



## Review Article: Direct Ethanol Fuel Cells as a Renewable Source of Energy



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### Abstract

An overview is reported about the history of prevailing direct ethanol fuel cells (DEFCs) as a renewable green source of energy. The review discussed the important features affecting the electrocatalytic performance of DEFCs. These features include: (1) operating DEFCs in alkaline media, (2) development of a suitable preparation method or technique of the catalyst to achieve more favorable dispersion and smaller particle size, (3) employing high surface area supports, (4) combining the catalyst with another metal, metal oxide, metal carbide or nitride, (5) addition of additives in the coating bath; on

*Key Words:* Fuel cells, Ethanol oxidation, Electrocatalyst, Alkaline media, Preparation methods, Supports

### 1. Introduction

A fuel cell is an electrochemical device that can directly convert the chemical energy produced by a fuel and oxidant into electricity without the efficiency limitations of the Carnot cycle inherent to internal combustion engines. A fuel cell can be thought of as a battery, only unlike a battery, the reactants flow continuously, and as long as they are supplied, there is no interruption in the power produced.

There are many different types of fuel cells according to their electrolyte or catalyst used. Direct ethanol fuel cells have drawn increasing attention because ethanol is a carbon neutral, sustainable fuel and possesses many unique physicochemical properties including high energy density (8 kWh/kg vs 10 -11 kWh/kg for gasoline, less toxic, ease of transportation, storage & handling as well as low price (from fermentation of biomass). Moreover, one mole of ethanol generates 12 electrons (for every mole oxidized) whereas only 2 electrons in the case of hydrogen. On the other hand, expensive noble metals are used as electro catalysts in these DEFCs which limit their commercialization.

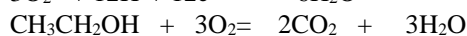
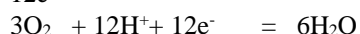
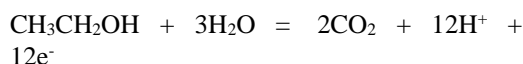
It is therefore of much interest to develop low cost, high efficient electrocatalyst for ethanol oxidation by suitable ways such as : operating DEFCs in alkaline

media, developing a suitable preparation method to achieve more favorable dispersion and nanoparticle size, employing high surface area supports, combining the catalyst with another metal (alloying), metal oxide, metal carbide or nitride, and addition of additives in the electrodeposition bath.

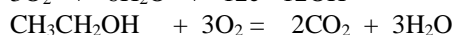
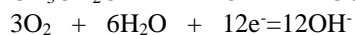
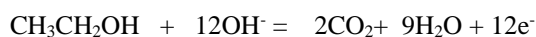
### 2. 2. Operating DEFCs in alkaline media

DEFCs can operate in either acidic or alkaline media according to the following equations:

In acidic medium



In alkaline medium



However, DEFCs that use acidic medium result in rather low performance than that operate in alkaline, even using the same ion conductors and catalysts. Such drastic improvement in performance is basically attributed [1 – 20] to the enhancement of the kinetics

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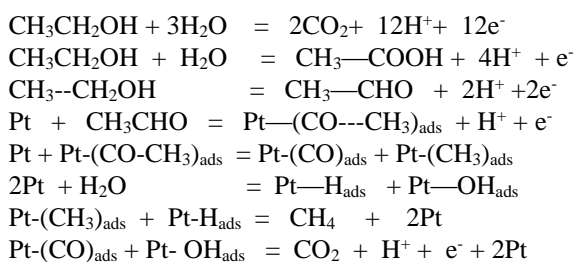
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of ethanol oxidation reaction (EOR) & oxygen reduction reaction (ORR), and increase the ionic transport capability. Other advantages of alkaline DEFCs are: simplicity, low cost, non-corrosive possibility of using non-noble metals as a catalyst and finally absence of electrode poisoning from the reaction intermediates. That is to say, poisoning by either adsorbed CO coming from the ethanol dissociative chemisorption or partial ethanol oxidation forming C<sub>2</sub> products (such as acetic acid or acetaldehyde) is greatly reduced leading to a significant enhancement of the electrode activity.

