DMFC Models and Applications - A Literature Survey, Part I

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Abstract

Fuel cell modeling is considered an effective tool for calculating various parameters of the fuel cell as well as understanding various phenomena occurring within the cell. In literature, various models of direct methanol fuel cell (DMFC) that include the analytical model, the semi-empirical model, and the mechanistic model have been developed and tested. Analytical model takes into account basic parameters of fuel cell such as cell voltage, current density and power to investigate the performance of the fuel cell. Analytical model uses assumptions in order to develop a simple model. Semi-empirical model predicts the cell performance as a function of operating conditions such as pressure, temperature and concentration using empirical equations. Mechanistic model describes the fundamental phenomena of the fuel cell using differential and algebraic equations. This paper reviews literature dedicated to various models that have been successfully developed for the DMFC.

Keywords
Fuel cell; Direct methanol fuel cell; Analytical model; Semi-empirical model; Mechanistic model; Electrochemical model.

Introduction
A fuel cell is an electrochemical device, which converts chemical energy into electrical energy without combustion. It takes fuel at anode side and oxidant at cathode side and in the presence of electrolyte, reaction occurs between them to produce electricity. Unlike battery, fuel cells can operate continuously as long as fuel is supplied. The fuel used is typically a hydrocarbon or any other Hydrogen-containing compound which would produce Hydrogen after reprocessing. Fuel cells, being renewable as well as environment-friendly, seem to be the most promising source of electrical energy. Beside these advantages, fuel cells have high efficiency, superlative dynamic response, and superior reliability and durability in almost all kinds of portable and transportation applications [1].

The first fuel cell that was reported in the literature is a polymer electrolyte membrane based fuel cell (PEMFC) which uses Hydrogen as the fuel. Other types of fuel cell are also reported in literature such as alkaline fuel cell (AFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC) and solid oxide fuel cell (SOFC). Hydrogen is used as fuel in all of which brought up the issues associated with safe transportation and storage of the fuel [2]. An alternative approach is to oxidize a liquid fuel and to produce Hydrogen.

The direct methanol fuel cell (DMFC) uses methanol (CH_3OH) as the fuel and operates at relatively low temperatures (below 130^{o}C) without the use of a reformer. The advantages of DMFCs include high efficiency, very low emission, and fast and convenient refueling capability [3]. Furthermore, DMFCs are reliable, flexible, durable and easily maintainable. Due to these properties, DMFC is gaining huge popularity in the field of fuel cell technologies.

A typical DMFC comprises of two flat electrodes with a thin layer of membrane electrode assembly (MEA) in the middle. The membrane electrode assembly is the key component of DMFC and consists of a catalyst layer and a diffusion layer for both anode and cathode [4]. Figure 1 illustrates the basic building blocks of a typical DMFC.

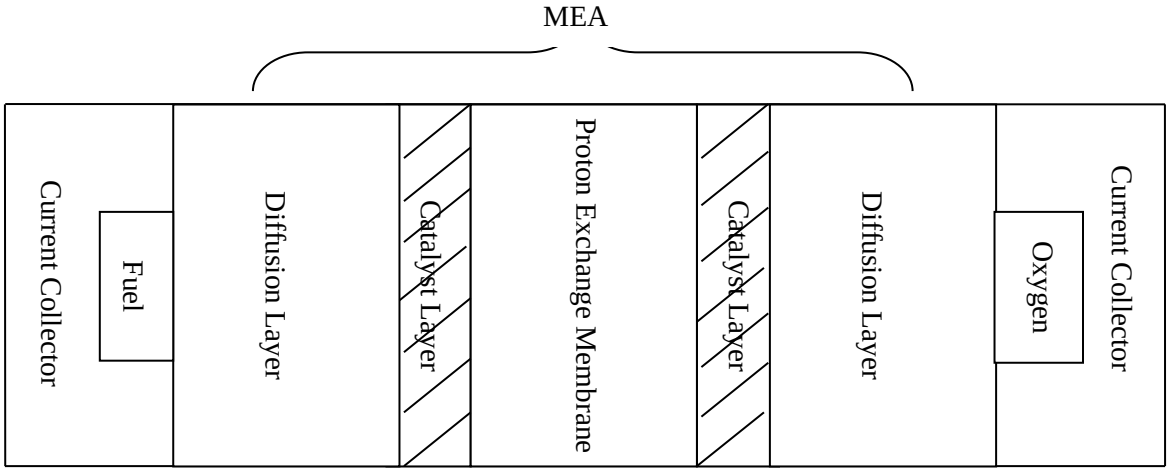

Figure 1. Basic building blocks of a typical DMFC [4].

DMFC produces electricity by electrochemical process. Methanol is fed with water at anode to produce Hydrogen atoms (protons and electrons) and carbon dioxide. Electrons travel to the cathode through an external circuit containing load while protons migrate through the membrane. At the cathode, Hydrogen protons and the electrons combine with oxygen from air to form water. The chemical reactions occurring in the DMFC are as follows [4]:

Anode:

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \quad (1)$$

Cathode:

$$\frac{3}{2} O_2 + 6H^+ + 6e^- \rightarrow 3H_2O \quad (2)$$

Overall:

$$CH_3OH + \frac{3}{2} O_2 \rightarrow CO_2 + 2H_2O \quad (3)$$

Acceptable level of carbon dioxide and water are produced as a byproduct, which ensures compliance with environmental pollution related constraints.

1. DMFC Models

Various DMFC models have been proposed and developed over the last few years which include analytical, semi-empirical, and mechanistic models [5-18]. Additionally, several research groups investigated the operational characteristics of DMFC such as the effects of operating parameters on DMFC performance [19-42].

