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Polyaniline films containing palladium microparticles for electrocatalytic purposes

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Abstract The deposition of palladium as microparticles on electrogenerated polyaniline (PAni) films accomplished by metal electroless precipitation or by electrodeposition has been used to prepare stable polymer-modified electrode systems. Its general morphology, metal particles size and distribution were obtained by AFM analysis. The PAni/Pd microparticles electrodes have been evaluated for their catalytic activity towards hydrogenation reactions upon organic compounds reduction using 4-nitro-benzaldehyde. Studies on rotating ring-disk electrodes have shown that relatively low Pd loadings are required to obtain effective electrocatalytic activity, provided a good metal particles dispersion of about 100 nm diameter is observed.

Keywords Polyaniline · Electroless precipitation · Electrodeposition · Palladium microparticles · 4-nitro-benzaldehyde electrohydrogenation

Introduction

The development and design of novel catalyst materials and systems have been the subject of several studies in the last years [1–8], and particular attention has been paid to the dispersion of micro/nano-sized metal particles in porous and electron-conducting polymer matrices [9, 10], with the aim to increase the exposed metal spe-

cific area for the enhancement of the systems electrocatalytic activity [11].

The ability of palladium to adsorb hydrogen forming metal-H bonds on its surface and the good reducing activity of the so-generated hydrogen monolayers are well known [12–15]. Nevertheless, these properties may turn into a problem if palladium films are used, since irreversible changes occur in the Pd bulk and on the Pd surface, namely the expansion of the lattice due to the hydrogen absorption and water molecules generation resulting from the combination of adsorbed hydrogen atoms with oxygen [15]. To overcome this difficulty, a possible route is the use of palladium micro/nanoparticles, dispersed onto conducting polymeric layers; as reported [16], the ratio between hydrogen absorbed in the bulk and adsorbed on the surface decreases with increasing ratio of surface-to-bulk Pd atoms. This can be achieved by using polyaniline (PAni) as host polymer matrix for electron transfer, modified by highly dispersed deposited Pd particles. [15]. The synthesis conditions for the PAni film formation as well as the deposition method for embedding the noble metal influence the distribution and size of the metallic particles and, therefore, the performance of these materials as catalysts [13, 15]. The metal incorporation on pre-formed polymer films has been carried out either by electrodeposition [15, 17–20] or electroless precipitation [21–24].

The performance of the polymer/metal composite electrodes as catalysts has already been described involving several reactions such as the reduction of oxygen [18, 25], the hydrogenation of organic molecules [26–29] and the oxidation of hydrogen [19, 30] or of small organic molecules [16, 31–35]. However, information concerning the electrocatalytic hydrogenation of aromatic hydrocarbons is still scarce due to their poor solubility in aqueous solutions and to the low detection limits usually required [36]. Several works report the use of rotating ring-disk electrodes (RRDE) for the detection and identification of reaction product species and for the kinetic study of electrochemical reactions [37–

Dedicated to Professor M. A. Vorotyntsev on the occasion of his 60th birthday

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41]. The advantage of these electrodes is the transport enhancement of the unstable intermediates or products generated on the disk, to the ring electrode, leading to higher currents and therefore, to a higher sensibility and reproducibility [42–44].

The present work is aimed at the correlation of the electrocatalytic activity of PANi films containing Pd particles obtained by electroless precipitation and by electrodeposition with the size and dispersion of the particles. Using the RRDE technique, the behaviour of these modified electrodes as catalysts in the electrohydrogenation of organic molecules, e.g. 4-nitro-benzaldehyde (NBA) and the detection of the hydrogenation products has been evaluated.

Materials and methods

PAni films were synthesised potentiodynamically at a sweep rate of 10 mV/s on polycrystalline Au electrodes, by cycling the potential between -0.20 and $+0.80$ V versus saturated calomel electrode (SCE) for the first 5 cycles, then lowering the anodic limit to 0.75 V for the next 3 cycles, and to 0.7 V after 8 cycles until 17 polymerisation cycles [24]. Two different Au-working electrodes (purity 99.99%) were used; a homemade rotating Au ring–Au disk electrode system, i.e. RRDE ($A_R = 0.061$ cm² and $A_D = 0.28$ cm²) and free gold disks ($A = 0.50$ cm²). The films grown onto the gold disk (RRDE) electrode were used to evaluate their electrocatalytic behaviour while those grown on the free disks were used for the microscopic characterisation. For each experiment, a fresh mirror-finish surface was generated by hand-polishing the electrode in an aqueous suspension of successively finer grades of alumina (down to 0.05 μ m). A Pt foil and an SCE were used as counter and reference electrode, respectively, in a three-compartment cell. The electrolyte solution was 0.1 M aniline (distilled and kept under N₂ atmosphere, at 4 °C) in 0.5 M H₂SO₄ (100%, Merck), degassed with Nitrogen (99.9999%) for 15 min prior to all measurements.

