



Understanding the electrocatalytic activity of Pt_xSn_y in direct ethanol fuel cells

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ABSTRACT

In the present work, the activity of Pt_xSn_y/C catalysts towards ethanol, acetaldehyde and acetic acid electrooxidation reactions is investigated for each one separately by means of cyclic voltammetry. To this purpose, a series of Pt_xSn_y/C catalysts with different atomic ratio ($x:y = 2:1, 3:2, 1:1$) and small particle size (~ 3 nm) are fast synthesized by using the pulse microwave assisted polyol method. The catalysts are well dispersed over the carbon support based on the physicochemical characterization by means of XRD and TEM. Concerning the ethanol electrooxidation, it is found that the Sn addition strongly enhances Pt's electrocatalytic activity and the contributing effect of Sn depends on: (i) the Sn content and (ii) the operating temperature. More precisely, at lower temperatures, Sn-rich catalysts exhibit better ethanol electrooxidation performance while at higher temperatures Sn-poor catalysts give better performance. In the case of acetaldehyde electrooxidation, Pt_1Sn_1/C catalyst exhibits the highest activity at all the investigated temperatures; due to the role of Sn, which could effectively remove C_2 species and inhibit the poison formation by supplying oxygen-containing species. Finally, it is found that the Pt_xSn_y/C catalysts are almost inactive (little current was measured) towards the acetic acid electrooxidation. The above findings indicate that Sn cannot substantially promote the electrooxidation of acetic acid to C_1 species.

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1. Introduction

Direct ethanol fuel cells (DEFCs) have been attracting the increasing interest of the scientific community due to the ethanol's renewability, low toxicity, easy storing and handling. Over the last decade, several experimental [1–7] and theoretical [8,9] work concerning DEFCs has been published in the literature. Since the very beginning, it has been recognized that the most interesting issue is the identification of a desirable electrocatalyst, which has the ability to both activate the C–C cleavage and remove the adsorbed C_1 and C_2 species. It is well known that Pt is the most active material for ethanol adsorption and activation, however, it is easily poisoned when it is used alone as an anode catalyst in DEFCs. Thus, the research on ethanol electrooxidation catalysts was targeted on doping Pt with a second or a third additive, such as Sn [6,10–17], Ru [18,19], Rh [20–22], Ce [23], Ti [24], Ni [25,26], P [27] and W [5,7]. According to the already published results, PtSn catalysts were found to exhibit the highest electrocatalytic activity towards ethanol electrooxidation. More precisely, the maximum power density values obtained during DEFC operation at 90 °C in

almost all the published results, ranged from 70 to 100 $mW\ cm^{-2}$ [7,28]. Moreover, it is known that the maximum power density recorded is strongly dependent on several parameters such as: (i) catalyst and membrane electrode assembly (MEA) preparation procedures, (ii) catalysts loading, (iii) ethanol feeding concentration, (iv) oxygen partial pressure at the cathode, and (v) the nature of the current collectors, etc.

Based on the state-of-the-art of DEFCs, ethanol can be electrooxidized mainly to acetaldehyde and acetic acid, while the complete electrooxidation of ethanol to CO_2 is difficult to happen in the range of the examined temperatures of DEFCs (30–90 °C) [2,29,30]. In order to enhance the maximum DEFC power density, novel electrocatalysts have to be developed with both higher activity toward for ethanol electrooxidation and higher selectivity to CO_2 production. As mentioned before, Pt_xSn_y electrocatalysts have been recognized to be the best choice for ethanol electrooxidation despite the fact that ethanol is mainly converted to C–C containing species even over these catalysts [28–32]. Here, it should be noted that recently it was demonstrated that the use of ternary $PtRhSnO_2/C$ electrocatalysts (synthesized by depositing Pt and Rh atoms on carbon supported tin oxide nanoparticles) could lead directly to the oxidation of ethanol towards CO_2 [20,22]. However, more studies concerning the products analysis distribution when the proposed ternary catalyst is used as anode catalyst during the DEFC operation should be made in order to strengthen this finding [20].

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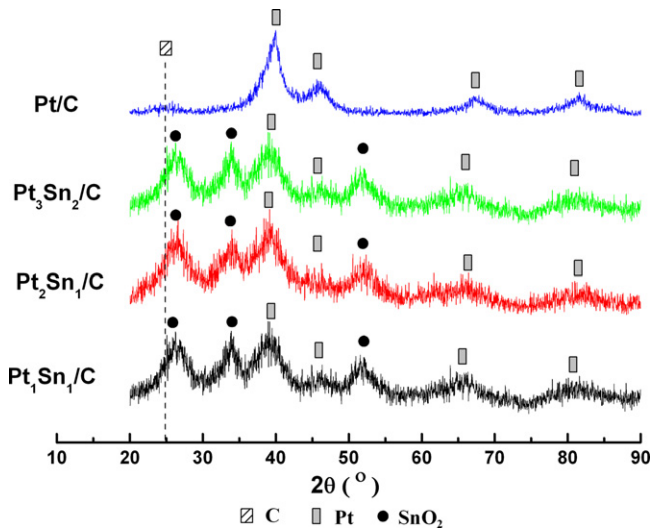


Fig. 1. XRD patterns of the as-prepared Pt_xSn_y/C and Pt/C electrocatalysts.

Consequently, in order to design novel and more efficient electrocatalysts for ethanol electrooxidation, it is firstly necessary to answer questions concerning the role of Sn in both the enhancement of Pt's activity and the activation of ethanol molecules and its intermediate oxidation products. Although many efforts have been devoted to the investigation on the activity of PtSn catalysts towards ethanol electrooxidation, most of them are focused on

the product detection and distribution. According to the literature there is lack of systematic evaluation of PtSn serials catalysts not only for the ethanol electrooxidation but also for the electrooxidation of the intermediate oxidation products of ethanol, such as acetaldehyde and acetic acid. Taking into account the above discussion, the activity of different PtSn electrocatalysts – in the temperature range of 30–80 °C towards the electrooxidation reaction separately for each one of: (a) ethanol, (b) acetaldehyde, and (c) acetic acid is investigated in the present work. To this purpose, a series of Pt_xSn_y/C catalysts with different Pt/Sn molar ratios were fast synthesized by the pulse microwave assisted polyol synthesis method. Their corresponding physico-chemical characteristics were obtained by using the techniques of *X-ray diffraction* (XRD) and *transmission electron microscopy* (TEM). The Pt_xSn_y 's activity towards the electrooxidation reaction of C_2H_5OH , CH_3CHO , and CH_3COOH was evaluated in acidic environment by the aid of *cyclic voltammetry* (CV) at different temperatures.

