Enhancement of the electrooxidation of ethanol on a Pt–PEM electrode modified by tin. Part I: Half cell study

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Abstract

The direct platinisation of a solid polymer electrolyte (Nafion® membrane) was realized by chemical reduction of a platinum salt. The Pt–PEM electrodes thus obtained were modified by tin to improve the electrocatalytic activity towards the electrooxidation of ethanol. The Pt–PEM and Pt–Sn–PEM electrodes were characterized by TEM, EDX and XRD analysis, cyclic voltammetry, and their polarisation curves for the electrooxidation of ethanol were determined under quasisteady state conditions.

1. Introduction

Over the last three decades, the electrooxidation of ethanol has been the subject of numerous studies by several methods [1]. So far, the best catalyst for the electrooxidation of ethanol in acid medium has been found to be platinum. However, many problems arise when using a platinum electrode for the direct electrochemical oxidation of ethanol. In fact, the adsorption of ethanol is a fast process but this leads to an autoinhibition of the reaction due to poisoning of the electrode surface through the formation of strongly adsorbed CO species as the result of the dissociative chemisorption of ethanol [2, 3].

To increase the electrocatalytic activity of a platinum electrode for the electrooxidation of ethanol by decreasing the poisoning phenomena, the electrode surface can be modified by adding a second metal, thus promoting the electrocatalytic activity of pure platinum. Metals suitable for such a modification are few for the oxidation of alcohols in acid medium. However, the following are noted:

(i) In the case of the electrooxidation of ethanol on pure platinum, previous studies showed that the electrode surface is rapidly covered by adsorbed CO species, which can be removed from the surface by oxidation to CO_2, only at rather positive potentials [4, 5]. At low potentials, using infrared reflectance spectroscopy, other adsorbed species were detected leading to the formation of C2 compounds such as acetaldehyde and acetic acid [2–6];

(ii) Recent work in our laboratory has led to the conclusion that the electrocatalytic couple Pt–Sn is

particularly interesting with a view to decreasing the poisoning phenomena observed during CO oxidation [7];

(iii) Previous studies showed the enhancement of the rate of ethanol electrooxidation by the catalytic couple Pt–Sn dispersed in a polyaniline matrix [8]. Such effects were also observed on smooth Pt–Sn electrodes [9].

Taking these arguments into account, we studied in more detail the effect of tin added to platinum on the electrode poisoning phenomena during ethanol oxidation. This study was carried out on platinum dispersed on a Nafion® membrane, so that the Pt–PEM electrode thus obtained is equivalent to a fuel cell model electrode. The prepared Pt–PEM and Pt–Sn–PEM electrodes were characterized by transmission electron microscopy (TEM), electron desexcitation X-ray microprobe (EDX) and X-ray diffraction analysis (XRD), cyclic voltammetry (CV), and the polarisation curves for ethanol electrooxidation were determined.

2. Experimental details

2.1. *Preparation of Pt–PEM electrodes*

The preparation of the Pt–PEM electrodes is detailed elsewhere [10]. Perfluorosulfonic acid polymer membranes (Dupont de Nemours Nafion®) were used as the solid polymer electrolyte. Before metal deposition a three-step standard cleaning procedure was followed for every sample [11]: immersion for 30 min in a boiling HNO_3–H_2O (1:1 by volume) solution, to remove impu-

rities; immersion for 1 h in boiling ultrapure water (milli-Q Millipore system, resistivity 18 MΩ cm at 25 °C) to introduce a reproducible amount of water into each sample; then immersion for 1 h in boiling 0.5 M H_2SO_4.

The chemical technique to platinise the surface of the Nafion® proton exchange membrane, for preparing a Pt–PEM electrode, was the impregnation–reduction method [11, 12]. The plating procedure conditions were optimised in previous work, to obtain high Pt surface areas [10]. A given amount of $[Pt(NH_3)_4](OH)_2$ was dissolved in water, and the Nafion® membrane (H^+ form) was soaked for 40 min in this $[Pt(NH_3)_4](OH)_2$ aqueous solution to replace hydrogen ions by the platinum complex ions $[Pt(NH_3)_4]^{2+}$. A given amount of $NaBH_4$ was then dissolved in a $LiOH/H_2O$ solution, and after the impregnation step, the platinum solution was removed from the plating cell and replaced by 40 cm^3 of this reducing solution. During both the impregnation and reduction steps, the solution was stirred.

