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Electronic effect in intermetallic electrocatalysts with low susceptibility to CO poisoning during hydrogen oxidation

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ABSTRACT

This paper reports the results of Hydrogen Oxidation Reaction (HOR) experiments over ordered intermetallic (PtSn and PdSn) nanoparticles under CO-free and CO-covered surface conditions. The activity of PtSn toward the HOR was comparable to the activity of commercially available Pt/C. In addition, PtSn/C presented low susceptibility to CO poisoning. In the case of CO-covered surfaces, it was found that the CO was weakly adsorbed at the surface of the PtSn nanoparticles and it did not inhibit the HOR; in fact, this catalyst performed better than Pt/C under the same experimental conditions. X-Ray Absorption assays conducted in the present work proved that the ability of Sn to donate electrons to the Pt adsorption sites was crucial for the resulting intermetallic catalyst to display high activity in the HOR and low susceptibility to CO poisoning.

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Introduction

One of the greatest challenges that scientists have to face to implement the use of hydrogen-fed proton-exchange membrane (PEM) fuel cells is to find a way to employ hydrogen fuel obtained from renewable biomass catalytic reform processes effectively. When it comes to producing electricity, hydrogen-fed PEM fuel cells constitute the most efficient electrochemical devices; however, if the fuel contains traces of CO (co-produced during the catalytic reforming process), this contaminant will rapidly poison the catalyst surface and reduce the device power to useless levels. Such passivation process is particularly important at the surface of Pt, the best electrocatalyst for hydrogen oxidation.

One widely applied strategy to overcome the limitation of Pt surface passivation has been to add oxophilic metals to the Pt structure. These metals act in two different ways: (1) they produce oxygenated species at less positive potentials and therefore aid CO removal via the Langmuir–Hinshelwood mechanism, and/or (2) they modify the electronic state of the Pt adsorption sites, which will influence CO adsorption. Both phenomena may contribute to the successful application of fuel cells fed with hydrogen produced from biomass catalytic reform processes. Hence, it is essential to know which of these mechanisms, if not both, underlies the development of CO-poisoning resistance in electrocatalysts. Unfortunately, this type of chemistry does not have a probing species. The electronic effect of the oxophilic metal takes place as soon as the foreign atom is introduced into the structure of the catalyst.

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Then, the bifunctional action may or may not occur. For this reason, it is hard to distinguish the effect through which the oxophilic metal acts in the catalyst, and it is difficult to provide a reliable explanation for the actual role of the foreign metal.

Tin is an oxophilic transition metal with frequent application in noble metal matrixes—Sn enhances the catalytic activity of fuel cell anodes for the oxidation of organic fuels. There is no consensus on whether Sn improves electrode activity via the electronic or bifunctional effect. Sn ([Kr] $4d^{10}5s^25p^2$) exerts an electron donor effect toward the Pt orbitals, which increases the electron density of the Pt ([Xe] $4f^{14}5d^96s^1$) adsorption sites. This action is particularly effective in the Pt sites because the half-filled d-orbital of Pt favors this phenomenon. In contrast, the electronic configuration of Pd ([Kr] $4d^{10}$) does not facilitate the donor action of Sn atoms because the Pd d-orbitals are already filled. In parallel, the oxophilic character of Sn atoms will always be present at the surface of noble metals, to generate oxygenated species ($-\text{OH}$, $-\text{OOH}$, $-\text{O}_2$) at less positive electrode potentials than in the case of the pure noble metals. On the basis of the aforementioned characteristics, the electronic and the bifunctional effect will predominate at the PtSn and the PdSn surfaces, respectively. In this context, this investigation has relied on the CO oxidation reaction to evaluate the ability of PtSn and PdSn surfaces to adsorb CO, suffer CO poisoning, and remain active for the HOR.

