



## Review

## Catalysts for direct ethanol fuel cells

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**Abstract**

By comparing the performance of fuel cells operating on some low molecular weight alcohols, it resulted that ethanol may replace methanol in a direct alcohol fuel cell. To improve the performance of a direct ethanol fuel cell (DEFC), it is of great importance to develop anode catalysts for ethanol electro-oxidation more active than platinum alone. This paper presents an overview of catalysts tested as anode and cathode materials for DEFCs, with particular attention on the relationship between the chemical and physical characteristics of the catalysts (catalyst composition, degree of alloying, and presence of oxides) and their activity for the ethanol oxidation reaction.

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*Keywords:* Ethanol oxidation; Direct ethanol fuel cells; Platinum alloys; Electrocatalysts**Contents**

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**1. Introduction**

In various applications, fuel cells are widely recognized as very attractive devices to obtain directly electric energy from the combustion of a chemical product. Low temperature fuel cells, generally conceived around a proton electrolyte membrane, seem able to be used for a large range of power applications.

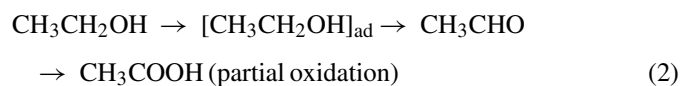
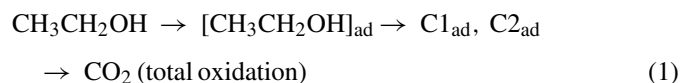
Alcohols and mainly methanol are widely proposed as possible fuels for mobile applications such as electric vehicles [1,2]. The direct oxidation of methanol in fuel cells has been widely investigated. However, the question of the toxicity of methanol remains crucial. Methanol is considered since a long time as a toxic product, in addition to possible environmental problems in relation to its large miscibility to water. Ethanol offers an attractive alternative as a fuel in low temperature fuel cells because it can be produced in large quantities from agricultural products and it is the major renewable biofuel from the fermentation of biomass. By comparing the performance of fuel cells employing

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an H<sub>3</sub>PO<sub>4</sub>-doped polybenzimidazole membrane and Pt–Ru as anode catalyst operating on various methanol-alternative fuels, Wang et al. [3] found that ethanol is a promising alternative fuel with an electrochemical activity comparable to that of methanol. These reasons motivate investigations on ethanol electro-oxidation in order to improve the electrical performances when using it in a direct ethanol fuel cell (DEFC), and to open the possibility of replacing methanol in a direct alcohol fuel cell.

Several studies on the electro-oxidation of ethanol have been devoted mainly to identifying the adsorbed intermediates on the 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 spectrometry (ECTDMS) [4–9]. Based on the foregoing work, the global oxidation mechanism of ethanol in acid solution may be summarized in the following scheme of parallel reactions:



The formation of CO<sub>2</sub> goes through two adsorbed intermediates C1<sub>ad</sub> and C2<sub>ad</sub>, which represent fragments with one and two carbon atoms, respectively. In spite of many advances in the understanding of the mechanism of ethanol oxidation, there are still some unclear aspects. For instance, there is some controversy on whether acetic acid is formed in one step or through the aldehyde. Also, there is no agreement regarding the nature of the adsorbed species. According to some workers, the carbon–carbon bond is preserved, so a larger quantity of intermediates of the type C2 are formed [4,5], but others claim that the main intermediates contain only one carbon atom and are of the type C1 [6,8]. Breaking the C–C bond for a total oxidation to CO<sub>2</sub> is a major problem in ethanol electrocatalysis. Thus, high yields of partial oxidation products, CH<sub>3</sub>CHO and CH<sub>3</sub>COOH, are formed at Pt catalysts [10,11]. These parallel reactions cause a considerable lowering of the fuel capacity to generate electricity and produce undesirable substances.

Carbon supported platinum is commonly used as anode catalyst in low temperature fuel cells. Because catalysis is a surface effect, the catalyst needs to have the highest possible surface area. So, the active phase is dispersed on a conductive support as carbon. Pure Pt, however, is not the most efficient anodic catalyst for the direct ethanol fuel cell. Indeed, the electro-oxidation of a partially oxygenated organic molecule, such as a primary alcohol, can only be performed with a multifunctional electrocatalyst. Platinum itself is known to be rapidly poisoned on its surface by strongly adsorbed species coming from the dissociative adsorption of ethanol [12]. Efforts to mitigate the poisoning of Pt have been concentrated on the addition of cocatalysts, particularly ruthenium and tin, to platinum.

On the other hand, it is known that in direct ethanol fuel cells the ethanol fed to the anode compartment can permeate through the electrolyte to the cathode, similar to the case of methanol in direct methanol fuel cells (DMFCs), i.e. ethanol crossover occurs. Song et al. [13] found that the ethanol permeated to the cathode exhibited a less serious effect on the cell performance compared to methanol because of both its smaller permeability through Nafion<sup>®</sup> membrane and its slower electrochemical oxidation kinetics over Pt/C cathode. However, due to the low activity for the oxygen reduction reaction (ORR) of Pt, research on cathode catalysts alternative to pure Pt are in progress. The requirements of a suitable cathode material for the DEFC are an improved ORR activity and an ethanol tolerance even or higher than those of Pt.

This paper presents an overview of catalysts tested as anode and cathode materials for DEFC by measurements in half-cell in acid environment and in fuel cell with proton exchange membrane, with particular attention on the relationship between the chemical and physical characteristics of the catalysts (catalyst composition, degree of alloying, and presence of oxides) and their activity for the ethanol oxidation reaction (EOR). Considering that ethanol could be used as fuel also in alkaline fuel cells [14], supported catalysts for ethanol oxidation in alkaline media are briefly reviewed.

## 2. Anode catalysts

The more extensively investigated anode materials for DEFCs are the binary Pt–Ru and Pt–Sn and the correlated ternary Pt–Ru-based and Pt–Sn-based catalysts. As in the case of the methanol oxidation, the superior performance of these binary and ternary electrocatalysts for the ethanol oxidation with respect to Pt alone was attributed to the bifunctional effect (promoted mechanism) [15,16] and to the electronic interaction between Pt and alloyed metals (intrinsic mechanism) [15,17,18]. According to the promoted mechanism, the oxidation of the strongly adsorbed oxygen-containing species is facilitated in the presence of Ru(Sn) oxides by supplying oxygen atoms at an adjacent site at a lower potential than that accomplished by pure Pt. The intrinsic mechanism postulates that the presence of Ru(Sn) modifies the electronic structure of Pt, and, as a consequence, the adsorption of oxygen-containing species. In the next paragraphs the characteristics and the electrochemical activity of these materials are presented. The last part of this section is addressed to ethanol oxidation in alkaline media.

### 2.1. Binary catalysts

#### 2.1.1. Pt–Ru/C

The crystal structure of pure Pt is face centered cubic (fcc), while that of Ru is hexagonal close packed (hcp). For Ru atomic fractions up to about 0.7, Pt and Ru form a solid solution with Ru atoms replacing Pt atoms on the lattice points of the fcc structure. The lattice constant decreases from 3.923 Å (pure Pt) to 3.83 Å at 0.675 atomic fraction Ru [19]. Above 0.7 at Ru, another solid solution is formed with Pt atoms replacing Ru in an hcp structure. While unsupported Pt–Ru alloys

are easily obtained, it is difficult to obtain carbon supported Pt–Ru with a Pt:Ru atomic ratio in the alloy like nominal Pt:Ru [20].

Regarding the oxidation mechanism of ethanol, Schmidt et al. [9] observed that the formation of chemisorbed species coming from dissolved ethanol is partially inhibited by the presence of Ru. This favours the oxidation pathway through weakly adsorbed species, and therefore the selectivity for ethanol production was found to be higher compared to that for pure Pt. In agreement with this result, Camara et al. [21] found that the dissociative adsorption of ethanol seems to be inhibited by Ru. Probably, this effect is due to the diminution of neighboring Pt sites, which are necessary for the scission of the C–C bond. On the other hand, according to Fujiwara et al. [22], the promoter action of Ru seems to enhance the oxidation of strongly-bound adsorbed intermediates to give a higher relative yield of CO<sub>2</sub> than on pure Pt. Lee et al. [23] investigated the temperature effect on ethanol electro-oxidation at carbon supported Pt and Pt–Ru by cyclic voltammetry (CV). With increasing temperature from 25 to 80 °C, the CV results showed that Pt/C increased currents only by a factor of 4 whereas Pt–Ru/C raised it about eight times for the same temperature range. According to the authors, the ruthenium addition remarkably enhanced ethanol oxidation performance probably due to the strong adsorption of OH. Pt–Ru/C showed larger apparent activation energies of oxidation than Pt/C, representing higher temperature dependence of OH adsorption on ruthenium.

