Available online at www.sciencedirect.com

International Journal of Heat and Mass Transfer 48 (2005) 3891–3920

International Journal of HEAT and MASS TRANSFER

www.elsevier.com/locate/ijhmt

Review

Challenges and opportunities of thermal management issues related to fuel cell technology and modeling

Amir Faghri *, Zhen Guo

Department of Mechanical Engineering, School of Engineering, University of Connecticut, Storrs, CT 06269-2237, United States

Received 20 February 2005; received in revised form 16 April 2005

Abstract

Development and application of fuel cell technology will be increased significantly through analysis and improvement of the heat transfer in the fuel cell stack and auxiliary components and by implementation of innovative heat transfer schemes that address those issues. A detailed review of these problems related to fuel cell technology, including recently developing challenges, is presented. Current technical limitations can be overcome through a combination of novel methodologies, increased efficiency of components, decreased component size and mass, and detailed modeling. This paper also outlines the existing fuel cell technologies and developers, fuel cell models, and unresolved issues in fuel cell modeling.

Contents

---

* Corresponding author. Tel.: +1 860 486 2221; fax: +1 860 486 0318.
E-mail address: faghri@engr.uconn.edu (A. Faghri).

0017-9310/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ijheatmasstransfer.2005.04.014

1. Introduction

A fuel cell is an electrochemical energy device that converts the chemical energy in the fuel directly into electrical energy. Unlike conventional power devices, i.e., steam turbines, gas turbines and internal combustion engines, which are based on certain thermal cycles, the maximum efficiency of fuel cells is not limited by the Carnot cycle principle. Fig. 1 is a schematic of a general fuel cell. A fuel cell generally functions as follows: electrons are released from the oxidation of fuel at the anode, protons (or ions) pass through a layer of electrolyte, and the electrons are required for reduction of an oxidant at the cathode. The desired output is the largest flow of electrons possible over the highest electric potential. Although other oxidants such as the halogens have been used where high efficiency is critical, oxygen is the standard because of its availability in the atmosphere. Fuel cells typically use hydrogen, carbon monoxide or hydrocarbon fuels (i.e., methane, methanol). The hydrogen and carbon monoxide fuels may be the products of catalytically processed hydrocarbons. Hydrogen from processed ammonia is also used as fuel.

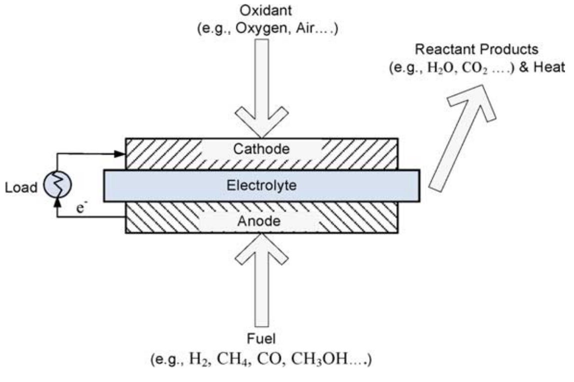

Fig. 1. General fuel cell.

Table 1 provides a summary of fuel cell types. The acronym used to describe the fuel cell type refers to the type of electrolyte or proton (or ion) conductor used, with the exception of direct methanol fuel cells (DMFCs), where the type is identified by the fuel used. Although, the electrolyte used in DMFCs, in most cases, is the same kind of membrane used in a polymer electrolyte membrane fuel cell (PEMFC). PEMFC is commonly referred to the fuel cell that uses hydrogen or hydrogen-rich gas (i.e., production from hydrocarbon reformers) as fuel. The electrolyte is provided in the first column. Selected operating parameters appear in the second column. The fuel listed is the crudest possible. Alkaline fuel cells, for example, require pure hydrogen, whereas the phosphoric acid fuel cell (PAFC) can tolerate hydrogen-rich gas from a hydrocarbon reformer. The reformate typically contains some impurities, such as CO, which can poison some fuel cells. The optimal operating temperature is listed for each fuel cell type. For example, molten carbonate fuel cells (MCFCs) operate at about 650 °C but not much lower, meaning they must be heated to near 650 °C before they will operate. Alkaline fuel cells can operate over a larger temperature range, and generally do not need to be heated before operating. Presently, PEMFCs operate at less than 100 °C, which is limited by the operation temperature range of Nafion®-based polymer electrolyte membrane. High temperature polymer electrolyte membranes capable of operation at 150–200 °C are at their early stage of development [1]. Higher temperature operation has several advantages, which include, at least, reducing the sensitivity of the electrocatalyst to CO in the anode stream and facilitating the issues of thermal management and water recovery. The efficiency listed in the table is the best that can be expected without

Table 1
Summary of fuel cell types

Fuel cell Electrolyte	Fuel oxidant T_{op}, η	Electrochemical reactions	Applications	Advantages	Disadvantages
Alkaline KOH (e.g.)	H_2 Air <100 °C, <70%	Anode: $H_2 + 2(OH)^- \rightarrow 2\,H_2O + 2e^-$ Cathode: $1/2O_2 + H_2O + 2e^- \rightarrow H_2O$ Cell: $H_2 + 1/2O_2 \rightarrow H_2O$	Space	Efficiency is highest of all fuel cells. Low operation capability reduces startup time. Technology has been successfully used in space	CO can poison the fuel cell so reformers are not yet suitable for delivery of H_2. CO_2 in the reactants causes carbonation of the electrolyte
PAFC Phosphoric acid	H_2 or Ref-H_2 Air ~ 190 °C, <45%	Anode: $H_2 \rightarrow 2H^+ + 2e^-$ Cathode: $1/2O_2 + 2H^+ \rightarrow H_2O$ Cell: $H_2 + 1/2O_2 \rightarrow H_2O$	Electric utilities transportation	PAFCs contribute >90% of fuel cell electricity generation currently. Waste heat utilization increases system efficiency	Typically limited to >100 kW applications. Heat required for startup
MCFC Molten carbonate	Many Air ~ 650 °C, <60%	Anode: $H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$ Cathode: $1/2O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$ Cell[a]: $H_2 + 1/2O_2 + CO_2 \rightarrow H_2O + CO_2$	Electric utilities	High quality waste heat suitable for Brayton or Rankine combined cycle to boost system efficiency. Internal reforming allows fuels from H_2 to diesel	High operating temperature leads to greater parasitic losses in small (kW) scale stacks. CO_2 must be added to the air side. Heat required for startup. Special materials required
SOFC Solid oxide (yttria-stabilized zirconia)	Many Air ~ 1000 °C, <60%	Anode: $H_2 + O^{2-} \rightarrow H_2O + 2e^-$ Cathode: $1/2O_2 + 2e^- \rightarrow O^{2-}$ Cell: $H_2 + 1/2O_2 \rightarrow H_2O$	Electric utilities	High quality waste heat suitable for Brayton or Rankine combined cycle to boost system efficiency. Internal reforming allows fuels from H_2 to diesel	High operating temperature leads to greater parasitic losses in small (kW) scale stacks. Heat required for startup. Special materials required
PEMFC Proton exchange membrane	H_2 or Ref-H_2 Air <100 °C, <55%	Anode: $H_2 \rightarrow 2H^+ + 2e^-$ Cathode: $1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$ Cell: $H_2 + 1/2O_2 \rightarrow H_2O$	Transportation Portable power Electric utilities	Low temperature leads to short startup time. Receiving most attention for mW–100 kW applications. Operating temperature is increasing for better waste heat utilization	Water management (Nafion hydration) is a major issue. CO poisoning is a problem with reformate
DMFC Proton exchange membrane	Methanol Air <100 °C, <55%	Anode: $CH_3OH + H_2O \rightarrow CO_2 + 6H^{2+} + 6e^-$ Cathode: $O_2 + 4H^+ + 4e^- \rightarrow H_2O$ Cell: $CH_3OH + O_2 \rightarrow CO_2 + 2H_2O$	Portable power	Same as PEMFC. DMFC has additional advantages such as liquid fuel increasing power density per system volume and convenient refueling	Direct methanol fuel cell is less efficient and has less power density. Liquid methanol crossover reduces efficiency

[a] CO_2 is produced at anode and circulated to cathode.

consideration of recovering waste heat or reformer requirements, just the fuel cell stack.

Fuel cells are versatile energy conversion devices with numerous potential applications: large electrical plants, stationary electricity generation, vehicle propulsion, and portable power. Overall, PEMFCs, DMFCs, SOFCs and MCFCs are the major types of fuel cell technologies that draw the most attention for commercialization. The advantages of fuel cells are both environmental and economic. Most fuel cell systems produce electrical energy at high efficiency that may range from 40% to 60% based on the lower heating value (LHV) of the fuel. The fuel conversion efficiency is higher than that of generators powered by internal combustion engines, such as piston engines and gas turbines. This efficiency advantage becomes more significant at the smaller scales since the efficiency of fuel cells is nearly constant with size. Furthermore, high temperature fuel cells, such as the molten carbonate and the solid oxide fuel cells, can be combined with gas turbines, thereby surpassing the efficiency of large combined power plants, while maintaining much lower levels of emission of NO_x, SO_x, CO_x, etc.

Heat and water are the sole byproducts of the electrochemical reactions in a hydrogen fuel cell vehicle. If hydrogen is produced by reforming hydrocarbons or using electrolyzers powered by fossil based electricity, the superior energy efficiency of fuel cell engines (~2× that of ICE's) helps reduce emissions of carbon dioxide. If hydrogen is produced using renewable sources (solar-thermal, wind, etc.) or nuclear energy, emission can be reduced to zero.

Fuel cells may be used efficiently in portable applications currently powered by batteries, from portable power tools requiring a few hundred watts to cell phones requiring a few watts of power. One of the key advantages of fuel cells over batteries is the separation of the power generation and energy storage components of a system. For a given application, if more power is required, a module having a greater cell area is used. If more energy is required, more fuel storage is provided to the system. One of the major advantages of portable fuel cells over rechargeable batteries is that they can operate for longer periods of time without recharging or interruption. Unlike batteries, these fuel cells can extend operation by instantly refueling with hydrogen or liquid methanol. Furthermore, batteries contain toxic materials and require proper disposal.

As one expects, numerous technical challenges exist in fuel cell technology development. This review article describes the issues and challenges of thermal management related to fuel cell technology for scientists who may not necessarily have a background in fuel cells and who want to contribute to this important field. The paper is organized as follows: Section 2 discusses thermal management of fuel cells from single cell to system level, and the challenges and opportunities associated with thermal management issues of low temperature and high temperature fuel cells; Section 2 provides a detailed description of the development of PEMFC, DMFC and SOFC models including unresolved issues in fuel cell modeling; and Section 3 concludes the paper with summary challenges and opportunities of thermal management issues related to fuel cell technology and modeling.

