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Review

Effect of synthesis method and structural characteristics of Pt–Sn fuel cell catalysts on the electro-oxidation of CH_3OH and CH_3CH_2OH in acid medium☆

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ABSTRACT

In view of a possible use as anode materials for low-temperature fuel cells, the electro catalytic activity of Pt–Sn catalysts for methanol and ethanol oxidation has been widely investigated. This short review examines the effects of Pt–Sn structural characteristics, such as degree of alloying and Sn oxidation state, depending on the synthesis method, on the electro catalytic activity for methanol and ethanol oxidation.

Contents

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1. Introduction

Platinum is commonly used as anode catalyst in low-temperature fuel cells fuelled with low molecular weight alcohols such as methanol (DMFC) and ethanol (DEFC). Pure Pt, however, is not the most efficient anodic catalyst for direct alcohol fuel cells, being rapidly poisoned on its surface by strongly adsorbed species coming from the dissociative adsorption of the alcohols [1,2]. Efforts to mitigate the poisoning of Pt have been concentrated on the addition of cocatalysts, particularly ruthenium and tin, to platinum.

Pt–Sn nanocomposites have been extensively studied as catalysts for the electro-oxidation of methanol and ethanol. Among various Pt-based binary catalysts, Pt–Sn has been reported as the most effective for the electro-oxidation of ethanol. Regarding the methanol electro-oxidation, instead, controversial results have been reported. In this review we examine the catalytic activity and the relationship of activity to structural characteristics of Pt–Sn catalysts for the electro-oxidation of CH_3OH and CH_3CH_2OH in acid medium. The question of the promotional role of Sn atoms is crucial, so we will discuss whether Sn has to be present in metallic form alloyed to Pt or in the oxide form, and whether the activity enhancement produced by Sn atoms has to be ascribed to a bifunctional or an electronic effect. As the degree of alloying depends on the synthesis method, a key role is played by the way of preparation of Pt–Sn catalysts. The different synthesis methods and their effect on the alloying degree are presented.

2. Structure of Pt–Sn fuel cell catalysts

In Pt–Sn fuel cell catalysts platinum alloys with tin to form mainly a face-centered-cubic (fcc) Pt_3Sn phase and, in some case, as a hexagonal-closed-packed (hcp) PtSn phase. Regarding the shift of the XRD fcc Pt peaks of Pt–Sn catalysts to lower angles than pure Pt but to higher angles than the Pt_3Sn phase, Kuznetsov et al. [3] asserted that Pt forms nearly all possible alloys with Sn, thus the shift of XRD Pt reflexions should reveal the formation of a solid solution between Pt and Sn. Radmilovic et al. [4] and Antolini and Gonzalez [5], instead, attributed the shift of XRD Pt reflexions to a mixture of Pt_3Sn and Pt_9Sn [4] or Pt [5] phases.

Generally, Pt–Sn catalysts are formed by fully alloyed (fcc Pt_3Sn), fully non-alloyed (Pt–SnO_x or Sn ad-atom modified Pt) or partially alloyed (fcc $Pt_{(1-x)}Sn_x$ alloy, with lattice parameter <0.40 nm, that is, Pt/Sn atomic ratio in the alloy >3, and SnO_x) platinum–tin structures. The most common type of tin oxide reported in Pt–Sn catalysts is tin dioxide, SnO_2. SnO_2 is usually regarded as an oxygen-deficient *n*-type semiconductor [6], which crystallizes with the rutile structure [7]. Considering the use of Pt–Sn in acidic fuel cells, it is important to remark that SnO_2 dissolves in sulfuric acid to give $Sn(SO_4)_2$ [8].

In addition to XRD, characterization techniques such as X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) are useful to better clarify the structure of Pt–Sn catalysts. Godoi et al. [9] and Kim et al. [10] used both XPS and XAS to characterize Pt–Sn catalysts with different alloying degree and different Sn contents, respectively. XPS and direct-XAS (DXAS) studies were carried out for three Pt–Sn/C catalysts [9]. To modify the catalysts surface without producing significant changes in the average particle size, the as-prepared sample was divided into three parts and two of them were heat-treated in mild temperature conditions (150 °C, 1 h, one in nitrogen and the other in a hydrogen atmosphere). In this way, the as-prepared and heat-treated Pt–Sn/C catalysts had exactly the same overall composition and particle size. The sample treated in H_2 atmosphere was partially alloyed, while the others were fully non-alloyed. The Pt 4f spectrum was deconvoluted into three doublets which correspond to Pt $4f_{7/2}$ and Pt $4f_{5/2}$ of different oxidation states. In general, Pt is found as metallic Pt (Pt(0)) and in oxidized forms, as $Pt(OH)_2$ and PtO_2. The data revealed that heat treatments in nitrogen and hydrogen produced an increase in Pt(0) amount in both Pt–Sn/C catalysts. The Sn $3d_{5/2}$ signal was deconvoluted into two different peaks. The first line centered at 485.1–485.5 eV was attributed to metallic tin (Sn(0)) while the second line (487.1–467.4 eV) was assigned to Sn(IV) species. The amount of Sn(0) for the Pt–Sn/C catalyst treated in nitrogen was similar to that for the as-prepared catalyst, and significantly larger for the hydrogen-treated material. Additionally, the amounts of Sn(0) and Sn oxides remained nearly the same for the material heat-treated in nitrogen while there was a substantial increase in Sn(0) content (with concomitant decrease in the content of Sn oxides) for the catalyst treated in hydrogen. From situ DXAS measurements, the decrease in the white line intensity observed for the Pt–Sn/C catalyst heat-treated in hydrogen was consistent with an increase in the degree of alloying, as evidenced by XRD data and the concomitant decrease in the amount of oxidized species in good agreement with XPS data. The fact that the white line intensity observed for the Pt–Sn/C catalyst heat-treated in nitrogen was similar to that of the as-prepared material was also in good agreement with XRD and XPS results, showing that the amounts of metallic Sn and Sn oxides in those two samples are comparable.

Kim et al. [10] reported XPS spectra of Pt 4f and Sn 3d for Pt/C and Pt–Sn/C catalysts with various Sn contents. They found that Pt(0) is the predominant species in all Pt–Sn/C catalysts, with small amounts of the oxidized Pt species. A binding energy shift to lower energies by 0.3–1.0 eV appeared in all Pt–Sn/C catalysts compared to Pt/C, due to electronegativity differences in the elemental Pt and Sn, leading to charge transfer from the less-electronegative Sn to the more-electronegative Pt. For Sn_{3d} XPS spectra they observed that the surface state of Sn is oxidic (e.g., SnO, SnO_2, or Sn hydroxides), independent of the amount of Sn content in the Pt–Sn/C catalysts. XPS data showed that the surface Sn/Pt atomic ratios are higher than the bulk values, indicating that the Pt–Sn/C catalysts may cause significant surface Sn enrichment by segregation of Sn onto the surface, especially in the samples with higher Sn content.

X-ray absorption near edge structure (XANES) spectra were obtained for Pt/C and Pt–Sn/C catalysts. The white line magnitudes were smaller in all Pt–Sn/C catalysts than that of Pt/C catalyst and showed a decreasing tendency with increasing Sn content up to Pt/Sn ratio of 2, ascribed to partial filling of the unoccupied Pt 5d orbital by electrons that are donated by adjacent Sn. Thus the electronic transition of 2p → 5d was suppressed along with the result of smaller white line intensities. It was correlated with the extended X-ray absorption fine structure (EXAFS) results, that is, the Pt–Sn bond distance seemed to slightly decrease with increasing Sn amount up to Pt/Sn ratio of 2 via a stronger interaction between Pt and Sn, although the white line intensities appeared to increase a little again for the catalysts with the highest Sn content, but still smaller than that of Pt.

3. Synthesis methods

Pt–Sn catalysts used for alcohols electro-oxidation are commonly prepared in form of films or carbon supported materials. The following synthesis methods of Pt–Sn film electrodes have been proposed:

(i) Electrochemical co-deposition: a Pt–Sn electrode is prepared by electrodeposition from a mixed solution of Pt and Sn precursors at constant potential [11] or by potential cycling [12].
(ii) Immersion method [13,14]: this consists of covering a hydrogen-covered platinum surface with tin ad-atoms by immersing it into an aqueous tin solution.
(iii) Underpotential deposition [15–18]: a submonolayer of tin ad-atoms is underpotential-deposited on a smooth platinum electrode from a tin solution.