The polymer films were washed with Milli-Q water and the redox activity characterised in 0.5 M H₂SO₄ (monomer-free solution) by cycling the potential between -0.20 and $+0.40$ V versus SCE at a sweep rate of 50 mV/s. The electrode potential was initially kept at -0.2 V for 10 min in order to observe a complete discharge of the film.

The polymer coated gold electrodes were used as substrates for the palladium deposition. The procedure for the electroless metal precipitation is described elsewhere [24]; it is achieved by immersing the PANi-modified electrodes in the reduced state (-0.20 V versus SCE for 10 min in 0.5 M H₂SO₄ and washed in Milli-Q water), in a solution containing 100 ppm Pd (II) in 0.0125 M HCl. Immersion times of 30 and 60 min were used and the so-obtained composite electrodes will be named thereafter as 17/10/Pd_{el-p}30 and 17/10/Pd_{el-p}60.

For the Pd electrodeposition, the polymer film, in its oxidised state, was transferred in the shortest lapse of time to a 0.001 M PdSO₄ (98%, Aldrich) in 0.5 M H₂SO₄ solution, where it was kept at $+0.40$ V versus SCE for 5 s; this procedure was developed to avoid the electroless precipitation of palladium in/on the polymer film. The potential was stepped from $+0.40$ to $+0.19$ V leading to the reduction of the Pd (II) species, until a deposition charge of ~ 15 and 33 mC cm⁻² was accomplished. The corresponding modified electrodes will be designated as 17/10/Pd_{ed}15 and 17/10/Pd_{ed}33, along the following sections.

The electrochemical measurements were performed using either a homemade potentiostat, a Waveform Generator PP R1 (Hi-Tek Instruments, England), and a Recorder X-Y Model 200 (The Recorder Company) or, for the RRDE experiments, an EG&G model 363 bipotentiostat and Yokogawa recorder (A3 X-Y, model 3023). The RRDE experiments were carried out at room temperature, in ethanol/water (2:3) + 0.5 M H₂SO₄ solutions containing 1 mM NBA ($>99.0\%$, Fluka), which were degassed with Nitrogen (99.9999%) for 15 min, before each measurement. The potential of the gold disk electrode was scanned from $+0.50$ V to different cathodic limits (-0.20 , -0.25 and -0.30 V) and then in the positive direction to $+0.50$ V at a scan rate of 0.020 V/s while keeping the ring potential at $+0.50$ V. A palladium electrode ($A = 7.9 \times 10^{-3}$ cm²) was also employed in order to compare its catalytic response with the PANi/Pd electrodes. The Pd electrode was hand-polished, by the same methodology applied to the Au electrodes.

The surface morphology of the modified electrodes was examined with a Nanoscope IIIa Multimode Atomic Force Microscope from Digital Instruments equipped with the Extended Electronics Module for topographic and phase imaging.

Results and discussion

PAni/Pd electrochemical synthesis and characterisation

Typical cyclic voltammograms of the potentiodynamically prepared PANi films, recorded in 0.5 M H₂SO₄, are shown in Fig. 1. The charge involved in the polymer oxidative conversion, Q_{ox} , observed within the potential range of -0.20 to $+0.40$ V, obtained from the anodic current, is $Q_{ox} = 6.12$ mC cm⁻².

