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Preparation and electrochemical characterization of Pt nanoparticles dispersed on niobium oxide

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(Endnotes)

Abstract: Electrodes consisting of Pt nanoparticles dispersed on thin films of niobium oxide were prepared onto titanium substrates by a sol-gel method. The physical characterization of these electrodes was carried out by X-ray diffraction, scanning electron microscopy and energy dispersive X-ray analysis. The mean size of the Pt particles was found to be 10.7 nm. The general aspects of the electrochemical behavior were studied by cyclic voltammetry in 1 mol L^{-1} $HClO_4$ aqueous solution. The response of these electrodes in relation to the oxidation of formaldehyde and methanol in acidic media was also studied.

Keywords: Pt nanoparticles, sol-gel, electrocatalysis, niobium oxide.

Introduction

A significant amount of research efforts is nowadays dedicated to the search for new electrode materials aiming to improve the efficiency of a number of electrochemical processes of practical interest. However, for many important electrochemical reactions, such as those related to clean energy generation like hydrogen oxidation, oxygen reduction and the oxidation of small organic molecules, Pt is the best catalyst and, therefore, Pt or Pt based alloys are used [1]. Pt based catalysts, obtained by alloying Pt with a second metal, such as Ru [2-6], Sn [6,7], W [7], Mo [7,8], or Os [9] (usually referred to as a co-catalyst) often show a better electrocatalytic activity toward the oxidation of CO and some small organic molecules than pure Pt [10]. Since Pt and most of co-catalysts are quite expensive, considerable attention has been given to their efficient use. The preparation of mono- and bimetallic nanoparticles has gained increasing attention in scientific and technological research throughout the last several years. Different methods for the preparation of high surface area electrocatalysts have been developed [11-13]. Nanoparticles of Pt and binary Pt alloys have been dispersed on a wide variety of substrates such as carbon powders [14,15], Nafion membranes [16,17], polymers [18,19], polymer-oxide nanocomposites [20], three-dimensional organic matrixes [21] and oxide matrixes [22-26].

Dispersion of Pt particles into an oxide matrix can lead, depending mainly on the oxide nature, to a Pt-oxide system that shows better behavior than pure Pt [23-25, 26]. On the other hand, if the oxide is not involved in the electrochemical reactions taking place onto the Pt sites, it might just provide a convenient matrix to produce a high surface area catalyst.

The sol-gel method is an interesting alternative route for the preparation of materials in form of coatings, nanoscale powders and porous systems. It requires inexpensive equipment and, in the case of coatings, it allows to work with rather

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Em homenagem ao Prof. Dr. Ernesto R. Gonzalez large surfaces in a controlled and homogeneous manner. Several excellent reviews about the sol-gel method can be found in the recent literature [27-29]. Reviews on the sol-gel preparation of Nb_2O_5 coatings are also available in the literature [30]. Very recently, sol-gel derived methods have also been used to prepare nanoparticulate thin films of Ir and Pt [31,32].

In this work, the preparation and characterization of niobium oxide supported Pt nanoparticles obtained by a sol-gel method are reported. The general features of the electrochemical behavior and some aspects of the catalytic properties toward the electro-oxidation of formaldehyde and methanol are also presented.

Experimental

Thin films of niobium oxide modified with dispersed Pt nanoparticles were prepared by a sol-gel method, as schematically shown in Fig. 1.

