

Short communication

Methanol and ethanol electrooxidation using Pt electrodes prepared by the polymeric precursor method

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Abstract

The results of methanol and ethanol oxidation in acidic medium on Pt electrodes deposited on Ti substrate using the Pechini method are presented. In this route the metallic salts were dissolved in a mixture of ethylene glycol (EG) and citric acid (CA) forming a polyester network, which is painted onto a Ti substrate and then heat treated at 600 °C in order to obtain the metallic Pt thin films. The X-ray diffraction analysis showed the presence of Pt pattern peaks. The presence of the (4 2 0) plane in a higher amount compared to bulk Pt was observed and the peak position of the planes (2 0 0) and (4 2 0) were displaced by approximately -0.3° . The roughness data presented almost the same values for Ti and Ti/Pt. The electrochemical characterization of the electrodes in 0.1 M HClO₄ showed a typical Pt voltammetric profile. Although the voltammetric profiles of Ti/Pt and bulk Pt were the same, the electrocatalytical behavior for methanol oxidation showed an enhancement of the oxidation current density peak, which increased by 170% compared to bulk platinum. Although, the current density peak for ethanol oxidation on Ti/Pt is smaller than for Pt, it began at 0.11 V less positive than the same process on bulk Pt. The chronoamperometric experiments for methanol and ethanol oxidation on Ti/Pt increased by almost 934% and 440%, respectively, compared with Pt bulk.

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1. Introduction

Fuel cells are widely recognized as very attractive devices to obtain electric energy directly from a chemical product. However, the final choice of the fuel is still difficult and depends on the field of the application. The use of direct organic fuels has been often considered despite their low electrochemical reactivity compared to hydrogen fuel cells [1]. Different authors have studied the electrochemical oxidation of primary alcohols [2–6]. One of the main advantages of methanol is its availability, low price, and its easy storage as a liquid. Ethanol appears also to be a good alternative due to its low toxicity and its ready availability (from biomass) [7,8].

Investigations have revealed that the electrochemical oxidation of primary alcohols have different reaction pathways [1,2], which could lead to aldehyde or to carboxylic acid formation and

not to CO₂ as the final product. It is also important to stress the presence of CO as an intermediate, which is strongly bounded to the electrode surface. Alkanes [9] and alkenes [10] have also been detected.

In the literature Pt–M-based binary catalysts are used where M = Ru, Rh, Ir, Sn, Mo, W, Os or Ni to enhance the catalytic activity by eliminating or inhibiting the CO poisoning effect on the basis of a bifunctional mechanism, an electronic effect or an ensemble effect [11–17]. Considerable effort continues to be focused on the development of new ternary or quaternary alloy catalysts [18–22].

Although Pt is poisoned by CO molecules adsorbed during the alcohol oxidation, the use of metallic Pt as electrocatalyst for the oxidation of small organic molecules has been widely investigated [2,23–26]. The catalytic dissociation of these molecules at electrode surface is a topic of longstanding interest in electrochemistry [27].

Pt has many applications in different areas despite its high price. Therefore, it is interesting to consider electrodes on cheap substrates with electrochemical and chemical properties of the

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bulk material. For this reason, platinum deposited onto titanium could be a good solution to decrease the cost of platinum-based metal electrodes.

The method utilized to prepare the thin Pt electrodes in this work is the polymeric precursor method (PPM) [28,29] (also called Pechini method). In the PPM, metallic salts are dissolved in a mixture of ethylene glycol and citric acid generating a polyester network containing the metallic ions homogeneously distributed. The polymeric solution is applied onto the support and the metallic thin film is obtained by the calcination at an adequate temperature.

To check the behavior of the electrodes prepared by PPM method, the methanol and ethanol oxidation was studied. These electrodes were characterized by X-ray diffraction (XRD), cyclic voltammetry (CV) and atomic force microscopy (AFM). The electrocatalytic activity for alcohols oxidation was studied using CV, and chronoamperometric method, CA.

2. Experimental

2.1. Electrodes preparation

The electrodes were prepared using a 10 mm × 5 mm × 0.5 mm titanium plate as substrate (TiBrasil 99.7%). The substrates were treated by sandblasting followed by a chemical treatment in hot aqueous oxalic acid 10% (w/w) for 30 min. After the chemical treatment, the substrates were washed with Millie-Q water and dried at 130 °C.

