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Electrocatalytic oxidation of methanol and C1 molecules on highly dispersed electrodes
Part II: Platinum–ruthenium in polyaniline

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The oxidation of methanol and C1 molecules at electrodes modified with polyaniline and particles of platinum and ruthenium has been studied in aqueous $HClO_4$ electrolyte. The platinum and ruthenium particles were incorporated into the polyaniline film by electrochemical reduction. The activity for the oxidation of C1 molecules is higher for bimetallic electrodes than for polyaniline-coated electrodes modified with platinum alone. Indeed, a negative shift of more than 100 mV is observed as compared to the potential obtained with a polyaniline film modified by pure platinum. Moreover, the oxidation of methanol is faster and more complete on the Pt–Ru modified polyaniline electrode, since carbon dioxide is the main reaction product.

1. Introduction

Electronic conducting polymers such as polypyrrole, polythiophene and polyaniline have been widely used as porous supports to disperse catalysts [1–13]. The physical and chemical properties of these polymers [14] and especially polyaniline [15–17], are now well known and allow the preparation of an appropriate support to incorporate electrocatalysts, which need a homogenous and strong adherent film, high surface area, and good stability in acid medium.

Platinum dispersion inside such a support, which leads to a decrease of the amount of noble metals used, allows improvement of the catalytic activity for the oxidation of methanol [5, 7, 8, 10–13] via a better utilization of the platinum crystallites and, especially, in decreasing the poisoning effect [8, 13]. However, platinum needs to be modified by other metals in order to obtain lower oxidation potentials, much more compatible with a working anode in a direct methanol fuel cell. Ruthenium and tin are two metals which give encouraging results [18, 19].

Swathirajan and Mikhail [10] and Hable and Wrighton [20] studied the simultaneous deposition of platinum and tin inside a conducting polymer and confirmed the promoting effect of tin for the oxidation of methanol, leading to a negative shift of the polarization curve [19]. The same effect on the electrocatalytic properties of platinum for the oxidation of methanol is also observed with the dispersion of ruthenium and platinum inside a conducting support, such as a Nafion® membrane [21, 22] or on a carbon support [23–26].

In this work the electrocatalytic properties of a polyaniline film, modified by the inclusion of a small amount of two metals, platinum and ruthenium, are investigated. The electrooxidation of small C1 molecules (HCOOH, HCHO, CH_3OH and CO) are taken as typical examples. Furthermore, a more complete study of the oxidation of methanol at this bimetallic electrode is realized using cyclic voltammetry and chromatographic techniques to monitor the reaction products formed during prolonged electrolysis, and is compared to that realised at a polyaniline electrode modified by pure platinum.

2. Experimental details

Solutions were prepared from ultrapure water (Millipore Milli Q system) and Merck reagents (p.a. for aniline, formic acid, methanol and paraformaldehyde, 'zur synthese' for H_2PtCl_6, $6H_2O$ and 'Suprapur' for $HClO_4$ and H_2SO_4); $RuCl_3$ was a Johnson Matthey reagent and carbon monoxide was provided by L'air Liquide (N47 grade). Aniline was purified by distillation under vacuum and formaldehyde obtained by refluxing paraformaldehyde at 40 °C for at least 4 h.

All experiments were performed under a nitrogen atmosphere in a three-electrode cell. The temperature of the cell was kept constant by circulating thermostated water. A vitreous carbon counter electrode and a mercury/mercurous sulphate electrode (MSE), as reference electrode, were used although the electrode potentials are given on the reversible hydrogen electrode (RHE) scale. A sheet of gold was used as substrate for the polymer film deposition.

Voltammograms were recorded using standard equipment (a Wenking PSG 77 potentiostat, a PAR 175 universal programmer and a Linseis LY 1700-X–Y recorder).

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The polyaniline films were deposited by cycling voltammetry, sweeping at $50\,\mathrm{mV\,s^{-1}}$ between 0.1 and 1.15 V vs RHE in $0.5\,\mathrm{M}$ H_2SO_4 containing $0.1\,\mathrm{M}$ of freshly distilled aniline. The thickness of the polymer layer was around $0.5\,\mu\mathrm{m}$.

Platinum and ruthenium particles were then incorporated by electrochemical deposition, from a solution containing 0.01 wt% hexachloroplatinic acid and $10^{-3}\,\mathrm{M}$ $RuCl_3$ in $0.5\,\mathrm{M}$ H_2SO_4, at a constant potential of 0.15 V vs RHE.

Prolonged electrolysis of methanol was carried out in an electrochemical cell with two compartments separated by an ionomeric membrane. This cell, which was gas-tight, allowed the working electrode compartment to be evacuated, by nitrogen bubbling, of all the gases produced during methanol oxidation, essentially carbon dioxide.

