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**PROTON EXCHANGE MEMBRANE FUEL CELL CATALYST:  
SYNTHESIS AND CHARACTERIZATION**

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**ABSTRACT**

Fuel cells are a promising technology to deal with energy sustainability, especially for mobility purposes the Proton Exchange Membrane Fuel Cell and hydrogen produced from biomass could be coupled to overcome the amount of CO<sub>2</sub> emissions. In order to improve fuel cells performances the search for new electrocatalysts has a great importance in this technology the challenge for a fuel cell catalyst that is less poisoned by CO is one of the most important field in low temperature fuel cell developments that use alcohol and hydrocarbons as primary fuels. In this work PtSm, PtTb, PtDy, PtU, PtRuMo and PtRuDy systems have been synthesized by the colloid method, investigated by the following techniques: X-rays fluorescence analysis (XFA), X-rays powder diffraction (XRD), X-rays photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), cyclic voltammetry (CV) and polarization curves (Exi). The results obtained in this work shows that PtRuMo is the best choice for direct methanol oxidation. For direct ethanol oxidation the higher activity was found in PtRuDy system. PtU system was investigated and showed an interesting behaviour in ethanol oxidation. After two cycles of H<sub>2</sub>/O<sub>2</sub> and ethanol/O<sub>2</sub> the catalyst was able to reach the initial figures on hydrogen/oxygen oxidation which means that no degradation of the catalyst was identified.

**INTRODUCTION**

The effects of the CO<sub>2</sub> emissions is playing an important role in nowadays, in fact the need for more efficient energy

conversion is evident as the world fossil fuel sources become scarcer and the cost of the fuels rises. Moreover, the urgent necessity of reducing the pollution in large urban centers imposes the use of biomass fuels for transportation. Hydrogen as an energy carrier and renewable primary fuels in large scale are expected to grow in the next decades [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].

For stationary applications the question of fuel choice is still pertinent and 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 [2].

Huge investments in the logistics of the Hydrogen Economy are necessary for worldwide demand or the use of other organic fuels locally produced should be employed [3].

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 electro-activity. Electrochemical experiments have shown that carbon dioxide, acetaldehyde and acetic acid are produced in the oxidation of ethanol on polycrystalline platinum electrodes [4-7]. CO tolerance is therefore crucial for further developments in fuel cell technology. The development of better performance anode electro-catalysts is associated with a co-catalyst that are able to generate oxygenated species at low potentials in the vicinity of the Pt active sites enhancing the oxidative desorption of CO at

those sites [8-11]. 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 and ternary electrocatalysts [12-16]. In the present work binary and ternary systems are being investigated in methanol and ethanol oxidation, based in Pt and co-catalysts, among them we employed Dy, Tb and Sm. These systems have a potential for fuel cell applications that one can see by the experiments of cyclic voltammetry. However further improvements of the structure of the catalysts, the preparation of the membrane electrode assembly and operational conditions are in our concern to obtain a good electrochemical behavior.

## EXPERIMENTAL

### Synthesis of the electro-catalyst:

The catalysts were synthesized by the colloid method. The first step of the method corresponds to obtain a NR4X-stabilized colloidal. Pt-X precursors were prepared via the reduction of anhydrous chlorides of the catalysts involved. Then a suspension of Vulcan XC-72 (Cabot inc.) in millipore water was impregnated with an appropriate amount of the colloidal solution. Details of the synthesis can be found in [14].

### Characterization of the electro-catalyst powder by XFA, XRD, TEM and XPS:

Metal loading and composition of the supported catalysts were measured using a Xlab 2000 (Spectro analytical instruments GmbH).

X-rays powder diffraction was carried out on a STOE STADI-P powder diffractometer, with germanium monochromatized  $\text{CuK}\alpha$  radiation and a position-sensitive detector with  $40^\circ$  aperture in transmission mode. A Philips CM 20 with an acceleration voltage of 200 kV and tungsten cathode was applied for high resolution images of the supported catalysts. Additionally the microscope was equipped with a nano-EDX device to check the catalysts 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.