2. Thermal management

Operating temperature affects the maximum theoretical voltage at which a fuel cell can operate. Higher temperatures correspond to lower theoretical maximum voltages and lower theoretical efficiency. However, higher temperature at the electrodes increases electrochemical activity, which in turn increases efficiency. Operating at a higher temperature also improves the quality of the waste heat. It should be noted that there is a moderate temperature range within which a specific type of fuel cell can operate well and reliably. The main purpose of thermal management in fuel cell systems is to ensure stack operation within the specific temperature range. Optimal thermal management also allows for effective use of the fuel cell system's byproduct, heat, leading to substantial increases in overall system efficiency. For example, a fuel cell operating at 1.0 kW and 50% efficiency generates 1.0 kW of waste heat. This heat may be dissipated by convection, conduction, radiation or phase change. The heat generated in a fuel cell stack may be dumped to the atmosphere, but often it is used in other system components requiring heat. In some cases the heat is used to run a thermodynamic cycle for additional power generation.

A methanol fed fuel cell system is illustrated in Fig. 2 to show how many processes requiring heat and mass transfer are present in a fuel cell [2]. This system consists of a number of support components, including some exothermic devices that produce heat while in use and require cooling and endothermic devices that require heat to be operational. A PEM fuel cell stack used in this system is fed by hydrogen-rich gas from a methanol reformer. The low PEM fuel cell operating temperature (~100 °C) limits the availability of the waste heat from the stack. A novel cooling system was incorporated into the fuel cell system to efficiently recover this low temperature heat as described later. In the methanol tank, the methanol is pumped into a mixing chamber and mixed with liquid water pumped from a water tank at an appropriate ratio. The pressure of the resulting mixture is substantially reduced after flowing through an expansion valve. Subsequently, the mixture enters a heat exchanger or evaporator and is vaporized while absorbing heat from the coolant of the fuel cell stack cooler. This pre-

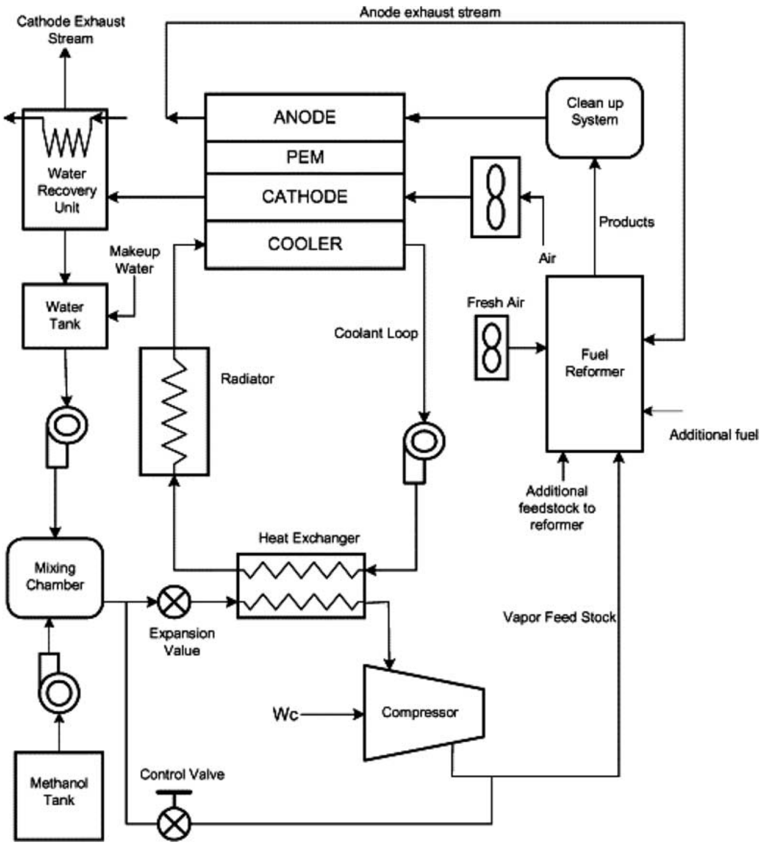

Fig. 2. Schematic of a typical PEM fuel cell power plant incorporating the energy recovery system [51].

heated mixture enters the methanol reformer and reacts to form hydrogen, carbon dioxide and a small amount of carbon monoxide. Additional thermal energy may be needed for the reforming reaction. This heat is usually provided through a burner in the reformer that burns the hydrogen remaining in the anode exhaust stream. The hydrogen-rich gas generally requires cooling and cleanup before it arrives at the stack.

Thermal management issues are closely related to the fuel cell operating temperature. For example, low temperature fuel cells (e.g., PEMFC and DMFC) usually operate below 100 °C, whereas solid oxide fuel cells (SOFC) operate near 1000 °C. Therefore, heat transfer problems could be dramatically different in low temperature fuel cells and SOFCs as illustrated in Sections 2.1 and 2.2, respectively. Particular heat transfer issues could arise from small fuel cells, which are discussed in Section 2.3.

2.1. Low temperature PEM fuel cells

Proton exchange membrane fuel cells (PEMFCs) work at a low temperature, having the advantage of a quick startup. Use of a thin solid electrolyte facilitates the compact PEM fuel cell design. Either hydrogen or methanol can be used as fuel. If hydrogen is used, over-potential occurs mainly at the cathode. In contrast, for fuel cells using methanol, activation over-potential at both electrodes is important. While crossover does occur with hydrogen fueled fuel cells, the problem of fuel crossover is much worse with methanol. Methanol crossover is the process by which methanol diffuses from the anode through the electrolyte to the cathode, where it will react directly with the oxygen, producing no current from the cell. Furthermore, methanol has a poisoning effect on the cathode catalyst that will reduce the performance of the cell. Therefore, the performance of direct methanol fuel cells is limited by the crossover of methanol and catalytic inefficiency [3].

Fig. 3 shows the basic structure of a PEMFC, which can be subdivided into three parts: the membrane electrode assemblies (MEAs), the gas diffusion layers (GDLs) and bipolar plates [4]. The MEA is the key component of PEMFCs. It is composed of a proton exchange membrane sandwiched between two fuel cell electrodes; the anode, where hydrogen is oxidized; and

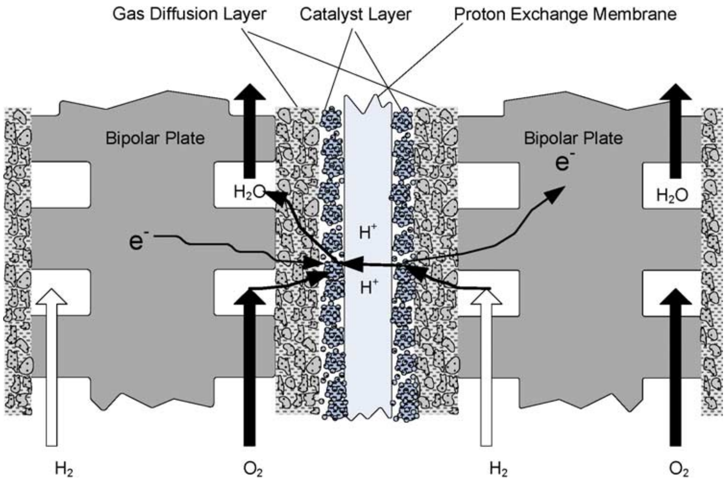

Fig. 3. Basic construction of a typical PEM fuel cell stack.

the cathode, where oxygen from air is reduced. A gas diffusion layer is formed from a porous material, which must have high electric conductivity, high gas permeability, high surface area and good water management characteristics. One side of the bipolar plate is next to the cathode of a cell, while the other side is next to the anode of the neighboring cell. The fuel cell stack consists of repeated interleaved structure of MEAs, GDLs and bipolar plates. All these components are clamped together with significant force to reduce electric contact resistance.

The mass transfer process that occurs within fuel cell channels is multi-component, multi-phase and multi-dimensional flow. For PEMFCs, hydrogen enters the anode flow channel, penetrates through the gas diffusion layer, and then reaches the catalyst layer. Air is forced into the cathode flow channel, penetrates through the gas diffusion layer, and then reaches the catalyst layer. As reactions proceed, water is produced at the cathode catalyst layer and must be removed to avoid flooding. The work of Um and Wang [5] shows that oxygen diffusivity through the air cathode is three to four times lower than the hydrogen diffusivity at the anode. As a result, mass transfer limitation occurs mainly at the cathode unless the cell is properly designed. Mass transport in the DMFC anode is a two-phase counter flow. Methanol needs to penetrate through the gas diffusion layer to the anode, where it reacts with water to produce carbon dioxide. Small bubbles produced by this process must be removed continuously to avoid blocking the access of methanol to the reaction sites.

There must be sufficient water content in the proton exchange membrane: otherwise, the ionic conductivity will decrease. The process of electroosmosis tends to move water from the anode to the cathode. If sufficient water is not present in the anode stream, the membrane will dry out. Another driving force for membrane dry out is the fact that cathode gas removes water from the cathode GDL. While protecting against dry out is important, there must not be so much water that it will flood the electrodes and block the pores in the electrodes or gas diffusion layer. The conductivity of the proton exchange membrane is not generally a problem for liquid-feed methanol fuel cells: the liquid at the anode does a good job of hydrating the membrane.

2.1.1. Heat transfer issues related to PEM fuel cell stacks

A typical hydrogen PEMFC has relatively high power generation efficiency, at approximately 50%. This means the remaining 50% is waste heat. The heat must be discharged efficiently from the fuel cell to protect the proton exchange membrane. Cooling methods are determined greatly by the size of the fuel cell [3]. Some commonly used cooling methods are summarized as follows:

- *Cooling with cathode air flow*. For a small fuel cell, the cathode can work in one of two modes: air-breathing (natural convection) or forced air flow (forced convection). Natural convection is the simplest way to cool the cell and evaporate water at the cathode. This is done with a fairly open structure at the cathode sides, which will increase the volume of the stack. Forced convection airflow is another convenient way to bring the waste heat out of the stack. This will result in a more compact stack structure and increase the cooling capability. However, very high cathode air flow velocity or a very large gas channel is necessary for removal of waste heat. When the power of the fuel cell is higher than a few hundreds watts, a more effective cooling approach must be applied.

- *Cooling with separate air flow*. Although simply increasing reactant air flow can remove more heat, too much reactant air may dry out the proton exchange membrane [3]. In such cases, fuel cells will generally need a separate reactant air supply and cooling system. Fig. 4 illustrates a PEM fuel cell structure with separate cooling plates, through which air is blown. The advantage of this structure is that it can extract more heat from the stack without affecting air flow.
- *Cooling with heat spreaders*. It is obvious that heat can be transferred more efficiently outside the stack. Heat spreaders can be used to transport heat out of the stack through conduction, then to dissipate the heat to surrounding air through natural or forced convection. To add as little extra weight and volume as possible to the stack, high performance heat spreaders must be used.
- *Water cooling*. For hydrogen PEMFCs larger than 10 kW, it is generally necessary to use water cooling. Units below 2 kW can be air cooled, and cells between 2 kW and 10 kW require judicious decision making as to use of water or air cooling [3]. Water cooling requires a more complex design: the temperature and pressure of the cooling water must be monitored and the flow of cooling water must be supplied via an oil-free water pump. Stack cooling in DMFCs is relatively simpler, since increasing circulation of dilute methanol solution at the anode could remove more waste heat from the stack.
- *Cooling with antifreeze/coolant*. The water cooling of PEM fuel cells gives rise to problems associated with water management, such as preventing the product water from freezing, and rapidly melting any frozen water during start-up whenever the fuel cell system is operated in sub-freezing conditions. An antifreeze/coolant is substituted for normal water in the cooling system for these situations [6,7].

