

# Electrocatalysis and related factors of platinum microparticles dispersed on/in polypyrrole film in methanol oxidation

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## Abstract

Platinum microparticles display effective electrocatalysis for methanol oxidation in 1 M MeOH + 1 M HClO<sub>4</sub> and polypyrrole film exhibits a promotive action for such electrocatalysis. The electrocatalytic activity is determined by the loading mass of the platinum microparticles, and the potential and medium used for the electropolymerization of PPy film. The thickness of the polypyrrole film under the chosen experimental conditions is less critical towards the electrocatalysis of MeOH oxidation. The effect of the increase in electrode area due to the high dispersion of platinum microparticles is substantially deducted in the evaluation of the catalytic activity because the real surface of the platinum microparticles, rather than the projected area of the electrode, is used in the calculation of the current density. © 1998 Elsevier Science S.A. All rights reserved.

**Keywords:** Electrolysis; Methanol; Polypyrrole; Platinum microparticles; Modified electrode

## 1. Introduction

It is well known that platinum is a powerful electrocatalyst for methanol oxidation [1–5], and the existence of a large surface energy due to a large surface area can enhance the activity of a catalyst. Some conducting polymers, e.g., polypyrrole, polyaniline and polythiophene, are desirable systems to support highly dispersed platinum particles. Such conducting polymers possess high electronic conductivity and a porous structure which can accommodate a dispersed catalyst with a large surface area as is necessary for efficient electrocatalysis. Various workers [6–8] have studied the electrocatalytic application of metal microparticles dispersed on different conducting polymer films for reduction of oxygen and the oxidation of hydrogen. Other studies have examined the electrocatalytic activity of platinum microparticles dispersed on/in polyaniline [9,10] and poly(*N*-methylpyrrole)-nafion composite film [11] for the electro-oxidation of methanol. We have reported [12] the electrocatalytic oxidation of methanol on polypyrrole film modified with platinum mi-

croparticles. This paper discusses various factors related to such electrocatalysis. In the paper, GC denotes glassy carbon, Pt/GC denotes platinum microparticles deposited on glassy carbon, PPy/GC is polypyrrole film deposited on the glassy carbon, and Pt/PPy/GC is platinum microparticles dispersed on PPy/GC.

## 2. Experimental

### 2.1. Chemicals

All the chemicals were analytical grade. Pyrrole and methanol were redistilled before use. Water was distilled twice.

### 2.2. Instrumentation

The electrochemical experiments were carried out using an EG&G Princeton Applied Research (PAR) Model 273 Potentiostat/Galvanostat. Data were acquired on an IBM PC computer. Scanning electron micrographs were ob-

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tained by means of a Hitachi Scanning Electron Microscope X-650.

### 2.3. Techniques

Pyrrole (Py) was electropolymerized by linear sweep voltammetry with a scanning rate of  $10 \text{ mV s}^{-1}$  from 0.6 to 0.9 V vs.  $\text{Ag}/\text{Ag}^+$  (0.01 M  $\text{AgNO}_3$  in MeCN) in an MeCN solution containing 0.0221 M Py and 0.1 M  $\text{LiClO}_4$ , or within the scanning range 0.5 to 0.7 vs. SCE in an aqueous solution of 0.0221 M Py and 1 M  $\text{HClO}_4$ . The thickness of the polypyrrole (PPy) film was estimated on the assumption that a charge of  $100 \text{ mC cm}^{-2}$  yielded a film of  $0.3 \text{ }\mu\text{m}$  thickness [7,8] under the chosen preparation conditions. Prior to the electropolymerization, the solution was purged with highly purified  $\text{N}_2$  for 10 min. During measurements, the solution was maintained under a blanket of  $\text{N}_2$ . Platinum was deposited by controlled potential coulometry (a technique which, like chronocoulometry, determines charge as a function of time under a constant potential) in an aqueous solution of 5 mM  $\text{K}_2\text{PtCl}_6$  in 1 M  $\text{HClO}_4$ . MeOH oxidation was studied in 1 M MeOH + 1 M  $\text{HClO}_4$  aqueous solution by means of cyclic voltammetry. A SCE was used as the reference electrode for Pt deposition, MeOH oxidation and Py electropolymerization in aqueous solution. A reference electrode of  $\text{Ag}/\text{Ag}^+$  (0.01 M  $\text{AgNO}_3$  + 0.1 M  $\text{LiClO}_4$  in MeCN) was used for Py polymerization in MeCN solution. It has been recognized by some authors [9–11] that the electrocatalytic activity in such a case depends on the loading mass of platinum microparticles. In addition, it is important to distinguish between the activity of the electrocatalyst itself and the effect of the increase in area due to the high dispersion of platinum microparticles. Therefore, estimation of the loading mass and the surface area of platinum microparticles play an important role in evaluating the electrocatalytic activity. The real surface area of platinum microparticles deposited on a bare GC electrode can be determined from the monolayer adsorption of underpotential-deposited (UPD) hydrogen, as commonly used by other authors [13–15] ( $\sim 210 \text{ }\mu\text{C cm}^{-2}$ ), but it is difficult to apply this procedure to the Pt/PPy/GC electrode due to the effects of the doping–dedoping behaviour of PPy [7,9]. We suggest that the real surface area,  $S$ , of the platinum microparticles in the latter system can be estimated by