The XPS measurements were carried out on a PHI 5700 MultiTechnique ESCA (Perkin Elmer) with  $\text{AlK}\alpha$  radiation at a power of 300 W. A suitable pass energy of 11.75 eV was chosen, while a pressure of  $3 \times 10^{-8}$  mbar was maintained within the spectrometer chamber. Samples were prepared by pressing a small amount of the supported catalyst powder into In-foils. The spectra were fitted and evaluated by the standard software Igor Pro (Wavemetrics Inc., Oregon, 1988) using a mixed Gauss-Lorentzian function.

### Electrochemical investigation with cyclic voltammetry:

Electrochemical studies of the electrocatalysts were carried out using the thin porous layer technique [11, 17, 18]. An amount of 20mg of the electrocatalysts was added to 20 g of water. The mixture was submitted to an ultrasound bath for 5 min, where drops of a PTFE (Polytetrafluorethylene) suspension were added. Again, the mixture was submitted to an ultrasound bath for 5 min, filtered and transferred to the cavity

(0.30mm deep and area with  $0.36 \text{ cm}^2$ ) of the working electrode. The quantity of the electrocatalysts in the working electrode was determined with a precision of 0.0001g. By the cyclic voltammetry experiments, the current values (I) were expressed in amperes and were normalized per gram of platinum. The reference electrode was RHE (Reversible Hydrogen Electrode) and the counter electrode was a platinized Pt net with  $4 \text{ cm}^2$ . Cyclic voltammetry was performed in a  $0.5 \text{ molL}^{-1} \text{ H}_2\text{SO}_4$  solution saturated with  $\text{N}_2$ . The evaluation of CO oxidation was performed in this way; the potential of the working electrode was fixed in 50mV vs. RHE and CO gas was boiled in the electrochemical cell solution for 2 h. After that,  $\text{N}_2$  was boiled in the electrochemical cell solution to remove the CO dissolved in the solution. The anodic sweeping was carried at  $10 \text{ mVs}^{-1}$  in  $\text{H}_2\text{SO}_4$   $0.5 \text{ molL}^{-1}$ .

For comparative purposes a commercial carbon supported PtRu catalysts from E-TEK (20%wt.%; Pt:Ru molar ratio 1:1) was used. Electrochemical measurements were made using a Microquimica (model MQPG01, Brazil) potentiostat/galvanostat coupled to a computer using the Microquimica Software.

### Electrochemical investigation in single cells:

The membrane electrode assemblies were produced by hybrid method of spraying and hot pressing.

For hydrogen operation, the anode gas was humidified at a temperature of  $85^\circ\text{C}$  using a hydrogen flow of  $150 \text{ mL}\cdot\text{min}^{-1}$ . Feed gas at the cathode was dry oxygen ( $75 \text{ mL}\cdot\text{min}^{-1}$ ) at a cell temperature of  $75^\circ\text{C}$ .

For methanol operation,  $1 \text{ mL}\cdot\text{min}^{-1}$  of a  $1.0 \text{ mol L}^{-1}$  aqueous methanol solution was evaporated and fed into the cell by a support gas flow of  $35 \text{ mL}\cdot\text{min}^{-1}$  of nitrogen. The cell temperature of  $95^\circ\text{C}$  was maintained, and cathode feed gas was dry oxygen.

For ethanol operation  $1 \text{ mL}\cdot\text{min}^{-1}$  of a  $1.0 \text{ mol L}^{-1}$  liquid ethanol was fed directly into the anode of the fuel cell and oxygen into the anode. The catalytic activity of the system was measured by recording the polarization (E/i) curves.

## RESULTS

### X-rays fluorescence analysis (XFA)

The compositions of the catalysts were investigated by XFA and the carbon content was verified by chemical analysis. The results are presented in Table 1.

