

# Electrode fabrication for proton exchange membrane fuel cells by pulse electrodeposition

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## Abstract

For low platinum loading, electrodeposition is used to fabricate electrodes for proton exchange membrane fuel cells. Pulse electrodeposition can form platinum deposits of about 15 Å directly on the surface of the electrode. With direct current electrodeposition at a current density of 25 mA cm<sup>-2</sup>, the electrode exhibits the best performance. At greater currents, the performance drops sharply because of the growth of dendritic crystals and the loss of the deposition layer due to generation of hydrogen. At a deposition current density of 50 mA cm<sup>-2</sup>, the optimum conditions of pulse electrodeposition are 100 ms on-time and 300 ms off-time, and the performance of the electrode is 320 mA cm<sup>-2</sup> at 0.7 V. Also, it is found that the brushing method for making carbon electrodes is favourable for electrodeposition because it can supply much more sites for the formation of nuclei. © 1998 Published by Elsevier Science S.A. All rights reserved.

**Keywords:** Pulse electrodeposition; Platinum deposits; Electrode performance; Proton exchange membrane; Fuel cell; Surface roughness; Deposition current density

## 1. Introduction

The proton exchange membrane fuel cell (PEMFC), which uses a polymer membrane as an electrolyte, has good energy efficiency, high current density per volume, and no corrosion problems. Also, it can be operated at low temperature [1–3]. It requires, however, a high initial investment cost due to the expensive noble metal catalyst and the electrolyte membrane. Many studies have been directed towards the development of an electrode with excellent performance at a low platinum loading [4–6].

Methods for fabricating electrodes for PEMFCs include silk screening, brushing and rolling. These methods are used to spread the Pt/C catalyst with PTFE on carbon cloth or carbon paper. If the electrode is made by these methods, inactive catalyst sites exist in the catalyst layer because the electrochemical reaction occurs only at the interface of the membrane and the electrode. Nafion solution is impregnated to expand the three-dimensional reaction zones in the electrode [7,8]. The addition of Nafion solution and the existence of inactive catalyst sites in-

crease, however, the manufacturing cost of the electrode. Therefore, it is essential to enlarge the effective surface area by diminishing the size of catalyst particles and to distribute the catalyst only on the surface of the electrode for a low platinum loading. Vilambi and Anderson [9] developed a method to distribute catalysts on the surface of the Nafion-coated electrode and Verbrugge [10] also studied this procedure. Jernstedt [11] obtained a densely deposited layer from copper cyanide solution at high current density by pulse electrodeposition, and Popkov [12] reported similar results.

In this study, electrodes have been fabricated by using direct current (DC) and pulse electrodeposition methods, and their performances compared. The effects of current density, pulse conditions, duty cycle in electrodeposition, and electrode surface condition on performance are examined.

## 2. Theory

It is known that pulse electrodeposition, as compared with DC electrodeposition, has many advantages in terms of controlled particle size, stronger adhesion, uniform elec-

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trodeposition, selectivity of hydrogen, reduction of internal stress, etc. Also, DC electrodeposition has only one variable, namely, current density, while pulse electrodeposition, as shown in Fig. 1, has three independent variables, namely,  $t_{\text{on}}$  (on-time),  $t_{\text{off}}$  (off-time) and  $i_p$  (peak current density). In electrodeposition, the duty cycle is defined as follows:

$$\text{duty cycle (\%)} = \frac{t_{\text{on}}}{t_{\text{on}} + t_{\text{off}}} \times 100. \quad (1)$$

In DC electrodeposition, as the deposition current density increases, the deposited metal ions near the cathode are exhausted and dendritic crystals are formed. Eventually, the ion concentration at the cathode surface becomes zero. The current density at which dendrite crystals begin to form is defined as the ‘limiting current density’. At this current density, the ion concentration at the deposited surface is zero. Pulse electrodeposition can raise the limiting current density considerably in comparison with DC electrodeposition because the deposited metal ions of the cathode surface can be supplied from the bulk solution during the off-time of the pulse. The mechanism of pulse electrodeposition, however, has still to be fully understood. Cheh [13] reported that the rate-determining step of pulse electrodeposition is controlled by mass transport. In other work, Ibl [14] claimed that the duty cycle can be an important factor because the properties of metal deposits can be influenced by both the on-time, during which formation of nuclei and growth of existing crystals occur, and the off-time, during which desorption of deposited ions takes place.

