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Electrocatalytic activities of graphite-supported platinum electrodes for methanol electrooxidation

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Electrooxidation of methanol in 1 M NaOH at 30 °C was studied on graphite-supported platinum electrodes prepared both in hydrogen and in air at various temperatures. Heating in hydrogen always produced higher surface area of Pt, and hence greater mass activity, than in air at a particular temperature. Nevertheless, both the graphite-supported platinum electrodes exhibited almost the same specific activity as a smooth Pt electrode for methanol electrooxidation irrespective of the preparation conditions. This indicates that the difference in mass activity is due to different surface areas produced by the different preparation methods. The Tafel slope of 110 mV decade^{-1} on all the electrodes studied indicated that the first charge transfer process was the rate-determining step.

1. Introduction

The electrooxidation of methanol has been a topic of extensive research since the 1960s in view of fuel cell applications. Numerous modifications of Pt electrodes have been studied using various foreign metals in different ways, namely, alloying [1–7], novel immersion techniques [7], underpotential deposition [8], etc. The underlying concept has been to oxidize CO-like species produced during the course of the methanol electrooxidation at potentials as low as possible, or suppressing the formation of CO-like species so that the electrooxidation occurs effectively and efficiently. Highly dispersed Pt catalysts on various carbon supports have also been investigated [9–14] in order to evaluate the particle size effect on the methanol electrooxidation. In this paper we report the effect of heating temperature for the decomposition of chloroplatinic acid into platinum to prepare graphite-supported platinum electrodes (C/Pt) in both hydrogen and air and to compare their catalytic activities to the activity of a smooth platinum electrode for methanol electrooxidation. Results indicate that heating in hydrogen at low temperature produces catalysts of higher electrocatalytic activities. This is due to the higher surface area obtained, but there is no intrinsic particle size effect in the range studied.

2. Experimental details

2.1. *Materials*

Alkaline supporting electrolytes were used as in earlier investigations [15, 16], as this work is concerned with basic properties of electrocatalysts. All the solutions were prepared using water purified in a Millipore water purification system. Methanol (Merck, 99.5%), NaOH (Merck, 99%) and $H_2PtCl_6.6H_2O$ (Cica, 37% as Pt) were used without further purification. Platinum foil (0.05 mm thick) and gauze (100 mesh) (both 99.98%), Ta wire (0.5 mm dia., 99.95%) and graphite plates (0.3 mm thick, 99.8%) were obtained from the Nilaco Corporation, Tokyo.

2.2. *Preparation of electrodes*

Graphite sheets (5 mm × 5 mm) were cleaned using acetone, alcohol and Millipore pure water in an ultrasonic vibrator, and were used as substrate. Platinum was deposited by wetting the substrates with a 2 wt % aqueous solution of H_2PtCl_6, followed by drying at 80 °C for 1 h and heating at various temperatures ranging from 220 to 650 °C under hydrogen and air. The platinum loading was about 0.3 mg cm^{-2}. The smooth platinum electrode used for comparison was cleaned in a similar manner as for the graphite sheets and treated with a freshly prepared 1 : 1 mixture of concentrated H_2SO_4 and HNO_3 for a few minutes followed by washing with the Millipore pure water.

Electrodes were clipped to Ta wire hair pins (exposed length about 25 mm), which were in turn sealed in Pyrex glass tubes; Ta is known to be inactive for the reaction investigated in this work.

A high resolution scanning electron microscope (SEM) (Hitachi F-900) was used to observe the morphology of the electrode surface.

2.3. *Electrochemical measurements*

The cyclic voltammetric and potentiostatic measurements were conducted in a conventional three-compartment glass cell. The measuring system comprised

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a potentiostat (Wenking, 68 FR 0.5), a function generator (Kowa, FG-101A) and an X–Y recorder (Rika-Denki, RW-201T). A saturated Ag/AgCl/KCl electrode (TOA, HS-205) was used as reference, but all the potential values are reported on the RHE scale. A Pt gauze was used as the counter electrode. A Luggin capillary was used to minimize *iR* drop; however, at high current density (c.d.), the ohmic drop was measured by the use of a current interruption circuit and correction was made accordingly. During all the electrochemical experiments, the cell temperature was maintained at 30 °C by means of a thermostated water bath.

