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Platinum–tin/carbon catalysts for ethanol oxidation: Influence of Sn content on the electroactivity and structural characteristics

Franz E. López-Suárez ^{a,*}, Carlos T. Carvalho-Filho ^a,
 Agustín Bueno-López ^b, Johana Arboleda ^c, Adriana Echavarría ^c,
 Katlin I.B. Eguiluz ^a, Giancarlo R. Salazar-Banda ^a

^a Electrochemistry and Nanotechnology Laboratory, Research and Technology Institute/Processes Engineering Post-graduation, Universidade Tiradentes, Av. Murilo Dantas, 300, Aracaju, SE, Brazil

^b MCMA Group, Department of Inorganic Chemistry, Faculty of Sciences, University of Alicante, Ap. 99, E-03080, Alicante, Spain

^c Grupo Catalizadores y Adsorbentes, Instituto de Química, Universidad de Antioquia U de A Calle 70 No. 52-21, Medellín, Colombia

ARTICLE INFO

Article history:

Received 27 April 2015

Received in revised form

4 July 2015

Accepted 25 July 2015

Available online 17 August 2015

Keywords:

Platinum

Tin

Alloy

Ethanol oxidation reaction

Fuel cell

ABSTRACT

Carbon-supported Pt–Sn catalysts commonly contain Pt–Sn alloy and/or Pt–Sn bimetallic systems (Sn oxides). Nevertheless, the origin of the promotion effect due to the presence of Sn in the Pt–Sn/C catalyst towards ethanol oxidation in acid media is still under debate and some contradictions. Herein, a series of Pt_x–Sn_y/C catalysts with different atomic ratios are synthesized by a deposition process using formic acid as the reducing agent. Catalysts structure and chemical compositions are investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) and their relationship with catalytic behavior towards ethanol electro-oxidation was established. Geometric structural changes are producing by highest Sn content (Pt₁–Sn₁/C) promoted the interaction of Pt and Sn forming a solid solution of Pt–Sn alloy phase, whereas, the intermediate and lowest Sn content (Pt₂–Sn₁/C and Pt₃–Sn₁/C, respectively) promoted the electronic structure modifications of Pt by Sn addition without the formation of a solid solution. The amount of Sn added affects the physical and chemical characteristics of the bimetallic catalysts as well as reducing the amount of Pt in the catalyst composition and maintaining the electrocatalytic activities at the anode. However, the influence of the Sn oxidation state in Pt–Sn/C catalysts surfaces and the alloy formation between Pt and Sn as well as with the atomic ratio on their catalytic activity towards ethanol oxidation appears minimal. Similar methodologies applied for synthesis of Pt_x–Sn_y/C catalysts with a small change show differences with the results obtained, thus highlighting the importance of the conditions of the preparation method. Copyright © 2015, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

* Corresponding author. Tel./fax: +55 079 3218 2190.

E-mail addresses: franzedwin@gmail.com (F.E. López-Suárez), trivellatoc@hotmail.com (C.T. Carvalho-Filho), agus@ua.es (A. Bueno-López), johana.arboleda@udea.edu.co (J. Arboleda), adriana.echavarría@udea.edu.co (A. Echavarría), katlinbarrios@gmail.com (K.I.B. Eguiluz), gianrsb@gmail.com (G.R. Salazar-Banda).

<http://dx.doi.org/10.1016/j.ijhydene.2015.07.135>

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Introduction

Interest in the development of fuel cells as power sources in portable electronic devices and electric vehicles has been increasing in recent years. The proton-exchange membrane fuel cells (PEMFCs) are the most promising because they are clean, silent, and efficient power sources [1]. In this kind of cell, hydrogen displays the best performance as a fuel; however, the problems in its storage, handling, and distribution are important barriers to its direct use. Hence, the direct use of liquid fuels in the cell has been investigated as a possible alternative to hydrogen. Ethanol is the most promising liquid fuel that can be used in PEMFCs, because it is a renewable and safe molecule, and it is easy to store and handle. The main disadvantage of ethanol comes from its molecular structure since it has two carbons with different functionalities, one containing a primary alcohol function and another with a methyl group. Its molecular configuration induces a hard conversion of ethanol into carbon dioxide due to the difficulty in both cleaving the C–C bond and the complete oxidation of the methyl group using platinum as an electrocatalyst [2].

In order to enhance the catalytic activity of this catalyst towards alcohol oxidation, a secondary metal is usually introduced as a co-catalyst. Different efforts have been realized in preparing binary Pt-based catalysts, which have showing a better the catalytic activity better than pure Pt catalyst. The secondary component in the catalyst composition can include Zn, Fe, Co, Ni, Ir, Pd [3–6] and Sn [5,7], which were incorporated with primary Pt species. A Pt–Sn catalyst is generally considered the best anode for ethanol oxidation compared to other bimetallic catalysts. While Pt-based anodes are the best catalysts for alcohol oxidation in acid medium, Sn provides surface oxygen species for the oxidation of CO or carbonyl species adsorbed on adjacent Pt, which are produced during the dissociative adsorption of ethanol on Pt active sites at low potentials [8]. Moreover, the addition of Sn contributes to reducing the amount of noble metal in the anode of direct alcohol fuel cells, which remains one of the challenges of making the technology commercially available.