Carbon supported catalysts are commonly used as electrode materials in low-temperature fuel cells. As metal particle growth takes place appreciably by thermal treatment at temperatures >600 °C [19], a way to tailor carbon supported Pt–Sn catalysts with small particle size is the simultaneous impregnation on the carbon support of Pt and Sn precursors, followed by reduction at low (<100 °C) or intermediate temperature (200–500 °C) [20]. The degree of alloying of Pt–Sn/C catalysts depends on the synthesis methods.

Bonnemann et al. [21,22] developed a colloidal method to prepare unsupported and supported metals. Metal salts of groups 6–12 were reduced using alkali hydrotriorganoborates in hydrocarbons between −20 and 80 °C to give boron-free powder metals. The use of tetraalkylammonium hydrotriorganoborates as reducing agents leads to colloidal transition metals in organic phases. The obtained particles are nearly amorphous. This synthesis method was used to prepare carbon supported fully non-alloyed Pt–Sn catalysts [2,23].

The polyol synthesis, in which an ethylene glycol solution of the metal precursor salt is slowly heated to produce colloidal metal, has recently been extended to produce carbon supported metal nanoparticles [24,25]. In this process, the polyol solution containing the metal salt is refluxed at 120 °C to decompose ethylene glycol to yield in situ generated reducing species for the reduction of the metal. The metal particles produced as such may be captured by a support material suspending in the solution. Pt–Sn/C catalysts synthesized using the polyol method presented a mean particle size of about 1.9 nm and a sharp particle distribution [24,25].

As a rapid, uniform and effective heating method, microwave heating has received considerable attention as a new promising method for nanosized materials synthesis. Polymer stabilized Pt colloids with small and uniform particle size have been prepared by microwave heating ethylene glycol solutions of metal precursor salts. Carbon supported Pt catalysts were prepared using a microwave heated polyol (MHP) process [26]. Liu et al. [27] prepared carbon supported Pt–Sn nanoparticles by a MHP process. The MHP process leads to the formation of small and uniform Pt–Sn particles and to a high dispersion on the carbon support.

Kim et al. [10] synthesized Pt–Sn/C using the borohydride reduction method (BM) followed by freeze-drying procedure without any heat treatment. All Pt–Sn catalysts prepared using this method were highly dispersed on the carbon support, demonstrating that BM with freeze-drying procedure could provide a convenient, inexpensive and suitable method to prepare nanosized catalysts.

Another way to prepare carbon supported catalysts is based on the reduction of the precursors with formic acid at room temperature (FAM method). The method consists in the treatment of carbon powder with formic acid before impregnation of metal precursors. The treated carbon reduces the precursors on its surface. Carbon supported Pt–Sn catalysts were successfully prepared using this method [28].

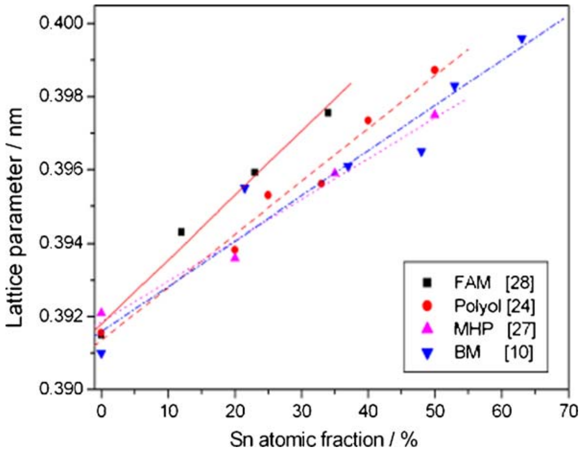

Fig. 1. The dependence of the lattice parameters of Pt–Sn catalysts prepared by different methods on Sn content.

All the Pt–Sn/C catalysts synthesized by the polyol method, the MHP, the BM and the FAM were partially alloyed. The dependence of the lattice parameters of Pt–Sn catalysts prepared by these methods on Sn content is shown in Fig. 1. The lattice parameters for all the Pt–Sn catalysts are larger than those for Pt/C and increase with the increase of Sn content in the catalyst, indicating the lattice expansion by alloying. The increase in the lattice parameters of the solid solution with Sn content in the catalyst reflects the progressive increase of tin content in the solid solution, due to the conversion of part of Sn into the alloyed state. Part of Sn, however, is present as SnO_x. The lattice parameters of all series of carbon supported catalysts linearly increased with the Sn content in the catalyst. The Pt–Sn catalysts synthesized by the FAM presented the highest slope of the lines obtained by fitting different data set, indicating that this method produces catalysts with the highest degree of alloying.

Thermal treatment of partially alloyed Pt–Sn/C (Pt:Sn = 3:1) catalysts in the temperature range 200–500 °C results in the formation of fully alloyed catalysts, with the formation of a predominant cubic Pt_3Sn phase and, to a lesser extent, a hexagonal PtSn phase [29]. The amount of the hexagonal PtSn phase as well as the particle size increased with increasing thermal treatment temperature. In the case of thermal treatment of partially alloyed Pt–Sn/C (Pt:Sn = 1:1) catalysts the formation of a main hexagonal PtSn phase and cubic Pt_3Sn as a secondary phase was observed [30].

4. Pt–Sn catalysts for methanol oxidation

4.1. A general overview

The total oxidation process of methanol consists of a pattern of parallel reactions which can be formulated as follows [31]:

$$CH_3OH \rightarrow \text{adsorbedintermediates} \rightarrow CO_{ad} \rightarrow CO_2 \tag{1}$$

$$CH_3OH \rightarrow \text{adsorbedintermediates} \rightarrow HCHO, \quad HCOOH \rightarrow CO_2 \tag{2}$$

Among CH_3OH, HCHO and HCOOH, methanol is the least reactive. Thus, in the stepwise oxidation of CH_3OH to CO_2, the first

$2e^-$ oxidation step, i.e., the conversion of methanol to formaldehyde is the rate-determining step [32]. The elementary step which determines the rate might be either C–H bond breaking or C–O bond formation. Studies on bare Pt have shown that the methanol oxidation reaction (MOR) is inhibited by formation of poison, identified as a –CO or a –COH species [1,31,33,34]. The –COH species have been suggested to be a detectable intermediate in the formation of –CO on Pt [35]. Generally, on Pt–Sn surfaces a lower onset for methanol oxidation currents is observed compared to bare Pt surfaces, attributed to earlier poison oxidation by the presence of excess O at the surface, supplied by Sn species. The presence of Sn atoms near to Pt, however, has negative effects on methanol adsorption and dehydrogenation.

Pt–Sn nanocomposites have been prepared by a variety of electrochemical or chemical methods, and inconsistencies in catalyst performance have been reported [14]. Indeed, an enhanced activity for methanol electro-oxidation, in contrast to no/negligible enhancement of the MOR rate over Pt–Sn catalysts was observed. As reported in detail in the following paragraphs of this section, the MOR activity of Pt–Sn catalysts depends on the chemical state of Sn, that is, Sn can be present in an oxidized form (Sn(II) and Sn(IV) and/or as Sn(0), alloyed with Pt or as Sn ad-atoms. We have separated the Pt–Sn catalysts for methanol electro-oxidation in non-alloyed, fully alloyed and partially alloyed catalysts.

