

Direct electrooxidation of methanol on highly dispersed platinum-based catalyst electrodes: temperature effect

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The direct electrooxidation of methanol in acid medium was studied on electrodes made of a perfluorinated membrane with small amounts of metal catalysts incorporated by chemical reduction. Platinum is a good electrocatalyst for this reaction, but needs to be modified by other metals in order to obtain oxidation potentials much more compatible with a working anode in a direct methanol fuel cell. Ruthenium and tin appear to give encouraging results, leading to a negative shift of more than 250 mV as compared to the potential obtained with pure platinum. Other parameters were investigated in this work, such as the working temperature, and the manner of introduction of the methanol into the cell. By gaseous supply, it was possible to carry out measurements at higher temperatures than with methanol in solution, and consequently to greatly improve the performance of the catalytic electrode.

1. Introduction

The direct methanol fuel cell (DMFC) allows the direct conversion of the chemical energy of methanol into electrical energy: this procedure avoids the use of a reformer to produce hydrogen, which increases the complexity and the price of the system and decreases the overall yield. However, the direct electrooxidation of methanol is difficult to perform, even with platinum, which appears to be the only acceptable catalyst. Moreover, even in this case, a decrease of the performances of the methanol anode is always observed with time as the consequence of poisoning effects [1–4]. This latter phenomenon is due to the formation of strongly adsorbed species, such as CO, as the result of the dissociative adsorption of methanol [5].

In order to enhance the performances of the platinum electrode, one possibility is to increase the active surface area, by dispersion of the catalyst as small particles on a convenient conducting support [6]. Moreover, this procedure also allows the use of very small amounts of precious metals, typically a few mg cm^{-2} . An important point in improving the performance of practical electrodes is to decrease poisoning. For this purpose, the use of bimetallic catalysts, either platinum-based alloys or adatom modified platinum electrodes, is a good solution [4, 7].

To obtain an efficient dispersion of the catalyst, it is necessary to use a convenient conducting support. Nafion[®] is a typical example of such a support. It is a perfluorinated membrane, which is known to be inert from a chemical point of view and to have good

stability [8]. This kind of membrane was used for several decades [9] as a solid polymer electrolyte (SPE[®]) for hydrogen/oxygen fuel cells. Small platinum particles are highly dispersed on both sides of the membrane, and are the main part of the so-called proton exchange membrane fuel cell (PEMFC).

Recent work has been published concerning the use of metallized Nafion[®] membranes as electrodes for electrocatalytic reactions. Thus, the electrooxidation of methanol was studied at pure platinum [10], or at platinum-based bimetallic [11–13] or trimetallic [14] alloys, deposited on a Nafion[®] membrane. This showed that such electrodes, with a platinum loading generally about 5 mg cm^{-2} , are very active. The use of plurimetallic compounds, with components such as Ru or Sn or Mo, led to a significant decrease of the poisoning effect observed with pure platinum [4, 11–14]. Such a decrease in poisoning was also observed when carbon substrate electrodes were used [15].

The aim of the present work was to investigate the electrocatalytic oxidation of methanol on such platinum-based membranes with a low amount of platinum, typically about 1 mg cm^{-2} . These electrodes were tested with methanol supplied both from liquid and gas phases. This latter manner of introducing methanol [10, 16] allows the use of operating temperatures higher than the boiling point of methanol.

2. Experimental details

The membrane used was Nafion 117[®] from Dupont De Nemours, the thickness being $178 \mu\text{m}$. The dispersion of platinum or bimetallic catalysts was performed

