



# Micro- Direct Methanol Fuel Cells: A Brief Review

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## Abstract:

Nowadays the portable power sources have great demand with increase in high energy density. A Micro electrochemical device with high efficiency is realized by keeping the compact size at electrode surface area. A Direct-methanol fuel cells or DMFCs is a renewable source of energy having an ease of liquid fuel storage which operates under room temperature and makes it essentially a potential device. The DMFC has an ability to convert liquid methanol fuel into electrical energy by chemical reaction process, with H<sub>2</sub>O and CO<sub>2</sub> as bi-products. At present DMFCs has a plenty of advantages as well as challenges to overcome, when compared to hydrogen fuelled PEMFCs. This review presents the current status of development of micro-direct methanol fuel cells for power application. The issues regarding the R&D on Design & methanol flow architecture, Micro- channels for flow of methanol, Working principle, Electrode for power output, Methanol diffusion layer, Proton exchange membrane, Proton conductivity, Effect of methanol crossover through membrane, Role of catalyst, Electrical performance of DMFC and applications are addressed.

## 1. INTRODUCTION

In recent years, there is a growing interest in the use of fuel cells for a variety of electronic systems, specially portable systems and electronic products. The benefits of fuel cells include better efficiency, environmentally benign emissions, silent low temperature operation, and modularity of design [1]. The energy density of methanol used in direct methanol fuel cells (DMFC) is much greater than that of compressed hydrogen and also than that of lithium ion batteries. Further, DMFC's are free from hydrogen storage and transportation problems as compared to PEMFC where hydrogen is used as a fuel. Cryogenic storage and safety measures are also not required of DMFC's, since methanol is a fuel [2]. One of the simplest and compact fuel cells is micro fuel cell ( $\mu$ FC) which includes micro proton exchange membrane fuel cell ( $\mu$ PEMFC) and its equivalent micro direct methanol fuel cell ( $\mu$ DMFC). The performance of  $\mu$ PEMFC is generally better than that of  $\mu$ DMFC. However, methanol has the advantage because it can be easily stored, transported and managed. This gives  $\mu$ DMFC a greater advantage in portable equipment [3, 4.]. Recently, micro-direct methanol fuel cells ( $\mu$ DMFCs) have attracted greater attention as compared to traditional Li-ion batteries as power sources because of higher energy density [5]. Among the several factors which contribute to the overall fuel cell performance. Methanol flow dynamics in the micro channels and crossover across in the membranes are important issues to be addressed. High methanol concentration leads to high energy density but also results in severe methanol crossover through the membrane causing a poor potential at the cathode there by lowering cell performance. The flow channel design determines the flow distribution in Micro-fuel cells [6]. The design optimization demands for a better understanding of the flow dynamics since the control of the methanol flow at the micro channel is a critical issue. Cha at al [7] used numerical simulation technique to compare the performance of many designs. Carbon dioxide (CO<sub>2</sub>) bubbles and their transport dynamics in micro-channels is another issue to be addressed in the design of fuel cells. Carbon dioxide (CO<sub>2</sub>) bubbles are generated at the anode of the fuel cells.

Hence, without efficient removal of CO<sub>2</sub> bubbles at the anode, the porous diffusion layer and the flow channel of the DMFC will be blocked. This causes methanol water-solution which is the anodic reactant to poorly distribute to the catalyst site, causing decrease of performance of the DMFC, possibly even causing failure of the device. For investigating the CO<sub>2</sub> bubble dynamics [8]. Lu and Wang [9] recorded the bubble flow in the anode side and water flooding in the cathode side using a video camera. Yang et al. [10] and Wong et al. [11] have also studied CO<sub>2</sub> bubble formation by In situ visualization in anode flow fields. These experimental techniques have become extremely useful to give us an understanding of the bubble dynamics in flow channels. However, when the large numbers of bubbles are released it is difficult to observe the detailed bubble dynamics experimentally within the non-transparent diffusion layers in anode flow fields which are in mm scale. Therefore, flow animation and micro fluidic analysis are good research tools to carry out a study of the bubble dynamics in such a micro-scale environment [12, 13]. On the cathode side, in active systems, the water generated is released into the air/O<sub>2</sub> channels where the two-phase flow plays a major role in water management of DMFC [8]. Hence, the channels should be designed for a low pressure drop in order to avoid excessive parasitic power losses so that the fuel cell would operate in a regime where overall water management of the DMFC is maintained. In this paper, we review some important aspects of  $\mu$ DMFCs which include design of micro channels and electrodes, diffusion layers, catalyst layers and proton exchange membrane.

