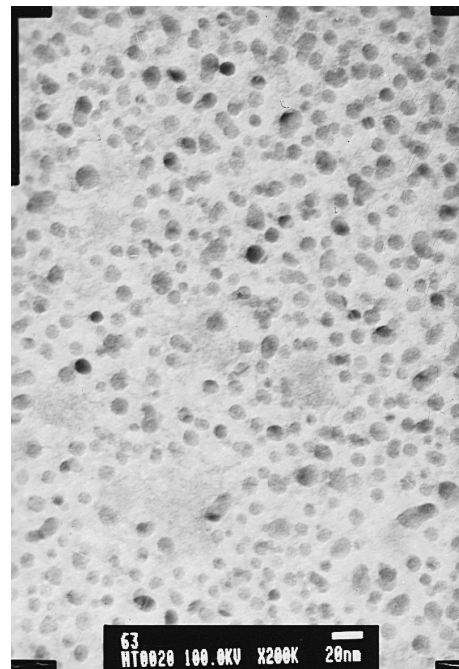


Fig. 3. TEM micrograph of pure 5 wt.% Nafion solution.

higher than the brushed electrode. According to the above method for calculation of platinum utilization, the utilization of Pt particles in the immersed and brushed E-TEK electrode is 77.8 and 22%, respectively. This shows that when the E-TEK electrode is impregnated by immersion so that sufficient proton passageways are provided to the catalyst particles, the platinum utilization can increase to 77.8%, which is higher than that of the thin-film catalyst layer obtained above.

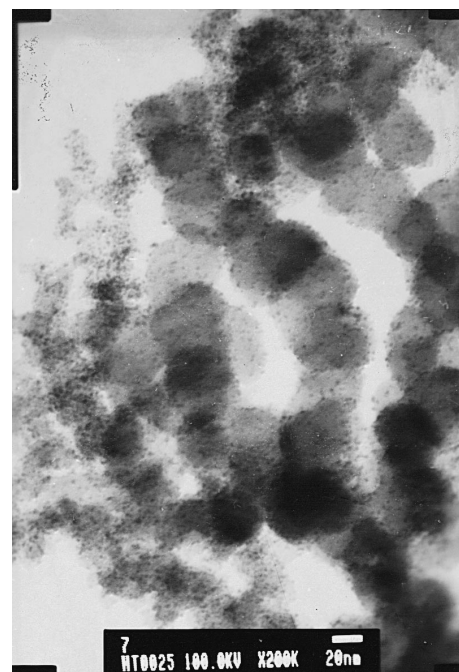


Fig. 4. TEM micrograph of 20% E-TEK Pt/C catalyst.

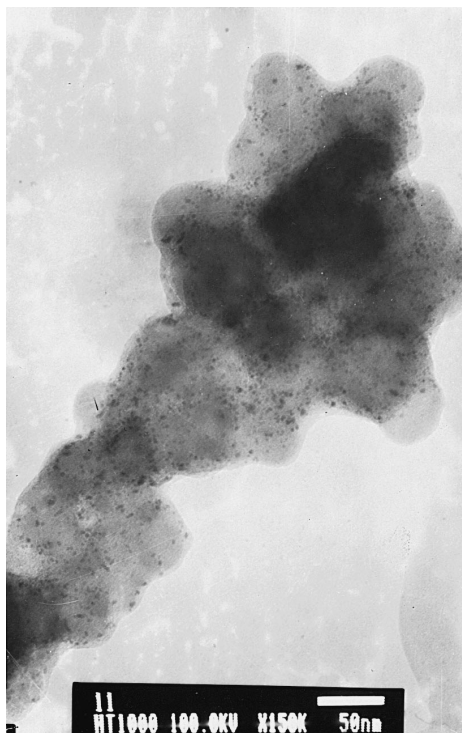


Fig. 5. TEM micrograph of a Pt/C+Nafion with $\text{weight}_{\text{Pt/C}} / \text{weight}_{\text{Nafion}} = 3:1$.

3.2. TEM micrographs of Pt / C + Nafion

A TEM micrograph of pure Nafion solution is presented in Fig. 3. Some Nafion balls can be observed with a diameter of about 4 to 10 nm. Obviously, the size of the Nafion molecules is smaller than these balls.