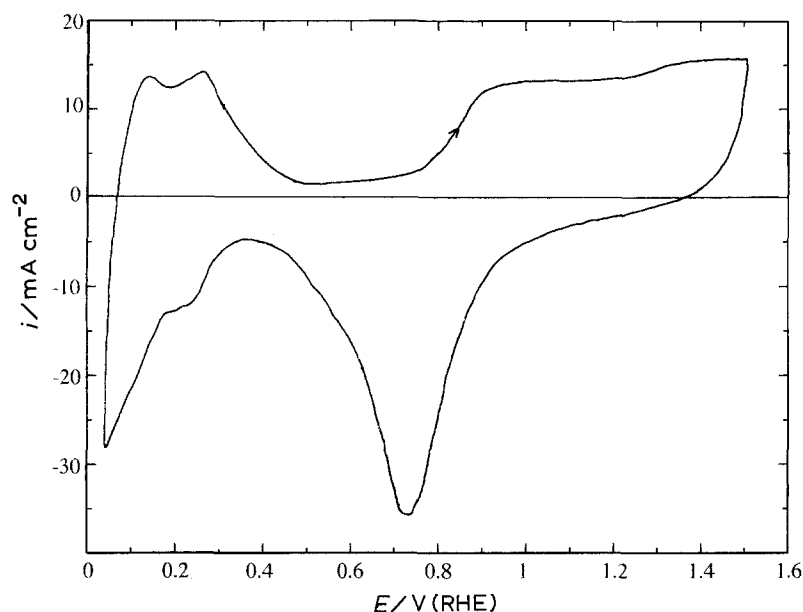


Fig. 1. Voltammogram of a Nafion[®] membrane covered with platinum particles in 1 M HClO₄; 25 °C, 50 mV s⁻¹, 1 mg cm⁻² of platinum.

according to the method initially proposed by Takenaka *et al.* [17]. With this latter method, the platinum particles were obtained by chemical reduction of a metallic salt. The nature, and especially the charge, of the metal precursor ion is important. Takenaka *et al.* used an anionic salt (chloroplatinate), while Millet *et al.* [18] proposed the use of cationic metallic salts. With these latter salts, the metallic ions are much more easily impregnated onto, and even inside, the membrane. In this work, the metallic platinum particles were deposited from cationic salts. The chemical reduction was carried out through the membrane by means of a reducing agent in contact with the opposite side. For the bimetallic catalyst modified membranes, the platinum particles were deposited by the same way, but the second metal was deposited from a cationic metallic salt reduced on the same side of the membrane by the reducing agent. The platinum loading was determined by absorption spectroscopy after dissolving the deposit in *aqua regia*.

For the electrocatalytic measurements, the solutions were prepared from Merck reactants (p.a. grade for methanol and suprapure grade for perchloric acid). All experiments were done under a nitrogen atmosphere, and the flow of nitrogen containing gaseous methanol was measured with a bubble flowmeter. A reversible hydrogen electrode (RHE) was used as reference electrode and a carbon felt as counter electrode. All the cyclic voltammetric measurements were carried out with standard equipment (a PSG77 Wenking potentiostat, a PAR 175 Universal programmer and a 17100 Linseis XY recorder). All the current densities noted in the text are given in mA cm⁻².

3. Results

3.1. Pure platinum Nafion[®] electrode

Figure 1 shows the voltammogram, in the supporting electrolyte alone (1 M HClO₄), of the Nafion[®] electrode

covered with a small amount of platinum (about 1 mg cm⁻²). The usual shape of the voltammogram of a platinum electrode is displayed in Fig. 1. Thus, from the hydrogen adsorption region, it is possible to estimate the real active surface area of such a platinum electrode. An approximate value of 380 cm² for a geometric surface area of 0.95 cm² was measured, which corresponds to a rugosity factor of about 400. This shows that the platinum particles are well dispersed on the Nafion[®] membrane.

With methanol in solution, i.e. 0.1 M methanol in 1 M HClO₄, the same electrode shows a good electrocatalytic activity for methanol oxidation, which begins at around 0.4 V/RHE with a maximum current density of 46 mA cm⁻² at 0.89 V/RHE (Fig. 2). This voltammogram is recorded at a sweep rate of 10 mV s⁻¹.

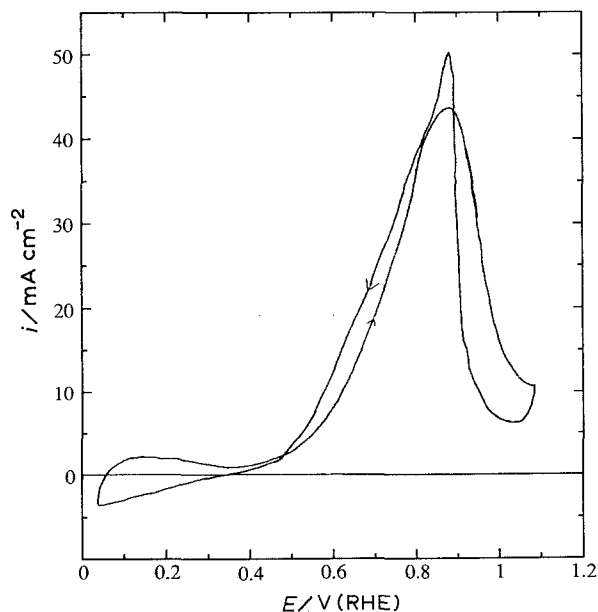


Fig. 2. Voltammogram of a Nafion[®] membrane covered with platinum particles in 1 M HClO₄ + 0.1 M methanol; 25 °C, 10 mV s⁻¹, 1 mg cm⁻² of platinum.