4.2. Methanol oxidation on non-alloyed Pt–Sn catalysts

4.2.1. Methanol oxidation on platinum–tin oxide/hydroxide catalysts

A positive effect of the presence of tin oxide/hydroxide on Pt MOR activity has been reported in both old and recent papers [11,12,17,36–41]. Firstly, Cathro [11] found that electrodeposited platinum–tin mixtures have higher activity towards methanol, formaldehyde and formic acid oxidation than platinum black. This enhancement was attributed to a redox mechanism, with the tin assumed to be present in an oxidic form. On the basis of the values of the standard potential of the redox couple $Sn(OH)_2/Sn(OH)_4$ ($E_o = 0.075$ V vs. NHE at 25 °C), he suggested that a direct redox reaction of $Sn(OH)_4$ with the strongly adsorbed residue from methanol takes place. Katayama [36], instead, asserted that the redox coupling of ionic tins is not likely to act towards the MOR enhancement, but rather the redox coupling of Pt^0/Pt^{2+} or Pt^{2+}/Pt^{4+}. Platinum stabilized in ionic forms by the presence of SnO_x is likely to enhance the catalytic activity of Pt–SnO_x. The assertion of Katayama [36] was supported by Aramata et al. [37] through studies of the MOR activities of M–Sn oxides (M = Pt, Rh and Ir). Sobkowski et al. [17] and Bittins-Cattaneo and Iwasita [38] reported that the catalytic effects of adsorbed tin on platinum upon methanol oxidation is due to the presence of Sn(I1) species. They found that tin is not adsorbed in the form of ad-atoms but rather as divalent hydroxy- or sulphate complexes. Taking into account the electronic configuration of Sn(I1) and Pt it seems quite possible that Sn(I1) forms a hydroxycomplex like $Sn(OH)^+$ which should offer oxygen atoms for the oxidation of methanol adsorbate to CO_2. In the presence of co-adsorbed tin, methanol adsorbate oxidation occurs at potentials 0.15 V lower than on pure platinum. Hable and Wrighton [12] observed that up to +0.5 V vs. SCE the MOR activity on Pt–SnO_x catalysts in aqueous H_2SO_4 at 25 °C is higher than on Pt alone. Above +0.5 V vs. SCE, the MOR activity was inhibited compared to Pt alone. More recently, De Oliveira et al. [39] studied the electro-oxidation of methanol on Pt–M_yO_x (M = Sn, Mo, Os or W) electrodes. Fig. 2 shows the anodic part of the cyclic voltammetry (CV) curves in CH_3OH/H_2SO_4 solutions for different electrodes: the $PtSn_yO_x$ electrodes presented the highest peak current values, and the oxidation process started at a potential 200 mV lower that that on Pt electrodes. The same research group [40] found that the current values for methanol electro-oxidation on electrodeposited platinum on SnO_2 thin films were up to 10 times higher than the current values on platinized platinum. The high MOR activity of the SnO_2 supported Pt was ascribed both to the high Pt dispersion (tin oxide film functions as an efficient matrix) and to the co-catalytic effect of SnO_2. Finally, Cui et al. [41] investigated the MOR activity of Pt and Pt–SnO_2 catalysts supported on graphitized mesoporous carbon: they found that the MOR activity of Pt–SnO_2 is much enhanced compared to that of Pt alone, although the Pt loading amount of the former is only half of the latter.

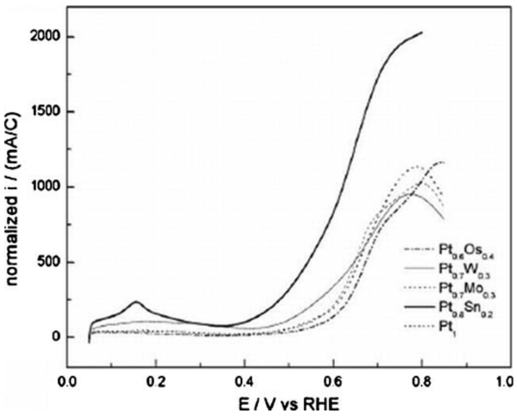

Fig. 2. Anodic sweep of binary electrodes in CH_3OH/H_2SO_4 solution at 20 mV s^{-1}. Current values normalized by the CO desorption charge. Reproduced from Ref. [39], copyright 2005, with permission from Elsevier.

4.2.2. Methanol oxidation on Pt catalysts modified by Sn ad-atoms

Conflicting results have been reported in the literature regarding the methanol oxidation on Pt catalysts modified by Sn ad-atoms. In earlier works, Janssen and Moolhuysen [13,42] and Watanabe at al. [43] reported a remarkable increase in the MOR activity on Sn ad-atom modified Pt, by a factor of 50 and 100, respectively, as compared with pure platinum. More recently, Wei et al. [18] observed that the rate of methanol electro-oxidation on underpotentially deposited-ruthenium-modified platinum electrode (upd-Ru/Pt) and on underpotentially deposited-tin-modified platinum electrode (upd-Sn/Pt) increased several times than on a pure Pt electrode. Methanol oxidation on the upd-Sn/Pt electrode shifted towards an even more negative potential than that on upd-Ru/Pt. The effects of tin were sensible to the potential range. In a potential range from 0 to 0.22 V, the current of methanol oxidation on upd-Sn/Pt with underpotential deposition of 100 s was larger than that on upd-Ru/Pt. Over the potential of 0.22 V, the low coverage of upd-Sn deposits on the Pt surface was favorable for methanol electro-oxidation. The enhancement effect of upd-Sn adatoms for the MOR disappeared as the electrode potential is beyond a certain value. Effects of potential and Sn content on the MOR activity of Sn ad-atom modified Pt were previously observed also by Beden et al. [16]. Conversely, Stalnionis et al. [44] and Campbell and Parsons [45] found that the methanol oxidation rate is not enhanced on the Sn-modified Pt surface, compared to the Pt electrode.

In well defined {1 1 1} and {1 0 0} Pt surfaces of single crystals, Campbell and Parsons [45] and Haner and Ross [46] found that Sn ad-atoms have no effect or decrease the electrocatalytic activity of pure platinum. The methanol oxidation rate decreased as the amount of irreversibly adsorbed tin increased.

To explain the effect of tin ad-atoms on methanol oxidation, Ishikawa et al. [47] carried out relativistic density functional theory

(DFT) calculations of the elementary steps of CH_3OH oxidation on pure platinum and mixed Pt–Sn metals. Cluster models of Pt_nSn_{10-n} were used to simulate the metal surfaces. They found that the presence of tin in the cluster weakens the platinum–methanol bond. The same is true for other adsorbates (CH_2OH, CHOH and CHO). On the $(Pt_3)(Sn_4Pt_3)$ cluster, with the highest Sn/Pt ratio, the adsorption energy on Pt is decreased dramatically in comparison to adsorption on pure platinum. Similar trends are found in other mixed cluster species. Tin is a poor electron acceptor: the tin site in $(Pt_3)(Pt_4Sn_3)$ does not adsorb CH_3OH ($E_{ads} = 0$). The dehydrogenation of CH_2OH on $(Pt_3)(Sn_2Pt_5)$ has an activation energy of 0.75 eV, 0.2 eV higher than that on pure platinum. On $(Pt_3)(Sn_4Pt_3)$, the dehydrogenation of CH_2OH has even higher activation energy (0.84 eV). The dehydrogenation energies of CH_3OH and CH_2OH on the cluster also become endothermic. The results indicated that a Pt–Sn surface with a high atomic percentage of tin is not conducive to CH_3OH dissociation (negative effect). Hence, the optimal tin surface coverage must be low. The dissociation of H_2O at a tin site in Pt–Sn is more favorable than at a platinum site (positive effect). The presence of Sn atoms reduces the Pt–CO bond strength substantially, indicating the existence of a ‘ligand effect’ (positive effect). They concluded that the activity of a platinum site in mixed Pt–Sn for CH_3OH dissociation should vary somewhat with atomic Sn/Pt ratio. With more tin, the activity at platinum becomes less.

On this basis, the conflicting MOR activity results observed in Sn ad-atoms polycrystalline Pt could likely be ascribed to different Sn coverages. Moreover, depending on the preparation method of the Sn ad-atoms modified Pt, that is, whether this arises from the operation of a cyclic Sn(II)/Sn(IV) redox system or from modification of the platinum surface by Sn(0), in some cases the presence of oxidized tin in Sn ad-atoms modified Pt was reported [44,48], increasing the MOR activity of the catalysts.

The poor MOR activity of Sn ad-atoms on well defined Pt crystal faces could also be due to the absence of a cooperative interplay between facets. Indeed, in polycrystalline Pt, Sn deposition takes place on both {1 0 0] and {1 1 1} facets, while in Pt single crystals Sn is deposited only on the {1 0 0} or {1 1 1} facet. As reported by Komanicky et al. [49] for the activity for oxygen reduction of platinum arrays containing different ratios of {1 1 1} and {1 0 0} facets, the increased catalytic activity of the arrays with respect to single {1 1 1} and {1 0 0} facets points to a possible cooperative interplay between facets.

