

Short communication

# PtM/C (M = Sn, Ru, Pd, W) based anode direct ethanol–PEMFCs: Structural characteristics and cell performance

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## Abstract

In the present work, the role of the structural characteristics of Pt-based catalysts on the single direct ethanol proton exchange membrane fuel cell (PEMFC) performance is examined. Several PtM/C (M = Sn, Ru, Pd, W) catalysts were characterized by means of transmission electron microscopy (TEM) and X-ray diffraction (XRD) and then evaluated as anode catalysts in single direct ethanol fuel cells. XRD spectra showed that Pt lattice parameter decreases with the addition of Ru or Pd and increases with the addition of Sn or W. According to the obtained experimental results, PtSn catalysts presented better electrocatalytic activity towards ethanol electro-oxidation. Based on these results, PtSn/C catalysts with different Pt/Sn atomic ratio were tested and compared. The maximum power density values obtained were correlated with the structural characteristics of the catalysts. A volcano type behaviour between the fuel cell maximum power density and the corresponding atomic percentage of Sn (Sn%) was observed. It was also observed that Sn% affects almost linearly the Pt<sub>x</sub>Sn<sub>y</sub> catalysts' lattice parameter.

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**Keywords:** Direct ethanol fuel cells; Pt-based catalysts; Lattice parameter

## 1. Introduction

*Direct alcohol fuel cells* (DAFCs) are promising candidates for use in power systems for portable applications, considering their easy handling of the fuel and flexibility in the cell operation. Among the alcohols that can be used as fuels, methanol and ethanol have been studied more extensively in proton exchange membrane fuel cells. However, for both alcohols, certain obstacles, such as the slow kinetics of alcohol electro-oxidation and fuel crossover through the electrolyte membrane, which still hinder the widespread commercial entry of DAFCs have to be overcome. Many works [1–4] have already been reported concerning direct methanol fuel cells (DMFCs). Recently, more studies [5–29] have also been devoted to *direct ethanol fuel cells* (DEFCs), due to the fact that ethanol provides many advantages over methanol as a fuel: ethanol is non-toxic, safer and has a greater energy density. Therefore, it is attractive and appears to meet most of the fuel requirements for low-temperature fuel cells.

The electro-oxidation of ethanol is more complicated than that of methanol, and imposes the necessity to develop more active and selective anode catalysts [5]. As known, the complete electro-oxidation of ethanol involves the release of 12 electrons per ethanol molecule and the cleavage of the C–C bond. The latter is believed to play a key role in ethanol electro-oxidation because it has a determining effect on the fuel cell efficiency and it has attracted scientific interest the last decade. Platinum is recognized to be the most active material for ethanol oxidation; however, self-poisoning occurs in the case of pure Pt [6]. Thus, there is a need to increase the electrocatalytic activity of Pt. As a consequence, research on ethanol electro-oxidation is targeted on modifying Pt with a second or a third additive. Additives such as Ru [7–9,10–12], Sn [7,9,13–15], W [7,9,16], Mo [17], Pd [7], and Ni [18] have already been studied in order to identify appropriate catalysts for ethanol electro-oxidation.

According to the reported results, it was found that better performance was achieved when PtSn/C catalysts were used. Furthermore, it is known that Sn or its oxides, can supply surface oxygen-containing species for the oxidative removal of CO-like species strongly adsorbed on adjacent Pt active sites, which is the so-called bi-functional mechanism and activate the

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chemisorbed CO-like intermediates. Thus, the addition of Sn to Pt enhances the ethanol electro-oxidation activity and consequently improves the fuel cell performance compared to a cell with pure Pt/C as anode catalyst. However, the optimum Pt/Sn atomic ratio of the catalyst still remains controversial. Moreover, the catalyst preparation procedure can affect the catalyst's nature and structure, which plays a crucial role in the ethanol adsorption onto the catalyst's surface, its electro-oxidation and consequently the overall cell's performance [7,13].

