

Direct Alcohol Fuel Cells: Challenges and Future Trends

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I. INTRODUCTION

Among the most considered future alternative energy conversion systems are fuel cells. A fuel cell is an electrochemical device that continuously and directly converts chemical energy to electricity with the most common technologies to be the Polymer Electrolyte Membrane Fuel Cells (PEMFC) and the Solid Oxide Fuel Cells (SOFC). In such devices hydrogen is considered as the preferred fuel in virtue of its high activity and its environmental benignity. Fuel supply is an important problem to be solved for the commercial application of fuel cells' technology. Conventional fuel-cell types require hydrogen as the fuel, which has to be free of impurities when operated at temperatures below 100°C. The storage and distribution of hydrogen is still one of the open questions in the context of a customer-oriented broad commercial market. The last two decades research effort has been devoted to Direct Alcohol Fuel Cells dedicated to overcome the hydrogen specific restrictions. In this direction direct alcohol fuel cells have been extensively studied and considered as possible power production systems for portable electronic devices and vehicles in the near future. However, because of the relatively low performances and the high cost of platinum-based catalysts, a number of research groups have oriented their efforts mainly towards the development: a) of low or non platinum electrocatalysts (anodes and cathodes) and b) of nanostructured electrocatalysts based on non-noble metals. The challenges and the prospects related to the low and non platinum anodes for direct alcohol (methanol and ethanol) PEM fuel cells are presented and discussed in the present work.

Keywords: *low and non platinum electrocatalysts, direct alcohol fuel cells, ethanol and methanol electrooxidation*

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It is generally accepted that between the most important problems that affect earth's future are: a) the progressive environmental degradation, b) the observed reduction of the mineral fuels reserves and c) the population growth and consequently the constant increase of energy demand. Due to the current situation there is an obvious need for better utilization of the existent energy reserves and a constant process of searching new *alternative sources of energy* and *more efficient energy conversion systems*. Concerning the later one, between the most considered future alternative energy conversion systems are Fuel Cells.

Fuel Cells are electrochemical devices (Galvanic cells), which convert directly the chemical energy of a fuel into electricity bypassing the intermediate and exergy intensive process of conversion of energy into heat and the transformation of it to mechanical, as it usual takes place in the conventional power production systems. The performance of fuel cells comparable with the one of the conventional power production systems (e.g. internal combustion engines) can be twofold enhanced. Indicative, it is referred that a fuel cell can yield up to 45%, while it is general known that the yield of an internal combustion system varies to ~25%. However, the combination of fuel cells with the conventional power generation systems can reach yields around 70%, as it is stated in the literature.

Of the several fuel cell types available, five have proved to be viable: i) Alkaline Fuel Cells (AFCs), ii) Proton Exchange Membrane Fuel Cells (PEMFCs), iii) Phosphoric Acid Fuel Cells (PAFCs), iv) Molten Carbonate Fuel Cells (MCFCs) and Solid Oxide Fuel Cells (SOFCs). From the aforementioned *Proton exchange membrane fuel cell* (PEMFCs) systems are the type that have been developed for transport applications as well as for stationary and portable fuel cell applications, due to their environmental benign, low temperature operation and quick start-up. In these operation systems, hydrogen is considered as the preferred fuel in virtue of its high activity and its environmental benignity. Along with the PEMFCs development, low molecular alcohols, especially methanol and ethanol, are also directly fed into the anode as the fuel because of the easy handle of liquid fuels and their high power density, 16 MJ/L and 23 MJ/L, respectively, contrary to the 9 MJ/L of the liquid hydrogen's [1].

Nonetheless, two major technical gaps hindering commercialization of Direct Alcohol Fuel Cells (DAFCs) have been identified: high cost and reliability/durability (5,000 hr lifetime). A great percentage (~50%) results from the fact that the most active catalyst, hitherto, is platinum and alloys of it for anode and cathode electrochemical reactions which is a high cost and scarce metal. Today the cost of a prototype PEMFC stack may exceed 1300-1500 €/kW. Consequently, in order PEMFC to compete with combustion engines and especially for being penetrated into the automotive area the cost of it should be lower than 36 €/kW. Based on this, for PEMFCs to have wide practical applications and become commercially viable, the challenging issue of the high catalyst cost resulting from the exclusive adoption of Pt or Pt-based catalysts must be addressed. Concerning the low-Pt catalysts aspect, the target of the community is to reduce the Pt loading to *ca.* 0.15 mgcm⁻² while maintaining high power densities [2].