## 2. WORKING PRINCIPLE OF MDMFC

The working principle of a typical  $\mu$ DMFC is shown in Fig. 1. The  $\mu$ DMFC mainly consists of a flow field having micro channels, a diffusion layer, a catalyst layer and proton exchange membrane (PEM)[14]. The diffusion layers are made up on carbon paper of porous structure. Pt-Ru and Pt are the catalyst used on the anode and the cathode end respectively. The methanol solution is fed at the anode side and oxygen at the cathode side. At the anode region, aqueous methanol

solution penetrates the diffusion layer and uniformly distributes over the surface of catalyst layers which results in oxidation producing proton, electrons and carbon dioxide. The carbon dioxide emerges from the anode diffusion layer as bubbles and is removed by the flowing CH<sub>3</sub>OH solution. Protons permeate to the cathode catalyst layer through proton

exchange membrane. Electrons flow through the external circuit as shown in figure 1. At the cathode region, air or oxygen combines with the protons at the catalyst to form water releasing electrons in the external circuit [15]. The overall electrochemical reaction at the anode and cathode side are as shown in the following equations; [16]

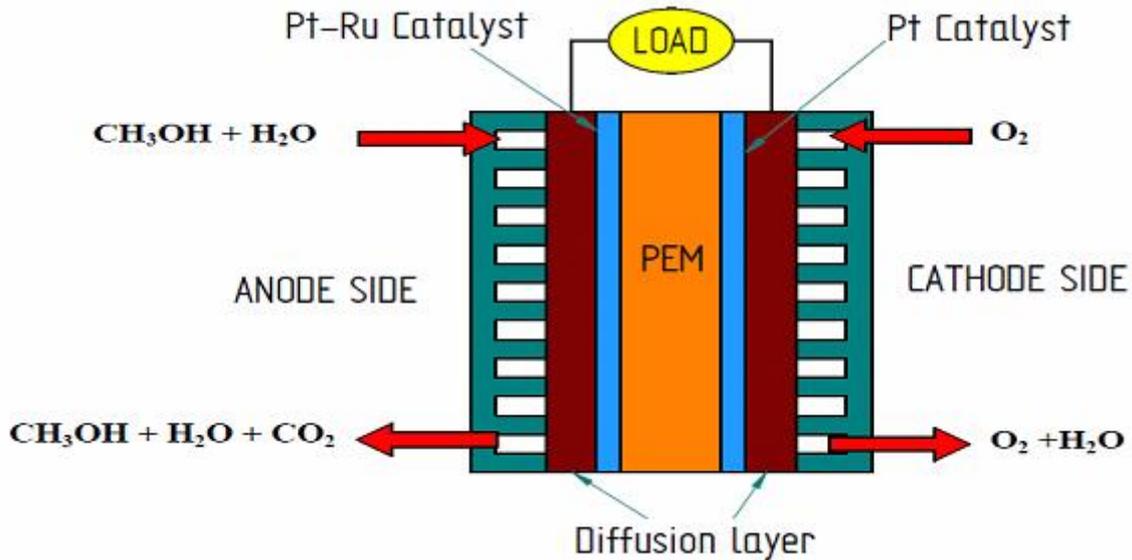
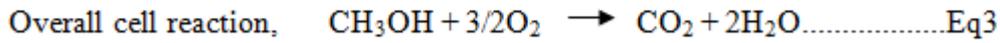
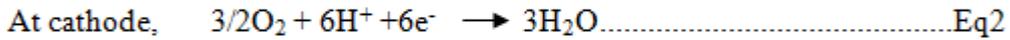
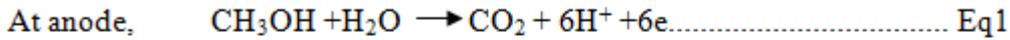


Figure.1. the basic structure of μDMFC

### 3. DESIGN & METHANOL FLOW ARCHITECTURE

#### 3.1 Micro- channels for flow of methanol

The channel design determines the flow distribution in Micro-DMFCs. C.W. Wong, [17] investigated flow field at the anode with parallel and single serpentine having micro channels with active area 1.0 cm×1.0 cm. The experimental results showed that the parallel flow field has less cell voltage than the serpentine flow field. Further, the experimental study indicated that for a given channel width there is an optimal channel depth for serpentine flow field configuration, similar open ratio, when the similar quantity of methanol flow rate is supplied. Lu et al. [18] evaluated the performance of an active fuel cell (active area of 2.25cm<sup>2</sup>) using four different types of flow fields: single serpentine, double serpentine and mixed multichannel serpentine with narrow channels, mixed multichannel serpentine with wide channels. This study describes that μDMFC with double-channel serpentine flow field showed the excellent performance and also μDMFC with mixed narrow multi- channel serpentine flow field indicated the poor performance. Wang et al. [19] evaluated (experimentally and by 3D simulations) the effect of four different types of flow field on an air breathing cell performance such as: double serpentine, parallel, helix and single serpentine (active area of 1.44cm<sup>2</sup>). Simulated results has found that the double serpentine flow field indicates more uniform temperature distribution with better flow velocity distribution, which would lead to a better performance. Further experimental investigation on the four types of flow fields also confirmed that the MicroDMFC with double-serpentine flow field structure exhibits a maximal power density at a variety of

inlet velocities, which is in good agreement with the simulated results. A flow field design with Inputs/Outputs parallel with rectangular convexes (active area of 0.64cm<sup>2</sup>) to reinforce methanol mass transport and reduce concentrate ion polarization was presented by Zhang et al. [21]. Their experimental and simulation studies indicated that fuel cell performance can be enhanced by the use of this flow field scheme.