It is known that the additives can enhance Pt's activity to some extent through both the bifunctional mechanism and the electronic effect. Taking into account what was mentioned in the previous paragraph, the main objective of the present work is to examine the effect of the PtM/C catalysts (where M = Ru, Sn, W, Pd) on the ethanol electro-oxidation activity. More precisely, experimental data for direct ethanol fuel cell performance from the literature and from the present work are examined and compared aiming at the comprehension of the effect of the catalyst's structure on its activity towards ethanol electro-oxidation. Nafion<sup>®</sup>-115 membrane was used as the electrolyte and commercial Pt/C as cathode catalyst for the oxygen reduction in all single fuel cell tests. The electrode preparation and the *membrane-electrode assembly* (MEA) preparation procedure were kept consistent. Anode catalyst was the only variable in the single fuel cell test. The structure and the chemical composition of the catalysts were investigated by means of TEM and XRD.

## 2. Experimental

All carbon supported Pt and PtSn catalysts were synthesized as follows [7,19]. An ethylene glycol solution containing precursors of Pt and Sn was mixed with carbon slurry, and kept at 120 °C for 3 h after pH was adjusted to 13. The reduced mixtures were then acidified at room temperature. The reduced metals supported on carbon were filtered and washed with copious distilled water. The in-house catalysts were obtained after the filter cake was dried in vacuum oven at 70 °C for 12 h. All catalysts were denoted as Pt<sub>x</sub>Sn<sub>y</sub> (subscript denotes the atomic ratio). Pt content in each sample was pre-determined to be 20 wt.%. XRD analysis was carried out to obtain all reflection peaks. Pt (220) reflection peak was scanned finely again and was fitted

using the Gaussian function to calculate the particle size and lattice parameters. The nanoparticle sizes of different Pt-based catalysts were also investigated by TEM. More than 300 particles were calculated to obtain the integrated information of each catalyst.

The *membrane electrode assemblies* (MEAs), in which the cathode was commercial Pt/C catalyst (20 wt.% Pt) with a metal loading of 1.0 mg Pt cm<sup>-2</sup>, were fabricated by pressing the electrodes onto both sides of Nafion<sup>®</sup>-115 membranes at 130 °C for 90 s [7,19]. The anode included the different in-house carbon supported Pt-based bimetallic catalysts with a Pt loading of 1.3 mg cm<sup>-2</sup> (except that the metal loading was 2.0 mg cm<sup>-2</sup> when Pt/C was used as anode catalyst). The MEAs were fastened between two stainless steel bipolar plates with a dotted flow field and fixed on an in-house single-cell test apparatus. Two aureate meshes were placed between the bipolar plates and MEAs to collect current. During the single DEFC tests, unhumidified oxygen with 2 atm (abs.) backpressure was directly fed to the cathode side and 1.0 mol L<sup>-1</sup> of ethanol solution without backpressure at a flow rate of 1.0 ml min<sup>-1</sup> was directly pumped to the anode side.

## 3. Results and discussion

### 3.1. Atomic radius and metal percentage correlation with lattice parameter

The mean particle size and the lattice parameter of several Pt-based catalysts used in the single fuel cell tests, obtained from XRD patterns and TEM results are summarized in Table 1 [7–9,20].

It is known that platinum is considered as the most active material for ethanol oxidation; however, it was found that self-poisoning occurs when Pt was used alone [6]. In order to enhance the electrocatalytic activity of Pt towards ethanol electro-oxidation, different carbon supported binary alloys of the type PtM had already been prepared, characterized and tested. The dependence of the Pt unit cell lattice parameter on the dopant metal's atomic radius and content in the alloy is depicted in Fig. 1. It can be distinguished that the lattice parameter of the Pt crystallite increases along with the atomic radius increment. The higher lattice parameter values of PtM/C were observed when

Table 1  
Characterization results of carbon supported Pt-based bimetallic catalysts [7]