After the reduction step was complete (2 h), the Pt–PEM composite electrode was soaked in a 0.5 M H_2SO_4 boiling solution for 2 h, followed by boiling in pure water for 1 h, and then kept in ultrapure water before being used. The determination of the active surface area of the Pt–PEM electrodes was made by hydrogen adsorption–desorption coulometry and by evaluating the quantity of electricity associated with the oxidation of a CO monolayer previously adsorbed [10]. Such a hydrogen adsorption–desorption region is not well defined in the case of a Pt–PEM electrode, so that the adsorption of CO is preferred to evaluate more accurately the active surface area [10].

2.2. Tin electrodeposition on Pt–PEM electrodes

For tin electrodeposition, the Pt–PEM electrode was placed in a cell shown in Figure 1. A 0.5 cm^2 disc of the membrane was exposed to a 1×10^{-3} M $SnCl_4$/0.5 M H_2SO_4 solution on the metallised side and to 0.5 M H_2SO_4 on the nonplatinised side of the Pt–PEM electrode. Tin deposition was carrried out at $+0.2$ V
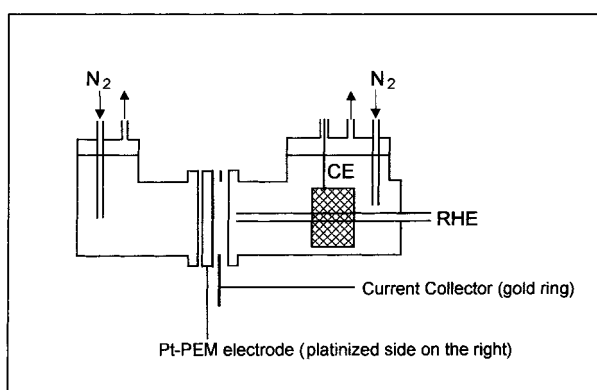

Fig. 1. Scheme of the cell used for tin electrodeposition.

vs RHE; such a potential value was chosen after recording the Sn^{4+} reduction current densities against E by voltammetry at a low sweep rate of $v = 1$ mV s^{-1} (i.e., under quasisteady state conditions). The current collector was a gold ring. A carbon counter electrode and a reversible hydrogen reference electrode were used. The amount of electrodeposited tin was estimated by coulometry, during the reduction process of the Sn^{4+} ions.

2.3. Characterization of the Pt–Nafion® and Pt–Sn–Nafion® electrodes

TEM analysis, to examine the surface morphology of the deposit (metal deposit thickness, depth of metal penetration into the Nafion® membrane, distribution of metal particle size), was realised with a Philips-CM 120 electron microscope. The composition of the Pt–Sn surface particles was determined by EDX analysis.

To evaluate the poisoning of a Pt–PEM or a Pt–Sn–PEM electrode during the electrooxidation of ethanol, current densities were recorded under quasisteady state conditions as a function of E, that is, i(E) curves (i being measured after 1 min at each potential), or as a function of time at constant potential, that is i(t) curves. For the active surface area measurements and for the evaluation of electrocatalytic activity, the Pt–PEM electrode was placed in a cell in which a 0.5 cm^2 disc of the membrane was exposed to a 0.5 M H_2SO_4 solution on the non-metallised side, and to $H_2O(g)$ or $(EtOH/H_2O)(g)$ on the platinised side [9]. The current collector was a gold ring. The reference electrode was placed directly against the Nafion® membrane on the nonmetallised side. A carbon counter electrode and a reversible hydrogen reference electrode (RHE) were used.

Electrolytic solutions were prepared with Millipore Milli-Q water and Merck suprapure chemicals. Cyclic voltammograms were recorded using a Wenking LT-87 potentiostat, a Wenking MVS-87 waveform generator, and a Linseis LY-1700 X–Y recorder.