2.1 DMFC Analytical Models

Analytical modeling is considered an important tool to understand the effects of basic parameters on the fuel cell performance. The analysis of the cell voltage as a function of the cell current density is essential to determine the fuel cell performance. The basic equation for the cell voltage for any model is given by the equation [3]:

$$V_{cell} = E_{cell} - \eta_a - \eta_c - \eta_{ohm} \quad (4)$$

where, V_{cell} is the cell voltage, η_{a} is the anode overpotential, η_{c} is the cathode overpotential and $\eta_{ohm} = jR_{cell}$ is the ohmic losses. j is the cell current density and R_{cell} is the resistance of the fuel cell. E_{cell} is the ideal electromotive force of the cell which depends on the temperature and pressure as follows [5]:

$$E_{cell} = E^0_{cell} + (T - T_0)\left(\frac{\partial E_{cell}}{\partial T}\right) - \Delta n \frac{RT}{vF} ln\left(\frac{P}{P_0}\right) \quad (5)$$

where E^0_{cell} is the open circuit voltage of DMFC that has a theoretical value of 1.21 V, $(T - T_0)$ is the difference between a given temperature T and a reference temperature T_o, R is the universal gas constant, v is the velocity, F is the Faraday's constant, P is the pressure, and P_0 is the reference pressure.

There are many analytical models reported in the literature [5-13]. Guo and Ma [5] described a two-dimensional (2D) analytical model of DMFC. The model is used to study the electrochemical reactions at the anode and cathode electrodes as well as the transport phenomenon in fuel cell. The phenomena include methanol crossover, diffusion of

reactants, fluid flow, etc. The analytical solution of the model is derived and used to predict the cell voltage as a function of the fuel cell current density. Furthermore, the model is used to analyze and determine fuel cell parameters. It is concluded that the methanol concentration decreases linearly along the flow direction of anode channel and anode catalyst layer.

Chen and Yeh [6] developed a one dimensional analytical model based on physiochemical processes of DMFC, which describe the behavior of electrochemical systems. DMFC can be divided into seven compartments namely the anodic flow channel, the anodic diffusion layer, the anodic catalyst layer, the proton exchange membrane, the cathodic catalyst layer, the cathodic diffusion layer and the cathodic flow channel. For each compartment, a governing equation has been developed. This model evaluates the flow channels, the methanol and oxygen transport, the reaction kinetics within anodic and cathodic catalyst layer and the mixed potential effect. The mixed potential, caused by oxidation of methanol crossover at the cathode, is calculated by evaluating the internal current generated by methanol permeation in cathodic catalyst layer. This model was validated in the laboratory to obtain the experimental data which was used to determine key parameter values from the I-V characteristics. It was found that mixed potential decreases the fuel cell voltage.

Kulikovsky [7] developed a fitting equation for voltage-current curve by taking into account the voltage losses due to transportation of reactants in diffusion layers and methanol crossover. Finally, the analytical model for optimal methanol concentration in the feed channel is derived and the analytical model was used to develop the DMFC performance characteristics [8]. The optimal methanol concentration in anode channel, $(c_h^a)_{opt}$, is determined using the following equation [7, 8]:

$$(c_h^a)_{opt} = \frac{2}{3}\left(\frac{1+\beta}{\beta}\right)\left(\frac{\gamma^a}{\gamma^a+\gamma^c}\right)\frac{D_b^c l_b^a}{D_b^a l_b^c} c_h^c \quad \text{..... (6)}$$

where,

$$\beta = \frac{D_m l_b^a}{D_b^a l_m} \quad \text{..... (7)}$$

In the above equation, D is the diffusion coefficient, l_b is the thickness of backing layer, l_m is the thickness of membrane, γ is the effective order of reaction, and c_h is the oxygen concentration in cathode channel. The subscript "b" indicates the backing layer.

The idea behind the fitting procedure is that there should be some common fitting parameters among the set of performance curves obtained for different methanol concentrations and they are fitted simultaneously by using a generic algorithm in two stages. In the first stage, common parameters are calculated independently whereas, in the second stage, a mean value is estimated for each common parameter and further iteration corrects the mean values. This fitting procedure is used to analyze the set of performance curves until acceptable physical parameters of the cell such as transfer coefficients, diffusion coefficients, conductivities of catalyst layers on both side of the cell, specific cell voltage and loss due to methanol crossover through membrane are attained. The fitting equation provides reasonable approximations for basic transport and kinetic parameters on both sides of the fuel cell and is given by following equation [7,8]:

$$\frac{\eta}{b} = \emptyset\left(\frac{j}{j_*}\right) ln\left(\frac{j}{j_*}\right) - ln(k_t) \quad \text{..... (8)}$$

where b is Tafel slope, j is current density, $j_* = \frac{2\sigma_t b}{l_t}$ is a characteristic current density, $k_t = \frac{l_t i_*}{j_*}\left(\frac{c_t}{c_{ref}}\right)^\gamma$ describes the variation of cell voltage as a function of concentrations of feed molecules. Here, σ_t and l_t are proton conductivity and thickness of catalyst layer respectively, i_* is exchange current density, c_t is the concentration of feed molecules in catalyst layer, and c_{ref} is the reference concentration.