Table 1: Metal loading composition of the catalysts by XFA.

Catalyst	C (%)	Pt (%)	2° (%)	3° (%)
PtDy	72.1	$14.3 \pm 0.1$	$10.3 \pm 0.1$	
PtSm	72.8	$7.9 \pm 0.1$	$18.3 \pm 0.2$	
PtTb	77.5	$8.6 \pm 0.1$	$12.8 \pm 0.1$	
PtU	80.0	$8.1 \pm 0.1$	$5.2 \pm 0.1$	
PtRuMo	87.9	$4.4 \pm 0.1$	$1.8 \pm 0.1$	$1.3 \pm 0.1$
PtRuDy	84.7	$10.4 \pm 0.1$	$2.1 \pm 0.1$	$2.8 \pm 0.1$

### Scanning electron microscopy (SEM):

In Figure 1 the morphology of the catalysts is investigated by SEM and revealed agglomerates with a medium size of 50  $\mu\text{m}$  in all samples. Due to the resolution limit in conventional SEM, it was not possible to identify the nanocrystals on the carbon support. Figure 2 shows the triple interface of a MEA after spraying.

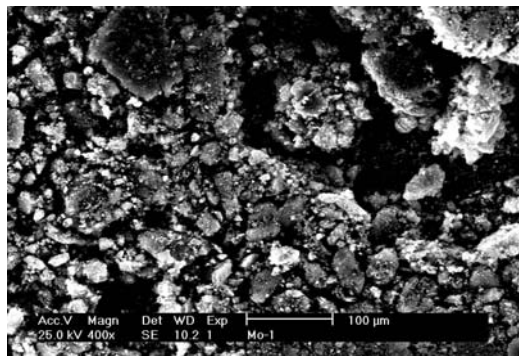


Figure 1 : SEM micrograph of the Pt-Ru-Mo

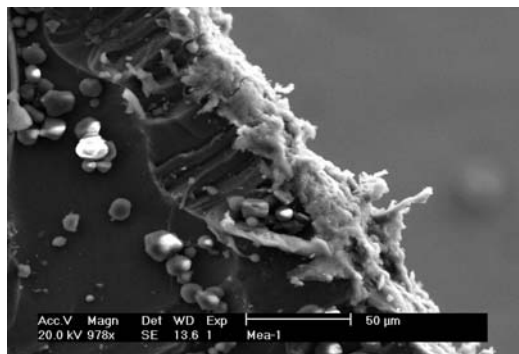


Figure 3: Electrode structure.

### High resolution transmission electron microscopy (HRTEM):

The high resolution microscopy was used to investigate the average crystallites diameter. Nanocrystallites with an average diameter of approximately 2 nm are displayed in Figure 4.

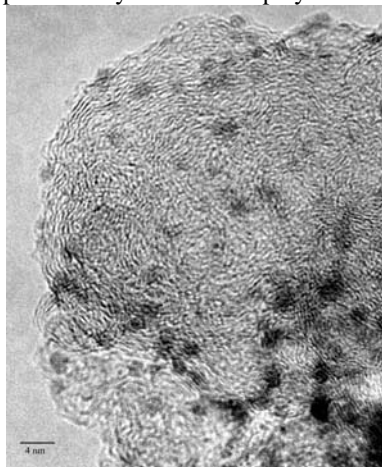


Figure 4: HRTEM images of the Pt-Ru-Mo catalysts.

The catalytic active particles are highly-dispersed on the support grains for both samples. In comparison with the results for PtRu published by Schmidt et al. [10] slightly bigger particle sizes were found, perhaps due to the addition of Mo. The other catalysts shows similar behavior for HRTEM.

### X-rays diffraction (XRD)

The diffractograms of the catalysts reveal platinum as the only crystalline phase showing reflections according to the ICDD data base. No evidence of other metallic phases or crystalline oxide species was found. In Figures 5,6,7 and 6 the diffractograms of the catalysts are presented.