The precursor solution was prepared dissolving citric acid (Synth) in ethylene glycol (Merck) at 60 °C. In this solution, H₂PtCl₆·7H₂O (Aldrich) was added at 1:12:96 molar ratios (Pt:CA:EG).

The precursor solution was painted with a brush onto the support (Ti) and the material was initially treated at 130 °C for 30 min to eliminate water and later at 600 °C for 10 min to eliminate the organic materials producing the metallic film. This procedure was repeated three times and at the end the electrode mass is 0.3 mg. At the third time, a cooling rate of 5 °C min⁻¹ was performed. All materials were obtained in static air atmosphere.

2.2. Electrodes characterization

The electrochemical characterization was accomplished using a potentiostat/galvanostat EG&G PARC model 263 A. All the electrochemical experiments were carried out at 25 °C. The voltammetric curves were measured in a 0.1 M HClO₄ solution in the potential range between 0.05 and 1.55 V (versus a reversible hydrogen electrode RHE). The methanol and ethanol oxidation was investigated in a 0.1 M HClO₄ solution containing 0.5 M methanol or 0.5 M ethanol by means of CV and CA. A Pt plate was used as auxiliary electrode. Prior to the experiments, the solutions were desaturated with N₂ for 30 min.

The X-ray diffraction (XRD) patterns were obtained using a SIEMENS diffractometer model D-5000 with Cu K α radiation and $\lambda = 1.5406 \text{ \AA}$.

The AFM images and roughness mean square data were obtained using a SPM LAB TOPOMETRIX Probe Microscope. To determine the electrode thickness it was used a cross-sectional micrograph measured in a scanning electron microscopy Zeiss model 940 A.

3. Results and discussion

The X-ray diffraction analysis for Ti/Pt films prepared from the precursor solution 1:12:96 (Pt:CA:EG) molar ratio and heat treated at 600 °C and also for a Pt polycrystalline electrode are presented in Fig. 1(a) and (b), respectively. The Ti/Pt film was very thin as shown in Fig. 1(a), since the titanium diffraction peaks are observed (JCPDS File #44-1294). The electrode thickness was measured using a cross-sectional SEM micrograph and was 6.7 μm . The platinum pattern peaks observed for Ti/Pt electrodes are $2\theta = 46.243^\circ$ (2 0 0), $2\theta = 81.286^\circ$ (3 1 1) and $2\theta = 122.807^\circ$ (4 2 0) according to JCPDS (PDF #04-0802). Not all pattern peaks for the polycrystalline Pt are observed in the Ti/Pt thin film. In addition, the pattern peak at $2\theta = 122.807^\circ$ (4 2 0) has a higher intensity compared with polycrystalline Pt. Finally, it was observed that the peaks related to the planes (2 0 0), and (4 2 0) are displaced by -0.37° and -0.31° , respectively. This means that the Pt film lattice is stressed. The (1 1 1) phase peak pattern ($2\theta = 39.743$) cannot be observed in Fig. 1(a), since it appears in the same 2θ region of titanium ($2\theta = 40.170$).

The tri-dimensional AFM images (25 $\mu\text{m} \times 25 \mu\text{m}$) of Ti and Ti/Pt electrodes are presented in Fig. 2(a) and (b), respectively. It can be seen that both electrodes are rough. Data of roughness mean square RMS are presented in Table 1. In this table, the RMS data confirm that the Pt electrode has almost the same roughness of the Ti electrodes.

The electrochemical characterization of the Pt electrode formed at Ti (solid line) and a polycrystalline Pt electrode (dotted line) are presented in Fig. 3 in 0.1 M HClO₄ solutions. In order to obtain a reproducible surface, prior to the experiments, all the electrodes were cycled between 0.05 and 1.55 V at 1 V s⁻¹ to

