

Electrochemical and morphologic studies of nickel incorporation on graphite electrodes modified with polytyramine

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Abstract Electrodes modified with electropolymerized films have received considerable attention in the development of catalysts and sensors, and their use is rapidly increasing. This work reports modification of the surface of graphite electrodes by electrochemical polymerization of tyramine. These modified electrodes were used to nickel incorporation and hydrogen evolution. Tyramine electrooxidation, in acid and basic media, yielded polymeric films onto graphite surface. In ferrocyanide/ferricyanide solution, the electrodes modified in acid medium showed higher electron transfer efficiency. Impedance studies indicated higher charge transfer resistance to electrodes modified with Ptyr prepared in basic pH. Scanning electron microscopy showed that the formed films present different morphology for the several pH values studied. Interferometry and scanning electron microscopy analysis showed higher coverage to films formed in acid medium. Polymers produced in more alkaline medium present growth self-limited. Nickel was incorporated in the films through immersion of the modified electrodes in solution of potassium hexafluoronickelate, followed of electrochemical reduction of the metal. The electrocatalytic activity of the modified electrodes with nickel incorporated was tested for hydrogen evolution reaction. The amount of nickel mass incorporated as well as the current density of

hydrogen evolution reaction was higher in electrodes modified with polytyramine produced in acid medium.

Introduction

Electrochemical methods of polymerization permit to tailor the chemical and physical properties of polymers to gain importance in the research and development of new materials. For the last years, electropolymerization of various aromatic compounds has been investigated with the goal of obtaining polymeric films to produce modified electrodes for specific applications, such as catalysis, sensors, electrochromic materials and new conducting, semi-conducting and insulating polymers [1–7].

Due to their high conductivity and stability, both in air and aqueous solution, polypyrrole, polyaniline, polyacetylene, polythiophene, polyindole and polythionine and has been extensively studied to application in sensors [8, 9] and catalysis [10–12].

Previous studies indicate that monomers containing aromatic groups directly bonded to oxygen are easier to polymerize, present high reproducibility and mechanical resistance of the obtained film, allowing higher stability to the modified electrode [13, 14]. Polymerization of tyramine [4-(2-aminoethyl)phenol] was studied for applications in biosensors [15–20]. This monomer can covalently attach the biorecognition molecule via the formation of a peptide bond through the free amino group.

Inorganic nanoparticles of different nature and size can be combined with conducting [21] or non-conducting polymers [22], producing nanocomposites with high porosity and activity. The literature to use of modified

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electrodes for confinement of metals is less common however the deposition of metallic particles has an increasing interest in catalysis. Previous incorporation of the respective salts or complexes of several metals have made it by ionic exchange in polymeric films deposited in electrodes, followed by electrochemical reduction [13, 14, 21, 23–29].

Catalysts, such as platinum, palladium or nickel, are used in catalytic hydrogenations of unsaturated organic compounds. The main hydrogenation catalysts in organic chemicals industry are Raney nickel for margarine and related processes, nickel and palladium or platinum on lithium oxide for hydrogenation of benzene to cyclohexane [30]. The reactions take place on the surface of the metals finely divided, often deposited on supporting material. The reduction of unsaturated organic compounds by hydrogen generated by electrochemical reaction (electrocatalytic hydrogenation) is advantageous compared to catalytic hydrogenation because it does not require hydrogen gas manipulation [22].

The purpose of this investigation was to study the morphology and some electrochemical characteristics of the tyramine electropolymerization on graphite electrode, for different pH values of film formation, nickel incorporation and hydrogen evolution in these modified electrodes.

To our knowledge, this is the first report of nickel incorporation and hydrogen generation in electrodes modified with polytyramine (Ptyr).

Experimental

Reagents

Tyramine was purchased from Sigma-Aldrich and potassium hexafluoronickelate from Acros. The electrolyte and monomer solutions were deoxygenated for 45 min with ultra pure nitrogen gas. All the reagents were of analytical grade and prepared using Millipore/Milli-Q water (resistivity = 18.2 M Ω cm).

Production and characterization of Ptyr films

The electrochemical studies were performed in three compartment glass cell, fitted with a graphite working electrode of 6 mm diameter, platinum plate as auxiliary electrode and a saturated calomel electrode (SCE) as reference, connected to a potentiostat PAR 273A. The working electrode was mechanically polished with alumina oxide (0.3 μ m slurry) before each electrochemical assay. After polishing, the electrode was rinsed with water from a Millipore Milli-Q system. The electrodes were then sonicated in ultrasound bath and rinsed again with water.