Quantitative analysis of the reaction products was performed by high performance liquid chromatography (HPLC). The soluble products were analysed after separation on an ion-exchange column, placed in a thermoregulated oven. Electrolysis products were detected with a differential refractometer, which allowed the concentration change to be monitored. The carbon dioxide was first flushed from the electrolyte solution by a stream of pure nitrogen, and then absorbed by bubbling in a solution of sodium hydroxide. The carbonates formed were finally analysed by high performance ionic chromatography (HPIC) using an ionic column and a conductimetric detector.

The investigated temperature range was 25–65 °C. The current densities were measured during the positive sweep of voltammograms recorded at $5\,\mathrm{mV\,s^{-1}}$. The electrolyte support was a $0.5\,\mathrm{M}$ H_2SO_4 solution, allowing higher temperature to be reached than in a $0.1\,\mathrm{M}$ $HClO_4$ solution.

3. Results and discussion

The cyclic voltammogram of a polyaniline film electrochemically grown from a $0.5\,\mathrm{M}$ sulphuric acid and $0.1\,\mathrm{M}$ aniline solution, at a sweep rate of $50\,\mathrm{mV\,s^{-1}}$ between 0.1 and 1.15 V vs RHE [13], is shown in Fig. 1 (thick solid line). This voltammogram in blank solution ($0.1\,\mathrm{M}$ $HClO_4$) gives the characteristic peaks of polyaniline and shows that the polymer is stable in such a medium when the upper potential is limited to 1 V vs RHE [13].

3.1. *Platinum and ruthenium microparticle deposition in a polyaniline film*

The electrochemical deposition of platinum and ruthenium particles in a polyaniline film was achieved

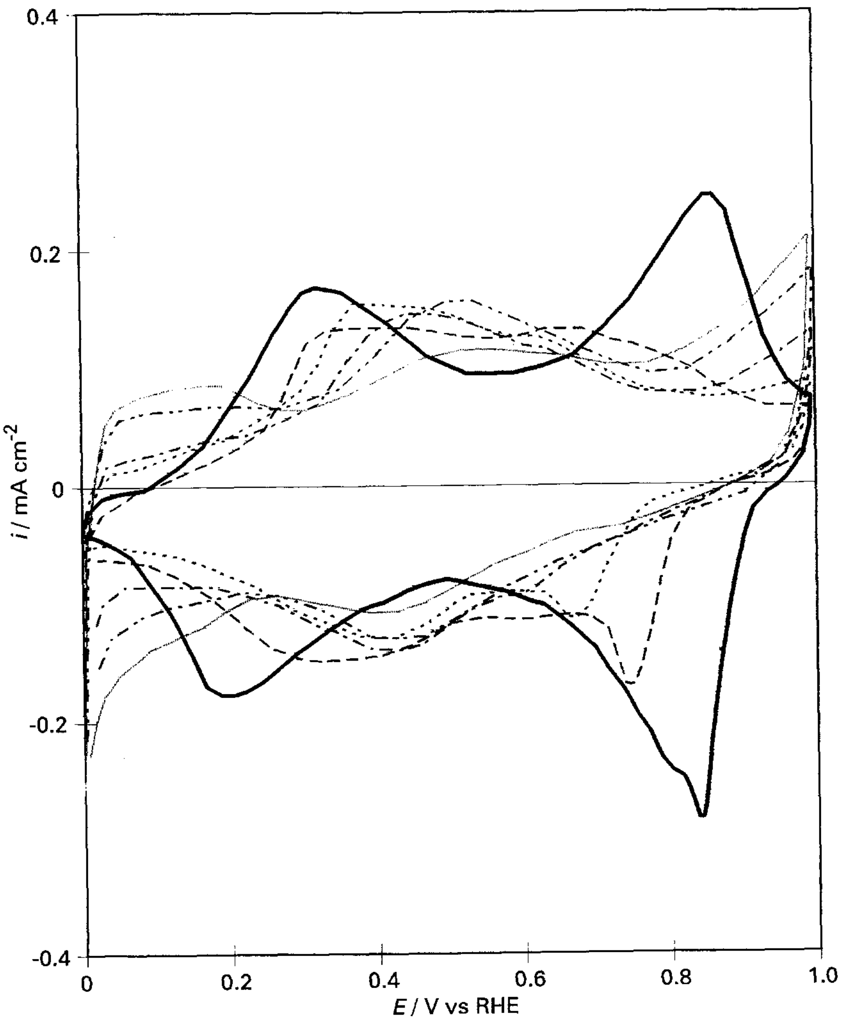

Fig. 1. Cyclic voltammograms of a polyaniline film modified by platinum and ruthenium particles, in $0.1\,\mathrm{M}$ $HClO_4$, recorded at $5\,\mathrm{mV\,s^{-1}}$, 25 °C. Catalyst amount: without platinum and ruthenium (——), $34\,\mu\mathrm{g\,cm^{-2}}$ of Pt + $12\,\mu\mathrm{g\,cm^{-2}}$ of Ru (– – –), $55\,\mu\mathrm{g\,cm^{-2}}$ of Pt + $29\,\mu\mathrm{g\,cm^{-2}}$ of Ru (· · · ·), $73\,\mu\mathrm{g\,cm^{-2}}$ of Pt + $52\,\mu\mathrm{g\,cm^{-2}}$ of Ru (–· – ·–), $94\,\mu\mathrm{g\,cm^{-2}}$ of Pt + $72\,\mu\mathrm{g\,cm^{-2}}$ of Ru (–·· – ·), $112\,\mu\mathrm{g\,cm^{-2}}$ of Pt + $90\,\mu\mathrm{g\,cm^{-2}}$ of Ru (——).

