

# Analysis of Catalyst Technology in Direct Alcohol Fuel Cell A Review

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## ABSTRACT

Direct alcohol fuel cells (DAFCs) are a type of electrochemical energy conversion device that directly convert the chemical energy stored in a liquid alcohol fuel, commonly methanol and ethanol, and also ethylene glycol, or *n*-propanol, to electricity. Because of their simplicity, high energy density, instantaneous recharging, and presumably long life, DAFCs have been identified as the most promising candidate to replace batteries in micro power applications. The role of catalyst is significant since by modifying the catalyst composition, it was confirmed that the overall electro catalytic activity is greatly enhanced at low potentials as it enables the breakdown of alcohols into proton and electron. Platinum is used as a catalyst for both half-reactions. Even though platinum is being used as a conventional catalyst, modifications like alloying or impregnations of other elements on it enables a better and cost effective catalyst. However, their dependence on expensive Pt-based catalysts for both the anode and the cathode make them unsuitable for large-scale commercialization. This paper deals with the recent evolution of catalyst technology in DAFC. Analysis is made about the anode catalysts and cathode catalyst. Critical analysis of catalyst technology is also made on Nano structures, New Carbon Materials as Catalyst Supports. The effective composition of catalyst is identified and reported as an outcome of the analysis.

**Keywords:** DAFC; Direct ethanol fuel cell; direct methanol fuel cells, Catalyst, Catalyst support.

## I. INTRODUCTION

A fuel cell is an electrochemical energy conversion device which constantly produces electricity using hydrogen and oxygen. Fuel cell on no account goes dead as long as there is a flow of chemical into the cell. Fuel cells generate electricity from an electrochemical reaction between oxygen in air and a fuel to form water. The electricity produced from fuel cells can be used to power all sorts of devices, from cars and buses to laptops and mobiles phones. However there are certain constraints that reduce its performance. Low temperature fuel cells, generally conceived around a proton electrolyte membrane, seem able to be used for a large range of power application. Electro-catalyst materials are a major obstacle for fuel cell technology. Pt catalysts suffer from several drawbacks including slow kinetics, low efficiency, high cost, and limited. Thus, current research is focused on the development of

catalyst materials with low cost [1], high performance [2], high stability, and durability. The basic function of a catalyst layer is to provide a conductive environment for electrochemical reactions. Alcohols mainly methanol and ethanol are widely proposed as possible fuel for mobile application such as electric vehicle. Ethanol offers an attractive alternative as a fuel in low temperature fuel cells because it can be produced in large quantities from agricultural products and it is the major renewable biofuel from the fermentation of biomass. By comparing the performance of fuel cells employing an H<sub>3</sub>PO<sub>4</sub> doped polybenzimidazole membrane and Pt–Ru as anode catalyst operating on various methanol-alternative fuels, Wang et al. found that ethanol is a promising alternative fuel with an electrochemical activity comparable to that of methanol. These reasons motivate investigations on ethanol electro oxidation in order to improve the electrical performances when using it in a direct ethanol fuel cell

(DEFC), and to open the possibility of replacing methanol in a direct alcohol fuel cell. Ethanol is one of the most important renewable fuels contributing to the reduction of negative environmental impacts generated by the worldwide utilization of fossil fuels. By modifying the catalyst used for both methanol and ethanol fuel cell, an efficient DAFC can be formed, which can be used for many portable applications.

## II. METHODS AND MATERIAL

### Catalyst Technology in DMFC

#### A. Anode Catalysts

Pt has been the most effective metal used as Anode. However, pure platinum is not efficient due to poisoning of CO intermediates. According to the dual pathway mechanism [2], the intermediate CO generated in the indirect pathway can be strongly adsorbed on the Pt surface, and the reaction active sites on the Pt become occupied, leading to a severe decrease in reaction kinetics. To address the poisoning by CO, modification of Pt with foreign metals (Me) (e.g., Ru, Ni, Co, and Sn) is necessary. Among the multifarious Pt-based catalysts, the Pt–Ru alloy has been identified to be the most effective for Methanol Oxidation reaction (MOR). Ru could produce active OH at a low potential to react with adsorbed intermediates on neighbouring Pt sites [3, 4]. Recently, by an accelerated degradation test and normal pulse voltammetry, scientists showed kinetic evidence favoring the electronic effect of Ru in the promotion of initial dissociative adsorption of methanol on Pt and weaken the adsorption strength of CO. Recently; considerable efforts have been dedicated to structure optimization to increase the electro catalytic activity of Pt–Ru for MOR [7]. For example, it was reported that the electro catalytic activity of a Pt–Ru catalyst with a Ru-decorated Pt surface in MOR was twice higher for optimised Ru coverage as compared to Pt–Ru black alloy catalysts.