Catalyst	Mean particle size (nm)		Lattice parameter (Å)	Atomic radius (Å)	Sn content (%)
	TEM	XRD			
Pt/C	2.7	2.6	3.9156	–	–
Pt <sub>1</sub> Ru <sub>1</sub> /C	1.9	1.8	3.8830	1.34	–
Pt <sub>1</sub> Pd <sub>1</sub> /C	3.0	2.8	3.9064	1.37	–
Pt <sub>1</sub> W <sub>1</sub> /C	3.4	3.2	3.9223	1.39	–
Pt <sub>1</sub> Sn <sub>1</sub> /C	2.3	2.1	3.9873	1.405	50
Pt <sub>2</sub> Sn <sub>1</sub> /C	3.0	2.6	3.9562	–	33.33
Pt <sub>3</sub> Sn <sub>1</sub> /C	2.2	1.9	3.9530	–	25
Pt <sub>3</sub> Sn <sub>2</sub> /C	2.2	1.9	3.9735	–	40
Pt <sub>4</sub> Sn <sub>1</sub> /C	2.3	1.9	3.9383	–	20

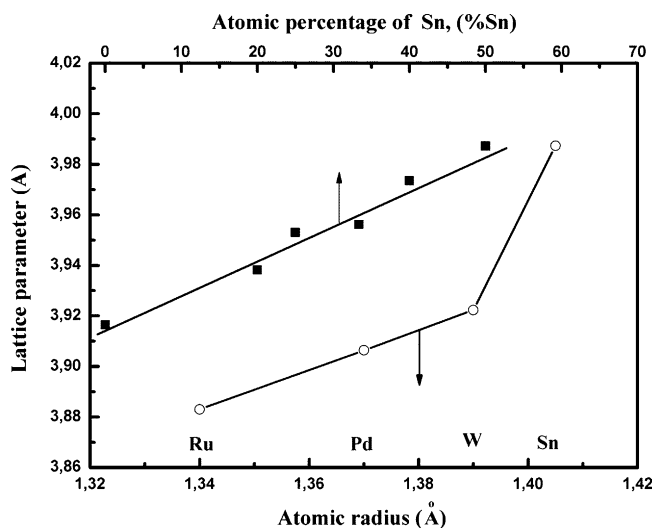


Fig. 1. The dependence of the Pt unit cell lattice parameter on the dopant metal's atomic radius and content in the alloy.

Pt was alloyed with Sn. A possible explanation for the enhancement of the cell current density with the use of a second metal and especially Sn is that the CO does not prefer to bind with Sn surface atoms [7]. As a consequence, the Sn surface sites are always free to adsorb  $\text{OH}^-$  species, due to the fact that abundant  $\text{OH}_{\text{ads}}^-$  species are necessary to completely oxidize the poisoning intermediates to  $\text{CO}_2$ . Moreover,  $\text{OH}^-$  species prefer to be adsorbed mostly on Sn, rather than on Pt sites enabling Sn or Sn-oxide to form oxygen-containing species at lower overpotentials than Pt. These oxygen containing surface species are necessary for the oxidation of adsorbed CO-like intermediates. This is the so-called bifunctional mechanism and explains partially the enhanced effect of the second metal on the Pt.

The dependence of the current density on the atomic radius of the dopant metal at 0.5 V cell voltage and at 90 °C, is presented in Fig. 2. As it can be seen from the comparison of four different Pt-based catalysts, the higher value of the current density was obtained when a Pt–Sn binary catalyst was used, while the lower

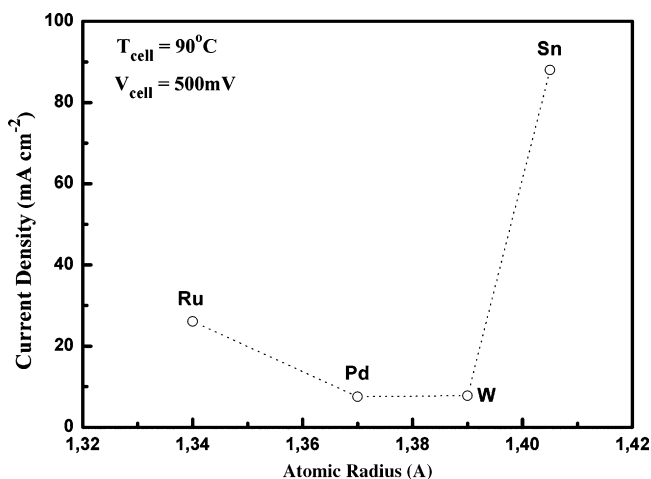


Fig. 2. The dependence of the cell current density on the dopant metal's atomic radius.

