

Electro-oxidation of methanol and ethanol on Pt–Ru/C and Pt–Ru–Mo/C electrocatalysts prepared by Bönemann's method

A. Oliveira Neto^a, E.G. Franco^a, E. Aricó^a, M. Linardi^{a,*}, E.R. Gonzalez^b

^a*Instituto de Pesquisas Energéticas e Nucleares, Centro de Ciência e Tecnologia de Materiais, Laboratório de Células a Combustível PEM, Travessa R, No. 400, SP, Brazil*

^b*Instituto de Química de São Carlos—USP, C.P. 780, 13560-970 São Carlos, SP, Brazil*

Abstract

Pt–Ru/C and Pt–Ru–Mo/C electrocatalysts prepared by Bönemann's method have been studied as porous thin films on high surface area carbon electrodes, in order to evaluate their electroactivity on CO desorption in PEM fuel cells. Electrode precursor powders with and without thermal treatment were considered for comparison. The morphology of these precursor powders was characterized in a high-resolution transmission electron microscope equipped with a nano-EDX device and also by XPS measurements. Cyclic voltammetry showed that addition of Mo in the well-established Pt/Ru system is very promising for methanol and ethanol oxidation. Infrared spectroscopic measurements revealed that a thermal treatment in a hydrogen atmosphere of the electrode precursor material was necessary to enhance the efficiency. In order to compare the electroactivity of different catalysts a normalization procedure based on the amount of Pt was used.

© 2003 Elsevier Ltd. All rights reserved.

Keywords: Catalyst; Electrocatalysis; Fuel cell; Platinum; Voltammetry

1. Introduction

The need for more efficient energy conversion is presently evident as the world fossil fuel sources become scarcer and the cost of the fuels rise. Moreover, the urgent necessity of reducing the pollution in large urban centers imposes the use of non-polluting fuels, like hydrogen and renewable primary fuels in large scale.¹ Fuel cells have shown to be an interesting and very promising alternative to solve the problem of clean electric power generation with high efficiency.¹

According to a recent review from a fuel company “The question of fuel choice, for fuel cell vehicles remains an open one”.² For stationary applications the question is also pertinent. Research for the best solution may lead to the definition of more convenient local options. As concluded in the “best” fuel solution is strongly influenced by the local conditions in the country, or region, being considered.^{3,4}

When considering the combustion heat per mass, hydrogen presents a large advantage over other fuels, but when the number of available electrical charges per

mass are compared the advantage is not significant. Hydrogen liquefaction would require an energy-spending equivalent of about 30% of its calorific power.⁴ Because of this, hydrogen gas utilization has been considered as safer techniques for handling it develop. Hydrogen production implies in additional questions.

Some organic substances are considered very promising as alternative fuels for electrochemical energy conversion. These substances are oxidized on the anode while oxygen, the pure gas or from ambient air, is reduced on the cathode in low temperature fuel cells. The use of methanol and ethanol in electrocatalytic processes has received recently great attention in many research groups, justified by the development of more efficient and less polluting electrochemical energy conversion systems. Ethanol is especially attractive for Brazil, since its production and distribution are well established in this country.¹ The oxidation of small organic molecules, like methanol and ethanol, on a Pt electrode is followed by the formation of intermediates, like CO, which are strongly adsorbed on the catalyst surface, reducing considerably its electroactivity. Electrochemical experiments have shown that carbon dioxide, acetaldehyde and acetic acid are produced in the oxidation of ethanol on polycrystalline platinum electrodes.^{5–8} CO tolerance is therefore crucial for further

* Corresponding author. Tel.: +55-11-38-16-9192; fax: +55-11-38-16-9370.