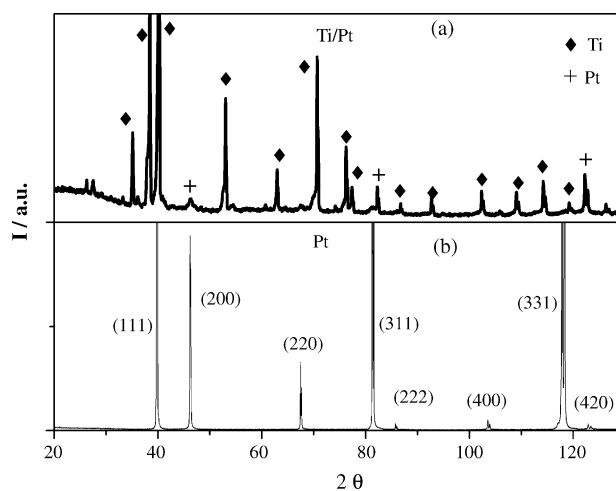


Fig. 1. X-ray diffraction analysis of (a) the platinum thin film (three painted layers) onto Ti substrate (precursor solution 1:12:96 (Pt/CA/EG) thermally treated at 600 °C) and (b) bulk Pt sample.

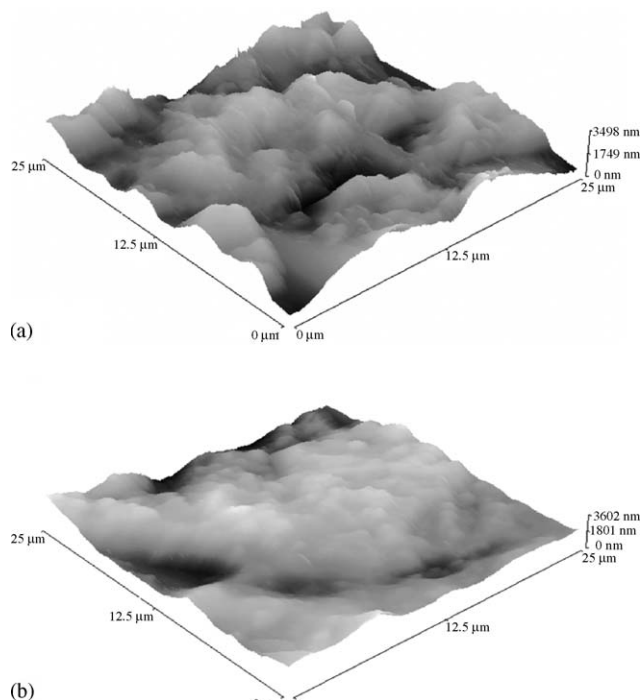


Fig. 2. The tri-dimensional AFM images: (a) Ti sandblasting and (b) Ti/Pt: three painted layers, precursor solution 1:12:96 (Pt:CA:EG) thermally treated at 600 °C.

Table 1
Roughness mean square (RMS) data for Ti and Ti/Pt

Roughness, Ti (nm)	Roughness, Ti/Pt (nm)
555.5 ± 0.06	425.02 ± 0.25
601.2 ± 0.01	643.02 ± 0.12
622.04 ± 0.04	646.70 ± 0.13
Mean: 592.91 ± 0.03	Mean: 571.58 ± 0.16

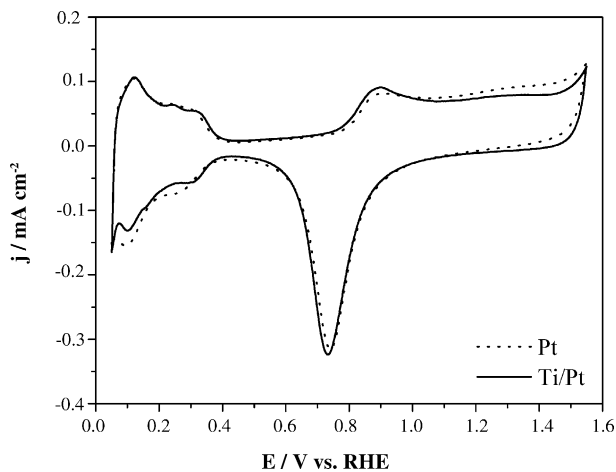


Fig. 3. Voltammetric profile for Pt electrodes in 0.1 M HClO₄ solution (solid line) three painted layers onto Ti substrate. Precursor solution 1:12:96 (Pt/CA/EG) thermally treated at 600 °C and (dotted line) polycrystalline Pt; sweep rate = 50 mV s⁻¹.

