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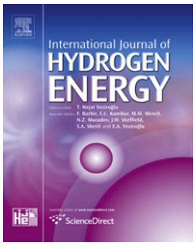

Review

Process system engineering in direct methanol fuel cell

S. Basri[a], S.K. Kamarudin[a,b,*]

[a] Fuel Cell Institute, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia
[b] Department of Chemical and Process Engineering, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia

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ABSTRACT

Among the different fuel cell technologies, the direct methanol fuel cell (DMFC) presents several interesting scientific and engineering problems such as feed and oxidant requirements, fuel utilization and recovery, scale-up, etc. There are many Process System Engineering (PSE) issues that remain unsolved. Notable among these are the structure of the DMFC and the modeling and optimization of design parameters. The PSE-related challenges discussed in this paper include the methanol and water crossover, the low kinetics rates of the reaction, heat and water management, the fuel management system, hydrodynamics studies and mass transport. Also presented in this paper are several important engineering factors for the successful stacking design of DMFCs for portable applications.

1. Introduction

PSE has to reassess and reposition its future research agenda on fuel cells. Emphasis should be placed on model-based applications in all PSE domains including product and process design, control and operations. Furthermore, systems thinking and systems problem solving have to be prioritized rather than the mere application of computational problem solving methods. This review reflects on the past, present and future of PSE from the DMFC point of view via diagnosis MEA cross section area. It redefines PSE as an active and future-proof research field that can play an active role in providing enabling technologies for DMFCs and process innovations in the chemical industries and beyond. Its major achievements include methodologies and tools to support process modeling, simulation and optimization (MSO) in terms of flow field and MEA on the DMFC system.

The direct methanol fuel cell (DMFC) presents several interesting scientific and engineering problems. There are many engineering issues that arise from the cell materials [1,2], feed and product management [3], mass and heat transport [4,5], etc. Among the various fuel cell technologies, the DMFC, which uses methanol directly to the system, has high-energy efficiency and a wide application prospect. A good design of the flow field can easily facilitate uniform distribution of reactants and by-product in electrodes to improve the performance of micro-DMFCs [6]. Thus, design fuel and heat management are related with the flow-field design.

Besides from engineering skills like design, simulation, fabrication, or material knowledge, microsystems engineering

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* Corresponding author. Department of Chemical and Process Engineering, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia. Tel.: +60 389216422; fax: +60 389216148.

E-mail address: ctie@vlsi.eng.ukm.my (S.K. Kamarudin).

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of DMFCs also requires thorough physical and chemical knowledge for functional design issues and device fabrication, as shown in Fig. 1. Chemistry part is focusing on catalyst and MEA fabrication with applied nanotechnology which describe in Section 2 while microsystem engineering in flow field and fuel management designs cover at Section 3. On the way to still smaller systems, microsystems technology is a major link to nanotechnology [7]. Process system engineering generate the simulation process for both microsystem and chemistry part cover in Sections 4–6 in this paper.

Furthermore, microsystems technology, which started in information technology and microelectronics, has entered many fields of daily life. Silicon chips and sensors can be found in cars, washing machines, and smart cards, with various functions; now DMFCs are being applied in MEMs technology.

Chemistry provides the background orientation and a multitude of applications for both process and microsystem disciplines [8–10], besides in fuel processing applications. The various ideas from all sides may inspire further development in the disciplines and result in increased possibilities and applications for innovations across the borders. A good overview is given by various authors with a clear and concise presentation of the fundamentals, design, fabrication and integration of a DMFC microprocess, as well as prominent applications to replace batteries.

Scott et al. [11] discuss several important engineering factors in the successful design of large-scale DMFCs including the use of vapor and liquid-feeds, thermal management, gas management, methanol fuel management, hydrodynamics and mass transport. Their modeling includes the mass transport of the gases in the diffusion layers and catalyst layers, the mass transport in the membrane, as well as the reaction and the potential distribution in the catalyst layers [12]. The performance of the fuel cell is adversely influenced by methanol permeation from the anode to the cathode. Moreover, the formation of a mixed potential is possible both at the anode and cathode and has a large negative effect on the energetic performance of the fuel cell. The model provides information concerning the impact of methanol permeation through the membrane on energy and mass yield and on the influence of the operating and structural parameters.

This article reviews on direct methanol fuel cell system design for active and passive system. Some sections like Section 3.1 only cover for active due to the limitation researches cover the flow-field design for passive system. Section 2 analyzed the chemistry of three main components in MEA DMFC such as backing layer, catalyst layer and membrane. Process system engineering issues were generated from the each layer. Section 3 investigates the microsystem engineering in outside and inside MEA such as fuel management and mass transport. Section 4 elaborates the process engineering which done to solve the issue that cover in previous Section 5 is focusing on the scaling up the DMFC for application purposes.

2. Chemistry diagnosis of direct methanol fuel cell

The micro or small DMFC for portable power application usually utilizes a passive operational mode. Fuel and oxidant are transferred into the electrodes by natural diffusion, which leads to auxiliary devices, such as the liquid pump for the fuel feed and the gas compressor for the oxidant supply, being completely eliminated. MEA consists of three important components which are backing layer, catalyst layer and membrane. Each layer has their engineering issue because the fuel will pass through to the each layer. During the permeation, mass and heat transfer occur which will explain further in Section 3.

2.1. *Backing layer*

The gas diffusion layer (GDL) is a critical component of fuel cell MEAs. The GDLs (or the backing layers), together with the flow fields [13,14] and current collectors [15,16], must be redesigned to achieve high performance from the operation of the direct

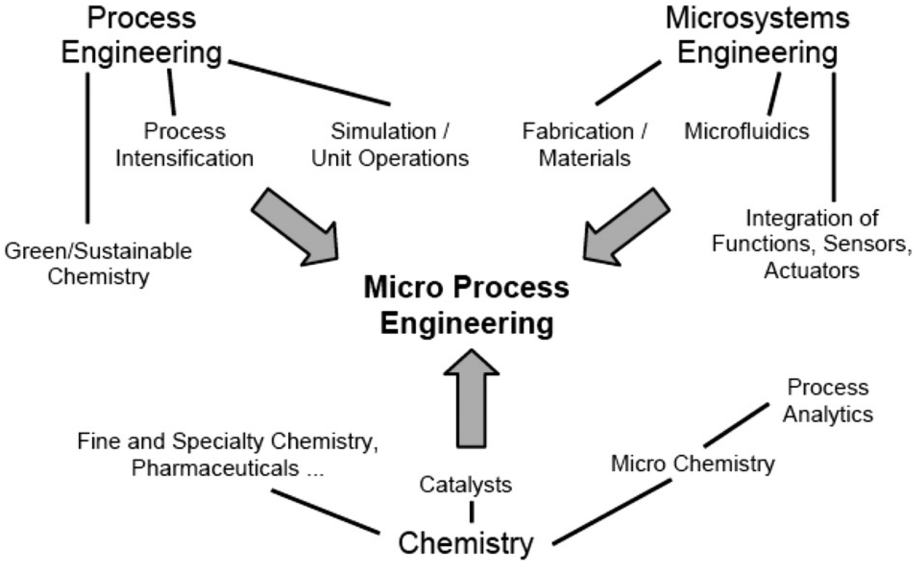

Fig. 1 – Micro process engineering as enabling and focusing technology as well as an interdisciplinary area for many engineering areas [7].

methanol fuel cell. The main function of the GDL is to diffuse the methanol to the catalyst layer. The porous nature of the backing material facilitates the effective diffusion of each reactant to the catalyst on the MEA. The GDL is also an electrical connection between the carbon-supported catalyst and the bipolar plate or other current collectors. In addition, the GDL manages water in the fuel cell while it carries the product water away from the electrolyte surface [17,18].

The GDL is usually made of a carbon-based porous substrate, such as carbon paper or carbon cloth, with a thickness of about 0.2–0.5 mm and a dual-layer structure. The great majority of engineering has come to include graphitic microstructures or disordered graphitic microstructures [19]. Also, most carbon engineering materials are derived from organic precursors by heat treatment in inert atmospheres (carbonization). During carbonization, the organic precursor is thermally degraded at temperatures in the range ~450–1,000 °C to form products that undergo condensation or volatilization reactions; the competition between these processes determines the carbon yield.

An ideal backing layer is required to effectively transport the gas reactants to the catalyst layers. It should have low electronic resistance, a surface that makes good electronic contact, and proper hydrophobicity for each application. In particular, for the highest power output when the fuel cell is operated at a relatively high current density, a higher flux of gas feed is needed, which requires the ideal GDL to effectively transport reactant gases to the catalyst surfaces at a fast rate.

The diffusion layer is composed of inactive carbon micromaterial or nanomaterial; no electrochemical reaction is expected within this region. Therefore, the water and methanol flux remains constant throughout this region [20]. The diffusion flux of oxygen in the cathode backing layer is then a sum of the fluxes required to consume the proton current j_o and to burn methanol.

The introduction of a GDL to the anode and cathode, as well as the decrease in polytetrafluoroethylene (PTFE) content of the backing layer and the use of the thinner electrolyte membrane under the premise of the existence of such a GDL are effective ways to reduce water crossover, increase methanol utilization, and improve cell performance. Xu and Zhao [21], also investigated the effect of a cathode MPL on cell performance and water crossover. They found that PTFE content affected cell performance and that increase in carbon loading can significantly decrease water crossover; however, too large a carbon loading increases the oxygen transport resistance and thus decreases the cell performance. Up to now, many models considering anisotropic effects of GDLs have been developed. Only a few of them considered the shape deformation effect and contact resistances [22].

