

## NOTES

## ELECTROCATALYTIC OXIDATION OF ETHANOL ON PLATINUM NANOPARTICLES MODIFIED POLYANILINE ELECTRODE

D. A. FUNGARO, A. OLIVEIRA - NETO and M. LINARDI

*Institute for Energy and Nuclear Research, Av. Prof. Lineu Prestes, 2242, CEP 05508-000, São Paulo, SP, Brazil  
dfungaro@ipen.br*

**Abstract**— The electrocatalytic properties of platinum nanoparticles incorporated into polyaniline films was investigated for oxidation of ethanol in sulfuric acid solutions. The electropolymerization of aniline and the electrochemical depositions of platinum particles into the polyaniline film were achieved by cyclic voltammetry. The effect of the formation conditions of platinum-modified polyaniline films (as cycle numbers, sweep rates) and alcohol concentration were evaluated. The platinum-modified polyaniline films formed by the optimization conditions can be used as a convenient conducting substrate for the ethanol electrooxidation.

**Keywords**— polyaniline films, ethanol, platinum particles.

## I. INTRODUCTION

Conducting polymers are a very important materials which are currently being investigated with regard their application in energy storage, microelectronics, electrochromic displays, electrocatalysis, chemical sensors, etc. (Inzelt *et al.*, 2000; Fungaro, 2001, 2004). These polymers, especially polyaniline, are usually used as matrix to incorporate noble metal catalysts in the application for electrooxidation of small molecules such as hydrogen, methanol and formic acid, etc. (Kost *et al.*, 1988; Gholamian and Contractor, 1990; Hable and Wrighton, 1991). The reason for incorporating metallic particles into porous matrixes is to increase the specific area of these materials and thus improve catalytic efficiency. Another reason is the higher tolerance of the platinum particles to poisoning effect due to adsorption of CO species, in comparison with the serious problem of poisoning effect on bulk platinum electrodes. On the other hand, it is of great importance to investigate the catalytic activity of low loading platinum catalysts and to determine the lowest metal loading necessary to reach the practical performances in terms of current density and power density because of relatively high cost of catalytic material.

Platinum particles are generally electrodeposited into the polyaniline films at a constant potential (Croissant *et al.*, 1998; Ficicoglu and Kadrigan, 1997; Mikhaylova *et al.*, 2001; Laborde *et al.*, 1994; Kitani *et al.*, 2001).

Apart from the constant potential method, in principle, cyclic voltammetry is also an alternative to deposit metal particles into polymer matrix within a fixed potential limit. In most cases as reported previously, the polyaniline films are electropolymerized from a solution containing aniline monomer and sulfuric acid electrolyte by cycling potentials until the films reach certain thickness around 0.5  $\mu\text{m}$  (Napporn *et al.*, 1996; Kelaidopoulou *et al.*, 1998; Kelaidopoulou *et al.*, 1999). However, no specific explanation is given to indicate whether it is the most reasonable film thickness to deposit platinum particles in terms of the electrocatalytic application.

Ethanol, among other small organic molecules, offers an attractive alternative as a liquid fuel with respect to methanol because is less toxic and it is the major renewable biofuel from the fermentation of biomass. However, few studies have been reported so far regarding ethanol oxidation on polyaniline film electrode (Hable and Wrighton, 1993). In view of its application prospects, fundamental insight for the electrooxidation of ethanol is important.

The purpose of the present work was to study the electrooxidation of ethanol as function of formation conditions of platinum-modified polyaniline films (cycle numbers, sweep rates) and alcohol concentration.

## II. EXPERIMENTAL

All the solutions were prepared with ultrapure water Millipore Milli-Q. Aniline (Aldrich) was purified by distillation with zinc dust and stored under nitrogen gas. All other reagents were of analytical grade and were used as-received: ethanol (Merck),  $\text{H}_2\text{SO}_4$  (Merck) e  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  (Acros Organics). The experiments were performed at ambient temperature (25 °C) and under a nitrogen atmosphere.

Electrochemical experiments were carried out using an Autolab 30 (EcoChemie - Netherlands) voltammetric analyzer. The cell assembly contained a 3 mm diameter glassy carbon electrode as working electrode, a platinum wire as auxiliary electrode and a Ag/AgCl (3 mol  $\text{L}^{-1}$  KCl) as reference electrode.