Towards this direction low, non platinum materials have been developed, while nanotechnology is an interesting emerging field through which has great potential for materials anodes and cathodes and could be the key for accelerating the commercialization for fuel cell applications. In the following parts the challenges and the prospects related to the low and non platinum anodes for DMFCs & DEFCs will be discussed.

II. ANODE DIRECT METHANOL FUEL CELLS' CATALYSTS

Direct methanol fuel cells in the last few years are penetrating the marketplace and constitute the replacements of batteries in consumer electronics like cellular phones and laptop computers. However, the still sluggish methanol oxidation kinetics even over the present well recognized PtRu catalysts is one of the main challenges for DMFCs commercialization in other fields such as in automotive field and in wide applications. Much worse, from the point of view of practical consideration, a quite high catalyst loading of 200-800 μgcm⁻² is necessary for the desirable DMFCs performance even with the optimal PtRu alloy catalysts [3]. Thereafter, in the novel methanol oxidation reaction (MOR) anode catalysts, not only performance (activity, reliability and durability) but also cost should be taken into account. One effective strategy consequently for anode catalysts with accepted performance and low cost is to dramatically decrease the Pt content in catalysts while still maintaining the accepted performance.

A. Low Platinum

Currently, Ando *et al.* [4] adopted a new synthetic method that involved the oxidation of carbon support, adsorption of Pb²⁺, its reduction and then galvanic displacement of Pb⁰ by Pt and Ru, to develop very thin Pt-Ru nanoplatelets on carbon nanoparticles. This catalyst exhibits 10 times Pt mass activity towards MOR higher than the commercial PtRu/C. They attributed to this significant activity improvement to the effect of underlying layer which strongly affects the activity of the catalyst's top layer. Another attractive future trend that increases the Pt utilization and simultaneously lowering its

loading is the core-shell structured catalysts. The metal is distributed only on the surface of a core composed of a transition metal other than Pt. The PtPd@Pt/C catalyst [5] with a low Pt content of about 8 wt%, (8.2 μgPt cm⁻²), exhibited three times higher activity towards MOR than the commercial Tanaka 50 wt% Pt/C, (20 μgPtcm⁻²), and the PtRu/C (14 μgPtcm⁻²).

Characteristic as it can be seen from Fig.1 is the novel catalyst that developed currently from Adzic's group. This comparable with the other bi-metallic platinum systems exhibits 8-fold higher performance towards methanol oxidation while the loading of the platinum reached only 0.6μg.

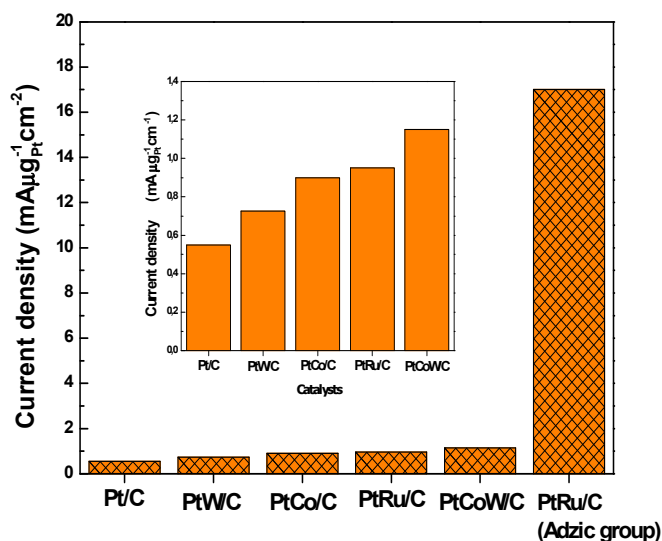


Fig.1. Mass specific activity for low platinum based bi-metallic catalysts for the methanol oxidation reaction *ca.* 0.7V [4, 6]. Index: Current density for the first five catalysts.

The use of nanotechnology in catalysts' support is very significant as it contributes to achieve a high Pt utilization, increasing the specific surface area by highly dispersing it on a high surface area support. Thus, an electrode with high population of the triple-phase boundary, as the carbon-nanotubes, is important for the development of high Pt utilization catalysts.

