



Preparation and characterization of composite polyaniline materials for catalytic purposes

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ARTICLE INFO

Article history:

Received 15 April 2008

Accepted 20 May 2008

Available online 24 June 2008

Keywords:

Carbon nanoparticles

Polyaniline

Platinum

Nichrome

Carbon monoxide

Methanol

ABSTRACT

Composite film electrodes were prepared by open-circuit Pt deposition on polymeric PANI films that were electrosynthesized from aniline acid solutions with suspended carbon particles (CPs). Gold, nickel, and a Ni-based alloy, Nichrome, were used as substrates, and carbon particles, carbon nanotubes (CNT), and Vulcan XC-72R carbon black, suspended in the monomer acid solution, were incorporated into the film. Pt particles were dispersed on films grown on Ni-based substrates by deposition from a Pt(IV) acid solution at open circuit (OC). CNT trapped into the PANI films have a favorable influence on Pt dispersion. The novel composite electrodes showed significant catalytic activity for methanol oxidation.

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1. Introduction

New conductive materials have been explored in the past decades as suitable matrices to disperse catalytic materials. Among the conducting polymers, polyaniline (PANI) has been extensively studied due to its potential applications as a substrate for environmental sensors of polluting gases and catalyst support in fuel cells [1–7]. PANI films with a three-dimensional structure can be grown easily on different metal substrates by applying electrochemical methods [8–12].

Different carbon particles (CPs) are widely used in electrochemistry because they fulfill the conditions imposed on electrode materials; i.e., they are capable of accumulating an electric charge and have good electrical and thermal conductance and a large inner area [13–15]. Thus, Vulcan XC-72R powder is commonly used as a support for catalytic material in fuel cell technology [16].

Since the 1960s, novel carbon structures have been developed, stimulating numerous researches in order to establish their practical and potential applications [15,16]. Carbon nanotubes (CNT) are new members of the carbon family with exceptional physicochemical properties; according to their structure, they can be present as multiwall and single-wall carbon nanotubes [17,18]. Their electronic properties and atomic arrangement let them behave as a metal or as a semiconductor, and they can be used to fabricate electrodes with outstanding properties. In this respect, it has been

reported that the incorporation of single-wall carbon nanotubes into an acid aniline aqueous solution accelerates the growth rate of PANI [19]. Different chemical and electrochemical ways to decorate polymer substrates with catalytic material have been described in the literature [4,20–25]. The composition, particle size, and dispersion grade of the catalysts on a proper substrate have to be controlled carefully to increase the use of noble metals for practical applications.

The aim of this work is to study the synthesis of composite electrodes (PANI/CPs/Pt) on different substrates and to evaluate their electrocatalytic behavior for methanol oxidation.

2. Materials and methods

A conventional three-electrode cell was used. The working electrode was a gold, Ni, or Ni-alloy wire on which PANI composite films containing CPs and dispersed Pt particles were built and physically and electrochemically characterized. The counterelectrode was a large Pt sheet and the reference electrode was a Ag/AgCl electrode. All potentials in the text are referred to the reversible hydrogen electrode (RHE). The experiments were carried out at room temperature.

2.1. Preparation of the composite films

The preparation routine comprised two steps: (i) PANI film formation, either from the pure monomer solution or with the addition of different suspended carbon particles, and (ii) Pt deposition on the composite film.

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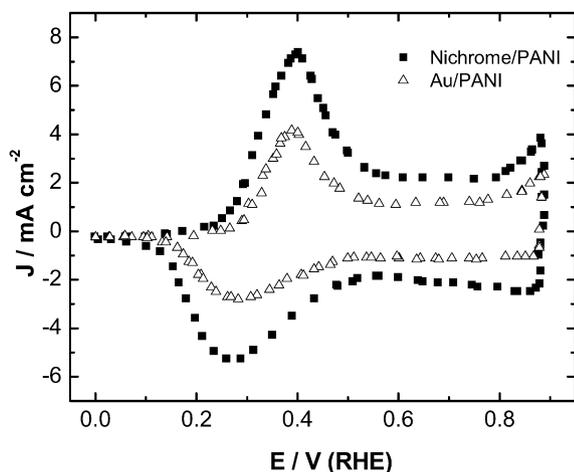


Fig. 1. Cyclic voltammograms of Au/PANI and Nichrome/PANI electrodes in 0.5 M H_2SO_4 , after a 50-min polymerization time, $\nu = 0.100 \text{ V s}^{-1}$.