$$S = \frac{3m}{dr} \quad (1)$$

where  $m$ ,  $d$  and  $r$  are the mass, density and radius of the platinum particles, respectively. The density of platinum is taken as  $21.45 \text{ g cm}^{-3}$  [16]. The radius of the platinum microparticles can be estimated from scanning electronmicrographs, one of which is shown in Fig. 1. The mass of platinum can be obtained from the net charge, denoted as

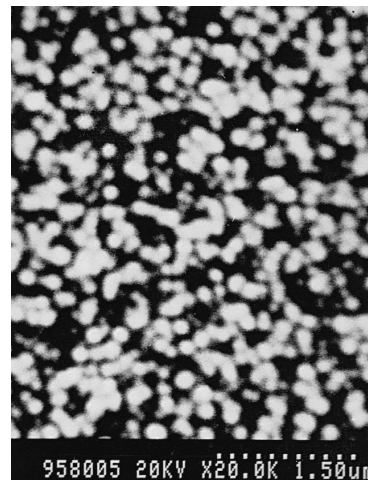


Fig. 1. Electron micrograph of platinum microparticles on a Pt/PPy/GC electrode, magnification  $\times 20000$ . Py was electropolymerized by linear sweep voltammetry from 0.6 to 0.9 V vs.  $\text{Ag}/\text{Ag}^+$  (0.01 M  $\text{AgNO}_3$  in MeCN) with a scanning rate of  $10 \text{ mV s}^{-1}$  in MeCN solution with 0.0221 M Py and 0.1 M  $\text{LiClO}_4$ . Pt was deposited by controlled potential coulometry in an aqueous solution of 5 mM  $\text{K}_2\text{PtCl}_6$  and 1 M  $\text{HClO}_4$  at a constant potential of  $-0.2 \text{ V vs. SCE}$  for 70 s.

$Q_{\text{net}}$ , consumed for platinum deposition. It is commonly accepted that a net charge of  $100 \text{ mC}$  corresponds to a platinum loading of  $51 \text{ }\mu\text{g}$  [7]. The net charge  $Q_{\text{net}}$  for platinum deposition must exclude the PPy dedoping charge  $Q_{\text{ded}}$ , when platinum is deposited on the PPy/GC electrode. Thus, a controlled potential coulometry experiment for a PPy/GC electrode was carried out first in a blank aqueous solution containing 1 M  $\text{HClO}_4$  but without  $\text{K}_2\text{PtO}_6$  before platinum was deposited on the electrode. The potential applied and the duration of the blank experiment were the same as those used for depositing platinum microparticles from the aqueous solution of 5 mM  $\text{K}_2\text{PtO}_6$  and 1 M  $\text{HClO}_4$  on to the PPy/GC electrode. The charge passed during the blank experiment was taken as the dedoping charge  $Q_{\text{ded}}$  of the PPy film on the PPy/GC electrode during platinum deposition. From the total charge  $Q_{\text{tot}}$  for platinum deposition in the aqueous solution of 5 mM  $\text{K}_2\text{PtO}_6$  and 1 M  $\text{HClO}_4$  on the PPy/GC electrode, the net charge for depositing Pt microparticles was obtained as follows:

$$Q_{\text{net}} = Q_{\text{tot}} - Q_{\text{ded}} \quad (2)$$

To evaluate the electrocatalytic activity, a comparison was made of the peak current densities of cyclic voltammograms under various conditions of methanol oxidation. In the current density calculation, the real surface area rather than the projected surface area was used. The former estimated by the method introduced in the paper is about 3 to 4 times larger than the latter. Thus, the effect of the increased area due to the high dispersion of platinum particles is substantially deducted in the evaluation of the catalytic activity.

