A Progress Review on Performance Improvement of Direct Methanol Fuel Cells Using Modified Nafion Membrane

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***Abstract*--Proton exchange membranes (PEMs) are important components of fuel cells in which either hydrogen or methanol are used as fuels. In this paper we propose to use methanol as fuel to realize micro direct methanol fuel cells (µDMFC). The membrane electrode assembly (MEA) of µ-DMFC consists of a micro-porous layer which regulates the flow of methanol to the catalyst at the anode, a high efficiency catalyst layer for the generation of protons (H+) from methanol, a high conductance membrane layer for the transfer of protons and a high efficiency catalyst at the cathode for the conversion of oxygen and H+ into water. Simulation results indicate that the cell voltage decreases with increase in membrane thickness from 50 µm to 200 µm.**

Keywords: **PEM, µDMFC, MEA, Nafion 117**

I. INTRODUCTION

The Fuel cells are leading contenders for clean energy generation for variety of applications especially for wearable and portable devices. It is an energy conversion device which converts chemical energy of fuel in to electrical energy. The Direct-Methanol Fuel Cell (DMFC) is a subcategory of proton-exchange fuel cells in which methanol is used as a fuel. The DMFC devices are growing rapidly, recognized internationally and these devices are increasingly finding applications in many types of electronic devices. In recent years there is much demand on portable electronic devices such as cell phones and laptop computers. Therefore various energy storage and conversion systems have emerged in order to provide electrical power for portable devices with mechanical stability and high efficiency as well as environmental benefit and cost-effectiveness. DMFC has lot of advantages, such as low energy consumption, high energy density, simple system, abundant and low-cost fuel, which is easy to carry, storage and supply, and also a long time for power supply. Therefore, DMFC will be the most promising substitute for secondary batteries which are being used widely.

However, in India, there is no major effort in the development of technology for DMFC. The DMFC consists of a proton conducting membrane (Nafion 117) which is sandwiched between two gas diffusion layers (GDL); this Membrane Electrode Assembly (MEA) is the heart of DMFC. The Methanol diffuses through the micro-porous layer which regulates the transport of methanol to the catalyst which generates protons. The protons then diffuse through the membrane to the cathode. The protons react with oxygen at the cathode to form water. The equations for the process are as below: Anode reaction:

$CH_3OH + H_2O \rightarrow 6\,H^+ + 6e^- + CO_2$ (Oxidation) ------(1.1)

Cathode reaction:

$3/2\,O_2 + 6\,H^+ + 6e^- \rightarrow 3H_2O$ (Reduction) -------(1.2)

Overall reaction:

$CH_3OH + O_2 \rightarrow 2H_2O + CO_2$(Overall Redox reaction) - (1.3)

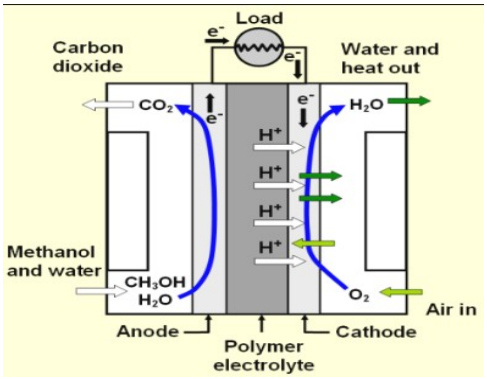


Figure1: Schematic of DMFC

The entire MEA is sandwiched between two silicon chips with micro channels which contain the flow of methanol at the anode and flow of air at cathode. The negative charge is collected by the metallic electrode, which moves into the external circuit from anode to cathode, thus balancing the charge transfer process. On the outside of the MEA, backing layers made of non-woven carbon paper or woven carbon cloth, are placed to fulfil several functions. The primary purpose of a backing layer is to provide lateral current collection from the catalyst layer to the ribs as well as optimized gas distribution to the catalyst layer through diffusion. It must also facilitate the transport of water out of the catalyst layer. This latter function is usually accomplished by adding a coating of hydrophobic polymer, polytetrafluoroethylene (PTFE), to the backing layer.