The polyaniline films were formed by cyclic voltammetry at 50  $\text{mV s}^{-1}$  between - 0.16 and + 0.94 V in solution of 0.1 mol  $\text{L}^{-1}$  of aniline + 0.5 mol  $\text{L}^{-1}$   $\text{H}_2\text{SO}_4$ . The

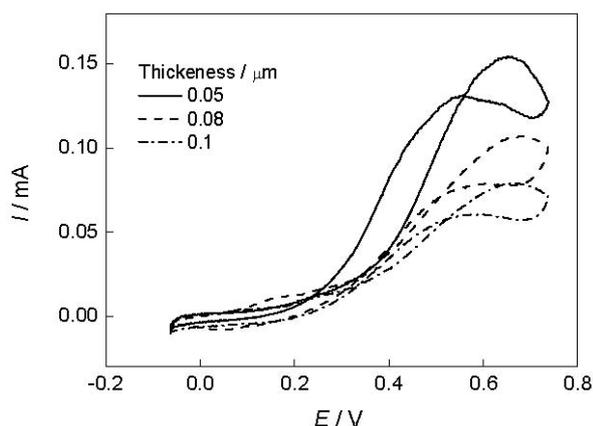


Fig 1. Effect of thickness of polyaniline films on the oxidation of  $0.5 \text{ mol L}^{-1} \text{ CH}_3\text{CH}_2\text{OH} + 0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  at  $5 \text{ mV s}^{-1}$ .

film thickness, varied by changing the number of potential cycles, was estimated using the cathodic charge value of the last cycle during film formation (Genies and Tsintavis, 1986). The dispersion of platinum into the polyaniline films was performed by cyclic voltammetry at  $50 \text{ mV s}^{-1}$  between  $-0.063$  and  $+0.84 \text{ V}$  in solution of  $3 \text{ mmol L}^{-1}$  of  $\text{H}_2\text{PtCl}_6 + 0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ , except for specific indication of sweep rates used. Prior to the reduction the electrode was soaked in the hexachloroplatinic acid solution for 15 min. The amount of platinum deposited into the polyaniline film can be estimated from measurements of the charge involved during the reduction of  $\text{Pt}^{4+}$  to  $\text{Pt}^0$  (Laborde *et al.*, 1994).

Electrocatalytic oxidation of ethanol on polyaniline films modified with platinum particles was examined in  $0.5 \text{ mol L}^{-1} \text{ CH}_3\text{CH}_2\text{OH} + 0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  by cyclic voltammetry at  $5 \text{ mV s}^{-1}$  between  $-0.063$  and  $0.74 \text{ V}$ .

### III. RESULTS AND DISCUSSION

#### A. Thickness of polyaniline films

Polyaniline is a very interesting material because is homogeneous, strongly adherent to the support, and chemically stable in acid medium. Electropolymerization offers the possibility of controlling the thickness and homogeneity of the conducting polymer film on the electrode surface.

The effect of polyaniline films on the electrodeposition of platinum particles and the subsequent electrocatalytic activity for ethanol oxidation was studied by changing the cycle sweep numbers to 13, 15 and 17. The thickness of the polyaniline films electropolymerized with the above three cycle numbers corresponds to 0.05, 0.08 e  $0.1 \mu\text{m}$ , respectively. Figure 1 shows the effect of thick-ness of polyaniline films modified with same amount of platinum particles (25 cycles) on the oxidation of ethanol.

The current of ethanol oxidation with the thicker polyaniline films ( $0.1 \mu\text{m}$ ) falls remarkably compared to that with two thinner polyaniline films due the more difficulty for the distribution of platinum particles in three dimensions. The superimposition of the curves during the positive and negative sweeps indicates that

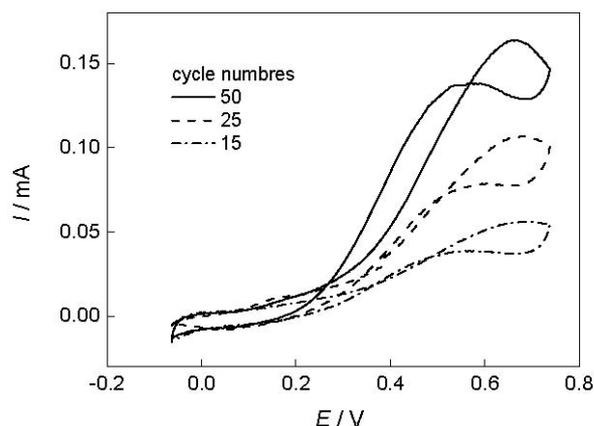


Fig 2. Effect of cycle numbers of platinum electrode-position on the oxidation of  $0.5 \text{ mol L}^{-1} \text{ CH}_3\text{CH}_2\text{OH} + 0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  at  $5 \text{ mV s}^{-1}$ .

strongly chemisorbed posing species are not formed extensively (Laborde *et al.*, 1994). The poisoning effect was less significant with the polyaniline film of intermediate thickness ( $0.08 \mu\text{m}$ ), which was used as the matrix to electrodeposit platinum particles in the following experiments.

