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Recent evolutions in modeling of direct methanol fuel cell

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ABSTRACT

Direct Methanol Fuel Cells (DMFC) offers one of the most promising alternatives to the replacement of fossil fuels. However effective the design of the fuel cell may be, it cannot perform effectively without proper modelling and simulation. The importance and the need for the modelling of a DMFC are discussed in detail. The modeling of the key components such as the gas diffusion layer, MEA, flow distribution, catalyst thickness which contributes to the performance of the fuel cell are discussed.

Introduction

Fuel cells are showing great potential in the replacement for fossil fuels. However the conventional polymer electrolyte membrane fuel cell with hydrogen as a fuel requires many external devices for safe and effective functioning of the device and therefore makes it difficult for use in small portable applications. Although active fuel cells are easily controllable to obtain the desired output they require additional equipment in order to function well. Therefore, calls in for more space and increases the complexity in portable systems. The passive type fuel cells are smaller in size when compared to their active counter parts but cannot be used to support fluctuating energy requirements in a standalone mode. Although they can be coupled to a battery to support fluctuating energy demands.

The chief advantage of DMFC over other variants of fuel cells is that, methanol can be transported and handled with ease. The fuel also has high stability. Besides, methanol can be easily produced by biological processes with high degree of purity. Direct alcohol fuel cells are expected to replace the conventional PEM fuel cells in the foreseeable future with DMFC taking the lead (1). The direct methanol fuel cell is a proton exchange membrane fuel cell that is fed with an aqueous solution of methanol. The two catalytic electrodes where the methanol oxidation (anode) and the oxygen reduction (cathode) occur are separated by a membrane which conducts protons from anode to cathode, while other compounds diffusion is blocked. The combination of electrodes and membranes is called Membrane Electrode Assembly (MEA). Each electrode is made of a gas diffusion layer and a catalytic layer (fig.1).the state of the art in membranes is nafion. It was created by addition of sulfonic acid groups into the bulk polymer matrix of teflon. These sites have strong ionic properties and act as proton exchange sites.

Aqueous methanol is fed at the anode side. It diffuses through the diffusion layer to the catalytic layer where it is electrochemically oxidized into electrons, protons, carbon dioxide. Protons formed during this reaction diffuse through the nafion membrane to the cathode catalytic layer. They participate in oxygen reduction to form water at cathode side. Oxygen may be pure but can also come from air (6).

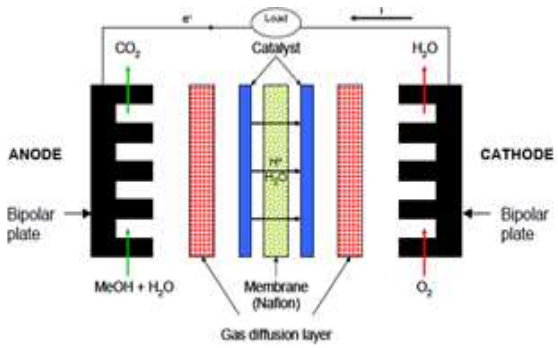

Fig 1. Schematic diagram of DMFC [20,22]

The mere design of fuel cells does not essentially mean fuel cells of higher efficiency. Modelling and control plays a vital role in the improvement of the fuel cell efficiencies. Modelling of fuel cells is necessary for better understanding of the working of DMFC fuel cells and also predicts the changes in a fuel cell performance when attached to its ancillary units. Modelling of all fuel cells is quite necessary but it takes an added importance in the case of a DMFC because of the following reasons

A) Fuel cannot be supplied at all concentrations, the methanol solutions must be suitably diluted and then supplied to the cell.

B) Gas liquid separation is present at the anode surface. Also since water is used to dilute the methanol solution it could lead to accumulation and affect the conditions inside the cell

An ideal DMFC is one which is able to operate in spite of various external and internal disturbances (2). Also it must deliver the required performance while operating safely without compromising on the life of the fuel cell. Following factors must always be considered while modelling DMFC,

I). Uniform velocity distribution of the reactants must be maintained, in order to ensure that there exists a uniform current distribution in the fuel cell.

