

Spontaneous Platinum Deposition on Polyaniline Films with Trapped Carbon Nanotubes

Marcela A. Bavio¹, Teresita Kessler¹ and Ana M. Castro Luna^{*2}

¹Facultad de Ingeniería, Universidad Nacional del Centro de la Provincia de Buenos Aires, Avda. Del Valle 5737 (7400) Olavarria, Buenos Aires, Argentina

²INIFTA-Facultad de Ciencias Exactas-UNLP, Diag.113 y 64 (1900) La Plata, Buenos Aires, Argentina

Abstract: A polyaniline film (PANI) with incorporated carbon nanotubes (CNTs) was used as substrate to prepare composite platinum electrodes. The polymeric film was grown electrochemically on Nichrome and gold wires from the monomer acid solution with suspended carbon nanotubes. Later, Pt catalytic particles were distributed onto the film by spontaneous deposition varying the deposition time. The results show that the codeposited CNTs significantly influence not only the amount but also the dispersion of the Pt particles. Methanol oxidation was chosen as model reaction to test the catalytic properties of the Pt composites. It was found that those with carbon nanotubes show better catalytic performance.

Keywords: Polyaniline, Spontaneous deposition, Methanol oxidation.

1. INTRODUCTION

New energy systems, namely fuel cells, have special constraints to be efficient arrangements and to lessen contamination problems. In this respect, metallic supported catalysts have to be properly distributed on adequate base materials. These substrates can be either carbon materials or tridimensional structures such as conducting polymers. Polyaniline (PANI) films have been studied extensively because this polymer is easy to synthesize electrochemically and has an outstanding capacity to undergo reversible switching between insulating (leucoemeraldine) and conducting (emeraldine) forms. The application of PANI as substrate to anchor well-dispersed catalytic particles of Pt or Pt-Ru for methanol oxidation reaction has been reported [1-4]. However, this polymer film application in long-term operation systems has failed because some problems related to its porous morphology and its low electron conductivity have to be solved [5].

The possibility of synthesizing polymeric films including carbon nanotubes (CNTs) in their structure has attracted great interest in recent years, since the incorporation of these carbon particles with their unique physicochemical and mechanic properties into PANI can result in tailored composite materials with enhanced characteristics [6,7]. Moreover, a better catalyst-carbon interaction can be achieved by increasing the number of oxygenated surface species on the carbon particles. The generation of functional groups on the carbon surface can be achieved, among others methods, through chemical oxidation treatments. Thus, CNTs enlarge the amount of oxygenated organic group on their surface after treatment with concentrated HNO₃ acid [8,9]. Different ways were proposed to add Pt as catalyst particles spread on the substrate such as electrochemical deposition, either under

potentiostatic conditions [10] or by applying cycling routines [11], and spontaneous deposition [12,13].

The aim of this work is to report about the preparation of PANI-CNT/Pt composite films varying the catalyst charge by controlling the time of the Pt spontaneous deposition process. These electrocatalysts were tested for the electrooxidation of methanol.

2. MATERIALS AND METHODOLOGY

A conventional three-electrode cell was used. The working electrode was a gold or Nichrome 80 alloy (80% nickel and 20% chromium) wire on which PANI composite films, containing codeposited CNTs, were built. Afterwards, Pt particles were dispersed. The composite electrodes were electrochemically characterized. 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. All 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 suspended carbon nanotubes and ii) Pt deposition on the composite film.

PANI films were built up on the metallic substrate (gold and Nichrome alloy) of ca. 0.08 cm² geometric area by electropolymerization of the monomer from 0.1 M aniline + 0.5 M H₂SO₄ cycling the potential between 0.0 V and 0.90 V at 0.1 V s⁻¹. The film thickness was ca. 0.1 μm.

The PANI-CNT films were grown under the same experimental conditions, but adding 0.1 mg ml⁻¹ of CNTs to the 0.1 M aniline + 0.5 M H₂SO₄ solution. CNTs have been previously functionalized through a chemical treatment with concentrated HNO₃. Before electropolymerization, the resulting suspension was stirred in an ultrasonic bath to minimize agglomeration.

