

COMPOSITE ELECTRODE MATERIAL WITH CATALYTIC ACTIVITY OBTAINED BY ELECTROCHEMICAL DEPOSITION OF POLYPYRROLE AND PLATINUM ON TITANIUM SUBSTRATES

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Cyclic voltammetric method was used in order to obtain highly stable and adherent polypyrrole (PPy) deposits on titanium substrates. It was found that a PPy loading within the range 0.2 to 0.4 mg cm⁻² ensures high active area and good conductivity of the polymer matrix. The possibility of achieving Pt-modification of the PPy layers was also investigated and it was observed that applying cathodic potential steps enables better control of the deposition process which allows obtaining Pt loadings lower than 100 μg cm⁻². The electrocatalytic activity for methanol oxidation of the composite material thus obtained compares quite well with that available by using platinum electrodes.

INTRODUCTION

It is widely accepted that the efficient use of noble metals as electrocatalysts relies on the maximization of the catalytic properties while limiting the precious metal loading. One way to minimize the amount of expensive electrocatalyst is to deposit it on a substrate which must be electrically conductive, stable and also high in surface area, in order that a large number of active sites are provided in a small volume. In this respect, the use of conducting polymers appears to be a promising approach because these compounds fulfill to a satisfactory extent the above requirements. Furthermore, the use of polymers (such as polyaniline or polypyrrole) as conducting matrix for metal clusters enables better separation and stabilization of the electrocatalyst microparticles, thus ensuring higher catalytic activity.¹⁻⁴

These findings triggered very active research in the field of composite materials consisting of metal aggregates and conducting polymers and a large variety of applications has been envisaged in the literature, including environmental science,⁵ microelectronics and amperometric biosensors.⁶⁻⁸ In most of the cases the preparation of such composite materials involves the deposition of polymers on appropriate substrates, followed by

their modification by electrodeposition of catalysts (mainly noble metals or transition metals) particles.^{9,10} However, the incorporation of metal particles during monomer polymerization has also been reported.^{3,4}

The present work is aimed at studying both the possibility of using titanium as a substrate for platinum-modified polypyrrole, and the way in which the electrocatalytic properties of this composite material can be improved by optimizing the obtaining conditions.

RESULTS AND DISCUSSION

Polypyrrole (PPy) deposition was carried out, according to a method described in the literature,¹¹ from a 0.2 M oxalic acid aqueous solution containing 0.1 M pyrrole (Py) by continuously cycling the potential of the electrode within the range -0.2 ÷ 1.0 V, at a scan rate of 200 mV s⁻¹. After being removed from the plating bath, the electrodes were thoroughly rinsed and then dried in air. The electrochemical activity of the PPy deposits was examined by cyclic voltammetry (scan rate 50 mV s⁻¹) within the same potential range (-0.2 ÷ 1.0 V), in a 0.5 M H₂SO₄ solution.

Fig. 1 shows characteristic voltammetric patterns recorded for electrodes obtained by

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increasing the number of deposition cycles. It appears that PPy deposition results in an important enhancement of the voltammetric current, due both

to the increase of the electrochemically active area and to the “pseudo-capacitive” faradaic behavior of the polymeric coatings.

