



Review

Mass and heat transport in direct methanol fuel cells

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ABSTRACT

The direct methanol fuel cell (DMFC) is a better alternative to the conventional battery. The DMFC offers several advantages, namely, faster building of potential and longer-lasting fuel, however, there are still several issues that need to be addressed to design a better DMFC system. This article is a wide-ranging review of the most up-to-date studies on mass and heat transfer in the DMFC. The discussion will be focused on the critical problems limiting the performance of DMFCs. In addition, a technique for upgrading the DMFC with an integrated system will be presented, along with existing numerical models for modeling mass and heat transfer as well as cell performance.

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Contents

1. Introduction.....	9847
2. Mass transfer in DMFC.....	9848
2.1. Methanol crossover.....	9848
2.2. Water transport.....	9849
2.3. One-phase model.....	9850
2.4. Two-phase model.....	9850
3. Heat transport in DMFC.....	9852
3.1. One-dimensional model.....	9852
3.2. Two-dimensional model.....	9852
4. Algebraic approaches for DMFC/ μ DMFC.....	9852
4.1. Numerical techniques.....	9852
4.2. Mathematical modeling.....	9853
4.3. Experimental approaches for DMFC.....	9853
4.4. Computational fluid dynamics (three-dimensional model).....	9854
5. Conclusion.....	9854
Acknowledgement.....	9854
References.....	9854

1. Introduction

A fuel cell is an electrochemical energy device that converts the chemical energy in a fuel directly into electrical energy [1,2]. New

findings in fuel cell research have led to a rapid development in new kinds of fuel cells. Among these, the direct methanol fuel cell (DMFC) is very promising in terms of its potential for high energy density, low pollution, quick recharging and operation at room temperature. Micro direct methanol fuel cell (μ DMFC) refers to a micro-scale version of the system, which could be used to power portable devices.

The most important features of the DMFCs are the mass and heat transport in the system. A DMFC system consists of many different species, such as water, methanol, oxygen and carbon dioxide;

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thus, mass transfer occurs frequently. Common DMFC operating temperatures are in the range of 50–120 °C, and systems are often pressurized to prevent methanol vaporization, however, methanol and oxygen (air) enter the DMFC system at ambient temperature (25 °C); hence, heat transfer occurs because of the difference between the ambient and operating temperatures. A better understanding of mass and heat transport is essential for improving fuel cell performance and operating stability in the DMFC system.

This article includes mass and heat transport in active and passive systems for DMFCs. Section 1 is an introduction of DMFC systems in terms of mass and heat transport, while Section 2 focuses solely on mass transport in these fuel cell systems. A description of heat transfer is reviewed in Section 3, and Sections 4 and 5 discuss DMFC modeling methodologies, both algebraic and experimental approaches. Finally, Section 6 discusses a computational fluid dynamics (CFD) model for DMFC.

2. Mass transfer in DMFC

DMFCs use methanol and oxygen as raw materials, and methanol provides electrons via oxidation. Hydrogen ions formed from this oxidation pass through a membrane layer, and more electrons are used to reduce oxygen at the cathode. The transportation of these different mass species in DMFC systems is a technical issue that needs to be solved. Mass transport not only affects the performance and operating stability of DMFCs but also influences the volumetric energy density of the DMFC system [3–9].

Over the past decade, mass transport in DMFC systems involving methanol, water, carbon dioxide and oxygen has been extensively studied. The management of these masses is crucial since it can affect the cell performance of DMFC. To obtain the best performance of DMFC, the concentrated methanol or pure methanol up to 5 M is desired [10–13]. With practice of pure methanol, the volumetric energy density of DMFC can be higher than the energy density of a state-of-art Li-ion battery (about 350 Wh L⁻¹ [14]), however, this scenario can cause methanol crossover which methanol permeates through the membrane and arrives at the cathode, where it is oxidized to create a so-called mixed potential that can decrease the cathode potential.

Because the fuel cell is a multi-layered planar structure, the requirements for mass transport of species involved in electrochemical reactions in the in-plane and through-plane directions are different [15]. According to Rice and Faghri [16], methanol can be fed to the fuel cell through the vapor phase by a passive means. The major transport phenomenon governing this process is methanol evaporation from a nearly pure liquid methanol source into a porous media, followed by condensation into a highly dilute methanol solution at the anode side of the fuel cell. The reverse transport of water vapor occurs slowly because water has a much lower vapor pressure than methanol at a given temperature. Carbon dioxide is generated from the oxidation reaction and leaves the fuel cell from a gas diffusion layer at the anode. Fig. 1 shows a schematic of the mass transport process with a vapor feed DMFC system.