Calegario et al. [24] used a sol–gel-based method to incorporate ruthenium and iridium oxides, either alone or combined, on a carbon supported platinum, with 25% in their total mass related to the Pt amount. Polarization curves showed that the ethanol oxidation can proceed more efficiently on Pt–RuO<sub>2</sub>/C than on commercially available Pt–Ru/C and Pt/C catalysts. Moreover, the addition of IrO<sub>2</sub> to Pt–RuO<sub>2</sub>/C composites can improve even more the EOR. The same research group [25] fixed the Pt–RuO<sub>2</sub>/C composite on the surface of a boron-doped diamond (BDD) electrode. By cyclic voltammetry, Tafel plots and chronoamperometry measurements the ethanol oxidation in H<sub>2</sub>SO<sub>4</sub> solutions on BDD supported Pt–RuO<sub>2</sub>/C occurred with larger current densities and increased stability than that on a commercial Pt/C catalyst.

The Ru amount in the Pt–Ru catalysts is an important parameter influencing the ethanol oxidation. Lamy et al. [12] observed a poor activity of Pt–Ru (Pt:Ru atomic ratio = 4:1) for the ethanol oxidation at room temperature. Camara et al. [21] found that there is a relatively narrow range of Pt–Ru compositions having a high rate of ethanol oxidation: for a Ru content lower than 20 at.%, there are not enough Ru sites to effectively assist the oxidation of adsorbed residues and the oxidation current remains almost at the levels obtained for pure Pt. On this basis, the low Ru content could explain the poor activity of the Pt–Ru (4:1) catalyst observed by Lamy et al. By cyclic voltammetry measurements, Spinacé et al. [26] found that the activity for the ethanol oxidation of Pt–Ru/C increases with the increase of ruthenium content in the catalysts (range investigated up to Pt:Ru 1:3). In the same way, Oliveira Neto et al. [27] also observed that the activity for the oxidation of ethanol of Pt–Ru/C increases with the content

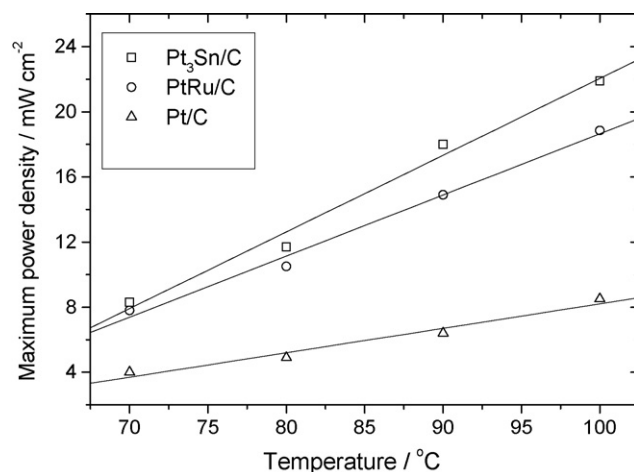


Fig. 1. Dependence of the maximum power density of DEFCs with Pt/C, Pt–Ru (1:1) and Pt–Sn/C (3:1) as anode catalysts on cell temperature. O<sub>2</sub> pressure: 3 atm; ethanol solution: 1 mol l<sup>-1</sup>. Anode metal loading 1 mg cm<sup>-2</sup>. Cathode 20 wt.% Pt/C, Pt loading 1 mg cm<sup>-2</sup>. Reprinted from Ref. [29], copyright 2006, with permission from Elsevier.

of the second metal (range investigated up to Pt:Ru 3:2). Camara et al. [21] found an optimum Pt:Ru composition of *ca.* 3:2.

Tests in direct ethanol fuel cells showed that the cells with Pt–Ru/C as anode material better perform than those with Pt/C [12,28,29]. Fig. 1 shows the dependence of the maximum power density (MPD) of single DEFCs with Pt/C, Pt–Ru/C (1:1) and Pt–Sn/C (3:1) as anode material on cell temperature in the range 70–100 °C. For all the investigated temperatures the MPD of the cell with Pt–Ru/C was considerably higher than that of the cell with Pt/C as anode catalyst.

### 2.1.2. Pt–Sn/C

Platinum and tin form five bimetallic intermetallic phases, Pt<sub>3</sub>Sn, PtSn, Pt<sub>2</sub>Sn<sub>3</sub>, PtSn<sub>2</sub>, and PtSn<sub>4</sub>, of which Pt<sub>3</sub>Sn and PtSn are congruently melting compositions. These intermetallic phases are distinguished by distinct crystalline structures and unique X-ray diffraction patterns. Kuznetsov et al. [30] asserted that Pt forms nearly all possible alloys with Sn. Then, the shift of the fcc Pt peaks of Pt–Sn catalysts to lower angles than pure Pt but to higher angles than the fcc Pt<sub>3</sub>Sn phase should reveal the formation of a solid solution between Pt and Sn, due to the incorporation of Sn in the fcc structure of Pt. Radmilovic et al. [31], instead, attributed the value of the lattice constant of 0.3965 nm found for a commercial carbon supported Pt:Sn 1.23:1 catalyst, prepared by a conventional precipitation route by decomposing Pt and Sn precursors at 500 °C, to a mixture of Pt<sub>9</sub>Sn (0.3934 nm) [32] and Pt<sub>3</sub>Sn phases. Given the near-coincidence of the Pt<sub>9</sub>Sn and Pt<sub>3</sub>Sn reflections and the particle size broadening, a mixture of Pt<sub>9</sub>Sn and stoichiometric Pt<sub>3</sub>Sn would produce a diffraction pattern very similar to that of a nonstoichiometric Pt<sub>3</sub>Sn phase.

Carbon supported Pt–Sn catalysts are commonly prepared in the absence of thermal treatment, and, as a consequence, are formed by a fcc Pt–Sn alloy (or a mixture of Pt<sub>9</sub>Sn and Pt<sub>3</sub>Sn phases) and Sn and Pt oxides. The relative amount of Pt–Sn alloy and SnO<sub>2</sub> affects the electrochemical activity of these catalysts.

Table 1  
Summary of performance of single direct ethanol fuel cell tests adopting different anode catalysts (90 °C)

Catalyst	Open circuit voltage (mV)	Voltage at 30 mA cm <sup>-2</sup> (mV)	Voltage at 60 mA cm <sup>-2</sup> (mV)	Maximum power density (mW cm <sup>-2</sup> )
Pt	547	275	177	10.85
Pt–Ru (1:1)	677	461	368	28.54
Pt–Sn (1:1)	811	662	576	52.22
Pt–Ru–W (1:1:1)	698	503	425	38.54
Pt–Ru–Mo (1:1:1)	720	486	389	31.19

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Conversely to DMFCs, DEFCs with Pt–Sn/C as anode material better performed than those with Pt–Ru/C [12,28,29], as shown in Fig. 1 and Table 1. Song et al. [33] compared the cell performances of direct ethanol fuel cells with various Pt–Sn/C (2:1) and Pt–Ru/C (1:1) catalysts as anode materials. As can be seen in Fig. 2, the cells with Pt–Sn/C catalysts prepared by different methods better performed than the cells with commercial and in-house prepared Pt–Ru/C.

