Mathematical modelling of Proton Exchange Membrane Fuel Cells – a brief Review

Salumuri S. Lingeswara Rao[a], A. Shaija[a], S. Jayaraj[a]
[a]Department of Mechanical Engineering
National Institute Technology-Calicut
Kerala - 673601, India.

Abstract
This paper presents a review of publications on mathematical modelling, steady state and dynamic behaviour of Proton Exchange Membrane (PEM) fuel cells. The scope of this review is limited to only the mathematical modelling of PEM fuel cells because of two reasons, firstly, mathematical modelling is an indispensible tool for studying the static and dynamic behaviour of fuel cells and is helpful for the fuel cell developers to design cheaper and more efficient fuel cells and secondly, Polymer Electrolyte Membrane fuel cell (PEMFC) is considered to be the most promising answer to the environmental and energy problems. PEMFC are expected to be the best option for automotive, stationary and portable applications, because of their high power density, low operating temperatures, quick start-up and zero emissions. The organisation of paper is as follows: section 1 gives a brief introduction about the types and working principle of a fuel cell, section 2 provides a literature review of studies on mathematical modelling of the PEM fuel cells with respect to the steady state, dynamic behaviour and spatial changes, section 3 deals with the review on the mathematical modelling with respect to the bipolar plates, section 4 deals with the review on the studies based on gas diffusion layer models, section 5 provides studies on the membrane models, section 6 provides studies on computational fluid dynamic models and section 7 provides concluding remarks.

Key words: PEM fuel cells; Mathematical modelling; Gas diffusion layer; Proton exchange membrane

1. Introduction

Fuel cells are set to become the power source of the future. The interest in fuel cells has increased during the past decade due to the fact that the use of fossil fuels for power has resulted in many negative consequences, like severe pollution, extensive mining of the world's resources, and political control and domination of countries that have extensive resources. A new power source is needed that is energy efficient, has low pollutant emissions, and has an unlimited supply of fuel. A fuel-cell system is expected to meet such demands because it is a chemical power generating device, which converts the chemical energy of a clean fuel (*e.g.* Hydrogen) directly into electrical energy. Fuel cells are now closer to commercialization, and have the ability to fulfil all the global power requirements while meeting the efficacy and environmental expectations. Its efficiency can reach as high as 60 % in electrical energy conversion and overall 80 % in co-generation of electrical and thermal energies with 90 % reduction in major pollutants. Five categories of fuel cells which have received attention are: (i) Polymer Electrolyte Membrane (PEM) fuel cells (PEFCs), (ii) Solid Oxide fuel cells (SOFCs), (iii) Alkaline fuel cells (AFCs), (iv) Phosphoric Acid fuel cells (PAFCs), and (v) Molten Carbonate fuel cells (MCFCs).

Among all these kinds of fuel cells, PEMFCs are considered to be the best possible answer to environmental and energy problems, and are expected to soon become the most promising

energy converts for automotive, stationary and portable applications, because of their high power density at low operating temperatures, quick start-up and zero emissions. Schematic diagram of a PEMFC is shown in Figure 1 which consists of two electrodes, a cathode and an anode, and an electrolyte membrane is sandwiched between them is called membrane electrode assembly (MEA). This is heart of the fuel cell.

Each of these electrodes is coated on one side with a thin catalyst layer that speeds up the reaction of oxygen and hydrogen. It is usually made of platinum powder very thinly coated onto carbon paper or cloth. The catalyst is rough and porous so the maximum surface area of the platinum can be exposed to the hydrogen and oxygen. The platinum coated side of the electrode faces the PEM. The catalyst layer between the anode and PEM is known as anode catalyst layer and catalyst layer between cathode and PEM is known as cathode catalyst layer. The fuel Hydrogen diffuses through the porous electrode and reaches the anode catalyst layer, where it is oxidized liberating electrons and producing protons (H+). The protons are transferred through the membrane to the cathode catalyst layer and the electrons flow via the external circuit to the cathode.

Similarly, humidified O_2 gas or air is supplied to the cathode flow channel where O_2 gas diffuses through the electrode and reaches the cathode catalyst layer and forms water reacting with protons and electrons. The PEM electrolyte plays a central role, because it allows protons to pass through, but block the passage of electrons and heavier gasses. PEM fuel cells have polymer electrolyte in the form of thin permeable sheet. Most popular and important electrolyte used in PEM fuel cell is Nafion (introduced by Dupont) due to its extremely high ionic conductivity. To maintain this extraordinary conductivity, however, Nafion must be fully hydrated with liquid water. Usually hydration is achieved by the humidifying the fuel and oxidant gases supplied to the fuel cell. Because of this hydration requirement, Nafion membranes are typically restricted to operating temperatures below 100 ^{o}C.

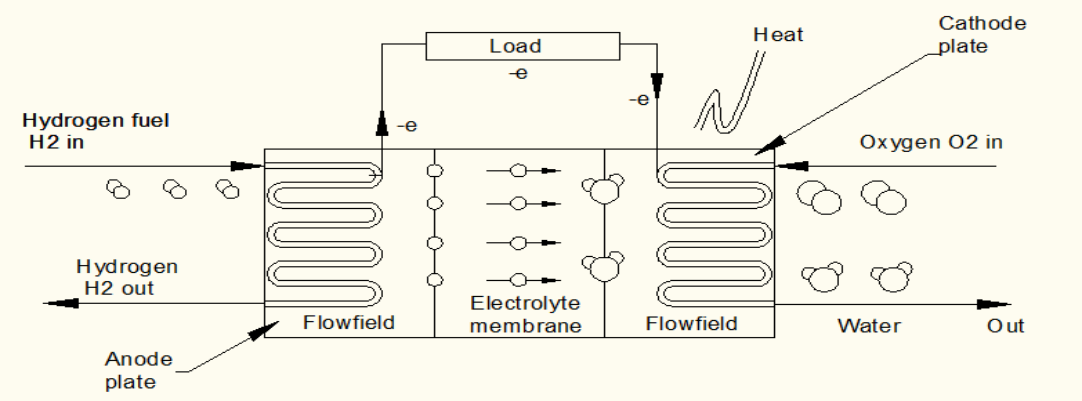

Fig.1 Schematic diagram of PEM fuel cell

At the membrane electrode interface, following two electrochemical reactions take place:

Anode reaction (HOR): $$H_2 \rightarrow 2H^+ + 2e^- \quad (1)$$

Cathode reaction (ORR): $$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \quad (2)$$

Overall reaction: $$H_2 + \frac{1}{2}O_2 \rightarrow H_2O + \text{Electrical energy} + \text{Waste heat} \quad (3)$$

This paper presents the comprehensive review of publications on mathematical modelling from the pioneer model developed by Springer *et al.* (1991) to the latest model formulated by Cao *et al.* (2013). The organisation of the rest of this paper is as follows: section 1 is based

on the studies on mathematical modelling on steady state, dynamic behaviour, spatial, section 2 provides a review based on the bipolar plates, section 3 deals with the review based on gas diffusion layer models, section 4 provides studies on the membrane models and section 5 provides studies on computational fluid dynamic models.