Before and during the cyclic voltammetric (CV) and potentiostatic measurements, the solutions, 1 M NaOH or 1 M NaOH + 1 M CH_3OH, were deaerated thoroughly by bubbling with purified Ar. The current data for the potentiostatic polarization experiments were obtained after polarization for 30 min. As the current obtained using potentiostatic polarization was more reliable than that obtained from cyclic voltammograms (CVs), the former was used to make the Tafel plots. True surface areas of platinum were determined coulometrically from the hydrogen desorption area on the anodic cyclic voltammetric sweep (0.05–0.5 V) in the background solution, 1 M NaOH, assuming 210 μC for the desorption of hydrogen from 1 cm^2 (true) of platinum [17].

3. Results and discussion

3.1. *SEM observations*

Figures 1(a) and (b) show the SEM photographs of the C/Pt electrodes prepared in air and in hydrogen, respectively, at 220 °C after the electrochemical measurements. White spots on the photographs are Pt particles. Comparison of Fig. 1(a) with (b) reveals that the mean particle size in the former case is larger than in the latter. If the surface areas are evaluated from these particle sizes, the areas are greater than those calculated from the hydrogen desorption waves on the CVs. This discrepancy is due to the fact that the dispersion of Pt particles prepared by wetting is not uniform and homogeneous throughout; some photographs reveal that there are some spots on the electrodes where Pt is deposited in mass.

3.2. *Voltammetry*

In Fig. 2, the curves represented by solid, dotted and broken lines show typical steady state CVs of the C/Pt electrodes prepared at 220 °C in hydrogen and in air and of the smooth Pt electrode, respectively, in 1 M NaOH at a sweep rate of 50 mV s^{-1} at 30 °C. Comparison of the solid curve with the dotted one clearly indicates that heating in hydrogen produced much greater surface area of Pt than heating in air. The three CVs are similar in shape except that the oxygen reduction peak appearing at about 0.7 V, indicated by an arrow, for the C/Pt electrode prepared in hydrogen appears at about 40 mV, and that prepared in air at about 50 mV, less positive potentials than that for the smooth Pt electrode. The ratios (P_1/P_2) of heights of oxidation peaks on the CVs represented by P_1 to those represented by P_2 are different for the three electrodes. In earlier work [15, 16], we reported that C/Pt electrodes prepared in hydrogen at 200 and 220 °C, respectively, exhibited almost the same specific activity as smooth Pt for methanol electrooxidation in 1 M NaOH at 30 °C, but the former were much less deactivated (by a factor