These PANi films were modified by electroless precipitation and by electrodeposition of palladium. The former process has been previously discussed in detail by the authors [24]. For the potentiostatic deposition of Pd, the polymer was kept in its oxidised state ($+0.40$ V vs. SCE), and after immersion of the PANi films in the solution containing palladium salt a potential pulse to $+0.19$ V was applied. From the analysis of the collected chronoamperograms, it has been concluded that Pd

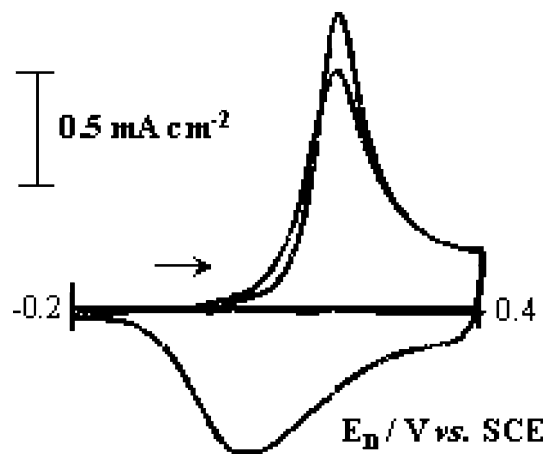


Fig. 1 Cyclic voltammograms (first and second scan) of the 17/10 film in monomer-free solution (0.5 M H₂SO₄), $v = 0.05$ mV/s

electrodeposition on PANi films can be described by an instantaneous nucleation and 3D growth, as discussed by the authors in a separate paper (A. Mourato et al., in preparation).

The charge consumed in the course of Pd electrodeposition was selected aiming to obtain metal amounts similar to those observed for the electroless precipitation. A crude estimate was made based on a statistical analysis of the number and size of Pd clusters through AFM images obtained for 17/10/Pd_{el-p}30- and 17/10/Pd_{el-p}60-modified electrodes; assuming the superficial area of the exposed particles as half spheres it results,

respectively, in requiring charges of ≈ 15 and 33 mC cm⁻², for observing the equivalent quantity of electro-deposited Pd. Topographic non-contact AFM images of the PANi/Pd-modified electrodes obtained by Pd electroless precipitation for 60 min and Pd electrodeposition attained with 33 mC cm⁻² are depicted in Fig. 2. Electrolessly precipitated spherical palladium particles (Fig. 2a) are distributed mainly on the top of the compact polymer layer which is formed by small globular features with diameters lower than 80 nm. The Pd clusters (average size, 80–150 nm) are highly distributed and no aggregation was observed. It is of interest to note that the number of the deposited metal clusters increases with the immersion time but the Pd particles average size remains. On the other hand, by the electrodeposition method, in agreement with an instantaneous nucleation and 3D growth, an increase in the consumed charge leads to an enlargement of the Pd particles diameter, namely from about ~ 50 nm when 15 mC cm⁻² to ~ 100 nm (Fig. 2 b) for 33 mC cm⁻². The larger number of dispersed smaller palladium particles provided by this approach as compared to the electroless precipitation is clearly distinguishable in Fig. 2.

Electrocatalytic hydrogenation of NBA at Au/PANi-Pd-modified electrodes

The hydrogenation of NBA was chosen to test the catalytic activity of PANi-Pd cathodes prepared under the

