



# Pt–Ru polymeric electrocatalysts used for the determination of carbon monoxide

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## ABSTRACT

Different PtRu polyaniline composite catalysts were studied for the electro-oxidation of carbon monoxide (CO) in order to ascertain their response to the changes in CO bulk concentration in acid solutions. The catalyst substrate consisted of polyaniline films with incorporated carbon nanotubes grown over a Ni wire. To build the electrode, PtRu particles were added to the polymeric film by immersion at open circuit from a solution containing Pt(IV) and Ru(III). The concentration relationship  $R = [\text{Pt(IV)}]/[\text{Ru(III)}]$  was established fixing the Pt(IV) concentration and varying Ru(III) concentration in order to have  $0.5 < R < 5$ .

CO electro-oxidation in acid media was studied applying cyclic voltammetry and chronoamperometry, carefully controlling the amount of CO that flowed into the cell. A linear relationship was established between the CO oxidation current density and its concentration in solution for the catalyst prepared with lower R.

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## 1. Introduction

Conducting polymers are organic materials with a three-dimensional matrix and a porous structure, presenting unique properties that can be modified by the addition of carbon particles [1–3]. These composite polymeric materials have been used as support due to the high surface area available for the dispersion of the catalytic material [4,5]. Platinum and its combinations with ruthenium are known as the most active catalysts for the oxidation of carbon monoxide (CO) [6–9]. Their superior electrocatalytic activity has been explained through the so-called bifunctional mechanism in which adsorbed CO is oxidized at lower potentials on Pt–Ru materials due to its reaction with adsorbed OH species provided by Ru sites [10,11]. Another interpretation suggests that there is a modification of the Pt electronic structure due to the presence of Ru and a weakening of the adsorption strength of CO on Pt atoms [12,13].

As carbon monoxide is a toxic gas, its accurate determination is crucial to guarantee safe environmental conditions to human beings. In this sense, electrochemical sensors are usually prepared with metal oxides in the so-called solid electrolyte based sensors, to be applied when working with gas streams at temperatures greater than 400 °C [14]. Moreover, catalytic materials can be selected from materials for methanol fuel cells, as CO is an intermediary specie in methanol oxidation process [15,16]. In particular, a sensor has been developed based on carbon nanotube self-assembled Pt-microelectrodes [17].

To build an electrochemical CO sensor, three main points must be fulfilled, i) firstly, the device has to detect CO (*specificity*); (ii) secondly,

different amounts of CO must be determined (*sensitivity*); (iii) thirdly linear relationships must be established, i.e. between the CO oxidation current density and the CO concentration (*linearity*).

The aim of the present paper is to describe the preparation steps of a suitable composite material to be used in the electrochemical detection of carbon monoxide, namely polyaniline (PANI) films containing trapped carbon nanotubes (CNTs) with dispersed catalytic metals. Thus, the behavior of electrosynthesized polymeric Pt–Ru catalysts was studied for the oxidation of CO, evaluating their response to changes in the gas bulk concentration in acid solutions.

## 2. Experimental details

### 2.1. Equipments and materials

The electrochemical equipment consisted of a potentiostat PAR 273 with a ramp function generator Lorenzo Y Paus and a recorder Houston X-Y. A conventional three-electrode thermostated cell was used and the experiments were carried out at 25 °C. The counter electrode was a large Pt sheet and the reference electrode was Ag/AgCl. All potential values in the text are referred to the reversible hydrogen electrode (RHE).

