

Electrocatalytic oxidation of methanol and C1 molecules on highly dispersed electrodes

Part 1: Platinum in polyaniline

H. LABORDE, J.-M. LÉGER, C. LAMY

Laboratoire de Chimie 1, URA au CNRS No. 350, Université de Poitiers, 40, avenue du Recteur Pineau, 86022 Poitiers, France

Received 2 April 1993; revised 5 July 1993

The oxidation of methanol and C1 molecules was investigated on platinum-modified polyaniline electrodes. It was found that such electrodes are conducting even at 0.0 V vs RHE. They were found to have a higher electrocatalytic activity than bulk platinum electrodes. Moreover, the poisoning effect is drastically decreased as proved by *in situ* EMIRS studies which show no significant CO_{ads} signal. Finally, kinetic results show that the methanol electrooxidation is first order with respect to methanol and that the main oxidation product is formaldehyde.

1. Introduction

Over several years, conducting polymers have been extensively studied in view of their potential applications [1]. Considerable effort has been devoted to the electrochemical preparation of conducting polymers such as polypyrrole, polythiophene and polyaniline. Polyaniline (PAni), which is easy to synthesize in aqueous medium, is a very interesting material [2]. It is generally homogeneous, strongly adherent to the support, and chemically stable in acid medium [3, 4].

The possibility of dispersing metallic particles inside these polymers gives electrocatalytic active electrodes. Indeed, the polymer provides the possibility of higher surface areas and is conducting in the potential range where the organic molecule is oxidized. Promising results have been reported for the oxidation of hydrogen [5], of small organic molecules such as formic acid [6] and of methanol [7–10] on Pt-based particles dispersed in a polymer film (poly(3-methyl)thiophene [7], polypyrrole [4, 8], polyaniline [5, 6, 9]) or a copolymer of pyrrole and dithiophene [10].

The aim of the present work is to investigate the electrocatalytic properties of polyaniline modified by the intercalation of a small amount of platinum. The electrooxidation of C1 organic molecules (CH₃OH, HCOOH, HCHO) and of CO and H₂ will be taken as typical examples. Furthermore, a more detailed study of methanol oxidation was realized using *in situ* spectroscopic methods to investigate adsorbed intermediates, and analytical techniques to monitor the reaction products formed during prolonged electrolysis.

2. Experimental details

The electrolytic solutions were prepared from ultra-pure water (Millipore Milli Q system) and Merck

reagents (p.a. for aniline, formaldehyde, formic acid and methanol, 'für synthese' for H₂PtCl₆, 6H₂O and 'Suprapur' for HClO₄ and H₂SO₄); hydrogen and carbon monoxide were 'U' quality from l'Air Liquide. Aniline was purified by distillation under vacuum and formaldehyde was obtained by refluxing paraformaldehyde.

All experiments were performed at room temperature under a nitrogen atmosphere in a three-electrode cell with a vitreous carbon counter-electrode and a mercury/mercurous sulphate electrode (MSE) as reference. However, the electrode potentials are given on the reversible hydrogen electrode (RHE) scale. A gold sheet was used as a 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-XY recorder).

The polyaniline films were deposited by cyclic voltammetry between 0.1 and 1.15 V vs RHE, at a sweep rate of 50 mV s⁻¹ in 0.5 M H₂SO₄ containing 0.1 M of freshly distilled aniline. The thickness of the polymer layer was estimated to be around 0.5 μm.

Platinum particles were then incorporated by electrochemical deposition from a solution containing 0.01 wt % hexachloroplatinic acid in 0.5 M H₂SO₄, at a constant potential of 0.15 V vs RHE. The electrode was allowed to remain in contact with the hexachloroplatinic acid solution for at least 15 min prior to the reduction. The amount of platinum deposited, calculated from the integral of the cathodic charge passed during the deposition process, was estimated by assuming that the reduction of Pt⁴⁺ to Pt⁰ is 100% efficient.

The experimental setup for electrochemically modulated infrared reflectance spectroscopy consisted of an EMIRS III grating spectrometer (Hi-Tek

Instruments, England) driven by a Commodore microcomputer. After a single reflection at the electrode surface, the infrared beam (from a Nernst filament) was monochromated and detected by a liquid nitrogen cooled HgCdTe detector (Infrared Associates Inc., USA). The resulting electric signal was then filtered and analysed by a PAR-5204 lock-in amplifier, locked at the frequency of the reference signal used to modulate the electrode potential (for ΔR measurements) or at the frequency of the light chopper (for R measurements). A Nicolet 4094 digital oscilloscope was used to store and to process the output signal to the final dimensionless ratio $\Delta R/R$.

Electrolysis was carried out in an electrochemical cell with two compartments separated by an ionic 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 using 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 HPLC using an ionic column and an u.v.-visible detector.

3. Results

Figure 1 gives a cyclic voltammogram showing the electropolymerisation of aniline prepared from a 0.5 M sulphuric acid and 0.1 M aniline solution. During the first cycle, the electrooxidation of aniline starts at 0.9 V vs RHE and leads to the first layer of polyaniline. Subsequent cycles indicate a regular growth of the polyaniline film as evidenced by the increase in the redox charge.