by electrolysis at constant potential using an acidic hexachloroplatinate solution and a ruthenium(III) chloride solution. From measurements of the cathodic charge involved during the reduction of Pt(IV) to Pt(0) or the reduction of Ru(III) to Ru(0), the amount of Pt or Ru deposited into the polyaniline film can be estimated. Indeed, the two metals were deposited successively and, thus, the amount of each metal deposited can be easily calculated.

Voltammograms of the modified electrodes were then recorded in the supporting electrolyte, a 0.1 M perchloric acid solution (Fig. 1).

The shape of the voltammograms of the polyaniline film becomes modified as the amount of platinum and ruthenium microparticles increases. If only platinum is deposited inside the polyaniline, the shape of the voltammograms is very slightly modified but no hydrogen adsorption–desorption region is apparent [13]. When a bimetallic system, such as platinum–ruthenium particles, is deposited, the shape of the voltammograms changes more notably (Fig. 1). For a low amount of metals ($0.034\,\mathrm{mg\,cm^{-2}}$ Pt + $0.012\,\mathrm{mg\,cm^{-2}}$ Ru), the first redox couple of polyaniline at 0.25 V vs RHE is slightly decreased and displaced to more positive potentials, and the second redox couple at 0.85 V vs RHE is drastically decreased and displaced to more negative potentials. For a larger amount of metal ($\geqslant 0.073\,\mathrm{mg\,cm^{-2}}$ Pt + $0.052\,\mathrm{mg\,cm^{-2}}$ Ru), the two redox couples of polyaniline completely disappear and are replaced by an ill-defined reversible peak near 0.5 V vs RHE (Fig. 1). Moreover, the appearance of large, but not intense, peaks is detected at lower potentials and may correspond to the hydrogen adsorption–desorption region on platinum.

SEM photomicrographs show that the bimetallic (platinum + ruthenium) particles in the polyaniline film form clusters having a larger size (about 100 nm) and a more non-homogeneous distribution than monometallic platinum particles. This means that the dispersion of the bimetallic particles is lower than the dispersion of pure platinum. Consequently, the presence of ruthenium leads, for a lower amount of catalyst, to the appearance of the hydrogen adsorption–desorption region, and to a decrease in the current densities corresponding to the polyaniline contribution.

3.2. *Catalytic activity*

The catalytic activity of the PAni electrode, modified with platinum and ruthenium, was evaluated by observing the electrooxidation of several small molecules and was compared with the catalytic activity of a PAni electrode, modified with $0.1\,\mathrm{mg\,cm^{-2}}$ of platinum. The amount of platinum and ruthenium dispersed in the polyaniline film is difficult to evaluate since, in this case, both metals are deposited together. The charge, resulting from the complete reduction of the precursor salts, was $166\,\mathrm{mC\,cm^{-2}}$ and corresponded to a maximum amount of platinum deposited of around $0.085\,\mathrm{mg\,cm^{-2}}$ and a maximum amount of ruthenium deposited of around $0.060\,\mathrm{mg\,cm^{-2}}$.

Figures 2, 3, 4 and 5 show the voltammograms of the platinum-ruthenium-modified polyaniline

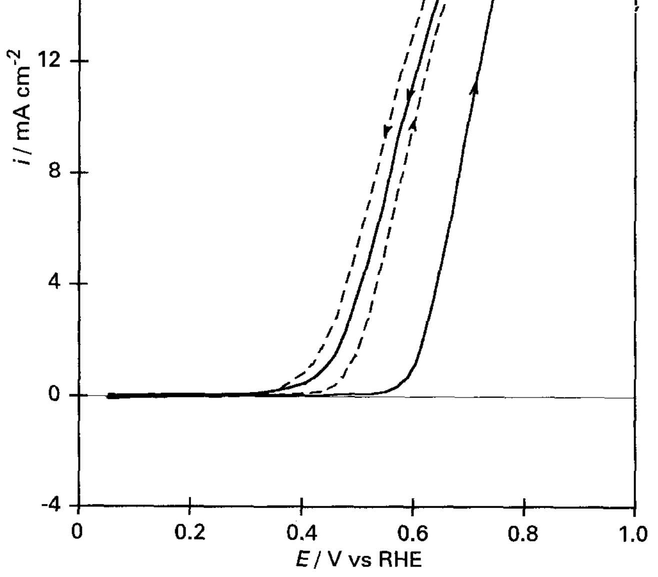

Fig. 2. Cyclic voltammograms of a polyaniline film modified by platinum (——) and platinum–ruthenium (– – –) particles, in 0.1 M $HClO_4$, recorded at $5\,\mathrm{mV\,s^{-1}}$, 25 °C, with 0.1 M HCHO.