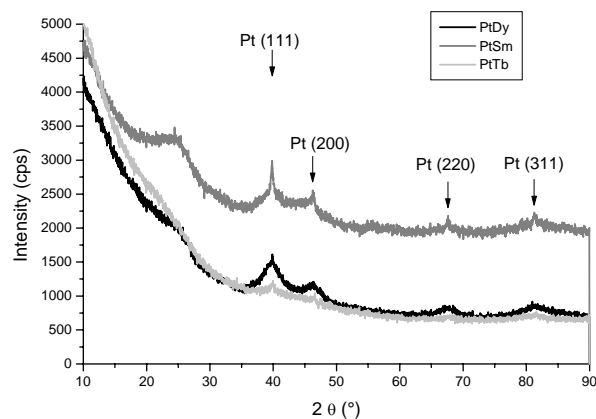


Figure 5: Diffractograms of the binary systems.

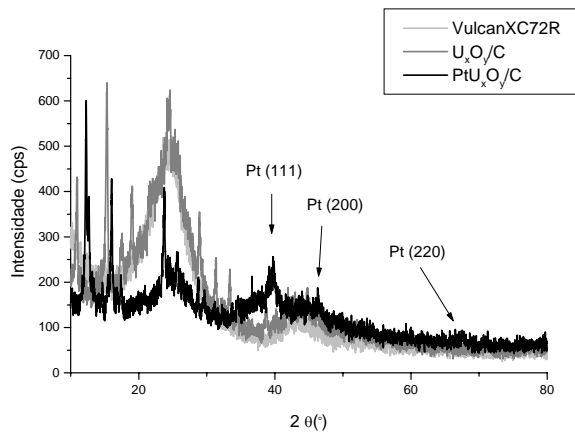


Figure 6: Diffractograms of the PtU system.

In the PtU system only the reflections of platinum were verified. In spite of this the carbon support and the precursor of the uranium diffractograms were performed to help the identification of the PtU catalyst even with these diffractograms we were not able to identify the uranium phases.

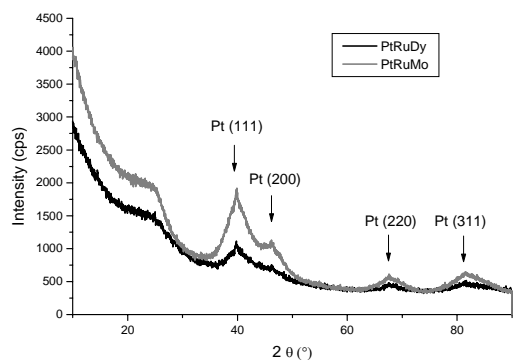


Figure 6: Diffractograms of the ternary systems.

With ternary systems again only the platinum reflections were identified.

In table 2 the average crystallite size are presented and it was calculated according to Scherer's equation.

Table 2: Crystallites sizes of the catalysts systems.

Radiation Cuk		
System	d (nm)	Scherer equation:
PtDy	2.6	$d = \frac{K(\lambda)}{(\beta \cos \theta)}$
PtSm	9.9	
PtTb	5.6	
PtRuMo	2.4	
PtRuDy	3.1	

**X-rays photoelectron spectroscopy (XPS):**

The surface composition of the catalysts was investigated by X-rays photoelectron spectroscopy. As the crystallites are very small, an approximation of obtaining nearly bulk information can be made. The results of the measurements are presented in Table 3 for the PtRuMo ternary catalysts.

Table 3: XPS measurements for PtRuMo.