Zhang et al. [20] also reported a study with a new flow field design (tapered single serpentine with an active area of 0.64cm<sup>2</sup>). Compared with conventional single serpentine design, the new flow field is able to enhance the pressure difference between any of the adjacent flow channels and thus improve the mass transport efficiency. In another experiment different cell configurations with different distances between anodic and cathodic channels in a planar fuel cell were studied by D'Urso et al. [22].

A maximum power density was achieved at room temperature with the smallest distance between anode and cathode (0.25 mm). Similar performance was obtained with the largest distance between anode and cathode (0.5mm) by using 10M methanol concentration at the anode. Serpentine configurations, both single and double, were used in most of the reports. Fuel cell performance improved with this type of channel configurations. Reported results indicated that a new tapered serpentine configuration led to better fuel cell performances than the ones reported for conventional serpentine flow channels. This new configuration appears to be an excellent alternative to conventional serpentine, although,

more work on this issue is needed. A typical micro cell DMFC

is showed in figure 2

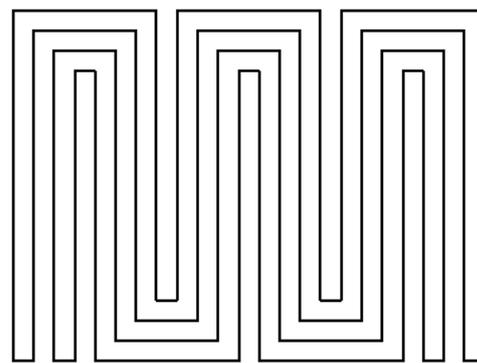
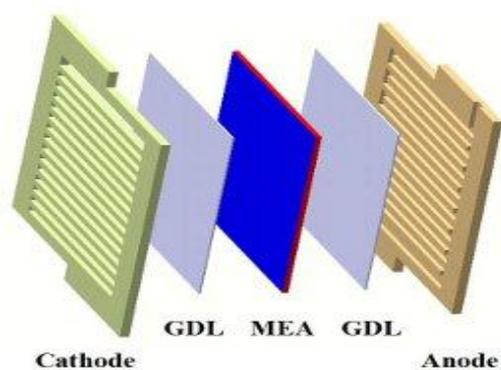


Figure.2.a:-Overall Micro DMFC designs: 2b:- Expanded view of double serpentine flow channel

### 3.2 Electrodes for power output

A DMFC made up of different layers including catalyst layers which enhance the rate of chemical reaction in the cell. The electrodes present at the anode and the cathode side primarily functions as the current collector for the cell. The perforation in the electrodes transport the fuel (Methanol at anode side and oxygen at cathode side) and are also responsible for letting out the waste products i.e. carbon dioxide at the anode side and water at the cathode side. The backing layer at the electrodes provides a better contact between the fuel and the catalyst layer where the chemical reaction takes place. Also backing layer decreases the occurrence of methanol crossover between the anode and cathode via proton exchange membrane [23]. A backing layer would increase the overall size of the cell and also makes the cell layers difficult to assemble. The flow field both at the anode and the cathode where chosen having a channel structure and a grid structure. Hence, channel structure used at the anode as the flow field is a suitable choice as methanol is fed by means of gravity and capillary action [24]. At the cathode, ambient air is drawn from the surroundings, where a grid structure allows for a greater oxygen/air flow. Since the air flow is not increased from the surroundings using auxiliary pump, a flow field design with minimum obstacles for the air flow is of great importance. Maximization of the contact area is another factor to be considered regarding the design of the flow fields. The contact area is defined as area having anode and cathode surface, i.e. the current collectors present on both the side of the PEM. The PEM is sandwiched between the two electrodes in direct methanol fuel cell. In order to overcome the problems of methanol solution entering the cathode side, the electrodes can be rotated 90° with respect to each other. This ensures that the inlet and outlet of the anode do not interfere with the inlet and outlet of the cathode

### 3.3 Methanol diffusion layer

The diffusion layer which are placed on the membrane electrode assembly (MEA) plays a critical role in DMFCs. The diffusion layers performs several function: electrical connection between the bipolar plates and the catalyst layers on the proton exchange membrane, bringing fuel and oxidant to the proton exchange membrane, heat transport, transporting water from the cathode side of the membrane to the cathode flow channels, transporting carbon dioxide to the anode flow channels and conducting the current. A Typical diffusion layers are made up carbon fiber based porous materials such as carbon paper. And also the conductivity of carbon paper can be increased by coating it with electrically conducting powder such as carbon black [25]. The diffusion layer water removal capacity can be improved by treating with a hydrophobic

material such as polytetrafluoroethylene (PTFE) [26]. Heinzel *et al* used Toray carbon paper filled with carbon black and PTFE to make the diffusion layer of their micro fuel cell [27]. Similarly, Lee *et al* [28] used carbon paper treated with carbon-supported platinum as the diffusion layer. Cha *et al* [29] used a polymeric frame filled with carbon black and PTFE as the diffusion layer. To reduce the overall thickness of the DMFC's many micro fuel cell designs eliminate the diffusion layer by using a thin catalyst layer sputtered directly on the PEM [30, 31, 32, and 33].