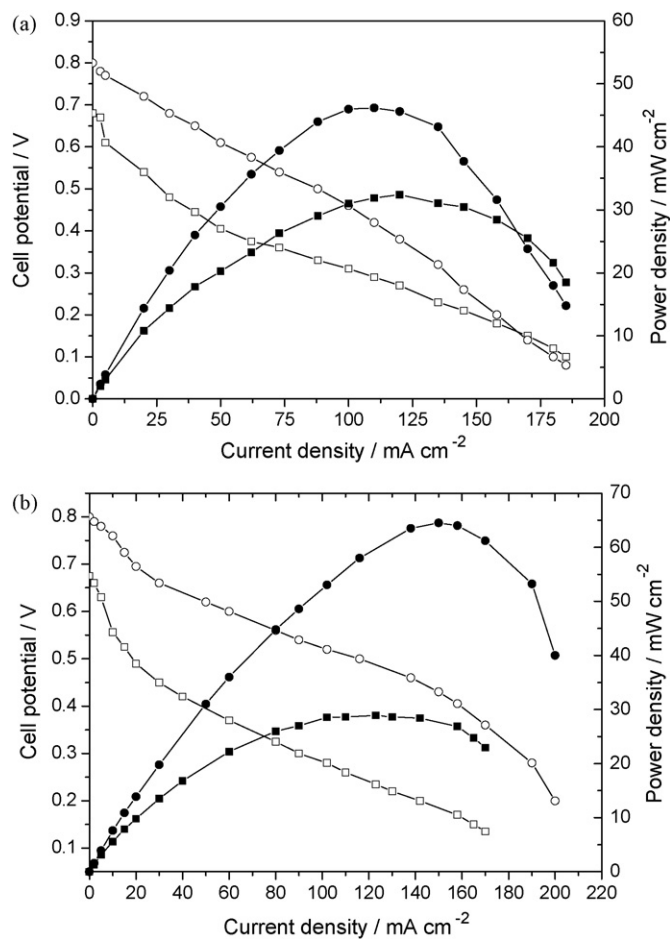


Fig. 2. Polarization curves and power density curves in single DEFC with Pt–Sn/C (2:1) and Pt–Ru/C (1:1) catalysts. (a) PtSn/C-a and commercial PtRu/C, (b) PtSn/C-b and in-house PtRu/C. Cell temperature: 90 °C. Anode Pt loading: 1.3 mg cm<sup>-2</sup>; ethanol solution: 1.0 M ethanol solution, flow rate: 1.0 ml min<sup>-1</sup>. Cathode: 20 wt.% Pt/C, Pt loading 1.0, oxygen pressure: 2 atm. Electrolyte: Nafion® 115 membrane. Circles: Pt–Sn/C; squares: Pt–Ru/C. Open symbols: cell potentials; full symbols: power densities. Reprinted from Ref. [33], copyright 2005, with permission from Elsevier.

The research groups of Lamy [12,34,35] and Xin [28,36–38] investigated the ethanol oxidation on carbon supported Pt–Sn catalysts prepared by the co-impregnation reduction method [34], the Bonneman's method [12] and a modified polyol process [28]. In all cases most of the Sn was in a non-alloyed oxidized state. Controversial results on the effect of the Sn content in the Pt–Sn catalysts on cell performance were reported. Lamy et al. [12] prepared Pt–Sn/C electrocatalysts with Pt:Sn atomic ratios varying from 90:10 to 50:50 and observed an optimum composition with tin in the range 10–20 at.%. Conversely, Zhou et al. [28] found that Pt–Sn/C electrocatalysts with Pt:Sn molar ratios of 66:33, 60:40 and 50:50 are more active than electrocatalysts with 75:25 and 80:20 molar ratios, with the optimum composition in the range 33–40 at.%, depending on DEFC operation temperature.

The activity for the ethanol oxidation of Pt–Sn/C electrocatalysts with different Sn content, prepared by the alcohol reduction process using ethylene glycol as solvent and reducing agent, was investigated by Spinacé et al. [39] using cyclic voltammetry. The results of CV measurements are shown in Fig. 3. The electro-oxidation of ethanol starts at low potentials (~0.25 V) for Pt–Sn/C electrocatalysts with Pt:Sn molar ratios of 50:50 and 25:75, showing similar current values in range of 0.25–0.40 V. Above 0.4 V the electrocatalysts with Pt:Sn molar ratio of 50:50 showed a superior performance. For the electrocatalyst with

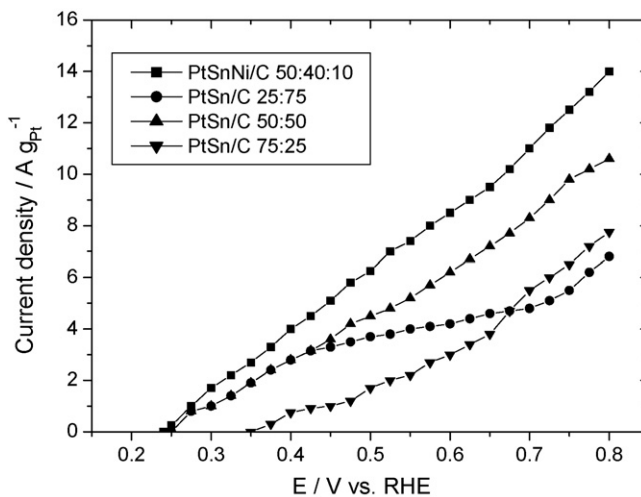


Fig. 3. Cyclic voltammetry of Pt–Sn/C and Pt–Sn–Ni/C electrocatalysts in 0.5 M H<sub>2</sub>SO<sub>4</sub> containing 1.0 M of ethanol with a sweep rate of 10 mV s<sup>-1</sup>, considering only the anodic sweep. Reprinted from Ref. [39], copyright 2005, with permission from Elsevier.

Pt:Sn molar ratio of 75:25 the oxidation starts only at about 0.35 V and the currents values were lower than those observed for the electrocatalysts with more tin content. These results were similar to those obtained by Zhou et al. [28] using Pt–Sn/C electrocatalysts prepared by a similar procedure but different from those obtained by Lamy et al. [12] using electrocatalysts prepared by co-impregnation reduction method. These observations suggest that the performance of Pt–Sn/C electrocatalysts greatly depends on its preparation procedure. The importance of the preparation method was shown by Song et al. [33]. They prepared carbon supported Pt–Sn catalysts by two ways. The Pt–Sn/C catalysts were prepared by the commonly used polyol method, by simultaneous deposition of Pt and Sn on the carbon support (denoted as PtSn/C-b) and by deposition of Sn on pre-formed Pt/C (denoted as PtSn/C-a). Based on the results reported in Fig. 2a and b, it is clear that the cells with different Pt–Sn/C show almost the similar behaviour in the low current density. By increasing the current density, however, the performance of the cell with PtSn/C-a becomes inferior to that with PtSn/C-b, and this difference increases as the current density increases. According to the authors, this could be attributed to a higher content of Sn oxide in PtSn/C-a than that in PtSn/C-b, leading to a higher internal cell resistance and consequently affecting the cell performance. In addition, the direct deposition of Sn onto Pt/C could partly cover the platinum active sites, hindering in this way the adsorption and oxidation of ethanol, and resulting in the inferior performance in the high current density range when PtSn/C-a was used as the anode catalyst.

Siné et al. [40] prepared bimetallic Pt–Sn nanoparticles supported on a boron-doped diamond substrate. These nanoparticles showed high activity toward ethanol oxidation. They believed that this substrate could promote the activation of the ethanol C–C bond scission, or increase the turnover frequency of product formation.

Controversial results regarding the effect of the degree of alloying on the EOR activity of Pt alloy catalysts have been reported. Jang et al. [41] compared the catalytic activity of a partially alloyed Pt–Sn catalyst with that of a quasinon-alloyed PtSnO<sub>x</sub> catalyst. From the results of chronoamperometry analysis and the performance of direct ethanol fuel cells, PtSnO<sub>x</sub> catalyst showed higher catalytic activity for ethanol electro-oxidation than Pt–Sn alloy. They deduced that the unchanged lattice parameter of Pt in the PtSnO<sub>x</sub> catalyst is favourable to ethanol adsorption and meanwhile, tin oxide in the vicinity of Pt nanoparticles could offer oxygen species conveniently to remove the CO-like species of ethanolic residues to free Pt active sites. Conversely, Colmenares et al. [42] compared the performance of the polyol-type Pt/C, Pt–Ru/C (1:1) and Pt–Sn/C (3:1) catalysts with that of the corresponding commercial catalysts. For all catalysts, incomplete ethanol oxidation prevails, and CO<sub>2</sub> formation contributes by ≤1%. The EOR activities of the polyol-type catalysts were lower than those of the commercial catalysts, due to the lower activity for acetaldehyde formation. This behaviour was ascribed to the lower degree of alloy formation in the polyol-type catalysts.