*Address correspondence to this author at the INIFTA-Suc4 CC 16 (1900) La Plata, Argentina; Tel: +542214257430; Fax: +542214254642; E-mail: castrolu@inifta.unlp.edu.ar

Films of PANI and PANI-CNT on Nichrome wires were decorated with Pt particles by spontaneous deposition, after immersion in 0.05 M H_2PtCl_6 + 0.1 M HCl solution, for different times, 5 min < t < 120 min.

2.2. Physical and Electrochemical Characterizations

SEM and EDX were used to characterize the composite electrodes.

Methanol oxidation was studied in 0.5 M H_2SO_4 + 0.5 M CH_3OH solution by cyclic voltammetry in the potential range from 0.05 V to 0.80 V. The current densities are referred to the CO-calculated real area. Real areas were determined by considering the anodic charge involved in the CO-stripping peak by assuming that 420 μC is equivalent to 1 cm^2 [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.

3. RESULTS AND DISCUSSION

3.1. PANI Film Growth Effect of the Metallic Substrate and the Added CNTs

PANI films were synthesized electrochemically by cyclic voltammetry on two different substrates, namely gold and Nichrome wires. The monomer solutions were prepared with and without the addition of CNTs. The film growth process could be followed by recording the I-V profiles at 0.10 V s^{-1} . The anodic current peak height assigned to the leucoemeraldine to emeraldine transition at ca. 0.4 V was used as a parameter to evaluate the film growth. In Fig. (1), the relationship between the current peak and the cycling time is presented for the PANI and PANI-CNT films formed on the two substrates under study. It is worth mentioning that there is an outstanding difference in the film growth rate on both gold and Nichrome substrates independently from the solution composition. It is believed that Nichrome wires can favor the polymeric film growth due to Ni species dissolved and deposited in the early stages of PANI growth that remain

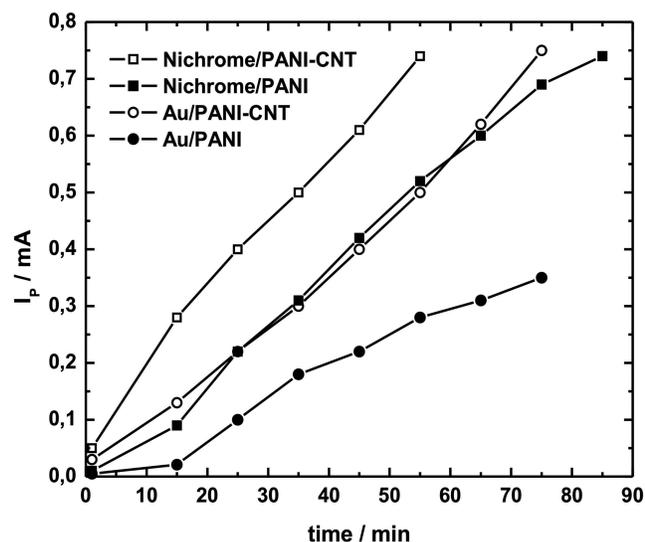


Fig. (1). Comparison of the growth rate for PANI and PANI-CNTs on gold and on Nichrome wires. (I_p : anodic current peak at ca. 0.40 V from cyclic voltammograms at 0.1 V s^{-1}).

blocked in the polymeric matrix [14]. The addition of CNTs to the monomer acid solution increases the growth rate on both substrates. The presence of carboxyl and carbonyl groups on the CNT surface can assist the anchoring of the initial aniline nuclei that cause a fast film growth [12].

As the composite films grown on Nichrome from a CNT containing aniline acid solution are thicker and the preparation time is shorter, we decided to continue the study taking into account only the Nichrome/ PANI composite films.

3.2. Addition of Catalytic Material by Spontaneous Deposition

The addition of platinum to the composite films was performed by spontaneous deposition controlling the immersion time in H_2PtCl_6 solution. Due to the deposition process itself, the presence of a nickel ionic species is a necessary requirement to cause the reduction of the ionic Pt.