2.1. Methanol crossover

One of the main issues concerning mass transport in DMFCs is methanol crossover from the anode to the cathode. This crossover not only wastes fuel but also lowers the cathode performance, especially for room temperature DMFC systems. Methanol transport across the membrane is driven by molecular diffusion, a pressure gradient and electro-osmotic drag [17], however, the effect of the pressure gradient is typically small and neglected in a first

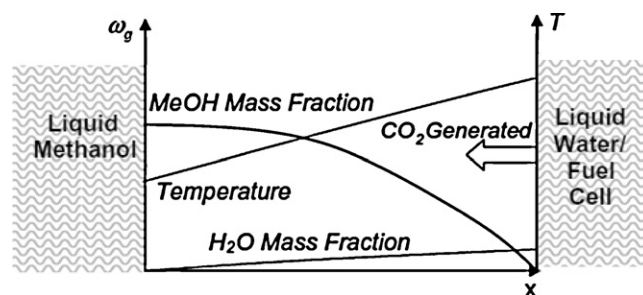


Fig. 1. Schematic of mass transport process for a vapor feed DMFC through a gaseous medium between a pure methanol source and the fuel cell [16].

approximation [18]. Assuming Fickian diffusion for methanol in the membrane, the molar flux of methanol can be written as [19]:

$$N_{\text{cross}} = n_d^m \frac{i}{F} - D_{m,\text{mem}}^{\text{eff}} \frac{dC_m}{dy} \Big|_{\text{mem}}, \quad (1)$$

where n_d^m is the electro-osmotic drag coefficient of methanol, defined as the number of methanol molecules dragged by a hydrogen ion moving in the membrane, and $D_{m,\text{mem}}^{\text{eff}}$ is the effective diffusion coefficient of methanol in the membrane, which is assumed to be independent of the concentration. The electro-osmotic drag coefficient of methanol is given as [20]:

$$n_d^m = \frac{W_w}{\rho_w} n_d^w C_{m,\text{acl}} \quad (2)$$

The electro-osmotic drag coefficient of water, n_d^w , is the number of water molecules dragged by a hydrogen ion moving in the membrane and is given by Guo and Ma [21] as:

$$n_d^w = 2.9 \exp \left[1029 \left(\frac{1}{333} - \frac{1}{T} \right) \right] \quad (3)$$

There are various expressions available in the literature for the effective diffusion coefficient of methanol in the membrane, $D_{m,\text{mem}}^{\text{eff}}$, at a range of operating temperatures for the DMFC system. According to Scott et al. [22], $D_{m,\text{mem}}^{\text{eff}}$ can be expressed as follows (in the range of temperatures of 298–363 K).

$$D_{m,\text{mem}}^{\text{eff}} = 4.9 \times 10^{-10} \exp \left[2436 \left(\frac{1}{333} - \frac{1}{T} \right) \right] (\text{m}^2 \text{s}^{-1}) \quad (4)$$

Because of their unique characteristics, DMFCs are considered potential power sources for stationary and transportation applications, however, improvements in DMFC performance are needed before its practical application can be realized, and indeed, significant research has targeted these challenges. Strategies employed for improved performance include increasing the efficiency of the catalyst, improving the fuel cell design and optimizing electrode structure. Arico et al. [23] studied the influence of flow field patterns on the performance of the DMFC, and this resulted in control of the methanol crossover and a more effective utilization of fuel using a Pt–Ru co-catalyst (which is accepted as the most effective anode catalyst).

The performance of liquid-feed DMFCs with Nafion membranes of various thicknesses and equivalent weights has been studied since the 1990s to measure the methanol crossover and electrical performance [24]. The results from these studies showed that Nafion EW 1500 is a very promising membrane material compared to Nafion EW 1100 and allows the DMFC to overcome problems with methanol crossover. Ravikumar and Shukla [11] reported on the effects of methanol crossover in a liquid-feed polymer-electrolyte DMFC using 2 M methanol. A liquid-feed DMFC with a proton-exchange membrane electrolyte with Pt–Ru/C as an anode and Pt/C as a cathode can deliver a power density of 0.2 W cm⁻² at 95 °C.

Valdez and Narayan [25] discussed techniques for quantifying the methanol crossover in a fuel cell and for separating the electrical performance of each electrode in a fuel cell. The cathode was found to be mass transfer limited when operating with a low air flow rate and high concentration of methanol. The development of a simple model to describe the permeation of methanol from the anode to the cathode in a DMFC was discussed by Cruickshank and Scott [17]. Using Nafion 117, the permeation rate was measured under various pressure differentials across the membrane to determine key parameters in the model. The three important parameters for methanol crossover are temperature, fuel flow rate and concentration [26]. The data from methanol crossover measurements are used to define a continuous loop model, which helps delineate the impact of parameter variations on the energy and power density.

Liu et al. [27] studied different thin membranes, including a catalyzed diffusion medium (CDM) anode, a thin Nafion membrane and a carbon cloth pre-coated with a highly hydrophobic cathode micro porous layer (MPL). They found that, when the net water transport coefficient through the membrane is smaller than 0.8 at 60 °C and 0.4 at 50 °C, the fuel efficiency is approximately 80%, and the steady-state power density at 60 °C and 0.4 V is 60 mW cm⁻² when a 3 M methanol solution is used. Methanol and water crossovers through a polymer electrolyte membrane (PEM) of a DMFC have been measured for different operating conditions using a mini-plant with full online material balancing of all DMFC inlet and outlet material flows [28]. In this study, the authors compared the experimental data with simulation results from a one-dimensional rigorous mathematical model of a DMFC, in which the main focus is a realistic description of mass and energy transport and the physical properties of the PEM material.

The effect of methanol crossover on the cathode behavior of a DMFC was also investigated using a half-cell method [29]. Significant oscillations in both current and open circuit potential at the cathode were found as a result of methanol crossover, which is one of the reasons for unstable operating behavior in DMFCs. The relation between methanol crossover and water crossover was studied for a passive liquid-feed DMFC based on a mass balance of the cell discharged under different current loads [30]. With a feed of 2–4 M of methanol, both water and methanol crossovers increase with an increase of current density. This can be concluded that reduction of water crossover from anode to the cathode was always related with a reduction of methanol crossover.