E-mail address: m. linardi@net.ipen.br (M. Linardi).

developments in fuel cell technology. The development of better performance anode electrocatalysts is associated to the introduction of a more oxidizable metal, in order to generate oxygenated species at lower potentials in the vicinity of the Pt active sites to enhance the oxidative desorption of CO at those sites.^{9–12}

The feasibility of the use of methanol and ethanol as primary fuels for proton exchange membrane fuel cells (PEMFC) has been studied and proven by several authors, employing electrodes based on binary electrocatalysts.^{13,14} However, less amount of work has been devoted to ternary electrocatalyst systems, which may show synergistic effects by the addition to platinum of two metals with similar characteristics.¹⁵ The Pt, Ru, Os, W, Mo, Sn, V, Ni and Pd elements, as co-catalysts, need to satisfy the following requirements:

- (i) These elements must have a potential equilibrium between the potential oxidation (CO) and methanol oxidation (0V vs NHE) and the potential oxidation of platinum (+0.98 vs NHE).
- (ii) These elements must have a fast kinetics by the formation of species containing oxygen and by adsorption/desorption reactions of CO.
- (iii) These elements need to be stable in anodic electrode.
- (iv) These elements may be produced as nanoparticles.

These requirements make them good co-catalysts candidates for H₂/CO and methanol oxidation in acid medium.

2. Experimental procedure

The Pt–Ru/C (1:1 at.%) and Pt–Ru–Mo/C (1:1:0.5 and 1:1:1%) electrocatalysts were prepared by a colloidal process known as the Bönemann's method, slightly-modified, according to procedures described in Refs.15 and 16 The Bönemann method was chosen as crystallite sizes between 1.5 and 2.5 nm can be obtained, showing enhanced electrocatalytic activities due to their favorable surface-to-bulk ratio. First NR₄X stabilized colloidal precursors (where X is the electrocatalyst particle) were prepared via the reduction of anhydrous PtCl₂, RuCl₃ and MoCl₅ dissolved in THF tetrahydrofuran. Then a suspension of Vulcan XC-72 carbon (Cabot Inc.) in water purified in a Millipore system was impregnated with the appropriate amount of the colloidal solution. All the chemicals were from Aldrich, and used without additional treatments. Thermal treatments were carried out in a H₂ reducing atmosphere at 300 °C for 120 min.

The characterization of the electrocatalysts was performed by high resolution transmission electron

microscopy (HRTEM), energy-dispersive X-ray spectroscopy (nano-EDX) and X-ray photoelectron spectroscopy (XPS). These techniques were used in order to investigate the crystallite sizes, particle size distribution and composition and particle dispersion on the support. A Philips CM 20 with an acceleration voltage of 200 kV and tungsten cathode was used for high-resolution images of the supported catalysts. Additionally, the microscope was equipped with a nano-EDX device to check the catalyst composition in nm-sized regions. Samples were prepared by suspending the catalyst powder in methanol and depositing a drop of the suspension on a standard copper grid covered with carbon. XPS measurements were carried out on a PHI 5700 Multi-Technique ESCA (Perkin Elmer) with Al K_α radiation at a power of 300 W. A pressure of 3×10⁻⁸ mbar was maintained within the spectrometer chamber, while a suitable pass energy of 11.75 eV was chosen. The supported catalyst was pressed against an In-foil. The spectra were fitted and evaluated by the Igor Pro software (Wavemetrics Inc., Oregon, 1998), using a Gauss-Lorentzian function. Infrared spectroscopic measurements were carried out on a Nicolet NEXUS 670 Spectrometer in the region of 4000–1000 cm⁻¹ in a CCl₄ suspension of the catalyst placed between CaF₂ plates.

The electrochemical characterization of the catalysts was performed at room temperature using cyclic voltammetry, with a EGG Princeton Applied Research Model 273 A potentiostat, in 0.5 mol l⁻¹ H₂SO₄, saturated with N₂. Methanol and ethanol 0.1, 0.5 and 1.0 mol l⁻¹ in 0.5 mol l⁻¹ H₂SO₄ solutions were used to test the activity of the catalysts. The electrochemical cell used, is described elsewhere.^{17,18} The working electrode was made of a thin porous layer of a high surface area carbon with nanodispersed electrocatalyst particles. Electrical contact was assured by a pyrolytic graphite wire inserted in a teflon support. The reference used was a reversible hydrogen electrode (RHE) and the counter electrode was a Pt foil.