### 3. Results

#### 3.1. Preparation of PPy/GC

Cyclic voltammograms for the electrochemical synthesis of PPy in MeCN are shown in Fig. 2. The solid line is for the first cycle and the broken line is for the second one. The oxidative peaks of Py appear at 1.232 V vs. Ag/Ag<sup>+</sup> (0.01 M AgNO<sub>3</sub> in MeCN). The peak current density of the second cycle is higher than that of the first. This is characteristic of conducting polymers. From Fig. 2, the sweep range used in the linear voltammetry for the preparation of PPy film on the GC electrode in MeCN was chosen to be 0.6 to 0.9 V in order to avoid over-oxidation and to maintain a proper reaction rate. The voltammograms of the PPy film in MeCN containing 0.1 M LiClO<sub>4</sub> for the 1st and 30th cycles are shown in Fig. 3. The curves are almost identical and this suggests that the doping–dedoping behaviour of the PPy film has excellent reversibility.

#### 3.2. Real surface area of platinum microparticles on Pt/PPy/GC electrode

An electron micrograph of platinum microparticles on a Pt/PPy/GC electrode is presented in Fig. 1. During preparation of the electrode, the projected surface area of the GC substrate of the electrode was 0.29 cm<sup>2</sup>. The charge consumed for PPy deposition was 112 mC, which

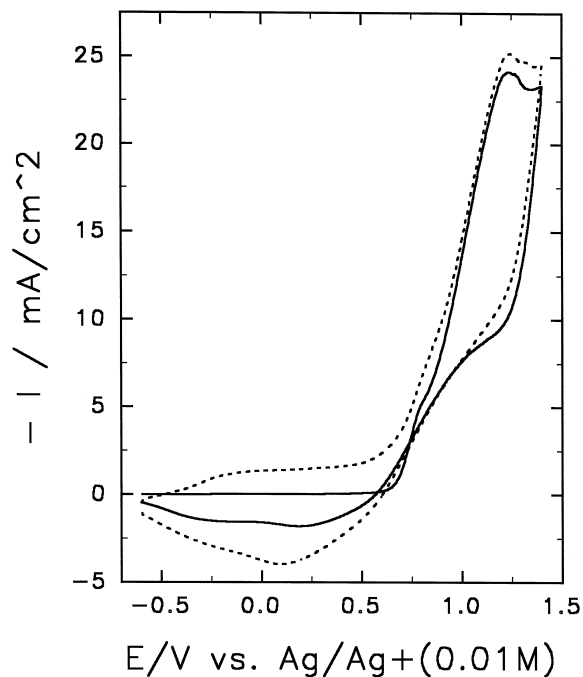


Fig. 2. Cyclic voltammograms for oxidative polymerization of 0.0221 M Py monomer in MeCN containing 0.1 M LiClO<sub>4</sub> on a GC electrode. The sweep rate is 100 mV s<sup>-1</sup>. The solid line (—) is for the 1st cycle; the dashed line (---) for the 2nd cycle.