3. Results and discussion

3.1. Electrooxidation of ethanol on a Pt–Sn–Nafion® electrode

Figure 2 shows the current densities for ethanol oxidation recorded on a Pt–Sn–PEM electrode as a function of the tin amount (related to the geometric surface area) deposited electrochemically on a Pt–Nafion® electrode (of roughness factor, ρ = active platinum surface area/geometric surface area = 310). The presence of tin produces enhanced current densities for the electrooxidation of ethanol. This experimental curve has a maximum, corresponding to a tin mass of approximately 20 μg cm^{-2}. For such an amount, the current density of ethanol oxidation is enhanced by a factor of 6 in comparison with the value obtained on the same Pt–
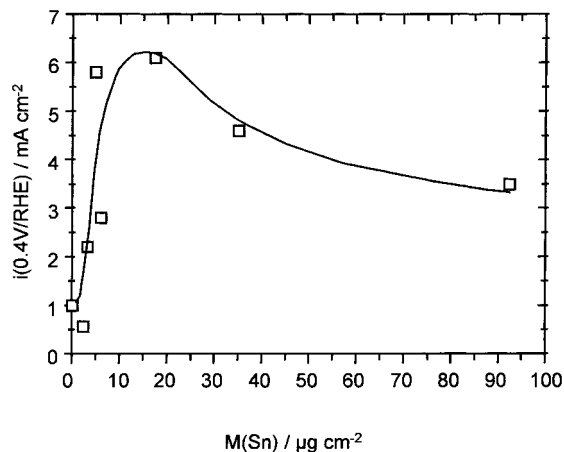
Fig. 2. Influence of the amount of electrochemically deposited tin on the activity of the Pt–Sn–Nafion® electrode (roughness factor, $\rho = 312$).

PEM electrode without added tin. With increase in tin coverage, however, the distribution of tin occupying platinum sites on the Pt–PEM electrode makes the adsorption of the organic species more difficult leading to a decrease in electrode activity for higher amounts of tin.

The increase in the current densities of ethanol electrooxidation is displayed by the shift of the oxidation peak potential to more negative values, indicating that a lower energy is necessary for the oxidation of ethanol. This shift in the electrooxidation potential is illustrated in Figure 3, which compares the voltammogramms of a Pt–PEM electrode, with and without the presence of tin. Moreover, measurements of polarisation curves under quasisteady state conditions (current measured after 10 s at a given potential) confirm the modification of the Pt–PEM electrochemical behaviour towards ethanol electrooxidation by the presence of tin. This appears in Figure 4, giving $i(E)$ curves, which shows a constant shift of the $i(E)$ curve in the presence
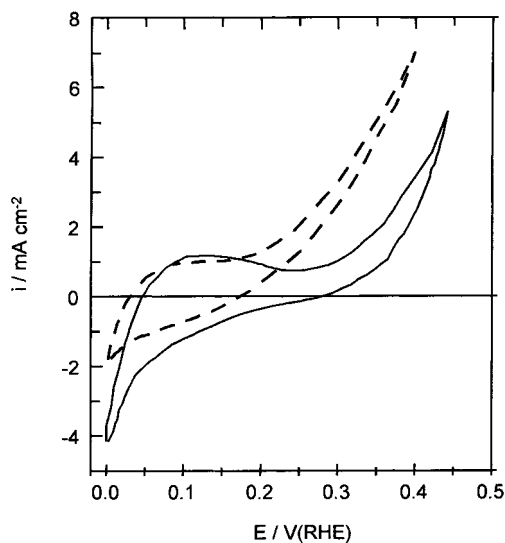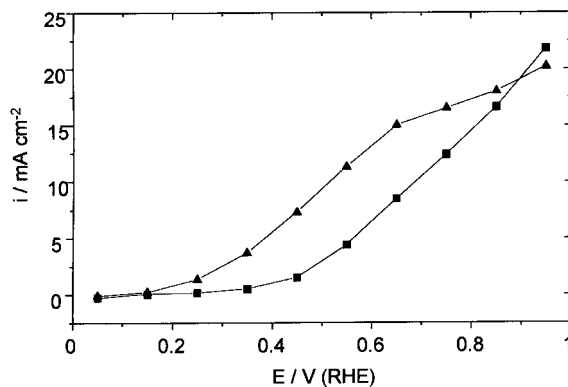

Fig. 4. $i(E)$ curves (recorded under quasisteady state conditions) of a Pt–PEM electrode with (▲) or without (■) added tin.

