

# Electrooxidation of Methanol and Formic Acid on Platinum Dispersed Polypyrrole Electrodes

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The present study was performed in order to investigate the electrocatalytic properties of platinum incorporated polypyrrole films for methanol and formic acid oxidations. The behaviour of this modified electrode was characterised in acidic media (0.1M HClO<sub>4</sub>). The electrodes exhibited excellent long-term stability in this media. After the modification and optimisation, the electrocatalytic properties of polypyrrole-metal particles and kinetics of the oxidation reactions were interpreted with regard to fuel cell applications.

**Key Words:** Polypyrrole, platinum particles, methanol, formic acid

## Introduction

Much effort has been devoted to the study of methanol (Me) and formic acid (FA) oxidation on metallic electrodes in recent decades<sup>1-6</sup>. This interest has been caused by several factors, which can be classified into two main groups. Firstly, there is fundamental interest in unraveling reaction mechanisms on electrodes, especially when dealing with small molecules that could be considered as models for electrocatalysis. Secondly, these molecules are candidates to be used in the development of direct fuel cells since they are cheap and have a high energy density. Most studies have dealt with platinum electrodes, reflecting the well-known performance of this electrocatalyst for the oxidations of methanol and formic acid. In spite of all this attention, there are several crucial mechanistic aspects that still demand elucidation. Several reaction sequences have been suggested; a dual pathway mechanism including both poison and reactive intermediates has often been proposed. For methanol and especially formic acid adsorbed CO on most platinum-group metals has been detected over wide potential ranges.

Recently, conducting polymers have gained importance in electrocatalysis. There has been a considerable effort in the electrochemical preparation and study of several conducting polymers including polypyrrole, polythiophene and polyaniline. Although polypyrrole (PPy) was first prepared at the beginning of the 20<sup>th</sup> century, it was not until the synthesis of continuous films by anodic oxidation was reported in 1979<sup>7</sup> that interest in PPy began to expand, prompting a large body of literature related to the various properties of this conducting polymer. As a conducting polymer substrate, PPy is one of the most attractive polymers on account of its stability and processibility in ambient conditions<sup>8-12</sup>.

Metal microparticles dispersed in polymer-modified electrodes have been recently recognized to have potential applications in electrocatalysis. Many research groups have studied the incorporation of catalyst particles in polymer-modified electrodes<sup>8–11,13–16</sup>. The insertion of transition metal (e.g. Pt, Pd, Ru, Sn) microparticles in conducting polymer-coated electrodes exhibit enhanced electrocatalytic activities as compared with the bulk-form metal electrodes in the oxidation of small organic molecules (e.g. CH<sub>3</sub>OH and HCOOH). The increase in the catalytic activities may be due to the decrease in the poisoning effect<sup>17–18</sup> and the synergistic effects of platinum microparticles and the PPy film<sup>19,20</sup>. Platinum particles electrodeposited at constant potential onto polypyrrole films are not evenly distributed within the films, but are preferentially segregated toward the polymer-solution boundary, whereas the region close to the substrate is practically free of the electrodeposited metal particles. This behaviour is expected if electrodeposition takes place onto an electronically conducting layer, where the potential drop occurs mostly at the interface between electronic and ionic conductors. This kind of modification typically concerns the insertion of small metallic particles into the polymer layer during or after the polymerisation process. The first way leads to a dispersion of the metallic particles inside the polymer layer, but none of these particles are accessible for the electrocatalytic reaction. The second way is to electrodeposit the metal after the electropolymerisation process. This electrodeposition can be carried out at a fixed potential, at a constant current or during continuous cycling.

In the present paper, the electrocatalytic oxidation of methanol and formic acid at the PPy-coated electrodes modified by Pt microparticles is reported. The factors that affect the electrocatalytic activities of the electrode were studied and optimised by cyclic voltammetry.