#### B. Effect of cycle numbers of platinum electrodeposition

The electroactivity for ethanol oxidation depends on the amount of deposited platinum. The platinum-modified polyaniline electrodes were prepared with different platinum loadings. The platinum particles were electrodeposited into polyaniline films ( $0.08 \mu\text{m}$ ) by cyclic voltammetry with same potential limits and sweep rate, but the cycle numbers increase from 15, 25 to 50. As expected, the platinum loadings increased successively with increasing cycle numbers of platinum electrodeposition. The platinum loadings calculated by the method used in literature (Laborde *et al.*, 1994) were 8.1, 9.3 e  $16.4 \mu\text{g cm}^2$ , corresponding to the cycle numbers 15, 25 and 50 used in the electrodeposition of platinum particles, respectively. Figure 2 shows the effect of cycle numbers of platinum electrodeposition on the oxidation of ethanol.

The anodic peak currents, which appear in the positive going sweeps, increased with the amount of deposited platinum. The platinum nanoparticles electrodeposited up to the 50 cycles were sufficiently dispersed in the overall structure of the polyaniline film. Figure 3 represents the variation of the maximum current density as a function of the amount of deposited platinum. The current density increase regularly up to  $9.5 \mu\text{g cm}^2$ , then reaches a plateau. The decrease observed after  $16.4 \mu\text{g cm}^2$  is probably due to the formation of platinum clusters, leading to a smaller dispersion (Laborde *et al.*, 1994).

#### C. Effect of sweep rates of platinum electrodeposition

The effect of sweep rate of platinum electrodeposition on the electrooxidation of ethanol was studied. The

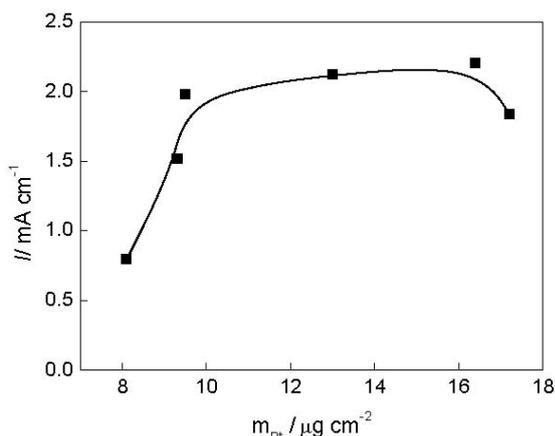


Fig 3. Maximum current density as a function of the amount of deposited platinum on the oxidation of  $0.5 \text{ mol L}^{-1} \text{CH}_3\text{CH}_2\text{OH} + 0.5 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$  at  $5 \text{ mV s}^{-1}$ .

platinum particles are electrodeposited into polyaniline films ( $0.08 \mu\text{m}$ ) by cyclic voltammetry with the same potential limits ( $-0.063$  to  $+0.84 \text{ V}$ ), and same cycle numbers (25 times), while the sweep rates increase from  $10$  to  $100 \text{ mV s}^{-1}$ . The current peak of ethanol oxidation increases with the decrease of the sweep rate from  $100$  to  $10 \text{ mV s}^{-1}$  (Fig. 4).

The current for ethanol oxidation reaches the highest value (about  $0.101 \text{ mA}$ ) at the lowest sweep rate ( $10 \text{ mV s}^{-1}$ ), owing to highest platinum loading ( $24.5 \mu\text{g cm}^{-2}$ ). However, since the sweep rate is slower, it will spend much longer time ( $75 \text{ min}$ ) compared to other two rates of  $80$  and  $50 \text{ mV s}^{-1}$  ( $9$  and  $15 \text{ min}$ , respectively) to accomplish the electrodeposition of platinum particles and may lead to a certain extent of degradation of polyaniline matrix. The platinum particles electrodeposited with sweep rate of  $100 \text{ mV s}^{-1}$  have no electrocatalytic activities on the oxidation of ethanol. Niu *et al.* (2003) found that the electrocatalytic activities of platinum particles electrodeposited into polyaniline films with sweep rate of  $100 \text{ mV s}^{-1}$  on methanol oxidation was not remarkable and decreased quickly during the consecutive potential cycle. From the point of view of both electrocatalytic activities of platinum particles and optimization of polymer matrix properties, therefore, an intermediate sweep rate of  $50 \text{ mV s}^{-1}$  is selected to deposit platinum particles within the polymer matrix.