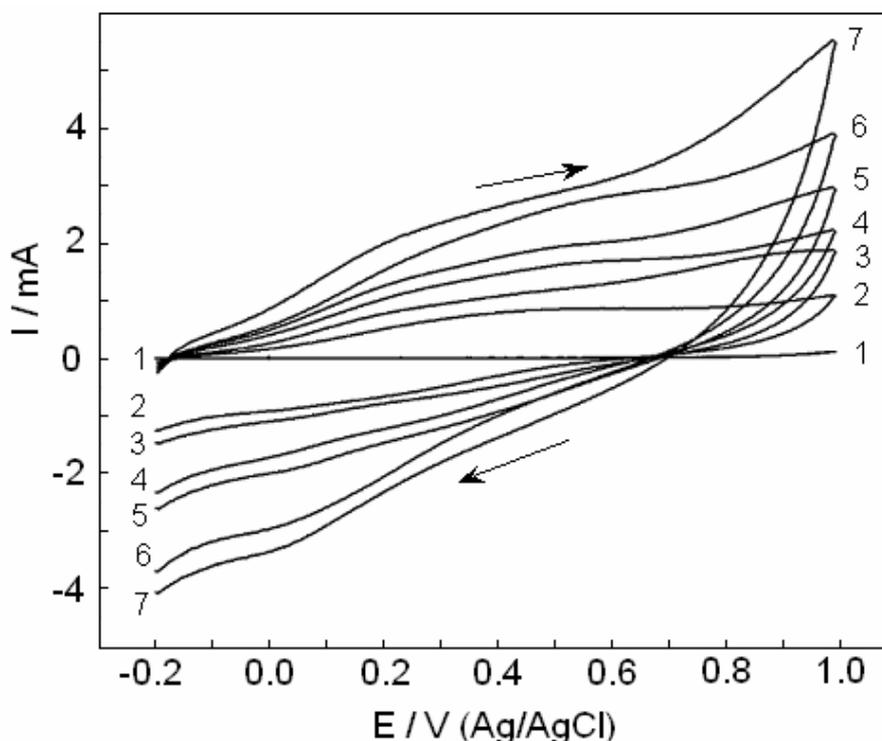


Fig. 1 – Cyclic voltammograms for titanium electrodes after polypyrrole deposition during: (1) 0, (2) 25, (3) 35, (4) 50, (5) 70, (6) 100, and (7) 150 deposition cycles. Electrolyte: 0.5 M H_2SO_4 ; scan rate 50 mV s^{-1} .

It was also found that, at potential values higher than ca. 0.7 V, increasing the PPy loading results in a rather sharp increase of the current during the anodic scan, as illustrated by curves 4 to 7 from Fig. 1. A possible explanation for this behavior is provided by assuming that under these circumstances a partial oxidation of the backbone of the polymer occurs. This is also in line with the fact that, as Fig. 1 shows, the oxidation current increases with the amount of deposited polypyrrole.

In order to put into a better perspective these results, both the anodic and the cathodic voltammetric charges were integrated within the potential range $-0.25 \div 0.7 \text{ V}$, for electrodes with increasing PPy loading, and the results are shown in Fig. 2.

An almost linear variation of the voltammetric charge as a function of the amount of deposited polymer was found for PPy loadings lower than ca. 0.5 mg cm^{-2} , and the least-squares analysis yielded a specific voltammetric charge of ca. 50.3 C g^{-1} , with $R^2 = 0.9831$. As Fig. 2 shows, further increase of the PPy loading resulted in a less important increase of the charge. This is an

indication of the fact that additional amounts of electrodeposited polypyrrole lead to a decrease of both the roughness and the porosity of the coating. It is also interesting to note that, within the investigated potential range, the cathodic charge is generally slightly higher than the corresponding value of the anodic one, although the overall voltammetric behavior is highly reversible. There are reasons to believe that this behavior could be ascribed to the partial oxidation of the backbone of the polymer which results in a p-doping of the electrodeposited PPy.

The study of the effect of the polypyrrole loading on the voltammetric behavior of the electrodes have shown that, under our experimental conditions, ca. 30 to 70 deposition cycles enable obtaining PPy layers (with loadings ranging from 0.2 to 0.4 mg cm^{-2}) that exhibit good conductivity, relatively large active area, and high stability and reproducibility of the electrochemical response. Based upon the above results, electrodes thus obtained were further Pt-modified.

Platinum electrochemical deposition was carried out from a $0.5 \text{ M H}_2\text{SO}_4$ solution containing

2.4 mM H_2PtCl_6 , by applying potential steps. The effect of both potential limits and deposition time on the electrochemical activity of the Pt-modified polypyrrole layers was also carefully investigated. It was found that, for PPy loadings within the range 0.2 to 0.4 mg cm^{-2} , applying for 5 minutes a potential step from 0.3 to -0.1 V results in

excellent electrochemical features of the electrodes. Under these experimental conditions high catalytic activity for methanol anodic oxidation is available, while the amount of deposited platinum is still less than *ca.* 100 $\mu\text{g cm}^{-2}$.