The voltammogram of the PANi film in blank solution (0.5 M H_2SO_4) is shown in Fig. 2 and gives four peaks with E_{pa} values of 0.37, 0.65, 0.72 and 0.95 V vs RHE. Upon repeated potential cycling, the peak currents associated with the processes at 0.37 and 0.95 V vs RHE decrease in magnitude while the peak currents for the redox couple at 0.65 and 0.72 V vs RHE increase in magnitude. It has been previously reported that complete oxidation of the polymer to the imine form at potentials greater than 1.0 V vs RHE results in hydrolysis of the imine nitrogen-carbon bonds to a quinone form [11–13]. The peaks at 0.65 and 0.72 V vs RHE may correspond to this quinoid structure.

On the other hand, under the same conditions, cyclic voltammograms in 0.1 M HClO_4 given in Fig. 3, show that the waves at 0.37 and 0.9 V vs RHE

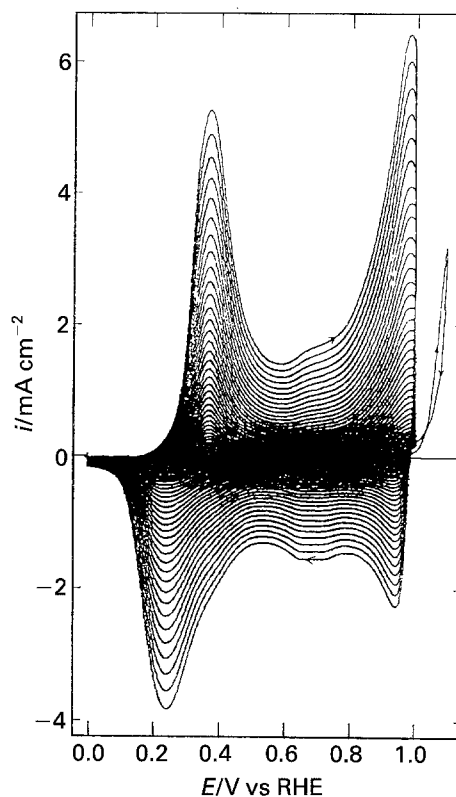


Fig. 1. Cyclic voltammograms during the electropolymerization of aniline from a solution containing 0.5 M sulphuric acid with 0.1 M aniline on a gold electrode, recorded at 50 mVs^{-1} , room temperature.

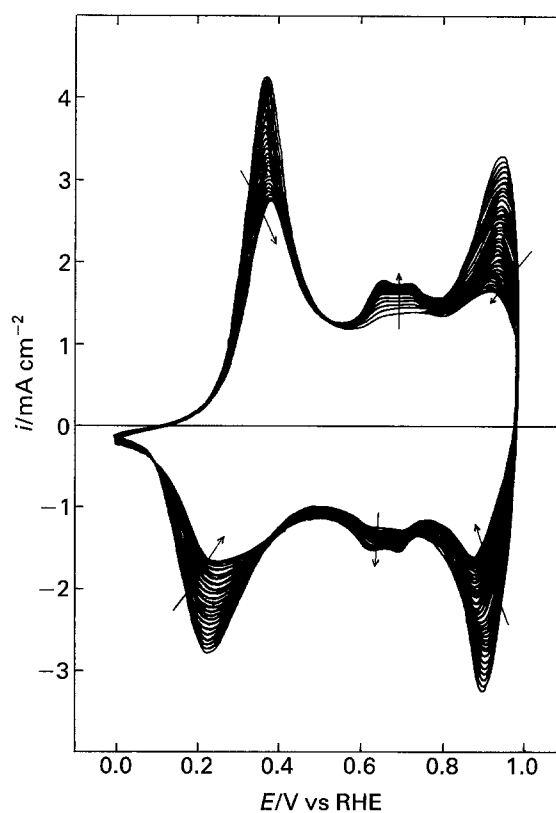


Fig. 2. Cyclic voltammograms of a polyaniline film in 0.5 M H_2SO_4 , recorded at 50 mVs^{-1} ; upper limit: 1 V vs RHE, room temperature.

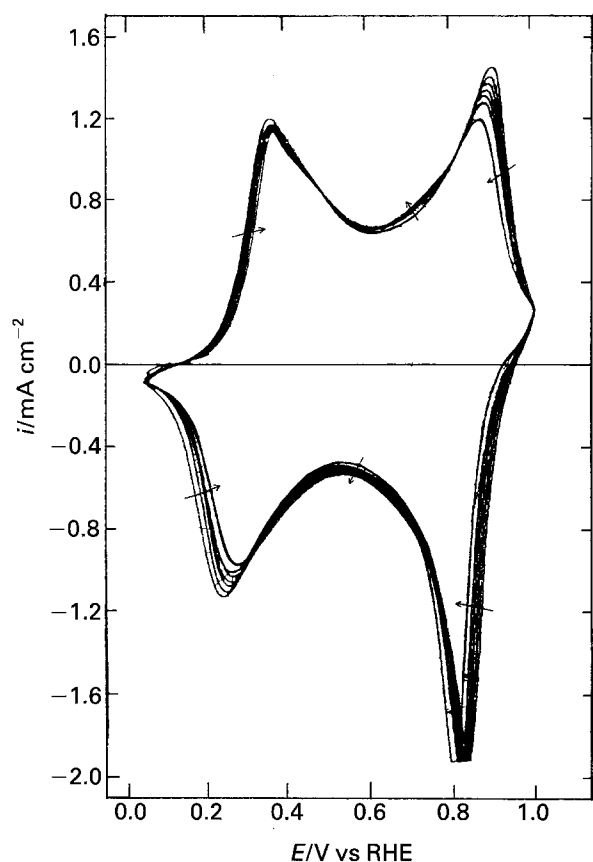


Fig. 3. Cyclic voltammograms of a polyaniline film in 0.1 M HClO₄, recorded at 50 mV s⁻¹; upper limit: 1 V vs RHE, room temperature.

remain quite constant, indicating the greater stability of the polymer in a such medium.