Colmati et al. [43] investigated the EOR activity of Pt–Sn/C catalysts (Pt:Sn=90:10, 75:25 and 66:33) prepared by the

formic acid method. They found that the activity of Pt–Sn catalysts for the ethanol oxidation reaction seems to depend on the amount of both non-alloyed and alloyed Sn. The rate-determining step for ethanol oxidation depends on the temperature of the reaction and determines the optimal distribution of Sn between the alloyed and non-alloyed states. At low temperatures and/or at low current densities, where the electro-oxidation of ethanol is not fast, the oxidation of adsorbed CO and CH<sub>3</sub>CO species determines the rate of the process. In this case the oxidation of ethanol is enhanced by the presence of tin oxides. At high temperatures and high current densities, instead, the oxidation of ethanol increases with the increase of the lattice parameter: in the hypothesis of the formation of a Pt–Sn 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. In the hypothesis of the formation of two phases, instead, it can be inferred that the activity for the EOR of the Pt<sub>3</sub>Sn phase is higher than that of the Pt<sub>9</sub>Sn<sub>1</sub> phase.

Regarding the C–C bond cleavage, it has to be pointed out that, while Gursahani et al. [44] showed that ethanol reacts on pure Pt to give CO, CH<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub> by cleavage of C–O and C–C bonds, a recent work of the same research group [45] reports that addition of Sn to Pt catalysts inhibits the decomposition of ethanol to CO and CH<sub>4</sub>, owing to the suppression of C–C bond cleavage. The inhibition of C–C bond cleavage reactions by addition of Sn to Pt catalysts was been attributed to changes in the geometric and electronic characteristics of the surface. Similarly, in DEFC experiments Rousseau et al. [46] found that 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: the formation of CO<sub>2</sub> and acetaldehyde is lowered whereas the formation of acetic acid is increased. The yield in CO<sub>2</sub> was twice as much with a Pt/C catalyst than with a Pt–Sn/C catalyst. This can be explained by the need to have several adjacent platinum sites to adsorb dissociatively the ethanol molecule and to break the C–C bond. When some tin atoms are introduced among the platinum atoms, the latter reaction is not favoured. As soon as acetaldehyde is formed, however, it can adsorb on platinum sites leading to a Pt–CH<sub>3</sub>–CO species: then, because Sn is known to activate water at lower potentials than platinum, some OH species can be formed at low potentials on Sn sites and adsorbed acetaldehyde species can react with adsorbed OH species to produce acetic acid.

Colmati et al. [47] thermally treated at 200 °C a carbon supported Pt–Sn electrocatalyst in the Pt:Sn atomic ratio 75:25, prepared by the reduction of Pt and Sn precursors with formic acid. In the case of the as-prepared catalyst, on the basis of the lattice parameter, lower than Pt alone and higher than Pt<sub>3</sub>Sn phase, the formation of a fcc Pt–Sn solid solution was hypothesized, together with the presence of SnO<sub>2</sub>. Alternatively, the presence of a mixture of Pt<sub>9</sub>Sn and Pt<sub>3</sub>Sn phases and SnO<sub>2</sub> was invoked. Thermal treatment at 200 °C of this Pt–Sn (3:1) catalyst gave rise to the formation of a cubic Pt<sub>3</sub>Sn phase. The activity for the

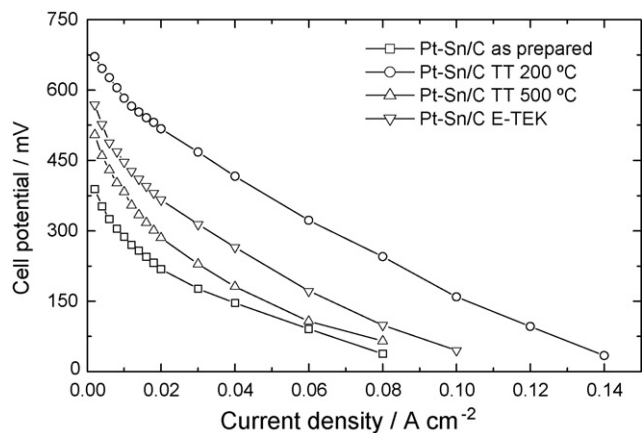


Fig. 4. Polarization curves and power density curves in single DEFC with as prepared and thermally treated Pt-Sn/C (75:25) prepared by FAM and commercial Pt/C and Pt<sub>3</sub>Sn/C by E-TEK as anode electrocatalysts for ethanol oxidation at 90 °C and 3 atm O<sub>2</sub> pressure using a 1 M ethanol solution. Anode metal loading 1 mg cm<sup>-2</sup>. Cathode: 20 wt.% Pt/C, Pt loading 1 mg cm<sup>-2</sup> (□) Pt-Sn/C as prepared; (○) Pt-Sn/C thermally treated at 200 °C; (△) Pt-Sn/C thermally treated at 500 °C; (▽) Pt<sub>3</sub>Sn/C E-TEK. Reprinted from Ref. [47], copyright 2007, with permission from Elsevier.

ethanol oxidation reaction and the performance in single direct ethanol fuel cell (see Fig. 4) of the catalyst thermally treated at 200 °C were better of those of the as-prepared catalyst. This result was explained on the basis of a superior catalytic activity of the Pt<sub>3</sub>Sn phase than that of the fcc Pt-Sn solid solution/SnO<sub>2</sub> mixture or of the Pt<sub>9</sub>Sn/Pt<sub>3</sub>Sn/SnO<sub>2</sub> mixture. Conversely, the EOR activity of the PtSn phase was lower than that of the Pt<sub>3</sub>Sn phase and of the fcc Pt-Sn solid solution/SnO<sub>2</sub> mixture [48].

### 2.1.3. Other binary Pt-based catalysts

Other binary Pt-M (M = W, Pd, Rh, Re, Mo, Ti, Ce) catalysts than Pt-Ru and Pt-Sn have been investigated for the ethanol oxidation reaction. Generally, these catalysts presented an EOR activity higher than that of Pt alone but lower than that of Pt-Ru and Pt-Sn.

Pt<sub>x</sub>-WO<sub>3</sub>/C electrocatalysts were prepared by loading Pt on WO<sub>3</sub> modified carbon [49]. Based on cyclic voltammetry, linear sweep voltammetry, and chronoamperometry, Pt<sub>x</sub>-WO<sub>3</sub>/C showed superior electrocatalytic activity to ethanol oxidation to Pt/C. The results also showed that the activity of the Pt<sub>x</sub>-WO<sub>3</sub>/C electrocatalysts with different Pt:W atomic ratios increases with the increase of the WO<sub>3</sub> content.

Tanaka et al. [50] prepared Pt-based binary and ternary electrocatalysts deposited onto a Au substrate by co-sputtering process. As can be seen in the voltammogram of Fig. 5, the EOR activity of Pt-W was higher than that of Pt-Sn and Pt-Ru. Conversely, Zhou et al. [51] found that Sn, Ru, Pd and W can enhance ethanol electro-oxidation activity over Pt in the following order: Pt-Sn/C > Pt-Ru/C > Pt-W/C > Pt-Pd/C > Pt/C.

Vigier et al. [34] investigated the ethanol electro-oxidation on carbon supported Pt, Pt-Sn and Pt-Re. By CV measurements and tests in single DEFC the activity for EOR was in the order: Pt-Sn/C > Pt-Re/C > Pt/C.

De Souza et al. [10] found that the combination of platinum and rhodium in bimetallic electrodes for ethanol oxidation pro-

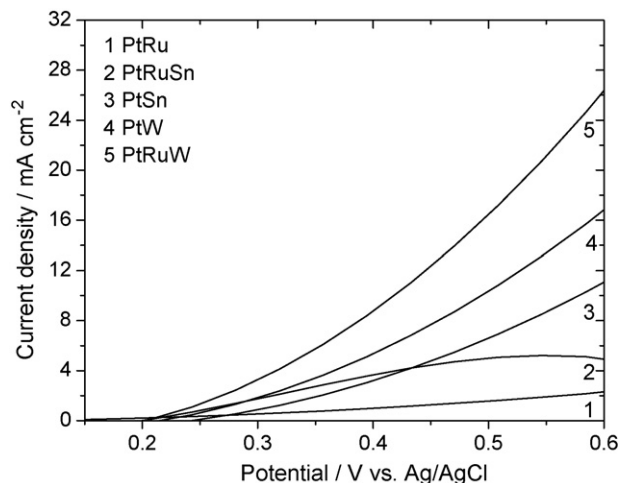


Fig. 5. Voltammograms of Pt-Metal alloy electrodes in 0.5 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> + 1 mol dm<sup>-3</sup> ethanol solution compared to Pt-Ru. Substrate, Au; heating temperature, 300 °C; scan rate, 10 mV s<sup>-1</sup>. Reprinted from Ref. [50], copyright 2005, with permission from Elsevier.