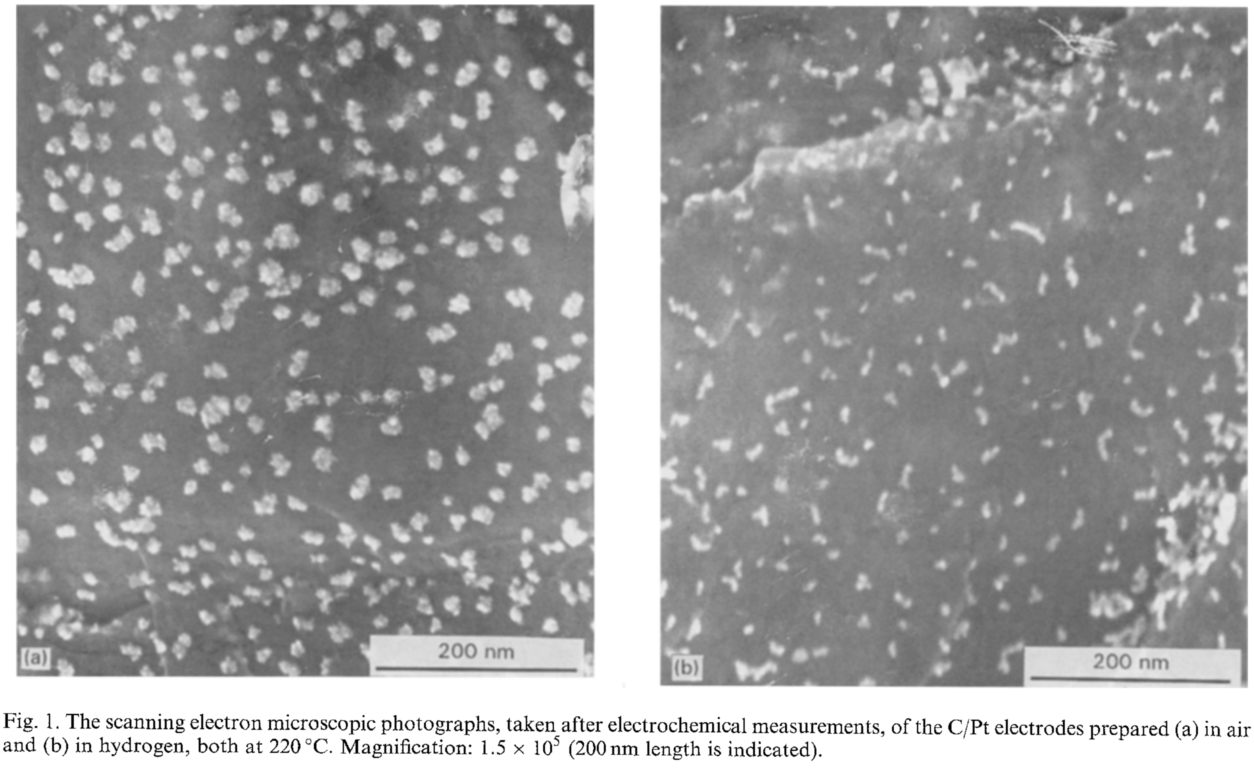

Fig. 1. The scanning electron microscopic photographs, taken after electrochemical measurements, of the C/Pt electrodes prepared (a) in air and (b) in hydrogen, both at 220 °C. Magnification: 1.5 × 10^5 (200 nm length is indicated).

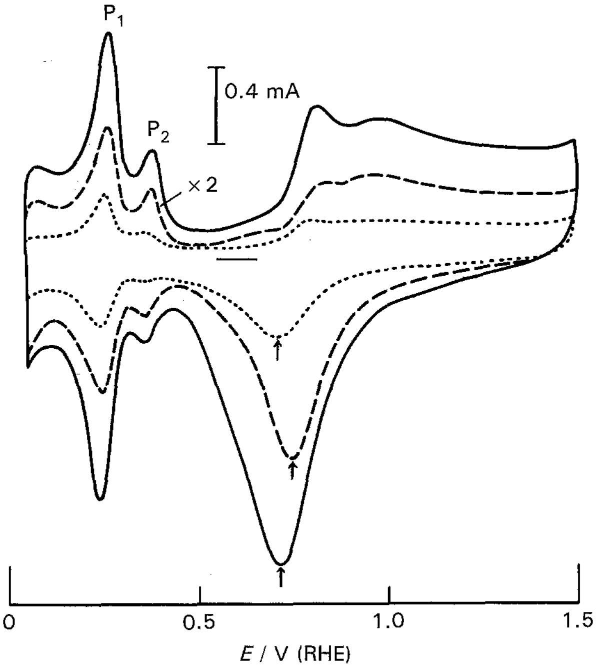

Fig. 2. Typical cyclic voltammograms and the peak height ratios (P_1/P_2) of the C/Pt electrodes prepared in hydrogen (——) and in air (. . . .) at 220 °C ($P_1/P_2 = 2.10$ and 2.35, respectively) and of the smooth Pt electrode (- - -) ($P_1/P_2 = 1.85$), in 1 M NaOH at 30 °C. Sweep rate: 50 mV s^{-1}. The reduction peak potentials are indicated by arrows.

of about 2) than the latter (by a factor of about 10) by continuous bubbling of CO during the electrochemical measurements.