## 4. PROTON EXCHANGE MEMBRANE

The core of DMFC is Proton exchange membrane (PEM). The main function of membrane is to transport of protons from anode side to cathode side for eventual reaction with oxidant by the catalyst at cathode side. Another important function of PEM is prevention of methanol crossover from anode side to cathode side thereby preventing direct reaction between methanol and oxidant. Hence, it is an insulating membrane for separating fuel and oxidizer to prevent a direct reaction. During the last few years many materials has been developed as proton exchange membranes. Qiu *et al.* used a new method based on a solution grafting technique to prepare polyvinylidene fluoride grafted polystyrene sulfonated acid proton exchange membrane [34]. Jung *et al.* produced nafion/silicon oxide hybrid proton exchange membranes via the in situ acid catalyzed sol-gel reaction of tetraethylorthosilicate in nafion perfluorosulfonic acid films [35,]. In another experiment Staiti *et al.* have investigated nafion-silica composite membranes doped with phosphotungstic and silicotungstic acids for application in DMFCs at high temperature [36]. Choi *et al.* proposed the concept of modifying the morphology of the protonconducting membrane for reducing methanol cross-over to the cathode in a DMFC [37]. Recently Kim *et al.* have presented a Pd-impregnated nanocomposite Nafion membrane for use of high-concentration methanol fuel in DMFC's [38]. Further, a novel modification method of the commercial proton exchange membrane Nafion®117 to produce an improved polymer electrolyte membrane for the  $\mu$ DMFC has been reported by Liu *et al* [39]. Also Ainla *et al.* have reported preparation of Nafion®-polybenzimidazole (PBI) composites by diffusing synthesized PBI from solution phase into Nafion® membranes, using different concentrations and drying temperatures [40]. More recently, performance characterization of polyaniline and silica modified Nafion membranes has been reported by Chen *et al* [41]. Verjullo *et al.* used carbon-supported  $\text{CoSe}_2$  as a Pt-free cathode catalyst in a passive, air-breathing, alkaline anion

exchange membrane  $\mu$ DMFC [42]. The progress made over the last few years in the functionalization of polybenzimidazole and polyetherketones with a view to increase their proton conduction properties without detriment to their thermohydrolytic and chemical stability has been reviewed by Jones et al [43].

#### 4.1 Proton Conductivity

Sufficient proton conductivity of the catalyst layer of the direct methanol fuel cell is important, because it enables the extension of the reaction zone from the membrane surface into the bulk of the catalyst layer. However, proton conductivity is difficult to determine because pseudo capacitances in the interface in the noble catalyst and the ionomer phase inside the catalyst layer enable the flow of an electronic current. Different methods were proposed in literature to avoid this problem. For example, the proton conductivity was estimated from well known specific conductivity of the nafion membrane in combination with the approximated value fraction of the nafion phase within the catalyst layer [44,45, and46]. This method is simple, but it tends to overestimate proton conductivity, because it does not consider the microstructure, eg the tortuosity of nafion phase. Other methods include the replacement of the electronically conducting catalyst by silica [47] or the introduction of an inactive catalyst layer sandwiched between two nafion membranes [48].The latter methods require the use of modified catalyst layer or membrane electrode assemblies different from those used in fuel cells under practical operating conditions

#### 4.2 Effect of methanol crossover at membrane

One of the vital problems in DMFCs is methanol crossover through the proton exchange membrane which occurs due to diffusion and electro-osmotic drag and an ion clustering with the membrane [49]. Methanol diffusion or crossover from the anode to the cathode lowers fuel utilization, increases cathode polarization and causes excess thermal load in the cell and consequently lowers the cell performance [49]. This methanol crossover results in a mixed cathode potential, and a reduction in power output of the fuel cell. Hence, suppression of methanol crossover has been a major research focus. Various methods for reducing methanol crossover have been examined which include the development of a new electrolyte [31], surface modification of a Nafion membrane [32] and the incorporation of Pt and hygroscopic oxides into the Nafion membrane [33]. At the cathode end, the reduction of oxygen to water takes place mainly supported by platinum as a catalyst. This reaction has been extensively examined during the last decades with the development of hydrogen-consuming low-temperature fuel cells (PEMFC)[50,51]. The reaction of conversion of methanol into protons at the anode is slower than hydrogen oxidation; hence, it is expected to play a major role in optimizing the performance of these cells. However, the methanol conversion reaction at the anode is slower than oxygen reduction at the cathode, it cannot be assumed to be the rate determining step in DMFCs under most operating conditions. This is primarily because a second reaction also takes place at the cathode platinum catalyst which is the direct oxidation of methanol permeating through the PEM. This undesired side reaction leads to a mixed potential formation at the cathode, which results in a severely reduced electrode potential, and therefore, also a severely reduced overall cell voltage. Thorsten Schultz et al [52] have compared the open circuit cell voltage of a DMFC with standard NAFION membrane to the thermodynamic cell voltage according to the Nernst equation. The large voltage difference between