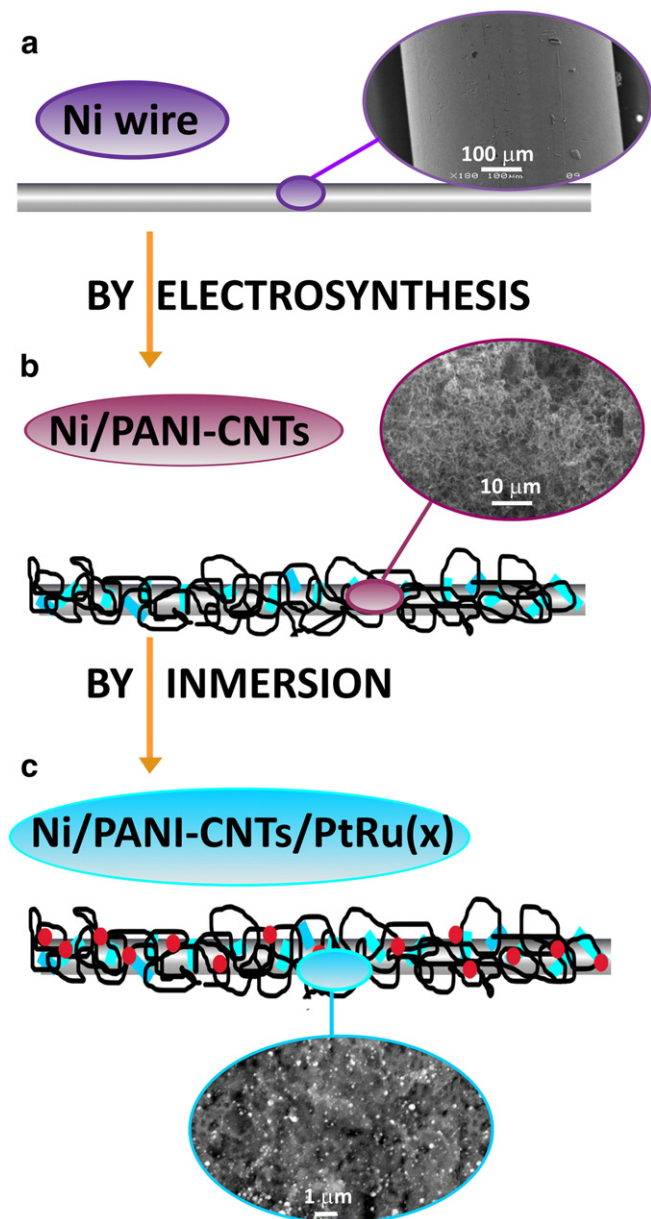
The working electrode was a nickel wire on which the polymeric catalyst was built through a two-steps process (Fig. 1). Firstly, the PANI-CNTs film was grown by electrosynthesis and secondly, Pt–Ru particles were dispersed by immersion onto the composite polymeric film.

CNTs were synthesized in our lab from graphite by thermal treatment at 1200 °C using AgNO<sub>3</sub> as catalyst [2]. They were characterized by Scanning electron microscopy (SEM), Transmission electron microscopy, X-ray diffraction and Fourier transform infrared spectroscopy,

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**Fig. 1.** Schematic representation of the electrocatalysts preparation. (a) Bare Ni wire. (b) Ni wire covered by the composite PANI-CNTs. (c) As (b) with dispersed PtRu particles.

being ca. 15 μm length and 40 nm in external diameter. Previous to their use, they were chemically treated with 2.2 M HNO<sub>3</sub> during 20 h to generate surface oxygenated groups, especially carboxylic species [18].

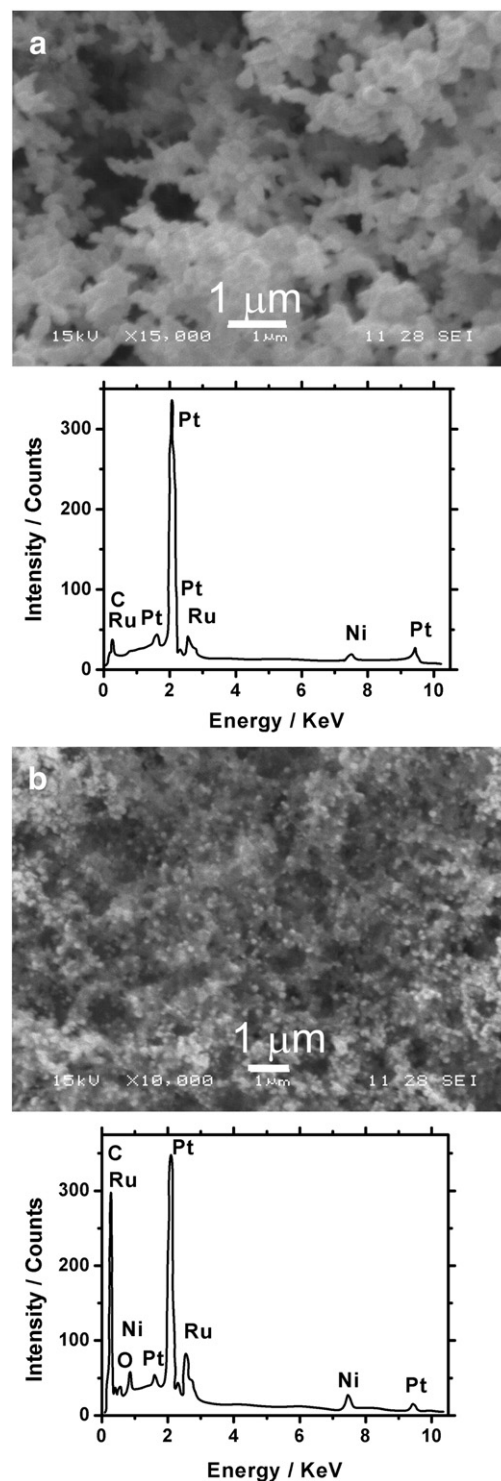
## 2.2. Preparation of the composite PANI-CNT films