duces a strong decrease in the acetaldehyde yield, compared to pure platinum electrodes. The CO<sub>2</sub> yield is improved relative to pure platinum on Pt-Rh in the atomic ratio 73:27 and 55:45. Gupta and Datta [52] carried out a comparative study on the EOR activity of electrodeposited Pt and Pt-Rh alloys by voltammetry, polarization study and electrochemical impedance spectroscopy. The best ethanol oxidation behaviour was observed on the Pt-Rh electrode in the atomic ratio 74:26. The authors ascribed the enhancement in the EOR activity of this Pt-Rh catalyst compared to Pt alone to an improvement of C-C bond cleavage rather than to a bifunctional mechanism. Colmati et al. [53] studied the EOR activity of Pt/C, Pt-Sn/C (1:1) and Pt-Rh/C (1:1) prepared by the FAM. LSV at 90 °C indicated that the EOR activity of Pt-Rh/C is slightly higher than that Pt/C but remarkably lower than that of Pt-Sn/C.

dos Anjos et al. [54] investigated the EOR activity on Pt-Mo prepared by an arc-melting furnace process. Pt-Mo alloy catalysts were more active than Pt alone. Mo dissolution was observed after voltammetric and chronoamperometric measurements. According to the authors, the dissolved Mo contributed to the catalytic effect of the electrode as underpotentially deposited ad-atoms. Moreover, Mo dissolution leads to an increase in the electrode surface roughness.

The group of Qiu investigated the effect of oxide presence on the EOR activity of supported platinum [55,56]. Carbon nanotube (CNT) supported Pt-TiO<sub>2</sub> were prepared by sol-gel and ethylene glycol reduction method [55]. CV, chronoamperometry and CO stripping voltammetry measurements indicated that Pt-TiO<sub>2</sub>/CNT catalysts have higher EOR activity and CO tolerance than Pt/C by E-TEK and Pt/CNT catalysts in acid media. The optimum Pt:TiO<sub>2</sub> molar ratio was 1:1. The activity for ethanol oxidation of carbon supported Pt-CeO<sub>2</sub> and Pt-Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub>/C catalysts was evaluated by CV, steady state polarization and CO stripping measurements [56]. Cyclic voltammetry results showed that the EOR activity of Pt-CeO<sub>2</sub>/C is higher than that of Pt/C. They found that the structure and

Ce/Zr ratio of Pt–Ce<sub>x</sub>Zr<sub>1–x</sub>O<sub>2</sub>/C influences the catalytic activity of the catalysts. CO stripping voltammetry indicated that the inclusion of CeO<sub>2</sub> and Ce<sub>x</sub>Zr<sub>1–x</sub>O<sub>2</sub> favours the CO oxidation at lower potential.

## 2.2. Ternary catalysts

It is worthy to note that even if Pt–Sn/C catalysts exhibit higher electrocatalytic activity for ethanol oxidation than Pt alone and other binary catalysts, the majority of the oxidation products are still the species containing C–C bond, which will have an obviously negative effect on the fuel cell performance. It is crucial and necessary to develop novel catalysts or add a third element to modify the Pt–Sn/C and Pt–Ru/C catalysts to present higher specific activity of dehydrogenation, C–O and C–C bond cleavage during the ethanol oxidation process.

### 2.2.1. Pt–Ru-based catalysts

Zhou et al. [28] tested the activity towards ethanol oxidation of carbon supported binary and ternary Pt–Ru-based catalysts, prepared using a modified polyol method, by cyclic voltammetry measurements and in single direct ethanol fuel cells. The respective additions of W and Mo to Pt–Ru/C have no obvious effect on its XRD pattern, showing that both additives do not change its crystal structure. Pt–Ru–W (1:1:1) and Pt–Ru–Mo (1:1:1) showed an excellent behaviour. The results of single DEFC tests adopting the ternary catalysts mentioned above are summarized in Table 1, in which is including the open circuit voltage of various single cells, the working output voltages at current densities of 30 and 60 mA cm<sup>–2</sup>, and the maximum power densities. As can be seen in Table 1, the addition of Mo increases the open circuit voltage, while the addition of W can greatly increase the maximum power density. The performance of the cells with Pt–Ru–W and Pt–Ru–Mo was higher than that with Pt–Ru (1:1), but still inferior to that employing Pt–Sn (1:1). Zhou et al. [51] also investigated the ethanol oxidation in single DEFC with a carbon supported Pt–Ru–Sn (1:1:1) catalyst as anode material. In the case of Pt–Ru–Sn, from XRD pattern it results that the lattice parameter ranges between the lattice parameter of Pt–Sn/C and that of Pt–Ru/C. The cell with Pt–Ru–Sn/C showed high performance as that with Pt–Ru–W/C, and the former was better than the latter in the intrinsic resistance-controlled region and activation-controlled region. Also in this case, however, the performance of the single fuel cell with Pt–Ru–Sn was higher than that of the cell with Pt–Ru (1:1), while still inferior to that of the cell with Pt–Sn (1:1).

Tanaka et al. [50] prepared Pt-based binary and ternary electrocatalysts deposited onto a Au substrate by co-sputtering process. Conversely to the results obtained by Zhou et al. [26], the performance of Pt–Ru–W was favourably compared with that of binary alloys, such as Pt–W, Pt–Sn, and Pt–Ru, which exhibit higher catalytic activity than single Pt metal layer electrode. Ethanol electro-oxidation at Pt–Ru–W alloy system showed a cathodic shift in the onset potential and a higher current density than the binary alloy electrodes comparatively. The results of linear sweep voltammograms of ternary alloy systems

deposited onto Au substrate at 300 °C in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1 M ethanol solution compared to Pt–Ru alloy electrodes are shown in Fig. 5. It makes clear that the Pt–Ru–W ternary electrocatalyst provides superior performance of ethanol oxidation as compared with binary alloy compositions.

Pt–Ru–Ni/C (6:3:1) and Pt–Ru/C (1:1), prepared by a chemical reduction method, were tested by Wang et al. [57] as catalysts for ethanol oxidation by cyclic voltammetry and chronoamperometry measurements in a half cell in a solution of 0.5 M CH<sub>3</sub>CH<sub>2</sub>OH and 0.5 M H<sub>2</sub>SO<sub>4</sub>. Taking into account that the amount of platinum atoms in the ternary catalyst is higher than that in the binary catalyst, the almost same value of the lattice constant for Pt–Ru/C (1:1) and Pt–Ru–Ni/C (6:3:1) clearly indicates that the formation of a ternary Pt–Ru–Ni alloy took place. No significant differences in the ethanol electro-oxidation on both electrodes were found using cyclic voltammetry, especially regarding the onset potential for ethanol electro-oxidation. The electrochemically active specific areas of the Pt–Ru–Ni/C and Pt–Ru/C catalysts were almost the same. But, the catalytic activity for ethanol electro-oxidation of the Pt–Ru–Ni/C catalyst was higher than that of the Pt–Ru/C catalyst. The promoting effect attributable to the addition of nickel to platinum–ruthenium on the electro-oxidation of ethanol is particularly significant at low potentials, as can be clearly seen in Fig. 6, which shows the ratio of the current densities, measured under quasisteady-state conditions, with and without the addition of nickel, as a function of the oxidation potential. This figure shows that the addition of nickel gives a maximum ratio at a potential of about 0.3 V (versus RHE), at which the current density for ethanol oxidation is enhanced by a factor of 5.4.