thermodynamic data and experimental result is to a large extent due to the oxidation of methanol which permeated through the membrane. Hence, to achieve a better performance, a significant reduction in the methanol permeation through the PEM is necessary. This can either be realised by PEM materials less permeable for methanol or by optimizing (dynamic) methanol feeding strategies. This can be best achieved by simply using low methanol feed concentrations (at the moment values around 1 mol/dm<sup>3</sup> show best performance) [53] or by realizing high methanol conversion efficiency at the anode (i.e. high fuel utilization). Hence, the concentration of methanol at the anode would be such that it should be small enough to reduce crossover as much as possible but also supply the anode catalytic layer with enough methanol to produce an acceptable current density. The effect of a barrier layer was investigated [54] to reduce crossover. Zirconia and silica nano-composite membranes were tested instead of Nafion and found to reduce crossover [54]. Finally another important consideration is possible water flooding of the cathode pore structure due to the water transport through the membrane (from the anode side) and the water production at the cathode side which also affects the power obtained from the cell.

### 5. ROLE OF CATALYST

Catalyst is very important for the electrochemical reactions. Good catalysts will increase the reaction rates and decrease over potential for electrochemical reactions. Development of catalysts is crucial to improve the performance of fuel cells, especially for DMFCs. The catalysts in DMFCs must have high kinetic properties for electrochemical reactions and good ability to resist methanol poisoning In DMFCs, Pt-Ru is widely used catalyst material at the anode side. This combination catalyst enhances better methanol oxidation reaction (MOR) due to its high electro-catalytic property. Further, the use of supporting material influences the catalyst which result in increasing MOR surface area and the oxygen reduction reaction (ORR) at the cathode side .Thus various supporting material like graphite nanofibers (GNF) and carbon nanotubes (CNTs) in the form of nano-structure were studied because of their better mechanical and electrical properties [39]. In addition, the design of catalyst layers were improved by incorporation of Pt-group metal nano particles having size range of 2-5 nm and the impregnation of ionomers with carbon support materials. Recently, PTFE which was used as a binder and hydrophobic agent were replaced by ionomers [40]. These measures reduced catalyst loadings from 4-10 mg Pt/cm<sup>2</sup> to about 1.0 mg Pt/cm<sup>2</sup> [41, 42,] the combination of ionomer with carbon/Pt forms phase-segregated, agglomerated morphologies in the colloidal ink solution. Agglomerates are the particles consisting of carbon particles by deposition of Pt nanoparticles on it.Ionomer molecules form a separate proton-conducting film without penetrating Pt/carbon clusters with a 10nm film thickness attached to the agglomerate surface. Ionomer molecules form a separate proton-conducting film without penetrating Pt/carbon clusters with a 10nm film thickness attached to the agglomerate surface .Various parameter describes the penetration of Nafion on to the agglomerates such as fabrication method, the concentration of nafion and the kinetics of the agglomeration technique. Basically at low polarization porous electrode are used to support high current densities, although due to charge and mass transfer in the structure current and over potential are non-uniform. In DMFC as the mechanism of Pt-Ru catalyst related to methanol electro oxidation is not properly understood, researchers accepted that

the Tafel or B-V equations do not represent the intrinsic methanol oxidation kinetics and a dual-site mechanism on surfaces Pt-Ru catalyst. Further it is important to include dual site mechanism of methanol oxidation to observe macro-kinetics at the anode side.

## 6. ELECTRICAL PERFORMANCE OF MDFMC

For high efficient  $\mu$ DMFCs the electrical performance should be better. Yingqi Jiang [55] developed a micro direct methanol fuel cell ( $\mu$ DMFC) with silicon-based air-breathing stacks (active area of 13 mm  $\times$  11 mm) having a unique 3D air-breathing cathode. The results showed an open circuit voltage (OCV) of 0.47 V and maximum power density of 2.31 mW cm<sup>-2</sup> when 1 M methanol solution at room temperature. M. Wang [56] demonstrated a monolithic  $\mu$ DMFC for the first time, integrated with silicon-based PEM, nanocatalysts and current collector layer together. The  $\mu$ DMFC prototype achieves an open circuit voltage of 0.3 V, a maximum power density of 5.5 mW/cm<sup>2</sup>. These results demonstrate the proposed monolithic integrated  $\mu$ DMFC shows great potentials for optimizing the size and performance of  $\mu$ DMFCs, furthermore, are quite promising for integrated micro systems. Xiaohong Wang [57] developed a silicon-based air-breathing  $\mu$ DMFC stack model having two air-breathing cathode plates and an anode plate. The stack with shared model and a single cell, which is the half of stack, are tested in the same operating condition. The results show that shared model has maximum power of 2.52 mW with an open circuit voltage of 0.46 V as compared to single cell having 0.47 V and 1.28 mW when 2M methanol solution fed under room temperature. The power obtained by shared model is almost double of that of a single cell which indicates the performance of  $\mu$ DMFC. Konrad Wozniak [58] demonstrated a  $\mu$ DMFC with an area of 0.25 cm<sup>2</sup>, the flow channels were designed using mathematical model and verified the polarization curves, which indicates cell output power. The electrode were fabricated using silicon as a substrate, and the membrane electrode assembly was provided by Ion. The power density of a 0.25 cm<sup>2</sup> cell and an open circuit voltage of 0.7 V were obtained. Hiroaki Houjou [59] designed a new concept of  $\mu$ DMFC based on the well considered electrochemical background and MEMS process. Use of the 3-D electrodes instead of the planar electrodes. To realize a metal pattern on 3-D structures, spray coating method was utilized. The experimental result shows that the  $\mu$ DMFC with 3-D electrodes succeeds in actual electrical power generation. The open circuit voltage (540mV) of the  $\mu$ DMFC is almost same or little higher than that of the other  $\mu$ DMFC.