2. Steady state, dynamic behaviour, spatial changes models

With respect to the spatial changes, the problem could be zero-dimensional (lumped model), one-dimensional (1D), two-dimensional (2D) or three-dimensional (3D), depending on the number of spatial independents of the resulting model.

Most of the modelling approach is variations or combinations of the two initial models: the models developed by Springer *et al.* [1] and Bernardi and Verbrugge [2]. Both of these models assumed steady state and isothermal conditions. The species transport through the MEA and along the gas channels was assumed to be one-dimensional. Bernardi and Verbrugge [2] assumed no pressure drop in the channel portion and species transport was only through convection and also assumed no pressure drop in the electrode layers and species transport was only through diffusion. They developed a mathematical model from the fundamental transport properties where the activation losses incurred by the anode and cathode reactions, the ohmic losses incurred by the membrane are considered. This model does not account for concentration overpotential region of the polarization curve. The membrane was assumed to be fully hydrated. The ion transport was governed by the Nernst-Plank equation, liquid water transport was described by Schlogl's equation and the gas transport by Stefan-Maxwell equation. The catalyst layers were considered to be porous media, and the diffusion of the reactant gases were characterised by Fick's law. Bernardi and Verbrugge [2] have also assumed that the water and charge transport in the membrane was constant. However, the water content in the membrane is not constant and proton conductivity is highly dependent upon water content. The pioneering fuel cell model proposed by Springer *et al*. [1] has allowed for variable hydration between anode and cathode and thus the variable ohmic resistance due to the hydration of the membrane. The diffusional velocity depends upon a potential gradient and is a function of membrane hydration. The water diffusion coefficient, electro-osmotic coefficient and electrical conductivity are all dependent upon membrane hydration, which is a function of humidity of the gasses. An empirical formula was used to relate the hydration of the membrane and the conductivity. Fuller and Newman [3] presented a mathematical model of transport between the gas channels and two-dimensional MEA. Water management, thermal management and utilization of fuel were investigated in this study. Stefan-Maxwell equation was used to explain the multi-component diffusion of gasses and system was modelled as a single phase. It was found that equilibrium sorption of water between gas phase and the polymer electrolyte depended strongly on temperature. The rate of heat removal was shown to be a critical parameter in the operation of the fuel cell. Springer *et al*. [4] presents a fit between model and experiment for well humidified PEM fuel cell. They collected experimental data with the cells that utilized thin film catalyst layers bonded directly to the membrane and a separate catalyst free hydrophobic backing layer. Amphlett *et al.* [5, 6] developed a mechanistic and empirical model for the Ballard Mark IV cell that combines performances losses into parametric equations based on cell operating conditions, such as current, temperature and partial pressures of the reactants. It considers only the activation and ohmic potential region. Activation overpotential was modelled as a function of operating temperature, the product of operating temperature and the logarithm of operating current, and the product of operating temperature and the logarithm of oxygen concentration at the catalyst reaction sites. The ohmic overpotential was modelled as a function of operating temperature and the current. Kim *et al.* [7] developed a curve fitting scheme based on

experimental data that fits the entire polarization curve of PEMFC over the complete operating range. Amphlett *et al.* [8] developed a model and predicted transient responses of Ballard mark V 35 cell, 5 kW PEM fuel cell. This electrochemical model calculates the power output of a PEM fuel cell stack through the prediction of cell voltage as a function of operating current, stack temperature, hydrogen and oxygen gas flow rates and partial pressures. Yi and Nguyen [9], developed an along the channel for evaluating the effects of various humidification designs, higher cathode gas pressure and heat removal schemes on the performance. The results show that humidification of anode gas is required to improve the conductivity of the membrane and higher humidification temperature can improve the cell performance by introducing more water into the anode. Applying higher cathode gas pressures helps to replenish the water loss by electro-osmosis and thereby making the membrane more conductive, resulting in a higher cell performance. The Gurau *et al*. [10] developed a single phase, two-dimensional model that includes the gas channels, gas diffusers, catalyst layers and polymer electrolyte membrane layer. The model representing the conservation of mass, momentum, species and energy equations in each layer had the same general form and differed only in the source terms. Liquid water transport was described by Schlogl's equation and this model was similar to the Bernardi and Verbrugge [2]. The gas diffusion media was modelled using a Darcy's equation and the catalyst layer was assumed to consist of a solid matrix with void space filled with the polymer electrolyte membrane. Ohm's law was used to model the current flow and proton conductivity in the membrane was allowed to vary with the membrane hydration using the model of Springer *et al.* [1]. Lee *et al*. [11] developed numerical modelling of the Membrane Electrode Assembly (MEA) for the PEMFC stacks which uses the family of empirical equations that describe the electrochemical characteristics of MEA. The main objective of developing this model was to simulate the performance of MEAs in large scale fuel cell stack for which performance data is available for laboratory scale single cell without extensive calculations. Later, Lee and Lalk [12] presented a technique for modelling fuel cell stack to determine the fundamental thermal-physical behaviour of a fuel cell stack for any operating and design configuration. They also investigated the performance variation from cell to cell in a stack. The variations in performance due to reactant gas flow rates, varying rates of water accumulation, differences in MEAs and differences in contact resistance between cells. Singh *et al.* [13] developed a two dimensional model using the same approach as Bernardi and Verbrugge [2] which takes into account diffusion of the humidified reactants through the porous electrodes, and convective and electro-osmotic transport of liquid water in the electrode and membrane. Thermodynamic equilibrium potential is calculated from the Nernst equation and reaction kinetics is determined using the Butler-Volmer equation. The influence of flow configuration and electrode porosity on predicted cell performance is also discussed. Shimpalee *et al*. [14] developed a three dimensional flow simulation of PEM fuel cell in which the addition of diffusion layer in both anode and cathode shows the mass transport behaviour caused by inlet velocity of reactants, chemical reactions and permeability of diffusion layers. The complete three dimensional Navier-stokes equations are solved to obtain the velocity and pressure distributions along the flow channel. Results indicate that the diffusion of hydrogen is aided by the flow toward the membrane in the anode side and diffusion of oxygen is opposed by the flow direction present in the cathode side. Shimpalee and Dutta [15] developed a three dimensional numerical model that includes the energy equation to predict the temperature distribution inside a straight channel of fuel cell and effect of heat produced by the electrochemical reactions on fuel cell performance. This model concludes that fuel cell performance depends not only on the inlet humidity conditions and initial setup, but also on the temperature rise inside the fuel cell. For this reason, the fuel cell model, including the energy equation, gives lower performance than the model without the heat transfer

