REVIEW PAPER

PEMFCs and AEMFCs directly fed with ethanol: a current status comparative review

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Abstract The last decade's research on the performance of proton-exchange membrane direct ethanol fuel cells (PEM-DEFCs) and anion exchange membrane direct ethanol fuel cells (AEM-DEFCs) is included in the present review. Future research challenges are identified along with potential strategies to overcome them. Pt-containing or Pt-free PEM-DEFCs that use acid proton-exchange membranes (typically Nafion type) exhibit relatively low performance (i.e., the state-of-the-art peak power density is 110 mW cm^{-2} at 145 °C over 4 mg of total Pt loading), while Pt-containing or Pt-free AEM-DEFCs that use low-cost anion-exchange membrane have recently exhibited better performance values (i.e., the state-of-the-art peak power density is about 185 mW cm^{-2} at 80 °C over Au-modified Pd catalysts supported on carbon nanotubes. The required faster kinetics of the ethanol oxidation and especially for the oxygen reduction reaction seem to be satisfied from one side by the AEM-DEFCs and from the other by PEM-DEFCs only if working at intermediate temperature values (>150 °C). Moreover, new possibilities of using less expensive metal catalysts (as silver, nickel, and palladium) are opening mainly for AEM-DEFCs and the last years for PEM-DEFCs too. Finally, it is worth to be noticed that the best value ever reported (peak power density is 360 mW cm^{-2} at 60 °C) has been obtained in a very promising alkaline-acid direct ethanol fuel cell (AA-DEFC).

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1 Introduction

Fuel cells technology is nowadays shifting from the fundamental research to real-world applications. Polymer electrolyte fuel cells (PEFCs) or solid polymer fuel cells (SPFCs) running on hydrogen in acidic environment were first used by NASA's Gemini program in the 1960s to provide with auxiliary power requirements in the space vehicles and drinking water for the astronauts [1]. They have been proved to represent an efficient energy conversion system and are currently being developed for many applications such as automotive and transportation in general, portable devices and auxiliary power units (APUs), because of the important improvements achieved in the field of electrocatalysis in the past decade [2–5]. In the last few years, the interest on alkaline fuel cells (AFCs) also increased, mainly due to more favorable oxygen reduction and fuel oxidation reactions with a variety of non-noble metal catalysts (e.g., Fe, Co, and Ni). AFC technology was the first fuel cell technology employed in applications such as the NASA's Apollo and Space Shuttle flights [6], while among the whole family of fuel cells, AFCs exhibit the best electrode performance when running on pure hydrogen and oxygen under similar operating conditions. A comparison of PEMFC versus AFC technologies using H$_2$ as a fuel is provided by McLean et al. [7]. However, a serious problem of AFCs, the progressive carbonation of the alkaline electrolyte due to carbon dioxide (CO$_2$) from air or the oxidation product of the fuel, hindered its further development. This problem was

addressed mainly by the application of alkaline anion-exchange membranes (AEMs) [8–14].

Alkaline AEMs conduct hydroxide ions (OH⁻) and represent the high pH equivalent to proton-exchange membranes (PEMs) employed in the acidic-type PEMFCs. Quaternary ammonium groups are used as anion-exchange groups in these materials. However, due to their low stability in highly pH (strongly alkaline) media [15], only a few membranes have been evaluated for use as AEMs in alkaline SPFCs. Yu and Scott [13] employed Solvay' MORG-ANE®—ADP membrane that belongs to another important class of membranes made from perfluorinated backbone polymers. This commercial AEM consisted of a cross-linked fluorinated polymer carrying quaternary ammonium as exchange groups, and the electrochemical performance of such an AEM-based DMFC was examined. However, the quaternary ammonium conductive groups may decompose in concentrated alkaline solution following the Hofmann degradation reaction [16], thus: it is crucial how these exchange groups are attached to the polymer backbone, especially if one considers that, during fuel cell operation, the pH may increase up to 14. Membranes with a C–H backbone are also of interest, considering their manufacturing and availability. According to Matsuoka et al. [10], an alcohol penetrating the AEM may protect it from a peroxide attack. They used a polyolefin backbone chain from Tokuyama (Japan), on which was fixed tetraalkylammonium groups. In the literature most of the AEMs are provided by Tokuyama Corporation [17, 18]. Scott's group, however, has recently reported striking advances in the field of AEM-based PEFCs operating on hydrogen using radiation grafted polymers. Mamlouk et al. [19, 20] studied radiation grafted polymers as an AEM for an alkaline DMFC, which exhibited enhanced oxygen reduction reaction (ORR) kinetics and superior performance and output. Moreover, high power output and durability cross-linked composite anion exchange membranes have been prepared and tested by Zhao et al. [21] and Lin et al. [22] using linear polymer and poly (ionic liquids), respectively.

AEM-based PEFCs have been attracting attention worldwide, mainly due to the prospect of using Pt-free electrocatalysts. Several advantages have been identified and reported over conventional AFCs: (i) there is no precipitated carbonate, since there is no mobile cation present, (ii) no electrolyte weeping, (iii) potentially simplified water management; in alkaline AEM-based SPFCs, water is produced at the anode and consumed at the cathode, and (v) potentially reduced corrosion [23]. DEFCs operating in alkaline (AEM) medium exhibit several advantages also over the ones operating in an acidic (PEM) medium, such as: (i) the ORR is faster under alkaline conditions than acidic ones, thus introducing lower activation overpotentials; (ii) non-precious metal catalysts can be used

effectively; (iii) due to the less corrosive environment, a number of cheap materials for the cell components can be employed; and (iv) EtOH crossover is less severe in AEM-based DEFCs, because the crossover takes place in the opposite way to the OH⁻ transport.

Concerning the fuel, hydrogen is the most suitable from the electrochemical and specific energy (energy per gram of fuel) point of view. However, the use of pure hydrogen has posed numerous storage and processing challenges that have inhibited its widespread use, especially in portable applications. Compared to the use of H₂ in fuel cells, liquid alcohol fuels are easy to store and transport. The direct oxidation of alcohol will also eliminate a heavy reformer needed to produce H₂ from liquid or gaseous carbonaceous fuels. Therefore, the use of H₂-rich and readily available alcohols, such as methanol (MeOH) [24–27] and ethanol (EtOH), as a fuel source has also attracted the interest of the fuel cells research community. EtOH, which is easily derived in large quantity via fermentation of biomass, is a green, sustainable, carbon–neutral fuel. Additionally, in comparison to MeOH, EtOH is non-toxic and its boiling point is relatively higher. Ideally, the electrochemical EtOH oxidation reaction (EOR) would produce twelve electrons per molecule of ethanol, whereas its energy density is 8.0 kWh kg⁻¹ (6.3 kWh L⁻¹). In this respect, fuel cells running on EtOH—direct EtOH fuel cells (DEFCs) represent a promising choice for sustainable energy conversion, and have been drawn a great deal of attention [28–43].

In terms of the catalysts employed in DEFCs, Pt and Pt-based catalysts are commonly used. In either acidic or alkaline media, the most extensively investigated anode catalysts, contain binary and ternary combinations based almost exclusively on PtRu and PtSn (see e.g., [4, 41, 44, 45]); adsorbed CO, however, resulting from EOR, poisons the electrode and reduces the activity of platinum [46]. The contribution of alloyed and non-alloyed platinum and tin to the EOR on PtSn/C catalysts for DEFCs was also evaluated via a simple model [47], that can predict the performance of a single DEFC by varying the Sn content and/or the degree of alloying of PtSn/C catalysts used as the anode material. Furthermore, EtOH cannot be totally electro-oxidized to CO₂ at temperature values below 100 °C, due to the difficulty in breaking the C–C bond in the EtOH molecule. This represents the major challenge in DEFC research [48].