Brandao et al. [31] modified a Nafion membrane by self-assembly of palladium composite nanoparticles to reduce methanol crossover in a DMFC system. The performance using this system was compared to a system with unmodified membranes, and it was found that the modified membranes reduced methanol crossover by 10–35%, depending on the self-assembly time, nanoparticle composition and test temperature. To control methanol crossover, a perforated metal sheet in which the pore diameter and the porosity were regularly controlled was used in a passive DMFC, and the influence of open ratio on power generation was studied [32]. The pore diameter of the metal sheet did not affect the power generation or methanol crossover, however, the methanol transport was increased by decreasing the open ratio below 3%. Wu et al. [33] used a microfluidic-structure flow field for passive DMFC which consists of plural micro flow passages to control methanol crossover even though high concentration of methanol is used. The advantage of this innovative flow field allows passive DMFCs to achieve good cell performance with a methanol concentration as high as 18.0 M, increasing the specific energy of the DMFC system by about five times compared with conventional designs.

2.2. Water transport

Water is needed in DMFC system to ensure the transport of protons. For methanol oxidation reaction, MOR, water is required with the ratio of water to methanol to be 1:1, however, the management of water needed to be addressed to overcome the problem, i.e., water crossover and water flooding. Water crossover through the membrane is greatly influenced by the membrane electrode assembly (MEA) design including the anode and cathode gas diffusion layer (GDL). Wu et al. [34,35] investigate the effect of cathode GDL on water transport and cell performance in DMFC. It was found that the optimal design not only attained better cell performance, but also achieved better water management in DMFC using PTFE (polytetrafluoroethylene) loading in the cathode backing layer as well as in the micro-porous layer (MPL) and the carbon loading in the MPL [34], however, this scenario can also cause an increase in the oxygen concentration loss of the cathode performance thus lowering the cell performance [35].

By using an anode MPL made of carbon powder and nanotubes, water crossover can be controlled [36]. The practice of MPL could decrease the water crossover through the membrane without sacrificing cell performance when the feed methanol concentration is increased, and thereby increases the fuel cell system energy density. The presence of a large amount of water can cause flooding in DMFC systems. Water is needed to dilute the fuel (methanol) solution to overcome the methanol crossover. Traditionally, a high cathode gas flow rate is employed to prevent flooding, which can increase power consumption and impair DMFC compactness, however, the difficult task of removing water from the cathode to avoid severe flooding and supplying water to the anode to make up for water loss due to water crossover through the membrane requires innovative water management in a portable DMFC [37].

The multiphase mixture model is used to simulate two-phase water transport in the anode. For one-dimensional water transport through the membrane, the governing equation can be written as [38]:

$$\frac{d}{dx}(\gamma_c u C_{H_2O}) + \frac{d}{dx} \left[\left(\frac{1 - c_1^{MeOH} M^{MeOH} / \rho^2}{M^{H_2O}} - \frac{c_{sat}^{H_2O}}{\rho_g} \right) j_1 \right] = 0 \quad (5)$$

The two terms on the left-hand side describe water transport via convection and capillary transport. $C_1^{MeOH} M^{MeOH} / \rho_1$ is the mass fraction of methanol in the liquid, and γ_c is the advection factor [39], which is expressed as:

$$\gamma_c = \frac{\rho}{c_{H_2O}} \left(\frac{\lambda_1}{M^{H_2O}} + \lambda_g \frac{c_{sat}^{H_2O}}{\rho_g} \right), \quad (6)$$

where ρ , λ_1 and λ_g are the two-phase mixture density and the relative mobility of the liquid and gas phases, respectively. The relative mobility of the liquid and gas phase, λ_1 and λ_g , can be described by the following equation:

$$\lambda_1 = \frac{k_{rl}/v_1}{(k_{rl}/v_1) + (k_{rg}/v_g)}, \quad \lambda_g = 1 - \lambda_1, \quad (7)$$

where k_{rg} and k_{rl} are the relative permeabilities of the individual phases, which are equal to the cube of the phase saturations. The total water concentration is expressed in terms of the liquid saturation, s , as [40]

$$C_{H_2O} = s C_1^{H_2O} + (1 - s) C_{sat}^{H_2O} \quad (8)$$

Water crossover can be determined in situ by measuring the water flow rate at the exit of the cathode flow field in a DMFC system [41]. Experimental data showed that diffusion dominated the total water crossover flux at low current densities due to the high water concentration difference across the membrane. Water transport