## Experimental

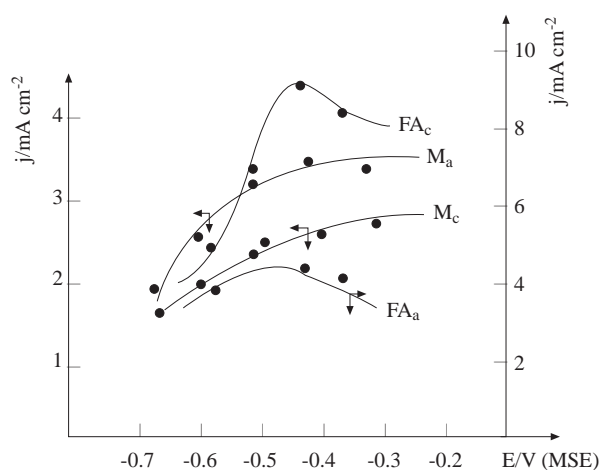
The electronic apparatus and the methods used for the determination of reaction kinetic have been described previously<sup>8,9,15</sup>. The polypyrrole films were grown by electropolymerisation in 0.1M LiClO<sub>4</sub> aqueous medium at constant potential (0.40 V/MSE). The mercury/mercury sulphate electrode (MSE) was used as the reference. The thickness of the polymer film was estimated as 1  $\mu\text{m}$ <sup>21</sup>. The electrochemical deposition of platinum particles onto the polymer matrix was achieved using solutions containing 0.01% H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O in 0.1M HClO<sub>4</sub> through electrolysis at a constant potential after electropolymerisation. The amount of platinum deposited onto the polymer surface is calculated from the integral of the cathodic charge passed during the deposition process, assuming that the reduction of Pt<sup>4+</sup> to Pt<sup>0</sup> is realised with 100% efficiency. It was reported that a charge  $Q_{Pt}$  of 200 mC.cm<sup>-2</sup> corresponds to a Pt loading of 100  $\mu\text{g.cm}^{-2}$ <sup>22</sup>. These films were tested in the presence of 0.1M Me or 0.1M FA in 0.1M HClO<sub>4</sub>. Surface characterisation was carried out using a Kratos ES3000 XPS spectrometer with Mg-K $\alpha$ X-rays at 1253.6 eV. Polymer coated (containing the dispersed metals) Pt electrode samples inserted into the vacuum chamber (vacuum lower than 10<sup>-8</sup> Torr) and analysed directly.

## Results

Firstly, we investigated optimum conditions for the preparation of the polypyrrole-metal particle modified system. A series of experiments were performed as a function of platinum deposition potential between (-0.30)–(-0.70) V/MSE since the electrochemical deposition potential may have control over the crystalline structure and grain morphology of the surface. These are the main factors affecting the electrocatalytic

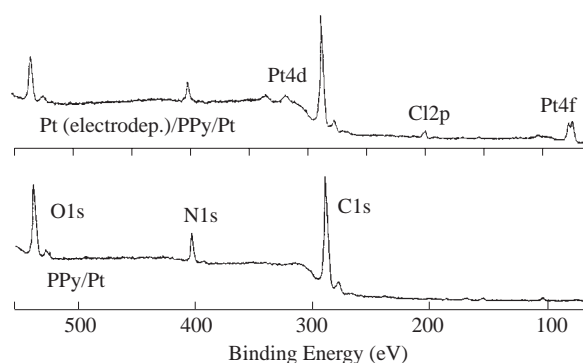
properties of the surface. The maximum current density of methanol and formic acid oxidation on metal dispersed polymer films was obtained with a Pt loading of approximately  $100 \mu\text{g}\cdot\text{cm}^{-2}$ (18). For this reason, Pt loading was kept constant at  $100 \mu\text{g}\cdot\text{cm}^{-2}$  and the deposition potential was varied. The effect of the platinum deposition potential on the electrooxidation of Me and FA was tested by recording the corresponding cyclic voltammogram after each deposition process in a solution containing  $0.1\text{M Me} + 0.1\text{M HClO}_4$  or  $0.1\text{FA} + 0.1\text{M HClO}_4$  individually. Figure 1 gives the variation of maximum anodic current densities as a function of platinum deposition potential.  $-0.46 \text{ V/MSE}$  was obtained as the optimum deposition potential, giving maximum current density of both electroactive species studied in the same conditions.

