

# Application of Controlled Surface Reactions for the preparation of highly active tin modified Pt/C catalysts for electrooxidation of ethanol

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## Introduction

Ethanol is the most attractive alcohol for Direct Alcohol Fuel Cells. A serious drawback to the implementation is the lack of efficient ethanol oxidation electrocatalysts. Such catalysts should combine high tolerance to CO and high ability to break the C-C bond. Pt-Sn bulk alloys are among the most studied bimetallic systems [1]. However, there is no method for the synthesis of nanosized Pt-Sn particles of a controlled composition. Exclusive formation of supported Sn-Pt alloy phases with different Sn/Pt ratios can be prepared by using Controlled Surface Reactions (CSRs) between hydrogen adsorbed on Pt sites and tetraethyltin [2]. The Sn-Pt/SiO<sub>2</sub> catalysts showed high activity in CO oxidation [2]. Tetra-*n*-butyltin has also been applied to prepare Sn-Pt/C catalysts for fuel cell application [3], however in this study no attempt was done to control the exclusive formation of bimetallic entities. In the present study general principles of CSRs were applied to prepare alloy-type Sn-Pt/C catalysts with different tin content. The bimetallic catalysts thus prepared displayed an outstanding performance in both the CO and ethanol electrooxidation reactions.

## Materials and Methods

The surface modification of Pt/C (40 wt% Pt/C, JM) leading to the exclusive formation of Pt-SnEt<sub>(4-x)</sub> surface complexes was accomplished at 70 and 120 °C as described earlier [2,3]. Final Sn/Pt ratio was controlled by both the amount of SnEt<sub>4</sub> introduced ([Sn]<sub>0</sub>/Pt, ratios) and temperature as shown in Table 1. Pt-SnEt<sub>(4-x)</sub> surface complexes were decomposed in hydrogen at 350 °C give rise to Sn-Pt bimetallic entities [2]. The prepared catalysts were characterized by XRD, HRTEM and XPS. Electrochemical performance was evaluated in 0.5 M HClO<sub>4</sub> at 25 °C with a PC controlled potentiostat. The catalysts were deposited onto the working electrode by means of an ink, the experimental protocol is described in [4].

## Results and Discussion

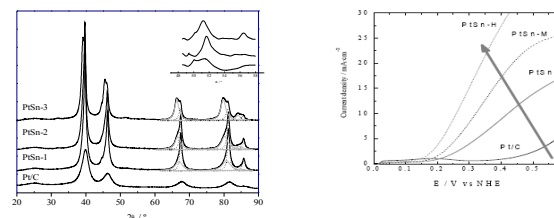
Figure 1 depicts the diffractograms of all the catalysts with reflections of the fcc structure of platinum being the only ones observed. A splitting of the peaks to lower 2θ with increasing tin loading is observed. This feature is in good agreement with the incorporation of tin into the fcc structure of platinum. Since the atomic radius of tin is larger than that of platinum, an expansion of the unit cell should be expected. Sn incorporation produces an increasing of the particle size from ca. 4.4 nm for Pt/C to 5.5-6.5 nm for the ones containing Sn. Fourier Transform of high-resolution images of the samples demonstrates the presence of Pt<sub>3</sub>Sn and Pt crystalline phases alone. In line with XRD analysis, this technique shows no evidence of the presence of SnO<sub>2</sub> phases in the samples.

The CO oxidation was evaluated by means of the CO-stripping technique. The onset potential for CO oxidation on Pt/C, PtSn-L, PtSn-M and PtSn-H is 620, 300, 220 and 210 mV, respectively. The presence of Sn strongly promotes CO electrooxidation. As a summary of electrochemical investigation the current density for the ethanol oxidation process on the different electrodes at 450 mV has been compared, the electrooxidation process increases as the amount of Pt<sub>3</sub>Sn phase increases. The comparison is clearly illustrated in Figure 2 where a magnification of the forward scan of the ethanol electrooxidation reaction on the different electrodes is depicted.

**Table 1.** General data related to tin anchoring.

No	Solvent	T <sub>r</sub> °C	[Sn] <sub>0</sub> /Pt <sub>0</sub>	time min.	n <sup>I</sup> <sup>a</sup>	n <sup>II</sup> <sup>b</sup>	x	Sn <sup>c</sup> wt%	Sn/Pt at/at
PtSn-L	C <sub>7</sub> H <sub>16</sub>	70	3.4	420	582.6	54.8	3.66	1.89	0.08
PtSn-M	C <sub>7</sub> H <sub>16</sub>	70	17.0	2000	1386.0	47.1	3.87	4.25	0.18
PtSn-H	C <sub>10</sub> H <sub>22</sub>	120	23.8	1020	1987.9	83.2	3.84	6.15	0.25

<sup>a</sup> Amount of ethane formed in step (1) (mol/g<sub>cat</sub> x 10<sup>-6</sup>); <sup>b</sup> Amount of ethane formed in step (2) (mol/g<sub>cat</sub> x 10<sup>-6</sup>); <sup>c</sup> Tin content calculated from the material balance of tin anchoring.



**Figure 1.** XRD pattern of the electrocatalysts. Contribution due to reflections ascribed to fcc Pt and Pt<sub>3</sub>Sn are depicted in dotted black and grey lines respectively.

**Figure 2.** Ethanol electrooxidation on Pt/C (black), PtSn-M (grey), PtSn-M (black-dotted) and PtSn-H (grey-dotted) in 0.5 M CH<sub>3</sub>CH<sub>2</sub>OH / 0.5 M HClO<sub>4</sub> at 10 mV/s.

## Significance

The results clearly demonstrated that upon using CSRs it is possible to prepare highly active alloy-type Sn-Pt/C electrocatalysts for electrooxidation of ethanol with high tolerance against poisoning with CO.

## References

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