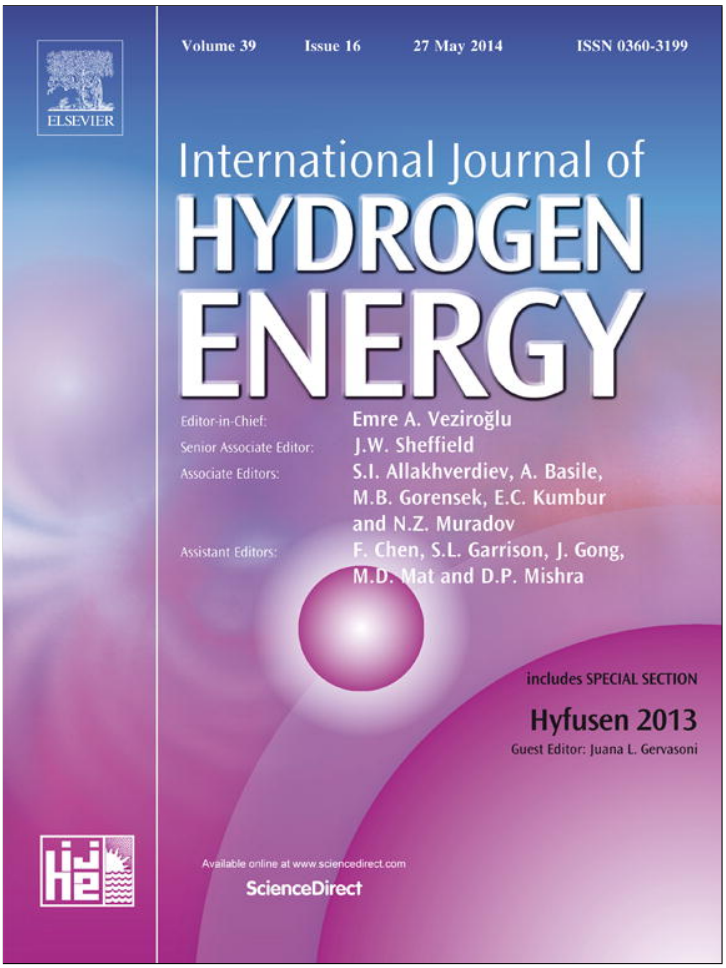

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Influence of metallic oxides on ethanol oxidation

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ABSTRACT

An improvement in ethanol oxidation electrocatalysis is possible with multifunctional Pt-based combinations. Thus, the addition to Pt of Sn, Ir or Ni enhances the ethanol oxidation reaction (EO) and shifts the onset oxidation potential to lower values. It has been suggested that metallic oxides in the vicinity of Pt have the capacity of promoting the oxidation of residues coming from alcohol oxidative adsorption. In order to get a deeper knowledge on the ethanol oxidation catalysis, supported catalysts prepared either by thermal decomposition of polymeric precursors (PP) or by microwave assisted poliol reduction (MW) methodology are studied to determine the role of the catalyst components and its oxides on the improvement of ethanol oxidation. The catalysts are physically and electrochemically characterized. According to the synthesis method, the amount of SnO_2 in the catalyst varies. Faceted particle structures for the microwave-synthesized catalysts are observed. By employing electrochemical techniques it is concluded that the catalyst with the highest amount of SnO_2 has the best catalytic behaviour for EO.

1. Introduction

Fuel cells that employ alcohols, such as direct ethanol fuel cells (DEFCs) are attractive to power portable devices because their theoretical cell voltage is similar to that obtained when hydrogen is oxidized [1,2]. Ethanol is a liquid easy to handle, transport and store and its complete electro-oxidation involves a 12-electron process. Nevertheless, the DEFC undergoes slow kinetics of alcohol oxidation on electrode surfaces. Efficiency is currently quite low for that fuel cell [3].

To achieve the maximum chemical energy from ethanol, it has to be completely oxidized to CO_2. Consequently, an acceptable ethanol catalysts need to have a great capability to convert it into CO_2 and water. It appears that an improvement in ethanol oxidation electrocatalysis is possible with multifunctional Pt-based combinations [4]. Thus, the binary PtSn/C or the ternary PtSnIr/C and PtSnNi/C supported catalysts enhance the EO and shift the onset oxidation potential to values lower than that on Pt/C supported catalyst [5–8]. The effect of Sn addition to Pt is related, to a certain extent, to alloy formation and a controversy is established regarding tin oxide

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in the vicinity of Pt nanoparticles. Some researchers found that the activity of PtSn catalysts for the ethanol oxidation reaction seems to be dependent on the amount of both non-alloyed and alloyed Sn [9].