## 7. CONCLUSION

In this review, the current technical developments in Micro DMFCs have been summarised. Many studies have focused on analysis and improvement of single components of Micro DMFCs systems and design optimisation are suggested. Factors such as methanol crossover through the membrane which effects overall cell performance of the MicroDMFCs have been discussed. As presented in this work, the cell performance can be increased by using different micro channel design and oxidant delivery systems. A great challenge on the development of this type of fuel cell, in order to be used in real applications, is the development of cost-effective materials. To achieve that, different materials have been, recently, explored as current collectors, membrane, and diffusion and catalyst layers both for the anode and cathode side, as well as, different micro- fabrication techniques achieving improved power

generation. However, additional studies on more cost-efficient electrode materials and optimization of configurations are needed. Another key factor when a micro-fuel cell is projected is the fuel cell design (conventional or planar). For some applications, the simplicity of planar design could be crucial. However, fuel cell performances are yet limited. Since the MicroDMFC systems involves electrochemical processes, energy, mass and charge transfer, a better understanding of the basic transport phenomena is essential to achieve the energy densities needed for real applications.

## 8. REFERENCES

- [1].Mench, M. M., Wang, Z. H., Bhatia, K., & Wang, C. Y. Design of a Micro Direct Methanol Fuel Cell ( $\mu$ DMFC). *International Mechanical Engineering Congress and Exposition*, 1–8.2001
- [2].V. V Joshi and M. B. Patil, "Recent Developments and Trends in Direct Methanol Fuel," vol. 5, no. 3, pp. 3–6, 2015.
- [3].Mallick RK, Thombre SB, Shrivastava NK. Vapor feed direct methanol fuel cells (DMFCs): A review [J]. *Renewable and Sustainable Energy Reviews*; 56:51–74.2016
- [4].An, M. G., Mehmood, A., Hwang, J., & Ha, H. Y. A novel method of methanol concentration control through feedback of the amplitudes of output voltage fluctuations for direct methanol fuel cells. *Energy*, 100, 217–226. 2016
- [5].Alotto, P., Guarnieri, M., & Moro, F. Optimal Design of Micro Direct Methanol Fuel Cells, 45(3), 1570–1573.2009
- [6].Falco, D. S., Oliveira, V. B., Rangel, C. M., & Pinto, A. M. F. R. Review on micro-direct methanol fuel cells. *Renewable and Sustainable Energy Reviews*, 34, 58–70. 2014
- [7].Cha SW, O'hayre R, Saito Y, Prinz F B. The scaling behavior of flow patterns: a model investigation. *J Power Sources*; 134(1):57–71.2004
- [8].Fei, K., Chen, T. S., & Hong, C. W. Direct methanol fuel cell bubble transport simulations via thermal lattice Boltzmann and volume of fluid methods. *Journal of Power Sources*, 195(7), 1940–1945.2010
- [9].Lu, G. Q., & Wang, C. Y. Electrochemical and flow characterization of a direct methanol fuel cell. *Journal of Power Sources*, 134(1), 33–40.2004
- [10].Yang, H., Zhao, T. S., & Ye, Q. In situ visualization study of CO<sub>2</sub> gas bubble behavior in DMFC anode flow fields. *Journal of Power Sources*, 139(1-2), 79–90. 2005
- [11].Wong, C. W., Zhao, T. S., Ye, Q., & Liu, J. G. Transient Capillary Blocking in the Flow Field of a Micro-DMFC and Its Effect on Cell Performance. *Journal of The Electrochemical Society*, 152(8), A1600.2005
- [12]. Fei K, Cheng CH, Hong CW. Lattice Boltzmann simulations of CO<sub>2</sub> bubble dynamics at the anode of a  $\mu$ DMFC. *Trans ASME J Fuel Cell Sci Technol* 3:180–187.2006
- [13].Fei, K., & Hong, C. W. All-angle removal of CO<sub>2</sub> bubbles from the anode microchannels of a micro fuel cell by lattice-

