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Synthesis of Electrocatalysts by the Bönnemann Method for the Oxidation of Methanol and the Mixture H$_2$/CO in a Proton Exchange Membrane Fuel Cell

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Novas formulações de eletrocatalisadores ternários do tipo Pt/Ru/Mo foram desenvolvidas pelo método de Bönnemann e caracterizadas pelas técnicas de análise por energia dispersiva de raios X (EDX), difração de raios X (XRD), voltametria cíclica (CV) e curvas de polarização (E *vs.* i), para a oxidação de H$_2$, mistura H$_2$/CO e metanol em células a combustível tipo PEMFC. A estrutura dos catalisadores obtida é formada por nanocristais altamente dispersos na matriz de carbono, com 2 nm de tamanho médio da nanopartícula. Os resultados da voltametria cíclica sugerem um aumento considerável da eletroatividade do catalisador com a adição de cocatalisadores. A análise das curvas de polarização sugere que o catalisador ternário Pt/Ru/Mo pode ser interessante do ponto de vista tecnológico.

The synthesis of ternary electrocatalysts Pt/Ru/Mo type were performed according to the Bönnemann method and characterized by the following techniques: energy dispersive analysis (EDX), X-rays diffraction (XRD), cyclic voltammetry (CV) and polarization curves (E *vs.* i) for the oxidation of H$_2$, H$_2$/CO and methanol in a Proton Exchange Membrane Fuel Cell (PEMFC). Catalysts structure consists of highly dispersed nanocrystals in carbon support, with an average particle size of 2 nm. The results of cyclic voltammetry suggest an enhancement of the catalyst electroactivity with the addition of cocatalysts. Polarization curves indicate that Pt/Ru/Mo systems could be employed as electrode material for PEM fuel cell for technological application.

Keywords: electrocatalyst, fuel cell, methanol oxidation, reformate gas

Introduction

The study and development of new electrocatalysts aim an increase in the electrocatalytic activity for the oxidation of H$_2$/CO or methanol in Proton Exchange Membrane Fuel Cell (PEMFC). A great challenge in the oxidation of H$_2$/CO and methanol is the synthesis of proper new electrocatalysts in order to minimize catalyst contamination caused by CO adsorption.[1-3] Some binary and ternary electrocatalysts systems developed by different methods have been previously investigated. Grgur *et al.*[4] reported interesting results for the binary system Pt/Mo, while Frelink *et al.*[5] and Lee *et al.*[6] investigated Pt/Sn and Pt/Ru/W systems, respectively.

The Bönnemann method was selected for the doping of carbon black (electrode material) with the electrocatalysts system,[7] in a modified version,[8] consisting of a colloidal system in a dry nitrogen atmosphere, employing anhydrous solvents and metal salts.

Experimental

Bönnemann's method

This method consists in the production of a stable colloid in an inert and dry atmosphere using non-hydrated chlorides of the desirable metals and solvent.

The anhydrous salts were dissolved in anhydrous tetrahydrofuran (THF) with an appropriate amount of tetraoctylammonium bromide [N(oct)$_4$Br]. The reducing agent was produced by dissolving [N(oct)$_4$Br] in THF and adding [KHBr(Et)$_3$], resulting in the formation of a stark reducing agent, triethylhydroborate of tetraoctyl-ammonium [N(oct)$_4$HBr(Et)$_3$] according to equation 1:

$$N(oct)_4Br + KHB(Et)_3 \xrightarrow{THF} N(oct)_4HB(Et)_3 + KBr \quad (1)$$
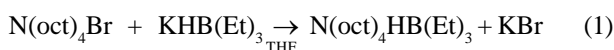
For the reduction of metallic ions, a 50% excess over the stoichiometric amount of [N(oct)$_4$HBr(Et)$_3$] is added to the solution of metal salts and heated under stirring.