PANI films were built up on wires of geometric area ca. 0.1 cm^2 by cycling the potential between 0.0 and 0.90 V at 0.10 V s^{-1} in a 0.1 M aniline + 0.5 M H_2SO_4 solution. The film thickness, between 0.04 and $0.3 \mu\text{m}$, was calculated from the anodic charge involved between 0.0 and 1.20 V in the voltammogram, recorded at 0.10 V s^{-1} in 0.5 M H_2SO_4 [4].

The PANI/CP films were grown under the same experimental conditions, but adding 0.1 mg ml^{-1} of different CPs to the 0.1 M aniline + 0.5 M H_2SO_4 solution. CPs such as multiwall CNT and Vulcan XC-72R were employed. Before electropolymerization, the resulting suspension was stirred in an ultrasonic bath to minimize agglomeration. The CNTs were synthesized from graphite by thermal treatment at 1200°C . When CNTs were used, they had been previously treated as described elsewhere, using nitric acid as oxidizing agent for different times to create surface oxygen groups, especially carboxylic groups [26]. PANI and PANI/CP films were decorated with Pt particles by open-circuit (OC) deposition, after contact with a 0.05 M H_2PtCl_6 + 0.1 M HCl solution, for different immersion times, t_i ($60 \text{ s} \leq t_i \leq 600 \text{ s}$).

2.2. Physical and electrochemical characterizations

The composite electrodes were characterized by scanning electron microscopy, SEM. Their chemical composition was analyzed by energy dispersive X-ray analysis, EDX.

Real areas were determined by considering the anodic charge involved in the CO-stripping peak by assuming that CO is linearly adsorbed on one Pt site and taking into account that $420 \mu\text{C}$ is equivalent to 1 cm^2 . The CO stripping voltammogram was run at 0.01 V s^{-1} , after CO adsorption at 0.05 V from a CO-saturated 0.5 M H_2SO_4 solution for 10 min, and subsequent bubbling of N_2 for 10 min.

Methanol oxidation was studied in 0.5 M H_2SO_4 + 0.5 M CH_3OH solution by cyclic voltammetry at 0.01 V s^{-1} in the potential range from 0.05 to 0.8 V. Chronoamperometric measurements were also recorded at 0.65 V. The current densities are referred to the CO calculated real area.

3. Results and discussion

3.1. Effect of the substrate and the added CPs on the film growth rate during the PANI polymerization process

PANI films were electrochemically grown on Au and on Ni and Nichrome. It was found that, for a constant polymerization time,

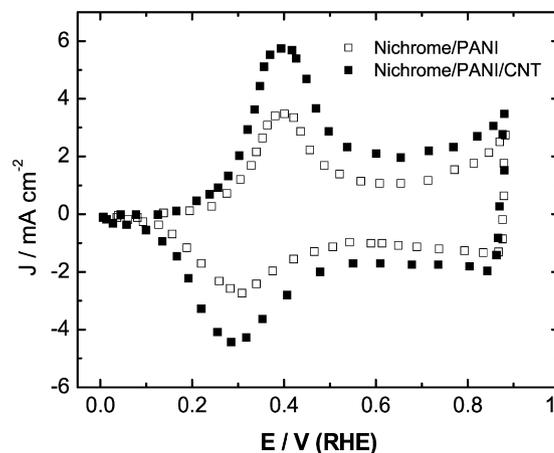
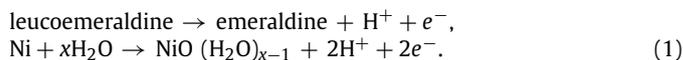


Fig. 2. Cyclic voltammograms of Nichrome/PANI electrodes in 0.5 M H_2SO_4 , with and without CNT, after a 35-min polymerization time, $\nu = 0.100 \text{ V s}^{-1}$.

polymer films are thicker on Ni and Ni-based alloy than on Au substrates. The cyclic voltammograms of PANI films grown during the same polymerization time on Au and Nichrome substrates are shown in Fig. 1. Both voltammograms show a noticeable anodic peak at ca. 0.43 V, which corresponds to the oxidation of leucoemeraldine to emeraldine, and a cathodic one at ca. 0.30 V attributed to leucoemeraldine reduction [8]. The participation of Ni in the polymerization process is envisaged. During the electropolymerization, aniline adsorption onto the Ni-containing wires prevents massive Ni oxidation. However, on a covered Ni/PANI electrode, Ni dissolution is even possible during the oxidation of leucoemeraldine to emeraldine, as the value of $E_{0\text{Ni}^{2+}/\text{Ni}}$ is -0.23 V versus NHE [27,28].