4.3. Methanol oxidation on Pt_3Sn and Pt–Sn alloys

4.3.1. Pt_3Sn single crystals

Haner and Ross [46] studied the effect of tin atoms on the platinum surface by using single crystal faces of the Pt_3Sn alloy. They found that none of the alloy surfaces were more effective catalysts than any of the pure platinum surfaces and that alloying platinum with tin to any extent significantly reduced the activity. They proposed that the effect of tin is primarily an electronic effect. The voltammetry data support the conclusion that there is a very strong “ligand effect” on the way methanol adsorbs on the Pt surface due alloying the Pt with Sn, but this effect is not beneficial for catalysis. Wang et al. [50] investigated the activity of the $Pt_3Sn(1\,1\,0)$ single crystal surface towards methanol oxidation in acid solution. A small enhancement of methanol oxidation was observed in long time potential step measurements. The steady-state activity of the $Pt_3Sn(1\,1\,0)$ surface showed a factor of 3 enhancement (which is small compared with that of Pt–Ru alloys) for methanol oxidation over the pure Pt, but for times smaller than ca. 10 s. the $Pt_3Sn(1\,1\,0)$ surface was less active than Pt. The other low index surfaces of Pt_3Sn showed no enhancement over Pt even at long times. The poor MOR activity of Pt_3Sn alloy was ascribed to the blocking of the multiple Pt atom sites needed to dehydrogenate methanol by CO adsorbed (CO_{ad}).

4.3.2. Polycrystalline Pt_3Sn and PtSn alloys

A reported by Colmati et al. [28] the performance of a DMFC with polycrystalline Pt_3Sn/C was lower than that of a cell with Pt/C as anode catalyst. A poor stability of polycrystalline Pt–Sn alloys in acid media, however, can positively influence their MOR activity, has been reported [13,16,42]. Polycrystalline PtSn and Pt_3Sn alloys were submitted to potential cycling in H_2SO_4/CH_3OH solutions. The evolution of the voltammograms showed that the Pt–Sn alloys are not at all stable, and that Sn is preferentially dissolved in the electrolyte solution. Moreover, the surface area decreased during the potential cycling, which can certainly be attributed to a superficial rearrangement of the platinum deposit. The change of the oxidation current of methanol during potential cycling showed that, when Sn electrode surface content decreases, due to its preferential dissolution in the electrolyte, the oxidation current increases, whereas the anodic polarization curve is shifted to more anodic potentials. Liu et al. [51], by potential cycling of Pt_3Sn particles in H_2SO_4 solution between −240 and 500 mV vs. SCE, suggested that the Pt_3Sn catalysts are structurally and chemically stable in the acid environment when the applied potential is lower than 500 mV. However, when the positive potential limit was extended to 1000 mV vs. SCE, the distinct hydrogen adsorption/desorption peaks characteristic of pure Pt were observed due to the dissolution of Sn on Pt_3Sn catalyst surface.

Summarizing, Pt–Sn alloy surfaces are not suitable catalysts for the MOR. Alloying platinum with tin to any extent significantly reduced the activity. However, catalyst surface modifications by Sn dissolution can improve the MOR activity of Pt–Sn alloy catalysts.

4.4. Methanol oxidation on partially alloyed Pt–Sn catalysts

Many papers reported methanol oxidation on partially alloyed Pt–Sn catalysts. Honma and Toda [52] investigated the temperature dependence of methanol oxidation for Pt and partially alloyed Pt–Sn catalysts in the range from 25 to 140 °C. In all the temperature range Pt–Sn catalysts exhibited electrocatalytic properties superior to those of Pt. Zhou et al. [53] studied DMFCs with Pt/C and partially alloyed Pt–Sn/C (1:1) and Pt–Ru/C (1:1) as anode catalysts, respectively. They found that the addition of Ru or Sn to the Pt considerably enhances the electro-oxidation of methanol, and that Pt–Ru/C is more suitable for use as DMFC anode catalyst than Pt–Sn/C.

The effect of Sn content in partially alloyed Pt–Sn catalysts formed by fcc $Pt_{(1-x)}Sn_x$ solid solution and SnO_x on the MOR activity has been reported in different papers [10,27,28,54]. Colmati et al. [28] investigated the MOR activity of Pt–Sn catalysts with different Sn contents and/or different alloying degree. The onset potential of methanol oxidation of all the Pt–Sn catalysts was lower than pure Pt, but increased with Sn content in the alloy. As shown in Fig. 3, the DMFC with partially alloyed $Pt_{75}Sn_{25}$/C showed the best performance, while the performance of the cell with fully alloyed $Pt_{75}Sn_{25}$/C was very poor, lower than that of the cell with Pt/C as anode material. The high performance of partially alloyed $Pt_{75}Sn_{25}$/C was ascribed to the optimal mixing of Sn content, degree of alloying and particle size. Liu et al. [27] and Lim et al. [54] investigated the MOR activity of Pt–Sn/C catalysts with Sn/Pt atomic ratio in the range 0–2. The catalysts with Sn/Pt = 0.54 and 0.33 showed the highest MOR activity at room temperature and at 40 °C, respectively. Kim et al. [10] investigated the electro-oxidation of methanol, ethanol, and 1-propanol on Pt–Sn/C catalysts with different Pt:Sn atomic ratios. They found that addition of Sn into Pt leads to substantial enhancements in the catalytic activity for the electro-oxidation of alcohols. The addition of Sn into Pt significantly

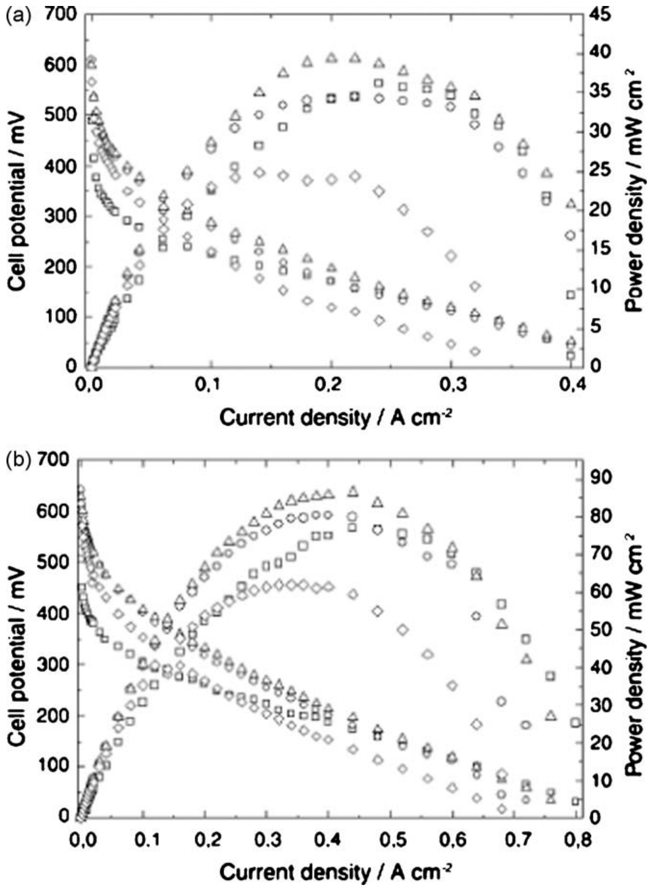

Fig. 3. Polarization and power density curves of DMFCs with $Pt_{90}Sn_{10}/C$ and $Pt_{75}Sn_{25}/C$ prepared by FAM and commercial Pt/C and $Pt_{75}Sn_{25}/C$ as anode electrocatalysts for methanol oxidation at 70 °C and 1 atm O_2 pressure (a) and at 90 °C and 3 atm O_2 pressure (b) using a 2 M methanol solution. Anode metal loading $0.4\,mg\,cm^{-2}$. Cathode 20 wt.% Pt/C, Pt loading $0.4\,mg\,cm^{-2}$. (□) Pt/C E-TEK; (○) $Pt_{90}Sn_{10}/C$; (△) $Pt_{75}Sn_{25}/C$; (◊) $Pt_{75}Sn_{25}/C$ E-TEK.

improves the reaction rate regardless of the Sn contents up to 50%. Interestingly, the activity enhancements with the addition of Sn become much larger by 2.5, 3.5 and 6.0 folds, considering the best composition of Pt and Sn to give maximum activity, for methanol, ethanol, and 1-propanol, respectively.

To evaluate the optimum Sn content and lattice parameter, we have plotted the Pt–Sn to Pt MOR activity ratio against Sn content (Fig. 4a) and lattice parameter (Fig. 4b), using data from different works [10,27,54]. According to both a Gaussian and a Lorentzian distribution, the maximum MOR activity is at a Sn/Pt atomic ratio of 0.40 (Pt:Sn = 2.5:1) and at a value of lattice parameter of 0.396 nm. In the hypothesis of the formation of a solid solution between Pt and Sn, due to the incorporation of Sn in the fcc structure of Pt, the amount of alloyed Sn in the Pt–Sn catalysts (x) can be evaluated approximately using Vegard's law. On this basis, x was calculated with the relationship:

$$x = \frac{a - a_o}{x_s(a_s - a_o)} \qquad (3)$$

where x_s is the Sn atomic fraction (0.25) of the Pt_3Sn catalyst, and a_s (0.400 nm) and a_o (0.392 nm) are the lattice parameter of Pt_3Sn and Pt, respectively. For $a = 0.396$ nm, it results a value of x of 0.125, corresponding to a Sn/Pt atomic ratio of 0.14. Being total Sn/Pt atomic ratio = 0.40, it can be inferred that the highest MOR activity is obtained with 1/3 Sn in an alloyed form and 2/3 Sn in a non-alloyed form.