Element	BE (eV)	State
Platinum	72.1	Pt
Pt 4f	74.2	PtO <sub>2</sub>
Ruthenium	463.1	RuO <sub>2</sub>
Ru 3p	465.6	RuO <sub>2</sub> ·x H <sub>2</sub> O
Molibdenum	232.1	(NH <sub>4</sub> ) <sub>4</sub> MoO <sub>4</sub>
Mo 3d5/2	232.8	MoO <sub>3</sub>

The 4f signal of platinum two binding energies (BE) can be obtained corresponding to metallic platinum and a Pt oxide species. Deconvolution of the Ru 3p peak gave two distinguishable peak pairs with BEs of 463.1 and 465.6 eV according to an oxide and a hydrous oxide species. For molybdenum only oxidized species can be found that are not easy to ascribe to a specific compound. The platinum signal

shows a shift to higher binding energies which can be either explained by the small particle size or an alloy formation.

In table 4 the results for PtRuDy catalysts are presented.

Table 4: XPS measurements for PtRuDy.

Element	BE (eV)	State
Platinum	71	Pt
Pt 4f	74	PtO <sub>2</sub>
Ruthenium	462	RuO <sub>2</sub>
Ru 3p		
Disprosium	168	Dy <sub>2</sub> O <sub>3</sub>
Dy 4d		

For the PtRuDy systems the metallic phase was only platinum the other elements were identified as oxides species.

**Cyclic voltammetry (CV):**

The catalysts systems were tested with cyclic voltammetry and CO stripping. The results are presented in the Figures 7, 8, 9, 10.

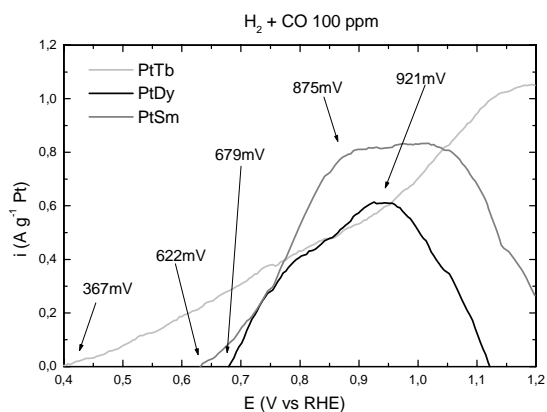


Figure 7: Anodic sweep of the catalysts systems PtTb, PtDy and PtSm.

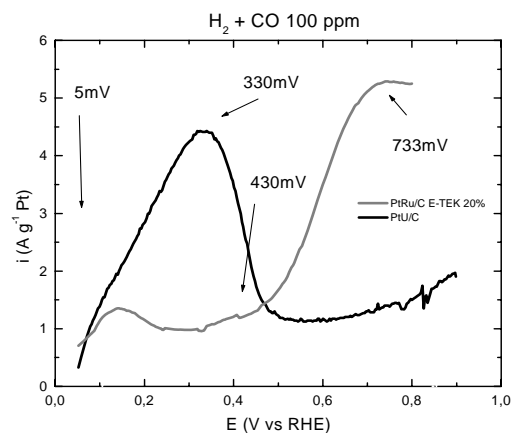


Figure 8: Anodic sweep of the catalysts systems PtU and PtRu.

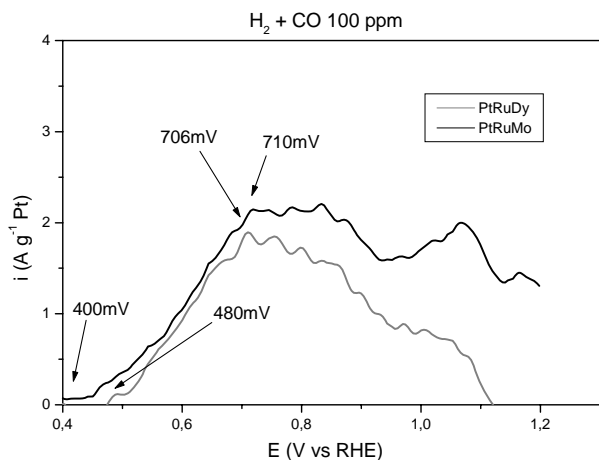


Figure 9: Anodic sweep of the ternary catalysts systems.