3. Results and discussion

The high-resolution transmission electron microscope was equipped with a nano-EDX device to perform analyses in small areas (range of some nm) of the specimen in order to verify the composition of the nanocrystals.

Table 1
Nano-EDX analysis of the catalyst nanocrystals

Element	PtRuMo (1:1:0.5) (%)	PtRuMo (1:1:1) (%)
Pt	42.33	35.40
Ru	32.71	27.47
Mo	24.96	37.13

The results are presented in Table 1 and Fig. 1. Nanocrystals with an average size of 2.0 nm appear in both catalysts with a good distribution on the carbon support.

The values obtained in Table 1 are close to the stoichiometric one, with more deviation for Ru probably due the statistical variation of samples and intrinsic variation of electrocatalysts producing method.

The HRTEM image is shown in Fig. 1 for the Pt–Ru–Mo/C (1:1:0.5 at.%) catalyst. In comparison with the results for Pt–Ru/C published by Schmidt et al.¹⁹ slightly bigger particle sizes were found in this work, perhaps due to the addition of Mo to the material.

Deconvolution of XPS measurements indicates the presence of two peaks for Pt 4f, one showing metallic platinum with a binding energy (BE) of 72.1 eV and the other showing PtO₂ with a BE of 74.2 eV, as shown in Table 2.

A shift in BE of Pt 4f to a higher value can be explained by the small particle size of the sample or by the formation of an alloy. The deconvolution of the ruthenium response gives two peaks: one for Ru 3p, detected as an oxide form RuO₂ for a BE of 463.1 eV and the other as a hydrous oxide form for a BE of 465.6 eV. The molybdenum deconvolution shows an oxidized species for Mo 3d that is not so easy to ascribe to a specific compound.

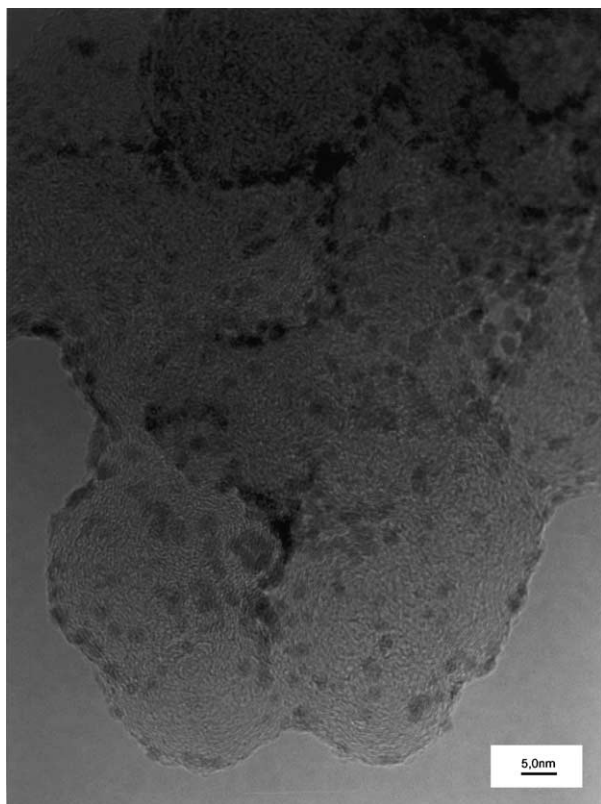


Fig. 1. High-resolution transmission electron microscopy of Pt–Ru–Mo/C (1:1:0.5 at.%) on carbon black nanoparticle.

The results of cyclic voltammetry experiments with the prepared Pt–Ru/C and Pt–Ru–Mo/C electrocatalysts by the Bönemann's method in the absence of methanol and ethanol in a 0.5 mol l⁻¹ H₂SO₄ solution are presented in Fig. 2.

