

# On reviewing the catalyst materials for direct alcohol fuel cells (DAFCs)

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**Abstract** - Direct alcohol fuel cells (DAFCs) are electrochemical devices that to be fed directly with alcohol fuel to undergo electrochemical oxidation producing electricity. The most famous among all DAFCs types, are direct ethanol fuel cells (DEFCs) and direct methanol fuel cells (DMFCs) as both liquid ethanol and methanol have high energy density and low cost. Ethanol and methanol are oxidized in DEFC and DMFC respectively producing electrical energy. The most complicated challenge for DMFC and DEFC operations are the slow kinetics of both oxygen reduction at the cathode and fuel oxidation (ethanol or methanol) at the anode. Thus, finding a catalyst material able to accelerate such reactions was the main objective for researchers and manufactures interested in fuel cell technology. In this work, it is hoped to review the pioneering research work done for more than 15 years to satisfy this ambition. Pt alloys and recently Pd alloys have the biggest fortune in this research theme.

**Keywords** - *Ethanol/Methanol Oxidation, Oxygen Reduction, Platinum/palladium catalysts*

## I. INTRODUCTION

A fuel cell is an electrochemical device that continuously and directly can convert the chemical energy of externally supplied fuel and oxidant to electricity. The five most common fuel cell technologies are polymer electrolyte membrane fuel cell PEMFCs, alkaline fuel cells AFCs, phosphoric acid fuel cells PAFCs, molten carbonate fuel cells MCFCs, and solid oxide fuel cells SOFCs [1]. The differences among all fuel cells systems could be revised to using variable electrolyte and fuel types. For instance, while the electrolyte for PEMFC is acidic, it is alkaline for AFCs.

This article focuses basically on the fuel cell operation and materials. It is organized as follows, introducing them; the modern economic and environmental impacts of fuel cell application are highlighted. Then, we give in-depth review on the operation of direct alcohol fuel cells DAFCs.

engine [7]. Adding the advantage of being friendly to the environment, fuel cells must be the objective of academics and governments. Since the fuel cell process is a combination of an electrochemical

Special attentions are given to direct ethanol fuel cells DEFCs and direct methanol fuel cells DMFCs. Also, the oxygen reduction reaction ORR is considered in both of them. Thirdly, we investigate the catalyst materials used for improving the electrochemical reactions. Material alloys based on platinum and palladium, are specially thought. Finally, the methods of synthesis used to amalgamate the catalysts.

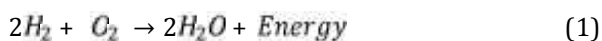
During the 20<sup>th</sup> century, fuel cells have been found hopeful as energy sources for diverse applications [2]. Hospitals, shelters, centers for elderly care, hotels, offices and schools have used more than 2500 fuel cell systems, which may be connected to the grid to supply additional power for the plant [3], or independent from the plant and will supply the whole required power [4]. Even for telecommunications and information systems purposes fuel cells have proved reliability about 99,999% thus they can compete with batteries producing power range 1-5 kW and can be used to feed DC power for telecommunications switching nodes, transmission towers, reception or other electronic devices [5,2]. Concerning buses, fuel cells have been used extensively during the last 8 years to supply buses power. The buses – powered by fuel cells - have exposed high efficiency as H<sub>2</sub> is produced from fossil fuels and hence reducing the CO<sub>2</sub> emissions and help reduce the noise contamination in large cities [2]. Moreover, motorcycles manufacturers currently use fuel cells to drive them [6].

The fuel cell can produce electrical energy continuously and directly due to the electrochemical reactions (fuel oxidation and oxygen reduction) and the energy conversion efficiency is high compared to the traditional methods of converting the chemical energy into heat – sometimes the efficiency is doubled - like internal combustion

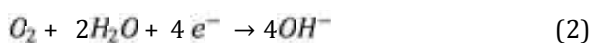
oxidation (of the fuel at the anode), and reduction (of the oxygen at the cathode), this processing does not result in formation of any pollutants. Moreover, the fossil fuels are the main sources of

energy productions during the last two centuries, however they are non-renewable sources inspiring the researchers to answer the challenging question; "what produces energy when these sources finish?" Beyond that, it is necessary to find new sources of energy which should be friendly environmentally [8]. Fuel cells are suitable energy source for portable devices as they have higher energy density, durability, simple design, and low cost [9].