2.2. *Catalyst layer*

For cost reasons, the foremost objective for the catalyst layers is to obtain the highest reactivity or transfer current density with a minimum amount of the catalyst. This requires a huge electrocatalytic active surface area, small kinetic barriers to bulk transport and interfacial transfer of protons, electrons and reactant gases, and proper handling of product water and waste heat. In DMFCs, the bimetallic Pt–Ru is the most widely used catalytic material because of its high electrocatalytic activity toward the methanol oxidation reaction (MOR) at the anode. Furthermore, it is interesting to mention that supporting material can also influence the electronic properties of the metal catalyst, especially in terms of increasing the surface area for the MOR and the oxygen reduction reaction (ORR) at the cathode side. Therefore, the idea of employing a nano-structured carbon material with a graphitic framework structure, including graphite nanofibers (GNF) and carbon nanotubes (CNTs), as supporting material for the Pt–Ru catalyst has received the attention of this study because of these materials' unique structural, electrical and mechanical properties [23]. In addition, two major improvements in the catalyst layer design have been the incorporation of Pt or Pt-group metal nanoparticles with sizes in the range of 2–5 nm and the impregnation or colloidal mixing of the high-surface area carbon support with an ionomer [24]. Ab initio quantum mechanical (QM) methods can complement these fundamental efforts but have traditionally been limited by their ability to capture the complex catalytic and electrochemical environments. The tremendous advances that have taken place over the past decade in the application of theory to understanding the surface reactivity of more traditional vapor-phase catalytic systems, however, has made it an invaluable partner in elucidating catalytic reaction mechanisms and aiding the design of new catalytic materials.

Currently, the ionomer completely replaces the PTFE that had formed a major component as a binder and hydrophobic agent in early fabrication methods. By these measures, catalyst loadings have been reduced from about 4–10 mg Pt/cm^2 (in the 1980s) to about 1.0 mg Pt/cm^2 today [25,26]. The self-organization of the ionomer and the carbon/Pt in the colloidal ink solution leads to the formation of phase-segregated, agglomerated morphologies. Agglomerates consist primary of carbon particles onto which Pt nanoparticles are deposited. It was found that ionomer molecules do not penetrate into the Pt/carbon clusters. Instead, they form a separate proton-conducting film with a thickness of ~10 nm that is attached to the surface of the agglomerates. Notice that the penetration of Nafion into the agglomerates depends on the fabrication technique, the Nafion concentration, the type of carbon, and the kinetics of the agglomeration process.

Generally porous electrode structures are used to support high current densities at low polarization, although typically current and overpotential are non-uniform due to the influence of mass and charge transfer in the structure. Even though the mechanism of methanol electro-oxidation on Pt–Ru catalyst in the DMFC is not fully understood, researchers have come to a common understanding, namely that simple Tafel or B–V equations are unable to represent the intrinsic methanol oxidation kinetics and a dual-site mechanism on Pt–Ru catalyst surfaces has been accepted. Consequently for a model of the observed or macro-kinetics of the DMFC anode it is important to include the appropriate dual-site mechanism of methanol oxidation.

2.3. *Membrane layer*

The main function of the membrane in a fuel cell system is to transport protons from the anode to the cathode. Membrane polymers facilitate the transport of protons (through their sulfonic groups) and keep the fuel and oxidant separated to prevent mixing of the two gases and to withstand harsh conditions, including active catalysts, high temperatures or temperature fluctuations, strong oxidants, and reactive radicals. Thus, the ideal polymer must have excellent proton conductivity, chemical and thermal stability, strength, flexibility, low methanol and water permeability, low-cost, and good availability.

Generally, it is the lifetime of the MEA that determines the lifetime of the DMFC. Thinner membranes, although they increase performance efficiency and proton conductivity, have lower physical strength and higher gas permeability, allowing more methanol crossover, which accelerates degradation. The technology for solid polymeric electrolytic membranes calls for the thinnest film that is electrochemically stable. At present, polymeric solid state fuel cell membranes, thinner than 50 μ, seldom work mechanically during fuel cell operation. When approaching the thin film limits, interfacial effects become significant to structure dynamics and consequently, the stability of the membranes.

At present, Nafion membranes are commonly used for DMFCs. Methanol crossover through this type of membrane is usually significant [27–29]. The common strategy to mitigate methanol crossover is to use a thicker Nafion membrane. However, this leads to an increase in the internal cell resistance, degrading cell performance. The compromise between these two effects is a Nafion membrane with an intermediate thickness, such as Nafion 115 or 117, which exhibits the best performance. Another active approach to reduce methanol crossover is to develop alternative materials that are less permeable to methanol, i.e., with low ethanol diffusivity and electro-osmotic drag coefficients. Extensive efforts have been devoted to the modification of fluorinated and non-fluorinated membrane such as PBI (polybenzimidazole) [30], SPEEK (sulfonated polyetheretherketone) [31], OPAs (asymmetric based organophosphorus acids) [32], DPS (diphenylsilicate) [33], etc. through the addition of inorganic components, or by depositing an ultra-thin barrier layer made of the methanol-impermeable proton-conducting (MIPC) materials such as Pd. However, the new membrane materials that have lower methanol permeability usually exhibit lower proton conductivity than the original Nafion membrane. Although this problem could be minimized by employing a thinner membrane, thinner membranes could potentially result in poor mechanical strength and long-term stability problems. Therefore, the development of an ideal low-cost membrane with a low methanol permeability and higher proton conductivity and durability are still underway. More detailed information about the state-of-the-art status of the membranes for DMFCs can be found elsewhere.

3. Microsystem engineering in direct methanol fuel cell

3.1. *Design flow field*

Flow-field design of direct methanol fuel cells (DMFCs) plays an important role in the cell performance. Like the water management at the cathode, the efficient removal of CO_2 at the anode is one of the most important research issues in the development of active DMFCs. Visual investigations of the CO_2 (g) evolution and flow behavior with flow beds are based on a stainless steel plate and mesh. According to several works, a number of flow designs are based on a stainless plate and mesh, which showed promising behavior in terms of gas removal characteristics, electrical performance [34,35] and size reduction [36,37]. To ensure free access for reactants to the electrodes especially at a high current density, products have to be removed from the active surface area and out of the cell. This removal is achieved via diffusion layers and flow channels that are manufactured into the plates. The main tasks of these flow-field plates are to guarantee distribution of fuel or air over the reaction surface area and remove products from the cell. Presently, a few investigations have been extended to the reactant flow fields [13,38] and to act as current collectors. Currently, mainly symmetrical grid, serpentine [39] and parallel flow fields are used at active system for both the anode and cathode [40] to facilitate mass transport to and from the active surface area. However, due to the long channels, serpentine flow-fields feature high pressure drops between the inlet and the outlet and result in large parasitic energy demands [13], which is shown in Fig. 2.

In addition, a method of fuel circulation with a fixed amount of fuel was employed by [41] to investigate a direct methanol fuel cell (DMFC) stack that was built with metal foam flow fields for the air and fuel flows. Fig. 3 shows an air-breathing DMFC

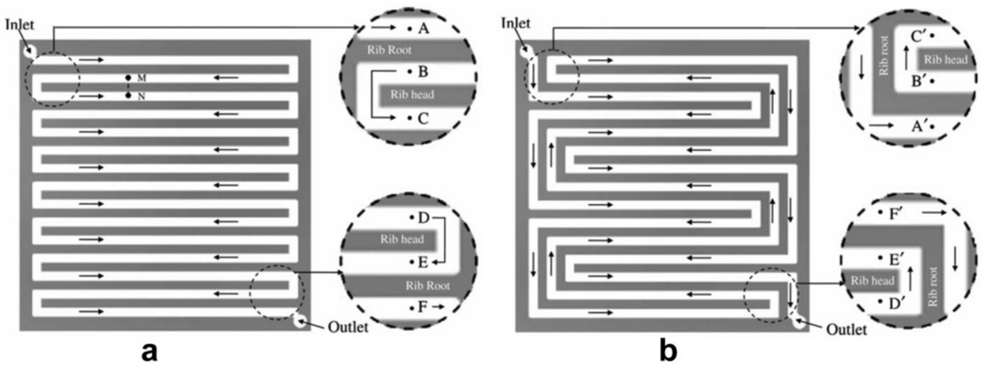

Fig. 2 – Designs of the flow fields (drawn to scale): (a) serpentine flow field SFF (b) convection enhanced serpentine flow field CESFF [13].