SEM images of the Nichrome/PANI/Pt and Nichrome/PANI-CNT/Pt composite films are shown in Fig. (2), for a 5-minute immersion time. It can be noticed that the incorporation of CNTs to the polymeric film strongly influences the catalytic particle size and its dispersion. The Nichrome/PANI-CNT/Pt catalysts exhibit smaller and properly distributed particles in comparison to Nichrome/PANI/Pt electrodes. Thus, the morphology and nanostructure of carbon materials are considered to be the main factors in obtaining a high dispersion of nanoparticle catalysts.

For deposition times between 20 and 30 min, the Pt particles are suitably spread all over the surface. For larger immersion times, a relatively thick Pt layer is formed.

3.3. Methanol Electrooxidation

The electrochemical activity of the composite PANI films was investigated by cyclic voltammetry in 0.5 M CH_3OH + 0.5 M H_2SO_4 aqueous solution. In Fig. (3), the cyclic voltammograms for methanol oxidation on Nichrome/PANI/Pt and Nichrome/PANI-CNT/Pt catalysts (after 30 min of Pt spontaneous deposition) are shown. The highest current density value is exhibited by Nichrome/PANI-CNT/Pt electrode. Its outstanding behavior is attributed to a better Pt dispersion on the (PANI-CNT) composite substrate.

The inset in Fig. (3) shows plots of current density versus time for the potentiostatic electro-oxidation of 0.5 M methanol on Nichrome/PANI/Pt and Nichrome/PANI-CNT/Pt catalysts at 0.50 V. A great initial current drop is followed by a region of more stable activity in which the current slowly decreases. The behavior is interpreted as an initial fast dehydrogenation of methanol adsorption followed by a slower oxidation of CO and/or related species derived from methanol that can poison the surface [15]. The Nichrome/PANI-CNT/Pt surface was the most active and stable.

Other catalytic Pt electrodes, (Nichrome/PANI-CNT/Pt) obtained after different immersion times in the PtCl_6H_2 solutions, were tested for methanol oxidation. In Fig. (4), the current density values for methanol oxidation at 0.50 V are plotted as a function of the immersion time. The electrochemical activity increased with increasing plating time reaching a maximum at 30 min, and then it decreased steadily.

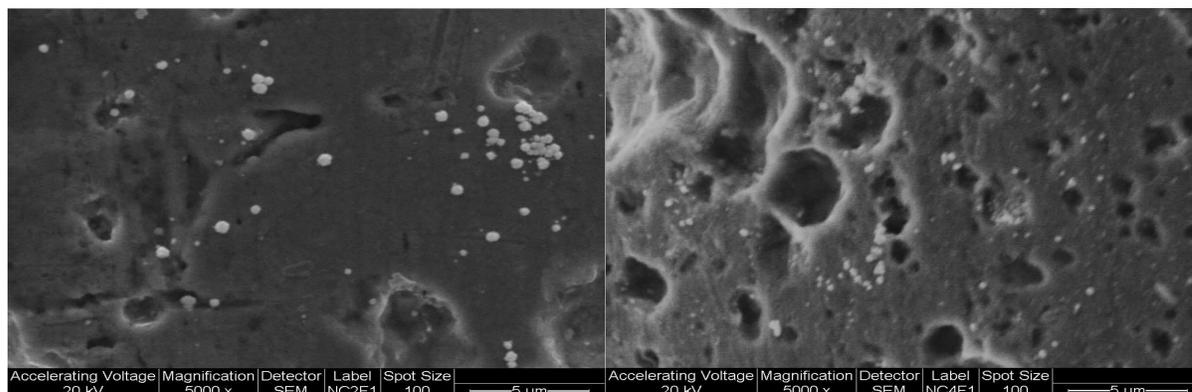


Fig. (2). SEM micrographs of the composite films developed on Nichrome wires, for a Pt immersion time of 5 min. (a) PANI/Pt, (b) PANI-CNTs/Pt.