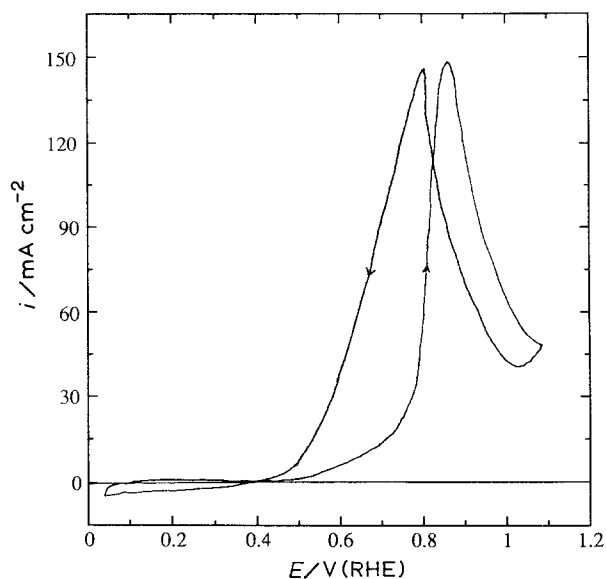


Fig. 3. Voltammogram of a Nafion® membrane covered with platinum particles in 1 M HClO₄ under gaseous methanol supply; 25°C, 10 mV s⁻¹, 1 mg cm⁻² of platinum.

It is possible to improve the oxidation rate of methanol when the cell is fed with gaseous methanol in a nitrogen flow, even at room temperature. Figure 3 shows a voltammogram of the electrooxidation of gaseous methanol at 25°C. The gaseous methanol was added by bubbling nitrogen in a methanol solution at a flow rate of 10 cm³ min⁻¹. The maximum current density obtained is around 150 mA cm⁻², which represents three times the value obtained with methanol dissolved in solution. However, the poisoning effect observed, visible on the voltammogram through the potential shift between the positive and the negative sweeps, is more significant under gaseous supply conditions (compare Figs 2 and 3).

It is easy to obtain larger current densities with increase in temperature. For example, Fig. 4 represents a voltammogram for the oxidation of gaseous methanol at 45°C. With an electrode having 1.1 mg cm⁻² of platinum, corresponding to a measured rugosity factor of about 400, it is possible to reach current densities of 250 mA cm⁻². All the other experimental conditions are the same as those described in Fig. 3. Such an increase in the activity is accompanied by a significant shift of the oxidation potential in the negative direction. This is particularly evident in Fig. 5, where the gaseous methanol is oxidized at 65°C. This shows that, under these experimental conditions (methanol gaseous supply), the poisoning effect observed with pure platinum is less significant at higher temperatures, compared to that observed when methanol is used in solution.

At 0.5 V/RHE, the current densities obtained for different temperatures were low as shown in Table 1. It is possible to estimate the activation energy and in the case of pure platinum deposits, a value of 35 kJ mol⁻¹ is obtained. This value is a little higher than those (between 20 and 33 kJ mol⁻¹) determined by Aramata *et al.* [11] with methanol in solution. It should also be noted that the electrodes studied by