consideration. Baschuk and Li [16] presented a one-dimensional steady state, isothermal model of PEM fuel cell which includes all the essential fundamental physical and electrochemical processes occurring in the membrane, cathode catalyst layer, electrode backing and flow channel and membrane is assumed to be fully hydrated. This model has considered the effect of variable degree of water flooding in the cathode catalyst layer on the cell performance. The study showed that increasing the fuel cell pressure increases significantly the extent of water flooding in the electrode and results in maximum flooding at low current densities. Maggio *et al.* [17] proposed a model to describe water transport in proton conductive membranes used in the PEM fuel cells. They used diffusional overpotential and convective overpotential instead of concentration overpotential to calculate the cell voltage. Rowe and Li [18] developed one-dimensional non-isothermal mathematical model to investigate the effect of various design and operating conditions on the cell performance. The model includes variable membrane hydration, ternary gas mixtures for both reactant streams, phase change of water in the electrodes and energy equation for the temperature distribution across the cell. Humidification was achieved via water vapour in the reactant gas streams. However, excessive water presence leads to the flooding of electrode pores, thereby limiting the gas transport to the reaction sites. This study showed that increase in operating temperature can decrease mass transport limitations and increase electrochemical reaction rates, but adverse effects on the maximum cell potential. Pisani *et al*. [19] developed a model using the same approach of Bernardi and Verbrugge [1], but this model contains a description of the flooding phenomena and a better description of cathode region where concentration overpotential start to appear. Kazim [20] proposed a new mathematical approach to determine the minimal PEM fuel cell efficiency below which it is not recommended to operate the fuel cell. Two dimensionless mathematical criteria were proposed for the annual fee cost and electricity cost. If fuel cell efficiency is below 37%, then the fuel cell is not recommended to operate.

Yerramalla *et al*. [21] developed a linear, as well as non-linear model that accounted for energy and mass transfer as well as electrochemical reactions. The linear model was not predicting well the fuel cell behaviour, but the dynamic behaviour of the fuel cell system was better understood when non-linearity in the system is considered. Ge and Yi [22] presented a steady state two-dimensional model for PEM fuel cell which describes the effect of flow mode, operation conditions and membrane thickness on water transport, water content of membrane and performance of fuel cell. Compared to co-flow mode, counter-flow mode improves the current density distribution with dry or low humidity gasses. Garcia *et al.* [23] developed a semi- analytical, one-dimensional, isothermal model for Direct Methanol Fuel Cell. The model predicts the concentration profile in the anode and membrane as well as methanol crossover. The model is compared with experimental polarization data. Grujicic and chittajallu [24] studied the performance of a single phase two-dimensional electrochemical model for PEM fuel cell. The electrical and electrochemical potential and species conservation equations were optimised with a non-linear constrained optimization algorithm. The model shows that the predicted electrical response of PEM fuel cell is highly dependent on the magnitude of number of parameters associated with the oxygen transport and reduction half-reaction. Hussain *et al*. [25] studied the thermodynamic modelling of PEM fuel cell for transport applications by dividing the fuel cell system in two major modules: fuel cell stack module and system module. System module includes air compressor, heat exchanger, humidifier and cooling loop. They found that, with increase in the external load (current density), the difference between gross stack power and net power increases. The largest irreversibility's occur in fuel cell stack which hinders the commercialization of fuel cell power system for transport applications. Pathapati *et al*. [26], developed a PEMFC dynamic model, accounted for the effect of charge double layer capacitance, the dynamics of

flow pressure in the anode and cathode channels, as well as mass and heat transfer response of the fuel cell body. The dynamic model predict the transient response of cell voltage, temperature of the cell, hydrogen and oxygen outflow rates and cathode and anode channel temperatures/pressures under sudden change in load current. This model demonstrates that the dynamic interaction effects within a PEMFC are significant and such transient effects are necessary. Mawardi *et al.* [27] presented a model based on optimization by considering a one dimensional, non isothermal description of a PEM fuel cell operating on reformates feed. Optimal operating conditions were presented for six fuel cell design cases to illustrate the effects of membrane and electrode thickness, constraint values and CO concentration in the feed stream on the anode side to optimize the power density. Meng and Wang [28] developed a mathematical model for two phase flow and flooding dynamics to describe liquid water transport in the GDL while mist flow model is used in the gas channel and potentially differentiating hydrophilic from hydrophobic GDLs in their effect of electrode flooding and cell performance. The model points to two distinctive mechanisms for electrode flooding: one is controlled by bulk transport of liquid water across the GDL thickness and the other dictated by the interfacial process occurring at the GDL surface. Dong *et al.* [29] studied the characteristic operating performance under low humidity operation. This paper presents series of experiments at various anode and cathode humidity levels with distributed current, species and high frequency resistance data. Results shows that degree of water saturation in the anode greatly influence local performance through anode dryout, even for the thin 18 μm electrolyte used in this study. Chen and Peng [30] developed a steady state thermodynamic model, which captures the crucial dynamic variables of the humidifier, including the pressure, flow rate, temperature and relative humidity of the air flow.

