

Pt-Sn Electrocatalysts for the ethanol oxidation reaction

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Objectives and Novelty

Electrochemical energy conversion and storage play essential roles in addressing the global energy challenge. In particular, direct ethanol fuel cells (DEFC) represent an attractive alternative to resources based on fossil fuel combustion for portable power generation. Ethanol is an eco-friendly and renewable fuel (naturally available in large quantities from biomass), and its complete oxidation to CO_2 and H_2O would lead to high energy densities. In addition, the easy handling, storage and transportation of liquid fuel, such as ethanol, avoids some of the problems associated with gaseous fuel (e.g. H_2) systems.

Over the past decades, platinum (Pt) has been shown to be the most active pure metal catalyst for the ethanol oxidation reaction (EOR). However, Pt is prone to deactivation by the adsorption of some intermediates (such as CO) and reaction by-products during the different pathways of the reaction. This fact, in combination with the high cost of Pt, has fueled the search for more active and stable EOR electrocatalysts. To achieve this objective, the synthesis of nanoparticle catalysts (with a high surface area to volume ratios), the combination of Pt with other metals and the control of the exposed Pt surface structure, have been extensively studied individually. However, the deliberate and integrated combination of these three approaches is clearly complex.

The most promising bimetallic catalysts for the EOR is Pt-Sn, resulting in a great improvement in the Pt pure catalytic activity. Furthermore, the EOR is a structure-sensitive surface reaction, which makes essential to control the surface morphology of the catalyst, and the catalyst support should be also considered since it can greatly influence the activity of the catalyst toward the EOR.

The present work aimed to outline important progress obtained from the study of the influence of the surface structure as well as the metal composition and catalyst support on the mechanism and electroactivity toward EOR. The knowledge generated in this works allowed the final synthesis of highly-active and stable shape-controlled Pt-Sn nanoparticles, which provides a promising electrocatalyst for DEFCs, in particular, and alcohol-based fuel cells, in general.

Results

In order to study the influence of the carbon support and the Pt-Sn composition on the activity toward EOR and CO oxidation reaction, Pt-Sn catalysts with different Pt-Sn atomic ratios and supported on CNF, Vulcan and oxidized Vulcan, were synthesized and

studied in acid and alkaline media in order to design an optimized material with the appropriate composition and carbon support to provide the highest catalytic activity toward EOR. The carbon materials employed were carbon nanofibers (CNF), commercial Vulcan XC-72R and normalized Vulcan XC-72R with nitric and sulfuric acid at room temperature 30 min (Vulcan NSTa0.5). X-ray photoelectron spectroscopy analyses (XPS) indicated that Sn is mostly in an oxidized state and promotes the oxidation of both metals in the catalysts. On the other hand, X-ray diffraction results (XRD) evidenced the presence of SnO_2 along with Pt, finding Pt crystallite sizes in the order of 3–5 nm. The relative quantity of Pt_3Sn_1 crystallite phase in the materials increased with Sn content, having an important effect on the whole catalytic behavior towards CO and EOR.

The addition of Sn shifted the onset potential for adsorbed CO oxidation to more negative values with respect to bare Pt. Instead, the atomic Pt:Sn ratio did not significantly influence the CO oxidation behavior, whereas the carbonaceous support affected the CO tolerance, being CNF the one with the lowest oxidation potential in both acid and alkaline electrolytes. The chemical functionalization of Vulcan did not significantly improve the tolerance toward CO oxidation.

Regarding the EOR, the addition of Sn and, consequently, the content of Pt_3Sn_1 crystallite phase, strongly improved the catalytic activity. Electrochemistry studies showed lower activity for Pt-Sn 1:3 than for the Pt-Sn 1:1 catalyst, but similar stationary currents for both formulations, regardless of the carbon support and electrolyte (Figure 1).

This is an important result considering the low noble metal content of the Pt-Sn 1:3 material. In all cases, the activity of the catalysts toward EOR was higher in alkaline media than in sulfuric acid media.

An effect of carbon support on the Pt-Sn catalytic activity was also found, being CNF the one which showed the highest activities toward CO stripping and EOR. The oxidation treatment of Vulcan was also found to positively influence the EOR activity.