A reaction scheme of the processes is



From Eq. (1), an increase in the local concentration of protons is evident, which probably promotes the ionization of the PANI chains, increasing the conductivity of the matrix. The abundance of free electrons also contributes to the delocalization of π -bonding electrons on the polymer [27]. As the polymerization process is accomplished by cyclic voltammetry, NiO, a product according to Eq. (1), is partially converted into Ni(0) during the electroreduction of emeraldine. Consequently, Ni clusters can be dispersed into the PANI matrix.

It has also been observed that the addition of CPs to the monomer acid solution increases the PANI formation rate. In this respect, experiments carried out on the same substrate, under almost the same conditions with and without CP addition, are shown in Fig. 2. The presence of surface oxygen groups in the CNTs, after their chemical treatment, can enhance hydrophilicity and therefore facilitate the access of the electrolyte to the internal pore structure, increasing the effective accessible surface area of the polymer films.

On Au or Ni-based alloy substrates, PANI films with added CPs grow faster. It is highly possible that CPs supply nuclei to begin the polymerization process and/or participate in a charge-transfer couple formation that promotes PANI growth [19,29].

3.2. Pt deposition

Pt deposition at open circuit is achieved on PANI films grown on Ni and Ni-based alloy wires by immersion of PANI and PANI/CP films in the chloroplatinic acid solution. The open-circuit potential