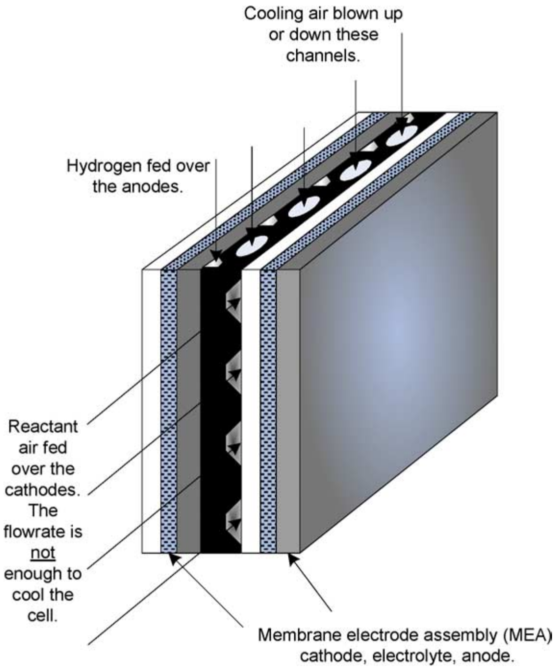

Fig. 4. Diagram showing two MEAs and one bipolar plate modified for separate reactant and cooling air in a PEM fuel cell (redrawing from [3]).

Heat transfer within the fuel cell stack itself leads to the issues of stack performance modeling as well as the integration of thermal management. The literature indicates that, for low temperature PEM fuel cells, higher operating temperatures allow for more efficient waste heat utilization and higher power densities. If this is so, modeling stack performance would focus more on achieving thermal uniformity within the stack. It also may be the basis for including heat spreaders at intervals between adjacent fuel cells, which would reduce the temperature in some regions, while increasing the temperature in others, thereby contributing to thermal uniformity. Reducing thermal gradients allows stack operation closer to the safety or material temperature limit, with the effect of higher quality waste heat as well as possible increased power density.

Fuel cell experiments and modeling have shown a correspondent, or even a dependent relationship between power density and temperature. Fuel cell data from various sources indicate the significance of operating temperature on fuel cell specific power [8–11]. This illustrates the benefit of being able to predict the temperature profile in a fuel cell stack, and it also indicates the benefit of reducing thermal gradients in the stack. While thermal gradient reduction may be achieved through clever routing of reactants through the stack, the addition of heat spreaders in a fuel cell stack to reduce temperature gradients may be a simpler and more effective solution. The key to the viability of a heat spreader is the specific power and specific energy (in the case of waste heat utilization) benefit, which can be determined based on the specifications of a given heat spreader.

2.1.2. Transport phenomena in gas–liquid flow within mini/micro channels

In a PEM fuel cell stack, many cells are electrically connected in series; the reactants are supplied to each cell through common manifolds, and then into an array of multiple channels within the anode and cathode of the bipolar plate. It is evident that flow channels are an essential component for flow distribution in many PEMFC deigns. The flow channels in a PEM fuel cell are typically on the order of a 1 mm hydraulic diameter, which falls into the range of minichannels (with hydraulic diameters from 200 μm to 3 mm). As shown in Fig. 3, one channel wall is porous (gas diffusion layer); mass transfer occurs on this wall along its length. Hydrogen is consumed on the anode side along the main flow dimension in minichannels. Oxygen from air is introduced on the cathode side to form water at catalyst sites at the cathode, which is transported into the minichannels through the gas diffusion layer and then is eventually removed from the cell by the gas flow and gravity if so oriented.

The reactant streams enter minichannels from manifolds in the gas phase. Water produced by oxygen reduction reaction is injected into channels along the main flow dimension. Two-phase flow will likely be developed along the channel depending on the pressure and temperature gradients. For many practical PEMFC design, the volumetric flux of water is very small, usually between two or three orders of magnitude less than that of the gas phase [12]. However, gas–liquid flow transport phenomena within minichannels play the central role in fuel cell water management and stable operation.

Water management is one of most complicated aspects of PEM fuel cell operation. The channels must be designed for low pressure drop to avoid excessive parasitic power losses and must be operated in a flow regime in which the overall water balance in the fuel cell can be maintained. From the standpoint of fuel cell design, the most common flow regimes occurring in minichannels are slug flow and annular flow. In the slug flow regime, a liquid water slug completely blocks an individual flow channel and thus diverts the flow to neighboring channels while maintaining an equal pressure gradient across each channel. The annular flow is preferably in PEMFC operation. Liquid water flows as a film along the channel wall in the annular flow regime. Reactant flow paths are through the central area of the channels and delivery of reactant gases to catalysts sites can be achieved. Furthermore, differences in liquid volume between channels result in small changes in liquid film thickness and flow distribution. The approximate gas velocity range necessary to achieve an annular flow within the fuel cell channels seems to be 5–6 m/s [12]. At this velocity and higher, the accumulation of water in the fuel cell channels can be avoided. In this regime, reactant gas flows are associated with higher current densities. However, operation of fuel cell at low power still can be outside the annular flow regime. The depletion of hydrogen (anode) and air (cathode), and therefore the reduction of gas superficial velocity, possibly causes a change in the two-phase flow regime along the channel from the inlet to outlet.

PEM fuel cell design demands a substantially better understanding within the minichannel, particularly on the flow regimes in small non-circular geometries as well as effects of surface energy on two-phase flow regime.

2.1.3. Heat transfer in auxiliary components

In a practical fuel cell power unit, the fuel cell stack must be accompanied by auxiliary components. Fig. 5 is a flow chart of reactants flowing into, and products flowing out of, a fuel cell stack. Items in parentheses are present depending on the fuel cell type and decision of the designers as to which auxiliary components to include. Ancillary electronics are typically required to convert the electrical power into a more useful form, 12 V for example. In the following sections, a few auxiliary components of particular relevance to heat transfer are discussed. The auxiliary components discussed are summarized in Table 2.

2.1.4. Compact heat exchangers

Heat exchangers as auxiliary devices in fuel cells can be used to perform tasks such as water recycling, preheating, and cooling. In fuel cells where hydration of the electrolyte is necessary, a condenser to reclaim water has been investigated as an ancillary device. As operating temperature increases, driven by the advantage of better current density and waste heat quality, the need for a condenser increases due to the higher tendency of the electrolyte to dry out. The ability to recycle water in a PEMFC or DMFC reduces or eliminates the requirement of a water supply. Fig. 6 shows the possible components to the stream requiring condensation. It was found that existing condenser technology leads to an unacceptable system weight increase, even though at this point water mixed with the methanol fuel is not ideal. The drive for a more compact condenser or heat exchanger may lead to a reduction or elimination of water needed in the fuel stream. For hydrogen-fed fuel cells, there also is a drive for a compact and efficient condenser. Current condensers and radiators require fans, but these draw electricity produced by the system. Increasing heat exchanger performance can lead to a system weight reduction as well as reduction in power needed to run auxiliary components.

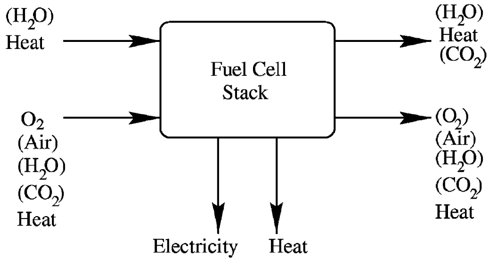

Fig. 5. Flow chart for possible reactants and products in a fuel cell stack.

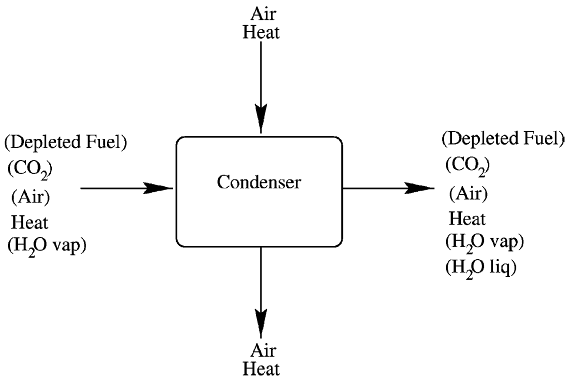

Fig. 6. Flow chart for possible components to flow streams in a fuel cell system condenser.

2.1.5. Heat transfer within the reformer

Development of a fuel cell reformer is driven by the availability and weight of a fuel supply for transportation or a portable fuel cell unit. Currently, the reactant fed into a fuel cell stack is either hydrogen or methanol for types other than solid oxide fuel cells and MCFC, which reform fuel internally. Ball Aerospace, for example, is marketing portable 50 W and 100 W fuel cell systems that appear compact until they are displayed with the requisite bottles containing the compressed hydrogen fuel supply. Hydrogen is more difficult than methanol to store and transport, hydrogen-fed fuel cell stacks have much higher specific power density than DMFCs'. Moore et al. [13] recognizes this, and is currently using metal hydrides to store hydrogen for a PEMFC portable field generator for military use. For logistical reasons, the military would like to be able to feed JP8 or diesel fuel into the fuel cell system. This requires reformation of the fuel. To respond to this demand for liquid fuel fed portable fuel cell systems, researchers at the Pacific Northwest National Laboratory (PNNL), InnovaTek and other organizations are working to develop a reformer designed for the US Army. Fig. 7 is a flow chart of the possible components to the streams entering and exiting a reformer. Although not exclusively relevant to portable fuel cell systems, an additional incentive for reformer development is in the use of ammonia as a hydrogen carrier. Heat transfer issues for reformers lie in the characteristics of the temperature-sensitive catalytic reactions necessary to convert the fuel to hydrogen with as little CO as possible. An alternative to the reformer is the use of an SOFC or MCFC. Although their characteristic high temperatures and corrosive electrolytes bring into question safety and dependability, Delphi Automotive has announced its 1 kW auxiliary power unit incorporating an SOFC to be used in BMW vehicles to supply electrical needs.