Several authors have reported that the bifunctional mechanism and the electronic effect account for the different electrocatalytic activities of PtSn/C and Pt/C during the methanol and ethanol electrooxidation reactions [1–4]. According to Mukerjee and McBreen [5], Sn acts as an electron donor that partially fills the Pt d band and increases the Pt–Pt bond length, which accounts for the distinct performances of PtSn/C and Pt/C. On the basis of XPS and XANES studies, Shukla et al. [6] have proposed that the different electronegativity of Sn and Pt atoms polarizes the Pt–Sn bond, so the donor effect of Sn will give rise to a distinct activity in PtSn/C. Shukla et al. [6] have provided a very consistent explanation for the electronic and bifunctional role that Sn plays in PtSn materials. These authors stated that CO chemisorption on Pt involves donation of an electron pair from CO anti-ligand orbitals to empty Pt 5d orbitals. Back donation of electrons from Pt to CO orbitals stabilizes the Pt–CO interaction even further. On the other hand, partial electron donation to the Pt adsorption site raises the electronic density on the Pt atom, which decreases the energy of the interaction between CO and the Pt adsorption sites. This phenomenon, combined with OH adsorption at the Sn surface sites, aids surface CO removal for anode oxidation of fuel alcohols [6]. Lee et al. [7] studied the CO tolerance in the hydrogen oxidation reaction on Pt/C, PtSn/C and PtRu/C nanoparticles, in PEM fuel cell. According to their results, the onset potential for each material was different, in the order PtSn/C < PtRu/C < Pt/C. The authors proposed that the process of CO adsorption took place through the hydrogen displacement step for PtSn/C, while for PtRu/C and Pt/C was through direct CO adsorption on the free site. Moreover, they observed that the CO adsorption configuration (bridge or linear) was dependent on the material and temperature of cell operation. It was concluded that the thermodynamic and

kinetic alterations provoked by the alloys were responsible for the higher tolerance to CO poisoning. Crabb, Marshall and Thompsett [8] prepared PtSn bimetallic catalysts supported on Carbon in different compositions, and they studied the influence of this on the CO electrooxidation reaction. The results obtained pointed to the lowering of the CO electrooxidation onset potential on the synthesized materials as compared to Pt/C. Wang and Hsing [9], by using impedance technique, studied H_2/CO electrooxidation kinetics at Pt and its alloys surfaces. The higher PtSn/C activity toward the H_2/CO oxidation was attributed by the authors to the combination of several factors, namely: promotion of the OH nucleation; excluding CO adsorption on Sn sites; and the minimization of the CO adsorption caused by the metallic bond. Arenz and co-workers [10] studied the catalytic activity of three PtSn catalysts supported on Carbon toward the CO and H_2/CO electrooxidation reaction. These catalysts differ because of the relative amounts of Pt_3Sn , PtSn and SnO_2 on the support. It was concluded that the material composed exclusively by Pt_3Sn showed the best performance toward the reaction investigated. However, any deeper conclusion on the influence of the materials properties is hard to be extracted due to the presence of a mixture of phases. García-Rodríguez et al. [11] synthesized nanoparticles by incorporating Sn on Pt/C. With these materials, the authors studied the ethanol and CO electrooxidation reactions. According to the results the performance of the materials was dependent on the amount of the Pt_3Sn phase, i.e. the higher the Pt_3Sn amount, lower the onset potentials and higher the current densities for both reactions. The higher ability to CO oxidation was attributed to the Sn- OH_{ads} formed at less positive potentials in comparison to pure Pt. Lim and co-workers [12] synthesized PtSn/C electrocatalysts and evaluated them as anode for low temperature fuel cell. On commercially available Pt/C material, the CO oxidation reaction onset potential and maximum current density potential were more positive than the obtained with PtSn/C catalysts. The authors stated that the Sn promoted the CO_{ads} oxidation in lower potentials due to the ability to adsorb OH specie. Pt_3Sn showed better performance than Pt/C toward the H_2 and H_2/CO oxidation reactions in fuel cell. Such a behavior was considered as consequence of the presence of PtSn alloys and coexistence of the Sn oxides species. A very interesting work was published by Liu, Jackson and Eichhorn [13] that synthesized PtSn alloy, core-shell and intermetallic nanoparticle materials with same composition and particle size and evaluated as anode for H_2 electrooxidation reaction in the presence of CO. RDE tests showed that intermetallic and core-shell structures presented higher performance than Pt, PtRu alloy and PtSn alloy. The authors attributed these results to the electronic effect provoked by PtSn in the core-shell structure while on intermetallic material it was due to the bifunctional effect. Liu et al. [14] reported the study performed with Pt_3Sn nanoparticles toward the CO and methanol electrooxidation reactions. The improved activity of the material for CO oxidation was proposed because of the Sn effect of weakening CO adsorption on Pt and promoting Sn- OH_{ads} formation that eases the near adsorbed CO oxidation process. Moreover, the authors reported that the particles were also very active toward the methanol oxidation reaction. Herranz and colleagues [15] synthesized Pt_3Sn (fcc) and PtSn (hcp)

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