Until now, electrocatalysts that provide sufficiently complete oxidation of EtOH to CO₂ in acid electrolytes (releasing 12 electrons per EtOH molecule) have remained unknown. Usually, the electrode process terminates with the formation of acetaldehyde (2e⁻) or acetic acid (4e⁻) [49–52]. However, recently it was demonstrated that the use of ternary PtRhSnO₂/C electrocatalysts—synthesized

by depositing Pt and Rh atoms on carbon-supported tin oxide nanoparticles—could lead directly to the oxidation of EtOH toward CO_2 in acidic media [53–55]. Very recently, De Souza et al. [42] reported that Pt-Etek/C presented different activity for the EOR depending on the support. Pt/C on carbon cloth was seen that facilitates the C–C bond cleavage of the EtOH molecule via a new ATR–FTIR setup introduced in [42] for in situ spectro-electrochemical studies in non-reflective and rough electrodes.

In an alkaline environment, it was shown [56] that an efficient oxidation of EtOH with the release of no less than 8–10 e^- per EtOH molecule is possible if carbon-supported nanosized RuM (M = Ni, Co, Fe) are used as anodic catalysts. Fang et al. [57] indicated that the C–C bond cleavage of EtOH on Pd occurred at NaOH concentrations lower than 0.5 M (pH values ≤13), an observation which was also supported via density functional theory (DFT) calculations [58]. However, important problems to be solved to ensure the efficiency of EtOH liquid fuel in alkaline media are: (a) the use of a cathode catalyst tolerant to EtOH and (b) the choice of an ion exchange membrane with a high electrical conductivity and good separation properties for EtOH.

The durability of the state-of-the-art catalyst employed in PEM-based DEFC research (e.g., PtSn/C) has been scarcely analyzed [59–61]. Hsieh et al. [60] investigated the electrochemical activity and durability of nanosized Pt–Sn binary catalysts on carbon nanotube grown on carbon paper (CNT/CP) composites. Accelerated durability test (ADT) was performed to accelerate the degradation of the Pt/C and PtSn/C catalysts by continuously cycling the potential in acidic environment in the work of Su et al. [61]. The potential cycling was conducted for 500 cycles, and the electrochemical stability of the electrocatalysts was studied by the linear sweep voltammetry after the ADT.

For the state-of-the-art Pd-based electrocatalysts for the oxidation of alcohols in alkaline media Bianchini and Shen [2] discuss on the catalyst lifetime among other research areas, whereas in a very recent study, Li and Zhao [40] reported on the durability test of an AEM-based DEFC that is composed of a Pd/C anode, an A201 membrane, and a Fe–Co cathode. They have shown that the major voltage loss occurs in the initial discharge stage, but the loss becomes smaller and more stable with the discharge time. It was also reported that the irreversible degradation rate of the fuel cell is around 0.02 mV h^{-1}, which is similar to the degradation rate of conventional PEM-based DMFCs. Furthermore, the performance loss of the AEM-DEFC was mainly attributed to the anode degradation, while the performance of the cathode and the membrane remains relatively stable. Nevertheless, the chemical stability of the catalysts over longer periods of time (fuel cell durability studies) is an important issue that still needs to be considered and is suggested for further investigations.

EtOH crossover is another major obstacle for DEFC commercialization, leading to a serious decrease in the cathode performance. Several studies have examined EtOH crossover [30, 35, 43, 51, 62], and its effect on mixed potential formation in DEFCs [32, 33]. Water uptake and transport properties, including diffusivity, electro-osmotic drag coefficient, and the mass transfer coefficient of water at the cathode catalyst were also examined for AEMs [63].

It was recently shown that in low temperature PEM-DEFCs, oxygen is also permeating from cathode and is able to chemically oxidize EtOH at the anode [36]. The same group, reported distribution of products of EtOH electrooxidation on Pt, PtRu, and PtSn as a function of fuel cell voltage (under load) and temperature for the first time [64].

Song and Tsiakaras [45] provided with a brief review of the research and development of PEM-DEFCs up to 2005, including (a) development of anode electrocatalysts for EOR, (b) MEA preparation procedure, (c) single DEFC performance, and (d) EtOH crossover phenomena, whereas Antolini [44] reviewed catalysts tested as anode and cathode materials also for PEM-DEFCs, with particular attention on the relationship between the chemical and physical characteristics of the catalysts (catalyst composition, degree of alloying, and the presence of oxides) and their activity for the EOR. In a recent review, Antolini and Gonzalez [65] provided with a short review that examines the effects of Pt–Sn structural characteristics, such as degree of alloying and Sn oxidation state, depending on the synthesis method, on the electrocatalytic activity for MeOH and EtOH oxidation. Very recently, Tsiakaras and co-workers [4] provided with the state-of-the-art of low- and non-Pt electrocatalysts (anodes and cathodes) for PEM-based fuel cells running on H_2, MeOH, or EtOH.

The progress achieved from 2005 to 2009 in the design of Pd-based electrocatalysts for the oxidation of alcohols in alkaline media is reviewed by Bianchini and Shen in [2]. Particular attention was dedicated to discuss the important role played by the Pd nanostructure and by the support material in governing the kinetics and selectivity of the oxidation process as well as the catalyst lifetime, whereas reviews of past research on the development of AEM-based direct alcohol fuel cells (DAFCs) were recently presented [66–69]. Antolini and Gonzalez [66] provided with an overview of catalysts and membranes for AEM-DAFCs and of their testing when fueled with methanol, ethanol, or ethylene glycol. Yu et al. [67] reviewed principles and mechanisms of alcohol oxidation and oxygen reduction in AEM-DAFCs. Different types of catalysts from conventional precious metal catalyst of Pt and Pt alloys to other lower cost Pd, Au, and Ag metal catalysts were compared. Non-precious metal catalysts, and lanthanum, strontium oxides and perovskite-type oxides were discussed, and

membranes like the ones used as polymer electrolytes and developed for AEM-DAFCs were also reviewed. Zhao et al. [68] reviewed past research on the development of AEM-DEFCs including the aspect of catalysis, AEMs, and single cell design and performance testing.

The present review provides a brief state-of-the-art of Pt and Pt-free PEM, and AEM-DEFCs and a comparison between their performance characteristics. Key references to the latest scientific literature and reviews are included, along with a brief overview of principles and mechanisms characterizing these electrochemical converters. In Sect. 2 the technological and economic barriers/challenges for PEM- and AEM-based DEFCs are listed, whereas in Sect. 3 the principles and mechanisms of acid and alkaline DEFCs are described. Next, in Sects. 4 and 5, the single fuel cell's performance and catalytic activity data are also reviewed.

2 Economic and technological challenges for PEM- and AEM-DEFCs

The U.S. Department of Energy (DoE) and its Fuel Cell Technologies Program disseminated a 2011 report concerning automotive fuel cells. Their cost was reduced by more than 82 % since 2002 (from $275/kW in 2002 to $49/kW in 2011, based on projections to high-volume manufacturing—500,000 units per year) [70]. These cost reductions reflect numerous individual advances in key areas, including the development of durable membrane electrode assemblies (MEAs) with low platinum group metal (PGM) content [71]. The balance of plant (includes assembly and testing) cost represents almost 55 %, whereas the stack cost represents 45 % of the total system cost. Here, the platinum cost represents about 30 % of the stack cost, assuming a Pt price of $35 per gram. We have to note, however, that the last 12 months (up to July 2012) average price for Pt is 46 Euro per gram. Table 1 [72] shows a list with average prices (of the last 12 months) of the metals employed in fuel cells electrocatalysis.

