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# On the design of Pt-Sn efficient catalyst for carbon monoxide and ethanol oxidation in acid and alkaline media

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## ABSTRACT

Pt-Sn catalysts supported on carbon, with different Pt-Sn atomic ratios (3:1, 1:1, 1:3), were prepared through the formic acid method (FAM) and supported on different carbon supports (nanofibers and carbon blacks) to study their behavior toward CO stripping and ethanol oxidation reaction (EOR). PtSn/C catalysts and supports were physicochemically characterized by XRD, EDX, XPS, TEM and TPD. Good particle dispersion onto the carbon support, similar particle sizes (around 4–5 nm) and the presence of tin oxides were observed in all cases. Sn insertion favored the development of the $Pt_3Sn_1$ phase and the presence of higher oxidation states of both metals in the catalyst. Ethanol and adsorbed CO oxidation were studied at these materials both in acid and alkaline media, by linear sweep voltammetry and chronoamperometry. Higher EOR current densities were obtained with the increase in the amount of Sn in the samples, been those materials supported on CNF the ones with the best CO tolerance and catalytic activity toward this reaction. As expected, a great improvement of the EOR activity was found in alkaline media compared to sulfuric acid media, providing good expectative for these materials as catalysts for alkaline direct ethanol fuel cells.

## 1. Introduction

Nowadays, the importance of finding alternatives to petroleum is a worldwide concern, as oil extraction is costly and environmentally damaging, the burn of hydrocarbons releases carbon dioxide to the atmosphere, contributing to the global warming, and oil reserves are becoming scarce. Hydrogen used as an energy vector is the simplest and most efficient way to convert energy, but the required infrastructure is yet limited mainly due to the production costs and storage difficulties.

One good alternative to hydrogen is the use of small organic molecules containing hydrogen atoms (methanol, ethanol, formic acid, etc.) directly as a fuel in low temperature fuel cells. Ethanol presents several advantages: it can be obtained from the fermentation of biomass in large quantities (renewable), it is not toxic like methanol and has a high energy density [1,2]. The catalytic activity of Pt for the electrooxidation of hydrogen is very satisfactory but, when electrooxidizing ethanol, the use of Pt as electrode entails some disadvantages. Among them, its low selectivity to the complete oxidation of ethanol to $CO_2$ leads to low fuel efficiency and, thus, low power densities when compared for example to methanol even if the former has a higher theoretical energy density. Actually, the main ethanol electrooxidation products are acetic acid and acetaldehyde [3–5]. Pt needs high overpotentials to break the C—C bond from ethanol, forming some adsorbed C2 species in addition to CO-like intermediates which also need high overpotentials to be oxidized [6–8]. As a consequence, a fast Pt surface poisoning takes place, resulting in low ethanol oxidation reaction (EOR) currents.

Pt-Sn catalysts are currently considered the best binary formulation toward EOR. The properties of Pt-Sn/C catalysts have been extensively investigated for their application as anode materials for direct ethanol fuel cells (DEFCs) in the last years. Tsiakaras et al. studied the influence of Pt-Sn composition on the ethanol oxidation reaction, with metallic ratios ranging from $Pt_1Sn_1$ to $Pt_4Sn_1$ catalysts that were prepared by reduction with ethylene glycol [9]. They showed that the maximum power density obtained in a DEFC exhibits a "volcano-type" behavior with the Sn content in the catalyst. The apex of the volcano was attributed to an interplay of

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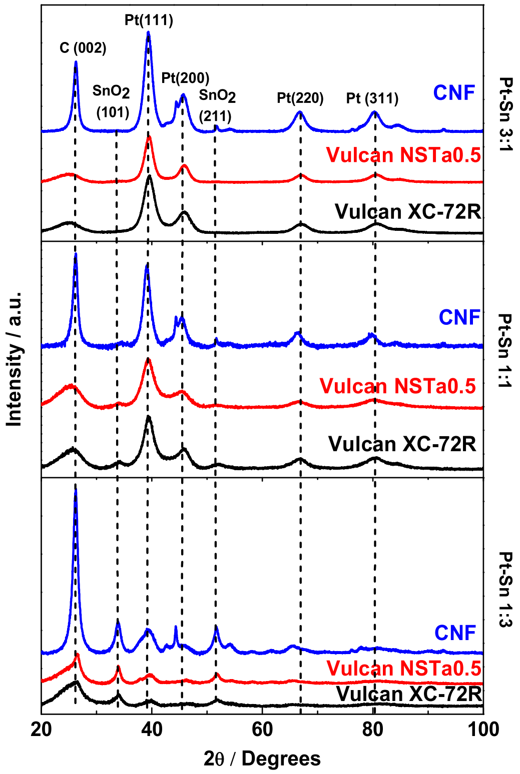