It has been suggested that metallic oxides in the vicinity of Pt have the ability to promote the oxidation of residues resulting from alcohol oxidative adsorption [10,11]. According to Jiang et al. [11], SnO_2 can supply surface oxygen-containing species for the removal of strongly adsorbed residues on adjacent Pt active sites, considering the bifunctional mechanism.

The SnO_2 amount may depend on the catalysts preparation method, and on the presence of other precursors [12].

The aim of the work is to highlight the role of the multi-components catalysts and to evaluate if the synthesis method could favour the formation of different amounts of SnO_2 in the catalyst and modify the particle morphology.

To achieve the goal, PtSnM/C catalysts with M = Ir or Ni have been prepared either by thermal decomposition of polymeric precursors, (PP) or by microwave assisted poliol reduction (MW) and tested for ethanol oxidation reaction.

2. Experimental

2.1. Catalysts synthesis

Metal nanoparticles are mostly prepared by the growth of particles starting from metal atoms, which are obtained from the chemical interaction between ionic precursors and a reductor agent. The methodology is suitable to obtain small and uniform nanoparticles. And controlling the atom aggregation is the most important step to manage the size and uniformity of the metal nanoparticles [13,14].

In accordance with the Pechini methodology, a PtSnIr/C (PP) catalyst with a fixed total metal loading on carbon (Vulcan XC-72R) of 40 wt% was synthesized employing ethylene glycol as a reactant and reducing agent together with citric acid [15]. The method is based on the thermal decomposition of a polymeric precursor obtained by the polymerization reaction between citric acid, the metallic ions and ethylene glycol to form an esterified chelate.

Briefly, Pt, Ir and Sn polymeric precursors were prepared separately by employing metallic salts namely, H_2PtCl_6, $IrCl_3 \cdot xH_2O$ and Sn citrate, dissolved in a mixture of ethylene glycol and citric acid at 60 °C. The molar ratio among citric acid, ethylene glycol and metallic salt was set as 4:16:1 for all the polymeric precursors. The mixture of the three polymer precursors was unified and the temperature was rised to 90 °C and kept under vigorous stirring for 3 h composing a polyester network that keeps the metallic ions homogeneously distributed. A calculated amount of the functionalized carbon black support was added. Finally, the mixture precursor solution/carbon was homogenized in an ultrasonic bath and then calcinated at different temperatures under an air atmosphere, using a temperature program reaching 350 °C to get rid of organic residues.

Employing chemical reduction by ethylene glycol, assisted by microwave heating, PtSnIr/C(MW), PtSnNi/C(MW), and PtSn/C(MW), catalysts have been prepared following [16,17]. In brief, a calculated amount of the different precursors were added to 25 mL of ethylene glycol. The mixture was stirred for 5 min in ultrasonic bath, and sufficient carbon Vulcan XC-72 powder was then added, in order to obtain a metal catalyst load of 40 wt%. The mixture was kept under ultrasound stirring for 30 min, until a homogeneous suspension was obtained. This suspension was then placed in a common household microwave oven (Likon, 2.45 GHz, 700 W) for 70 s. Finally, the suspension was filtered and washed repeatedly with water, and then dried in an oven at 80 °C for 24 h.

2.2. Characterization methodology

The physical characterization of the materials was accomplished by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and energy dispersive spectroscopy (EDS).

For the electrochemical characterization linear voltammetry (LV), chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS) were employed.

A conventional three-electrode cell was employed, the working electrode consisted of a glassy carbon disk (0.071 cm^2 geometric area) covered by a thin layer of catalyst (28 $\mu g\ cm^{-2}$ Pt loading) embedded in a Nafion polymer electrolyte film (0.1 μm thick) [18]. A Pt foil of ca 1 cm^2 geometric area was used as counterelectrode and a saturated calomel electrode as reference electrode. In this work, the potentials refer to that of the reversible hydrogen electrode (RHE).