of tin, in comparison with the $i(E)$ curve recorded on the Pt–PEM electrode. Experimental evidence has been accumulated during the past decade that the oxidation of the CO poisoning species is the key point and that it is necessary to remove CO from the electrode surface at lower potentials [2]. The presence of an oxidised form of tin on the platinum surface allows the beginning of ethanol oxidation to be displaced to lower potentials, probably due to the oxidation of the adsorbed residues formed during its dissociative adsorption by adsorbed OH species present on tin sites. Figure 4 also shows that, for a potential higher than 0.65 V vs RHE, Sn_xO_y surface oxides are formed on the Sn sites; these oxides do not promote the electrooxidation of ethanol. It should be noted that the oxidation of Sn leads to only a slight dissolution of the electrodeposited tin, since the Pt–Sn surface is not in contact with liquid solution (the oxidation reaction takes place in the gas phase). Consequently, there is a decrease in the $i(E)$ curve for a potential greater than 0.65 V vs RHE due to oxidised Sn sites, which are inactive at such potentials.

The promoting effect attributable to the addition of tin to platinum for the electrooxidation of ethanol is particularly significant at low potentials, as clearly seen in Figure 5, which shows the ratio of the current
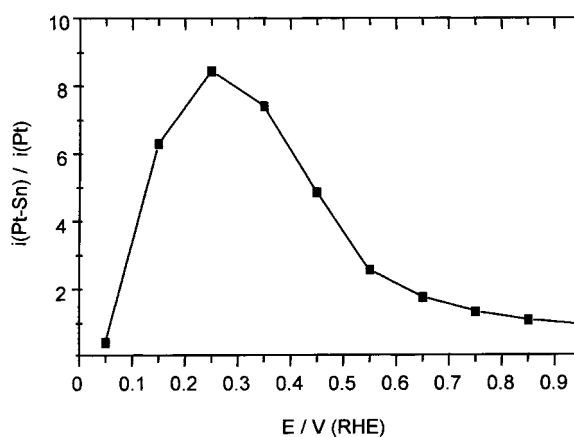

Fig. 3. Voltammograms from 0 to 0.45 V vs RHE of a Pt–PEM electrode with (– – –) or without (——) added tin in the presence of 1.5×10^{-2} M ethanol.

Fig. 5. Ratio of the current densities of ethanol oxidation recorded on a Pt–PEM electrode with or without added tin as a function of the potential (measured vs RHE).

densities, measured under quasisteady state conditions, with and without added tin, as a function of the oxidation potential (data taken from Figure 4). This figure shows that the benefit of tin is maximum for a potential of about 0.25 V vs RHE, at which the current density for ethanol oxidation (measured under steady conditions) is enhanced by a factor of 8. This shift of the oxidation potential is also clearly shown in Figure 6, presenting the Tafel plots obtained with and without added tin to the Pt–PEM electrode, which also demonstrates that there is no significant change in the rate determining step in the oxidation mechanism.

The better performances of the Pt–Sn catalyst in comparison to platinum is the result of weaker electrode poisoning, due to strongly adsorbed residues. It is possible to visualize this electrode poisoning by measuring the current densities of ethanol electrooxidation (at a constant potential of 0.4 V vs RHE) as a function of time, under steady conditions (Figure 7). In Figure 7, for a tin amount of 30 μg cm^{-2}, the current density associated with the electrooxidation of ethanol is greater by a factor of 10 after 20 min in comparison with the same Pt–PEM electrode without added tin.
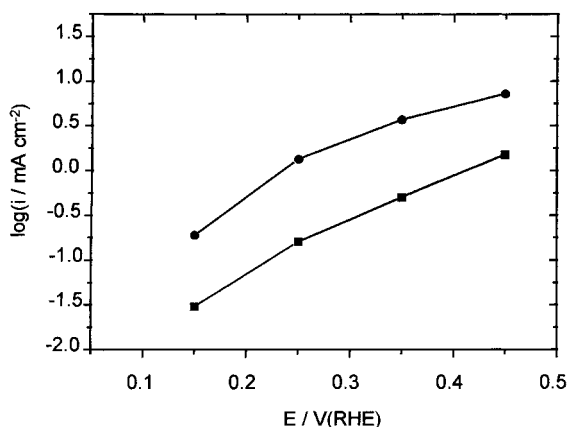