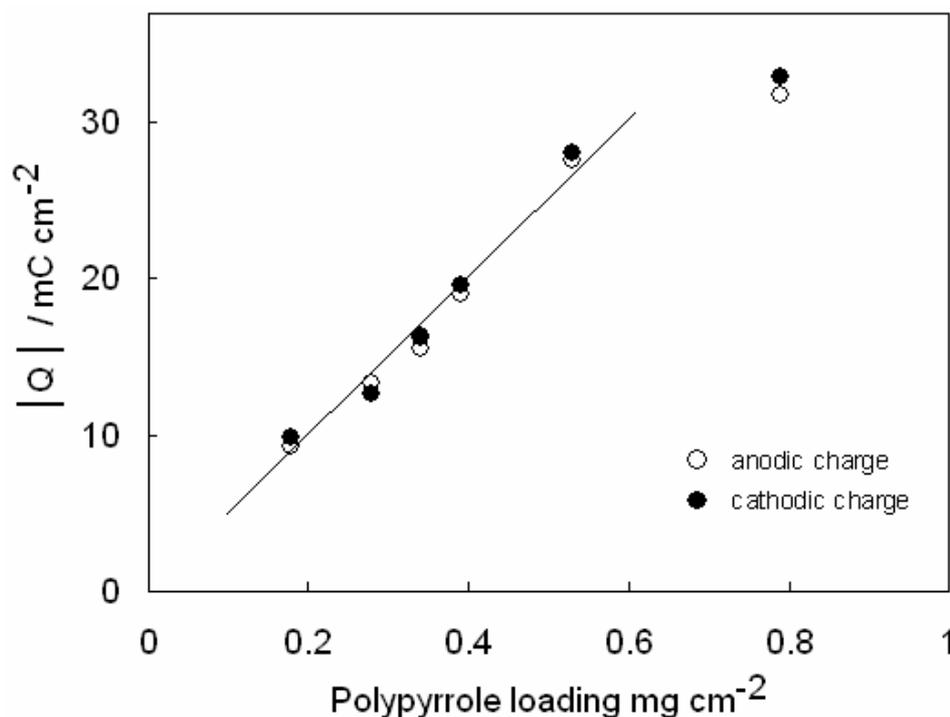


Fig. 2 – The variation of the absolute value of the voltammetric charge as a function of polypyrrole loading.

In order to calculate the quantity of electricity, Q_{tot} , involved during the Pt deposition process at -0.1 V, current vs. time curves were recorded and Fig. 3 shows a typical I/t transient response obtained for a 0.34 mg cm^{-2} PPy loading (corresponding to 50 deposition cycles). Because at potential values higher than *ca.* -0.2 V the hydrogen evolution is negligible, a current efficiency close to 100 % is expected for platinum electrodeposition. Thus, the quantity of electricity used for this process (Q_{Pt} in mC cm^{-2}) is

$$Q_{\text{Pt}} = Q_{\text{tot}} - Q_{\text{dl}} \quad (1)$$

in which Q_{dl} (in mC cm^{-2}) stands for the quantity of electricity associated with the charging of the double layer and the reduction processes at the PPy surface. By integrating the I/t response from Fig. 3, a value of 169.7 mC cm^{-2} can be calculated for Q_{tot} , while a Q_{dl} value of 7.3 mC cm^{-2} is estimated for the same electrode, within the potential range 0.3 ÷ -0.1 V, from the corresponding cyclic voltammogram (curve 4 from Fig. 1). The amount

of deposited platinum (W in $\mu\text{g cm}^{-2}$) can be calculated as

$$W = \frac{Q_{\text{Pt}} M}{zF} \times 10^3 \quad (2)$$

Where $M = 195.1 \text{ g mol}^{-1}$ is the atomic weight of Pt, $z = 4$ the number of exchanged electrons and $F = 96500 \text{ C mol}^{-1}$, the faradaic constant. Thus, from the above data, a platinum loading of 82.1 $\mu\text{g cm}^{-2}$ can be calculated.

In order to assess the electrocatalytic activity of the Pt-modified polypyrrole layers, cyclic voltammetric experiments (scan rate 50 mV s^{-1}) were performed in a 0.5 M H_2SO_4 solution containing 1 M CH_3OH , within the potential range -0.2 ÷ 1.0 V. It was observed that reproducible voltammetric signals are obtained after *ca.* five consecutive cycles, and typical voltammograms are shown in Fig. 4. In the absence of methanol (curve 1 from Fig. 4) the shape of the voltammogram can be explained in terms of the main electrochemical

processes, typical for platinum behavior in acidic media. Thus, the broad anodic peak located at ca. 0.05 V can be ascribed to the oxidation of the adsorbed hydrogen while, at potential values higher than ca. 0.6 V, platinum oxidation is responsible for the increase of the anodic current.