2. Experimental

2.1. Preparation of electrocatalysts

Pt/C and Pt_xSn_y/C catalysts (x and y denotes the respective nominal atomic number of Pt and Sn.) were obtained by a pulse-microwave assisted polyol synthesis procedure as described in our previous work [33]. In all samples, the Pt loading was kept at 40 wt.% while the minimal Pt/Sn atomic ratio was different ($x:y=2:1$, $3:2$ and $1:1$). Typically, an appropriate amount of $H_2PtCl_6 \cdot 6H_2O$ and $SnCl_2 \cdot 2H_2O$ was well mixed with *ethylene glycol* (EG) in

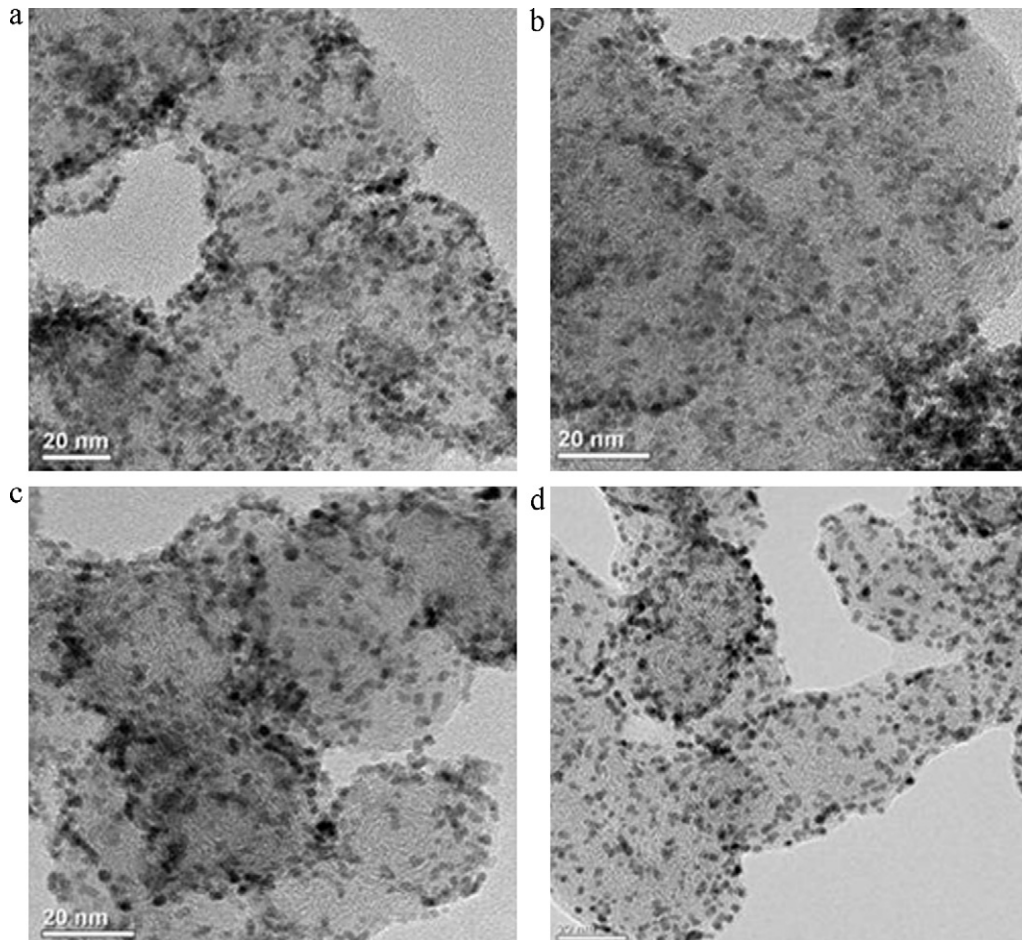


Fig. 2. TEM images of (a) Pt_1Sn_1/C , (b) Pt_2Sn_1/C , (c) Pt_3Sn_2/C , and (d) Pt/C.

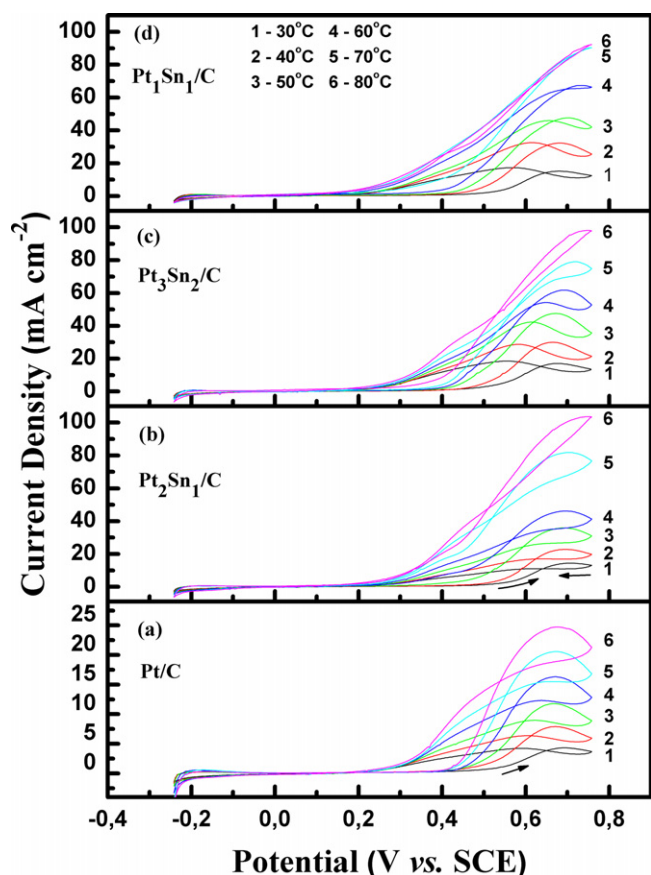


Fig. 3. Ethanol electrooxidation rate in terms of current density over (a) Pt/C, (b) Pt₂Sn₁/C, (c) Pt₃Sn₂/C, and (d) Pt₁Sn₁/C in 0.5 mol L⁻¹ H₂SO₄ + 1.0 mol L⁻¹ C₂H₅OH aqueous solution recorded at a sweep rate of 50 mV s⁻¹.

an ultrasonic bath, and then XC-72R carbon black (Cabot Corp., $S_{\text{BET}} = 236.8 \text{ m}^2 \text{ g}^{-1}$) was added into the mixture. After the pH value of the system was adjusted to more than 10 by the dropwise addition of 1.0 mol L⁻¹ NaOH/EG, the well-dispersed slurry was obtained with stirring and ultrasonication for 30 min. Thereafter, the slurry was microwave-heated in the pulse form of 5s-ON/5s-OFF for several times in a domestic microwave (Galanz WP750, 2450 MHz, the maximum power output of 750 W). After that, the slurry was re-acidified. Finally, the resulting black solid sample was filtered, washed with hot water until no chloride anion could be detected in the filtrate by 1.0 mol L⁻¹ AgNO₃ aqueous solution and then dried at 80 °C overnight in a vacuum oven.