PANI films were built up on a Ni wire of ca. 0.08 cm<sup>2</sup> geometric area by electropolymerization, using as electrolyte in the electrochemical cell a solution containing 0.1 M aniline + 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.1 mg mL<sup>-1</sup> CNTs (Fig. 1). The composite film was grown by cyclic voltammetry varying the potential between 0 V and 0.90 V at 0.1 V s<sup>-1</sup>, controlling its thickness up to 0.5 μm. The film thickness was computed by integrating the total anodic charge involved between 0.0 V and 1.20 V of the anodic linear potential sweep at 0.10 V s<sup>-1</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub> assuming that a charge of 1 mC cm<sup>-2</sup> corresponds to a thickness of 4.4 nm, according to Park [19,3]. The established 0.5 μm film thickness guarantees its mechanical stability for nearly fifty CO electrooxidation runs, since the electrochemically determined active surface area remained

constant. When using higher thicknesses, the composite film fell off the metal substrate.

## 2.3. Dispersion of the PtRu particles

The catalytic particles, Pt and Ru, were distributed onto the PANI-CNT composite film by immersion at open circuit in a 0.05 M H<sub>2</sub>PtCl<sub>6</sub> + x M RuCl<sub>3</sub> + 0.1 M HCl solution for 15 min (Fig. 1). The concentration relationship  $R = [\text{Pt(IV)}]/[\text{Ru(III)}]$  was established by fixing



**Fig. 2.** SEM images and EDX spectra of (a) Ni/PANI-CNTs/PtRu(5) and (b) Ni/PANI-CNTs/PtRu(0.5) electrodes.



the Pt(IV) concentration and varying Ru(III) concentration in 0.1 M and 0.01 M in order to have a ratio value  $R$  of 0.5 and 5, respectively.

The preparation steps of the composite catalytic electrode are presented in Fig. 1. Ni is the primary substrate on which the composite polymeric film is grown (Fig. 1a); PANI-CNTs stands for the electrosynthesized composite film (Fig. 1b) and PtRu are the catalytic particles added at open circuit by immersion (Fig. 1c). The expression Ni/PANI-CNTs/PtRu( $x$ ) represents the polymeric electrocatalyst, where  $x$  corresponds to the value of the precursors' concentrations relationship,  $R$ .

#### 2.4. Characterization methods

Scanning electron microscopy (SEM, Jeol JSM-6460LV) and energy dispersive X-ray spectroscopy (EDX, EDAX Genesis XM4-Sys 60) operated at 15 kV were used to characterize the composite electrodes; EDX chemical analysis dot maps were also obtained in order to examine the distribution of the different components.

CO electrooxidation was studied through electrochemical methods, namely stripping voltammetry and chronoamperometry. The stripping voltammograms were run at  $0.01 \text{ V s}^{-1}$ , after CO adsorption at  $0.05 \text{ V}$  from a CO-saturated  $0.5 \text{ M H}_2\text{SO}_4$  solution for 20 min, and subsequent bubbling of  $\text{N}_2$  for 10 min. Chronoamperometric measurements were utilized to determine the quasi-steady state current for different CO concentrations in the acidic solution. An experimental routine was applied to reach  $0.65 \text{ V}$ , the CO oxidation potential. The routine sequence was as follows: firstly, CO– $\text{N}_2$  gas mixtures with different CO concentrations were bubbled into the cell solution at open circuit for 3 min; secondly, the potential was held at  $E = 0.05 \text{ V}$  for 7 s in order to achieve an equilibrium coverage of the active surface and to ensure initial steady-state conditions for each CO concentration. The potential was then rapidly changed to  $0.65 \text{ V}$  to oxidize all CO species. At this potential value, the variation of the CO electrooxidation current intensity with time was recorded for the CO concentration in solution. Different CO concentrations were tested varying from 3 to  $25 \mu\text{g CO L}^{-1}$  range. Current density values vs CO bulk concentrations were then graphically presented to determine a linear relationship. The current density values are referred to active areas determined by considering the anodic charge involved in the CO-anodic stripping peak and taking into account that  $420 \mu\text{C}$  is equivalent to  $1 \text{ cm}^2$  [20].

