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Characterization of bismuth adatom-modified palladium electrodes The electrocatalytic oxidation of aliphatic aldehydes in alkaline solutions

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Abstract

Palladium–bismuth films supported on glassy carbon substrates were prepared by cathodic electrodeposition of palladium ad subsequent adsorption of bismuth species on the electrode surface. A mechanism regarding the irreversible adorption process of bismuth species on the palladium surface, was described. The resulting active film was characterized, and in particular, the electrooxidation of some aliphatic aldehydes was investigated in moderately alkaline solutions. The bismuth adlayer increases the overall rate of the oxidative processes through a combination of a third body mechanism and a true catalyst. The oxidation currents of propionaldehyde, evaluated in cyclic voltammetry increased linearly on increasing analyte concentration up to 8 mM. Under chronoamperometric conditions at the constant applied potential of −0.2 V versus SCE, the resulting calibration plot for propionaldehyde analysis was linear over the range of 1.5–8 mM with a correlation coefficient better than 0.97. Throughout the XPS investigation Pd 3d and Bi 4f detailed regions an average chemical composition of the surface composite film of $Pd_{96\pm2}Bi_{4\pm2}$ was evaluated.

Keywords: Palladium; Bismuth; Oxides; Aldehydes oxidation; XPS

1. Introduction

The electrochemical oxidation of organic species in aqueous solutions constitutes an interesting topic in the field of the electrosynthesis, electroanalysis and hydrocarbon–air fuel cells. In general, the efficiency of electrode reactions, depend strictly upon the chemical and physical nature of the electrode substrates. Noble metals such as gold and platinum are ideal electrode substrates for the electrochemical oxidation of several electroactive molecules because they show a high catalytic activity and a good corrosion resistance. Unfortunately, a serious consequence of strong adsorption of organic reactants, intermediate and/or products species can be the reason fouling of these electrodes when are used as anodic materials. Hence, the scarcely electrocatalytic efficiency of these electrodes is the result, in many instances, of strong adsorption of organic molecules with subsequent poisoning of the substrate electrodes. Metal adatoms have been widely studied and proposed in order to improve the electrocatalytic activity of traditional noble metals for the oxidation of organic molecules [1,2]. These metal adatoms can affect the initial activity of the noble electrode substrate through different mechanism such as: (i) blocking the active sites of the electrode in order to avoid the adsorption of poisoning species; (ii) providing a favourable and distinct catalytic interaction with the reactants and reaction intermediates (i.e., oxygen species necessary for the surface electrode reactions); (iii) modifying the electronic properties of the electrode surface in a such a way that the poisoning species cannot be adsorbed on the active sites. In this way, electrodeposition or irreversible adsorption of As, Se, Sb, Sn, Pb, Hg, Cd, Bi, etc. on noble metal substrates have been proposed as electrodes in order to obtain significant enhancements in the electrocatalytic activity towards the electrooxidation of small organic electroactive molecules [3–11].

Because of its strong adsorption and subsequent formation of stable adlayer, bismuth adatom has been widely characterized and used as modifier species in order to enhance the electrocatalytic properties of platinum or palladium surfaces [12–17]. It has been suggested that bismuth enhances the cat-

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alytic activity of platinum substrate electrodes toward formic acid through an electronic effect [7], however bismuth may also act as a third body, decreasing the ensemble size for poison formation [16]. On the other hand, theoretical model calculation has suggested that bismuth acts as a catalyst in the electrooxidation processes (bifunctional mechanism) [7]. Recently, we have compared the electrocatalytic activity of polycrystalline gold and platinum electrodes modified with adsorbed bismuth oxide adlayers toward the electrooxidation of several sugar acid molecules in moderately alkaline medium [18]. In this study, the bismuth adsorbed species acts as a true catalyst on the direct electrooxidation pathway, providing the oxygen necessary for the oxidation of organic molecules adsorbed on the platinum or gold active sites.

In the present work, we report a procedure for the electrochemical deposition of palladium film onto a traditional glassy carbon electrode substrate (GC/Pd) and its surface modification with bismuth adlayer (GC/Pd/Bi). The resulting modified films were characterized by electrochemical and X-ray photoelectron spectroscopy (XPS) techniques. The electrocatalytic properties of the GC/Pd and GC/Pd/Bi electrodes were investigated in 50 mM NaOH solutions towards the electrocatalytic oxidation of some saturated aliphatic aldehydes.

2. Experimental

2.1. Reagents

Solutions were prepared from analytical-reagent grade chemicals without further purification and by using doubly distilled deionized water. NaOH pellets (99%), $HClO_4$ (70%), Na_2PdCl_6, $Bi(NO_3)_3{\cdot}5H_2O$ and aliphatic aldehydes are purchased from Aldrich Chemical Co. (St. Louis, MO).

2.2. Apparatus

The voltammetric experiments were performed with an Autolab PGSTAT 30 Potentiostat/Galvanostat (Eco Chemie, Utrecht, The Netherlands) and the data were acquired using an Autolab GPES software package Version 4.8. Cyclic voltammetry (CV), was done in a three-electrode cell using a glassy carbon electrode modified with palladium film and bismuth adlayer as a working electrode, a SCE reference electrode and a platinum foil counter-electrode. The electrode substrate (3 mm diameter) used in CV was purchased from Amel (Milan, Italy). Current density values ($mA\,cm^{-2}$) are quoted with respect to apparent geometric area of electrode substrate. Unless otherwise specified, experiments were carried out at an ambient temperature (21 °C ± 2). When necessary, the solutions were deoxygenated by bubbling with nitrogen prior to the electrochemical experiments.

X-ray photoelectron spectra were collected using a Leybold LH X1 spectrometer using unmonochromatized Al Kα radiation (1486.6 eV). The source was operated at 15 kV and 20 mA. The binding energy (BE) scale was calibrated with respect to the Cu $2p_{3/2}$ (932.7 eV, with a full-width at half-maximum (FWHM) of 1.75 eV) and Au $4f_{7/2}$ (84.0 eV with a FWHM of 1.20 eV) signals. Spectra were recorded only after the wide scan showed that no features arose from the copper tape and from the sample rod. Wide and detailed spectra were collected in fixed analyser transmission (FAT) mode with a pass energy of 50 eV and a channel width of 1.0 and 0.1 eV, respectively. The vacuum in the analysis chamber was always better than 5×10^{-9} mbar.