The supporting electrolyte was 0.5 M H_2SO_4 and the working solution was 1 M C_2H_5OH + 0.5 M H_2SO_4. After the assembly, the composite catalytic disk electrode was cycled in 0.5 M H_2SO_4 for 5 min at 0.10 V s^{-1} between 0.05 and 1.24 V to clean the surface. Real areas were determined by considering the anodic charge corresponding to the CO-stripping peak and assuming that CO is linearly adsorbed on one Pt site and taking into account that 420 μC is equivalent to 1 cm^2.

To establish the catalytic activity of the synthesized materials, current–potential curves for EO were recorded at 0.01 V s^{-1}. The alcohol was added to the supporting electrolyte at 0.05 V and its oxidation was measured. The temporal stability of the electrode at 0.5 V was determined by chronoamperometry. The current densities refer to the CO calculated real area. Electrochemical impedance spectroscopy (EIS) was also employed to identify the materials with the best EO performance. The impedance spectra were recorded by polarizing in a constant voltage mode at 0.5 V at frequencies from 100 kHz to 10 mHz. The amplitude of the applied potential perturbation was 0.010 V. All electrochemical measurements were performed at 60 °C.

Prior to each EIS measurement, the electrolyte was replaced by fresh solution and the electrode was cycled to get a clean and reproducible surface. A 30 min holding time was applied at each potential to approach a near steady state before the data were collected.

3. Results and discussion

3.1. Physical characterization

In Fig. 1 TEM images of all the synthesized catalysts are shown: Fig. 1a, PtSnIr/C (PP), Fig. 1b, c and d, PtSnIr/C (MW),