In the double layer region an increase in the double layer capacity is observed as the content of the second and third metal is increased. In the case of Ru this phenomenon is related to the formation of oxygenated species at low potentials.¹⁹ The same explanation is also valid for Mo, but in this case it is also necessary to consider the oxidation of the Mo (see below). In the region of adsorption/desorption of hydrogen (between 0.0 and 0.4 V) the corresponding peaks are suppressed due to oxide formation at lower potential than 0.4 V.¹⁹

The Pt/C electrocatalyst curve shows a strong blockage in the hydrogen region. This phenomenon suggests that the electrocatalyst's surface is covered by species from the reducing agent used in Bönemann's method. Another peak next to 0.5 V is observed for the Pt–Ru–Mo/C systems. This peak corresponds to a change in the oxidation state of Mo from +IV to Mo +VI. Infrared spectroscopic measurements revealed an electrocatalyst's surface covered by impurities. The spectra of the electrocatalyst without thermal treatment showed absorption bands near 2900 and 2800 cm⁻¹, corresponding to the asymmetrical stretching ($\nu_{as}CH_2$) and

Table 2
XPS results for the Pt–Ru–Mo/C (1:1:1 at.%) catalyst

Element	Binding energy (eV)	Compound
Platinum	72.1	Pt
Pt 4f	74.2	PtO ₂
Ruthenium	463.1	RuO ₂
Ru 3p	465.6	RuO ₂ ×H ₂ O

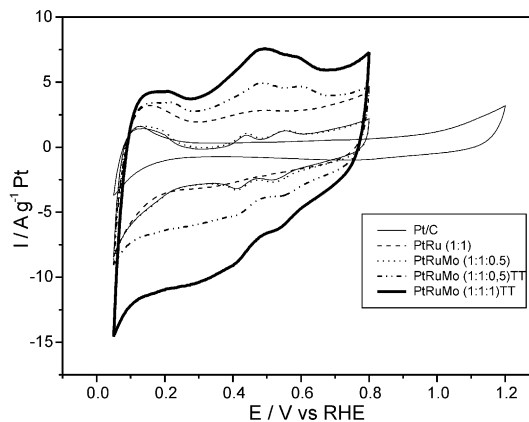


Fig. 2. Cyclic voltammograms of the Pt–Ru/C and Pt–Ru–Mo/C electrocatalysts prepared by Bönemann's method in 0.5 mol l⁻¹ H₂SO₄ solution. $\nu = 10$ mV s⁻¹.

symmetrical stretching ($\nu_s\text{CH}_2$) as expected from tetraoctylammonium species, present in the preparation of the catalyst. This is shown in Fig. 3 for Pt–Ru–Mo/C (1:1:1).

Fig. 4A shows cyclic voltammetry curves for Pt–Ru–Mo/C (1:1:0.5, atom%) TT electrocatalysts in the presence of different concentrations of methanol, ranging from 0.1 to 1.0 mol l⁻¹, in 0.5 mol l⁻¹ H₂SO₄. Fig. 4B shows cyclic voltammetry curves for Pt–Ru–Mo/C (1:1:1 at.%) TT electrocatalysts in the presence of the different concentrations of ethanol, ranging from 0.1 to 1.0 mol l⁻¹, in 0.5 mol l⁻¹ H₂SO₄.

An increase in the oxidation current above 0.5 V is observed in Fig. 4A, as the methanol concentration increases. The same behavior is observed for Pt–Ru–Mo/C TT (1:1:1, with thermal treatment) in the presence of ethanol, as presented in Fig. 4B.

The increase in the observed current is not proportional to the increase of alcohol concentration in the solution. This behavior indicates a poisoning of the catalyst sites with increasing alcohol concentration due to the adsorption of the alcohol on the catalyst surface.