Table 1. Maximum current density, onset and peak potentials for the oxidation of C1 molecules, upper potential limit: 0.95 V vs RHE

		C1 molecules			
		HCHO	*HCOOH*	*CH_3OH*	*CO*
PAni/Pt	Maximum current density/mA cm^{-2}	21	15.5	14	1.1
	Onset potential/V vs RHE	0.55	0.2	0.55	0.72
	Peak potential/V vs RHE	0.85	0.82	0.86	0.83
PAni/Pt–Ru	Maximum current density/mA cm^{-2}	20.5	15	12	0.7
	Onset potential/V vs RHE	0.4	0.2	0.45	0.58
	Peak potential/V vs RHE	0.8	0.75	0.75	0.65

electrode for the oxidation of formaldehyde, formic acid, methanol and carbon monoxide respectively. The voltammograms represent the first sweep, but the second and the following sweeps display the same shape. In the same figure, the voltammograms for the polyaniline electrode modified only by platinum are represented. These curves were recorded at a sweep rate of 5 mV s^{-1} in a solution saturated by bubbling CO or in solutions containing 0.1 M HCHO or 0.1 M HCOOH or 0.1 M CH_3OH. The supporting electrolyte was 0.1 M $HClO_4$.

3.2.1. Electrooxidation of formaldehyde. The electrooxidation of formaldehyde is shown in Fig. 2. On the platinum-ruthenium-modified polyaniline electrode, represented by the dotted curve, the oxidation starts at 0.4 V vs RHE and reaches a maximum of 20.5 mA cm^{-2} at 0.8 V vs RHE (Table 1). The negative sweep is practically superimposed on the curve corresponding to the positive sweep. This shows a very small poisoning effect in comparison to the case of pure platinum particles. In this latter case, poisoning by strongly adsorbed species, like CO_{ads} [18, 27], exists [13]. The modification of platinum by alloying with ruthenium leads to a 150 mV negative shift of the electrochemical oxidation of formaldehyde.

3.2.2. Electrooxidation of formic acid. Figure 3 shows the voltammograms for the electrooxidation of formic acid at Pt–Ru-modified polyaniline and Pt-modified polyaniline electrodes. The oxidation of formic acid starts at 0.2 V vs RHE with a low rate up to 0.4 V vs RHE, meaning that the surface is covered preferentially by the strongly chemisorbed species

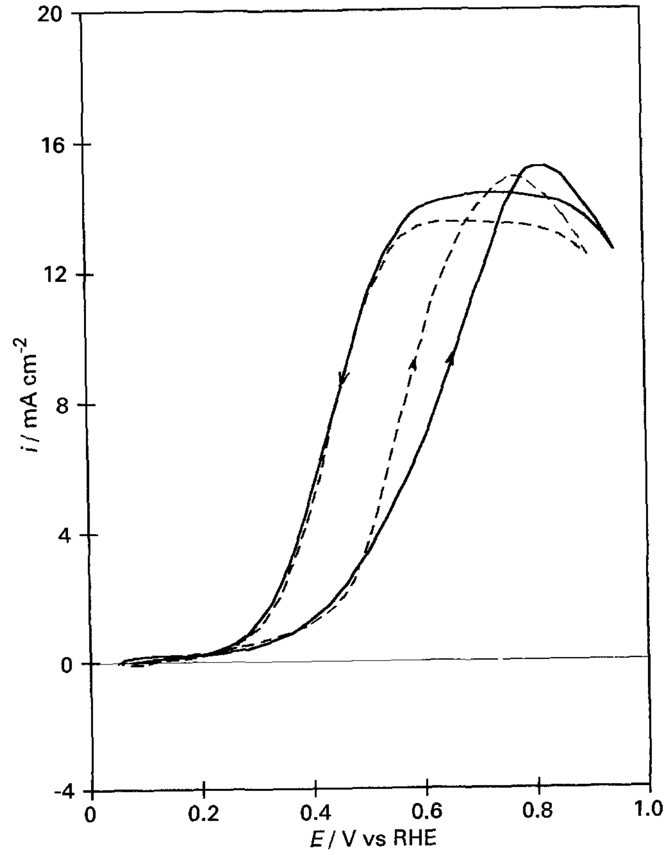

Fig. 3. Cyclic voltammograms of a polyaniline film modified by platinum (——) and platinum–ruthenium (– – –) particles, in 0.1 M $HClO_4$, recorded at 5 mV s^{-1}, 25 °C, with 0.1 M HCOOH.