Tsang et al investigated the dependence of the electro catalytic activity of Pt–Ru catalysts on Ru coverage. Page et al investigated Pt–Ni, Pt–Co, Pt–Fe and Pt–Cu catalysts for MOR [9]. They found that Pt–Co/C catalysts were better catalysts for MOR than Pt and other transition metal alloy catalysts. In addition, the CO tolerance of Pt–Co catalysts was recently investigated

and their results showed that the CO adsorption rate for the Pt–Co alloys was much slower than that for pure Pt, which might be attributed to the electronic effect of Co on Pt. Pt–Mo and Pt–Sn catalysts, with high CO tolerance, have long attracted significant attention. In the study of the binding energies and geometries of CO and OH, for Pt–Ru, Pt–Mo and Pt–Sn catalysts [12], the Pt–Mo and Pt–Sn catalysts seemed to be better CO oxidation catalysts than Pt–Ru catalysts.

Experimentally, found that both a Pt 0.8 Mo0.2 alloy and core-shell catalysts showed negligible over potential for oxidation of a H<sub>2</sub>/CO mixture. Until now, Ru has been the most effective metal for improving the CO tolerance of Pt catalysts. However, as Ru is a precious metal with relatively high cost and low production, the development of Pt–Me catalytic systems is beneficial to obtaining low-cost alternative catalysts for MOR.

#### B. Cathode Catalysts

With the cathode, the fundamental challenges are how to address the sluggish ORR kinetics and the methanol crossover. The sluggish ORR kinetics require high loading of Pt in the cathode for acceptable power density. Correspondingly, methanol crossover not only decreases fuel efficiency but also causes mixed potentials due to the occurrence of MOR on Pt. Therefore, the development of low-platinum/non-platinum and methanol tolerant cathode catalysts is highly desired for implementation in DMFCs. Generally, the smaller the Pt particles are, the larger surface area the Pt particles possess, leading to good electro catalytic performance of Pt catalysts. Pt alloys have been studied for many years as an effective tactic to improve the electro catalytic activity of Pt and simultaneously reduce Pt loading. To maximize Pt utilization, the ideal structure of a Pt-based catalyst is where the total available Pt atoms are distributed on the electrochemical reaction interface.

Until now, Pt-based catalysts were considered state-of-the-art catalysts for oxygen reduction reaction (ORR). Nevertheless, from a long-term viewpoint, considering the limited mining capability and prohibitive cost of Pt metal, the development of non-platinum catalysts such as Pd based catalysts, Ru–Se and heat-treated MeN<sub>x</sub>Cy-based catalysts is significant for widespread application of DMFCs. Although Pd-based and Ru–Se catalysts show promise as alternatives to Pt, this is still one

precious metal replacing another. Thus, virtually all non-precious metal catalysts (NPMC) are of interest for large scale and cost-competitive DMFCs. Recently, MeNxCy catalysts have been receiving increased attention due to their reasonable activity and remarkable selectivity towards ORR. MeNxCy catalysts are usually obtained through heat treatment of a mixture of metal salts, carbon, and N-containing molecular precursors.

### C. Technology for Catalyst Support

Among new carbon-based materials, nanotubes are the most investigated catalyst support for low-temperature fuel cells. The highly crystalline structure of CNTs provides high conductivity, surface area and porosity, resulting in exceptional diffusivity. Moreover, CNTs and CNFs have a positive effect on catalyst structure, yielding higher catalytic activity and stability than carbon black. On the other hand, few studies have been conducted on carbon nanohorns, nanocoils and fibers as Pt catalyst supports. A considerable amount of research has been focused on reducing Pt and/or PteRu poisoning and improving the performance of DMFCs. Oxide-supported Au catalysts are promising candidates for the selective oxidation of CO in gas phase reactions. Kim et al.[9] added Au/TiO<sub>2</sub> to a PteRu/C electrode to improve the performance of DMFC, Catalyst performance was improved by the removal and selective oxidation of CO and other poisonous species generated during the oxidation of methanol. Park et al.[17] enhanced the catalytic activity of a PteRueRheNi in a direct methanol fuel cell. PteRueRheNi showed a high oxidation current, power density, and excellent long-term stability in electrochemical half- and single-cell particles on carbon and metal supports. Thus, carbon supports may improve stability, properties, and cost of the catalyst.