Fig. 5A shows current-potential results for methanol oxidation from 0.1 mol l⁻¹ solutions on the different

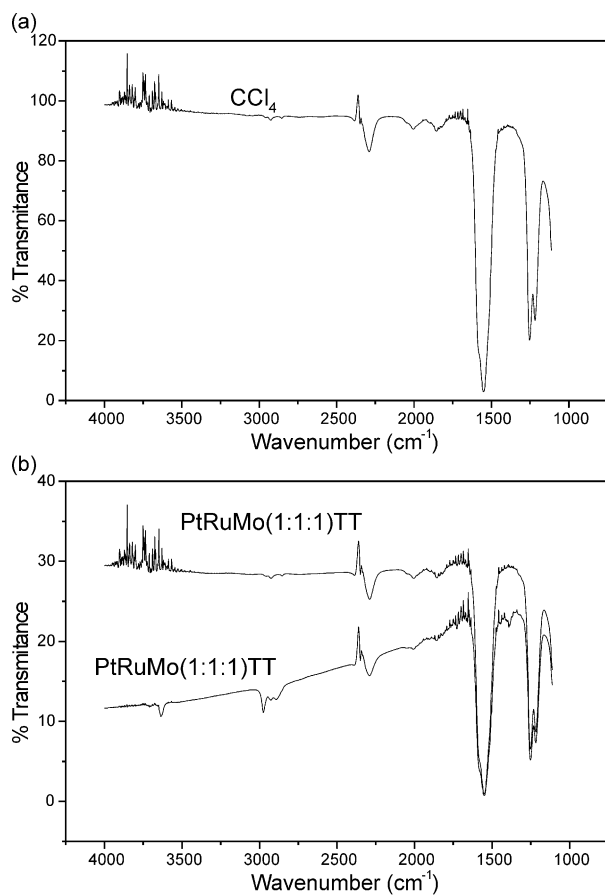


Fig. 3. Infrared spectra of (A) CCl₄ and (B) Pt–Ru–Mo/C (1:1:1) in CCl₄ and Pt–Ru–Mo/C (1:1:1) with thermal treatment in CCl₄.

electrocatalysts prepared by Bönemann's method. Fig. 5B shows the performance of the different catalysts when the concentration of methanol is increased to 1.0 mol l⁻¹.

The potential region around 0.6 V is of great interest for operational regime of fuel cells for the direct oxidation of methanol. In this region the normalized currents may be considered low, but it can be observed that the Pt–Ru–Mo/C (1:1/0.5) TT and the Pt–Ru–Mo/C (1:1:1) TT electrocatalysts present similar currents and higher than only Pt–Ru by the same method. This fact indicates that the addition of Mo to Pt–Ru electrocatalysts has a beneficial effect on the oxidation of methanol.

PtRu catalyst produced by the formic acid method shows significant values in comparison with those produced by Bönemann method (Fig. 5A). The better apparent results of the Pt–Ru/C (1.4/0.8) catalyst can be explained by the higher platinum content (Fig. 5A).

In Fig. 5B currents are much larger, particularly around 0.5 V. Also it is seen that in this case the Pt–Ru–Mo/C TT (1:1:1) shows the best performance, probably

