

Spectroelectrochemical Evaluation of Rh Microparticles as Electrocatalyst for Carbon Monoxide and Formic Acid Oxidation

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Abstract

Electrooxidation of carbon monoxide and formic acid was performed on Rh microparticles deposited on both, Glassy Carbon (Rh/GC) and polyaniline films (Rh/PANI), to evaluate the electrocatalytic activity of those electrodes. The deposit of Rh microparticles on those substrates provides a higher surface and exhibits a better electrocatalytic activity compared with that shown by smooth Rh for the electrochemical oxidation of formic acid in sulphuric acid. The oxidation of CO and HCOOH on Rh/GC and Rh/PANI was followed using *in situ* Multi-Step FTIR Spectroscopy (MS-FTIRS). Either linear or bridge bonded adsorbed CO (CO_l , CO_b), has been observed by FTIRS as the main species. In comparison to the adsorption of CO on smooth Rh surface, the IR features of CO adsorbed on Rh/GC and Rh/PANI electrodes showed an anomalous behaviour.

Keywords: rhodium microparticles, electrocatalysis, carbon monoxide, formic acid, FTIR study.

Introduction

Oxidation of small organic molecules on bulk noble metals has been extensively studied [1]. Recently, some researchers have been dealing with highly dispersed metal microparticles on graphite, glassy carbon, as well as on conducting polymer films [2-9], by reduction of metal ions with consecutive potential cycling as the favourite method suitable for the desired electrodeposition. Platinum microparticles have been used for the electrooxidation of carbon

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monoxide, methanol and formic acid [5, 6, 8, 9], while palladium microparticles were used for electrooxidation of CO [8], and gold microparticles for oxidation of formaldehyde [10]. Previous studies have shown that rhodium exhibits electrocatalytic activity towards oxidation of CO and HCOOH [11-14]. However, no preceding report using Rh microparticles for these reactions is known. The aim of this work was to evaluate the electrocatalytic activity of Rh microparticles deposited on glassy carbon as well as on polyaniline, for the oxidation of carbon monoxide and formic acid in sulphuric acid, and detection of absorbing species using *in situ* FTIR spectroscopy.

Experimental

All chemicals were reagent grade. Solutions were prepared with ultra pure water (Millipore, 18 MΩ). The complete instrumental setup for electrochemical and spectroelectrochemical measurements has been reported in previous works [15,16]. A Pt wire was used as the counter electrode. All potentials are reported against the reversible hydrogen electrode (RHE). GC and Rh disks (12 and 9 mm diameter, respectively) were used as working electrodes; the GC and Rh disks were sequentially polished with decreasing grades of alumina up to 0.05 μ and then sonicated in ultra pure water prior to use.

Polyaniline films were prepared by electrochemical oxidation of 0.1 M aniline on Glassy Carbon in 1 M HCl under cyclic voltammetric conditions. The dispersed thin layer of Rh was electrochemically deposited on Glassy Carbon (Rh/GC) and polyaniline film (Rh/PANI), by consecutive potential cycling from solutions containing 20 mM RhCl₃ in HCl; adjusting the pH to 4 by adding 1 M NaOH. The particle size was estimated by Scanning Electron Microscopy (SEM) and the purity of deposited microparticles was tested by EDAX and X-ray Photoelectron Spectroscopy (XPS).

The electrocatalytic activity of the Rh/GC and Rh/PANI electrodes for the oxidation of CO was evaluated performing cyclic voltammetry in 0.5 M H₂SO₄ for both dissolved and adsorbed CO. To prepare dissolved CO, 0.5 M H₂SO₄ solution was first deoxygenated with N₂ and then saturated with pure CO, holding the working electrode at 0.01 V. The study of solely adsorbed CO, was performed by removing the dissolved CO from the solution by bubbling N₂. For HCOOH oxidation, a solution containing 0.1 M HCOOH and 1 M H₂SO₄ was put into the electrochemical cell, left at open circuit and then the working electrode potential was switched to 0.01 V, to allow adsorption of HCOOH.

Multi-step FTIR Spectroscopy [MS-FTIRS] [17] was applied for spectroelectrochemical investigations; the resulting spectra were calculated as:

$$\frac{\Delta R}{R} = \left(\frac{R_s - R_r}{R_r} \right) \quad (1)$$

where $[\Delta R/R]$ is the resulting differential normalised spectrum, R_s is the single-beam background spectrum acquired at the sample potential, and R_r is the single-beam background spectrum acquired at the reference potential. R_r was first measured at the adsorption potential of CO or HCOOH; then, the sample

potential was varied stepwise to a more positive potential and R_s measured at each potential.