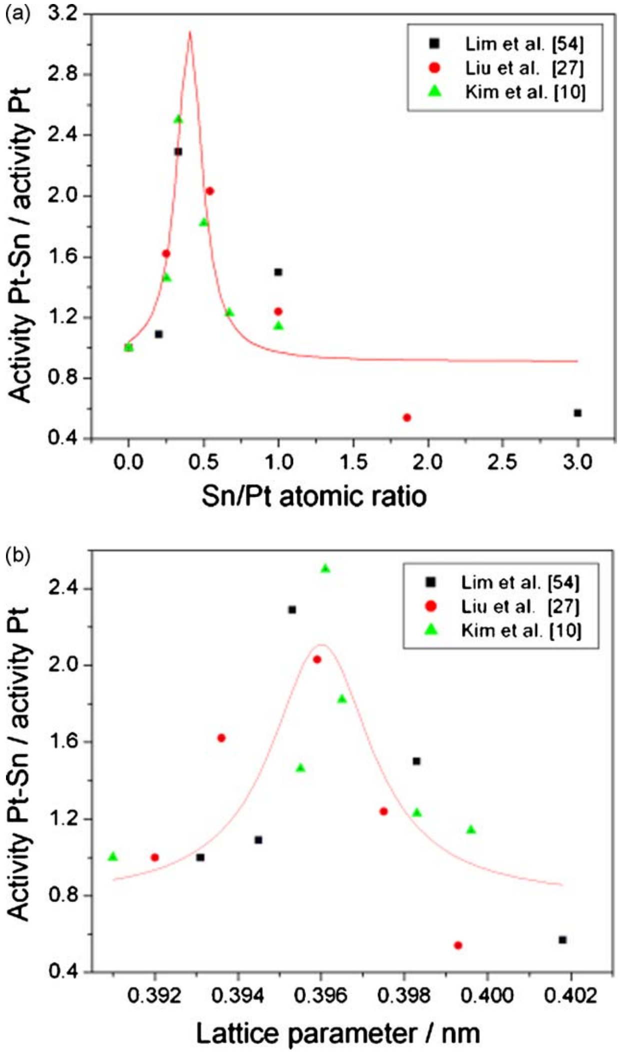

Fig. 4. Dependence of the Pt–Sn to Pt MOR activity ratio against Sn content (a) and lattice parameter (b), obtained using data from different works [10,27,54]. The full lines represent the Lorentzian fit of all the data.

5. Pt–Sn catalysts for ethanol oxidation

5.1. A general overview

Several studies on the electro-oxidation of ethanol have been devoted mainly to identifying the adsorbed intermediates on the Pt electrode and elucidating the reaction mechanism by means of various techniques, as differential electrochemical mass spectrometry (DEMS), in situ Fourier transform infrared spectroscopy (FTIRS) and electrochemical thermal desorption mass spectroscopy (ECTDMS) [55–60]. Based on the foregoing works, the global oxidation mechanism of ethanol in acid solution may be summarized in the following scheme of parallel reactions:

$$CH_3CH_2OH \rightarrow [CH_3CH_2OH]_{ad} \rightarrow C_{1ads}, \quad C_{2ads} \rightarrow CO_2(\text{totaloxidation}) \qquad (4)$$

$$CH_3CH_2OH \rightarrow [CH_3CH_2OH]_{ad} \rightarrow CH_3CHO \rightarrow CH_3COOH(\text{partialoxidation}) \qquad (5)$$

The formation of CO_2 goes through two adsorbed intermediates C_{1ads} and C_{2ads}, which represent fragments with one and two carbon atoms, respectively. Breaking the C–C bond for a total oxidation to CO_2 is a major problem in ethanol electrocatalysis. Thus, high yields of partial oxidation products, CH_3CHO and CH_3COOH, are formed at Pt catalysts [61,62]. DFT calculations on Pt(1 1 1) provide a starting point to probe ethanol C–C and C–O bond cleavage reactions on supported Pt catalysts [63,64]. Ethanol conversion on supported Pt catalysts at temperatures above 217 °C resulted in higher selectivity for C–C bond cleavage products (methane and CO) compared to C–O bond cleavage product (ethane) selectivity [63]. Alcalá et al. [64] estimated that the rate constant for C–C bond cleavage in ethanol is faster than for C–O bond cleavage on Pt(1 1 1) at temperatures higher than about 277 °C. This prediction is in agreement with experimental results for ethanol decomposition and ethanol reforming on Pt catalysts at these temperatures. In addition, the calculated value of the rate constant for C–C bond cleavage in ethanol at temperatures near 277 °C was much higher than for C–C bond cleavage in ethane. Similarly, the rate of C–O bond cleavage in ethanol is expected to be much higher than for C–O bond cleavage in carbon monoxide on Pt(1 1 1).

Pure Pt, however, is not the most efficient anodic catalyst for direct ethanol fuel cells, being rapidly poisoned on its surface by strongly adsorbed species coming from the dissociative adsorption of ethanol [2]. Efforts to mitigate the poisoning of Pt have been concentrated on the addition of cocatalysts, particularly ruthenium and tin, to platinum. Conversely to the methanol oxidation, the best binary catalyst for ethanol oxidation in acid environment is not Pt–Ru but Pt–Sn [65]. In the following part of Section 5, we report the ethanol oxidation reaction on non-alloyed, fully alloyed and partially alloyed Pt–Sn catalysts.

5.2. Ethanol electro-oxidation on non-alloyed Pt–Sn catalysts

5.2.1. Pt–SnO_x catalysts

Hable and Wrighton [35,66] found that the activity for the ethanol oxidation reaction (EOR) of the Pt–SnO_2 catalyst was superior to that of Pt and Pt–Ru catalysts. The Pt–SnO_2 catalyst, however, offers no benefit over Pt alone with respect to C–C bond oxidation. Ethanol and acetaldehyde are both oxidizable at relatively negative potentials on surfaces modified by Pt–SnO_2 electrodeposits, but acetic acid is practically inert on Pt–SnO_2. Product analysis showed acetic acid to be the ultimate product from oxidation of ethanol at potentials more negative than 0.5 V vs. SCE at room temperature. In alcohols that have a C–C bond, CO poisoning at Pt–SnO_2 does not occur at low temperatures and low potentials to the same extent as for methanol, because C–C bond breaking does not occur on Pt–SnO_2 under such conditions. Lamy et al. [2] prepared Pt–Sn/C catalysts in the Pt:Sn atomic ratio 9:1, 4:1 and 3:1 using the "Bönneman" method. In particular, for the Pt–Sn (9:1) catalyst, the absence of shift of the Pt XRD peaks clearly showed that no alloy is formed during the co-reduction process. Likely, tin should be present in the oxide form. The effect of the Pt:Sn atomic ratio on ethanol electro-oxidation is shown in Fig. 5. With 10 at.% Sn, the electrocatalytic activity is greatly enhanced mainly at low potentials. Small enhancements exist also for higher Sn contents (Pt:Sn 4:1), but for Sn contents >30 at.%, the electroactivity decreases in comparison to pure platinum. Regarding the electro-oxidation of ethanol on Pt–Sn (9:1), in a next work [67] they found that the presence of tin lead to an important change in the product distribution, i.e., increase of the acetic acid (AA) and decrease of the acetaldehyde (AAL) and CO_2 chemical yields. They suggested that the electro-oxidation observed for potentials greater than 0.2–0.3 V with Pt–Sn is due mainly to the oxidation of ethanol without breaking of the C–C bond. With pure platinum, the CO poisoning remains significant until 0.6 V, meaning that ethanol is still dissociated, with breaking of the C–C bond. When Pt is modified by Sn, the CO poisoning becomes negligible above 0.2 V, and ethanol goes through the direct oxidation of the alcohol group producing acetaldehyde and finally acetic acid. This was explained by the ability of tin to activate water dissociation at potentials lower than on platinum, leading to the formation of OH species necessary to complete the oxidation of ethanol via AAL adsorbed species according to the bifunctional mechanism. Jiang et al. [23] found that the EOR activity of Pt–SnO_x/C catalysts with different Pt:Sn atomic ratios prepared by a colloidal method decreased with tin content at room temperature, but increased at 80 °C. On all Pt–SnO_x/C catalysts, AA and AAL represent dominant products, while CO_2 formation contributes 1–3%. With increasing potential, AAL yield decreased and AA yield increased. DEFC measurements at 90 °C indicated that the cell performance depends on SnO_x content and available Pt active sites. High amounts of tin oxides result in smaller metal particle sizes and consequently a larger active surface area, more OH species for removing ethanol residues, partial blocking of Pt active sites, and higher resistance of the catalytic materials due to the semiconducting tin oxides. Among these, the former two are positive factors for ethanol electro-oxidation, while the contribution of the latter two is negative, resulting in a maximum power density (MPD) at a SnO_x/Pt ratio of about 0.57. Simoes et al. [68] prepared Pt–SnO_2 electrocatalysts with various Sn contents by thermal decomposition. These Pt–SnO_2 catalysts displayed high EOR activity. The $Pt_{0.9}Sn_{0.1}O_2$ composition presented the largest power density in a DEFC. The results showed that the electrocatalytic oxidation of ethanol on Pt–SnO_2 catalysts lead mainly to AAL and AA. Adsorbed intermediates such as CO_L and CO_2 were also observed by in situ infrared spectroscopy and high pressure liquid chromatography (HPLC) analysis. The presence of the last species suggested a rupture of the C–C bond, which occurred during ethanol oxidation on the Pt–SnO_2 catalysts.

