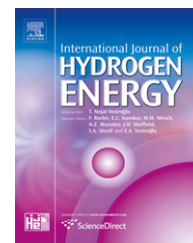


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# Co oxidation on spontaneous Pt–Ru deposits on composite polymeric electrodes

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## ARTICLE INFO

### Article history:

Received 1 December 2009

Accepted 17 December 2009

Available online 12 January 2010

### Keywords:

Polyaniline

Carbon nanotubes

Pt–Ru

CO

## ABSTRACT

Composite polyaniline electrodes containing carbon nanotubes incorporated in the film and spontaneous Pt–Ru deposits as catalytic material for CO oxidation are reported.

PANI films were electrosynthesized from a monomer acid solution with the addition of carbon nanotubes. Then, Pt–Ru deposits were obtained by immersing the polymeric film in  $\text{H}_2\text{PtCl}_6$  and/or  $\text{RuCl}_3$  in HCl. Three series of deposits were prepared by either immersion in a solution containing both metallic ions during a fixed time or successive immersion in different solutions containing only one of the metallic ions during half of the established time and varying the sequence as follows: (i) first in  $\text{H}_2\text{PtCl}_6$  and then in  $\text{RuCl}_3$  or (ii) first in  $\text{RuCl}_3$  and then in  $\text{H}_2\text{PtCl}_6$ . Adsorbed CO oxidation was studied by cyclic voltammetry in  $\text{H}_2\text{SO}_4$  solution.

The electrodes were characterized through SEM and EDX. The different ways to obtain spontaneous Pt–Ru deposits are analyzed and their influence on CO oxidation is discussed.

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## 1. Introduction

Polyaniline, polypyrrol and polythiophene are conduction polymers used as substrates for catalysts applied to the electro-oxidation reaction of many organic compounds [1,2]. Different ways to improve their electrocatalytic behavior have been reported, such as addition of either metallic particles [3] or carbon particles [4] during the polymer synthesis and application of different deposit techniques to distribute the catalytic material onto the polymeric matrix [5,6]. It is well known that Pt and its Ru-containing alloys are excellent catalysts for CO oxidation in acid solution [7,8].

The growth of polyaniline films on different metallic substrates and the co-deposition of carbon particles (activated carbon, Vulcan, carbon nanotubes) have been studied in our lab, establishing that activated carbon nanotubes notably influenced not only the film growth but also its final

characteristics. For nickel as substrate, the effect of the film thickness and the deposit time for Pt was reported [9].

In this work the catalytic activity for CO oxidation is presented for composite polyaniline electrodes with carbon nanotubes (CNT) incorporated in the film and spontaneous Pt–Ru deposits as catalytic material (Ni/PANI/CNT/Pt–Ru). The appearance of different dispersion patterns and particle size is discussed.

## 2. Experimental

### 2.1. Preparation of composite electrodes

The polyaniline composite film, PANI/CNT, was grown electrochemically on nickel wires, ca.  $0.08 \text{ cm}^2$  geometric area. A conventional three-electrode cell was used with a Pt sheet as

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doi:10.1016/j.ijhydene.2009.12.105

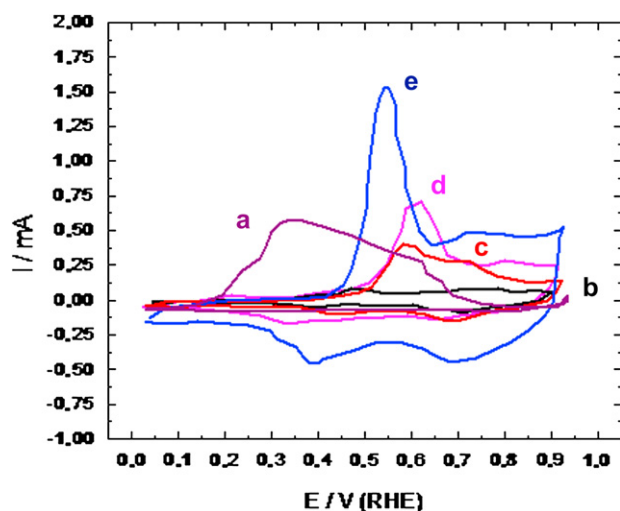


Fig. 1 – Composite Ni/PANI/CNT film growth,  $0.1 \text{ V s}^{-1}$  in  $0.1 \text{ M}$  aniline +  $0.5 \text{ M H}_2\text{SO}_4$ . (a) First cycle. (b) After two cycles. (c) After 15-min cycling. (d) After 25-min cycling. (e) After 35-min cycling.

counterelectrode and Ag/AgCl as reference electrode. The potential values in the text are referred to the hydrogen electrode in  $\text{H}_2\text{SO}_4$   $0.5 \text{ M}$ .