Pt–Sn catalysts, with optimized compositions and structures, have exhibit enhanced activity towards ethanol electro-oxidation, mainly due to a weakening of CO adsorption, as well as a facilitated split of the C–C bond of the adsorbed alcohol [9]. Nevertheless, the origin of the promotion effect due to the presence of Sn in the Pt–Sn catalyst towards ethanol oxidation is still under debate and some contradictions are found in the literature [10–16]. Generally, it can be established that the effect of Sn addition to Pt in the Pt–Sn/C electrocatalysts performance strongly depends on their preparation procedures, Pt:Sn atomic ratio, and the amount of Sn alloy in the catalyst composition.

The procedure of synthesis has a major influence on the physical properties of Pt–Sn nanoparticle, such as composition, structure, and degree of alloying, which results in different electrocatalytic activities. Pt–Sn catalysts supported on carbon are commonly prepared in the absence of thermal treatment, and, as a consequence, a crystalline face-centered cubic Pt–Sn alloy and/or Sn oxides can be formed. The relative amounts of Pt–Sn alloy and SnO₂ affects the electrochemical

activity of these catalysts. The debate about the effects of either alloyed Sn with Pt or adding SnO₂ to improve catalytic activity as well as the contribution of oxidation state of Sn (Sn or SnO₂) have been controversial and remains open [7,17]. García-Rodríguez et al. [6] compared PtSn/C catalysts prepared by colloidal and impregnation – reduction methods suggesting that PtSn/C catalyst prepared by impregnation reduction method showed better activity than that by colloidal method. Pt–Sn/C nanocatalysts synthesized by a polyol/alcohol procedure at which the ethylene glycol:ethanol:water solution ratio is changed, showed that the synthesis conditions have an important effect on the chemical composition, lattice parameter and degree of alloying [7,18]. Delime et al. [19] prepared bimetallic non-alloyed Pt–Sn catalysts and observed that the presence of non-alloyed Sn led to increased current densities during the ethanol electro-oxidation. Jang et al. [10] compared the catalytic activity of a partially alloyed Pt–Sn catalyst with that of a quasi-non-alloyed Pt–SnO_x catalyst, and the Pt–SnO_x catalyst showed higher catalytic activity during ethanol electro-oxidation than the Pt–Sn alloy. The improvement in the activity suggests that the unchanged lattice parameter of Pt in the Pt–SnO_x catalyst is favorable for ethanol adsorption, and the tin oxide present in the vicinity of Pt nanoparticles could provide active oxygen species to remove the CO-like ethanolic residues and clean the Pt active sites. Colmati et al. [12,20] and Zignani et al. [13] prepared the carbon-supported Pt–Sn alloys by the formic acid method, and found that the activity of these catalysts for the ethanol oxidation reaction seems to depend on the amount of both non-alloyed and alloyed Sn, in addition to the overall content of Sn in the catalyst. Vigier et al. [16] prepared Pt–Sn/C catalysts using the co-impregnation reduction method. The presence of bimetallic Pt–Sn alloy phases, Pt particles, and Pt–O–Sn²⁺ species was detected in these catalysts. Others reports [8,11,14–16,18] show that a good degree of alloying between Pt and Sn leads to the highest electrocatalytic activity towards ethanol electro-oxidation.

Both the preparation procedures and the Pt:Sn atomic ratios influence the performance of Pt–Sn/C electrocatalysts. Lamy et al. [8,21] suggested an optimum composition for Sn in the 10–20 mol.% range for catalysts prepared by a co-impregnation-reduction method, varying from 90:10 to 50:50 (Pt:Sn). Zhou et al. [22] reported the optimum composition as being 33–40 mol.% of Sn, depending on the direct alcohol fuel cell operation temperature. Jiang et al. [23] showed that Pt–Sn/C electrocatalysts with Pt:Sn molar ratios of 66:33, 60:40, and 50:50 were more active than electrocatalysts with 75:25 and 80:20 atomic ratios. Spinacé et al. [24] investigated the activity of Pt–Sn/C electrocatalysts with varied Sn contents during ethanol oxidation, and showed that the electro-oxidation of ethanol begins at low potentials (~0.25 V) for 50:50 and 25:75 Pt:Sn molar ratios, with similar current values in the range 0.25–0.40 V. Above 0.4 V, the electrocatalysts with a Pt:Sn molar ratio of 50:50 displayed a superior performance. Wang et al. [25] studied the activity of Pt_x–Sn_y/C catalysts with different atomic ratios (x:y = 1:1, 2:1, 3:2) towards ethanol oxidation, establishing that the addition of Sn strongly improves the activity depending on the Sn content and the operating temperature. At lower temperatures, Sn-

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