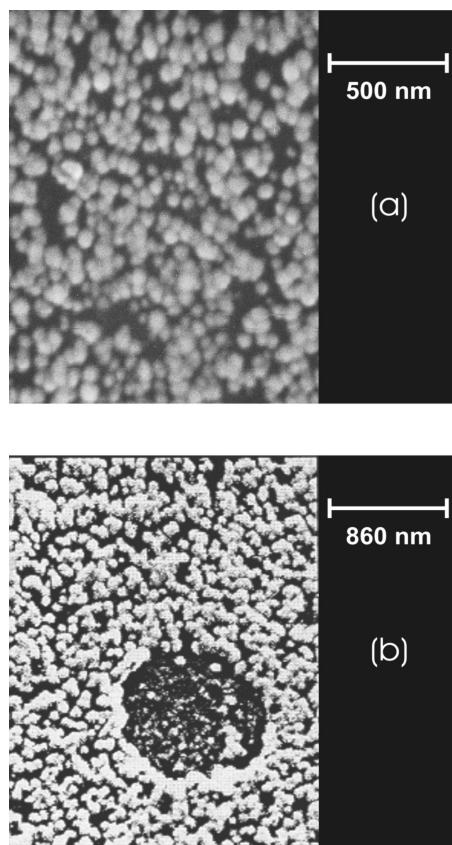


Figure 1. SEM pictures of (a) Rh deposited on GC disk and (b) Rh deposited on PANI film supported on GC disk. Both pictures were taken after 10 consecutive scans.

Results and discussion

Electrodeposition of rhodium

Rhodium was electrodeposited on both bare glassy carbon and GC coated with PANI, by repetitive cycling at 50 mV.s^{-1} within 0.00 V and -0.20 V vs. SCE, in a solution containing 0.1 M RhCl_3 prepared in HCl 1 M , adjusted to pH 4 with 1 M NaOH . A Faradaic efficiency higher than 90% was expected [14]. In both cases after 10 scans, an adherent, shiny deposit of Rh was obtained. A SEM evaluation of the surface after 10 scans on both, GC and PANI coated GC electrodes, showed the formation of microparticles of Rh of about $30 \text{ nm} - 150 \text{ nm}$ wide (Fig. 1). EDAX and XPS (Fig. 2) analyses of the microparticles showed the presence of Rh as the unique metallic element.

Cyclic voltammetry

Cyclic voltammetry in 0.5 M H_2SO_4 , swept at 1 mV.s^{-1} , was performed to compare the response of microparticles deposited on GC and PANI coated GC with the response observed on polished rhodium disk. Cyclic voltammograms 3a and 3b, are quite similar each other: during the anodic scan, hydrogen desorption

peaks are observed at 0.07 and 0.060 V, respectively, as well as formation of surface oxides at about 0.70 V. During the cathodic scan, reduction of the oxides at 0.40 V and adsorption of hydrogen at 0.05 V and 0.02 V takes place. For the Rh/PANI electrode (Fig. 3c), the response due to capacitive charge and the redox process of PANI is shown at 0.40 V and 0.30 V, respectively. Moreover, at those less anodic potentials over the range at which PANI is not conducting, hydrogen adsorption–desorption peaks on Rh particles are observed. In this case, the background current due to oxidation-reduction of polyaniline film, masks the signals due to formation and reduction of Rh oxides.