CNT were lab prepared from graphite by thermal treatment at  $1200^\circ\text{C}$  and then characterized. Before incorporating them in the aniline solution, they were treated with  $\text{HNO}_3$   $2.2 \text{ M}$  for  $20 \text{ h}$  and washed repetitively. These activated CNT were added

to the acid aniline solution,  $0.1 \text{ M} + \text{H}_2\text{SO}_4$   $0.5 \text{ M}$ , to obtain a  $0.1 \text{ mg mL}^{-1}$  concentration. The latter solution was sonicated to prevent the agglomeration of the carbon particles and favor their dispersion. Afterwards, the electrosynthesis of the PANI/CNT films was performed by cyclic voltammetry between  $0$  and  $0.9 \text{ V}$  at  $0.1 \text{ V s}^{-1}$ . The film thickness was calculated from the anodic charge of a voltammogram recorded at  $0.1 \text{ V s}^{-1}$  between  $0$  and  $1.2 \text{ V}$ , in  $0.5 \text{ M H}_2\text{SO}_4$  [10].

## 2.2. Catalytic composite films

The composite films were immersed for  $15 \text{ min}$  in  $0.05 \text{ M H}_2\text{PtCl}_6$  and/or  $0.1 \text{ M RuCl}_3$ , in  $0.1 \text{ M HCl}$  solutions. Three different ways to obtain Pt–Ru deposits were tested.

- Routine 1: immersion in Pt (IV) + Ru (III) solution for  $15 \text{ min}$ .
- Routine 2: immersion firstly in Pt (IV) solution for  $7 \text{ min}$  and  $30 \text{ s}$ , and then, in Ru (III) solution for the same time.
- Routine 3: immersion firstly in Ru (III) solution for  $7 \text{ min}$  and  $30 \text{ s}$ , and then, in Pt (IV) solution for the same time.

## 2.3. Characterization of the composite electrodes

The physical characterization and the dispersion degree of the Pt–Ru particles were obtained through SEM images, EDX analysis provided the chemical composition.

CO-stripping measurements were performed in saturated  $\text{CO H}_2\text{SO}_4$   $0.5 \text{ M}$  solutions. CO was adsorbed at  $E = 0.05 \text{ V}$  for  $20 \text{ min}$ ; then  $\text{N}_2$  was bubbled to remove CO from the solution. The CO electro-oxidation was achieved by cyclic voltammetry.

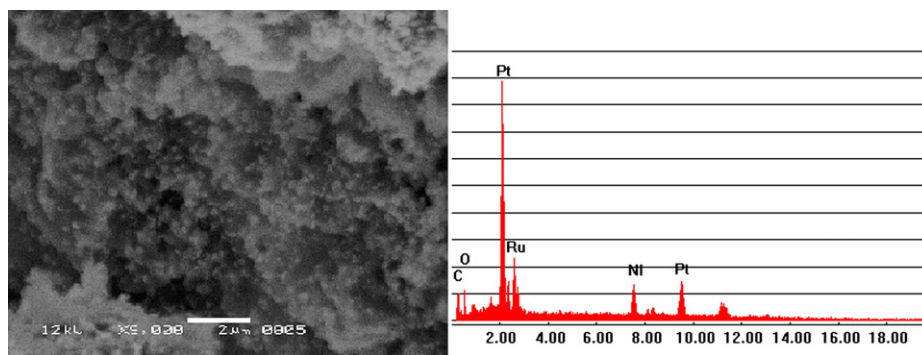


Fig. 2 – SEM – EDX for routine 1 Pt–Ru deposits.

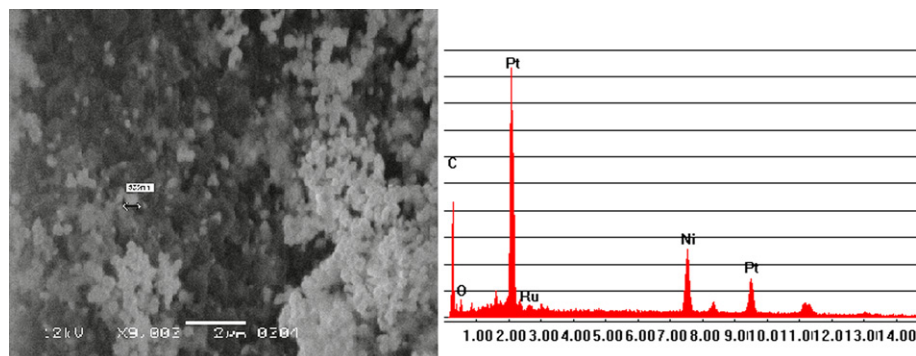


Fig. 3 – SEM – EDX for routine 2 Pt–Ru deposits.

