Journal of Applied Electrochemistry **31**: 379–386, 2001.
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Investigation of ternary catalysts for methanol electrooxidation

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Received 11 July 2000; accepted in revised form 12 December 2000

Key words: direct methanol fuel cell, electrocatalysis, electronic conducting polymer, methanol electrooxidation, polyaniline, Pt–Ru–Mo catalyst, ternary catalyst

Abstract

The electrochemical oxidation of methanol was investigated on Pt–Ru–X ternary metallic catalysts (with X = Au, Co, Cu, Fe, Mo, Ni, Sn or W). The catalysts were prepared by electrochemical deposition and dispersed in a conductive three-dimensional matrix, an electronic conducting polymer, polyaniline (PAni). A comparative study of the behaviour of several ternary catalysts towards the electro-oxidation of methanol shows that PAni/Pt–Ru–Mo is the most efficient anode at potentials up to 500 mV vs RHE. This latter ternary electrocatalyst leads to current densities up to 10 times higher than those measured with PAni/Pt–Ru in this potential range. Moreover, the catalyst appears to be stable for potentials lower than 550 mV vs RHE. According to EDX analysis, the good behaviour of the Pt–Ru–Mo ternary catalyst seems to result from the presence of a small amount of the third metal, at an atomic ratio close to 5%. This set of encouraging results has also been confirmed by preliminary measurements in a single cell direct methanol fuel cell (DMFC) containing a home made PAni/Pt–Ru–Mo anode. The ternary catalyst leads to higher power densities than the PAni/Pt–Ru binary catalyst under the same experimental conditions.

1. Introduction

The development of the direct methanol fuel cell (DMFC) has been the target of many research efforts for more than 30 years [1, 2]. The DMFC, based on a proton exchange membrane fuel cell (PEMFC) technology, is a promising candidate for several applications, mainly electric vehicle [3]. This is because methanol is a liquid fuel which can be easily stored, handled and produced from oil, natural gas, coal or biomass [4–7]. Thus, methanol should be widely available and cheap. Moreover, the DMFC can run at low temperatures (around 100 °C) and does not require fuel processing.

Despite all efforts devoted to the DMFC development, there still remain problems to be overcomed in terms of efficiency and power density. The thermodynamic reversible cell potential (1.21 V) of a methanol/oxygen fuel cell is close to that of a hydrogen/oxygen fuel cell (1.23 V). But under operating conditions, the methanol/oxygen cell output voltage is much lower, about 0.5 to 0.6 V, as a result of two main problems. The first is the permeation of methanol through the membrane [8–10], which causes a mixed potential at the oxygen cathode, thus decreasing its potential. The second is the relatively slow kinetics of the methanol oxidation reaction at the anode, which leads to high overpotentials.

The electrooxidation of methanol bas been studied for more than 30 years and all efficient catalysts have been based on platinum. This noble metal is known to activate the dissociative adsorption of methanol at an appreciable rate. The main problem is that methanol oxidation at a platinum electrode is a self poisoning reaction, since strongly adsorbed CO (CO_{ADS}) are produced by chemisorption of methanol [11–14]. This leads to the blocking of the catalyst surface causing a significant anodic overpotential and, therefore, a lower cell output voltage and smaller power densities of the DMFC.

Since the mid-1970s, to promote methanol electrooxidation at platinum, modification of the catalyst surface has been made by the addition of a second metal to platinum [15–27].

The Pt–Ru binary metallic catalyst is commonly accepted as the best electrocatalyst for methanol oxidation. Ru is believed to provide for oxygenated species at low potentials in the vicinity of Pt sites, creating additional active sites for CO_{ADS} oxidation.

The addition of other elements to platinum, such as W, Sn, Mo etc., has also been intensively studied. Many authors have reported improved catalytic performances with these binary catalysts for methanol oxidation. However, controversy exists concerning the real improvement of the methanol electrooxidation kinetics and, until now, Pt–Ru remains the best candidate for the realization of a DMFC anode. As an example, when combined to Pt under specific synthesis conditions, tin has been shown to have a beneficial effect on CO oxidation, leading to a negative shift of about 400 mV in the oxidation potential compared to pure platinum [19]. But the same effect was not observed for methanol oxidation and some doubt still remains concerning the real improvement of the anode kinetics due to the addition of tin to platinum.

From these different results, it appears that the best catalyst for methanol electrooxidation should be multimetallic, by combining synergistically the properties of different elements. The aim of this work is, therefore, an experimental investigation of Pt–Ru–X electrocatalysts to improve the behaviour of the Pt–Ru binary catalyst by the incorporation of a third metal. The realization of the ternary catalysts was entirely controlled by electrochemistry: the electrodeposition of the metals was carried out on a gold electrode substrate covered with an electronic conducting polymer, polyaniline (PAni). PAni is easy to prepare by oxidizing aniline during several voltammetric cycles, and its electrodeposition is highly reproducible. PAni is generally known to be a fibrous material and its high roughness allows high dipersion of the catalysts [28–33]. Moreover, in previous studies, infrared reflectance spectroscopy has shown that platinum catalysts dispersed in PAni leads to lower electrode poisoning than bulk platinum [34–37].