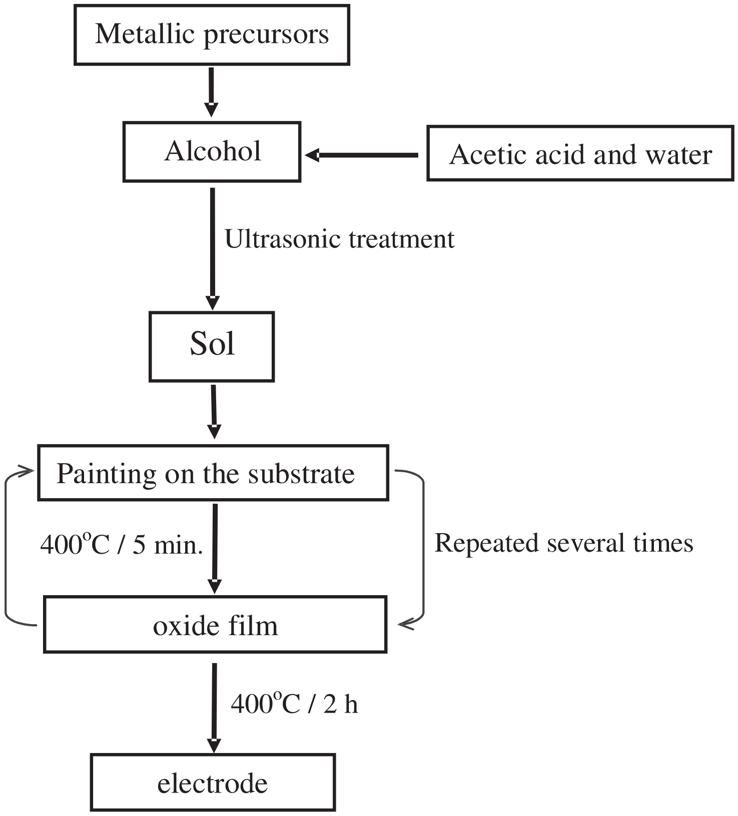

Figure 1. Schematic representation of the process of preparation of the electrodes.

The sols were prepared by dissolving the precursors ($H_2PtCl_6.6H_2O$ - Aldrich and $NH_4H_2[NbO(C_2O_4)_3].3H_2O$ - CBMM, Brazil) in isopropanol with later addition of acetic acid to promote the formation of the polymeric chains and water to produce the hydrolysis reactions. The sols, prepared with a nominal composition (in atoms) Nb:Pt 60:40, were then submitted to an ultrasonic treatment to ensure complete dissolution of the precursors and stabilization. The titanium sheets that were used as substrates were sand blasted to increase their roughness in order to enhance the adherence of oxide films. Before applying the sol-gel coating, the Ti substrates were washed in a hot solution of oxalic acid, rinsed with pure water and dried. Pt-modified Ti/Nb_2O_5 electrodes were obtained by a painting procedure followed by evaporation of the solvents in a flux of hot air. Each dried layer was subsequently heated in a furnace at 400^{o}C for 5 minutes. The painting procedure was repeated several times until a mass corresponding to a nominal thickness of ~2 mm was reached. A final heat treatment, aiming to promote stabilization and densification of the films and to remove unreacted organic residues, was carried out in a furnace at 400^{o}C during 2 hours.

The phases present in the sol-gel prepared electrodes were identified by X-ray diffraction. The incident wavelength was 1.5406 Å (K±Cu).

All the electrochemical experiments were carried out in a conventional electrochemical cell, with a Pt foil counter-electrode and a reversible hydrogen reference electrode in the same solution. The working electrodes had geometric areas of 1 cm^2. Cyclic voltammetry experiments carried out to determine the general behavior of the Ti/Nb_2O_5-Pt electrodes were done in 1 mol L^{-1} $HClO_4$ (Merck) solution, at room temperature (25 ± 1^{o}C). Measurements to investigate the catalytic activity toward the oxidation of formaldehyde and methanol were done in 0.5 mol L^{-1} solutions of the organic compound (Mallinckrodt) in 1 mol L^{-1} $HClO_4$ solution (Merck). Pure nitrogen was bubbled through the solution prior the electrochemical experiments.

Aiming to facilitate the evaluation of the performance of the Pt modified Ti/Nb_2O_5 electrodes toward the oxidation of formaldehyde and methanol, thin layers of nanoparticulated platinum were prepared onto Ti from the adequate sols and following the same procedure, and used for comparison.

Results and discussion

Physical characterization

The X-ray diffraction pattern obtained for the sol-gel prepared Pt modified Ti/Nb_2O_5 electrodes is shown in Fig. 2. The diffraction peaks at 2q values of approximately 53, 63, 71, 76 and 77^o are associated to the Ti base. The presence of metallic platinum is revealed by the characteristic peaks of the [200] and [220] planes at 2q values of approximately 47 and 67^o (Powder Diffraction Files, card 04-0802). The fact that no peaks related to Nb compounds are observed serves as indication of the formation of an Nb_5O_2 amorphous phase, as observed for niobium oxide layers treated at 400^{o}C [33-35]. Since the 100% intensity diffraction peak of Ti (2q = 40.1^o) is too close to the main diffraction peak of the metallic platinum ([111] planes at 2q = 39.8^o), the peak 2q = 46.2^o ([200] planes, 53% relative intensity) was used to calculate the average size of the Pt nanoparticles, using Scherrer's. equation [36]. The average particle size was found to be 10.7 nm.