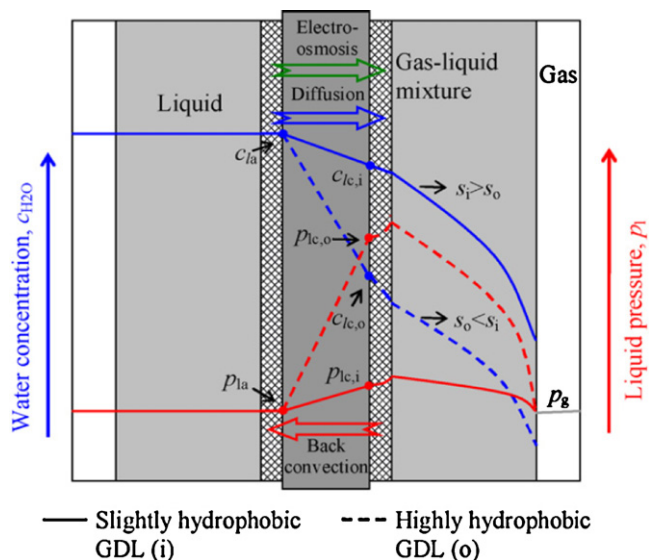


Fig. 2. Schematic illustrating water transports in a DMFC [40].

through a polymer electrolyte membrane used in a DMFC is generally due to three transport mechanisms: electro-osmotic drag by proton transport, diffusion driven by water concentration gradients and convection caused by hydraulic pressure gradients. Fig. 2 illustrates the water transport in a DMFC system through the membrane in a liquid-fed DMFC [41]. Liquid water in the fed dilute methanol solutions is transported from the anode channel membrane to the cathode layer, where part of it reacts with methanol to form the gas carbon dioxide.

Nafion 112 is used as a membrane in DMFC systems to manage water [42]. Excessive water crossover through the membrane results in water loss in the anode and flooding of the cathode. To investigate the water transport through MEA for a liquid feed DMFC, Xu et al. [43] developed a one-dimensional, isothermal two-phase mass transport model. The model enables quantification of the water flux corresponding to the water transport mechanism through the membrane for DMFCs. Using this model, the effects of MEA design parameters on water crossover and cell performance under various operating conditions can be numerically investigated.

Liu and Wang [39] studied water transport in DMFCs using an experimental method to evaluate the effect of the anode diffusion media. A two-phase water transport model was also employed to theoretically study their effects on water transport and saturation level in a DMFC anode. Another two-dimensional, two-phase mass transport model was developed to investigate the water transport characteristics in a passive liquid-feed DMFC [44]. Water transport was shown to be influenced by the ambient relative humidity.

2.3. One-phase model

A one-phase model for a DMFC/ μ DMFC depends on the phase of the methanol feed, and it can be either liquid-feed or gas-feed. Although we find a two-phase model more favorable, a few investigators are still focused on single-phase models to investigate DMFC performance. Scott et al. [22] developed a single-phase, semi-empirical DMFC model and investigated the impact of methanol crossover on cell performance. The results from the study were compared with experimental data measured with a methanol feed concentration of 1 M.

Liu et al. [45] studied the use of supported and unsupported catalysts to discern the effects of the catalyst loading, fuel concentration and temperature on the anode, cathode and full fuel cell

performance using a liquid-feed DMFC. All the investigations in this study were done using experimental methods. Using a liquid feed, the performance of a DMFC was evaluated with a Nafion solid polymer electrolyte membrane [4]. In this study, the authors included the mass transfer characteristics of the anode reaction in terms of the influence on carbon dioxide gas evolution and methanol diffusion on the cathode potential and thus cell voltage. Wang and Wang [18] used a liquid-phase DMFC model that included the transport phenomena and electrochemical kinetics to determine the effect of the methanol feed concentration on cell performance. They found that an increase in the methanol feed concentration leads to a slight decrease in cell voltage and a proportional increase in the mass-transport limiting current density for methanol concentrations below 1 M.

An isothermal, two-dimensional, liquid-phase DMFC model for the conservation of mass, momentum and species in the anode channel and porous media was used to demonstrate the relative importance of mass transfer resistance in both the flow channel and the adjacent porous backing [46]. Saarinen et al. [47] developed a free-breathing DMFC by assuming steady-state, isothermal and single-phase conditions. They included the mass transport phenomena and current production in the free-breathing DMFC when different operating parameters were varied.

Oliveira et al. [48] presented a one-dimensional, single-phase DMFC model and precisely studied methanol crossover and water transport across the membrane. They compared simulation results with experimental data measured at low methanol feed concentrations (i.e., 0.1, 0.2 and 0.5 M) and at an operating temperature of 70 °C. The limiting current density and the methanol crossover phenomena in a DMFC were studied using a one-dimensional, single-phase model [49]. The methanol crossover flux was decomposed into electro-osmotic and diffusion-driven methanol fluxes, and the behavior of methanol crossover over a wide range of methanol feed concentrations (i.e., 0.125–5.0 M) was intensively analyzed. Recently, Yang et al. [50] modeled a passive DMFC operating with neat methanol operation 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. The results showed under the neat methanol operating condition, water distribution across the MEA is greatly influenced by the membrane thickness, the cathode design, the operating temperature and the ambient relative humidity.

2.4. Two-phase model

A two-phase flow pattern in the anode channel under various operating conditions has been studied by Argyropoulos et al. [51] and Apyropoulos et al. [52]. This flow visualization on the anode side can lead to a valuable understanding of CO₂ bubble dynamics in a DMFC, however, the drawback of their studies is that they were done under low cell performance. To further flow visualization studies, Lu and Wang [53] have developed a transparent DMFC that allows for visualization of bubble dynamics on the anode side and liquid droplet dynamics on the cathode.