2. Experimental details

2.1. *Electrode fabrication*

The process of electrode fabrication was electrochemically controlled with a classical three-electrode EGG setup (model 362) coupled to an X–Y recorder (Goerz, Servogor 790). Although all potentials are given with respect to the reversible hydrogen electrode, a mercury–mercurous sulfate electrode was used as reference electrode. The counter electrode was a graphite sheet. The stationary working electrode was a 1 cm^2 gold sheet.

All solutions were prepared with ultrapure water (milliQ Millipore) and suprapure acids (Merck, suprapure grade). They were outgassed before use with N_2 (Air Liquide, U grade) for 30 min. All electrochemical experiments were conducted at room temperature.

Polyaniline (PAni) was electrodeposited on the stationary gold electrode from an aqueous solution containing 0.1 M freshly distilled aniline (Merck 'zur synthesis') in 0.5 M H_2SO_4. The polymer film was deposited by cyclic voltammetry at a sweep rate of 50 mV s^{-1}. The initial potential was fixed at 0 V. The first sweep was run until + 1.100 V to initiate the aniline oxidation, while the following cycles were stopped at an upper potential limit of + 1.000 V. The polymerization process was terminated at the initial potential when the first oxidation peak reached 7 mA cm^{-2}; this value was previously determined to correspond to a film thickness of 0.5 μm for similar experiments [34–37]. The resulting film was stabilized (doping/undoping processes) in an aqueous solution of 0.5 M H_2SO_4 by cycling at 50 mV s^{-1} between 0 V and + 0.650 V over a few cycles.

The metals were then dispersed into the polymer matrix by the electroreduction of the corresponding metal salts at fixed potential (+ 0.100 V). The deposition process was carried out in an aqueous solution containing 0.5 M H_2SO_4 and the following metallic salts: 2×10^{-4} M K_2PtCl_6 (Alfa), 1.5×10^{-4} M K_2RuCl_5 (Alfa) and 4×10^{-5} M of the third metallic salt ($MoCl_5$, $CoSO_4$, $CuSO_4$, $NiSO_4$, $FeSO_4$, $SnCl_4$, WCl_6, $HAuCl_4$). We observed that, in most experiments, the successive electrodeposition of the different metals was not possible: the deposition of ruthenium on platinum modified electrodes leads to a partial coverage of the platinum surface, therefore decreasing the available surface for methanol adsorption. We also observed that the addition of the other metals to a platinum–ruthenium modified electrode was difficult to control because of the small current densities measured. It was, therefore, decided to perform the codeposition of the metals, from an aqueous solution containing the three metal salts. The composition of the several anodes then obtained was controlled by EDX analysis. The amount of deposited metals was controlled by chronocoulometry. We assumed that the amount of platinum deposited under these conditions is 0.1 mg for a cathodic charge of 0.2 °C [34–37].

Several metals have been investigated in this study. To allow a better comparison between the different electrodes concerning their catalytic activity towards methanol oxidation, the same cathodic charge was used for all electrode combinations. The deposition process was performed during five successive steps of 40 mC in order to optimize the particles dispersion, as observed previously [34–37]. After each step, the electrode was placed in an aqueous solution of 0.1 M perchloric acid and submitted to three voltammetric cycles between 0 V and + 0.350 V at 5 mV s^{-1}. This step has been previously demonstrated to be necessary to stabilize the electrode [36, 37].

Finally, the resulting electrode was tested towards methanol oxidation. All tests were carried out in an aqueous solution containing 0.1 M perchloric acid and 1 M methanol. Both voltammetric and potentiostatic measurements were realized. The voltammetric measurements were performed between 0 and + 1.000 V at 5 mV s^{-1}. Concerning the potentiostatic measurements, the steps were controlled by a computer driven device. A simple potential program for potentiostatic steps has been applied, consisting in succesive steps (400, 450, 500, 550 mV vs RHE, etc.) of 30 min long. The resulting current was then recorded as a function of time.

2.2. *EDX and TEM sample preparation*

To determine the anode composition and to observe their structure, we performed EDX analysis and TEM photographs on several electrode catalysts before the tests concerning methanol oxidation. To prepare the samples, before analysis, the electrode catalysts were dissolved in ethanol with an ultrasonic stirring bath. Part of the suspension was then deposited on a copper grid and the ethanol was evaporated before any measurement.

The measurements were performed with a Philips CM 120 microscope/EDX analyser, equipped with a La B6 filament.

The TEM photographs (Figure 1) clearly show metallic particles (black aggregates) dispersed into the conducting polymer matrix (gray fibres). The metallic aggregates generally have a diameter of about 50 nm and are composed of small metallic particles of 4 nm size.