The kinetic energy axis origin in all spectra was not corrected for surface charging, but peak positions (BE) in the text are corrected by referring to the C 1s peak after setting its BE to 284.6 eV. Satellites and a non-linear Shirley background were substracted from the spectrum before curve fitting analysis. Elemental surface stoichiometries were obtained from peak area ratios corrected by appropriate sensitivity. Gaussian/Lorenzian sum functions were used to fit Pd 3d, Bi 4f, O 1s and C 1s peaks line-shapes.

2.3. Electrode modification

The palladium electrodeposition on the glassy carbon electrodes was performed by voltage cycling ($50\,mV\,s^{-1}$) between 0.0 and −0.4 V versus SCE for 50 cycles in non-deaerated solution containing 0. 5 mM Na_2PdCl_6, 50 mM $HClO_4$ and 25 mM HCl. The bismuth-modified palladium electrodes were prepared by immersion of the GC/Pd electrode in non-deaerated 50 mM $HClO_4$ solution containing 200 μM $Bi(NO_3)_3$ at open circuit for a given time. Occasionally, bismuth film was electrodeposited on the glassy carbon surface at −0.6 V versus SCE for 10 min in solution 50 mM $HClO_4$ containing 200 μM $Bi(NO_3)_3$. The resulting GC/Pd/Bi electrodes were then rinsed with pure water and transferred to an electrochemical cell containing 50 mM NaOH solution. Traces of palladium–bismuth oxides were removed from the glassy carbon substrate by polishing the surface electrode with 0.05 μm α-alumina powder on a polished micro-cloth and washing it with twice distilled water.

Quantitative analysis for evaluating the film composition was mainly based on the relative areas of the XP signal of the Pd 3d and Bi 4f corrected for the relevant sensitivity factors. Moreover, the surface coverage of Bi (Γ_{Bi}) and the surface film composition of the investigated composite electrodes were also evaluated by electrochemical analysis considering the charge under the Ia_1 and Ic_1 waves associated at the oxidation and reduction of bismuth and palladium species, respectively. In this respect, the charge under the Ia_1 wave was referred to $Bi^0 \rightarrow Bi^{III}$ redox process while the Ic_1 wave was referred to $Pd^{II} \rightarrow Pd^0$ redox process.

3. Results and discussion

3.1. Preparation and electrochemical behaviour of the GC/Pd and GC/Pd/Bi electrodes

In order to minimize the hydrogen gas evolution from the electrode surface and to improve the adherence and mechanical film properties, the electrodeposition of palladium film was performed by voltage cycling between 0.0 and −0.4 V versus SCE for 50 cycles in deaerated solution containing 0.5 mM Na_2PdCl_6, 50 mM $HClO_4$ and 25 mM HCl. Fig. 1 shows a typical growth of palladium film on the glassy carbon electrode during continuous

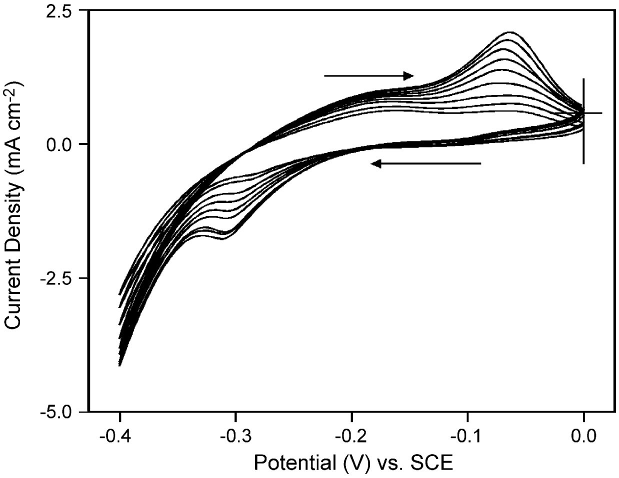

Fig. 1. Consecutive cyclic voltammograms (recorded after each fifth scan) at 50 mV s^{-1} of palladium film growth on a glassy carbon electrode in a solution containing 0. 5 mM Na_2PdCl_6, 50 mM $HClO_4$ and 25 mM HCl.

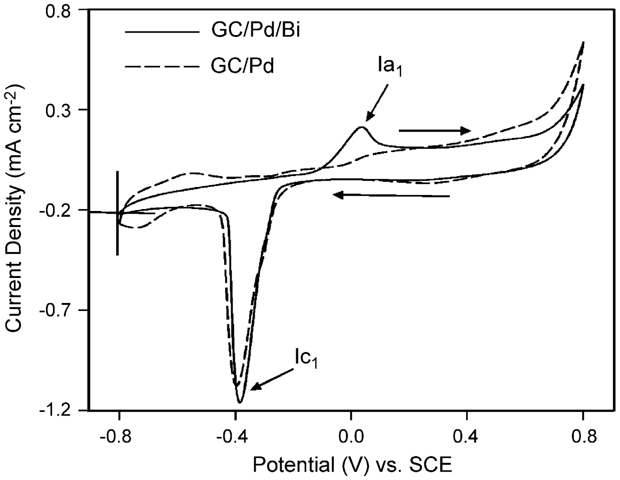

Fig. 2. Comparison of the voltammogram profiles of a GC/Pd/Bi and GC/Pd electrodes in 50 mM NaOH solution. The bismuth oxide adlayers were deposited on the palladium film by direct immersion of the GC/Pd electrode in solution containing 200 μM $Bi(NO_3)_3$ at open circuit for 10 min. Other experimental conditions as in Fig. 1.

potential cycling. After 50 potential scans, an uniform and well adherent deposit film appeared on the glassy carbon surface. It is well known that in the negative potential range, hydrogen is strongly adsorbed on the Pd surface and can be absorbed to a large extent into the Pd lattice [19,20]. In general, two superficially forms (i.e., α-PdH and β-PdH) of hydrogen species on the Pd surface are reported [21] and the complex redox waves observed, can be attributed to the β-PdH formation/desorption processes of hydrogen from the Pd lattice to the surface and from there into the electrolyte [22]. In fact, depending on the potential and time, the diffusion of hydrogen atoms into bulk palladium film (absorption processes) can result in the formation of either α or the β phase [23,24].