When focusing on portable appliances and consumer electronics equipment, however, where DAFCs are considered as the systems of choice, the percentage of the catalyst cost contribution on the total system cost may be significantly higher due to higher amounts of precious metals used. Thus, despite the fluctuating metal market prices, it is clear that every improvement in electrochemical kinetics will eventually be reflected in lower stack and fuel cell system cost. In this respect, the maximum mass specific power density (max-MSPD), which will be discussed in Sect. 4 with respect to several PEM- and AEM-DEFC power density data, is of foremost importance.

Table 1 Average prices (Euros per gram) for the last 12 months of the most used metals in fuel cells electrocatalysts [72]

Metal	Average price (Euros per gram)
Pt	46.0
Rh	44.0
Au	42.5
Ir	31.0
Pd	19.0
Re	4.8
Ru	3.0
Ag	0.72
Co	0.02
Ni	0.01
Sn	0.01
Cu	0.00612
Al	0.00152

Hereafter, barriers/challenges for both technologies are listed.

2.1 PEM-based DEFCs

- The cost of the system, not only because a considerable amount of Pt-based catalysts at both the anode and cathode is required, but also because acid electrolyte membranes (e.g., Nafion, and Nafion-based) are expensive.
- The incomplete oxidation of EtOH to acetaldehyde and acetic acid that liberates only 2 and 4 electrons, respectively, and greatly reduces the Faradaic efficiency of the fuel cell.
- The kinetics of the EOR in acid media is slow, leading to a large activation loss.
- EtOH crossover from the anode to the cathode within the PEM that leads to a parasitic current generation (mixed potential formation).
- The use of a cathode catalyst tolerant to EtOH.
- The durability of the state-of-the-art catalyst employed (e.g., PtSn/C) has been scarcely analyzed. Thus, the chemical stability of the catalysts over longer periods of time is an issue of foremost importance that still needs to be considered and is suggested for further investigations.

2.2 AEM-based DEFCs

- The complete oxidation of EtOH to CO_2 remains a challenging issue (the most important one). Nowadays, Pd-based catalysts show appreciable performance toward the EOR in alkaline media. However, EOR is incomplete and EtOH is selectively oxidized to acetate.
- The activity and durability of the Pd catalyst. The activity and durability of the Pd catalyst for the EOR in

alkaline media needs to be further enhanced, and the design of multi-metallic electrocatalysts is essential.

- A challenging issue in the cathode catalyst material is how to enhance the catalytic activity of non-Pt catalysts, making them comparable to that of Pt. For example, so far, Ag-based cathode catalysts for the ORR in alkaline media have a larger particle size than Pt-based catalysts do. Hence, a target in the cathode electrode is to develop new synthesis methods that can lead to high electrochemical surface area Ag-based catalysts.

- A significant improvement is needed to upgrade the OH^- conductivity, chemical, mechanical, and thermal stability of the existing AEMs. The OH^- conductivity can be improved by increasing the amount of charged groups in the membrane; however, there is a trade-off with the mechanical properties. A loss of the mechanical properties by promoting excessive water uptake is the result of increasing the concentration of the charged groups. The thinness of the AEM is an important requirement related to mechanical stability; to keep good mechanical stability when immersed in water, an AEM as thin as ~ 50 μm is necessary. AEM suffers also of a poor chemical stability in alkaline media, stemming from the hydroxide attack on the cationic group. The result of this degradation is an important loss in the number of anionic exchange groups, and a decrease of the ionic conductivity.

- Like the AEM, both the ionic conductivity and the thermal and chemical stability of the nowadays ionomers present within the catalyst layers are still low. Hence, significant work is needed to enhance the ionic conductivity and stability of ionomers. Recently, Mamlouk et al. [19, 73] studied the effect of ionomer content on the cell performance and the effect of catalyst layer thickness without ionomer on cell performance.

Water transport management is a key issue for both PEM- and AEM-DEFCs. The appropriate management of this process is necessary so as to avoid either cathode flooding (high water crossover) or a high cathode activation loss (too low water crossover). EtOH transport management is another key issue for both PEM- and AEM-DEFCs. Note that in AEM-DEFCs, as the cathode catalyst (non-Pt) is generally tolerant to EtOH oxidation, the mixed potential problem as a result of fuel crossover is not as serious as in PEM-DEFCs. Furthermore, the effect of the EtOH crossover in AEM-DEFCs is suppressed; the EtOH crossover within the membrane takes place in the opposite way to the OH^- transport, thereby diminishing that detrimental process. EtOH crossover, adversely affects fuel efficiency (i.e., energy density) due to the wasteful oxidation on the cathode side leading to a mixed potential formation [32, 33]. This mixed potential on the cathode causes a decrease in

DEFC voltage, and eventually results in decreased fuel efficiency, thereby lowering the energy density of the system. Low EtOH flow rates and low concentrations enable very high fuel efficiencies. However, mass transport limitations prevent the attainment of useful power densities under those conditions that enable high fuel efficiencies [74]. Moreover, the electro-oxidation reaction of EtOH in acid PEM-based DEFCs evolves through multiple steps resulting in the production of mainly acetic acid and acetaldehyde [49]. On the other hand, the EtOH electro-oxidation in alkaline AEM-based DEFCs evolves through a simpler path producing less acetic acid in the form of ions (CH_3COO^-) and favoring the formation of acetate [75]. This results in fuel utilization much higher than the one achieved in the PEM-based DEFCs, better cell performances, and a higher energy density.

An important drawback, however, of the AEM-based DEFC is the formation of a pH gradient with time (more alkaline at the cathode, more acidic at the anode) that will cause the occurrence of an electromotive force in opposition to the electromotive force of the reaction itself [76, 77]. In case of a high pH gradient, this will strongly deteriorate the polarization performance. Wang et al. [76] discussed in their study this thermodynamic disadvantage for an AEM-based DMFC. As reported, the significant reduction of activation overpotential in alkaline media can compensate for the voltage loss due to the thermodynamic effects associated to the pH gradient. Furthermore, Aricò et al. [77] mentioned in their work that recirculation of the liquid electrolyte through the device not only enhances conductivity but also significantly reduces the pH gradient.

Nevertheless, PEM- and AEM-DEFCs are attracting increasing interest, as electrochemical energy converters for portable appliances; as a result there exist a blossoming research activity focused on PEM- and AEM-DEFCs (see Fig. 1).
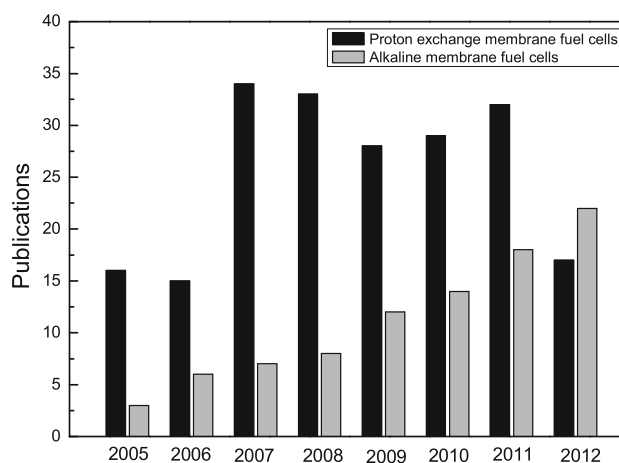

Fig. 1 Publications for proton-exchange membrane and alkaline membrane fuel cells running on EtOH from the WEB of knowledge from the year 2005 to 2012

It can be seen that for a period of 5 years (2007–2011) an average of almost 30 research papers per year on PEM-DEFCs appeared, reflecting the constant interest of the research community in this type of DEFC, mainly due to the reliability of the existing Nafion membranes and to the interest toward new catalyst developments for breaking the C–C bond and fully oxidize the EtOH molecule to CO_2. On the other hand, the scarcity of reliable and cost competitive AEMs has certainly contributed to moderate the interest of many researchers in Pd-based electrocatalysts and AEM-DEFCs. With the advent, however, of efficient and commercially available AEMs, together with the progress achieved in the development of new and more active catalytic systems, the situation has changed and the research on anode and cathode catalytic architectures for AEM-DEFCs increases steadily from 2005 to 2012 (see Fig. 1).