clean the platinum surface. A typical behavior for Pt electrodes in perchloric acid medium was observed [30,31]. The processes can be associated with: (i) hydrogen adsorption and desorption between 0.05 and 0.4 V, (ii) double layer region between 0.4 and 0.8 V, and (iii) formation and reduction of PtO, between 0.8 and 1.55 V and 1.55 and 0.4 V, respectively. The surface areas of the electrodes were calculated using the procedure well established in the literature [32], which considers a charge density of 210 μC cm⁻² as being equivalent to the desorption of one hydrogen monolayer on Pt. Using this procedure the electrode electroactive surface area is 6.2 cm². Differences were not observed between the electrochemical profile for Pt electrode formed on Ti and the polycrystalline Pt electrode. From the X-ray diffraction we observed the Pt pattern peaks for the Ti/Pt sample, even though the plane for (4 2 0) peaks have enhanced intensity and the other peaks are displaced compared to bulk Pt as described before. From the voltammetric data the electrochemical Pt profile was observed for both substrates in acid media. As will be described below, the changes observed in the X-ray pattern lead to important electrocatalytical changes for methanol and ethanol oxidation.

In Fig. 4(a) and (b), the voltammetric profiles for methanol and ethanol oxidation on Pt (dotted line) and Ti/Pt (solid line) are presented, respectively. All the measurements were performed in acidic media (0.1 M HClO₄). In the presence of methanol the Pt substrate shows the well-known oxidation profile [4,33] characterized by two oxidation peaks at 0.85 and 1.25 V during the positive sweep. The first process is attributed to the oxidative removal of adsorbed/dehydrogenated methanol fragments (CO_{ads} for example) by oxygen-containing species PtOH [34,35]. During this process, which occurs at 0.85 V, CO, CO₂, HCOOH, HCOH and HCOOCH₃ are formed and CO molecules can be re-adsorbed, poisoning the surface [4,36]. For the second anodic process (current peak at 1.25 V) it is known that, for primary alcohols, the main species produced are HCOH, CO₂, and HCOOH [36,37]. During the negative potential sweep, the Pt oxide is reduced. This last process reactivates the surface and an oxidation reaction occurs as indicated by the presence of an intense anodic peak for methanol oxidation at 0.69 V.

A good electrocatalyst must fulfill at least two requirements: (i) high current peak density for the process investigated and (ii) low energy (E/V) to supply the current peak density. Over the Ti/Pt electrodes, an increase of 170% in the current peak density for methanol oxidation was observed, as seen in Fig. 4(a) (solid line). It is important to point out that this increase is not related to an increase of active surface area since the current for both substrates was divided by the active areas. During methanol oxidation on Ti/Pt there is also a shoulder at 0.7 V (which does not appear on Pt [3]). Fig. 4(a) (solid line) also shows that there is a displacement of the current density peak potential towards more positive values for methanol oxidation in Ti/Pt compared with bulk Pt (0.1 V). During the reverse sweep a displacement in the current density peak was observed for the reactivation process of 0.02 V. In addition, it is important to stress that these results do not necessarily imply that the methanol oxidation reaction mechanism is the same for Pt and Ti/Pt electrodes.