2.3. *Electrochemical measurements*

The cyclic voltammograms were recorded with the same electronic set-up used for the electrode fabrication (see Section 2.1).

2.4. *Fuel cell tests*

The cathode was provided by E-TEK (2 mg cm^{-2} platinum, 30% Teflon, 0.8 mg cm^{-2} Nafion®). The anode was home-made: an E-TEK carbon cloth covered with a diffusion layer (4 mg cm^{-2} carbon, 40% Teflon) on which were successively deposited a layer of PAni and the trimetallic catalysts (2 mg cm^{-2}). The manufacturing conditions of these anodes were similar to those previously reported for small electrodes. The solid electrolyte was a Nafion® 117 membrane (DuPont) which was treated before use: the membrane was first placed in a boiling aqueous solution containing 3% H_2O_2 for 1 h. After an abundant rinsing with ultrapure water, the membrane was placed for 1 h in a boiling aqueous solution containing 1 M H_2SO_4. The membrane was finally rinsed with ultrapure water and was ready for use. The membrane–electrode assembly (MEA) was then realized by pressing the three elements at 130 °C, with a pressure of 14.2×10^3 kg cm^{-2}, for 90 s.

The final available geometric area of the fuel cell electrode was 5 cm^2.

The experiments were performed at a fuel cell temperature of 110 °C; the DMFC was fed with a 2 M methanol aqueous solution at a temperature of 95 °C, with a flow rate of 2 ml min^{-1}, and a pressure of 1.7 bar. The cathode was fed with oxygen at 95 °C, with a flow rate of 1 l min^{-1}, and at a pressure of 2 bar.

3. Results and discussion

The first step of this study consisted in the selection of the third metal. Many aspects have to be considered to select the best Pt–Ru–X combinations for methanol electrooxidation. The resulting material has to be more

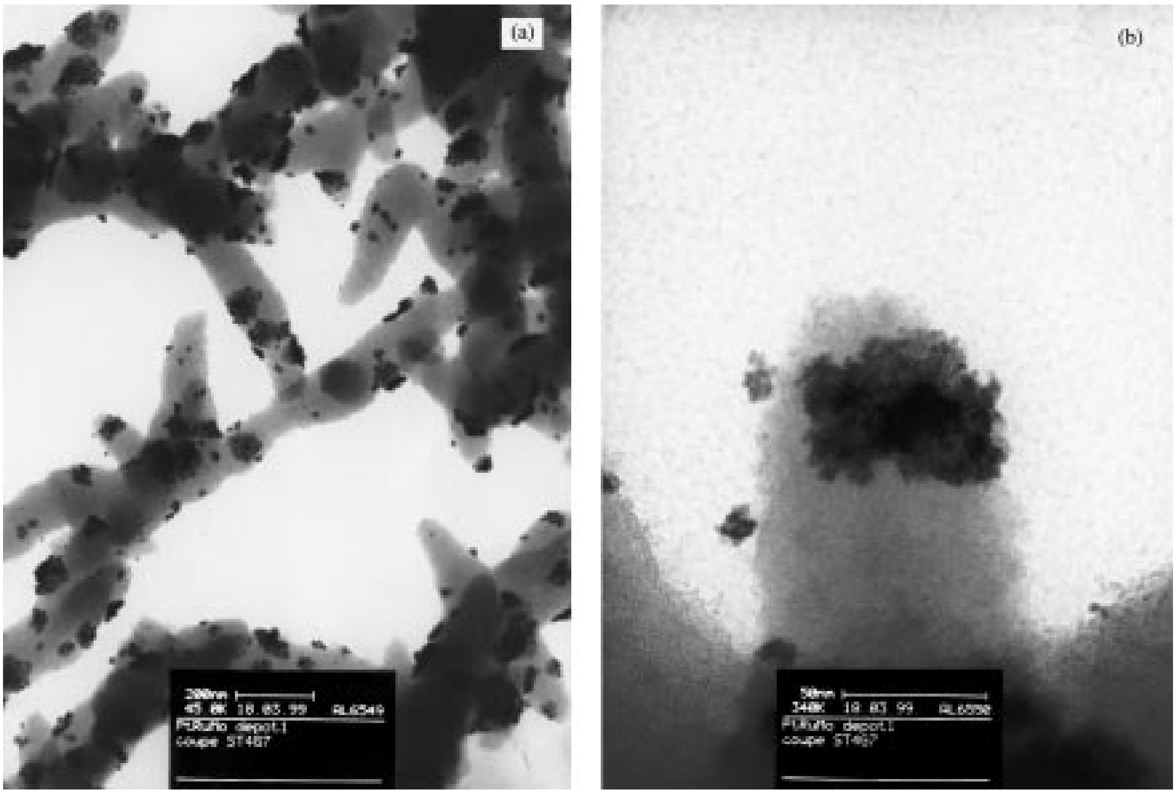

Fig. 1. TEM photographs of a PAni/Pt–Ru–Mo electrode. Scale: (a) 200 nm and (b) 50 nm.

