

Catalysts for fuel cell: Production and characterization

CATALISADORES PARA CÉLULAS A COMBUSTÍVEL: PRODUÇÃO E CARACTERIZAÇÃO

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ABSTRACT

Fuel cells technology is one of the most promising technologies for this century to deal with energy sustainability. In order to improve fuel cells performances the search for new electrocatalysts has a great importance in this technology. The colloidal method was chosen to produce the catalysts because a good nanocrystal distribution can be obtained. This method consists in the production of a stable colloid that will be anchored in the support (carbon black Vulcan XC 72 R). The catalysts were investigated by the following techniques: energy dispersive analysis (EDX), X-rays powder diffraction (XRD), X-rays photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM) and polarization curves (Exi). The binary and ternary catalysts systems synthesized in this work were tested for the oxidation of hydrogen, H₂/CO mixtures (150 ppm of CO), methanol and ethanol. The catalyst systems produced by the colloidal method presents a highly-dispersed nanocrystals structure with an average size of 2.0 to 3.1 nm. The electrocatalytic activity of the synthesized Pt-Ru-Mo catalysts for reformat and methanol oxidation was evidenced by polarization curves showing a very promising system to be optimized. PtRuDy behavior is compared to state of the art catalysts for direct ethanol fuel cells (DEFC) and should be tested in long term experiments in direct ethanol fuel cells. Only both structural and electrochemical characterization together will result in a detailed understanding of the effect of the structure on the electrocatalytic activity of catalysts in real fuel cell systems. This work is part of a systematic research of the fuel cell group of IPEN/CNEN-SP and further investigations in the performance of these catalysts will be done. The PtRuMo system could be used for technical applications.

KEYWORDS

Fuel cell. Oxidation. Hydrogen. Methanol. Ethanol.

RESUMO

A tecnologia de células a combustível é uma das mais promissoras para a geração de energia sustentável para este novo século. O desenvolvimento e estudo de novos eletrocatalisadores, que devem aumentar o desempenho destas células, é de grande importância nesta tecnologia. O método coloidal foi escolhido para a produção de catalisadores devido à excelente distribuição de nanocristais que pode ser obtida com esse processo. Esse método consiste na produção de um colóide estável que é ancorado num suporte (negro de fumo Vulcan XC 72R). As seguintes técnicas foram utilizadas na caracterização dos catalisadores produzidos: EDX, XRD, XPS, SEM, HRTEM e curvas de polarização. Os sistemas de catalisadores binários e ternários sintetizados neste trabalho foram testados para a oxidação da mistura H₂/CO (150 ppm de CO), metanol e etanol. Os sistemas produzidos pelo método coloidal apresentaram estrutura de nanocristais altamente dispersos, com um tamanho médio de partícula de 2,0 a 3,1 nm. A atividade eletrocatalítica do sistema Pt-Ru-Mo para a oxidação da mistura H₂/CO e metanol foi evidenciada pelas curvas de polarização, mostrando ser um sistema bastante promissor a ser otimizado. O comportamento do sistema Pt-Ru-Dy é comparável ao estado da arte de catalisadores para células a combustível e etanol direto (DEFC) e deve ser testado em experimentos de longa duração. Somente as caracterizações estrutural e eletroquímica dos sistemas resultam numa compreensão detalhada dos efeitos da estrutura sobre a eletroatividade do catalisador nas condições reais de uma célula a combustível. Este trabalho é parte de uma investigação sistemática do Grupo de Células a Combustível do IPEN/CNEN-SP, que

continua atuando nesta atividade. O sistema Pt-Ru-Mo é promissor para aplicações técnicas.

PALAVRAS CHAVE

Oxidação. Hidrogênio. Metanol. Etanol.

INTRODUCTION

The demand for energy has increased since the industrial revolution, but in the last two decades environmental issues are playing an important role in the development of new technologies to generate electricity.

The growth of greenhouse gas emissions by the internal combustion engine and the raising demand of electricity has multiplied the interest in fuel cell technologies for mobile and stationary applications. In this context, proton exchange membrane fuel cell has been quoted as the most promising technology to substitute the internal combustion engine and a valuable decentralized power plant for the electricity generation (Linardi; Arico; Franco, 2001). A great challenge for this technology relies on the choice of the fuel, that could be hydrogen, reformat gas, methanol and ethanol (Gonzalez, 2000). The development of new electro-catalysts systems for each choice of fuel becomes an important issue to be solved. While for pure hydrogen systems, the state of the art is well established, platinum is the catalyst of choice for both anode and cathode. Therefore, for other systems, we should develop new catalysts systems that presents lower contamination by adsorbed CO, while operating with reformat gas, methanol and ethanol.