Several investigators [12, 18–21] have reported that the activities of Pt electrodes for methanol and formic acid electrooxidation are greatly affected by the exposed crystal planes of Pt. For example, Yahikozawa *et al.* [14] reported that the (1 1 0) plane of Pt deposited on glassy carbon was active for methanol electrooxidation, whereas the (1 0 0) plane was active for formic acid electrooxidation. Motoo and Furuya [22] observed that the (2 2 1) plane of Pt gave the highest electrocatalytic activity in the electrooxidation of methanol, while (1 1 0) plane was the most active among the three lowest index planes, (1 0 0), (1 1 0) and (1 1 1). In parallel to this finding, it seems reasonable to assume that some of the exposed crystallographic planes of Pt may adsorb CO more strongly than others and the fractions of such planes may be dominating on the smooth Pt electrode compared to the C/Pt electrode prepared in hydrogen. This argument, together with the different values of P_1/P_2 and of the reduction peak potentials for these three electrodes, indicates that the ratios of various crystallographic planes exposed may be different. It is likely that heating in hydrogen favours the development of certain crystal planes, whereas that in air, other kinds. Further investigation is necessary.

In Fig. 3, the solid and the dotted lines show typical steady state CVs for the C/Pt electrodes prepared in hydrogen and in air, respectively, at 310 °C. The CVs are similar in shape. The difference is that the ratios of the heights of peaks, P_1/P_2, as indicated on the figure, are different for two electrodes as in the case of Fig. 2 and the area of Pt for the electrode prepared in hydrogen is greater than for that prepared in air. The difference in surface areas of the Pt prepared in hydrogen and in air in this case is not as marked as in the case of the heating temperature of 220 °C. A small difference in the reduction peak potentials, as indicated by arrows on the figure, also exists, as in the case of Fig. 2.

The CVs on the C/Pt electrodes prepared in hydrogen and in air at 410 °C also exhibited similar features, namely, different values of P_1/P_2, 2.00 for the former and 2.22 for the latter, and also small difference in the reduction peak potentials compared to those prepared in hydrogen and in air, respectively, at 220 °C (Fig. 2) and 310 °C (Fig. 3).

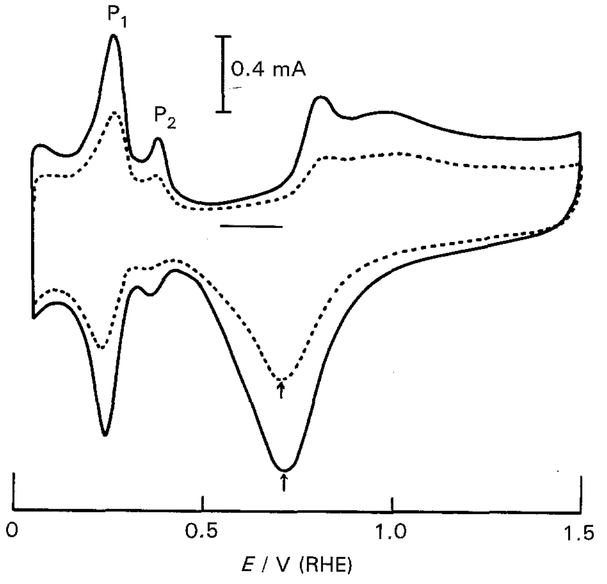

Fig. 3. Typical cyclic voltammograms and the peak height ratios of the C/Pt electrodes prepared in hydrogen (——), $P_1/P_2 = 2.15$, and in air (. . .), $P_1/P_2 = 2.27$, both at 310 °C, in 1 M NaOH at 30 °C. Sweep rate: 50 mV s^{-1}. The reduction peak potentials are indicated by arrows.

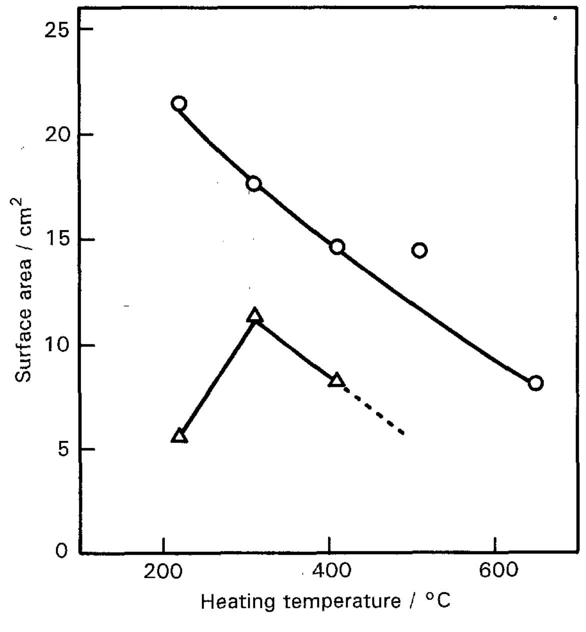

Fig. 4. The effect of the heating temperature upon the true surface area of Pt produced on the C/Pt electrodes prepared in hydrogen (○) and in air (△).