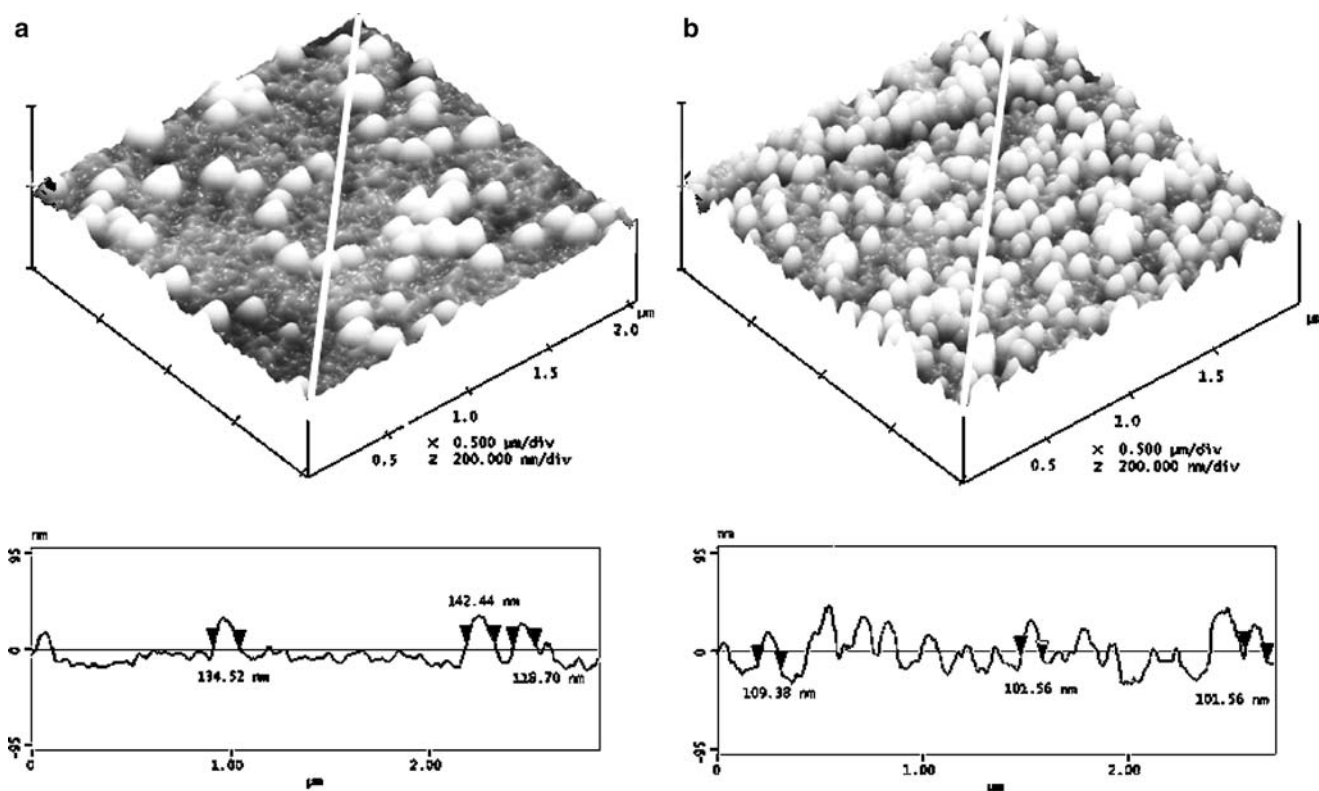
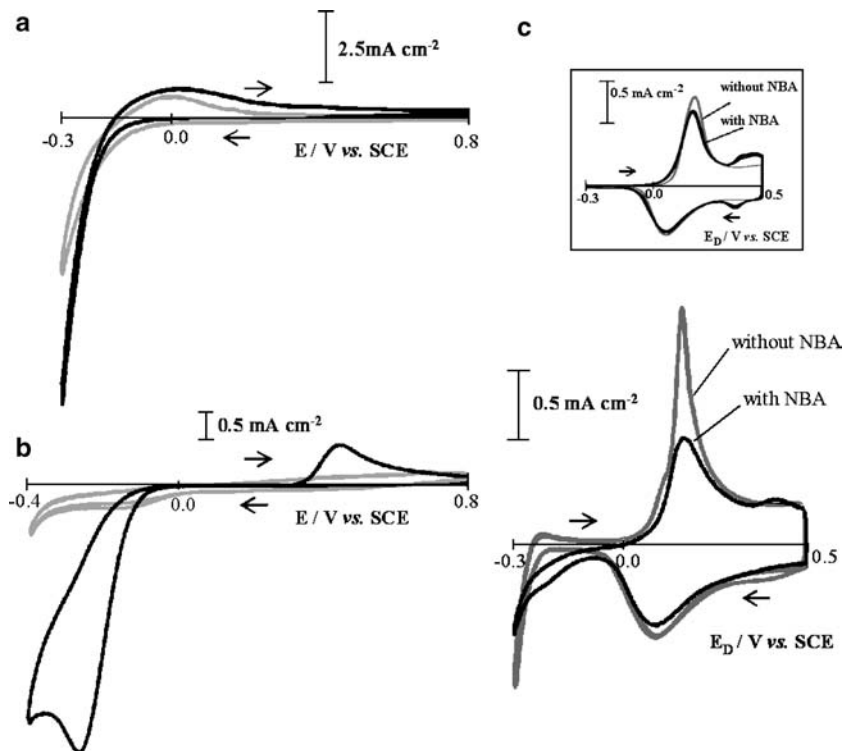


Fig. 2 3D-processed topographic AFM-tapping mode images of the 17/10/Pd_{el-p}60 (a) and 17/10/Pd_{ed}33 (b)

Fig. 3 Cyclic voltammograms at $v = 0.02$ V/s of the Pd electrode (a), Au polycrystalline electrode (b) and 17/10/Pd_{cl}-p₃₀-modified electrode (c), in ethanol/water (2:3) + 0.5 M H₂SO₄ solutions (grey line) and in electrolyte containing 1 mM 4-nitro-benzaldehyde (NBA) (dark line); inset: voltammetric response of pristine PANi in NBA free (grey line) and NBA containing (dark line) background electrolyte



above mentioned experimental conditions and with different metal loadings.