The hydrophobic character of the polymer allows the excess water in the cathode catalyst layer to be expelled from the cell by the gas flowing inside the channels, thereby alleviating flooding. Methanol releases six protons and electrons per molecule during its oxidation. Its high energy density makes methanol a suitable fuel for fuel cells. DMFC works at low and intermediate temperatures (up to 150ºC) and are fed with a dilute aqueous solution of methanol in water. Cells operation in gas phase also gives good performance. Actually, the higher temperature enhances kinetics and methanol crossover is lowered with a gas phase feed. When providing current, methanol is electrochemically oxidized at the anode electro catalyst to produce electrons which travel through the external circuit to the cathode electro catalyst where they are consumed together with oxygen in a reduction reaction. The circuit is maintained within the cell by the conduction of protons in the electrolyte.

II. LITERATURE REVIEW

Based on the reference papers we have subdivided them into 5 categories they are:

1. Based on membranes

There are 17 reference papers under this category. Authors have analysed the effect of channel width on the fuel cell performance, by considering different channel widths employing different distributions and dimensions.

Table1: The following are the design parameters of the model.

Cell Length	20.0mm
Channel height	1.0mm
Channel width	0.7mm
Rib width	0.9mm
GDL width	0.3mm
Contact dimension for 1 contact	200im
Porous electrode thickness	0.5mm
Membrane thickness	0.05mm
GDL Porosity	0.4
GDL electric conductivity	1000S/m
Contact electric conductivity	100000S/m
Inlet H2 mass fraction (anode)	0.743
Inlet H2O mass fraction (cathode)	0.023
Inlet oxygen mass fraction (cathode)	0.228
Anode inlet flow velocity	0.2m/s
Cathode inlet flow velocity	0.5m/s
Anode viscosity	1.19?10- 5Pa.s
Cathode viscosity	2.46?10- 5Pa.s
Permeability (porous electrode)	2.36?10- 12 m2
Membrane conductivity	10 S/m

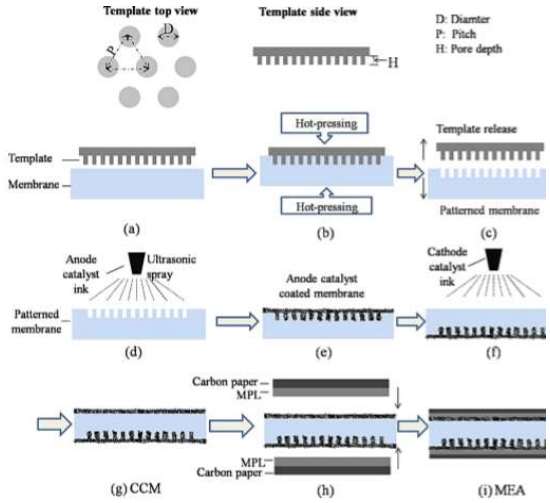


Fig2: Schematic Illustration of Micropatterned Nafionmembrane And MEA Fabrication processes.

2. Based on Characteristics

There are 4 reference papers under this category. Authors have described the heat and the power management of a direct methanol fuel cell system. The system consists mainly of a direct methanol fuel cell stack, an anode feed loop with a heat exchanger and on the cathode side, a compressor/expander unit. The model computations are carried out by analytical solutions for both mass and energy flows. The study is based on the measurements on laboratory scale single cells to obtain data concerning mass and voltage efficiencies and temperature dependence of the cell power.

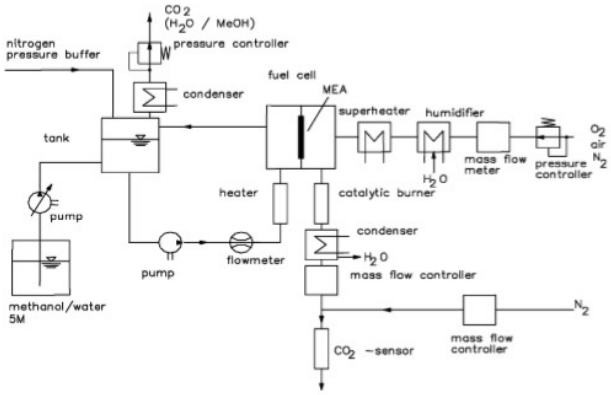


Fig 3:DMFC system with air

3. Based on Micro-Porous Layer

There are 2 reference papers under this category. They have explained that PolyPyrrole Nanowire Networks (PPNNs), as anodic Micro-Porous Layer (MPL) of passive direct methanol fuel cells, are grown in-situ on the surface of carbon paper through an electrochemical polymerization. The typical morphology of Toray carbon paper coated with 20wt.%.The hydrophobic open pores within the carbon fiber matrix usually promote the mass transfer of the produced CO2 better than the methanol aqueous solution.