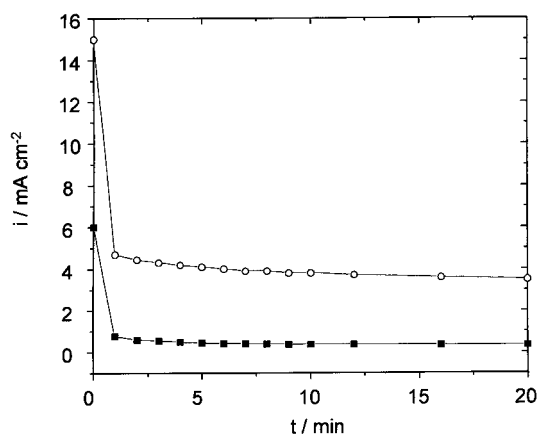*Fig. 6.* Tafel plots for ethanol oxidation on a Pt–PEM electrode with (●) and without (■) added tin.

Moreover, Figure 8, presenting a $(\mathrm{d}i/\mathrm{d}t) = f(t)$ plot (normalised scale) at small time values allows evaluation of the initial poisoning rate for the Pt–PEM electrode, with and without tin, by comparing the two experimental slopes; the greater the slope, the greater the initial poisoning of the electrode surface. It appears that added tin leads to less poisoning, since the experimental slope with added tin is lower by a factor of 1.3, compared to that obtained without added tin, that is, 0.32 and 0.41, respectively.

Recent work demonstrates the ability of Pt–Sn catalysts to shift the oxidation potential of CO [7, 13, 14] to more negative potentials. Whatever the adsorption mechanism of ethanol on platinum (dissociative or not), the ethanol oxidation to CO_2 necessitates the breaking of the C—C bond of the alcohol, leading to CO_{ads} species on the platinum surface, which act more as catalytic poisons than as reactive intermediates [2, 3, 15]. If tin favours the low potential oxidation of CO_{ads}, formed during the adsorption of ethanol, the presence of tin must allow ethanol oxidation at lower potentials, by increasing the reaction rate. The same approach is used to explain the promoting effect of tin in the bimetallic catalyst platinum–tin, which has been demonstrated to enhance, to a small extent, the oxidation of methanol, during which CO_{ads} species are also formed [6, 15, 16].

3.2. Electrooxidation of ethanol on a Pt–Sn–Nafion® electrode: Influence of platinum dispersion

Figure 9 shows the influence of the amount of added tin to a Pt–PEM electrode with a higher roughness factor ($\rho = 620$). The curve obtained has a maximum for a tin content of about 90 μg cm^{-2}. For this tin content, the electrode activity enhancement factor is about 2.

As the active surface area of this electrode is greater by a factor of 2 in comparison with the previous studied electrode (for which $\rho = 312$), the expected tin content required to improve the electrode activity should be twice as great, which is not the case experimentally. In
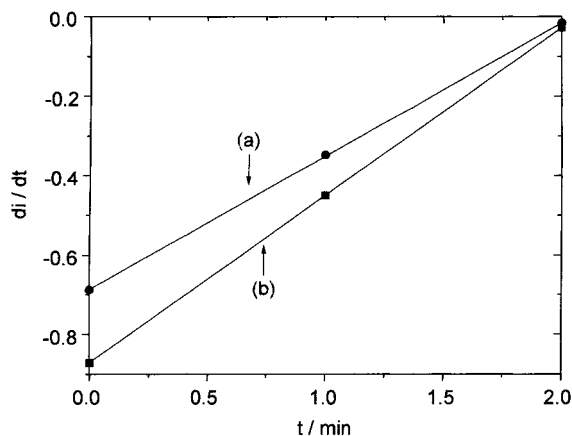

Fig. 7. Ethanol oxidation current densities, measured under quasi-steady state conditions at $E = 0.4$ V vs RHE *as a function of* time, for a Pt–PEM electrode with (○) or without (■) added tin.