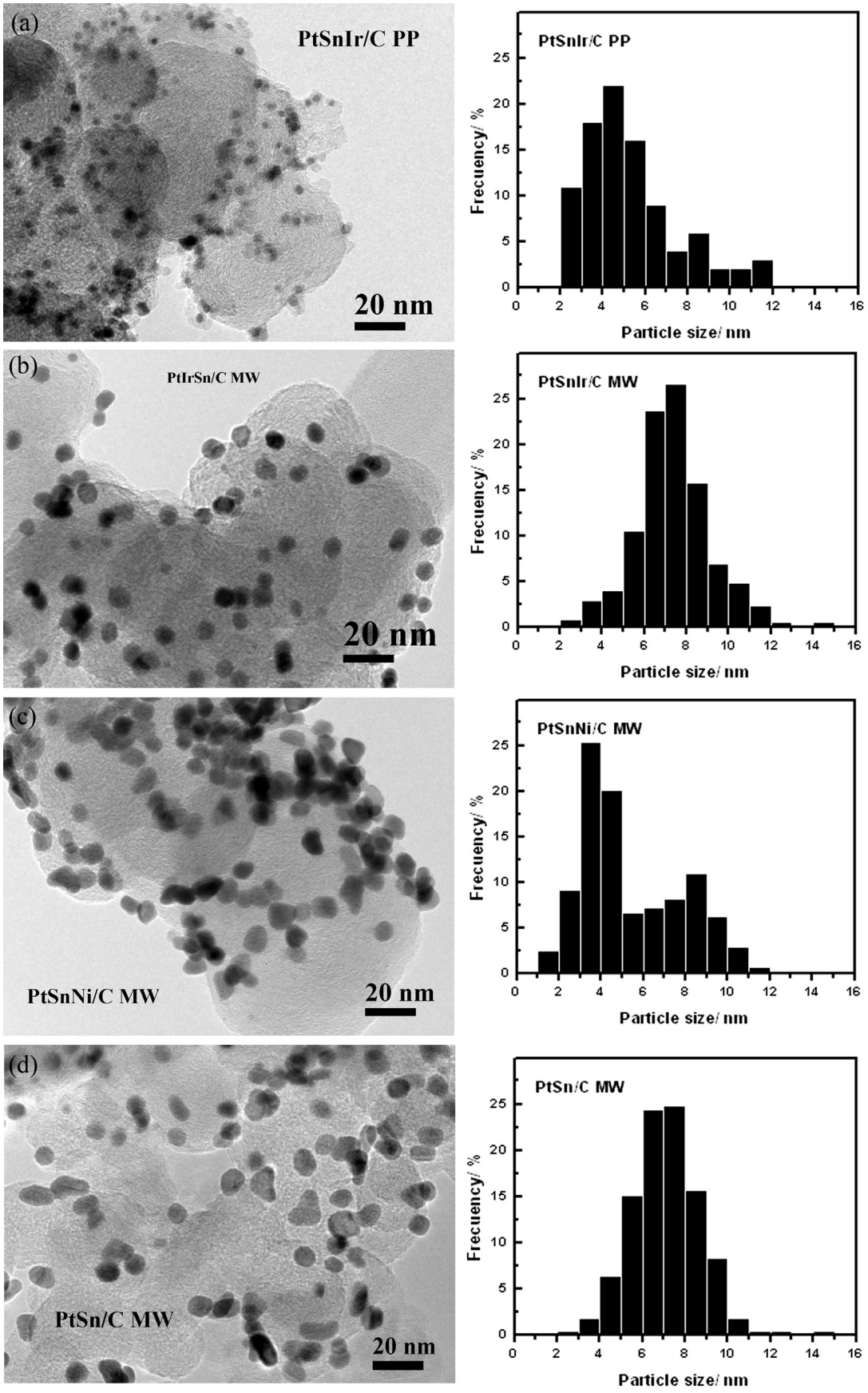

Fig. 1 – TEM micrographs and histograms for (a) PtSnIr/C (PP), (b) PtSnIr/C (MW), (c) PtSnNi/C (MW) and PtSn/C (MW) catalysts.

Table 1 – Atomic percentage determined by XPS and EDS.

Catalyst	XPS	EDX
PtSn/C (MW)	95-5	97-3
PtSnIr (MW)	84-16-0	84-10-6
PtSnNi (MW)	75-25-0	78-22-0
PtSnIr (PP)	71-29-0	73-12-15

PtSnNi/C (MW), and PtSn/C (MW), respectively. A difference in the particle size depending on the synthesis method employed can be noticed. Accordingly, PtSnIr/C (PP) shows the smallest particle size confirmed by the corresponding histogram. It appears that the citric chelate helps to prevent particle aggregation, to a certain extent, and induces nanoparticles to get high dispersion.

The MW synthesized particles depict faceted structure, clearly shown in Fig. 1d. It has been claimed that the homogeneous microwave heating of liquid samples reduces the temperature and concentration gradients in the reaction medium, providing a uniform environment for the nucleation and growth of metal particles. The fast heating by microwave accelerates the reduction of the metal precursor and the nucleation and growth of the metal clusters. The carbon surface may contain sites suitable for heterogeneous nucleation [19].

The atomic percentages of the component in the binary and ternary catalysts, listed in Table 1, have been determined by EDS and XPS. It can be highlighted that EDS is a surface technique that goes through less than 10 μm whereas XPS measures the elemental composition of the surface from the top to 4 nm depth. A significant surface Sn enrichment by segregation of Sn onto the surface can be noticed from Table 1. Due to the great affinity of Sn for oxygen, the migration of Sn of the catalyst towards the surface occurs.

In Fig. 2 the Sn 3d 5/2 XPS spectra of the synthesized catalysts, in the binding energy region between 480 and 490 eV are shown. All the Sn(3d) spectra have been deconvoluted into two components and are ascribed to elemental Sn (0) and Sn(IV) oxide, respectively. From the spectra, an important distinction between the diverse catalysts can be notice; Sn is