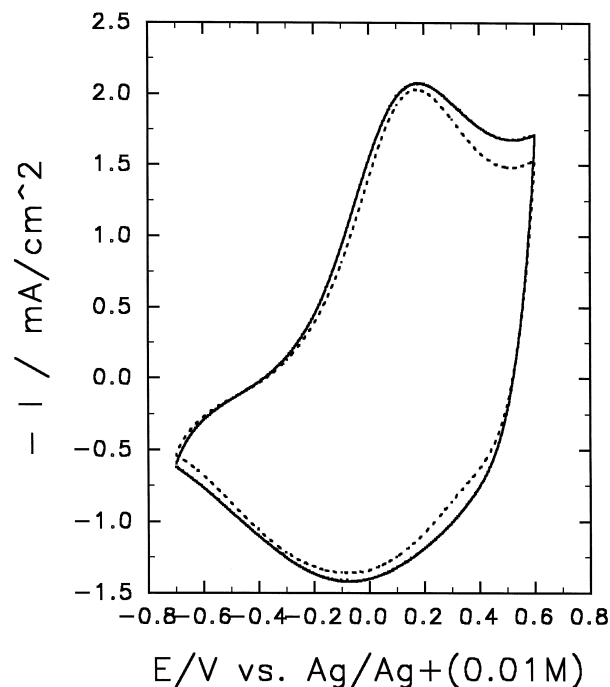


Fig. 3. Cyclic voltammograms for PPy film with thickness of 1.2 μm in 0.1 M LiClO<sub>4</sub>/MeCN. Solid line (—): 1st cycle. Dashed line (---): 30th cycle. Sweep rate = 50 mV s<sup>-1</sup>.

corresponds to a film of 1.1 μm thickness. The net charge for platinum deposition was 93.8 mC obtained from Eq. (2); this corresponds to a platinum loading mass of 48 μg on the electrode, or 165 μg cm<sup>-2</sup>. The micrograph (Fig. 1) shows that the platinum microparticles are highly dispersed on/in the PPy film. The particle size is quite even, with a diameter of around 0.15 μm. Thus, according to Eq. (1), the real surface area of platinum microparticles on the Pt/PPy/GC electrode is estimated to be 0.90 cm<sup>2</sup>, i.e., about three times the projected area of the electrode. Indeed, it should be realized that such an estimate of the radius of platinum particles by means of SEM photomicrographs is not accurate because of the variation in the radius. In general, however, it may be acceptable when the estimate is used for qualitative purposes.

#### 3.3. Electrocatalysis of Pt/PPy/GC for methanol oxidation

Steady-state cyclic voltammograms for methanol oxidation on bulk platinum disc, Pt/GC, and Pt/PPy/GC electrodes are presented in Fig. 5. The substrate for the Pt/GC and Pt/PPy/GC electrodes is glassy carbon which has no electrocatalytic activity for methanol oxidation, as shown in Fig. 4. The loading mass of Pt on the Pt/GC and Pt/PPy/GC electrodes is expressed in μg of platinum microparticles per cm<sup>2</sup> of projected surface area of the electrodes. The current density is in mA per cm<sup>2</sup> of the real surface area of platinum, which is estimated by use of the methods mentioned above. Thus, the effect of the

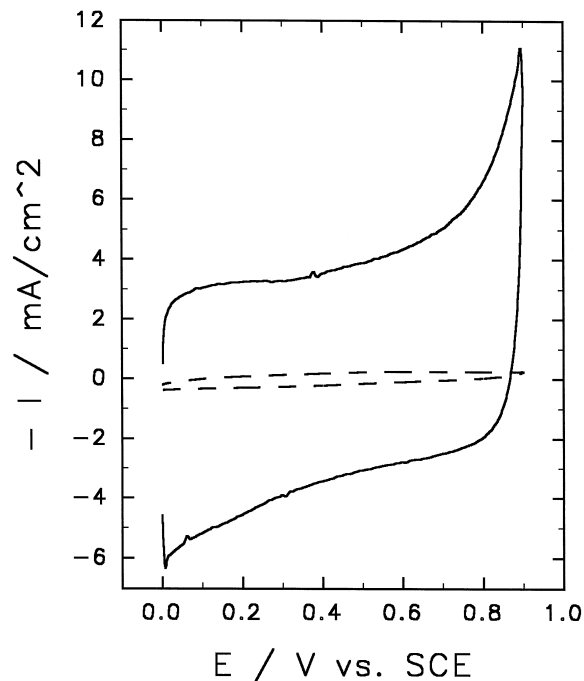


Fig. 4. Steady-state cyclic voltammograms for methanol oxidation in 1 M MeOH+1 M HClO<sub>4</sub> aqueous solution on bare GC (--- line) and Pt/PPy/GC (— line) electrodes. Thickness of PPy film is 0.9 μm on the Pt/PPy/GC electrode. Sweep rate = 100 mV s<sup>-1</sup>.