The rate of nuclei formation,  $\nu$ , is given by:

$$\nu = k_1 \exp(-k_2/\eta^2), \quad (2)$$

where  $k_1$ ,  $k_2$  are constants and  $\eta$  is the overpotential [15]. Therefore, the rate of nuclei formation depends on the

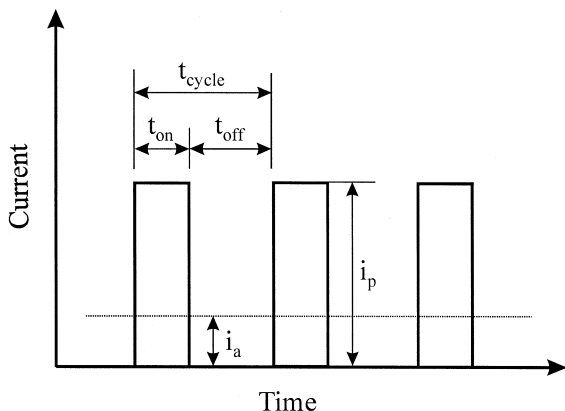


Fig. 1. General concept of pulse-current technique.

anodic overpotential,  $\eta_a$ . The anodic overpotential of DC electrodeposition is given by:

$$\eta_{a,DC} = \eta_o \ln \left( \frac{i_{DC}}{i_o} \right), \quad (3)$$

where  $\eta_o$  is the overpotential at the exchange current density. The anodic overpotential of pulse electrodeposition is expressed as:

$$\eta_{a,PC} = \eta_o \ln \left( \frac{i_a}{i_o} \right) + \eta_o \ln \left( \frac{t_{\text{off}}}{t_{\text{on}}} + 1 \right). \quad (4)$$

The average current density,  $i_a$  in Eq. (4) is equal to  $i_{DC}$  because it determines the surface concentration of deposited metal ions, i.e.,

$$i_{DC} = i_a, \quad (5)$$

$$\eta_{a,PC} = \eta_{a,DC} + \eta_o \ln \left( \frac{t_{\text{off}}}{t_{\text{on}}} + 1 \right). \quad (6)$$

As the anodic overpotential of pulse electrodeposition is larger than that of DC electrodeposition by  $\eta_o \ln(t_{\text{off}}/t_{\text{on}} + 1)$ , the rate of nuclei formation increases and the size of metal deposits becomes smaller.

### 3. Experimental

#### 3.1. Electrode fabrication by electrodeposition

The process of electrode fabrication by electrodeposition consisted of three steps. The first step was to make the carbon electrode without catalyst, the second was deposition of platinum on the carbon electrode, and third was drying.

In the first step, a carbon black (Vulcan XC-72) catalyst support was treated to remove organic matter for 3 h at 600°C. Glycerin, PTFE and pretreated carbon black were mixed with isopropyl alcohol in a supersonic mixer in a weight ratio of 1:3.5:0.3. This mixture was brushed on the carbon cloth and then dried at 80°C for 12 h. Electrodeposition was performed in a plating bath which contained a solution of  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  at room temperature. A platinum gauze anode and a carbon cathode were used. A pulse generator controlled both the pulse wave and the deposition current density. A schematic diagram of the plating bath is shown in Fig. 2. The solution was agitated well to bring up a fresh supply of metal ions to the cathode and to sweep away gas bubbles. The concentration of the solution was fixed at 18 mM. The conditions of electrodeposition were: current density = 10 to 50  $\text{mA cm}^{-2}$ ; on-time and off-time = 10 to 100 ms; total amount of charge = 4  $\text{C cm}^{-2}$  in all cases.