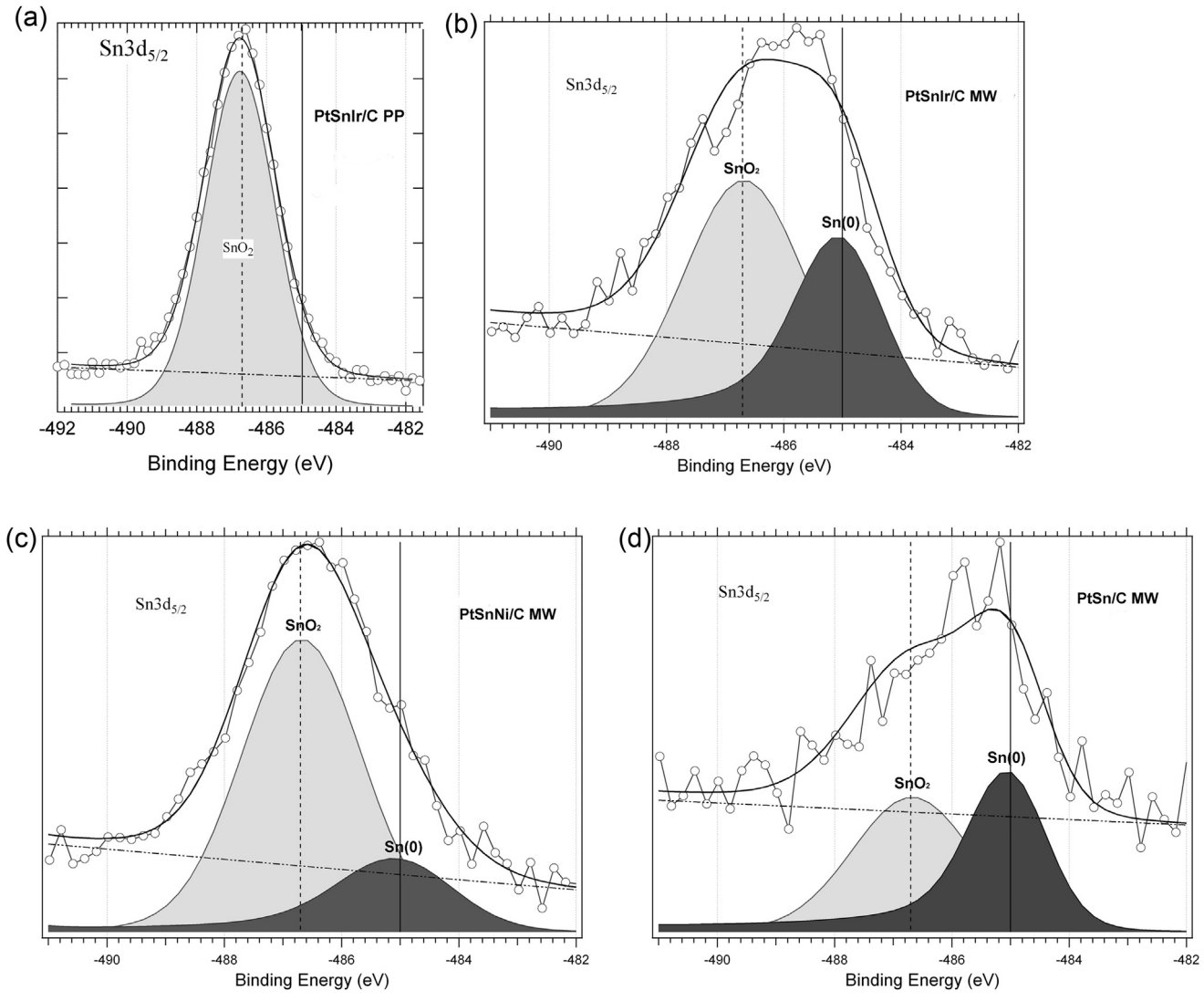

Fig. 2 – XPS spectra (a) PtSnIr/C (PP), (b) PtSnIr/C (MW), (c) PtSnNi/C (MW) and (d) PtSn/C (MW) catalysts in the Sn 3d 5/2 binding energy region.

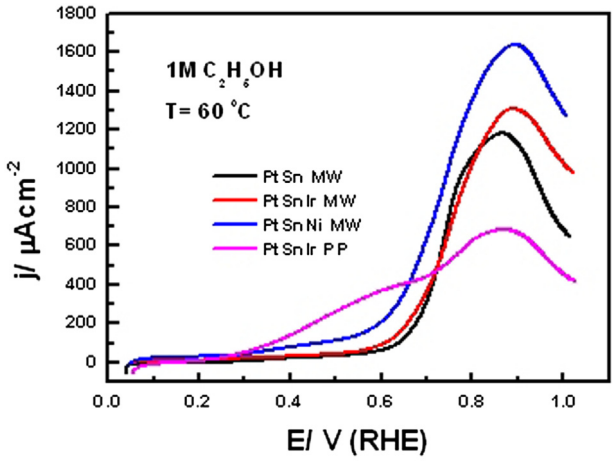

Fig. 3 – Linear sweep voltammetry at 0.010 V s^{-1} for EO at 60 °C on PtSnIr/C (PP), PtSnIr/C (MW), PtSnNi/C (MW) and PtSn/C (MW).

mostly in an oxidized state as SnO_2 in PtSnIr/C (PP), and the microwave-prepared catalyst show different SnO_2 amounts, being the one for PtSnNi/C (MW), the highest, and that for PtSn/C (MW) catalyst the lowest, in agreement with the oxophilicity of Sn [20].