increase in area due to the high dispersion of platinum microparticles on Pt/GC and Pt/PPy/GC electrodes has been deduced. From Fig. 5, the peak current densities of the cyclic voltammograms of Pt/GC and Pt/PPy/GC electrodes are higher than that of the bulk platinum disc electrode, showing that the platinum microparticles have higher electrocatalytic activity for methanol electro-oxidation than the bulk platinum. Laborde et al. [10] have suggested that the greater electrocatalytic activity on dispersed platinum particles might come from a smaller amount of adsorbed CO formed during methanol oxidation than on the bulk platinum. Our in situ FTIR experiments [12] have shown that CO<sub>2</sub>, from the oxidation of the linearly adsorbed CO, starts to form at 0 V vs. SCE, i.e., negative shift of ~280 mV compared with the results for the bulk platinum electrode. In Fig. 5, the loading mass of platinum on Pt/GC and Pt/PPy/GC electrodes is almost the same, but the oxidation peak current density of Pt/PPy/GC is much higher than that of Pt/GC. This is similar to that for platinum microparticles in polyaniline film reported by Kost and Bartak [9]. These authors concluded that the higher current density of the Pt/PA/GC electrode is due to the fact that the polyaniline matrix stabilizes the redox coupling of platinum in different oxidation states. This also appears to be an acceptable assumption for polypyrrole. We observed Pt 4f<sub>7/2</sub> and 4f<sub>5/2</sub> peaks on a Pt/PPy/GC electrode before and after 13 min of etching in XPS experiments [12], which showed that platinum microparticles exist both on and in the PPy film.

Furthermore, the experiments revealed that the binding energies of Pt 4f<sub>7/2</sub> and 4f<sub>5/2</sub> on the sample after 13 min etching were greater than those on the unetched sample. This implies that there is a certain interaction between the platinum microparticles and PPy. It is noted that polypyrrole itself has no electrocatalytic activity for methanol oxidation, as shown in Fig. 4. Polypyrrole on Pt/PPy/GC electrode only plays a somewhat promotive function for the electro-oxidation of methanol.

### 3.4. Related factors affecting the electrocatalysis of Pt/PPy/GC

#### 3.4.1. Platinum loading mass

Steady-state cyclic voltammograms for Pt/PPy/GC with different platinum loading masses but equal thickness of PPy film are shown in Fig. 6. Within a certain range, higher loading masses produce a greater oxidative peak current density and a more effective electrocatalysis of methanol electro-oxidation. This result agrees with other studies [9–11].

#### 3.4.2. Thickness of PPy

Steady-state cyclic voltammograms for Pt/PPy/GC electrodes with various thicknesses of PPy film, but equal platinum loading mass, are presented in Fig. 7. The curves possess different oxidative peak heights. Considering the background arising from the effects of capacity for PPy

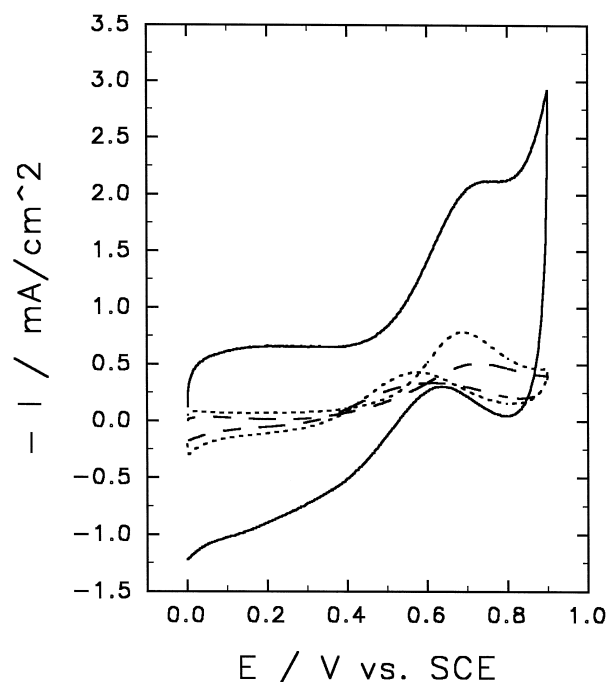


Fig. 5. Steady-state cyclic voltammograms for platinum disc (long dash line ---), Pt/GC (short dash line ····, 147 μg cm<sup>-2</sup> Pt microparticles deposited on GC), and Pt (145 μg cm<sup>-2</sup>)/PPy (0.7 μm)/GC (solid line —) electrodes in 1 M MeOH+1 M HClO<sub>4</sub> aqueous solution. Sweep rate = 100 mV s<sup>-1</sup>.