II). Flow of water through the cell is the most vital part in a fuel cell. The electrolyte membrane must be hydrated to ensure protonic conductivity (9) and at the same time water formed from the reaction must be removed from the cathode. The movement of water in the cell is governed by both drag and

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mass diffusion. Non removal of water could lead to flooding and results in deterioration of the fuel cell system III) The heat produced from the reactions must be removed so that the cell temperature remains uniform and fuel crossover i.e. Transportation of unreacted fuel through the membrane.

In a DMFC, the various processes taking place include transfer of mass and energy through gas channels and electrochemical reactions at the surfaces of the electrodes (3). Though a lot of modelling and analysis have been done for a conventional PEMFC, adequate literature is not available for modelling of a DMFC. The factors that makes the modelling of DMFC difficult is,

A) Methanol crossover that takes place from the anode side to cathode side. This action leads to a decrease in cell efficiency and corrodes the cathode.

B) The slow kinetics of the methanol oxidation process. This reaction takes a significantly longer time than the reaction that occurs in a similar direct alcohol fuel cell.

Advances in DMFC modelling

Even though numerous articles regarding the various processes occurring in DMFC has been published, very few deals with the modeling of fuel cells. This led to the development of various models and designs which intends to solve the problems encountered in DMFCs like corrosion of stacks due to liquid fuels, methanol cross over, water hold up, corrosion of current collectors. High energy density. DMFC system modelling is important to provide performance prediction and leads to design optimization. Problems encountered in DMFC vary from gas diffusion layer, catalyst layers, fluid flow, electrochemical kinetics, multi-component transport to methanol crossover, water hold up. Liquid fuel causes the corrosion the stack and therefore the performance drop as a result (4).

Gas diffusion layer

Transport phenomena in the Gas Diffusion Layer (GDL) are of vital importance for the operation of Direct Methanol Fuel Cells (DMFCs). A two-phase mass transport model was developed to investigate the effects of anisotropic characteristics of a GDL, including the inherent anisotropy, deformation, and electrical and thermal contact resistances, on the coupled species, charges and thermal transport processes in a DMFC. In this model, methanol crossover and non-equilibrium evaporation/condensation of water and methanol are considered. The multistep electrochemical mechanisms are used to obtain a detailed description of the kinetics of Methanol Oxidization Reaction (MOR) in both the anode and Cathode Catalyst Layers (CCL). The numerical results show that the anisotropy of the GDL has a great effect on the distribution of species concentration, over potential, local current density, and temperature (8, 21).

The deformation of the GDL depresses the transport of species through the GDL, particularly methanol diffusion in anode GDL, but facilitates the transport of electron and the removal of heat. The electrical contact resistance plays an important role in determining the cell performance. The use of adequate materials for the gas diffusion layers (carbon paper at the anode GDL and carbon cloth at the cathode GDL) enables the use of thinner membranes enhancing the water back diffusion which is essential to work at high methanol concentrations.

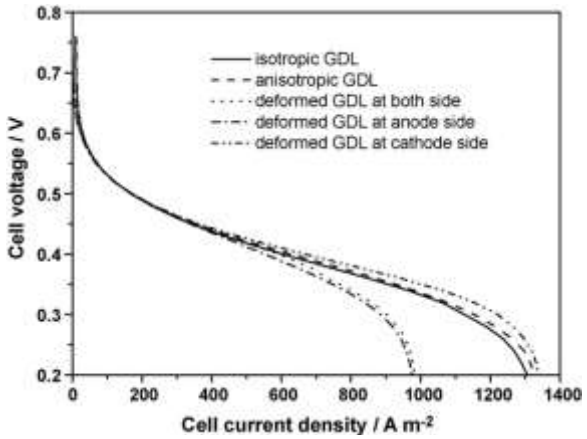

Fig 2: polarization curves for the DMFCs with different GDL shape and properties [8]