It is well known that at catalytically active electrodes, such as Devarda copper [45] or Raney nickel [46], nitrobenzene can be reduced to aniline with good yields. For the conversion of nitrobenzene to phenyl hydroxylamine an electron–protonation mechanism is widely accepted; further reduction to aniline is often considered to involve an electrocatalytic hydrogenation [47]. In substituted aromatic nitro compounds, a similar reaction path is expected since the nitro group usually is the more easily reducible site; consequently, for the NBA hydrogenation the following pathway has been considered [48, 49]:

The behaviour of NBA (1 mM) was first analysed using polycrystalline palladium and gold electrodes, and the obtained voltammograms are illustrated in Fig. 3. At bulk palladium (Fig. 3a) no current peak can be observed before the discharge of protons. The hydrogen adsorption cannot be seen, since it is masked by the hydrogen absorption reaction [15] and its counterpart

only denoted by the weak current shoulder in the reverse potential scan. Moreover, there are no significant differences in the current responses collected in free and NBA containing solutions, to support the occurrence of the organic compound hydrogenation, even in small extent.

The voltammograms recorded with the Au electrode (Fig. 3b), in the presence of NBA, show a well-defined cathodic peak at -0.265 V. Its assignment to the NBA electroreduction to hydroxylamine-benzaldehyde is corroborated by the development, in the reverse scan, of the anodic peak at $+0.45$ V, which shall correspond to the product re-oxidation very likely to nitroso-benzaldehyde. Although a search in the literature only provided information for aprotic solvents, indicating a reduction at -0.375 V versus SCE on a platinum electrode in dimethylsulfoxide with 0.1 M tetra-*n*-butylammonium bromide [50], the observed NBA reduction at a less negative potential is to be expected in aqueous acidic solutions.

The voltammograms obtained with the 17/10/Pd_{cl}-p₃₀-modified electrodes are presented in Fig. 3c. In

Scheme 1. 1

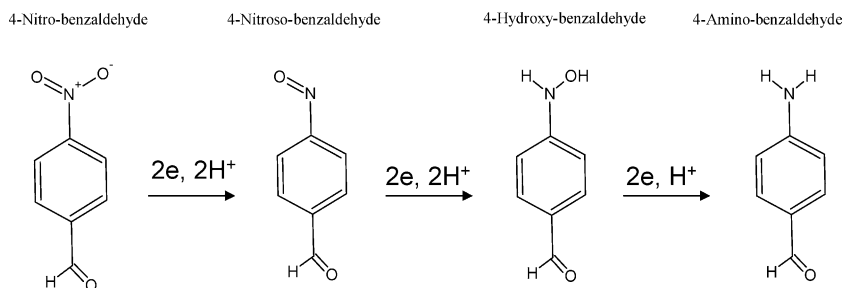
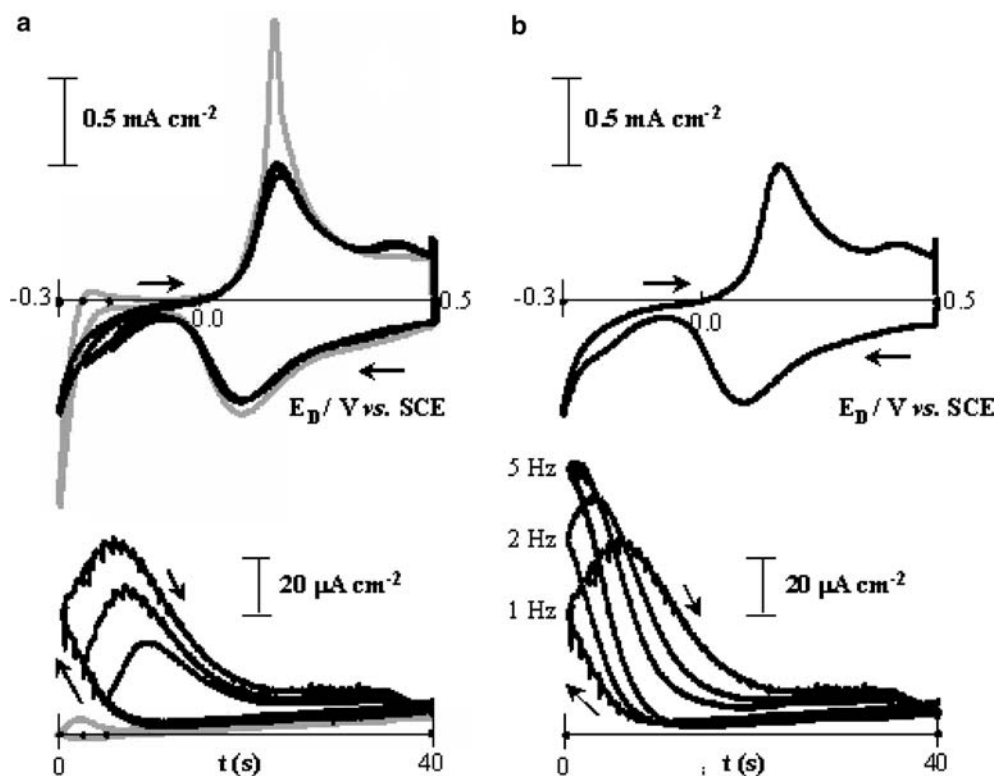