Xue and Tang [31] developed a highly non-linear system level dynamic model which accounts in to the phase change effect. The model describes the complicated transient behaviour of temperature, gas flow, phase change in the anode and cathode channels and membrane humidification under operating conditions. The results show that the vapour in the cathode channel is more likely to be in over-saturated state if the load current is large resulting in the phase change. In the anode channel, however, the vapour generally is not saturated even if the inlet hydrogen is humidified with a 90% relative humidity. Pukrushpan *et al*. [32] developed a model suitable for control oriented modelling analysis for PEM fuel cells for automotive applications. The transient phenomena captured in the model include the flow inertia dynamics of the compressor, the manifold for both anode and cathode, reactant partial pressures and membrane humidity. The fuel cell polarization curve used in this study is a function of oxygen and hydrogen partial pressures, stack temperature and membrane water content helping to assess the effect of varying oxygen concentration and membrane humidity on the fuel cell voltage. Tanrioven and Alam [33] developed a reliability modelling and analysis of stand-alone PEM fuel cell power plants. The proposed fuel cell power plant evaluation algorithm can be used for replacement time for bipolar plates and MEAs in order to lengthen the lifetime of fuel cell power plants. Shan and Choe [34] proposed a highly dynamic PEM fuel cell stack model, taking into account the most important property of temperature effecting performance and dynamics. Simulation has been conducted to analyse the static and dynamic behaviour of stack. Results show that heat generated in the cathode side is higher than in the anodic side. The heat conductivity of the membrane varies during operations because of the continuous variation of water content which results in an increase of electrical and thermal resistance. Chang *et al.* [35] presented a stack model which couples flow distribution with unit cell performance. Individual parameters for each unit cell can be varied and the model can be used to investigate the effects of different designs, operating conditions and manufacturing requirements to minimize the impact on stack operability. Al-Baghdadi [36] presented a simple one-dimensional, steady state, isothermal mathematical

model for PEM fuel cells and effect of the operation conditions on the cell performance has been investigated. This study shows that the effect of temperature on the inlet gas composition is particularly strong in the 1 to 3 atm pressure range. Rodriguez *et al.* [37] presented a study of the design and functionality characterisation of current, voltage and power of PEM fuel cell. The experimental design applies four different pressure levels inside the cathode compartment. Results show that greater current densities are obtained when working with cross current flow, where as greater electrical power levels are observed in the co-current flow. Kolodziej [38] presented a non-linear control method for accurately maintaining cooling temperature within fuel cell stack by controlling cooling flow rate. The control algorithm utilizes a nonlinear continuous flow stirred tank reactor model of the fuel cell for feedback linearization. Park and Choe [39] developed a model for a 20-cell stack to investigate start up and transient behaviour. Start up behaviour under different conditions of load current, temperature and flow rate of coolant and extra heating of the end plates where as transient analysis considered the dynamics of temperature, oxygen and vapour concentration in the GDL, liquid water saturation and variation of water content in the membrane. The model concluded that voltage difference between a single phase model and two phase model were predominantly affected by activation overpotentials caused by changes in the oxygen concentration. Also, four cells from each end showed a temperature gradient while the rest of cell maintained a relatively uniform temperature distribution. Zhang *et al*. [40] developed a three dimensional steady state electrochemical mathematical model to study the influence of the parameters like porosity, permeability, the thickness of gas diffusion layer and the inlet gas stoichiometry on the fuel cell performance. The results show that the pressure drop across the cathode GDL is slightly influenced by gas inlet stoichiometric ratio. Relatively high potential occurs at large permeability as more oxygen is transferred to the catalyst layer.

Jung *et al*. [41] developed a steady state two-dimensional numerical model to predict the performance of large active area with the water cooling thermal management system. The results show that the changes in local electric resistance due to temperature distribution cause fuel cell power to decrease. Therefore, the coolant temperature and flow rate should be controlled properly depending on the operating conditions. Martins *et al.* [42] developed a simple steady state model with temperature dependence on space and current and experimentally validated by direct comparison with output voltage and power measurement in the laboratory. Infrared image temperature measurements show that the actual temperature distribution of a single cell is not uniform even at low current levels. As the cell current increases, the operating current increases, the temperature spatial gradients increase since more heat is generated through electrochemical reactions. Lottin *et al*. [43] presented a simple pseudo-2D model to underline the limits of one-dimensional modelling of the MEA. The overpotential at anode and cathode are evaluated by a Tafel law and it allows determining the fuel cell limiting current density as a function of the gas composition and stoichiometry. One- dimensional, steady state model accounting for coupled heat and mass transfer with a special attention to the water transport through a PEM fuel cell has been presented by Falcao *et al*. [44]. They studied the conditions corresponding to relatively low values of relative humidity, conditions of special interest in the automobile applications. The model predicts that humidification of anode and cathode streams are must to avoid membrane dehydration, particularly at high current densities. Zhou *et al*. [45] developed a multiphysics model to simulate the entire process including the effects of mechanical deformation, mass transfer resistance and electrical contact resistance. The model concludes that the assembly pressure has significant effects on PEM fuel cell performance. High assembly pressure increases the mass transfer resistance and decreases the current density. As assembly pressure increases, the power output increases first and then decreases over a wide range of powers.

Min *et al.* [46] developed a one-dimensional dynamic model of stationary PEM fuel cell. The system model consists of fuel processing system, PEM stack with coolant, humidifier and an enthalpy wheel. The unit cell model contains a five control volumes of anode gas, anode GDL, electrolyte, cathode GDL, cathode gas for solving the dynamic species and mass conservation equations and seven control volumes to solve the dynamic energy balance and to capture the MEA behaviour. Baschuk and Li [47] presented a comprehensive, consistent and systematic mathematical model for PEM fuel cells. This model is applied to an isothermal, steady state, two-dimensional PEM fuel cells and it includes the transport of gas in the gas flow channels, electrode backing and catalyst layers. Water and ion transport in the polymer electrolyte was modelled using the generalised Stefan-Maxwell equations based on non-equilibrium thermodynamics. The model result shows that the some of the water required by the anode is supplied by the water produced in the cathode. But this is not sufficient to keep the anode hydrated. Therefore, anode gas must be humidified to avoid anode side dehydration of the membrane. The length of gas channel has a significant effect on the current production with longer channel length having a lower performance relative to a shorter channel length. Das *et al.* [48] demonstrated a one-dimensional analytical solution of liquid water transport in cathode catalyst layer (CCL) of PEM fuel cells. They concluded that wetting characteristic of a CCL plays a significant role on the liquid water transport and cell performance and the liquid water saturation in a hydrophilic CCL can be significantly reduced by increasing the surface wettability or lowering the contact angle.