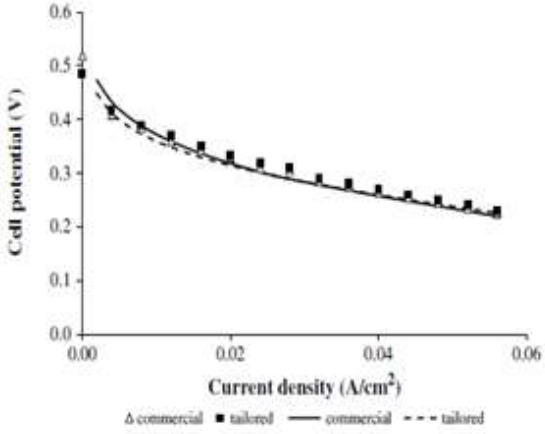

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Fig 3: influence of mea properties on cell performance. Model predictions [9]

A number of issues need to be resolved before DMFC can be commercially viable such as the methanol crossover and water crossover which must be minimized in portable DMFCs. A one dimensional (1-d), isothermal model for a Direct Methanol Fuel Cell (DMFC) was developed. This model accounts for the kinetics of the multi-step methanol oxidation reaction at the anode. Diffusion and crossover of methanol are modelled and the mixed potential of the oxygen cathode due to methanol crossover is included. Kinetic and diffusion parameters are estimated by comparing the model to data from a 25 cm^2 DMFC. This semi-analytical model can be solved rapidly so that it is suitable for inclusion in real-time system level DMFC simulations

A detailed experimental study on the performance of a DMFC with 25 cm^2 of active membrane area, working near the ambient conditions is described. Tailored MEAs (Membrane-Electrode Assemblies), with different structures and combinations of gas diffusion layers (GDLs), were designed and tested in order to select optimal working conditions at high methanol concentration levels without sacrificing performance. The experimental polarization and power density curves were successfully compared with the predictions of a steady state, one-dimensional model accounting for coupled heat and mass transfer, along with the electrochemical reactions occurring in the DMFC recently developed earlier (10,21). A tailored mea build-up with the common available commercial materials was proposed to achieve relatively low methanol crossover, operating at high methanol concentrations.

Catalyst layer

The cathode catalyst layer in Direct Methanol Fuel Cells (DMFCs) features a large thickness and mass transport loss due to higher pt loading, and therefore must be carefully designed to increase the performance. The effects of nafion loading, porosity distribution, and macro-pores on electrochemical characteristics of a DMFC cathode cl have been studied with a macro-homogeneous model, to theoretically interpret the related experimental results. Transport properties in the cathode catalyst layers are correlated to both the composition and microstructure. The optimized ionomer weight fraction (22%) is found to be much smaller than that in h_2 polymer electrolyte fuel cells, as a result of an optimum balance of proton transport and oxygen diffusion. Different porosity distributions in the cathode cls are investigated and a stepwise distribution is found to give the best performance and oxygen concentration profile. Influence of pore defects in the cls is discussed and the location of macro-pores is found to play a dual role in affecting both oxygen transport and proton conduction, hence the performance. The reaction zone is extended toward the membrane side and the proton conduction is facilitated when the macro-pores are near the gas diffusion layer. The effects of cathode catalyst layer (ccl) thickness on the detrimental effect of methanol cross-over in a direct methanol fuel cell (DMFC) under various operating conditions.