In order to detect if the Pt substrate has any effect on the oxidation of Me and FA on a Pt dispersed PPy coated electrode, the surface sensitive XPS spectra of Pt(substrate)/PPy and Pt(substrate)/PPy/Pt electrodes were recorded. No peak related to Pt was observed in the case of PPy, as shown in Figure 2. This observation proves that substrate does not play a role in the electrooxidation of Me and FA on the polymer matrix. Additionally, the stability of each electrode system was investigated by testing the successive voltammograms of the electrodes. Even after 100 cycles, the electrodes showed good stability.



**Figure 1.** Maximum peak currents ( $i_p$ ) vs deposition potential (E)

FA<sub>a</sub>: Anodic sweep for the electroox. of 0. 1M FA  
 FA<sub>c</sub>: Cathodic sweep for the electroox. of 0. 1M FA  
 M<sub>a</sub>: Anodic sweep for the electroox. of 0. 1M Me  
 M<sub>c</sub>: Cathodic sweep for the electroox. of 0. 1M Me  
 $v = 50 \text{ mVs}^{-1}$ ,  $m_{Pt} = 100 \mu\text{gcm}^{-2}$



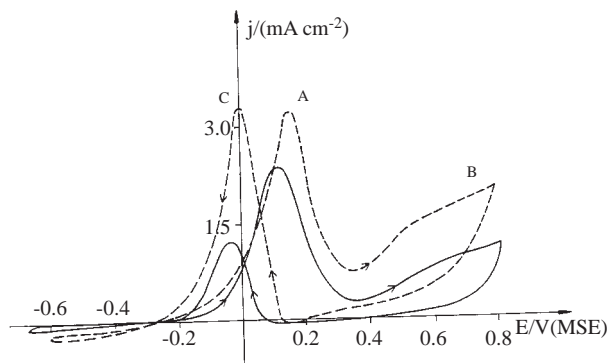
**Figure 2.** XPS spectrum of the electrode after PPy deposition on Pt substrate, Thickness of PPy:  $1 \mu\text{m}$

#### *a) Oxidation of Methanol on Pt Dispersed Polypyrrole Electrodes*

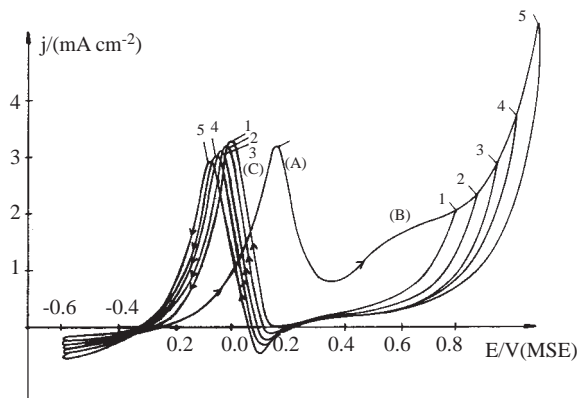
Figure 3 shows the electrooxidation of  $0.1\text{M}$  methanol on a platinum dispersed polypyrrole electrode in  $0.1\text{M HClO}_4$  with a sweep rate of  $50 \text{ mVs}^{-1}$ . During the positive scan, an oxidation peak (A) at  $0.18 \text{ V/MSE}$  and peak (B) at  $0.55 \text{ V/MSE}$  were observed. Throughout the reverse scan, an oxidation peak (C) at  $0.00 \text{ V/MSE}$  was obtained.