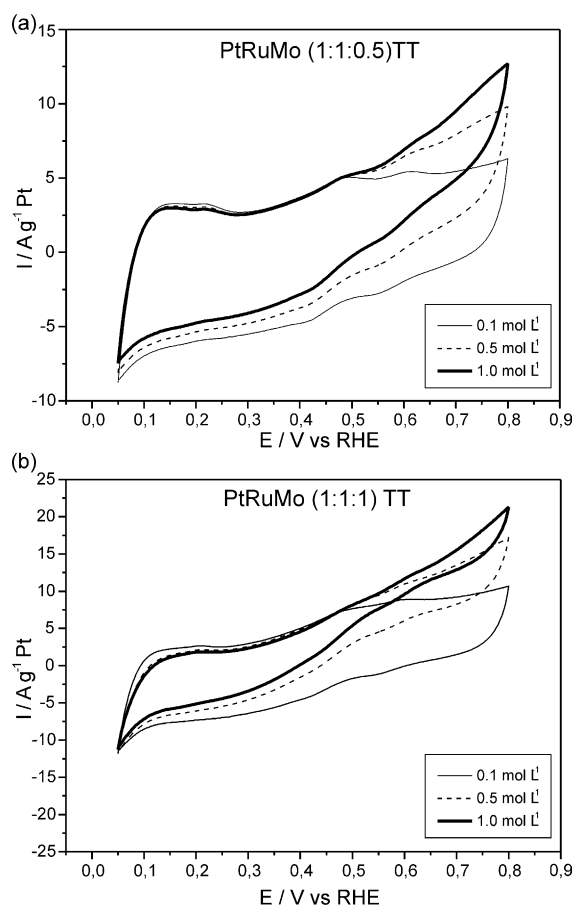


Fig. 4. (A) Cyclic voltammograms for Pt–Ru–Mo (1:1:0.5) TT in the presence of different concentrations of methanol between 0.1 and 1.0 mol l⁻¹. $\nu = 10 \text{ mV s}^{-1}$. (B) Cyclic voltammograms for Pt–Ru–Mo/C (1:1:1) with thermal treatment in the presence of different concentrations of ethanol between 0.1 and 1.0 mol l⁻¹. $\nu = 10 \text{ mV s}^{-1}$.

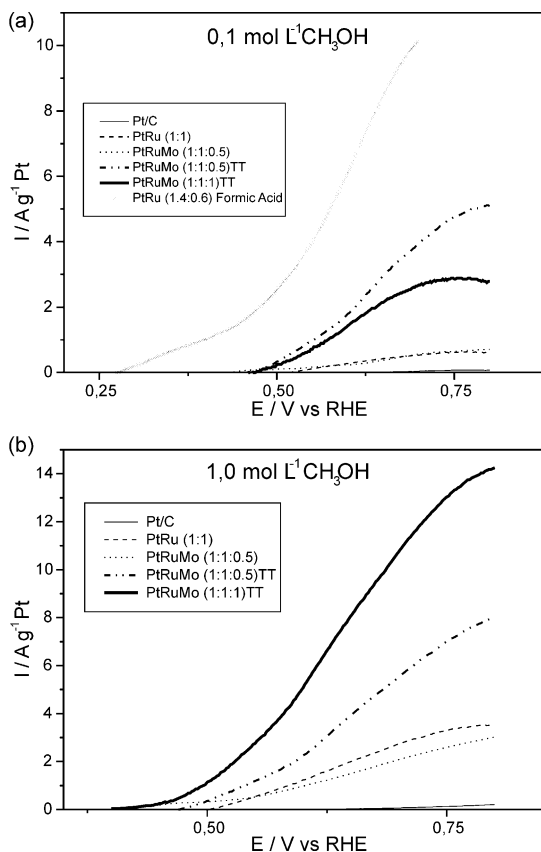


Fig. 5. (A) Anodic scans in a 0.1 mol l⁻¹ methanol solution with the different electrocatalysts prepared by Bönemann's method. $\nu = 10$ mV s⁻¹. (B) Anodic scans in a 1.0 mol l⁻¹ methanol solution with the different electrocatalysts prepared by Bönemann's method. $\nu = 10$ mV s⁻¹.

because it is less sensitive to the adsorption of methanol at higher concentrations.

Fig. 6A shows the results for 0.1 mol l⁻¹ ethanol. The results of increasing the concentration of ethanol to 1.0 mol l⁻¹ are shown in Fig. 6B.

In Fig. 6A the best catalyst is Pt–Ru–Mo/C TT (1:1:1) and the results show that not only the presence but the amount of Mo is important because the performance of the Pt–Ru–Mo/C TT (1:1:0.5) is much poorer.