By examining the polyaniline films with SEM, it was found that they display a porous and rough morphology and provide a high area surface which may be exploited when they are used as a catalyst support.

3.1. Platinum microparticles deposition in polyaniline films

The electrochemical deposition of platinum particles in the polyaniline films was achieved by electrolysis at constant potential using an acidic hexachloroplatinate solution.

Voltammograms of the modified electrodes were then recorded in the supporting electrolyte (Fig. 4). These do not exhibit any well-defined peaks corresponding to the adsorption-desorption region of hydrogen on platinum. This observation confirms that the polymer contains only a small amount of platinum and that a good dispersion of platinum is achieved, since there are no platinum islands which should have the adsorption properties of the bulk metal. But, when a higher amount of platinum is deposited (a few mg cm⁻²), the voltammogram of this PANi/Pt electrode looks like the voltammogram of a bulk platinum electrode and shows a hydrogen adsorption-desorption region.

SEM photomicrographs show that platinum atoms form small clusters inside the PANi film. However,

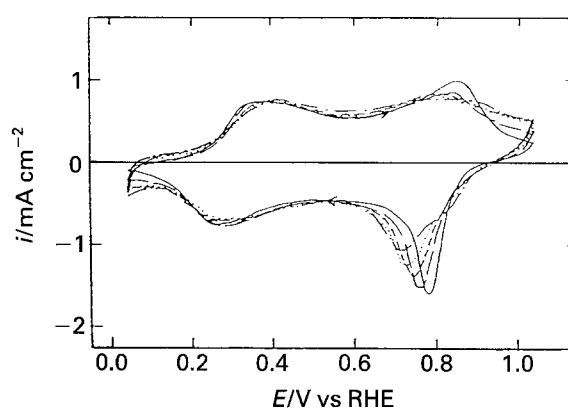


Fig. 4. Voltammograms of a polyaniline film modified by platinum particles, in 0.1 M HClO₄, recorded at 5 mV s⁻¹; 25°C. Platinum amount: (—) 33, (—) 54, (---) 69, (····) 82, (-·-·-) 109 μg cm⁻².

owing to the porous nature of the polymer, these clusters appear to be sufficiently dispersed in the overall structure of the PANi film.

3.2. Catalytic activity

The catalytic activity of the PANi electrode, modified with 0.1 mg cm⁻² of platinum, was evaluated by observing the electrooxidation of several small molecules.

Figs 5 and 6 show the voltammograms of the platinum-modified polyaniline electrode for the oxidation of hydrogen and formaldehyde, formic acid, methanol and carbon monoxide respectively. These curves were recorded at a sweep rate of 5 mV s⁻¹ in a solution saturated by bubbling H₂ and CO or in solutions containing 0.1 M HCHO or 0.1 M HCOOH or 0.1 M CH₃OH. The supporting electrolyte was 0.1 M HClO₄.

3.2.1. *Electrooxidation of hydrogen.* Figure 5 represents the electrooxidation of hydrogen dissolved at saturation in a perchloric acid solution. In

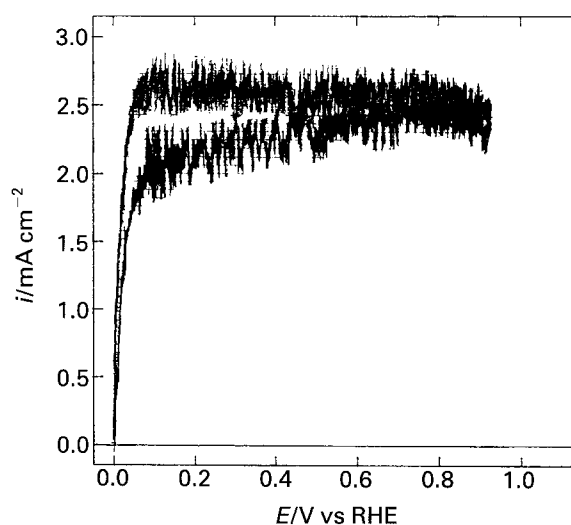


Fig. 5. Voltammogram of a polyaniline film modified with 0.1 mg cm⁻² of platinum, in a 0.1 M HClO₄ solution saturated with hydrogen; 5 mV s⁻¹, 25°C.

