



Carbon monoxide and ethanol oxidation on PtSn supported catalysts: Effect of the nature of the carbon support and Pt:Sn composition



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ABSTRACT

This paper presents the behavior of 20 wt.% PtSn supported catalysts as anodes for direct ethanol fuel cell (DEFC), which is fed with an aqueous ethanol solution. PtSn nanoparticles with different Pt:Sn ratios (1:1 and 3:1) were supported on carbon black and carbon nanofibers. Physicochemical characterization showed high particle dispersion onto the carbon supports and similar particle size (around 4.0 nm). XRD analysis indicated the presence of SnO₂ and similar lattice parameter for PtSn (1:1) to those of pure Pt₃Sn₁. Prepared catalysts were electrochemically studied in acidic medium by carbon monoxide (CO) stripping voltammetry, cyclic voltammetry, lineal sweep voltammetry and chronoamperometry in three-electrode cell experiments. In addition, cell voltage vs. current density curves were recorded in a DEFC. It was found that PtSn anodes exhibit good activity toward ethanol electrooxidation in half-cell experiments under fuel cell relevant conditions. Specifically, PtSn supported catalysts on carbon black showed higher catalytic activity compared to those supported on carbon nanofibers. The low activity for ethanol adsorption/deprotonation and C–C cleavage appear as the main causes for the low performance for ethanol oxidation reaction on catalysts supported on carbon nanofibers. A similar behavior was observed in single fuel cell experiments.

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1. Introduction

Direct liquid ethanol fuel cells (DEFC) are promising energy sources for portable applications. Ethanol has several advantages, such as its high energy density (8.03 kWh kg⁻¹) compared to that of methanol (6.1 kWh kg⁻¹), in addition to its higher solubility in liquid electrolytes, availability at low cost, easier handling, transport and storage [1]. Furthermore, ethanol is a non-toxic fuel and it can be produced in large quantities by the fermentation process of sugar-containing biomass or agricultural products. Although the feasibility of DEFC has been established by single cell experiments [2–6], the commercial development of these systems is still far away, and further progresses are necessary to improve their performance and efficiency [7], due to the limitations related to the ethanol electrooxidation reaction. It is well known that the main oxidation products are soluble acetic acid and acetaldehyde,

instead the complete oxidation to CO₂ [8–11]. Ethanol electrooxidation at low temperature (<100 °C) on PdSn based catalysts yields a products mixture with the following composition (ordered according to their concentration): acetic acid > acetaldehyde ≫ CO₂ [4]. The activation for the C–C bond of ethanol appears as an important challenge for its oxidation to CO₂ that is not necessary for formic acid or methanol oxidation reactions. Consequently, under electrocatalytic conditions, the current density produced via the total oxidation to CO₂ (as the result of C–C bond activation), is only a few percent. Most of the current is produced from the ethanol partial oxidation to acetaldehyde or acetic acid [12]. The formation of CO₂, CH₃CHO and CH₃COOH has been confirmed by spectroelectrochemical and chromatographic measurements [13].

Recently, considerable effort has been directed toward the development of high catalytic activity anodes for ethanol electrooxidation (EOR). The electrocatalyst optimization has involved two routes: (i) the development of new catalysts syntheses with attention to alloy composition, that is, the enhancement of the platinum activity by using binary and ternary electrocatalysts [14], like

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Pt–X where X = Ru, Sn, Rh, Mo [15–17], Pt–Sn–Ru, Pt–Sn–W and Pt–Rh–SnO₂ [18–20] among others; and (ii) the development of new carbon supports of high electric conductivity with a high accessible surface area to allow a good dispersion of metal nanoparticles.

Traditionally, catalyst supports have received less attention, despite the catalyst–support interaction strongly influences the physicochemical and electrochemical properties of the catalysts and, as a consequence, its performance under fuel cell operation [21,22]. It is usually suggested that the use of carbon materials with an ordered structure and high electrical conductivity improves the fuel cell performance, and because of this, many research groups have recently made efforts to synthesize and use different novel carbon supports such as nanotubes [23–27], nanofibers [28,29], carbon microspheres [30,31], hard carbon spherules [32], carbon aerogels and xerogels [33,34], and mesoporous carbons for fuel cell applications [35]. In particular, carbon nanofibers (CNF) have been extensively studied as catalyst support for the electrooxidation of alcohols, mainly for their high resistance to corrosion [36–38] and their high electrical conductivity that make them good candidates to replace the commercial Vulcan XC-72R support. In this context, recently was observed that catalysts supported on CNF shown an enhanced activity toward CO and alcohol oxidation reactions, respect to commercial catalyst supported on carbon back [36]. In addition, both their structural properties and surface chemistry can be easily tailored to obtain a material with the desired properties [29,39].

Another important factor is the metal–support interaction that plays an important role in catalysis, since this interaction determines the physicochemical and electrochemical properties of the materials. Regarding the physicochemical properties, the size and morphology of the metal particles depend on the nature of the support. High crystalline grade of the support (graphitic character) induces the formation of small metal particles with high crystallinity, which is associated with a strong metal–carbon interaction. On the other side, amorphous carbon support produces spherical metal particles with high size and mass density. The last features are related with a weak metal–carbon interaction [40].