2.2. Catalysts characterization

The XRD measurements were carried out by the aid of a D/Max-III A (Rigaku Co., Japan) employing Cu K α ($\lambda = 0.15406 \text{ nm}$) as the radiation source, operating at 40 kV and 40 mA. The morphology and the particle size distributions of the as-prepared catalysts were obtained by TEM. For sample preparation, the catalysts were ultrasonically dispersed in ethanol solution to get uniform catalyst ink and fixed onto a copper grids covered with holey carbon film. The TEM investigations were performed on a JEOL TEM-2010 (HR) operating at 200 kV.

All the electrochemical measurements were conducted on a PARSTAT 2273 instrument in a three-electrode cell mounted in a thermostatic water bath, with a saturated calomel electrode (SCE) as the reference electrode and a platinum foil as the counter electrode, respectively. The thin catalyst film was prepared onto the glassy carbon disk surface with a diameter of 0.5 cm. Typically, a mix-

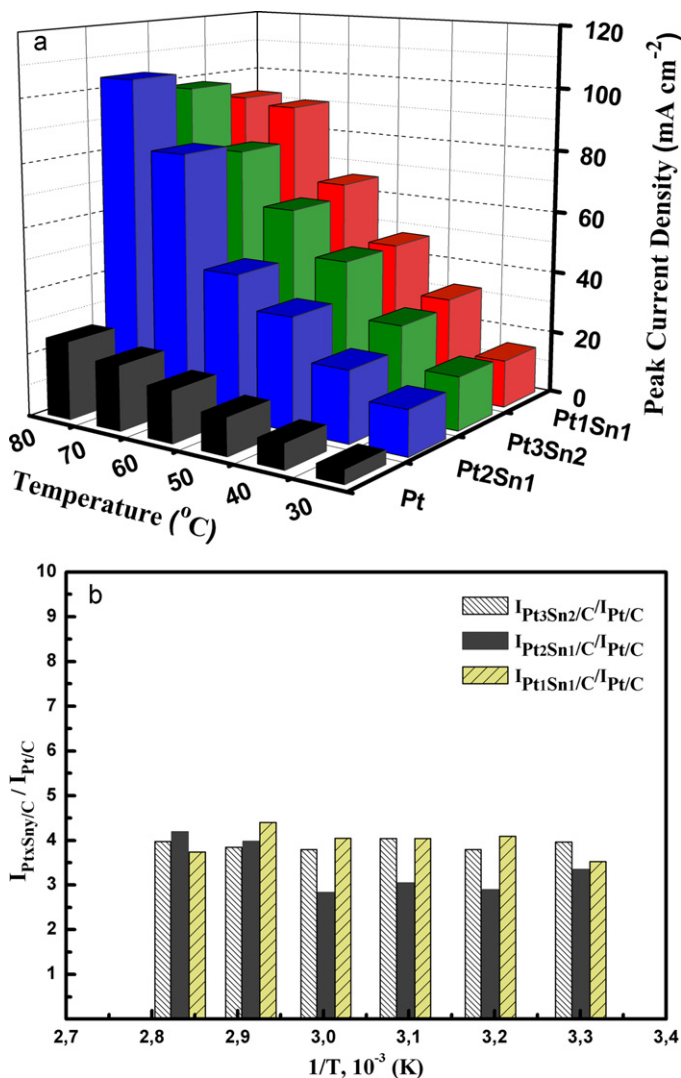


Fig. 4. (a) Comparative results of the temperature effect on the ethanol electrooxidation over different catalysts and (b) the effect of temperature on the peak current density enhancement ratio.

ture containing 5.0 mg electrocatalyst, 1.8 mL ethanol and 0.2 mL Nafion solution (5 wt.%, DuPont Company, USA) was ultrasonicated for 15 min to obtain a well-dispersed ink. The catalyst ink was then quantitatively transferred onto the surface of the glassy carbon electrode and dried under an infrared lamp to obtain the thin catalyst film. The electrochemical tests were performed in 0.5 mol L⁻¹ H₂SO₄ aqueous solution as the blank experiment and in 0.5 mol L⁻¹ H₂SO₄ aqueous solutions containing: (a) 1.0 mol L⁻¹ C₂H₅OH, (b) 0.5 mol L⁻¹ CH₃CHO and (c) 0.5 mol L⁻¹ CH₃COOH for the electrochemical activity evaluation, respectively. Before each experiment, the electrolyte solution was bubbled with high-purity N₂ for 30 min in order to remove the dissolved oxygen inside. It should be noted that without specification, all the potentials are referred to the SCE.

3. Results and discussion

3.1. Physico-chemical characterization

The different diffractograms of the as-prepared Pt/C and Pt_xSn_y/C catalysts are shown in Fig. 1. The diffraction peaks at about 39°, 46°, 68°, and 81° are assigned to Pt (1 1 1), (2 0 0), (2 2 0), and (3 1 1) planes, respectively, which represent the typical characteristics of a crystalline Pt face centered cubic (fcc) phase. The