The bismuth adlayers on the palladium surface were prepared by direct immersion of the GC/Pd electrode in solution containing 200 μM $Bi(NO_3)_3$ at open circuit for 10 min. Typical voltammogram profiles are shown in Fig. 2. The electrochemical processes occurring at the GC/Pd electrode are relatively complexes because several palladium oxide species are involved during the redox transition [19,25–27] such as PdO, $Pd(OH)_{ads}$, $Pd(OH)_2$, PdO_2, PdO_3, etc. These electrochemical surface reactions are assumed to occur in a stepwise fashion, superimposed by a significant metal dissolution process strongly dependent on the experimental conditions, such as applied potentials, pH and chemical composition of the electrolytic solutions, etc. The GC/Pd electrode shows during the anodic sweep, a broad peak centred in the potential range between −0.7 and −0.5 V. This peak is likely related to the desorption process of hydrogen species from the palladium surface. Upon further anodic scanning, the major redox process includes a large anodic peak at about 0.0 V corresponding to the formation of $Pd(OH)_2$ and/or PdO monolayers [27,28]. Moreover, a simultaneous formation of hydrous oxide above 0.0 V via formation of $Pd(OH)_{ads}$ species can be postulated. Oxygen evolution, observed at potentials >0.5 V, obscures the overall processes regarding the formation of higher valence oxides of palladium such as PdO_2 and PdO_3 species. During the cathodic sweep, there is a peak at −0.4 V (Ic_1) corresponding to the reduction of oxide species and reformation of a clean surface of Pd^0 layers. At potential values more negative than −0.6 V there is a broad wave corresponding to the hydrogen adsorption process. The voltammogram profile of the GC/Pd/Bi electrode, shows some distinct features if is compared with that of GC/Pd electrode. At sufficiently high coverage, the adsorbed bismuth species suppresses completely the adsorption/desorption processes of hydrogen on Pd surface. In addition, the adsorbed bismuth induces a partial inhibition of the formation of palladium oxides and oxygen evolution. It is interesting to observe that during the positive sweep, there is a wave (Ia_1) that occurs at about 0. 1 V versus SCE and can be related to the formation of a Bi(III) oxide film [29], according to the following reaction:

$$2Bi_{ads} + 6OH^- \Leftrightarrow (Bi_2O_3)_{ads} + 3H_2O + 6e^- \quad (1)$$

The reduction of Bi_2O_3 and/or other bismuth oxide species such as $Bi(OH)_3$, BiOOH, $Bi(OH)^{2+}$, $Bi_6(OH)_{12}{}^{6+}$, etc., is usually observed as a single cathodic peak occurring prior to hydrogen region. This reduction process can be accompanied by a partial dissolution of bismuth oxide into the ionic species $BiO_2{}^-$ and formation of BiO_{ads}, $(Bi(OH)_2)_{ads}$ and Bi_{ads} species.

The experimental data reported here established that when a palladium surface is exposed to an acidic solution containing Bi^{3+} ions, a spontaneous adsorption process of bismuth species occurs. This behaviour is in agreement with previous studies [30,31], where an irreversible adsorption process of bismuth species on platinized or platinum electrodes substrates is observed. Taking into account our experimental data, and in agreement with the literature [29,30], we believe that the adsorption process of the bismuth species, proceeds through the ionization of adsorbed hydrogen species with subsequent formation of hydroxyl and bismuth adsorbed species. Thus, a general scheme regarding the irreversible adsorption process of bismuth

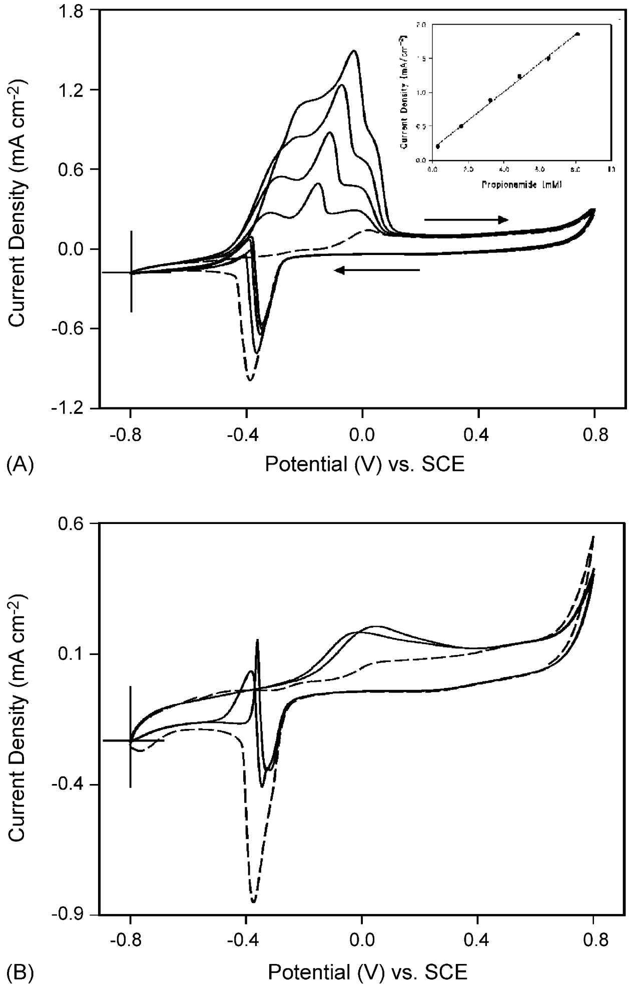

Fig. 3. (A) Voltammograms at a GC/Pd/Bi in 50 mM NaOH (dashed curve) and in solution containing increasing concentration of propionaldehyde (in 1.6 mM steps). *Inset*: calibration graph of peak currents versus concentration of the propionaldehyde. In the calibration graph, the peak currents are not corrected for the background contribute. (B). Voltammograms at a GC/Pd electrode in 50 mM NaOH (dashed curve) and in solution containing increasing concentration of propionaldehyde. Other experimental conditions as in (A).