The monomer solutions were deoxygenated with N₂ prior to electropolymerization. Ptyr films were grown by potentiodynamic electropolymerization on graphite electrodes from tyramine solution (15 mmol L⁻¹). HClO₄ solution (0.5 mol L⁻¹) was used for all experiments and pH adjustment was carried out using NaOH solution.

The graphite electrode behavior was analyzed in K₃[Fe(CN)₆] (5.0 mmol L⁻¹)/K₄[Fe(CN)₆] (5.0 mmol L⁻¹)/KNO₃ (0.1 mol L⁻¹) solution, and HClO₄ solution (0.1 mol L⁻¹), before and after tyramine electropolymerization.

Electrochemical impedance spectra were measured for electrodes modified with Ptyr electropolymerized in pH 1.0 and 12.0, before and after nickel incorporation, in solution containing 5.0 mmol L⁻¹ K₄Fe(CN)₆/K₃Fe(CN)₆ as redox couple. A constant potential of 250 mV with 5 mV sinusoidal excitation amplitude was applied. The impedance data were measured and collected for harmonic frequencies from 10 KHz to 10 MHz. A conventional three-electrode cell was used containing platinum plate as counter electrode and SCE as reference electrode. Fitting of impedance spectra was performed using CHI Instruments model 760C modeling software CHI Version 6.21.

Morphology of the films was assessed by scanning electron microscopy (SEM) LEO 940A microscope, interferometry (Microfocus Expert 3D laser interferometer, UBM) and atomic force microscopy (AFM) (Nanoscope IIIa, Digital Instruments). Roughness was evaluated by AFM using the non-contact method.

Nickel incorporation on modified electrodes

After formation of the modified electrode, it was immersed in potassium hexafluoronickelate solution (2 \times 10⁻² mol L⁻¹) during 20 min. The modified electrode with nickel complex incorporated was washed carefully and transferred to the cell contain KCl solution (0.1 mol L⁻¹), being applied potential of -1.0 V during 120 s. The incorporation procedure was repeated by three times to all modified electrodes. The nickel mass incorporated in Ptyr produced in different pH had been calculated by Faraday's law for electrochemical reduction of ions incorporated.

Hydrogen evolution reaction in the modified electrodes

The modified electrodes with nickel incorporated had been connected to the electrochemical cell contain HCl solution (0.1 mol L⁻¹) and submitted to voltammetry in the potential interval from 0.0 V to -1.0 V, 10 mV s⁻¹. The current density of the hydrogen evolution reaction was observed by current in -1.0 V in function of the geometric area re-covered for the film in the modified electrode [14, 22].

The stability of the composite material formed by nickel and Ptyr produced in pH 1.0 or 12.0 was investigated in

deaerated (0.5 mol L^{-1}) HCl solution, through the application of -0.85 V (vs. SCE) during 24 h, with stirring, and determination of current values.

Results and discussion

Electrochemical behavior of tyramine

Cyclic voltammograms of tyramine oxidation in different pH values are shown in Fig. 1.

The oxidation of tyramine at pH 1.0 was observed at about $+1.05 \text{ V}$ versus SCE. The oxidation peak of tyramine in basic medium shifted to lower potentials and two peaks were observed. Since the pK_a of the phenolic hydroxyl group of tyramine is 10.52 [15], the two peaks can be attributed to the oxidation of the tyramine and phenolate species, such as was observed for other phenolic compounds [31], through a shift in the phenol/phenolate equilibrium, resulting in easier oxidation due to higher electronic density. The phenolate oxidation peak is localized at $+0.43 \text{ V}$.

Tyramine oxidation occurs through the ortho position, similar to electrochemical polymerization of other phenols [17]. Scheme 1 represents the electropolymerization of tyramine.

Cyclic voltammograms (CV) for the oxidative polymerization of tyramine in solutions (pH 1.0 and 12.0) are presented in Fig. 2.