2.1.6. Secondary cycle: waste heat utilization

Waste heat utilization in a fuel cell system would require the addition of a Rankine or Brayton cycle. Fig. 8 shows the flow of gases into and out of an auxiliary secondary cycle unit. As fuel cell operating temperature increases, so does the quality of the waste heat. From 100 °C waste heat, cycle efficiency can be expected to

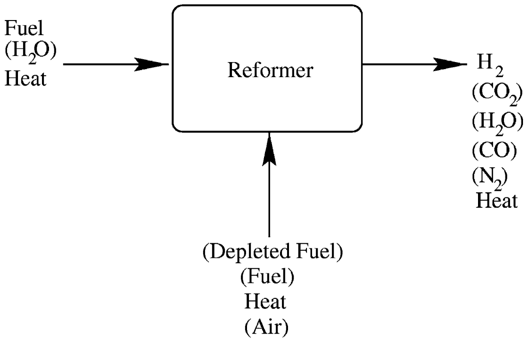

Fig. 7. Flow chart for possible components to flow streams in a fuel cell system reformer.

Table 2
Summary of auxiliary components for a fuel cell system

Ancillary component	Benefits	Challenges	Alternatives
Condenser	Recycle water for electrolyte hydration of reformer steam	Specific volume, mass reduction	Water supply, MCFCs, SOFCs
Pre-heater	Lower thermal gradients in fuel cell stack, waste heat utilization	Specific volume, mass reduction	Internal heating
Radiator	Maintain operating temperature under safety or material limit	Specific volume, mass reduction	Air cooling
Reformer	Allow liquid hydrocarbon fuels for fuel cells other than DMFCs, SOFCs, MCFCs	Specific volume, mass reduction	DMFCs, SOFCs, MCFCs, hydrogen gas storage
Secondary cycle	Waste heat utilization	Specific power increase; specific volume, mass reduction; control and reliability	Thermoelectric, infrared photovoltaics

be ∼20% when heat is rejected to an ambient 30 °C. For a 50% fuel efficient fuel cell stack, this would boost the system efficiency by 20%. Provided the added cycle is of the same characteristic power density by weight and volume as the fuel cell stack, and as robust, its addition would be justified due to the lower fuel consumption or larger system energy density. The possibility of fuel cell stack temperature regulation by control of the added cycle would be an additional benefit, and may reduce the system weight as other stack temperature control components are made redundant. The key to the benefit of the added cycle is the power density evaluation.

2.1.7. Methodology for heat transfer approach

The following is a possible layout for applying heat transfer analysis to the fuel cell stack. The plan takes place in four steps. The first is to determine the benefit of isothermal cell operation. The next is to determine a heat transfer scheme aimed at achieving isothermal operation. The scheme is then optimized for a fuel cell stack. Finally, the analysis can be extended, for example, to employing phase change material (PCM) as a thermal reservoir to cope with transient operation.

The evaluation of isothermal fuel cell operation can be performed using a simple experiment. Fig. 9 shows an experimental setup for isothermal fuel cell operation. In this case a PEM is used for the electrolyte, and the membrane electrode assembly (MEA) is attached or integrated with the bottom plate of a thermosyphon heat exchanger. The fuel and oxygen streams are fed into the heat exchanger to be pre-heated, after which they enter the fuel cell. Heat from the reacting products conducts to the thermosyphon, evaporating the fluid that is spread using a porous wick. The vapor in the thermosyphon can condense either on the tubes containing the product streams or on a tube containing water from a constant temperature circulator. Hotter regions of the MEA are thereby cooled, and the fuel cell can be operated closer to an isothermal condition.

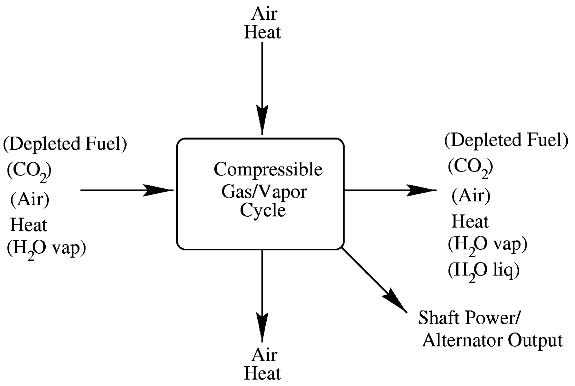

Fig. 8. Flow chart for possible components to flow streams in a secondary cycle generator.

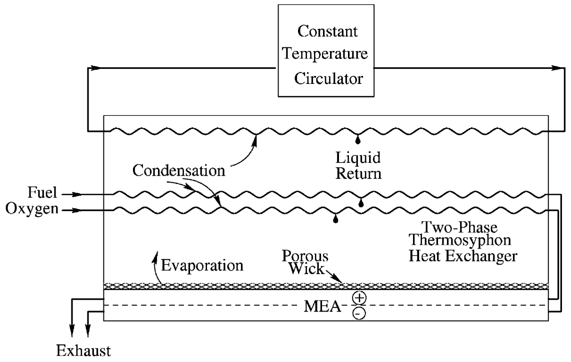

Fig. 9. Experimental setup for investigation of current density augmentation through isothermal operation.

From the experimental setup, data can be collected to show how isothermal operation affects current density. The setup is run over a range of temperatures, and the current density data is compared to that collected for temperature profiles similar to those reported in the literature. The maximum temperature of the profile is necessary for comparison, because the objective of isothermal operation is not to increase the maximum operating temperature, but rather to increase the average operating temperature given a particular maximum.

Once the benefit of the heat exchanger is established, a method for lowering thermal gradients in the fuel cell stack can be designed. This may take the form of heat pipes embedded in the current collectors or walls of the flow paths, or the device may be a thin thermal spreader sandwiched between adjacent cells. Modeling, combined with prototype testing, can be used to optimize the interval at which the devices are located.

With this task completed, the investigation can be extended to the identification of other means by which to apply the benefit of isothermal operation. Provided the heat transfer can be accomplished effectively enough, the use of PCM may be justified. This could be used to supply heat during periods of increasing load, such as startup. When excess heat is available, it may be stored again in the PCM. Such an addition could also lead to more reliable control of power and water management.

2.1.8. Miscellaneous

Durability of PEMFCs is a major issue that has received more attention in recent years. The life capability of the PEM fuel cells used for the GEMINI missions in the 1960s seldom exceeded 500 h, the advent of fluorinated membranes such as Nafion extended lifetimes beyond 10,000 h. However, this durability performance was achieved on a high-cost cell optimized for performance and durability. With significant market demand for low-cost fuel cells to meet residential and automotive needs, the injection of low-cost technology has reduced effective cell lifetimes to several hundred to a few thousand hours of invariant operation. Curtin et al. [14] reported that DuPont began a series of process and product development programs specific to Nafion membranes since 1995. These ongoing programs are focused on providing the required performance, mechanical durability, and chemical stability necessary for successful PEM fuel cell applications. Takahisa et al. [15] developed a proton exchange membrane with high durability that is capable of inhibiting production of peroxide radicals. Siroma et al. [16] examined the degree of dissolution of Nafion membrane in mixtures of methanol and water at various temperatures up to 80 °C. At 80 °C, more than 30% of the membrane was dissolved in mixed solvents with methanol concentration of higher than 80%. Knights et al. [17] examined various operating conditions that can significantly affect the durability of PEMFCs and DMFCs. These conditions include: low reactant flows, high and low humidification levels, and high and low temperatures. Mohtadi et al. [18] reported that air impurities such as SO_2, NO_2, and H_2S negatively affect the performance of PEMFCs and severity of the performance degradation varies depending on the impurity, its concentration and dosage. In general, the impurities containing sulfur showed a stronger effect than those containing NO_2.

Durability is also one of essential aspects in the development of SOFC technology. Liu et al. [19] studied whether and how the impurities introduced during anode fabrication influence SOFC durability. Specifically, they examined the influence on the microstructure of Ni/YSZ cermet anode and of the interface toward the YSZ electrolyte. Long-term test results showed that the mobility and reactivity of the impurities are increased by forming a sodium silicate glass phase with low viscosity, and further enhanced by the presence of a high water pressure developed in the central region of the cell due to the conversion of hydrogen to water and the diffusion restriction. Finnerty and Ormerod [20] evaluated the durability of the anode in terms of reforming activity and carbon deposition. This work was performed on a small diameter, thin-walled extruded YSZ tubular SOFC and test results showed that a 90-vol% nickel/zirconia anode demonstrated higher activity and better durability than a 50-vol% Ni anode at higher reforming temperatures. Livermore et al. [21] studied the electrical performance and durability of planar ceria-gadolinia (CGO)-based SOFCs over temperatures ranging 500–600 °C. Their test results showed that the SOFC with 75-mol% Ni/CGO anode gave poor power output and durability. The same SOFC, but with 85%-mol% Ni/CGO, gave excellent durability over 100 h operation and temperature cycling. Mazumder et al. [22] used a computational model to analyze the effects of a SOFC power-conditioning system and electrical application load on the performance and durability of the SOFCs. They demonstrated that, over a short time frame, fast scale current ripple imposed by the power-electronics subsystem has negligible impact on the SOFC.

System-level thermal design. How can system components be integrated to offer improved performance and reduce overall cost, weight, and size? An example is a hydrogen fuel cell supplied with fuel that is stored using metal hydrides, a very common scenario. Extraction of hydrogen from metal hydrides constitutes an endothermic chemical reaction. On the other hand, the waste heat generated by a hydrogen fuel cell very closely matches the thermal energy required to release the hydrogen from the storage medium. Viewed as a system, overall cost can be reduced if efficient ways can be identified to transfer the waste heat from the fuel cell and deliver it to the metal hydride in order to release the hydrogen from the interstices of the metal lattices.

Thermal processing of materials must be better understood to reduce system cost. This includes operations such as injection molding or stamping of bipolar plates, as opposed to the current practice of machining these plates, one-at-a-time, from solid graphite.

Truly optimized thermal design. How can new manufacturing methods, such as additive manufacturing techniques, be exploited to improve thermal conditions in the fuel cell? Additive manufacturing has advanced to the state where the engineer is no longer constrained to consider only the geometries that can be fabricated using conventional material removal operations. Manufacture of molds for injection molding operation has been transformed by additive manufacturing. Ten years ago, the cooling channels embedded in the molds were carefully designed, but options regarding the cooling channel geometry and layout were limited to those that could be fabricated using conventional boring and casting methods. Today, truly thermally optimized internal cooling channel configurations are used, since the geometry and placement of the channels are no longer limited by conventional manufacturing methods. A specific opportunity is the design of bipolar plates with extremely complex (or very simple) geometries that cannot be fabricated with the manufacturing techniques of 10 years ago.

Water management. The key to obtaining maximum performance and life in a PEMFC is effective water management within the cells. Insufficient water results in high membrane resistance and premature membrane failure. An excess of water causes local reactant starvation, resulting in performance losses and permanent cell degradation. This constitutes a rather unique thermal systems design challenge, in that cooling or heating rates should not be minimized or maximized, but adjusted in response to changes in the environmental conditions (temperature and relative humidity) to provide a specific "sweet spot" temperature interval to the fuel cell. UTC

Fuel Cells has developed proprietary PEMFC technology that effectively overcomes this water-management challenge in a simple and passive manner [23–26]. Water flow from the cathode of one cell to the anode of an adjacent cell is provided by water transport plates. The gas crossover between cells is blocked by bubble pressure of the water transport plate. This may be achieved by a careful balance of pore size and pressure differential between the reactant gases and the coolant water. This technology greatly simplifies the system and dramatically improves the performance and lifetime of the stack.