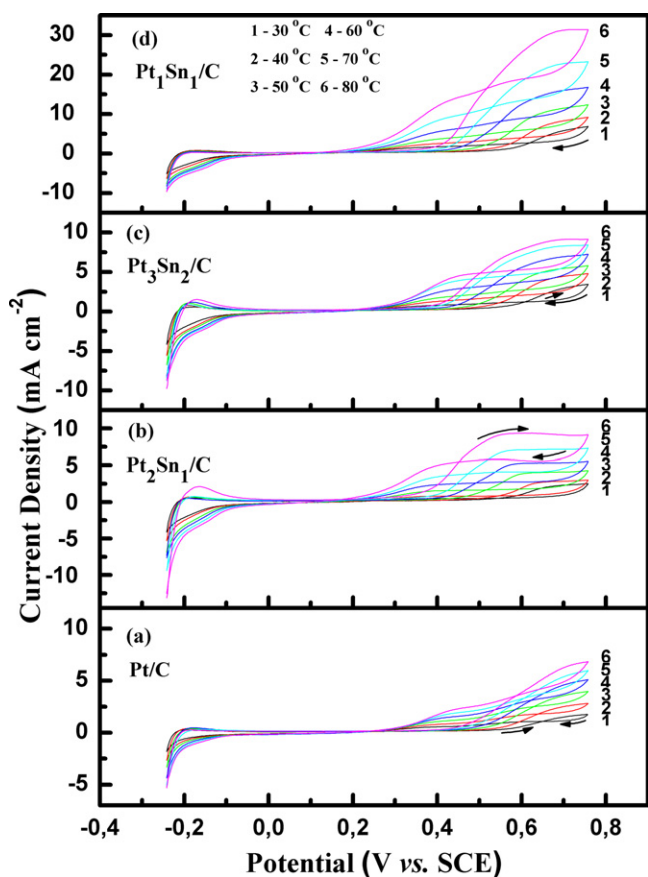


Fig. 5. Acetaldehyde electrooxidation rate in terms of current density over (a) Pt/C, (b) Pt₂Sn₁/C, (c) Pt₃Sn₂/C and (d) Pt₁Sn₁/C in 0.5 mol L⁻¹ H₂SO₄ + 0.5 mol L⁻¹ CH₃CHO aqueous solution recorded at a sweep rate of 50 mV s⁻¹.

diffraction peak at 20–25° observed in all the XRD patterns of the carbon-supported catalysts is attributed to the (002) plane of the hexagonal structure of Vulcan XC-72 carbon. In the case of Pt_xSn_y/C catalysts, the corresponding diffraction peaks at about 26°, 34° and 52° are assigned to SnO₂ (1 1 0), (1 0 1), and (2 1 1) planes, respectively, indicating that Sn has been successfully introduced into Pt/C catalysts in the form of SnO₂. By comparing the XRD patterns of Pt/C and Pt_xSn_y/C, one can distinguish that the diffraction peak at ~25° appears more intensive in the case of Pt_xSn_y/C, which is probably attributed to the more intensive diffraction of SnO₂(1 1 0). Consequently, this could lead to the corresponding peak shift to a little higher degree compared with C(0 0 2). The respective mean particle size of Pt₁Sn₁/C, Pt₃Sn₂/C, Pt₂Sn₁/C, and Pt/C are 3.1, 3.1, 3.3, and 3.1 nm estimated from the (2 2 0) reflection parameters according to the Scherrer formula. By comparing the XRD results presented in Fig. 1, it is observed that the addition of Sn to Pt can induce the Pt (2 2 0) diffraction peak to shift to a lower position, which is helpful for enhancing Pt's catalytic activity to ethanol electrooxidation. This is in agreement with the reported results, where Pt_xSn_y/C catalysts were prepared by polyol method [16]. Moreover, from the TEM results depicted in Fig. 2, it can be distinguished that the metal particles are uniformly dispersed on the carbon supports.

3.2. Ethanol electrooxidation

The CVs of ethanol electrooxidation in 0.5 mol L⁻¹ H₂SO₄ + 1.0 mol L⁻¹ C₂H₅OH at different temperatures over Pt/C, Pt₂Sn₁/C, Pt₃Sn₁/C, and Pt₁Sn₁/C catalysts are given in Fig. 3. In order to avoid the Sn dissolution at high potential, the upper limit of scanning

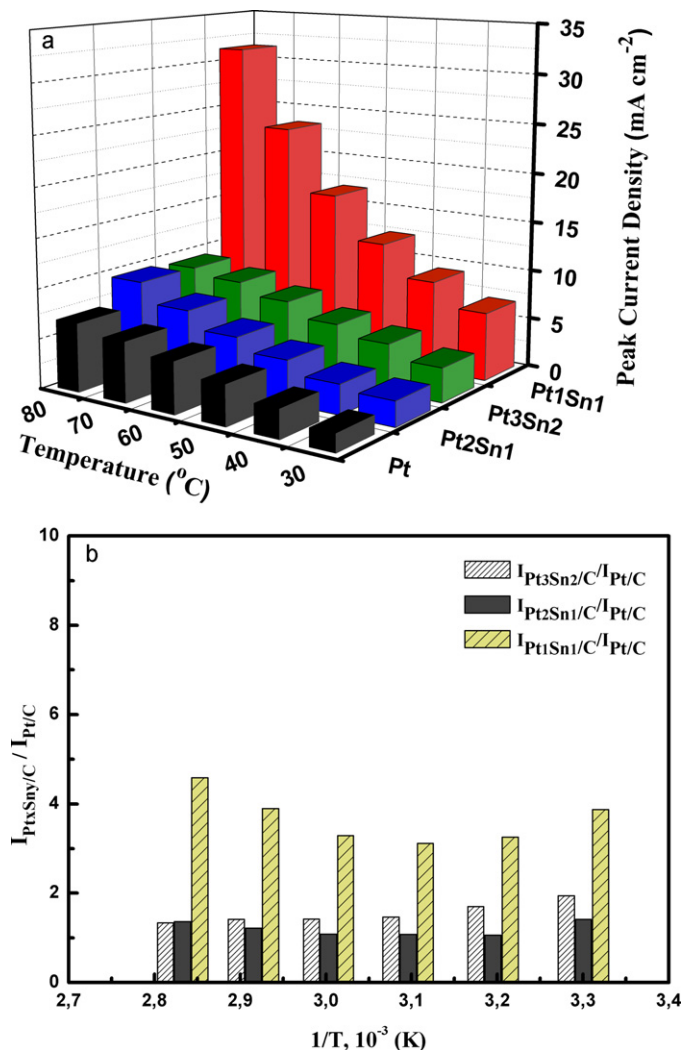


Fig. 6. (a) Comparative results of the temperature effect on acetaldehyde electrooxidation over different catalysts and (b) the effect of temperature on the peak current density enhancement ratio.

potential was set to 0.75 V. In the investigated potential range, there are different peak current density values during the forward and the reversed sweep. The reversed sweep is ascribed to the renewed electrooxidation of ethanol. It is found that at lower temperatures the current densities in the reversed scanning for all samples are higher than the counterparts in the forward scans at the high potential range. In the case of Pt alone, the current densities in the reversed scanning are obviously lower than those in the forward scanning at higher potentials. As the Sn content in the catalysts is increased, the difference between the current densities recorded during the forward and the reversed scans becomes insignificant and even disappears in the case of Pt₁Sn₁/C at higher temperatures (80 °C). Based on the above comparisons the following conclusion could be drawn. The contributing effect of Sn is beneficial for refreshing the active Pt surface and supplying enough Pt active sites for ethanol adsorption and dissociation, especially at high potentials and higher temperatures.