It is interesting to note that, during the reverse scan the corresponding cathodic reactions (*i.e.* platinum oxide reduction and hydrogen adsorption) are not evidenced, indicating that the presence of the PPy matrix affects the reversibility of these processes.

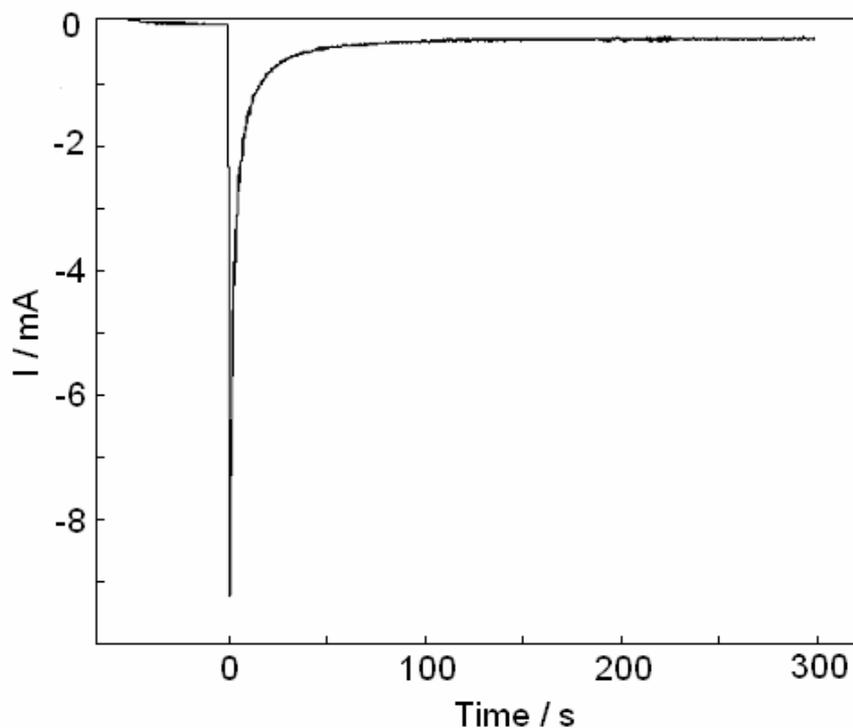


Fig. 3 – Current vs. time response for a potential step from 0.3 to -0.1 V recorded in a 0.5 M H_2SO_4 + 2.4 mM H_2PtCl_6 solution for an electrode with a PPy loading of 0.34 mg cm^{-2} .

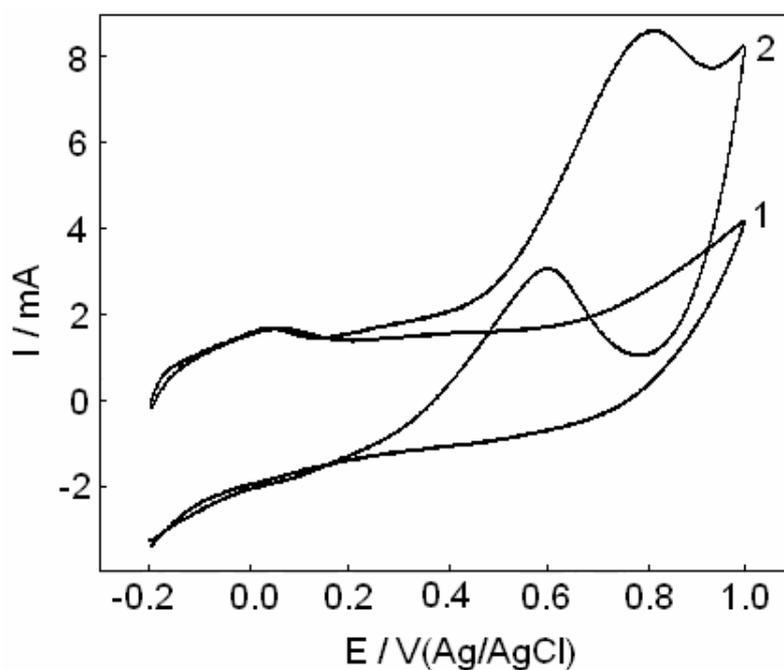


Fig. 4 – Cyclic voltammograms recorded for an electrode with a 0.34 mg cm^{-2} PPy loading, modified with 82 μg cm^{-2} Pt in a 0.5 M H_2SO_4 solution containing: (1) 0 M and (2) 1 M CH_3OH . Scan rate: 50 mV s^{-1} .