The first cycle shows that oxidation of tyramine is irreversible for all pH values. During continuous potential cycling (Fig. 2a) a gradual decrease in the peak current is observed, but oxidation of the monomer continues after 200 scans. The increase in current between $+0.2$ and

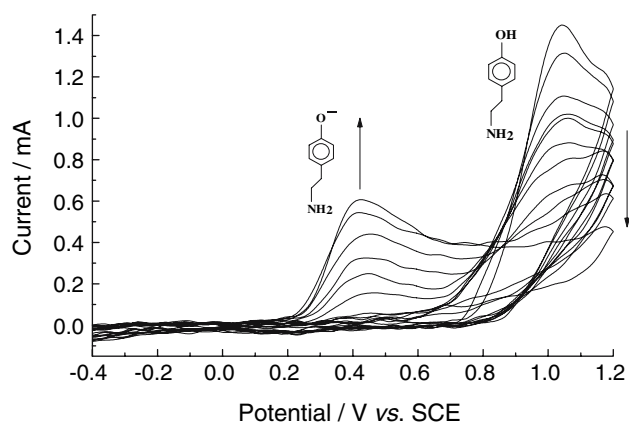
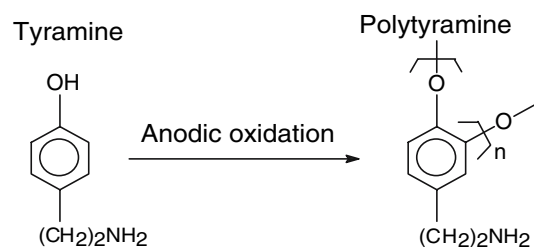


Fig. 1 Effect of pH on the electrochemical behavior of tyramine (15 mmol L^{-1}) on a graphite electrode, 50 mV s^{-1} , pH 1.0–12.0. The arrows indicate pH increase



Scheme 1 Schematic of the electropolymerization of tyramine

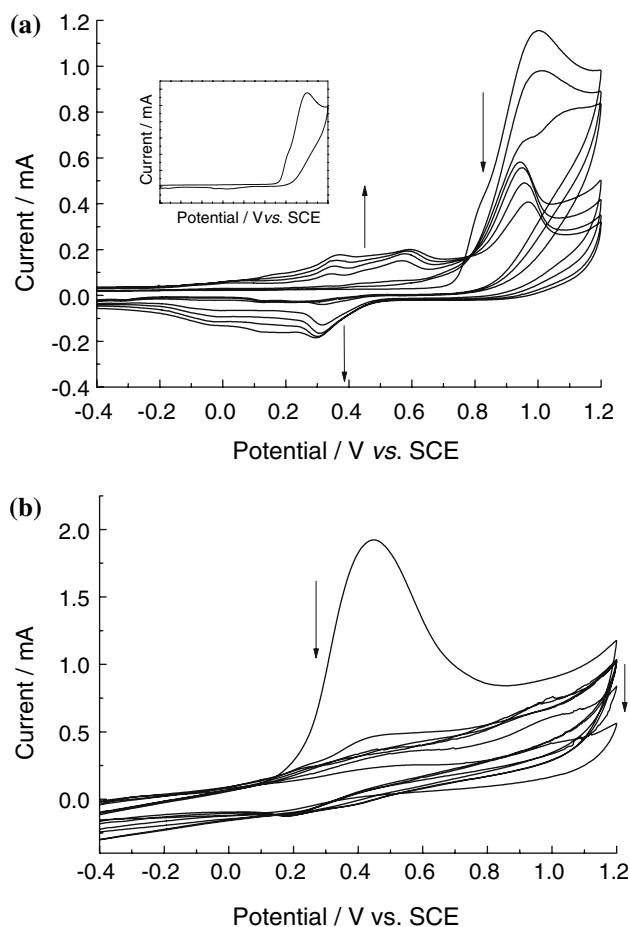


Fig. 2 Cyclic voltammograms of tyramine (15 mmol L^{-1}), recorded continuously (a) pH 1.0. Inset: first cycle of tyramine oxidation (b) pH 12.0; 50 mV s^{-1} , 200 scans. The arrows indicate scans increase

$+0.7 \text{ V}$, after the first cycle, reflects the covering of the electrode surface by the electroactive polymer film.

In alkaline medium (Fig. 2b), increasing the number of cycles, results in drastic decrease in electrodeposition. After several cycles small oxidation currents were observed, suggesting electrode passivation.

The electrochemical behavior of the modified electrodes prepared in acid and basic pH values is shown in Fig. 3.