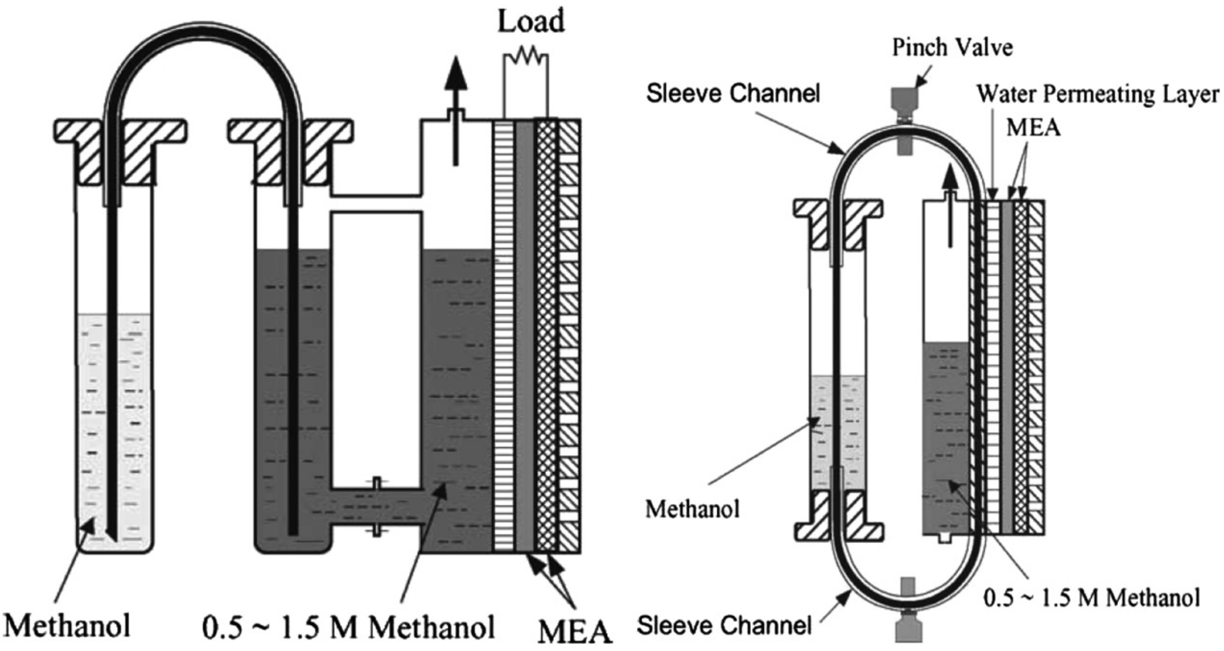

Fig. 3 – The air-breathing DMFC with a passive fuel delivery system (a) with methanol storage (b) with an enhanced fuel delivery mechanism [42].

with a passive fuel delivery system with methanol storage and an enhanced fuel delivery mechanism [42].

Xu et al. [43] come out with the unique idea to design flow field for high concentration. Vaporize methanol solution in the flow field by utilizing the heat generated from the fuel cell then the methanol concentration in the anode catalyst layer can be controlled to an appropriate level.

3.2. *Fuel management*

Fuel cells are being considered as an important technology that can be used for various power applications. For portable electronic devices such as laptops, digital cameras, cell phone, etc., the direct methanol fuel cell (DMFC) is a very promising candidate as a power source. However many issues related to the design, fabrication and operation of miniaturized DMFC power systems still remain unsolved. Fuel delivery is one of the key issues that will determine the performance of the DMFC. To maintain a desired performance, an efficient fuel delivery system is required to provide an adequate amount of fuel for consumption and to remove carbon dioxide generated from fuel cell devices at the same time.

Zhang and Wang [44] have developed a novel methanol fuel delivery system combined with a miniaturized DMFC, as shown in Fig. 4. The core component of this system is a piezoelectric valveless micropump that can convert the reciprocating movement of a diaphragm activated by a piezoelectric actuator into a pumping effect. or as shown in Fig. 5,

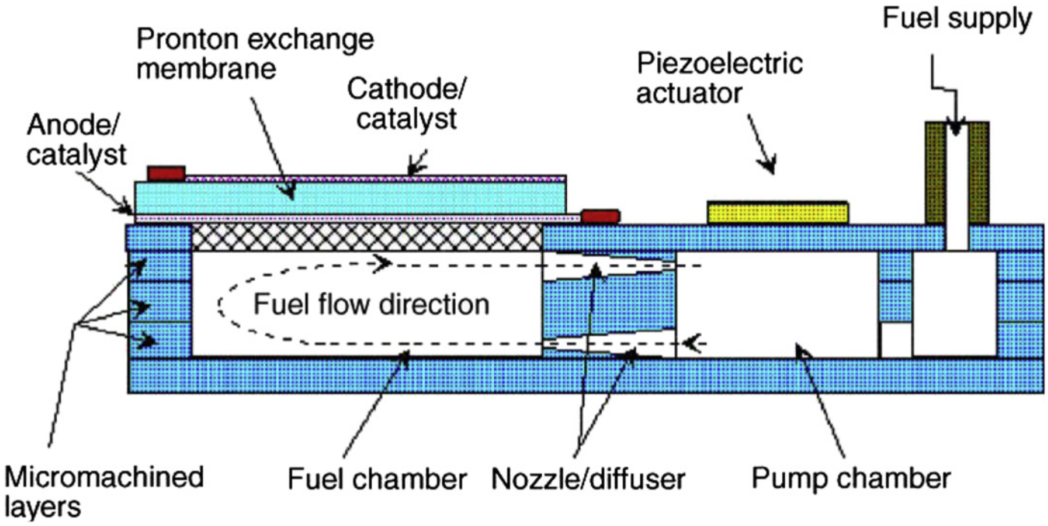

Fig. 4 – Schematic of the miniaturized DMFC system driven by piezoelectric valveless micropump [44].

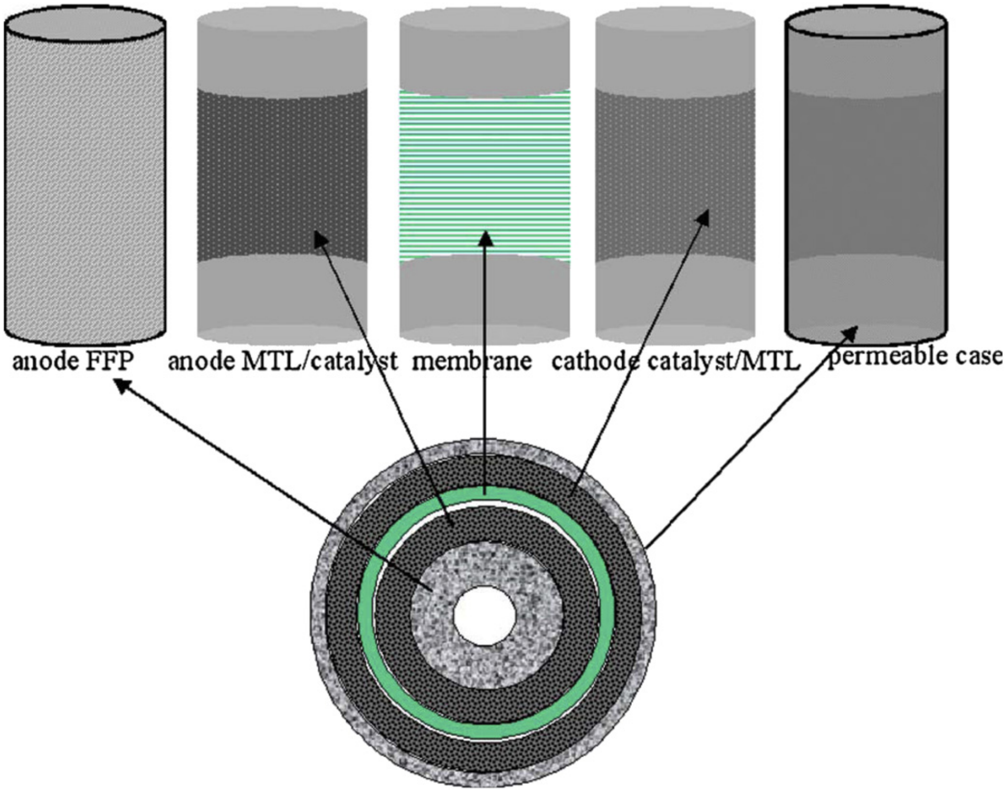

Fig. 5 – Schematic of expanded graphite based cylindrical fuel cell construction representing assembly order [45].

Yazici [45] has developed an air management system for the purpose of controlling diffusion for higher performance cylindrical fuel cells. A passive cylindrical fuel cell with an expanded graphite diffusion medium was constructed and operated with hydrogen. A very stable open circuit potential was obtained with this volume-efficient self-sealing construction. Paust et al. [46] fabricated and tested a microfluidic fuel supply concept for passive and portable direct methanol fuel cells (DMFCs) that operates in all spatial orientations, as shown in Fig. 6.

Consciously, the volumetric or gravimetric theoretical energy density of methanol is about 10 times higher than that of the currently used Li-ion battery. On the other hand, the DMFC usually shows a maximum power at a methanol low concentration such as 1–3 M under active conditions and about 5 M under passive conditions due to the methanol crossover (MCO). Tsujiguchi et al. [47] have proposed a novel electrode structure with a porous carbon plate, PCP, for the DMFC [48–50] and we have demonstrated that the DMFC with PCP can be operated at very high methanol concentrations, even 100%, because the DMFC with PCP efficiently uses a high concentration of methanol with a significantly reduced MCO, and the system does not require any additional devices such as pumps and sensors.

3.3. *Heat and mass transfer*

Transport processes are involved when a current is passed through a fuel cell. Ions and neutral species that participate in the electrochemical reaction at the anode or cathode have to be transported to the respective electrode surfaces. The charge transfer kinetics-controlled electrode reactions are those in which the rates of mass transfer processes are very rapid in comparison to those of all associated chemical reactions. The Tafel characteristic is representative of an irreversible electrode reaction in which the exchange current density is very small. Another case is the mass-transfer-controlled reactions in which the rates of all associated chemical reactions are very rapid compared to those of the mass transfer processes [51].