Methanol solution is supplied through the anode diffusion layer to the anode catalyst layer using an anode flow field. It is also used to transport carbon dioxide gas from the cell. As a result, two phases (gas-liquid) form in the flow field. Because the two-phase flow behavior in the flow field affects not only the mass transport of methanol to the anode catalyst layer but also the removal of carbon dioxide gas from the cell, two-phase flow behavior can have a large impact on cell performance [54–63]. Two-phase flow behavior in different anode flow fields was studied to obtain a better understanding of the mass transport of methanol and carbon dioxide gas on the DMFC anode [37,63–71]. The most commonly used

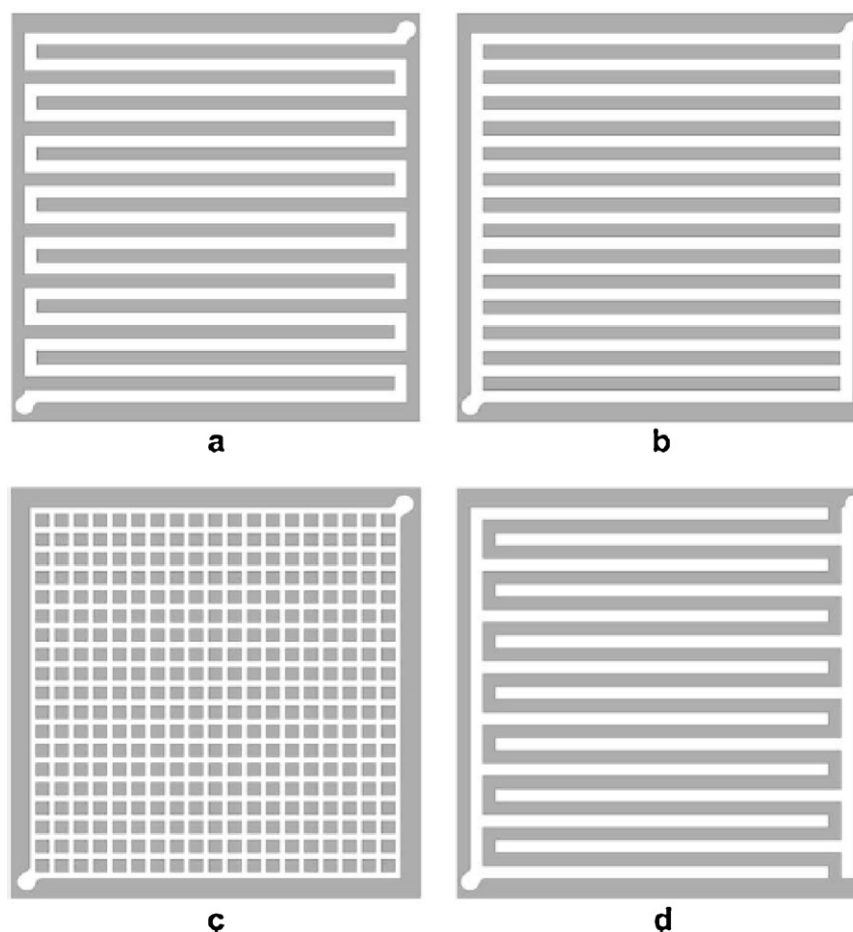


Fig. 3. Different flow fields for DMFCs: (a) serpentine, (b) parallel, (c) spot, and (d) interdigitated [15].

flow fields are shown in Fig. 3. A comparison between the flow fields has been summarized by Qian et al. [61] and is shown in Table 1.

Mass transport in an air-breathing DMFC was discussed using a three-dimensional [72] and two-dimensional [73] two-phase liquid feed to examine the water crossover through the membrane [72] and the cathode [73]. Various processes that affect DMFC behaviors are numerically studied using a two-dimensional, isothermal two-phase mass transport model [74] and a transient two-phase mass transport model [42] for a liquid-feed DMFC. In addition, Oliveira et al. [48] developed a one-dimensional model to predict the correct trends for the influence of current density and methanol feed concentration on both methanol and water crossovers. A two-dimensional, transient, multiphase, and

multicomponent model that considers mass transport in the feed delivery system was developed and compared to existing experimental data with a high level of agreement [75].

Complexity-reduced mathematical modeling was used to describe both mass and heat transport in a realistic, but fast, computation for the prediction and analysis of a DMFC prototype design [76]. The simulation results were validated against experimental data with good agreement and suggested that both optimization of the flow-field structure and fuel cell operating parameters are important factors for DMFC performance. He et al. [77] offered a two-dimensional, two-phase mass transport model that can be numerically solved with an in-house code and validated this model with published experimental data. The results showed that mass

Table 1
Comparison of different flow fields used in portable direct fuel cells [61].

Flow field	Advantages	Disadvantages	Applications
Straight (parallel)	Lower pressure drops	Prone to inhomogeneous reactant distribution and product removal	Active DMFC Passive DMFC
Serpentine (meander)	Helpful to remove gas product at the anode and water at the cathode, and to enhance two-phase mass transport	Higher pressure drops	Active DMFC
Spot (pin or grid)	Similar to straight flow fields as above	More parasitic energy required Similar to straight flow fields as above	Active DMFC
Interdigitated	Enhanced local mass transport by both diffusion and forced convection	High-pressure difference required between channels High parasitic energy required	Active DMFC
Porous media diffusion	Simple, low cost and compact	Lower mass transfer rates dependent on porous media Separate current collector needed	Passive DMFC

transfer of methanol is predominated by a resistance from the porous structure.