3 Principles and mechanisms of a direct ethanol fuel cell

In a PEM-DEFC, EtOH together with water is supplied to the anode, where it undergoes electro-oxidation. Figure 2a shows a schematic principle of a proton-conducting DEFC with a mixture of EtOH and water circulating in the anode, and oxygen in the cathode, whereas Fig. 2b shows a schematic principle of an AEM-DEFC with a mixture of EtOH and water circulating in the anode, and oxygen in the cathode. Electrons are subsequently transferred via the external circuit to the cathode, where they are utilized in the ORR process. The reactants and mobile species in the polymer electrolyte are intimately tied to its pH.
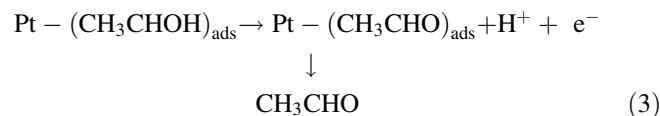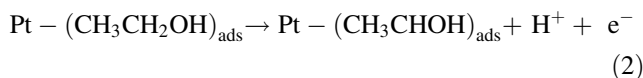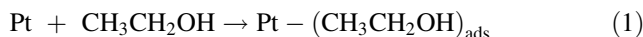
At low pH levels (acidic environment), water is consumed in the anode process together with EtOH, while protons are transported from the anode electrocatalytic layer across the electrolyte and consumed in the cathode process to form water. This is the case for the proton-conducting membrane DEFC.

In high pH systems (alkaline environment), on the other hand, the effect is reversed: water is consumed on the cathode side in the ORR process, forming hydroxyl ions. These ions are now transported across the cell to the anode, where they are consumed together with EtOH fuel to form mainly acetaldehyde and acetic acid and to a lesser extend CO_2.

3.1 Ethanol oxidation reaction

3.1.1 EOR in acidic media

Many different Pt-based anode catalysts such as PtRu and PtSn have been investigated and reported to increase the EOR activity (see e.g., [4, 45]). Among these binary and ternary alloy catalysts, PtSn catalysts are state-of-the-art catalysts for the EOR. EtOH electrooxidation over PtSn catalysts was described in [44, 45]. Li et al. [78] determined the rate-determining step of PtSn/C in different potential regions. The dissociative adsorption of EtOH on the Pt surface is the main step in the lower potential region:

$$Pt + CH_3CH_2OH \rightarrow Pt-(CH_3CH_2OH)_{ads} \qquad (1)$$

$$Pt-(CH_3CH_2OH)_{ads} \rightarrow Pt-(CH_3CHOH)_{ads} + H^+ + e^- \qquad (2)$$

$$Pt-(CH_3CHOH)_{ads} \rightarrow Pt-(CH_3CHO)_{ads} + H^+ + e^-$$
$$\downarrow$$
$$CH_3CHO \qquad (3)$$

For the higher potential region, the rate-determining step is the activation of H_2O oxidation to OH^-. The mechanism in the higher potential region can be described by the following equations:

$$Sn + H_2O \rightarrow Sn-OH_{ads} + H^+ + e^- \qquad (4)$$

$$Pt-(CH_3CHO)_{ads} + OH_{ads} \rightarrow Pt + CH_3COOH + H^+ + e^- \qquad (5)$$
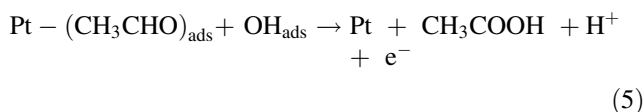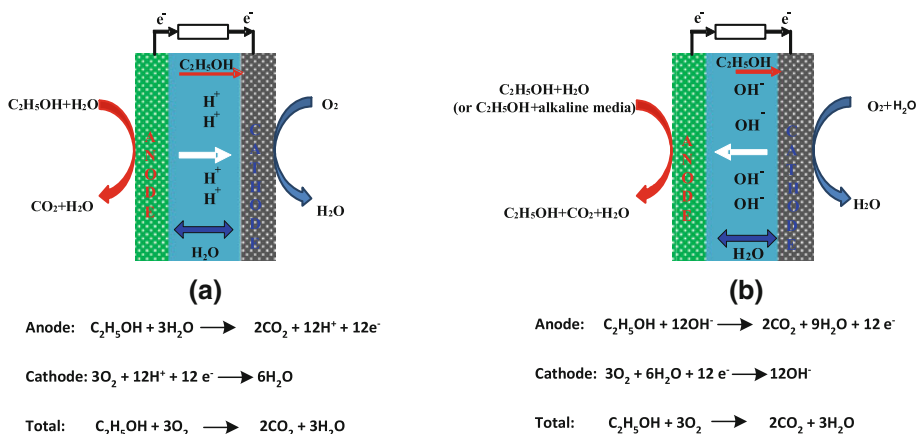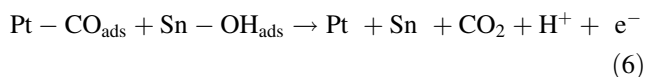

Fig. 2 The operational principle of a DEFC with: an anion-conducting (a) and a proton-conducting (b) polymer electrolyte

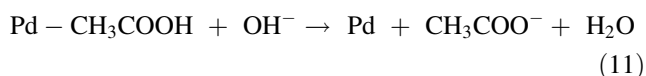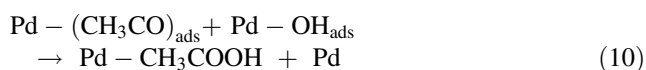$$Pt - CO_{ads} + Sn - OH_{ads} \rightarrow Pt + Sn + CO_2 + H^+ + e^- \tag{6}$$
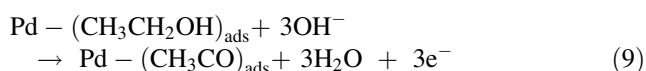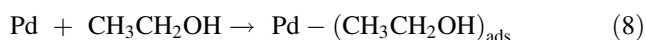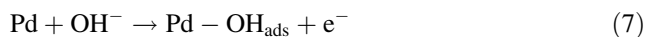
OH species can further react with the adsorbed acetaldehyde molecules to produce acetic acid [79]. Moreover, based on the bifunctional mechanism and the ligand effect [80] some researchers have also shown that SnO_2 can provide O-species for the oxidation of the CO that is produced on the Pt active sites during the dissociative adsorption of EtOH [81, 82]. The role of SnO_2 during the EOR activity of the PtSn catalysts has been proposed in [65, 83]. The authors showed that SnO_2 can increase the Pt surface area or help remove the adsorbed intermediates. SnO_2 can improve Pt for the quick dissociation of EtOH in higher potential region. However, there may be too many oxides on the alloy surface to block the active sites on the Pt particles, which would deteriorate the electrochemical activity [84].