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The reduction is followed by darkening and hydrogen evolution, as shown in the equation 2:

$$MeX_n + N(oct)_4HB(Et)_3 \xrightarrow{THF} Me*[N(oct)_4]^+ + nB(Et)_3 + n/2\ H_2 + nX^- \quad (2)$$
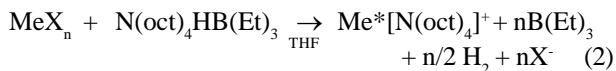
The colloid is formed by the adsorption of the ion $[N(oct)_4]^+$ on the metallic surface resulting in a stable particle with an average size from 1.5 to 3.0 nm. All of these steps were performed under an inert and dry atmosphere. In Figure 1 a schematic drawing of the stable colloid is shown.[7]
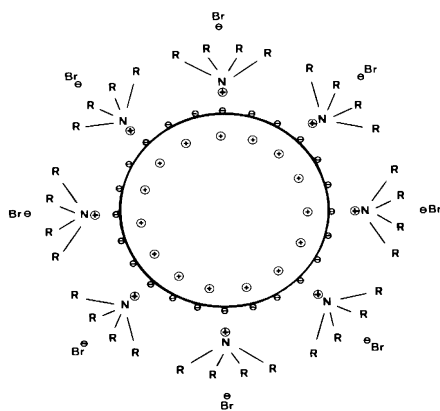

Figure 1. Schematic drawing of the stabilized colloid.[7]

After the synthesis of the stable colloid a suspension of carbon black in THF was prepared and the colloid solution is dropwise added to the carbon black solution, finishing the preparation of the powder catalyst with filtration and several washes with THF and ethanol.

Characterization of the electrocatalyst powder by EDX, XRD, HRTEM and XPS

X-ray powder diffraction was carried out on a STOE STADI-P powder diffractometer, with germanium monochromatized CuK_α radiation and a position-sensitive detector with 40° aperture in transmission mode.

A Philips CM 20 microscope 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 AlK_a radiation at a power of 300 W. A suitable pass energy of 11.75 eV was chosen, while a pressure of 3×10^{-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 investigations

The electrochemical investigations were performed by cyclic voltammetry (CV) and polarization curves (E *vs*. i).

Cyclic voltammetry was performed in a EGG Princeton Applied Research Model 273A in a 0.5 mol L^{-1} H_2SO_4 solution saturated with N_2. The evaluation of methanol oxidation was performed in three different concentrations of methanol: 0.1 mol L^{-1}, 0.5 mol L^{-1}, 1.0 mol L^{-1}, at 25°C. The working electrode was made of a thin porous layer of the catalysts with dispersed nanoparticles in a high surface area carbon black. The reference electrode was a RHE and the counter electrode was a platinized Pt plate. The electrocatalyst produced by the Bönnemann method usually remains with some adsorbed species that come from the protective shell formed around the colloid. These species block the active platinum sites. In spite of this, a thermal treatment with reducing atmosphere (H_2) could improve the electroactivity of the catalysts. Neto *et. al.*[9] showed that PtRuNi electrocatalyst prepared by the Bönnemann method and thermally treated presents higher electroactivity than the same catalysts without thermal treatment. Results obtained by cyclic voltammetry suggest the use of a thermal treatment for the catalyst. This thermal treatment was performed under hydrogen atmosphere for 2 h.

The preparation of membrane electrode assemblies (MEA) was carried out using the hot spray method developed by Wilson and Gottesfeld[10] and modified by Fischer *et al.*[11] According to this method an appropriate amount of ink was prepared for each electrode and sprayed onto an area of 25 cm^2 to yield a metal loading of 0.4 mg cm^{-2}. The MEA was fit into a commercially available graphite cell block from Electrochem® (USA) using teflonized carbon paper (Toray TGPR-090) as gas distributor on each electrode. For hydrogen operation, the anode gas was humidified at a temperature of 85 °C using a hydrogen flow of 150 mL min^{-1}. Feed gas at the cathode was dry oxygen (75 mL min^{-1}) at a cell temperature of 75 °C.