3.2. *Electrochemical characterization*

3.2.1. *Linear sweep voltammetry*

The linear sweep voltammograms at 0.010 V s^{-1} and 60 °C for EO, with PtSnIr/C (PP) and the microwave-prepared PtSnIr/C (MW), PtSnNi/C (MW) and PtSn/C (MW) catalysts are shown in Fig. 3. The catalytic activity for EO, follows the order PtSnIr/C (PP) > PtSnNi/C (MW) > PtSnIr/C (MW) > PtSn/C (MW); the amount of SnO_2 oxide follows the same trend, confirming the need of metal oxides, mainly SnO_2, to improve the ethanol oxidation reaction. Accordingly, PtSn/C (MW) catalyst which has the lowest amount of SnO_2 has also the lowest catalytic activity for EO. Some researchers claimed that Sn and Ir activate water dissociation at lower potentials than on platinum, leading to the formation of OH species and promoting EO, according to the bifunctional mechanism [21].

It is interesting to remark that the initial composition of the precursors to obtain PtSnIr/C in both (PP and MW) methods is the same, but the atomic percentage of Pt is higher in the microwave synthesized catalyst. Moreover, independently of the synthesis methodology no atomic percentage of Ir is determined on the surface, according to Table 1. The Sn segregation is higher in the (PP) catalyst, which also has the highest SnO_2 amount.

An analysis between the microwave-synthesized catalysts behaviour for EO shows that PtSnNi/C (MW) is the most active catalyst and the performance of all of them is proportional to the surface SnO_2 amount. The reaction rate for EO increases with potential and there is a competition between fresh ethanol and water molecules for the liberated Pt sites, so that, as the oxidation reaction progresses, the Pt catalytic sites are occupied either by new ethanol molecules, or water molecules. From Table 1 no Ni atoms percentage is informed neither in the bulk or on the surface. Consequently, it appears that Ni has an active role during the PtSnMx microwave synthesis. We postulate according to XPS analysis that during the synthesis, fresh Ni atoms can go to spontaneous Ni dissolution, favouring Sn deposition in the catalyst. Accordingly, a higher amount of Sn and its oxide is present in PtSnNi/C (MW).

3.2.2. *Chronoamperometry*

In Fig. 4 the chronoamperogram at 0.5 V for EO with the synthesized catalysts shows higher currents with PtSnIr/C (PP), the good performance of this catalyst is followed by PtSnNi (MW), PtSnIr (MW) and PtSn (MW) catalysts, respectively. The current for EO on all the catalysts decreases rapidly at first and then becomes relatively stable. A softer decrease is observed at longer times. The temporal stabilization of the oxidation current is an important parameter to take into account in catalysts for DEFC.

In reference to microwave catalysts it is known that crystallites with high-index planes have high densities of atomic steps, ledges, and kinks and consequently show higher

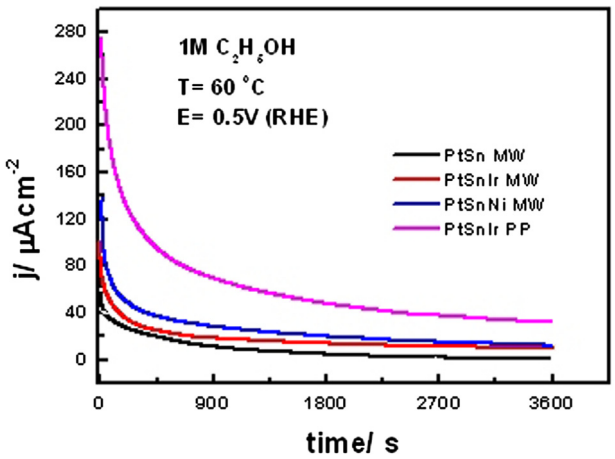

Fig. 4 – Chronoamperograms at E = 0.5 V and 60 °C for EO on PtSnIr/C (PP), PtSnIr/C (MW), PtSnNi/C (MW) and PtSn/C (MW).