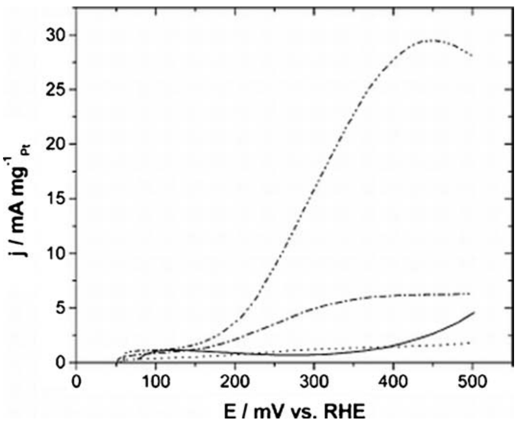

Fig. 5. Electro-oxidation of ethanol on Pt–Sn catalysts. Effect of Sn content; 0.1M $HClO_4$ + 0.1 M C_2H_5OH; 5 mV s^{-1}, 3000 rpm; 25 °C. (–) Pt–Sn/C (3:1); (–·–) Pt–Sn/C (4:1); (··–··) Pt–Sn/C (9:1); (—) Pt/C. Reproduced from Ref. [2], copyright 2004, with permission from Elsevier.

5.2.2. Sn ad-atoms modified Pt and Pt_3Sn catalysts

Tripković et al. [69] studied the electro-oxidation of ethanol at Sn ad-atoms modified and unmodified Pt_3Sn/C and Pt/C catalysts. The activity of Pt/C and Pt_3Sn/C catalysts was significantly improved by Sn ad-atoms. The onset potential was shifted for ~0.05 V towards more negative potentials and the current densities in the potential region <0.3 V (SCE)) were two times higher than unmodified catalysts. The results indicated that Sn in alloy and electrodeposited Sn exhibit different effects on the catalytic activity. Promotional effect of Sn ad-atoms on the ethanol oxidation is related to the enhancement of CO oxidation rate by the bifunctional mechanism. Sn ad-atoms tend to nucleate on the particle edges due to their high mobility and low surface energy. As the coverage with Sn ad-atoms is low, ~10%, it is reasonable to assume that Sn is deposited mostly on the edges. Edges as the defect sites are highly active for CO and OH adsorption. Blocking the edges by Sn ad-atoms prevents strong adsorption of CO at the same sites, but simultaneously permits adsorption of OH species on Sn_{ads} at lower potentials than on Pt. Consequently, less strongly bonded CO species on the facet sites neighboring to the edge sites can be easily oxidized to CO_2. In fact, Sn ad-atoms on the edge sites increase the CO oxidation rate in bifunctional reaction mechanism operative for oxidation of CO on the Pt_3Sn/C catalyst, resulting in the enhanced CO_2 production as a final consequence.

5.3. *Ethanol oxidation on alloyed (fcc Pt_3Sn and hcp PtSn) Pt–Sn catalysts*

5.3.1. *$Pt_3Sn(h\,k\,l)$ single-crystal electrode*

Electronic structure calculations employing periodic, self-consistent DFT were used to study the relative stabilities of various species derived from ethanol and acetic acid on $Pt_3Sn(1\,1\,1)$, and these results are compared with the behavior on $Pt(1\,1\,1)$ [70]. The lowest energy transition states for C–O and C–C bond cleavage on $Pt_3Sn(1\,1\,1)$ involve reactions of adsorbed 1-hydroxyethylidene (CH_3COH) and acetyl (CH_3CO) species, respectively. The energies of these transition state on $Pt_3Sn(1\,1\,1)$ are 25–60 kJ mol^{-1} higher compared to $Pt(1\,1\,1)$, indicating that C–O and C–C bond cleavage reactions are inhibited on $Pt_3Sn(1\,1\,1)$. In contrast, energies of transition states for dehydrogenation–hydrogenation reactions increase by only 5–10 kJ mol^{-1} on $Pt_3Sn(1\,1\,1)$ compared to $Pt(1\,1\,1)$. These results are in agreement with experimental results which show that the rate of ethanol dehydrogenation reaction is fast on Pt_3Sn catalysts as well as on Pt catalysts, whereas ethanol decomposition reactions leading to CO, CH_4, and C_2H_6 and involving C–C and C–O bond cleavage are inhibited by the presence of Sn [71].

5.3.2. *Polycrystalline Pt_3Sn and PtSn alloys*

The EOR activity of Pt_3Sn/C by E-Tek, essentially formed by the Pt_3Sn phase [4,72], and its selectivity for complete oxidation were evaluated by using CV combined with on-line DEMS measurements and compared to those of a Pt/C catalyst [71]. Addition of Sn in Pt catalysts lowers the onset potential for ethanol electro-oxidation and leads to an increase of the total activity of the Pt_3Sn/C catalyst. It does not improve, however, the selectivity for complete oxidation to CO_2, which is about 1%. Dissociative adsorption of ethanol to form CO_2 is more facile on Pt/C than on Pt_3Sn/C catalyst within the potential range of technical interests (<0.6 V), but Pt/C is rapidly blocked by CO_{ad}. In all cases acetaldehyde and acetic acid are dominant products, CO_2 formation contributes less than 2% to the total current. The higher ethanol oxidation current density on the Pt_3Sn/C catalyst results from higher yields of C_2 products. Colmati et al. [72] investigated the electrochemical oxidation of ethanol on commercial Pt/C, Pt–Ru/C and Pt_3Sn/C catalysts in acid solution at room temperature and in single DEFCs in the temperature range 70–100 °C. In all the experiments, an enhancement of the EOR activity was observed on the binary catalysts. In acid solution the improvement at low current densities was higher on Pt–Ru than on Pt_3Sn. In DEFC tests, at 70 °C the cells with Pt–Ru and Pt_3Sn showed about the same performance, while for $T > 70$ °C the cells with Pt_3Sn better performed than those with Pt–Ru as anode material. They also thermally treated at 200 and 500 °C a Pt–Sn/C (Pt:Sn = 3:1) electrocatalyst prepared by the FAM [29]. Thermal treatments gave rise to the formation of a predominant phase of cubic Pt_3Sn and, to a lesser extent, a hexagonal PtSn phase. The EOR activity and the performance in a single DEFC of fully alloyed Pt–Sn/C thermally treated at 200 °C were better than that of as-prepared partially alloyed catalyst. Garcia-Rodriguez et al. [73] prepared Pt–Sn/C catalysts by controlled surface reactions between $Sn(C_2H_5)_4$ and Pt/C. The incorporation of Sn results in the exclusive formation of intermetallic $Pt_{1-x}Sn_x$ and Pt_3Sn alloy phases. They demonstrated that the formation of Pt_3Sn intermetallic phase can substantially be increased by high reaction temperature, high Sn/Pt ratio, and the use of several consecutive tin anchoring periods. The EOR activity of these alloyed catalysts increased with increasing the amount of Pt_3Sn phase.