- Boltzmann simulation. *Microfluidics and Nanofluidics*, 3(1), 77–88.2007
- [14]. Mahmoud Ahmed and Ibrahim Dincer A review on methanol crossover in direct methanol fuel cells: challenges and achievements international journal of energy research Int. J. Energy Res. 2011; 35:1213–1228
- [15]. Xueye Chen, Zhen Zhang, Jienan Shen and Zengliang Hu Micro direct methanol fuel cell: functional components, supplies management, packaging technology and application. international journal of energy research Int. J. Energy Res. (2016)
- [16]. Ahmad H, Kamarudin SK, Hasran UA, Daud WRW. International Journal of Hydrogen Energy 2010; 35:2160–2175.
- [17]. Wong, C. W., Zhao, T. S., Ye, Q., & Liu, J. G. Experimental investigations of the anode flow field of a micro direct methanol fuel cell. *Journal of Power Sources*, 155(2), 291–296.2006
- [18]. Lu, Y., & Reddy, R. G. Effect of flow fields on the performance of micro-direct methanol fuel cells. *International Journal of Hydrogen Energy*, 36(1), 822–829.2011
- [19]. Wang, S.-J., Huo, W.-W., Zou, Z.-Q., Qiao, Y.-J., & Yang, H. Computational simulation and experimental evaluation on anodic flow field structures of micro direct methanol fuel cells. *Applied Thermal Engineering*, 31(14-15), 2877–2884.2011
- [20]. Zhang, Y., Zhang, P., Yuan, Z., He, H., Zhao, Y., & Liu, X. A tapered serpentine flow field for the anode of micro direct methanol fuel cells. *Journal of Power Sources*, 196(6), 3255–3259.2011
- [21]. Zhang, Y. F., Wang, L. W., Yuan, Z. Y., Wang, S. B., Li, J. M., & Liu, X. W. Silicon-based micro direct methanol fuel cell with an N-inputs-N-outputs anode flow pattern. *Chinese Science Bulletin*, 56(8), 826–829. 2011
- [22]. D'Urso, C., Baglio, V., Antonucci, V., Aric, A. S., Specchia, S., Icardi, U.A., ... D'Arrigo, G. (2011). Development of a planar ?? dMFC operating at room temperature. *International Journal of Hydrogen Energy*, 36(13), 8088–8093.
- [23]. Kim, Y. M., Park, K. W., Choi, J. H., Park, I. S., & Sung, Y. E. A Pd-impregnated nanocomposite Nafion membrane for use in high-concentration methanol fuel in DMFC. *Electrochemistry Communications*, 5(7), 571–574.2003
- [24]. Kanamura, K., Mitsui, T., & Munakata, H. Preparation of composite membrane between a uniform porous silica matrix and injected proton conductive gel polymer. *Chemistry of Materials*, 17(19), 4845–4851.2005
- [25]. Stanley, K. G., Czyzewska, E. K., Vanderhoek, T. P. K., Fan, L. L. Y., Abel, K. a, Wu, Q. M. J., & Parameswaran, M. (Ash). A hybrid sequential deposition fabrication technique for micro fuel cells. *Journal of Micromechanics and Micro engineering*, 15(10), 1979–1987.2005
- [26]. Bevers, D., Rogers, R., & Von Bradke, M. Examination of the influence of PTFE coating on the properties of carbon paper in polymer electrolyte fuel cells. *Journal of Power Sources*, 63(2), 193–201.1996
- [27]. Heinzl, A., Hebling, C., Müller, M., Zedda, M., & Müller, C. Fuel cells for low power applications. *Journal of Power Sources*, 105(2), 250–255.2002
- [28]. Lee, S. J., Chang-Chien, A., Cha, S. W., O'Hayre, R., Park, Y. I., Saito, Y., & Prinz, F. B. Design and fabrication of a micro fuel cell array with “flip-flop” interconnection. *Journal of Power Sources*, 112(2), 410–418.2002
- [29]. Cha, H. Y., Choi, H. G., Nam, J. Do, Lee, Y., Cho, S. M., Lee, E. S., Chung, and C. H. Fabrication of all-polymer micro-DMFCs using UV-sensitive photoresist. *Electrochimica Acta*, 50(2-3 SPEC. ISS.), 795–799.2004
- [30]. Hsieh S-S, Huang C-F, Kuo J-K, Tsai H-H, Yang S-H. SU-8. flow field plates for a micro PEMFC. *J Solid State Electrochem*, 9, 121–31.2005
- [31]. Hsieh S S, Kuo J K, Hwang C F and Tsai H H .A novel design and micro fabrication of a micro PEMFC *Microsyst. Technol.* 10 121–6.2004
- [32]. Shah K, Shin W C and Besser R S. A PDMS micro proton exchange membrane fuel cell by conventional and non-conventional micro fabrication techniques *Sensors Actuators B* 97 157–67.2004
- [33]. A ravamudhan S, Rahman A R A and Bhansali S .Porous silicon based orientation independent, self-priming micro direct ethanol fuel cell *Sensors Actuators A* 123–124 497–504.2005
- [34]. J.I. Ozaki, S.I. Tanifuji, N. Kimura, A. Furuichi, A. Oya, . Catalysts for Alcohol-Fuelled Direct Oxidation Fuel Cells 44-1324.2006
- [35]. Weinmueller C, Tautschnig G, Hotz N, Poulikakos D. A flexible direct methanol micro-fuel cell based on a metalized, photosensitive polymer film. *J Power Sources*; 195 (12):3849–57.2010
- [36]. Lu, G. Q., Wang, C. Y., Yen, T. J., & Zhang, X. Development and characterization of a silicon-based micro direct methanol fuel cell. *Electrochimica Acta*.2004
- [37]. Kelley S C, Deluga GA, Smyrl W H. A miniature methanol/air polymer electrolyte fuel cell. *Electrochem Solid-State Lett*; 3(9):407–9.2000
- [38]. Esquivel JP, Senn T, Hernández-Fernández P, Santander J, Lörger M, Rojas S, Löchel B, Cané C, Sabaté N. Towards a compact SU-8 micro-direct methanol fuel cell. *J Power Sources* 195(24):8110–5.2010
- [39]. D'Urso, C., Baglio, V., Antonucci, V., Aric, A. S., Specchia, S., Icardi, U. A. ... D'Arrigo, G. Development of a planar ?? dMFC operating at room temperature. *International Journal of Hydrogen Energy*, 36(13), 8088–8093.2011
- [40]. En, M., Walter, S., Dovat, L. S., & Gijs, M. A. M. Planar micro-direct methanol fuel cell prototyped by rapid powder blasting. *Microelectronic Engineering*, 88(8), 1884–1886. 2011