Furthermore, Kulikovsky [9] derived an extended model which takes into account the transportation of methanol and oxygen within the cell including methanol crossover. The model incorporates the new effect of mixed potential, i.e. the formation of the narrow bridge of local current near the channel inlet. Asymptotic solutions are determined to see the properties of the bridge. The bridge formation in case of different methanol and oxygen stoichiometries are analyzed. The stoichiometries are related to mean current density J, respectively as follows [9]:

$$\lambda^a = \frac{6Fh^a v^a c^a \psi^0}{LJ},\ \lambda^c = \frac{4Fh^c v^c c^c \xi^0}{LJ} \quad \text{..... (9)}$$

where h is the channel height, v is the flow velocity, c is the total molar concentration of the mixture in the channel, L is the channel length and J is the mean current density. ψ and ξ are the molar fractions of methanol and oxygen

respectively. Superscript “a and c” are for anode and cathode channel respectively and subscript “0” is the value at the inlet channel. At equal methanol and oxygen stoichiometries with small current, the bridge formed is minimal with finite current density near the feed channel inlet. This bridge causes the electrodes to be short-circuited, hence reducing the open-circuit voltage of the cell. When methanol stoichiometry becomes greater than that of the oxygen, the current bridge seems to spread over a finite region on the cell surface. The bridge smears out over a large region of the cell when oxygen stoichiometry becomes greater than that of the methanol. For all of these three cases, the local current density in the bridge is proportional to the crossover rate and inversely proportional to the stoichiometry flow rate.

Cruickshank and Scott [10] presented a simple model which accounts for methanol crossover in DMFC. Permeation rates were measured through Nafion 117 membrane to determine key parameter of the model. This model is used to analyze the effect of methanol crossover, cathodic pressure and methanol concentration on the cell performance. The equation for the cell voltage is given by [10]:

$$V_{cell} = E_{cell} - \eta_a - \eta_c - \eta_{xover} - \eta_{ohmic} \quad \text{..... (10)}$$

where η_{xover} is the losses due to methanol crossover in the membrane.

Bahrami et al., [11] presented an analytical, one-dimensional steady state model to explain the overpotentials at the catalyst layers as well as methanol distribution and oxygen transport in anode and cathode respectively. Furthermore, an exergy analysis of the cell is performed under normal operating condition. It is concluded that of the overpotentials due to methanol crossover are the major exergy destruction sources inside the cell which lowers the current in the cell.

Xiao et al., [12] analyzed a two-dimensional, multiphase model for a vapor feed DMFC system. The model is used to study the transient and polarization characteristics of DMFC including methanol crossover, temperature evolution and overpotentials. It is observed from the results that anode flow channel for feeding methanol solution played a vital role in optimizing the cell performance. Additionally, the authors presented a multi-component, non-isothermal model to resolve the heat and mass transport in passive and semi passive liquid-feed DMFC [13]. The transient characteristics were investigated. The comparison of voltage and power density between passive and semi passive system indicates that the performance of passive cell is superior to that of a semi-passive cell.

2.2 DMFC Semi-Empirical Models

A number of semi-empirical models for DMFC are reported in the literature [14-21]. Semi-empirical model is used to evaluate the performance of fuel cell as a function of various operating conditions such as pressure, temperature and heat using empirical models. The advantage of this type of models is that it is small, uses basic algebraic equations, and requires less computational effort.

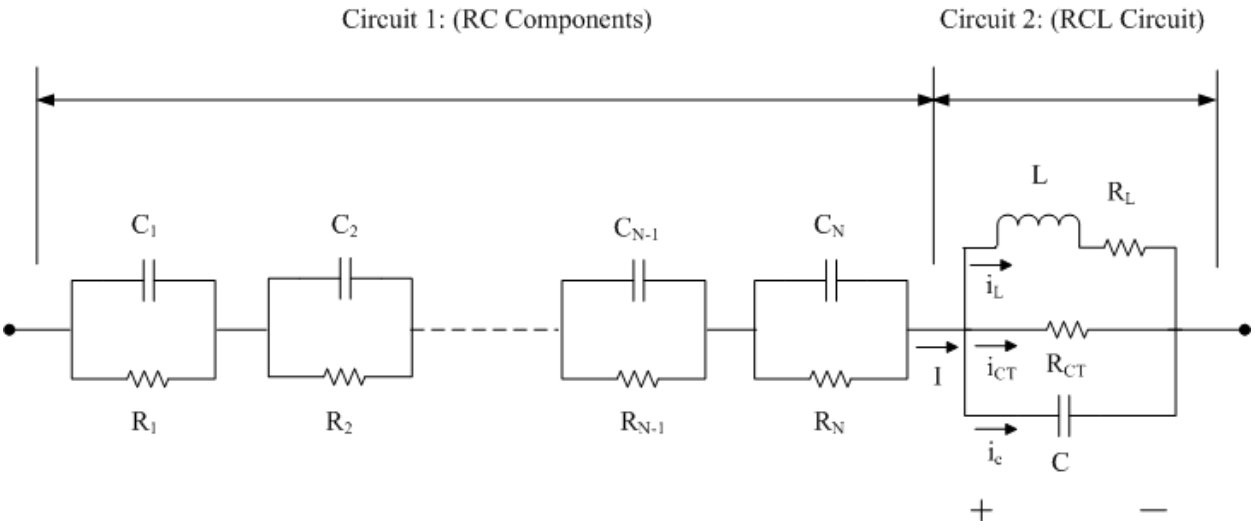

Figure 2. The plot of equivalent circuit of DMFC [14].