In Figure 7 one can see that the PtTb catalysts starts CO oxidation with 367 mV x RHE, while for the PtSm starts with 622 mV x RHE and PtDy 679 mV x RHE. The oxidation peak of the systems are 875 mV x RHE for PtSm and 921 mV x RHE for PtDy.

In Figure 8 PtU catalysts starts oxidizing CO at 5 mV x RHE while PtRu starts with 430 mV x RHE and its oxidation peak of CO is 330 mV x RHE. This is a very promising result.

In Figure 9 are presented the results for ternary systems and one can see that PtRuMo and PtRuDy shows similar behavior, but PtRuMo starts oxidizing CO before than PtRuDy that leads to a better performance of the catalysts.

#### Polarization curves (E/i):

The MEAs were operated in a fuel cell system with 25 cm<sup>2</sup> active electrode area first with pure hydrogen, hydrogen contaminated with CO, methanol and ethanol. The results are summarized in Figures 10, 11 and 12.

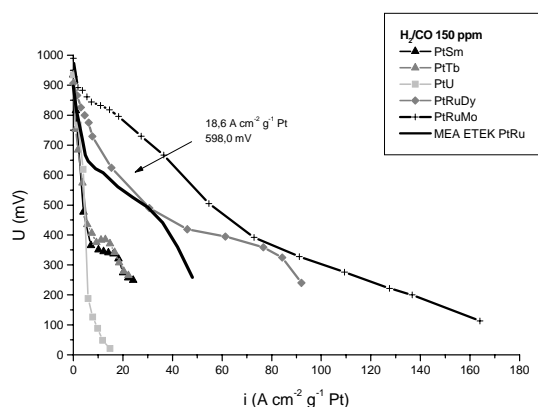


Figure 10: Polarization curves of the catalyst systems operating with H<sub>2</sub> - CO (150 ppm).

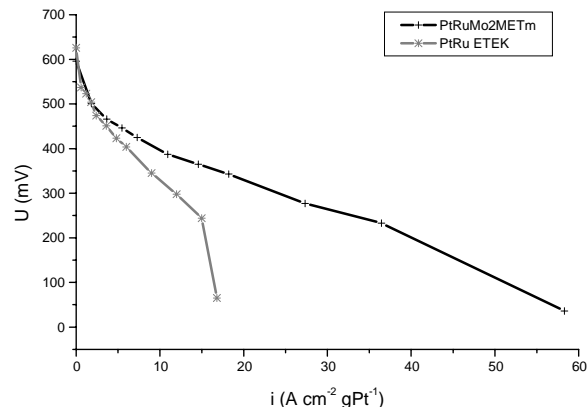


Figure 11: Polarization curve for PtRuMo system operating with methanol 1.0 mol L<sup>-1</sup>.

PtRuMo system presents the best electrochemical activity among all other systems for methanol oxidation, when compared, in term of Pt mass, with PtRu ETEK system one can verify the electrochemical activity performance of PtRuMo, specially on higher current densities.

The best catalysts system for direct oxidation of liquid ethanol was PtRuDy system and PtU shows a different behavior among all other catalysts systems.

PtU system is the only system that after operating with ethanol one can turn to operate with hydrogen and the figures obtained are the same as the figures of hydrogen operation before the use of ethanol.

These findings can be found in Figures 12 and 13.

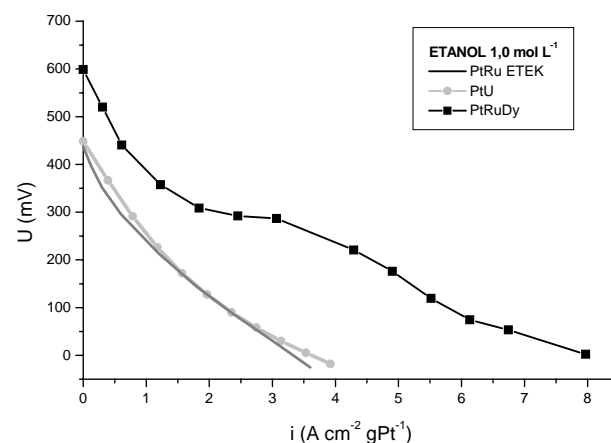


Figure 12: Polarization curve for PtRuDy, PtU and PtRu ETEK for direct ethanol oxidation.