#### D. Effect of the concentration of ethanol

The investigation of the effect of varying the ethanol concentration on oxidation electrocatalytic at polyaniline/Pt electrode was examined and was shown in Fig. 5.

The concentration of ethanol was varied from  $0.10$  to  $1.0 \text{ mol L}^{-1}$  and maximum current peak of oxidation was obtained for  $0.50 \text{ mol L}^{-1}$ . The main products observed during ethanol electrochemical oxidation on platinum electrodes are acetaldehyde, acetic acid and carbon dioxide, with predominance for acetic acid and acetaldehyde (Souza *et al.*, 1997; Ianniello *et al.*, 1999; Fujiwara *et al.*, 1999; Iwasita, 2002; Iwasita and Pastor, 1994). The formation of  $\text{CO}_2$  goes through strongly

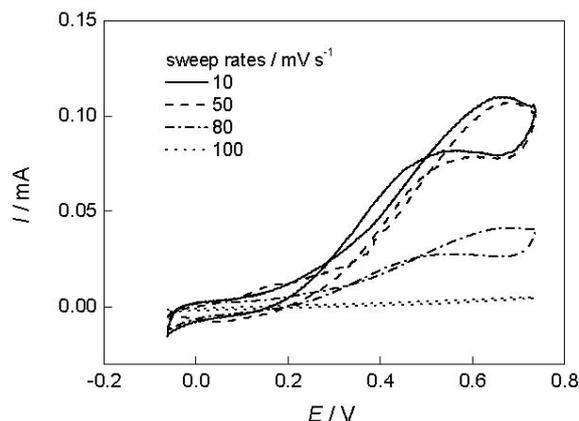


Fig 4. Effect of sweep rates of platinum electrodeposition on the oxidation of  $0.5 \text{ mol L}^{-1} \text{CH}_3\text{CH}_2\text{OH} + 0.5 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$  at  $5 \text{ mV s}^{-1}$ .

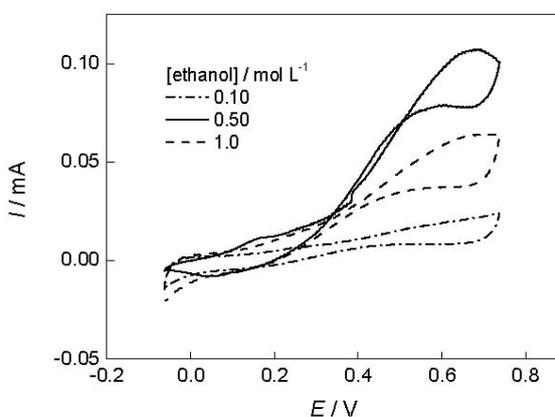


Fig 5. Effect of alcohol concentration on the oxidation of  $\text{CH}_3\text{CH}_2\text{OH} + 0.5 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$  at  $5 \text{ mV s}^{-1}$ .

chemisorbed intermediates, CO and hydrogenated absorbates, whereas acetaldehyde, etc, are formed through a weakly adsorbed ethanol intermediate (Iwasita and Pastor, 1994). It has been reported that the production of the partially oxidized acetaldehyde increases as the ethanol concentration increases (Bergamaski, 2003). The activity of electrode is limited because polyaniline can be degraded by the acidic solutions of acetaldehyde.

#### IV. CONCLUSIONS

Polyaniline films can be used as a convenient conducting substrate for the dispersion of platinum nanoparticles for electrooxidation of ethanol. It was found that the oxidation of ethanol depends on the nature of both polymer matrix and platinum particles. The optimum catalytic activity for a polyaniline film of  $0.08 \mu\text{m}$  thickness was obtained for the following conditions: amount of deposited platinum =  $9.5 \mu\text{g cm}^{-2}$ , sweep rate =  $50 \text{ mV s}^{-1}$  and ethanol concentration =  $0.50 \text{ mol L}^{-1}$ . Experiments of current-potential curves using platinum-modified polyaniline films in direct ethanol fuel cell are currently in progress.

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