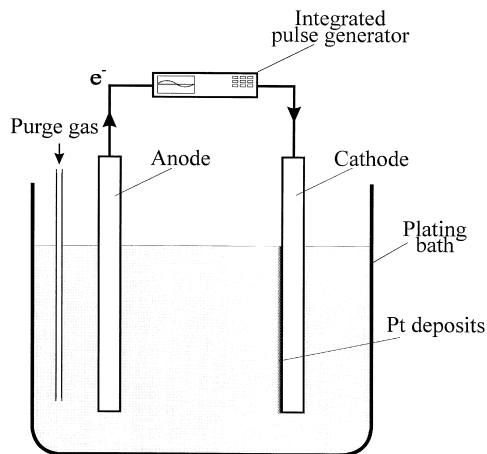


Fig. 2. Schematic of electrodeposition cell.

### 3.2. Performance test of single cell

The electrode and membrane assemblies were made by hot-pressing at 120°C and 140 atm for 3 min. The fuel cell test station was composed of a gas supply, a single cell, and measuring devices. The reaction gases were supplied through a humidifier and a mass-flow controller (Teledyne Hastings-Raydist) from hydrogen and oxygen tanks. The cell operation was conducted at 70°C and the cell performance was measured by an electronic load (HP-6060B, Hewlett Packard) which was connected to a computer via a GPIB interface.

### 3.3. Measuring of particle size and effective surface area of platinum

The surface of the electrode fabricated by electrodeposition was observed by scanning electron microscopy (H-6010, Hitachi), and platinum scanning by energy dispersive X-ray spectroscopy (EDXS) was performed in order to measure the degree of distribution in the deposits. The size of the platinum particles on the surface of the electrode was determined by means of transmission electron microscopy (H-600, Hitachi). The effective surface area of the platinum catalyst was determined by cyclic voltammetry (CV) in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 25°C. Undertaken in the range of -1.9–1.4 V (vs. SCE) using a triangular potential sweep at a scan rate of 50 mV s<sup>-1</sup>.

## 4. Results and discussion

### 4.1. Effect of deposition current density

The performance of electrodes fabricated by DC electrodeposition at the various deposition current densities is shown in Fig. 3. The best performance was observed at 20 mA cm<sup>-2</sup>. The deposition current density exerts an impor-

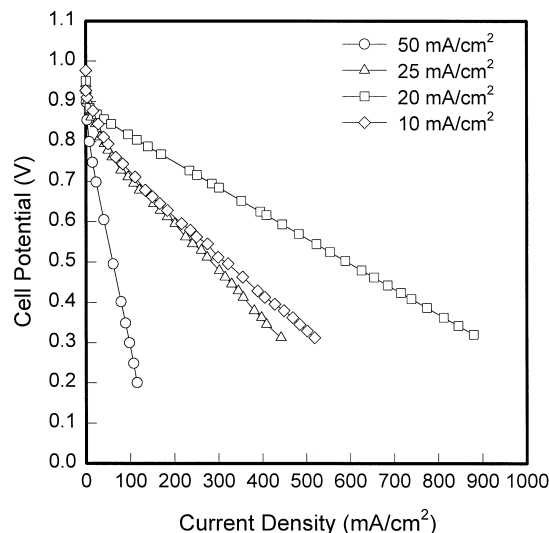


Fig. 3. Effect of deposition current density on performance in DC electrodeposition.

tant effect on properties such as the size, shape and distribution of the deposit. At low current density, the growth of existing crystals is superior to the formation of nuclei because the rate of movement of electrons at the surface is so slow as compared with the diffusion rate of deposited metal ions that the latter are crystallized at stable places on the surface with sufficient time. This decreases the surface area of the catalyst. As the deposition current density increases, however, the overpotential at the cathode rises because the rate of electron movement at the surface is no longer slower than the diffusion rate of the metal ions. In other words, as new nuclei are formed and crystallized before the deposited metal ion diffuses to the stable places, the rate of nuclei formation increases in proportion to the overpotential. Table 1 displays the effective surface area of platinum obtained from cyclic voltammograms. The effective surface area is 100.9 and 70.5 m<sup>2</sup> g<sup>-1</sup> at 20 and 10 mA cm<sup>-2</sup>, respectively. These results confirm that the effective surface area is larger at higher current densities.