species on the palladium surface, may be the following:

$$\mathrm{Pd} + \mathrm{H_2O} \Leftrightarrow \mathrm{Pd(OH)_{ads}} + \mathrm{Pd(H)_{ads}} \qquad (2)$$

$$\mathrm{Bi^{3+}} + \mathrm{Pd(H)_{ads}} \Leftrightarrow \mathrm{Pd(Bi^{*})_{ads}} + \mathrm{H^{+}} \qquad (3)$$

where $(\mathrm{Bi}^{*})_{\mathrm{ads}}$ indicates the bismuth ions and/or its oxides species adsorbed on the palladium surface. Thus, the proposed mechanism of bismuth adsorption, combining hydroxyl species formation with bismuth adsorption, would lead to the simultaneous accumulation at the surface of oxygenated and bismuth species (vide infra). Nevertheless, more experimental information is necessary in order to confirm and/or define a better detailed adsorption mechanism.

Typical cyclic voltammograms on GC/Pd/Bi and GC/Pd electrodes in 50 mM NaOH solution containing increasing concentrations of propionaldehyde are shown in Fig. 3A and B, respectively. When propionaldehyde was added to alkaline solution, the GC/Pd/Bi electrode shows, during the positive sweep, a complex wave that appears in the range of potentials comprised between −0.4 and 0.1 V. The currents increased linearly on increasing analyte concentration up to 8 mM and the relevant peak potential shifted in the positive direction on increasing concentration of analyte. The inset in Fig. 3A, shows the relevant calibration graph for the analysed propionaldehyde. Similar current–potential profiles and linear ranges of the concentrations were observed for the other aliphatic aldehydes investigated such as formaldehyde, acetaldehyde, butyraldehyde, valeraldehyde and hexanale. In all cases, no significant electrooxidation currents attributable to aliphatic aldehydes could be observed at glassy carbon electrodes modified with electrodeposited bismuth film, in the same alkaline medium and within the same potential window. The GC/Pd electrode shows, a very low elctrocatalytic activity for potentials higher than −0.2 V, where the electrooxidation of the aldehyde is simultaneously accompanied with the formation of higher oxidation state of the palladium. The anodic currents are not linearly proportional to analyte concentrations, but approach a limiting value with increasing concentrations (i.e., up to 1.5–2.0 mM). Moreover, the comparison between the electrochemical behaviour of the GC/Pd/Bi and GC/Pd electrodes (see Fig. 3A and B) reveals, in presence of analyte, a diminution of the charge under the Ic1 cathodic peak of about 20% and 75%, respectively. Similarly, in presence of hexanale (3 mM), was observed a diminution of the Ic1 peak of about 25% and 91% for the GC/Pd/Bi and GC/Pd electrodes, respectively. The differences in the electrochemical behaviour of the GC/Pd/Bi and GC/Pd electrodes are particularly evidenced for aliphatic aldehydes with longer aliphatic chains (i.e., valeraldehyde and hexanale). Thus the influence of the bismuth adlayer on the catalytic activity should increase in the order: formaldehyde < acethaldehyde < propionaldehyde < butyraldehyde < valeraldehyde < hexanale. It is likely, that bismuth adlayer on the palladium film induces a partial inhibition of the adsorption processes of organic reactants and/or intermediate reaction species on the catalytic active sites. Thus, bismuth adatom acts as a third body type mechanism in decreasing the reaction ensemble size. Similarly, on platinum electrodes modified with bismuth adlayers, a third body mechanism during the formic acid electrooxidation process has been hypothesized [32]. On the other hand, the potential needed for the incipient electrooxidation process of the aldehydic molecules on the GC/Pd/Bi electrode is significantly less positive than that observed in absence of bismuth adlayer (see Fig. 3A and B). The total shift of the anodic polarization curve (towards the more negative potentials) reaches approximately $0.25 - 0.40$ V, which is an interesting catalytic effect because the oxidation overpotential is significantly reduced. As comparison, Fig. 4 shows the relevant voltammograms obtained for the electrooxidation of 3.2 mM hexanale in 50 mM NaOH solution at a GC/Pd/Bi and GC/Pd electrodes. As can be seen, with bismuth adatoms a significantly enhancement of the catalytic currents, during the anodic sweep, is observed. In addition, on the GC/Pd/Bi electrode the electrooxidation process is shifted towards negative potentials by more than 0.4 V. Although it appears that bismuth acts as third body in decreasing the reaction ensemble size, it may be contributing

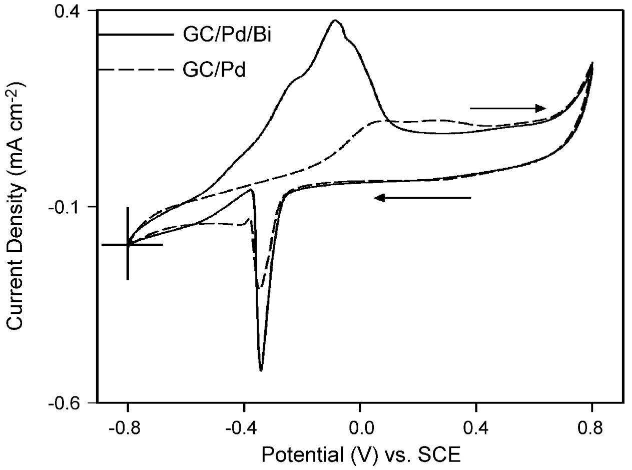

Fig. 4. Comparison of the voltammograms relevant to the GC/Pd/Bi (solid curve) and GC/Pd (dashed curve) electrodes in presence of 3.2 mM hexanale. Other experimental conditions as in Fig. 3A.

to the enhancement of the kinetics of the electrooxidation processes through a bifunctional mechanism [33,34] in which Pd and Bi species promote specific interactions with reactants and/or reaction intermediate.