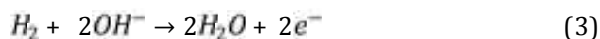
Although fuel cells and batteries share the same working theory depending *faradaic redox* reactions, there is crucial difference between them in application. While batteries are used to store energy, fuel cells are energy converters. After, the energy stored in battery is finished; a new one is required for application instead; except some battery systems known as "secondary" that can be recharged. On the other hand fuel cells convert chemical energy into electricity as continuously as they are supplied by fuel. Fuel cells are much lighter and durable than batteries [10]. For instance direct methanol fuel cells DMFCs have been used widely in space application because of the longer life time than lithium ion batteries. Companies like Panasonic, Samsung, Toshiba, NEC, etc have manufactured DMFC. Panasonic seeks to produce portable generator – by combining fuel cell and lithium ion battery – with a 100 V output which will be more compact than engine-based generator [11]. T. Burchardt et al. [12] have studied the recent contribution and current limitations to AFCs. The working theory of a fuel cell involves the H<sub>2</sub> oxidation and O<sub>2</sub> reduction as follows:



The alkaline oxygen reduction can be represented by:



While the hydrogen oxidation reaction can be:



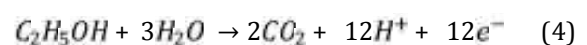
## II. DIRECT ALCOHOL FUEL CELLS (DAFCS)

Direct alcohol fuel cells (DAFCs) are new energy source that recently became the focus of research attention. They belong to the family alkaline fuel cells AFCs. The ACFs grasped the academics attention from 1960 to 1980 [13]. Liquid fuels such as low molecular weight alcohols, have several advantages compared to pure hydrogen. First, they can be handled, stored and transported easily. Second, they have considerable higher energy densities compared to that of gasoline. Although

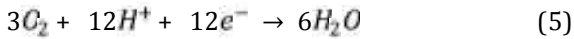
the AFCs can produce higher exchange current densities than polymer exchange membrane fuel cells PEMFCs, PEMFCs use solid electrolyte and avoid the electrolyte leakage [14]. Conversely, AFCs have lower cost and corrosiveness and they can use non-noble metal as catalysts for the reaction acceleration especially for the oxygen reduction reaction ORR [3]. The oxygen reduction reaction (ORR) kinetics occur faster in case of alkaline medium more than acidic one [15,16]. The faster ORR kinetics affords the use of non-noble metal catalyst like silver, and nickel proposing a reduction of the cell cost. The DAFCs severe problem is related to CO<sub>2</sub>, which may come from the air entering to cathode or result from the fuel oxidation reaction in the anode. Using an acidic membrane electrolyte in the current DAFC system, argues for CO<sub>2</sub> formation in the anode reaction. CO<sub>2</sub> causes the progressive carbonation of the alkaline electrolyte which leads to the application of alkaline anion exchange membrane AAEMs or AEM-DAFCs [17,18,19]. The direction of ion transport species in case of alkaline (OH<sup>-</sup>) is opposite to that species in case of acidic one (H<sup>+</sup>). The direction reverse reduces the fuel permeation rate through membrane. Direct Alkaline fuel cells AEM-DAFCs have some advantages than traditional AFCs; i) no mobile cation (no precipitated carbon), ii) no electrolyte sweeping, iii) reduced alcohol cross over rate, and iv) simple water management, and v) reduced corrosion [20]. One of the main feature advantages of DAFC is the low working temperature which makes them suitable for vehicle application [21].

### A. Direct Ethanol Fuel Cells (DEFCs)

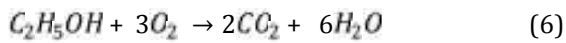
Direct ethanol fuel cells are a DAFC type that uses ethanol as the fuel to be oxidized in the anode. The ethanol has been used recently in fuel cell as it has higher energy density compared to methanol, less cross over rate (from the anode to cathode), and can be produced from agriculture and biomass products [22]. The complete oxidation of ethanol molecule to CO<sub>2</sub> involves the release of 12 electrons and the cleavage of the C-C bond, which is between two atoms with little electron affinity or ionization energy, thus making it difficult to employ low temperature [23]. The anodic ethanol oxidation and cathodic oxygen reduction reaction can be represented as follows: while the ethanol would be oxidized in the anode according to Eq. (4),



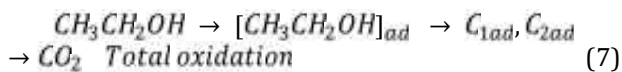
The oxygen reduction reaction shall run as illustrated by Eq. (5)



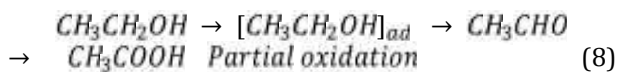
And the global reaction of the cell can be illustrated by Eq. (6),



Indeed, the ethanol oxidation is not fully interpreted as it may be oxidized totally or partially, which can be represented by eq. (4), and eq. (5) respectively. Questions can be asked like, "Is the acetic acid formed in one step through aldehyde?" And "What is the nature of the adsorbed species?" Such questions need more thought endeavors to be responded. These questions were answered by Liang et al. [24] who have shown the acetate is the final product and acetaldehyde is an active intermediate. The content of the carbonate ions indicated less than 5% of ethanol was converted to carbonate ions.