The effect of the anodic and cathodic limits was also investigated (Figure 4). While an increase in the upper limit ( $E_a$ ) does not cause a change in the current density of peak A, it causes a decrease in the intensity of peak C. At the same time, the potential of peak C shifts to more negative values, whereas the

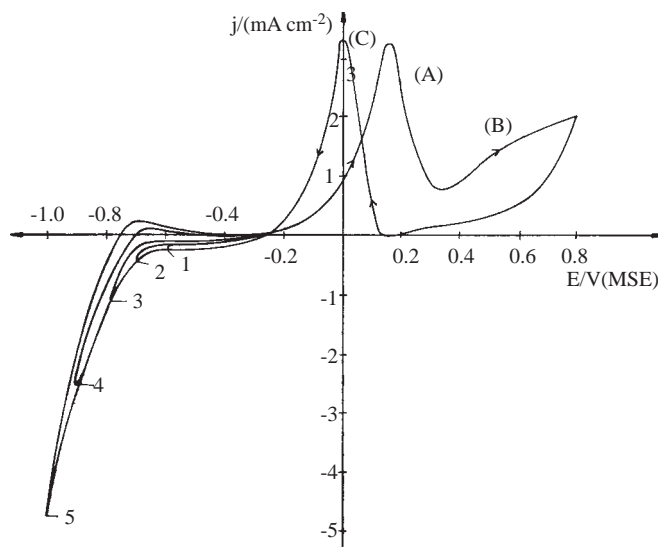
effect of cathodic limit ( $E_c$ ) is negligible for the same system (Figure 5). This means that adsorbed hydrogen has no effect on the oxidation reaction.



**Figure 3.** Cyclic voltammogram of 0. 1M Me on pure platinum (—) and platinum dispersed polypyrrole (- - -) electrodes in 0. 1M HClO<sub>4</sub>,  $v = 50 \text{ mVs}^{-1}$ ,  $m_{Pt} = 100 \mu\text{gcm}^{-2}$



**Figure 4.** Effect of the anodic sweep ( $E_a$ ) on the electrooxidation of 0. 1M Me  $v = 50 \text{ mVs}^{-1}$ ,  $m_{Pt} = 100 \mu\text{gcm}^{-2}$

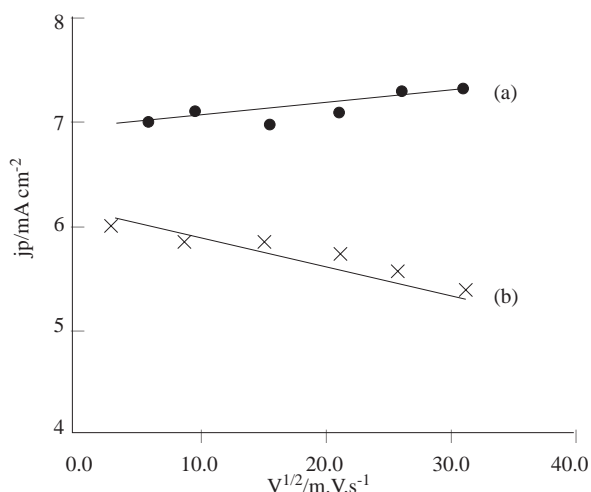


**Figure 5.** Effect of the cathodic sweep ( $E_c$ ) on the electrooxidation of 0. 1M Me  $v = 50 \text{ mVs}^{-1}$ ,  $m_{Pt} = 100 \mu\text{gcm}^{-2}$

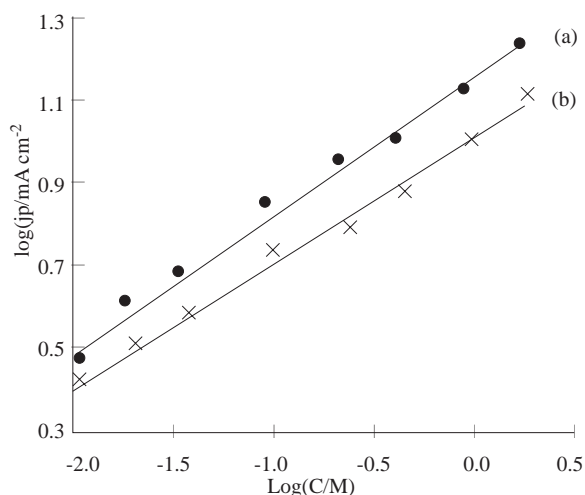
The variation of the sweep rate ( $v$ ) from 0.01 to  $1.0 \text{ Vs}^{-1}$  was studied for 0.1M Me oxidation. Figure 6 shows the variation in maximum current density ( $\log i_p$ ) vs  $v^{1/2}$ . The current density increases linearly with increasing scan rate for the anodic peak, whereas it declines for the cathodic peak. Peak potentials do not depend on the scan rate. These facts mean that the electron transfers are reversible and controlled by diffusion.