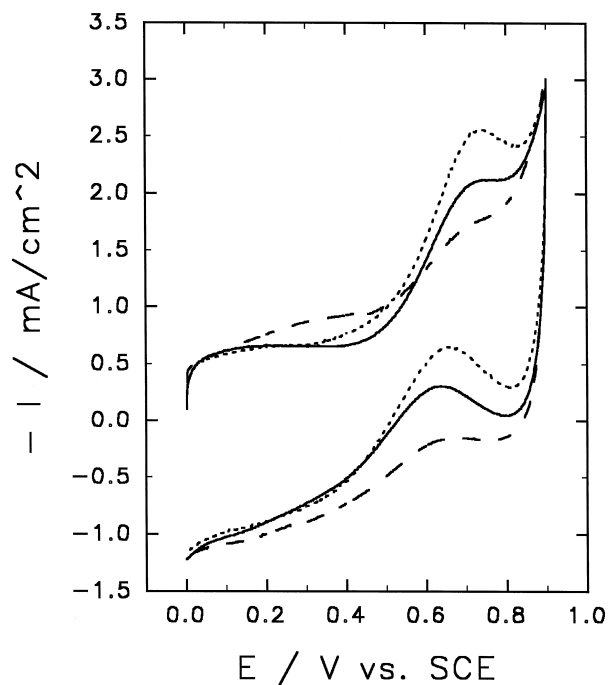


Fig. 6. Steady-state cyclic voltammograms for methanol oxidation in 1 M MeOH+1 M HClO<sub>4</sub> aqueous solution on Pt/PPy/GC electrodes of approximately equal thickness of PPy film (around 0.7  $\mu\text{m}$ ) but different platinum loading mass. Dotted line ( $\cdots$ ): 220  $\mu\text{g cm}^{-2}$  Pt. Solid line ( $—$ ): 145  $\mu\text{g cm}^{-2}$  Pt. Dashed line ( $- - -$ ): 73.2  $\mu\text{g cm}^{-2}$  Pt. Sweep rate = 100  $\text{mV s}^{-1}$ .

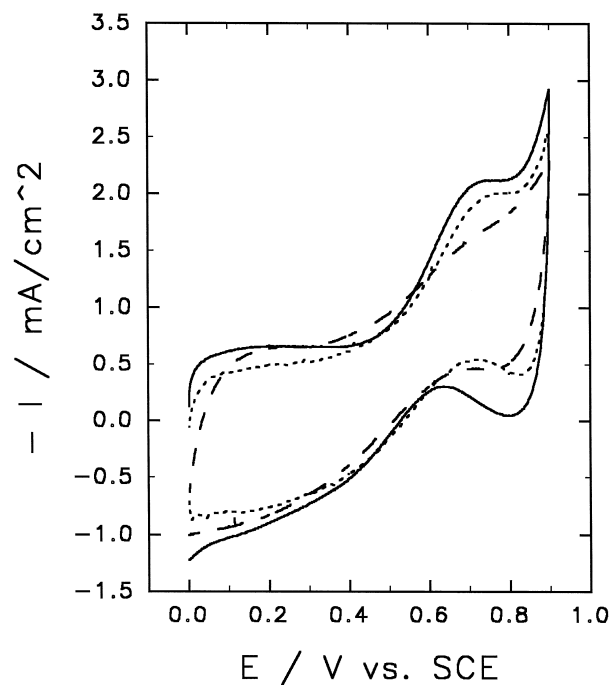


Fig. 8. Steady-state cyclic voltammograms for methanol oxidation in 1 M MeOH+1 M HClO<sub>4</sub> aqueous solution on Pt/PPy/GC electrodes with approximately equal platinum loading mass (around 145  $\mu\text{g cm}^{-2}$ ) and nearly equal thickness of PPy film (around 0.7  $\mu\text{m}$ ). Films were deposited by linear sweep voltammetry with the same initial potential of 0.6 V, but at different final potentials. Solid line ( $—$ ): 0.9 V. Dotted line ( $\cdots$ ): 1.2 V. Dashed line ( $- - -$ ): 1.6 V. Sweep rate = 100  $\text{mV s}^{-1}$ .