The oxidation that usually happens is the partial oxidation shown in eq. (8).



The C<sub>1</sub> and C<sub>2</sub> which are produced as intermediates before CO<sub>2</sub> represent fragments with 1 and 2 C- atoms respectively. Some previous research examinations have argued that the C-C bond is preserved so that a larger quantity of the intermediates type C<sub>2</sub> will be formed [17,18] although others declare that the biggest part of the intermediates belongs to the single carbon atom C<sub>1</sub> type [19].

Previously, R. Alcalá group [25] reported that ethanol reacts on pure Pt to produce CO, CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> due to the C-C bond cleavage, but recently [26] they have found that Sn addition to Pt catalysts inhibits the decomposition of ethanol to CO and CH<sub>4</sub> owing to the C-C cleavage suppression. In DEFC experiments, Rousseau et al. have found the Sn addition both increases the EOR activity and changes the product distribution increasing the acetic acid and reducing the CO<sub>2</sub> and acetaldehyde [27]. That can be explained as the CO<sub>2</sub> formation needs more adjacent Pt sites for the dissociative ethanol oxidation and the Sn addition among Pt atoms does not favor this reaction and the acetaldehyde can be adsorbed on the Pt sites as Pt-CH-CO<sub>3</sub> species leading the OH species formation due to Sn is known to activate water at lower potential more than Pt.

At low current densities, only the activation losses are significant while the diffusion (concentration)

and ohmic losses are negligible so that the kinetic parameters can be determined easily. In case of using pure O<sub>2</sub> instead of air, the diffusion losses are practically eliminated and only the ohmic and activation losses will remain. Hence particle to particle and particle to current collector resistances can be measured through the conductivity of electrode [28]. The ethanol can be used *directly* (DEFC application) or *indirectly* in fuel cell as it can be used for the H<sub>2</sub> supply for H<sub>2</sub>/PEMFC system since it is rich of hydrogen [29]. The electro-oxidation of ethanol involves more intermediates and pathways more than that of methanol, hence appears the need to more active catalysts at lower temperature. The nature and structure of the catalyst have dominant effect on ethanol adsorption and oxidation and the preparation method also define that structure of the catalyst [16].

Many research labors have been forwarded to the definition of the ethanol oxidation reaction intermediates and used many techniques to characterize them like different electrochemical mass spectroscopy DEMS, in *Stiu Fourier transform infrared spectroscopy FTIRS*, and electrochemical thermal adsorption mass spectroscopy (ECDTMS) [30,31,32,33]. Several studies have been made to investigate the possibility of ethanol oxidation in alkaline media [34]. Generally palladium and platinum are used as a catalyst-base for ethanol oxidation in alkaline media. C. Xu et al. [35] have studied the ethanol oxidation on Pt/C and Pt-CeO<sub>2</sub>/C catalysts in alkaline medium. The optimum composition was found Pt: CeO<sub>2</sub> 2:1 with platinum loading 0,3 mg cm<sup>-2</sup>. That could be explained as CeO<sub>2</sub> have the same of Ru in Pt-Ru/C catalysts, while it helps to form easily the oxygen containing species on CeO<sub>2</sub> surface. As the oxygen containing species can transform CO-like poisoning species into CO<sub>2</sub> on Pt surface. The same group prepared Pd/C promoted with non-crystal oxides (CeO<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub>, Mn<sub>3</sub>O<sub>4</sub> and NiO) catalysts by the intermittent microwave heating IMH [36]. These electro-catalysts showed better EOR performance and more prominently the onset potential for Pd-NiO/C was shifted 300 mV negatively compared to Pt/C. The same result was concluded by Hu et al [37]. Bai et al. have concluded that the electrocatalytic activity of Pt-ZrO<sub>2</sub> is higher than Pt/C for EOR in alkaline media and the lowest onset potential was achieved by catalyst composition Pt(1):ZrO<sub>2</sub>(4) [38]. Pd catalysts supported on carbonized TiO<sub>2</sub> nanotube were prepared by Hu et al. [39]. They found that Pd/TiO<sub>2</sub>C (with atomic ration Pd: TiO<sub>2</sub>C=1:1) have EOR activity and stability during constant current polarization in alkaline media. Xu et al. [40] investigated the Pt- and Pd- based catalysts promoted with metal oxides CeO<sub>2</sub> and NiO in alkaline media. They realized that higher activity for