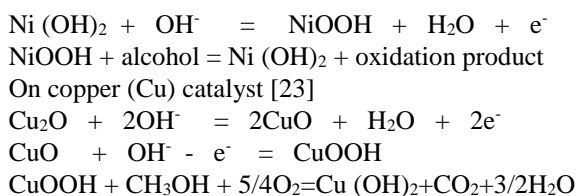
### 3. Catalysts and their role in fuel cells

A catalyst is a material that accelerates the rate of a reaction without itself being consumed in the process. In alcoholic fuel cells, catalysts are necessary to split oxygen molecules at the cathode and breakdown the complex fuel at the anode. In other words, electrocatalyst activates both alcohol chemisorptions and water molecule to provide preferential site for OH<sup>-</sup> adsorption [21] as represented by the following equations in acid medium:

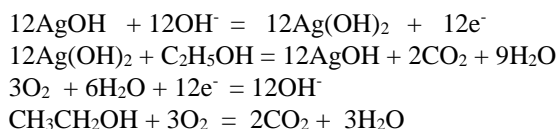


It is also well known that, the electrooxidation of organic compounds, as a general, in alkaline media, requires the presence of oxyhydroxide group [14, 15, 22–25]. The corresponding electrocatalytic mechanisms of alcohol electrooxidation in alkaline media on Ni, Cu, or Ag catalyst electrodes have been represented, respectively, as follows:

On nickel (Ni) catalyst [14, 15]



On silver (Ag) catalyst [24, 25]



The most common catalyst for fuel cells is platinum (Pt) [26–34] and it is typically supported on XC-72 carbon. Palladium (Pd) is also recognized as the most efficient catalyst of the pure metals for the (EOR) in alkaline media. Pd is at least fifty times more abundant than Pt on earth [35]. F. Hu et al. [36] investigated the EOR activities of Pd electro catalysts supported on TiO<sub>2</sub> nanotube and carbonized TiO<sub>2</sub> nanotube. The latter showed the better activity. H.T. Zheng et al. [37] found that the Pd catalyst supported on multiwall carbon nanotube exhibited the best performance than that supported on either carbon black or activated carbon. Xu et al. [35] found that Pd supported on carbon microspheres gave better performance than that supported on carbon black. Y.H. Qin et al. [38] fabricated Pd on three types of carbon nanofibers (platelet, fish-bone & tubular CNFs). Platelet-CNF was the best because it has the highest ratio of edge atoms to basal atoms. V. Bambagioni et al. [39] deposited very small (0.5 – 1.0 nm), highly dispersed, and highly crystalline Pd clusters as well as single Pd sites. The specific activity for the EOR in alkaline media at room temperature was as high as 3600 A/g Pd.

In an attempt to develop low cost less noble electrocatalysts with comparable efficiency towards oxidation of organic compounds, Ag has been considered. Y.Q. Liang et al. [40] found that Ag nanoparticles supported on TiO<sub>2</sub> nanotubes, prepared by the polyol process (reduction method), is an active catalyst for ethanol oxidation. D.G. Guo et al. [41] prepared a highly dispersed Ag nanoparticles on functional multiwall nano carbon tube (MWNCT) surfaces for methanol oxidation in alkaline solution. X. Xinhua et al. [42] prepared carbon black supported ultra-high loading Ag nanoparticles catalyst by modified ethylene glycol reduction method. The catalyst had a considerably stable ORR activity. Y. Yanan et al. [43] fabricated Ag ion implementation modified electrode which showed prominent electrocatalytic activity towards the oxidation of formaldehyde with long term stability in fuel cells. R. Sandra et al. [44] claimed that Ag is a powerful electrocatalyst for organic halides reduction. A. Abdirisak et al. [45] deposited Ag nanoparticles on glassy carbon by a single potential pulse method which have remarkable electrocatalytic activity for the reduction of benzyl chloride. T. Chang et al. [46] synthesized carbon black-Ag hybrid catalysts by a mixing method of acid-oxidized carbon black and the colloidal dispersion of Ag nanoparticles which was pre-synthesized through a chemical reduction of AgNO<sub>3</sub> by dimethyl sulfoxide in the presence of trisodium citrate dehydrate as capping agent. The