For the sake of further comparison, the peak current densities during the forward scanning are taken and summarized in Fig. 4(a). It is obvious that the addition of Sn strongly enhances the activity of Pt towards ethanol electrooxidation. In order to determine the positive effect of Sn addition, the peak current density enhancement ratio, ρ , is calculated through Eq. (1) and the corresponding

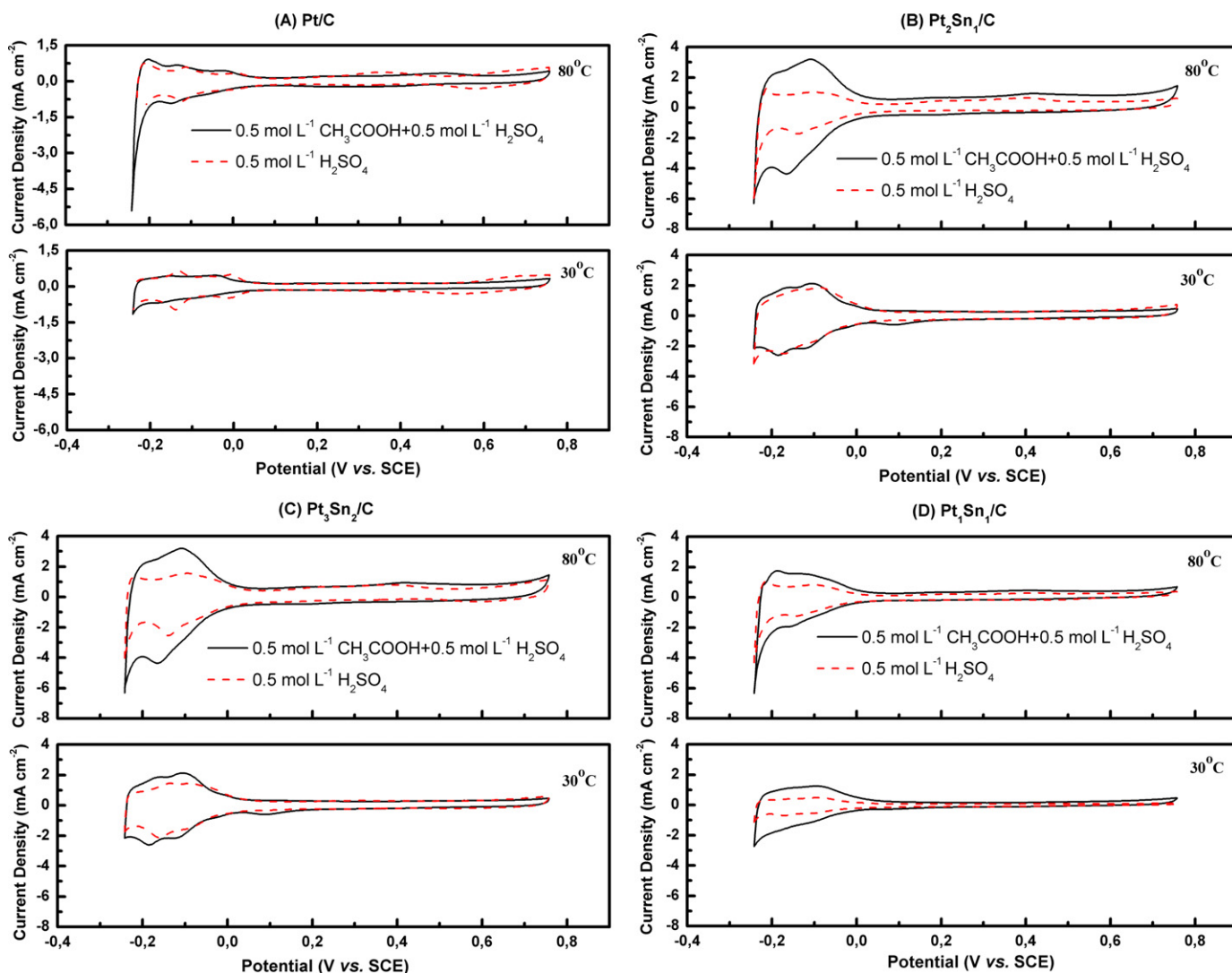


Fig. 7. Acetic acid electrooxidation rate in terms of current density over (a) Pt/C, (b) Pt₂Sn₁/C, (c) Pt₃Sn₂/C and (d) Pt₁Sn₁/C in 0.5 mol L⁻¹ H₂SO₄ + 0.5 mol L⁻¹ CH₃COOH aqueous solution recorded at a sweep rate of 50 mV s⁻¹.

values versus temperature are plotted in Fig. 4(b).

$$\rho = \frac{I_{\text{Pt}_x\text{Sn}_y/\text{C}}}{I_{\text{Pt}/\text{C}}} \quad (1)$$

where $I_{\text{Pt}_x\text{Sn}_y/\text{C}}$ and $I_{\text{Pt}/\text{C}}$ stand for the peak current densities recorded during ethanol electrooxidation over Pt_xSn_y/C and Pt/C, respectively. As it can be seen the enhancement ratio in all cases is between 3 and 4. However, it can be concluded that the contributing effect of Sn seems to become more significant at higher temperatures. This is due to the fact that at higher temperatures, the ability of Sn to supply oxygen-containing species for the oxidative removal of CO and CH₃CO species adsorbed on Pt active sites is enhanced. The above mentioned behavior is known as the bifunctional mechanism, improving the activity of Pt towards ethanol electrooxidation [34]. As it concerns the Sn content effect, it is found that at lower temperatures ($\leq 60^\circ\text{C}$), the Sn-rich Pt_xSn_y/C catalysts (i.e. Pt₁Sn₁/C, Pt₃Sn₂/C) present higher activity. However, at higher temperatures ($\geq 70^\circ\text{C}$) the Sn-poor Pt_xSn_y/C catalyst (Pt₂Sn₁/C) exhibits better performance. This could be explained by the fact that at higher temperatures ethanol adsorption is the rate-determining step, while Pt is the only metal providing sites for ethanol adsorption and dehydrogenation [34]. In the case of the higher Sn content, the relative Pt content in catalyst particles decreases, and moreover,

Pt active sites could be partly blocked by Sn or its oxides. This consequently lowers the density of Pt active sites, which are available for ethanol adsorption, activation and breaking.