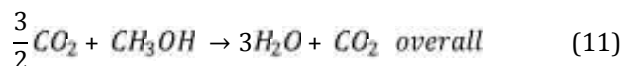
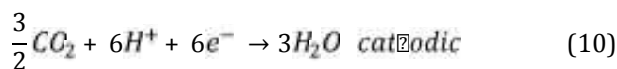
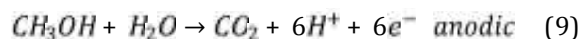
Pd-based catalyst and the highest values went for noble metal – CeO<sub>2</sub> (2:1), and noble metal – NiO (6:1). The oxide function is the same as that of Ru with Pt-oxide and Pd-oxide because OH<sub>ad</sub> species could form on the oxide surface. The OH<sub>ad</sub> formation can transform the CO-like poisoning species on the metal surface to other products at lower potentials.

#### B. Direct Methanol Fuel Cells (DMFCs)

Methanol is the most common alcohol to be used in DAFCs and it was used essentially with the acidic medium PEMFC. Methanol has fascinated fuel cell researchers and manufactures because it is renewable energy source, easily stored and handled, and eagerly available [41]. Platinum from all pure metals has shown the best catalytic performance for methanol oxidation reaction MOR both in alkaline and acidic media. In both methanol oxidation reaction MOR and ethanol oxidation reaction EOR, the leading intermediate product is CO, while other surface intermediates are detected like small C1, and C2 molecular ethoxyl and acetyl [42,43]. During DMFC operation methanol is oxidized producing CO<sub>2</sub> and protons at the anode [44]. In alkaline solution, the activity of MOR is enhanced due two main reasons; first the lack of specifically-adsorbing spectator ions, and second is the higher coverage of the adsorbed OH at lower potential. [45]. The rate determining step in MOR is that involving a reaction of the adsorbed intermediates, e.g. CO or CHO, and adsorbed OH [46]. Yet, the final product of MOR in alkaline media is not well justified. A dual path reaction mechanism was proposed by Tripkovic et al [47]; HCO is produced in the main reaction path and CO<sub>2</sub> is produced – from the poisoning species – in the parallel path. Moreover, Tripkovic et al [106] prepared Pt (111) catalyst for methanol, ethanol, and n-propanol electrooxidation. They noticed the reversible OH<sub>ad</sub> formation is faster than irreversible OH<sub>ad</sub> species, which could be generated only during the time-dependent adsorption.

Although the high methanol concentration increases the energy density, it increases the methanol cross over rate from anode to cathode and hence reducing the cell performance. Electrochemically, the methanol molecules will diffuse through the electrolyte to cathode and will be oxidized there by oxygen molecules. In his review article, A. M. Zainoodin argued that the methanol concentration, temperature, and water, and CO<sub>2</sub> extents vary with time in a *passive* DMFC (DMFC without fuel pump and air power) [48]. Kuver et al. have shown the maximum operating voltage goal can be achieved by the light methanol

feed rate below 50% by volume [49]. On the other hand the cathode performance is not affected by increasing the methanol concentration in the anode and the cross over is present at low concentrations. The methanol oxidation reaction has poor kinetics [50]. The DMFC reactions can be represented in Eqs. (9), (10), and (11).



Both DMFC anode and cathode reactions are irreversible and hence they suffer from over-potential phenomena [51]. The anodic methanol oxidation procedure entails the formation of CO, which adsorbs strongly on the Pt-catalysts surface raising the potential more than the needed thermodynamic value to obtain reasonable reaction rate [46]. Due to the poor electrode kinetics, a higher anodic positive potential (over-potential) and a higher cathodic negative potential are required to draw a current from a DMFC [20].