Table 2 : Schemes of current collection

Case No	No of Contacts	Contact Dimension	Contacts Position
1	1	200 µm	Center
2	3	66.667 µm	Evenly distributed
3	5	66.667 µm	Evenly distributed
4	7	28.5 µm	Evenly distributed

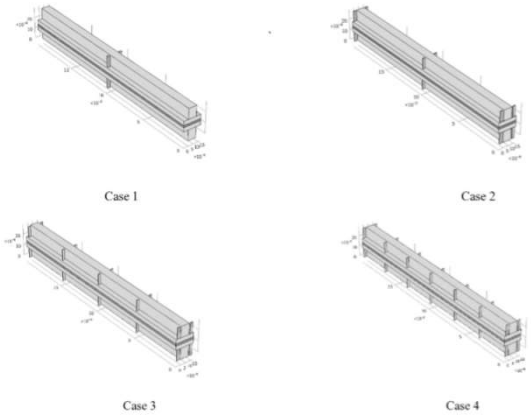


Fig4: DMFC models with segmented contacts

4. Based on Methanol crossover

There are 3 reference papers under this category. Authors have synthesised various composite membranes and studied the performance of these composites membrane in DMFC. The addition of composites like (SI-PBI), Phospho Tungstic Acid (PTA) to Graphene Oxide (GO) /Nafion creates n composite polymer electrolyte that is a reasonable proton conductor while reducing the crossover of methanol.

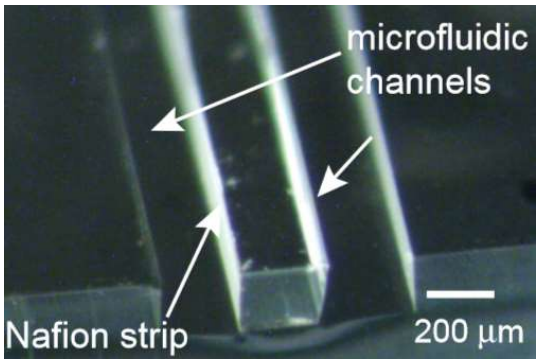
5. Based on structure

There is 1 reference paper under this category. **Wang et al** [20] have stated that the all basic parameters were gained from experiment datum. Inside dimension and structure were determined by calculating, admeasuring and devising elaborately. Three-dimensional model was devised through ProlE, planar diagrammatic drawing was created by the software also, and detail drawing was drew with CAD further. Tubular membrane electrode assembly without the fluid field's bipolar plates was used in this conceptual design, which was made up of titanium mesh anode layer, anode catalyst layer, Nafion membrane layer, cathode catalyst layer, gas diffusion layer and titanium mesh cathode layer in turn. A novel conceptual design of "DMFCs" was proposed firstly, which was faced to market demands and based on normal batteries.

III. RESULTS & DISCUSSION

The cross-sectional microscopic picture of the Nafion strip-integrated PDMS chip is shown in Figure 3a. The 200 µm-wide guiding channel in the PDMS chip allows precise positioning of the rigid Nafion strip. A planar µ−DMFC mounted in its experimental setup is shown in Figure 3b.

(a)



(b)

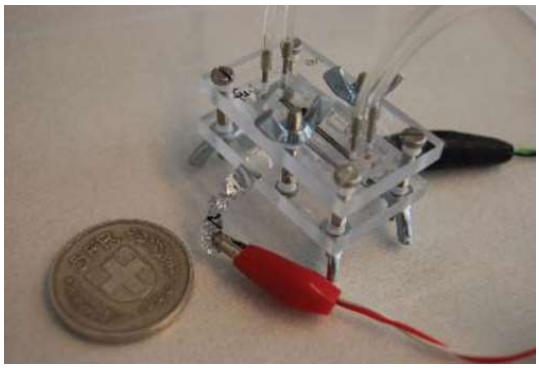


Figure 4: Photographs of (a)the cross-section of the channel and (b) the µ− DMFC assembled in its experimental setup.