As curve 2 from Fig. 4 shows, platinum modification of the deposited polypyrrole enables achieving high catalytic activity for CH₃OH electrochemical oxidation. In this case the voltammogram exhibits a well defined peak located at ca. 0.8 V, together with a smaller additional oxidation peak (peak potential ca. 0.6 V) on the reverse scan, corresponding to methanol oxidation on clean, oxide-free platinum surface. The peak current measured for methanol oxidation during the forward scan, and corrected for the double layer charging contribution, is generally used for the evaluation of the so called "mass activity", an important parameter for the characterization of an electrocatalyst.¹² In our case, for an electrode with a platinum loading of 82 μg cm⁻², the mass activity calculated from Fig. 4 was ca. 70 A g⁻¹. This value compares well with those reported in the literature for the catalytic activity for CH₃OH oxidation of Pt nanoparticles deposited onto porous carbon substrates.¹²

It was also found that platinum-modified polypyrrole films deposited on titanium substrates could be successfully used for amperometric detection of glucose, and the results will be published in detail elsewhere.

EXPERIMENTAL

Electrochemical deposition of polypyrrole was carried out on titanium (Pierce Inorganics B.V.) substrate from a 0.2 M oxalic acid aqueous solution containing 0.1 M pyrrole. Before polymer deposition the Ti foils (20×5×0.67 mm) were polished with alumina suspensions and then ultrasonically cleaned with ethanol and distilled water for 10 minutes. By using Teflon tape, a deposition area of 1 cm² was delimited. All the electrochemical experiments were performed by means of a computer-controlled PAR 273A potentiostat in a conventional three-electrode glass cell at room temperature under ambient air. A platinum wire and a Ag/AgCl electrode were used as the counter and reference electrode, respectively.

PPy was deposited onto the Ti foil by cyclic voltammetry (from -0.2 to 1.0 V at 200 mV s⁻¹). After deposition, in order to determine the mass of polypyrrole the electrodes were washed with distilled water and then dried at 40 °C. The platinum electrodeposition was performed by applying potential steps and the plating bath consisted of a 2.4 mM H₂PtCl₆ and 0.5 M H₂SO₄

aqueous solution. In a typical experiment the potential steps were applied from 0.3 to -0.1 V and a deposition time of 5 minutes was used.

Pyrrole (98 %) from Aldrich was used without further purification and the hexachloroplatinic acid (40 % Pt) was purchased from Fluka. All the other substances were analytical-reagent grade, and all solutions were prepared from bidistilled water.

CONCLUSIONS

The outstanding electrochemical properties of conductive polymers-based nanocomposite materials prompted us to investigate the possibility of using polypyrrole as a matrix for platinum particles. It was found that the cyclic voltammetric method enables obtaining highly stable and adherent PPy layers on titanium substrates. Thus, after 30 to 70 deposition cycles a polypyrrole loading within the range 0.2 to 0.4 mg cm⁻² was obtained, that ensures high active area and conductivity of the polymer matrix. The possibility of achieving Pt-modification of the PPy layers was also investigated and it was found that by applying cathodic potential steps, the deposition process is better controlled which allows obtaining platinum loadings lower than 100 μg cm⁻².

Cyclic voltammetric measurements performed in the presence of methanol have shown that the electrochemical deposition of an amount of platinum as low as 80 μg cm⁻² on the PPy matrix enables obtaining catalysts with an activity for CH₃OH oxidation that compares quite well with that available by using Pt electrodes. For assessing the application of Pt-PPy composite materials for methanol fuel cells, further experiments are in progress in order to study the possibility of Pt-Ru alloys electrochemical deposition.

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