A conventional two-phase mass transport model was developed to determine the liquid water distribution in the anode diffusion medium of a liquid-feed DMFC [78]. A simple theoretical approach combined with in situ measurements for water-crossover flux in a DMFC resulted in a model for water distribution that was much more realistic than previously predicted models. Using a multi-fluid approach, a two-dimensional, two-phase model was developed for a passive vapor-feed DMFC to investigate the effect of various operating parameters and cell configurations on the mass transport and cell performance [79]. Recently, Basri et al. [80] presented a two-phase, unsteady state model for a liquid-feed DMFC that considers mass and heat transport. This study revealed that the optimum performance, in terms of methanol crossover, occurs at a methanol concentration of 4 M, and the authors described the effects of the methanol feed concentration in the reservoir and the current density on mass transport of the catalyst layer.

3. Heat transport in DMFC

3.1. One-dimensional model

In recent years, interest in fuel cells has increased for a range of applications, such as power for transport and smaller scale static systems. Because fuel cells are developed to generate electricity, heat transportation in DMFC system can be obtained. A fuel cell is an electrochemical device that directly converts chemical energy into electrical energy. Argyropoulos et al. [81] presented a one-dimensional thermal model for a DMFC stack based on the differential thermal energy conservation equation. In the first part of their study, they developed the model, and in a second party, the model was used to assess the effect of operating parameters on the temperature profile along the stack.

In addition, Argyropoulos et al. [82] developed a thermal energy one-dimensional model for a DMFC based on the differential thermal energy behavior of a DMFC stack composed of many large cells in a bipolar arrangement. This model allows for an assessment of the effect of operating parameters and system design on the temperature profile. A one-dimensional model for a passive liquid-feed DMFC was developed by considering the inherently coupled heat and mass transport, along with the electrochemical reactions [12]. It seems that the improved performance with higher methanol concentrations in DMFC systems is due to the increased operating temperature resulting from the exothermic reaction between permeated methanol and oxygen on the cathode.

Kulikovsky developed a model of heat transport in a membrane-electrode assembly [83] and a fragment of a DMFC stack [84]. These models included heat release in the reaction on both sides of the cell and heat transfer to the anode flow. Oliveira et al. [85] presented a one-dimensional and non-isothermal model for a passive DMFC to predict the methanol, oxygen and water concentration profiles in the anode, cathode and membrane and to estimate the methanol and water crossovers and the temperature profile across the cell.

3.2. Two-dimensional model

Compared to models of a PEM fuel cell, the DMFC models are less developed, and some problems remain to be solved. Heat transport in DMFC systems needs to be improved to overcome problems such as methanol and water crossovers and carbon dioxide diffusion. Kulikovsky [86] developed a two-dimensional numerical model of a DMFC. This model is based equations of conservation of mass and current. The results from this study showed that the transport of methanol near the fuel channel is determined mainly by the

pressure gradient, whereas methanol transport in the active layer and the membrane is dominated by diffusion.

The inherently coupled heat and mass transport in a passive DMFC was modeled based on unsaturated flow theory in porous media for a two-dimensional, two-phase thermal model [87]. The model is solved numerically using a home-written computer code, and the results showed that cell performance increases with increasing methanol concentrations from 1.0 to 4.0 M due to the increased operating temperature. Management of heat transport is crucial for DMFC systems because the electrochemical reaction rate and coefficients of diffusion depend on the temperature of the catalyst layer. Another developed model of a two-dimensional, two-phase non-isothermal system used natural convection heat transfer at the outer surface of the current collector as the thermal boundary condition [88]. Established models such as these can be used to predict cell performance of a DMFC under different operating conditions.

Analysis of heat and mass transport was performed using a two-dimensional, transient, multi-phase, multi-component and non-isothermal model in a miniature passive and semi-passive liquid-feed DMFC [89]. The cell temperature can increase during operation due to heat generation by internal phase changes and electrochemical reactions. Bahrami and Faghri [90] offered a two-dimensional, steady-state, non-isothermal, multi-fluid, two-phase flow model of a semi-passive DMFC to investigate the effect of different air flow rates (as an oxidant) in the cathode channel on the temperature, oxygen and water vapor mass fractions and the liquid saturation.

4. Algebraic approaches for DMFC/ μ DMFC

4.1. Numerical techniques

In recent years, varied and extensive research on numerical techniques has been done to solve problems in DMFC systems. In general, a DMFC exhibits lower power densities than those of a H₂/air polymer electrolyte fuel cell (PEFC), which requires anode and cathode platinum loadings less than 1 mg cm⁻² to achieve a power density of 0.6–0.7 W cm⁻², however, a DMFC offers several advantages, such as easier fuel storage, no humidification requirement and a simpler design, and it is considered a leading contender for portable power applications. The thermodynamic equilibrium potential and efficiency of a fuel cell can be calculated from the following:

$$\Delta E = -\frac{\Delta g}{nF} = \frac{\Delta h - T \Delta s}{nF} \quad (9)$$

$$\eta_{rev} = \frac{\Delta g}{\Delta h} = \frac{\Delta F \Delta E}{-\Delta h} \quad (10)$$

The thermodynamic cell potential for a general liquid-feed DMFC is 1.21 V, which is similar to that of the H₂/air PEFC. The theoretical thermodynamic efficiency of DMFC reaches 97% at 25 °C, however, the practical energy efficiency is much lower after accounting for voltage and fuel losses. In a DMFC, fuel efficiency is affected by methanol crossover and is defined as:

$$\eta_{fuel} = \frac{I}{I + I_{xover}}, \quad (11)$$

where I_{xover} is an equivalent current density caused by methanol crossover under the operating current density of I .