3.1.2 EOR in alkaline media

The mechanism of electrochemical oxidation of EtOH in alkaline systems was investigated on polycrystalline gold electrodes [85, 86] and on palladium catalysts [87, 88]. For EtOH oxidation on palladium, the formation of acetaldehyde and/or acetic acid was reported [89, 90], and takes place according to the following steps:

$$Pd + OH^- \rightarrow Pd - OH_{ads} + e^- \tag{7}$$

$$Pd + CH_3CH_2OH \rightarrow Pd - (CH_3CH_2OH)_{ads} \tag{8}$$

$$\begin{aligned} Pd - (CH_3CH_2OH)_{ads} &+ 3OH^- \\ &\rightarrow Pd - (CH_3CO)_{ads} + 3H_2O + 3e^- \end{aligned} \tag{9}$$

$$\begin{aligned} Pd - (CH_3CO)_{ads} &+ Pd - OH_{ads} \\ &\rightarrow Pd - CH_3COOH + Pd \end{aligned} \tag{10}$$

$$Pd - CH_3COOH + OH^- \rightarrow Pd + CH_3COO^- + H_2O \tag{11}$$

The rate-determining step is the one described in Eq. [10]. There, the adsorbed ethoxy intermediate is removed by adsorbed hydroxyl ions to form acetate. The mechanism of EtOH electrooxidation on a palladium electrode in alkaline solution with various concentrations of NaOH (0.01–5 M) was also studied in [57, 58]. The same research [57] suggested that the EtOH oxidation to CO_2 on Pd in moderate alkaline media either proceeds with no intermediacy of CO_{ads} (non-poisoning path) or by fast oxidation of weakly adsorbed CO by the abundant OH^-_{ads} species. The latter eventuality is less likely in view of a specific study of CO electrooxidation on either Pt or Pt-based electrocatalysts [91], where it was shown that the CO coverage on Pt is larger than that on Pd but the overpotential for CO oxidation is higher on Pd than on Pt.

3.2 Oxygen reduction reaction

3.2.1 ORR in acidic media

The ORR in acidic media has been studied extensively. Effects of different pH, electrolytes, temperature, and pre-conditioning of electrodes on ORR have been investigated. The most accepted mechanism of ORR was first proposed by Damjanovic et al. [92, 93]. They suggested that the ORR proceeds along two parallel reaction paths with comparable rates. One is the direct four-electron transfer reduction from oxygen to water; the other is the formation of hydrogen peroxide as an intermediate in a two-electron transfer reaction.

Using Pt-based electrocatalyst the oxygen reduction intermediate species share the electrode's surface with platinum oxide and/or hydroxide compounds as well as with other adsorbed species. The formation of platinum oxide and/or hydroxide compounds shows an irreversible behavior and so the performance of a Pt electrode may also depend on this. The recent state-of-the-art for low-Pt and Pt-free electrocatalysts for ORR, reviewed by Palacin and co-workers [94], revealed that the research community adopted many different methods to reduce Pt loading, such as using nanoparticles on various supports, preparing Pt-monolayers supported on suitable metal nanoparticles, 1-D, 2-D, and 3-D nanostructures, etc.

Table 2 reports some recent results [95–97] of low-Pt cathode electrocatalysts for the ORR in the presence and in the absence of EtOH, characterized with the rotating disk electrode (RDE) technique. In the absence of EtOH, Pt-M oxides exhibited relatively good mass activity toward ORR except in case of PtCeOx/MWCNT. In the presence of EtOH, despite the fact that there were no current peaks associated to the oxidation of EtOH, a higher overpotential (in comparison to the absence of EtOH) was observed, with $Pt_{0.7}–Co_{0.3}$/MWCNT to be more tolerant compared to the other catalysts.

Table 2 Mass activities (mA $\mu g_{Pt^{-1}}$) (@ 0.8 V, 1,600 rpm) for oxygen reduction reaction in acidic media over platinum-based electrocatalysts in the presence and in the absence of EtOH

Catalysts	Mass activity (mA $\mu g_{Pt^{-1}}$) In the absence of ethanol	Mass activity (mA $\mu g_{Pt^{-1}}$) In the presence of ethanol	Ref.
$Pt_{0.5}Sn_{0.5}O_x$/C[a]	0.072	0.024	[95]
$Pt_{0.7}Ni_{0.3}O_x$/C[a]	0.072	0.015	[95]
$Pt_{0.6}Co_{0.4}O_x$/C	0.072	0.013	[95]
$Pt_{0.7}Co_{0.3}$/MWCNT	0.014	0.002	[96]
PtCeO$_x$/MWCNT[a]	0.003	0.001	[97]

[a] 1,200 rpm

Table 3 Kinetic current values (mA cm^{-2}) (@ 0.8 V, 1,600 rpm) for oxygen reduction reaction in acidic media over non-platinum electrocatalysts in the presence and in the absence of EtOH

Catalysts	Kinetic current density (mA cm^{-2}) In the absence of ethanol	Kinetic current density (mA cm^{-2}) In the presence of ethanol	Ref.
Ru/C	1.8	1.8	[98]
PdCoMo/ CDX-975	1.6	0.58	[99]
PdCoMo/C	1.5	1.21	[99]
PdCo/C	1.5	0.7	[100]
CoSe/C	0.1	0.1	[101]
Pd$_3$Fe/C	0.1	0.1	[102]

Concerning the Pt-free ORR electrocatalysts, one of the major challenges is the poor performance compared to the Pt-based ORR electrocatalysts for PEM-DEFCs. In Table 3 some of Pt-free electrocatalysts [98–102] that have been examined under the RDE toward ORR in the presence and in the absence of EtOH are included.

The Ru/C presents the highest kinetic current density 1.8 mA cm^{-2} versus RHE, which in the presence of EtOH does not change. The performance of a DEFC based on a 20 % Ru/C cathode (5 mW cm^{-2}; anode Pt loading: 1 mg cm^{-2}) was lower than that observed over 20 % Pt/C cathode (17 mW cm^{-2}). Also as it is shown in Table 2, Pd-based alloys ORR electrocatalysts in combination with cobalt exhibited good activity values and close to that of Pt/C, presenting very good tolerance in the presence of EtOH. The Pd–Co–Mo/Carbon black—heat treated at 973 K was also examined successfully as cathode in a DEFC whose performance peak power density was 8 mW cm^{-2} with anode catalyst loaded with 1 mg cm^{-2} of Pt.

3.2.2 ORR in alkaline media

One of the main advantages of alkaline media comes from the fact that the electrode's reaction kinetics in these media is higher than those exhibited in acidic media, enabling the use of Pt-free catalysts. Moreover, the alkaline media provides a less corrosive environment to the electrodes. Pd-based catalysts have shown a surprisingly high ORR activity, particularly in the alkaline medium, with an ORR activity close to that of Pt.

The most examined cathode electrocatalyst, according to the literature is Hypermec^{TM} provided by Acta S.p.A [18, 90, 103–106]. Zhiani et al. [39] compared platinum supported on carbon and Hypermec^{TM} as non-noble metal cathode catalyst, in AEM-DEFCs, indicating that active DEFC made by non-noble cathode catalyst showed superior performance compared to the cell made by 10 wt% Pt/C cathode catalysts in terms of power density and OCV at 60 °C and at ambient pressure. This result is related to the higher ORR kinetic of the non-noble metal cathode catalyst in alkaline media. A different, Au-modified Pd electrocatalyst supported on carbon nanotubes was studied as cathode from Xu et al. [107] and non-platinum cathode. According to their results the fuel cell performance reached 185 mW cm^{-2} and the Au-modified Pd is also a potential ORR electrocatalyst in AEM-DEFCs.

