

Direct Chloro Ethanol Fuel Cells: Challenges and Future Trends

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Abstract

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 Cell (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 type requires hydrogen as the fuel, which has to be free of impurities when operated at temperatures below 100⁰c. 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 efforts have been devoted to Direct alcohol fuel cells dedicated to overcome the hydrogen specific restriction. In this direction direct chloro ethanol 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) non platinum electro catalysts (anode and cathode) and b) of nanostructure electro catalysts based on non-noble metals.

The challenge and the prospects related to the non platinum anodes for direct chloro ethanol fuel cell PEM fuel cells are presented and discussed in the presented work.

Keywords: Non platinum electro catalyst, electro oxidation, nanostructure, chloro ethanol electro oxidation.

Introduction

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 reserve 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 by passing the intermediate and energy intensive process of conversion of energy into heat and the transformation of it to mechanical, as it usually take 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 be yield up to 45%, while it is general known that the yield of an internal combustion system varies~25%. However the combination of fuel cells with the conventional power generation system 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: 1) 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) system are the type that have been developed for transport application as well as for stationary and portable fuel cell application, due to their environmental benignity, 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 it environmental benignity. Along with the PEMFCs development, low molecular alcohols, especially methanol and chloro 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 23MJ/L, respectively, contrary to the 9 MJ/L of the liquid hydrogen [1].

Nonetheless, two major technical gaps hindering commercialization of direct Chloro ethanol fuel cells (DCLEFs) have been identified: high cost and reliability/durability (5,000 hr lifetimes). A great percentage (~50%) results from the fact that the most active catalyst, hitherto, is platinum and alloy of it for anode and cathode electrochemical reaction 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 mg cm^{-2} while maintaining high power densities [2].

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

Anode Direct Chloro Ethanol Fuel Cell

Chloro ethanol is a hydrogen-rich liquid and it has a higher energy density (8.0 KWh/kg) compared to methanol (6.1KWh/kg). The use of chloro ethanol would also overcome both the storage and infrastructure challenge of hydrogen for fuel cell application, 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 most efficient materials for the oxidation chloro ethanol too. In PEMFCs, based on the state-of-the-art of chloro ethanol electro oxidation anode catalysts, the main products from chloro ethanol electro oxidation reaction (EOR) are mainly chloro acetaldehyde and chloro acetic acid [3], with small quantity of CO_2 [4]. This consequently decreases the fuel utilization coefficient and faraday's efficiency. Identifying electro catalysts for oxidizing chloro ethanol to CO_2 that can break the C-C bonds in chloro ethanol molecules has been become a practical challenge for DEFCs development.

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 is presented an additional problem: the C-C bond cleavage for the complete oxidation of chloro ethanol to carbon dioxide. This fact decreases the electrical efficiency of the process.

Indicative recently, Adzic's group [5] reported a ternary PtRhSnO_2 electro catalyst consisted of 30 nmol ($5.85 \mu\text{g}_{\text{pt}}$) of Pt and 8 nmol ($0.82 \mu\text{g}_{\text{rh}}$) of Rh. Despite the fact that Rh was in a small amount it was very important for considerably increasing the catalytic activity of PtSnO_2 , PtRhSnO_2 can effectively break the C-C bonds in chloro ethanol molecule at room temperature in acid solutions by taking advantage of the specific properties each constitute 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.* [6] 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 $28 \mu\text{g cm}^{-2}$.

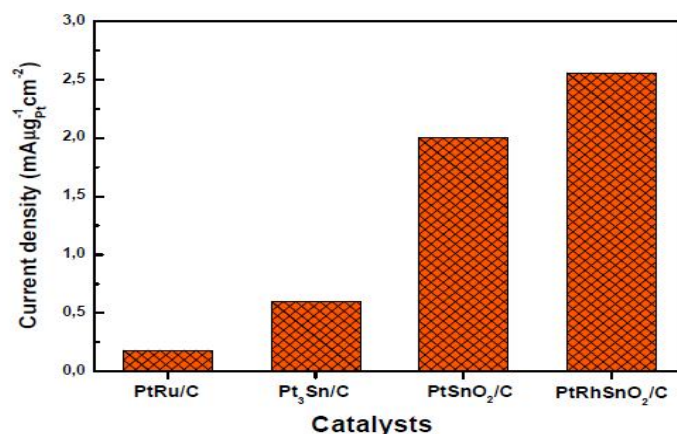


Figure 1: Mass specific activity for low platinum based catalysts for the chloro ethanol oxidation reaction, ca 0.7V [4].

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 Figure 1. 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 Figure 1 the tin oxide can promote more the chloro ethanol electro-oxidation through synergetic interaction with Pt. Consequently, Adzic's group combining the advantage of the tin oxides can promote more the chloro ethanol electro oxidation through synergetic interaction with Pt. Consequently, Adzic's group combining the advantage of the tin oxide, 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 DEFC's performance.