In order to elucidate some aspects of the kinetics of the bismuth adsorption, various time of immersion of the GC/Pd electrode in non-deaerated 200 μM $Bi(NO_3)_3$ solution at open circuit and under various applied potentials were investigated. Assuming that the bismuth oxidation and palladium reduction processes (i.e., Bi^0/Bi^{3+}; Pd^{2+}/Pd) are 100% efficient on the voltammetric time scale, and assuming an almost homogeneous surface distribution of the Pd–Bi species, the film composition can be tentatively evaluated by electrochemical technique measuring the charge associated under the wave Ia_1 and Ic_1 related to the oxidation and reduction of bismuth and palladium species, respectively. Table 1 summarizes the relevant results. As can be seen, after 5 min of time immersion, the bismuth coverage reached about 30% of the maximum coverage value (i.e., 25 min of electrode immersion at open circuit), while the catalytic efficiency towards the electrooxidation of propionaldehyde reached about the 90% of the maximum observed value. Thus, the catalytic efficiency for the electrooxidation of aldehydes increases linearly with the bismuth loading up to values of about 1 nmol cm^{-2} and increases slowly for higher surface concentration of bismuth species.

Table 1
Effect of the immersion time of the GC/Pd electrode in non-deaerated 50 mM $HClO_4$ solution containing 200 μM $Bi(NO_3)_3$ on the bismuth surface concentration (Γ_{Bi}) and charge associated to the oxidation process of 3 mM propionaldehyde

Immersion time (min)	Γ_{Bi} (nmol cm^{-2})	Pd_xBi_y	Charge (mC)
0.0	–	Pd	0.087
2.0	0.32	$Pd_{98}Bi_2$	0.223
5.0	0.54	$Pd_{96}Bi_4$	0.255
10.0	1.01	$Pd_{91}Bi_9$	0.261
15.0	1.18	$Pd_{92}Bi_8$	0.282
25.0	1.94	$Pd_{88}Bi_{12}$	0.290

The charge (mC) was evaluated by integration of the oxidation wave during the anodic sweep between −0.5 and 0.15 V at 50 mV s^{-1} in 50 mM NaOH solution containing 3 mM propionaldehyde.
The bismuth surface concentration (Γ_{Bi}) and the film composition (Pd_xBi_y) were evaluated by integration of the Ia_1 and Ic_1 peaks considering the $Bi^0 \rightarrow B^{III}$ and $Pd^{II} \rightarrow Pd^0$ redox process, respectively. The GC/Pd electrode was obtained by cycling the potentials between 0.0 and −0.4 V vs. SCE for 50 cycles in non-deaerated solution containing 0. 5 mM Na_2PdCl_6, 50 mM $HClO_4$ and 25 mM HCl.

Table 2
Effect of the applied potential on the GC/Pd electrode in non-deaerated 50 mM $HClO_4$ solution containing 200 μM $Bi(NO_3)_3$ on the bismuth surface concentration (Γ_{Bi}) and charge associated to the oxidation process of 3 mM propionaldehyde

Applied potential (V)	Γ_{Bi} (nmol cm^{-2})	Pd_xBi_y	Charge (mC)
−0.8	2.36	$Pd_{78}Bi_{22}$	0.236
−0.4	1.74	$Pd_{85}Bi_{15}$	0.249
0.0	1.41	$Pd_{88}Bi_{12}$	0.285
0.4	1.29	$Pd_{86}Bi_{14}$	0.273
0.8	–	Pd	0.095

The potential was applied for 10 min under stirred solution with a magnetic bar at about 300 rpm.
Other experimental conditions as in Table 1.

The effect of applied potential during the deposition procedure on the efficiency of bismuth adsorption and catalytic performance are also evaluated. Table 2 shows the relevant results. As can be seen, increasing the applied potentials in the range comprised between −0.8 and 0.4 V during the deposition procedure, the surface concentration of bismuth species (Γ_{Bi} nmol cm^{-2}) exhibit a decrease, while the resulting composite films show an electrocatalytic activity almost independent from the deposition conditions and film composition. On the contrary, for higher applied potentials, a sensible decrease of the bismuth coverage with subsequent attenuation of the catalytic performance was observed. This result suggests that, at high applied potentials a partial transformation of bismuth oxide into the cationic species such as $Bi(OH)^{2+}$, $Bi_6(OH)_{12}{}^{6+}$ or negatively charged $BiO_m(OH)_n{}^{(2m+n-3)-}$ species may facilitate the desorption process of the bismuth adlayer from the electrode surface. Alternatively, the formation of higher valence oxides of palladium such as PdO_2 and PdO_3 species can induce a partial inhibition of the adsorption process of bismuth species on the electrode surface.