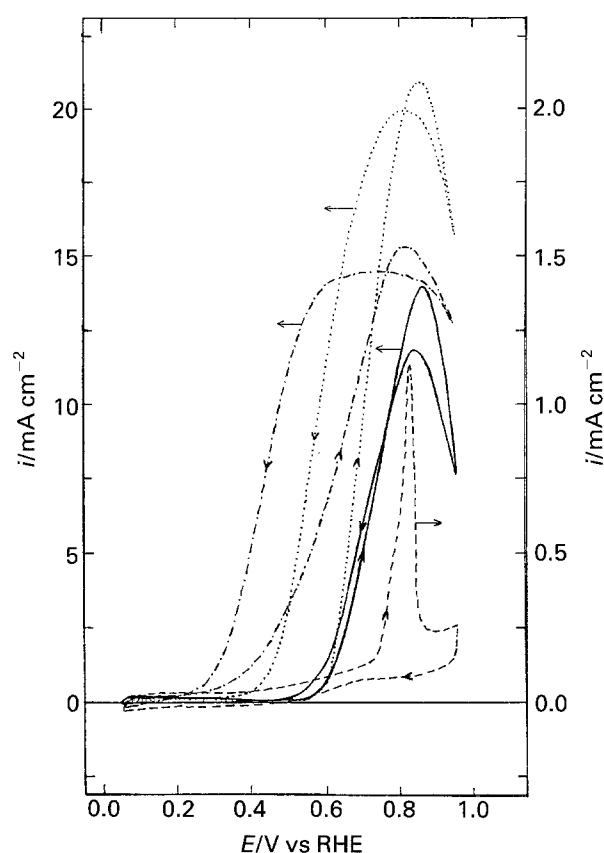


Fig. 6. Voltammograms of a polyaniline film modified with 0.1 mg cm^{-2} of platinum, in 0.1 M HClO_4 , recorded at 5 mV s^{-1} , 25°C ; with $0.1 \text{ M CH}_3\text{OH}$ (—), with 0.1 M HCHO (.....), with 0.1 M HCOOH (-.-.-), and in a CO saturated solution (- - - -).

contrast to the results of Vork *et al.* [5] who found that hydrogen is not oxidized on a platinum modified-polyaniline electrode at potentials lower than 0.35 V vs RHE, the oxidation starts at 0.0 V vs RHE. This is normal for an active catalytic electrode, the hydrogen overpotential being small for such electrodes. The current density reaches a limiting value due to a kinetic control of the overall process by diffusion of the electroactive species H_2 . Under these conditions of stirring (magnetic stirrer), the limiting current is around 2.5 mA cm^{-2} . The general shape of the curve confirms that the platinum-modified polyaniline electrode is conducting at lower potentials, in contrast with the case of polymer electrodes without platinum particles.

Recent u.v.-visible reflectance spectroscopic results show that the deposition of platinum inside polyaniline led to a state of the polymer at 0.0 V vs RHE which does not correspond to the insulating and neutral form. Conversely, it seems that the reduction of the nitrogen atoms up to the amine form is not complete in the presence of platinum particles.

3.2.2. Electrooxidation of C1 molecules. Figure 6 shows the electrooxidation of several C1 molecules, dissolved in 0.1 M HClO_4 , on a polyaniline electrode modified by 0.1 mg cm^{-2} of platinum. The voltammograms represent the first sweep, but the second and the following sweeps display the same shape.

The electrooxidation of 0.1 M HCHO , shown in Fig. 6, starts at 0.55 V vs RHE and reaches a maximum of about 21 mA cm^{-2} at 0.85 V vs RHE (Table 1). During the negative sweep, the oxidation current is represented by a wide peak, meaning that a small poisoning effect is detected due to the formation of strongly adsorbed species [14]. This effect is less important and the current densities are higher than on a bulk platinum electrode.

The electrooxidation of 0.1 M HCOOH , shown in Fig. 6, starts at around 0.2 V vs RHE and reaches a maximum of 16 mA cm^{-2} at 0.82 V vs RHE (Table 1). This peak is generally attributed to oxidation of the strongly chemisorbed species. During the negative sweep, the oxidation peak is wider than during the positive sweep. This is due to the inhibition of the weakly bound intermediate pathway by the presence of strongly chemisorbed species. Gholamian *et al.* [6] observed that this weakly bound intermediate pathway is favoured on platinum microparticles. The maximum current densities against geometric area for formaldehyde and formic acid oxidation obtained with the platinum-modified polyaniline electrode are much higher than those obtained with a bulk platinum electrode (by a factor of around 10 under the same experimental conditions).

The electrocatalytic oxidation of carbon monoxide is weak on this dispersed electrode. The small current density of the CO oxidation ($i_{\text{max}} = 1.1 \text{ mA cm}^{-2}$ at 0.83 V vs RHE) is an unexpected phenomenon but was predicted by a previous spectroscopic result; the EMIRS signal of the linear CO_{ads} species decreases with increase in the platinum dispersion [15], indicating that the CO adsorption decreases with electrode roughness. Thus, CO is adsorbed weakly on dispersed platinum-based electrodes and these electrodes are less poisoned than massive platinum electrodes, on which poisoning species are easily formed during the oxidation of organic molecules such as formic acid or methanol [14].

Moreover, for methanol oxidation, the poisoning effect is less significant owing to the quasisuperimposition of the oxidation currents during the positive and the negative sweeps (Table 1).

All the maximum current densities and the peak potentials are reported in Table 1 where the two first

Table 1. Maximum current density and peak potential for the oxidation of C1 molecules on a polyaniline film modified with 0.1 mg cm^{-2} of platinum, upper potential limit: 0.95 V vs RHE

Sweep	C1 molecules			
	HCHO	HCOOH	CH ₃ OH	CO
<i>Positive</i>				
Maximum current density mA cm^{-2}	21	16	14	1.1
Potential/V vs RHE	0.85	0.82	0.86	0.83
<i>Negative</i>				
Maximum current density mA cm^{-2}	20	14.5	12	—
Potential/V vs RHE	0.8	0.7	0.83	—