The results show that, when a thicker ccl, approximately twice the thickness of the base case, is used, the fuel cell performance increases significantly. The increase in performance with a thicker ccl is attributed to the oxidation of the methanol crossed-over in part of the catalyst layer and leaving the rest of the catalyst layer free from methanol contamination, leading to mitigations of the effects of mixed potentials. The results of Electrochemical Impedance Spectroscopy (EIS) show that the charge transfer resistance for the fuel cell with twice the thickness of ccl is 30% lower compared to that for the base case, indicating that the active catalyst area available for Oxygen Reduction Reaction (ORR) is indeed greater. The results of the Electrochemical Active Surface Areas (ECA) show that without methanol contamination, the ECA of the thicker ccl is actually lower, indicating that the better performance and the lower charge transfer resistance are not caused by a higher original ECA, but a higher active area for ORR. A much thicker ccl, about 5 times of that for the base case, is also used and the cell performance is also higher than that for the base case. The results show that there exists an optimum cathode catalyst layer thickness and the thickness of cathode catalyst layer has a significant effect on DMFC performance.

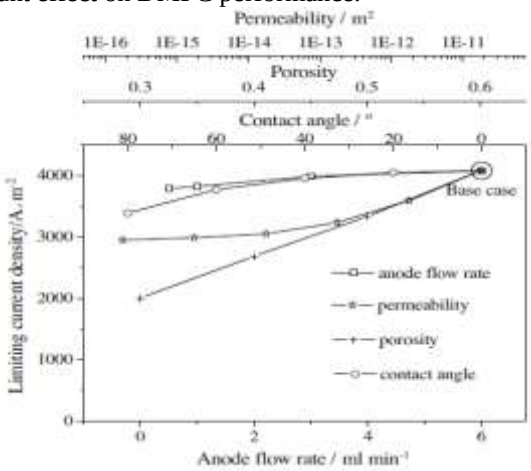


Fig 4: effects of flow rate, permeability, and contact angle towards limiting current density. [10]

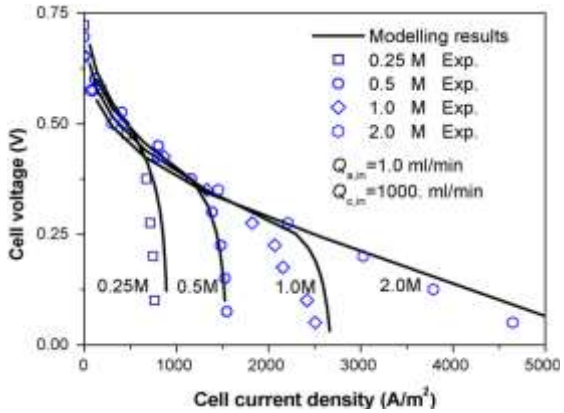


Fig 5: current density vs cell voltage [11]

The physical characteristics of the anode plays a significant role in the performance of DMFC. A two-dimensional, two-phase mass transport model for a direct methanol fuel cell (6) was developed. The numerical results show that the mass transfer of methanol is predominated by the resistance in the anode porous structure, which is affected by physical properties of the porous medium, such as porosity, permeability, and contacting angle. It is further shown that cell performance can be improved by increasing the porosity and permeability, and decreasing the contacting angle of the porous medium for a given feed methanol concentration.

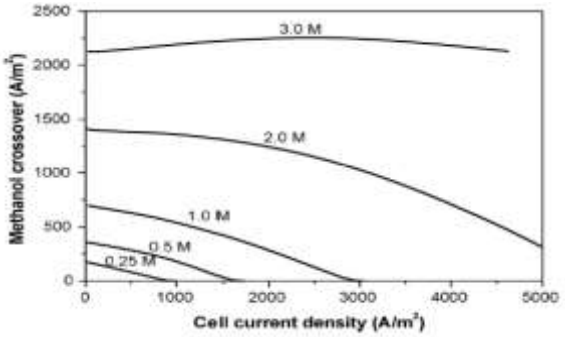


Fig 6: Methanol crossover as predicted by model [11]

Membrane electrode assembly

For a membrane in contact with liquid methanol and water on one side and conditioned air on the other, the corresponding differential equations and boundary conditions were derived in a polymer-related coordinate system taking into account the polymers three-dimensional swelling.