The synthesis of new electro-catalysts systems has been researched by different authors, and in this paper we pointed out some of these researches. Janssen and Moolhuysen (1976) investigated different elements as co-catalysts for Pt aiming to improve the oxidation of methanol. In this work the elements investigated were: Ru, Os, Re, V, Ge, Hg, As, Sb, Te, Nb, Dy, U, Sn, Mo, Ti, Pb, Se. The binary systems PtRu (Watanabe, 1975; Gasteiger, 1993, 1994 a, 1994 b, 1995; Schmidt, 1998, 1999; Friedrich, 1996), PtMo (Grgur, 1998, 1999; Santiago, 2003, 2004) and PtSn (Bittins-Cattaneo, 1987; Wang, 1996) were the most interesting systems reviewed in the literature. For this work we chose the ternary systems PtRuMo and PtRuDy to investigate the oxidation of different fuels.

The colloidal method was chosen to produce the electrocatalyst in spite of the good particle size and

distribution (Roth, 2001). The structural characterization of the new electrocatalysts were performed by the following techniques: X-ray fluorescence analysis (XFA), nanosize energy-dispersive analysis (nano-EDX), X-ray diffraction (XRD), X-ray photoelectron microscopy (XPS), high resolution transmission electron microscopy (HRTEM) and for the electrochemical characterization were performed the polarization curves.

EXPERIMENTAL PROCEDURE

PRODUCTION OF THE ELECTROCATALYST BY THE COLLOIDAL METHOD

The colloidal method or the Bönemann method consists in the production of a stable metallic colloid with nanocrystals. Schmidt (1998) found for the PtRu system nanocrystals with a mean average diameter of 1.7 ± 0.5 nm. The synthesis of the catalysts was performed by a little modification in the colloidal method, in a dry nitrogen atmosphere using dry solvents and non-hydrated salts as the precursors of the catalyst described by Franco (2003a).

The first step is the production of the reducing agent responsible for the reduction of the salts, this agent was done by mixing stoichiometric amounts of 0.5 M solution of tetraoctylammonium bromide in THF and a 0.5 M solution of potassium triethylhydroborate in THF forming a 0,25 M solution of tetraoctylammoniumtriethyl hydroborate and a precipitated of KBr. The KBr is separated from the solution by filtration. The non-hydrated metal salts were dissolved in tetrahydrofurane (THF) with an appropriate amount of tetraoctylammonium bromide, and the reducing agent solution was dropwised to the stirred suspension of the metal salts at 40°C. After stirring, a solution of the carbon support (Vulcan XC-72R) in THF was prepared and the colloidal solution was slowly added to a stirred suspension of the carbon support, followed by filtration.

CHARACTERIZATION OF THE ELECTROCATALYST 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 CuK_α radiation and a position-sensitive detector with 40° 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 AlK_{α} 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.

PREPARATION OF THE MEMBRANE ELECTRODE ASSEMBLY (MEA)

The preparation of membrane electrode assemblies (MEAs) were performed according to the hybrid method developed by Linardi (2003).

ELECTROCHEMICAL INVESTIGATION IN SINGLE CELLS

For hydro-gen operation, the anode gas was humidified by passing it through water at a temperature of 85°C. The cell temperature was 65°C and cathode gas was dry oxygen.

For methanol and ethanol operation a 1.0 mol L⁻¹ aqueous solution of the alcohol was fed into the cell. The flow rate of the liquid solution was 1 mL/min, the cell temperature was 95°C and cathode gas was dry oxygen. The catalytic activity of the systems were evaluated by comparing the polarization curves ($i \times V$).

RESULTS

A detailed characterization of the PtRuMo and PtRuDy electrocatalysts should cover chemical analysis (bulk composition of the catalyst was checked by XFA and nano-EDX), structural and electrochemical characterization.

X-RAYS FLUORESCENCE ANALYSIS (XFA)

The noble metal loading and stoichiometry were verified by XFA measurements (Franco 2002) and the

results presented in Table 1. The figures were suitable according to the stoichiometric amounts employed for the synthesis.

Table 1 - Metal loading and molar composition of noble metals by XFA

System	C	Pt	2 nd Metal	3 rd Metal
PtRuMo (at%)		42.3	32.8	24.9
PtRuMo (wt%)	87.9	4.4	1.8	1.3
PtRuDy (at %)		58.7	22.5	18.8
PtRuDy (wt %)	84.7	10.4	2.1	2.8

NANOSIZE-ENERGY DISPERSIVE X-RAYS ANALYSIS

The transmission electron microscope is equipped with a nano-EDX device to perform analyses in small areas of the specimen in order to verify the stoichiometry of the nanocrystals. Table 2 shows The composition of the nanocrystals for the catalyst Pt-Ru-Mo.