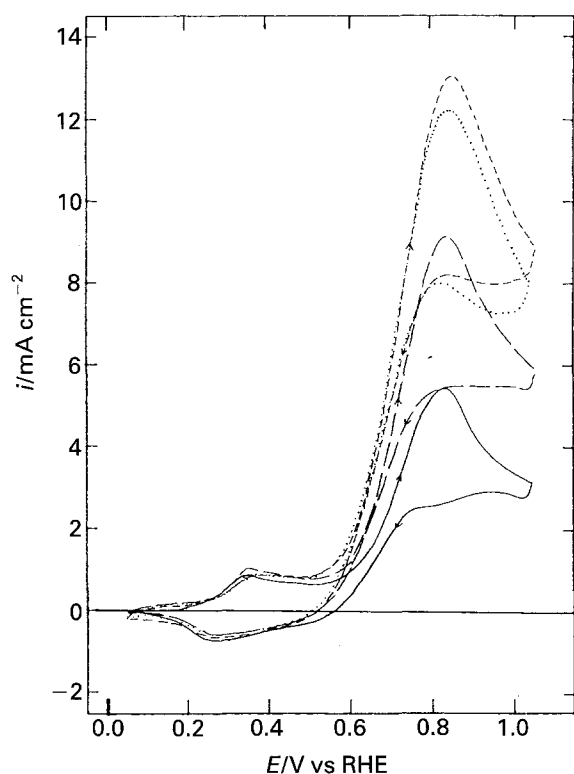


Fig. 7. Voltammograms of a polyaniline film modified with different loadings of platinum, in 0.1 M HClO₄ + 0.1 M CH₃OH, recorded at 5 mV s⁻¹, 25 °C; Platinum amount: (—) 33, (---) 54, (- - - -) 69, (.....) 82 μg cm⁻².

lines are the data for the positive sweep and the two last lines for the negative sweep.

3.2.3. Influence of the platinum loading. The electroactivity for methanol oxidation depends on the amount of deposited platinum. The methanol oxidation starts at 0.55 V vs RHE and the maximum of the current density is observed between 0.84 and 0.91 V vs RHE for a platinum amount varying from 0 to 110 μg cm⁻². The voltammograms are shown in Fig. 7. The shift to more positive potentials of the current peak increases with the amount of deposited platinum.

Figure 8 represents the variation of the maximum current density as a function of the amount of deposited platinum. In this curve, the current

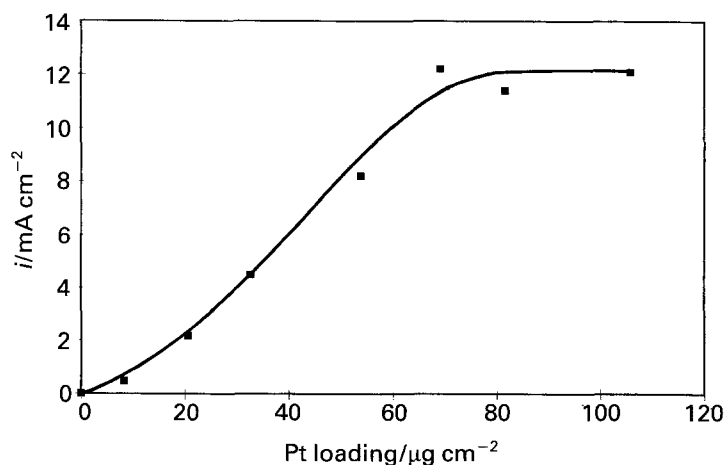


Fig. 8. Maximum current density of methanol oxidation as a function of the platinum loading of a platinum modified-polyaniline electrode. Electrolyte was 0.1 M HClO₄ + 0.1 M CH₃OH; 25 °C.

density increases regularly up to 70 μg cm⁻², then reaches a plateau: (i) for an amount of platinum smaller than 70 μg cm⁻², the maximum current density increases proportionally with the platinum loading, and (ii) after 70 μg cm⁻², the maximum current density becomes nearly constant. The slight decrease observed is probably due to the formation of platinum clusters, leading to a smaller dispersion.

3.3. Electrochemically modulated infrared reflectance spectroscopy

The nature of the adsorbed species formed by chemisorption of methanol at platinum modified-polyaniline electrodes was investigated by EMIRS.

The EMIRS spectrum, in Fig. 9, was obtained using 0.5 M H₂SO₄ as a supporting electrolyte and a 0.1 M CH₃OH solution in order to compare with the spectrum obtained with a bulk platinum electrode. The electrode potential is modulated between 0.05 V and 0.35 V vs RHE (mean potential \bar{E} = 0.2 V vs RHE; modulation amplitude ΔE = 300 mV).

The maximum contribution of the band centred at 1680 cm⁻¹ of the platinum-modified polyaniline electrode spectrum can be attributed to organic radicals, either formyl species (CHO)_{ads}, or acid species (HCOO)_{ads} [15–17]. But, in the region between 1500 and 1700 cm⁻¹, there are also characteristic bands of polyaniline [18–21]. Most notable, however, is the absence of a CO_{ads} signal in the region 1800–2200 cm⁻¹ with platinum modified-polyaniline electrodes (Fig. 9(b)) compared with a bulk platinum electrode (Fig. 9(a)). This fact confirms the lower degree of poisoning observed on electrodispersed platinum [15] and the results obtained with cyclic voltammetry. Moreover, these spectra show a contribution of adsorbed CO₂ at 2350 cm⁻¹. CO₂ was formed during the electrooxidation process.