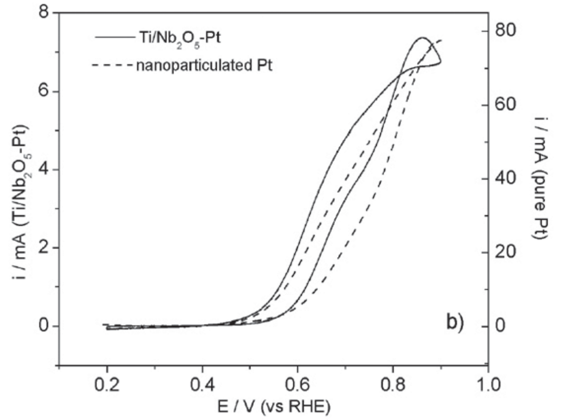

Figure 2. X-ray diffraction pattern for the Ti/Nb_2O_5-Pt electrode of nominal composition Nb:Pt 60:40.

Examination of surface morphology was carried out by scanning electron microscopy (SEM). Figure 3 shows the microphotographs obtained with two different magnifications. It is clearly seen that the surface of the sol-gel prepared Ti/Nb_2O_5-Pt electrodes is quite rough and relatively compact. At low magnification, the general aspect of the surface differs from the so-called "cracked mud" morphology observed for RuO_2-Nb_2O_5 and IrO_2-Nb_2O_5 [37,38]. As it can be seen in Fig. 3a, some regions appear to be more compact while others present small cracks.

The composition Nb_2O_5-Pt layer was qualitatively determined by energy dispersive X-ray analysis (EDX), by integration of the dispersion peaks in the energy region of 0.1 – 10.3 keV. In a general manner, the values obtained for the Pt content were around 50%, a value higher than the 40% Pt of nominal composition.

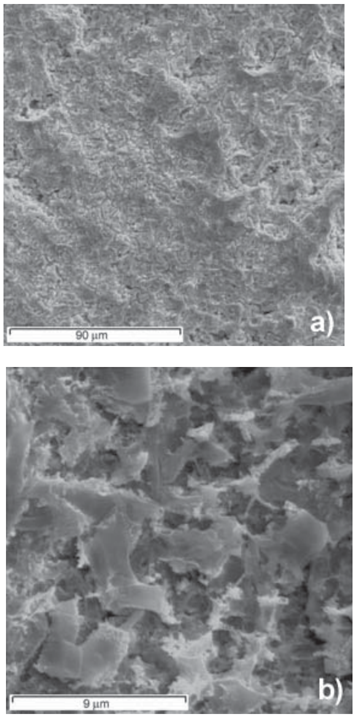

Figure 3. SEM microphotographs for the Ti/Nb_2O_5-Pt electrode a) x 500 b) x 5000

Electrochemical characterization

The Ti/Nb_2O_5-Pt electrodes were initially characterized by cyclic voltammetry at 50 mV s^{-1}, in a 1 mol L^{-1} $HClO_4$ acid solution, between 0.4 and 1.4V, as usually done for many oxide systems, particularly for those of DSA^{Ò} type [39]. As shown in Figure 4, the voltammetric curves change significantly during continuous cycling. The oxidation-reduction peaks characteristic of Pt are initially poorly defined but, as the number of successive cycles within this potential region increases, these peaks become better defined and the voltammetric curves reached a steady-state. Despite the variation in the general shape of the voltammetric curve during the prolonged cycling, the anodic and cathodic charges were equal and remained constant.