Some other technical challenges remain in water management and some examples include: How can the internal temperature and humidity be measured accurately and inexpensively, and how can the thermal management system be adjusted (on board) to provide for the desired temperatures?

Cold start-up. The typical cold weather specifications for an internal combustion engine vehicle include

- ambient temperature tolerance: −40 °C to 52 °C;
- start-up within 30 s in low ambient temperatures such as −40 °C;
- stable operation in low ambient temperatures.

Fuel cell vehicles will probably be required to meet similar cold weather specifications to meet consumer expectations [27]. Several approaches have been provided for starting a fuel cell vehicle in sub-freezing temperatures. For example, Fuller and Wheeler [28] disclosed a method to heat a PEM fuel cell to operating temperature during cold start-up. In this embodiment, a dilute hydrogen/air mixture is introduced into the normal process oxidant channels of the fuel cell where it reacts with a catalyst to produce heat at sub-flame temperatures. The catalyst can be provided in a structure between the cathode and the process oxidant channels. Rock and Plant [29] provided a method of heating a cold MEA to accelerate cold start-up of a PEM fuel cell. The MEA is locally heated from below freezing to a suitable operating temperature by the exothermal chemical reaction between H_2 and O_2 on the anode and/or cathode catalysts. During start-up, H_2 is introduced into the O_2-rich cathode feed stream and/or O_2 is introduced into the H_2-rich anode feed stream. Reiser [30] disclosed an electrical heating method by using a battery to force current through a frozen fuel cell stack, thereby to cause it to rapidly become operational.

2.2. High temperature SOFC fuel cells

The solid oxide fuel cell is similar to the PEMFC and DMFC in that a solid ion conducting electrolyte layer is sandwiched between a porous anode and cathode. For a SOFC, this electrolyte is usually yttria-stabilized zirconia (YSZ). A SOFC with YSZ electrolyte is operated at temperatures between 800 and 1000 °C. One of the technical trends in SOFC developments is to reduce the operating temperatures to 500–700 °C in order to reduce the overall system costs. Reducing the cost of electrolyte materials is the key to achieving this goal. The most promising alternatives to an YSZ electrolyte for these intermediate temperature SOFCs include Sr- and Mg-doped $LaGaO_3$ (LSGM), Sc2-doped ZrO_2 (ScSZ) and CeO_2-based materials (GDC, YDC). The high operating temperature of SOFCs has numerous advantages: there is no need for a precious catalyst, units enjoy fuel flexibility, and heat cogeneration is possible for even higher efficiency. Methane (CH_4) can also be used as fuels.

2.2.1. Heat transfer issues related to SOFC stacks

The two principal types of SOFCs are tubular and planar. In the tubular configuration, bundles of tubes are arranged in parallel. For a closed-end tubular design (e.g., Siemens, Westinghouse), air is introduced to the inside of each tube while fuel flows over the outside of the cells [31]. Fig. 10 shows a Westinghouse 100 kW tubular SOFC structure. Operating at 900–1000 °C, tubular SOFCs have relatively high electrical resistance but are simple to seal. Recent technology developments in the planar type SOFC cell components and materials have been the change to a thinner electrolyte layer, anode-supported cells, the use of metallic interconnect plates, and more conductive materials for electrolytes. A typical planar SOFC has a structure similar to that of a PEMFC as shown in Fig. 3.

The high operating temperature can lead to extremely stringent requirements for materials. The thermal expansion coefficients for cell components must be closely matched to reduce thermal stress arising from differential expansion between components. Chemical compatibility of the stack components with gases in the high oxidizing and reducing environments is also of primary concern [31].

2.2.2. Heat and fuel recovery cycle

The ability to combine a SOFC with a bottoming cycle has been known in concept for many years. A general thermodynamic model has shown that combined fuel cell/heat engine systems may reach an energy conversion efficiency of more than 80% [33]. These systems, and variations on them, are described in the literature [34–36]. Fig. 11 shows a cogenerative Brayton cycle SOFC power system [31]. The hot air and fuel streams leave the stack and enter the combustor, where they mix and the residual fuel burns. The combustion product enters the expander to generate additional power and to drive the compressor, which is connected to the expander. The compressor is used to compress the air flow to the stack. The flow then passes through a pre-heater to recover heat from the combustion product gases leaving the expander.

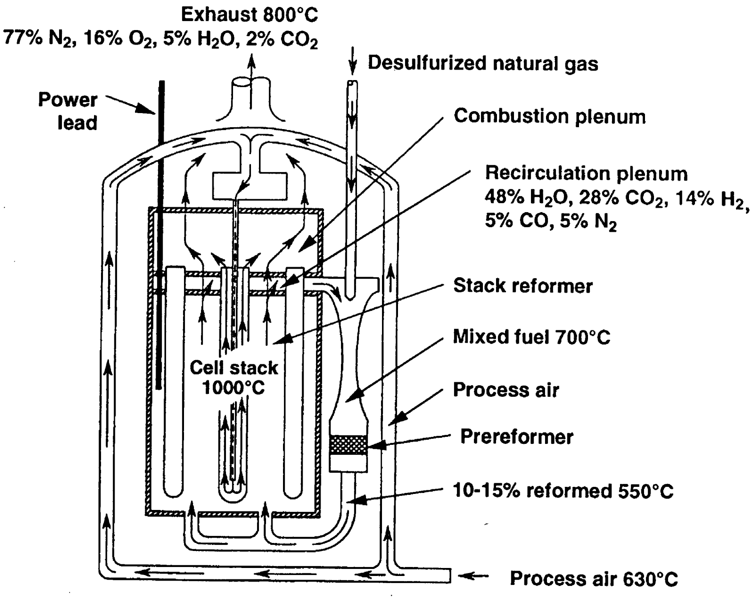

Fig. 10. Westinghouse 100 kW tubular SOFC stack gas flows [32].

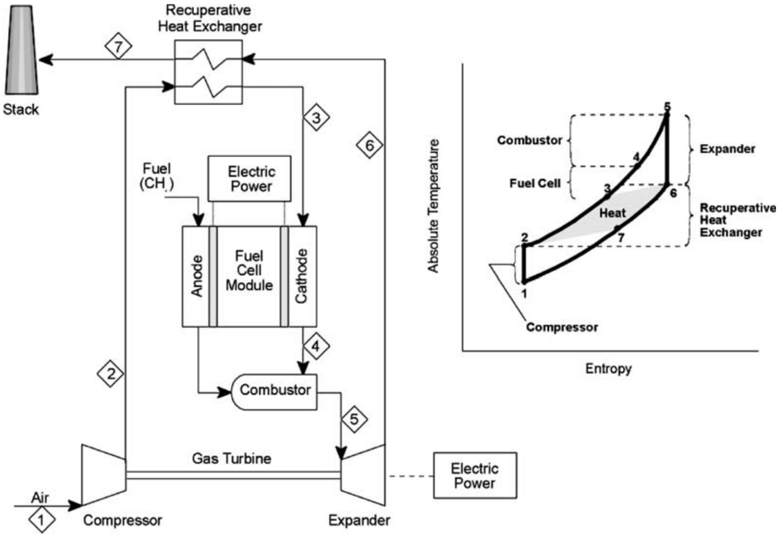

Fig. 11. A cogenerative Brayton cycle SOFC power system [31].

Winkler and Lorenz [33] summarized the tasks of thermal engineering in a cogenerative SOFC power system: (1) choice of heat engine and integration; (2) integration of fuel processing; (3) integration of pre-heaters; and (4) satisfaction of restrictions by ceramic cells. The most significant design variables are the fuel cell operating temperature range and the temperature and pressure at the gas turbine expander inlet [31].

2.2.3. Heat transfer in auxiliary components

The exhaust from the turbine in a cogenerative Brayton cycle SOFC power system could be used to heat fuel and air that enter the anode and cathode. There are at least two purposes for this pre-heating process: to recover waste heat and to prevent the SOFC stack from undergoing thermal shock. Ceramic materials of a SOFC cannot withstand steep temperature gradients.

To obtain a uniform temperature distribution in the cell, a higher air-flow rate than that required for fuel cell oxidation must be fed to the cell at high temperature. As a consequence, the air pre-heater and the air blower become bulky and expensive. Costamagna [34] proposed an integrated air pre-heater for a planar SOFC, which will dramatically reduce the size of a conventional pre-heater.

2.2.4. Material properties and prediction capability

Local reaction rates are highly dependent upon local temperatures. The local temperature distributions are established primarily by both surface and volumetric radiation transfer and conduction. We know very little about the spectral radiation heat transfer properties of the layered, semi-transparent ceramic structures that constitute the cathode/anode/electrolytic structure within which the electrochemical reactions occur. Even if these properties were known, what computational methods are available to predict the performance, or intelligently design, an entire stack of these materials? How are the (unknown) radiation and electrochemical properties affected by the methods by which these ceramics are produced? How are the coupled, multi-mode heat transfer effects coupled to the electrochemical reaction rates? What is the optimal design of such ceramic layers?

2.3. Portable/miniature/micro fuel cells

Fuel cell development has benefited greatly from attempts to create larger power systems for automotive, residential and stationary applications. In recent years, interest in using fuel cells to power portable electronic devices and other small equipment has increased partly due to the promise of fuel cells having higher energy density and instant recharge. In developing these smaller fuel cell systems, one cannot simply use scaled-down system architectures and components used in their larger counterparts. Several fuel cell manufacturers (see Tables 3 and 4) have recognized this and are already developing novel system architectures and redesigning subsystem components to address the particular technical issues related to these smaller fuel cells. The initial efforts for small fuel cells use externally supplied hydrogen to generate electricity [37]. Due to the challenge of hydrogen storage, the technical trend is shifting to DMFC and reformate hydrogen fuel cell (RHFC) technology in very recent years [38]. Small solid oxide fuel cells also offer the possibility of using fuels other than hydrogen.

For descriptive purposes, small fuel cell systems are further divided into portable fuel cells (>100 W), miniature fuel cells (10–100 W) and micro fuel cells (0–10 W). The general heat transfer issues in these small fuel cell systems are the same as in the larger counterparts systems, which are discussed in other parts of this paper. The particular heat transfer issues related to small fuel cell systems will be presented in the following subsections.

2.3.1. Portable fuel cells (>100 W)

A complete fuel cell system consists of three major parts [39]:

(1) The fuel cell stack, which is the "heart" of the fuel cell. Its size is directly related to the power output.
(2) The fuel tank, the volume is proportional to the energy stored in the system.
(3) The Balance of Plant (BOP), which includes all of the additional parts (reformer, pumps, fan, valves, sensors, control circuit, etc.) of the system that support the power generation process.

The weight and cost of BOP are proportional to the power output, but it has a minimum size and weight. This is especially important when the stack and fuel tank are reduced, as is the case for portable fuel cells. The cost of the BOP also becomes predominant for portable fuel cells.