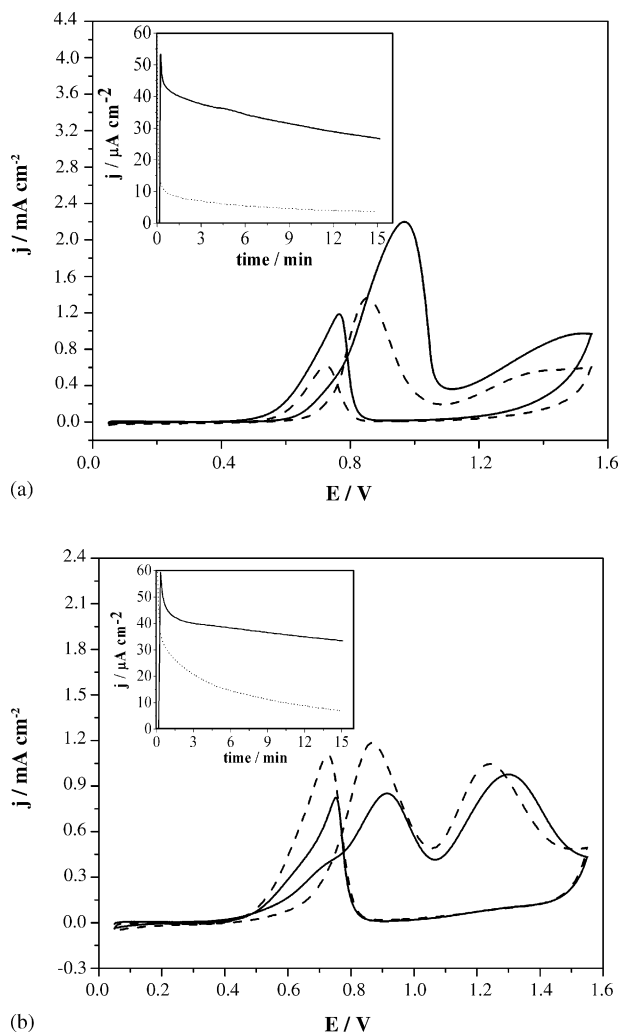


Fig. 4. Cyclic voltammograms and chronoamperometric measurements for alcohols oxidation in 0.1 M HClO₄ at Ti/Pt (solid line) and at polycrystalline Pt electrode (dotted line). Sweep rate = 20 mV s⁻¹. Insert are the curves (a) 0.5 M H₃COH, $E_{ox} = 0.6$ V and $t = 15$ min and (b) 0.5 M H₃CCH₂OH, $E_{ox} = 0.5$ V and $t = 15$ min.

In Fig. 4(b), the voltammetric profiles for ethanol oxidation on Pt (dotted line) and Ti/Pt (solid line) are presented. Ethanol oxidation on Pt is characterized by the presence of two peaks at 0.83 and 1.23 V [38]. The first peak in the cyclic voltammogram appears at a potential where surface-bonded OH is formed on Pt (and begins to form rapidly with a steep rise in current that follows the hydrogen peaks during the positive sweep results). The formation of the OH species has an important role in ethanol oxidation. A two-path mechanism can occur, with the formation of CO_{ads} strongly bonded to the Pt substrate and also bulk oxidation [38]. The peaks in the oxide region of the CVs for Pt in acid solution are caused by the production of CO₂ and carboxylic acid [38]. The main products of ethanol oxidation are adsorbed CO, adsorbed CH₃CO, CH₃CHO, CH₃COOH and CO₂, which were detected by in situ reflectance spectroscopy and chromatography techniques [26]. Similar species have already been described in previous papers [39,40].

In an analysis of the oxidation of ethanol on the Ti/Pt, Fig. 4(b) (solid line), it was observed that the first peak was displaced to

more positive values by 0.04 V and the second one by 0.06 V compared with Pt (dotted line). The reason for this behavior is not yet clear and new experiments will be done in a further work. The oxidation current density peak is smaller for Ti/Pt compared to bulk Pt. However, the ethanol oxidation process on Ti/Pt starts at 0.11 V less positive than on Pt with a wave at 0.7 V more pronounced than for methanol oxidation. This wave for ethanol oxidation, as such as for methanol oxidation process, does not appear on Pt [41,42] and probably it can be associated with a change in the oxidation reaction mechanism.

It is known from the literature that the Pt crystallographic orientation can change both the reaction mechanism and the potential or current density for methanol [3,43] and ethanol [44] oxidation processes. Also, lattice stresses lead to a change in the energy surface [45]. Considering the results presented here, we suggest that for methanol and ethanol oxidation the changes in the current peak density, the peak potentials and potentials where the processes start using Ti/Pt could be explained by a change of the crystallographic orientation and lattice stresses observed for this substrate compared to the polycrystalline platinum. A deep understanding of the mechanism of the observed effect is beyond the purpose of this paper.