A TEM micrograph of pure Pt/C catalyst is given in Fig. 4. The carbon particles are balls with a diameter of about 30 nm. Many small black Pt particles are visible on the surfaces of the carbon particles.

A TEM micrograph of Pt/C catalyst blended with Nafion is presented in Fig. 5. There are many Pt particles on the surface of carbon particles, but no such kind of Pt particles should exist in the Nafion solid. This difference can therefore be used to distinguish carbon particles and Nafion solids. As the electron beam of the TEM passes through the carbon particles from the top to the bottom, the Nafion solids on the top or bottom surface of the carbon particles cannot be distinguished from carbon particles. Only the thicker Nafion layer on the edge of the carbon agglomerates can be detected.

Assuming that Nafion is spread very uniformly on the carbon particles and that the size of the carbon particles is 30 nm, it can be calculated that when the $\text{weight}_{\text{Pt/C}} / \text{weight}_{\text{Nafion}}$ ratio is 3:1, the thickness of the Nafion layer on the carbon surface is about 3 nm, which is a little too thin to be detected clearly. From the micrograph in Fig. 5, it can be seen that some Nafion layers are present on the edge of the carbon particles, especially in the upper-left area of the micrograph. In some places, the Nafion layers are more than 10 nm in thickness. This indicates that the thickness of Nafion layer is not uniform. From examination of all the TEM micrographs, it is found that although some thick Nafion layers or clumps are present in the catalyst layer, these are no Nafion clumps larger than 100 nm. Almost all the Nafion clumps are fixed to the surface of the carbon. The distribution of Nafion in the catalyst layer is essentially even.

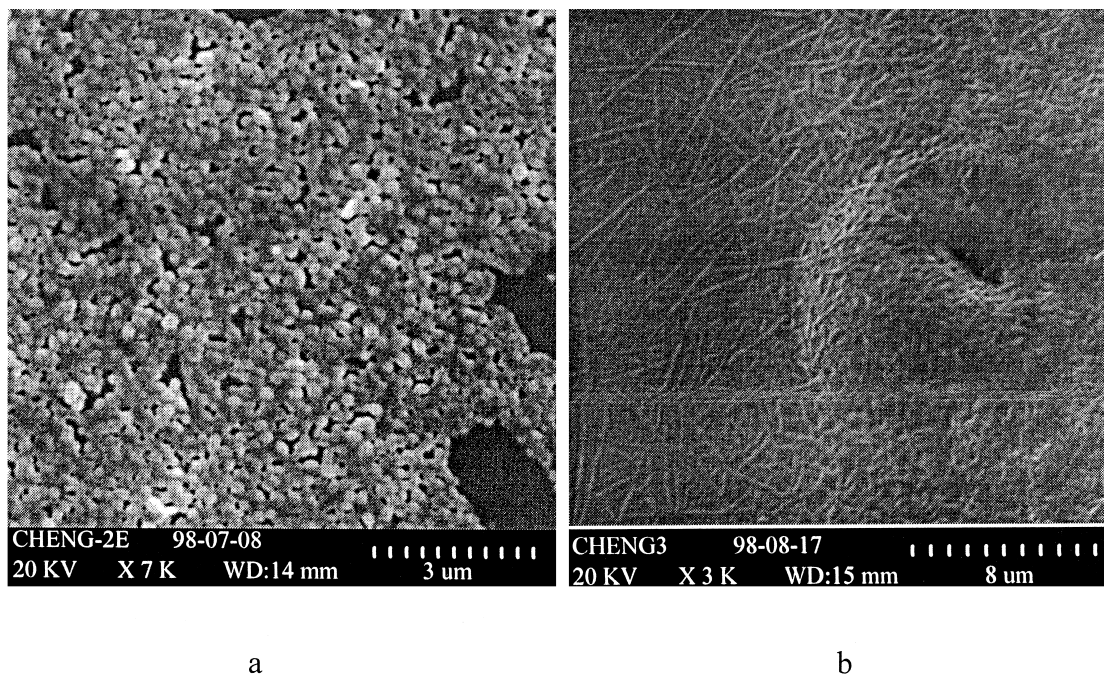


Fig. 6. SEM micrographs of pure PTFE emulsion: (a) before heat-treatment at 340°C; (b) after heat-treatment at 340°C.