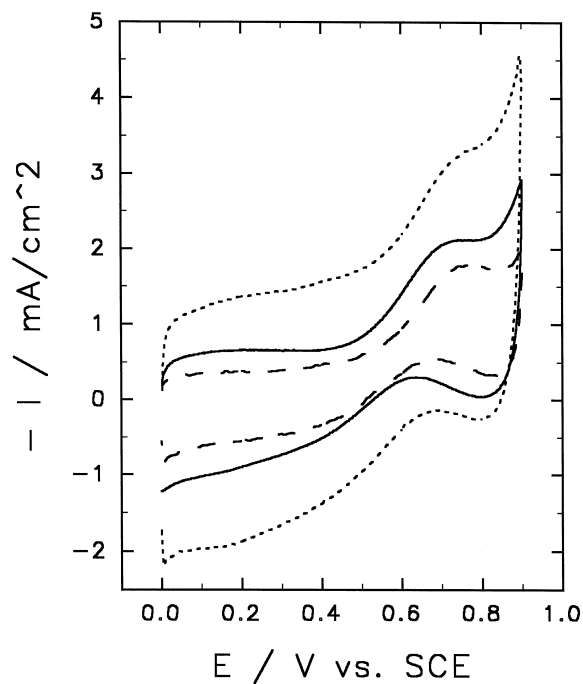


Fig. 7. Steady-state cyclic voltammograms for methanol oxidation in 1 M MeOH+1 M HClO<sub>4</sub> aqueous solution on Pt/PPy/GC electrodes with approximately equal amounts of dispersed platinum (around 145  $\mu\text{g cm}^{-2}$ ), but with different PPy film thickness. Dotted line ( $\cdots$ ): 1.6  $\mu\text{m}$ . Solid line ( $—$ ): 0.7  $\mu\text{m}$ . Dashed line ( $- - -$ ): 0.4  $\mu\text{m}$ . Sweep rate = 100  $\text{mV s}^{-1}$ .

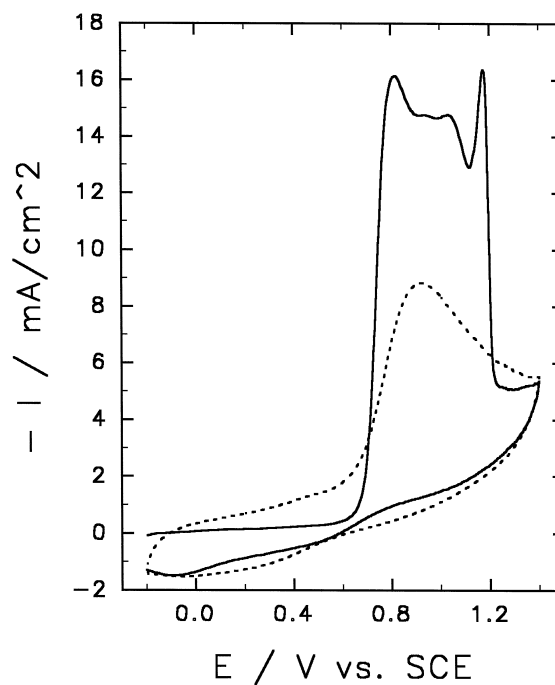


Fig. 9. Cyclic voltammograms for oxidative polymerization of 0.0221 M Py in an aqueous solution containing 1 M HClO<sub>4</sub> on a GC electrode. Sweep rate = 100  $\text{mV s}^{-1}$ . Solid line ( $—$ ) is for the 1st cycle; dashed line ( $- - -$ ) is for the 2nd cycle.

