Nanostructured Electrocatalysts Pt_3Sn/C and $SnO_2@Pt/C$: Effect on Low Temperature Direct Ethanol Fuel Cells Performance

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Brazil has a great renewable energy potential, such as ethanol, which is less toxic and has a higher energy density (8.01 kWh kg^{-1}) compared to methanol (6.09 kWh kg^{-1}), being attractive for low temperature fuel cells. However, ethanol electrochemical oxidation is more complex than that of methanol. Hence, one of the aims of the research for direct application of this fuel is the developing of electrocatalysts that can change its structure with new constituents (auxiliary metals), also modifying their electronic properties. Besides, obtaining materials with a lower content of Pt, low cost, but no less efficiency and able to reduce the effect caused by poisoning intermediates on the Pt surface in the oxidation of small organic molecules is one of the main goals in this research area. In the case of ethanol, it is desired to facilitate the breaking of the C-C bond, since without breaking this bond is formed acetic acid and there are no materials effective to promote oxidation of this latter process. Sn has been widely studied as aPt auxiliary metal, presenting, in most of the cases, the best performance for the oxidation of ethanol in a 3:1 ratio (Pt:Sn). The main goal of the present study is to develop binary nanostructured electrocatalysts Pt_3Sn/C [1] and Sn@Pt /C [2] core-shell structures in order to evaluate its electrocatalytic activity as anodes in the ethanol oxidation, aiming at the application as materials for direct ethanol fuel cells. The materials were prepared using the polymeric precursor and chemical reduction methods and subsequently supported on high surface area carbon. In UV-Visible spectrophotometry analysis it was observed absorbance spectrum on the preliminary formation of the core-shell structure. By XRD it was detected displacement of Pt 2Θ degrees for lower values in the presence of Sn, which characterizes the alloy phase Pt_3Sn formation in the electrocatalyst produced by the polymeric precursor method. For core-shell structure were observed peaks associated to Pt with the presence of SnO_2 in the noise level. The images from TEM showed surfaces with good dispersion and distribution of particle sizes on the support. The particle sizes are from 3-4 nm for the alloy and 3-16 nm for the core-shell structure. The electrocatalytic activity was studied by cyclic voltammetry and chronoamperometry. Analysis of reaction products and intermediates were performed by in-situ infrared spectroscopy. The highest electrocatalytical effect obtained was for Pt_3Sn/C as anode having as main product acetic acid, generated during ethanol oxidation. These results were confirmed in a single direct ethanol fuel cell experiment, maximum power density of 56.64 mW cm^{-2} using Pt_3Sn/C as anode (four times higher than that presented by the core-shell structure as anode). The theoretical results were obtained using First Principles Calculations based on Density Functional Theory (DFT) using PAW potentials. The effects of quantum confinement were checked: when the diameter of SnO_2 nanoparticles was decreased, its energy gap was increased. By Pt doping, it was noticed that it tends to decorate SnO_2 nanoparticle favoring the formation of the shell. However, it is observed a deformation of the core structure with the adsorption of Pt in the surface which could reduce the stability of the core-shell structure compared to Pt_3Sn/C alloy structure.

Keywords: Nanomaterials, Electrocatalysis, Pt_3Sn/C, Core-shell, DEFC, First Principles.

[1] J. C. M. Silva, R. F. B. De Souza, L. S. Parreira, E. T. Neto, M. L. Calegaro, M. C. Santos. *Appl. Catal. B,* Vol. 99 **(2010)** 265–271.

[2] L. S. Parreira, D. C. Rascio, J. C. M. Silva, R. F. B. De Souza & M. D'Villa-Silva. *I. J. Chem.*, Vol. 4 (2) **(2012)** 38-48.

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