The comparison of the Pt (dotted line) and Ti/Pt (solid line) electrodes under constant-potential polarization for methanol and ethanol oxidation are presented in inserts in Fig. 4(a) and 4(b), respectively. As shown, even for the polarization times of 15 min, the current density (at 0.6 V) is almost 940% higher for Ti/Pt than pure Pt electrodes for 0.5 M methanol in 0.1 M HClO₄. For 0.5 M ethanol in 0.1 M HClO₄ the current density (at 0.5 V) was 440% higher for Ti/Pt than pure Pt electrodes. This fact indicates that the Ti/Pt structure decreases the poisoning effects of the strongly adsorbed species (e.g., CO) generated during methanol and ethanol oxidation. Further experiments will be necessary to describe the mechanism of these effects.

4. Conclusions

In this paper, a polycrystalline platinum electrode thin film deposited on Ti was prepared by the polymeric precursor method and the properties characterized. The electrocatalytic behavior of methanol and ethanol was measured on a Ti/Pt substrate and compared with polycrystalline platinum electrodes. The X-ray diffraction analysis of the Ti/Pt substrate showed characteristic platinum pattern peaks and the electrochemical characterization was totally confirmed as a typical polycrystalline platinum voltammogram in the acidic medium 0.1 M HClO₄. The AFM images and roughness data showed that the morphology and roughness of Ti and Ti/Pt were almost the same. The current peak density of methanol on Ti/Pt showed an increase of 170%. Additionally, a voltametric wave related to methanol oxidation at 0.7 V was observed. Although, for ethanol oxidation the current density peak is smaller for the Ti/Pt, the beginning of the ethanol oxidation on Ti/Pt was shifted to less positive potentials (0.11 V) than on Pt. The chronoamperometric measurements for methanol and ethanol oxidation on Ti/Pt presented increased by almost 940 and 440%, respectively, for the oxidation current of

alcohols over Pt. We suggest that the results could be explained by a change in the crystallographic orientation of Pt over Ti and the lattice stresses measured using X-ray diffraction. Further experiments are necessary to explain the mechanism of the phenomena.