Oxidation waves ($+215 \text{ mV}$, $+427 \text{ mV}$ and $+602 \text{ mV}$) and reduction waves ($+186 \text{ mV}$, $+270 \text{ mV}$ and $+354 \text{ mV}$)

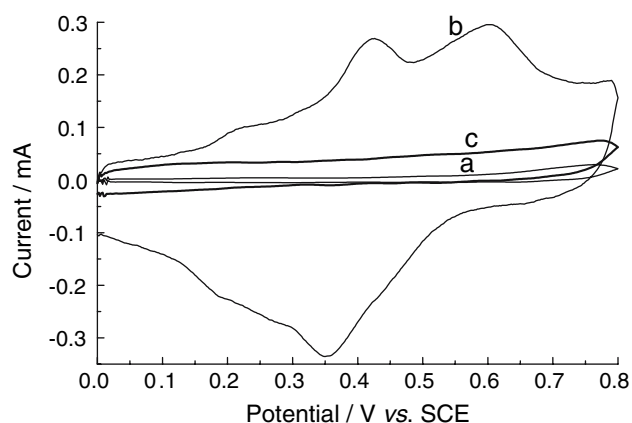


Fig. 3 Cyclic voltammogram of graphite electrode or electrodes modified with Ptyr in HClO_4 solution (0.5 mol L^{-1}), 50 mV s^{-1} , 200 scans. (a) Bare graphite electrode; (b) Ptyr prepared at pH 1.0 and (c) Ptyr prepared at pH 12.0

of Ptyr were observed in modified electrode prepared in pH 1.0. The electrochemical oxidation and reduction waves of Ptyr were observed in modified electrodes prepared until pH 8.0. For pH higher than 10.0 no polymer electroactivity was observed.

The cyclic voltammograms of the electrodes modified with Ptyr in ferrocyanide/ferricyanide solution are shown in Fig. 4.

Situmorang et al. [17] described the electropolymerization of tyramine in methanol–phosphate buffer on platinum electrode. Formation of Ptyr resulted in passivation of the electrode. Kuramitz et al. [31] showed the formation of

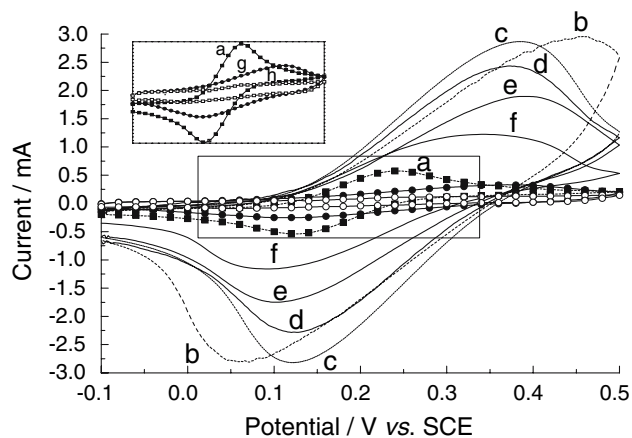


Fig. 4 Cyclic voltammogram in $\text{K}_3\text{Fe}(\text{CN})_6$ (5 mmol L^{-1}), $\text{K}_4\text{Fe}(\text{CN})_6$ (5 mmol L^{-1}) and KNO_3 (0.1 mol L^{-1}) of bare graphite electrode and graphite electrode modified with Ptyr, electropolymerized in aqueous solution of tyramine (15 mmol L^{-1}), 100 mV s^{-1} , 200 scans. (a) bare graphite electrode and electrode modified with Ptyr prepared at (b) pH 1.0; (c) pH 2.0; (d) pH 4.0; (e) pH 6.0; (f) pH 8.0; (g) pH 10.0; (h) pH 12.0. Inset: magnifying of polymeric film in (g) pH 10.0; (h) pH 12.0

insulating polymer film by electropolymerization of bisphenol in sodium sulfate buffer solution on glassy carbon. This behavior was observed in Ptyr produced in high pH on the graphite, whereas this polymer decreased the ferricyanide/ferricyanide current (Fig. 4).

The electrodes modified with Ptyr, prepared in acid media, present increase in the electrochemical response of the redox pair, when compared to the graphite electrode, suggesting formation of Ptyr with different structures, presenting a larger electrode surface area. Significant shift in E_{p_a} to more positive values are observed, suggesting a slower electron transport across the polymer.

The current of $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ couple is much higher under acid conditions when compared to more basic conditions. Considering the geometric surface areas of the graphite electrodes are similar this can only be understood assuming the Ptyr-films formed in acid solutions present areas much higher. This is consistent with the globular structure observed by scanning electron microscopy for films prepared under the more acidic conditions (Fig. 5).