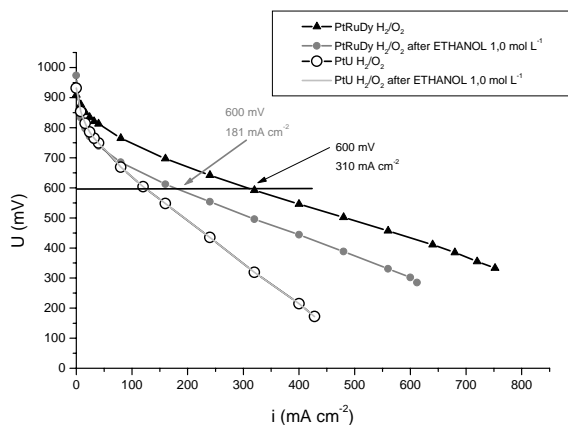


Figure 13: Degradation of PtRuDy and PtU systems after operating with liquid ethanol.

In Figure 13 the one can see a operation cycle that consists on the operation of a MEA with  $H_2/O_2$ , a polarization curve is recorded. After that we turn the system for direct ethanol oxidation and finally we turn the system to  $H_2/O_2$ . When comparing the electrochemical activity of PtRuDy and PtU systems one can observe that PtRuDy system for the second polarization curve shows a degradation of 41.2% on 600 mV. This behavior is typical for all catalysts systems described in the literature. PtU system presents a totally different behavior than other catalysts systems PtU presents no degradation at all. Direct ethanol fuel cell are a long term possibility to avoid GHG emissions from transport system [19,20].

#### FINAL CONSIDERATIONS

Ethanol is an effective fuel for GHG emissions mitigations in transport systems.

The Bönemann method is an effective synthesis for the preparation of new catalyst systems for PEMFC, DMFC and DEFC. Nanocrystals with an average size of 2.0 nm highly dispersed and well distributed were obtained.

The PtRuMo system was the most effective system to oxidize  $H_2 - CO$  (150 ppm) and methanol.

For ethanol operation the most promising system is PtRuDy that presents electrochemical activity similar to Pt3Sn described in literature in term of Pt content.

PtU system presents a different behavior among all other catalysts showing no degradation after operating with ethanol and turning back to hydrogen again.

#### REFERENCES

- [1] Wendt, H.; Gotz, M. e Linardi M., 2000, Tecnologia de Células a Combustível. Química Nova, , **4**, 538-546.
- [2] Faltenbacher, M., 2000, Alternative Fuels for Fuel Cell Powered Buses Compared to Diesel powered Buses, University of Stuttgart, , SAE 2000-01-1484.
- [3] Franco, E. G.; Linardi, M.; Colosio, M. A.et al. *Fuel cells and ethanol: a technological advantage*. Células a Combustível e Etanol: Uma Vantagem Tecnológica. In: 12°. Congresso e Exposição

Internacionais de Tecnologia da Mobilidade, 2003, São Paulo. Anais do 12°. Congresso e Exposição Internacionais de Tecnologia da Mobilidade. Danvers, USA: Global Mobility Database, 2003. v. 1. p. 3623-3623.

[4] Souza, J.P.I.;Rabelo, F.J.B.; De Moraes, I.R.; Nart, F.C., 1997, Performance of a co-electrodeposited Pt-Ru electrode for the electro-oxidation of ethanol studied by in situ FTIR spectroscopy. J. Electroanal. Chem., **420**, 17-20.