A great majority of the research efforts have been focused on developing new electrocatalysis to enhance the methanol oxidation and new electrolyte materials to minimize methanol crossover through the membrane. Methanol crossover is one of the most important problems to overcome in DMFCs because it causes depolarization losses at the cathode and conversion losses in terms of lost fuel, leading to poor performance. The present state-of-the-art optimized operating conditions are elevated cell temperatures to improve the anode reaction, high air stoichiometries to prevent cathode flooding, and dilute methanol solutions to mitigate methanol crossover. These very dilute fuel solutions require the presence of a high amount of water, leading to a reduction in the energy density of the system. More concentrated methanol solutions would be preferable in order to achieve energy densities needed for portable power applications. However, the possibility of using highly concentrated methanol solutions at the anode is limited by the significant water loss from the anode to the cathode that occurs in the DMFC due to electro-osmotic drag and molecular diffusion through the membrane. Hence, besides minimizing methanol crossover, water crossover must also be mitigated in portable DMFCs.

Heinzel and Barragán [52] have presented a comprehensive review of the state-of-the-art studies of mass transport of different species, including the reactants (methanol, oxygen and water) and the products (water and carbon dioxide) in DMFCs. The overview of the mass transport of the reactants (methanol, oxygen and water) and the products (water and carbon dioxide) revealed that the designs of MEAs and flow fields as well as operating conditions affect the cell performance and operating stability by affecting the mass transport of each species.

Another key issue in the portable DMFC system is thermal management, so several attempts have been made to develop thermal models for fuel cell systems. Argyropoulos et al. [53] have designed a thermal energy model for the direct methanol fuel cell (DMFC) based on the differential thermal energy conservation equation. The model is used to predict the thermal behavior of a DMFC stack [54] comprised of many large cells in a bipolar arrangement. The model allows an assessment of the effect of various operating parameters: feed and oxidant inlet temperatures, flow rate and pressure, operating current density, and the system design active area.

Chen and Zhao [55] have developed a one-dimensional model by considering the inherently coupled heat and mass transport along with the electrochemical reactions that occur in passive DMFCs. They obtained the analytical solutions to predict the performance of this type of fuel cell operating with different methanol concentrations and showed that the performance of passive DMFCs increases with methanol concentration. The model then revealed that the improved performance with higher methanol concentrations is primarily due to the increased operating temperature resulting from the exothermic reaction between the permeated methanol and the oxygen on the cathode.

3.4. *Hydrodynamic study*

Krewer et al. [56] investigated the hydrodynamic behavior of different anode flow-field designs of liquid-fed direct methanol fuel cells (DMFCs), as shown in Fig. 7. Experiments, as well as CFD simulations, of the transient concentration distribution and of the residence time behavior were analyzed. Investigations at different flow rates showed a negligible change of the flow pattern within a certain flow rate interval. Based on these results, reduced models consisting of ideal reactor networks were developed. Delavar et al. [57] study Lattice Boltzmann Method (LBM) as an alternative of conventional computational fluid dynamics method. In flow pattern simulation, flow velocity in cathode channel is very higher than anode channel. This has been made several problems in convergence at two-channel interface.

4. Process engineering of the direct methanol fuel cell

The DMFC is a multiphase system involving simultaneous mass, charge and energy transfer. Because several simultaneous processes occur in a DMFC, the development of a mathematical model is critical to the design and optimization of this type of cell. While novel materials are being developed to solve the problems referred to above, there is an urgent need for understanding and predicting the main heat, mass and electrochemical processes.

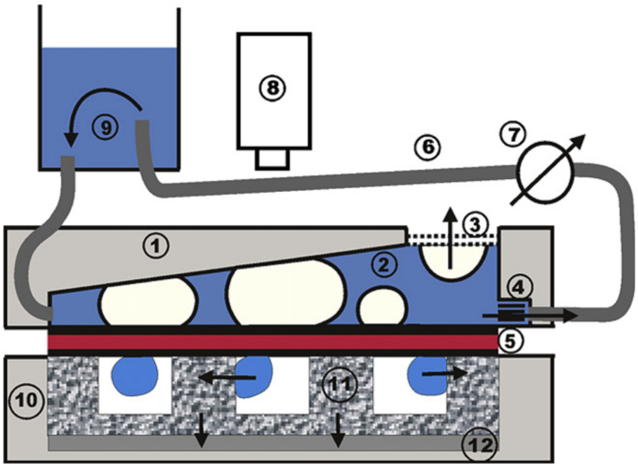

Fig. 6 – Schematic of the passive DMFC. (1) Transparent anode flow field; (2) tapered channel; (3) hydrophobic membrane; (4) bubble fence; (5) PTL and MEA; (6) tubing; (7) flow sensor; (8) camera; (9) reservoir; (10) cathode mount; (11) cathode flow field; (12) non-woven material for capillary water transport [46].

4.1. *Model development*

The methanol concentration in the anode flow channel is defined as the feed concentration. The feed concentration

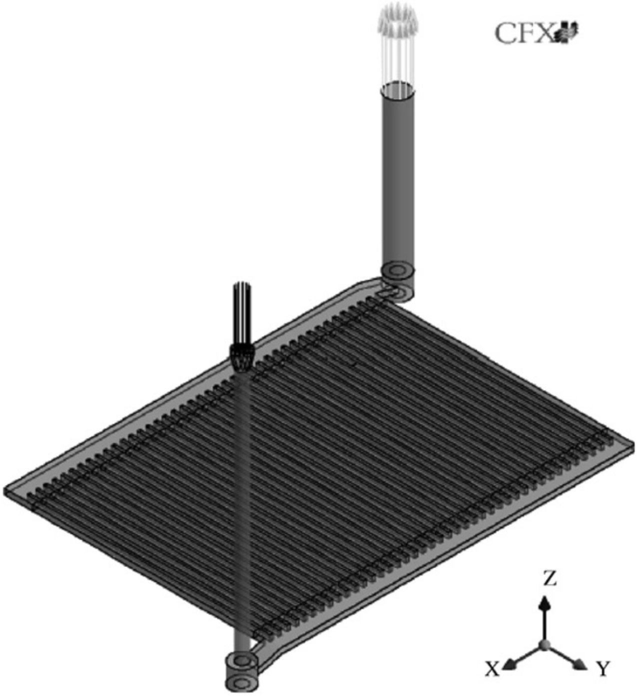

Fig. 7 – Simulation domain for the parallel channel design [56].

decreases as the methanol solution flows downstream. As the variation in the methanol concentration is small under general operating conditions, one can consider the feed concentration to be constant. Carbon dioxide is generated in the anode electrode from the electrochemical reaction. Gas bubbles are then formed (because of the moderate solubility of carbon dioxide in a methanol solution) and released into the flow channel [58]. The released bubbles stir the flowing methanol solution, which complicates the methanol transport in the flow channel.

4.1.1. *1D model*

Methanol transport in a DMFC occurs by both diffusion and convection. Fig. 8 shows a schematic diagram of an unsteady-state model developed by Basri et al. [59] for a liquid-feed direct methanol fuel cell (DMFC) delivery as a two-phase system. The model considered the mass and heat transport in the feed delivery system attached to the anode and cathode of the fuel cell. Kulikovsky [60] analyzed 1D + 1D model of DMFC which takes into account gaseous bubbles in the anode channel. Asymptotic solution to model equations for the case of small rate of bubbles formation is derived. The formula for the change in cell mean current density due to bubbles formation is obtained. The formula for the change in the mean current density of the cell due to bubbles is obtained and the effect of bubbles on the limiting current density is rationalized. Physically, the bubbles (i) decrease time-average methanol concentration in the anode channel, which reduces cell performance and (ii) decrease methanol crossover, which improves it.

Numerous modeling works have determined the major limitations of direct methanol fuel cells: methanol and water crossover [61], water [62] and heat [4,55] management and the kinetics of the reaction [63]. Oliveira et al. [64] have done a comparative study of approaches to direct methanol fuel cell modeling. Analytical, semi-empirical and mechanistic models for direct methanol fuel cells (DMFC) are reviewed. Effective models were, until now, developed describing the fundamental electrochemical and transport phenomena taking place in the cell. More research is required to develop models that can account for the electrochemical processes and catalyst poisoning [65] occurring at the anode and cathode of the DMFC and the water and methanol fluxes in the membrane.

In regards to the problem of methanol crossover, different groups have carried out a lot of researches [66,67]. The additional catalyst layer coupled with the cathode formed an assistant cell that could use the crossover methanol to generate electric power [9]. This complex MEA system can provide a novel way to reduce the methanol crossover and the consequent mixed potential at the cathode and favorable information for improving DMFC performance. Recently, [68] Colpan et al. evaluated the performance characteristics of a flowing electrolyte-direct methanol fuel cell (FE-DMFC) and a direct methanol fuel cell (DMFC) are by computer simulations.

4.1.2. *2D model*

In a study by Xiao et al. [69], a 2D, non-isothermal, transient model-based on the multi-fluid approach was developed to capture the advantage of a non-isothermal model over an isothermal one for a passive DMFC system. They used a semi-passive DMFC channel at the cathode side to facilitate the oxidant transport. Even though the cell temperature increases during the operation, the temperature distribution is almost uniform throughout all of the porous layers including the fuel delivery system and fuel cell.