Wang et al. [14] have demonstrated a semi-empirical DMFC model by mathematically deriving a nonlinear equivalent electrical circuit consisting of a special group of impedance. Figure 2 shows the plot of equivalent electrical circuit of DMFC. The circuit obtained for DMFC is similar to Mueller's impedance fuel cell model, but the lumped elements (capacitor, resistor and inductor) are basically nonlinear. The model does not consider mass transport losses at anode and cathode. The obtained model provides a good approximation of the static and transient behaviors of the fuel cell under various load conditions. The model is verified by comparing the numerical simulation results with the polarization curve and dynamic behavior of DMFC using square current pulses with different high and low current levels. The basic equations used for verification of static and dynamic performances in this model are, respectively [14]:

$$V = V_{OCV} - A\ ln\left(\frac{I}{I_0}\right) - R_{ohm}I \quad (11)$$

$$V = V_{OCV} - V_{RCL} - R_t(I)I \quad (12)$$

where V is the cell voltage, V_{OCV} is the open circuit voltage, A is the Tafel parameter for oxygen reduction, I is the cell current, I_0 is the exchange current, R_{ohm} is the cell ohmic resistance, and V_{RCL} is the voltage drop on the RCL circuit.

Sundmacher et al., [15] operated a liquid-feed DMFC under different methanol feeding conditions with proton exchange membrane (PEM) as the electrolyte. The cell voltage response for different methanol concentration showed a noteworthy variation in voltage as the methanol concentration is varied. A mathematical model is developed to analyze the behavior of the fuel cell. The analysis includes anode mass balances, charge balances of both electrodes and electrode kinetic expressions. This model also takes into account the undesired methanol crossover. This model was simulated to evaluate the steady-state as well as the dynamic response of the fuel cell by varying the methanol concentration. It is observed that with periodically pulsed methanol feeding, the crossover could be effectively reduced.

Dohle and Wippermann [16] developed a semi-empirical model for DMFC based on various experimentation and observation of the anode overpotential, the cathode overpotential and the methanol permeation. The anode overpotential, η_{an} and the cathode overpotential, η_c are fitted using given semi-empirical equations [16]:

$$\eta_{an} = f_1 + f_2 \ln(i) + f_3 exp\left(\frac{f_4 i}{c_M}\right) \quad (13)$$

$$\eta_c = \frac{RT}{\alpha F} ln\left(\frac{i}{l_t i_*}\left(\frac{c_{O_{2,ref}}}{c_{O_2}}\right)^{\gamma}\right) + k(i) i_p \quad (14)$$

with f_{1-4} being the fitting parameters, i is the current density, i_* is the exchange current density, i_p is the local methanol permeation, α is the transfer coefficient, c_M is the methanol concentration, c_{O_2} is the oxygen concentration, $c_{O_{2,ref}}$ is the reference molar concentration, and k is an empirical factor. The developed model is used to predict the I-V characteristics of the fuel cell for a wide range of operating conditions. It is seen that the methanol permeation have a significant impact on the current density and the efficiency of the fuel cell.

Argyropoulos et al., [17] have developed a semi-empirical model to determine the I-V characteristics of liquid feed DMFC for a wide range of operating conditions. This model is based on the Tafel type kinetics for methanol oxidation and oxygen reduction combined with mass transport coefficients for fuel cell electrodes. Furthermore, this model seems to be valid even for extremely low current densities unlike most DMFC models which are valid only for narrow range of operating conditions. The basic model equation used by this paper is [17]:

$$E_{cell} = E_0^* - b_{cell} \log j - R_e j + C_1 \ln(1 - C_2 j) \quad (15)$$

with

$$E_0^* = E_{ocell} - \frac{RT}{\alpha_c F} ln\left(\frac{p_0^{ref}}{j_{oc} p_0}\right) - \frac{RT}{\alpha_a F} ln\left(\frac{C_M^{ref}}{j_{oc} C_M^N}\right) \quad (16)$$

where, b_{cell}, C_1 and C_2 are constants, α is the transfer coefficient, R_e is the ohmic resistance, E_{ocell} is the open circuit voltage, j_{oc} is the exchange current density and N is the reaction order.

An algebraic semi-empirical model is proposed by Chiu [18] to evaluate the fuel crossover phenomenon in DMFC. An experimental setup is established to predict the methanol crossover fluxes under various temperature, methanol concentration and current density. The proposed model is used to study the effects of operating variables and physical parameters on the methanol crossover fluxes. A semi-empirical model has been presented in [19, 20] to evaluate the efficiency of a DMFC as a function of current density. The real fuel cell efficiency, η_{real} is the combination of fuel efficiency, η_{fuel}, thermodynamic efficiency, η_{thermo} and voltage efficiency, $\eta_{voltage}$ [20].

$$\eta_{real} = \eta_{fuel} \cdot \eta_{thermo} \cdot \eta_{voltage} = \left(\frac{I}{I+I_c}\right) \cdot \left(\frac{\Delta g}{\Delta h}\right) \cdot \left(\frac{V_{cell}}{V_{th}}\right) \quad (17)$$

where I is the operating current, I_c is the crossover current, Δg is the Gibbs free energy change per mole of fuel, Δh is the enthalpy change per mole of fuel, V_{cell} is the operating voltage and V_{th} is the theoretical maximum voltage.
In [21], the author has developed a semi-empirical model to predict the performance of DMFC along with the illustration of the design and analysis for the optimal operating conditions. The proposed model basically focused on the balance between increasing the methanol concentration and reducing methanol crossover.

2.3 DMFC Mechanistic Models

Mechanistic model is a transport model that describes the fundamental phenomena such as heat, momentum, mass transport and other electrochemical processes. This type of model uses differential and algebraic equations and is more complex than the alternate models. However, mechanistic model helps to understand the details of fundamental phenomena occurring in the fuel cell. There are many mechanistic models that have been developed [22- 28].and a few attractive models are summarized below.