[5] Ianniello R.; Schmidt V.M.; Rodrigues, J.L.; Pastor, E., 1999, Electrochemical surface reactions of intermediates formed in the oxidative ethanol adsorption on porous Pt and PtRu. J. Electroanal. Chem., **471**, 167-179.

[6] Fujiwara, N.; Friedrich, K.A.; Stimming, U., 1999, Ethanol oxidation on PtRu electrodes studied by differential electrochemical mass spectrometry. J. Electroanal. Chem., **472**, 120-125.

[7] Hitmi, H.; Belgsir, E.M.; Léger, J.M.; Lamy, C.; Lezna, R.O., 1994, A kinetic, analysis of the electrooxidation of ethanol at a platinum electrode in acid-medium. Electrochim. Acta, **39**, 407-15.

[8] Oliveira Neto, A.; Perez, J.; Napporn, W.T.; Ticianelli, E.A.; Gonzalez, E. R., 1999, 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, 83-6.

[9] Fujiwara, N.; Friedrich, K.A.; Stimming, U., 1999, Ethanol oxidation on PtRu electrodes studied by differential electrochemical mass spectrometry. J. Electroanal. Chem., **472**, 120-125.

[11] Oliveira Neto, A., Giz , M.J., Perez, J., Ticianelli, E.A. and Gonzalez, E.R., 2002, The Electro-oxidation of ethanol on Pt-Ru and Pt-Mo particles supported on high surface area carbon. J. Electrochem. Soc., **149**, A272-A279.

[12] Hable, C.T.; Wrighton, M.S., 1993, Electrocatalytic oxidation of methanol and ethanol: a comparison of platinum-tin and platinum-ruthenium catalyst in a conduction polyaniline matrix. Langmuir, **9**, 3284-90.

[13] Wang, J.; Wasmus, S.; Savinelli, R.F., 1995, Real-time mass-spectrometric investigation of the methanol oxidation in a direct methanol fuel cell. J. of Electrochem. Soc., **142**, 4218-24.

[14] Franco, E.G.; Linardi, M.; Aricó, E., 2001, Formulação de novos eletrocatalisadores pelo método de Bönemann para a oxidação da mistura  $H_2/CO$  e metanol em células PEM. Proceedings of the XII SIBEE Simpósio Brasileiro de Eletroquímica e Eletroanalítica, Gramado – RS – Brasil.

[15] Franco, E.G.; Aricó, E.; Linardi, M.; Roth, C.; Martz, N. and Fuess H.; 2001, Third International Latin-American Conference on Powder Technology, Nov, 26 to 28, Florianópolis, Brazil.

[16] Franco EG, Arico E, Linardi M, Roth C, Martz N, Fuess H; 2003, Synthesis and characterization of electrocatalyst powders for application in PEM fuel cells; Advanced Powder Technology III, Materials Science Forum; 416-4: 4-10.

[17] Spinacé, E.V., Oliveira Neto, A., Vasconcelos, T.R.R.; Linardi, M., Journal of Power Sources, v.137, p.17, (2004).

[18] Schmidt, T.J., Jusys, Z., Gasteiger, H.A., Behm, R.J., Endruschat, U., Boennemann, H., J. of Electroanalytical Chemistry, 501, (2001), 132-149.

[19] Franco, E. G.; Taioli, F.; Burani, G.F. et al.. Sustainable energy: hydrogen, ethanol and fuel cells. Abstracts and Proceedings UNINDU 2007. Perugia: Italy.

[20] FRANCO, E. G. ; Dantas Filho, P.L. ; BURANI, G.F. ; CARMO, M. ; LINARDI, Marcelo . PtU/C electrocatalysts for direct ethanol fuel cell. In: 2nd. European Fuel Cell Technology and Applications Conference, 2007, Roma. Proceedings of the 2nd. European Fuel Cell Technology and Applications Conference, 2007. v. 1. p. 237-238.