In recent years, many researchers suggested that *carbon nanotubes* (CNTs) are suitable for electrode materials and catalyst supports in DMFCs due to their high accessible surface areas, low resistance and high stability properties. It was found that [6] higher Pt utilization catalysts could be obtained with the single walled CNTs (SWNTs) as support because it could be made full use of their high surface area, conductivity, and porosity. Specifically, it was observed that Pt/SWCNTs had a significantly enhanced electrocatalytic activity for MOR over the Pt/SWCNTs composite [7]. In Fig.2 the enhancement and the improved resistance to CO poisoning

than the Pt/SWCNTs catalyst is mainly the result of the unique structures of SWCNTs, and the uniform dispersion of Pt nanoparticles on the SWCNTs surfaces [8]. A number of earlier investigations have demonstrated that Pt-based electrocatalysts supported by properly pre-treated MWCNTs would show enhanced electrocatalytic activity for the oxidation of CO [9] and methanol at the anode.

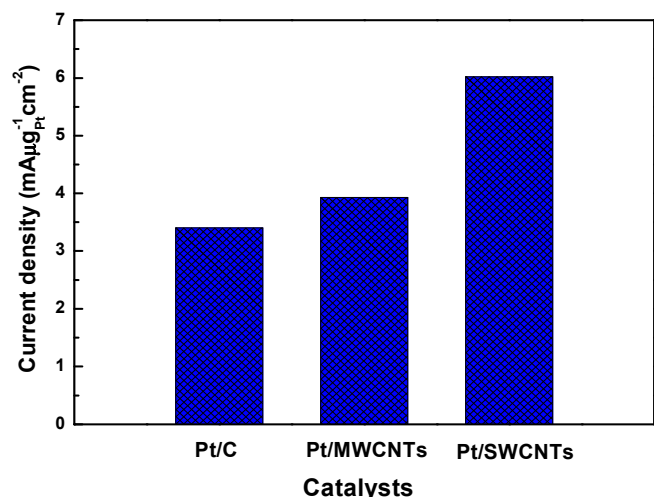


Fig.2. Mass specific activity for low Pt catalysts supported on different carbon nanotubes measured for methanol oxidation ca.0.7V [10].

B. Non platinum

Recently, several works have dealt with tungsten and molybdenum materials as non-precious metal and non Pt anode electrocatalysts for DMFCs. However, these works are few. The investigations over the stability of WC and W₂C [11] revealed that WC is stable at anode in an acid electrochemical environment at 0.6 V, demonstrating the potential application of WC in the electrochemical system. Moreover, novel Co-W alloys for MOR in alkaline and acidic media, exhibited low overpotential even on prolonged electrolysis, and they had good corrosion resistance in acidic and alkaline media [12].

In the recent works, it is observed that the non-Pt catalysts for MOR are investigated mostly in alkaline media. According to the literature, Pd-alloys are the most promising catalysts in alkaline media. Liu *et al.* [13] investigated Pd and PdNi nanoparticles supported on Vulcan XC-72 carbon. The PdNi/C catalyst had higher electrocatalytic activity for MOR in alkaline media than a comparative Pd/C catalyst. Additionally the explored Pd-MnO₂/MWCNTs electrocatalysts [14] exhibited higher electrocatalytic activity and stability than Pd/MWCNTs and Pd/Vulcan XC-72C. While Li *et al.* [15] synthesized CNTs-supported Pd-Ag (1:1) catalyst, which exhibited even better catalytic activity, benefiting from bigger electrochemical surface area and better intrinsic catalytic activity than the carbon black supported bimetallic palladium silver (Pd-Ag/C) catalyst. Hollow Pd nanospheres (HPNs)-

decorated CNT was developed for MOR in alkaline media by Liu *et al.* [16].

In Fig.3, the peak current densities of Pd-based catalysts for the MOR in alkaline media are depicted. As it can be observed the materials, much cheaper than platinum, present great interest since they gave comparable values of peak current density with the platinum based ones due to their faculty to lower the electronic binding energy in Pt [12, 15-19].