Yu *et al.* [49] studied a 1 kW PEM fuel cell for residential power generation. The dynamic simulation model of the PEMFC contains turbo blower, membrane humidifier, two cooling circuits and a PEMFC stack. The efficiency of this model has been increased by supplying the electricity and hot water to the house. The model demonstrates that the parasitic power consumption of the blower is significant at low current densities. Contreras *et al*. [50] developed a semi-empirical mathematical model representing the main technical and economic features involved in the operation of PEM fuel cells in rural villages of Venezuela. The simulation spans 20-years from 2001. The simulation also considers the annual linear increase in equipment cost and decrease in fuel cell cost due to technological improvements. The results shows that the main operating variables like current density, efficiency and generated voltage show the typical behaviour of this type of cell where as cost of electricity produced by the stack decreases asymptotically for the same year. Sharifi *et al*. [51] proposed two models to simulate the steady state and transient phenomena in a PEM fuel cell system where mathematical and theoretical equations are considered for determining the humidity of the membrane in steady state condition. Transient response of voltage under sudden change in load current was also studied and found that the sudden increase or decrease in load, decrease or increase of voltage due to capacitance effect of fuel cell, is decreased. Paja *et al*. [52] presented a mathematical analysis of the efficiency of common series and parallel hybrid topologies based on PEM fuel cell and auxiliary storage device. The new topology exhibits a higher efficiency in non-degenerative operation and eventually effected in reduction of the fuel cell hydrogen consumption. Youssef *et al*. [53] developed a lumped model depending on linear algebra for PEM fuel cell which is used to study the effects of several operating parameters, such as input temperature, pressure, stoichiometric ratio, membrane thickness and fuel cell performance. The results show that the voltage of fuel cell increases with the temperature of fuel cell and pressure of the gasses and decreases with the increase of the membrane thickness. Mangold *et al*. [54] developed a model for the freeze start behaviour of a PEM fuel cell stack which covers a wide range of temperatures from below the freezing point of water to usual operating temperature of the fuel cell. The model has been derived from the first principles and shows a good agreement with the experimental data. Simulation studies are helpful to improve the process control strategies during a freeze start. Ameri and

Oroojie [55] developed an isothermal, steady state, two-dimensional model for PEM fuel cells operating at different voltages to investigate the fuel cell performance parameters such as the mass concentration, the velocity distribution of reactants, current density distribution and polarization curve using COMSOL multi physics software. Water and ion transport in the membrane has been modelled using the Stefan-Maxwell equations and reactant gas flow in the gas channel has been modelled using Navier –Stokes equations. The model shows that fuel mass fraction decreases faster when the cell works at low voltage and high current densities. Ziogou *et al*. [56] developed a dynamic fuel cell model using the gPROMS software modelling environment and validated with the experimental data. The model relies on mass and energy conservation equations combined with equations having experimentally defined parametric coefficients thus resulting in a semi-empirical dynamic model. The equation of voltage as a function of the current and relationship between current drawn from the fuel cell and consumption of reactants describes the operation of the fuel cell.

3. Bipolar plate models

Kazim *et al*. [57] developed a simple mathematical model to investigate the superiority of interdigitated flow field design over the conventional one in terms of maximum power density where Darcy's equation for porous media and Butler-Volmer equation is used at the catalyst layer interface. The results show that the limiting current density of a fuel cell with an interdigitated flow field is about three times the conventional flow field and double the maximum power density of a fuel cell. Dutta *et al.* [58] developed a numerical model to predict the mass flow rate through the cathode and anode channels with a serpentine flow path. The complete three-dimensional Navier-Stokes equations with multi species mixtures are solved and electrochemical reactions are modelled in the control volumes. The results show that the flow directions are significantly dependent on the mass consumption pattern on the MEA. Cha *et al.* [59] developed a model based on three-dimensional computational flow dynamics to study the effect of flow channel scaling on fuel cell performance and explained the advantage of using micro channels in small fuel cell. The results show that the discrepancy between model expectations and experimental data are for channels which are smaller than 100 μm due to flooding in the cathode. Yi *et al.* [60] developed a water flux model for vapour and liquid phases along a gas flow channel and scaled up for fuel cell stack for different applications. The results show that for good fuel cell stack water management, lower reactant utilization and higher pressure drop in the reactant stream are desirable. In contrast, higher reactant utilization and lower pressure drop in the reactant are preferred for overall system efficiency. Liu *et al.* [61] studied water flooding and two phase flow of reactants and products in cathode flow channels with different flow fields including parallel flow field, interdigitated flow field and cascade flow field. The results show that the water in flow channels at high temperature is much less than that at low temperature. When water flooding appears, increasing cathode flow rate can remove excess water and leads to good cell performance. The water and gas transfer can be enhanced and the water removal is easier in the interdigitated channels. Wang *et al*. [62] developed a continuum model of two phase channel flow based on two phase Darcy's law and M^2 formulism to derive the liquid water saturation and species concentration along the channel. The results reveal that liquid water builds up quickly at the entrance region followed by a slow increase downstream, under full humidification inlet conditions. Lee *et al.* [63], developed a single phase three dimensional simulation model for both anode and cathode flow field for examine the micro flow channel with electrochemical reaction. It is found that the amount of water in cathode channel was determined by water formation due to electrochemical reaction plus electro-osmotic mass flux directing toward the cathode side. Ous and Arcoumanis [64] studied experimentally the effect of air stoichiometry, hydrogen stoichiometry, temperature and electric load on the

accumulation of water in the anode and cathode flow channels with transparent flow visualisation. The study show that the increasing the cell temperature to 60 ^{o}C was sufficient to evaporate all water from the channels. Kumar and Kolar [65] studied a three dimensional, steady state, non-isothermal and single phase model to find the effect of cathode channel dimensions on the performance. The results show that the cell performance can be improved by increasing the depth and width and reducing the height of the channel. With a cathode channel depth of 2 m the performance of cell is limited by the flow resistance offered by the channel, where as for channel depths of 6 mm and 10 mm the performance is limited due to channel flow and diffusion resistance offered by the porous media. Darling and Badrinarayana [66] studied the oxygen transport in interdigitated air channels in porous bipolar plates and found that convective flow through the GDL caused by incorporating interdigitated channels into air flow field significantly improves oxygen transport to the cathode catalyst layer provided that the membrane electrode assembly is well hydrated.