When compared to the spectrum of bulk platinum [16], this spectrum has a significant contribution of the band located at 1680 cm⁻¹, which is certainly related to the disappearance of the (CO)_{ads} signal. Thus, the electrocatalytic oxidation of methanol on platinum modified-polyaniline leads to the formation

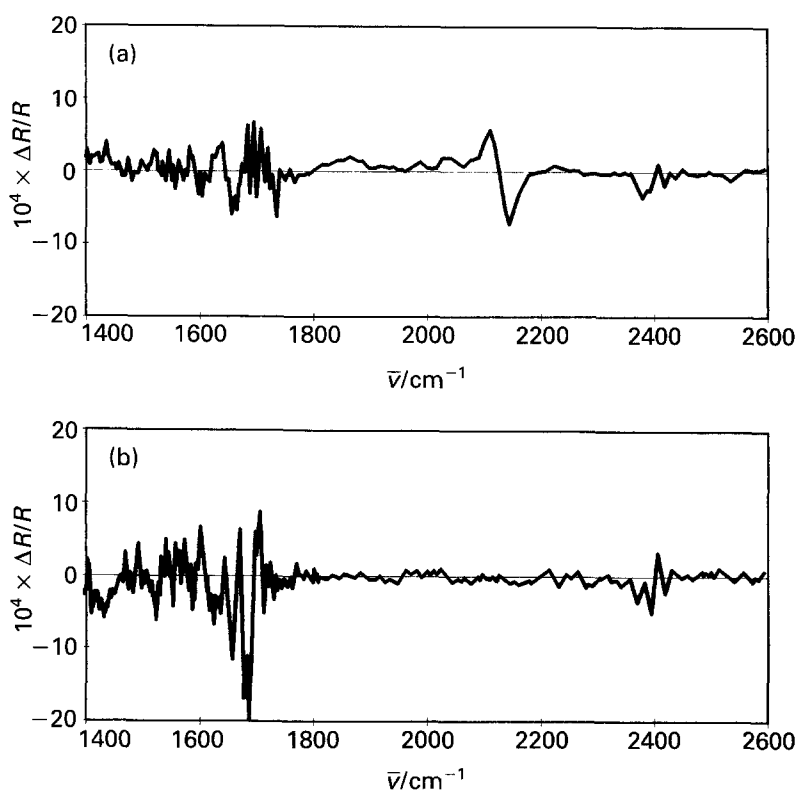


Fig. 9. EMIRS spectra of the adsorbed species resulting from the dissociation of 0.1 M CH_3OH in 0.5 M H_2SO_4 . Modulation frequency $f = 13.5$ Hz, modulation amplitude $\Delta E = 300$ mV, 5 scans, mean electrode potential $\bar{E} = 0.2$ V vs RHE, room temperature, (a) platinum bulk electrode, (b) platinum modified-polyaniline electrode.

of a formyl intermediate $(\text{CHO})_{\text{ads}}$, characterized by an EMIRS band at around 1680 cm^{-1} . The oxidation of this intermediate gives carbon dioxide directly without forming a poisoning species, such as $(\text{CO})_{\text{ads}}$, which is not detected.

3.4. Electrolysis

To study the overall reaction mechanisms, quantitative analyses of the reaction products were done during prolonged electrolyses of 0.1 M CH_3OH in 0.1 M HClO_4 on platinum modified-polyaniline electrodes.

The electrolysis of methanol was performed using a potential program, consisting of a potential plateau at 0.7 V vs RHE for several minutes (typically 20 min). This plateau was then followed by a voltammetric sweep between two given limits, allowing the electrode surface to be 'cleaned' by oxidizing the strongly adsorbed intermediates.

The plot of the current density during prolonged CH_3OH oxidation, at constant potential, is represented in Fig. 10(a), where each point of the curve corresponds to the current density at the beginning of the potential plateau. Between two points, there were the potential plateau during which the current density slightly decreased, and the cyclic voltammogram before the new plateau. This voltammogram sweep allowed the electrode to recover its initial activity.

HPLC analysis detected several products: the remaining methanol, carbon dioxide, formaldehyde and formic acid. Formaldehyde was always the main product detected. A significant amount of carbon dioxide and some weak traces of formic acid were detected only after 3 h of electrolysis, as reported in Table 2.

A notable point is that the disappearance of methanol follows a linear $\log C$ against time law (Fig. 10). This means that first-order reaction kinetics prevail, the intrinsic rate constant being $0.014\text{ h}^{-1}\text{ cm}^{-2}$.

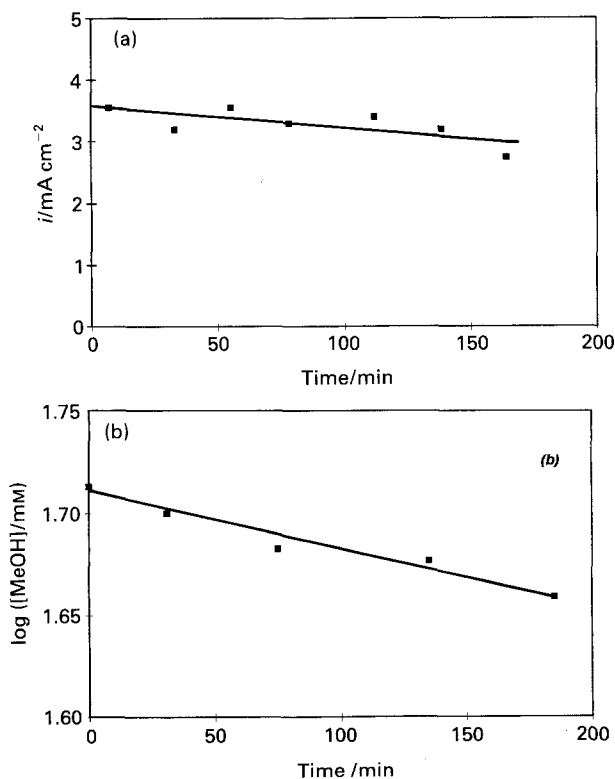


Fig. 10. (a) Variation of the current density of methanol oxidation as a function of the electrolysis time, (b) variation of the logarithm of methanol concentration as a function of the electrolysis time; 0.1 M HClO_4 + 0.1 M CH_3OH ; electrolysis potential 0.7 V vs RHE, room temperature.