#### C. Oxygen Reduction Reaction (ORR)

The oxygen reduction reaction is very sluggish due to the fact that each single oxygen molecule needs 4 electrons to be reduced while the simultaneous transfer of those electrons from anode is intricate. Meanwhile, a partial electron transfer occurs leading to the formation of surface intermediates. Therefore it appears the need for a strong catalyst aiming to stabilize these intermediates and lets the reaction proceed at reasonable speed [46]. The multi-electron-charge transfer kinetics – associated with oxygen reduction reaction – depends on the catalyst surface structure and the electrolytic solution [52,53]. Therefore, many publication papers tried to deduce the minimum Pt catalyst usage combined with the maximum performance of it through the control of the structural arrangement [54,55,56,57]. In their recent article, D. M.-Casillas et al. [58] have considered the main disadvantages of the PEM fuel cell are the high over-potential in the cathodic oxygen reduction and the consumed noble - Pt amount at the cathode to achieve higher current densities, and they synthesized ternary catalysts of Pd, Pt, and Cu aiming to eliminate those drawbacks. Moreover other efforts were contributed to minimize the Pt content without decreasing the catalytic activity through the synthesis of binary Pd-M (M=metal) catalysts like PdCu and PdSn and the resulting effect was revised to the *d*-band property

that accelerated the ORR dissociative adsorption during the rate determining step [52,59,60].

Considering the facts that the noble Pt catalyst is raising the fuel cell cost and the cathodic Pt-loading and consumption are high, there is a need to innovate alternative catalysts that can be used as cathode catalysts. Fe and Co ions are among those alternatives [61]. The carbon support nature was justified to affect the ORR activity [62] and the peroxide release [63] while using Fe-N/C catalysts. The iron acetate species were adsorbed and various C supports and then polarized at high temperature in  $\text{NH}_3$ . A conclusion was drawn with a higher N content the higher ORR activity and lower peroxide release. Upon reaction with ammonia, some support species are rich with  $\text{NH}_3$  while others have poor contact with ammonia leading a conclusion the higher N content is favored for raising the activity [64]. J. Herranz et al. [61] have shown that all what is wanted for ORR is a micro-porous carbon support bearing the N-functionalities and can coordinate the position of the Fe- or Co ions. They used a single heat treatment step (in the classical synthesis method) to produce a carbon support doing 3 functions; 1- the gasification of disordered carbon (producing micro porous host sites), 2- the addition of surface N-bearing functionalities, and 3- the coordination of Fe or Co ions.

### III. MATERIALS FOR CATALYST SYNTHESIS

There is a great motivation for institutions to develop new catalyst materials for energy application purposes and the key aspect is considered to be the structure-performance relationship which can assist improve the catalytic performance, selectivity and stability at low cost [65,66]. Catalysis is a surface effect, so that a good catalyst acquires a large surface area. Consequently, the active phase is dispersed over a conductive support such as carbon. It has been appreciated that the catalyst activity depends on the particle size and shape, catalyst surface structure, local composition, chemical bonding, and the particle surface-support interaction [67,68].

#### A. Platinum catalysts

For decades, the most recorded material used as electrocatalyst for DAFCs has been platinum and platinum alloys supported on carbon for low temperature fuel cell application. Many papers have tried to address and optimize the use of Pt catalyst for methanol oxidation reaction MOR in acid and alkaline solutions. Petrii et al [69] have compared

the polarization curves for MOR in alkaline medium on both Pt and PtRu catalysts. MOR was running under steady state condition and the ratio Pt:Ru was 9:1. They resulted in the MOR over-potential while using PtRu is 60-70 mV lower than that using Pt. Tripkovic et al [70] have investigated MOR kinetics on supported Pt and PtRu (Pt:Ru atomic ratios 3:2 and 2:3) catalysts in 0.5 M  $\text{H}_2\text{SO}_4$  and 0.1M NaOH at 22° and 60° C. The PtRu activity for methanol oxidation at room temperature was slightly better than Pt suggesting the promoting effect of OH species. Kardigan et al [71] prepared Pt-Pd alloy catalysts for MOR in alkaline, acid, and neutral solutions. In alkaline, the maximum noticed exchange current density was recorded for catalyst containing 15% Pd, while this value is 10 times higher for pure platinum. On the other side, for neutral and acid media, there was no such maximum and the exchange current densities were reduced monotonically from pure Pt to pure Pd.

While using Pt catalysts, the major problem was the C-C bond aiming the complete oxidation of ethanol to  $\text{CO}_2$  which involves the partial oxidation products of  $\text{CH}_3\text{CHO}$ , and  $\text{CH}_3\text{COOH}$  [72,73]. The reaction parallelism produces undesirable materials and reduces the electricity from fuel. On the other hand Pt can be poisoned easily with the strongly adsorbed species coming from the dissociative ethanol adsorption [74]. So that the co-catalysts are proposing better behavior to reduce species adsorption on Pt surface like Ru, and Sn. On the intrinsic mechanism clarify the presence of Ru and Sn modifies the electronic structure of Pt, resulting changing the adsorbed oxygen-containing species.