Dohle et al., [22] introduced an one dimensional mathematical model for DMFC based on finite integration technique and verified it experimentally. This model is used to interpret various phenomena occurring in DMFC. The model consists of mass transport of gases in diffusion layers, the catalyst layers and the membrane along with the electrochemical reactions that takes place in catalyst layers.
The total mass transport in diffusion layer can be evaluated using [22]:

$$N_i = N_d^i + N_i^p \quad (18)$$

where,

$$\frac{N_i^d}{D_i} + \sum_{j=1}^{n} \frac{y_j N_i^d - y_i N_j^d}{D_{i,j}^m} = -c_{tot} \frac{dy_i}{dx} \quad (19)$$

$$N_i^p = -y_i B_i \frac{dc_{tot}}{dx} \quad (20)$$

Here, N is the molar flux, "*d*" and "*p*" indicates diffusion and permeation respectively and i is the species i in the mixture. D is the diffusion coefficient, y is the mole fraction, c_{tot} is the total concentration, and B_i is the transport coefficient of species i in mixture.
For the catalyst layers, the cathodic and anodic reactions are, respectively, expressed as [22]:

$$i_c = i_{o,ref}^c \frac{P_{o_2}}{P_{o_{2,ref}}} \exp\left[-\frac{\alpha_c F}{RT}(\varphi_{el} - \varphi_{ion} - \varphi_{o,ref}^c\right] \quad (21)$$

$$i_{a=} i_{o,ref}^a \frac{P_{MEOH}}{P_{MEOH,ref}} \frac{P_{H_2O}}{P_{H_2O,ref}} \exp\left[+\frac{\alpha_a F}{RT}(\varphi_{el} - \varphi_{ion} - \varphi_{o,ref}^a\right] \quad (22)$$

where i_c and i_a are the current densities at cathode and anode, $i_{o,ref}^c$ and $i_{o,ref}^a$ are the reference current densities at standard conditions, α is the transfer matrix coefficient, and T is the temperature. φ_{el}, φ_{ion}, $\varphi_{o,ref}^c$ and $\varphi_{o,ref}^a$ are the electronic potential, ionic potential, cathodic reference potential at standard condition and anodic reference potential at standard condition, respectively. P_{o_2}, P_{MEOH}, P_{H_2O} are, respectively, the pressure of oxygen, methanol, water and $P_{o_{2,ref}}$, $P_{MEOH,ref}$, $P_{H_2O,ref}$ are the reference pressure of oxygen, methanol and water, respectively. Furthermore, the water transport in the membrane is comprised of osmotic drag and diffusion due to gradients in water content. ψ [22].

$$N_{H_2O,diff} = -D_\psi^{mem} \frac{d\psi}{dx} \quad (23)$$

and

$$N_{H_2O,drag} = n_{drag}^{H_2O} \frac{I_{ion}}{F} \frac{\psi}{22} \quad (24)$$

where, $N_{H_2O,diff}$ is the diffusion due to molar flux of water, D_ψ^{mem} is the diffusion coefficient of water content in membrane, $N_{H_2O,drag}$ is the electroosmosis due to molar flux of water in membrane, $n_{drag}^{H_2O}$ is the drag coefficient of water, and I_{ion} is the ionic current. Similarly, methanol diffusion and methanol drag is, respectively, expressed as [22]:

$$N_{MEOH,diff} = -D_\gamma^{mem} \frac{d\psi}{dx} \quad (25)$$

and

$$N_{MEOH,drag} = n_{drag}^{MEOH} \frac{I_{ion}}{F} \frac{P_{MEOH}}{P_{MEOH,sat}} \quad (26)$$

It is seen from the results in [22] that methanol permeation rate from the anode to the cathode is a function of methanol concentration and current density and it increases as the concentration increases. At low concentration, methanol permeation rate decreases with increasing current density. Therefore, less amount of methanol is diffused from the anode to the cathode i.e., the total transport decreases. In addition, the possibility of formation of mixed potential at both anode and cathode creates a huge negative impact on energetic performance of the fuel cell. Overall, it is concluded that methanol permeation and the formation of mixed potential could have an adverse effect in the performance of the fuel cell. In [23], the authors developed a one-dimensional, steady-state, two-phase model to investigate complex physiochemical phenomena in DMFC. The model comprises of Maxwell-Stefan diffusion equation to represent the species transportation through porous membrane and Darcy's equation to describe the capillary-induced liquid flow in porous media. The results indicate the influence of those physiochemical parameters on the performance and the efficiency of the fuel cell.

Zou et al., [24] presented a two-dimensional, two-phase non-isothermal model for DMFC to analyze the heat transfer, mass transfer and other electrochemical phenomena occurring in the cell. The modeling domain of the fuel cell is shown in Figure 3.