In Fig. 6B the currents are appreciably larger and the Pt–Ru–Mo/C TT (1:1:1) catalyst shows also the best performance, particularly around 0.6 V.

The results in Figs. 4A–6B show the beneficial effects of the addition of Mo to the Pt–Ru catalyst and also of the thermal treatment at 300 °C in a hydrogen atmosphere. It is also important to point out that the Pt–Ru–Mo/C TT (1:1:1) catalyst shows a much better performance for the oxidation of ethanol than for the oxidation of methanol. Thus, it may be concluded that the addition of Mo not only has a beneficial effect to promote the oxidative desorption of intermediates like CO but also promotes the breaking of the C–C bond.

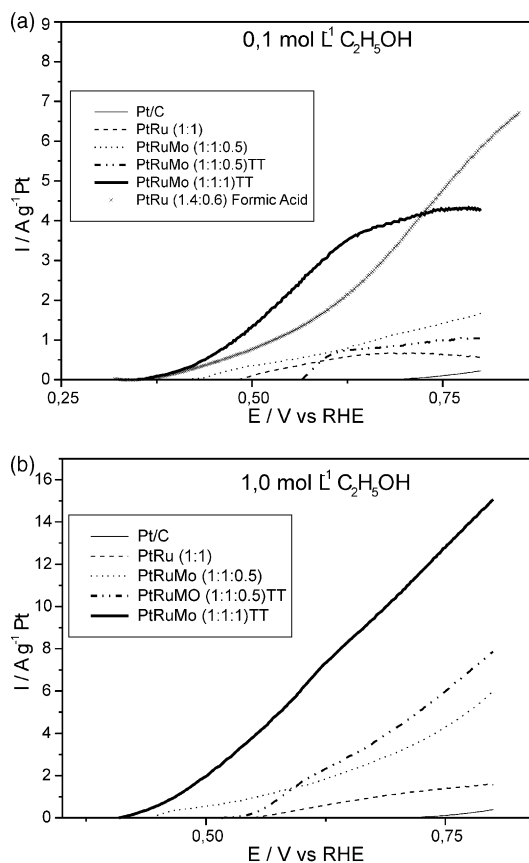


Fig. 6. (A) Anodic scans in a 0.1 mol l⁻¹ ethanol solution with the different electrocatalysts prepared by Bönemann's method. $\nu = 10$ mV s⁻¹. (B) Anodic scans in a 1.0 mol l⁻¹ ethanol solution with the different electrocatalysts prepared by Bönemann's method. $\nu = 10$ mV s⁻¹.

4. Conclusions

Bönemann's method showed to be an effective procedure to develop Pt based alloys as active catalyst systems for the oxidation of methanol and ethanol in PEMFC. The results suggest a considerably enhanced catalyst electroactivity when the catalyst is submitted to a thermal treatment at 300 °C in a hydrogen atmosphere. The system Pt–Ru–Mo/C TT (1:1:1), submitted to thermal treatment, showed to be very promising for practical application in fuel cells and more active for the oxidation of ethanol than for the oxidation of methanol.

Acknowledgements

Thanks are due to the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) and the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for financial support. The authors also thank the Technical University of Darmstadt, Germany, for the HRTEM and nano-EDX

measurements and Professor Dr. T. B. Iwasita from IQSC/USP for helpful discussions.