### 3. Results and discussion

#### 3.1. Characterization of the electrocatalysts

Ni/PANI-CNT/PtRu electrodes were prepared as described in the experimental section adding the catalytic particles from precursor solutions with  $R$  of 5 and 0.5. Fig. 2a,b shows SEM micrographs and EDX spectra for both types of catalysts. When the Ru(III) concentration was low, leading to  $R = 5$  solution, EDX composition of the catalyst was 95 at.% Pt and 5 at.% Ru (Fig. 2a), providing a considerably good particle dispersion. On the other hand, when using  $R = 0.5$  solution, a more uniform catalyst distribution with ca. 100 nm particle size is obtained (Fig. 2b). In this case, the catalyst composition was 81 at.% Pt and 19 at.% Ru.

Fig. 3 depicts the EDX digital X-ray dot maps showing the distribution of the most important components of the electrodes, specifically Ni, C, Pt and Ru of Ni/PANI-CNTs/PtRu(5) and Ni/PANI-CNTs/PtRu(0.5) electrodes. Particular distribution patterns can be pointed out for Pt and Ru in relation to the constituents of the substrate. Thus, when comparing the figures, the distribution of Pt dots matches the pattern of Ni dots, and the Ru dot map agrees with the one displayed by C.

The coincidence of Pt–Ni dots can be explained by considering that Ni dissolution is the driving force for the Pt spontaneous deposition process [2]. Thus, in the early steps of the electropolymerization process, Ni wire is dissolved in the acidic electrolyte media and became trapped in the polymeric matrix inducing Pt deposition onto those Ni sites [2]. On the other hand, as the Ru spot distribution is similar to the one displayed for carbon, a preference of the Ru particles for the carbon sites in the composite polymeric configuration can be envisaged, considering the total C positions corresponding to the PANI matrix and the ones of the functionalized carbon nanotubes trapped in the electrosynthesized film. In this sense, it can be mentioned that for Pt–Ru nanoparticles obtained from Pt–Ru–C cluster precursors and supported on carbon, it was suggested the formation of a Ru–C compound [21]. Moreover, the presence of RuOH species could also interact with the carbon particles of the support [22].

Furthermore, when overlapping the Pt and Ru distributions, some spots of both components are located at the same place; this fact can be associated with the presence of PtRu particles. In the sketch of Fig. 1c, Pt, Ru and PtRu catalytic particles are symbolized by dots localized in and onto the composite film.