- [41].Sun, L., Liu, C., Liang, J., Zhu, X., & Cui, T.A self-pumping and self-breathing micro direct methanol fuel cell with polymer bipolar plates. *Journal of Power Sources*, 196(18), 7533–7540.2011
- [42].Zhang YF, Zhang P, Zhang B. *J Funct Mater Devices*; 14(2):408.2008
- [43].Tang XC, Zhang YF, Zhang B,Wang XL, Liu XW. Design and fabrication of micro direct methanol fuel cells based on MEMS technology. *Nami Jishu yu Jingmi Gongcheng/Nanotechnol Precis Eng* ;7(1):76–80.2009
- [44].F. Gloaguen and R. Durand, *J. Appl. Electrochem.* 27 - 1029,1997
- [45].D. Bernardi and V. Verbrugge, *J. Electrochem. Soc.*139 - 2477,1992
- [46].K.R. Weisbrod, S.A. Grot and N.E. Vanderborgh, *Proc. of Proton Conducting Membrane Fuel Cells I*, Eds.: S. Gottesfeld, G. Halpert and A. Landgrebe, The Electrochemical Society Proceedings, Pennington, N, PV 95-23, p. 152.1995
- [47]. T.E. Springer, M.S. Wilson and S. Gottesfeld, *J. Electrochem. Soc.* 140 - 3513,
- [48].Boyer, S. Gamburzev, O. Velez, S. Srinivasan and A.J. Appleby, *Electrochim. Acta* 43 (1998) 3703.1993
- [49].M. W. Verbrugge, *J. Electrochem. Soc.*, 136, 417 .1989
- [50].M. Eikerling, A. A. Kornyshev, *J. Electroanal. Chem.*, 453, pp. 89±106.1998
- [51].K. Broka, P. Ekdunge, *J. Appl. Electrochem.*, 27, pp. 281 ±289.1997
- [52].Current Status of and Recent Developments in the Direct Methanol Fuel Cell by Thorsten Schultz, SuZhou and Kai Sundmacher, *Chem. Eng. Technol.*, 24, 12 .2001
- [53].X. Ren, P. Zelenay, S. Thomas and J. Davey, S. Gottesfeld, *J. Power Sources*, 86, pp.111±116.2000
- [54].Mr.Nirmal Ramkrishna Joshi.Development in Direct Methanol – Oxygen Fuel Cell (DMFC). *IOSR Journal of Applied Chemistry (IOSR-JAC)* e-ISSN: 2278-5736.Volume 7, Issue 9 Ver. II, PP 24-26.2014
- [55]. Y. Jiang, X. Wang, L. Zhong, and L. Liu, “Design, fabrication and testing of a silicon-based air-breathing micro direct methanol fuel cell,” vol. 233, pp. 1–8.
- [56].M. Wang, Y. X. Lu, L. T. Liu and X. H. Wang, “A monolithic integrated micro direct methanol fuel cell based on sulfo functionalized porous silicon.” *Journal of Physics: Conference Series* 773 (2016) 012017 pp 1-4
- [57].X. Wang, Y. Zhou, Q. Zhang, Y. Zhu, and L. Liu, “An air-breathing micro direct methanol fuel cell stack employing a single shared anode using silicon microfabrication technologies,” vol. 94012
- [58].K. Wozniak, D. Johansson, M. Bring, A. Sanz-Velasco, and P. Enoksson, “A micro direct methanol fuel cell demonstrator,” *J. Micromechanics Microengineering*, vol. 14, no. 9, p. S59, 2004.
- [59]. H. Houjou, M. Ishizuka, and J. Mizuno, “3E4.35 Metallization on,” pp. 1437–1440, 2005.