Fig. 4 Cyclic voltammograms of 17/10/Pd_{el-p}30-modified disk and simultaneous Au ring currents in ethanol/water (2:3) + 0.5 M H₂SO₄ + 1 mM NBA as a function of the disk potential [+0.50, (E = -0.20, -0.25, -0.30)] V versus SCE, $\nu = 0.02$ V/s, keeping the ring potential at +0.50 V versus SCE; $\omega = 1$ Hz (a) and $\omega = 1, 2$ and 5 Hz (b). The grey line in (a) shows the response in NBA free electrolyte solution



addition to the response due to the redox process and capacitive charging of PANi, in the NBA-free electrolyte, the hydrogen evolution reaction (HER) occurs at a potential lower than -0.30 V and during the positive scan, besides the hydrogen desorption from the palladium clusters, responsible for the small anodic current at far negative potential values, the oxidation of molecular hydrogen entrapped in the polymer matrix [18] contributes for the peak at ca. $+0.17$ V. In the presence of NBA, an adsorption process seems to occur [51] related to a current shoulder ($E \approx -0.23$ V) observed within the potential region where PANi is electronically non-conductive and the HER much less pronounced at -0.30 V; these features strongly indicate the co-adsorption of NBA and H on the dispersed palladium particles, and a subsequent NBA hydrogenation. The additional oxidation wave, at ca. $+0.45$ V, in the capacitive region of the PANi, is also addressable to the oxidation of the hydrogenated species. Since adsorption of NBA on the pristine PANi can be considered negligible (inset in

Fig. 3), the modified electrodes appear suitable for the electrocatalytic hydrogenation of NBA, under the potential range in analysis.