The morphology of the electrode modified with Ptyr shows different topographies as function of pH. Up to pH 8 the coating presents a globular structure randomly distributed on the electrode surface. For pH 10.0 and 12.0, the coating is not capable of filling the graphite cavities, possibly due to the formation of a passivating layer of Ptyr. This is consistent with the CV behavior of Fig. 2b which shows a strong reduction of the current after the first potential cycle.

The profile obtained by interferometry (Fig. 6) shows a small amount of cavities in the polymeric films formed at acid pH. This result suggests that at acid pH values occurs major covering of the graphite electrode.

Impedance spectroscopy is an effective method to probe the electron transfer rates at the electrode for active redox species in solution [1]. Results for the graphite modified with Ptyr prepared in different values are shown in Fig. 7.

The complex plane plots show the initial part of a semi-circle, in the high frequency domain to Ptyr prepared in pH 1.0 and pH 12.0. These results indicate that the electrode process is under kinetic control in the high frequency [32].

It is worth emphasizing that the charge transfer resistance (R_{ct}) value of Ptyr prepared in pH 12.0 is three orders of magnitude higher (in the order of $\text{k}\Omega$) than the Ptyr prepared in pH 1.0. This behavior is in agreement with the CV in aqueous solution containing $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ couple (see Fig. 4).

In relation to the electrooxidation of phenols, it is complex and the predominance of intermediates in this process, as well as the product distribution and the reaction pathway may be affected by the following factors: medium pH, solvent–electrolyte system, electrode material,

Fig. 5 Scanning electron micrograph of bare graphite electrode (a) and Ptyr prepared at (b) pH 1.0; (c) pH 2.0; (d) pH 4.0; (e) pH 6.0; (f) pH 8.0; (g) pH 10.0; (h) 12.0; 50 mV^{-1} , 200 scans, magnification: $1000\times$

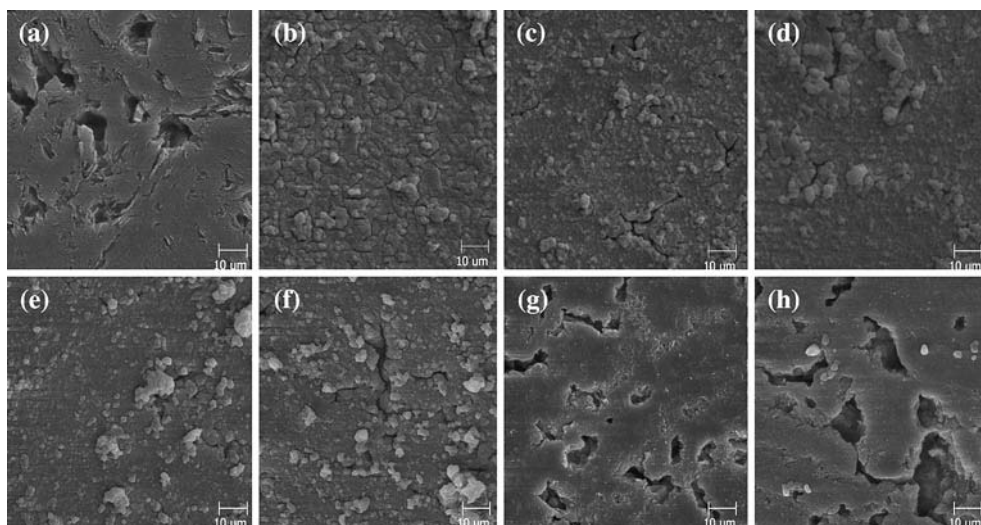
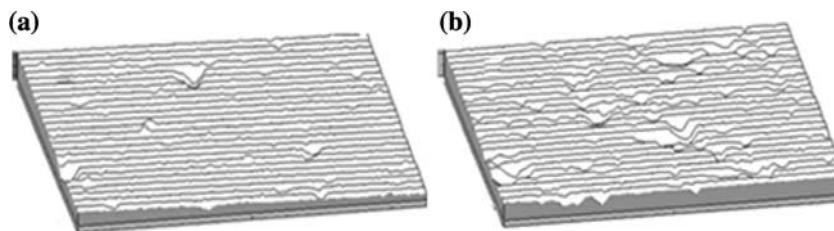


Fig. 6 Surface analysis by interferometry of a graphite electrode modified with Ptyr prepared at (a) pH 1.0; (b) pH 12.0; 50 mV s^{-1} , 200 scans



concentration of phenolic compounds, current density or potential applied [33, 34].