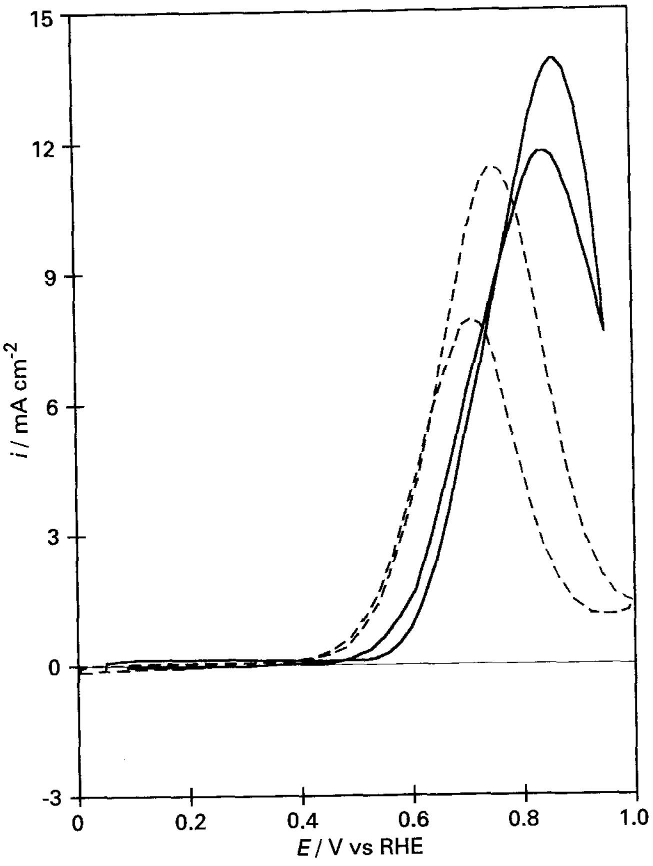

Fig. 4. Cyclic voltammograms of a polyaniline film modified by platinum (——) and platinum-ruthenium (– – –) particles, in 0.1 M $HClO_4$, recorded at 5 mV s^{-1}, 25 °C, with 0.1 M CH_3OH.

[4, 9]. For the bimetallic dispersed electrode, the maximum of the current density ($i_m \approx 15\,\mathrm{mA\,cm^{-2}}$) is observed at 0.75 V vs RHE (Table 1) and can be attributed to the oxidation of the strongly chemisorbed species. During the negative sweep, the oxidation peak is wider than during the positive sweep and this fact confirms that a poisoning effect is detected. These platinum-based electrodes are much more active (by a factor around 10 under the same experimental conditions) than a bulk platinum electrode, especially during the positive sweep. The oxidation onset occurs at a more negative potential than on a bulk platinum electrode where the catalytic surface is blocked by strongly adsorbed species up to 0.65 V vs RHE [27]. There is no significant difference between the Pt and Pt–Ru-modified polyaniline electrodes for the electrooxidation of formic acid.

3.2.3. Electrooxidation of methanol. Figure 4 represents the electrooxidation of methanol dissolved in perchloric acid solution at Pt–Ru-modified polyaniline and Pt-modified polyaniline electrodes. On the Pt–Ru electrode, the oxidation starts at 0.45 V vs RHE and reaches a maximum of 12 mA cm^{-2} at 0.75 V vs RHE (Table 1). With respect to the Pt-modified polyaniline electrode, the maximum of the current density of the methanol oxidation is similar, but the notable point is the 100 mV negative shift observed with the bimetallic dispersed electrode. Moreover, the superimposition of the curves during the positive and the negative sweeps indicates that strongly chemisorbed poisoning species are not formed extensively.

3.2.4. Electrooxidation of carbon monoxide. As at a Pt-modified polyaniline electrode, the electrocatalytic oxidation of carbon monoxide is weak on the Pt–Ru-modified polyaniline electrode (Fig. 5). CO is poorly reactive on pure dispersed platinum [13]. The small oxidation current density ($i_m = 0.7\,\mathrm{mA\,cm^{-2}}$ at 0.65 V vs RHE) confirms that CO adsorption decreases as the electrode roughness and dispersion increase [28]. The modification of platinum by alloying with ruthenium leads to a 150 mV negative shift for the electrochemical oxidation of carbon monoxide. Consequently, the poisoning effect is less significant.

All the maximum current densities obtained, the potential onsets and the peak potentials are reported in Table 1. It is clear that the presence of ruthenium promotes the electrooxidation of C1 molecules. Figure 6 shows Tafel plots for the oxidation of methanol at pure platinum and platinum–ruthenium deposits. The potential shift observed in the curves due to the presence of ruthenium is clearly seen.