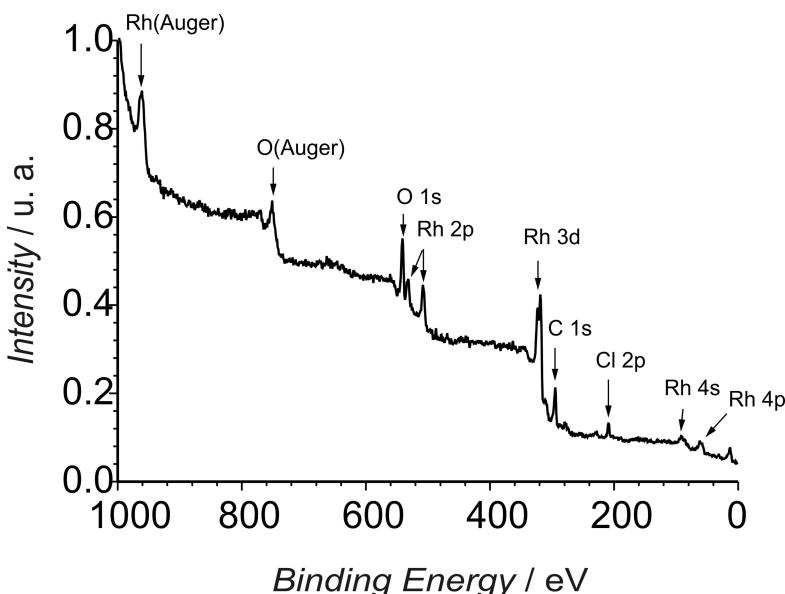


Figure 2. XPS spectrogram of Rh microparticles deposited on glassy carbon.

If we assume 211 mC.cm^{-2} as the charge due to the hydrogen adsorption on Rh [12], the rugosity factor obtained for the Rh disk is 1.09 and a range from 130 to 175 is obtained for different films of Rh on GC. For the deposit Rh on PANI/GC, the estimated rugosity factor (calculated by measuring the area under the hydrogen peak), was within 60–80.

To compare the electrocatalytic activity of the electrodes Rh/GC and Rh/PANI with that of polished Rh disk, they were used to follow the electrooxidation of CO and formic acid in H_2SO_4 solution.

Fig. 4a to 4c show the cyclic voltammograms in 0.5 M H_2SO_4 of a Rh disk, a Rh / GC and a Rh / PANI electrodes respectively in the presence of both dissolved (solid line) and adsorbed CO (dotted line). In all cases, the gas was admitted into the cell at 0.01 V vs. RHE. The broken lines show the background voltammogram.

The response of Rh and Rh / GC electrodes are quite similar for both, dissolved and quimisorbed CO. Initially, a complete disappearance of the hydrogen adsorption peaks is observed which means that, in both cases, there is a high coverage of quimisorbed

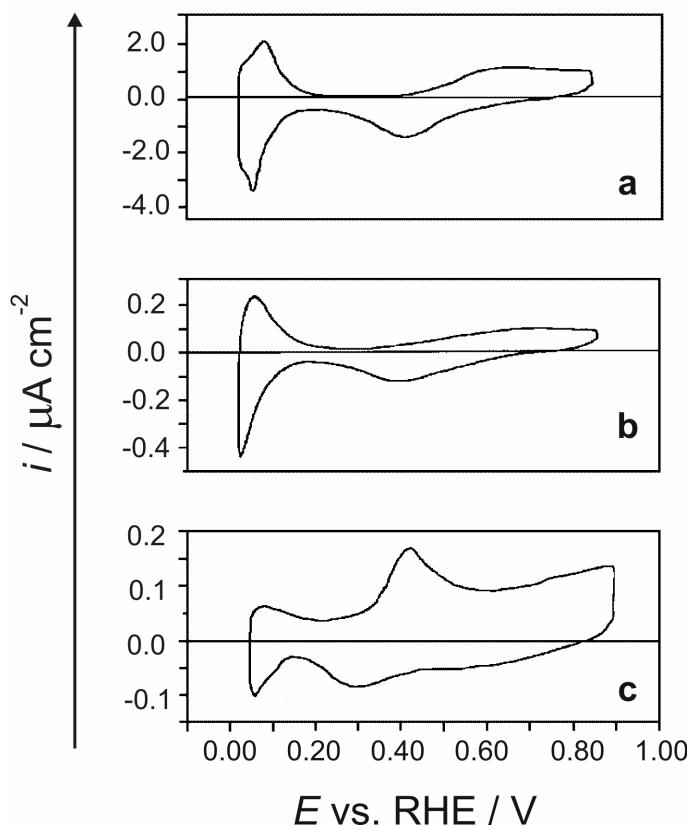


Figure 3. Cyclic voltammogram in 0.5 M H_2SO_4 of: (a) Rh polished disk; (b) Rh / GC electrode; c) Rh / PANI electrode.