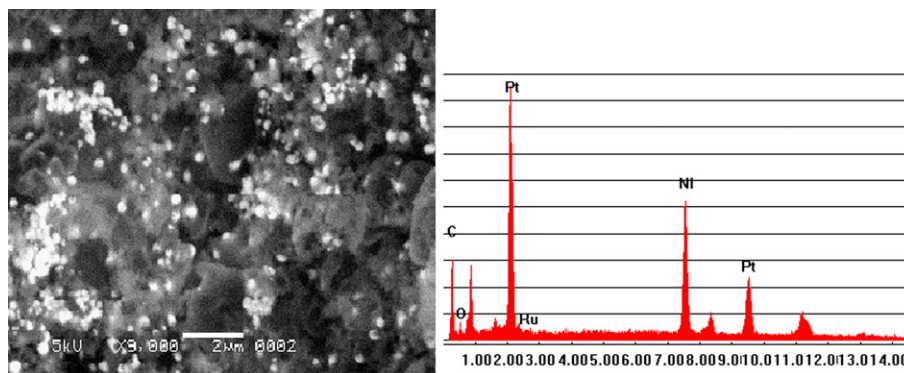


Fig. 4 – SEM – EDX for routine 3 Pt-Ru deposits.

### 3. Results and discussion

#### 3.1. Preparation of the polymeric electrodes

PANI/CNT film thickness was followed by cyclic voltammetry. In Fig. 1, a complex current peak appeared at ca. 0.37 V in the

first anodic-going scan. This is accounted for by assuming initial nickel dissolution in the acid monomer solution and taking into account that the peak disappears in the third voltammetric cycle. Thus, in the very first steps of PANI synthesis, not only Ni partial dissolution occurs but also the polymeric film starts to grow. Proton concentration in the