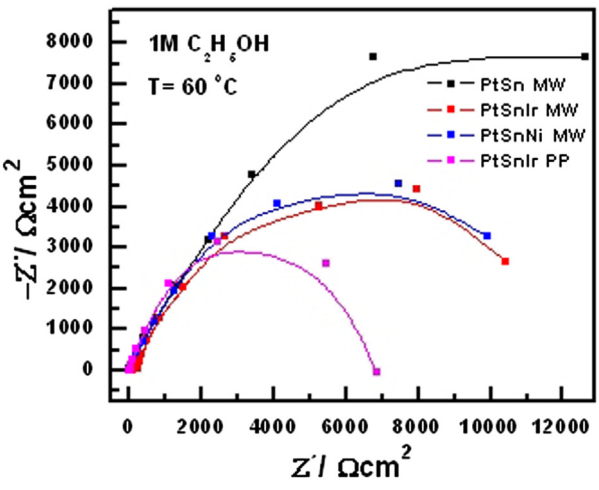

Fig. 5 – EIS spectra for EO at 60 °C on PtSnIr/C (PP), PtSnIr/C (MW), PtSnNi/C (MW) and PtSn/C (MW) at E = 0.50 V.

catalytic activity and stability [22]. It would be desirable to take advantage of the catalyst morphology in futures studies.

3.2.3. *Electrochemical impedance spectroscopy*

The electrochemical impedance spectra carried out at 0.5 V employing the analysed catalysts PtSnIr/C (PP) is shown as Nyquist plots in Fig. 5. It is observed that the smaller semi-circle fitted the PtSnIr/C (PP) followed by PtSnNi/C (MW), PtSnIr/C (MW), and PtSn/C (MW). It is generally predicted that the lower the charge transfer resistance the better the catalyst [23]. The good behaviour of PtSnNi/C (MW) would be linked to the particles morphology. Thus, the oxidation of adsorbed intermediates is expected to be easier on the facetted particles. It is well established that to accomplish the oxidation of ethanol, EO, the reactants and adsorbed intermediates need to assemble M–OH species produced by dissociative adsorption of H_2O on the catalyst surface. Liang et al. claimed that the microwave-irradiated polyol plus annealing prepared PtRuIr/C catalyst displayed an enhanced activity for COads electro-oxidation [20].

4. Conclusions

The microwave-synthesized PtSnNi/C (MW), PtSnIr/C (MW) and PtSn/C (MW) catalysts present different amounts of SnO_2 according to XPS analysis.

The PtSnIr/C (PP) catalyst contains the highest amount of SnO_2 and has the best catalytic activity for EO.

By employing electrochemical techniques it is concluded that PtSnIr/C (PP) has the best catalytic behaviour for ethanol oxidation, the improvement is attributed to the presence of metal oxides.

The particle size and distribution of the catalysts on carbon reveals that the microwave methodology produces facetted particles.

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REFERENCES

[1] Aricò AS, Baglio V, Antonucci V. In: Liu Hansan, Zhang Jiujun, editors. Direct methanol fuel cells: history, status and perspectives, electrocatalysis of direct methanol fuel cells. Weinheim: WILEY-VCH. KGaA; 2009, ISBN 978-3-527-32377-7; 2009.

[2] Liu H, Song C, Zhang L, Zhang J, Wang H, Wilkinson DP. A review of anode catalysis in the direct methanol fuel cell. J Power Sources 2006;155:95.

[3] Antolini E. Catalysis for direct ethanol fuel cells. J Power Sources 2007;170:1–12.

[4] Lamy C, Rousseau S, Belgsir EM, Coutanceau C, Leger JM. Recent progress in the direct ethanol fuel cell: development of new platinum–tin electrocatalysts. Electrochim Acta 2004;49:3901–9.

[5] Bonesi A, Garaventa G, Triaca WE, Castro Luna AM. Synthesis and characterization of new electrocatalysts for ethanol oxidation. Int J Hydrogen Energy 2008;33:3499–501.

[6] Purgato FLS, Pronier S, Olivi P, De Andrade AR, Léger JM, Tremiliosi-Filho G, et al. Direct ethanol fuel cell: electrochemical performance at 90 °C on Pt and PtSn/C electrocatalysts. J Power Sources 2012;198:95–9.