Fig. 8. $\mathrm{d}i/\mathrm{d}t = f(t)$ curves (from $t = 0$ to $t = 2$ min) for a Pt–PEM electrode with or without added tin (normalized scale). Slopes: (a) 0.32 for Pt–Sn–Nafion® and (b) 0.41 for Pt–Nafion®.
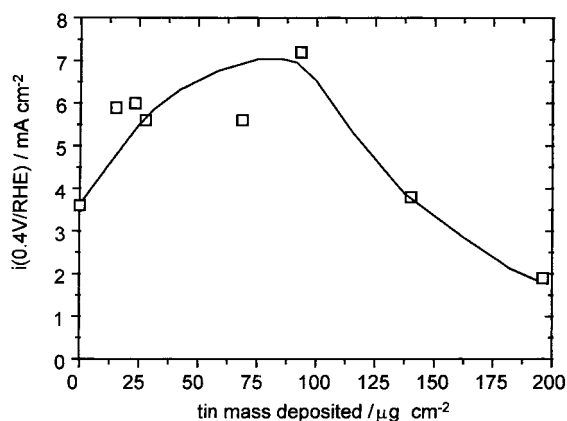
Fig. 9. Influence of the amount of electrochemically deposited tin on the activity of the Pt–Sn–Nafion® electrode (roughness factor, ρ = 620).

fact, the required amount of tin is not proportional to the active surface area of the electrode, probably because a greater number of tin germination sites are formed when the active surface area of the electrode increases. Otherwise, the enhancement of the Pt–PEM electrode activity by added tin is less significant when the active surface area, and therefore the roughness factor of the electrode, increases, as shown in Table 1.

3.3. *Microscopic observation of a Pt–Sn–Nafion® electrode*

To determine the microscopic distribution of tin on the Pt–Sn–Nafion® electrode, we carried out a TEM study of the Pt–Sn–PEM electrode with a tin content of about 20 μg cm^{-2} (corresponding to the best macroscopic composition) coupled with an EDX analysis. The TEM photographs are shown in Figure 10. These suggest that tin is particularly deposited on the surface of the Pt–Sn–Nafion® electrode, leading to large spherical particles about 100 nm in size. The EDX analysis of such particles (Figure 11), with a very small electron beam, distinguishes both the presence of tin and platinum, with an atomic ratio of 20% tin and 80% platinum. These two techniques give the optimum composition of Pt–Sn particles for enhancing the electrooxidation of ethanol.

Moreover, an XRD study of the particle itself was carried out to determine its crystallographic structure. It appears that the Pt–Sn particles are bimetallic, but no alloy was found. This result is in good agreement with previous results obtained by Mac Breen and Mukerjee, using EXAFS, who did not detect Pt–Sn alloy in the

Table 1. Enhancement factor in the catalytic activity for the ethanol electrooxidation at a Pt–PEM electrode modified by added tin

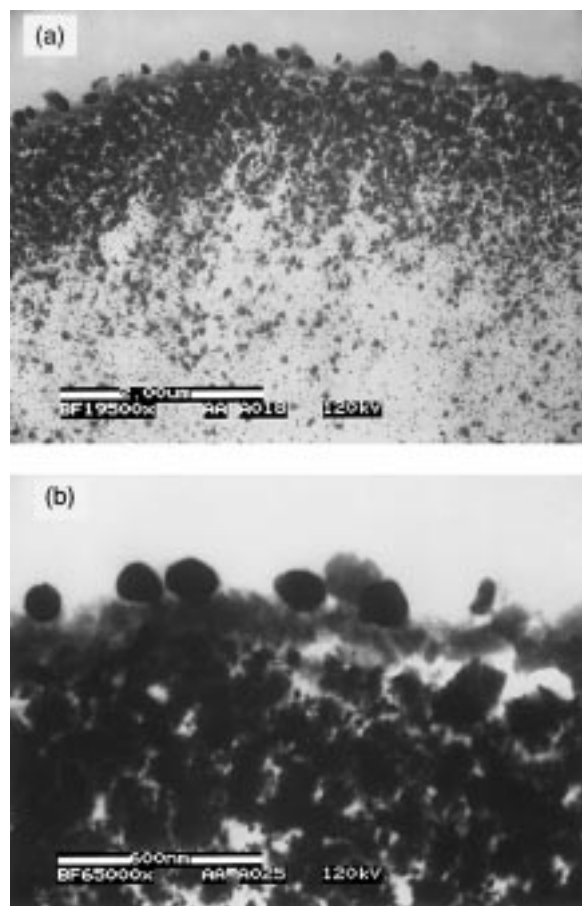| Active surface area /cm^2	$m_{(Sn)opt}$ /μg cm^{-2}	Enhancement factor at 0.4 V vs RHE
156	20	6
310	90	2