3.3. Acetaldehyde electrooxidation

Based on the literature results, it is known that acetaldehyde is one of the main products during ethanol electrooxidation in DEFCs when the temperature is lower than 100 °C [31]. From ethanol to acetaldehyde, only two electrons are transferred. Considering from the Faradaic efficiency of the cell, it is crucial to extract all the electrons from ethanol molecules. Consequently, it is necessary to explore the PtSn's activity towards acetaldehyde electrooxidation and to determine its effect on ethanol electrooxidation process. The corresponding CV curves of acetaldehyde electrooxidation in 0.5 mol L⁻¹ H₂SO₄ + 0.5 mol L⁻¹ CH₃CHO aqueous solution were recorded over different catalysts at different temperatures and the results are shown in Fig. 5. It can be seen that, at higher potential, the current densities in the reversed scanning are always lower than those in the forward scanning in all the cases no matter what the catalyst or the temperature is. This behavior is not like the one reported in the case of ethanol electrooxidation. This could be attributed to the fact that the strong adsorption of acetalde-

hyde onto the Pt surface almost completely inhibits the hydrogen adsorption. Additionally, the adsorbed coverage on the catalyst can reach a limited value which is sufficient to hinder the further C–C bond breaking and CO_{ad} formation but without influencing the partial electrooxidation of acetaldehyde to acetic acid [35,36].

For a better description of the performance comparison, the corresponding peak current densities for acetaldehyde electrooxidation are summarized and presented in Fig. 6. From Fig. 6(a) it can be concluded that the addition of Sn can improve the ability of Pt to electro-oxidize acetaldehyde. However, the Sn content has an obvious effect on its contributing role. As it is clearly shown in Fig. 6(a), the acetaldehyde electrooxidation reaction rate enhances along with the increase of the Sn content in the catalyst. In the case of $\text{Pt}_2\text{Sn}_1/\text{C}$ and $\text{Pt}_3\text{Sn}_2/\text{C}$ the current density enhancement ratio is approximately 2, while in the case of $\text{Pt}_1\text{Sn}_1/\text{C}$ the corresponding value is between 3 and 4.5 as it can be distinguished from Fig. 6(b). More precisely, in the case of $\text{Pt}_1\text{Sn}_1/\text{C}$, the peak current density is enhanced approximately by 200% compared with those of $\text{Pt}_3\text{Sn}_2/\text{C}$ and $\text{Pt}_2\text{Sn}_1/\text{C}$ at lower temperatures. At higher temperatures, the enhancement ratio between the $\text{Pt}_1\text{Sn}_1/\text{C}$ and Pt/C becomes more significant than the others. According to the literature it is known that the acetic acid is the main product of acetaldehyde electrooxidation over Pt alloy catalysts with negligible CO_2 production. The role of Sn in enhancing Pt's activity towards acetaldehyde electrooxidation is attributed mainly to the effective removal of C_2 species and the inhibition of catalyst poisoning by supplying oxygen-containing species [36]. Thus in the case of a DEFC, as the cell voltage decreases, the acetaldehyde concentration increases. Consequently, the use of the $\text{Pt}_1\text{Sn}_1/\text{C}$ catalyst, which presents the highest activity towards acetaldehyde electrooxidation, would be helpful for avoiding the accumulation of acetaldehyde during the DEFC operation. The above finding is in good agreement with other results reported in the literature, where a series of $\text{Pt}_x\text{Sn}_y/\text{C}$ catalysts were also prepared by the same preparation method [16]. Combined with the above results for ethanol electrooxidation, in order to obtain the improved DEFCs performance, it is expected to adopt the dual catalyst layer, with the first catalyst layer containing $\text{Pt}_2\text{Sn}_1/\text{C}$ while the second catalyst layer containing $\text{Pt}_1\text{Sn}_1/\text{C}$ close to the electrolyte membrane.

3.4. Acetic acid electrooxidation

The products of the acetic acid electrooxidation should be C_1 species. Obviously, this process involves the C–C bond cleavage, which is the determinable factor for the complete ethanol electrooxidation. In order to investigate the role of Sn in the C–C cleavage during the acetic acid electrooxidation, the corresponding CVs of all the prepared catalyst samples in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4 + 0.5 \text{ mol L}^{-1} \text{ CH}_3\text{COOH}$ aqueous solution were performed at different temperatures. For the sake of comparison, the CVs were also recorded in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ aqueous solution as the blank experiment.

Fig. 7 shows the corresponding and comparative CV curves for the acetic acid electrooxidation and the blank experiments, respectively, at 30°C and 80°C . In the case of $\text{Pt}_x\text{Sn}_y/\text{C}$ catalysts, there is little current production, with respect to the case of Pt alone, especially at higher temperature. The detected current density could be attributed to the acetic acid electrooxidation over $\text{Pt}_x\text{Sn}_y/\text{C}$ catalysts. It is also observed that in the case of acetic acid electrooxidation at higher temperature and over the Sn-rich catalysts the current slightly increases. This increment indicates the positive effect of the operating temperature on the acetic acid electrooxidation. Furthermore, the observed behavior is in agreement with other reported results in literature [36,37]. The observed results suggest that the presence of Sn seems to have a minor effect on the activation of C–C bond, and consequently it cannot substan-