In order to obtain higher efficiency and stability of the behavior of the DEFC's catalyst, attempt has been made to draw 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. Nano materials 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 carbon, hollow graphite nanoparticles, carbon nanotubes, carbon nanocoils and graphitic carbon nanofibers were reported [7, 8]. One subcategory is the carbon nanotubes (multi-walled carbon nanotubes & single walled carbon nanotubes) which are new Nano material with unique structure and properties. This kind of materials as it can be seen from Figure 2 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 Figure 2. it shows superior performance towards the other supports.

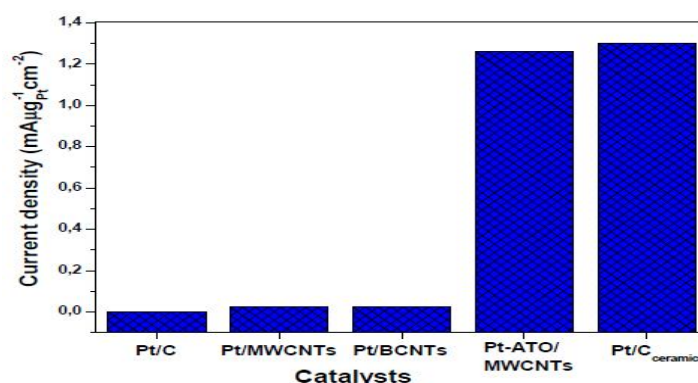


Figure 2: Mass specific activity for low platinum based catalysts on different supports for the chloro ethanol oxidation reaction, ca 0.6V [9-11].

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 macro cycles, and transition metal chalcogenides. However, these approaches are as yet in the research stage and are very few for DEFC's, as the catalyst activities and stabilities are still too low to be practical in comparison with Pt-based catalysts. Sun group [12] developed Ir-based catalysts with a higher activity towards EOR than Pt-based catalysts in the activation control region. The Ir₃Sn/C shown 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 chloro ethanol electro oxidation has attracted 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 electro oxidation on non platinum catalysts in alkaline media. It has recently been reported that catalyst based on Ni, Co, and Fe have activity comparable to that of Pt for chloro ethanol oxidation in alkaline media, but with a much higher selectivity for CO₂ formation [5]. Among the non platinum metals palladium have raised the interest as a non platinum catalyst for intensive researches. This can present current densities sometimes equal to platinum this constitute a problem, 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 electro catalyst for chloro ethanol oxidation and showed higher activity than that of Pt in alkaline media [13-15].

Anode Direct Methanol Fuel Cells' Catalysts

Direct methanol fuel cells in the last few years are penetrating the marketplace and constitute the replacement 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 $200\text{--}800\mu\text{gcm}^{-2}$ is necessary for the desirable DMFCs performance even with the optimal PtRu alloy catalyst [16]. Thereafter, in the novel methanol oxidation reaction (MOR) anode catalysts, not only performance (activity, reliability and durability) but also cost should be taken 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.

Low platinum

Currently, Ando *et al.* [17] adopted a new synthetic method that involved the oxidation of carbon support, adsorption of Pb^{2+} , its reduction and then galvanic displacement of Pb^0 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 [18] with a low Pt content of about 8 wt% ($8.2\mu\text{g}_{\text{Pt}}\text{cm}^{-2}$), exhibited three times higher activity towards MOR than the commercial Tanaka 50 wt% Pt/C, ($20\mu\text{g}_{\text{Pt}}\text{cm}^{-2}$) and the PtRu/C ($14\mu\text{g}_{\text{Pt}}\text{cm}^{-2}$).

Characteristic as it can be seen from Figure 3 is the novel catalyst that developed currently from Adzic's group. This comparable with the other bi-metallic platinum systems exhibit 8-fold higher performance towards methanol oxidation while the loading of the platinum reached only $0.6\mu\text{g}$.

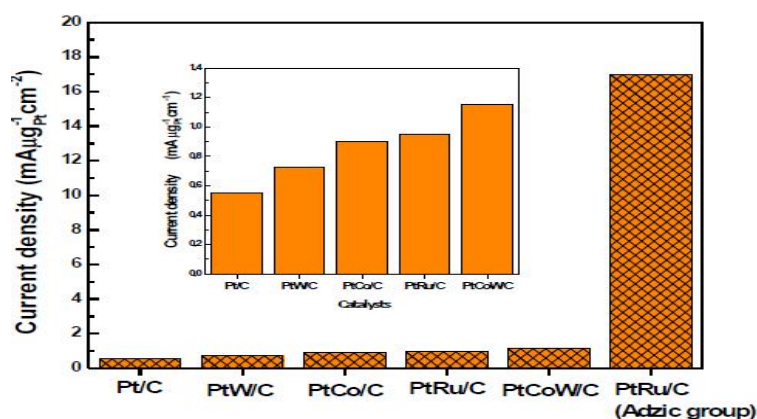


Figure 3. Mass specific activity for low platinum based bi-metallic catalysts for the methanol oxidation reaction ca.0.7v [17,19] index: current density for the first five catalysts.