4. Gas diffusion layer Models

Ridge *et al.* [67] developed a mathematical model for Teflon bonded, platinum black porous electrode for predicting the performance of a PEM test cell cathode. Transport and reaction of both oxygen and hydrogen ions were included in this model. Model prediction showed that transport of hydrogen ions to the catalyst site has an effect on the performance of the electrode and the performance of gas-fed electrodes could be improved by making agglomerates with small radii. Bernardi and Verbrugge [68] developed mathematical frame work to describe a gas diffusion electrode bonded to a solid polymer electrolyte, which served as a stepping stone to the development of a complete fuel cell model. Their model was focussed on cell polarization characteristics, water transport and catalyst utilization. Resistance due to the oxygen reduction reaction appears to be important during all practical operating current densities. Results show that at low current densities, water is forced out from the cathode of the membrane side of the electrode due to the pressure differential. In contrast, at higher current densities water is forced out of the gas chamber side of the electrode. Gloaguen and Durand [69] developed a macro-homogeneous and agglomerate model applied to different kinds of oxygen cathodes. The results show that, the gas pores must exist, even within real active layers thinner than 10 μm. The cathode performance is significantly affected by the diffusion through the agglomerate and by the ionic conduction along the layer thickness. Bevers *et al*. [70] presented a one dimensional dynamic model of a gas diffusion electrode (GDE) of a complete fuel cell. The model includes mass, momentum and energy transport in the gas diffusion, catalyst and membrane layers. A significant outcome of the simulation is the importance of keeping the cathode potential above the potential in which the change of the Tafel slope occurs. Vidts and White [71] developed governing equations for porous electrode containing three phases using the volume-averaging technique. These equations include the mass transfer in each phase and ohmic drop in the liquid and solid phase. Marr and Li [72] investigated the catalyst utilization as well as the optimum composition and structure for the cathode catalyst layer, such as catalyst loading, catalyst type, catalyst layer thickness, void fraction and membrane content in the void region. It concluded that the optimal void fraction for the catalyst layer is about 60% and fairly independent of current density and a 40% supported platinum catalyst yields the best performance. Bultel *et al*. [73] presented a model to show the influence of parameters characterizing the active layer on the working behaviour of PEM electrodes. This model takes into account diffusion and electrochemical reaction without ohmic drop limitations. The competition between neighbour particles participate in electrochemical reaction and diffusion effects at the particle level, almost negligible for oxygen reduction, are significantly influent for hydrogen oxidation. He *et al.* [74] developed a two-dimensional, two phase, and multi-

component transport model to investigate the effects of the gas and liquid water hydrodynamics on the performance of air cathode of a PEM fuel cell in contact with interdigitated gas distributor. Darcy's law was used to describe the transport of the gas phase and transport of liquid water through the porous electrode is driven by the shear force of gas flow and capillary force. This model conclude that a higher pressure difference between inlet and outlet channels improve the electrode performance due to better oxygen transport and water removal. The electrode thickness needs to be optimized as thinner electrode reduce gas flow rate and thicker electrode increase the diffusion layer thickness. Natarajan and Nguyen [75] developed a two-dimensional, two phase multicomponent, and transient model for the cathode of PEM fuel cells. Gas transport was addressed by multicomponent diffusion equations while Darcy's law was adapted to account for the capillary flow of liquid water in the Gas diffusion layer. They found that performance of cathode increased with increasing the porosity and decreasing the thickness of diffusion layer. Wang *et al*. [76] studied two phase flow and transport in the air cathode of PEM fuel cells to predict water formation and its effects on the electrochemical kinetics at the membrane/cathode interface and reactant and product transport. The water and vapour transport is controlled by capillary action and molecular diffusion respectively due to negligible small air velocity within the porous electrode. Jaouen *et al.* [77] developed one dimensional, steady state agglomerate model to describe the functioning and the mass limitations of the cathode. The model includes Tafel kinetics of the oxygen reduction reaction, proton migration, oxygen diffusion in the agglomerate and diffusion of ternary gas mixtures (O_2/N_2/water vapour) in the pores of active layer and the gas backing. The model show that limitations by proton migration in the active layer or by oxygen diffusion in the agglomerate lead to double of the Tafel slope at higher current densities. You and Liu [78] presented a two-dimensional, two phase and multi-component model to describe the flow transport in the gas channel and porous gas diffuser. The model concludes that the net water transport coefficient depends on the operating current density, water activity on the cathode and anode sides, water partial pressures and membrane properties. The threshold current density needed to form two phase flow and distribution of liquid saturation on the cathode side depend on the fuel cell operating temperature, cathode and anode humidification temperature and characteristic of the porous gas diffuser. Natarajan and Nguyen [79] presented a three dimensional model for the cathode using conventional gas distributor. The model includes dimension along the channel for the drop in oxygen concentration in the channel due to consumption and dilution and its effect on the performance of cathode. The model conclude that water transport mechanism is the slowest and most dominant in influencing the performance of cathode and the current density distribution is strongly dependent on the concentration profile along the channel. He *et al*. [80] designed an electrode flooding monitoring device with interdigitated flow distributors to correlate fuel cell performance and the water saturation level in the backing layers with the various operating parameters. The results show that inadequate water removal causes water build up in the cathode and it was observed that more than 30 minutes were required for a cell to reach a new steady state when subjected to current density changes. Increasing air flow rate or cell temperature helps water removal. Birgersson *et al.* [81] developed an isothermal, two-dimensional liquid phase model for the mass, momentum and species in the anode of direct methanol fuel cell [DMFC]. The governing equations and boundary conditions were normalized and reduced model was then derived. The advantage of reduced approach leads to a better understanding of the important transport mechanisms for mass momentum and species. Weber *et al.* [82] developed a sandwich two phase model to examine the effects of flooding on the operation quantitatively. It described the change in maximum power as a function of structural properties of diffusion media, including the bulk porosity, wet ability, thickness and pore size distribution. The simulation results demonstrated interplays between

mass transfer effects related to flooding of the diffusion media and ohmic effects. Lin *et al*. [83] presented a two phase, one-dimensional steady state, isothermal model to study the liquid water effects in the gas diffusion layer and catalyst layer of the cathode on the overall cell performance. The results confirmed that the water flooding in the catalyst layer is more severe than the back diffusion layer since water is first produced in the catalyst layer. The simulation results on the effect of the catalyst loading and thickness of catalyst layer suggested that excessive catalyst loading would not help the overall cell performance. Weber and Newman [84] studied the effect of microporous layers (MPL) in PEM fuel cells. The results show that MPL provides less ohmic resistance and minimise the flooding by pushing water away from the GDL through the membrane. The better membrane hydration can be achieved by using MPLs and provides highest maximum power.