Table 2 - Nano-EDX analysis of the catalyst PtRuMo

Element	PtRuMo	
	wt%	at%
Pt	49	32
Ru	25	33
Mo	26	35

SCANNING ELECTRON MICROSCOPY (SEM)

The powder morphology revealed by SEM (Figure 1) presents agglomerates with a medium size of 50 nm. It was not possible to identify the nanoparticles on the carbon support, due to the resolution limit in conventional SEM. Figure 2 shows the triple reactional interface of an MEA. By the hybrid process a micropore structure is produced facilitating the diffusion of educts and products during the reaction. Anode and cathode side of the MEA exhibit the same structure, as can be seen in Figure 3.

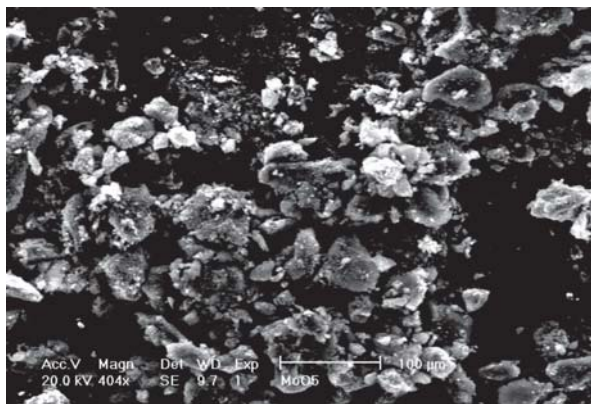


Figure 1 - SEM micrograph of the Pt-Ru-Mo catalyst

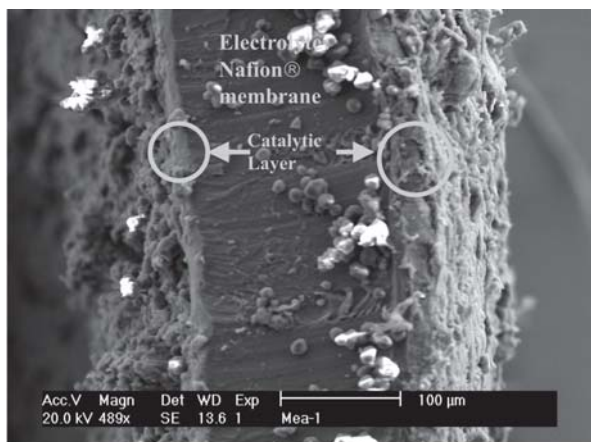


Figure 2 - MEA with anode and cathode thickness of 20 μm

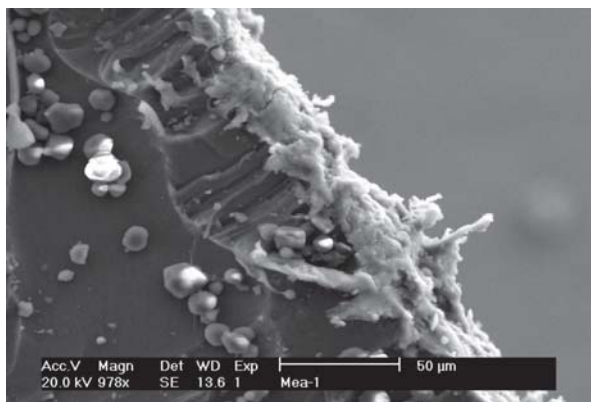


Figure 3 - Anode structure of the MEA similar to the cathode structure

HIGH RESOLUTION TRANSMISSION ELECTRON MICROSCOPY (HRTEM)

Nanocrystallites with an average diameter of approximately 2.0 nm are displayed in Figure 4. The catalytic active particles are highly-dispersed on the support grains for both samples. In comparison with

the results for PtRu published by Schmidt (1998) slightly bigger particle sizes were found, probably due to the addition of the third element.