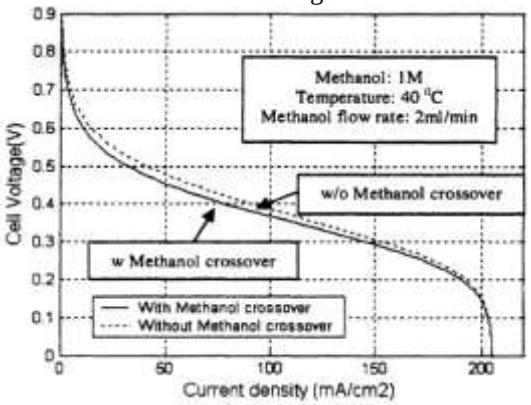


Fig 7: methanol crossover at concentration of methanol at 40^0 c at 2ml/min of methanol and 300 ml/min air [14]

Phase equilibrium parameters and unknown diffusion coefficients for nafion-117 were obtained by comparing the simulation results to water and methanol concentration profiles measured with confocal Raman spectroscopy. The effectiveness of the diffusion membrane is determined by the ability to resist

methanol crossover. It is generally observed that Methanol Crossover (MCO) as shown in fig 3 increases as the concentration of the feed solution increases which is shown in fig. The influence of methanol concentration, temperature and air flow rate was predicted by the model with a maximum relative mean deviation between measurement and simulation of 8.6% for methanol and 3.4% for water.

A mathematical model to simulate the fundamental transport phenomena in a passive direct methanol fuel cell (DMFC) operating with neat methanol. The neat methanol operation is realized by using a 'pervaporation' membrane that allows the methanol concentration from the neat methanol in the fuel reservoir to be declined to an appropriate level in the Anode Catalyst Layer (ACL). The water required by the methanol oxidation reaction on the anode is passively obtained by diffusion from the cathode through the membrane. The numerical results indicate that the methanol delivery rate from the fuel reservoir to the anode cl is predominately controlled by the pervaporation process. It is also found that under the neat methanol operating condition, water distribution across the membrane electrode assembly is greatly influenced by the membrane thickness, the cathode design, the operating temperature, and the ambient relative humidity.

A two-dimensional numerical model of the direct methanol fuel cell with gas fuel was developed (7). Simulation of the cell with current collectors of conventional geometry reveal the formation of fuel-depleted, "shaded" regions in the cathode and anode catalyst layers. These regions are positioned in front of current collectors, farther from the gas channel windows. Another disadvantage of the conventional geometry is the concentration of electron current at the edges of current collectors embedded current collectors may significantly improve the performance of the fuel cell. Based on the simulation results, a new design of current collectors was suggested. It was concluded that it is beneficial to position current collectors inside the backing and catalyst layers, parallel to the flow of the fuel. These embedded collectors do not produce shaded regions in the catalyst layers. Two plausible geometries of such collectors are considered: of rectangular and circular shape. Simulations show that depending on the transport properties of the backing and catalyst layers the

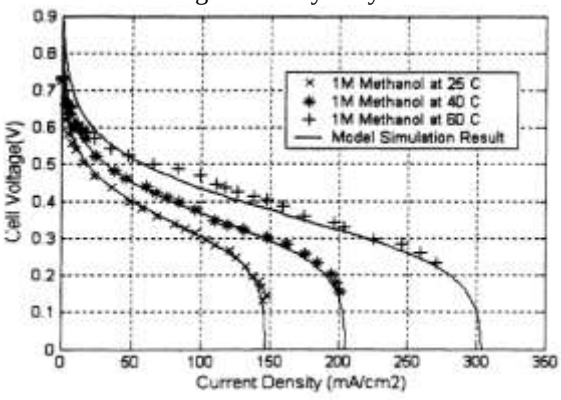


Fig 8: Current density vs cell voltage at methanol concentration of 1m. Flow rate of methanol is 2 ml/ min and the flow rate of air is 300 ml/min [14]