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

time for one MEA in a single cell test was 10 days. The catalytic activity of the system was measured and compared with a commercial catalyst from ETEK® (USA) by recording the polarization (E *vs.* i) curves.

Results and discussion

The high-resolution transmission electron microscope (HRTEM) was equipped with a nano-EDX device to perform analyses in small areas, with 10 nm of particle diameter corresponding to a few nanocrystals of the specimen, meaning that some variation of the nominal composition is expected. The results of nano-EDX are presented in Table 1.

Table 1. Nano-EDX analysis of the catalyst nanocrystals

Element	Pt/Ru/Mo (1/1/0.5) at. %	Pt/Ru/Mo (1/1/1) at. %
Pt	42.33	35.40
Ru	32.71	27.47
Mo	24.96	37.13

Nanocrystals with an average size of 2.0 nm appear in both catalysts higly dispersed on its carbon support. A HRTEM image is shown in Figure 2 for the Pt/Ru/Mo (1:1:0.5) catalyst and in Figure 3 for Pt/Ru/Mo (1:1:1). Both catalysts have nanocrystals diameters around 2 nm. These results are comparable to those reported for Pt/Ru,
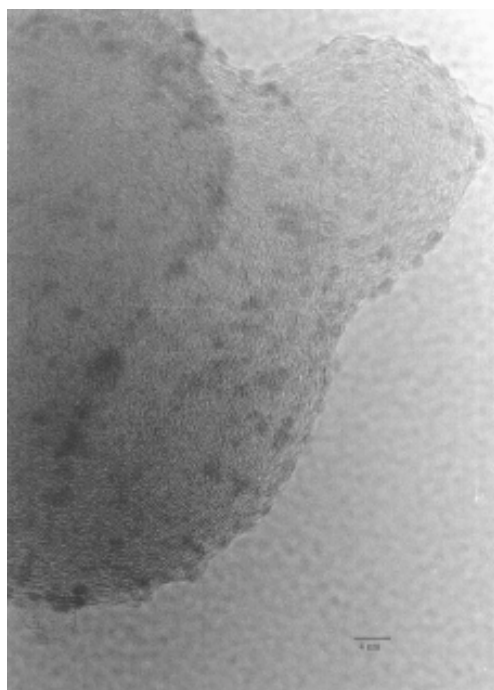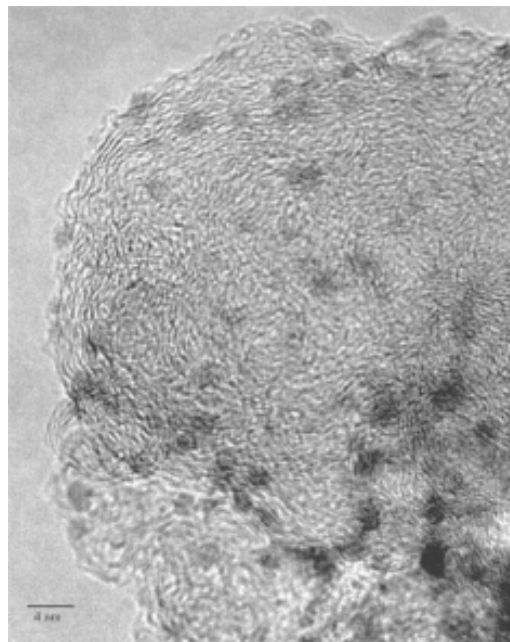

Figure 3. Nanoparticles of Pt/Ru/Mo (1:1:1) dispersed in carbon black.

by Schmidt *et al.*[12] The small increase in the average nanocrystals size is probably due to the addition of Mo.

The XRD measurements for both catalysts were similar and reveal the predominance of the carbon support response around $2\theta = 20°$, while the responses of Pt, Ru and Mo are difficult to find. Only the peaks ascribed to Pt could be resolved in the diffractogram, this occurs because most of the crystals formed are too small to be detected by XRD[13,14] or due to the formation of amorphous phases. The presence of Pt as indicated in Figure 4 for the Pt/Ru/Mo (1:1:0.5) was corroborated by the XPS measurements.