Fig. 5 shows some of the chronoamperometric curves (*I*–*t*) for the GC/Pd electrode recorded at a constant potential of −0.2 V versus SCE in 50 mM NaOH solution in presence of 2 mM propionaldehyde. After the addition of 50 μM Bi^{3+} in solutions (curve A), immediately the electrooxidation current increases without undesired electrode poisoning effects. In contrast, in absence of Bi^{3+} ions in solution (curve B), the GC/Pd electrode shows a rapid and sensible attenuation of the catalytic performance and the relevant electrooxidation current decreases rapidly. It is interesting to observe that, Bi^{3+} ions absorb efficiently on the palladium surface also in presence of adsorbed analytes and/or their intermediates. Thus, bismuth adatoms are able to prevent the poison formation or to remove the formed organic adsorbate molecules on the electrode surface through a third-body type mechanism or through an electronic effect [35]. Fig. 6 com-

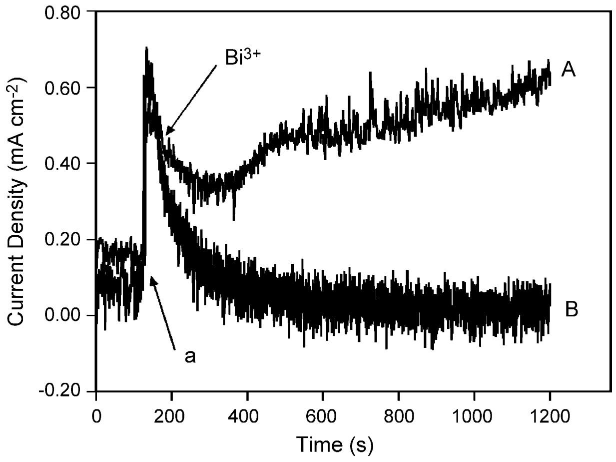

Fig. 5. Chronoamperometric measurements obtained at a GC/Pd electrode in 50 mM NaOH solution. (a) Addition of 2 mM propionaldehyde; after 200 s were added 50 μM Bi^{3+} ions (curve A). The curve B is obtained in absence of Bi^{3+} ions. The solution was stirred with a magnetic bar at about 500 rpm. Electrode potential: −0.2 V vs. SCE.

pares the chronoamperometric responses of the GC/Pd/Bi and GC/Pd electrodes, obtained at a constant potential of −0.2 V versus SCE in 50 mM NaOH solution in presence of increasing concentration of propionaldehyde. As a consequence of poisoning effects, the chronoamperometric profile of the GC/Pd electrode appears rather insensitive to the propionaldehyde addition. On the contrary, the GC/Pd/Bi electrode responds rapidly to millimolar concentration changes and the resulting calibration plot for propionaldehyde analysis is linear over the range of 1.5–8 mM with a correlation coefficient better than 0.97.

3.2. XPS characterization of GC/Pd and GC/Pd/Bi electrodes in alkaline solutions

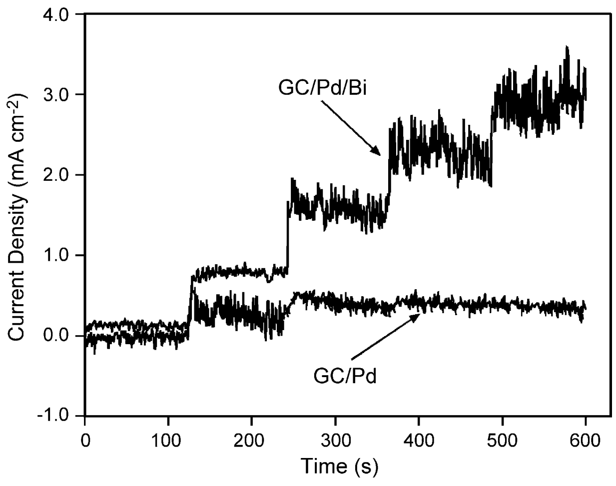

Fig. 6. Chronoamperometric measurements obtained at a GC/Pd/Bi and GC/Pd electrode in 50 mM NaOH solution containing increasing concentration in 2.0 mM steps of propionaldehyde. Other experimental conditions as in Fig. 5.

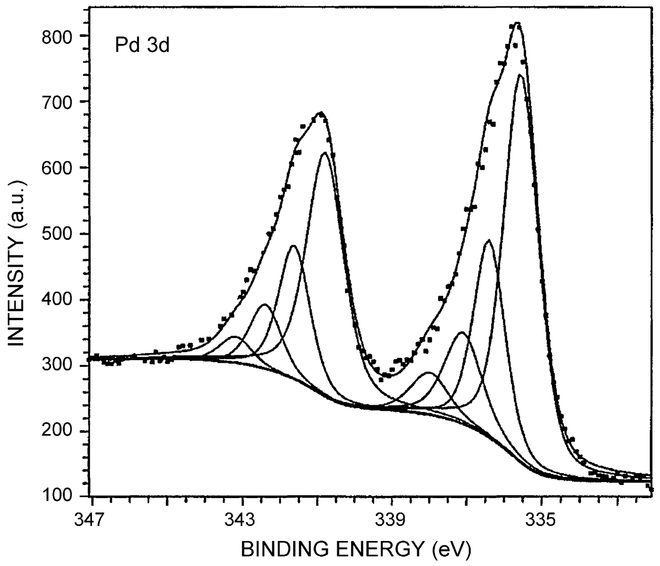

Fig. 7. XP detailed Pd 3d spectra of the composite Pd–Bi film obtained as in Fig. 2.

In order to investigate the chemical nature and surface composition of the catalysts we first analyse the detailed spectra of the GG/Pd/Bi composite electrodes and then compare the results with those obtained from the GC/Pd electrodes. Throughout this investigation Pd 3d, Bi 4f, O 1s and C 1s regions were collected and analysed for each specimen. Typical XP spectra of Pd 3d and Bi 4f of a GC/Pd/Bi electrode are shown in Figs. 7 and 8, respectively. As can be seen, the energy spectrum of the Pd 3d shows two asymmetrical signals corresponding to the Pd $3d_{5/2}$ and Pd $3d_{3/2}$ with a spin-orbit splitting, in agreement with the literature [36], of about 6.0 eV. In this study, the Pd $3d_{5/2}$ peak gives four contributions at 335.2 ± 0.1, 336.0 ± 0.2, 337.1 ± 0.3 and 338.1 ± 0.5 eV, which on the basis of their BEs can be tentatively assigned to Pd metal, PdO_{ads}, PdO and PdO_2 species, respectively [36–40].