Flow distribution

Until recently, there were mainly two approaches in the modelling of DMFC, namely to derive through full CFD and to go through electrochemical reactions involving mass and electrons flux transport. The latter had the advantage of reduced computational complexity, however without considering the physics of two phase flow caused by anode methanol oxidation. Whereas, such effects are modelled using CFD techniques for accurate performance analysis. However extensive mathematical modelling has been conducted on the design and optimization of liquid-feed direct methanol fuel cells (DMFCs). Detailed modelling of DMFC operations reveals that a two-phase flow phenomenon at the anode contribute significantly to mass-transfer in a DMFC and its output performance (15). In practice, comprehensive simulations based on the finite volume technique for two-phase flow require a high level of numerical complexity in computation. To solve this problem, a complexity-reduced mathematical model was developed to cover both phenomena for a realistic, but fast, in computation for the prediction and analysis of a DMFC prototype design (16). Analysis of the DMFC mass-transfer was made, to investigate methanol distribution at anode and its crossover through the proton-exchange membrane. The influence of two-phase flow and under-rib mass-transfer on DMFC performance, the significance of gas-phase methanol transport was established. Simulation results as shown in fig 10 suggest that both the optimization of the flow-field structure and the fuel cell operating parameters (flow rate, methanol concentration and operating temperature) are important factors for competitive DMFC performance output.

The gas management on the anode side is an important issue in DMFC design and it greatly influences the performance of the fuel cell. A 3d DMFC model for gas evolution and flow patterns was developed to design optimal flow field for gas management (18, 19). The flow field is related to gas management and distribution. Since experiment for the optimal design of various flow fields is difficult and expensive and due to high bipolar pate cost, computational fluid dynamics (CFD) is mostly implemented to solve the problem.

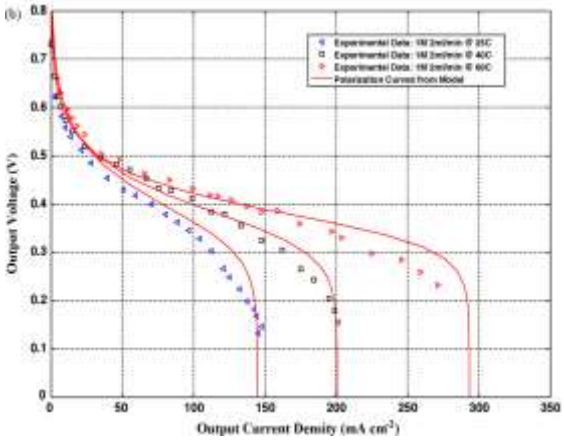


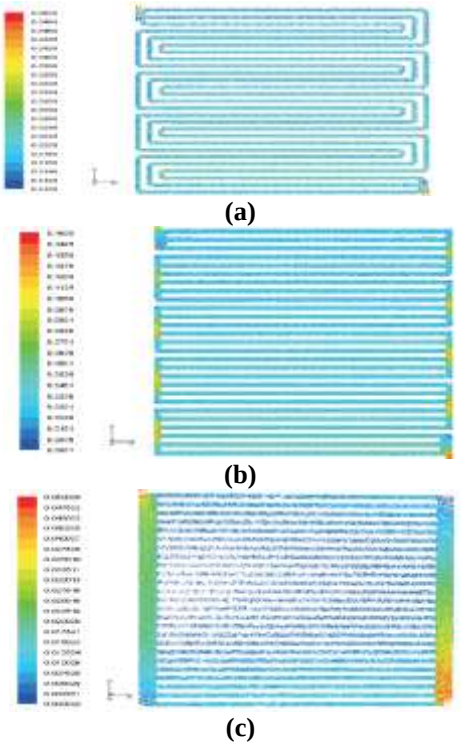
Fig 9: Model performance under different operating temperatures, 25, 40 and 60 ◦c, with 1m feeding methanol solution. Flow rate of methanol in anode channel is 2mlmin^{-1}. Air is supplied at cathode with flow rate of 300 ml min−1 in all cases. [13]