The XPS technique was used to investigate the chemical surface composition of the catalyst, because the improvement in the catalyst activity described by the bi-functional mechanism is strongly dependent on the surface of the catalyst and on the species adsorbed on it. Deconvolution of XPS measurements indicates the presence
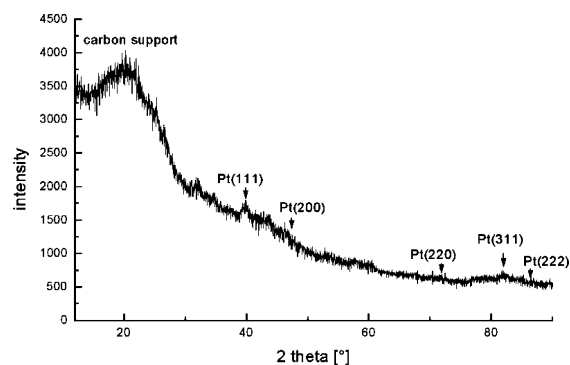

Figure 2. Nanoparticles of Pt/Ru/Mo (1:1:0.5) dispersed in carbon black.

Figure 4. Pt/Ru/Mo (1:1:0.5) X-ray diffractogram.

of two peaks for Pt 4f, one showing metallic platinum with a binding energy (BE) of 72.1 eV and other showing PtO_2 with a BE of 74.2 eV. These results are shown in Table 2. A shift in BE of Pt 4f to a higher value can be explained by the small particle size considered or by an alloy formation. Ruthenium deconvolution gives two peaks for Ru 3p, detected as oxide form RuO_2 for a BE of 463.1 eV and hydrous oxide form for a BE of 465.6 eV. Molybdenium deconvolution shows oxidized species for Mo 3d that are not so easy to ascribe to a specific compound.

Table 2. XPS results for Pt/Ru/Mo (1:1:1) catalyst

Element	Binding energy (eV)	State
Platinum	72.1	Pt
Pt 4f	74.2	PtO_2
Ruthenium	463.1	RuO_2
Ru 3p	465.6	RuO_2x H_2O

As one can see the results of XPS indicate that the cocatalysts chosen appear as oxygen-rich species that could facilitate the oxidation of adsorbed CO in the platinum sites.

The results of cyclic voltammetry experiments with the Pt/C and Pt/Ru/Mo/C electrocatalysts prepared by the Bönnemamm´s method, in the absence of methanol, are presented in Figure 5.
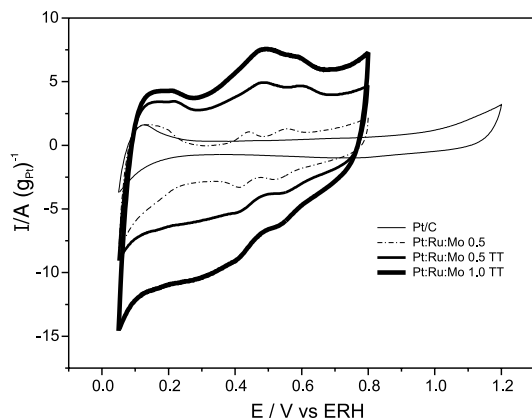

Figure 5. Cyclic voltammetry of the catalyst systems in 0.5 mol L^{-1} H_2SO_4 with a sweep rate of 10 mVs^{-1}.