Oliveira Neto et al. [58] compared the electrooxidation of methanol and ethanol of carbon supported Pt–Ru and Pt–Ru–Mo catalysts, prepared by a modified version of the Bonnemant method, using cyclic and linear voltammetry. XPS measurements indicate the presence of metallic platinum, PtO<sub>2</sub>, RuO<sub>2</sub> and an oxidized form of Mo. They found that the Pt–Ru–Mo/C (1:1:1) catalyst shows a much better performance for the oxidation of ethanol than for the oxidation of methanol. Thus, the authors inferred that the addition of Mo not only has a beneficial

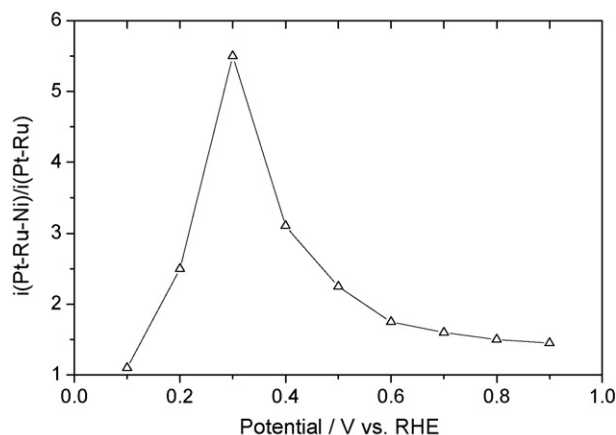


Fig. 6. Ratio of the current densities of ethanol oxidation recorded on the Pt–Ru–Ni/C and Pt–Ru/C electrodes as a function of the potential. Reprinted from Ref. [57], copyright 2006, with permission from Elsevier.

effect to promote the oxidative desorption of intermediates like CO but also promotes the breaking of the C–C bond.

Li and Pickup [59] prepared Pt–Pb and Pt–Ru–Pb by deposition of Pb on Pt and Pt–Ru catalysts. No Pt–Pb and Pt–Ru–Pb alloys were formed. The addition of Pb to Pt and Pt–Ru increases the EOR activity, especially at high potentials.

Salazar-Banda et al. [60] investigated the ethanol oxidation on boron-doped diamond electrode surface modified with Pt, Pt–RuO<sub>2</sub> and Pt–RuO<sub>2</sub>–RhO<sub>2</sub>. CV measurements in acid medium indicated that the CO poisoning effect for the ethanol oxidation is clearly inhibited on the Pt–RuO<sub>2</sub>–RhO<sub>2</sub>/BDD electrode. Polarization curves and the corresponding Tafel plots showed that the addition of RuO<sub>2</sub> and RhO<sub>2</sub> to Pt/BDD produces a more reactive catalyst, changing the reaction onset by 180 mV towards less positive potentials. Moreover, the stationary current density for ethanol oxidation on the Pt–RuO<sub>2</sub>–RhO<sub>2</sub>/BDD measured at a fixed potential was more than one order of magnitude larger than that on a Pt/BDD surface.

### 2.2.2. Pt–Sn-based catalysts

Spinacé et al. [39] studied the electro-oxidation of ethanol on a ternary Pt–Sn–Ni/C electrocatalyst (50:40:10), prepared by alcohol reduction process, using cyclic voltammetry and chronoamperometry. The XRD pattern of Pt–Sn–Ni/C electrocatalyst showed the characteristic peaks of the platinum fcc structure and the presence of cassiterite phase like observed for Pt–Sn/C (50:50) electrocatalyst. By CV measurements they found that the substitution of a small amount of tin by nickel practically did not change the onset potential ( $\sim 0.25$  V) but the current values were greater than those obtained for Pt–Sn/C (50:50) electrocatalyst in the whole range of the potential (see Fig. 3). The superior performance of the Pt–Sn–Ni/C electrocatalyst was also observed by chronoamperometry measurements. In all current-time curves there is an initial current drop in the first 5 min followed by a slower decay, but the current values obtained for Pt–Sn–Ni/C electrocatalyst were always higher than those obtained for Pt–Sn/C (50:50) electrocatalyst.

Rousseau et al. [46] investigated the ethanol electro-oxidation at Pt, Pt–Sn (90:10) and Pt–Sn–Ru (86:10:4) in a single DEFC in terms of reaction product distribution depending on the anode catalyst. The addition of Ru to Pt–Sn greatly enhanced the electrical performance of the DEFC, i.e. the activity of the catalyst, but did not modify the product distribution. In the XRD pattern of the Sn-containing catalysts the absence of shift of the Pt diffraction peaks clearly shows that no alloy is formed during the co-reduction process. On this basis, the ratio of non-alloyed Ru to non-alloyed Sn in the ternary Pt–Sn–Ru (86:10:4) is  $\leq 0.4$ .

Antolini et al. [61] prepared carbon supported binary Pt–Sn (1:1) and ternary Pt–Ru–Sn (1:1:0.3 and 1:1:1) alloy catalysts by reduction of the metal precursors with formic acid, and their activity for ethanol oxidation was compared with that of commercial Pt/C and Pt–Ru/C. Both the ternary catalysts were formed by a mixture of fcc Pt–Sn alloy, Sn and Ru oxides. The ratios of non-alloyed Ru to non-alloyed Sn were 0.43 and 0.86 for Pt–Sn–Ru (1:1:0.3) and Pt–Sn–Ru (1:1:1), respectively. This ratio could play an important role regarding the electrochemical activity of these catalysts. Both by LSV measurements and tests

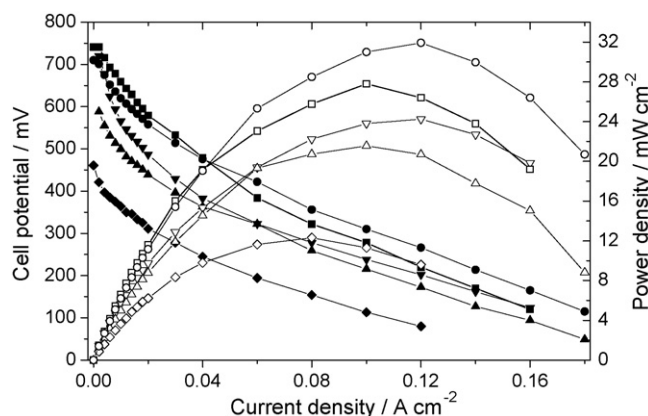


Fig. 7. Polarization curves and power density curves in single DEFC with binary Pt–Sn/C (1:1) and ternary Pt–Sn–Ru/C (1:1:0.3 and 1:1:1) catalysts prepared by the FAM and on commercial Pt/C and PtRu/C by E-TEK as anode electrocatalysts for ethanol oxidation at 110 °C and 3 atm O<sub>2</sub> pressure using a 1 M ethanol solution. Anode metal loading 1 mg cm<sup>-2</sup>. Cathode: 20 wt.% Pt/C, Pt loading 1 mg cm<sup>-2</sup> (□) Pt–Sn/C (1:1); (○) Pt–Sn–Ru/C (1:1:0.3); (△) Pt–Sn–Ru/C (1:1:1); (▽) Pt–Ru (1:1)/C E-TEK; (◇) Pt E-TEK. Full symbols: polarization curves; open symbols: power density curves. Reprinted from Ref. [61], copyright 2007, with permission from Elsevier.

in DEFC (see Fig. 7), the Pt–Sn–Ru (1:1:0.3) catalyst showed the highest activity for the ethanol electro-oxidation compared to the binary Pt–Sn and Pt–Ru and the ternary Pt–Sn–Ru (1:1:1) catalysts. The positive effect of Ru presence in ternary Pt–Sn–Ru (1:1:0.3) catalyst was ascribed mainly to the interactions between Sn and Ru oxides. Conversely, the activity of the Pt–Sn–Ru (1:1:1) catalyst was lower than that of the binary Pt–Sn and Pt–Ru catalysts in the same (1:1) composition. In the ternary catalyst with higher Ru content the interactions between Pt and SnO<sub>2</sub> were replaced with Pt–RuO<sub>2</sub> interactions, so the behaviour of this catalyst was similar to that of binary Pt–Ru.

Siné et al. [62] investigated the methanol and ethanol electro-oxidation on ternary Pt–Ru–Sn (80:10:10) nanoparticles synthesized by the microemulsion route and deposited onto boron-doped diamond electrode. The amount of Ru and Sn oxides was not reported. As in the case of methanol electro-oxidation, the ternary catalyst exhibited lower onset potential for ethanol oxidation than either pure Pt or the corresponding bimetallic Pt–Ru and Pt–Sn catalysts. The ternary Pt–Ru–Sn catalyst, however, was more efficient for methanol oxidation than for complete oxidation of ethanol, because ethanol electro-oxidation was stopped at acetaldehyde and/or acetic acid formation, the ternary catalyst being unable to activate the C–C bond scission.