An equally important factor is the improved material stability when employing alkaline electrolytes. Few electrode materials are stable under strongly acidic conditions, especially under the strongly oxidizing conditions encountered at oxygen cathodes. In contrast, a much wider range of materials are stable in alkaline environments, including much less expensive materials such as Ni [108] and Ag [109], etc. In the literature, studies on materials for ORR in alkaline media include mainly manganese oxides [110–113], Co and its binary alloys [114–118], and Ni [108, 118, 119], materials that have low cost and with improved catalytic activity and selectivity toward the 4-way ORR pathway. Moreover, the alkaline environment gives the rating to the carbon materials to act as metal-free electrocatalysts and to have much better electrocatalytic activity, long-term stability, and tolerance to cross-over effect [120, 121].

The ORR electrocatalysts for AEM-DEFCs are in the stage of early development as it is obvious from Table 4 which includes the catalysts [107, 122], which are palladium-based, that have been examined in alkaline media in the presence and

Table 4 ORR electrocatalysts for AEM-DEFCs

Catalysts	Kinetic current density (mA cm^{-2}) In the absence of ethanol	Kinetic current density (mA cm^{-2}) In the presence of ethanol	Experimental conditions	Ref.
PdAg (8 at %)/C	1	0.5	LSV-5 mV s^{-1} 1 M NaOH or 1 M NaOH + 0.1 M EtOH	[122]
Modified Pd$_3$Au/CNT	370	40[a] (in absence of ethanol: 2 mA cm^{-2})[a]	Room temperature, 1 M KOH, 3,500 rpm	[107]

[a] CV-measurement: 1 M KOH + 1 M EtOH

Fig. 3 DEFC operational results: maximum DEFCs power density (mW cm^{-2}) at 60 °C of Pt-based and Pt-free electrocatalysts in acidic and alkaline environment dependency on platinum or palladium loading (µg cm^{-2}); (T_{room}: room temperature; T_{40}: 40 °C; T_{80}: 80 °C; T_{100}: 100 °C; T_{145}: 145 °C; *open triangle* Pt-containing PEM-DEFC, *filled triangle* Pt-containing AEM-DEFC, *open square* Pd-containing PEM-DEFC, *filled square* Pd-containing AEM-DEFC, *open circle* Pd or Pt-containing alkaline-acid DEFC
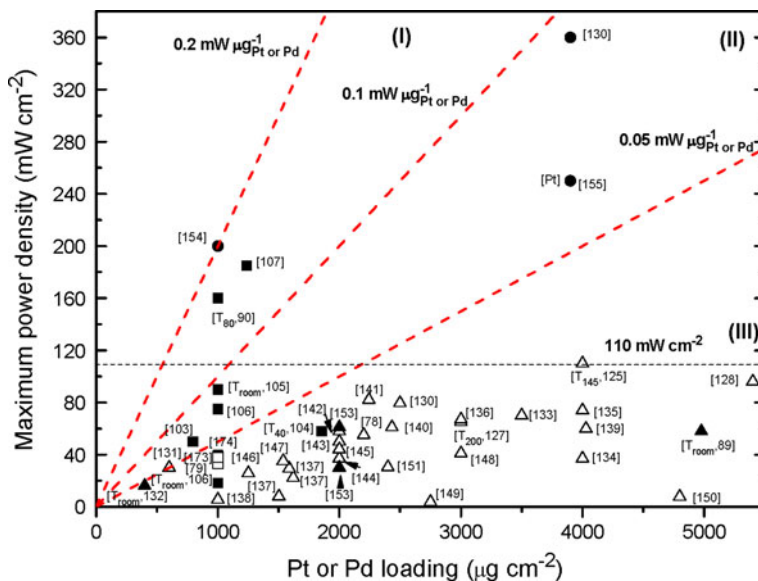
in the absence of EtOH. Compared to Table 3 the modified Pd$_3$Au/CNT exhibited very high kinetic current density. Its EtOH tolerance was examined with the cyclic voltammetry technique, showing activity toward EOR.

4 Single fuel cell performance (polarization curves)

To accelerate breakthroughs in PEFCs' R&D and their sustainable commercialization, great effort has been devoted by a number of research groups worldwide in order to decrease the Pt loading at a level of <150µg$_{Pt}$ cm$^{-2}_{MEA}$ [123] (or <200 mg$_{pt}$ kW^{-1} or <15 g$_{pt}$ for a 75 kW vehicle). Gottesfeld's survey on the central milestones in the development for low temperature fuel cells operating in acidic environment indicate that the most recent improvements in Pt catalyst utilization by optimization of catalyst layer composition and structure have led to catalyst utilizations as high as 80 % or more [5]. It was Zhang et al. [124] whose work focused on moving from preparation of homogenous Pt alloy particles to tailoring of core-and-shell alloy particles, targeting (i) further lowering of the mass of precious metal per unit power output and (ii) further boost of catalytic activity per square centimeter of catalyst area.

Single cell polarization performance data for PEM- and AEM-DEFCs were collected and depicted in Fig. 3. It presents the dependency of the maximum (peak) power density per square centimeter of geometric area (or maximum area-specific power density, max-ASPD) on total metal loading (MEA's metal loading; here metal can be either Pt and Pt-based catalysts for PEM-DEFCs, or Pt-based and Pd-based catalysts for AEM-DEFCs. Lines of constant maximum mass specific power density (max-MSPD) can be drawn.

As it can be distinguished in Fig. 3, the best performing PEM-DEFCs up today are limited to 110 mW cm^{-2}, reported by Aricò et al. [125]. They have achieved the highest ever area-specific power density (110 mW cm^{-2}, or 0.0275 mW µg$^{-1}_{Pt_{total}}$ in terms of the max-MSPD) in a PEM-DEFC at 145 °C, employing a PtRu (2 mg$_{Pt}$ cm^{-2}) binary anode electrocatalyst and a Pt (2 mg$_{Pt}$ cm^{-2}) cathode, both supported on carbon. Another high PEM-DEFC performance of 77 mW cm^{-2} was achieved and reported by Wang et al. [126] at 170 °C, but with very high platinum loading, 6,653 µg$_{Pt}$ cm^{-2} (0.0115 mW µg$^{-1}_{Pt_{total}}$), (not shown in Fig. 3 for practical reasons). Also, interesting results were recently presented by Lobato et al. [127], reporting fuel cell performance of 67 mW cm^{-2} (3,000 µg$_{Pt}$ cm^{-2}) at 200 °C. Peak power densities of 96 mW cm^{-2} (or 0.017 mW µg$^{-1}_{Pt_{total}}$) and 79.5 mW cm^2 at 90 °C for PEM-DEFC have been obtained by Wang et al. [128], over a double-layer anode that consisted of one layer Pt$_3$Sn and a second layer PtRu, and by Jiang et al. [129], respectively. The best fuel cell performance was observed in the case the Pt$_3$Sn was the first layer (close to the anode diffusion layer) and the PtRu (adjacent to the Nafion) the second one.