The concentration of Me was varied from 0.001 to 2M in 0.1M HClO<sub>4</sub> aqueous solutions. With increasing concentration, peaks A and C were shifted towards more negative potentials and their current densities were increased. Peak B became more intensive when the concentration was greater than 0.1M. Plots

of the logarithm of current densities ( $\log i_p$ ) vs the logarithm of the concentration of Me on the modified electrode surface are given in Figure 7. The reaction orders, derived from the slope of the straight line, are 0.35 and 0.31 for the anodic and cathodic peak, respectively. Tafel plot analysis of the left-hand side of the first oxidation peak (A) was also realised. The  $\alpha n$  values calculated from the slopes of the straight lines are given in Table 1. If we assume  $\alpha = 0.5$ ,  $n$  is calculated to be 0.7 ( $n$ : number of electrons transferred).



**Figure 6.** The anodic peak current ( $\log i_p$ ) vs square root of scan rate ( $v^{1/2}$ ) for the electrooxidation of 0.1M Me, a: anodic sweep, b: cathodic sweep



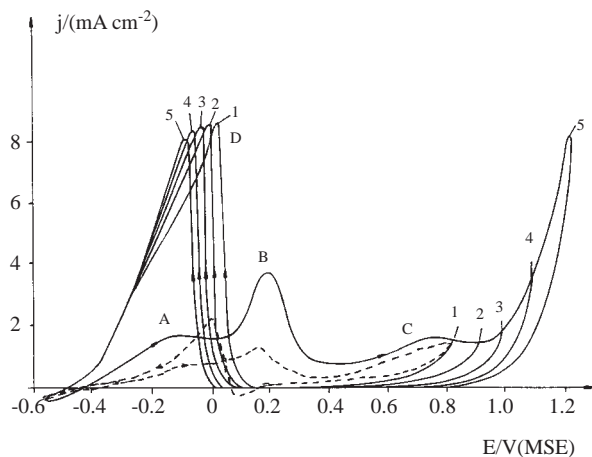
**Figure 7.** The log. of anodic peak current ( $\log i_p$ ) vs the log. of Me concentration ( $\log C_M$ ) on Pt(subs)/PPy/Pt electrode, a: anodic sweep, b: cathodic sweep

**Table 1.** Transfer coefficients for the electrooxidation of 0.1M Me on the PPy/Pt electrode

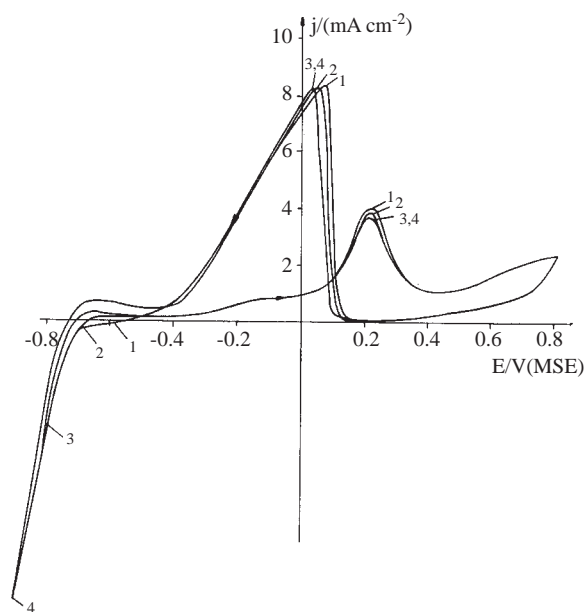
$C_M$ (M)	$\alpha n$	$C_M$ (M)	$\alpha n$	$C_M$ (M)	$\alpha n$
0.01	0.13	0.05	0.28	0.5	0.35
0.02	0.15	0.10	0.37	1.0	0.36
0.03	0.18	0.20	0.34	2.0	0.35