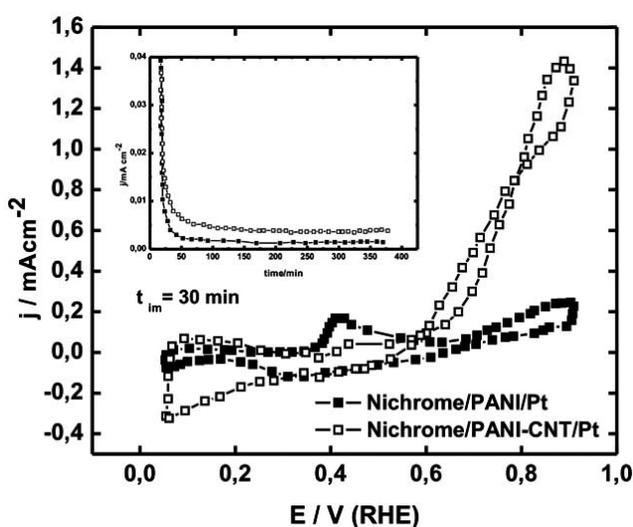


Fig. (3). Voltammograms for Nichrome/PANI/Pt and Nichrome/PANI-CNT/Pt electrodes, both prepared for 30-minute immersion time in 0.5 M CH₃OH + 0.5 M H₂SO₄, $v = 0.05 \text{ V s}^{-1}$. The inset shows the potentiostatic methanol oxidation at 0.50 V.

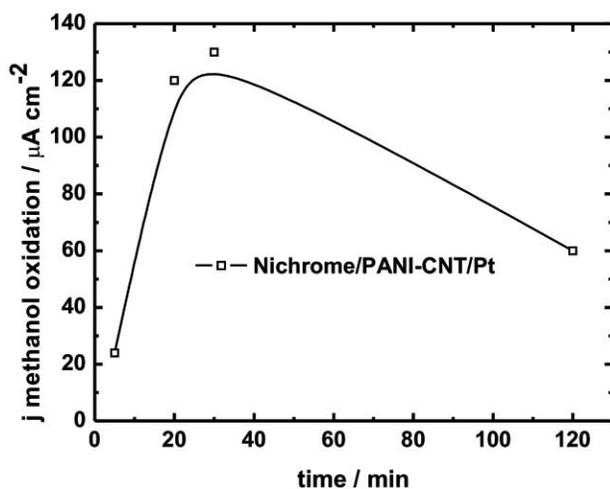


Fig. (4). Relationship between the current density at 0.50 V (taken from voltammograms at 0.020 V s^{-1} in 0.5 M CH₃OH + 0.5 M H₂SO₄) and the Pt-deposition time.

The highest activity is attributed to an enhanced specific surface area originated from a joint effect of adequate particle size and a proper relation between aggregation and dispersion of the catalyst on the composite polymeric film.

4. CONCLUSION

PANI composite films were electro synthesized on gold and Nichrome wires, the film growth being faster when nickel species from the substrate and CNTs added to the monomer solution are present.

- Spontaneous Pt deposition was obtained on polymeric films grown on Nichrome wires independently from the presence of CNTs.
- A greater amount of smaller and well-distributed Pt particles is obtained for the same plating time when CNTs are added to the polymeric film.
- An optimum value for the plating time was established in 30-minute immersion in the chloroplatinic acid solution.
- The Nichrome/PANI-CNT/Pt catalysts render better electrocatalytic activity for methanol oxidation than the Nichrome/PANI/Pt ones prepared under the same experimental conditions.

ACKNOWLEDGEMENT

The authors are grateful to Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CIC) and SE-CyT-UNCPBA for financial support. Fellowship from CONICET-Argentina (M.A.B.) is gratefully acknowledged. T.K. and A.M.C.L. are members of the research career at CIC.