in the case of Pt–W [9,13,20–21]. Based on the above results that  $\text{Pt}_1\text{Sn}_1/\text{C}$  appears to be very active anode catalyst for the direct ethanol electro-oxidation in a low temperature fuel cell, a wide range of  $\text{Pt}_x\text{Sn}_y/\text{C}$  catalysts have been prepared, characterized and tested in order to correlate their structural characteristics with their activity towards ethanol electro-oxidation.

### 3.2. Single direct ethanol PtM/C PEM fuel cell performance

In Figs. 3 the characteristic  $V-I$  and  $P-I$  curves of the performance of single direct ethanol fuel cells with different PtM/C anode catalysts at 90, 75 and 60 °C are presented [7,29]. As it can be distinguished from the single direct ethanol fuel cell tests in the chosen experimental conditions,  $\text{Pt}_2\text{Sn}_1/\text{C}$  and  $\text{Pt}_3\text{Sn}_2/\text{C}$  showed higher activity with respect to Pt/C and the other bimetallic catalysts. It can also be distinguished that in the case of  $\text{Pt}_2\text{Sn}_1/\text{C}$  the open circuit voltage approaches 790 mV, about 130 mV higher than that of  $\text{Pt}_1\text{Ru}_1/\text{C}$  under the same cell operational conditions. The single cell tests demonstrated that Pt/C itself does not seem to be a good catalyst for ethanol electro-oxidation, while, as it can be clearly seen, when Pt is doped with Sn, there is a noticeable cell power density enhancement. It has been already recognized that the role of tin is mainly to promote the cleavage of C–C bond and to improve the removal of  $\text{CO}_{\text{ads}}$  species formed on the platinum surface during ethanol electro-oxidation, and consequently enhance the ethanol electro-oxidation [7].

In Fig. 4, the cell's power density is plotted against the percentage of Sn for different operating temperatures, while the current density was kept constant at 30, 40 and 100  $\text{mA cm}^{-2}$ , respectively. In all cases the catalyst power density increases with tin's content in the catalyst. When the latter reaches a value of about 33% the power density begins to decrease slightly. A similar behavior has also been observed for the case of direct electro-oxidation of methanol over  $\text{Pt}_x\text{Ru}_y/\text{C}$  [22]. This is probably due to the fact that the active sites of Pt are partly covered by Sn or its oxides increasing at the same time the internal resistance of the cell, because of the poor electronic conductivity of  $\text{Sn}_x\text{O}_y$ . Finally, as it also can be seen in Fig. 4, the power density increases as the temperature increases as well due to the effect of temperature on the reaction kinetic constant.

### 3.3. Atomic percentage of Sn and catalyst lattice parameter constant

Fig. 5 depicts the dependence of the cell maximum power density on the Sn content at three different operating temperature values. It can be distinguished that there is a region where  $P_{\text{max}}$  presents its higher values. The dashed line indicates the whole tendency. More precisely, the optimum values of the maximum power density mainly correspond to the  $\text{Pt}_2\text{Sn}_1/\text{C}$  and the  $\text{Pt}_3\text{Sn}_2/\text{C}$  catalyst, depending on the operational temperature. A similar behavior is also reported in the literature and concerns the case of methanol electro-oxidation over a PtRu/C catalyst [30]. Moreover, it has also been reported [31] that the catalyst exchange current density decrement is related with the decrease