When current density reaches 25 mA cm<sup>-2</sup>, the concentration polarization is large (Fig. 3) and the metal deposits move to the tips of the crystals and the crystals grow. Thus, the shape of the crystal becomes dendritic, as shown in Fig. 4. This diminishes the surface area of the catalyst

Table 1  
Comparison of effective surface area of platinum deposits

Electrodeposition	Deposition current density (mA cm <sup>-2</sup> )	Effective surface area of platinum (m <sup>2</sup> g <sup>-1</sup> )
DC	10	70.5
DC	20	100.9
Pulse	50	124.5

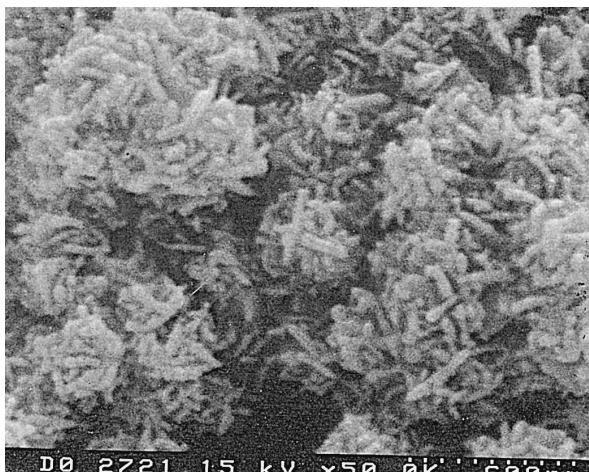


Fig. 4. Scanning electron micrograph of dendritic growth of platinum deposits.

and decreases the performance of the electrode. At 50 mA  $\text{cm}^{-2}$ , the deposition layer is lost due to the generation of hydrogen at the surface of the electrode and the perfor-

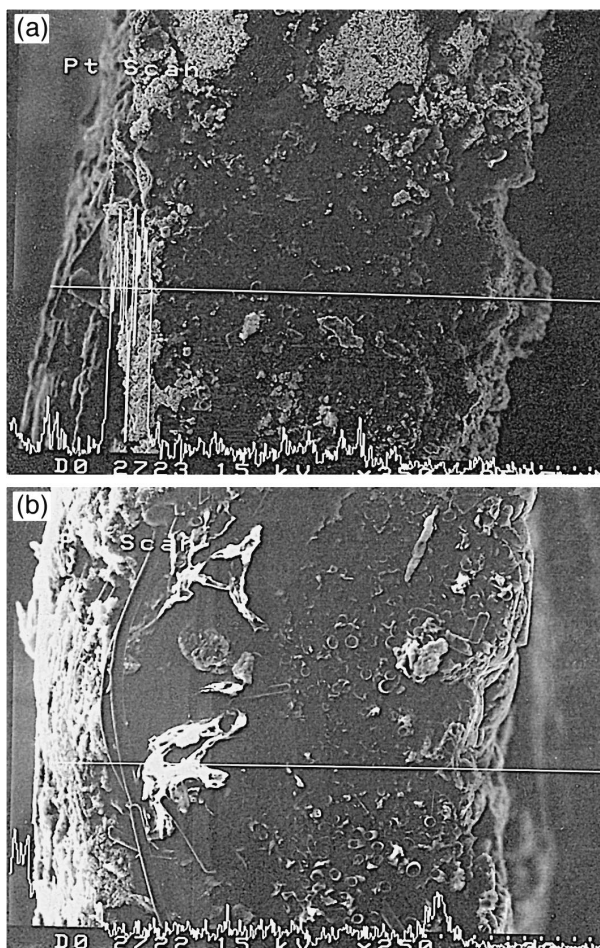


Fig. 5. Linear mapping of platinum distribution across cross-section of electrode fabricated by electrodeposition: (a) 20 mA  $\text{cm}^{-2}$ ; (b) 50 mA  $\text{cm}^{-2}$ .