efficient for CO oxidation than Pt–Ru. Since ruthenium and the third metal are believed to provide for oxygenated species at low potentials, mainly through –OH groups, the third metal has to be able to split the water molecule. Moreover, the catalyst needs to be stable in a strong acidic medium, which is necessary for the DMFC operation. With these assumptions, the choice of the third metal was guided by data available in the literature. From a theoretical point of view, Anderson et al. [38–40] performed quantum chemistry calculations to identify elements that would be able, when placed as substitutional atoms in a Pt(1 1 1) surface, to activate the water molecule leading to the formation of OH_{ADS}. The results, reported in terms of water binding energies and activation energies for OH bond scission, suggested some elements that would be convenient for methanol oxidation, when combined with platinum. Many experimental works are also available, mainly on methanol oxidation at binary electrocatalysts [15–17].

A screening was performed to identify at least one element that would, when combined with Pt–Ru, exhibit an enhancement in methanol oxidation rate at low potentials.

It can be seen in Figure 2 that the nine investigated anodes show a different behaviour towards methanol oxidation. From this Figure, a histogram based representation was built to allow a better comparison of the results (Figure 3). This representation was limited to low potentials, which are of best interest for fuel cell application.

At low potentials, the Pt–Ru–Mo ternary catalyst shows the highest current densities compared to other ternary electrocatalysts. This catalyst exhibits a current density 10 times greater than Pt–Ru at a potential of 400 mV vs RHE after 5 min of methanol oxidation, as can be seen in Table 1. At 450 mV vs RHE, Pt–Ru–Mo still shows a current density more than five times higher than Pt–Ru and at 500 mV vs RHE twice as high. Moreover, the electrocatalytic activity of the ternary catalyst Pt–Ru–Mo is very reproducible (at ±5%).

In this potential range, ternary catalysts such as Pt–Ru–Co, Pt–Ru–Ni or Pt–Ru–Fe, also exhibit good

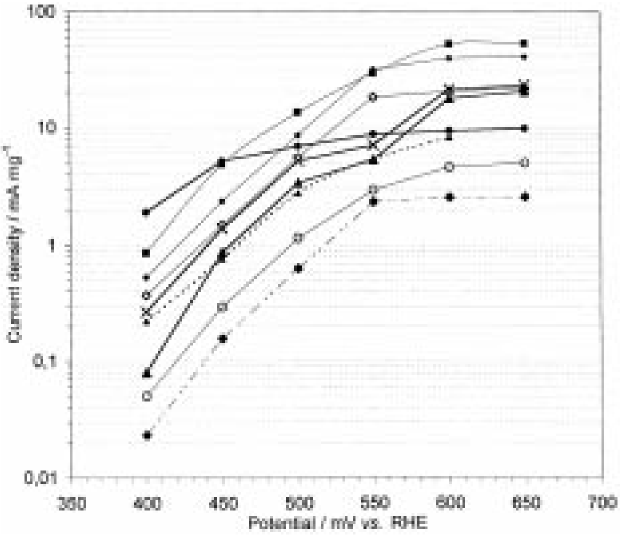

Fig. 2. Polarization curves for the oxidation of 1 M methanol in 0.1 M $HClO_4$ on different electrodes Pt–Ru–X recorded after 5 min of potential hold. Key: (- - ▲- -) PAni/Pt–Ru, (●) PAni/Pt–Ru–Mo, (■) PAni/Pt–Ru–Co, (◆) PAni/Pt–Ru–W, (◇) PAni/Pt–Ru–Fe, (×) PAni/Pt–Ru–Ni, (▲) PAni/Pt–Ru–Cu, (○) PAni/Pt–Ru–Sn, (◆) PAni/Pt–Ru–Au.