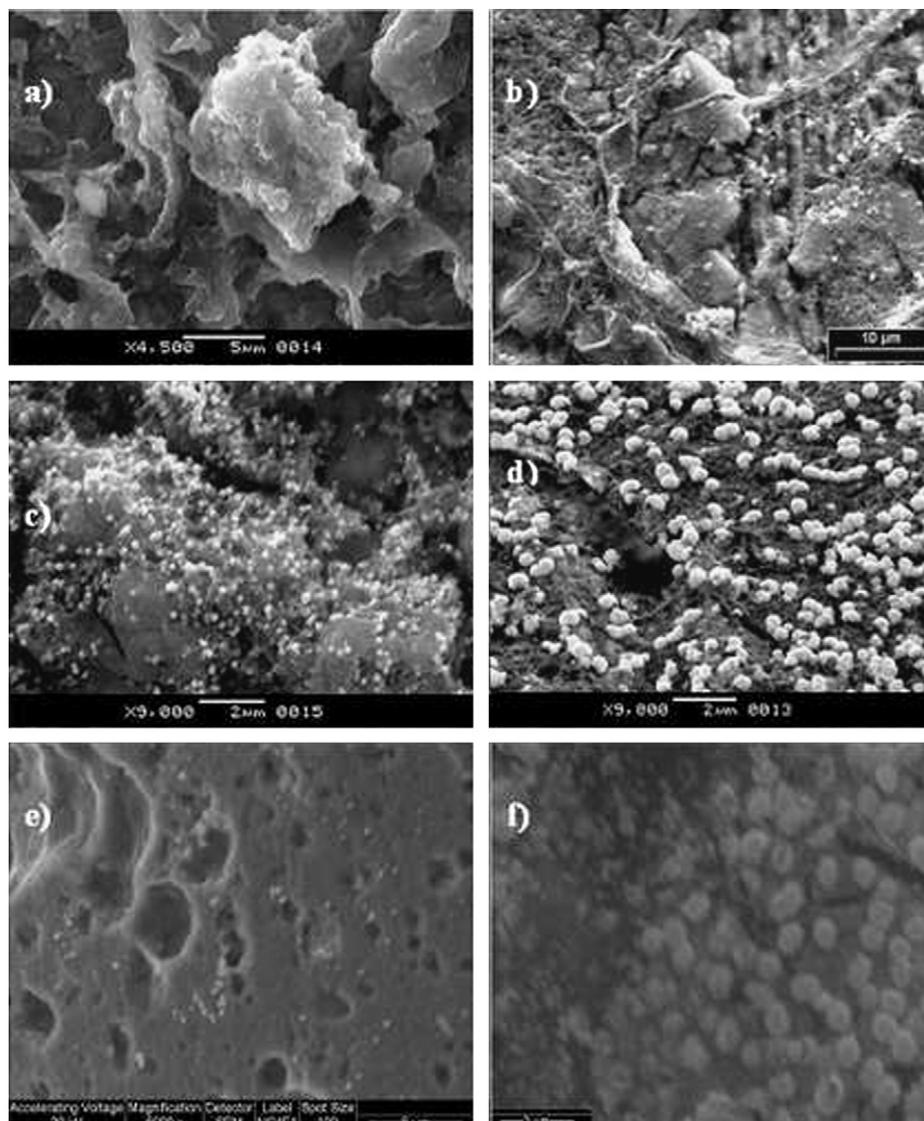


Fig. 3. SEM micrographs for different polymer-based electrodes, obtained after different times at OC in Pt(IV) solution: (a) Ni/PANI/Pt, $t = 100$ s; (b) Ni/PANI/Vulcan/Pt, $t = 100$ s; (c) Ni/PANI/CNT/Pt, $t = 60$ s; (d) Ni/PANI/CNT/Pt, $t = 100$ s; (e) Nichrome/PANI/CNT/Pt, $t = 300$ s; (f) Nichrome/PANI/CNT/Pt, $t = 600$ s.

of the composite electrodes, initially at ca. 0.7 V, decays rapidly to ca. 0.1 V. Novel metal deposition can be attributed to the dissolution of Ni underneath the polymeric film acting as driving force.

SEM micrographs of Ni or Nichrome/PANI/Pt, for a film thickness of 0.2 μm , are shown in Fig. 3. In Fig. 3a the micrograph of composite Ni/PANI/Pt clearly exhibits the uneven distribution of Pt crystallites on the film. However, the composite Ni/PANI/Vulcan/Pt, Fig. 3b, shows an improved crystallite distribution. Nanosized Pt agglomerates are observed on PANI/CNT/Pt (Figs. 3c, 3d) for two different Pt deposition times (60 and 100 s). It is believed that the carboxylic groups from treated CNT will have the strongest influence on Pt dispersion for application of these materials in electrocatalysis. When the composite consisted of Nichrome/PANI/Pt grown with or without CNT, a higher Pt scattering in the film was achieved on films with CNT. In Figs. 3f and 3g two different immersion times are shown. It is evident that the addition of CNT to the polymeric matrix grown on Ni or Nichrome facilitates a more uniform distribution of Pt nanoparticles on the film.

Under the same experimental conditions, when Au is the substrate, no open-circuit Pt deposition is possible.

3.3. Electrocatalytic characterization of composite electrodes

3.3.1. Adsorbed CO oxidation

The oxidation of adsorbed CO on Ni-based composite electrodes was recorded at 0.010 V s^{-1} . The CO stripping voltammogram with Ni/PANI/CNT/Pt and Ni/PANI/Vulcan/Pt electrodes is shown in Fig. 4. The CO stripping voltammogram is recorded after the potential is held for 10 min at 0.05 V. When conducting polymers are held at a potential value in their insulating state for some time, the voltammetric profile during the first positive-going half cycle differs from the steady-state profile. The peak features (potential E_p , ca. 0.4 V, current density J , etc.) depend on the time spent in the insulating state. This effect is called the first-cycle effect, or “slow relaxation” [30]. Some researchers have attributed this effect to the incomplete reduction of the polymer. The complete reduction of the polymer is a relatively slow process that depends on the external proton concentration and the film thickness. The rate of this process should be related to proton entrance into the film and to the subsequent ionic equilibrium within the polymer phase. The onset oxidation potential of CO shifts toward lower values when the electrode is Ni/PANI/CNT/Pt. The CO oxidation peak is set at 0.8–0.9 V.