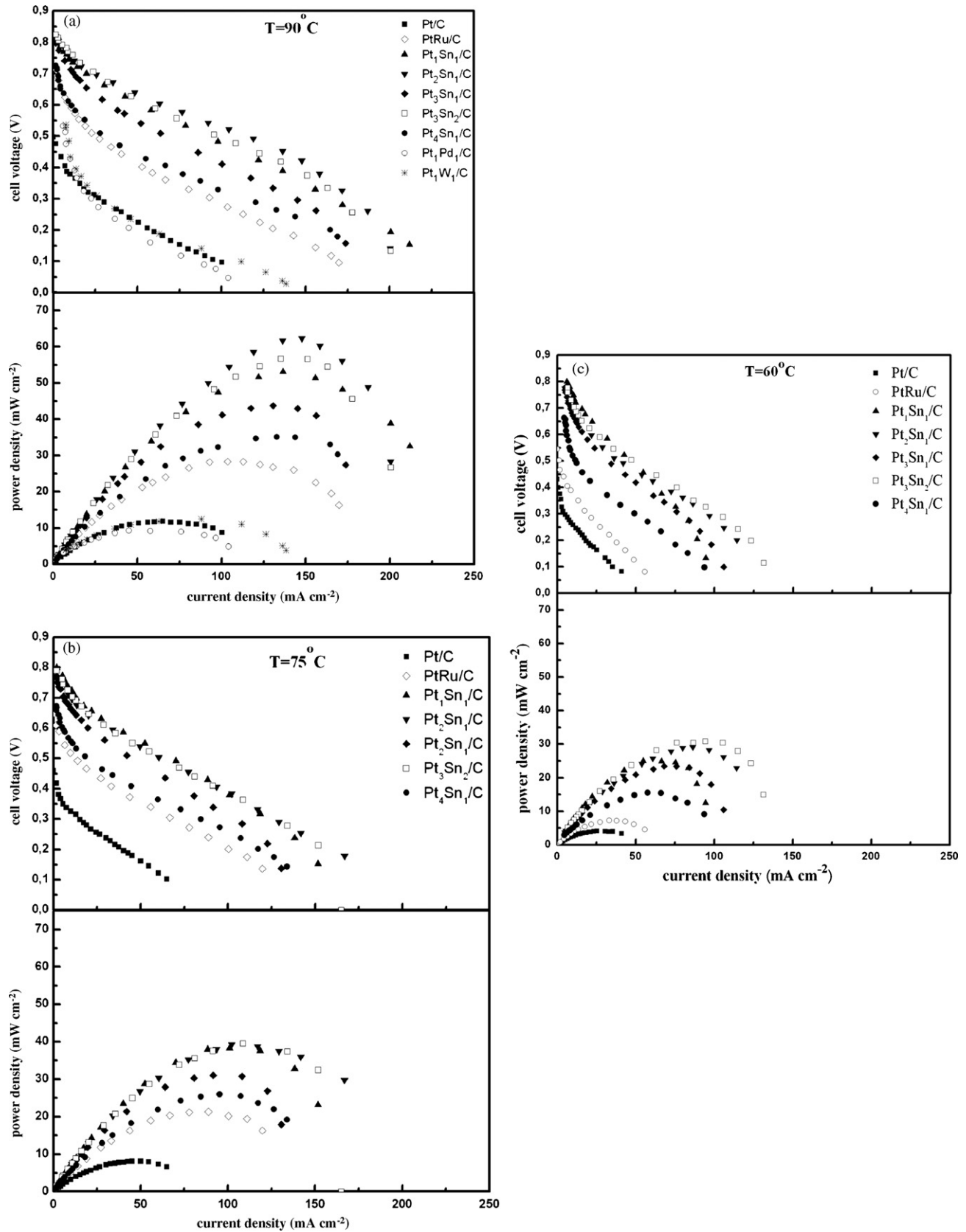


Fig. 3. Comparison of direct ethanol fuel cell operation with different bimetallic anode catalysts at 90, 75 and 60 °C. Ethanol aqueous solution was 1.0 mol L<sup>-1</sup> and its flow rate was 1.0 ml min<sup>-1</sup>, cathode catalyst was Pt/C.