mance of the electrode drops sharply. This is confirmed by a comparison (Fig. 5) of platinum scans of cross-section of electrodes fabricated at 20 and 50 mA  $\text{cm}^{-2}$ . At 20 mA  $\text{cm}^{-2}$ , a strong peak is observed due to platinum deposits forming mainly at the surface. At 50 mA  $\text{cm}^{-2}$ , however, the peak is shrunk markedly due to the loss of platinum under the action of excess current density. The limiting point to improve the properties of the layer of deposits produced by DC electrodeposition is considered to be 25 mA  $\text{cm}^{-2}$ ; beyond this, dendrites begin to form.

#### 4.2. Effect of operating conditions of pulse electrodeposition

Fig. 6 presents the performance plots of electrodes fabricated by pulse electrodeposition with a varying duty cycle at a deposition current density of 50 mA  $\text{cm}^{-2}$ , i.e., at a value which is higher than the limiting current density of DC electrodeposition. The on-time was fixed at 100 ms and the off-time was varied between 100 and 500 ms. For a duty cycle of 25%, the size of the platinum deposits is about 15 Å (Fig. 7), i.e., far smaller than the 50 Å found with the colloidal method [16]. This duty cycle also produces the best electrode performance. At a duty cycle of 50%, however, a white-coloured matter begins to appear on the surface of the electrode and particles with a diameter of 150 nm are formed, as shown in Fig. 8. If the duty cycle is 50%, the average current density of pulse electrodeposition is 25 mA  $\text{cm}^{-2}$  and this value is identical to that at which dendrites are formed in DC electrodeposition. Therefore, to prevent a drop in performance with pulse electrodeposition, the average current density must be kept below the limiting current density of DC electrodeposition.

The influence of pulse frequency on electrode performance is shown in Fig. 9. The duty cycle was fixed at 25%

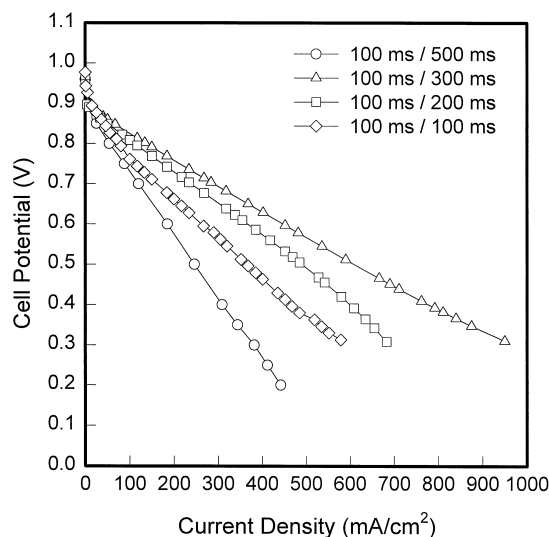


Fig. 6. Effect of duty cycle (on-time/off-time) on performance in pulse electrodeposition; deposition current density = 50 mA  $\text{cm}^{-2}$ .