Carbon supported ternary Pt–Sn–Rh (1:1:0.3 and 1:1:1) alloy catalysts were synthesized by reduction of the metal precursors with formic acid by the same research group [53] and their activity for ethanol oxidation was compared with that of binary Pt–Sn/C and Pt–Rh/C prepared with the same method. XRD analysis indicated that both the lattice parameter and the crystallite size of the Pt–Sn–Rh alloy catalysts were higher than those of Pt–Rh/C and lower than those of Pt–Sn/C. The formation of a ternary Pt–Sn–Rh alloy in both the Pt–Sn–Rh/C catalysts likely occurred. Linear sweep voltammetry measurements indicated



that, for potentials higher than 0.45 V versus RHE, the ternary Pt–Sn–Rh alloy catalysts possess the highest activity for ethanol electro-oxidation, while for potentials lower than 0.45 V versus RHE the electrochemical activity of the ternary catalysts was lower than that of the binary Pt–Sn catalyst.

### 2.3. Ethanol oxidation in alkaline media

Several studies have been carried out on the ethanol oxidation in alkaline media due to a possible use of this alcohol as fuel in alkaline fuel cells [14]. Apart from the work of Verma and Basu [14], it has to be promptly pointed out, however, that none of these studies has been performed in a fuel cell. Platinum and palladium are generally used as electrocatalysts for the EOR in alkaline environment. To improve the electrocatalytic activity of these metals, the ethanol oxidation of different bimetallic and oxide promoted Pt- and Pd-based electrocatalysts have been investigated in alkaline media. Firstly, El-Shafei et al. [63] studied the electrocatalytic effect of some metal ad-atoms (Pb, Tl, Cd) on ethanol oxidation at a Pt electrode in alkaline medium. All three metal ad-atoms, particularly Pb and Tl, improved the EOR activity of Pt.

More recently, a lot of papers have been devoted to the effect of oxide presence on the EOR activity of Pt and Pd catalysts in alkaline media. Xu and Shen [64] investigated the activities of Pt/C and Pt–CeO<sub>2</sub>/C for electrochemical oxidation of ethanol in 1.0 M KOH solution by cyclic voltammetry, chronopotentiometry and electrochemical impedance spectroscopy. The results showed that the composite of Pt–CeO<sub>2</sub>/C better performs than Pt/C. The content of CeO<sub>2</sub> in the Pt–CeO<sub>2</sub>/C catalysts affects the catalytic activity for ethanol oxidation. The electrode with the weight ratio of Pt to CeO<sub>2</sub> of 2:1 with a platinum loading of 0.30 mg cm<sup>-2</sup> showed the highest electro-catalytic activity. According to the authors, it is possible that CeO<sub>2</sub> functions as Ru does in Pt–Ru/C catalysts because oxygen-containing species could easier form on the surface of CeO<sub>2</sub>. The formation of oxygen-containing species at lower potential can transform CO-like poisoning species on Pt to CO<sub>2</sub>. The same authors [65] prepared Pd/C promoted with nanocrystalline oxides (CeO<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub>, Mn<sub>3</sub>O<sub>4</sub> and NiO) catalysts by the intermittent microwave heating (IMH). Such electrocatalysts showed a higher EOR activity and poison tolerance than Pt-based electrocatalysts. The most important result was that the onset potential for ethanol oxidation on Pd–NiO/C is shifted negatively by 300 mV compared with that of Pt/C. Regarding NiO promoted catalysts, Hu et al. [66] prepared NiO promoted Pt/C and Pd/C catalysts by IMH method and tested the ethanol oxidation in an ethanol solution with or without the presence of CO. Pd–NiO/C presented higher activity and less poisoning than that of Pt–NiO/C. Bai et al. [67] compared the electrochemical activity for ethanol oxidation of Pt/C and Pt–ZrO<sub>2</sub>/C catalysts by cyclic voltammetry, Tafel plot and electrochemical impedance in alkaline solutions. The Pt–ZrO<sub>2</sub>/C catalyst showed higher catalytic activity for the EOR than Pt. The electrode with the molar ratio of Pt to ZrO<sub>2</sub> of 1:4 showed the lowest peak potential for ethanol oxidation. Xu et al. [68] prepared MgO promoted Pt/C electrocatalysts by IMH method, and compared the electro-

oxidation of ethanol in alkaline media on Pt–MgO/C with that on Pt/C. The EOR activity of Pt–MgO/C catalysts was higher than that of Pt/C. The catalyst with a weight ratio of Pt to MgO of 4:1 presented the highest activity for ethanol oxidation. The exchange current density for the EOR was  $1.8 \times 10^{-5}$  A cm<sup>-2</sup> on Pt–MgO/Pt and  $3.3 \times 10^{-7}$  A cm<sup>-2</sup> on Pt/C. Hu et al. [69] prepared Pd electrocatalysts supported on carbonised TiO<sub>2</sub> nanotube (Pd/TiO<sub>2</sub>C) and compared their EOR activity in alkaline media with that of Pd/C. They found that the Pd/TiO<sub>2</sub>C catalysts with the Pd:TiO<sub>2</sub>C mass ratio = 1:1 gives the best performance. The results indicated that the Pd/TiO<sub>2</sub>C catalyst has higher EOR activity and higher stability during the constant current density polarization in alkaline media than the Pd/C catalyst. Finally, Xu et al. [70] investigated Pd-based catalyst as replacement for Pt-based catalysts for the ethanol oxidation in alkaline media. They observed a higher activity for ethanol oxidation on Pd/C catalyst than that on the Pt/C catalyst. Tests carried out on CeO<sub>2</sub> and NiO promoted noble metals (Pt, Pd) indicated that the catalysts with a weight ratio of noble metal to CeO<sub>2</sub> of 2:1 and a noble metal to NiO ratio of 6:1 has the highest EOR activity. The oxide promoted Pt/C and Pd/C catalysts presented a higher activity than the Pt–Ru/C by E-TEK.

Some studies have been focused to the influence of the support on the EOR activity in alkaline media of Pt and Pd catalysts. Zheng et al. [71] investigated the effect of various carbon supports (multiwall carbon nanotube, carbon black and activate carbon) on the EOR activity of Pd electrocatalysts. Pd supported on multiwall carbon nanotube showed the best performance for ethanol oxidation in alkaline media. Xu et al. [72] used Pt and Pd catalysts supported on carbon microspheres (CMS) for ethanol oxidation in alkaline media. They found that noble metals catalysts supported on CMS give better performance than those supported on carbon black.

Bagchi and Bhattacharya [73] investigated the effect of the composition of nickel supported Pt–Ru catalysts on the ethanol oxidation in alkaline media. They found that the best catalytic activity is presented by the Pt–Ru catalysts with Ru content in the range 32–47 at.%. Moreover, for high current densities, the optimum composition is shifted to higher Ru, while a lower Ru content is favoured for low current densities.

A new group of Ru–Ni and Ru–Ni–Co catalysts for ethanol oxidation in alkaline media was investigated by Kim and Park [74] and Tarasevich et al. [75]. Kim and Park [74] evaluated electrodeposited nickel oxide electrodes with additives such as cobalt, ruthenium and their combination as the anode materials for the electro-oxidation of ethanol in alkaline media using *in situ* X-ray absorption near edge structure (XANES). The Ni–Co–Ru electrode showed the best performance with increased anodic peak currents and lower overvoltages for electrochemical oxidation of ethanol. XANES data for the Ni and Co K-edges of these composite electrodes indicated that both Ni and Co are in the Ni<sup>3+</sup>–Ni<sup>4+</sup> and Co<sup>3+</sup>–Co<sup>4+</sup> mixed states, respectively, depending on applied potentials. The presence of cobalt and/or ruthenium in nickel oxide films enhanced the electrode performances for ethanol oxidation due to generation of highly oxidized states of cobalt and ruthenium via electrogenerated nickel oxides. Tarasevich et al. [75] investigated the ethanol oxi-

dation on carbon supported Ru–Ni catalysts in alkaline media. The catalysts consisted of dispersed metallic ruthenium decorated by nickel oxides. The optimum Ru:Ni composition was in the ratio of 70:30. The difference in ethanol oxidation kinetics indicated the change of Ru properties in Ru–Ni as compared to pure ruthenium.

### 3. Cathode catalysts

The requirements of a material for the use as DEFC cathode are a high activity for the oxygen reduction reaction and a high ethanol tolerance. Some alloys of the first-row transition metals present a higher activity for ORR than platinum in low temperature fuel cell operated on hydrogen [76–79]. The enhancement in the ORR activity observed when using supported Pt–M alloy electrocatalysts was ascribed to both geometric (decrease of the Pt–Pt bond distance) [80] and electronic factors (increase of Pt d-electron vacancy) [77].