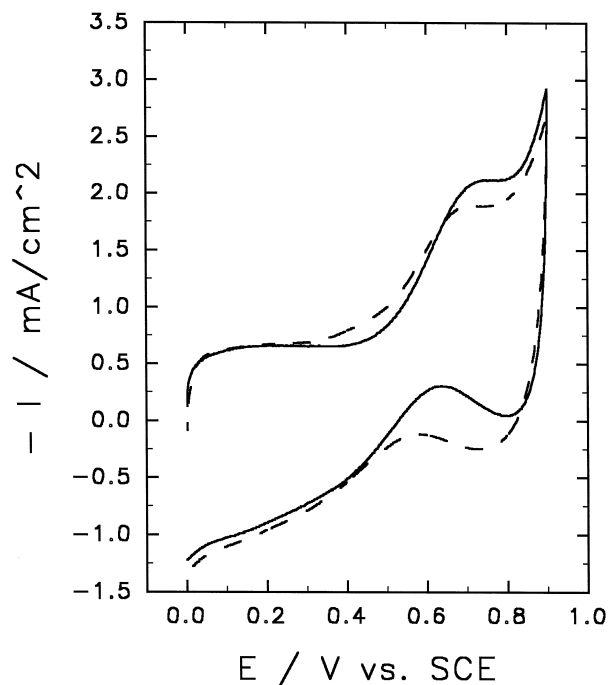


Fig. 10. Steady-state cyclic voltammograms for methanol oxidation in 1 M MeOH+1 M HClO<sub>4</sub> aqueous solution on different Pt/PPy/GC electrodes. PPy film on one electrode (--- line) was formed in aqueous solution of 0.0221 M Py+1 M HClO<sub>4</sub>, but PPy film of the other (— line) was deposited in MeCN solution containing 0.0221 M Py+0.1 M LiClO<sub>4</sub>. Thickness of both PPy films was  $\sim 0.7 \mu\text{m}$  and platinum loading amounts in both cases were  $\sim 145 \mu\text{g cm}^{-2}$ . Sweep rate = 100 mV s<sup>-1</sup>.

films of different thickness, the peak current densities are approximately equal. This implies that the thickness of the PPy film on Pt/PPy/GC electrodes is not particularly sensitive towards the electrocatalysis of methanol oxidation. Given that the same is true for the PPy/GC electrode, as shown in Fig. 4, this conclusion is reasonable.

#### 3.4.3. Deposition potential in the preparation PPy films

Steady-state cyclic voltammograms are shown in Fig. 8 for different final potentials but from the same initial potential, viz., 0.6 V vs. Ag/Ag<sup>+</sup> (0.01 M AgNO<sub>3</sub> + 0.1 M LiClO<sub>4</sub> in MeCN), in the preparation of PPy films. The oxidative peak current density for a final potential of 1.6 V is much smaller than the others. It has been recognized [7,17–19] that the application of a high potential can degrade polypyrrole and decrease its conductivity. This may cause some loss in electrocatalytic activity.

#### 3.4.4. Media used in preparation of PPy films

All the PPy films used in the above experiments were synthesized electrochemically in a medium of acetonitrile that contained 0.1 M LiClO<sub>4</sub>. Cyclic voltammograms for the oxidation of 0.0221 M Py in 1 M HClO<sub>4</sub> aqueous solution on a GC electrode are given in Fig. 9. The peak current density of the second cycle is much smaller than that of the first cycle. Comparison with the data in Fig. 2

suggests that the electronic conductivity of a PPy film synthesized electrochemically in an aqueous solution is less than that synthesized in MeCN, as reported elsewhere [17]. Cyclic voltammograms for MeOH oxidation on two Pt/PPy/GC electrodes are given in Fig. 10; one curve is for a PPy film prepared in MeCN, the other is for a PPy film prepared in aqueous solution. The PPy film prepared in aqueous solution is able to promote MeOH electrocatalysis in the presence of platinum microparticles, although it is not as good as the PPy film prepared in MeCN. Higgin and Hamnett [20] applied dynamic ellipsometry to the study of polypyrrole film growth and found that films grown in aqueous solution were somewhat denser than those grown in acetonitrile. Since the three-dimensional matrix of the PPy film electropolymerized in MeCN solution has a higher conductivity [17] and a smaller density [20] than that of the film electropolymerized in aqueous solution, it is understandable that the former will be a better support for platinum microparticles on Pt/PPy/GC electrodes.

## 4. Conclusions

Platinum microparticles dispersed on/in PPy films deposited on GC electrodes exhibit effective electrocatalysis for methanol oxidation in 1 M HClO<sub>4</sub> aqueous solution. The electrocatalytic activity is determined by the loading mass of platinum microparticles, the final potential of linear sweep voltammetry, and the medium used in the preparation of the PPy film. The thickness of the PPy film on Pt/PPy/GC appears to be less critical towards the electrocatalysis of methanol oxidation. To enhance electrocatalysis it is preferred to increase the platinum loading level to within a certain range and to keep the potential used in the polymerization of the PPy film to under 1.2 V in MeCN, and to under 0.7 V in aqueous solution [19], to avoid overoxidation.

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