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Effect of decreasing platinum amount in Pt–Sn–Ni alloys supported on carbon as electrocatalysts for ethanol electrooxidation

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ABSTRACT

Literature describes the influence of morphological and structural electrocatalysts characteristics, on the catalytic activity toward ethanol electrooxidation. Thus, in this work Pt and ternary Pt–Sn–Ni alloys nanoparticles, supported on Vulcan carbon, were obtained by impregnation/reduction method. The aim of this work was to evaluate the influence of the decrease of platinum and increase of nickel content of the electrocatalysts obtained. The electrocatalysts were characterized by Rutherford backscattering spectroscopy, X-ray diffraction, transmission electronic microscopy, cyclic voltammetry and electrochemical impedance spectroscopy. The results obtained showed that it was possible to obtain Pt–Sn–Ni nanoparticles with a uniform size distribution in a narrow particle size range with a composition control. Moreover, the simultaneous addition of Sn and Ni to Pt did not affect reticular lattice *a* value, but the crystallite size decreases significantly. Besides, electrochemical results suggest that the substitution of platinum by nickel, in the electrocatalyst alloys studied, does not compromise the catalytic activity toward ethanol electrooxidation.

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1. Introduction

Fuel cells have been considered as a technology of clean energy production regardless of the kind of cell. The success between these systems is related to different factors as

electrochemistry combustion efficiency in opposite to chemistry combustion efficiency [1,2]. In the meanings of stability and efficiency of proton exchange membrane fuel cells (PEMFCs), it is necessary to control the influences of various operational parameters as well as the use of high activity

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catalysts [3]. In this way, platinum supported on carbon Vulcan is considered the state of the art in the meanings of catalyses [4,5]. However, when impure hydrogen, methanol or ethanol are used as fuel, a lot of impurities, mainly reaction products, are incorporated into the system, contaminating the catalyst [6].

Among PEMFCs, it is necessary to take account that the ethanol used as fuel has some advantages over hydrogen. Ethanol is a liquid at room temperature, which facilitates the transport and storage when compared to pure hydrogen [7,8].

Alcohol and, mainly methanol [9], have been widely proposed as possible fuels for applications in mobile fuel cells employed in electric vehicles. The direct methanol oxidation has been widely investigated. However, the toxicity of methanol is still a crucial question. Methanol is considered toxic [10], besides it can cause environmental problems due its high miscibility in water. In this way, ethanol is an attractive alternative [11] as fuel for low temperature fuel cells because it can be produced in large scale from agricultural products and it is the biggest renewable source from biomass fermentation. These reasons motivated the electric development of direct ethanol fuel cells (DEFCs).

Ethanol is a molecule with a C–C bond, hard to be broken [12], and its complete oxidation pass through a complex mechanism, involving 12 electrons and many adsorbed intermediates [10]. Moreover, DEFCs operate at low temperature ranges, which makes ethanol oxidation slower. Thus, it is necessary to use electrocatalysts to accelerate this reaction.

Platinum supported on carbon is commonly used as anode catalyst in low temperature fuel cell. Since the catalysis process is a superficial effect, it is necessary that the catalyst has the highest superficial area as possible. Thus, the active phase is dispersed on a conductive support as carbon. Nevertheless, pure platinum is not the most effective catalyst to DEFCs, it is known to be rapidly poisoned on its surface by strongly adsorbed species coming from the dissociative adsorption of ethanol [13]. Efforts to mitigate the poisoning of Pt have been concentrated on the addition of co-catalysts to platinum, particularly constituted of tin to ethanol electrooxidation (EOR) [13].

Two mechanisms have been proposed to superior performance of binary and ternary platinum based electrocatalysts: bifunctional effect (promoted mechanism) and the electronic interaction among Pt and other metals (intrinsic mechanism) [13]. According to the promoted mechanism, the oxidation of strongly adsorbed species containing oxygen is facilitated in the presence of tin oxides by providing oxygen atoms in adjacent sites in a lowest potential than pure platinum. The intrinsic mechanism postulates that the presence of tin modifies the electronic structure of platinum and, as a consequence, the adsorption of species containing oxygen [13].

Spinacé et al. [14] studied the ethanol electrooxidation with a ternary electrocatalyst PtSnNi/C and they verified that the substitution of a little part of tin by nickel increased considerably the current values related to a PtSn/C electrocatalyst.

Literature also describes the importance in studying morphological and structural electrocatalysts characteristics. Jiang et al. [15] synthesized platinum based catalysts with the intent to produce reduced tin, alloyed with platinum, and tin oxides, recovered by platinum. They verified that catalysts

containing tin oxides (tin non-alloyed) could improve catalytic activity through ethanol electrooxidation, because it can provide oxygen containing species that react with intermediate species. However, Sn alloyed to Pt causes a favorable dilatation of crystal lattice, improving the ethanol electrooxidation.

One of the easiest and fastest routes to obtain the catalysts is the impregnation/reduction method. This method consists in reducing platinum and other metals simultaneously by a reducing agent, at high temperatures, and deposition (impregnation) of particles on a high surface material, as carbon. Ethylene glycol used as a reducing agent is known to produce nanoparticles of noble metals [16].

Inside this context, the present work aims to study PtSnNi/C catalysts, with different metals compositions, with the intent to correlate the composition with electrochemical results. Thus, it was synthesized PtSnNi nanoparticles supported on Vulcan carbon, through impregnation/reduction method, using ethylene glycol as a reducing agent. The characterization techniques used were Rutherford backscattering spectroscopy (RBS), X-ray diffraction (XRD), transmission electronic microscopy (TEM), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS).

2. Experimental

2.1. Electrocatalysts preparation

To obtain the PtSnNi alloys supported on carbon, the impregnation/reduction method was used [17]. Ethylene glycol was used as a reduction agent and carbon Vulcan XC72R as support. Initially, a solution containing the salts $H_2PtCl_6 \cdot 6H_2O$, $SnCl_2 \cdot 2H_2O$ and $NiCl_2$ was prepared (with a metal charge of 40 wt%) in ethylene glycol and water (75/25 v/v), followed by carbon addition and agitation in ultrasonic bath to the dissolution of the salts. The composition of the alloys was modified, varying the atomic proportion among Pt, Sn and Ni, added as salts mentioned above. Pure platinum and PtSn/C alloys with the same Pt/Sn ratio present in ternary alloys were also synthesized aiming to compare catalytic activity toward ethanol electrooxidation. The compositions are described in Table 1. The pH solution was adjusted in alkaline range (about pH 12) and heated at 130 °C, under agitation to enable the metals reduction. The samples passed through a centrifugation process and, after that, they were dried. The samples obtained were analyzed by Rutherford backscattering spectrometry (RBS), X-ray diffraction (XRD),

Table 1 – Composition of the synthesized alloys.

Alloy	Nominal composition (%)	Pt/Sn ratio	Pt/Ni ratio
Pt/C	Pt 100	–	–
PtSnNi/C – A	Pt–Sn–Ni 75:15:10	5	7.5
PtSnNi/C – B	Pt–Sn–Ni 55:17:28	3	2
PtSn/C – C	Pt–Sn–Ni 83:17	5	–
PtSn/C – C	Pt–Sn–Ni 77:23	3	–

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