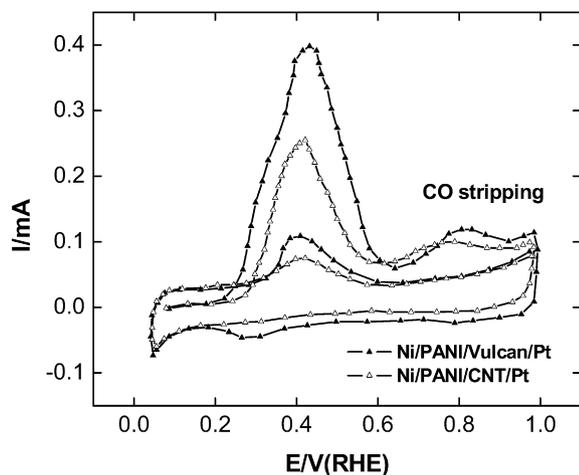
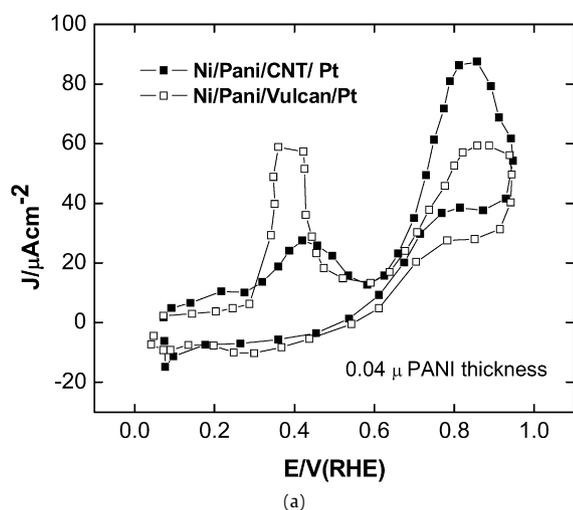
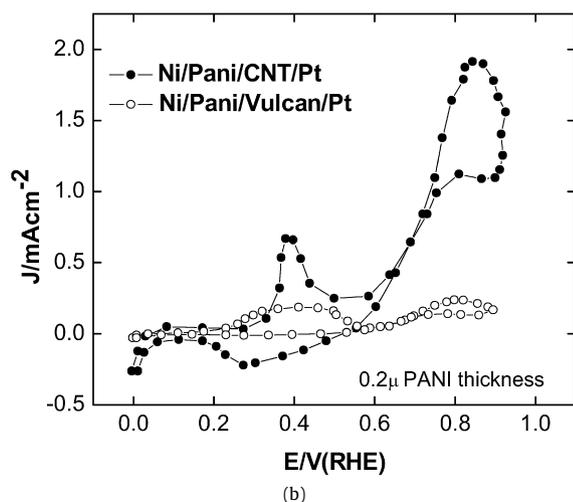


Fig. 4. CO stripping recorded at $v = 0.010 \text{ Vs}^{-1}$ in $0.5 \text{ M H}_2\text{SO}_4$.



(a)



(b)

Fig. 5. Cyclic voltammograms of Ni/PANI/CP/Pt electrodes with two different film thicknesses in $0.5 \text{ M CH}_3\text{OH} + 0.5 \text{ M H}_2\text{SO}_4$ at $v = 0.010 \text{ Vs}^{-1}$.

3.3.2. Methanol oxidation

The catalytic activity toward methanol electro-oxidation was evaluated by employing cyclic voltammetry, starting from 0.05 V . The voltammetric oxidation of methanol on two Ni/PANI/CP/Pt electrodes with different PANI thickness is shown in Figs. 5a and 5b. Irrespective of the PANI thickness, PANI/CNT/Pt showed the best performance. The fact that higher methanol oxidation current

Table 1

Oxidation current density values after 10 min at $E = 0.65 \text{ V}$, in $0.5 \text{ M CH}_3\text{OH}$

Electrode	Thickness (μm)	Area (cm^2)	J (μAcm^{-2})
Ni/PANI/CNT/Pt	0.04	2.9	3.5
Ni/PANI/Vulcan/Pt	0.02	2.89	0.7
Ni/PANI/CNT/Pt	0.23	0.7	85
Ni/PANI/Vulcan/Pt	0.26	1.66	15

densities are obtained on thicker PANI films can be understood, considering that now many Pt nuclei turn into small Pt clusters, providing better catalyst dispersion and consequently a greater catalytic area for methanol oxidation. Besides, thicker PANI films prevent Ni substrate dissolution better.

Chronoamperometric measurements in $0.5 \text{ M CH}_3\text{OH}$ were performed at 0.65 V with different composite electrodes constructed on Ni. The methanol oxidation current densities measured after 10 min are shown in Table 1. The most stable I versus t profile and the highest current intensity are recorded with PANI/CNT/Pt.

The good performance of the PANI/CNT/Pt composite electrodes in comparison to PANI/Vulcan/Pt films is the result of the better Pt dispersion on the PANI film prepared by adding CNT.

4. Summary

Ni, Ni-based alloy, Nichrome, wires were used as substrate to assemble new composite polymer-based electrodes, having a fundamental effect not only on the film assembly but also on the subsequent metal deposition process.

Open-circuit Pt particle deposition is possible on PANI films grown on Ni and Ni-based alloy.

Pt particles are smaller and better dispersed when the polymeric matrix contains carbon nanotubes.

The electrode materials developed with the incorporation of CNT yield effective methanol electrocatalysts.

Acknowledgments

The authors are grateful to the Comisión de Investigaciones de la Provincia de Buenos Aires (CIC), CONICET, UNLP, and UNCPBA for financial support. T.K. and A.M.C.L. are members of the research career at CIC.

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