Ge and Wang [85] developed transparent PEM fuel cell with parallel and serpentine channel flow field to study liquid water formation and transport on the anode side. Results show that GDL wettability plays an influential role in liquid water transport and distribution in the anode. Using hydrophobic GDL at low current density, water is prone to condense on the channel walls rather than inside the hydrophobic GDL. Current density is a controlling parameter for water condensation and liquid water formation in the anode. Schulz *et al*. [86] presented a model to determine the two phase characteristics of a compressed gas diffusion layer is determined based on its full 3D microstructure. The importance of clamping pressure on the two phase characteristics is demonstrated through the evaluation of capillary pressure curves for various levels of compression. The results shows that increased compression leads to more tortuous pore structure which in turn requires increasing capillary pressure for the invasion of the non wetting phase into wetting phase saturated GDL in order to achieve the same level of saturation. Seigel *et al.* [87] studied the operation and accumulation of liquid water within the cell structure with a dead-ended anode using neutron imaging. They measured the rate of accumulation of liquid water and its impact on the rate of cell voltage drop for a range of temperature, current density, cathode inlet relative humidity and air stoichiometric conditions. Wang [88] developed a three dimensional, two phase transport model in the diffusion media to investigate the species transport and electrochemical process in the fuel cell. Simulation results revealed that two phase flow can occur in both anode and cathode and that at low humidity, single and multiphase flow coexists in the fuel cell. In the co-flow configuration, liquid emerges downstream due to water production, while flooding is more severe in the middle of the fuel cell for the counter flow configuration due to the internal humidification. Benziger *et al.* [89] examined oxygen transport across the cathode gas diffusion layer (GDL) by varying O_2/N_2 ratio and area of the GDL. The results show that oxygen dilution by nitrogen increases mass transport resistance from the gas flow channel to the cathode catalyst layer. Convection is dominant at high mole fraction and diffusion is dominant at low oxygen mole fraction across the GDL. Yablecki *et al.* [90] determined the anisotropic effective thermal conductivity of the fuel cell GDL using 2-D and 3-D two phase conjugate fluid-solid thermal lattice Boltzman models. It was found that the through plane and in-plane thermal conductivities strongly depend on the porosity and fibre orientation.

5. Membrane models

Sakai *et al*. [91] investigated gas diffusivity and solubility in Nafion in dried and hydrated states. The results show that the water contained in the membrane decreased the solubility and increased the diffusivity. Also, diffusivity decreased when palladium metal was deposited in the membrane. Verbrugge and Hill [92] developed and analyzed a model for the simulation of ion and solvent transport within an ion-exchange membrane. A Nernst-Planck equation is employed for the description of ion transport by diffusion, migration and convection. The set of equations used in the simulation are presented in a dimensionless

form so that important dimensionless parameters can be evaluated. Bernardi [93] presented a model that identifies operating conditions that result in water balance and demonstrate the sensitivity of water balance to change in temperature, pressure, inlet humidity and flow of the reactant gases. The result show that the water balance is more sensitive to change in inlet air humidity and flow rates than inlet fuel humidity and flow rates, however, humidification of fuel is preferable. The analysis also identified that high operating pressure can significantly reduce water evaporation relative to the operation at atmospheric conditions. Nguyen and white [94] presented a water and heat management model to study the efficacy of various humidification designs. The model includes water transport across the membrane by electro-osmosis and diffusion, heat transfer from the solid phase to the gas phase and the latent heat associated with water evaporation and condensation in the flow channels. The model results show that at high current densities, ohmic loss in the membrane had the strongest effect on the voltage loss and that the water back diffusion from the cathode side of the membrane was not enough to keep the membrane sufficiently hydrated to provide high conductivity. It was concluded that anode stream must be humidified to minimise the ohmic loss. Hinatsu *et al*. [95] investigated the water uptake of Nafion membranes over the temperature range 25 to 130 ^{o}C and form water vapour at 80 ^{o}C. The results show that membrane water uptake from liquid water depended on the immersion temperature, the ion exchange capacity of the membrane and pre treatment conditions. For water uptake from water vapour from some membranes that are found to give relatively good performance than Nafion 117, possibly as a result of slight structural differences. Ren and Gottesfeld [96] measured the elector-osmotic drag of water in preflurosulfonic acid membranes. Measurements performed on Nafion, C and Dow membranes showed that water drag coefficients of all membranes increase with temperature. For a series of Nafion membranes, a membrane with high equivalent weight has lower water drag coefficient, where as water drag coefficient of Dow membrane is unusually low compared to that of a Nafion membrane of similar equivalent weight. Kulikovsky [97] developed a quasi-3D model of water transport in a membrane electrode assembly which takes into account nonlinear diffusion of liquid water in the membrane. The model developed by springer *et al.* [4] was used to model the transport in the membrane and the gas transport in the catalyst layer was assumed to be Knudsen diffusion only. Teranishi *et al.* [98] examined the distribution of water content in a PEM of three different thicknesses using Magnetic Resonance Imaging (MRI) and Impedance Spectroscopy. Cell with thinnest membrane had better performance than the cell with the thicker membranes because it had low ohmic resistance. Water content in all three membranes decreased with an increase in cell current density. Ge *et al.*[99] presented a pseudo-two-dimensional, steady state model for the water transport through the membrane to determine the mass transfer coefficients for the absorption and desorption of water and water diffusion coefficient. The model concluded that the rate of water absorption is much lower than that of desorption at a specific value of water content in the membrane and transport of water vapour through the Nafion membrane is controlled by two membranes/GDL interface and diffusion of water in the membrane. Nazarov and Promislow [100] presented a non-equilibrium force balance model of water and ion transport for PEM. The model predicts that the membrane compression will have a significant impact not only on membrane hydration but also on membrane water distribution and water balance. The model show that mechanical compression of membrane leads to a more uniform distribution of water through the thickness of the membrane and decrease membrane water content by 5-30% and decrease back-diffusion of water within the membrane by 20%. Steinkamp *et al*. [101] presented a non-isothermal, two-dimensional model which includes two phase flow of water (gaseous and liquid) in the gas diffusion layers and in the catalyst layers, as well as the transport of species in the gas phase. The electrochemical reactions in catalyst layers are modelled with simple Tafel approach via

source/sink terms in the Poisson equations and in the mass balance equations. Heat transport via conduction and convection is modelled in the gas diffusion layers and catalyst layers.