### D. Nanostructures as Catalyst Support

Currently, carbon black supports (Vulcan XC-72R, Black Pearls 2000, etc.) are widely used in platinum catalysts. However, recent publications suggest that novel carbon supports, such as ordered mesoporous carbon [3,4], carbon aero and xerogels, carbon nanofibers (CNFs) [5], and carbon nanotubes (CNTs) may improve efficiency of electro catalysts and reduce Pt loading [6,7] and increase surface area of the catalyst. This results to the high reaction area of alcohol and water to produce electron and proton. CNT-supported

electro catalysts commonly exist in unusual shapes and have bulky specific volumes compared to conductive carbon black. As a result, CNT-supported electro catalysts are difficult to fabricate into fuel cell electrodes by conventional means such as painting, brushing [8, 9], spraying [6, 11, 12], screen printing etc. Additionally, high catalyst loadings required for DMFC are also difficult to achieve in CNT-supported electro catalysts [12]. Common obstacles include thick catalyst layers, loose structures in coated layers, poor cell performance, and high ionomer content, leading to high electrode resistance. These problems are exacerbated when catalysts with low amounts of metal and high amounts of CNT are used in the electrode catalyst layer. Innovative solutions for common problems are urgently needed in practical applications. Recently, electrophoretic deposition (EPD) has been investigated as a novel method for fabricating electrodes for membrane fuel cells [13, 14]. This method is generally conducted in non-aqueous suspensions under high-voltage conditions. At present, studies in this field are limited.

## III. RESULTS AND DISCUSSION

### New Carbon Materials as Catalyst Supports

In order to improve the proton transport capacity in an electro catalytic reaction, Nafion solution was added into the catalyst slurry during the preparation of the catalyst ink. The proper amount of Nafion ranged from 10% to 30%. The addition of Nafion can improve proton transport capacity, but it will inevitably cover some of the catalyst active sites, thereby reducing the utilization of the precious metals. To improve the utilization of the precious metal catalysts, the modification of the carbon support is also another useful approach [18]. This not only improves the transport capacity of protons but also reduces the amount of Nafion, which can reduce the cost of the fuel cell. Furthermore, with regard to the carbon support for the oxygen reduction catalyst, in order to allow the product (water) to be quickly and effectively removed from the active sites, and reactant (oxygen) to access the active sites, the carbon supports are required to be hydrophobic. On the contrary, the methanol oxidation catalyst needs a certain degree of hydrophilic support. These can be achieved by the modification of the carbon support. By the combination of new carbon materials and modification of the support, it can be

possible to get an ideal support for electro catalysts. The commercial carbon support, such as Vulcan XC-72R, has a relatively large surface area, good electrical conductivity, and proper particle.

#### IV. CONCLUSION

Alcohols are a hydrogen-rich liquid and have a higher energy density ranging from 6.1 to 8.0 kWh/kg. Also Ethanol can be obtained in great quantity from biomass. Among new carbon-based materials, nanotubes are the most investigated catalyst support for low-temperature fuel cells. The highly crystalline structure of CNTs provides high conductivity, surface area and porosity, resulting in exceptional diffusivity. Moreover, CNTs and CNFs have a positive effect on catalyst structure, yielding higher catalytic activity and stability than carbon black. Technologically significant nanomaterials come in many shapes, sizes and structures. Nanomaterials range from small molecules to complex composites and mixtures. Depending upon the spatial dimensions of the system and properties under investigation, molecular modeling of nanomaterials can be accomplished. This review illustrates a variety of modeling techniques through recent applications. To replace carbon black with carbon nanostructures in catalyst supports, further experiments in fuel cells must be performed to evaluate electrochemical activity and long-term stability of catalysts supported on these new promising materials. Also, We placed our results in context of the state-of-the-art in the development of improved PEM materials for DMFCs, and showed that the proposed approach is comparable to the most promising results available in the literature. We also highlighted the importance of accounting for variations in some of the key experimental methods while comparing results of different researchers.

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