As Tsiakaras and co-workers [4] pointed out, the best performing PEM-DEFC compared to PEM-based DMFCs, exhibited a maximum power density per square centimeter of geometric area three times lower. On the other hand, it has been demonstrated that with a Pd-based electrocatalyst, the peak power density of an AEM-DEFC can be as high as 185 mW cm^2 at 60 °C [107]. Recently, Zhao's group [130] demonstrated an alkaline–acidic DEFC (AA-DEFC) with a thin membrane (25 µm) and peak power density as high as 360 mW cm^2 at 60 °C, which is about two times higher than the performance of the best performing AEM-DEFC, and 3.42 times higher than the performance of the best
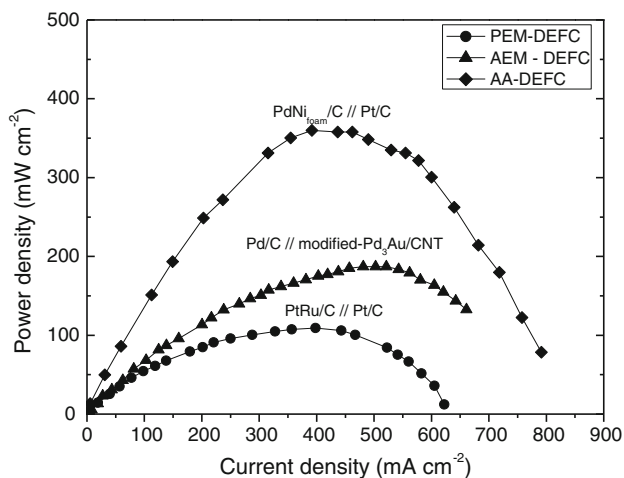
Fig. 4 The performances of the three-best performing DEFCs appeared in the literature

performing PEM-DEFC reported in the literature. Figure 4 hereafter depicts the polarization performances (in terms of the power density) for the three best performing DEFCs discussed above.

If we look now at the lines of constant maximum mass specific power density (max-MSPD) in Fig. 3, the following observations can be drawn:

(a) Three regions are distinguished: (I) with max-MSPD values between 0.2 mW $\mu g_{Pt\,or\,Pd}^{-1}$ and 0.1 mW $\mu g_{Pt\,or\,Pd}^{-1}$, (II) with max-MSPD values between 0.1 mW $\mu g_{Pt\,or\,Pd}^{-1}$ and 0.05 mW $\mu g_{Pt\,or\,Pd}^{-1}$, and (III) with max-MSPD values lower than 0.05 mW $\mu g_{Pt\,or\,Pd}^{-1}$. Each line has been drawn at the maximum MSPD of each catalyst's category that is reported in Fig. 3 (Pt-containing AEM, Pd-containing PEM-DEFC, Pd-containing AEM-DEFC, Pt–Pd-containing alkaline-acid DEFC)

(b) The best performing PEM-DEFC with low Pt-based electrocatalysts is the one reported Fatih et al. [131] with a max-MSPD of ca. 0.05 mW $\mu g_{Pt_{total}}^{-1}$

(c) An AEM-based DEFC, also with low Pt-based electrocatalysts, achieved a similar max-MSPD (0.04 mW $\mu g_{Pt_{total}}^{-1}$), representing the best performing AEM-based low-Pt DEFC, operating at room temperature, reported in the literature [132]. All other Pt-based PEMs [78, 125, 127–129, 133–151] and AEM-DEFC studies [104, 152, 153] found in the open literature reported lower max-MSPD values, as it can be also seen from Fig. 3

(d) Pd-based AEM-DEFCs exhibited a power output per unit mass of Pd as high as 0.16 mW $\mu g_{Pd\,total}^{-1}$ [90], whereas all other Pd-based AEM-DEFC studies [103,

105, 106] found in the open literature reported lower max-MSPD values

(e) AA-DEFCs exhibited a power output per unit mass of metal as high as 0.2 mW $\mu g_{Pd\,total}^{-1}$ [154], whereas all other AA-DEFC studies [130, 155] found in the open literature, reported lower max-MSPD values

According to Fig. 3, the AEM-DEFCs, in most of the cases not only present higher activity than PEM-DEFCs mainly due to the lower ethanol's crossover effect, but also provide the possibility of using non-Pt cheap electrocatalysts. Moreover, the most interesting thing about the AEM-DEFCs is that they operate at lower temperature values (60 °C) than the one's of PEM-DEFCs' (80 °C). Finally, a new interesting approach is the development of alkaline-acid fuel cells. Those also exhibit very high and comparable polarization performance to Pt-based PEM-DEFCs and Pd-based AEM-DEFCs. However, they are still questioned since the number of works in the literature is very limited and much further investigation is necessary.

5 Catalytic activity data

Further literature enhancement of the up-to-date developed and examined Pt- and Pd-based electrocatalysts under CV's technique in alkaline and in acidic media is presented in Fig. 5. Three distinct regions are shown: (I) where the max-mass specific current density values are higher than 15 mA $\mu g_{Pt\,or\,Pd}^{-1}$, (II) where the max-mass specific current density values are between 15 mA $\mu g_{Pt\,or\,Pd}^{-1}$ and 0.5 mA $\mu g_{Pt\,or\,Pd}^{-1}$, and (III) where the max-mass specific current density values are lower than 0.5 mA $\mu g_{Pt\,or\,Pd}^{-1}$.

(a) The best activity in acidic media with Pt-based electrocatalysts is the one reported Li et al. [156] with a max-mass specific current density of 15.4 mA μg_{Pt}^{-1}. The rest of the catalysts [37, 55, 157–163] present much lower values

(b) The highest max-mass specific current density for Pt-based electrocatalysts, 9 mA μg_{Pt}^{-1}, in alkaline media is reported by Tusi et al. [164]. The rest electrocatalyst [75, 91, 152, 165–172] presented lower max-mass specific current density

(c) In acidic media, Pt-free electrocatalysts [79, 173, 174] achieved very small mass specific current density with the maximum value 0.7 mA μg_{Pd}^{-1}

(d) In alkaline media, Pd-based electrocatalysts achieved a very much higher max-mass specific current density, 442 mA μg_{Pd}^{-1} [175] and 45.7 mA μg_{Pd}^{-1} [176], reported in the literature. The rest of the electrocatalysts [104, 105, 140, 177–196] exhibited

Fig. 5 Cyclic voltammetry results: comparison of maximum current density (mA cm^{-2}, 50 mV s^{-1}, room temperature) of Pt-based and Pt-free electrocatalysts in acidic and alkaline environment dependency of metal loading (μg cm^{-2}). *Ni, r_1: 100 mV s^{-1}, r_2: 10 mV s^{-1}, r_3: 1 mV s^{-1}, t: 303 K). *Inset* enlarged area, x: from 0 to 200 μg cm^{-2} and y: from 0 to 70 mA cm^{-2}). *Open triangle* Pt-containing PEM-DEFC, *filled triangle* Pt-containing AEM-DEFC, *open square* Pd-containing PEM-DEFC, *filled square* Pd-containing AEM-DEFC
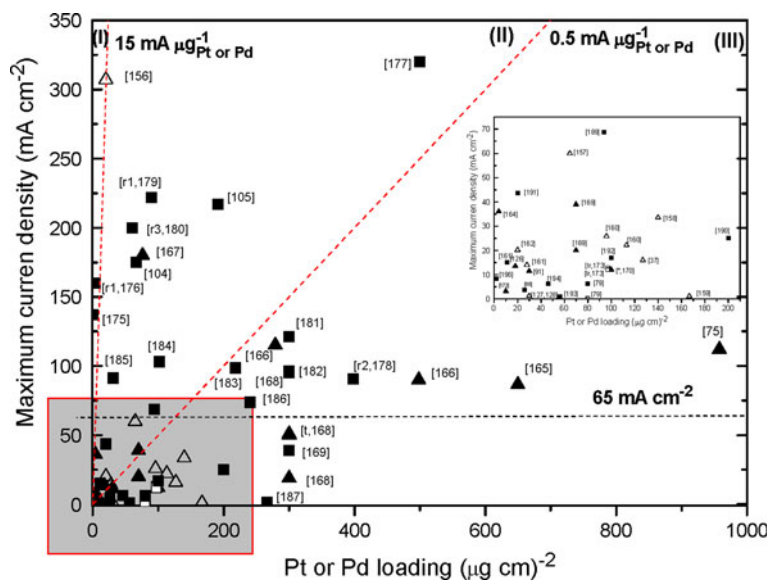
lower values, however, higher than acidic electrocatalysts