results clearly showed that this catalyst is highly active for oxidation of hydrazine. G. Khadige et al [47] fabricated Ag nanoparticles-poly pyrrole nanofiber also for high electrocatalytic oxidation of hydrazine. Chatenet et al. [48] studied the kinetics of sodium borohydride direct oxidation and oxygen reduction in sodium hydroxide electrolyte on Au and Ag catalysts and concluded that Ag exhibits the best activity of all. Wen et al. [49] published a review article on the recent advances in Ag-based heterogeneous catalysts for green chemistry processes including oxidation catalysis & electrocatalysis. In a series of extended program at CMRDI, our group firstly studied the effect of the electrochemical deposition techniques namely: pulsed-current [24] and double-pulse [25] on the catalytic activity and long-term stability of Ag in alkaline media and concluded that: (1) Ag can be used as an alternative active cheap electrocatalyst for DEFCS, (2) both techniques are suitable for synthesizing of Ag catalyst and (3) double-pulse technique shows higher efficiency (40 mA/cm<sup>2</sup> peak current density vs 30 mA/cm<sup>2</sup> for pulsed-current technique). Commercial E-TEK PtRu (2:1 by weight)/C electrode displays only 20 mA/cm<sup>2</sup> peak current density under the same testing conditions [50].

In literature, there have been some attempts to improve the performance of pure metal catalysts by combining with another metal (alloying), metal oxides, metal carbides or metal nitrides [5, 51 – 70]. The enhancement is interpreted on basis of bifunctional mechanism where second metal or oxide providing oxygen-containing species (OH)<sub>ads</sub> needed to oxidize reaction intermediates leaving the domain metal for alcohol electrooxidation.

The most common alloying metals used with Pt in alcohol fuel cells are: Ru, Sn, Fe, Co, Ni, & Cu [71, 72]. Alloying changes the surface characteristic of the catalyst by creating a 2-dimensional alloy metal at the surface of the catalyst. Alloying can also affect the selectivity of a catalyst towards a specific product. Pd have also been combined with metals such as : Au, Pt, Ru, Sn, Ag, Ni, Cu, & Pb [73 – 76]. Pd<sub>4</sub>Au/C catalyst displayed the best catalytic activity for the EOR in alkaline media. Electrochemical results demonstrated that for the PdPb/C catalysts, the Pd<sub>4</sub>Pb<sub>1</sub>/C catalyst gave the highest activity for EOR in alkaline media, whereas it was Pd<sub>1</sub>Ag<sub>1</sub>/C for the PdAg/C catalysts. The promoting effect of the addition of both Pb or Ag could be explained by the bifunctional mechanism and d-band theory. With the addition of Pb or Ag into Pd, the d-band center of Pd can be shifted up and result in more adsorbed (OH)<sub>ads</sub> species onto the catalyst surface, assisting in the removal of the adsorbed ethoxy species.

Enhancement effect of Ag for Pd/C towards EOR in alkaline media was also reported [72]. PdAg/C catalyst was prepared using co-reduction method. A highly active Pd coated Ag electrocatalyst for ORR in alkaline media [77] was prepared by coating carbon supported Ag with Pd via a galvanic displacement method. High EOR activity of Nb-doped-TiO<sub>2</sub> supported PdAg catalyst in alkaline media was investigated [75]. Various mesoporous Nb-doped titania materials were synthesized by a hydrothermal method and examined as catalyst support for PdAg alloy particles. Pd and Ag contents were deposited by a reduction method using ethylene glycol. Zhang et al. [78] demonstrated that incorporation of Ru to Pd with 1 : 1 atomic ratio greatly improves its catalytic activity for EOR in alkaline media with onset potential shift about 150 mV in the negative direction. L. Jou et al. [79] electrodeposited PdCu alloys on indium tin oxide (ITO) and compared their catalytic activities for EOR in alkaline media with that of Pd/ITO. The Pd<sub>9</sub>Cu/ITO catalyst possessed an onset potential of – 0.55V vs MMO, Peak density of 82 mA/cm<sup>2</sup>, and a ratio of 4 of forward peak current density to backward peak current density, while for Pd/ITO catalyst – 0.4 V vs MMO, 17 mA/cm<sup>2</sup> and 1.0 respectively.