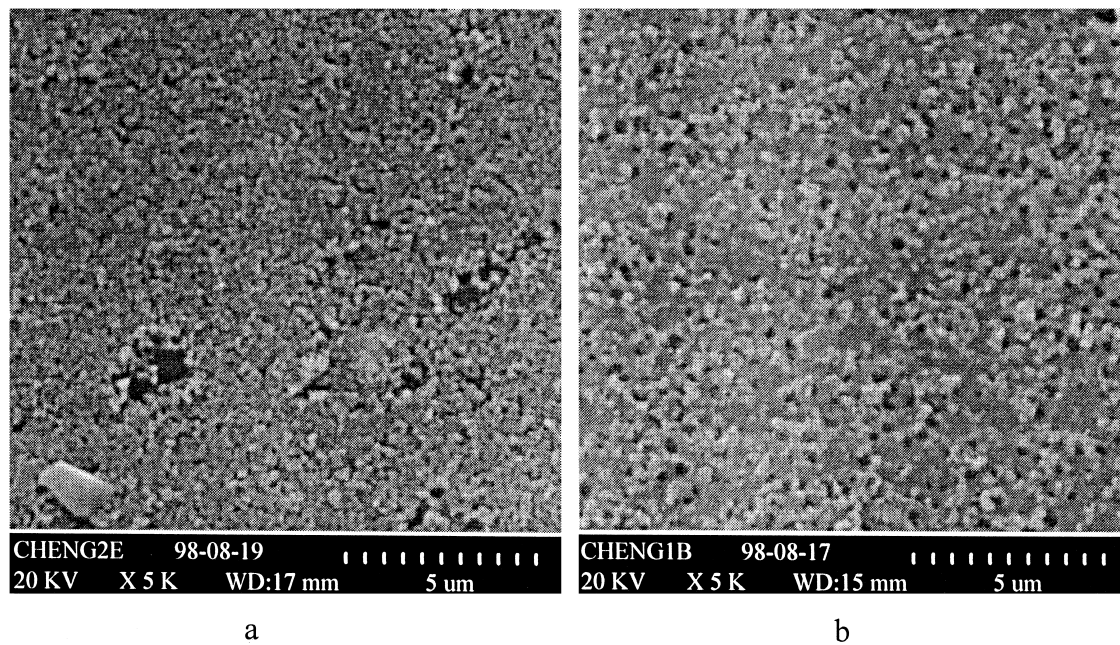


Fig. 7. SEM micrographs of Pt/C + PTFE emulsion with $\text{weight}_{\text{Pt/C}}/\text{weight}_{\text{PTFE}} = 1:5$: (a) before heat-treatment at 340°C; (b) after heat-treatment at 340°C.

3.3. SEM micrographs of PTFE + Pt/C layer

SEM micrographs of pure PTFE before and after melting treatment are shown in Fig. 6(a) and (b), respectively. In Fig. 6(a) it is seen that PTFE balls with diameters of about 0.2 μm are spread evenly on the glass plate. The dark areas in the lower right of the micrograph are glass

plate. Similar dark areas are visible in Figs. 7 and 8. From Fig. 6(b), it is seen that after treatment at 340°C, the PTFE balls have melted together and formed fibres. Micrographs of the PTFE + Pt/C layer at a $\text{weight}_{\text{PTFE}}/\text{weight}_{\text{Pt/C}}$ ratio of 5:1 are presented in Fig. 7. From Fig. 7(a), it is seen that the Pt/C agglomerates and PTFE balls are mixed together before the melting treatment. At this stage, it is