6. Computational fluid dynamic models

Um *et al*. [102] developed a transient CFD multidimensional model which account for electrochemical kinetics, current distribution, hydrodynamics and multi component transport. This model is applied to explore the hydrogen dilution effects in the anode feed when the reformate gas is used and show a substantial anode mass transport polarization and hence lower current density. Berning and Djilali [103] developed a CFD multiphase model which includes gas diffusion layer and gas flow channels for both anode and cathode as well as cooling channel. The results show that the amount of water strongly depends on the material properties particularly hydraulic permeability of GDL material. The large value of GDL permeability, water saturation in excess of 20% can be attained at the anode side. The saturation levels decrease with permeability, whereas at cathode side the opposite is true. Berning and Djilali [104] presented a three dimensional, non-isothermal model to investigate the effect of operational parameters such as temperature and pressure on the cell performance. In addition, effect of geometrical and material parameters such as GDL thickness and porosity as well as the ratio between channel width and land area were also investigated. The results show that the porosity of the GDL has a strong effect on the limiting current density. Ju *et al*. [105] developed a three dimensional, non isothermal model applied to 50 cm^2 cell under various humidity and cell voltage conditions and is validated with the experimental data of current distribution. Different shapes of current distribution are illustrated depending on the inlet humidity conditions. Under fully humidified conditions, the local current density is controlled by concentration polarization and thus continuously decreases from cell inlet to outlet. Low humidity operation shows initially increasing current density as the membrane gains moisture from product water. When the membrane gets fully hydrated, oxygen depletion effects begin to control the current density distribution, showing decreasing current density towards the cell outlet. Carcadea *et al.* [106] developed a three dimensional, steady state, single phase model to study the mass and charge transfer within a PEM fuel cell. The governing equations are solved numerically using a finite-volume based CFD technique. The model studied phase potential distribution and multi-component transport in the fuel cell. The results show that the maximum phase potential occurs at the inlet of the channel, due to the highest oxygen concentration and decreases along the flow direction because of oxygen consumption. Guvelioglu and Stenger [107] developed a detailed steady-state, isothermal, two-dimensional model based on finite element method to solve multi-component transport model coupled with flow in a porous media, charge balance, electrochemical kinetics and water balance in the membrane. The complex water balance in the membrane was investigated and the operating conditions where the membrane becomes dehydrated were identified. The results shows that smaller sized channels and bipolar plate shoulders are required to obtain higher current densities and the effect of relative humidity of the anode gas stream was found to be the most critical condition affecting the fuel cell performance. Sivertsen and Djilali [108] developed non-isothermal, three-dimensional model accounts for convective and diffusive transport and allows the concentration of species and distributed heat generation associated with the electrochemical reaction in the cathode and anode. The results show good agreement between the model and experimental values. The study shows that changing the conductivity radically alters the current distribution by changing the relative influence of ohmic to activation overpotentials. Chi *et al*. [109] developed a three dimensional numerically solved using a finite volume based on CFD technique to predict species concentration, current density distribution, temperature distribution and cell performance. The model concludes that, for lower cell temperature, the

saturation pressure will decrease from inlet to cell, flooding phenomena occurs due to increase in water content. For higher cell temperature, the water saturation pressure will increase inlet to cell which decrease the water content results membrane dry out. These two situations lower the cell performance. Low temperature self humidified fuel cell could be the best option for the portable PEMFC. Shan *et al*. [110] proposed unsteady, two dimensional model to describe dynamic behaviour of stack with two adjoining cells and end plate assembly. The model can calculate dynamic distribution of pressure and reactants, current density, temperature and potentials in a stack. Zhang and Pitchumani [111] presented a comprehensive two-dimensional, non-isothermal multicomponant numerical model is developed to simulate the mass transport and electrochemical phenomena and effects of fuel cell orientation on the cell performance. The vertical orientation of the fuel cell leads to the largest cell performance while the horizontal orientation is least effective for the cell performance at the low cell voltages. Increasing the anode pressure anode relative humidity significantly improves the cell performance while the cell performance is relatively less sensitive to anode temperature and anode flow rate. Carcadea *et al*. [112] presented a three dimensional steady state single phase model using the fluent CFD software for multicomponant species transport electrochemical kinetics, water management. Mulone and Orsi [113] introduced a numerical design procedure based on CFD to evaluate the performance of different fuel cell layouts. The design procedure has been applied to a co-flow design, characterised by large active area, moderate temperature and liquid cooling. The results show that humidity has a large influence on cell performance. Operating pressures influences performance greatly for the concurrent effects of increase in the water production and reactant partial pressures. Performance decay was observed by increasing the cathode stoichiometry. Perng and Wu [114] studied the effect of tapered flow channel installed with a baffle plate on the performance of PEM fuel cell. The results shows that the stronger composite effect of tapered flow channel and baffle blockage provides a better convection heat transfer performance and a higher fuel flow velocity and thus enhances the cell performance. Wang *et al.* [115] presented a three-dimensional, two-phase, non-isothermal model to implement the parameter sensitivity analysis for PEM fuel cell with parallel flow field design. This study shows that tortuosities and porosities of cathode GDL and CL, permeabilities of cathode GDL, electron conductivities of cathode and anode GDL, proton conductivities of cathode and anode CL, exchange current densities on cathode and anode sides, cathodic transfer coefficient on cathode side, and anodic transfer coefficient on anode side are strongly sensitive parameters on the performance of fuel cell. Alvarado *et al.* [116] proposed a two-phase non-equilibrium one dimensional and two dimensional models based on experimentally determined porosity, capillary pressure relationships, and permeability of the gas diffusion material in order to demonstrate whether or not the use of these properties enhances the accuracy of PEM fuel cell models to predict the liquid water saturation distribution. It was found that the implementation of the experimentally determined water transport characteristics of the GDL predicts more liquid water saturation than using empirical correlations for the capillary pressure curves and permeability. Ismail et al. [117] developed a simple two dimensional numerical model for air-breathing PEM fuel cell to investigate the thermal situation over the cathode surface of the fuel cell. They concluded that the heat is dissipated more effectively if the fuel cell is oriented vertically or horizontally facing upwards than if it is oriented horizontally facing downwards. Cao *et al.* [118] presented a three dimensional, two phase, non-isothermal model of a PEM fuel cell to investigate the interaction between water and thermal transport process. The numerical simulation results show that the boundary temperature greatly affects the local temperature distribution and indirectly influences the saturation profile. By increasing the inlet gas relative humidity, the saturation level of cathode GDL is increased.

7. Concluding remarks

The mathematical models from the pioneer models developed by Springer *et al.* (1991) to the latest model formulated by Cao *et al.* (2013) have been reviewed in this paper. Mathematical models can help to examine the effect of different parameters, new materials, and different designs on the cell performance. A good model should predict fuel cell performance under a wide range of fuel cell operating conditions and reduce the number of experimental tests required to study the fuel cell systematically. Simulation studies can determine the effects of various operating parameters like temperature, pressure, humidity of reactants, stack design etc. on the performance of the fuel cell. However, parameters such as, size, shape and number of gas channels during membrane flooding and drying should also be taken into account when considering analytical behavioural model. The simulation results should also be validated with experimental data from laboratory tests to ensure credibility.

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