Numerical simulations were carried out [70] to explore the transient and polarization characteristics of the DMFC, including methanol crossover through the membrane, temperature evolution, and anodic and cathodic overpotentials. Conservation equations of mass, momentum, species transport, and the potential with electrochemical reaction were numerically solved in a coupled manner.

Yang and Zhao [71] presented the model developments in different regions and validated the model with experimental data. They also reported the numerical results obtained with the model in order to investigate the effects of some key DMFC parameters on cell performance. As shown in the schematic illustrated in Fig. 9, the two-phase mass transport in the anode and cathode porous regions is formulated based on the classical multiphase flow in porous media with neither the

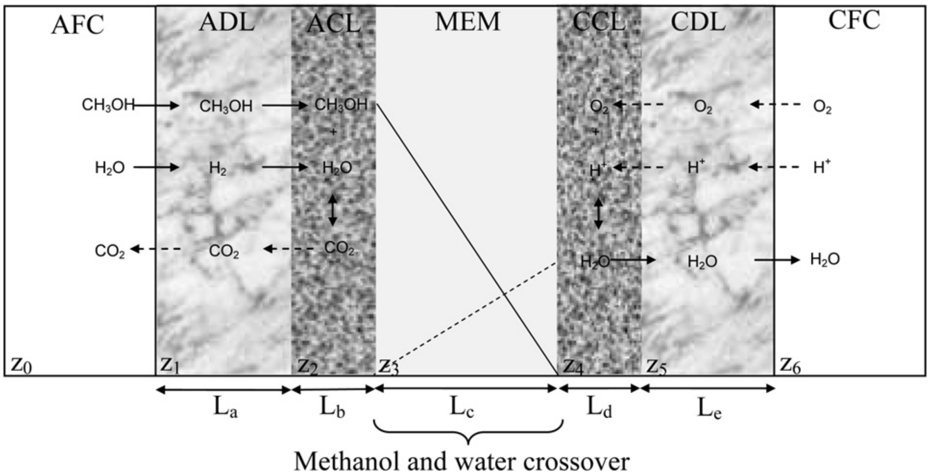

Fig. 8 – Schematic diagram of a passive liquid-feed DMFC [59].

assumption of constant gas pressure in the unsaturated flow theory nor the definition of mixture pressure of gas and liquid in the mixture multiphase flow model.

Xu and Fagri [62] developed a two-dimensional, two-phase, non-isothermal model to investigate the water transport characteristics in a passive liquid-feed direct methanol fuel cell. The liquid-gas two-phase mass transport in the porous anode and cathode was formulated based on a multi-fluid model in porous media, and water and methanol crossover through the membrane were considered with the effect of diffusion, electro-osmotic drag, and convection. Equation (1) shows the governing equation for the dissolved water concentration in the membrane. Here, it shown that the water crossover in DMFCs can be dominated by each of the three mechanisms depending on the operating conditions and cell structure, and no mechanism should be omitted in the model.

$$\nabla\cdot N_{H_2Ocr} = \nabla\cdot(-D_{we}(\lambda)\nabla C_{we}) + \nabla\cdot\left(n_{d,H_2O}\frac{1}{F}\right) = 0 \tag{1}$$

This analytical model is a valuable tool for understanding the effect of basic parameters on fuel cell performance. In 2004, a two-dimensional (2D) full cell model of the direct methanol fuel cell was developed by Guo and Ma [72] to describe not only the electrochemical reactions on the anode and cathode electrodes, but also the elaborate transport phenomena in fuel cells. Fig. 10 shows the 2D distribution of the methanol concentration in the membrane electrode assembly of a self-made DMFC with a 50 cm^2 active area.

4.1.3. 3D model

A three-dimensional, two-phase, multi-component model has been developed for a liquid-feed DMFC by Ge and Liu [73], as shown in Fig. 11. Furthermore, the model presented by Sivertsen and Djilali [74] is a full three-dimensional model that resolves coupled transport processes in the membrane, catalyst layer, gas diffusion electrodes and reactant flow channels of a PEM fuel cell. The model was implemented via a set of user-defined subroutines in a commercial CFD code, Fluent 6.1. The implementation allows simulations using parallel processing.

In addition, a three-dimensional model for the free-breathing direct methanol fuel cell (DMFC), as shown in Fig. 12, has been developed by Saarinen et al. [75] by assuming steady-state isothermal and single-phase conditions. It describes mass transfer phenomena and current production in a free-breathing DMFC when different operating parameters such as cell temperature, methanol concentration and reactant flow rates are varied on a large-scale. The detail of the model also describes with reasonable accuracy the existence of the measured electrolytic domains, such as regions of negative current densities. The molar flux of oxygen and water vapor in the cathode flow field is shown in equations (2) and (3) based on Stefan–Maxwell equation. Fig. 13 shows flow-field design for this paper.

$$N_{O_2} = -c\frac{D_{O_2,H_2O}D_{N_2,O_2}}{D_{N_2,O_2}X_{H_2O} + D_{N_2,H_2O}X_{O_2} + D_{O_2,H_2O}X_{N_2}} \times \left(\frac{D_{N_2,H_2O}X_{O_2}}{D_{O_2,H_2O}X_{N_2}}(\nabla X_{H_2O} + \nabla X_{O_2}) + \nabla X_{O_2}\right) \tag{2}$$

$$N_{H_2O} = -c\frac{D_{O_2,H_2O}D_{N_2,H_2O}}{D_{N_2,O_2}X_{H_2O} + D_{N_2,H_2O}X_{O_2} + D_{O_2,H_2O}X_{N_2}} \times \left(\frac{D_{N_2,H_2O}X_{H_2O}}{D_{O_2,H_2O}X_{N_2}}(\nabla X_{H_2O} + \nabla X_{O_2}) + \nabla X_{H_2O}\right) \tag{3}$$

Proper water management in direct methanol fuel cells is critical and complicated because of the many interacting physicochemical phenomena. This was the motivation for Liu and Wang [76] to numerically investigate a 3D two-phase model that employs an interfacial liquid coverage model at the interface between the cathode backing layer and flow

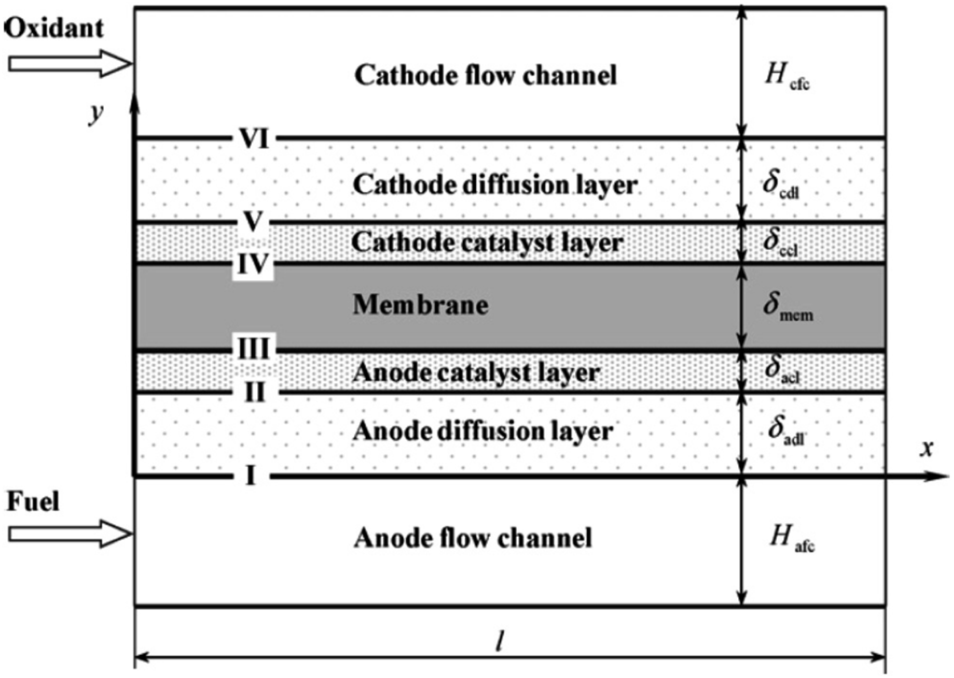

Fig. 9 – Schematic of a liquid-feed DMFC and the coordinate system [71].

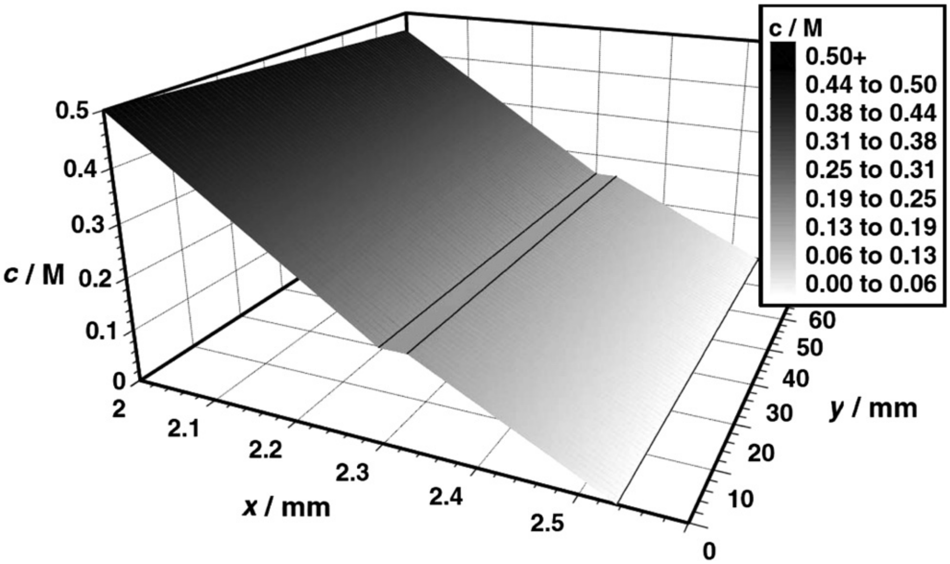

Fig. 10 – 2D distribution of the methanol concentration in the membrane electrode assembly of a self-made DMFC with 50 cm^2 active area [72].

channel. Additionally, the effects on the net water transport coefficient distribution in a DMFC are explored under typical operating conditions for portable applications.