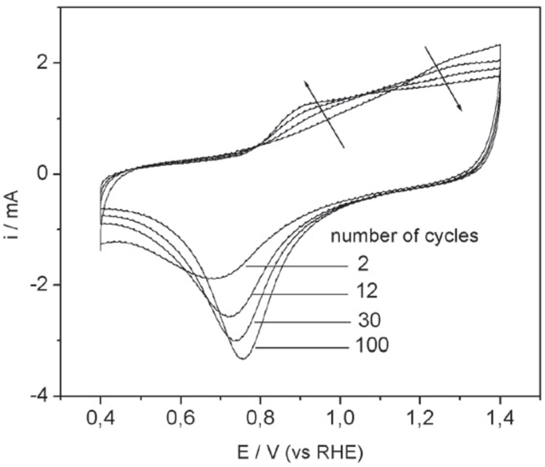

Figure 4. Voltammetric curves for the Ti/Nb_2O_5-Pt electrode in 1mol L^{-1} $HClO_4$ acid taken between 0.4 and 1.4 V at 50 mVs^{-1}. Number of cycles is indicated in the figure.

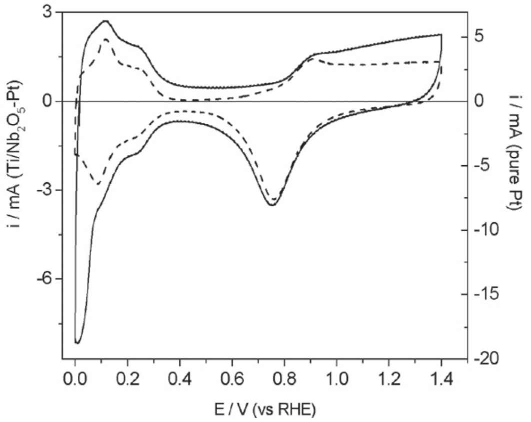

Figure 5. Voltammetric curves obtained between 0 and 1.4 V at 50 mV s^{-1} in 1 mol L^{-1} $HClO_4$. (¾) Ti/Nb_2O_5-Pt electrode; (- - - -) nanoparticulated Pt electrode.

Figure 5 shows the voltammetric curves obtained for the Ti/Nb_2O_5-Pt electrode when the negative potential limit was set at 0 V, compared with the curve of a nanoparticulated sol-gel derived Pt electrode, under the same conditions. As it can be seen in the figure, there are significant differences in the overall shape of the current-potential curves caused by the presence of the Nb_2O_5 matrix. In the region of most negative potentials, *ca* below 0.1 V, the adsorption of hydrogen on the Pt nanoparticles overlaps with another reduction process that probably involves the reduction of Nb(V) to Nb(IV) taking place at the oxide/solution interface simultaneously with the intercalation of H^+ ions into the Nb_2O_5 lattice [40]. Other differences are also observed in the potential region between *ca.* 0.4 and 0.6 V and, in the positive potential scan, above 0.9 V.

Electrocatalytic properties

In order to evaluate the electrocatalytic activity of the Ti/Nb_2O_5-Pt electrodes toward the oxidation of formaldehyde and methanol, cyclic voltammetry measurements were done in solutions containing 0.1 and 0.5 mol L^{-1} of the organic compound in 1 mol L^{-1} $HClO_4$ solution.

For these measurements the negative potential limit was kept at 0.2 V in order to avoid the potential region of intercalation of H^+ ions into the Nb_2O_5 lattice (see Fig. 5). In some experiments a constant potential (E_{ads}) at which the organic compound adsorbed on the surface was applied during a time (t_{ads}) before each potential scan was registered. The quantity of species adsorbed on the surface was thus varied by applying a constant potential E_{ads} (in the region of 0.2 - 0.3 V) during different adsoption times ($10 < t_{ads} < 360$ s). Figure 6 shows the effect of the adsorption time at E_{ads} = 0.2 V on the current-potential profiles obtained at 10 mVs^{-1} in the 0.2 - 0.9V potential range in a solution containing 0.1 mol L^{-1} formaldehyde (Fig. 6a) and in 0.1 mol L^{-1} methanol (Fig.6b). Anodic currents are observed in the negative scan and, in both cases, the oxidation charge increases with t_{ads}. The dependences of the total charges of oxidation (Q_{ox}) on the adsorption time are presented in the graphs inserted in Figs. 6a and 6b, showing that the amount of species adsorbed increases with t_{ads} and tends toward a saturation value. When the same type of experiment was carried out in 0.5 mol L^{-1} solutions of the organic compound, the curves were almost independent of the time of adsorption, indicating the saturation of the surface sites with the adsorbed species. Aiming to facilate comparison with the behavior of pure Pt electrodes, the same kind of experiments were performed on high surface (nanoparticulated) Pt