Electrocatalytic activity of Ni, as a catalyst, is also markedly enhanced by addition of either boron (B) or molybdenum (Mo): H.B. Hassan et al. [13] evaluated electrodeless Ni-B supported on carbon, with 5 wt.% B for ethanol & methanol oxidation reaction. Ni-B/C catalyst displayed a higher electrocatalytic activity compared to Ni-P/C. The promoting of the alloying B on the oxidation activity of alcohols includes both structural and electronic effect. H.B. Hassan et al. [15] electrodeposited ternary Ni-Mo-P thin films from citrate-based electrolyte onto graphite substrates for EOR. The results showed an increase in the oxidation peak current density of ethanol with increasing the Mo at. % in the deposited alloy films. Also, Ni-Mo-P/C displayed significantly improved catalytic activity and stability compared with Ni-P/C electrode, due to the strong synergy between Ni and Mo and the maximum synergy was found at 5.1 at.% Mo. Ni-Mo-P/C is extensively used for hydrogen evolution reaction and can be used as excellent anode materials for DAFCs

Composites have also been found to be highly beneficial for the activity of the catalysts: C. Xu et al. [80] investigated the activities of Pt-CeO<sub>2</sub>/C for EOR in 1.0 M KOH solution. The results showed that the composite gave the better performance than Pt/C. The weight ratio of Pt to CeO<sub>2</sub> of 2:1 showed the highest electrocatalytic activity. C. Xu et al. [56] prepared

MgO promoted Pt/C electrocatalysts by intermittent microwave heating (IMH) method and characterized the activity towards EOR in alkaline media. Such composite electrocatalysts were superior to pure Pt/C electrode. The highest activity achieved with 4 :1 weight ratio of Pt to MgO. P.K. Shen et al. [5] studied electrooxidation of methanol, ethanol, glycerol and ethylene glycol on  $\text{CeO}_2$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{Mn}_3\text{O}_4$  and NiO promoted Pd/C catalysts in alkaline media. The most significant result is the onset potential for EOR on Pd-NiO/C catalyst which be shifted negatively by 300 mV compared with that of Pt/C under the same experimental conditions. F. Hu et al. [81] prepared NiO supported Pt/C and Pd/C electrocatalysts by IMH method. Results showed that the higher activity and less poisoning of the Pd-NiO/C electrocatalyst than that of the Pt-NiO/C for EOR is possibly due to the lower CO coverage on the Pd-Ni/C which leads to the favorable adsorption of ethanol instead of CO and consequently the less poisoning effect. C. Xu et al. [50] studied the effect of the addition of  $\text{CeO}_2$  and NiO to the Pt/C and Pd/C electrocatalysts on EOR in alkaline media. The electrocatalysts with a weight ratio of Pt or Pd to  $\text{CeO}_2$  of 2 :1 and a noble metal to NiO ratio 6 : 1 showed the highest catalytic activity. The oxide promoted Pt/C and Pd/C electrocatalysts showed a high activity than the commercial E-TEK PtRu/C electrode. C. Xu et al. [82] indicated that the addition of oxides like  $\text{CeO}_2$ , NiO,  $\text{Co}_3\text{O}_4$ , and  $\text{Mn}_3\text{O}_4$  significantly promotes catalytic activity and stability of the Pd/C electrocatalysts for alcohol electrooxidation. The most active catalyst for EOR was Pd-NiO (6 :1, w : w)/C whereas Pd- $\text{Mn}_3\text{O}_4$ /C showed the better performance stability. The poor stability of the Pd- $\text{Co}_3\text{O}_4$ /C is most likely related to the limited solubility of Co oxide in alkaline media. R.N. Singh [54] investigated the catalytic activity of binary and ternary composite films of Pd, Ni, and MWCNTs for EOR in alkaline media. Pd-1%MWCNT-1%Ni composite electrode exhibited the greatest apparent electrocatalytic activity. H.B. Hassan et al. [14] prepared nanocomposite coatings of Ni- $\text{Cr}_2\text{O}_3$  supported on carbon electrodes by electrodeposited technique from Ni Watts bath in presence of  $\text{Cr}_2\text{O}_3$  nanoparticles. Electrocatalytic activity and stability towards EOR was increased with increasing the volume fraction percent of  $\text{Cr}_2\text{O}_3$  up to 7% and better than that of Ni/C electrode. Results were interpreted on the light of higher kinetic parameters such as charge transfer coefficient and charge transfer rate constant in the redox species of Ni at Ni- $\text{Cr}_2\text{O}_3$ /C compared with Ni/C. A higher diffusion coefficient of ethanol as well as a higher catalytic rate constant is obtained at Ni- $\text{Cr}_2\text{O}_3$ /C