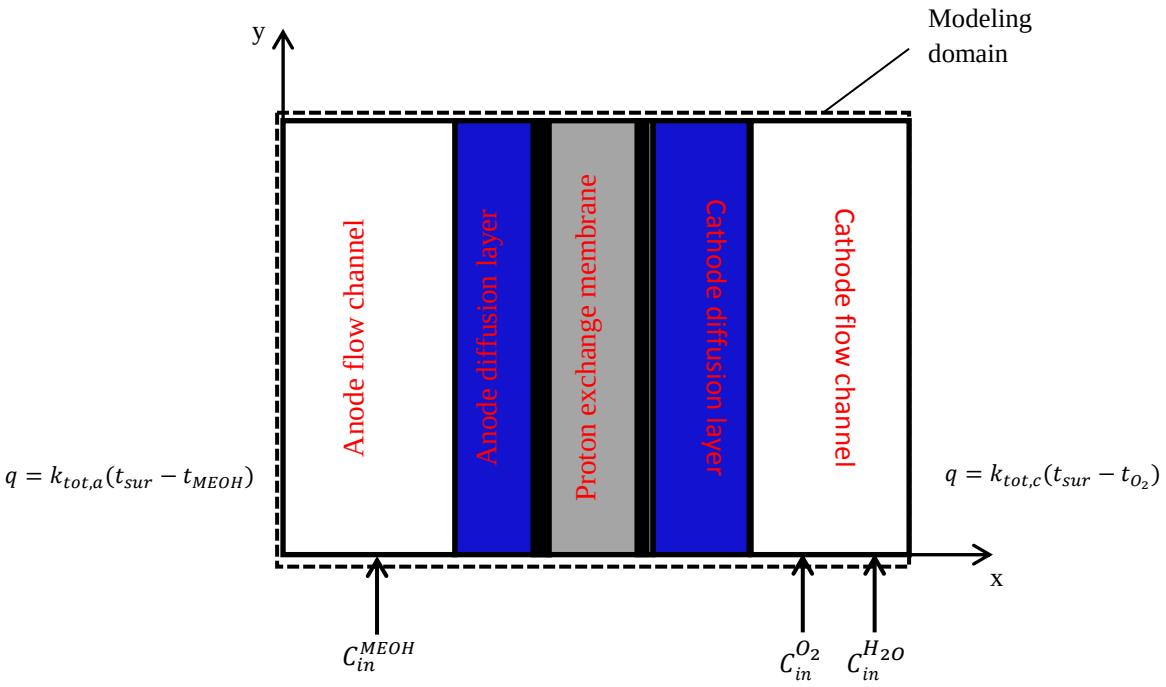

Figure 3. Schematic of the modeling domain of DMFC with C_{in}^{MEOH} being the mass fraction of methanol at the anode, $C_{in}^{O_2}$ the mass faction of oxygen in cathode and $C_{in}^{H_2O}$ the mass fraction of water in cathode [24].

The overall heat transfer, q, from surroundings to the anode and cathode of the fuel cell is, respectively, derived as [24]:

$$q = k_{tot,a}(t_{sur} - t_{MEOH}) \quad (27)$$

$$q = k_{tot,c}(t_{sur} - t_{O_2}) \quad (28)$$

where $k_{tot,a}$ and $k_{tot,c}$ are the heat transfer coefficient of anode and cathode, t_{sur} is the thickness of the surrounding, t_{MEOH} is the temperature of methanol solution in ^{o}C, and $t_{O_2}$is the temperature of the oxygen in ^{o}C. Furthermore, the electrochemical reaction in anode catalyst layers is expressed as [24]:

$$i_a = i_{a,ref} \frac{s_1 C_{MEOH}}{C_{MEOH,ref}} exp\left(\frac{\alpha_a F}{RT}\eta_a\right) \quad (29)$$

with i_a being electrochemical reaction rate in anode, $i_{a,ref}$ the reference electrochemical reaction rate in anode, s_1 the liquid saturation, C_{MEOH} the mass fraction of methanol, $C_{MEOH,ref}$ the reference mass fraction of methanol, α_a

the transfer coefficient of anode, and η_a the anode overpotential. Since, current is generated by electrochemical reaction of methanol, the average current density, I_{cell} is calculated as a function of i_a as [24]:

$$I_{cell} = \frac{\iint i_a dxdy}{L} \quad (30)$$

where L is the length of the anode catalyst layer (ACL). Finally, the fuel cell operating voltage is given by [24]:

$$E_{cell} = E_0 - \eta_a - \eta_c - I_{cell}\left(\frac{t_m}{\sigma_m}\right) \quad (31)$$

where t_m is the thickness of the membrane and σ_m is the membrane ionic conductivity. The results indicate that the cell performance is highly enhanced if the inlet temperature is increased.

Divisek et al., [25] developed 1-dimensional and 2-dimensional model for DMFC. A simulation model is set up to obtain different limiting processes for various operating conditions. Two phase flow model is used to describe transport process while Stefan-Maxwell equation is used to describe how molar gas fluxes depend on the pressure gradients.

Keeping in mind that the performance of the fuel is highly influenced by flow field effects, Vera [26] developed a novel 3-dimensional/1-dimensional (3D/1D), isothermal and a single-phase model for liquid-feed DMFC. The 3D model accounts for modeling mass, momentum and species transport in anode channel and gas diffusion layer. Figure 4 illustrates the schematic of the modeling domains covered by the 1D and 3D models.