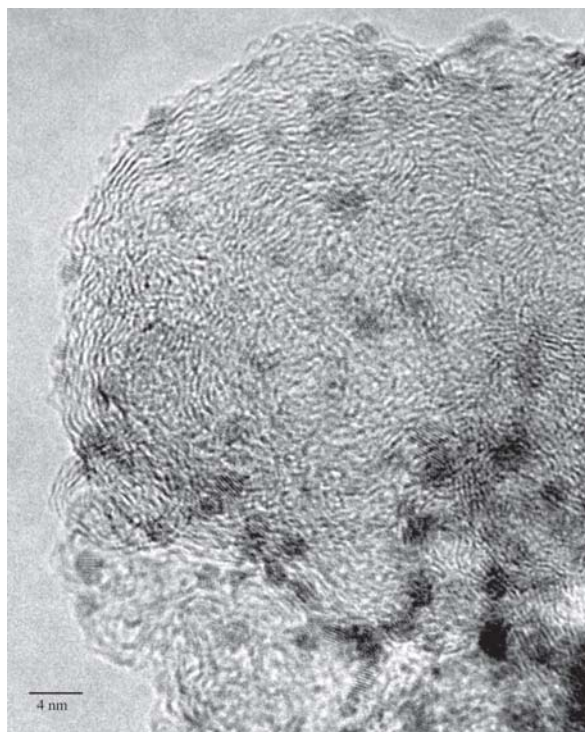


Figure 5: HRTEM images of the Pt-Ru-Mo catalysts: crystallite size = 2.0 + 0.5nm

X-RAYS DIFFRACTION (XRD)

The diffractograms of the ternary catalysts PtRuMo and PtRuDy are showed in Figure 6 and 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. Almost complete reduction of the educts was achieved, as no reflections of any metal chlorides appear in the patterns. The size of the nanocrystals were also evaluated by Scherer equation using Pt(220) reflection to evaluate it. The average nanocrystals size for PtRuMo was 2.2 nm and for PtRuDy 3.1 nm.

X-RAYS PHOTOELECTRON SPECTROSCOPY (XPS)

The surface composition of the catalysts was investigated by X-rays photoelectron spectroscopy (Igarashi, 2001 and Franco 2003b). As the particles are very small, the approximation of obtaining nearly bulk information can be made. The results of the measurements are presented in Table 3. For the 4f signal of platinum two binding energies (BE) can be obtained corresponding to metallic platinum and a Pt

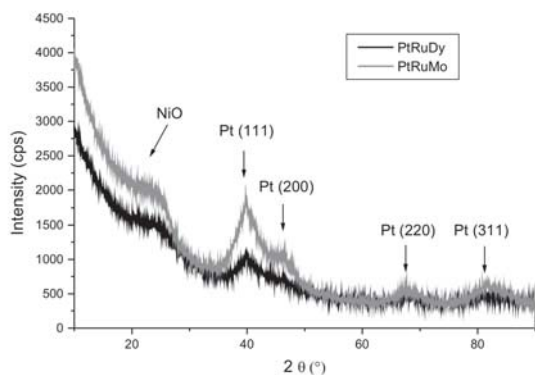


Figure 6 - Diffractograms of the ternary catalysts PtRuMo and PtRuDy

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 and dysprosium 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.

Table 3 - XPS measurements of PtRuMo

Element	Binding energy (eV)	State
Platinum Pt 4f	72.1	Pt
	74.2	PtO ₂
Ruthenium Ru 3p	463.1	RuO ₂
	465.6	RuO ₂ ·x H ₂ O
Molybdenum Mo 3d5/2	232.1	(NH ₄) ₄ MoO ₄
	232.8	MoO ₃
Dysprosium Dy 4d	168	Dy ₂ O ₃

POLARIZATION CURVES (E/i)

The MEAs were operated in a fuel cell system with 25 cm² active electrode area first with pure hydrogen, then with (H₂,CO) mixture to simulate reformat gas and afterwards with methanol and ethanol 1.0 mol L⁻¹. Both ternary catalysts shows a decrease of the CO-sensitivity compared with pure Pt catalysts. In accordance with Lasch, Jorssen e Gorce (1999) it was found that ternary catalysts are able to sustain higher current densities than the binary ones, as can be seen in Fig. 7 and 8. In Fig 9 and 10 one can see the polarization curves recorded for the catalysts systems

produced. In Fig 9 the performance of the catalysts were tested in a Direct Methanol Fuel Cell (DMFC) while in Fig. 10 the catalysts were tested in a Direct Ethanol Fuel Cell (DEFC).