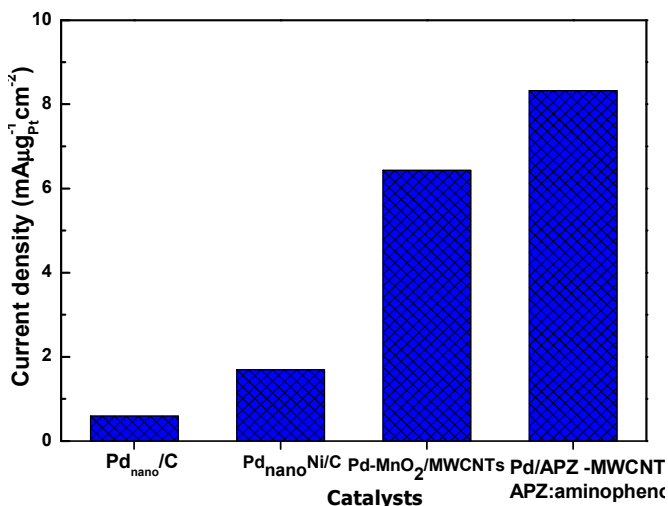


Fig.3. Mass specific activity for non platinum catalysts for methanol oxidation in alkaline media, ca.-0.2V [13, 14].

III. ANODE DIRECT ETHANOL FUEL CELLS' CATALYSTS

Ethanol is a hydrogen-rich liquid and it has a higher energy density (8.0 kWh/kg) compared to methanol (6.1 kWh/kg). The use of ethanol would also overcome both the storage and infrastructure challenge of hydrogen for fuel cell applications. In a fuel cell, the oxidation of any fuel requires the use of a catalyst in order to achieve the current densities required for commercially viable fuel cells, and platinum-based catalysts are some of the most efficient materials for the oxidation of ethanol too. In PEMFCs, based on the state-of-the-art of ethanol electrooxidation anode catalysts, the main products from *ethanol electrooxidation reaction* (EOR) are mainly acetaldehyde and acetic acid [18], with small quantity of CO₂ [19]. This consequently decreases the fuel utilization coefficient and Faraday's efficiency. Identifying electrocatalysts for oxidizing ethanol to CO₂ that can break the C-C bonds in ethanol molecules has become a practical challenge for DEFCs development.

A. Low Platinum

The nature and structure of the electrode material, directly affect the adsorption mode and kinetics of the reaction, and control the formation of adsorbed intermediates, determining the oxidation end products. In comparison with DMFCs in the DEFCs is presented an additional problem: the C-C bond cleavage for the complete oxidation of ethanol to carbon

dioxide. This fact decreases the electrical efficiency of the process.

Indicative recently, Adzic's group [20] reported a ternary PtRhSnO₂ electrocatalyst consisted only of 30 nmol (5.85 μg_{Pt}) of Pt and 8 nmol (0.82 μg_{Rh}) of Rh. Despite the fact that Rh was in a small amount it was very important for considerably increasing the catalytic activity of PtSnO₂. PtRhSnO₂ can effectively break the C-C bonds in ethanol molecules at room temperature in acid solutions by taking advantage of the specific properties each constituent caused by their synergy. Although the additive can improve Pt's activity, the composite catalyst is still the Pt-rich materials, which is still of high cost not mention that the price of Rh surpasses that of Pt's. Sun and Behm *et al.* [21] also examined PtSnO_x/C and compared them with PtRu and Pt/C catalysts. The characteristic of this works is the very low platinum loading of 28 μgcm⁻².

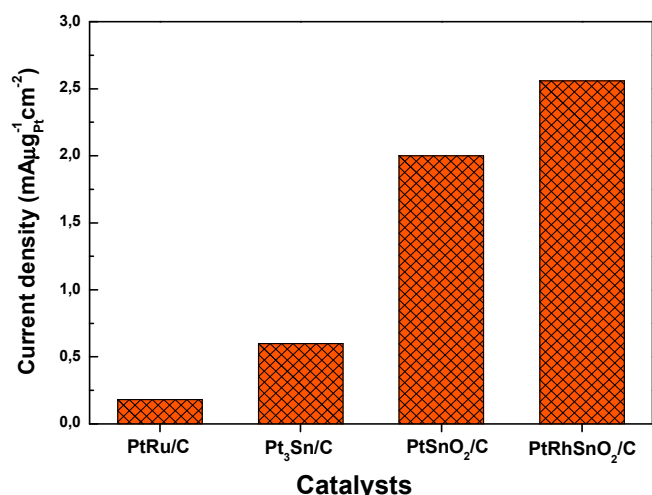


Fig.4. Mass specific activity for low platinum based catalysts for the ethanol oxidation reaction , ca.0.7V [19].