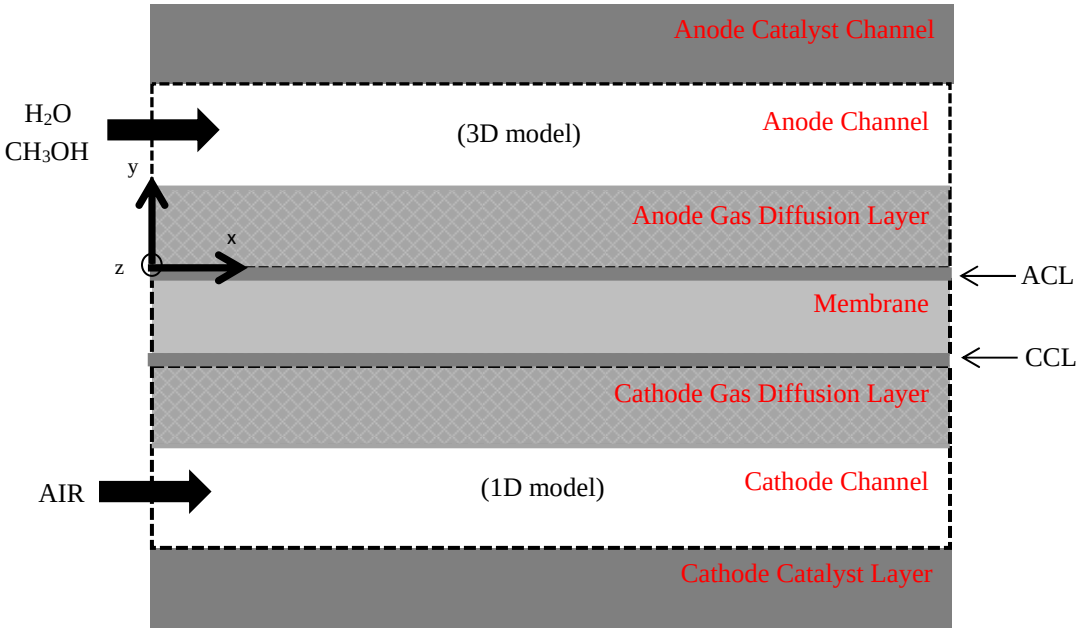

Figure 4. Schematic of the modeling domains covered by the 3D/1D models; ACL is the anode catalyst layer and CCL is the cathode catalyst layer; 3D modeling used for anode and 1D modeling used for ACL, membrane, and cathode [26].

The Navier-Stokes equations are solved in three dimensional (3D) domain to obtain the velocity and pressure distribution along with the methanol concentration in anode channel (AC) and gas diffusion layer (GDL) [26].

$$\nabla \cdot u = 0 \quad (32)$$

$$\frac{\rho}{\epsilon^2}(u \cdot \nabla)u = -\nabla P + \frac{\mu}{\epsilon}\nabla^2 u + S_u \quad (33)$$

where ρ is the density, μ is the viscosity, ϵ is the porosity, P is the pressure, and S_u is the term in momentum equation. The velocity field, u, is related to methanol concentration, C_m by the convection/diffusion equation [26]:

$$\nabla \cdot (uC_m) = D_m^{eff}\nabla^2 C_m \quad (34)$$

Here, D_m^{eff} is the effective diffusion coefficient of methanol in water.

On the other hand, one dimensional (1D) domain is used for mathematical solution of catalyst layers, membrane and cathode flow field. The molar flux for oxygen in cathode catalyst layer (CCL) is [26]:

$$N_{O_2} = \frac{i}{4F} + \frac{3}{2} N_{cross} \quad (35)$$

with N_{cross} being the molar flux of methanol that permeates through the membrane, which depends on the current density, i, the electroosmotic drag coefficient of methanol, n_d^m and the effective diffusion coefficient of methanol in the membrane, $D_{m,mem}^{eff}$ as [26]:

$$N_{cross} = n_d^m \frac{i}{F} - D_{m,mem}^{eff} \frac{dC_m}{dy}\Big|_{mem} \quad (36)$$

Again, the molar flux of methanol, N_m is given by [26]:

$$N_m = \frac{i}{6F} + N_{cross} \quad (37)$$

Now, the cathodic exchange current density, $i_{0,c}$ as a function of temperature, T is given by [26]:

$$i_{0,c} = i_{0,c}^{ref} exp\left[\frac{73200}{R}\left(\frac{1}{353} - \frac{1}{T}\right)\right] \quad (38)$$

where, $i_{0,c}^{ref}$ is the reference exchange current density in cathode at 353 K. Similarly, the anodic exchange current density, $i_{0,a}$ is given by [26]:

$$i_{0,a} = i_{0,a}^{ref} exp\left[\frac{35570}{R}\left(\frac{1}{353} - \frac{1}{T}\right)\right] \quad (39)$$

with $i_{0,a}^{ref}$ being the reference exchange current density in anode at 353 K. Coupling the 3D/1D model together, the system is used to compute polarization curves for different methanol concentrations, temperatures, and methanol flow.

Delavar et al., [27] developed a two-dimensional Lattice Boltzman model to predict the flow pattern and feed methanol concentrations in both clear and porous channels of a DMFC. The model is used to evaluate the cell performance as a function of flow speed and methanol concentration.

Basri et al., [28] reviews the process system engineering (PSE) of DMFC from construction and modeling perspective. Along with various PSE-related challenges such as methanol and water crossover, low kinetics rates of reaction, heat and water management, fuel management, hydrodynamics studies and mass transport, the authors have discussed important engineering factors for successful stacking design of DMFC for various portable applications.

2. Conclusions

This paper is an effort to introduce a literature review of all the publication in the field of DMFC. Reviews for analytical model, semi-empirical model, and mechanistic model show their own importance in understanding various processes and performance of the fuel cell. The main purpose of modeling is to understand the performance and the various phenomena occurring in the DMFC. Analytical model and semi-empirical models are basically used to predict the performance of the fuel cell while mechanistic model is developed to understand the various processes occurring in the fuel cell. Oliveira et al., [3] have discussed the merits and demerits of analytical, semi-empirical and mechanistic models of DMFC. Along with the discussion, case study for analytical and semi-empirical models is performed to compare between two techniques in the real-time system level DMFC calculations. It is concluded that semi-empirical models provides better evaluations for existing designs but proves unbeneficial for new designs. On the other hand, analytical models prove to be efficient for rapid calculations of voltage losses for simple as well as complex DMFC systems. Finally it is concluded that analytical model is considered suitable for implementation in real-time system level DMFC calculations. With the completion of this literature survey, a conclusion can be drawn that even though DMFC is gaining large popularity in the field of fuel cell technology, there are still some unsolved issues that needs intense research.

References

[1] J. M. Correa, F. A. Farret, L.N. Canha and M. G. Simoes, "An Electrochemical-Based Fuel Cell Model Suitable for Electrical Engineering Automation Approach," *IEEE Transactions on Industrial Electronics*, vol. 51, pp. 1-18, 2004.