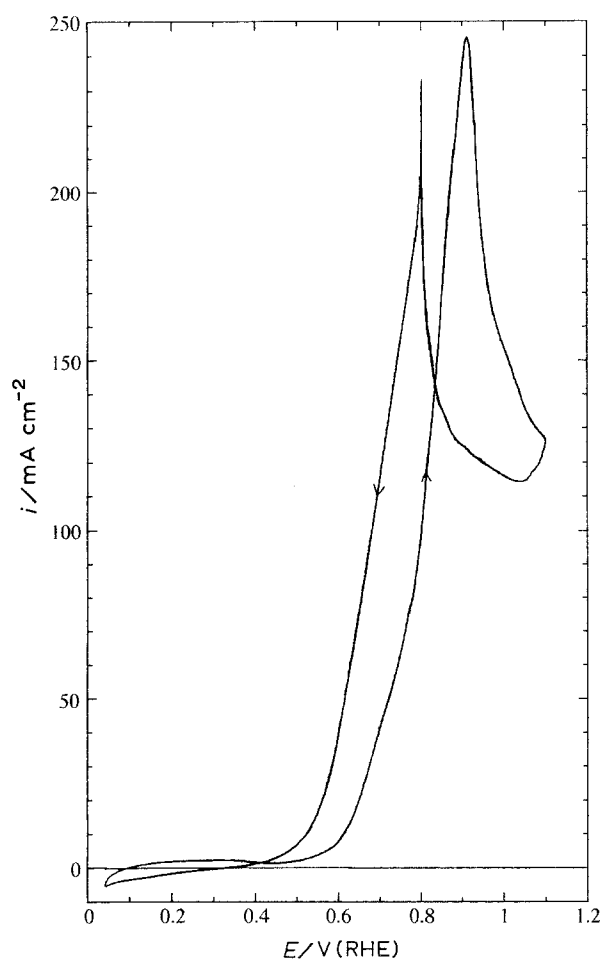


Fig. 4. Voltammogram of a Nafion® membrane covered with platinum particles in 0.5 M H₂SO₄ under gaseous methanol supply; 45°C, 10 mV s⁻¹, 1.1 mg cm⁻² of platinum.

Aramata *et al.* had a platinum loading around 5 times greater than the present ones.

It is thus clearly shown that it is possible to obtain platinum electrodes with a large active area by dispersion of small platinum particles into the surface of a Nafion® membrane. The use of gaseous methanol, even at low temperatures, allows current densities much higher than those obtained with methanol in solution. However, with pure platinum, the problem of poisoning remains critical, even if it is weaker at higher temperatures and the potentials, at which methanol is oxidized, remain too high, and are thus not convenient for fuel cell applications. The onset of the oxidation is at around 0.5 V/RHE, and it needs to be shifted 200 to 300 mV negatively to be useful in a direct methanol fuel cell. Such potential shifts cannot be obtained with pure platinum, even with highly dispersed catalysts. The only way is to use pluri-metallic platinum based catalysts.

3.2. Modified platinum-based Nafion® membrane

Other metallic components can be added to platinum in order to stabilize the metallic oxidation state at lower potentials; such electrodes are thought to favour (at lower potentials) the oxidation of the poisoning species formed from methanol chemisorption, or to prevent the formation of such poisons.

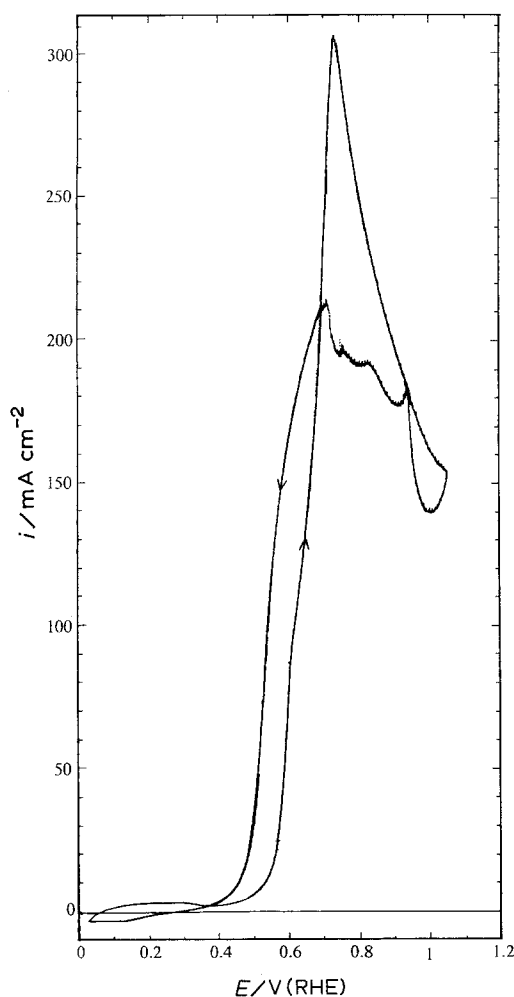


Fig. 5. Voltammogram of a Nafion® membrane covered with platinum particles in 0.5 M H₂SO₄ under gaseous methanol supply; 65°C, 10 mV s⁻¹, 1.1 mg cm⁻² of platinum.

Several components (ruthenium, tin, molybdenum . . .) have been proposed in the literature as activity modifiers of platinum electrocatalysts dispersed either on carbon substrates [15], or on ionomeric membranes [11–14].