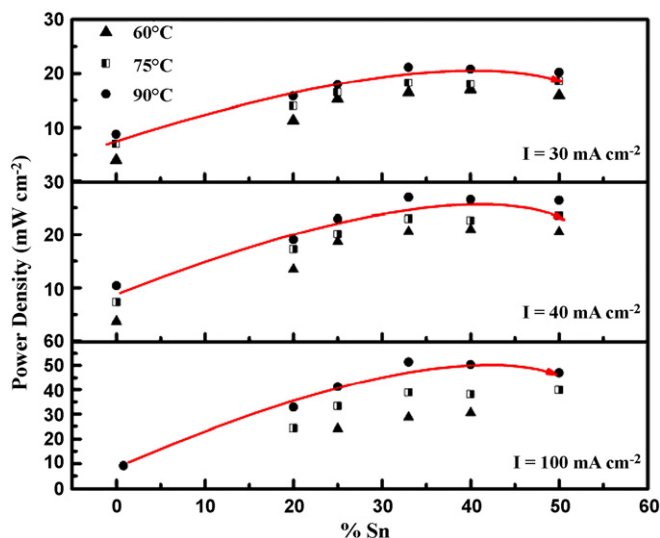


Fig. 4. The effect of Sn percentage on the DEFC power density for different current density values at three different operating temperatures.

of the crystal lattice parameter, as it was determined from the XRD analysis of the electrode material.

Fig. 6a shows the effect of the dopant metal atomic radius on both the maximum power density and the catalyst lattice parameter. It can be seen that the maximum power density obtained for each bimetallic catalyst, is related to the size of the dopant metal indicating that the dopant’s size and therefore the structure of the bimetallic catalyst, somehow affects its activity towards ethanol electro-oxidation.

Here, as mentioned above, the anode catalyst is the only variable, while other factors such as the cathode, the electrolyte and the MEA preparation procedure were kept constant. It is worth noting that all the catalysts were prepared following the same procedure and their mean particle size ranges from 1.9 to 3.2 nm [7]. Therefore, the single fuel cell tests could be used, to a certain extent, to examine the influence of the electrocatalyst structural features towards direct ethanol electro-oxidation activity and cell’s performance.

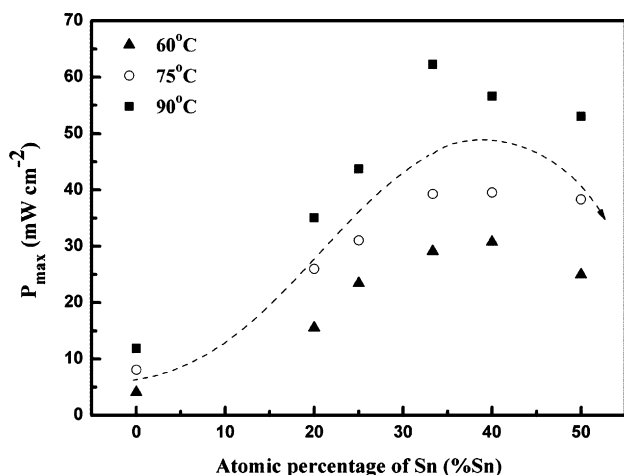


Fig. 5. Maximum power density along with the atomic percentage of Sn in a Pt<sub>x</sub>Sn<sub>y</sub>/C catalyst at different operating temperatures.