4.1.4. *Quantum theory*

Nanotechnology has recently been important to the worldwide application of direct methanol fuel cells as a one of the most suitable and promising options for portable devices. Therefore, computational approaches for theoretical modeling of nanomaterials such as carbon nanotubes (CNT) through molecular dynamic techniques significantly aid these investigations [23]. Density Functional Theory (DFT), a computational method based on this type of approach, is called an ab initio or first-principles method.

Gokhale et al. [77] conducted microkinetic analysis in conjunction with DFT calculations to form a powerful combination of methodologies to allow quantitative information to be derived about catalytic reactions at the molecular level. Because CO poisoning is acute on platinum surfaces, to aid the design of more CO tolerant anode catalysts, a deeper understanding of the surface chemistry on platinum CO on platinum is required.

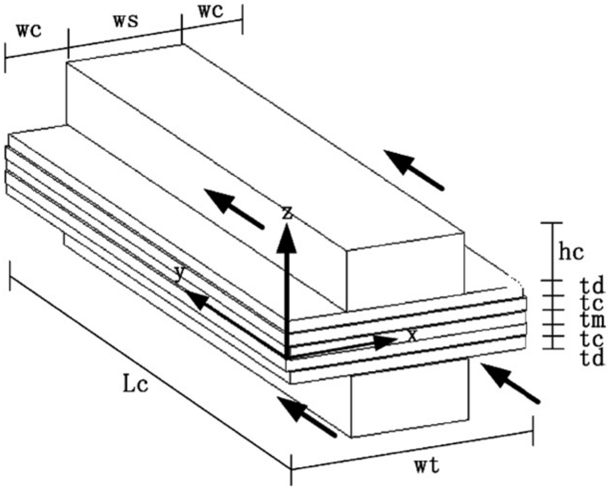

Fig. 11 – The schematic of the modeling domain [73].

First principles analysis investigate by Janik et al. [78] with approach termed the double reference method that can be used to simulate chemistry at an electrified interface. The simulations mimic the half-cell analysis that is used to evaluate electrochemical systems experimentally where the potential is set via an external potentiostat. In addition, by using linear scaling relations between the adsorption free energies of various intermediates in the reaction network, adsorption energies can be estimated by knowing only two key descriptors for each metal surface: the free energies of OH and CO on the surface [79]. Two mechanisms for methanol oxidation to CO$_2$ are investigated: an indirect mechanism that goes through a CO intermediate and a direct mechanism where methanol is oxidized to CO$_2$ without the formation of a CO intermediate.

4.2. *Challenges in DMFC modeling*

Methanol and water crossover plays a key role in the DMFC mechanism. These phenomena have to be accounted for correctly in mathematical models of the DMFC. Many researchers have tried to develop a novel MEA for the DMFC to fix the problem. Unfortunately, the typical membrane materials, which are sulfonated fluoropolymers (called NAFION™ by DuPont), have some parameters that make a realistic model description using classical mass transport models (Fick diffusion, Nernst–Planck and Maxwell–Stefan models [55,59,80,81]) difficult. The reason for this is that the classical models are based on some major simplifications such as the fact that body forces (like e.g., electrostatic forces, which are

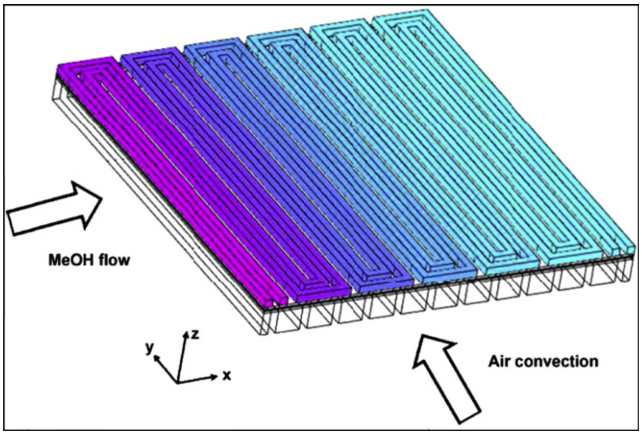

Fig. 12 – The modeled geometry and the main flow directions of reactants [75].

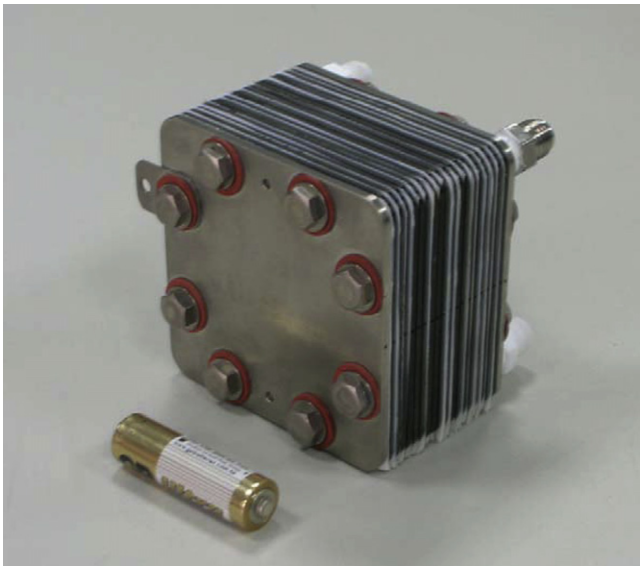

Fig. 13 – An experimental 18-cell bipolar plate stack [96].

important in electrochemical systems) are not taken into account, and that convective flow has to be considered separately [82]. Also, as described by Ko et al. [83], the parameters of those models (Fick's diffusivities, etc.) often show a strong dependence on operating conditions and are often not predictable.

Therefore, for the DMFC with its additional component methanol in liquid state, an alternative approach is necessary to obtain a realistic model for mass transport inside the materials. Generally, the typical PEM material shows significant swelling when in contact with water and even more so when in contact with methanol. The material is proton conductive only when it has taken up some amount of water, which is a necessary property in a DMFC. In this swollen state, the material is highly anisotropic, with regions where only the polymer backbone material can be found and a pore system filled with water (all mass transport driving forces known for flows through microporous systems can be found

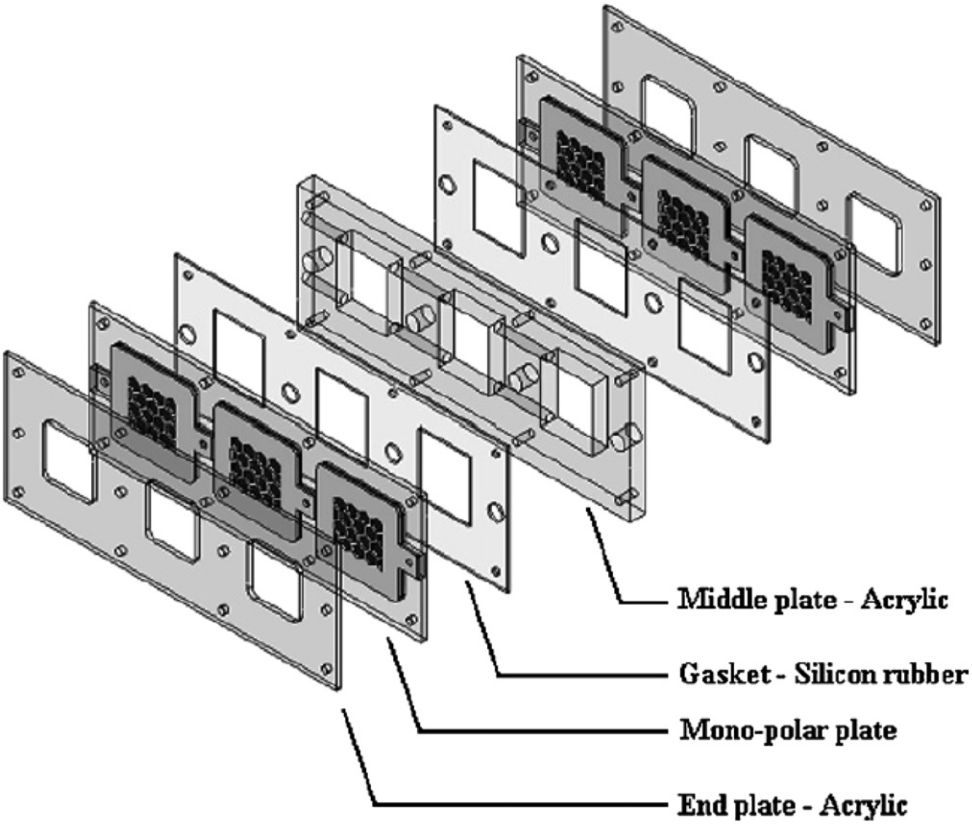

Fig. 14 – Schematic of the passive DMFC stack [97].