[7] Beyhan S, Leger JM, Kadırgan F. Pronounced synergetic effect of the nano-sized PtSnNi/C catalyst for ethanol oxidation in direct ethanol fuel cell. Appl Catal B Environ 2013;130–131:305–13.

[8] Tayal J, Rawat B, Basu S. Bimetallic and trimetallic PtSn/C, PtIr/C, PtIrSn/C catalysts for electro-oxidation of ethanol in direct ethanol fuel cell. Int J Hydrogen Energy 2011;36:14884–97.

[9] Colmati EF, Antolini E, Gonzalez ER. Effect of temperature on the mechanism of ethanol oxidation on carbon supported Pt, PtRu and Pt3Sn electrocatalysts. J Power Sources 2006;157:98–103.

[10] Calegaro ML, Suffredini HB, Machado SAS, Avaca LA. Preparation, characterization and utilization of a new electrocatalyst for ethanol oxidation obtained by the sol–gel method. J Power Sources 2006;156:300–5.

[11] Jiang L, Sun G, Zhou Z, Sun S, Wang Q, Yan S, et al. Size-controllable synthesis of monodispersed SnO_2 nanoparticles and application in electrocatalysts. J Phys Chem B 2005;109:8774–8.

[12] Antolini E, Colmati F, Gonzalez ER. Ethanol oxidation on carbon supported (PtSn)alloy/SnO_2 and (PtSnPd)alloy/SnO_2 catalysts with a fixed Pt/SnO_2 atomic ratio: effect of the alloy phase characteristics. J Power Sources 2009;193:555–61.

[13] Ye F, Li J, Wang T, Liu Y, WeiH Li J, Wang X. Electrocatalytic properties of platinum catalysts prepared by pulse electrodeposition method using SnO_2 as an assisting reagent. J Phys Chem C 2008;112:12894–8.

[14] Liu B, Chi ZW, Lee ZY, Cheng CH, Lee JY, Liu ZL. The importance of water in the polyol synthesis of carbon supported platinum–tin oxide catalysts for ethanol electrooxidation. J Power Sources 2012;206:97–102.

[15] Ribeiro J, dos Anjos DM, Kokoh KB, Coutanceau C, Léger J-M, Olivi P, et al. Carbon-supported ternary PtSnIr catalysts for direct ethanol fuel cell. Electrochim Acta 2007;52:6997–7006.

[16] Liu Z, Guo B, Hong L, Lim TH. Microwave heated polyol synthesis of carbon-supported PtSn nanoparticles for methanol electrooxidation. Electrochem Commun 2006;8:83–90.

[17] Almeida TS, Palma LM, Leonello PH, Morais C, Kokoh KB, De Andrade AR. An optimization study of PtSn/C catalysts applied to direct ethanol fuel cell: effect of the preparation method on the electrocatalytic activity of the catalysts. J Power Sources 2012;215:53–62.

[18] Paulus UA, Schmidt TJ, Gasteiger HA, Behm RJ. Oxygen reduction on a high-surface area Pt/Vulcan carbon catalyst: a thin-film rotating ring-disk electrode study. J Electroanal Chem 2001;495:134–45.

[19] Song S, Liu J, Shi J, Liu H, Maragou V, Wang Y, et al. The effect of microwave operation parameters on the electrochemical performance of Pt/C catalysts. Appl Catal B Environ 2011;103:287–93.

[20] Zhou Z-Y, Tian N, Huang ZZ, Chen DJ, Sun SG. Nanoparticle catalysts with high energy surfaces and enhanced activity synthesized by electrochemical method. Faraday Discuss 2008;140:81–92.

[21] Liang Y, Zhang H, Zhong H, Zhu X, Tian Z, Xu D, et al. Preparation and characterization of carbon-supported PtRuIr catalyst with excellent CO-tolerant performance for proton-exchange membrane fuel cells. J Catal 2006;238:468–76.
[22] Silveira Parreira L, Martins da Silva JC, D'Villa-Silva M, Carmona Simoes F, Garcia S, Gaubeur I, et al. PtSnNi/C nanoparticle electrocatalysts for the ethanol oxidation reaction: Ni stability study. Electrochim Acta 2013;96:243–52.
[23] Melnick RE, Palmore GTR. Time-dependent impedance of the electro-oxidation of methanol on polished polycrystalline platinum. J Phys Chem B 2001;105:9449.