(7%). H.B. Hassan et al. [16] also prepared Ni-MgO nanocomposites on carbon anodes by electrodeposition and their performance as electrocatalysts for methanol and ethanol oxidation in alkaline media was compared with Ni/C. The inclusion of MgO greatly promoted the catalytic activity and enhanced its poisoning resistance. The results reveal a lower charge transfer resistance and enhance roughness for the Ni-MgO/C compared with those of Ni/C.

#### 4. Methods of preparation of the catalyst

It is well established that catalyst activity, as a general, is attributed to their size and distribution i.e. narrow size distribution of nanoparticles is required to achieve large surface area to volume ratio concept. However, the development of a preparation method to achieve this is still a challenge. Many approaches were reported [83 – 92] such as: Chemical vapor deposition, arc discharge, laser ablation, wet chemistry, templates, thermal evaporation, electrochemistry, and hydrothermal process.

#### 5. Catalyst supports

The promoting effect of different supporting materials on catalytic activity of the EOR in alkaline media for the Pd-based catalysts was studied intensively, including the commonly used carbon black, carbon nanotubes [54], carbon microspheres [35], coin-like hollow carbon [93], tungsten carbide nanocrystals / nanotubes [94], carbonized porous anodic alumina, carbonized  $\text{TiO}_2$  nanotubes [95], activated carbon nanofibers [96, 97], zeolite graphite and the conducting polymers (PEDOT, PANI and PA6). These forms of supports have extremely beneficial properties [98] such as high surface area, high electronic conductivity, low weight, and anti-corrosion ability.

#### 6. Methods of fabrication of catalyst electrode

Methods for fabricating catalyst electrode are divided into two types: powder and non-powder type. In the powder type method [99 -102] catalyst, prepared by reduction method, and support agglomerates are mixed with Nafion then applied to the graphite substrate. On the other hand, in non-powder type [99, 100, 103] electrophoretic deposition of support followed by electrodeposition of the catalyst on support have been conducted.

#### 7. Effect of additives

It is also reported [104 -106] that, addition of suitable additives to the coating bath, in electrodeposition technique, may change the surface chemistry of metal particles (catalyst) and restrain the aggregate of metal

nuclei. They may also be a kind of capping reagents, which absorb on the surface of the metal particles and lower the surface energy[107]. They are mainly organic surfactants such as :dodecanesulphonate, benzyl mercaptan or poly vinyl pyrrolidone [106].

## 8. Conclusions

Ethanol fuel cells have drawn a considerable attention during recent years as a renewable clean source of energy. A lot of scientific research work has been trying to improve the efficiency of these fuel cells in aspects of cheap catalytic materials in order to achieve good balance between cost and performance. In this respect authors reported different ways:

- (i) Selection of cheaper catalyst materials.
- (ii) Suitable methods or techniques for the preparation of the catalyst, its alloys or composites.
- (iii) Operating the cell in alkaline media.
- (iv) Employing high surface area supports.
- (v) Addition of additives in the electrodeposition bath.

## 9. Conflicts of interest

“There are no conflicts to declare”.

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