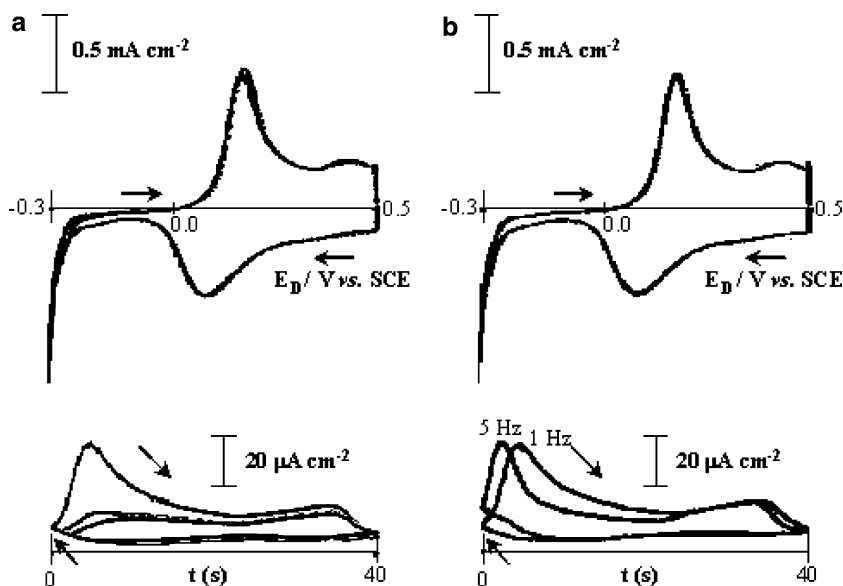
In order to give a better basis to the origin of the voltammetric characteristics, steady state hydrodynamic voltammetry was used. Figure 4a compares the data obtained using different cathodic potential limits (-0.20 , -0.25 and -0.30 V) at the 17/10/Pd_{el-p}30-modified gold disk electrode and the simultaneous response of the gold ring electrode ($E_R = +0.50$ V); the measurements were performed at a scan rate of 0.02 V/s and at 1 Hz angular velocity, ω . The ring current (I_R) increases as soon as the disk potential reaches the domain where the above mentioned current shoulder is observed, confirming that the co-adsorption of NBA and H on the disk is followed by the formation of an hydrogenated product being reduced at the disk. The extent of the hydrogenation reaction proceeding at the disk, most likely the reduction of NBA to 4-hydroxylamine-benzaldehyde, depends on the electrodes cathodic potential limit increasing from

Table 1 Oxidation charges obtained on the gold ring electrode

$Q_{ox} / \text{mC cm}^{-2}$	PANi-Modified Electrodes			
	17/10/Pd _{el-p} 30	17/10/Pd _{el-p} 60	17/10/Pd _{ed} 15	17/10/Pd _{ed} 33
$\omega = 1$ Hz	1.18	0.84	0.81	1.02
$\omega = 5$ Hz	1.26	0.74	0.72	1.05

$E_D = [+0.50, -0.30]$ V and $E_R = +0.50$ V versus SCE (other conditions as stated in Fig. 4b)

Fig. 5 Cyclic voltammograms of 17/10/Pd_{el-p}60-modified disk and simultaneous Au ring currents in ethanol/water (2:3) + 0.5 M H₂SO₄ + 1 mM NBA as a function of the disk potential [+0.50, ($E = -0.20, -0.25, -0.30$)] V versus SCE, $v = 0.02$ V/s, keeping the ring potential at +0.50 V versus SCE; $\omega = 1$ Hz (a) and $\omega = 1$ and 5 Hz (b)



-0.20 to -0.30 V; the ring anodic currents are due to the oxidation of the reaction intermediate (hydroxylamine-benzaldehyde to nitroso-benzaldehyde).

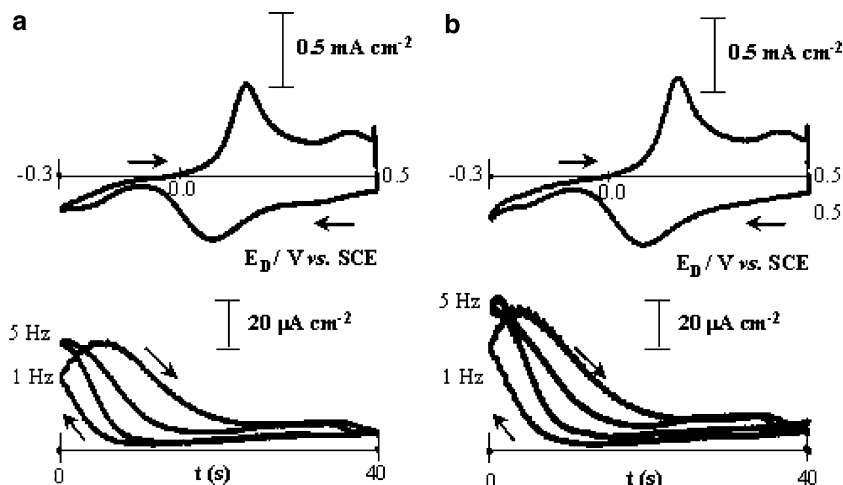
Taking into account that the efficiency of an organic compound hydrogenation should mainly depend on its co-adsorption with atomic hydrogen, no reagent-diffusion-controlled step is expected. Indeed, no alteration in the voltammetric response of the polymer/Pd-modified disk electrode has been registered with the increase of ω up to 5 Hz (Fig. 4b). On the other hand, the electrode rotation rate influences the detection of NBA-hydrogenated products oxidation since the ring current density increases with the angular velocity, i.e. as the hydrogenated species produced on the disk are transferred to the ring more easily. As expected, the charge of the anodic peak at the gold ring electrode did not depend significantly on the rotation rate (Table 1).