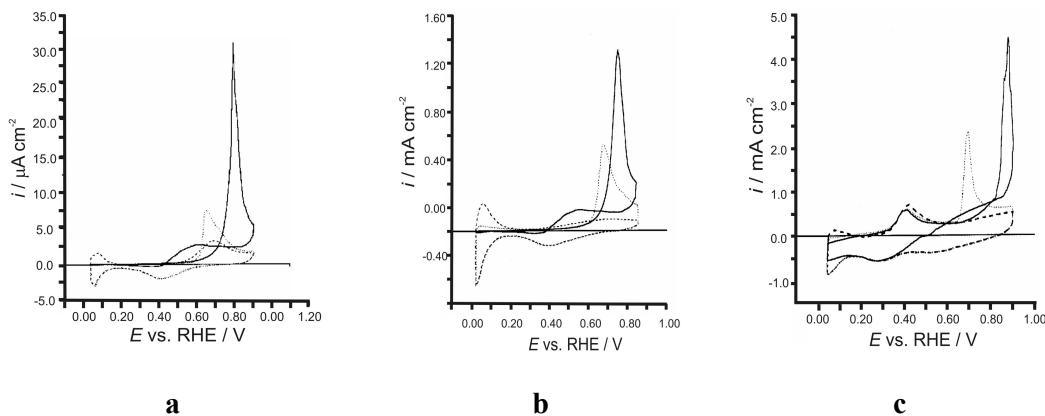


Figure 4. Cyclic voltammograms of (a) polished Rh disk, (b) Rh / GC electrode, and (c) Rh / PANI in 0.5 M H_2SO_4 in the presence of dissolved CO (—) and quimisorbed CO (.....). The broken lines correspond to the supporting electrolyte response.

CO. For dissolved CO, the oxidation peak is observed at 0.80 V on the Rh disk and Rh / GC electrodes, but peak intensity is 50 times higher in the latter case (this value is lower than that expected for an increase of the effective area). In the absence of dissolved CO, the peak potential due to oxidation of quimisorbed CO is 0.70 V on both electrodes. However, the peak current for quimisorbed CO on

Rh / GC is about 110 times higher than that on the massive metallic electrode (of the same magnitude expected for an increase of the effective area).

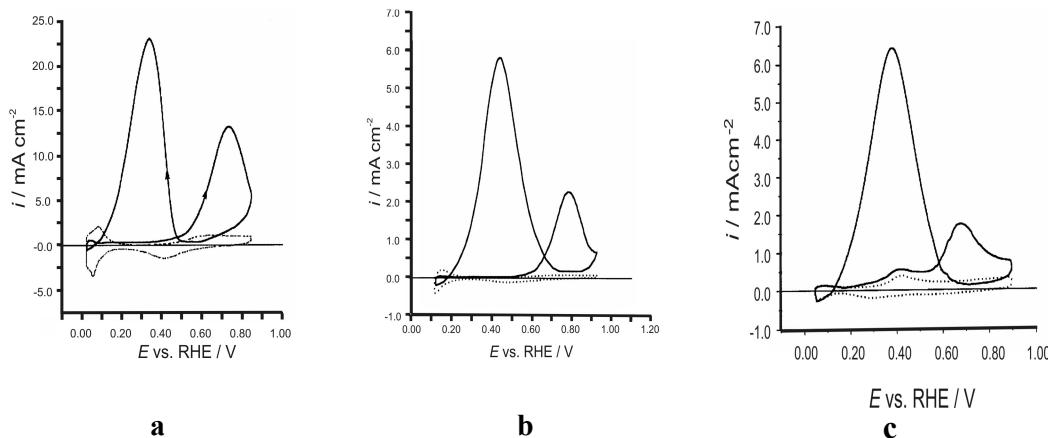


Figure 5. Cyclic voltammograms of (a) polished Rh disk, (b) Rh / GC, and (c) Rh / PANI electrode in 1 M H_2SO_4 in the presence of 0.1 M HCOOH (—). The broken lines correspond to the supporting electrolyte.

The potential peak observed for oxidation of dissolved CO on Rh / PANI was 0.90 V, which is 0.10 V higher than the potential observed for the Rh disk and the Rh / GC electrode; nevertheless, the peak current is 150 times higher than that observed for Rh disk, which is more than twice the value expected for an increase of the effective area. On the other hand, in the absence of dissolved CO, the oxidation peak of quimisorbed CO shows up at 0.70 V, the same value observed for Rh disk and Rh / GC electrodes, the peak intensity being 300 times higher than that obtained on the Rh disk (more than four times the value expected for an increase of the effective area).