The crystal structure of Pt is face centered cubic *fcc* and of Ru is hexagonal close packed *hcp*. Pt and Ru form solid solutions by the replacement of some Pt atoms by Ru atoms in the lattice points of the *fcc* structure. W. Zhou et al. have presented several binary and ternary based catalysts on Pt for the ethanol oxidation [29]. This study has concluded that the addition of W and Mo can increase the activity of  $\text{Pt}_1\text{Ru}_1/\text{C}$  for ethanol oxidation and has proved that  $\text{Pt}_1\text{Sn}_1/\text{C}$  has better ethanol oxidation performance than  $\text{Pt}_1\text{Ru}_1/\text{C}$  and other binary Pt- based catalysts [29]. Fujiwara et al. have another view that Ru promotes the ethanol oxidation of strongly adsorbed intermediates to give high yield for  $\text{CO}_2$  formation more than on Pt [75]. Above 0,7 fraction Ru, another solid solution is formed by the replacing the Ru atoms with Pt atoms in the *hcp* Ru atoms. The unsupported Pt-Ru is easily synthesized but the carbon supported bimetallic catalyst does not have the same easiness [76]. The ethanol oxidation mechanism was studied by Schmidt et al [33]. The presence of Ru inhibits the formation of chemisorbed species coming from the dissolved ethanol. Similar result was deduced

about the adsorption of species seems to be inhibited by Ru presence [77]. C. Lee et al. have examined the effect of increasing temperature on ethanol oxidation on Pt/C, and Pt-Ru/C. The authors have concluded the current densities have increased – by raising temperature from 25 to 80°C – 2 times in case of using Pt-Ru/C more than Pt/C and consequently a final argument that Ru addition enhances ethanol oxidation probably due to OH [78]. Along with this result, the addition of IrO<sub>2</sub> can improve even more the EOR if added to Pt-RuO<sub>2</sub>/C. H. Suffredini et al. used fixed Pt-RuO<sub>2</sub>/C composition on boron-doped diamond (BDD) [79]. C. Lamy group observed the lower activity of the Pt-Ru (Pt:Ru = 4:1) for ethanol oxidation at room temperature [80]. This can be explained by the results shown by Camara et al. [77] who proved decreasing the Ru content less than 20% will reduce the ethanol oxidation activity as there are not enough Ru sites for assisting the adsorbed residues oxidation and found also the optimum composition to be Pt:Ru (3:2).

In his review, E. Antolini [81] argued that Pt and Sn form 5 bimetallic intermetallic phases Pt<sub>3</sub>Sn, PtSn, Pt<sub>2</sub>Sn<sub>3</sub>PtSn<sub>2</sub>, and PtSn<sub>4</sub> of which PtSn and Pt<sub>3</sub>Sn are melting compositions while the others are distinguished with unique X-ray diffraction patterns and crystal structures. Kuznetsov et al. [82] assured forming a solid solution between Pt and Sn because the XRD peaks of the *fcc* Pt-Sn are higher than pure Pt and lower than Pt<sub>3</sub>Sn which confirms the incorporation of the Sn atom in the Pt lattice. Pt-Sn/C alloys are usually prepared without thermal treatment and the relative amount of Pt, Sn and SnO<sub>2</sub> affects the electrocatalytic activity [28]. Pt-Sn/C catalysts have higher activity - for ethanol oxidation reaction EOR – more than Pt-Ru/C while the opposite is correct for methanol oxidation reaction MOR [34,41,83]. The Sn amount effect in Pt-Sn catalysts has been studied and contrasting results have been deduced. While Lamy et al. [74] prepared the catalysts with atomic ratios Pt:Sn 90:10 to 50:50 and deduced the optimum performance for the Sn content 10-20%, Zhou et al [29] prepared the catalysts with molar ratios Pt:Sn 66:34, 60:40, 50:50; 75:25, and 80:20 and concluded the best performance for the 33-40% Sn amount catalyst depending on DEFC temperature. Similar conclusion to Zhou was obtained by Spinacé et al. who prepared the PtSn catalysts with different Sn contents by alcohol reduction process using ethylene glycol as a reducing and solvent agent [84]. On the other hand, Jang et al. have deduced higher activity for Pt-SnO<sub>x</sub> more than Pt-Sn for ethanol oxidation revising the fixed lattice parameter in Pt-SnO<sub>x</sub> like Pt is favorable for ethanol adsorption and more probable to remove CO-like species by offering oxygen species in the Pt vicinity [85]. F. Clomati et al. [86] have studied the EOR of

PtSn/C prepared by formic acid (Pt:Sn = 90:10, 75:25, 66:34). They have found that the EOR activity depends both on Sn and SnO<sub>x</sub> states. The rate determining step depends on the reaction temperature. At low temperature (low current density) the rate determining step is determined by the oxidation of CO and CH<sub>3</sub>CO species which is enhanced by SnO<sub>x</sub> presence. At high temperature (high current density), increasing the lattice parameter improves the EOR as the larger lattice parameter should support the C-C cleavage. On the other side, the larger lattice parameter is assisted by the presence of PtSn pairs which are necessary to complete the ethanol oxidation.