when the fuel and oxidant are fed into the chip, a limiting current density of 2.7 mA/cm^2 and a maximum power density of 0.52 mW/cm2 are obtained with a fuel and oxidant flow rate of 20 µL/min and 160 µL/min, respectively. A higher flow rate of oxidant results in a better refreshment of the oxidant solution and, thus, a higher limiting current and power density. This can be explained by the low dissolubility of oxygen in the oxidant solution (1.2 mmol/kg at ambient pressure and room temperature) [9]. It is noticeable that the flow rate of the fuel is not performance-determining, due to the cathode-limited behaviour of the DMFC [11]. Crossover of methanol through the Nafion strip from the anodic microfluidic channel can reduce the oxidant concentration near the cathode [21], an effect which can be reduced by having a better refreshment of oxidant using a higher flow rate.

IV. CONCLUSION

The batteries are no longer capable of competing in enhancing potential and intricacy of devices. A direct methanol fuel cell is able to replace batteries in many electronic devices. It is smaller, improved, limited in cost environmental receptive and more efficient than batteries. Refueling of the direct methanol fuel cell is fast and can last several months.

As we have refered above IEEE papers, we come to know that the direct methanol fuel cell performance depends on membrane thickness, as membrane thickness increases the efficiency of the fuel cell decreases.

REFERENCES

[1]. Swathi Rai , K. R. Rashmi , M. B. Savitha , A. Jayarama , R.Pinto and S.P. Duttagupta "Simulation study of proton exchange membrane thickness on cell voltage in micro methanol fuel cells", Vol 1, Issue 1, December 2015

[2]. H.Ozu, L.J.Hobson, M.Yamaguchi and S.Hayase, "Modified Nafion 117 as an improved polymer electrolyte membrane for direct methanol fue cells", Journals of the Electrochemical society, 148(10), September 13, 2001.

[3]. PhornpussadeeUmsarika, SairungChangkhamchom, NophawanParadee, AnuvatSirivat, Pitt Supaphol and PimpaHormnirun, "Proton Exchange Membrane Based on Sulfonated Poly (Aromatic Imide-Co-Aliphatic Imide) for Direct Methanol Fuel Cell",Materials Research. 2018; Vol 21, Issue 1, e20170823,November 10, 2017

[4]. B.MullaiSudarolia and Ajit Kumar Kolar, "Heat and Mass Transfer Characteristics of Direct Methanol Fuel Cell": Experiments and Model, 4th International Conference on Advances in Energy Research 2013, ICAER 2013.

[5]. Longjuan Pu, Jingjing Jiang. Ting Yuan, Jieshi Chai, Haifeng Zhang, ZhiqingZou, Xue-Mei Li and Hui Yang, "Performance improvement of passive direct methanol fuel cells with surface-patterned Nafion membrane", Applied Surface Science, 24 november 2014.

[6]. Jae Hyung Cho, Jang Mi Kim, JogheePrabhuram, sang Youp Hwang, Dong June Ahn, Heung Yong Ha and Soo-Kil Kim, "Fabrication and evalution of membrane electode assemblies by low- temperature decal methods for direct methanol fuelcells", Jounal of Power Sources, 7 November 2008.

[7]. Y.Hu, X.Li, L.Yan and B.Yue, "Improving the Overall Characteristics of Proton Exchange Membranes via Nanophase Separation Technologies": A Progress Review, January20,2017.

[8]. P. Ramesh and S.P Duttagupta, "Effect of Segmented Current Collection Contacts Attached to Gas Diffusion Layer in Micro PEM Fuel Cells with Ceramic Flow Field Plates", Int. J. Electrochem. Sci., 9 (2014) 4331 – 4344, 19 May 2014.

[9]. H. Dohle, J. Mergel and D. Stolten, "Heat and power management of a direct-methanol-fuel-cell system", Journal of Power Sources 111 (2002) 268–282, 27 May 2002.

[10]. Hongjun Kim, Sunghwan Lee, Suran Kim, Chungik Oh, JeongjaeRyu, Jaegyu Kim, Eugene Park, Seungbum Hong and 0KwangsooNo,"Membrane crystallinity and fuel crossover in direct ethanol fuel cells with Nafion composite membranes containing phosphotungstic acid", Springer Science+Business Media New York 2016.