Previous studies have shown that the addition of Ru, Sn and Rh compared to until now studied catalysts improve the kinetics of CO oxidation in comparison to platinum, as it is depicted in Fig.4. These catalysts are able to provide OH species (intermediates) reducing at the same time the poisoning of the catalyst of the carbon monoxide. Moreover as it can be deduced from Fig.4 the tin oxide can promote more the ethanol electro-oxidation through synergetic interaction with Pt. Consequently, Adzic's group combining the advantages of the tin oxides, platinum and rhodium managed, with a really small amount of platinum and rhodium, to have an extremely advantageous performance in comparison with until now proposed catalysts. However, taking into consideration that the average annual cost of platinum for the last year reached ~40 €/g and the rhodium ~60 €/g it is indicated that there is still much room to further improve DEFCs performance.

In order to obtain higher efficiency and stability of the behaviour of the DEFCs' catalysts the research groups drew attention to well distribute the catalyst on the support in order to improve the catalysts' utilization coefficient and consequently to reduce the fuel cell cost. Nanomaterials have attracted great interest towards this direction, in recent years because of their unusual catalytic, mechanical, electrical and optical properties. Recently different kinds of carbon materials, such as mesoporous carbons, hollow graphitic nanoparticles, carbon nanotubes, carbon nanocoils, and graphitic carbon nanofibers were reported [22, 23]. One subcategory is the carbon nanotubes (multi-walled carbon nanotubes & single walled carbon nanotubes) which are new nanomaterials with unique structure and properties. These kinds of materials as it can be seen from Fig.5 can exhibit superior performance in comparison with the pure carbon support. Another kind of support that is applicable due to its stability, permeability, simplicity and especially to its low cost, easy production and porosity is the ceramic carbon. As it can be deduced from Fig.5 it shows superior performance towards the other supports.

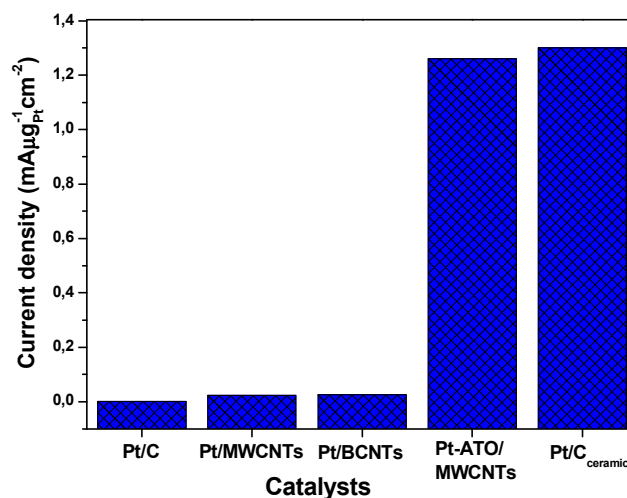


Fig.5. Mass specific activity for low platinum based catalysts on different supports for the ethanol oxidation reaction , ca.0.6V [24-26].

B. Non platinum

In the search for alternative low-cost non-Pt catalysts, researchers have looked at several others, including supported platinum group metal (PGM) types such as Pd-, Ru-, and Ir-based catalysts, bimetallic alloy catalysts, transition metal macrocycles, and transition metal chalcogenides. However, these approaches are as yet in the research stage and are very few for DEFCs, as the catalyst activities and stabilities are still too low to be practical in comparison with Pt-based catalysts. Sun's Group [27] developed Ir-based catalysts with a higher activity towards EOR than Pt-based catalysts in the activation control region. The Ir₃Sn/C shows a comparable single DEFC performance to Pt₃Sn/C, which makes it a potential interesting DEFCs non-Pt anode material. On the other hand, the world

reserve of Ir is much lower than that of Pt, leading to the same problem as Pt with shortage and high cost.

According to the literature non platinum catalysts for ethanol electrooxidation has attained little attention due to the fact that most of them are unstable in acid media. Thus a new trend that is appeared is the study of electrooxidation on non platinum catalysts in alkaline media. It has recently been reported that catalysts based on Ni, Co, and Fe have activity comparable to that of Pt for ethanol oxidation in alkaline media, but with a much higher selectivity for CO₂ formation [20]. Among the non platinum metals palladium has raised the interest as a non platinum catalyst for intensive researches. This can present current densities sometimes equal to platinum. This constitutes a pro, if it is taken into account that the abundance of Pd on the earth is at least fifty times more than that of Pt. Xu et al. reported that Pd is a good electrocatalyst for ethanol oxidation and showed higher activity than that of Pt in alkaline media [28-30]

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