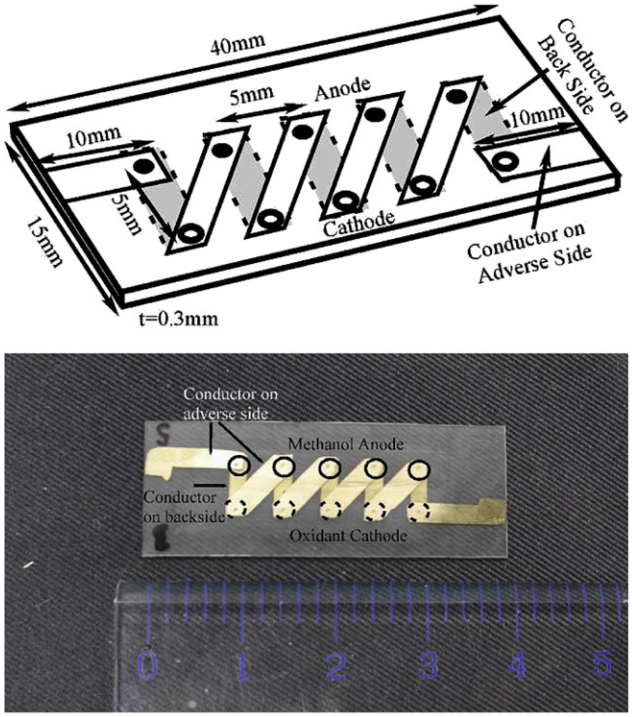

Fig. 15 – Schematic and photograph of the fabricated micro-DMFCs array [98].

simultaneously: diffusion driven by activity gradients, migration of protons in the electric field, pressure-driven convective flow, and finally electro-osmotic flow of uncharged species due to forces exerted on them by the migrating protons).

Thus, it is necessary to analyze all of these transport mechanisms simultaneously [84]. This is achieved in the following by applying the generalized Maxwell–Stefan mass transport equations. As mentioned previously, the membrane material can be seen as a porous material with solid walls, but unfortunately this system is flexible, i.e., it swells depending on the local water and methanol content in the pore fluid [3]. Moreover, the pore diameters are only one order of magnitude larger than the sizes of water and methanol molecules. Therefore, the activities of the pore fluid components cannot be calculated from free-liquid-phase models like UNIFAC. To calculate activities within polymer-solvent mixtures, the Flory–Huggins approach is widely used; this model will be discussed and applied further on.

In particular, understanding thermal effects, which are inseparable from the management of water in the cell, is necessary to optimize the performance of these fuel cells. A number of studies have reported simulating PEM fuel cells [85] and DMFCs [59], but most of them were isothermal models, except for a few papers that took into account thermal effects [55].

The anode and cathode electrochemical reactions, diffusion and convection of both gas and liquid phases in the backing layers and flow channels [86], the mixed potential effect due to methanol crossover, and the effect of methanol feed concentration were explored. Shaffer and Wang [87] discovered the role of hydrophobic anode MPL in controlling water crossover in DMFCs. A one-dimensional two-phase transport model was developed to account for capillary-induced liquid flow in porous media to explain how a hydrophobic anode MPL controls the water crossover from anode to cathode. Further studies show that a lower water crossover can lead to a lower methanol crossover via dilution of methanol in the anode catalyst layer. Xu and Faghri [62] found that the use of a hydrophobic air filter layer at the cathode can achieve a negative water crossover from the cathode to the anode, although the cell performance is degraded to some extent as a result of the significantly increased water accumulation in the cathode.

4.3. *Optimization*

Fuel cell design is a multi-objective, multi-variable problem. In order to design fuel cells by computational design, a mathematical formulation of the design problem needs to be developed. The problem can then be solved using numerical optimization algorithms and a computational fuel cell model. Apparently, very few design and optimization models have been developed for DMFCs. Cong Xu et al. [88] examined the DMFC model from Sundmacher et al. [89] and then performed a dynamic optimization to provide a constant feeding strategy and achieved the highest power density at given operating condition conditions specified by a given current density. They identified the optimal feed concentration, which provides the highest power density output for a given current density.

A non-isothermal dynamic optimization model of direct methanol fuel cells (DMFCs) was developed by Ko et al. [90] to predict their performance with an effective optimum-operating strategy. After investigating the sensitivities of the transient behavior (the outlet temperature, crossovers of methanol and water, and cell voltage) to operating conditions (the inlet flow rates into anode and cathode compartments, and feed concentration) through dynamic simulations, they found that the anode feed concentration has a significantly larger impact on methanol crossover, temperature, and cell voltage than the anode and cathode flow rates.

In advance, Basri et al. [91,92] develop optimization based on the single and stacking DMFC. Moreover, this method is different from others with respect to the cost minimization as guide for power generation.

Due to the increasingly competitive and global market demand for the DMFC, there is a need for a standard procedure for the system design of optimum DMFCs. From this perspective, it would be necessary to develop tools dedicated to the first design steps in order to propose a rapid preliminary solution with a high quality product. A toolset of this sort has been developed by Basri et al. [93].

The review by Secanell et al. [94] discusses the strengths, limitations, advantages, and disadvantages of optimization formulations and numerical optimization algorithms, and insight obtained from previous studies. The potential of novel fuel cells can only be gathered by developing designs and operating conditions that maximizing the power output of the fuel cells while minimizing their weaknesses e.g., cost and overpotential. In light of the recent progress made in new materials for fuel cells, the necessity for design methodologies

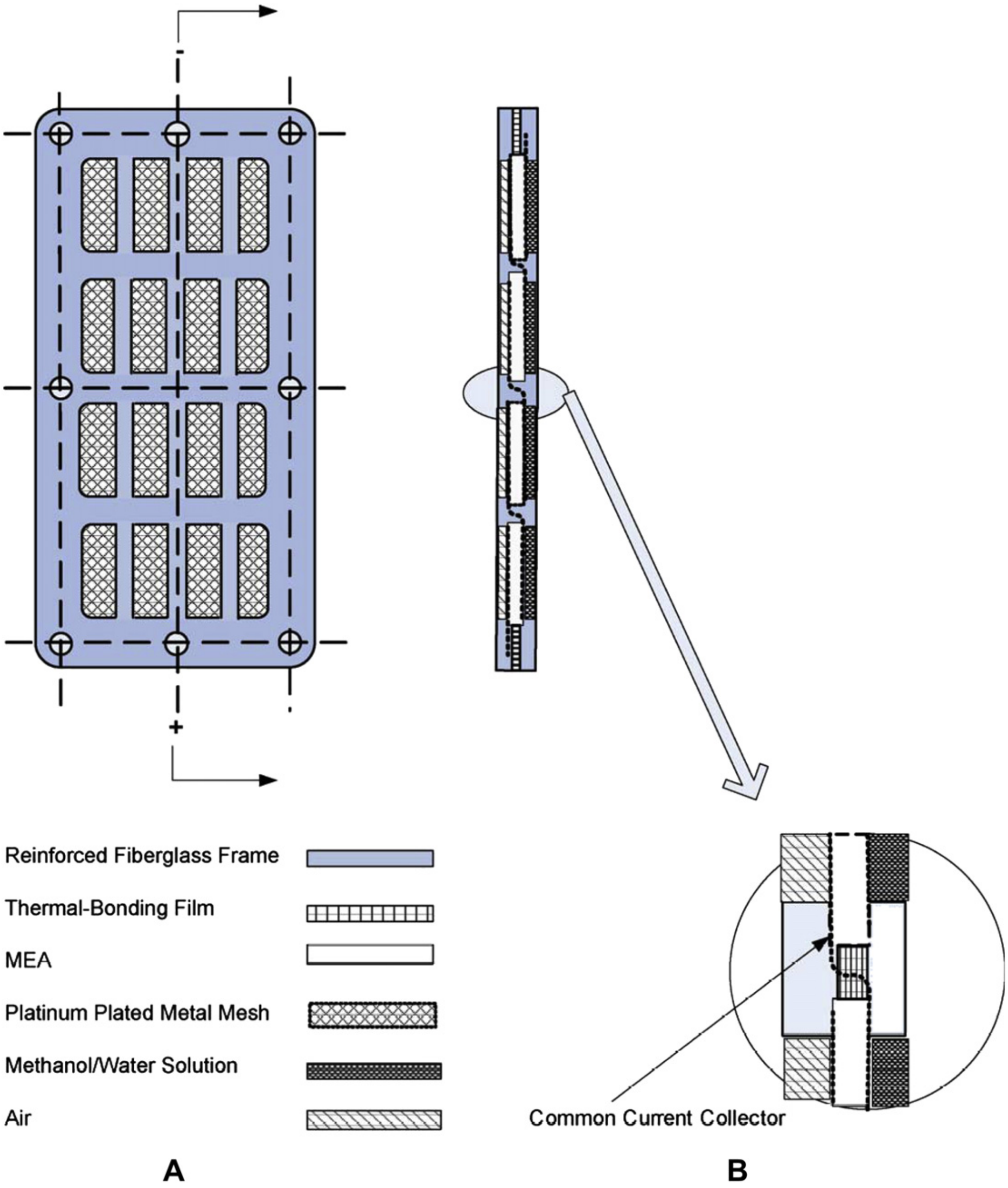

Fig. 16 – A four-cell stack with the window-type fixture frame structure suitable for air-breathing and fuel diffusion. (A) Four-cell stack; (B) an enlarged view of interconnections between adjacent cells by using a common current collector [99].

that are fast and reliable is tremendous. If a novel material is introduced in a current cell design, it might only perform slightly better or even worse simply because the design was optimized to achieve the best performance for the current materials.