PEM fuel cell stack performance has improved dramatically in recent years, leading to enhanced specific power density and reduced cost. Although PEM fuel cells operating on pure hydrogen gas have high efficiency and power density, the difficulties associated with handling high-pressure compressed hydrogen gas and the lack of a hydrogen storage method could prevent widespread use of PEM fuel cells in the near future. As a result, PEM fuel cells using hydrogen extracted from a liquid fuel such as methanol, gasoline, or diesel/JP-8 are actively under development. Methanol is selected as the leading fuel candidate to provide hydrogen for portable fuel cells, because it has several unique properties, including:

- methanol is a liquid at atmospheric conditions;
- methanol has a high hydrogen-to-carbon ratio relative to gasoline;
- methanol can be reformed to hydrogen at much lower temperatures (180–270 °C) and more efficiently than gasoline (800–900 °C).

A comprehensive methanol reformer is shown in Fig. 2. A simplified version can be used for portable power applications. However, unique requirements such as light weight, insulation and integration with fuel cells impose new challenges to the portable methanol reformer design.

The use of liquid fuel offers convenient use and higher energy density stored in the system. For this reason, the DMFC appears to be a good solution for portable applications. However, stack and BOP sections of DMFC systems are still heavier and more complicated than comparable hydrogen PEM systems mainly due to the methanol crossover and catalytic inefficiency.

Table 3
Summary of portable and miniature (>10 W) fuel cell developers

Investigator Type, Fuel	Power, T_{op}, size, weight, power density	Technology	Application comments
Ball Aerospace http://www.ball.com/aerospace PEMFC, Hydrogen	50, 100 W, NA, NA, 4.3 dm^3, 5.6 dm^3	The systems use oxygen from ambient air and externally supplied hydrogen. The hydrogen is held in two commercially available, refillable high-pressure tanks. An air filter having a gas permeable, hydrophobic, micro porous polymer film is used to exclude liquids and solids from the fuel cell enclosure	Electronics power
Smart Fuel Cell GmbH http://www.smartfuelcell.com DMFC, Methanol	25 W, −20 to +40 °C, 21.8 dm^3, 9.7 kg	This is a 25 W DMFC-lead acid battery hybrid system. The fuel cell is used to trickle charge the battery, which then powers the load. The fuel cell is fueled by ‘‘neat’’ methanol that is prepackaged in 2500 mL containers. One of primary drawbacks of the unit is the heavy initial system weight of 9.7 kg. Another major limitation of the system is that the unit must be operated in a perfectly upright position. Otherwise, the unit may be damaged and begins to leak methanol [43]	Consumer electronics, mobile office systems, remote sensors, power tools
Lynntech, Inc. Cisar [40] DMFC	15 W, ambient temperature, NA, NA, NA	This 15 W prototype DMFC system utilizes a monopolar design concept—an adjacent anode and cathode pair is fabricated using a common conductive element, with that conductive element serving to conduct the current from one cell to the adjacent one	Laptop PCs, cameras
Samsung Chang [41]	30 W, 70 W, 100 W, 30–40 °C, 0.6 dm^3, 0.97 dm^3, 1.26 dm^3, NA, NA	Chang developed a low methanol crossover membrane at Samsung. The membrane maintained the same proton conductivity and near 30% crossover vs. Nafion® when 5 mol/L or higher concentrations of methanol were used	Portable power, laptop PC
Dohle et al. [9] PEMFC, Methanol	500 W, 70 °C, 22% sys, 4.2 dm^3, NA power density: 50 mW/cm^2	This 500 W DMFC system consists of the stack, a water/methanol tank, a heat exchanger, a pump and compressors. The auxiliary components are powered by the DMFC itself. The stack consists of 71 cells and each cell has an area of 144 cm^2. The current collectors are manufactured of stainless steel with a cell pitch of 2 mm	Portable power, stack demonstration
Manhattan Scientifics http://www.mhtx.com PEMFC, H_2	Several watts to several kilowatts, NA, NA	These hydrogen fueled PEM fuel cell system operate with air as a cooling gas and have cooling layers comprising the external cooling fins. The cooling layers bring out the heat of reaction process, at first from the inside of the stack to the cooling fins and further from the cooling fins to ambient air or another cooling fluid. The cooling layer may be an extension of the one electrode and covers the whole active area	Laptop computers and other portable electronics, golf carts, wheel chairs, cordless power tools

(continued on next page)

Table 3 (*continued*)

Investigator Type, Fuel	Power, T_{op}, size, weight, power density	Technology	Application comments
Moore et al. [13] PEMFC, H_2	50 W, NA, 2.3 cm^3, 3.3 kg System: 85 W h/kg, 123 W h/L	This 50 W power source consists of a PEM stack, rechargeable metal hydride and voltage regulation equipment. On the first attempt, using 1 wt% hydrogen storage, the performance of the fuel cell system exceeded that of the batteries	Military battery replacement
Motorola Hallmark [42] PEMFC, Reformate	25 W, NA, 2.54 kg, 708 W h/kg	This is a 25 W reformed methanol fuel cell system. The methanol steam reformer operates between 200 and 230 °C. The high temperature fuel cell operates between 150 and 200 °C. This allows to simplify BOP—no CO clean-up device needed	

Solid oxide fuel cells have enjoyed some success in stationary applications. In recent years, SOFCs have adapted to portable applications. A start-up device is needed to heat the fuel cell system quickly to full-scale operation. Operation at high temperature requires efficient thermal insulation methods to prevent heat loss from the stack. Furthermore, it is necessary to consider coupled thermal and structural designs to reduce thermal stresses.

2.3.2. Miniature fuel cells (10–100 W)

Currently, several advanced prototype fuel cell units are commercially available in this power range. The most developed fuel cell system is the PEM fuel cell, which uses hydrogen gas as a fuel stored in a high-pressure tank. The second option is direct methanol fuel cells. Miniature fuel cell systems commercially available from Ball Aerospace and Smart Fuel Cell are briefly discussed below to illuminate the technical advancements.

Ball Aerospace provides two miniature PEM fuel cell systems (see Table 3): 50 W and 100 W. The systems use externally supplied hydrogen, which is held in two commercially available, refillable high-pressure tanks. This is the simplest solution, but appears not to be efficient for a miniature fuel cell in terms of energy density. For example, a combination of this 50 W unit and a 900 W h high-pressure hydrogen tank gives a power density of 173 W h/kg and 102 W h/L for the system [39], which is the same power density level of a Li-ion battery. But for a smaller size unit, it will be extremely difficult to compete with Li-ion batteries. As claimed by the manufacturer, the power systems have been extensively tested by the Army Research Laboratory, under which they were subjected to thermal and humidity testing. The systems are self-regulating and will turn themselves off if excessive temperature, pressure, current, voltage, etc., conditions occur.

The Smart Fuel Cell A25 is a direct methanol fuel cell hybrid, which uses a 25 W fuel cell stack and a 12 V lead acid battery linked in series. This unit is fueled by "neat" methanol that is prepackaged in 2500 mL containers. Bostic et al. [43] performed a series of tests on this unit. Fuel consumption tests provided an average system efficiency of 13.1% based on a load of 25 W under ambient conditions. The environmental testing showed that the system did not start at 15 °C and could not carry a load at 40 °C.

2.3.3. Micro fuel cells (0–10 W)

Micro fuel cells face intense competition with batteries in the low power range (0–10 W). Mostly due to the lack of effective hydrogen storage technologies, a liquid fuel appears to be the only good option to achieve a high power density capable of competing with batteries. Direct methanol fuel cells are the most developed liquid feeding fuel cell system thus far. The key challenge relating to micro DMFCs is how to achieve the desired power performance while simplifying the design of the BOP in order to miniaturize the whole system and reduce cost. Certainly, a number of diverging systems with emphasis on the BOP design have been provided, each with its own merits and limitations. As shown in Table 4, there are two types of fuel cell technologies developed in this power range: "active" and "passive". An active system requires moving parts such as a pump or fan to feed fuel and oxygen into the fuel cell stack, which are inherently unreliable and require power to operate. Conversely, a passive fuel cell system supplies fuel to the anode in a passive method requiring no external power and moving parts. Air-breathing operation mode is usually used in passive fuel cell systems.

Micro DMFC stacks can operate preferentially at a higher temperature to improve the power output. For example, Dohle et al. [9] reported power densities obtained from a DMFC of 7.6 mW/cm^2 at 22 °C and 16.0 mW/cm^2 at 45 °C, respectively. Xie et al. [58] developed a 2 W direct methanol fuel cell at Motorola Labs. The stack was insulated with a Zircar® alumina blanket.

Table 4
Summary of micro fuel cell (<10 W) developers

Investigator Type, Fuel	Power, T_{op}, size, weight, power density	Technology	Application comments
MTI Micro Fuel Cells Gottesfeld [44,45] DMFC, Methanol	1–2 W, ambient temperature, NA, NA, NA	The system uses effluent gases (CO_2) to drive liquids (methanol and water) among elements of the fuel cell system. A number of valves are used to control this operation. Mass manufacturable technology for DMFC cell array fabrication was used	Cell phones
Motorola Hallmark [46] PEMFC, Reformate	0.7 W, 150–170 °C, NA, NA, 120 mW/cm^2	The system consists of a miniature in situ H_2 generator (methanol fuel processor) and a high temperature (∼150 °C) membrane fuel cell	Cell phones
Manhattan Scientifics http://www.mhtx.xom Hockaday [47] DMFC, Methanol	80 mW, NA, NA, 65 cm^3, NA	A fuel ampoule is use to deliver methanol fuel by diffusion through the ampoule walls. The methanol vapor condenses at the anode surface and combines with water to form a water/methanol solution	Cell phones
Motorola Pavio [48] DMFC, Methanol	0.1 W, ambient temperature, NA, NA, NA	The DMFCs developed at Motorola operate in an actively driven mode. The active components used in the system include: methanol sensor, CO_2 separator, electronic controls, methanol feed pump, circulation pump and pump drivers	Cell phones
Samsung Chang [41] Kim [49] DMFC, Methanol	5 W, ambient temperature, 0.2 dm^3, NA, NA	A low methanol crossover membrane was developed at Samsung. The Nano composite membrane with layered proton conductor has ionic conductivity of 0.07–0.16 s/cm [49]. The membrane could maintain the same proton conductivity and near 30% crossover vs. Nafion when 5 M or higher concentrations of methanol were used. The system could use 10 M or higher concentration of methanol fueling [41]	4 G mobile phones
Toshiba Yonetsu et al. [50]	NA	A wick structure is used to deliver liquid methanol solution into the cell. The fuel is vaporized within the cell and supplied to the anode. The liquid fuel tank is equipped with a pressure control mechanism for controlling the fuel flow rate	NA
Florida International University Guo and Cao [51,52] DMFC, Methanol	75 mW, ambient temperature, NA, NA, 3.0 mW/cm^2	In this passive system, methanol fuel and water are stored separately in two containers. A wick is placed between these containers in a siphon fashion, with the container of the aqueous methanol solution communicating with the anode of the DMFC. Methanol is siphoned from the methanol container to the aqueous solution container in situ. Combining with air-breathing cathode, this is a completely passive DMFC system	Micro power source
Renew Power, Inc. Ha et al. [53] Liquid feed fuel cell, formic acid	12 mW, ambient temperature, 6.72 cm^3, NA, 12.2 mW/cm^2	Formic acid is used as fuel in this liquid feed fuel cell system due to its low crossover in Nafion membrane. Formic acid has two orders of magnitude smaller crossover flux through a Nafion membrane than methanol [59]. Neat formic acid has a much lower theoretical specific energy density than neat methanol (1724 W h/kg, for formic acid versus 6098 W h/kg for methanol)	Micro power source
University of Texas at Austin Chen et al. [54] Biofuel cell, glucose	280 nW, ambient temperature, NA, NA, 64 μW/cm^2	This biofuel cell is made from two 7-μm-diameter, electrocatalyst-coated carbon fiber electrodes placed in 1-mm grooves machined into a polycarbonate support. One electrode is a glucose-oxidizing anode, and the other is an oxygen-reducing cathode	Biological sensors