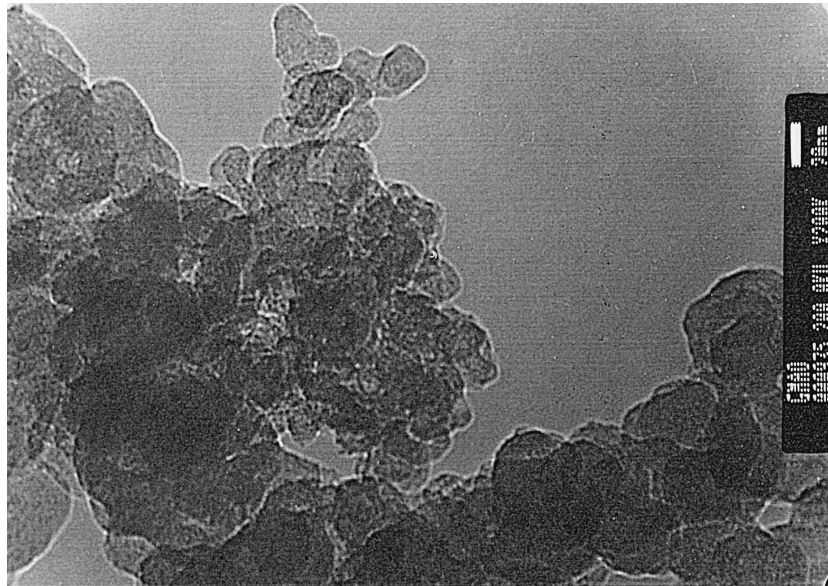


Fig. 7. Transmission electron micrograph of platinum deposits formed by pulse electrodeposition at  $50 \text{ mA cm}^{-2}$  (100 ms on-time/300 ms off-time).

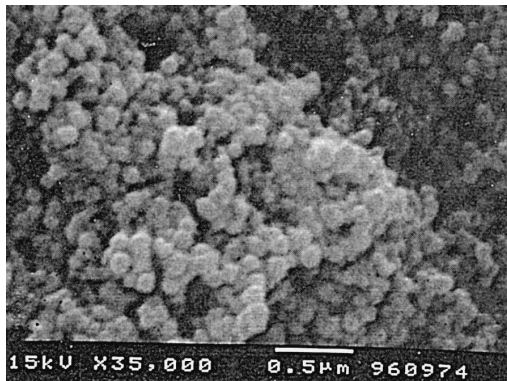


Fig. 8. Scanning electron micrograph of surface of electrode fabricated by pulse electrodeposition.

according to the results of Fig. 6 and the conditions of electrodeposition were: (i) on-time and off-time = 3 s; (ii) on-time = 100 ms, off-time = 300 ms; (iii) on-time = 10 ms, off-time = 30 ms; (iv) DC electrodeposition. Electrodes fabricated under pulse conditions display better performance; pulse electrodeposition increases the effective surface area of the platinum deposits, as shown in Table 1. In addition, the overpotential rises gradually during deposition with DC, but remains constant under pulse conditions. These results indicate that pulse electrodeposition is favorable for manufacturing electrodes for PEMFCs. The optimum conditions are an on-time of 100 ms and an off-time of 300 ms.

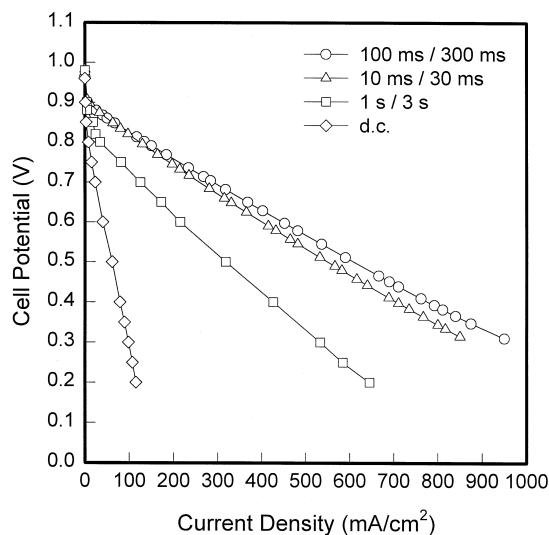


Fig. 9. Effect of frequency (on-time/off-time) on performance in pulse electrodeposition; deposition current density =  $50 \text{ mA cm}^{-2}$ .