In this figure an increase in the thickness of voltammetry is observed as the content of the second and third metals is increased. This phenomenon is related to oxygen species formation in the vicinity of Pt. Alloys with 50% of Ru do not have a very defined hydrogen oxidation region in the cyclic voltammetry, with a large capacity in the double layer region. When the concentration is reduced to 30% and 10% of Ru, the current on the double layer decreases and the hydrogen

region becomes similar to the Pt region. Gasteiger *et. al.* [15] believe that the differences in the voltammetry responses with Ru came from the formation of oxygen species. It is observed that the addition of ruthenium promotes oxide formation at potentials lower than 0.25 V. The Pt catalyst is not efficient to methanol electro-oxidation because it is quickly poisoned by intermediate species and by adsorbed CO (CO_{ads}). The oxygen species are formed at potentials of 0.8V for Pt catalyst lowering the power output of the fuel cell. A second chemical element is added to the Pt, for example Ru, to promote *oxygen-rich* species at lower potentials. The bifunctional mechanism explains how the addition of a second metal, like Ru, to the Pt catalyst that can adsorb oxygen species and lower the potential of the spill over mechanism, improves the performance of the catalyst in methanol and H_2/CO oxidation. The role of the cocatalyst is to offer oxygen species that could oxidize the CO adsorbed in the Pt sites into CO_2 improving the electroactivity of the catalyst.

The Pt/Ru optimum surface composition can be determined by the maximum probability of one ensemble of three Pt atoms that are necessary to adsorb methanol, connected to an adjacent Ru atom that can offer the oxygen atom to produce the oxidation of CO to CO_2.

The region of adsorption/desorption hydrogen (between 0.0 V and 0.4 V) is suppressed due to oxide formation at potentials lower than 0.25 V.[15]

The Pt/C electrocatalyst curve shows no peak in the hydrogen evolution region. This phenomenon suggests an electrocatalyst surface recovery by species of the reducing agent used in the Bönnemann's method. The catalysts were submitted to thermal treatment under hydrogen atmosphere. A peak next to 0.5 V is observed for Pt/Ru/Mo/C systems. This peak corresponds to a change in the oxidation state of Mo from IV to VI.[16]

Figure 6 shows cyclic voltammetry curves for Pt/Ru/Mo (1:1:0.5) electrocatalyst in presence of different concentrations of methanol, ranging from 0.1 to 1.0 mol L^{-1}.

An increase in the oxidation current by 0.8 V was observed, as methanol concentration increases.

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

Figures 7, 8 and 9 show results for, respectively, methanol oxidation in 0.1 mol L^{-1}, 0.5 mol L^{-1} and 1.0 mol L^{-1} solution by different electrocatalysts prepared by the Bönnemann's method.

At 0.5 V, a potential of great interest in fuel cell applications, the Pt/Ru/Mo TT (1:1:0.5) electrocatalyst in
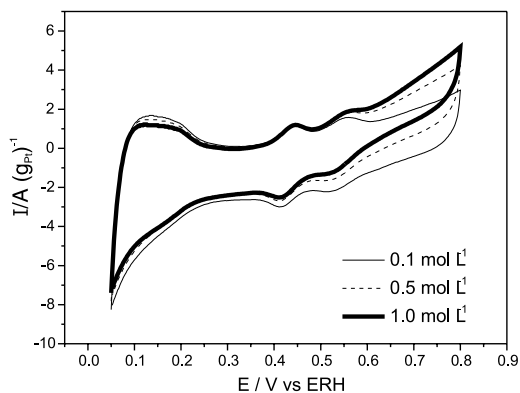
Figure 6. Cyclic voltammetry of the Pt/Ru/Mo (1:1:0,5) catalyst system in 0.5 mol L^{-1} H$_2$SO$_4$ with a sweep rate of 10 mVs^{-1} with different concentrations of methanol.
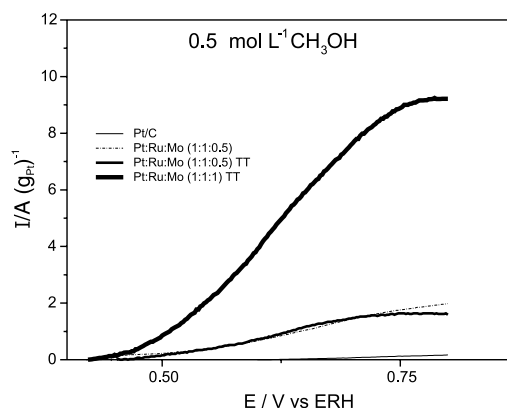