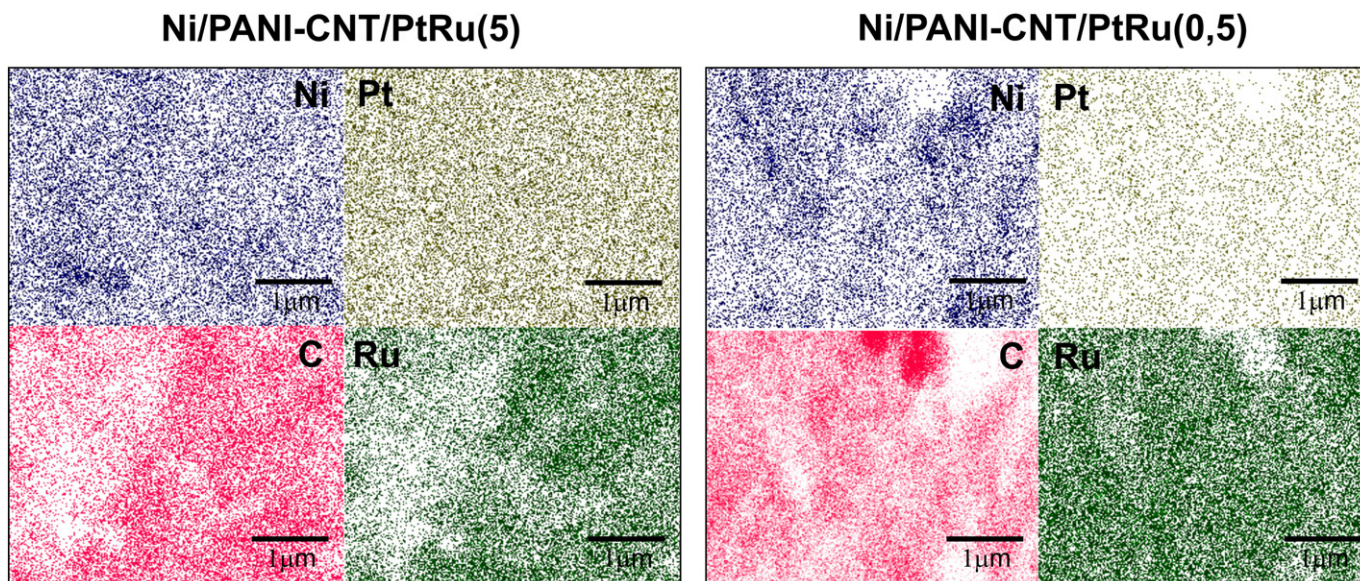


Fig. 3. EDX chemical analysis dot map figures showing Ni, Pt, C and Ru distribution of Ni/PANI-CNTs/PtRu(5) and Ni/PANI-CNTs/PtRu(0.5) electrodes.

### 3.2. CO electro-oxidation from saturated solutions

CO-electrooxidation was studied by voltammetry in a CO free-solution. The CO stripping voltammograms corresponding to the oxidation of adsorbed CO from a saturated acid solution at 0.05 V are shown for Ni/PANI-CNT/PtRu(5) and Ni/PANI-CNT/PtRu(0.5) electrodes in Fig. 4. The experimental routine ensures that the dissolved CO gas was swept away from the solution before the stripping run by N<sub>2</sub> gas bubbling.

The major activity of the Ni/PANI-CNT/PtRu(0.5) electrode can be attributed to the superior dispersion of the nanosized Pt–Ru particles that determine the position of CO<sub>ads</sub>–OH<sub>ads</sub> reactive pairs according to the bifunctional oxidation mechanism [10]. In this sense, reported infrared spectroscopy data have shown that the surface structure of the CO adlayer differs if the electrode is Pt, Ru or Pt–Ru, indicating either the formation of a compact adlayer when the electrodes are made of pure metals or a loose adlayer when a Pt–Ru alloy is used [23]. Other parameters, such as particle size and/or the addition of carbon nanoparticles onto polyaniline films [17] enhance the electrode activity towards CO oxidation.

Fig. 5 shows the current density vs. time curves for the CO oxidation from saturated solutions for Ni/PANI-CNTs/PtRu(5) and Ni/PANI-CNTs/PtRu(0.5) catalysts measured at the CO peak potential of each electrode, 0.69 V and 0.60 V, respectively. In the first few seconds, a fast decrease is observed and then the current density decays steadily reaching constant values after ca. 60 s. This behavior was explained as a first step corresponding to the oxidation of a high CO covered surface followed by a transition to a final steady state for the adsorption–oxidation

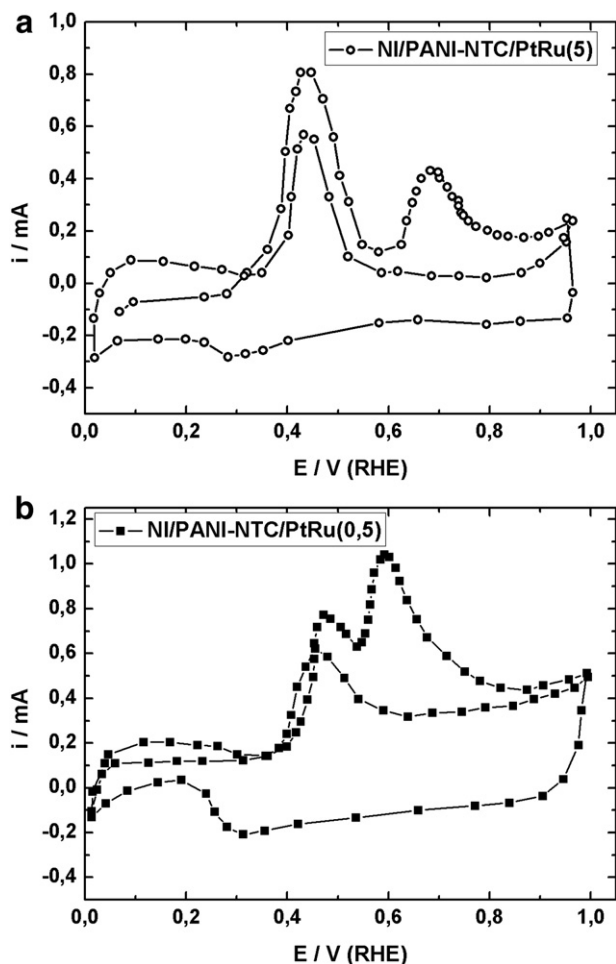


Fig. 4. CO-stripping voltammograms of (a) Ni/PANI-CNTs/PtRu(5) and (b) Ni/PANI-CNTs/PtRu(0.5) electrodes in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> recorded at 0.010 V s<sup>-1</sup>.