In this work, preliminary results with platinum-based bimetallic electrodes containing tin or ruthenium are presented. The Nafion® composite electrodes are made according to the same procedure as that described for pure platinum but with a solution containing a mixture of the two salts. The nature and the concentration of the metallic salts, and the reduction process, are critical.

3.2.1. Platinum–ruthenium deposited on a Nafion® membrane. Ruthenium is known to be a good promoter of the electrooxidation of methanol on platinum. With codeposits of Pt and Ru on a Nafion® membrane, in the presence of methanol under gaseous supply, the electroactivity is improved in comparison with that of pure platinum, as can be seen in Fig. 6. By

Table 1.

Temperature/°C	25	45	65	75
$i/\text{mA cm}^{-2}$	≈ 1	1.4	2.8	4.5

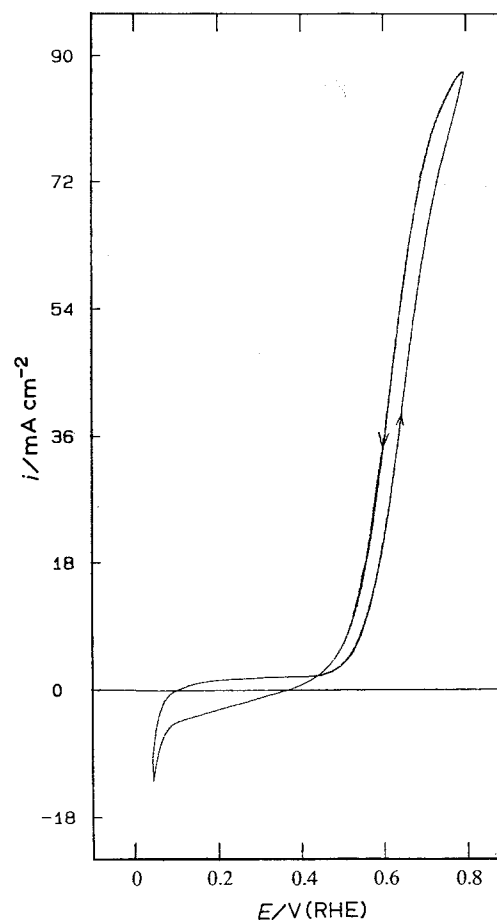


Fig. 6. Voltammogram of a Nafion® membrane covered with platinum and ruthenium particles in 0.5 M H₂SO₄ under gaseous methanol supply; 25°C, 10 mV s⁻¹, 1.5 mg cm⁻² of platinum.

increasing the operating temperature, the current densities obtained at 0.5 V/RHE, with the Pt–Ru deposit electrodes, increases greatly as seen in the Table 2.

Comparison of the values of the activation energy obtained with Pt–Ru deposits (65 kJ mol⁻¹) with that for pure platinum (35 kJ mol⁻¹) demonstrates the interest in increasing the operating temperature with the bimetallic Pt–Ru electrodes.

3.2.2. Platinum–tin deposited on a Nafion® membrane. Among the metals able to modify a platinum electrode for the electrocatalytic oxidation of methanol, tin is often proposed, mainly when it is deposited as adatoms. The nature of the tin salt used is critical; with tin sulphate, the platinum–tin electrodes obtained by chemical reduction are much less active than pure platinum electrodes, but with a chloride salt, it is possible to reach activities better than those with a pure platinum deposit. Figure 7 shows a voltammogram of such an electrode containing 2.1 mg cm⁻² of platinum modified by tin. As can be seen, the current densities reach values of about 105 mA cm⁻² at 0.75 V/RHE and at 25°C. A potential shift is also observed leading to oxidation of methanol at more negative

Table 2.

Temperature/°C	25	45	65	75
$i/\text{mA cm}^{-2}$	3.7	13.6	106	156

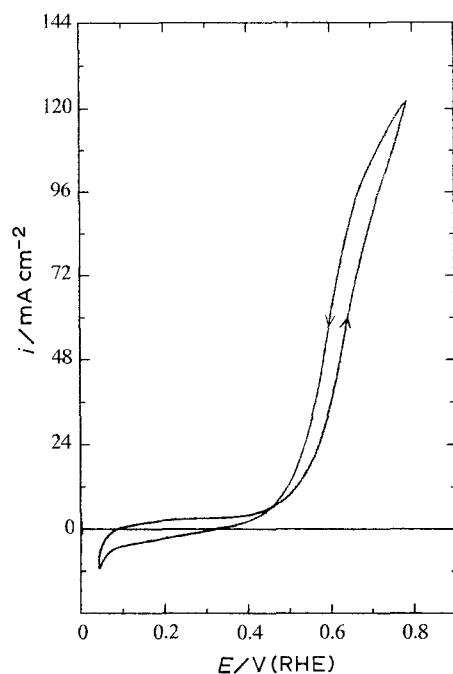


Fig. 7. Voltammogram of a Nafion[®] membrane covered with platinum and tin particles in 0.5 M H₂SO₄ under gaseous methanol supply; 25 °C, 10 mV s⁻¹, 2.1 mg cm⁻² of platinum.