To evaluate the activity for ethanol oxidation of the hexagonal PtSn phase, a Pt–Sn/C (Pt:Sn = 1:1) catalyst was thermally treated at 200 °C [30]. XRD pattern showed the formation of a main hcp PtSn phase and fcc Pt_3Sn as a secondary phase. The EOR activity of thermally treated $Pt_{50}Sn_{50}$ was lower than that of as-prepared $Pt_{50}Sn_{50}$ and of both as-prepared and thermally treated $Pt_{75}Sn_{25}$. From this result it was inferred that the EOR activity of the hcp PtSn phase is lower than that of both the fcc Pt_3Sn phase and non-alloyed Pt–Sn.

5.4. *Ethanol oxidation on partially alloyed Pt–Sn catalysts*

Many papers reported ethanol oxidation on partially alloyed Pt–Sn catalysts [65]. Vigier et al. [74] prepared Pt–Sn/C catalysts using the co-impregnation reduction method. The presence of PtSn alloy phases, Pt particles, and $Pt–O–Sn^{2+}$ species in these catalysts was suggested from XAFS results [75]. The catalytic activity of Pt–Sn/C was almost double that of Pt/C. By HPLC, subtractively normalized interfacial FTIRS (SNIFTIRS) and single potential alteration infrared reflectance spectroscopy (SPAIRS) the following species were detected: adsorbed CO, adsorbed CH_3CO, CH_3CHO, CH_3COOH and CO_2. By SNIFTIR and SPAIR measurements, it appeared that two effects are involved in ethanol electro-oxidation on Pt–Sn: the bifunctional mechanism, mainly due to non-alloyed tin, and the ligand effect, ascribed to alloyed Sn. The presence of tin allows ethanol to adsorb dissociatively, then to break the C–C bond, at lower potentials and with a higher selectivity than on pure Pt. Tin is able to adsorb water molecules dissociatively to form adsorbed OH species, so that Pt–Sn allows the formation of CO_2 and CH_3COOH at lower potentials than Pt by oxidation of adsorbed CO and CH_3CO species respectively, according to the bifunctional mechanism. Electronic interactions could be involved not only during the adsorption of ethanol, but also to explain CO_2 production at lower potentials on Pt–Sn than on Pt [74].

The optimum Sn content for ethanol oxidation in partially alloyed Pt–Sn catalysts is not well determined, depending on both catalyst structural characteristic, such as the ratio of alloyed and non-alloyed tin, and operational parameters, such as cell temperature [65]. Colmati et al. [76] tested Pt–Sn/C catalysts with different

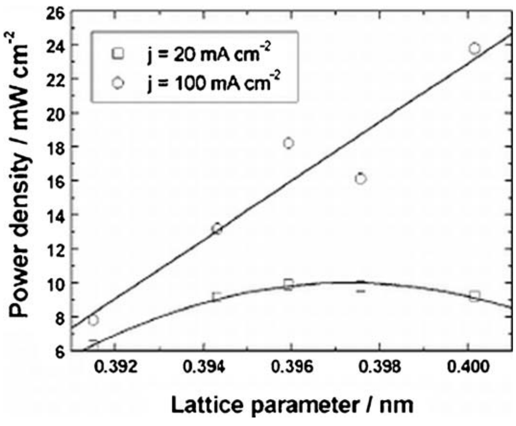

Fig. 6. Dependence of the power density of DEFCs, operating at 110 °C, at j = 20 and 100 mA cm^{-2} on Pt–Sn lattice parameter. Reprinted from Ref. [76], copyright 2007, with permission from The Electrochemical Society.

Table 1
Electrochemical activity and catalytic effects for the oxidation of CH_3OH and CH_3CH_2OH of Pt–Sn catalyst with different structures.

Fuel	Catalyst	Activity	Effect	References
CH_3OH	Pt/SnO_x	Moderate/high	Oxidation of adsorbed CO and CHO at lower potentials as compared to Pt/C. No effect on methanol adsorption and C–H bond dissociation	[11,12,17,36–41]
	Sn ad-atoms modified Pt	From moderate/high (low potentials and low Sn coverage) to poor with increasing tin content	Positive effect on H_2O dissociation and Pt–CO bond strength reduction. Inhibiting effect on the methanol adsorption/dehydrogenation	[13,16,18,42–48]
	Pt_3Sn	Poor	Inhibiting effect on methanol adsorption and C–H bond dissociation. Oxidation of adsorbed CO and CHO at lower potentials as compared to Pt/C. Increase activity by Sn dissolution	[13,16,42,46,50]
	Partially alloyed Pt–Sn	From moderate/high (optimum Sn/Pt: ratio 0.4; optimum lattice parameter 0.396 nm) to poor with increasing the amount of tin alloyed	Positive effect of SnO_x and low amount of tin alloyed on H_2O dissociation and Pt–CO bond strength reduction. Inhibiting effect of high content of alloyed tin on the methanol adsorption/dehydrogenation	[10,27,28,52–54]
CH_3CH_2OH	Pt/SnO_x	High	Sn provides OH species to oxidize adsorbed residues. Formation of AA and AAL. Inhibition of C–C bond cleavage	[2,23,32,66–68]
	Pt_3Sn	Very high	Sn provides OH species to oxidize adsorbed residues. Formation of AA and AAL. C–O and C–C bond cleavage reactions inhibited on Pt_3Sn(1 1 1). Ethanol dehydrogenation on Pt_3Sn(1 1 1) similar than that on Pt(1 1 1).	[29,70–73]
	Partially alloyed Pt–Sn	High (optimum Sn/Pt ratio 0.5; optimum lattice parameter 0.396 nm)	Oxidation of adsorbed CO and CH_3CO species, according to the bifunctional mechanism. Supportimg C–C bond cleavage at lower potential than Pt.	[10,24,25,74–77]

Sn contents and/or alloying degree in DEFCs. The best performance was not presented by the cell with the catalyst having the higher Sn content (partially alloyed Pt–Sn (2:1)), but by the cell with the fully alloyed Pt–Sn (3:1) catalyst. Fig. 6 shows the dependence of the power density at 110 °C, at low ($20\,mA\,cm^{-2}$) and high ($100\,mA\,cm^{-2}$) current densities, on the lattice parameter. At low current densities the power density increases going from the cell with pure Pt to the cells with the Pt–Sn catalysts as anode materials, but with little effect of the Sn content in the alloy. Instead, at high current density, an almost linear dependence of the power density on the lattice parameter can be observed. At low current density, only the positive effect of tin oxide on CO_{ad} oxidation is relevant. On the other hand, at high current densities, in the hypothesis of the formation of a $Pt_{(1-x)}Sn_x$ solid solution, a larger lattice parameter should support the cleavage of the C–C bond, or, conversely, the increase of the lattice parameter is associated with an increased number of Pt–Sn pairs, necessary to complete the oxidation of ethanol via acetaldehyde, i.e. without C–C bond cleavage. Zhou et al. [24,25] investigated the effect of tin content in partially alloyed Pt–Sn anode catalysts on the performance of single DEFCs operating at different temperatures. They found that in terms of MPD, the best catalyst goes from Pt_3Sn_2/C (lattice parameter, $a = 0.3974$ nm) to Pt_2Sn_1/C ($a = 0.3956$ nm) with increasing temperature from 60 to 90 °C. Kim et al. [10] and Tsiakaras [77] tested the EOR activity of Pt–Sn catalysts with different Sn contents in a single DEFC and by CV: in both works, the best results was obtained using as anode material the Pt–Sn catalyst with a nominal Pt:Sn atomic ratio of 2:1 and a lattice parameter of ca. 0.396 nm. As shown in Fig. 7, a volcano-type curve between both the MPD of DEFCs [77] and the maximum current density by CV [10] and the Sn content in the catalyst, and as a consequence the lattice parameter of the PtSn alloy, was observed.