Those results show that the electrolytic activity of the Rh microparticles electrodeposited on GC for electrooxidation of CO is not better than that on smooth Rh, since the CO poisoned both, the massive metal and the microparticles surfaces. Furthermore, the observance of a peak current lower than that expected for an increase of the effective area indicates that CO is a stronger poisoning agent for the Rh microparticles.

When oxidation is performed with CO quimisorbed on Rh / PANI, the oxidation peak current is much higher than that expected for an increase of the calculated effective area. This could mean that the proper effective area is higher than that calculated through the charge due to hydrogen adsorption, since not all microparticles of Rh would be activated for oxidation of H^+ and adsorption of H_2 due to the low conductivity of PANI within the potential range at which the adsorption occurs. This phenomenon has been previously observed for Pd electrodeposited on PANI [3]. However, CO could easily be quimisorbed, even on microparticles electrically isolated, at which CO is oxidised when a sufficiently high potential is reached (indeed, at this potential, PANI is electrically conducting). The effective area of the microparticles array, calculated from the oxidation peak of CO quimisorbed is, at least, four times higher than

that calculated using the area from hydrogen signal. Thus, although the current density of dissolved CO is much higher on the Rh microparticles electrodes than it is on the massive metal, it is still lower than the current expected for an increase of the effective area. This means that there is not an electrocatalytic effect and, the increase of the current is due to a considerable increase of the effective area because of the microparticles array.

Cyclic voltammograms for anodic oxidation of 0.1 M formic acid on a Rh disk, as well as Rh / GC and Rh / PANI electrodes, are shown in figures 5a to 5c. In all cases, an oxidation peak is observed at 0.70 V on Rh and, in the reverse scan, peaks at 0.34 V, 0.35 V and 0.38 V are observed for Rh, Rh / GC and Rh / PANI, respectively. The peak potential for oxidation of formic acid on Rh is higher than it is on Rh / GC and Rh / PANI, respectively. However, the current densities obtained are considerably higher, exceeding the expected values for an increase of the effective area. For Rh / GC, the oxidation current is about 250 times the current observed for smooth Rh, while the rugosity factor for the Rh film shown in figure 7 is only 130 (the maximum rugosity factor found for Rh / GC was 170). Evenly, the observed currents on Rh / PANI for the electrooxidation of formic acid are higher than those expected for an increase of the rugosity factor, compared with the currents observed on the Rh disk in figure 5a, where the oxidation currents are about 290 times higher on the modified electrodes than it is on Rh, while the estimated rugosity factor for the hydrogen zone charge in the forward scan, is 60. Even if we consider that the actual rugosity factor for Rh / PANI is four times higher than the estimated value, as it was mentioned before, the oxidation current of HCOOH is still 10 times higher than the expected value for an increase of effective area.

These results evidence that the increase of oxidation current of formic acid on microparticles of Rh is due to a great increase of the effective area as well as a real increase of the electrocatalytic activity of the electrodeposited metal. This feature agrees with the results obtained for Pt deposited on PANI and other conducting polymers [4, 5]. This corresponds to an oxidation process following a mechanism that involves the formation of strongly adsorbed intermediates by dissociative quimisorption or by an oxidation process. The opposite behaviour observed for the electrooxidation of CO, can be attributed to a direct quimisorption of CO on the metallic surface and, therefore, a previous dissociative quimisorption is not required. This suggests that, for the coverage levels of the deposit used in this work, the quimisorption of CO from dissolved CO is equally favoured on the massive metal than on the microparticles.

FTIR spectroscopy

Rhodium disk

Adsorption and oxidation of CO and HCOOH on a polished surface of Rh, has been widely studied [1,18-20], reporting in all cases linear quimisorption of CO (CO_L) as well as bridge-bonded (CO_B) and CO_2 as the oxidation product. In this work, we have observed formation of CO_L and CO_B as the direct adsorption species as well as the dissociative quimisorption of formic acid. Fig. 6a shows

the MS-FTIR spectra obtained as a response of a polished Rh surface with CO quimisorbed, when it is immersed in 0.5 M H₂SO₄. It clearly shows the formation of a couple of bipolar bands within (2069 – 2033) cm⁻¹ and (1960 – 1912) cm⁻¹ corresponding to CO_L and CO_B absorption, respectively. On these spectra, the maximum intensity of the bipolar band (1.5 %) was obtained for a potential gradient of 0.50 V. As it should be expected, the negative lobe of the bipolar band appears at higher frequencies than the positive lobe. The centre of the bipolar band shifts towards higher frequencies as the electrode potential becomes more positive, at a rate of 40 cm⁻¹ and 36 cm⁻¹ for CO_L and CO_B, respectively.