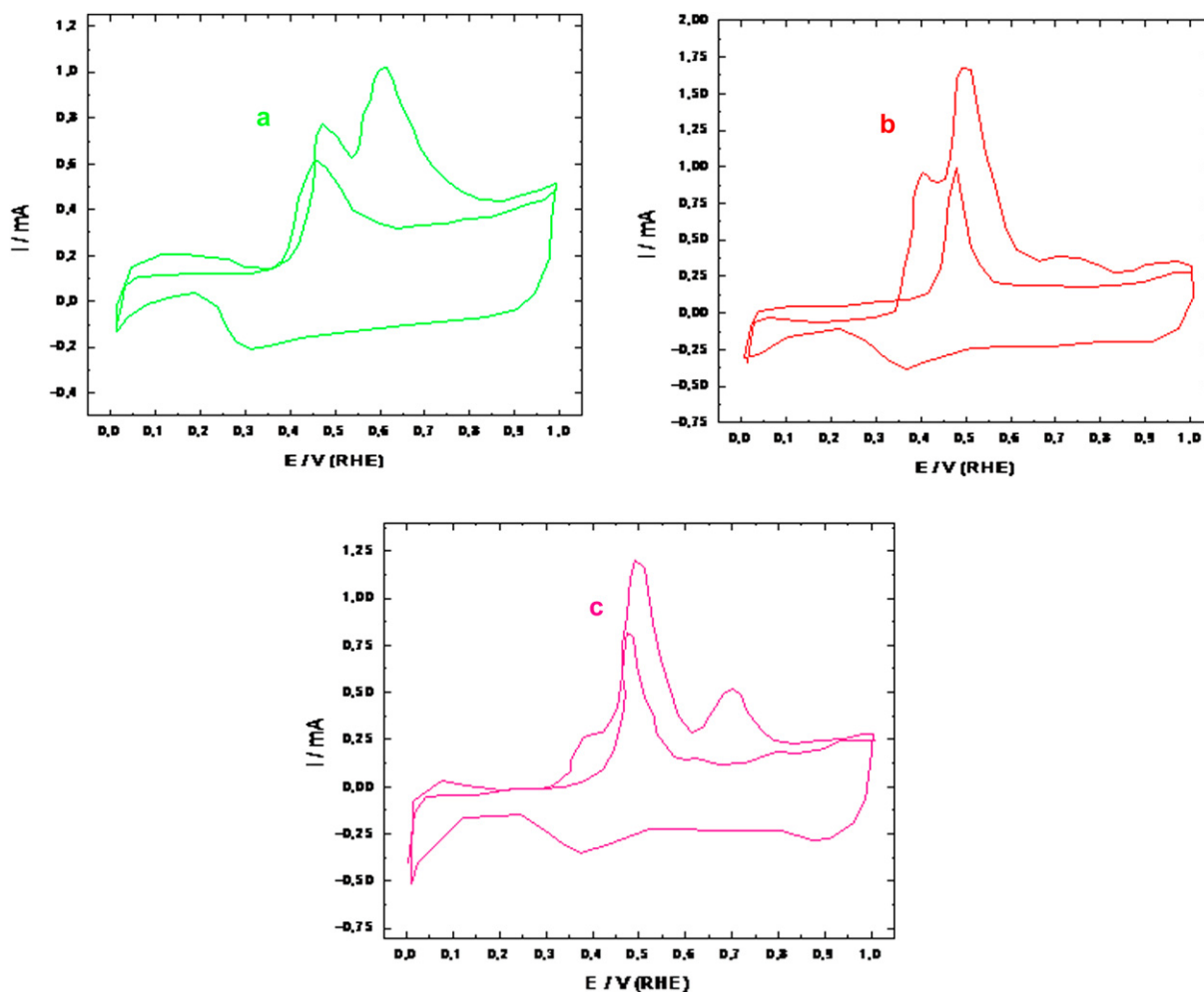


Fig. 5 – CO oxidation voltammograms on Ni/PANI/CNT/Pt-Ru electrodes prepared through the three routines. (a) Routine 1. (b) Routine 2. (c) Routine 3.

interface rises; this fact probably affects PANI chain protonation increasing the film conductivity and partial Ni dissolution also induces leucoemeraldine–emeraldine transition [10]. After 25-min cycling, an anodic current peak is clearly distinguished, which can be attributed to the leucoemeraldine/emeraldine pair.

The electrode substrate being an active metal and the addition of CNT to the monomer solution favor the growth of the anodic peak changing its potential as well. After 35-min cycling, the film thickness is 0.5  $\mu\text{m}$  and the anodic peak potential reaches 0.55 V.

### 3.2. Catalytic material deposit

The catalytic deposit was built at open circuit by controlling the electrode potential variation during the immersion in the metallic precursor solutions. A fast potential drop from 0.75 V to ca. 0.20 V in the first 4 min was observed; afterwards the potential value remained almost constant. This behavior is attained in the three routine experiments.

### 3.3. Characterization of the composite electrodes

In Figs. 2–4, SEM micrographs and EDX results are presented for the Pt–Ru deposits formed by applying routines 1, 2 and 3, respectively. The catalytic particles obtained through routine 1 are dispersed uniformly and present the smallest size in comparison to the other deposit routines.

The chemical composition expressed in weight percent of the catalytic metals depends on the deposit routine. When using the solution with both ions present (routine 1), a Pt:Ru 75:25 content relationship is established. When applying sequence 2 or 3, the Ru content is noticeably low.

CO electro-oxidation was recorded at 0.010  $\text{V s}^{-1}$ . In Fig. 5, the stripping voltammograms for the adsorbed CO and the following voltammetric cycles are shown for the composite electrodes Ni/PANI/CNT/Pt–Ru with catalytic material added through the three described routines.

For the three specimens, the CO peak potential lies in the 0.50–0.75 V range. In the case of electrodes obtained through routine 1, only one stripping peak is observed at 0.6 V. It can be attributed to CO oxidation on Pt–Ru particles. For routine 2, two peaks are distinguished at ca. 0.5 and 0.7 V and for routine 3, the peak at ca. 0.7 V is attributed to CO oxidation. It is important to highlight that intents to deposit Ru massively on PANI fail because the potential to deposit Ru(0) has to be shifted towards a region where PANI is nonconductive [5]. Consequently, for routine 3, a small Ru content is determined by EDX, and CO is adsorbed and oxidized on Pt sites.

When Pt is firstly deposited, a subsequent Ru deposit can be formed on Pt particles (routine 2). The voltammogram then shows two CO oxidation peaks attributed either to Ru or Pt sites.

## 4. Conclusions

- Pt–Ru particles can be deposited at open circuit on composite polymeric films (PANI + NTC) grown on nickel.
- CO oxidation occurs at different potentials according to the routine used in the spontaneous deposit.
- The dispersion of the catalytic material is better when applying routine 1 with the solution of both ions for Pt–Ru deposition in comparison to routines 2 and 3.

## Acknowledgements

The authors acknowledge financial support from UNLP, UNCPBA, CICPBA and CONICET. TK and AMCL are CICPBA researchers.

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