Figure 8. Cyclic voltammetry of the catalyst systems in 0.5 mol L^{-1} H$_2$SO$_4$ and 0.5 mol L^{-1} of methanol, with a sweep rate of 10 mVs^{-1}, considering only the anodic sweep.
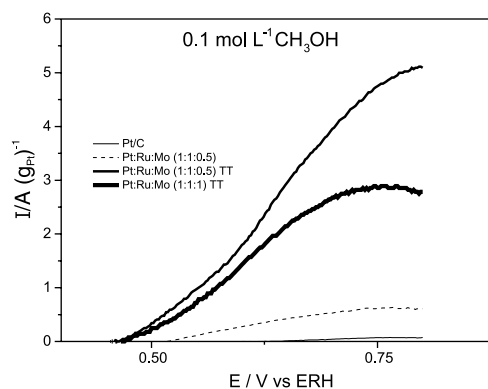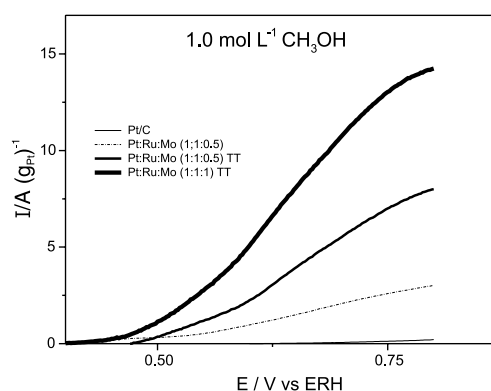

Figure 7. Cyclic voltammetry of the catalyst systems in 0.5 mol L^{-1} H$_2$SO$_4$ and 0.1 mol L^{-1} of methanol, with a sweep rate of 10 mVs^{-1}, considering only the anodic sweep.

Figure 9. Cyclic voltammetry of the catalyst systems in 0.5 mol L^{-1} H$_2$SO$_4$ and 1.0 mol L^{-1} of methanol, with a sweep rate of 10 mVs^{-1}, considering only the anodic sweep.

0.1 mol L^{-1} of methanol solution, presents larger currents compared to other electrocatalyst formulations. This observation indicates that Pt/Ru/Mo TT (1:1:0.5) is the best catalysts for methanol oxidation due to the fact that oxidation starts at lower potential.

Figure 8 and 9 present cyclic voltammetry results of methanol oxidation at 0.5 mol L^{-1} and 1.0 mol L^{-1}, at 25 °C.

Pt/Ru/Mo/C TT (1:1:1) showed the best activity at 0.5 V for both concentrations. Another very interesting observation is that current values, at 0.5 V both for methanol and ethanol are very similar, when using the Pt/Ru/Mo/C TT (1:1:1) formulation.[9]

The oxidation of the mixture H$_2$/CO with 150 ppm of CO was analyzed by cyclic voltammetry and the results obtained for Pt/C and PtRuMo/C are presented in the Figures 10, 11 and 12.

In Figure 11 one can note that for all the potentials in the anodic sweep the current for the PtRuMo catalyst was higher than the ones obtained for Pt catalyst, hence we can conclude that PtRuMo catalyst has a higher electroactivity.
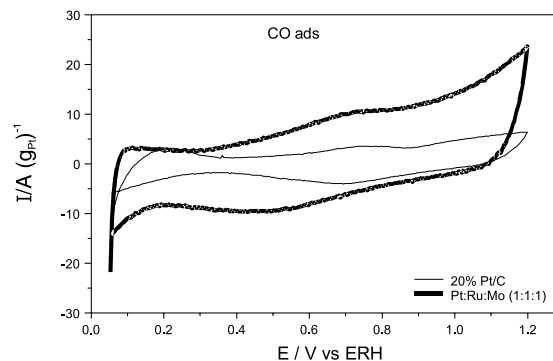

Figure 10. Cyclic voltammetry of the catalyst systems in 0.5 mol L^{-1} H$_2$SO$_4$ and mixture H$_2$/CO 150 ppm with a sweep rate of 10 mVs^{-1}.