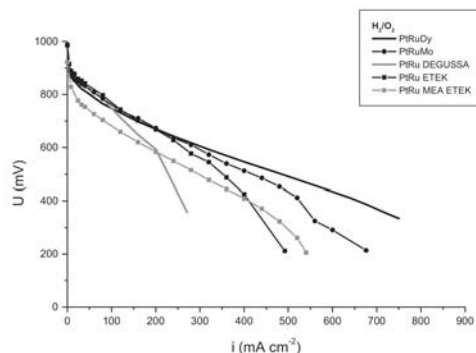


Figure 7 - Polarization curves for PtRuMo and PtRu ETEK with pure hydrogen

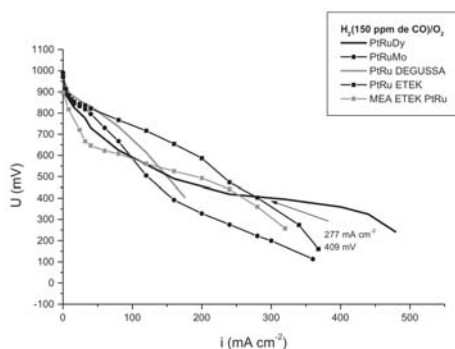


Figure 8 - Polarization curves for with reformat gas (H₂,CO - 150 ppm of CO/O₂)

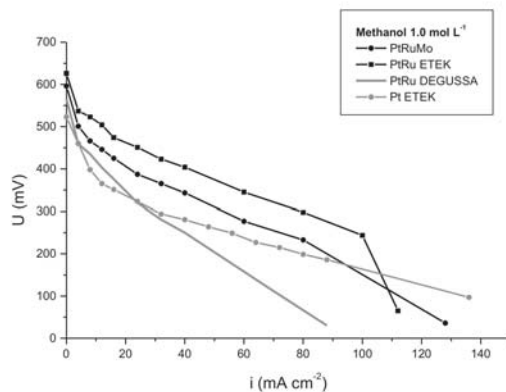


Figure 9 - Polarization curves for with methanol 1.0 mol L⁻¹

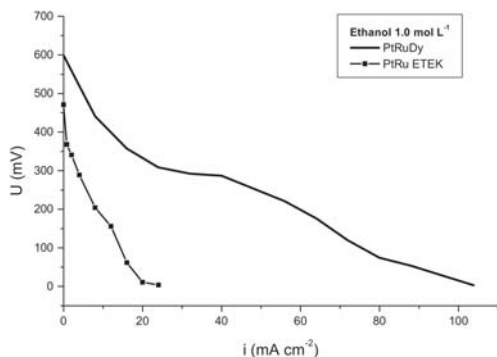


Figure 10 - Polarization curves for with ethanol 1.0 mol L⁻¹

According to Fig. 7, 8, 9 and 10 one can conclude that the performance of the ternary systems with (H₂, CO) mixtures, methanol is similar to the commercial Pt-Ru catalyst (E-TEK inc.) and they could be used as commercial catalysts. For ethanol oxidation the ternary system PtRuDy is more electroactive than the PtRu ETEK commercial catalyst. In Fig. 11 PtRuDy catalyst is compared to other catalysts developed for ethanol oxidation, when operating in a Direct Ethanol Fuel Cell (DEFC). The catalyst system compared to PtRuDy is PtSn₃ developed by Lamy (2004), Jiang (2004) and Song (2004).

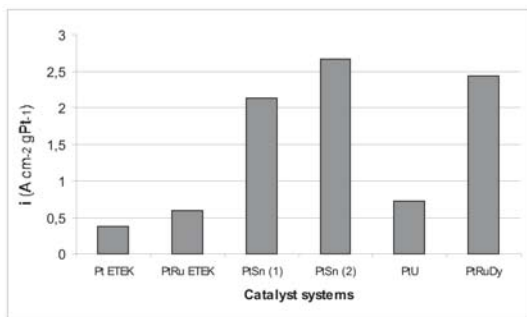


Figure 11 - Electro-oxidation of ethanol 1.0 mol L⁻¹ at 300 mV for different catalysts systems

CONCLUSION

The colloidal method is an effective synthesis for the preparation of new catalyst systems for PEMFC, DMFC and DEFC. Highly-dispersed nanocrystals with an average size of 2.0 to 3.1 nm were obtained and characterized in detail by spectroscopy, microscopy and diffraction in the present work.

Scanning electron microscopy (SEM), nanosize-energy dispersive analysis (nano-EDX), X-rays fluorescence analysis (XFA), X-rays diffraction (XRD), X-rays photoelectron spectroscopy (XPS) and high

resolution transmission electron microscopy (HRTEM) were used for the structural characterization of the ternary catalyst systems. Only both structural and electrochemical characterization together will result in a detailed understanding of the effect of the structure on the electrocatalytic activity of catalysts in real fuel cell systems.

The electrocatalytic activity of the synthesized Pt-Ru-Mo catalysts for reformate and methanol oxidation was evidenced by polarization curves showing a very promising system to be optimized. PtRuDy behavior is compared to state of the art catalysts for direct ethanol fuel cells (DEFC) and should be tested in long term experiments in direct ethanol fuel cells.

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