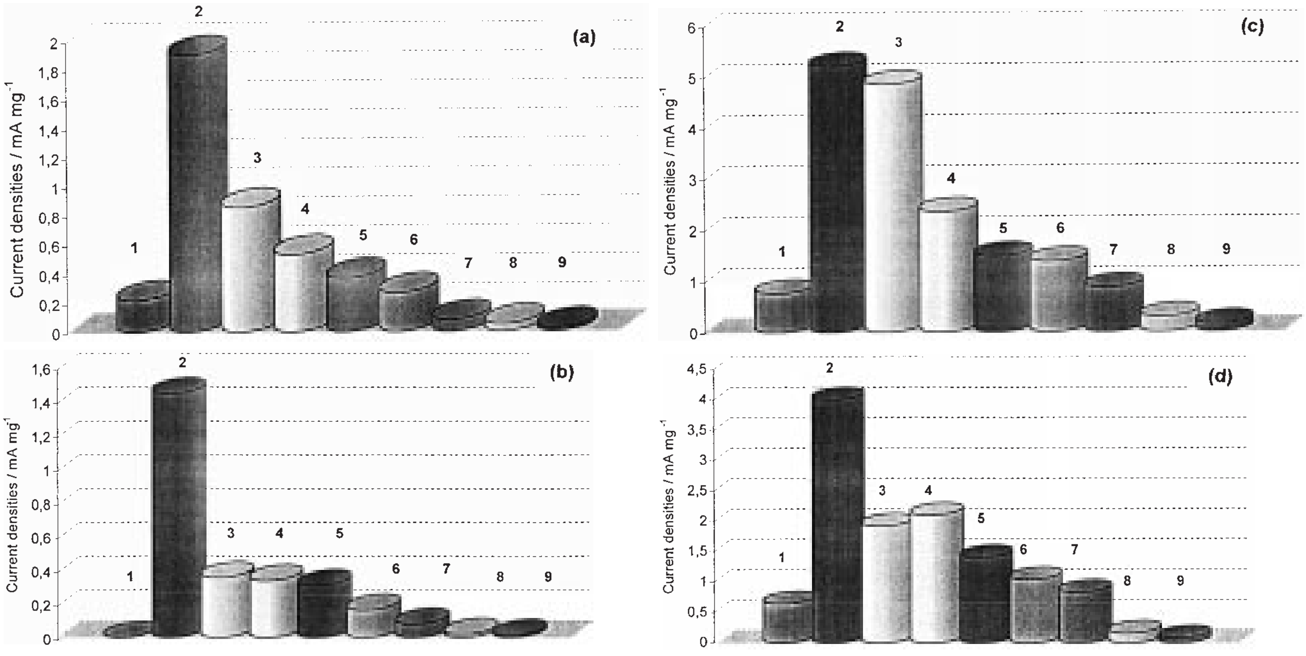

Fig. 3. Current densities for the oxidation of 1 M methanol in 0.1 M $HClO_4$ on several electrodes recorded after 5 min and 30 min of potential hold, respectively. At 400 mV vs RHE: (a) after 5 min and (b) after 30 min. At 450 mv vs RHE: (c) after 5 min and (d) after 30 min. (1) PAni/Pt–Ru, (2) PAni/Pt–Ru–Mo, (3) PAni/Pt–Ru–Co, (4) PAni/Pt–Ru–W, (5) PAni/Pt–Ru–Fe, (6) PAni/Pt–Ru–Ni, (7) PAni/Pt–Ru–Cu, (8) PAni/Pt–Ru–Sn, (9) PAni/Pt–Ru–Au.

Table 1. Mass activity (mA mg^{-1}) measured after 5 and 30 min during the oxidation of 1 M methanol in 0.1 M $HClO_4$ on three selected electrodes: PAni/Pt, PAni/Pt–Ru and PAni/Pt–Ru–Mo

Catalyst	E = 400 mV vs RHE		E = 450 mV vs RHE		E = 500 mV vs RHE	
	i at t = 5 min /mA mg^{-1}	i at t = 30 min /mA mg^{-1}	i at t = 5 min /mA mg^{-1}	i at t = 30 min /mA mg^{-1}	i at t = 5 min /mA mg^{-1}	i at t = 30 min /mA mg^{-1}
PAni/Pt	–	–	–	–	0.7	0.5
PAni/Pt–Ru	0.2	–	0.8	0.6	2.8	2.3
PAni/Pt–Ru–Mo	1.9	1.4	5.2	4.0	7	5.5

performances but showed however a poor stability under our working conditions: the reproducibility of the experiments was poor and the performances towards methanol oxidation clearly decreased after some hours of experiment at higher potentials. According to Pourbaix diagrams [41], the corrosion of these three metals occurs in strong acidic media. Therefore, the behaviour of the three ternary catalysts can probably be explained by the release of the third metal, even if there are evidences that the third metal, chosen for its ability to provide for OH_{ADS} species, could be stabilized in the ternary electrocatalyst.

Several of the tested electrocatalysts show weaker performances than Pt–Ru, irrespective of the anode potential. From this point of view, it was interesting to investigate the ternary Pt–Ru–Au catalyst, therefore serving as reference. This catalyst shows the worst performances under our working conditions. Indeed, gold is known for its poor ability to adsorb OH species in acidic media in this explored potential range [42]. That confirms the commonly accepted assumption that OH adsorbed species are necessary for a complete methanol oxidation.

These results obviously show an improved catalytic behaviour of PAni/Pt–Ru–Mo anodes compared to other electrocatalysts, especially PAni/Pt–Ru. The catalytic performances of PAni/Pt–Ru–Mo ternary system were also observed with cyclic voltammetry. Figure 4 displays cyclic voltammograms for two PAni/Pt–Ru–Mo and PAni/Pt–Ru electrodes. Higher current densities were obtained with the ternary catalyst in the whole potential range [0–650 mV vs RHE], confirming therefore the observations made during quasi-stationary potentiostatic measurements (Figures 2 and 3).