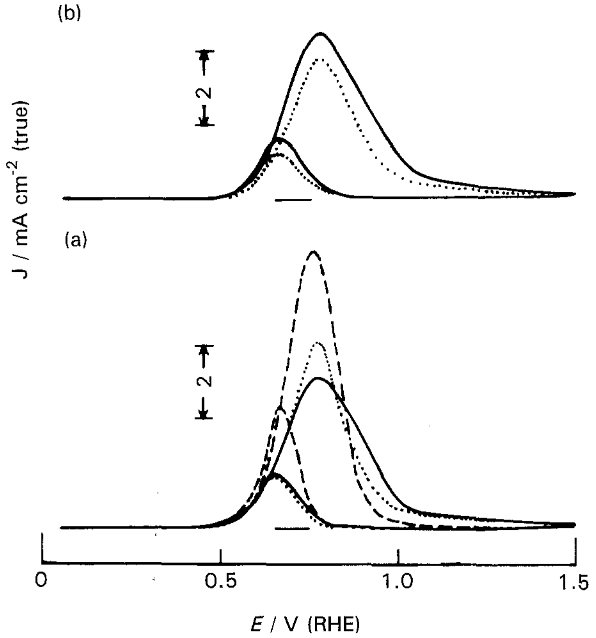

Fig. 5. Typical cyclic voltammograms (a) on the C/Pt electrodes prepared in hydrogen (——) and in air (. . . .) both at 220 °C, and on the smooth Pt electrode (- - -) and (b) on the C/Pt electrode prepared in hydrogen (——) and in air (. . . .) both at 310 °C, in 1 M NaOH + 1 M CH_3OH at 30 °C. Sweep rate: 50 mV s^{-1}.

Figure 4 shows the effect of the heating temperature upon the true area of Pt produced in air and in hydrogen. This figure indicates that the surface area produced in hydrogen at a particular temperature is always greater than that produced in air at the same temperature. The very large differences in the surface area produced in hydrogen and in air at 220 °C may indicate that the decomposition of H_2PtCl_6 into Pt at 220 °C in the latter case may be incomplete. On the other hand, in the former case, the heating temperature of 220 °C seems to be sufficient. In hydrogen, the surface area of the Pt decreases with increase in temperature, indicating that the usual sintering process is taking place. In the latter case, the surface area first increases with increase in temperature up to 310 °C, then decreases significantly, indicating the usual sintering tendency with increase in temperature. Another important point to be noted is that in hydrogen at lower temperature, namely, 220 °C as compared to 310 °C, a greater surface area was produced. This finding is in agreement with the work of Attwood *et al.* [9], who reported that Pt-salt supported on chemically/electrochemically oxidized pyrographite coated carbon fibre paper by impregnation/ion exchange when heated in hydrogen produced a larger surface area of Pt than when heated in air, and the decomposition temperature of the Pt-salt was less in hydrogen than in air.

Figure 5(a) shows typical CVs on (a) the C/Pt electrodes prepared in hydrogen and in air both at 220 °C and on the smooth Pt electrode and (b) on the C/Pt electrodes prepared in hydrogen and in air both at 310 °C in 1 M NaOH + 1 M CH_3OH at a sweep rate of 50 mV s^{-1} at 30 °C. All the CVs are similar in shape but the CVs show that C/Pt electrodes are a little more resistant to passivation than smooth Pt. It is likely that the difference in passivation among the electrodes may be due to different crystallographic orientations of the electrodes.