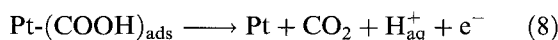
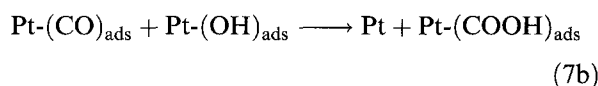
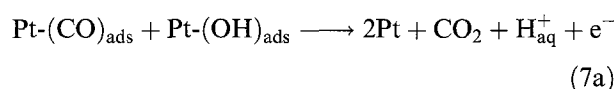
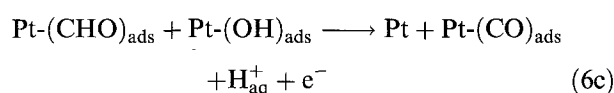
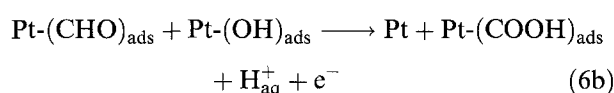
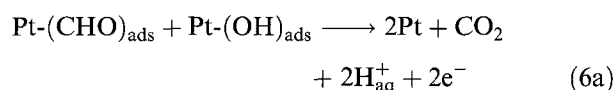
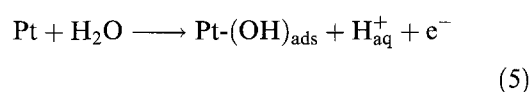
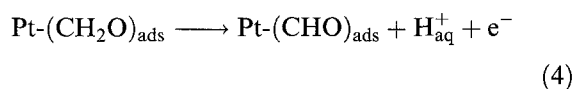
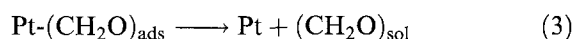
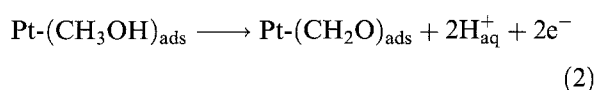
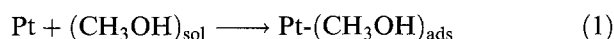
Table 2. Distribution of the reaction products of methanol oxidation after 3 h of electrolysis

Reaction products	HCHO	HCOOH	CO ₂
%	65	1	34

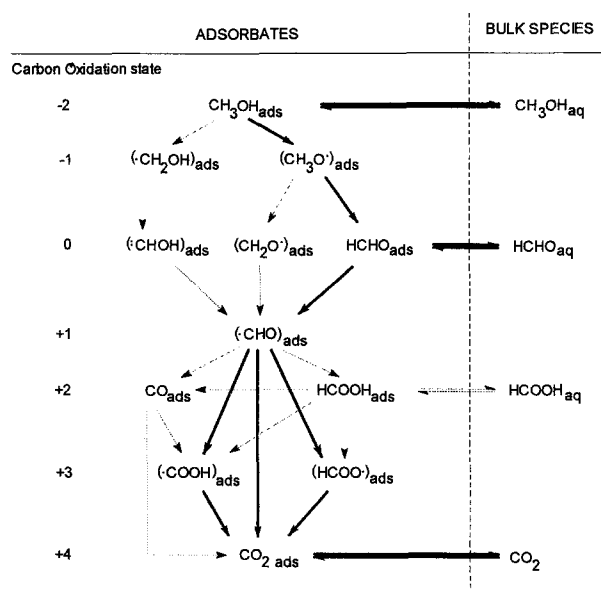
This value is about ten-fold higher on a platinum modified-polyaniline electrode than the intrinsic rate constant obtained on platinum-based electrodes [23], indicating that the methanol oxidation is faster on platinum dispersed electrodes.

4. Discussion

On the basis of these results, a mechanism can be proposed for methanol oxidation on platinum modified-polyaniline electrodes in acid medium. The steps are provided in the following sequence:



First, methanol is adsorbed and transformed to $(\text{CH}_2\text{O})_{\text{ads}}$ (Reactions 1–3). Then, $(\text{CH}_2\text{O})_{\text{ads}}$ leads to the formation of the reactive intermediate $(\text{CHO})_{\text{ads}}$ (Reaction 4) and its further oxidation (Reactions 6). This reactive species is oxidized, either directly to CO_2 (Reaction 6a) or through $(\text{COOH})_{\text{ads}}$ (Reaction 6b), which is further oxidized to CO_2 (Reaction 8). The formation of the poisoning species $(\text{CO})_{\text{ads}}$ is minimized (Reaction 6c). $(\text{CO})_{\text{ads}}$ can also be oxidized to CO_2 , either directly (Reaction 7a) or through $(\text{COOH})_{\text{ads}}$ (Reaction 7b, followed by Reaction 8).



Scheme 1. Methanol oxidation on platinum-modified polyaniline electrode.

The main difference with respect to the mechanism on bulk platinum in acid medium [24], is that the amount of $(\text{CO})_{\text{ads}}$ formed on dispersed platinum is smaller, leading to a greater electrocatalytic activity.