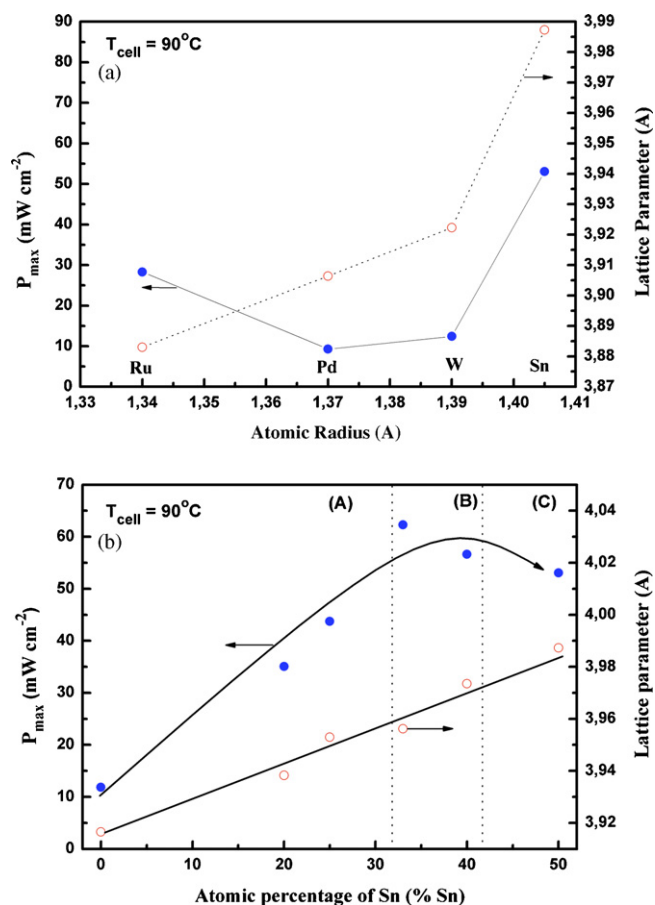


Fig. 6. (a) The cell maximum power density along with the atomic radius of the dopant ion and the catalyst lattice parameter. (b) The maximum power density along with the atomic percentage of Sn and the catalyst lattice parameter at 90 °C. Fig. 1 The dependence of the Pt unit cell lattice parameter on the dopant metal’s atomic radius and content in the alloy.

The dependence of both the cell power output and the catalyst’s lattice parameter on the Sn content and the lattice parameter value of the anode catalyst are reported in Fig. 6b. The experimental data concerning different Pt-based electrocatalysts for ethanol electro-oxidation at 90 °C are presented [7,9]. It is obvious that all data present a similar tendency, as in Fig. 4, and they can be “distributed” in three discrete regions A, B, C. In the region A, where the Sn content in the catalyst increases from 0 to 33%, the cell’s maximum power density increases. By further increasing the Sn content (33–45%, region B) the highest values of the maximum power density are achieved. Finally, when the Sn content is above 45% the maximum power density decreases (region C). As one can also observe in Fig. 6b, the catalyst lattice parameter linearly increases with the Sn content. Taking into account the above, and the controversial results in the literature concerning the optimum Pt/Sn atomic ratio for ethanol electro-oxidation [7,10,13,32] it could be considered that a region of optimum catalyst lattice parameter values exists. A possible explanation of the observed behaviour between the Sn percentage, maximum power density value and lattice parameter could be the following: The increment of the lattice parameter enhances the adsorption of ethanol and favors the cleavage of the C–C bond, improving the fuel utilization and consequently the



performance of the cell [7]. After a critical value of the Sn content, a decrement of the anode electronic conductivity occurs, due to the poor electronic conductivity of tin oxide, which has as a consequence an increased internal resistance of the catalyst [29]. Moreover, the presence of high Sn content could partly block the active sites of the Pt hindering the ethanol adsorption, which is a very important stage for the ethanol electro-oxidation reaction, resulting in high overpotentials. Concerning the volcano behaviour some possible explanations are already reported in the literature [30]. It is worth noting that Pt<sub>x</sub>Sn<sub>y</sub> catalysts having the same Sn content and different structure (i.e. lattice parameter) showed different activity towards ethanol electro-oxidation, indicating that the atomic percentage of Sn is not the only parameter affecting the bimetallic catalysts activity and eventually the role of lattice parameter should be further investigated [13].

#### 4. Conclusions

In the present study, the role of the structural features of Pt-based catalysts used in direct ethanol fuel cells is investigated. Pt was alloyed with a second metal in order to enhance its performance towards ethanol electro-oxidation. More precisely, PtSn/C electrocatalysts showed a better activity compared to PtW/C, PtPd/C and PtRu/C. In order to elucidate the best atomic ratio between Pt and Sn in the PtSn/C catalyst, several PtSn/C catalysts with different Pt/Sn atomic ratio were tested in single direct ethanol fuel cells. It was found that the ratio between these two components affects the catalyst lattice parameter and the fuel cell performance. It was noted that there is an almost “volcano type” behavior of the maximum power density value obtained in a DEFC along with the catalyst %Sn content, which linearly affects the catalyst’s lattice parameter. Finally, the single direct ethanol fuel cell tests are presented.

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