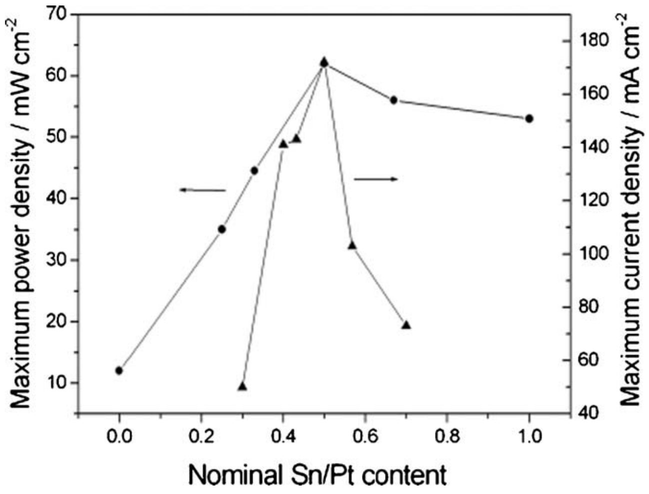

Fig. 7. Dependence of maximum power density of DEFCs [77] and maximum current density by CV [10] on nominal Sn content in the catalyst.

6. Conclusions

Commonly, the catalytic activity of Pt–Sn catalysts is compared with that of Pt and Pt–Ru. Generally, independent of the preparation method and catalyst structure, the order of activity for ethanol oxidation it is Pt–Sn > Pt–Ru > Pt. In the case of methanol oxidation, instead, the activity of Pt–Sn is lower than that of Pt–Ru, but can be higher or lower than that of Pt, depending on the synthesis method and structural characteristic of Pt–Sn. The catalytic activities of Pt–Sn catalysts with different structural characteristics for the oxidation of CH_3OH and CH_3CH_2OH are summarized in Table 1.

6.1. *Methanol oxidation*

There is a general consensus that the MOR activity of Pt–SnO_2 catalysts is higher than that of Pt. Controversial results of methanol oxidation on Sn ad-atoms modified polycrystalline Pt, instead, are reported in literature. These conflicting results can be explained by different ways. Firstly, the different Sn contents in the deposition solution and the different time of deposition used in the different works can result in different Sn coverages. As reported by Ishikawa et al. [47], the effect of tin coverage on the MOR activity changes with Sn amount: the optimal tin surface coverage must be low. Moreover, depending on the preparation method of the Sn ad-atoms modified Pt, that is, whether this arises from the operation of a cyclic Sn(II)/Sn(IV) redox system or from modification of the platinum surface by Sn(0), in some cases the presence of oxidized tin in Sn ad-atoms modified Pt was reported [44,48], increasing the MOR activity of the catalysts. The poor MOR activity of Sn ad-atoms on well defined Pt crystal faces could also be due to the absence of a cooperative interplay between facets. Indeed, in polycrystalline Pt, Sn deposition takes place on both {1 0 0] and {1 1 1} facets, while in Pt single crystals Sn is deposited only on the {1 0 0} or {1 1 1} facet.

Fully alloyed Pt_3Sn catalysts have a very poor activity for methanol oxidation. However, catalyst surface modifications by Sn dissolution can improve their MOR activity.

Regarding the partially alloyed Pt–Sn catalysts, the MOR activity of these catalysts goes trough a maximum, due to a positive effect of both $Pt_{(1-x)}Sn_x$ solid solution with low Sn content and SnO_x, and a negative effect of high amount of both Sn alloyed and SnO_x. The highest MOR activity is presented by a catalyst with a Sn/Pt atomic ratio of 0.40, with 1/3 Sn in an alloyed form and 2/3 Sn in a non-alloyed form. It is difficult to determine, however, for the same tin content, the best Pt–Sn structure among partially alloyed Pt–Sn and non-alloyed $PtSnO_x$ catalysts, as a direct comparison has not been carried out.

The different catalytic behavior for methanol oxidation between Pt–SnO_2, Sn ad-atoms modified Pt, partially alloyed Pt–Sn and Pt–Sn alloy catalysts as compared to bare Pt can be summarized as the following: (1) Pt–SnO_2: increase of the MOR activity; (2) Sn ad-atom modified Pt: increase of the MOR activity only for low Sn content; (3) partially alloyed Pt–Sn: increase of the MOR activity only for low Sn content in the alloy; (4) Pt_3Sn alloy: decrease of the MOR activity. An overall explanation, bringing together all the type of Pt–Sn catalysts is based on the enhancement of poison species oxidation rate by SnO_x (bifunctional mechanism) and on electronic effects of Sn atoms on Pt atoms. Electronic effects of Sn on Pt are positive regarding H_2O dissociation and Pt–CO bond strength reduction, but negative for methanol adsorption/dehydrogenation. The negative effects of tin increase with increasing Sn content in the catalyst. These effects are present in Sn ad-atom modified Pt, in partially alloyed Pt–Sn and in Pt_3Sn alloy, but not in Pt–SnO_x. SnO_x only supplies oxygenated species to oxidize –CO or–COH species. No effect of tin oxide presence on methanol adsorption and C–H bond dissociation. In Sn ad-atoms modified Pt and in partially alloyed Pt–Sn, the electronic effect goes from positive for low Sn content to negative with increasing Sn content in the catalyst and in the alloy, respectively. In Pt_3Sn alloy, due to the high Sn content, the effect of tin is always negative.

6.2. Ethanol oxidation

The addition of tin to platinum not only increases the activity of the catalyst towards the oxidation of ethanol and therefore the electrical performance of the DEFC, but also changes the product distribution, improving the ethanol oxidation to acetaldehyde and acetic acid.

C–C bond cleavage on Pt is inhibited by Sn presence in both fully alloyed and fully non-alloyed catalysts. Pt–SnO_2 catalyst offers no benefit over Pt alone with respect to C–C bond oxidation. Ethanol and acetaldehyde are both oxidizable at relatively negative potentials on surfaces modified by Pt–SnO_2 electrodeposits, but acetic acid is practically inert on Pt–SnO_2 [32,67]. In the same way, ethanol decomposition reactions on single crystals and polycrystalline Pt_3Sn leading to CO, CH_4, and C_2H_6 and involving C–C bond cleavage are inhibited by the presence of Sn [70,71]. On partially alloyed Pt–Sn catalysts, instead, it seems that the presence of tin allows ethanol to adsorb dissociatively, then to break the C–C bond, at lower potentials and with a higher selectivity than on pure Pt [74]. The coexistence of Sn in different states could support C–C cleavage. However, further studies have to be carried out to confirm this result.

The effect of Pt–Sn structural characteristics on the overall EOR activity was evaluated by comparing Pt–Sn catalysts in the same Pt:Sn atomic ratio (3:1), but different degree of alloying [29,78–80]: fully alloyed Pt_3Sn always better performed than partially alloyed Pt–Sn [29,79,80], but conflicting results have been reported regarding the activity of non-alloyed and partially alloyed Pt–Sn catalysts [79,80].

Very recently, the effect of alloying on the EOR activity of Pt–Sn/C catalysts with the same Pt:Sn composition and particle size was studied [9]. At fixed Pt:Sn atomic ratio (7:3) and particle size (3.0 nm), the EOR activity of the partially alloyed catalyst was higher than that of non-alloyed catalysts.

Thus, excluding the result of Jiang et al. [80], there is a general consensus regarding the superior effect of alloyed tin than non-alloyed tin on the EOR activity of Pt–Sn catalysts. The different catalytic behavior for ethanol oxidation between alloy and Pt–SnO_2 catalysts can be summarized as the following: (1) Pt–SnO2: good EOR activity by the bifunctional mechanism. (2) Pt_3Sn alloy: very good EOR activity by the bifunctional mechanism and electronic effects. In both alloyed and non-alloyed catalysts Sn provides OH species to oxidize adsorbed residues, and overall formation of AA and AAL occurs.

Interestingly, a different optimum Sn amount in partially alloyed Pt–Sn catalysts was found for methanol and ethanol oxidation. For the MOR the optimum Pt:Sn atomic ratio was 2.5:1, whereas for the EOR the optimum Pt:Sn was 2:1 and 1.5:1, depending on operation temperature. This comparison, however, does not take into account of the degree of alloying, and results in the sum of the effects of alloyed and non-alloyed tin. The effect of Pt–Sn alloying degree on the catalytic activity for methanol and ethanol oxidation has been reported [76]. For the same Sn content in the catalyst (Pt:Sn = 3:1), going from partially alloyed to fully alloyed tin, it results in a different effect on methanol and ethanol oxidation: the increased amount of alloyed tin gives rise to an enhancement in the EOR activity, but to a decrease in the MOR activity.

In conclusion, we recommend for methanol oxidation the use of non-alloyed Pt–SnO_x or partially alloyed Pt–Sn catalysts in the Sn/Pt atomic ratio = 0.40 with about 1/3 Sn in alloyed form and 2/3 Sn in the oxide form, and for ethanol oxidation the use of fully alloyed Pt_3Sn catalysts.

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