The Pt-Sn and Pt-Ru binary and ternary catalysts have achieved superior performance for methanol oxidation due to the bi-functional effect (promoted mechanism), [87,88] and to the electronic interaction between Pt and alloyed metals (intrinsic mechanism) [89,90]. The promoted mechanism shows that the presence of Ru and Sn oxides facilitates the oxidation of the strongly adsorbed oxygen-containing species more than the case of using single Pt at lower potential.

## B. Palladium catalysts

The introduction of alkaline electrolyte has a very good advantage which is the use of non-noble metal (which can survive longer time in alkaline more than acidic medium) as catalyst for alcohol oxidation reaction in DAFCs [91]. Recently, palladium has grasped high interest from academics to be alternative of platinum as a base catalyst material as it has shown the best catalytic performance as pure metal used ethanol electrooxidation catalysis. Moreover Pd has shown higher activity for alcohol oxidation reaction in alkaline medium than platinum in acidic one [92,93,94]. Pd is available 200 times more than Pt so that Pd price is 30-40% that of Pt. Consequently, it is very interesting to use Pd as a base catalyst material due to the ambition to reduce the large fuel cell application [17,36,95]. Furthermore, palladium from all pure metals has been proved more active for ethanol oxidation reaction EOR in alkaline medium. Many research papers reports that Pd-catalyst is more efficient than Pt for ethanol oxidation reaction and oxidation reaction also. Z. Zhou et al have combined the Pd catalyst with alkaline medium to oxidize ethanol [96]. V. Bambagioni et al have deposited Pd particles spontaneously on nickel –zinc materials to activate the ethanol electrooxidation in alkaline electrolyte [97]. C. Bianchiniet et al. [98] have also prepared Pd catalyst to be used for alcohol oxidation in fuel cells and direct ethanol fuel cells. J. Varcoe et al

have found that Pd catalyst in alkaline electrolyte has superior activity for oxygen reduction reaction [18]. Moreover, Pd catalysts have demonstrated higher ability than Pt for breaking the C-C bond in ethanol oxidation reaction.

The PdNi/C and the PdSn/C are the most famous two catalyst compositions for fuel cell application. Bambagioni V. et al. has shown that PdNi catalysts have superior performance than the monometallic Pd because Ni is oxophilic like Ru, which has the capacity to generate  $\text{OH}_{\text{ads}}$  at a lower potential and facilitates the oxidative desorption of the intermediate compounds [97]. Furthermore, the surface Pd-Ni alloy and NiO or NiOOH species can modify the adsorption capacity toward ethanol, and provide an oxygen source for CO oxidation at lower potential [99]. Z. Zhiyong et al. have shown that Ni refreshes the Pd- active sites [94]. The  $\text{Pd}_x\text{Ni}_y/\text{C}$  compositions have been investigated and proved to increase the EOR activity [100,101] although it does not increase the  $\text{CO}_2$  selectivity [102]. Furthermore S. Shen et al. used the simultaneous reduction method to synthesis PdNi catalysts and concluded the superior activity comes with  $\text{Pd}_2\text{Ni}_3/\text{C}$  composition towards EOR in alkaline electrolyte [103]. The PdSn binary catalysts supported on carbon and have proved higher activity than single Pd catalysts [8]. F. Hu et al. have shown that Pd-NiO catalysts have better catalytic performance for ethanol oxidation than Pt-NiO ones [39]. The same group has found that the carbonized  $\text{TiO}_2$  nanotube can significantly improve the Pd-based catalyst for ethanol oxidation in alkaline medium [40].

#### A. Other catalysts

Noble (Au) [104] and non-noble (Cd, Pb, Bi, Ti) [46] ad-atoms were investigated as MOR in alkaline media. When these metals are present in alkaline solutions at low concentrations, methanol oxidation on Pt electrodes is enhanced in the low potential range. At higher ad-atoms concentrations, is suppressed due to excessive coverage by foreign ad-atoms. The ad-electrode of AuPt presented the same electrocatalytic characteristics of AuPt alloy electrode. Thus, it shows the important role that ad-atoms can play. Another catalyst type is the perovskite structure to advance MOR in alkaline electrolyte on Pt. The perovskite-modified ( $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$  and  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ) Pt/C electrode were more active than Pt/C electrode in alkaline solution. The improvement can be revised to the perovskite structure which can form active platinum oxides/hydroxides, providing oxy-species at less positive potentials [105].