[2] E. Birgersson, "Mathematical modeling of transport phenomenon in polymer electrolyte and direct methanol fuel cells," *Doctoral Thesis,* Stockholm, pp. 1-44, 2004.

[3] V. B. Oliveira, D. S. Falcao, C. M. Rangel and A. M. F.R. Pinto, "A comparative study of approaches to direct methanol fuel cells modeling," *International Journal of Hydrogen Energy*, vol. 32, pp. 415-424, 2007.

[4] L. Xianglin, H. Yaling, Y. Benhao, M. Zheng and L. Xiaoyue, "Exergy flow and energy utilization of direct methanol fuel cells based on a mathematical model," *Journal of Power Sources,* vol. 178, pp. 344-352, 2008.
[5] H. Guo, and C. Ma, "2D analytical model of a direct methanol fuel cell," *Electrochemistry Communications*, vol. 6, pp. 306-312, 2004.
[6] C. Chen and T. Yeh, "A mathematical model for simulating methanol permeation and the mixed potential effect in a direct methanol fuel cell," *Journal of Power Sources*, vol. 160, pp. 1131-1141, 2006.
[7] A. A. Kulikovsky, "The voltage-current curve of a direct methanol fuel cell: "exact" and fitting equations," *Electrochemistry Communications*, vol. 4, pp. 939-946, 2002.
[8] A. A. Kulikovsky, "A method for analysis of DMFC performance curves," *Electrochemistry Communications*, vol. 5, pp. 1030-1036, 2003.
[9] A. Kulikovsky, "1D + 1D model of a DMFC: localized solutions and mixed potential," *Electrochemistry Communications*, vol. 6, pp. 1259-1265, 2004.
[10] J. Cruickshank and K. Scott, "The degree and effect of methanol crossover in the direct methanol fuel cell," *Journal of Power Sources*, vol. 70, pp. 40-47, 1998.
[11] H. Bahrami and A. Faghri, "Exergy analysis of a passive direct methanol fuel cell," *Journal*
[12] B. Xiao and A. Faghri, "Numerical analysis for a vapor feed miniature direct methanol fuel cell system," *International Journal of Heat and Mass Transfer*, vol. 52, pp. 3525-3533, 2009.
[13] B. Xiao, H. Bahrami and A. Faghri, "Analysis of heat and mass transport in a miniature passive and semi passive liquid-feed direct methanol fuel cell," *Journal of Power Sources*, vol. 195, pp. 2248-2259, 2010.
[14] Y. Wang, G. Au, E. J. Plichta, and J. P. Zheng, "A semi-empirical method for electrically modeling of fuel cell: Executed on a direct methanol fuel cell," *Journal of Power Sources*, vol. 175, pp. 851-860, 2008.
[15] K. Sundmacher, T. Schultz, S. Zhou, K. Scott, M. Ginkel and E.D. Gilles, "Dynamics of the direct methanol fuel cell (DMFC): experiments and model-based analysis," *Chemical Engineering Science*, vol. 56, pp. 333-341, 2001.
[16] H. Dohle and K. Wippermann, "Experimental evaluation and semi-empirical modeling of U/I characteristics and methanol permeation of a direct methanol fuel cell," *Journal of Power Sources*, vol. 135, pp. 152–164, 2004.
[17] P. Argyropoulos, K. Scott, A. K. Shukla and C. Jackson, "A semi-empirical model of the direct methanol fuel cell performance Part I. Model development and verification," *Journal of Power Sources*, vol. 123, pp. 190–199, 2003.
[18] Y. Chiu, "An algebraic semi-empirical model for evaluating fuel crossover fluxes of a DMFC under various operating conditions," *International Journal of Hydrogen Energy*, vol. 35, pp. 6418-6430, 2010.
[19] Y. Chiu, T. L. Yu and Y. Chung, "A semi-empirical model for efficiency evaluation of a direct methanol fuel cell", *Journal of Power Sources*, 2011.
[20] S. H. Seo and C. S. Lee, "A study on the overall efficiency of direct methanol fuel cell by methanol crossover current," *Applied Energy*, vol. 87, pp. 2597-2604, 2010.
[21] C. R. Buie, "Application of electroosmotic pumps to low temperature fuel cells," *Doctoral Dissertation,* Stanford University, pp. 157, 2009.
[22] H. Dohle, J. Divisek and R. Jung, "Process engineering of the direct methanol fuel cell*," Journal of Power Sources*, vol. 86, pp. 469-477, 2000.
[23] J. Ko, P. Chippar and H. Ju, "A one-dimensional, two-phase model for direct methanol fuel cells – Part I: Model development and parametric study," *Energy*, pp. 2149-2159, 2010.
[24] J. Zou, Y. He, Z. Miao and X. Li, "Non-isothermal modeling of direct methanol fuel cell," *International Journal of Hydrogen Energy*, vol. 35, pp. 7206-7216, 2010.
[25] J. Divisek, R. Jung, K. Gartner and J. Fuhrmann, "Numerical Simulation of Direct Methanol Fuel Cells (DMFC)," *3rd European Congress of Chemical Engineering*, Nuremberg, pp. 26-28, 2001.
[26] M. Vera, "A single-phase model for liquid-feed DMFCs with non-Tafel kinetics," *Journal of Power Sources*, vol. 171, issue. 2, pp 763-777, 2007.
[27] M. A. Delavar, M. Farhadi and K. Sedighi, "Numerical simulation of direct methanol fuel cells using lattice Boltzmann method," *International Journal of Hydrogen Energy*, vol. 35, pp. 9306-9317, 2010.
[28] S. Basri and S. K. Kamarudin, "Process system engineering in direct methanol fuel cell," *International Journal of Hydrogen Energy*, pp. 1-18, 2011.