(*continued on next page*)

Table 4 (*continued*)

Investigator Type, Fuel	Power, T_{op}, size, weight, power density	Technology	Application comments
The Pennsylvania State University Logan et al. [55] Biofuel cell, organic matter	NA, ambient temperature, NA, NA, 39 mW/m^2	In this microbial fuel cell, power is produced from the oxidation of cysteine at the cathode, with reduction of oxygen at the cathode. The maximum power density is 39 mW/m^2 at cysteine concentrations of 770 mg/L	Micro power sources
Brown University Palmore and Kim [56] Palmore [57] Biofuel cell, glucose	NA, ambient temperature, NA, NA, NA	A biocatalyst was used in the cathode compartment of an operation dihydrogen/dioxygen fuel cell. Biocatalysts are renewable and could be developed for more complex fuels (e.g., methanol, alkanes)	Micro power sources

Under normal operating conditions, stack temperature can reach 50–60 °C. This self-heating effect plays an important role in enhancing micro DMFC performance.

Micro DMFC systems usually work at near-ambient temperatures. It seems that there are no special needs for handling heat transfer issues. This is true in mild temperatures. Under extreme environmental conditions, such as sub-freezing and dry hot weather, special treatments must be implemented to ensure the system remains capable of delivering power from a "cold start" and to optimize the fuel cell operation. One possible solution to the difficulties associated with cold weather is to reuse the heat from the electronic device to keep the fuel cell warm.

Formic acid is another attractive fuel choice for direct liquid fed fuel cell technologies. If platinum–ruthenium black, the standard anode catalyst for methanol oxidation in DMFCs, is used for formic acid oxidation, a direct formic acid fuel cell can produce power densities up to 33 mW/cm^2 at ambient conditions [53]. Palladium-based anode catalysts can produce significant performance enhancements for direct formic acid fuel cells [59]. Although formic acid crossover through the Nafion membrane is lower than that of methanol, the operation of direct formic acid fuel cells with highly concentrated formic acid is still questionable due to accumulate poisoning adsorbant of formic acid on the palladium catalyst layer [60]. Gottesfeld [45] argued that neat formic acid (1.9 W h/g) has a lower specific energy density than neat methanol (6.1 W h/g) and the methanol crossover problem can be solved at the system level (e.g., diluting methanol before it is fed to the anode).

Biofuel cells use biocatalysts for the conversion of chemical energy to electrical energy. Abundant organic raw materials such as alcohols, organic acids, or glucose can be used as fuel, and oxygen or H_2O_2 can act as an oxidant. Another important use of biofuel cells is their in situ assembly of human body fluids, e.g., blood. The extractable electrical power could be used to activate implanted devices such as pacemakers, pumps (e.g., insulin pumps), sensors and prosthetics [54,57,61].

3. Fuel cell modeling

There are a number of reasons to model fuel cells. Fuel cell modeling is a useful tool to gain better insight into the inner working mechanism so that the fuel cell design can be improved. It is faster and cheaper to run a "modeled fuel cell" than a real one, so modeling can speed up the design process. During the past 10 years, extensive research efforts have been devoted to developing comprehensive computational fuel cell models. This work concerned modeling, simulation and numerical analysis of heat transfer, mass transfer/species flow, material issues, electrochemical kinetics, water management, and system integration. In the past few years, research interest in modeling DMFCs and SOFCs has also increased.

In many cases, modeling efforts focused on one aspect or area in a fuel cell, as summarized in Table 5. Some other criteria are also included in the table. For instance, spatial dimension could be from simple zero-dimension to complex three-dimension. Complexity defines the area of interest of the model, from the fundamental sub-cell level including the electrodes, electrolytes and single cell—to the level at which individual fuel cells are assembled in a fuel cell stack; from the fuel cell system level, consisting of a fuel cell stack with its auxiliary system of compressor, pumps and so forth—to the fuel cell plant level, including a fuel cell system and some other combined cycles such as a gas turbine system. The state of the model is referred to as steady state or transient. Two-phase (gas and liquid-phase) flow occurs in PEMFCs and DMFCs. However, there are no experimental results available for two-phase flow in fuel cells. Numerical investigations could help to reveal the relationships among the liquid water saturation, the proton conductivity, and the level of gas diffusion layer flooding. In SOFCs, only gas exists at high operating temperatures. Modeling also needs to be performed at the macro system level to evaluate how fuel cells integrate with other power and energy storage components.

At present, ongoing efforts on fuel cell modeling are mainly focused on three types of fuel cells: PEMFCs, DMFCs and SOFCs, which are summarized sequentially below.

3.1. PEM fuel cell models

As shown in Table 5, the numerical models published in the open literature are mostly focused on the single cell modeling. Nguyen et al. [62], Um and Wang [5], Li et al. [63] and Liu and Zhou [64] published 3-D computational fluid dynamics models. The computational domain in Nguyen et al. [62] is one turn of a serpentine channel. This model accounts for the major transport phenomena in a PEM fuel cell: convective and diffusive heat and mass transfer, electrode kinetics, and potential fields. The governing equations and appropriate boundary conditions were implemented and solved using a 3-D commercial CFD package (CFX-4.3) that employs a finite volume formulation. The Um and Wang [5] model focuses on obtaining a basis of understanding of how a 3-D flow and transport phenomena in the air cathode impact the electrochemical process. The model results indicate that forced convection induced by the interdigitated flow field substantially improves mass transport of oxygen to, and water removal from, the catalyst layer, thus leading to a higher mass-transport limiting current density as compared with that of the straight flow field. Liu and Zhou [64] used 3-D modeling to study mass transfer enhancement of the interdigitated flow field design. Furthermore, the effects of various design parameters such as gas channel width, GDL thickness and GDL porosity were presented. Li et al. [63] built a 3-D model to simulate the performance of a PEM fuel cell with complicated gas channels. The results showed that mass diffusion is strong in the hydrogen channel but is rather weak in the air channel. Meng and Wang [65] introduced a 3-D, electrochemical-transport fully coupled PEMFC model using massively parallel computational methodology.

Several two-dimensional numerical models were published by Mennola et al. [66], Ferng et al. [67] and Siegel et al. [68]. Most of these models limited the computational domain to the cross section of a single cell along the flow direction and omitted the variations across the flow channels. Fig. 12a and b show the effect of increasing pressure on the fuel cell performance and the comparison of numerical results and experimental data [68]. Mennola et al. [66] developed a 2-D, isothermal and steady-state model for the cathode of a free-breathing PEM fuel cell to identify the limiting processes of mass transport. The modeled domain consists of the cathode gas channel and the gas diffusion layer. Experimental data from current distribution measurements were used to provide boundary conditions for oxygen consumption and water production. The model results indicated that at a cell temperature of 40 °C the performance of the cell was limited by water removal. At a cell temperature of 60 °C, the current distribution was determined by the partial pressure of oxygen. The PEMFC model developed by Ferng et al. [67] adopted a two-phase multi-component flow model and simplified electrochemical reaction equations. Modeling and experimental work were conducted to investigate the performance of a PEMFC, the effects of operating temperature and pressure on performance, and flow characteristics within the cell. Siegel et al. [68] developed a 2-D steady-state PEMFC model, which includes the transport of liquid water within the porous electrodes as well as the transport of gaseous species, protons, energy, and water dissolved in the proton-conducting polymer. Electrochemical kinetics is modeled with standard rate equations adapted to an agglomerate catalyst layer structure. Some of the physical properties used in constructing the model are determined experimentally. Natarajan and Nguyen [69] developed a transient model for the cathode of a PEMFC using conventional gas distributors. The model was validated with experimental results and qualitative information on the effects of various operating conditions and design parameters. The performance of the cathode was found to be dominated by the dynamics of liquid water, especially in the high current density range. Berning and Djilali [70] presented a 3-D fuel cell model that accounts for phase change and heat transfer. Transport of liquid water inside the gas-diffusion layers is modeled using viscous forces and capillary pressure terms. The liquid water saturation does not exceed 10% at either anode or cathode under conditions investigated in this paper. Furthermore, the transport of liquid water in the membrane is one of most important aspects of the water management in PEMFC. Gurau et al. [112] developed a 2-D model to study liquid water velocity distribution in the membrane. The results showed that the transport of liquid water in the membrane is due to the superposition of certain effects: the pressure field, the proton drag, friction with the pore walls and water concentration field.