Rh deposited on glassy carbon and glassy carbon / polyaniline

MS-FTIR spectra for the oxidation of CO quimisorbed on Rh / GC, are shown in Fig. 6b. The appearance of two bipolar bands centred between [2050 – 2020] cm⁻¹ and [1915 – 18800] cm⁻¹, that becomes negative monopolar at 0.60 V, at wave numbers attributable to CO_L and CO_B [$\sim 2025\text{ cm}^{-1}$ for CO_L and 1883 cm^{-1} for CO_B]. The frequency of these bands decreases as the potential becomes more positive and the bipolar band becomes a negative monopolar one, and no further shift of the frequency is observed as the electrode potential becomes more positive. A similar behaviour was observed during oxidation of 0.1 M formic acid on Rh / GC (Fig. 7a) and CO on Rh / PANI (Fig. 6c). Spectra in Fig. 7a are focused in the range of [2600 – 1800] cm⁻¹ for a better monitoring of CO and CO₂ bands.

During the oxidation of CO quimisorbed on Rh / GC and Rh / PANI, formation of CO₂ (negative band at 2345 cm^{-1}) from 0.60 V is observed. The band assigned to CO₂ reaches a maximum [1%] at 0.70 V and those bands at 2025 cm^{-1} and 1883 cm^{-1} reach a maximum intensity of about 1 % and 0.8 %, respectively. These bands could be assigned to oxidation of CO_L and CO_B, formed by direct quimisorption of CO at the reference potential. Due to the convention used in this work to determine $\Delta R / R$ (Eq.1), as it was mentioned before, the attributable bands for CO_L and CO_B must be positive when they are completely oxidised; however, the sign of the bands is opposite to the expected. The same abnormal behaviour of these bands has been reported for quimisorbed CO on Pt microparticles deposited on graphite [6], CO quimisorbed on Pt and Pd microparticles deposited on Glassy Carbon [8], and CO quimisorbed on Ir microparticles [21]. An explanation for the negative sign of the bands has been attributed to the particular structure of the thin layers [8]. However, we have proposed that this behaviour occurs only in low reflectivity substrates and it is related to an increase of reflectivity due to differences in optical properties between metal particles and the substrate [21]. To confirm that such unexpected behaviour is related to the low reflectivity of the substrate and to the optical properties of microparticles, we performed MS-FTIRS experiments for the oxidation of CO on Rh microparticles deposited on smooth Rh disk (Rh / Rh electrode). Following the procedure described for preparation of Rh / GC electrode, we performed electrodeposition of Rh microparticles on polished Rh disk, obtaining Rh microparticles of the same size and a similar distribution as that obtained on glassy carbon. Fig. 7b shows the obtained spectra that clearly

show the normal behaviour for the IR features of the quimisorbed CO_L and CO_B on Rh / Rh surface, i.e., in agreement with the convention used to obtain reflectance spectra, the complete oxidation of quimisorbed CO species produces a positive upwards band. That band appears with intensity higher than that observed on the smooth bare Rh, due to the high coverage of quimisorbed CO on microparticles.