References

1. Wendt, H., Gotz, M. and Linardi, M., Tecnologia de Células a Combustível. *Química Nova*, 2000, **4**, 538–546.
2. Berlowitz, P., Exxon Mobil Research et Engineering in SAE Word Congress Preview, “Global Automotive Network”. *SAE International*, **11** February 2001.
3. Faltenbacher, M., Alternative Fuels for Fuel Cell Powered Buses Compared to Diesel powered Buses, University of Stuttgart. 2000 (SAE 2000-01-1484).
4. Thomas, C.E., Societal Impacts of Fuel Options for Fuel Cell Vehicles, Directed Technologies, 1998 (SAE 982496).
5. Souza, J. P. I., Rabelo, F. J. B., De Moraes, I. R. and Nart, F. C., Performance of a co-electrodeposited Pt–Ru electrode for the electro-oxidation of ethanol studied by in situ FTIR spectroscopy. *J. Electroanal. Chem.*, 1997, **420**, 17–20.
6. Ianniello, R., Schmidt, V. M., Rodrigues, J. L. and Pastor, E., Electrochemical surface reactions of intermediates formed in the oxidative ethanol adsorption on porous Pt and PtRu. *J. Electroanal. Chem.*, 1999, **471**, 167–179.
7. Fujiwara, N., Friedrich, K. A., Stimming, U. and Ethanol oxidation on PtRu electrodes studied by differential electrochemical mass spectrometry. *J. Electroanal. Chem.*, 1999, **472**, 120–125.
8. Hitmi, H., Belgsir, E. M., Léger, J. M., Lamy, C. and Lezna, R. O., A kinetic, analysis of the electrooxidation of ethanol at a platinum electrode in acid-medium. *Electrochim. Acta*, 1994, **39**, 407–415.
9. Oliveira Neto, A., Perez, J., Napporn, W. T., Ticianelli, E. A., Gonzalez, E. R., Electrooxidation of methanol on binary platinum based catalysts. In: *Workshop Electrocatalysis in Indirect and Direct Methanol PEM Fuel Cells, 3rd International Symposium in Electrocatalysis*. Portoroz, Slovenia, 1999, pp. 83–86.
10. Willson, J., Heitbaum, J., Elementary steps of ethanol oxidation on Pt in sulfuric acid as evidenced by isotopic labelling. *J. Electroanal. Chem.* 1985, **194**, 27–35.
11. Hitmi, H., Belgsir, E. M., Léger, J. M., Lamy, C. and Lezna, R. O., A kinetic, analysis of the electrooxidation of ethanol at a platinum electrode in acid-medium. *Electrochim. Acta*, 1994, **39**, 407–415.
12. Oliveira Neto, A., Giz, M. J., Perez, J., Ticianelli, E. A. and Gonzalez, E. R., The Electro-oxidation of ethanol on Pt–Ru and Pt–Mo particles supported on high surface area carbon. *J. Electrochem. Soc.*, 2002, **149**, A272–A279.
13. Hable, C. T. and Wrighton, M. S., Electrocatalytic oxidation of methanol and ethanol: a comparison of platinum–tin and platinum–ruthenium catalyst in a conduction polyaniline matrix. *Langmuir*, 1993, **9**, 3284–3290.
14. Wang, J., Wasmus, S. and Savinelli, R. F., Real-time mass-spectrometric investigation of the methanol oxidation in a direct methanol fuel cell. *J. Electrochem. Soc.*, 1995, **142**, 4218–4224.
15. Gotz, M. and Wendt, H., *Electrochim. Acta*, 1998, **43–24**, 3637.
16. Franco, E. G., Linardi, M. and Aricó, E., *Proceedings of the XII SIBEE Simpósio*. Brasileiro de Eletroquímica e Eletroanalítica, Gramado, RS, Brasil, 2001.
17. Oliveira Neto, A., *Estudos Eletroquímicos sobre Electrocatalisadores a Base de Platina Dispersos em Carbono de Alta Área Superficial*, PhD thesis, University of São Paulo, Brazil, 2001.
18. Oliveira Neto, A., Perez, J., Napporn, W. T., Ticianelli, E. A. and Gonzalez, E. R., Electrocatalytic oxidation of methanol: study with Pt:Mo dispersed catalysts. *J. of B. Chem. Soc.*, 2000, **11**(1), 39–43.
19. Schimidt, T. J., Gasteiger, H. A. and Behm, R. J., Methanol electrooxidation on a colloidal PtRu-alloy fuel-cell catalyst. *Electrochem. Communications*, 1999, **1**, 1–4.