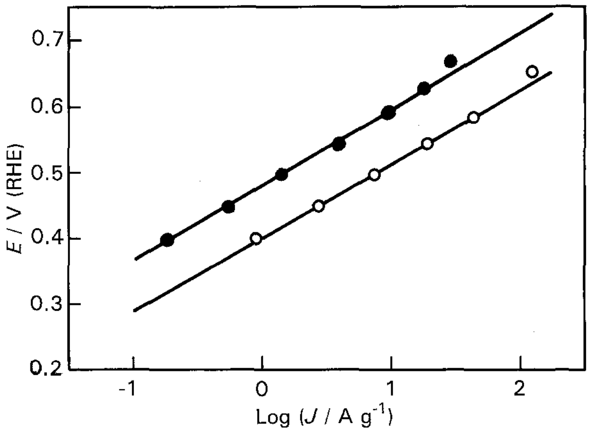

Fig. 6. Tafel plots of oxidation current densities of 1 M CH_3OH in 1 M NaOH at 30 °C, in terms of mass activity, on the C/Pt electrodes prepared in hydrogen (○) and in air (●), both at 220 °C.

3.3. *Electrocatalytic activity*

The catalytic activities of the C/Pt electrodes, prepared at 220 °C in both hydrogen and air, in terms of mass activities (current in A gm^{-1} of Pt), are shown in Fig. 6. The figure reveals that the C/Pt electrode prepared in hydrogen exhibits much greater (about five times) catalytic activity than that prepared in air for methanol electrooxidation in 1 M NaOH at 30 °C. From Fig. 4, it is evident that the surface area of Pt on the C/Pt electrode prepared in hydrogen at 220 °C is about five times greater than that on the C/Pt electrode prepared in air at the same temperature. Comparison of Fig. 4 with Fig. 6 possibly reveals that all the Pt on the C/Pt electrodes is catalytically active.

The mass activities of the C/Pt electrodes prepared at 310 °C in both hydrogen and air for methanol electrooxidation in 1 M NaOH at 30 °C are presented in Fig. 7. The difference between the mass activities of these two electrodes is less significant than that for the electrodes prepared at 220 °C (Fig. 6). This

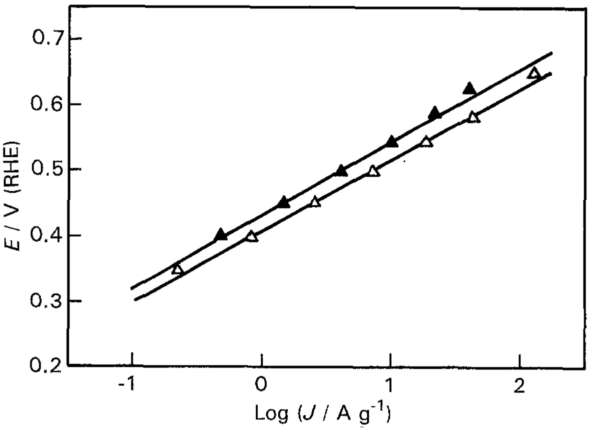

Fig. 7. Tafel plots of oxidation current densities of 1 M CH_3OH in 1 M NaOH at 30 °C, in terms of mass activity, on the C/Pt electrodes prepared in hydrogen (△) and in air (▲), both at 310 °C.

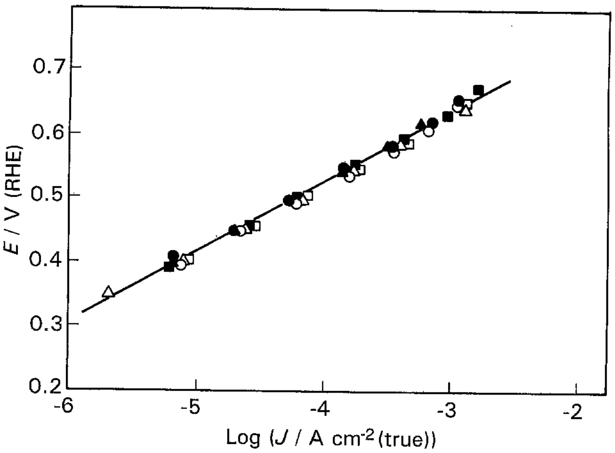

Fig. 8. Tafel plots of oxidation current densities per true area of Pt toward the methanol electrooxidation in 1 M NaOH + 1 M CH_3OH at 30 °C on the C/Pt electrodes prepared in hydrogen (○) and in air (●) both at 220 °C, in hydrogen (△) and in air (▲) both at 310 °C, and in hydrogen (□) and in air (■) both at 410 °C.