Additionally, not only the reactivity but also the influence of the carbon support and the metal composition on the mechanism toward EOR was studied by employing *in situ* spectroelectrochemical techniques, like *in situ* Fourier transform infrared (*in situ* FTIR) or differential electrochemical mass spectrometry (DEMS). These techniques allowed us to identify adsorbed reaction intermediates and products as well as volatile reaction products during the EOR. In a simplified manner, it is well established that the EOR on Pt occurs via two possible general

pathways. The incomplete oxidation of ethanol does not entail the breaking of the C-C bond and during this pathway, 2 electrons release to form acetaldehyde and 2 more for its further oxidation to acetic acid. On the other hand, the complete oxidation of ethanol can

also take place, leading to higher energy densities (12 electrons releases during the process) but also to the breaking of the C-C bond and the formation of C1 poisoning intermediates (CO_{ad} , $\text{CH}_{\text{x,ad}}$).

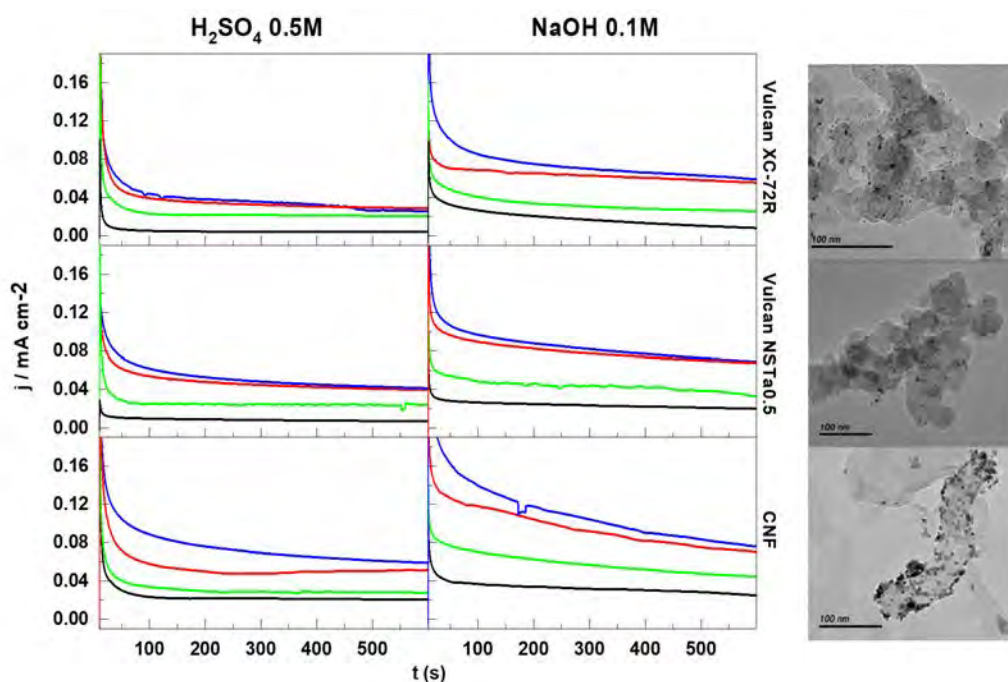


Figure 1. Current-time curves for ethanol 1 M electrooxidation: comparison of Pt (black solid line), Pt-Sn 3:1 (green solid line), Pt-Sn 1:1 (blue solid line) and Pt-Sn 1:3 (red solid line) recorded at 0.5 V in 0.5 M H_2SO_4 (left) and 0.1 M NaOH (right) at 20 °C. The insets correspond to the TEM images of Pt-Sn 3:1 supported on the respective carbon support.

In the present study, we found that that CNF shows the highest selectivity to acetaldehyde/acetic acid, which means that the enhancement of current density for this catalyst results from obtaining a higher amount of C2 products during the incomplete oxidation of ethanol.

Furthermore, studies about the influence of the composition in the mechanism showed that the C-C scission occurs at low overpotentials and at the same values independently of the Sn loading. Additionally, it was detected that acetic acid and acetaldehyde increases meanwhile CO formation decreases with the Sn loading, indicating that the enhanced catalytic activity toward the EOR is mainly due to the incomplete EOR.