Indeed, water molecules and their adsorbed residues (H_{ads}, OH_{ads}, O_{ads}) have a key role in the oxidation mechanism which requires an additional oxygen atom, especially in the case of the oxidation of alcohols up to carboxylic acids or carbon dioxide [27]. This oxygen atom may come from an adsorbed water molecule (H_2O_{ads}) or, more probably, from residues such as adsorbed hydroxyl (OH_{ads}). Moreover,

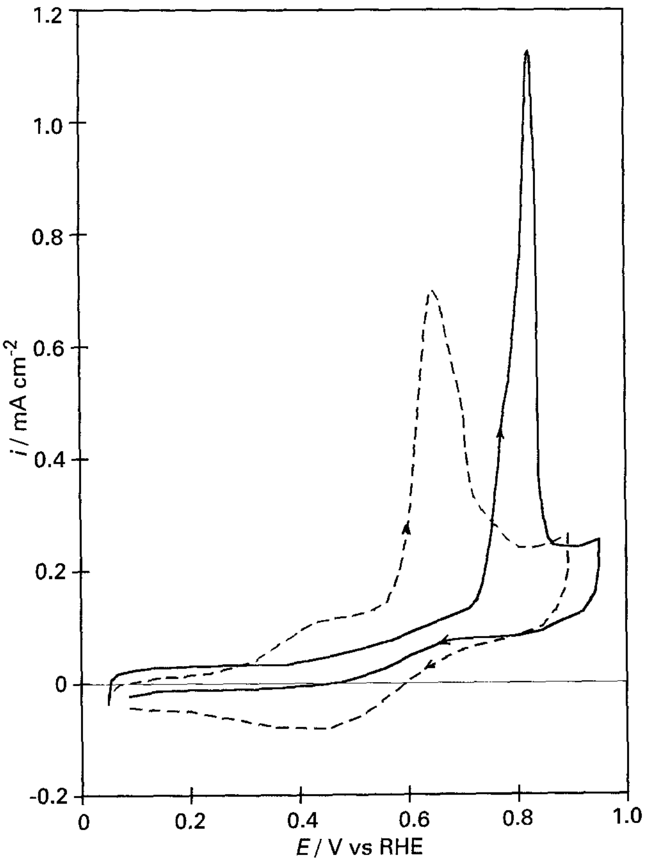

Fig. 5. Cyclic voltammograms of a polyaniline film modified by platinum (——) and platinum–ruthenium (– – –) particles, in 0.1 M $HClO_4$, recorded at $5 mV s^{-1}$, 25 °C, in a CO saturated solution.

the oxidation of the adsorbed CO species, responsible for the electrode poisoning, up to carbon dioxide, also requires the presence of oxygenated residues. It depends on the electrode potential and is responsible for the overpotential. Ruthenium leads to the formation of adsorbed surface oxygenated species at lower potentials than platinum and this explains the negative shift of the polarization curves during the oxidation of methanol, formaldehyde and carbon monoxide.

3.3. *Electrolysis of methanol*

Prolonged electrolysis of 0.1 M CH_3OH in 0.1 M $HClO_4$ was carried out in order to study the overall reaction mechanism. Quantitative HPLC analyses were carried out and led to the detection of several products: the remaining methanol, carbon dioxide, formaldehyde and formic acid or methyl formate [29] which are impossible to separate under the present conditions.

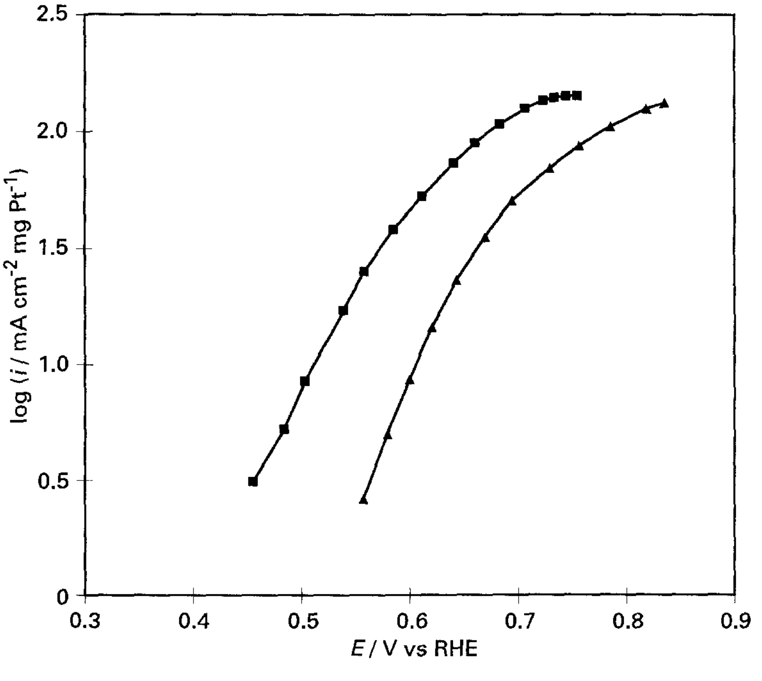

Fig. 6. Variation of the logarithm of the current density of methanol oxidation as a function of the electrode potential, 0.1 M $HClO_4$ + 0.1 M CH_3OH, $5 mV s^{-1}$, 25 °C, platinum–polyaniline (▲), platinum–ruthenium-polyaniline (■).