REFERENCES

- [1] Croissant, M.J.; Napporn, T.; Leger, J. M.; Lamy, C. Electrocatalytic oxidation of hydrogen at platinum-modified polyaniline electrodes. *Electrochim. Acta.*, **1998**, *43*, 2447-2457.
- [2] Castro Luna, A.M. A novel electrocatalytic polyaniline electrode for methanol oxidation. *J. Appl. Electrochem.*, **2000**, *30*, 1137-1142.
- [3] Mikhaylova, A.A.; Molodkina, E.B.; Khazova, O.A.; Bagotzky, V.S. Electrocatalytic and adsorption properties of platinum micro-particles electrodeposited into polyaniline films. *J. Electroanal. Chem.*, **2001**, *509*, 119-127.

- [4] Kessler, T.; Castro Luna, A.M. A catalytic platinum-ruthenium-polyaniline electrode for methanol oxidation. *J. Appl. Electrochem.*, **2002**, *32*, 825-830.
- [5] Mottaghtalab, V.; Spinks, G.M.; Wallace, G.G. The influence of carbon nanotubes on mechanical and electrical properties of polyaniline fibers. *Synth. Met.* **2005**, *152*, 77-80.
- [6] Liu, H.S.; Song, C.J.; Zhang, L.; Zhang, J.; Wang, H.; Wilkinson, D. P. A review of anode catalysis in the direct methanol fuel cell. *J. Power Sources* **2006**, *155*, 95-110.
- [7] Reddy, K. R.; Sin, B.C.; Ryu, K.S.; Noh, J.; Lee, Y. In situ self-organization of carbon black-polyaniline composites from nanospheres to nanorods: Synthesis, morphology, structure and electrical conductivity. *Synth. Met.* **2009**, *159*, 1934-1939.
- [8] Wang, Z.; Yuan, J.; Li, M.; Han, D.; Zhang, Y.; Shen, Y.; Niu, L.; Ivaska, A. Electropolymerization and catalysis of well-dispersed polyaniline/carbon nanotube/gold composite. *J. Electroanal. Chem.* **2007**, *599*, 121-126.
- [9] Strelko V.; Malik D. J.; Streat, M. Characterisation of the surface of oxidised carbon adsorbents. *Carbon*, **2002**, *40*, 95-80.
- [10] Franz, M.; Arafat, H.; Pinto, N. G. Effect of chemical surface heterogeneity on the adsorption mechanism of dissolved aromatics on activated carbon. *Carbon*, **2000**, *38* 1807-1819.
- [11] Guha, A.; Lu, W.; Zawodzinski, Jr. T.A.; Schiraldi, D.A. Surface-modified carbons as platinum catalyst support for PEM fuel cells. *Carbon*, **2007**, *45*, 1506.
- [12] Bavio, M.A.; Kessler, T.; Castro Luna, A.M. Preparation and characterization of composite polyaniline materials for catalytic purposes. *J. Colloid Interf. Sci.*, **2008**, *325*, 414-418.
- [13] Tremiliosi-Filho, H.; Kim, W.; Chrzanowski, A.; Wieckowski, B.; Grzybowska, P.; Kulesza, K. Reactivity and activation parameters in methanol oxidation on platinum single crystal electrodes 'decorated' by ruthenium adlayers. *J. Electroanal. Chem.*, **1999**, *467*, 143-156.
- [14] Trung, T.; Trung, T.H.; Ha, C.S. Preparation and cyclic voltammetry studies on nickel-nanoclusters containing polyaniline composites having layer-by-layer structures. *Electrochim. Acta*, **2005**, *51*, 984-990.
- [15] Iwasita, T. Electrocatalysis of methanol oxidation. *Electrochim. Acta*, **2002**, *47*, 3663-3674.

Received: October 28, 2009

Revised: November 13, 2009

Accepted: November 24, 2009

© Bavio *et al.*; Licensee Bentham Open.

This is an open access article licensed under the terms of the Creative Commons Attribution Non-Commercial License (<http://creativecommons.org/licenses/by-nc/3.0/>) which permits unrestricted, non-commercial use, distribution and reproduction in any medium, provided the work is properly cited.