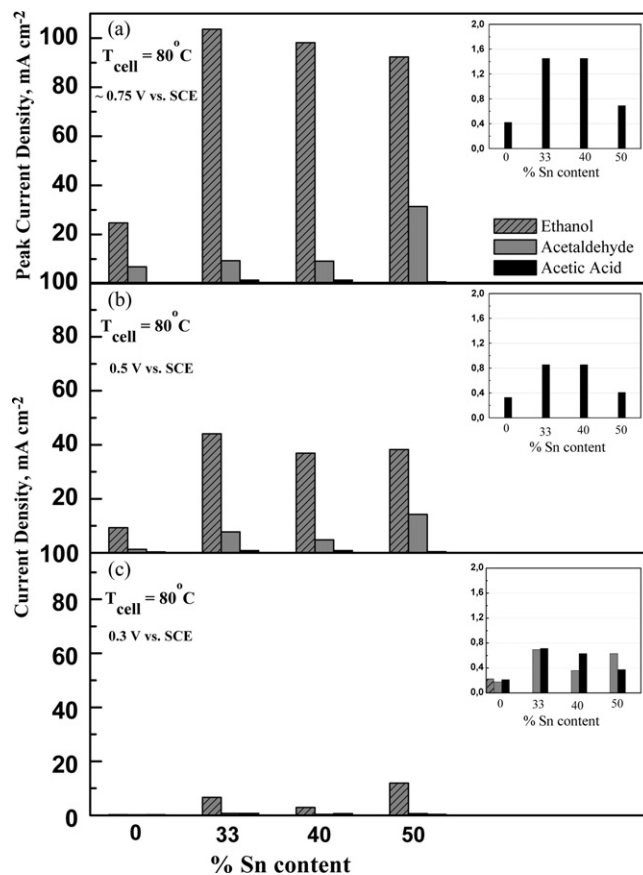


Fig. 8. Comparison of (a) peak current densities, (b) current densities at 0.5 V (vs. SCE), and (c) current densities at 0.3 V (vs. SCE), during ethanol, acetaldehyde and acetic acid electrooxidation over the examined catalysts, Pt/C (0% Sn), $\text{Pt}_2\text{Sn}_1/\text{C}$ (33% Sn), $\text{Pt}_3\text{Sn}_2/\text{C}$ (40%) and $\text{Pt}_1\text{Sn}_1/\text{C}$ (50% Sn).

tially promote the electrooxidation of acetic acid to C_1 species. This conclusion could be further supported by the comparison between the peak current densities recorded during the electrooxidation of ethanol, acetaldehyde and acetic acid over the examined catalysts, as shown in Fig. 8. Furthermore, it should be noted that in Fig. 7 the current in the hydrogen adsorption/desorption region in $\text{CH}_3\text{COOH} + \text{H}_2\text{SO}_4$ is higher than that in H_2SO_4 solution. This phenomenon can be explained as follows. The acetic acid can be considered as adsorbing in undissociated form on top of inner-layer water molecules, involving hydrogen-bonding interaction with the carbonyl oxygen [38]. Such an adsorption geometry has been proposed to account for the increase in the extent of acetic acid adsorption as the electrode charge becomes more positive [39], since the greater polarization of the adsorbed water molecules under these conditions should aid such hydrogen bonding.

3.5. The role of Sn content on the catalysts electrocatalytic activity

The peak current density recorded during the electrooxidation of a compound over a catalyst, could be used as a qualitative measurement for the catalyst activity towards this reaction. In the present case, the comparison of the peak current densities during the electrooxidation of ethanol, acetaldehyde and acetic acid over the examined catalysts at 80°C is depicted in Fig. 8(a). As it can be seen, the addition of Sn strongly enhances the electrocatalytic activity of Pt towards ethanol electrooxidation. The peak current density for the $\text{Pt}_x\text{Sn}_y/\text{C}$ catalysts is found to be approximately 100 mA cm^{-2} , while in the case of Pt/C the corresponding

value is only 25 mA cm^{-2} . In the case of acetaldehyde electrooxidation, the Sn addition only slightly improves the catalysts activity with respect to Pt alone, with the exception of $\text{Pt}_1\text{Sn}_1/\text{C}$, where the electrocatalytic activity is strongly enhanced, by a factor of approximately 300% compared to the other samples. Finally, as it can be better distinguished from the inset of Fig. 8(a), in the case of the acetic acid electrooxidation, the Sn addition improves the peak current density. The peak current density values recorded over the $\text{Pt}_x\text{Sn}_y/\text{C}$ samples are between 0.7 and 1.5 mA cm^{-2} , almost 2–3 times higher than that of Pt/C (0.4 mA cm^{-2}). However, the very low current density values recorded during the acetic acid electrooxidation, compared to those obtained during ethanol and acetaldehyde electrooxidation; indicate that the presence of Sn cannot substantially promote the further electrooxidation of acetic acid to C_1 species.

In order to examine the anode potential effect on the catalysts activity, the current densities recorded at lower potentials of 0.5 and 0.3 V are also reported in Fig. 8(b) and (c). As it is shown, the positive effect of the Sn content on the electrooxidation of each compound is also obvious at lower potentials, although the current density values are smaller. In the case of ethanol electrooxidation, there is a significant reaction rate enhancement with the addition of Sn into Pt/C. The same conclusion could be reached in the case of acetaldehyde electrooxidation at 0.5 V. At 0.3 V, the electrooxidation reaction rate is also enhanced with respect to that over Pt/C, but the recorded current densities are very low. In the case of the acetic acid electrooxidation at both potentials, it is found that there exists current density enhancement over $\text{Pt}_x\text{Sn}_y/\text{C}$ with respect to Pt/C. However, the current densities in both cases are very low, indicating that the presence of Sn cannot substantially promote the electrooxidation of acetic acid to C_1 species (break the C–C bond).

4. Conclusions

In the present work, the activity of $\text{Pt}_x\text{Sn}_y/\text{C}$ catalysts towards ethanol, acetaldehyde and acetic acid electrooxidation was investigated. A series of $\text{Pt}_x\text{Sn}_y/\text{C}$ catalysts with different atomic ratio ($x:y=2:1, 3:2, 1:1$) were fast synthesized by using the pulse microwave assisted polyol method. The physico-chemical characteristics showed that the mean particle size of all the as-prepared catalysts was approximately 3 nm and there was good dispersion over the carbon support. Based on the electrochemical results, the following conclusions could be drawn: (i) In the case of ethanol electrooxidation, the addition of Sn strongly improves Pt's activity with different contributing effect depending on the Sn content and the operating temperature. At lower temperatures, Sn-rich catalysts exhibited better performance, while at higher temperatures Sn-poor catalysts gave better performance. This behavior is attributed to the effect of Sn content on the surface oxygen-containing species, on the catalyst lattice parameter, and on the ohmic resistance. (ii) As it concerns the acetaldehyde electrooxidation, $\text{Pt}_1\text{Sn}_1/\text{C}$ demonstrated the highest activity at all the investigated temperatures, which is due to the fact that Sn existence can effectively remove C_2 species and inhibit the poison formation by supplying oxygen-containing species. (iii) In the case of acetic acid electrooxidation, there was little current recorded, giving an indicator that Sn can not substantially promote the C–C bond breakage. Finally, taking into account the results reported in the literature concerning the product analysis during the DEFCs operation and those obtained in the present work, the following further conclusions could be drawn: (i) the current densities obtained during ethanol electrooxidation over the examined catalysts are mainly related to its electrooxidation towards acetaldehyde, acetic acid and small amounts of CO_2 , (ii) the current densities recorded during acetaldehyde electrooxidation are

most probably due to its electrooxidation towards acetic acid and small amounts of CO_2 , and (iii) the very low current densities during acetic acid electrooxidation are related to its electrooxidation towards CO_2 .