### *b) Oxidation of Formic Acid on Pt Dispersed Polypyrrole Electrodes*

Figure 8 shows the electrooxidation of 0.1M FA on a platinum dispersed polypyrrole electrode in 0.1M HClO<sub>4</sub> with a sweep rate of 50 mVs<sup>-1</sup>. During the positive scan, oxidation peaks (A) at -0.10 V/MSE, (B) at 0.22 and (C) at 0.68 V/MSE were observed. During the reverse scan, an oxidation peak (D) at 0.00 V/MSE was obtained. The increase in the upper limit ( $E_a$ ) causes a change in the current density of cathodic peak D which shifts towards a more negative value. No changes were observed for peaks A and B (Figure 8). The shift in the cathodic peak may be due to the adsorption of oxygen at positive potentials during which it is reduced. The effects of changing the negative potential limit ( $E_c$ ) are shown in Figure 9. When the  $E_c$  was more negative, the current density of peak B decreased slightly but that of D remained constant, and the potential of peak D shifted to a more negative scale.



**Figure 8.** Cyclic voltammogram of (0. 1M FA) on pure platinum (- - -) and platinum dispersed polypyrrole (—) in 0. 1M HClO<sub>4</sub>, Effect of the anodic sweep ( $E_a$ ) on the electrooxidation of 0. 1M FA  $v = 50 \text{ mVs}^{-1}$ ,  $m_{Pt} = 100 \mu\text{gcm}^{-2}$



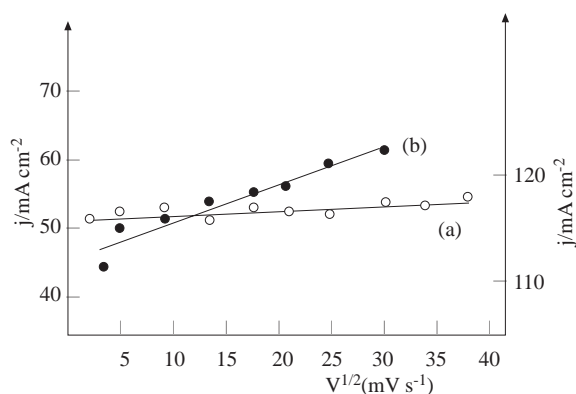
**Figure 9.** Effect of the cathodic sweep ( $E_c$ ) on the electrooxidation of 0. 1M FA  $v = 50 \text{ mVs}^{-1}$ ,  $m_{Pt} = 100 \mu\text{gcm}^{-2}$

By increasing the sweep rate from  $0.01$  to  $1 \text{Vs}^{-1}$  for  $0.1 \text{M}$  FA, the intensities of all peaks (A,B,C,D) increase and peak C also appears as a clear peak at more positive potentials. This means that shortening the time spent in the hydrogen region lowers the amount of poisoning species produced in this potential range. The current density ( $i_p$ ) varies linearly with increasing scan rate ( $v^{1/2}$ ) (Figure 10). In the case of diffusion and charge transfer control, the peak potential varies with the sweep rate according to following equation:

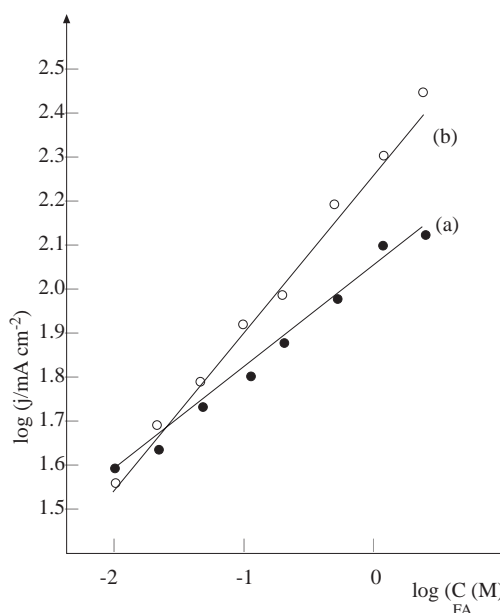
$$E_p = E_o + b' [ 0.78 + \ln(D_o/b')^{1/2} + \ln v^{1/2} - \ln k_s ]$$

$b' = RT/nF$ ,  $E_o$ : Standard potential,  $D_o$ : Diffusion coefficient,  $k_s$ : Heterogeneous rate constant at the standard potential. Herein, diffusion may be accepted considered to be the rate-determining factor for the oxidation reaction of FA.

The concentration of FA was varied from  $0.01$  to  $2 \text{M}$  in  $0.1 \text{M}$  HClO<sub>4</sub>. With the increasing concentration, peaks A and D were shifted towards more positive potentials, with a higher current density. Peak B also became more intense for higher concentration values. Plots of the logarithm of current densities ( $\log i$ ) vs the logarithm of concentration ( $\log C$ ) give the overall reaction order with respect to the initial concentration of FA (Figure 11). The reaction orders, derived from the slope of the straight line, are  $0.25$  and  $0.36$  for the anodic and cathodic sweeps respectively. Tafel plot analysis of the left-hand side of the first oxidation peak (A) was carried out and the  $\alpha n$  values were calculated from the slopes of the straight lines as given in Table 2. If one assume  $\alpha = 0.5$ ,  $n$  is calculated to be  $0.5$ .



**Figure 10.** The anodic peak current ( $i_p$ ) vs square root of scan rate ( $v^{1/2}$ ) for the electrooxidation of 0.1 M FA, a: anodic sweep, b: cathodic sweep



**Figure 11.** The log of the peak current ( $\log i_p$ ) vs the log of FA concentration ( $\log C_{FA}$ ) a: anodic sweep, b: cathodic sweep

**Table 2.** Transfer coefficients for the electrooxidation of 0.1 FA on the PPy/Pt electrode

$C_{FA}(M)$	$\alpha n$	$C_{FA}(M)$	$\alpha n$	$C_{FA}(M)$	$\alpha n$
0.01	0.12	0.05	0.19	0.5	0.27
0.02	0.14	0.10	0.28	1.0	0.25
0.03	0.15	0.20	0.25	2.0	0.21

## Conclusion

It is concluded that polypyrrole films may be used as a convenient substrate for the dispersion of platinum particles and these electrodes may be of interest for the oxidations of methanol and formic acid. The electroactivity of the catalytic system depends on the deposition potential of platinum. Maximum current density was observed both for methanol and formic acid oxidations at approximately the same deposition potential of platinum (-0.46 V/MSE). An increase in the current density was obtained on a Pt dispersed PPy electrode both for Me and FA oxidations. The rate-determining step was diffusion and charge transfer controlling for both cases. The formation of strongly adsorbed poisoning intermediate on bulk Pt sites (mainly linearly and bridge bonded CO<sup>2,10</sup>) were found to be more relevant processes for the oxidation of small organic molecules on bulk Pt. Since the main poisoning intermediates of Me and FA are similar, increased activity can also be expected on the Pt dispersed PPy coated electrode surface for the two materials, since the surface concentration of adsorbed residues on Pt sites is lowered by the quantity of Pt particles.

In conclusion, we observed that Pt dispersed PPy coated electrodes increase the electrooxidation rates of methanol and formic acid and their use as electrode materials may be attractive in direct fuel cells.

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