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.

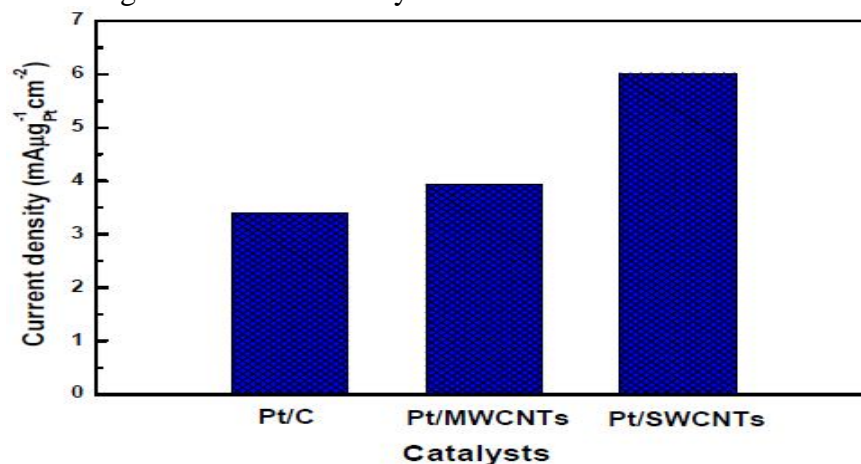


Figure 4: Mass specific activity for low Pt catalysts supported on different carbon nanotubes measured for methanol oxidation ca. 0.7V [23].

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 [19] higher Pt utilization catalysts could be obtained with a 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 electro catalytic activity for MOR over the Pt/SWCNTs composite [20]. In Figure 3 the enhancement and the improved resistance to CO poisoning than the Pt/SWCNTs catalyst is mainly the result of the unique structure of SWCNTs, and the uniform dispersion of Pt nano particles on the SWCNTs surface [21]. A number of earlier investigations have demonstrated that Pt-based electro catalysts supported by properly pre-treated MWCNTs would show enhanced electro catalytic activity for the oxidation of CO [22] and methanol at the anode.

Non platinum

Recently, several works have dealt with tungsten and molybdenum material as non-precious metal and non Pt anode electro catalysts for DMFCs. However, these works are few. The investigations over the stability of WC and W₂C [24] revealed that WC is stable at anode in an acid electrochemical environment at 0.6V, demonstrating the potential application of WC in the electrochemical system. Moreover, novel Co-W alloys for MOR in alkaline and acidic media, exhibited low over potential even on prolonged electrolysis, and they had good corrosion resistance in acidic and alkaline media [25].

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.* [26] investigated Pd and PdNi nanoparticles supported on Vulcan XC-72 carbon. The PdNi/C catalyst had higher electro catalytic activity for MOR in alkaline media than a comparative Pd/C catalyst. Additionally the explored Pd-MnO₂/MWCNTs electro catalysts [27] exhibited higher electro catalytic activity and stability than Pd/MWCNT's and Pd/Vulcan XC-72. While Li *et al.* [28] 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.* [29]

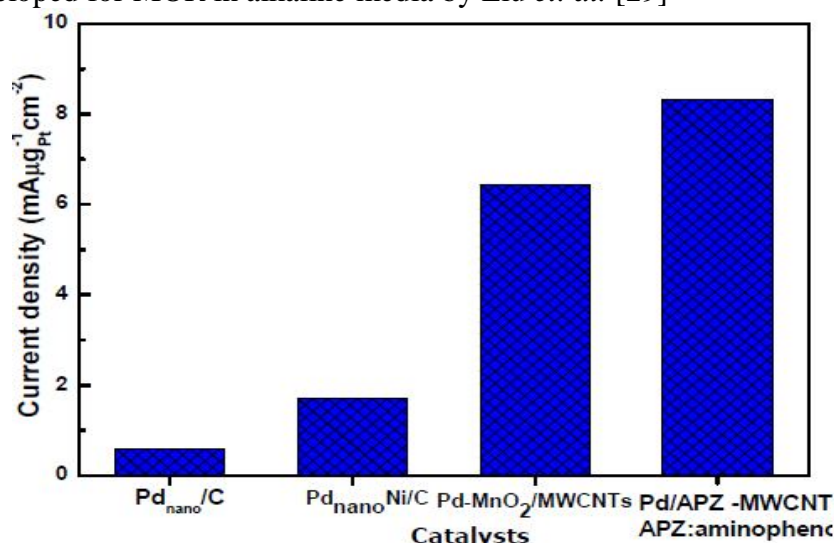


Figure 5: Mass specific activity for non platinum catalysts for methanol oxidation in alkaline media, ca-0.2V [26,27].

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