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References

- [1] C. Lamy, S. Rousseau, E.M. Belgsir, C. Coutanceau, J.M. Léger, *Electrochim. Acta* 49 (2004) 3901.
- [2] E.A. Batista, G.R.P. Malpass, A.J. Motheo, T. Iwasita, *Electrochem. Commun.* 5 (2003) 843.
- [3] T. Iwasita, *Electrochim. Acta* 47 (2002) 3663.
- [4] M. González Pereira, M. Dávila Jiménez, M.P. Elizalde, A. Manzo-Robledo, N. Alonso-Vante, *Electrochim. Acta* 49 (2004) 3917.
- [5] H. Nonaka, Y. Matsumura, *J. Electroanal. Chem.* 520 (2002) 101.
- [6] Shengli Chen, Mark Schell, *Electrochim. Acta* 45 (2000) 3069.
- [7] E. Peled, T. Duvdevani, A. Aharon, A. Melman, *Electrochem. Solid State Lett.* 4 (40) (2001) A38.
- [8] J. Wang, S. Wasmus, R.F. Savinell, *J. Electrochem. Soc.* 142 (1995) 4218.
- [9] T. Iwasita, E. Pastor, *Electrochim. Acta* 39 (1994) 531.
- [10] N.H. Li, S.G. Sun, *J. Electroanal. Chem.* 436 (1997) 65.
- [11] M. Watanabe, S. Motoo, *J. Electroanal. Chem.* 60 (1975) 275.
- [12] V. Radmilovic, H.A. Gasteiger, P.N. Ross, *J. Catal.* 154 (1995) 96.
- [13] H. Zhang, Y. Wang, E.S. Fachini, C.R. Cabrera, *Electrochem. Solid State Lett.* 2 (1999) 437.
- [14] Y. Ishikawa, M.S. Liao, C.R. Cabrera, *Surf. Sci.* 66 (2000) 463.
- [15] P.K. Shen, A.C.C. Tseung, *J. Electrochem. Soc.* 141 (1994) 382.
- [16] Y.E. Sung, H. Kin, S. Thomas, A. Wieckowski, R. Liu, H. Iddir, Q. Fan, G. Hou, A. Bo, K.L. Ley, E.S. Smotkin, *J. Phys. Chem. B.* 104 (2000) 3518.
- [17] K.W. Park, J.H. Choi, B.K. Kwon, S.A. Lee, Y.E. Sung, H.Y. Ha, S.A. Hong, H. Kim, A. Wieckowski, *J. Phys. Chem. B.* 106 (2002) 1869.
- [18] B. Gurau, R. Viswanathan, R. Liu, T.J. Lafrenz, K.L. Ley, E.S. Smotkin, E. reddington, A. Sapienza, B.C. Chan, T.E. Mallouk, S. Sarangapani, *J. Phys. Chem. B* 102 (1998) 9997.
- [19] A. Lima, C. Countanceau, J.M. Leger, C. Lamy, *J. Appl. Electrochem.* 31 (2001) 379.
- [20] M. Gotz, H. Wendt, *Electrochim. Acta* 43 (1998) 3637.
- [21] J.H. Choi, K.W. Park, B.K. Kwon, Y.E. Sung, *J. Electrochem. Soc.* 150 (2003) A973.
- [22] W.C. Choi, J.D. Choi, S.I. Woo, *Catal. Today* 74 (2002) 235.
- [23] A. Miki, S. Ye, T. Senzaki, M. Osawa, *J. Electroanal. Chem.* 563 (2004) 23.
- [24] H. Nonaka, Y. Matsumura, *J. Electroanal. Chem.* 563 (2004) 23.
- [25] M.C. Santos, L.O.S. Bulhões, *Electrochim. Acta* 49 (2004) 1893.
- [26] F. Vigier, C. Coutanceau, F. Hahn, E.M. Belgsir, C. Lamy, *J. Electroanal. Chem.* 563 (2004) 81.
- [27] B. Beden, J.M. Leger, C. Lamy, in: J.O. Bockris, B.E. Conway, R.E. White (Eds.), *Modern Aspects of Electrochemistry*, vol. 22, Plenum Press, New York, 1992, p. 97.
- [28] P.M. Pechini, United States Patent Office, 3 330 697, 1967.
- [29] M. Kakihana, *J. Sol Gel Sci. Technol.* 6 (1996) 7.
- [30] B.E. Conway, *Program Surf. Sci.* 49 (1995) 331.
- [31] M.C. Santos, D.W. Miwa, S.A.S. Machado, *Electrochem. Commun.* 2 (2000) 692.
- [32] S. Trassati, O.A. Petrii, *Pure Appl. Chem.* 63 (1991) 719.
- [33] F. Kardigan, B. Beden, J.M. Leger, C. Lamy, *J. Electroanal. Chem.* 127 (1981) 75.
- [34] H.A. Gasteiger, N. Markovic, P.N. Ross, E.J. Cairns, *J. Electrochem. Soc.* 141 (1994) 1795.
- [35] T. Zerihun, P. Grundler, *J. Electroanal. Chem.* 441 (1998) 57.
- [36] L.-W.H. Leung, M.J. Weaver, *J. Phys. Chem.* 92 (1988) 4019.
- [37] Y. Xu, A. Armini, M. Schell, *J. Electroanal. Chem.* 398 (1995) 95.
- [38] S. Chen, M. Schell, *J. Electroanal. Chem.* 478 (1999) 108.
- [39] J.P.I. de Souza, S.L. Queiroz, K. Bergamaski, E.R. Gonzalez, F.C. Nart, *J. Phys. Chem. B* 106 (2002) 9825.
- [40] R. Ianniello, V.M. Schmidt, J.L. Rodriguez, E.P. Pastor, *J. Electroanal. Chem.* 471 (1999) 167.
- [41] G.A. Camara, T. Iwasita, *J. Electroanal. Chem.* 578 (2005) 315.
- [42] R.T.S. Oliveira, M.C. Santos, B.G. Marcussi, P.A.P. Nascente, L.O.S. Bulhões, E.C. Pereira, *J. Electroanal. Chem.* 575 (2005) 177.
- [43] A.V. Tripkovi, K.D.J. Pofqvic, *Electrochim. Acta* 41 (1996) 2385.
- [44] V.P. Santos, G. Tremiliosi-Filho, *J. Electroanal. Chem.* 554 (2003) 395.
- [45] W.D. Kingery, H.K. Bowen, D.R. Uhlmann, *Introduction to Ceramics*, 2nd ed., John Wiley and Sons, 1976, p. 448 (Chapter 10).