4.4. *System and design advisor tool development for the DMFC*

Traditionally the development and study of the direct methanol fuel cell has been done experimentally. However, the experimental work has turned out to be rather slow and difficult and it has not been able to give full understanding to the transport mechanisms in each layer of the DMFC. The increasing computational resources and development of molecular dynamics (MD) software have opened a new way to study polymer electrolytes by atomistic molecular modeling. In addition to the studies of material transport in polymers, MD studies of gas diffusion in pure water have also been published. However, we have not found any modeling studies in the literature concerning gas transport in polymer electrolyte systems or even in neutral polymer systems containing a substantial amount of water. Because conducting polyelectrolytes typically contain 20–40 wt% of water, it is important to understand the influence of large amounts of water and ionic co-penetrants to the diffusional behavior of the gases in polymers. This knowledge will allow for the control of the gas transport properties of polymer electrolytes. The aim of this work is to use MD to study the transport

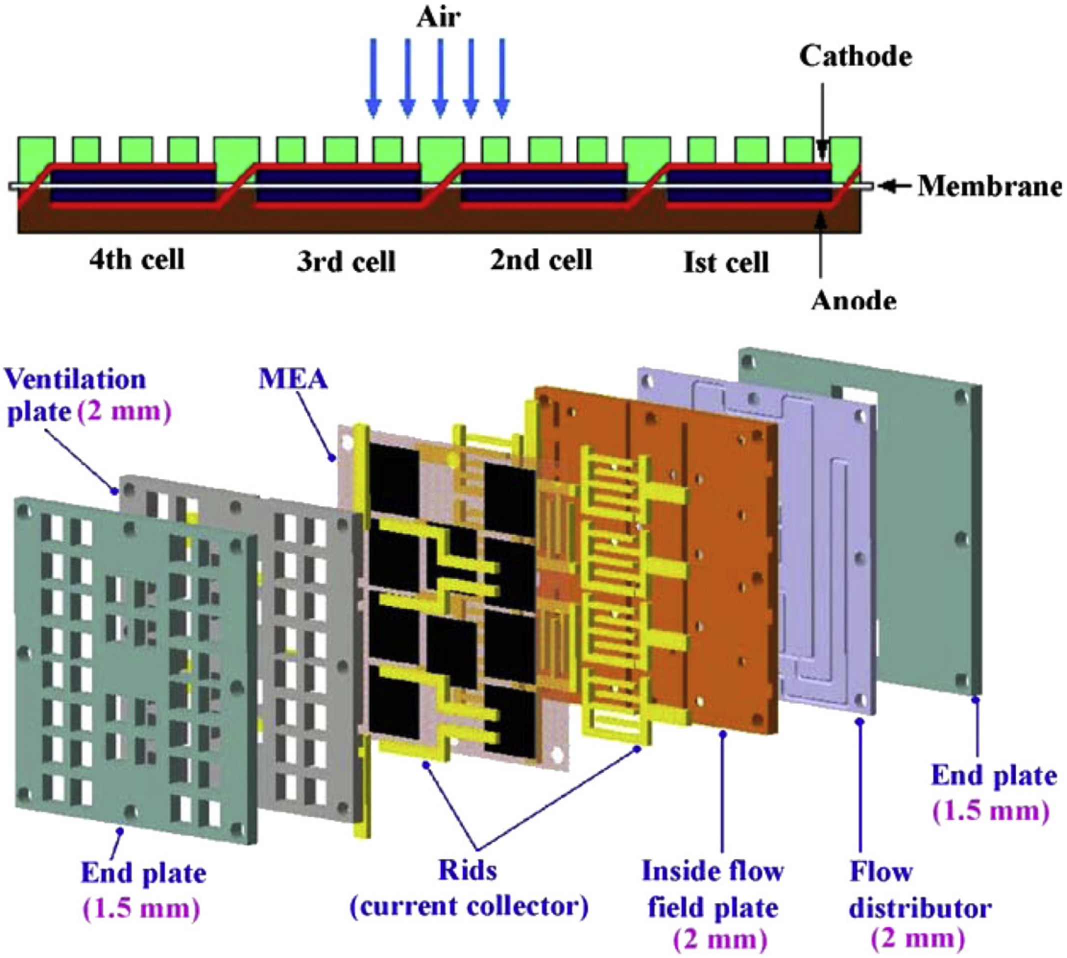

Fig. 17 – Schematic drawing for planar arrangement [100].

properties of several gases in polymer electrolytes containing 0, 35 or 90 wt% of water and small cations. The diffusion coefficients are calculated and the movements of the gas molecules are explored. MD as an atomistic modeling method gives a unique opportunity to study any individual molecules in the system. The possibility to study separate penetrants is used previously in many papers and also in this work.

Zenith and Krewer [95] has dynamically modeled a DMFC system in which each ancillary unit performs only one task. This simplified version is termed a reference system. The objective is to synthesize a dynamic model of a DMFC system, propose control strategies for it, and investigate under which conditions the system can be considered autonomous.

5. Stacking technology

From an operational point of view, passive air-breathing DMFCs can be designed to operate at ambient temperature without a fuel pump or other ancillary devices. The fuel supply relies on the diffusion from an accessible fuel reservoir, while the oxidant is supplied from the ambient air. This arrangement results in the elimination of parasitic power loss from ancillary devices, much simpler structures, and more compact system designs than active DMFCs. These features can potentially result in higher reliability, lower cost, higher fuel utilization, and higher energy density, which are favorable attributes for power sources in future electronic devices. Significant work has been reported on passive air-breathing DMFCs by organizations across the world on important issues, such as fuel concentration, membrane thickness, membrane electrode assembly (MEA) and fabrication. However, this work has mostly been based on single cell architectures. In practice, fuel cell power systems require a scale-up with stack of multiple cells connected in series to achieve a useful output voltage.

The main important operating parameters in scale-up are the air flow rate, the methanol concentration and the stack temperature. Insulation of the methanol–water tank and piping reduces the heat losses and improves the start-up behavior by increasing the temperature [38]. In the passive air-breathing operating mode, a DMFC stack can hardly utilize a conventional “bipolar plate” structure [96]. A special stack structure is required for passive diffusion of the liquid fuel and to provide access to ambient air, as shown in Fig. 14 [97].

Ito et al. [98] propose a novel design and fabrication technique for a micro direct methanol fuel cell. Ten μ-DMFCs were fabricated on a polymeric flexible substrate containing a micro-hole array, as shown in Fig. 15. Fig. 16 shows the planar air-breathing DMFC with the window-type fixture frame structure that was developed by Guo and Faghri [99]. This design provides a large open area for more efficient mass transfer.

Chen et al. [100] have designed a planar stacking PEMFC, as shown in Fig. 17, to power a handphone directly without converters/inverters. A 10-cell air-breathing miniature PEMFC is then used to demonstrate an advantage of the array stack design. The main material of the flow-field plates is acrylonitrile–butadiene–styrene (ABS), which allows the fuel cell be mass-manufactured by plastic injection molding technology for fast commercial design and low-cost manufacturing.

In fuel cells, model for a single element cannot describe large-scale effects in a stack. For example, large temperature non-uniformity spanning several elements is beyond the scope in [101] model. To rationalize the large-scale 3D effects, a promising approach is a hybrid of analytical and CFD calculations. Scott et al. [102] has been designed and built a prototype direct methanol fuel cell (DMFC) stack based on a flow bed design developed with the aid of a flow visualization study and fluid flow modeling. A number of limitations existed in the models; for instance the thermal model was based on a different flow bed design, of 57 parallel channels, to that used here, and the flow bed temperature profiles for the other models were based on a linear formulation between the inlet and the outlet port.

Simoglau et al. [103] using empirical state space models such as canonical variates analysis (CVA) models for the scale-up and scale-down of direct methanol fuel cells. The feasibility of using a dynamic state space canonical variates analysis (CVA) model of the small-scale single cell to predict the voltage responses of the scaled up three-cell stack system. In addition the feasibility of using the three-cell system model to predict the dynamic behavior of the small system is also studied (scale-down). The results achieved are encouraging and indicate the potential of using a CVA state space representations as an aid to cell scale-up and scale-down.

6. Conclusions

In this review, the process system engineering of the direct methanol fuel cell has been illustrated from the DMFC construction and modeling perspective. Overall, DMFC systems have unique PSE issues to investigate. Mature DMFCs have been penetrating into all fields of chemical engineering and also into commercially available technologies. MSO technologies for DMFCs have become a commodity; they are not a distinguishing feature of the PSE field any more. Consequently, PSE has to reassess and to reposition its future research agenda. Emphasis should be placed on model-based applications in all PSE of DMFC domains including product and process design, control and operations. Due to the limitation of DMFC fabrication, as described in Section 4.2, a strong effort as describe in Sections 4.3 and 4.4 is needed to establish the DMFC until it can be commercialized.

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