Fig. 10. TEM photograph (a) of a Pt–Sn–PEM electrode, (b) showing detail of the large Pt–Sn particles at the electrode surface.

case of tin deposited electrochemically on platinum electrodes in bulk [17]. For the Pt–Sn particles observed, two different sites are present: tin and platinum sites. Tin plays a role in the oxidation step, by providing adsorbed hydroxyls at low potentials, as already noted by Villar and Rabockai [9].

4. Conclusion

This study clearly shows that the presence of tin leads to increased current densities for the electrooxidation of ethanol, by decreasing the poisoning phenomena during ethanol adsorption. A weaker poisoning effect is illustrated as follows:

(i) By the constant shift of the $i(E)$ curve (under steady state conditions) recorded in the presence of tin in comparison with the $i(E)$ curve recorded on the Pt–PEM electrode. At E = 0.25 V vs RHE, the current density of ethanol oxidation is enhanced by a factor of 8 in the presence of tin (Figure 5).

(ii) By the same value of the Tafel plots obtained with and without added tin at the Pt–PEM electrode.

(iii) By the $i(t)$ study, which shows that the current density associated with the electrooxidation of ethanol is 10 times greater after 20 min in comparison with that at the same Pt–PEM electrode
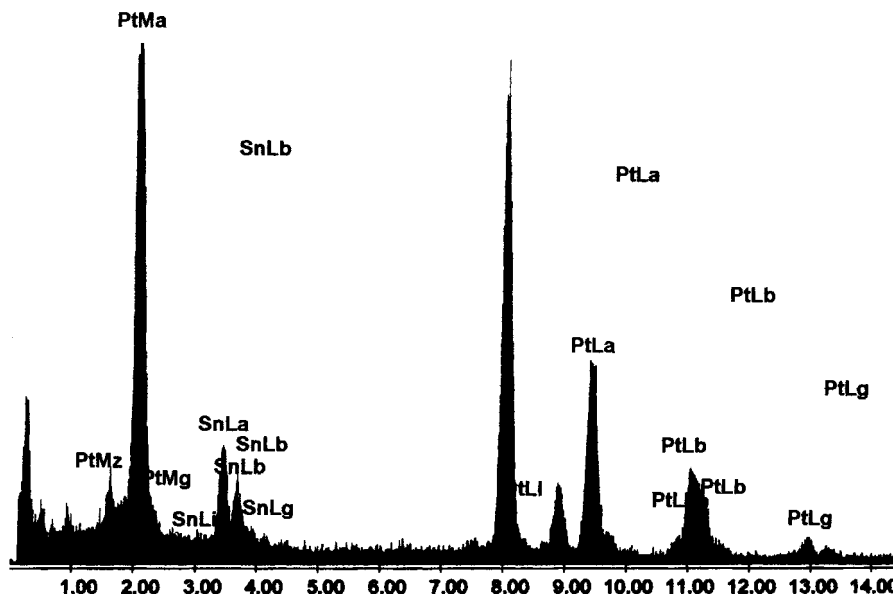
Fig. 11. EDX analysis of the Pt–Sn surface particles.

with no added tin. The different slope of the $(\mathrm{d}i/\mathrm{d}t) = f(t)$ plots shows a lower initial poisoning rate for the Pt–Sn–PEM electrode in comparison with the Pt–PEM electrode.

TEM photographs allowed us to characterize the Pt–Sn–PEM electrode surface morphology (observation of Pt–Sn particles of about 100 nm). An EDX analysis of the Pt–Sn particles gave the composition of the observed bimetallic Pt–Sn particles: thus, the optimum atomic composition of the Pt–Sn particles appears to be 20% Sn/80% Pt for increasing the electrode activity towards the electrooxidation of ethanol.

Acknowledgements

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