**Fig. 1.** X-ray diffractograms of samples.

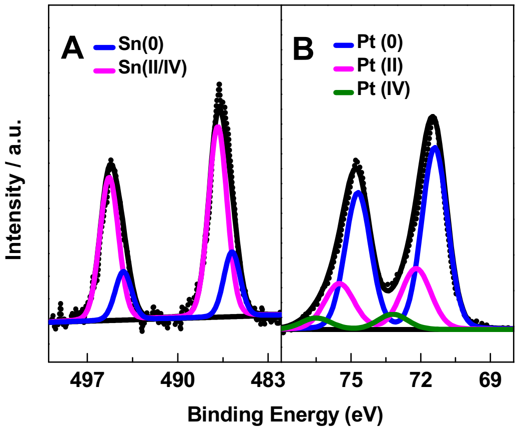

**Fig. 2.** (A) Sn 3d and (B) Pt 4f XPS spectra of Pt-Sn 3:1/Vulcan XC-72R.

enhanced activity with expanding lattice parameter and decreased conductivity with higher amounts of semiconducting tin oxide or decreased number of active sites of Pt partly covered by Sn [9]. The optimal Sn content for temperatures from 60 to 90 °C was found to be 30–40% [10], whereas a slightly higher optimum value of 50% [11,12] was reported for EOR at room temperature.

The higher electroactivity of this bimetallic formulation with respect to Pt has been explained by a bifunctional mechanism, i.e. Sn provides OH species at lower overpotentials than Pt, favoring the oxidation of intermediate species [13–15]. Other explanation is based on an electronic effect, which consists of the change of the electronic state of Pt atoms with the introduction of Sn, forcing the former to acquire different energy levels from the equilibrium. In this way, the weakening of Pt-CO bond is favored, which results in an easier removal of this adsorbate during the EOR [16]. However, the currents obtained in acid electrolytes by using Pt-Sn catalysts, although better than those for Pt, are still low.

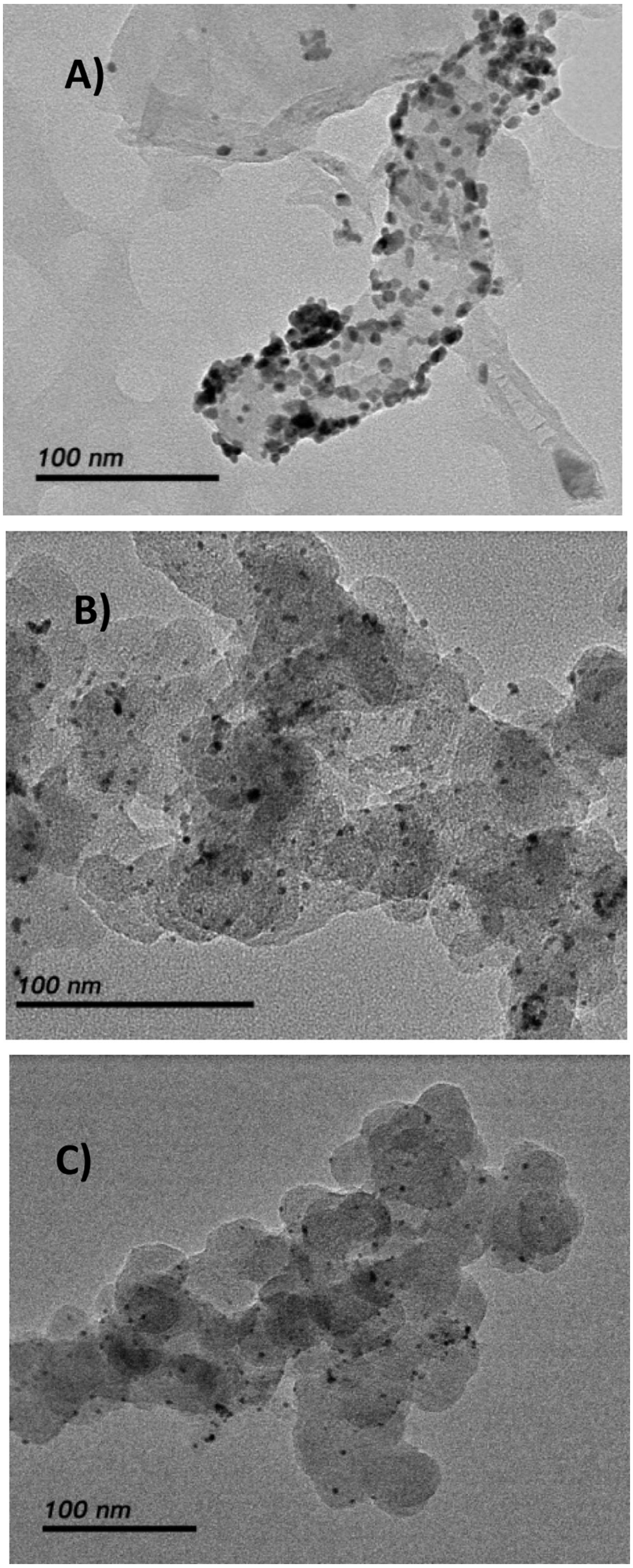

**Fig. 3.** TEM images of Pt-Sn 3:1 supported on: A) CNF B) Vulcan XC-72R C) Vulcan NSTa0.5.