Methanol crossover combined with slow anode kinetics can lead to a power density in a DMFC system that is three to four times lower than that of a hydrogen fuel cell [91]. Thus, much work has been done to overcome this problem. The activation overpotential

of the methanol oxidation reaction (MOR) can be calculated using Tafel kinetics as follows:

$$\eta_a = b_a \log \left(\frac{I}{I_{0,a}} \right), \quad (12)$$

where b_a and $I_{0,a}$ are the Tafel slope and exchange current density of MOR, respectively. According to Wikipedia [92], the Tafel equation is related to the rate of an electrochemical reaction and the overpotential. The Tafel slope, b_a , can be measured by experimental work.

The oxygen reduction reaction (ORR) on the DMFC cathode can cause high cathode overpotential. Similar to the equation for the MOR, the ORR can also be described using Tafel kinetics, as shown below:

$$\eta_c = b_c \log \left(\frac{I}{I_{0,c}} \right), \quad (13)$$

The Tafel slope for ORR is approximately 70 mV decade⁻¹ in the absence of methanol oxidation. In a DMFC system, however, the ORR takes place simultaneously with the oxidation of crossover methanol, and consequently, b_c for a DMFC becomes greater than that in a PEFC system. A DMFC model that captures the essence of electrode kinetics and methanol crossover has been developed to establish a relationship between the methanol feed concentration and power density at a given current density [93]. This model also included a sensitivity analysis of cell voltage and methanol feed concentration to identify the optimal feed concentration.

Sun et al. [94] described new numerical techniques for a three-dimensional, two-phase transport model of a liquid-feed DMFC where flow, species, charge-transport and energy equations are simultaneously addressed. Based on the numerical techniques presented, a fast nonlinear iteration (130 iteration steps) and numerical solutions were obtained, in contrast with non-convergent numerical solutions using the standard in-house finite element/volume code without new numerical techniques. Using a multiphase mixture formulation, a two-dimensional model was presented and analyzed for a vapor-feed DMFC system [95]. An iterative numerical scheme is used to solve the governing equations to explore the transient and polarization characteristics of a DMFC, including methanol crossover through the membrane, temperature evolution, and anodic and cathodic overpotentials.

4.2. Mathematical modeling

Attempts to elucidate the fundamental electrochemical reaction mechanism, explore new compositions and structures of catalysts, and develop new membranes and methods to prevent important system issues relevant to DMFCs are emerging. Issues such as water management, gas management, flow field design and optimization and scaling for different applications have been researched by various authors to solve problems encountered with DMFC systems.

Mathematical modeling is one attempt at describing DMFCs that has many advantages over an experimental approach. Mathematical modeling does not involve experimental preparations, and complex systems can be handled easily, making this technique more favorable to researchers. Scott et al. [56], Sundmacher and Scott [64] and Argyropoulos et al. [96] developed several simplified single-phase models to study transport and electrochemical processes in DMFCs. Baxter et al. [97] developed a one-dimensional mathematical model for a liquid feed DMFC anode. The authors assumed that carbon dioxide is only dissolved in the liquid; therefore, the model is defined as a single phase anode model.

Kulikovskiy et al. [98] developed a two-dimensional model to study the vapor feed in DMFC systems, however, in the study, the important phenomenon of methanol crossover was ignored. A

different, one-dimensional model was developed by Dohle et al. [99] for a vapor-feed DMFC that considered the crossover phenomenon and the effects of methanol concentration on cell performance.

Modeling can be used to define concentration and gas content profiles in anode channels because the parameters are difficult to measure in situ. Argyropoulos et al. [100] offered a liquid-feed DMFC model to predict the local pressure and chemical composition in the anode and cathode sides. Rice and Faghri [101] developed a two-dimensional, transient multi-phase, multi-component fuel cell model that captures evaporation/condensation rates. This model is formulated in a manner to capture non-equilibrium effects between the phases. For electrochemical kinetics, the Tafel equation, incorporating the effects of two phases, was used to predict the methanol crossover for a three-dimensional, two-phase and multi-component liquid-feed DMFC [102].

A non-isothermal, dynamic optimization model of a DMFC was developed to investigate the sensitivities of the transient behavior on the operating conditions through a dynamic solution [103]. It was revealed that anode feed concentration has a significantly larger impact on methanol crossover, temperature and cell voltage than the anode and cathode flow rates. Yan and Jen [104] presented a two-phase flow model to evaluate the effect of operating parameters on DMFC performance. The model considered fluid flow, electrochemical kinetics, current density distribution, hydrodynamics, multi-component transport and methanol crossover. Process control in portable DMFC systems is important because it can maintain the system output and stabilize the whole system. Zenith and Krewer [105] developed a dynamic model for a DMFC to analyze the system's losses and main dynamics for stability and the time constant. This system was found to be stable for all dynamics except for that of water holdup, which decoupled with single-input, single-output and feedback controllers.