From the general scheme [24], the methanol oxidation on platinum-modified polyaniline electrode can be summarized according to Scheme 1. The preferential reactions are represented with thick arrows.

5. Conclusion

Electrodes modified by platinum particles dispersed inside a polyaniline film show high activity with respect to methanol electrocatalytic oxidation and other C1 molecules such as formaldehyde and formic acid. Furthermore, the oxidation of hydrogen at low potentials proves that such electrodes are conducting even at 0.0 V vs RHE.

The enhancement effect observed in the methanol oxidation rate appears to occur mainly because the formation of the strongly chemisorbed species, $(\text{CO})_{\text{ads}}$, seems to be drastically decreased. This was confirmed by the EMIRS spectrum where no significant $(\text{CO})_{\text{ads}}$ signal was detected. The increase in activity is also due to the expected increase of the platinum area available.

The results, based on the quantitative analysis, by HPLC, of the reaction products of methanol oxidation, confirmed that this electrochemical reaction follows first order kinetics with respect to methanol [23]. It appears that the rate constant is increased markedly by the dispersion of platinum. The main oxidation product is formaldehyde, showing that the oxidation is incomplete.

More extensive work on plurimetalllic dispersed electrodes, and on their electrocatalytic properties, are currently in progress.

References

- [1] T. A. Skotheim, 'Handbook of Conducting Polymers', Marcel Dekker, New York (1986).
- [2] E. M. Génies, A. Boyle, M. Lapkowski and C. Tsintavis, *Synth. Metals* **36** (1990) 139.
- [3] W. S. Huang, B. D. Humphrey and A. G. MacDiarmid, *J. Chem. Soc., Faraday Trans. 1* **52** (1986) 2385.
- [4] E. M. Génies and C. Tsintavis, *J. Electroanal. Chem.* **195** (1985) 109.
- [5] F. T. A. Vork, L. J. J. Janssen and E. Barendrecht, *Electrochim. Acta* **31** (1986) 1569.
- [6] (a) M. Gholamian and A. Q. Contractor, *J. Electroanal. Chem.* **289** (1990) 69; (b) M. Gholamian, J. Sundaram and A. Q. Contractor, *Langmuir* **3** (1987) 741.
- [7] S. Swathirajan and Y.M. Mikhail, *J. Electrochem. Soc.* **139** (1992) 2105.
- [8] (a) D. J. Strike, N. F. De Rooij, M. Koudelka-Hep, M. Ulmann and J. Augustynski, *J. Appl. Electrochem.* **22** (1992) 922; (b) M. Ulmann, R. Kostecki, J. Augustynski, D. J. Strike and M. Koudelka-Hep, *Chimia* **46** (1992) 138.
- [9] (a) K. M. Kost, D. E. Bartak, B. Kazee and T. Kuwana, *Anal. Chem.* **60** (1988) 2379; (b) P. Ocon Esteban, J.-M. Léger, C. Lamy and E. Génies, *J. Appl. Electrochem.* **19** (1989) 462.
- [10] H. Laborde, J.-M. Léger, C. Lamy, F. Garnier and A. Yassar, *J. Appl. Electrochem.* **20** (1990) 524.
- [11] E. M. Génies and C. Tsintavis, *J. Electroanal. Chem.* **200** (1986) 127.
- [12] D. E. Stilwell and S. M. Park, *J. Electrochem. Soc.* **135** (1988) 2497; **136** (1989) 688.
- [13] T. Kobayashi, H. Yoneyama and H. Tamura, *J. Electroanal. Chem.* **161** (1984) 419; **177** (1984) 281, 293.
- [14] C. Lamy, *Electrochim. Acta* **29** (1984) 1581.
- [15] B. Beden, F. Hahn, J.-M. Léger, C. Lamy, C. L. Perdriel, N. R. de Tacconi, R. O. Lezna and A. J. Arvia, *J. Electroanal. Chem.* **301** (1991) 129.
- [16] (a) B. Beden, F. Hahn, J.-M. Léger, C. Lamy and M. I. S. Lopes, *J. Electroanal. Chem.* **258** (1989) 463; (b) M. I. S. Lopes, B. Beden, F. Hahn, J.-M. Léger and C. Lamy, *ibid.* **313** (1991) 323.
- [17] B. Beden, F. Hahn, C. Lamy, J.-M. Léger, N. R. de Tacconi, R. O. Lezna and A. J. Arvia, *ibid.* **261** (1989) 401.
- [18] E. M. Génies, M. Lapkowski and J. F. Penneau, *ibid.* **249** (1988) 97.
- [19] Y. Sun, A. G. MacDiarmid and A. J. Epstein, *J. Chem. Soc. Chem. Commun.* (1990) 529.
- [20] E. M. Génies and P. Noël, *J. Electroanal. Chem.* **296** (1990) 473.
- [21] J. Tang, X. Jing, B. Wang and F. Wang, *Synth. Metals* **24** (1988) 231.
- [22] K. I. Ota, Y. Nakagawa and M. Takahashi, *J. Electroanal. Chem.* **179** (1984) 179.
- [23] E. M. Belgsir, H. Huser, J.-M. Léger and C. Lamy, *ibid.* **225** (1987) 281.
- [24] B. Beden, J.-M. Léger and C. Lamy, in 'Modern Aspect of Electrochemistry', Vol. 22, (edited by J. O'M. Bockris, R. E. White and B. E. Conway), Plenum Press, New York, (1992) Chap. 2, p. 97.