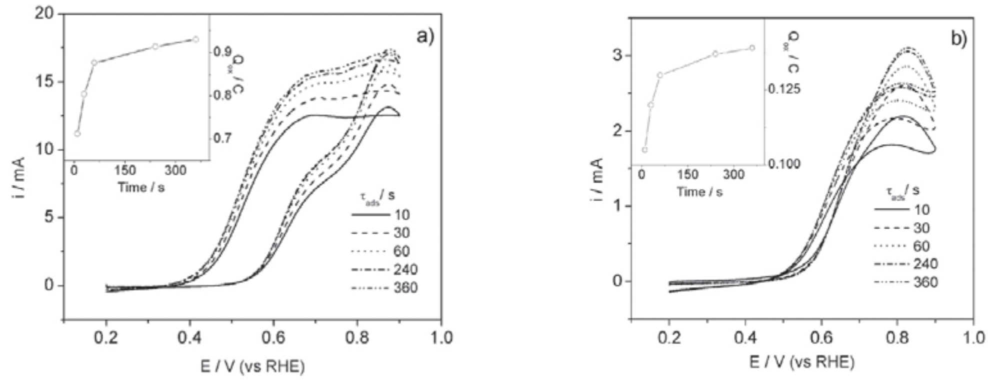

Figure 6. Effect of the adsoption time at 0.2 V on the voltammetric curves of Ti/Nb_2O_5-Pt electrode in 1 mol L^{-1} $HClO_4$ solution containing 0.1 mol L^{-1} formaldehyde (a) and 0.1 mol L^{-1} methanol. Adsorption times are indicated in the figure. v = 10 mV s^{-1}. The inserted figures show the oxidation charges plotted against the adsorption time.

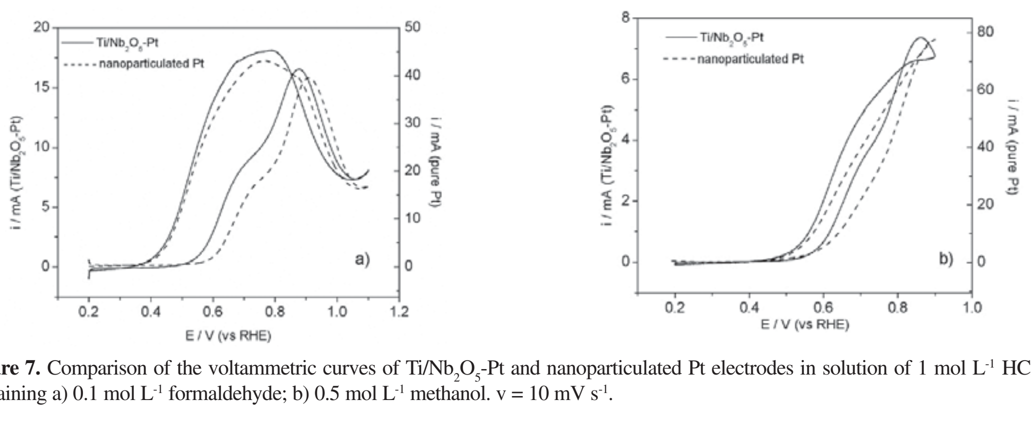

Figure 7. Comparison of the voltammetric curves of Ti/Nb_2O_5-Pt and nanoparticulated Pt electrodes in solution of 1 mol L^{-1} $HClO_4$ containing a) 0.1 mol L^{-1} formaldehyde; b) 0.5 mol L^{-1} methanol. v = 10 mV s^{-1}.

electrodes that were prepared by a similar sol-gel procedure. As a whole, the behavior of the Ti/Nb_2O_5-Pt electrodes was found to be similar to that of Pt what suggests that the electro-oxidation reactions take place on the Pt nanoparticles dispersed on the Nb_2O_5 matrix involving basically the same reaction mechanisms than on pure Pt.