The presence of nonionized phenol is observed at acidic medium, and the structure formed at basic pH is the phenolate ion. These species produce, by a series of proton and electron transfers, the electropolymerization onto electrode surface and bimolecular reactions in solution.

The first oxidation of phenols produces a cation-radical. By losing one electron and one proton, this intermediate produces phenoxonium ion or, by losing one proton, it produces phenoxy radical.

The oxidation of phenolate ion produces a phenoxy radical. This intermediate can produce *ortho* or *para*-benzoquinones, quinol ethers and C–C coupling process, producing biphenyls. The possible phenoxonium ion products are quinone derivatives and/or products of coupling with solvent and electrolyte [33, 34].

This variety of products suggests that the formation of polymers derived from phenols with different structures and properties is possible. This observation is in agreement with the different electrochemical behavior showed in investigations of passivation (Fig. 3), electron transfer (Fig. 4) and impedance (Fig. 7), or different morphological characteristics showed in studies of SEM (Fig. 5) and interferometry (Fig. 6) presented by polytyramine prepared in different pH values, on the graphite surface.

Nickel incorporation in modified electrode

Figure 8 shows the electrochemical behavior of nickel reduction in electrodes modified with Ptyr films prepared in different pH.

Figure 8 shows that the current values of nickel reduction were higher in films produced in acid medium, diminishing gradually with pH increase of preparation.

The nickel mass, calculated by charge of nickel reduction, and the current density values of electrodes modified with Ptyr in HCl solution at -1.0 V are indicated in Table 1.

Table 1 shows higher values to nickel incorporated and current density of hydrogen generation to electrodes modified with Ptyr prepared under more acidic conditions. This is in agreement with the area higher of these films, suggested by cyclic voltammograms (Fig. 4) and scanning electron microscopy, (Fig. 5). These results suggest that the higher area of the polymer increased the nickel incorporation.

Figure 9 presents the voltammograms of modified electrodes, prepared in different pH, with incorporated nickel, in acid solution.

The HER rate is determined by adsorption and desorption of hydrogen and is associated to the surface coverage of the catalytic metal. In all modified electrodes containing

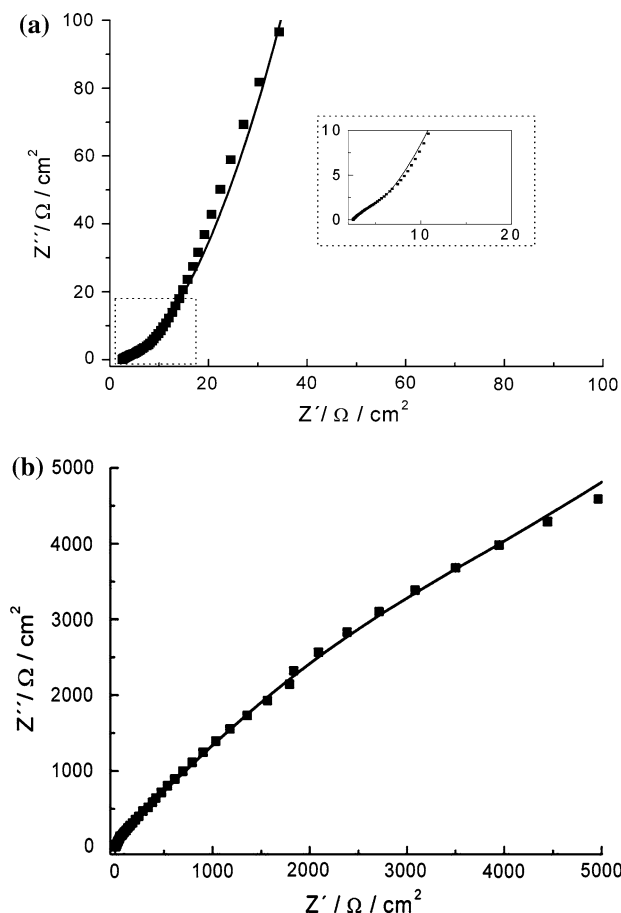


Fig. 7 Nyquist diagrams (Z'' vs. Z') in $0.1 \text{ mol L}^{-1} \text{ KNO}_3$ containing $\text{K}_3\text{Fe}(\text{CN})_6$ (5 mmol L^{-1}), $\text{K}_4\text{Fe}(\text{CN})_6$ (5 mmol L^{-1}) at graphite electrode modified with Ptyr prepared at (a) pH 1.0 and (b) pH 12.0; 50 mV^{-1} , 200 scans