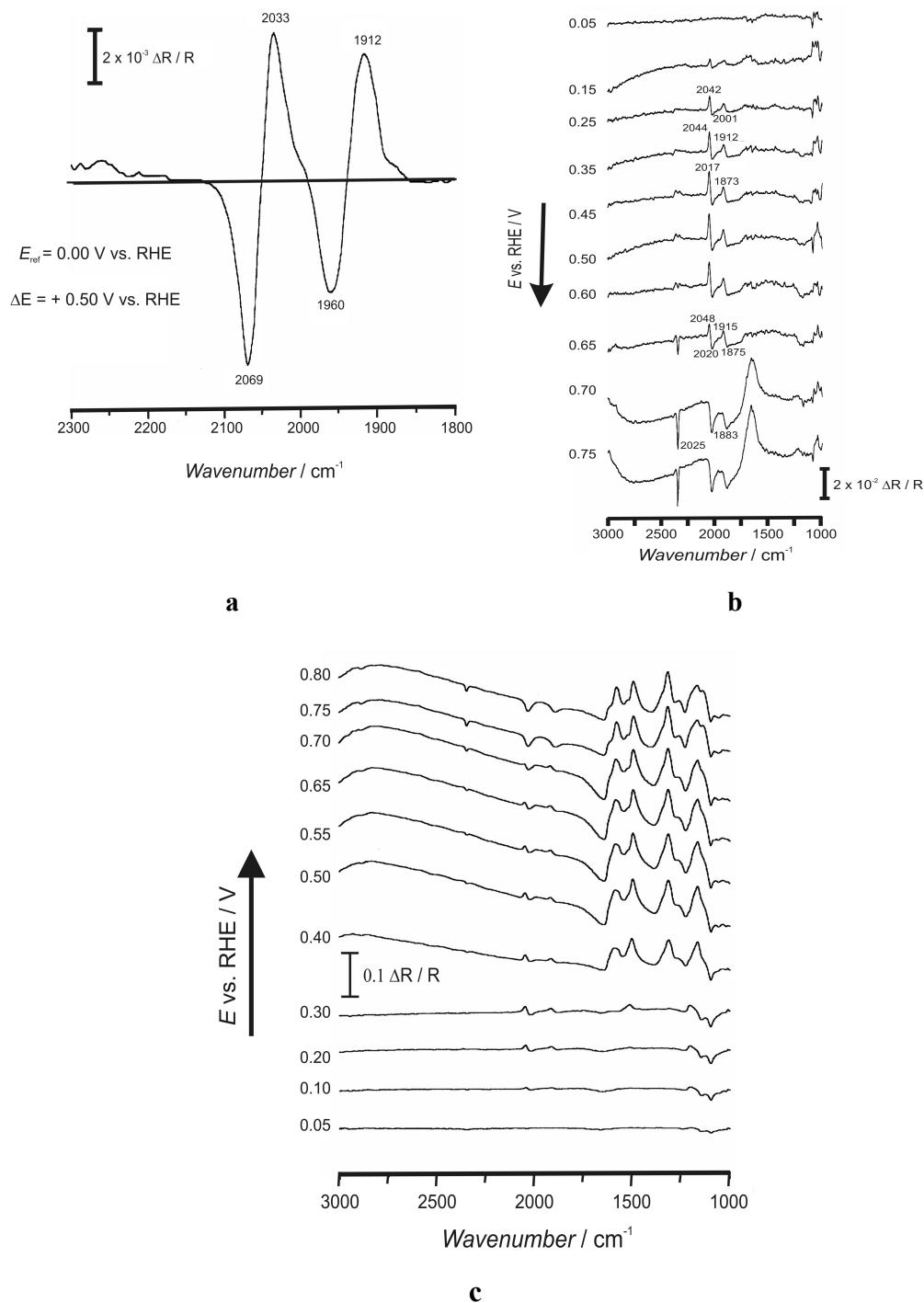


Figure 6. In situ MS – FTIR spectra obtained during oxidation of CO on (a) smooth Rh surface, (b) Rh / GC, and (c) Rh / Rh electrode, in 0.5 M H₂SO₄.