The high-resolution spectrum of the Bi 4f shows two asymmetrical main signals with a spin-orbit splitting of about 5.4 eV, corresponding to Bi $4f_{7/2}$ and Bi $4f_{5/2}$ contributes [36]. The deconvolution of the Bi $4f_{7/2}$ signal produces gen-

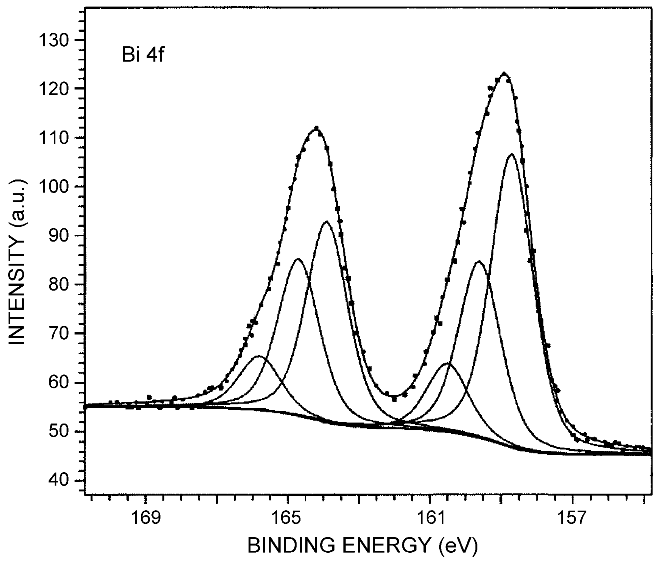

Fig. 8. XP detailed Bi 4f spectra of the composite Pd–Bi film obtained as in Fig. 2.

erally three contributes centred at 158.1 ± 0.3, 158.9 ± 0.4 and 159.8 ± 0.4 eV with a full-width at half-maximum of about 1.4 ± 0.1 eV. The significant dispersions of the binding energies can be explained by the fact that the bismuth forms a mixture of complexes species on the electrode surface and not pure metal oxides species [40]. In addition, a shift to higher BE values compared with those obtained with bismuth metal samples was previously observed [15], and can be understood as a consequence of an electronic charge transfer to the Pd oxides. Thus, in agreement with the literature data [15,40–42], the signal at 158.1 ± 0.3 eV can be attributed to Bi^0, while the signals at 158.9 ± 0.4 and 159.8 ± 0.4 eV can be related to Bi^{III} oxide species. Tentatively, the peak at 158.9 ± 0.4 eV can be attributed to BiOOH, $Bi(OH)_3$ and/or the $BiO_m(OH)_n{}^{(2m+n-3)-}$ species, while the peak at 159.8 ± 0.4 eV can be attributed to Bi_2O_3 oxides. In this study the surface composition of the GC/Pd/Bi electrode was mainly based on the measured areas of the XP signal for the Pd 3d and Bi 4f peaks. Thus the chemical composition of the film, was monitored as a function of the immersion time of the GC/Pd electrode in non-deaerated 200 μM $Bi(NO_3)_3$ solution at open circuit. In addition, the chemical composition of the films evaluated by XPS technique was compared with the surface concentration of adsorbed Bi species (Γ_{Bi}) calculated by electrochemical technique. The relevant results are summarized in Table 3. As can be seen, after 5 min of the immersion time in solution containing 200 μM $Bi(NO_3)_3$, the average composition of the film was $Pd_{95}Bi_5$. These results are in agreement with those obtained in the previous section, where a fast and irreversible adsorption process is established between palladium and bismuth complexes species. The further examination of Table 3 reveals that the shape and the BEs of the various contributions of the Pd 3d signal relevant to GC/Pd/Bi electrode are identical to those obtained for the GC/Pd electrode. Thus, although the Pd–Bi film shows interesting electrocatalytic activity towards the electrooxidation of aliphatic aldehydes, the present XPS study does not indicate any chemical interaction between the palladium and bismuth active species.

Table 3
XPS data (BEs, eV) of the GC/Pd/Bi electrodes and chemical composition of the active film in terms of Pd_xBi_y as a function of the immersion time of the GC/Pd electrode in non-deaerated 200 μM $Bi(NO_3)_3$ solution at open circuit

Immersion time (min)	Pd $3d_{5/2}$	Bi $4f_{7/2}$	(Γ_{Bi} nmol cm^{-2})	Pd_xBi_y
0.0	335.1 336.0 336.9 338.0	– – –	–	–
5.0	335.2 336.2 337.4 338.6	158.0 159.2 160.2	1.56	$Pd_{95}Bi_5$
10.0	335.3 336.2 337.3 338.6	158.2 159.3 160.2	1.66	$Pd_{93}Bi_7$
20.0	335.2 336.0 337.1 338.1	158.2 159.2 160.1	1.81	$Pd_{92}Bi_8$

The chemical film composition (Pd_xBi_y) was evaluated by measuring the areas of the XP signal of the Pd 3d and Bi 4f corrected for the relevant sensitivity factors.
The GC/Pd electrode was obtained as reported in Table 1.

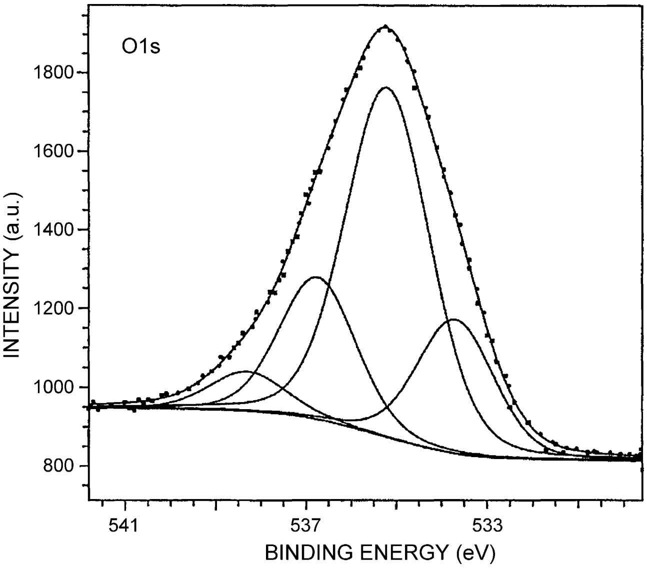

Fig. 9. XP detailed O 1s spectra of the composite Pd–Bi film obtained as in Fig. 2 and polarized at −0.4 V vs. SCE for 5 min in 50 mM NaOH solution.