Moreover, fundamental studies of the influence of the surface structure of the catalyst in the activity and mechanism toward the EOR were also carried out. For this purpose, Sn-modified Pt single crystals (Pt basal planes) were employed and enhanced activity, in terms of lower onset potential and a higher oxidation current, was found in the modified electrodes. The results revealed that the optimum Sn coverage depends on the Pt crystallography and the Sn/Pt(110) system is the surface that exhibits the highest activity. Additionally, DEMS experiments showed that on Pt(111) and Pt(110), the presence of Sn enhances the oxidation of ethanol to acetaldehyde. However, the further oxidation of acetaldehyde is sensitive to the Pt surface structure: on Pt(110) there are sites able to break the C-C bond in acetaldehyde to form

CO_2 , whereas on Pt(111) such sites are not available and acetaldehyde is oxidized further to acetic acid.

All of the knowledge acquired was also finally employed for the synthesis of highly-active cubic Pt-Sn NPs. They possessed a core-shell nanostructure with a Sn-rich shell and Pt-rich core. The electrochemical activity of this material was found to be about three times higher than that obtained with unshaped Pt-Sn nanoparticles and six times higher than that of Pt nanocubes (Figure 2).

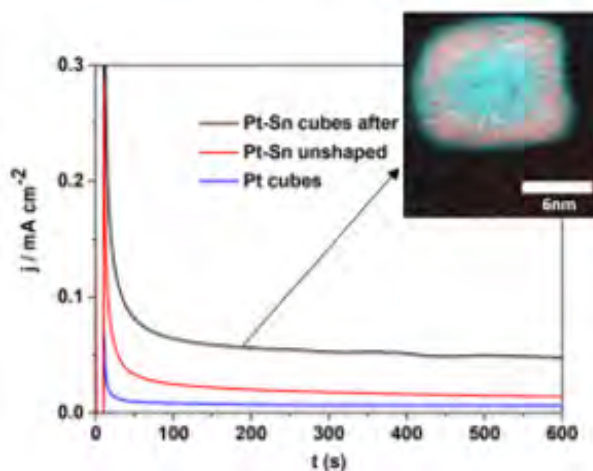


Figure 2. Current transients at 0.50 V of Pt:Sn nanocubes (black), unshaped Pt:Sn NPs (red), and Pt-cubic NPs (blue) in 0.5 M H_2SO_4 + 1 M EtOH solution. The inset corresponds to the STEM-EELS data of the Pt-Sn cubic NPs with Sn in red and Pt in cyan.

In addition, stability tests indicated that the electrocatalyst preserves its morphology and remains well-dispersed on the carbon support after 5000 potential cycles, while a cubic (pure) Pt catalyst exhibited severe agglomeration of the nanoparticles after a similar stability testing protocol. A detailed analysis of the elemental distribution in the nanoparticles by STEM-EELS indicated that Sn dissolves from the outer part of the shell after potential cycling, forming a ≈ 0.5 nm Pt skin. This particular atomic composition profile having a Pt-rich core, a Sn-rich subsurface layer, and a Pt-skin surface structure is responsible for the high activity and stability.

CONCLUSIONS

The influence of the composition, surface structure and carbon support of Pt-Sn catalysts on the activity and mechanism toward EOR, was studied. In the presence of Sn and CNF as catalyst support, the incomplete oxidation is more favored but also the oxidation of poisoning intermediates, which results in higher activity and lower onset potential for EOR because of the higher oxidation efficiency via C2 products formation. Regarding surface structure studies, fundamental experiments demonstrated that the presence of Sn improve the electrode activity regardless of the Pt crystallographic orientation but the Sn/Pt(110) surface is the one which showed the highest EOR currents. Finally, guided by the acquired knowledge, highly active and stable shape-controlled Pt-Sn catalysts were synthesized, which can be considered as a promising electrocatalyst for DEFCs, in particular, and alcohol-based fuel cells, in general.

RELATED PUBLICATIONS

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