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References

- [1] E. Antolini, *J. Power Sources* 170 (2007) 1–12.
- [2] C. Lamy, A. Lima, V. LeRhun, F. Delime, C. Coutanceau, J.M. Leger, *J. Power Sources* 105 (2002) 283–296.
- [3] S. Song, P. Tsiakaras, *Appl. Catal. B: Environ.* 63 (2006) 187–193.
- [4] S. Song, V. Maragou, P. Tsiakaras, *J. Fuel Cell Sci. Technol.* 4 (2007) 203–209.
- [5] P.E. Tsiakaras, PtM/C, *J. Power Sources* 171 (2007) 107–112.
- [6] C. Lamy, S. Rousseau, E.M. Belgsir, C. Coutanceau, J.M. Leger, *Electrochim. Acta* 49 (2004) 3901–3908.
- [7] W. Zhou, Z. Zhou, S. Song, W. Li, G. Sun, P. Tsiakaras, Q. Xin, *Appl. Catal. B: Environ.* 46 (2003) 273–285.
- [8] G. Andreadis, P. Tsiakaras, *Chem. Eng. Sci.* 61 (2006) 7497–7508.
- [9] G. Andreadis, A. Podias, P. Tsiakaras, *J. Power Sources* 194 (2009) 397–407.
- [10] E. Antolini, F. Colmati, E. Gonzalez, *J. Power Sources* 193 (2009) 555–561.
- [11] Y. Guo, Y. Zheng, M. Huang, *Electrochim. Acta* 53 (2008) 3102–3108.
- [12] L. Jiang, G. Sun, S. Sun, J. Liu, S. Tang, H. Li, B. Zhou, Q. Xin, *Electrochim. Acta* 50 (2005) 5384–5389.
- [13] H. Li, G. Sun, L. Cao, L. Jiang, Q. Xin, *Electrochim. Acta* 52 (2007) 6622–6629.
- [14] D.R. Lycke, E.L. Gyenge, *Electrochim. Acta* 52 (2007) 4287–4298.
- [15] F.C. Simoes, D.M. dos Anjos, F. Vigier, J.M. Leger, F. Hahn, C. Coutanceau, E.R. Gonzalez, G. Tremiliosi-Filho, A.R. de Andrade, P. Olivi, K.B. Kokoh, *J. Power Sources* 167 (2007) 1–10.
- [16] W.J. Zhou, S.Q. Song, W.Z. Li, Z.H. Zhou, G.Q. Sun, Q. Xin, S. Douvartzides, P. Tsiakaras, *J. Power Sources* 140 (2005) 50–58.
- [17] M. Zhu, G. Sun, Q. Xin, *Electrochim. Acta* 54 (2009) 1511–1518.
- [18] E. Antolini, F. Colmati, E.R. Gonzalez, *Electrochim. Commun.* 9 (2007) 398–404.
- [19] Z. Liu, X.Y. Ling, X. Su, J.Y. Lee, L.M. Gan, *J. Power Sources* 149 (2005) 1–7.
- [20] M. Li, A. Kowal, K. Sasaki, N. Marinkovic, D. Su, E. Korach, P. Liu, R.R. Adzic, *Electrochim. Acta* 55 (2010) 4331–4338.
- [21] K. Bergamaski, E.R. Gonzalez, F.C. Nart, *Electrochim. Acta* 53 (2008) 4396–4406.
- [22] A. Kowal, M. Li, M. Shao, K. Sasaki, M.B. Vukmirovic, J. Zhang, N.S. Marinkovic, P. Liu, A.I. Frenkel, R.R. Adzic, *Nat. Mater.* 8 (2009) 325–330.
- [23] A.O. Neto, L.A. Farias, R.R. Dias, M. Brandalise, M. Linardi, E.V. Spinace, *Electrochim. Commun.* 10 (2008) 1315–1317.
- [24] H. Song, X. Qiu, F. Li, W. Zhu, L. Chen, *Electrochim. Commun.* 9 (2007) 1416–1421.
- [25] E. Ribadeneira, B.A. Hoyos, *J. Power Sources* 180 (2008) 238–242.
- [26] E.V. Spinace, M. Linardi, A.O. Neto, *Electrochim. Commun.* 7 (2005) 365–369.
- [27] X. Xue, J. Ge, T. Tian, C. Liu, W. Xing, T. Lu, *J. Power Sources* 172 (2007) 560–569.
- [28] Q. Wang, G.Q. Sun, L. Cao, L.H. Jiang, G.X. Wang, S.L. Wang, S.H. Yang, Q. Xin, *J. Power Sources* 177 (2008) 142–147.
- [29] D.D. James, D.V. Bennett, G. Li, A. Ghumman, R.J. Helleur, P.G. Pickup, *Electrochim. Commun.* 11 (2009) 1877–1880.
- [30] G. Andreadis, V. Stergiopoulos, S. Song, P. Tsiakaras, *Appl. Catal. B: Environ.* 100 (2010) 157–164.
- [31] S. Rousseau, C. Coutanceau, C. Lamy, J.M. Leger, *J. Power Sources* 158 (2006) 18–24.
- [32] F. Vigier, C. Coutanceau, F. Hahn, E.M. Belgsir, C. Lamy, *J. Electroanal. Chem.* 563 (2004) 81–89.
- [33] S. Song, Y. Wang, P. Tsiakaras, P.K. Shen, *Appl. Catal. B: Environ.* 78 (2008) 381–387.
- [34] T.E. Shubina, M.T.M. Koper, *Electrochim. Acta* 47 (2002) 3621–3628.
- [35] K. Taneda, Y. Yamazaki, *Electrochim. Acta* 52 (2006) 1627–1631.
- [36] G. Wu, R. Swaidan, G. Cui, *J. Power Sources* 172 (2007) 180–188.
- [37] G. Sine, D. Smida, M. Limat, G. Foti, Ch. Comninellis, *J. Electrochim. Soc.* 154 (2007) B170–B174.
- [38] D.S. Corrigan, E.K. Krauskopf, L.M. Rice, A. Wieckowski, M.J. Weaver, *J. Phys. Chem.* 92 (1988) 1596–1601.
- [39] A. Wieckowski, J. Sobkowski, P. Zelenay, K. Franaszczuk, *Electrochim. Acta* 26 (1998) 1111–1119.