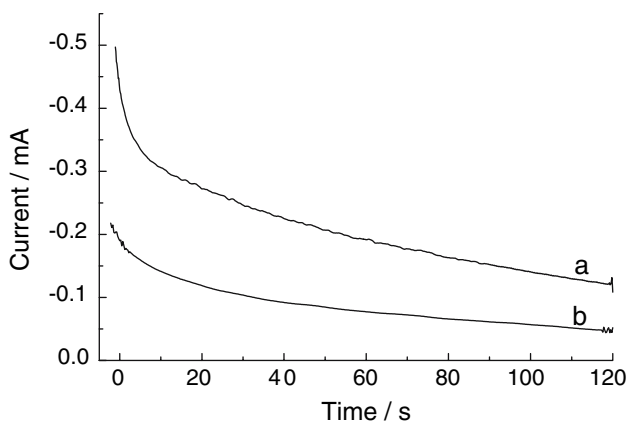


Fig. 8 Electrochemical reduction in KCl solution (0.1 mol L^{-1}) of hexafluoronickelate incorporated in graphite electrodes modified with Ptyr prepared at (a) pH 1.0; (b) pH 12.0. Potential: -1.0 V , 120 s

nickel, the presence of cathodic peaks suggests adsorption of hydrogen on metal. At more cathodic potentials, the hydrogen evaluation reaction predominates. The pH of

Table 1 Nickel mass incorporated and current density of bare graphite and modified electrodes with Ptyr in HCl solution (0.1 mol L^{-1}) at -1.0 V

Graphite electrode	Nickel deposited (g cm^{-2})	Current density in -1.0 V (mA cm^{-2})
Ptyr pH 1	5.1×10^{-5}	2.0
Ptyr pH 12	3.1×10^{-5}	1.2

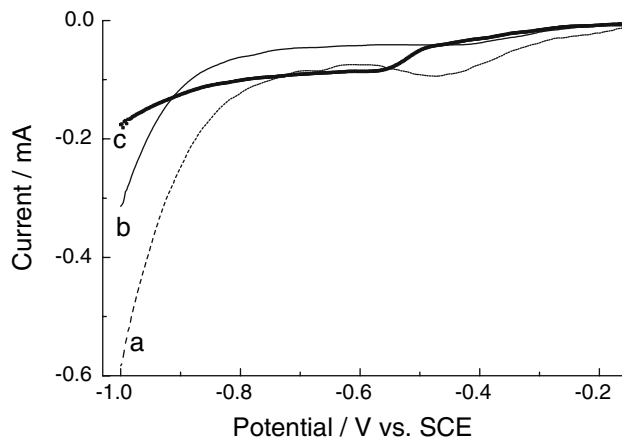


Fig. 9 Voltammograms in $0.1 \text{ mol L}^{-1} \text{ HCl}$ solution of electrodes modified with Ptyr prepared at pH 1.0 (a), 6.0 (b) and 12.0 (c), containing nickel incorporated; 10 mV s^{-1}

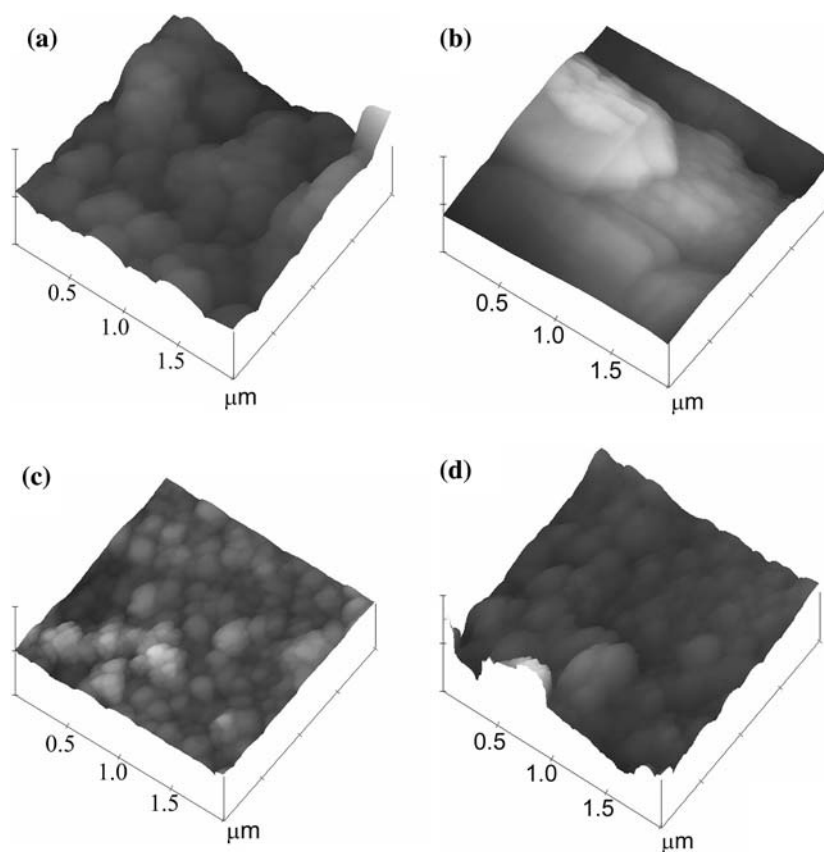
electropolymerization influences the hydrogen generation. The difference in the current recorded in the potential range from about -0.7 V to -0.9 V indicates that the hydrogen is adsorbed at the modified electrode prepared in pH 12.0 for a larger period of time than at the modified electrode prepared in pH 6.0 or and pH 1.0.