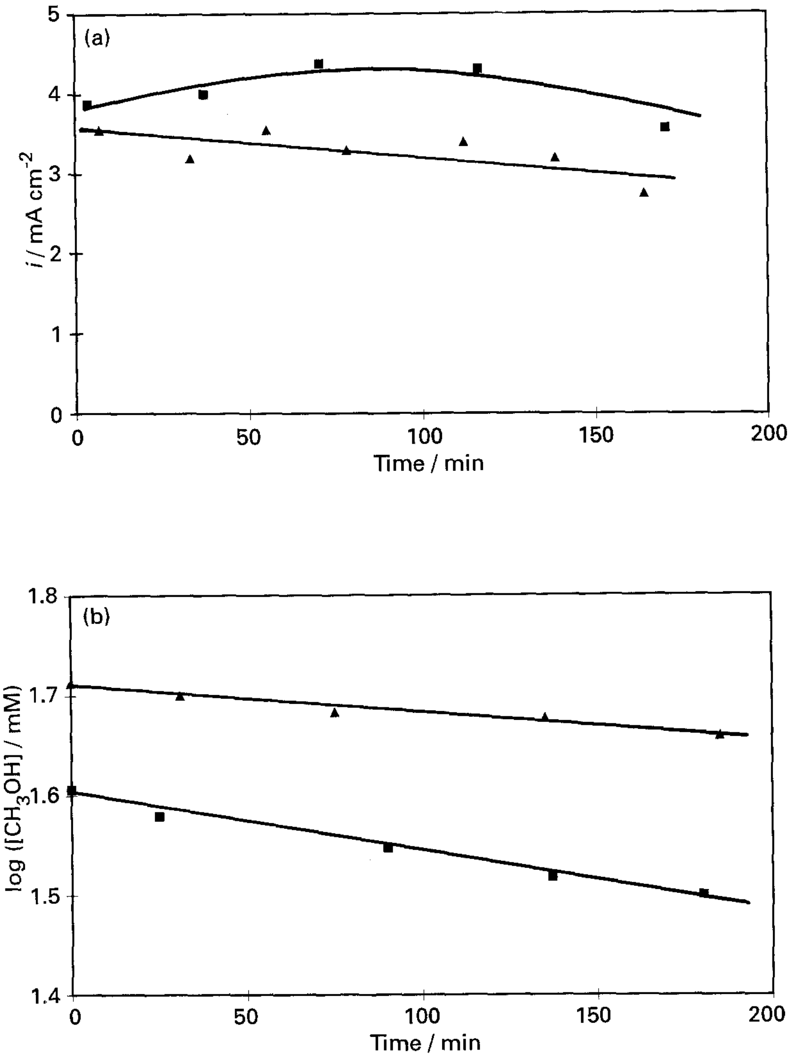

Fig. 7. (a) Variation of the current density of methanol oxidation as a function of the electrolysis time, (b) variation of the logarithm of methanol concentration as a function of the electrolysis time; 0.1 M $HClO_4$ + 0.1 M CH_3OH; electrolysis potential 0.7 V vs RHE, room temperature, platinum-polyaniline (▲), platinum–ruthenium-polyaniline (■).

The electrolysis of methanol was performed using a potential program, consisting of a potential plateau at 0.7 V vs RHE for several minutes, followed by a voltammetric sweep at 5 mV s^{-1} between two given limits (0 and 0.9 V vs RHE). This sweep, triggered when the current density became lower than 25% of the initial current density, allowed the electrode surface to be 'cleaned' by oxidizing the strongly adsorbed intermediates.

The plot of the current density during prolonged CH_3OH oxidation, at a constant potential, is represented in Fig. 7(a), where each point of the curve corresponds to the current density at the beginning of the potential plateau. The time elapsed between two experimental points thus represents the period of the potential program, which is usually several tens of minutes. Therefore, the higher is the number of experimental points in Fig. 7(a), the faster is the deactivation process of the catalytic anode, as observed with the monometallic platinum electrode which needs to be reactivated more frequently by the voltammetric sweep. Moreover, the activity of this electrode decreases slightly with time, showing that the active sites of the electrode are progressively poisoned. On the other hand, the bimetallic electrode displays the same activity during the first two hours of electrolysis. Indeed, this electrode is less sensitive to poisoning, since the oxidation of carbon monoxide occurred at much more negative potentials. After 2 h, the activity decreases slightly because of methanol consumption.

It must be pointed out that, during the potential plateau, the decrease in current is lower on these dispersed electrodes than on a platinum bulk electrode, thus allowing the maintenance of constant potential for several minutes.

After 3 h of electrolysis, the main product detected at the monometallic electrode is formaldehyde (65%), rather than carbon dioxide as at the platinum bulk electrode [30] (Table 2). The formaldehyde formation is not of interest for fuel cell application since it gives only 2 F mol^{-1} of oxidized methanol.