6 Conclusions

EtOH's effective and efficient conversion into electricity inside a fuel cell is a challenging target. Among the challenges, reducing the catalyst loading is perhaps the major one. The development of PEM-based DEFCs and more recently of solid AEM-based DEFCs brings new opportunities to the use of EtOH in a direct fuel cell, working either in acidic or alkaline environment.

PEM-DEFCs allow for power densities as high as 70–100 mW cm^{-2} to be reached at a temperature of 90 °C, with a PtSn/PtRu layered anode catalytic structure. The most interesting issue in PEM-DEFC research is the identification of a desirable electrocatalyst, which has the ability to both: (i) contribute in breaking of the C–C bond toward complete oxidation into CO$_2$, thereby leading to an increase of the fuel utilization and fuel cell efficiency, and (ii) remove the adsorbed intermediate species. Pt is the most active material for the EOR, however, it is easily poisoned when it is used alone as an anode catalyst. Thus, the research on EtOH electrooxidation catalysts was targeted on doping Pt with a second or a third additive, such as Sn, Ru, Rh, Ce, Ti, Ni, and W. PtSn catalysts were found to exhibit the highest electrocatalytic activity toward EtOH electrooxidation in acidic media so far. The need for Pt-based catalysts, however, may prevent wider applications for portable electronic devices. Furthermore, EtOH crossover adversely affects fuel efficiency (i.e., energy density) due to the wasteful oxidation on the cathode side, leading to a mixed potential formation.

The most important advantage of using a membrane (AEM-based PEFCs), instead of a liquid electrolyte, which is the case of the AFC (conventional aqueous KOH electrolyte fuel cells), is the elimination of the negative effects of CO$_2$. Carbonate formation is eliminated, and the need to frequently regenerate the electrolyte is not the case. In AEM-PEFCs, the conducting species is now in a fixed solid polymer; therefore, there will be some carbonates due to the reaction of the OH$^-$ with CO$_2$, but because there are no mobile cations (K$^+$), solid crystals of metal carbonate will neither be formed to block the electrodes, nor liquid caustic will be present. Thus, electrode weeping and corrosion will be minimized.

The required faster kinetics of the EtOH oxidation and especially for the ORR seem to be satisfied from one side by the AEM-DEFCs and from the other by PEM-DEFCs only if working at intermediate temperature values (>150 °C). While, however, a higher operating temperature promotes the EtOH electro-oxidation, it also increases the crossover rate, thereby reducing the fuel efficiency and the energy density of the fuel cell system. DEFCs operating in alkaline (AEM) medium exhibit several advantages over the ones operating in an acidic (PEM) medium. In addition to the faster electrochemical kinetics under alkaline conditions, non-precious metal catalysts (as Ag, Ni, and Pd) can be used effectively: the activity of non-noble catalysts for EOR and ORR is sufficient to reach power densities as high as 60 mW cm^{-2} at room temperature. This opens up a window of opportunity toward the development of AEM-based DEFCs that are particularly efficient for portable applications. Furthermore, it is known that water is produced at the anode and consumed at the cathode, thereby implying a simplified water management. Additionally, EtOH crossover is less severe in AEM-based DEFCs, because the alcohol transport mechanism takes place in the

opposite way to the OH^- transport. There are, however, some drawbacks which concern the formation of a pH gradient between anode and cathode, and the need to increase the operating temperature to enhance the conductivity of the AEMs, which may be not useful for portable applications. The suppression of the crossover in the AEMs would increase DEFC performance and fuel efficiency (i.e., energy density).

Our review summarizes the following observations:

- The highest peak power density value, 360 mW cm^{-2} (mass specific power density, 0.092 mW μg_{Pd}^{-1}), and the highest max-mass specific power density, 0.2 mW μg_{Pd}^{-1} (peak power density, 200 mW cm^{-2}) have been performed by platinum-free alkaline-acid DEFCs.
- A high peak power density of 185 mW cm^{-2} (mass specific power density, 0.15 mW μg_{Pd}^{-1}) and a high max-mass specific power density 0.16 mW μg_{Pd}^{-1} (peak power density, 160 mW cm^{-2}) have also been exhibited by platinum-free, palladium-based AEM-DEFCs.
- The majority of the Pt-based and Pt-free PEM-DEFCs presented peak power density values below 120 mW cm^{-2} and mass specific power density values below 0.05 mW μg_{Pt}^{-1}. The best power density value of PEM-DEFCs of 110 mW cm^{-2} (mass specific power density, 0.0275 mW μg_{Pd}^{-1}, 145 °C operating temperature) was reported in 1999 by Arico and his co-workers, over PtRu/C and Pt/C anode and cathode, respectively.

Concerning the cyclic voltammetry's measurements, the highest current density value (320 mA cm^{-2}) and the highest mass specific current density value (442 mA μg_{Pd}^{-1}) toward EOR have been observed in alkaline media over Pd-based electrocatalysts. All the examined electrocatalysts in acidic media have shown maximum current density values lower than 64 mW cm^{-2} (about six times lower than that obtained in alkaline media) and mass specific current density values $\sim$0.9 mA μg_{Pt}^{-1}, taking into account that all were Pt-based. The current density peak on Pd-based electrocatalysts in alkaline media has been found to be higher than that obtained on Pt-based electrocatalysts in alkaline or in acidic media, indicating the notable progress that is carried out to partially overcome the cost barrier. The catalytic cost seems to be potentially reduced two and a half times, if it is considered that palladium costs 19 euros per gram, while platinum costs 44 euros per gram (cf. Table 1).

The differences among the different types of fuel cells is not only observed with respect to the mass specific power density values, where the AA-DEFCs and AEM-DEFCs performances exceed over the ones of the PEM-DEFCs, but also to the operating temperature values. The latter ones operate usually at 80 °C, while the former at 60 °C,

providing additionally an energy cost advantage. Concluding, we point out that key issues/challenges that must be overcome for both PEM- and AEM-DEFCs to become competitive are: water transport management, EtOH crossover, and EOR kinetics on the anode. The appropriate management of the water transport process is necessary so as to avoid either cathode flooding (high water crossover) or a high cathode activation loss (too low water crossover). EtOH transport management is another key issue for both PEM- and AEM-DEFCs. In AEM-DEFCs, as the cathode catalyst (non-Pt) is generally tolerant to EtOH oxidation, the mixed potential problem as a result of fuel crossover is not as serious as in PEM-DEFCs. More active catalysts for the EOR would enable a certain power density to be achieved at higher cell voltages, and would hence directly impact the energy efficiency of the DEFC, which translates to the energy density if the amount of the fuel carried by a DEFC system is fixed.

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