Ethanol adsorption and oxygen adsorption are competing with each other for the surface sites. As in the case of methanol, the dissociative chemisorption of ethanol requires the existence of several adjacent Pt ensembles [81,82] and the presence of atoms of the second metal around Pt active sites could block ethanol adsorption on Pt sites due to the dilution effect. Consequently, methanol oxidation on the binary-component electrocatalyst is more difficult. On the other hand, oxygen adsorption, which usually can be regarded as dissociative chemisorption, requires only two adjacent sites and is not affected by the presence of the second metal. Among various catalysts, Pt–Ni and Pt–Co alloys, in addition to a high ORR activity, also presented a good methanol tolerance [83–86]. On this basis, Lopes et al. [87] investigated the EOR activity and the behaviour as cathode material in a single DEFC of a commer-

cial carbon supported Pt–Co (3:1) electrocatalyst. Linear sweep voltammetry measurements indicated that in the cathode region of the potential (0.7–0.9 V versus RHE) Pt/C and Pt–Co/C have the same activity for the ethanol oxidation. As shown in Fig. 8, the performances of Pt–Co/C as cathode material in DEFC operating in the temperature range 60–100 °C were better than those with Pt/C.

By measurements of oxygen reduction in H<sub>2</sub>SO<sub>4</sub> in the presence and in the absence of ethanol, promising results were obtained using a Pt–Pd (9:1) catalyst [88]. The Pt–Pd/C catalyst possess about the same ORR activity, but a higher ethanol tolerance than Pt. The enhanced performance of a single DEFC operating at 90 °C using this catalyst as cathode material confirmed the results observed in out-of-cell measurements.

### 4. Conclusions

Conversely to the methanol oxidation, the best binary catalyst for ethanol oxidation in acid environment is not Pt–Ru but Pt–Sn. The optimum Sn content in the catalyst is not well determined, and depends on the ratio of alloyed and non-alloyed tin and on cell temperature. Controversial results regarding the effect of the degree of alloying of Sn in the Pt fcc structure on the EOR activity have been reported [41–43], depending both on the intrinsic characteristics of the material (surface composition, particle size and particle size distribution of the alloy and the oxide, alloy/oxide interactions) and on the external conditions (current density, temperature, type of measurement). The addition of Sn to Pt catalysts, however, notwithstanding the enhancement of the activity for ethanol oxidation, inhibits the C–C bond cleavage reactions. The addition of Rh to Pt seems to promote the C–C bond cleavage [10,52], but the overall EOR activity of these catalysts is lower than that of Pt–Sn [53].

All ternary Pt–Ru-based catalysts tested for the ethanol oxidation reaction always better performed than Pt–Ru, but counteracting results regarding their EOR activity with respect to that of Pt–Sn have been reported [26,50,51]. Conversely, ternary Pt–Sn-based catalysts seem to better perform than Pt–Sn [39,46,61], so, in the light of these results, upcoming research on materials for ethanol oxidation should be focused on Pt–Sn-based instead of Pt–Ru-based ternary catalysts. Ternary Pt–Sn–Ru catalysts with nominal Ru/Sn atomic ratio <1 seems to be the most promising anode materials for the use in direct ethanol fuel cells. DEFCs with these catalysts as anode materials better performed than those with binary Pt–Ru and Pt–Sn. A suitable non-alloyed Ru to non-alloyed Sn ratio seems to be *ca.* 0.4 [46,61]. RuO<sub>2</sub>–SnO<sub>2</sub> interaction promotes the formation of hydroxyl species by dissociating water at a lower potential with respect to the Pt–Ru systems. Moreover, this interaction could also weaken the bonding between the hydroxyl species and the catalyst surface as compared with the bonding on Pt–Ru nanoparticles. The more weakly adsorbed hydroxyl species further promotes electro-oxidation of adsorbed CO and/or acetaldehyde species on the active metal sites at a lower potential, thus improving the performance. On the other hand, for higher Ru contents, as in the case of Pt–Sn–Ru (1:1:1) (the RuO<sub>2</sub>/SnO<sub>2</sub> ratio in Pt–Sn–Ru (1:1:1) is twice than that in

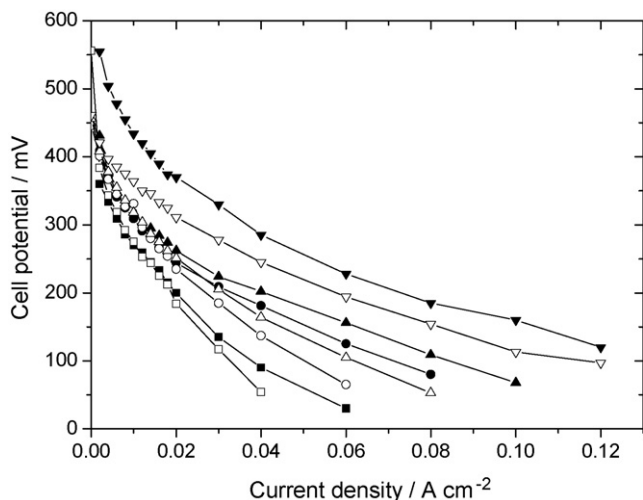


Fig. 8. Polarization curves in single DEFC with Pt–Sn/C (3:1) and Pt/C electrocatalyst by E-TEK as cathode materials for oxygen reduction at 60, 80, 90 and 100 °C and 3 atm O<sub>2</sub> pressure using a 1 M ethanol solution. Cathode Pt loading 1 mg cm<sup>-2</sup>. Anode: 20 wt.% Pt/C, Pt loading 1 mg cm<sup>-2</sup>. (□) 60 °C; (○) 80 °C; (△) 90 °C; (▽) 100 °C. Open symbols: Pt/C; full symbols: Pt–Co/C. Currents are expressed in terms of mass activity (numerically equal to the current normalized with respect to the geometric surface area). Reprinted from Ref. [87], copyright 2007, with permission from Elsevier.

Pt–Sn–Ru (1:1:0.3)), RuO<sub>2</sub> substitutes SnO<sub>2</sub> in the interaction with Pt. Moreover, the presence of RuO<sub>2</sub> on the particle surface of Pt–Sn–Ru catalyst decreases the active surface area of Pt particles. As a consequence, part of the noble metal becomes inactive due to the blocking of the Pt surface by the Ru oxide. Obviously, the active surface area loss by the presence of Ru oxides increases with increasing Ru content in the catalyst: these effects could explain the inferior performance of the Pt–Sn–Ru/C catalyst in the atomic ratio (1:1:1) than that of Pt–Sn/C (1:1) [51,61]. On this basis, another important parameter affecting the EOR activity of these catalysts is the ratio of the Pt content and the oxide content (SnO<sub>2</sub> + RuO<sub>2</sub>). It has to be pointed out, however, that the addition of Ru to Pt–Sn enhances the electrical performance of the DEFC, i.e. the EOR activity of the catalyst, but do not modify the product distribution, the ternary Pt–Sn–Ru catalyst being unable to activate the C–C bond cleavage [46,62]. So, basically the C–C bond scission remains the main problem in the ethanol oxidation reaction. At this point in time, to attain the performance of DMFCs, the DEFC catalyst development targets require a two- to threefold enhancement of activity for ethanol oxidation and have not been achieved, but Pt–Sn–M catalysts appear to be a feasible pathway towards meeting them. The C–C bond cleavage is the primary condition to achieve this result, then particular efforts should be addressed in the formulation of ternary Pt–Sn–M catalysts, the third metal being able to promote the C–C bond scission. The same experimental and theoretical combinatorial and/or high-throughput screening methods applied to the development of new anode fuel cell alloy catalysts with improved CO tolerance [89] or enhanced activity for methanol oxidation [90] could be used to the achievement of suitable ternary catalysts for the use in direct ethanol fuel cells. Apart of the control of particle size and particle size distribution, of fundamental importance is the optimization of the nominal composition, the surface composition, the degree of alloying and the oxide content of these promising materials. Considering that the chemical and physical characteristics of these catalysts depend on the synthesis method, the way of preparation becomes a key factor regarding their electrochemical activity.

In alkaline media Pd-based electrocatalysts seems to be superior to Pt-based catalysts in terms of activity for ethanol oxidation and poison tolerance. The oxide promoted Pt and Pd catalysts showed a higher EOR activity than pure metal catalysts.

On the other hand, Pt–Pd (9:1) showed higher ethanol tolerance than Pt when used as cathode material in DEFCs.

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