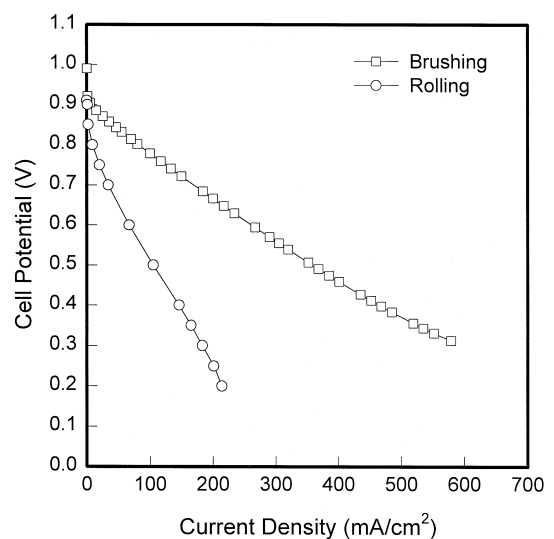


Fig. 10. Effect of surface condition on performance in pulse electrodeposition; deposition current density =  $50 \text{ mA cm}^{-2}$ .

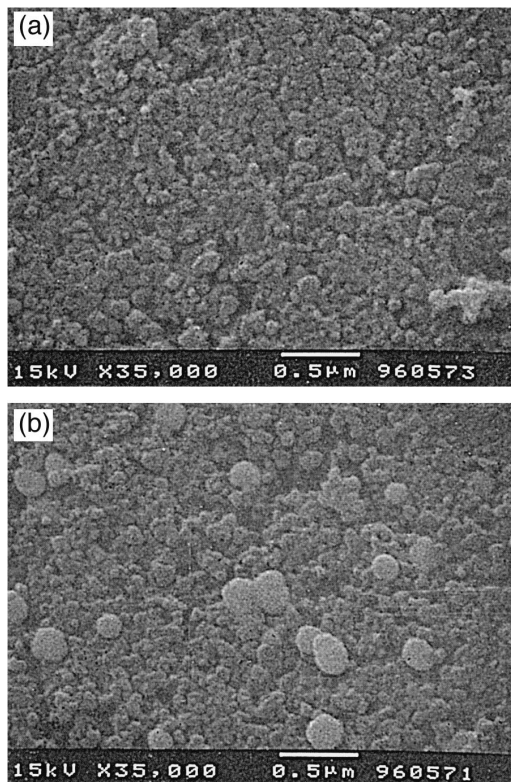


Fig. 11. Scanning electron micrographs (a) and (b) after electrodeposition of a carbon electrode made by rolling.

#### 4.3. Effect of roughness of the electrode surface

To investigate the effect of electrode roughness on electrodeposition, carbon electrodes were made by the rolling and brushing methods and subjected to pulse electrodeposition. The deposition current density was  $50 \text{ mA cm}^{-2}$ , the on-time was 100 ms, and the off-time was 10 ms. The brushed carbon electrode exhibits much better performance than the rolled one (Fig. 10). This suggests that the formation of nuclei and the growth of crystals are influenced markedly by the surface state of the electrode. The states before and after electrodeposition of the carbon electrode fabricated by the rolling method are compared in Fig. 11. The size of the platinum deposits formed on the smooth surface is about 250 nm. This value is larger than that of 150 nm found on the rough surface of the electrode produced by the brushing method. It is considered that the brushing method can supply much more sites for the formation of nuclei because it is able to increase the

surface area of the electrode as compared with the rolling method.

## 5. Conclusions

In general, the colloidal method has been used to impregnate the carbon support with platinum and the size of the deposited particles is about 50 Å. On the other hand, the pulse electrodeposition method can form deposits of about 15 Å directly on the surface of the electrode and can be operated at a higher current density than DC electrodeposition. In the latter, a current density of  $25 \text{ mA cm}^{-2}$  produces the electrode with the best performance. At greater currents, the performance decreases sharply due to both the growth of dendritic crystals and loss of the deposition layer through generation of hydrogen. At a deposition current density of  $50 \text{ mA cm}^{-2}$ , the optimum conditions of pulse electrodeposition are 100 ms on-time and 300 ms off-time, and the performance of the electrode is  $320 \text{ mA cm}^{-2}$  at 0.7 V. The brushing method for making carbon electrodes is suitable for electrodeposition because it can supply many more sites for the formation of nuclei.

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