4.3. Experimental approaches for DMFC

Many experimental investigations of DMFC behavior have been performed. Lee et al. [106] developed a DMFC/battery hybrid power system used for portable application. The setup of a connection apparatus with a DMFC and a battery has been done to measure and analyze load share and the fuel cell/battery dynamic characteristic. They concluded that the results from this study can be used to design an interface module for fuel cell/battery hybrid systems and to determine the fuel cell design requirements for portable applications. In another experimental study, Drake et al. [107] measured the methanol crossover in a DMFC system and found that the anodic CO₂ contributes to the total cathodic flux, which has a positive implication for fuel cell efficiency.

A 75 h life test of a DMFC was done at a low current density of 100 mA cm⁻², and the MEA system was characterized using electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) [108]. The results indicated that the agglomeration of the electro catalyst, together with delamination of MEA, contribute to the degradation of a DMFC. Bae et al. [13] used a passive DMFC single cell to investigate the effects of methanol concentration, catalyst loading of electrodes, fuel and oxidant supply modes and long-term operation on performance. It was ascertained, the highest single cell performance was 45 mW cm⁻² with 5 M methanol feed at room temperature and ambient pressure for a passive DMFC system.

The colloidal method was used to characterize high metal content Pt–Ru alloy catalysts (80 and 90 wt.%) with various carbon blacks for use in DMFCs [109]. The analysis is accomplished using high metal content catalyst with various supports for the anode of DMFCs with different type of electrolyte, i.e., liquid and solid. The results showed that 90 wt.% Pt–Ru/Ketjen Black gave the best

performance as the anode catalyst in a unit cell as the thin catalyst layer helps mass transport easy and the exposure of nanoparticles to form effective triple phase boundary with Nafion ionomer. Whereas, the 80 wt.% Pt–Ru/Ketjen Black showed the highest activity for methanol oxidation in electrochemical experiments. Flow field design has been experimentally studied to test the performance of a DMFC with stainless steel 316 (SS 316) end plates, which are fabricated with an intricate modified serpentine [110]. A long-term test was carried out for 100 h, and the stack efficiency was found to be 51%. Abdelkareem and Nakagawa [111] investigated the effect of oxygen and methanol supply modes through the MEA of a DMFC with and without a porous plate. In the case of a MEA with a porous plate, the flow of oxygen and methanol had no significant effect on cell performance.

Reference cells are used to distinguish between polarization losses of the anode and cathode electrodes. In a DMFC a reference electrode can either be attached using a salt bridge or be printed directly on the same ionomer as the working electrode. Eccarius et al. [112] developed a new technique to improve the alignment of the electrodes to prevent boundary effects. The results were validated using SEM, showing that the relative error in distinguishing anode polarization losses using the reference cell is well below 1%. Development of a MEA has been experimentally studied using four different methods tested under different temperatures and different methanol concentrations [113]. The results from these studies showed that the different methods give different MEA performances in DMFC system.

4.4. Computational fluid dynamics (three-dimensional model)

Optimum flow field design is important for improving flow patterns and gas evolution in anode channels. Computational fluid dynamic (CFD) simulations are widely used for PEMFC flow-field design [114–117] to integrate electrochemical processes with water/proton co-transport to enable multiphysics modeling and large-scale simulation, however, compared with H₂/air PEFCs, three-dimensional mathematical modeling has not been widely applied to DMFCs due to more complex interactions between two-phase species transport and electrochemical reactions.

Liu and Wang [8] presented a three-dimensional, two-phase DMFC model based on the mixture framework of Wang et al. [18,118,119] that revealed an intricate interaction between species transport and electrical current in three dimensions. The model was extended to further study the net water transport coefficient distribution and interfacial liquid water coverage effect [62]. CFD can be used in a three-dimensional model to capture performance limiting effects such as mass transfer and gas evolution. A CFD model was used to estimate the interfacial mass transfer without empirical correlations [120]. The improved two-phase model was developed for gas evolution and current distribution in a DMFC and showed that an increase in inlet flow rate corresponds to a decrease in the gas content in the outlet of the anode channels.

CFD-based simulations were used to visualize and analyze the gas evolution and flow patterns in anode channels [121]. Using a three-dimensional model, case studies of typical flow field designs such as parallel and serpentine flow fields illustrated applications of the CFD model. Ye et al. [122] performed a three-dimensional numerical simulation of mass transport of methanol in the DMFC anode under open-circuit conditions. They managed to obtain the mass flux of methanol through the porous layer for different permeability values.

Vera [19] described three-dimensional mass, momentum and species transport in anode channels and the gas diffusion layer using a commercial, finite-volume based, CFD software complemented with user supplied subroutines. The outcomes in terms of methanol feed concentrations, temperatures and volumetric

methanol flow rate agreed with experimental results found in the literature. A three-dimensional mathematical model incorporated with FLUENT computer code was presented to investigate the flow and heat transfer in μ DMFC with serpentine flow fields [123]. Using CFD code, the continuity, momentum, and energy equations can be simultaneously solved.

5. Conclusion

In this review, DMFCs have been discussed in terms of mass and heat transport and other subjects related to these systems. Application of DMFC systems can be found in many aspects of life because this system can replace electricity sources and offers several advantages to conventional batteries. Therefore, it is important to identify issues related to DMFC performance to make this system more favorable over other types of fuel cells.

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