It is interesting to observe that the film composition evaluated here, is in good accordance with those calculated by electrochemical technique. The small differences in the metal percent composition (i.e., Pd_xBi_y) of the composite films can be explained by considering, in first approximation, the different depth-profile sampling between the electrochemical and XPS technique. Thus the surface composition of the GC/Pd/Bi electrodes estimated by electrochemical and XPS techniques are in good agreement, indicating that the quantitative analysis procedures adopted here are sufficiently reliable.

The deconvolution of the O 1s signal exhibits generally four well-resolved contributions with BEs ranging between 530 and 536 eV. A typical O 1s curve fitting of a GC/Pd/Bi electrode polarized at −0.4 V versus SCE is shown in Fig. 9. Unfortunately, the O 1s signal do not contribute to an exhaustive elucidation of the chemical surface composition of the film, because the specific assignment of the O 1s peaks is more complex and rather ambiguous owing to partial overlapping of the various oxygen species such as OH^- ions, chemisorbed water and oxygen-containing organic compounds derived by oxidized carbonaceous species (i.e., glassy carbon substrate, adventitious carbon contaminants derived by diffusion pump oil in the residual gas, etc.). In addition, the contemporary presence of palladium and bismuth oxides induces further complications and the analysis of the O 1s peak is further complicated by the interference with the neighbouring Pd $3p_{3/2}$ signal [37] (BE = 531.4 eV). Nevertheless, in this study an analytical approach regarding the comparison of the relative areas of the Pd 3d, Bi 4f and O 1s peaks

Table 4
XPS data (BEs, eV) of the GC/Pd/Bi and GC/Pd electrodes polarized for 5 min at various potentials in 50 mM NaOH solution

Sample	Potential (V)	Pd $3d_{5/2}$	Bi $4f_{7/2}$	O 1s	O 1s/M	Pd_xBi_y
GC/Pd/Bi	−0.4	335.1	157.8	531.0	24.8	$Pd_{95}Bi_5$
		335.8	158.6	532.5		
		336.8	159.5	534.0		
		337.9		535.6		
GC/Pd	−0.4	335.2		530.5	2.1	
		336.0		532.4		
		336.6		534.1		
		337.6		536.3		
GC/Pd/Bi	0.15	335.1	157.9	530.6	5.2	$Pd_{96}Bi_4$
		336.0	158.5	532.1		
		337.0	159.5	533.7		
		337.8		535.5		
GC/Pd	0.15	335.2		530.4	2.1	
		355.9		532.1		
		336.7		533.9		
		337.7		536.2		
GC/Pd/Bi	0.8	335.2	158.5	530.6	7.4	$Pd_{98}Bi_2$
		336.0	159.4	532.2		
		337.2		533.9		
		338.3		535.9		
GC/Pd	0.8	335.3		530.2	3.1	
		336.2		531.9		
		337.1		533.8		
		337.8		535.8		

The GC/Pd film was obtained as reported in Table 1.
The composite Pd–Bi film was obtained by immersion of the GC/Pd electrode in non-deaerated 200 μM $Bi(NO_3)_3$ solution at open circuit for 10 min.
O 1s/M represents the atomic ratios taken between the areas of O 1s signal and the sum of the Pd 3d + Bi 4f signals, corrected for the relevant sensitivity factors.

is adopted, as consequence the exact assignment of the relevant contributions under the O 1s signal is not essential. Looking at Table 4 it is interesting to observe that the atomic ratios O 1s/M, expressed as:

$$\frac{\mathrm{O\,1s}}{\mathrm{M}}=\frac{\mathrm{O\,1s}}{\mathrm{Pd\,3d}+\mathrm{Bi\,4f}}$$

is strictly correlated to the presence of adsorbed bismuth species on the palladium electrode surface and the applied potential. In particular, under prolonged polarization at −0.4 V versus SCE the GC/Pd/Bi and GC/Pd electrodes shown an atomic ratios O 1s/M of 24.8 and 2.1, respectively. The above results clearly show that the adsorbed bismuth adlayer undergoes a surface redox process that leads, particularly in the double layer region, to the formation of adsorbed oxygen-containing complexes species. The significant high value of the O 1s/M atomic ratio observed in the double layer region, suggests, that the Bi species (i.e., in particular the Bi at lower oxidation state) adsorb preferentially and efficiently oxygen and/or hydroxyl ions on the electrode surface [43]. Thus, in agreement with the results obtained in the previous section, the bismuth adsorption process leads to significant formation of hydroxyl-adsorbed species on the modified palladium surface.

4. Conclusions

Surface modification of palladium sites electrodeposited on the glassy carbon electrodes were readily obtained in non-deaerated 200 μM $Bi(NO_3)_3$ solution under open circuit conditions for a given time. The spontaneous adsorption of bismuth species induces the simultaneous formation of hydroxyl-adsorbed species on the palladium film. The catalytic activity of the GC/Pd/Bi electrode towards the electrooxidation of some aliphatic aldehydes was evaluated by cyclic voltammetry and chronoamperometric techniques in moderately alkaline solutions. The surface coverage of bismuth (Γ_{Bi}) was evaluated by electrochemical measurements and a direct correlation with the catalytic reactivity towards the electrooxidation of aliphatic aldehydes was verified. The surface composition of the active Pd–Bi composite film was evaluated by XPS analysis throughout the investigation of the detailed Pd 3d, Bi 4f and O 1s regions. After various electrochemical treatments, an average chemical composition of the composite film of $Pd_{96\pm2}Bi_{4\pm2}$ was obtained. An unexpected high value of the O 1s/M atomic ratio (i.e., O 1s/M = 24.8) in the double region of potentials was also observed, indicating that the Bi adsorbs efficiently and irreversibly oxygen and/or hydroxyl species on the electrode surface.

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