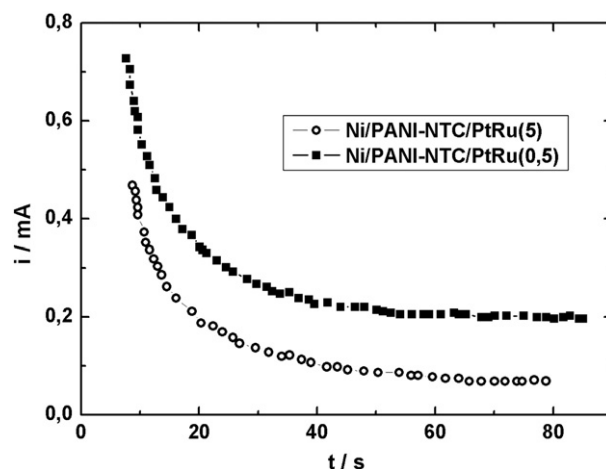


Fig. 5. Chronoamperometric runs for CO electrooxidation on Ni/PANI-CNTs/PtRu(5) and Ni/PANI-CNTs/PtRu(0.5) electrodes in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>.

process [24]. The highest current density value corresponds to the catalyst prepared from R = 0.5 precursor solution, providing these electrodes the improved potential values for the electrooxidation process.

In order to fix the potential value for the sensitivity measurements, chronoamperometric runs were recorded at different potential values in the 0.50–0.70 V potential range, with CO saturated solutions employing the Ni/PANI-CNTs/PtRu(0.5) catalyst. The largest current density value corresponds to 0.65 V.

### 3.3. Sensitivity to CO concentration changes

As Ni/PANI-CNT/PtRu(0.5) electrodes presented the best behavior in CO-saturated solutions, this catalyst was probed for the sensitivity measurements. Chronoamperograms were recorded at 0.65 V with CO bulk concentration ranging from 3 to 25 μg CO L<sup>-1</sup>.

The relationship between the current density values after 60 s and CO concentration is represented in Fig. 6, with a linear correlation fit. These results indicate that the composite polymeric catalysts are promising candidates for recognition and detection of CO gas.

## 4. Conclusions

Composite polymeric films were prepared by electrosynthesis from solutions containing aniline and functionalized carbon nanotubes. The catalytic material, Pt and Ru particles, was added onto the polymeric film by immersion in the precursors solution at open circuit. The

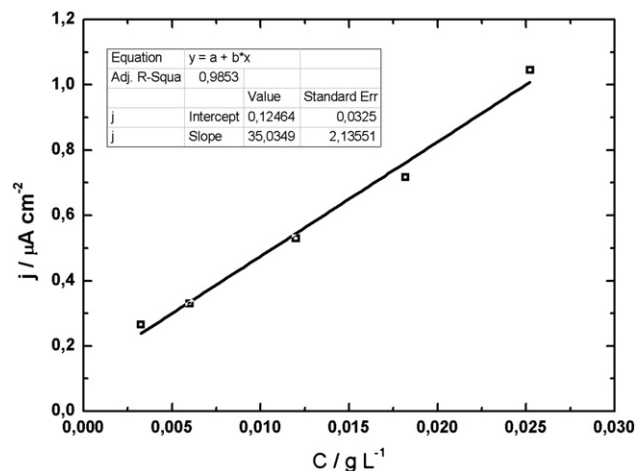


Fig. 6. Relationship between the stabilized current density and the CO bulk concentration for Ni/PANI-CNTs/PtRu(0.5) electrode.

relationship between Pt(IV) and Ru(III) concentrations in the precursor solution determines the dispersion and size of the catalytic particles. There is a better dispersion of smaller particles for the catalysts prepared from solutions with  $R=0.5$ . These composite catalysts presented an improved catalytic activity for the CO oxidation reaction, compared to the other developed catalysts. Moreover, the relationship between the oxidation current and the bulk concentration of CO is linear.

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