Figure 7 shows a comparison of the voltammetric curves for the oxidation of formaldehyde and methanol obtained with the Ti/Nb_2O_5-Pt electrode and with the nanoparticulated pure Pt electrode. It should be stressed that different current scales were used because the electrodes compared have significantly different effective areas. As it can be seen in the figure, the overall shape of the electro-oxidation curves are almost identical. It is important to observe, however, that the voltammetric curves of the Ti/Nb_2O_5-Pt electrodes are shifted toward more negative potentials. This depolarization effect indicates that the presence of the Nb_2O_5 matrix improves, even though in a rather small amount, the electrocatalytic properties.

In general terms, the literature shows that the improvement in the electrocatalytic activity of Pt produced by the presence of a co-catalyst has been always interpreted as related to the removal of the adsorbed CO that blocks the Pt active sites and, although some controversy exists in relation to the mechanism through which the oxidation of the adsorbed CO is promoted, a facilitated adsorption of the OH species on the co-catalyst and the participation of oxygenated co-catalyst species have been proposed [41]. Even in the case of Pt-Ru bimetallic alloys, currently considered the best materials for the oxidation of methanol, it has been recently suggested that bulk quantities of electron-proton conducting RuOxHy would produce a significantly better electrocatalytic activity [42,43]. Moreover, results obtained recently in our laboratory show that, in fact, Pt nanoparticles dispersed in a RuO_2 matrix exhibit a quite significant electrocatalytic activity for methanol oxidation [44].

Figs. 7a and 7b show that the differences between the onset potentials of the electro-oxidation reactions on the Ti/Nb_2O_5-Pt and pure nanoparticulated Pt electrodes are rather small to consider advantageous the utilization of the Ti/Nb_2O_5-Pt system for practical applications. However, a depolarization effect is, indeed, observed for the oxidations of formaldehyde and methanol. Even though, at this point, it is difficult to speculate on the possible ways through which the niobium oxide matrix may contribute to remove the strongly adsorbed CO from the electroactive sites it is clear that the niobium pentoxide matrix that surrounds the Pt nanoparticles plays a role in the electro-oxidation reactions.

Conclusions

It was possible to prepare Pt nanoparticles dispersed on thin films of niobium oxide grown on Ti substrates by a sol-gel method. The Ti/Nb_2O_5-Pt prepared from sols of nominal composition Nb:Pt 60:40 (in atoms) exhibited a rough surface and a rather high surface area. The average size of the nanoparticles was determined from XRD and found to be 10.7 nm. The studies carried out by cyclic voltammetry in acid media show that the Ti/Nb_2O_5-Pt electrodes are stable during prolonged cycling. The voltammetric curves exhibit the characteristic peaks of the oxidation-reduction processes of Pt and at more negative potentials the adsorption-desorption of hydrogen overlapping in the cathodic scan with a reduction process that can be associated to the simultaneous reduction of Nb (V) and incorporation of protons into the oxide lattice. The electrocatalytic activity of these electrodes toward the oxidation of formaldehyde and methanol was found to be very similar to that of nanoparticulated pure platinum electrodes. A slight improvement in the electrocatalytic response was found indicating the participation of Nb_2O_5.

Acknowledgments

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R.L.S. Mello, F.I. Mattos-Costa, H.M. Villullas, L.O.S. Bulhões. Preparação e caracterização eletroquímica de nanoparticulas de Pt dispersas em óxido de nióbio.

Resumo: Eletrodos contendo nanopartículas de Pt dispersas em filmes finos de óxido de nióbio foram preparados sobre substratos de titânio pelo método sol-gel. A caracterização física dos eletrodos foi realizada através das técnicas de difração de raios X, microscopia eletrônica de varredura e espectroscopia de dispersão de raios X. O valor obtido para o tamanho médio das nanopartículas foi 10,7 nm. Os aspectos gerais do comportamento eletroquímico foram estudados em soluções aquosas de $HClO_4$ 1 mol L^{-1}. A resposta dos eletrodos de Ti/Nb_2O_5-Pt em relação à oxidação de formaldeído e metanol em meio ácido também foi investigada.

Palavras-chave: nanopartículas de Pt, sol-gel, eletrocatálise, óxido de nióbio.

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