The atomic recombination and subsequent hydrogen evolution appears to occur faster in the modified electrode prepared in pH 1.0, and this reaction is influenced by a major area of the polymer and amount of nickel incorporated, appearing as a promising material for electrocatalytic hydrogenations.

In the composite Ptyr (pH 1.0)/nickel, we observed an initial current value of ca. 1 mA , increase of current with the time and stabilization of these values in ca. 10 mA at $\sim 16 \text{ h}$. This increase of current suggests an activation of the composite by cathodic current, and remotion of any spontaneously formed oxide.

The investigation with the composite Ptyr (pH12.0)/nickel showed that the initial current was ca. 1 mA , with a decrease of current with the time and stabilization of these values in ca. 0.3 mA at $\sim 12 \text{ h}$ (results not shown). These results are in agreement with the major covering of the graphite electrode by the polymer produced in acid pH, determined by interferometry and major nickel mass

Fig. 10 AFM images of graphite electrode modified with Ptyr prepared at pH 1.0 without nickel (a) and with nickel (b); Ptyr prepared at pH 12.0 without nickel (c) and with nickel (d); 50 mV s⁻¹, 200 scans



deposited in this modified electrode, calculated by charge of nickel reduction.

Typical 3-D AFM images of Ptyr and composites with nickel incorporated are shown in Fig. 10.

Surface morphology of Ptyr without nickel is different from the composites containing nickel.

The AFM images reveal that Ptyr prepared in pH 1.0 (Fig. 10a) or 12.0 (Fig. 10c) present globular morphology that recovers the whole surface. Ptyr prepared in pH 1.0 presents a rougher morphology with globules having a higher diameter, producing an increase in roughness. Ptyr prepared in pH 12.0 presents a more homogeneous surface, with lesser globules. Roughness values for Ptyr (pH 1.0) and Ptyr (pH 12.0) are 582 nm and 244 nm, respectively. The higher roughness observed for Ptyr (pH 1.0) is in agreement with the increase of current of the modified electrode in the presence of the $K_3Fe(CN)_6/K_4Fe(CN)_6$ redox couple (see Fig. 4). The higher incorporation of nickel (Table 1) in Ptyr (pH 1.0) may be due, in part, to its bigger rugosity in relation to Ptyr (pH 12.0).

Roughness values for the composites Ptyr (pH 1.0)/nickel (Fig. 10b) and Ptyr (pH 12.0)/nickel (Fig. 10d) are 190 nm and 498 nm, respectively.

Conclusions

It is possible to prepare electrodes modified with Ptyr film over the range of pH studied (1.0–12.0). The films formed at different pH values showed changes in electron transport across the polymeric matrix. The films show globular morphology covering all electrode surface, when the modified electrodes was prepared in the pH 1–8 range. Ptyr preparation in pH 12.0 had growth self-limited, possibly due the formation of a Ptyr passivating layer that was not enough to fill the graphite cavities. Impedance analyses indicate that this polymer presents bigger resistance charge transference than Ptyr prepared in pH 1.0.

The nickel incorporation on graphite electrodes modified with Ptyr was more efficient in acid medium due the higher surface area. The higher nickel mass incorporated in modified electrodes prepared in more acid medium produced bigger current density of hydrogen generation.

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