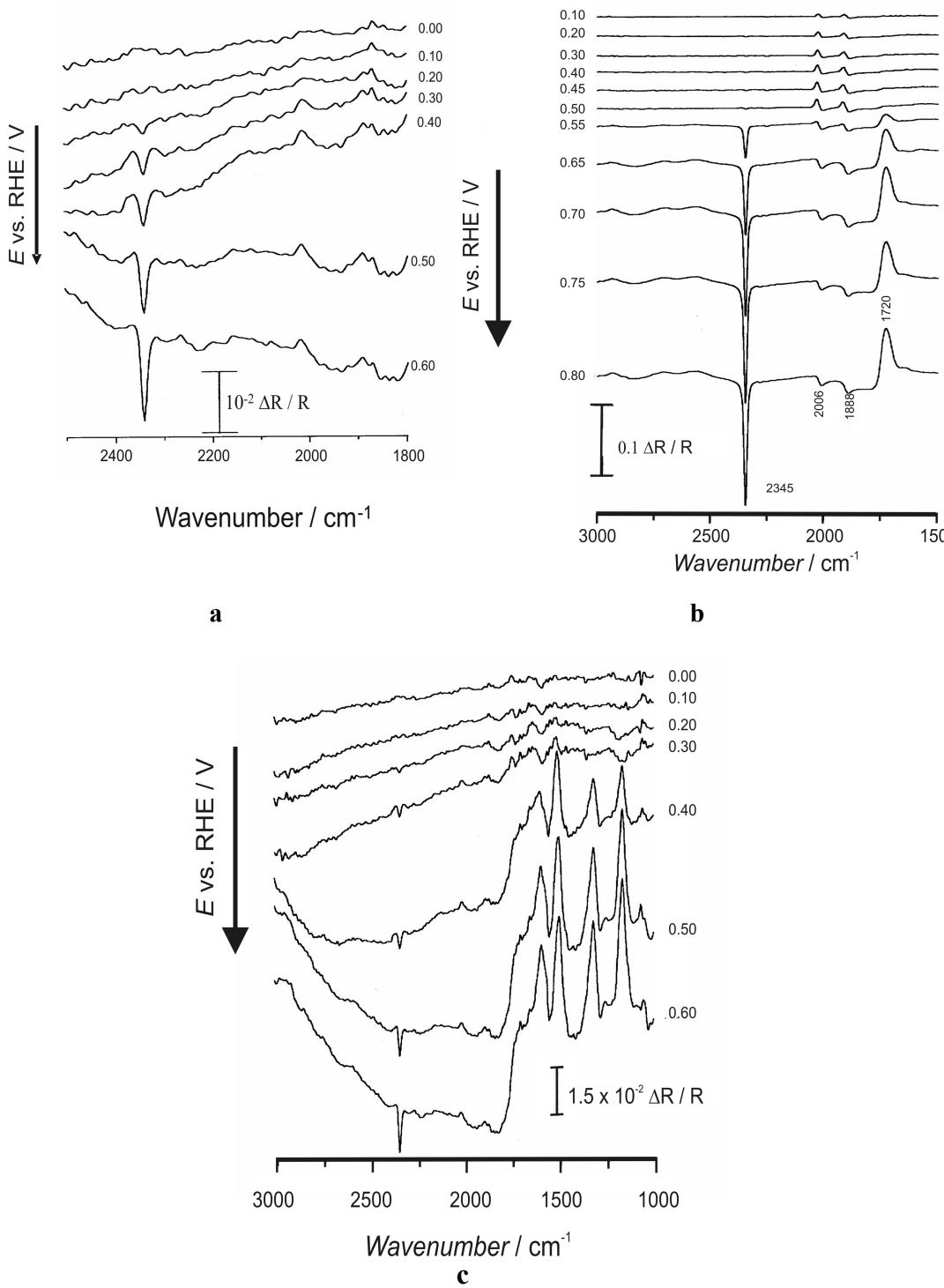


Figure 7. In situ MS - FTIR spectra obtained during oxidation of (a) oxidation of CO on Rh / Rh electrode, (b) oxidation of HCOOH on Rh / GC electrode, and (c) oxidation of CHCOOH on Rh / PANI electrode, in 0.5 M H₂SO₄.

Unlike the results obtained on Rh / GC, the spectra observed for oxidation of formic acid on Rh / PANI (Fig. 7c) no bands attributable to adsorbed CO can be distinguished. Strong negative band at 2435 cm⁻¹ corresponding to formation of

CO₂ is observed from 0.40 V, as well as the bands due to the oxidation of PANI film with the influence of the band for disappearance of the H₂O consumed during the oxidation of formic acid. In those spectra the absence of CO bands does not completely prove the total absence of adsorbed CO species, since the noise within the range 2100 cm⁻¹ and 1800 cm⁻¹ reaches 0.1 % and CO low bands could be hidden in it. In other words, if HCOOH dissociative adsorption takes place, the coverage by remaining adsorbed species should be very low.

Conclusions

Rh can be efficiently electrodeposited on GC and PANI to obtain thin layers consisting of deposited microparticles showing very high active surface areas. The Rh microparticles, deposited on GC and PANI show a considerable improvement of the electrocatalytic activity towards oxidation of formic acid. This rise of electroactivity is related to the rise of the current values that surmounted the estimated value due to only an increment of the effective area. From the FTIR spectra, it is possible to infer that the poisoning species during oxidation of CO and HCOOH on Rh microparticles are CO_L and CO_B. In agreement with previous reported observations [21] for the CO adsorption on Pt, Pd and Ir microparticles deposited on low reflective substrates, abnormal IR features for CO adsorbed on Rh microparticles supported on both glassy carbon and polyaniline have been observed in this work. In the other hand, we confirm that the anomalous behaviour does not occur on microparticles deposited on the metal smooth surface.

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