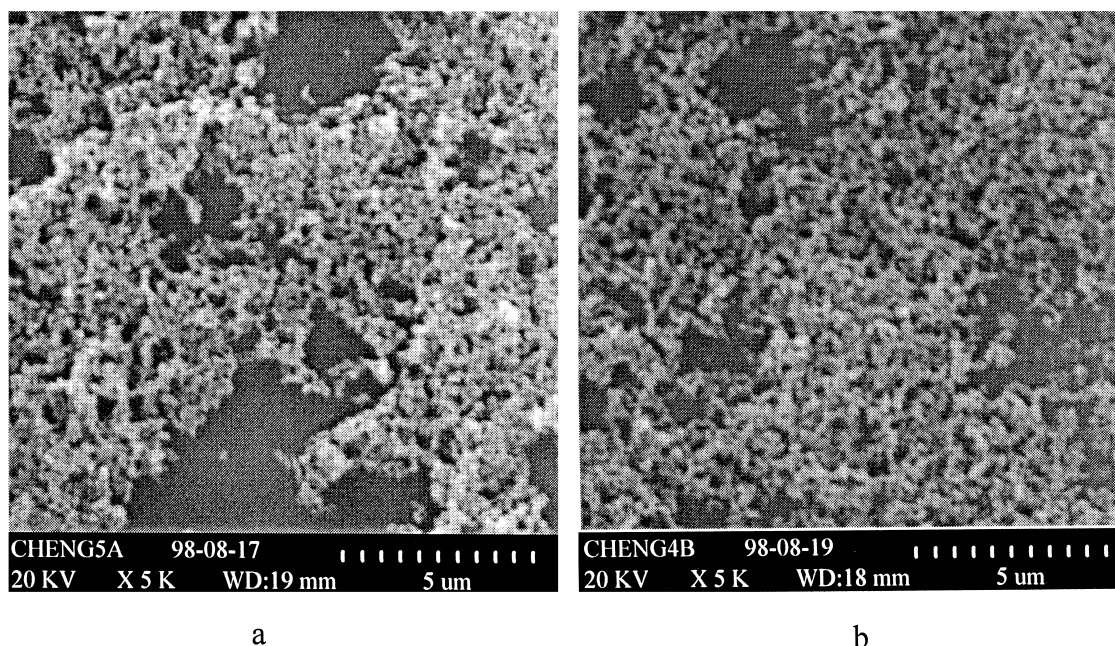


Fig. 8. SEM micrographs of Pt/C + PTFE emulsion with $\text{weight}_{\text{Pt/C}}/\text{weight}_{\text{PTFE}} = 1:1$: (a) before heat-treatment at 340°C; (b) after heat-treatment at 340°C.

rather difficult to distinguish the Pt/C agglomerates and the PTFE balls. When the specimen is heat-treated at 340°C, as shown in Fig. 7(b), the PTFE balls melt together. The particles, which can still be observed, should be the catalyst agglomerates because only PTFE are melted at this temperature. From Fig. 7(b) it is also observed that the catalyst agglomerates disperse uniformly in the melted PTFE. This indicates that the blending of catalyst and PTFE is very even. Most catalyst agglomerates are surrounded by the melted PTFE to a large degree. No PTFE fibres of the type displayed in Fig. 6(b) can be observed. When the weight ratio of PTFE and Pt/C is 1:1, as shown in Fig. 8, no pronounced change occurs after heat-treatment at 340°C. (cf., Fig. 8(a) and (b)). The encapsulating effect of melted PTFE on Pt/C agglomerates is not evident. Neither the PTFE fibres observed in Fig. 6(b) nor the melting structure of PTFE observed in Fig. 7(b) is evident. Neither PTFE net nor large clumps are present. This indicates that the mixing of Pt/C and PTFE is quite uniform.

4. Discussion

It is known that for any active site, which can sustain an electrochemical reaction, three passageways—electron conduction, proton conduction and gas diffusion must exist [1]. When the catalyst layer is not very thick, gas diffusion is not a restricting factor, especially for the gas-diffusion electrode [2]. Thus, the factors which influence platinum utilization are electron conduction and proton conduction. In PEMFC, proton conduction is provided by Nafion. Such conduction may be blocked, however, by melted PTFE which covers the catalyst surface. In the case of electron conduction, when the thickness of Nafion or PTFE between the carbon particles is sufficiently thin, electrons can still be conducted through a tunneling effect. When the thickness is large, however, electron conduction will be blocked by the solid Nafion or PTFE between the carbon particles or agglomerates (note: both Nafion and PTFE are electron insulators).