Table 2. Distribution of the reaction products of methanol oxidation after 3 h of electrolysis at 0.7V vs RHE

Electrode	*Reaction products*		
	% HCHO	*% HCOOH*	*% CO_2*
PAni/Pt	65	1	34
PAni/Pt–Ru	19	15	66

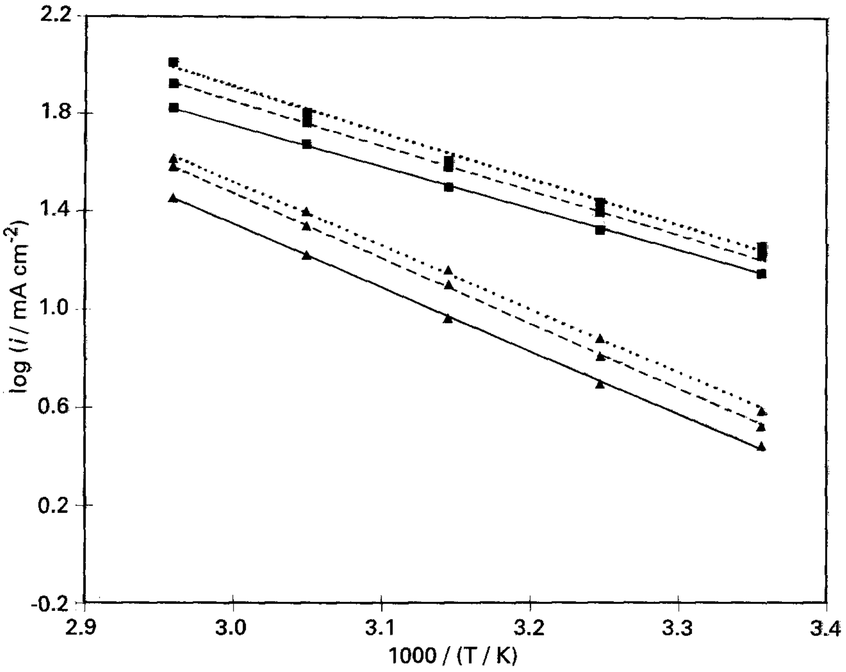

Fig. 8. Arrhenius plot for methanol oxidation on platinum-polyaniline (▲), and platinum–ruthenium-polyaniline (■); 0.5 M H_2SO_4 + 1 M CH_3OH; 0.7 V (——), 0.75 V (– – –) and 0.8 V vs RHE (· · · ·).

However, if ruthenium is added to platinum, the main product detected is now carbon dioxide (66%). A greater quantity of formic acid (15%) is formed, meaning that the oxidation reaction is more complete.

The reaction products and their distribution are reported in Table 2.

A notable point is that the disappearance of methanol follows a linear log C against time law (Fig. 7(b)). This means that a first-order reaction kinetics prevails, the intrinsic rate constants being 0.014 and 0.032 $h^{-1} cm^{-2}$ for the monometallic and bimetallic electrodes, respectively. The intrinsic rate constant obtained on a platinum-ruthenium modified polyaniline electrode is about two-fold higher than that obtained on a platinum-modified polyaniline electrode and is about twenty-fold higher than the intrinsic rate constant obtained on platinum bulk electrodes [30]. This indicates that the methanol oxidation is faster on platinum–ruthenium dispersed electrodes.

3.4. *Effect of temperature*

The effect of temperature allowed calculation of the apparent activation energy for the methanol oxidation reaction. The plots of log i against $1/T$ for the Pt–Ru-modified polyaniline and Pt-modified polyaniline electrodes (Fig. 8) reveal lower activation energies for methanol oxidation reaction on the bimetallic electrode than on the monometallic electrode (32 kJ mol^{-1} for PAni/Pt–Ru and 51 kJ mol^{-1} for PAni/Pt). Therefore, improvement in the performance of methanol oxidation on the bimetallic electrode is not only due to the formation of ruthenium oxides at lower potential but may also be due to a lower activation energy for methanol oxidation resulting from a different mechanism.

4. Conclusion

Electrodes modified by platinum and ruthenium particles dispersed inside a polyaniline film show higher activity, with respect to the electrocatalytic oxidation of methanol, than a polyaniline film modified only by platinum particles. This fact confirms the promoting effect of ruthenium on the electrocatalytic properties of platinum, even when platinum is dispersed in a conducting polymer like polyaniline. It is characterized by a 100 mV negative shift of the methanol oxidation curves, and a 150 mV negative shift of the oxidation of formaldehyde and carbon monoxide.

Moreover, the presence of ruthenium, which leads to the formation of oxides at lower potential, increases the kinetics of methanol oxidation and decreases the activation energy. The rate constant is increased by alloying dispersed platinum with ruthenium. The electrochemical reaction of methanol oxidation follows first order kinetics with respect to methanol.

Finally, the oxidation of methanol is much more complete at a Pt–Ru-modified polyaniline electrode than at a Pt-modified polyaniline electrode since carbon dioxide becomes the main reaction product.

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