Many studies are available in the literature concerning the behaviour of binary catalysts, such as Pt–Ru, Pt–Mo for methanol or for H_2/CO oxidation [18, 19, 22, 24], but very few concern ternary catalysts containing molybdenum [15]. As far as we know, there are no reports about how molybdenum operates during methanol oxidation in such catalysts.

It is commonly accepted that the OH adsorption is necessary to oxidize the strongly adsorbed CO on the platinum surface and that it is the rate determining step during the methanol oxidation process [43]. Therefore, OH formation has to be as easy as possible, implying a water binding energy to the molybdenum substituting atoms as high as possible. Moreover, to oxidize CO_{ADS}, the activation energy (E_a) of OH bond scission has to be as low as possible. The behaviour of molybdenum–platinum catalyst towards methanol oxidation has been theoretically predicted by Anderson et al. [38, 39]. According to the authors, molybdenum shows an outstanding behaviour, with energy values close to those of ruthenium: a binding energy of 2.5 eV (2.6 eV for ruthenium) and an activation energy of 0.25 eV for water splitting (0.3 for ruthenium).

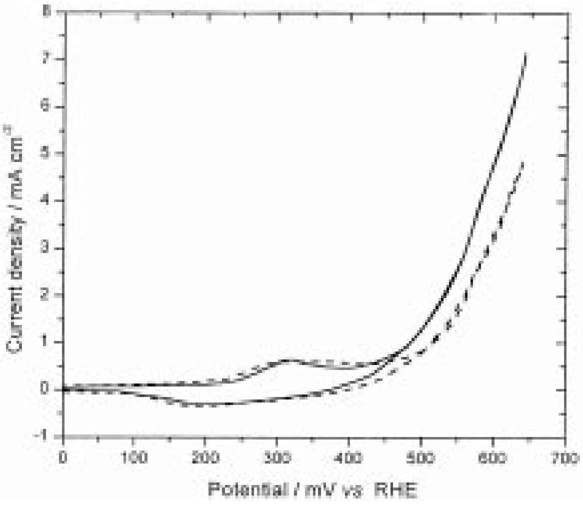

Fig. 4. Cyclic voltammograms of modified electrodes (PAni/Pt–Ru (- - - -) and PAni/Pt–Ru–Mo (——)) in the presence of 1 M methanol in 0.1 M $HClO_4$. Sweep rate 5 mV s^{-1}.

From an experimental point of view, Shropshire [44] already reported (1965) the beneficial effect, for methanol oxidation, of the adsorption of molybdates on the platinum surface. It was found then that, at low potentials, the measured current densities could be up to 10^4 times higher in the presence of adsorbed molybdates than in their absence, thus demonstrating the catalytic effect of molybdenum on the methanol oxidation process. Kita and coworkers [16, 18, 45] also found a promoting effect of molybdenum when combined to Pt, but their conclusions were quite different. They suggested that the enhancement of methanol oxidation was not due to a catalytic behaviour of Mo, but rather due to its redox properties.

More recently, Götz and Wendt [20] reported an experimental study concerning the electrooxidation of methanol on several binary and ternary catalysts. They also noticed the promoting effect of molybdenum on the properties of Pt–Ru catalysts. Their observations were however slightly different from ours, as they found that Pt–Ru–W was the most active catalyst. Comparison is difficult since their catalysts were chemically synthesized while ours were entirely electrochemically prepared.

All these studies confirm the beneficial effect of molybdenum addition, either to Pt (for CO oxidation) or to Pt–Ru for methanol oxidation. The enhanced behaviour of this catalyst is moreover strengthened by its relatively good stability. We applied a simple potential program to the ternary catalyst in the presence of methanol (Figure 5) in order to evaluate the potential at which the electrode is irreversibly altered. As can be seen in Figure 6, it appears that the ternary PAni/Pt–Ru–Mo electrocatalyst seems to be stable after 5 min of methanol oxidation up to 550 mV vs RHE, while the binary catalyst Pt–Ru seems to be stable for the whole explored potential range. We also obtained similar results after 10 minutes of methanol oxidation. The relative good stability of the ternary catalyst, suggested by this simple test but also by the electrochemical measurements, is somewhat unexpected, especially for the third element, molybdenum. According to Pourbaix diagrams [41], under our working conditions, molybdenum is expected to be completely oxidized to Mo(III) or to Mo(VI) (MoO_3), depending on the anodic potential and the pH. The metal corrosion should then occur and our catalyst is expected to be altered by the release of molybdenum. Despite these expectations, the ternary catalyst seems to be stable up to 550 mV vs RHE, which is a convenient potential range for the operation of a DMFC anode.