From Fig. 1, it was found that for a thin-film catalyst layer, the platinum utilization was 45.4%. In the preparation process of thin-film catalyst layers, as Pt/C catalyst and Nafion solution are blended ultrasonically and the molecule size of Nafion is very small so that it can enter Pt/C agglomerates, there should be no problem with the contact between Pt/C and Nafion. Even if some of the Pt/C is not contacted directly with Nafion, the distance of separation would not be very long, and there is always water in the catalyst layer that can conduct protons between Pt/C and Nafion. Thus, the Pt/C catalyst always has a proton passageway and the low platinum utilization (45.4%) should not be due to a restricted proton passageway. From TEM micrographs, it is found that the thickness of the Nafion layer on the carbon surface is not uniform. Therefore, it is possible that many carbon particles or

agglomerates may be separated or covered by Nafion layers or clumps which are too thick to be electron-conducting. As a result, for the thin-film catalyst layer, the loss of platinum utilization may be due mainly to the blocking effect of the Nafion solid on electron conduction.

For the Nafion-impregnated, gas-diffusion electrode, when the electrode is impregnated by immersion in Nafion solutions, the platinum utilization reached to 77.8%. (Fig. 2). This result shows that the platinum utilization of the gas-diffusion electrode is affected mainly by the proton passageway. When Nafion is impregnated sufficiently into the catalyst layer by means of the immersion method, a fairly high utilization of platinum can be obtained. This result also indicates that the blocking effect of PTFE on the electron or proton passageway is relatively slight when the content of PTFE is lower than 50%. As shown in SEM micrographs, when the $\text{weight}_{\text{PTFE}}/\text{weight}_{\text{Pt/C}}$ ratio is 5:1 (Fig. 7(b)) the Pt/C agglomerates are surrounded by melted PTFE. This will decrease the platinum utilization appreciably. When the weight ratio is 1:1, encapsulation of the Pt/C agglomerates with PTFE is not so obvious. The blocking effect of PTFE may be caused mainly by coverage by discrete PTFE clumps.

In the Nafion impregnated E-TEK electrode, the impregnated Nafion is only a provider of the proton passageway. Before impregnation with Nafion, the structure of the Pt/C particles in the catalyst layer has been fixed by the melted PTFE. Therefore, the impregnated Nafion cannot block the electron conduction of carbon particles in a manner similar to that which occurs in the thin-film catalyst layer. This explains why the platinum utilization of the immersed E-TEK electrode is higher than that of the thin-film catalyst layer.

From SEM micrographs of PTFE, it is seen that the morphology of PTFE changes greatly with the content in the Pt/C + PTFE layer. The Pt/C and PTFE particles are blended thoroughly and uniformly. When the content of PTFE is 50%, no PTFE fibres, large PTFE clumps or a wide PTFE net are formed. The reactant gas may have to diffuse evenly into the catalyst layer. As water is produced in the electrochemical reaction process in the catalyst layer, the efficiency of this type of uniform diffusion cannot be very high. In fact, the permeability of O_2 through water or Nafion in a short distance ($< 5 \mu\text{m}$) is sufficient for the reaction [2]. There is no particular advantage to be gained from the presence of PTFE in the immediate vicinity of the catalyst sites, because it will decrease the humidity of Nafion and block the proton or electron passageway in parts of the catalyst. Therefore, it is necessary to design a more efficient structure for gas diffusion in the catalyst layer.

The TEM micrographs of Nafion + Pt/C show that for the thin-film catalyst layer, although the thickness of Nafion layer is not uniform, the distribution of Nafion in the catalyst layer is essentially uniform. Thus, there should be no difficulties with proton conduction.

5. Conclusions

For the thin-film catalyst layer, the platinum utilization is 45.4%, the low utilization is due to the blocking effect of Nafion solid on the electron passageway in the catalyst. For the gas-diffusion electrode (E-TEK), platinum-utilization is affected mainly by the proton passageway provided by Nafion, while the blocking effect of PTFE is relatively small. By impregnating the catalyst with Nafion by means of an immersion method, the platinum utilization can be used to 77.8%.

Melted PTFE disperses very uniformly in the catalyst layer. No large PTFE clumps or wide net-like structure were found. The reactant gas may have to diffuse evenly into the catalyst layer. In the thin-film catalyst layer, although some thick Nafion layers and clumps are observed in the Pt/C + Nafion layer, there is an essentially uniform distribution of Nafion in the catalyst layer.

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