potentials than those with a pure platinum electrode. With an increase of temperature, the activities observed, at 0.5 V/RHE, are greatly improved as seen in Table 3. In this case, the apparent activation energy is 46 kJ mol⁻¹.

Table 3.

Temperature/°C	25	45	65	75
$i/\text{mA cm}^{-2}$	8.7	17.6	82	100

From the results described in this section, it is clear that ruthenium presents a good promotion effect for the electrooxidation of methanol under gaseous conditions. Figure 8 shows the Tafel plots of the oxidation curves at two different temperatures for the pure platinum deposit and different modified platinum deposits. The potential shift observed in the presence of ruthenium is clearly seen at 25 °C (Fig. 8a), whereas the modification by tin shifts the curves further in the negative direction. At 75 °C (Fig. 8b), the shift observed is enhanced, and reaches more than 200 mV in comparison to that obtained with pure platinum.

An interesting comment may be given on the values of activation energy determined in this work. The following table summarizes the difference values obtained above:

Table 4.

Electrode:	Pt	Pt-Sn	Pt-Ru
$\Delta H/\text{kJ mol}^{-1}$	35	46	65

It is interesting to compare the activation energy values to those obtained by Aramata *et al.* [11], between 20 and 33 kJ mol⁻¹ for different types of

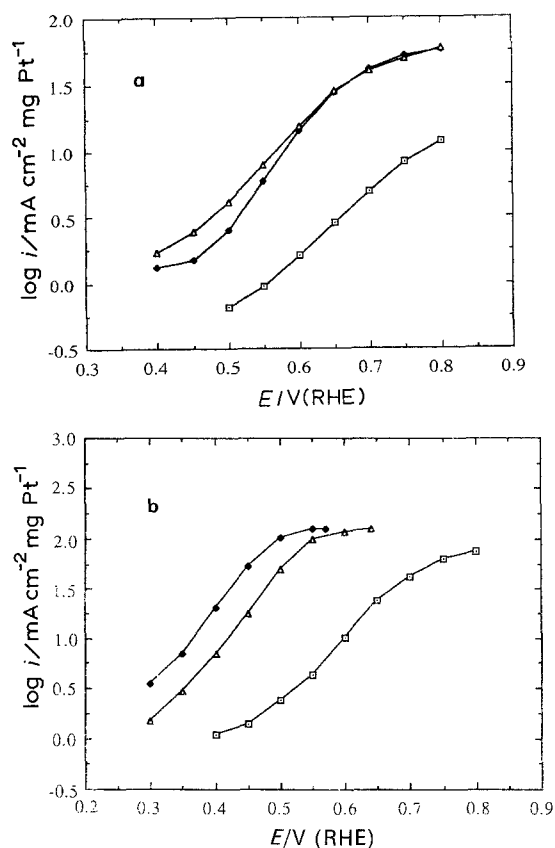


Fig. 8. Plots of the logarithm of the current densities versus the potential for different deposits. The data are taken from curves recorded under the same conditions as Figs 3-7. (a) 25 °C; (b) 75 °C. (□) Pt; (◆) Pt-Ru; (△) Pt-Sn.

metallized Nafion[®] membranes (Pt and Ru or Sn or Ir modified Pt). Thus it appears that, under gaseous methanol supply conditions, the two bimetallic electrodes considered in this work lead to values of activation energy much higher than those found when methanol is dissolved in aqueous solution. For Pt-Ru, the value of 65 kJ mol⁻¹ found suggests that the adsorption step is rate determining, conversely to pure platinum for which the diffusion process determines the reaction rate.

In conclusion, these preliminary results show that the use of methanol under gaseous supply conditions allows larger current densities in comparison with that obtained under liquid supply conditions. Decrease of the poisoning effect is possible by using modified electrodes with platinum deposited on a Nafion[®] membrane. Such preliminary results are promising for the direct oxidation of methanol and plurimetallic deposits on an ionic conducting membrane may be a good solution for practical electrodes working in acid medium.

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