To analyse the Pd loading effect on the catalytic activity of the PANi-modified cathodes, similar experi-

ments were performed with 17/10/Pd_{el-p}60 leading to data illustrated by Fig. 5. When compared with the results presented in Fig. 4, besides a higher I_D at -0.30 V due to HER taking place on a larger metallic area, the main difference is that the current shoulder related to the adsorption processes is almost undetectable. This is consistent with the development of a very small I_R up to the end of the cathodic potential scan of the disk. The increase of I_R when the disk potential sweep is reversed suggests that the hitherto formed molecular hydrogen participates in the hydrogenation reaction. This is also supported by the very small ring current recorded when the cathodic potential limit in the disk voltammetric sweep is decreased to -0.275 and -0.25 V (still allowing the formation of H_{ads} but hindering the HER).

The collected results clearly prove that the Pd particles incorporated in PANi by electroless precipitation are catalytically active for the electrogeneration of hydrogen, but for organic hydrogenation purposes an increase

Fig. 6 Cyclic voltammograms of a 17/10/Pd_{ed}15- and b 17/10/Pd_{ed}33-modified disk and simultaneous Au ring currents in ethanol/water (2:3) + 0.5 M H₂SO₄ + 1 mM NBA as a function of the disk potential [+0.50, ($E = -0.20, -0.25, -0.30$)] V versus SCE, $v = 0.02$ V/s, keeping the ring potential at +0.50 V versus SCE; $\omega = 1$ and 5 Hz



in the number of deposited Pd clusters on the polymer film surface, as is the case of 17/10/Pd_{el-p}60 when compared with 17/10/Pd_{el-p}30, may consist in a disadvantage.

For the case of the modified electrodes prepared by electrodeposition of palladium in PANi, to change the loading level (deposition charge) corresponds to obtain different sized but still uniformly dispersed Pd particles (A. Mourato et al., in preparation). The behaviour of 17/10/Pd_{ed}15 and 17/10/Pd_{ed}33 towards the hydrogenation of NBA is shown in Fig. 6. Both modified electrodes are less catalytic for the HER than the PANi/Pd composites prepared by electroless precipitation, and thus appear more adequate for the present purpose, since the efficiency of the electrocatalytic hydrogenation is determined by the competition between hydrogenation of the organic substrate and HER.

In contrast with 17/10/Pd_{el-p}, the increase in the size of the electrodeposited Pd particles do not significantly affect the disk voltammetric responses, but the increase in the charge of the oxidation process occurring at the ring points to a better performance of 17/10/Pd_{ed}33 and thus to a beneficial effect of enlarging the Pd particles size from ~50 nm (17/10/Pd_{ed}15) to ~100 nm (17/10/Pd_{ed}33). The relative similarity of behaviours displayed by 17/10/Pd_{ed}33 and 17/10/Pd_{el-p}30, where the Pd deposits diameters are in the 80–150 nm range, also emphasises the effect of the Pd particles size.

Conclusions

The incorporation of palladium in electrogenerated PANi films, either by metal electroless precipitation or by electrodeposition, provides good dispersion of metallic microparticles (i.e. diameters less than 0.2 μm) as revealed by AFM images. In particular, the AFM analyses show that the size of the microparticles varies with the conditions and type of deposition methodology. These modified electrodes exhibit interesting electrocatalytic activities with regard to the hydrogenation of organics.

By employing the RRDE to study the electrohydrogenation of NBA, the hydrogenated product produced at the disk can be detected by the ring, provided it is kept at an adequate oxidative potential. The results show the role of the metal-loading level, imparted by the time/charge used in the incorporation procedure on the modified electrodes catalytic activity. Data analysis reveals that relatively low Pd loadings with good dispersion of particles of about 100 nm diameter, as observed both for 17/10/Pd_{ed}33 and for 17/10/Pd_{el-p}30, are effective electrocatalysts for hydrogenation purposes.

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