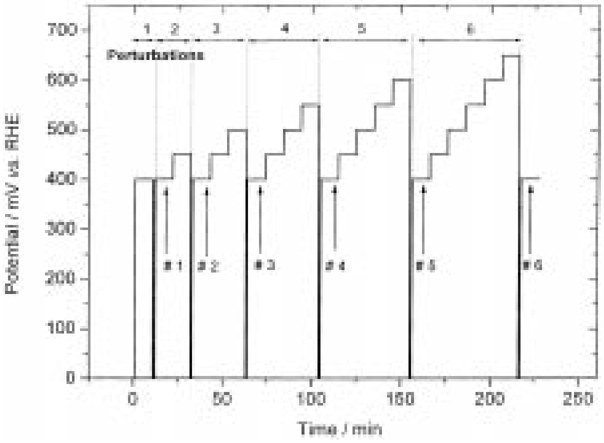

Fig. 5. Potential program used for stability testing of the catalysts. Each current density measurement (indicated by an arrow) is done after the corresponding potential perturbation, the duration of each step being 10 min.

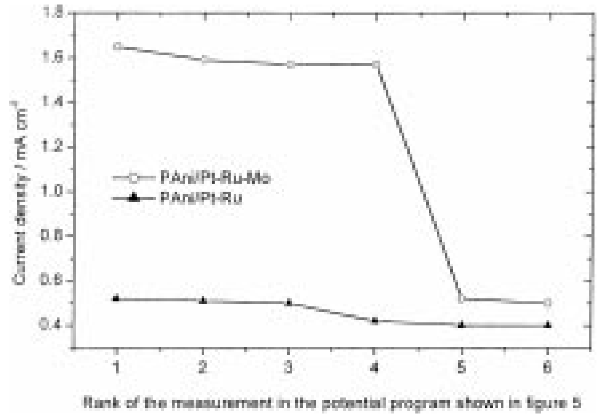

Fig. 6. Current densities for the oxidation of 1 M methanol in 0.1 M $HClO_4$ measured at 400 mV vs RHE after 5 min, during the potential program described in Figure 5, for two catalyst Pt–Ru (▲) and Pt–Ru–Mo (○).

Some authors previously suggested that the beneficial effect of the addition of a non-noble metal to platinum, rather than a real catalytic effect, could be interpreted by the corrosion of the additive metal, leading to the formation of a high-porosity platinum surface, thus increasing its catalytic activity [13]. Since an alteration of the ternary electrode occurs for potentials above 550 mV vs RHE, we believe that our observations on the beneficial effect of Mo for potentials up to 500 mV vs RHE can not only be explained by its possible corrosion but also by providing a small amount of the third metal in the anode formulation, as reported in Table 2 and Figure 7. In the ternary catalyst, Mo is present at an atomic ratio of 4%, according to EDX analysis, irrespective of the analyzed area. We also notice that the presence of Mo leads to a ternary catalyst with a different Pt:Ru ratio, which becomes 2.7 in the ternary catalyst while it was 4 in the binary catalyst. The Pourbaix diagrams, which predict molybdenum corrosion, have been established for pure elements and for thermodynamical equilibria. Our system is far more complex and these considerations might not be adapted to our working conditions. We can make the assumption that molybdenum is stabilized by neighbouring atoms of Pt or Ru so that molybdenum can provide for OH species at low potentials without being completely oxidized to Mo(III) or Mo(VI).

Preliminary results, obtained with *in situ* spectroscopic techniques, will be reported in a forthcoming paper [46] and seem to confirm that there are large differences in the catalytic behaviour of the ternary catalyst during methanol and CO electrooxidation compared to that of the Pt–Ru binary catalyst.

All the results described previously on methanol oxidation were obtained in a classical electrochemical cell. Encouraging results with the Pt–Ru–Mo ternary catalysts were observed for methanol oxidation. However, the operating conditions in a direct methanol fuel cell are drastically different from those in a classical cell so that we performed some preliminary tests in a single

Table 2. Sample atomic compositions (%) measured by EDX for PAni/Pt–Ru and PAni/Pt–Ru–Mo electrodes

Elements	PAni/Pt–Ru	PAni/Pt–Ru–Mo
Pt	80	70
Ru	20	26
Mo	–	4

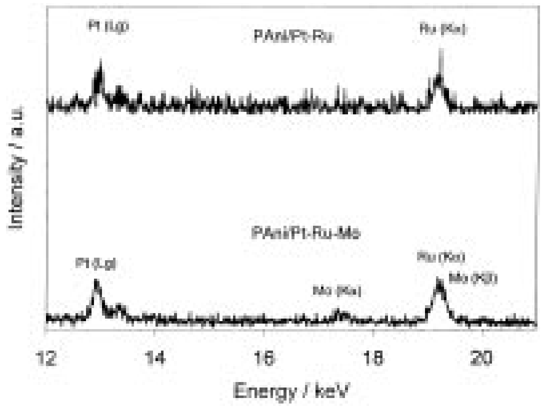

Fig. 7. EDX measurements on PAni/Pt–Ru and PAni/Pt–Ru–Mo electrodes.