[11]. Huijuan Wu, Ting Yuan, Qinghong Huang, Haifeng Zhang, ZhiqingZou, Junwei Zheng and Hui Yang, "Polypyrrole nanowire networks as anodic micro-porous layer forpassive direct methanol fuel cell", Journals of the ElectrochimicaActa 141 (2014).

[12]. ParitoshAgnihotri and V. N. Lad, "Membrane-less Fuel Cells: Microfluidic Fuel Cells", Asian International Conference on Science, Engineering & Technology AAICSET-2015.

[13]. P. Ramesh and S.P Duttagupta, "Effect of Segmented Current Collection Contacts Attached to Gas Diffusion Layer in Micro PEM Fuel Cells with Ceramic Flow Field Plates", Int. J. Electrochem. Sci., 9 (2014) 4331 – 4344.

[14]. Lunyang Liu, Wenduo Chen and Yunqi Li, "An Overview of the ProtonConductivity of Nafion Membranes Through a Statistical Analysis", Journal of Membrane Science 27 December 2015.

[15]. Seema S. Munjewar, Shashikant B. Thombre and Ranjan K. Mallick, "A comprehensive review on recent material development of passive direct methanol fuel cell", Ionics (2017) 23:Page 1–18.

[16]. Ai Hua Tian, Zhe Sheng Hou, Xiao Feng Sun and Dong Hui Shen, "Sodium Dodecyl "Sulfate/Pd/Modified Nafion Membrane for Direct Methanol Fuel Cells Applications", IEEE(2013).

[17]. K. Scott, "The direct methknol fuel cell", The Institution of Electrical Engineers, 1996.

[18]. Rajkumar B. Chadge, Jayant P. Giri, Naveen Shrivastava and PritamAhire, "Effect of Ethanol Concentration and Cell Orientation on the performance of passive direct ethanol fuel cell", International conference on industrial and information system(ICIIS),11th 2016.

[19]. Gregg A. Deluga, Shawn C. Kelley, Bryan Pivovar, David A. Shores, and William H. Smyrl, "Composite Membranes to Reduce Crossover in PEM Fuel Cells", Corrosion Research Center, 2000(IEEE). [19] Xingxing Wang, Hongjun Ni, Yu Zhu, Mingyu Huang and Ping Liaos, "Study of Direct Methanol Fuel Cells for Commercial Market Applications", 2011 IEEE.

[20]. Muhammad Tawalbeh, Amani Al-Othman and Mamdouh El Haj Assad, "Graphene oxide – Nafion composite membrane for effective methanol crossover reduction in passive direct methanol fuel cells", International Conference on Renewable Energy: Generation and Applications (ICREGA), 5th 2018.

[21]. M. Shen, S. Walter and M.A.M. Gijs,"rapid prototyping of micro-direct methanol fuel cell in pdms with microchannel-integrated nafion strip", 2009 IEEE.

[22]. S. Al-Batty, C. Dawson, S. P. Shanmukham, E. P. L. Roberts and S. M. Holmes, "Improvement of direct methanol fuel cell performance using a novel mordenite barrier layer", journal of Royal Society, 2013.

[23]. J.G. Liu, T.S. Zhao, Z.X. Liang and R. Chen, "Effect of membrane thickness on the performance and efficiency of passive direct methanol fuel cells", Journal of Power Sources 153 (2006) 61–67.

[24]. ChaiwatYoonoo, Craig P. Dawson, Edward P.L. Roberts and Stuart M. Holmes, "Nafion mordenite composite membranes for improved direct methanol fuel cell performance", Journal of Membrane Science 369 (2011) 367–374.

[25]. L. J. Hobson, H. Ozu, M. Yamaguchi and S. Hayasea, "Modified Nafion 117 as an Improved Polymer Electrolyte Membrane for Direct Methanol Fuel Cells", Journal of The Electrochemical Society, 148 ~10! A1185-A1190 ,2001.

[26]. H.S. Thiam, W.R.W. Daud, S.K. Kamarudin, A.B. Mohamad , A.A.H. Kadhum, K.S. Loh and E.H. Majlan, "Performance of direct methanol fuel cell with a palladium–silica nanofibre/Nafion composite membrane", journals of Energy Conversion and Management 75 (2013) 718–726.