Regarding to the electrochemical properties, the carbon support changes the electronic structure of the supported metal particles and consequently the electronic structure of the catalyst (metal–support interaction). Thus, it is expected that different carbon materials change the electronic structure of the catalysts in a different way. The metal–support interaction may affect the electron transfer from metal particles to the carbon support during the electrochemical reactions, thus changing the catalyst performance in the fuel cell [41]. In addition, the metal–support interaction can be attained through the oxygenated groups of the carbon surface, which play an important role in the electron transfer from metal particles to the support.

An efficient catalyst for ethanol electrooxidation should have a suitable surface for alcohol adsorption and a high tolerance toward CO and other intermediate ad-species during alcohol electrooxidation, and the ability to cleavage the C–C bond of the ethanol molecule at operating conditions compatible with the other fuel cell components. As it is pointed above, Pt has been modified with more oxophilic metals, like Ru, Sn, Rh, Mo, to improve its CO tolerance, because these atoms promote the formation of oxygenated species (e.g. OH_{ad}) at more negative potentials than Pt. Among these materials, Pt–Sn based electrocatalysts have presented the best performance during the ethanol oxidation in acidic media [2–4,42]. In Ref. [4], the best results were obtained using a Pt:Sn atomic ratio of 83:17, meanwhile in Ref. [43] the same authors suggested that the optimum Sn composition in the catalyst was in the range of 10–20% (atomic ratio). In fact, the optimum atomic composition of Pt–Sn has not yet been well established. The last is consequence of different factors, though catalyst preparation methods appear as

the most important issue [44–46]. In this sense, the choice of the catalyst synthesis will provide diverse Pt–Sn ratios (in the bulk and on the surface) and alloy degree with a tremendous effect of the catalyst performance [15].

In this paper we report the synthesis and the electrochemical behavior of Pt–Sn nanoparticles supported on carbon black and carbon nanofibers toward ethanol electrooxidation in half-cell and single direct ethanol fuel cell (DEFC), under operating conditions used in practical fuel cells, in addition to their suitability for their use as anodic electrocatalysts in these systems.

2. Experimental

2.1. Synthesis of catalysts and physical characterization

Carbon nanofibers (CNFs) have been prepared using the methodology described in our earlier works [47]. Briefly, the CNFs were grown by decomposition of a methane flow on a Ni:Cu:Al catalyst (atomic ratio = 78:6:16) at 700 °C for 10 h. Then, both the CNFs and commercial carbon Vulcan XC-72R were treated in a HNO₃–H₂SO₄ 1:1 (v/v) mixture for 0.5 h at room temperature during 30 min to create surface oxygenated groups. The original prepared CNF contains around 8 wt.% of metals, which act as catalyst for the carbon nanofibers production process. After that, the catalyst is eliminated during the acid treatment used to create oxygenated groups at the CNF surface.

N₂ adsorption–desorption isotherms of the carbon supports were measured at –196 °C using a Micromeritics ASAP 2020. The total surface area was calculated from BET (Brunauer, Emmett and Teller) equation and the total pore volume was determined using the single point method at $P/P_0 = 0.99$. Pore size distribution (PSD) curves were obtained from the analysis of the desorption branch of the N₂ isotherm using the BJH (Barrett, Joyner and Halenda) method.

The surface chemistry of functionalized CNFs was analyzed by temperature programmed desorption (TPD). The experiments were performed in a Micromeritics Pulse Chemisorb 2700 instrument, under a flow of helium and using a heating rate of 10 °C min^{–1} from 150 °C up to 1050 °C. The amounts of CO and CO₂ desorbed from the samples were analyzed by gas chromatography.

The carbon Vulcan XC-72R and CNF supported electrocatalysts (Pt₁Sn₁/C, Pt₃Sn₁/C, Pt₁Sn₁/CNF, Pt₃Sn₁/CNF) were prepared by the formic acid method (FAM) [48]. Appropriate amounts of metal precursor (H₂PtCl₆ and SnSO₄, Sigma–Aldrich) were used to obtain nominal metal loading of 20 wt.% on the support material.

X-ray diffractograms (XRD) of the electrocatalysts were obtained with an universal diffractometer Carl Zeiss–Jena, URD-6, operating with CuK α radiation ($\lambda = 0.15406$ nm) generated at 40 kV and 20 mA. Scans were done at 38 min^{–1} for 2θ values between 20° and 100°. In order to estimate the particle size from XRD, the Scherrer equation was used [49]. In order to improve the fitting of the peak, diffractograms for specific 2θ values ranges were recorded at 0.028 min^{–1}. The lattice parameters were obtained by refining the unit cell dimensions applying the least squares method [50].

Transmission electron microscope (TEM) micrographs for the PtSn electrocatalysts were obtained using a JEOL-2000 FXII microscope equipped with a LaB₆ gun. The samples were grounded, dispersed in ethanol and a drop of solution was then deposited on a copper grid.

The atomic ratios for Pt:Sn were determined by energy dispersive X-ray analysis (EDX) coupled to the scanning electron microscopy LEO Mod. 440, with a silicon detector and Be window, applying 20 keV.

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