cell DMFC. We also wanted to explore the possibility to validate the obtained results in a DMFC. More precisely, it was interesting to confirm the beneficial addition of molybdenum to the binary Pt–Ru catalyst. Preliminary results are reported in Figure 8 for two kinds of home-made electrodes: C/PAni/Pt–Ru and C/PAni/Pt–Ru–Mo. Although the performances are modest regarding to those generally obtained in a DMFC [3], the results that we obtained in a classical three-electrode electrochemical cell are fully confirmed. We notice a real difference in the behaviour of the two electrodes. Even at low cell voltages, which correspond to high anodic potentials, increased performances are observed with the ternary catalyst compared to Pt–Ru.

The modest performances of the DMFC were somewhat predictable since the used electrodes were optimized for electrochemical studies in a classical three-electrode cell rather than for the single cell DMFC operating conditions. We can probably partly explain the poor performances by the presence of the PAni layer over the diffusion layer. Recasting the Nafion® layer with an hot pressing (130 °C) of the MEA is necessary for an optimal contact between the electrodes and the membrane. At this temperature, the conducting polymer may be altered. The literature generally reports the possible loss of the doping agents in this temperature range, leading to the loss of part of the electronic conductivity of the polymer.

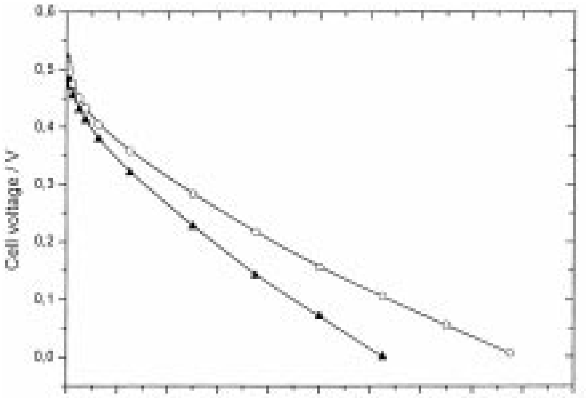

Fig. 8. Cell voltage against current density curves of a DMFC single cell. Operating conditions: $T_{\mathrm{CELL}} = 110$ °C; $T_{\mathrm{OXYGEN}} = 95$ °C; $T_{\mathrm{METHANOL}} = 95$ °C; $P_{\mathrm{OXYGEN}} = 2$ bar and $P_{\mathrm{METHANOL}} = 1.7$ bar. Key: (▲) PAni/Pt–Ru and (○) PAni/Pt–Ru–Mo.

4. Conclusion

This preliminary experimental study allowed us to investigate several ternary metallic electrocatalysts dispersed in a conducting polymer matrix and active towards methanol oxidation. The addition of a third metal to the binary Pt–Ru catalyst has shown that the behavior towards the oxidation of methanol could be modified. Particularly, the Pt–Ru–Mo ternary catalyst has shown enhanced performances compared to Pt–Ru, at low potentials (typically under 500 mV vs RHE) under stationary conditions. The current densities measured with PAni/Pt–Ru–Mo during methanol electrooxidation are up to 10 times greater than those observed with PAni/Pt–Ru. Moreover, this catalyst exhibits a good stability in a single cell at potentials lower than 550 mV vs RHE during methanol oxidation. These encouraging results were confirmed in an operating single cell DMFC.

Our main objectives are now the improvement of this promising ternary catalyst in terms of composition and structure, in order to increase the anode performances. To obtain a better understanding of the differences observed in the catalytic behavior, we are also currently performing experiments with *in situ* infrared reflectance spectroscopy. This will allow us to identify some of the intermediate species involved in the oxidation of methanol at these catalysts. The details of these results will be reported in a forthcoming paper [46] and show clearly that the oxidation of methanol to CO_2 occurs at lower potentials on PAni/Pt–Ru–Mo electrodes than on PAni/Pt–Ru and above all than on PAni/Pt electrodes (Table 3).

Acknowledgements

This work was carried out under the framework of the Commision of the European Union through the NEMECEL program (Joule III, JOE3-CT97-0063).

Table 3. Potentials at which CO_2 formed from the oxidation of 1 M methanol in 0.5 M $HClO_4$ on several electrodes (PAni/Pt, PAni/Pt–Ru and PAni/Pt–Ru–Mo) is detected by infrared reflectance spectroscopy

Electrode	Potential, mV vs RHE at which CO_2 formed during methanol oxidation is detected by IR spectroscopy/mV
PAni/Pt	550
PAni/Pt–Ru	450
PAni/Pt–Ru–Mo	350

The authors also would like to thank Stephane Pronier for his fruitful contribution in TEM/EDX experiments.

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