A two-fluid model was developed for CFD based flow field design. The CFD analysis is used to visualize and to analyze the flow pattern and to reduce the number of experiments. Case studies of typical flow field designs such as serpentine, zigzag and parallel type illustrate application of the model. A two-fluid model was developed for CFD based flow field design. The improved two-fluid model allows studying gas evolution in anode channels in a DMFC design without empirical correlations. The velocity and pressure are visualized and evaluated with characteristics of flow fields. The most widely used flow field design is the serpentine flow field. Though the serpentine design has high flow resistance, it is shown to

provide more uniform distribution of velocity and better performance than those with typical designs.

Simulation results revealed specific stagnant zones located at the corner where bubbles are growing in size, disturbing and blocking the reactant flow in channel. The simulation results of zigzag design are similar to the serpentine ones. The parallel flow field is a typical design for the straight flow. The simulation results predicted non uniform distribution of velocity in anode channels. It should be noted that the parallel flow field design is similar to a short straight pipe with a small pressure drop along the channel. Peculiarity of flow distribution is that the velocity in the middle section is lower than velocity in side area of the flow field. The disadvantage of the design is that flow distribution causes a stagnant zone and a reverse flow from the upper part to the exit. Carbon dioxide produced in the stagnant zone may obstruct reactant flow in channels. Flow fields are found to affect the fuel cell performance and pressure drop. This study revealed that the rectangular and straight flow channels are inefficient designs for gas management in a DMFC. The parallel type design with low resistance and serpentine design with high one are combined to fit the pumping power consumed by the fuel supply system in fuel cell systems. To improve overall fuel cell system performance new flow field design can be developed with an optimal pumping power and pressure drop for gas removal. For a fuel cell to function at its best the membrane plays a vital role. A multi-component transport model was developed to describe the diffusion driven mass transport of water and methanol in fuel cell membranes (5).

It was realized that for improving the efficiency of a fuel cell effectively it is necessary to consider the physics of the two phased flow caused by anode methanol oxidation. In essence, the hydrodynamic behaviour of the fluid should be modelled under transient condition for better operation of the fuel cell. In effect an investigation of hydrodynamic behaviour of different anode flow field designs of liquid-fed direct methanol fuel cells (DMFCs) was carried out.



(a)

(b)

(c)

Fig 10: velocity distribution diagram (a) serpentine flow (b) zig zag flow (c) parallel flow [15]

Experiments as well as CFD simulations of the transient concentration distribution and of the residence time behavior are analysed. Investigations at different flow rates show a negligible change of the flow pattern within a certain flow rate interval. Based on these results reduced models consisting of ideal reactor networks are developed. The studies highlight advantages and disadvantages of the various flow field designs with respect to hydrodynamics aspects. The CFD models as well as the reduced models can quantitatively reproduced the experimentally observed behaviour. Due to their small size, negligible computation times and modularity the reduced models are suitable for integration into dynamic DMFC models. With these, the influence of flow field design on DMFC behaviour was studied.

Conclusion

The various challenges in the modelling of a DMFC were addressed. After analysing the models on the gas diffusion layer it was concluded that rectangular and straight flow channels are inefficient designs for gas management in a DMFC. The combination of the parallel type design with low resistance and serpentine design with high one are effective in gas management. Various flow distribution patterns were discussed and it was deduced that though the serpentine design has high flow resistance, it is shown to provide more uniform distribution of velocity and better performance than those with typical parallel and zig zag designs. From the analysis, based on cathode catalysis models, there is an increase in performance as well as methanol crossover with increase in the thickness of cathode catalyst layer and methanol concentration.

Acknowledgements

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