For methanol oxidation, nickel is considered promising Pt-alternative in alkaline solution. When Ni gets in contact with aqueous solution, the surface would be covered by  $\text{Ni}(\text{OH})_2$ . According to [106] the oxidation state of nickel changes between +2 and +4 in a range of potentials. On the other hand, the oxidation of primary alcohols at Ni/NiOOH electrode will form organic acids. It was found the methanol oxidation in alkaline electrolyte commences in the potential range where multi layers of NiOOH have been formed on the electrode surface. It occurs on two steps; formate formation in the range 0.36-0.44V (vs. SCE), followed by further oxidation to carbonate at potential range above 0.45V. Recently, a titanium supported nano-scale catalyst (nano Ni/Ti) with flaky structure was prepared by Yi et al. [107]. Both the cyclic voltammetry and chronoamperometry results have shown higher performance for nano Ni/Ti than polycrystalline Ni.

#### IV. CATALYST SYNTHESIS METHODS

Calegro et al. [108] used the sol-gel method to incorporate ruthenium and iridium oxides, either alone or combine, on a carbon supported platinum with 25% in their total mass related to the Pt amount. This study has proved that the Pt-RuO<sub>2</sub>/C have better performance for ethanol oxidation more than commercially Pt-Ru/C and Pt/C. Lamy research group used the co-impregnation reduction and the Bonneman's methods to prepare Pt-Sn/C catalysts [109]. But Xin group used the modified polyol process to prepare the same catalysts [85]. Song et al used two methods to synthesize Pt-Sn catalysts; the polyol process (by simultaneous deposition of Pt and Sn on the carbon support), and the Sn deposition on prepared Pt/C catalyst [110]. The authors concluded at low current densities, the two methods prepared catalysts have similar performance, however when current density increases, the performance of the catalysts prepared by polyol becomes inferior to that of deposition. They attributed that to the higher Sn content in the polyol prepared catalyst leads to higher internal resistance, while Sn deposition on Pt/C can hinder the Pt active sites complication the species adsorption of ethanol oxidation EOR and lowering the performance. However, the EOR activities of Pt/C, PtRu/C (1:1), and PtSn/C (3:1) have been compared by Colmenares et al. [111] who have shown that commercial Pt/C catalysts have higher EOR activity than PtRu/C and PtSn/C polyol type. The impregnation/reduction method was used to prepare the Pd, Ni, and Sn bi-metallic catalysts supported on Vulcan carbon (XC-72) functionalized with  $\text{HNO}_3$  to prepare nano-catalyst materials [112,113]. The borohydride reduction

process was used successfully by J. Pascual et al. [55] to prepare spherical powder agglomerates composed of Pd<sub>45</sub>Pt<sub>5</sub>Sn<sub>50</sub> catalyst with particles less than 100 nm containing crystallites about 6 nm in size and this catalyst has proven high activity for oxygen reduction reaction ORR. R. Allen et al. [44] have fabricated Pt-based catalysts deposited on titanium mesh by thermal decomposition and electro-deposition of metal salt precursors. Their objective was to replace the carbon support with titanium mesh. The titanium mesh has shown promising use as a support for the catalyst for methanol oxidation in acidic medium.

## CONCLUSION

The materials used to catalyze ethanol and methanol oxidation reaction in the fuel cell anode have been assessed. Also, the catalyst materials for oxygen reduction reaction were thought in this review. Based on this study, the ethanol oxidation reaction is more complex than methanol since it contains C-C bond which is not easily broken. Pt alloys form the major part to catalyze ethanol and methanol reactions, and oxygen reduction reaction also. Another conclusion, with the introduction of alkaline medium for DEFC and DMFC, it became possible to use non-noble metal as catalyst instead of platinum. Pd alloys have shown higher catalytic activity than Pt alloys for ethanol and methanol oxidation reaction in alkaline electrolytes. On the other hand, more research endeavors shall be run to facilitate the sluggish kinetics of the oxidation of ethanol and methanol and the reduction of the oxygen reduction which is slower than methanol/ethanol oxidation. Hence, the performance DEFC and DMFC can be enhanced by increasing the catalytic activity.

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