may be due to the fact that the surface area of the C/Pt electrode prepared in hydrogen decreases due to sintering with increase in temperature, whereas increase in the surface area of the C/Pt electrode prepared in air at 310° C may be due to complete decomposition of H_2PtCl_6 into Pt, but this increase is not as much as in the case of the C/Pt electrode prepared at 220° C in hydrogen. This may be due to the fact that in air at 310° C the decomposition of H_2PtCl_6 is complete, but at the same time sintering is taking place at the higher temperature (310 vs 220° C). In the light of the discussion of Figs 6 and 7, it is evident that the heating in hydrogen at a low temperature is better than heating in air at a high temperature for the decomposition of H_2PtCl_6 into Pt.

Figure 8 shows the Tafel plots of oxidation current densities (c.ds) for methanol electrooxidation on C/Pt electrodes prepared in hydrogen and air at different temperatures. This figure clearly indicates that the catalytic activities of all the C/Pt electrodes, whether prepared in air or in hydrogen, on specific activity (c.ds per true surface area) basis, are almost the same.

Figure 9 shows Tafel plots for oxidation c.ds of the methanol electrooxidation on the C/Pt electrodes prepared in hydrogen and air both at 220 °C and on the smooth Pt electrode in 1 M NaOH + 1 M CH_3OH at 30 °C. Both the C/Pt's and the smooth Pt electrodes exhibited almost the same specific activity. Comparison of Fig. 9 with Fig. 8, reveals that the C/Pt electrodes prepared in both hydrogen and air atmospheres at 220, 310 and 410 °C exhibited almost the same specific activity as the smooth Pt electrode, irrespective of the different preparation conditions and, consequently, of the different structures of the C/Pt electrodes, in terms of crystallographic orientations, from that of smooth Pt.

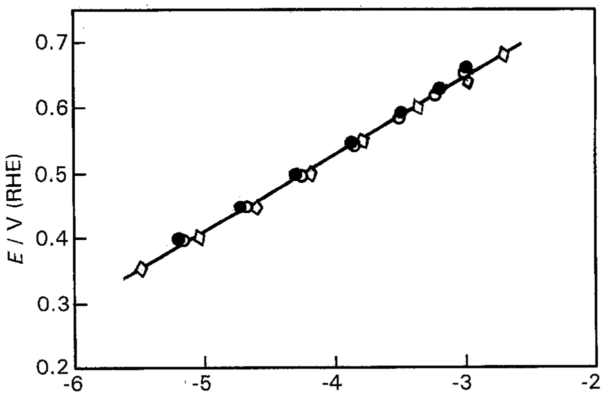

Fig. 9. Tafel plots of oxidation current densities per true area of Pt toward the methanol electrooxidation in 1 M NaOH + 1 M CH_3OH at 30 °C on the C/Pt electrodes prepared in hydrogen (○) and in air (●), both at 220 °C, and on the smooth Pt electrode (◇).

The catalytic activities of the C/Pt's and the smooth Pt electrodes toward methanol electrooxidation in 0.5 M H_2SO_4 also exhibited similar behaviour as that in 1 M NaOH.

The Tafel slope for all the C/Pt electrodes and the smooth Pt electrode for methanol electrooxidation in 1 M NaOH at 30 °C is about 110 mV decade^{-1}, which suggests that the first charge transfer process is the rate-determining step.

4. Conclusions

Heating in hydrogen produces a larger surface area of Pt than does heating in air. C/Pt electrodes prepared in hydrogen exhibited higher mass activity for methanol electrooxidation than those prepared in air. The C/Pt electrodes prepared in hydrogen and in air at different temperatures and the smooth Pt electrode exhibited almost the same specific activity for methanol electrooxidation in 1 M NaOH at 30 °C, although they may have different crystallographic orientations due to the different preparation conditions. These results altogether indicate that there is no intrinsic particle size effect in the range studied. The Tafel slope of 110 mV decade^{-1} reveals that in the methanol electrooxidation on both the C/Pt's and the smooth Pt electrodes in 1 M NaOH at 30 °C, the first charge transfer process is the rate-determining step.

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