The polarization curves for Pt/Ru/Mo (1:1:0.5) operating with H$_2$ and methanol in a single PEM fuel cell are presented in Figures 12 and 13.

The catalysts prepared by the Bönnemann method showed to be promising for future technological applications in direct methanol fuel cells.
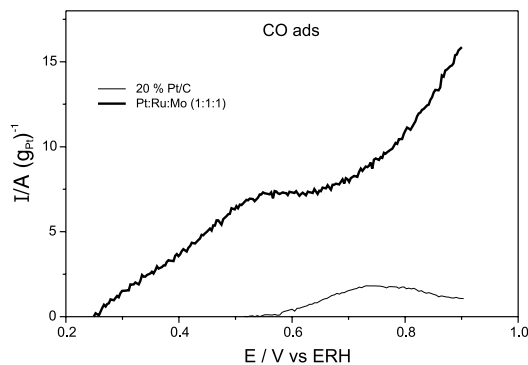
Figure 11. Cyclic voltammetry of the catalysts systems in 0.5 mol L^{-1} H$_2$SO$_4$ and mixture H$_2$/CO (150 ppm of CO) with a sweep rate of 10 mVs^{-1}, considering only the anodic sweep.
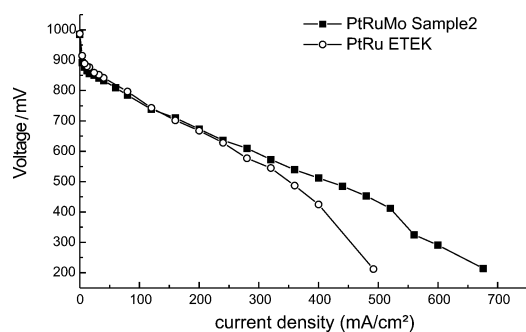

Figure 12. Polarization curves for: PtRuMo (1:1:0.5) and Pt/Ru (1:1) ETEK with pure hydrogen.
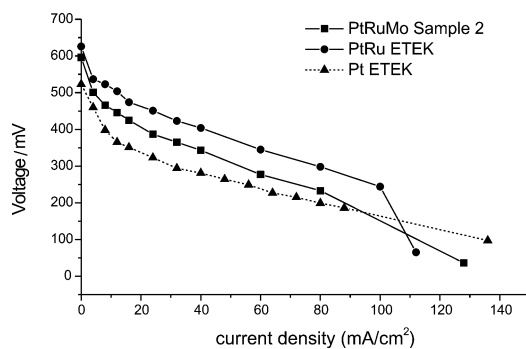

Figure 13. Polarization curves for: PtRuMo (1:1:0.5), Pt/Ru (1:1) ETEK and Pt ETEK with 1.0 mol L^{-1} methanol solution.

Conclusions

Bönnemann method appeared to be appropriate for the dopping of ternary electrocatalysts systems, aiming the production of MEA for PEM type fuel cells, according to the results obtained by the characterization methods employed.

The energy dispersive analysis (EDX) results of the catalysts are in good agreement with the method limitations.

The catalysts structure consists of highly dispersed nanocrystals in carbon support, with average size of 2 nm, verified by the HRTEM images and X-ray diffraction.

XPS measurements indicate that the catalyst surface is composed by Pt alloy, and oxides and hydroxides of the metals employed.

The results of cyclic voltammetry suggest a considerable enhancement of the catalyst electroactivity with the addition of cocatalysts.

Polarization curves indicate that Pt/Ru/Mo systems could be employed as electrode material for PEM fuel cell. The system Pt/Ru/Mo TT, submitted to thermal treatment, showed to be very promising for technological application.

Acknowledgments

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