The semi-empirical models developed by Jemei et al. [71] and Lee et al. [72] were unable to analyze the inner microscopic phenomena of the fuel cells, but the models are useful for system level design and analysis. Jemei et al. [71] developed a system level semi-empirical model on the basis of neural network methodology. This model simulated the steady state of fuel cells for automotive applications. Lee et al. [72] also used the neural network technique to derive a non-parametric empirical model

Table 5
A summary of features of selected fuel cell models developed in recent years

	Technology	Fuel	Methodology	Dimension	Complexity	Phases	State[a]	Electro[b]	Potential field	Heat and mass transfer
Gurau et al. [112]	PEM	H_2	Numerical	2-D	Single-cell	Two	SS	Yes	Yes	Heat and mass
Natarajan and Nguyen [69]	PEM	H_2	Numerical	2-D	Single-cell	Two	TR	Yes	Yes	Heat and mass
You and Liu [106]	PEM	H_2	Numerical	2-D	Cathode	Two	SS	Yes	Yes	Heat and mass
Berning and Djilali [70]	PEM	H_2	Numerical	3-D	Single-cell	Two	SS	Yes	Yes	Heat and mass
Li et al. [63]	PEM	H_2	Numerical	3-D	Single-cell	Two	SS	Yes	Yes	Heat and mass
Liu and Zhou [64]	PEM	H_2	Numerical	3-D	Single-cell	Two	SS	Yes	Yes	Mass
Mazumder and Cole [107]	PEM	H_2	Numerical	3-D	Single-cell	Two	SS	Yes	Yes	Heat and mass
Mennola et al. [66]	PEM	H_2	Numerical	2-D	GDL	Two	SS	NA	NA	Heat and mass
Nam and Kaviany [73]	PEM	H_2	Theoretical	1-D	GDL	Two	SS	Yes	Yes	Mass
Li et al. [74]	PEM	H_2	Theoretical	1-D	Cath.-GDL	Two	SS	Yes	Yes	Mass
Jemei et al. [71]	PEM	H_2	Semi-empirical	0-D	System	NA	SS	NA	NA	NA
Lee et al. [72]	PEM	H_2	Semi-empirical	0-D	Single-cell	NA	SS	NA	NA	NA
Meng and Wang [65]	PEM	H_2	Numerical	3-D	Single-cell	Single	SS	Yes	Yes	Mass
Nguyen et al. [62]	PEM	H_2	Numerical	3-D	Single-cell	Single	SS	Yes	Yes	Heat and mass
Um and Wang [5]	PEM	H_2	Numerical	3-D	Single-cell	Two	SS	Yes	Yes	Heat and mass
Ferng et al. [67]	PEM	H_2	Numerical	2-D	Single-cell	Two	SS	Yes	Yes	Heat and mass
Siegel et al. [68]	PEM	H_2	Numerical	2-D	Single-cell	Two	SS	Yes	Yes	Heat and mass
Weber and Newman [75]	PEM	H_2	Numerical	2-D	Single-cell	Two	SS	Yes	Yes	Mass
Argyropoulos et al. [77]	DMFC	CH_3OH	Numerical	1-D	Stack	NA	SS	NA	NA	Heat and mass
Kulikovsky [78]	DMFC	CH_3OH	Numerical	1-D	Single-cell	Single	SS	Yes	Yes	Mass
Sundmacher et al. [79]	DMFC	CH_3OH	Numerical	2-D	Single-cell	Single	TR	Yes	Yes	Mass
Jeng and Chen [80]	DMFC	CH_3OH	Theoretical	1-D	Anode	Single	SS	Yes	Yes	Mass
Argyropoulos et al. [83]	DMFC	CH_3OH	Semi-empirical	1-D	Single-cell	Single	SS	Yes	Yes	Mass
Kulikovsky [81]	DMFC	CH_3OH	Theoretical	1-D	Anode-GDL	Single	SS	Yes	Yes	Mass
García et al. [82]	DMFC	CH_3OH	Theoretical	1-D	Single-cell	Single	SS	Yes	Yes	Mass
Palsson et al. [36]	SOFC	H_2, CO	Semi-empirical	2-D	Plant	NA	SS	NA	NA	NA
Padullés et al. [35]	SOFC	H_2	Semi-empirical	0-D	Plant	NA	SS	NA	NA	NA
Haynes and Wepfer [96]	SOFC	H_2, CO	Theoretical	1-D	Single-cell	Single	SS	NA	NA	Heat and mass
Chan et al. [102]	SOFC	CH_4, H_2	Theoretical	0-D	Plant	NA	SS	NA	NA	NA
Winkler and Lorenz [33]	SOFC	NA	Semi-empirical	0-D	Plant	NA	SS	NA	NA	NA
Chan et al. [85]	SOFC	H_2	Theoretical	1-D	Electrolyte	NA	SS	Yes	Yes	NA
Dotelli et al. [101]	SOFC	NA	Numerical	2-D	Electrolyte	NA	SS	NA	NA	NA
Walters et al. [91]	SOFC	CH_4	Numerical	1-D	Anode	Single	SS	Yes	Yes	Heat and mass
Petruzzi et al. [88]	SOFC	H_2, CO	Numerical	3-D	System	Single	TR	Yes	Yes	Heat and mass
Tanner and Virkar [93]	SOFC	NA	Theoretical	2-D	Interconnect	NA	SS	NA	Yes	NA
Van herle et al. [87]	SOFC	Biogas	Semi-empirical	0-D	Plant	Single	SS	Yes	Yes	Heat and mass

Khaleel et al. [98]	SOFC	H_2, CO	Numerical	3-D	Single-cell	Single	SS	Yes	Yes	Heat and mass
Chen et al. [89]	SOFC	NA	Theoretical	1-D	Cathode	Single	SS	Yes	Yes	Mass
Jurado [86]	SOFC	H_2	Numerical	0-D	Stack	NA	TR	NA	NA	NA

[a] SS: steady state; TR: transient.

[b] Electrochemistry.

including process variations to estimate the performance of fuel cells without extensive calculations.

Nam and Kaviany [73] developed network models for the PEMFC diffusion layer and liquid water distribution. Li et al. [74] did the theoretical analysis of the free-convection at the cathode surface. The results indicated that the mass-transfer rate depends strongly on the oxygen concentration at the cathode, which can be viewed in terms of the relationship of the current density and voltage.

Weber and Newman [75] developed a mathematical model for polymer-electrolyte membranes. This model was placed in a simple pseudo 2-D fuel cell model to form a complete fuel cell model, which was validated and shown to be generally applicable for describing water transport in a polymer-electrolyte membrane. Meng and Wang [76] investigated effects of electron transport in the gas diffusion layer through a 3-D, single-phase, isothermal numerical model. The modeling results showed the lateral electric resistance of GDL and gas channel played a critical role in determining the current distribution and cell performance.

3.2. Direct methanol fuel cell models

Compared with PEM fuel cell modeling, the DMFC fuel cell models are at a less mature stage. Argyropoulos et al. [77] developed a thermal energy one-dimensional model for the DMFC, based on the differential thermal energy conservation equation. The model is used to predict the thermal behavior of a DMFC stack comprised of many large cells in a bipolar arrangement. The model allows an assessment of the effect of operating parameters (fuel and oxidant inlet temperature, flow rate and pressure, operating current density) and the system design (active area, material properties and geometry) on the temperature profile along the stack and the interactions among the various components in the stack. Kulikovsky [78] developed two-dimensional numerical modeling of a DMFC. The model is based on mass and current conservation equations. The velocity of the liquid is governed by gradients of membrane phase potential (electroosmotic effect) and pressure. The results show that, near the fuel channel, transport of methanol is determined mainly by the pressure gradient, whereas in the active layers and in the membrane, diffusion transport dominates. "Shaded" zones, where there is a lack of methanol, are formed in front of the current collectors. Sundmacher et al. [79] observed that pulsed methanol feeding could achieve a significant, sustained increase of the time-averaged cell voltage combined with a substantial reduction of the overall methanol consumption of the DMFC system. Their model has shown to be capable of describing the stationary behaviors of the DMFC quantitatively. Moreover, even the dynamic behavior as a result of changes in methanol

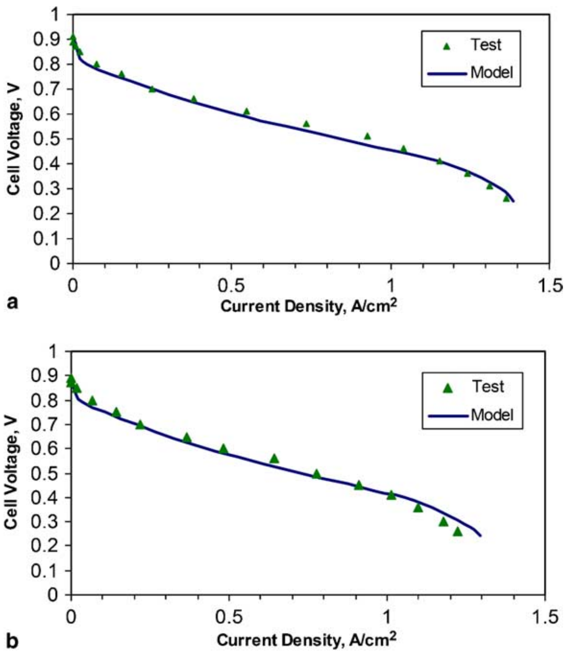

Fig. 12. The effect of increasing pressure on the fuel cell performance: (a) model comparison with test data at 30 psi (base case); (b) model comparison with test data at 20 psi [68].

feed concentration could be described qualitatively as shown in Fig. 13.

Jeng and Chen [80] presented a mathematical model for the anode of a DMFC. This model considers the mass transport in the whole anode compartment and the proton exchange membrane, together with the kinetic and ohmic resistance effects through the catalyst layer. The influence of key parameters on methanol crossover and anode performance is investigated. For a DMFC operated under low current density and high methanol feed concentration conditions, a large portion of the methanol fed into the fuel cell is wasted due to methanol crossover, thus producing low fuel efficiency. Kulikovsky [81] developed an analytical model of the anode side of a DMFC. The model takes into account non-Tafel kinetics of the electrochemical reaction of methanol oxidation, diffusion transport of methanol through the backing layer, and methanol crossover. The model offers an exact solution to the problem of performance of the anode catalyst layer of a DMFC. García et al. [82] provided a semi-analytical DMFC model. This model can be solved rapidly and can be included in real time system level DMFC simulations. This model accounts for both of the kinetics of the multi-step methanol oxidation reaction at the anode and the mixed potential of the oxygen on the cathode due to methanol crossover.

Argyropoulos et al. [83] developed a DMFC model to predict the cell voltage versus current density response of a liquid feed DMFC. The model is based on a semi-empirical approach in which methanol oxidation and oxygen reduction kinetics are combined with effective mass transport coefficients for the fuel cell electrodes.

Wang and Wang [84], in their mathematical modeling of a DMFC, do not attempt to model heat transfer, but rather to show that the predicted effect of operating temperature on diffusion coefficients is supported by experimental data. Their conclusion is that increased operating temperature leads to increased power density. Since the study lacks a heat transfer model, this is supportive of the dependence of power density on temperature.

3.3. Solid oxide fuel cell models

The recent intensive increase in interest in SOFCs has been accompanied by an increase in the use of mathematical modeling as a tool for interpreting experimental results and providing insight on how to improve SOFC design and performance. This subsection reviews the models and operation of SOFCs, noting the requirements of thermal management and the restrictions based on materials. Various mathematical models provided by investigators concern the theoretical fundamentals and practical operation of a SOFC. The fundamental models' concern is the ideal efficiency of SOFC combined cycle plants. Chan et al. [85] developed a thermodynamic model for simple SOFC power systems (only waste heat recovery used for pre-heating the fuel and air) fed by hydrogen and methane, respectively. Winkler and Lorenz [33] estimate that simple combined SOFC and gas turbine cycle efficiency is between 60% and 70%. They proposed a RH–SOFC–GT–ST (ReHeat–SOFC–Gas Turbine–Steam Turbine) cycle, which has an efficiency of more than 80% and confirms predictions of the theoretical thermodynamic model.

To determine the potential impacts of fuel cells on future distribution systems, a dynamic model for computing low-order linear system models of SOFCs from the time domain was created by Jurado [86]. This model uses the Box-Jenkins algorithm for calculating the transfer function of a linear system from samples of its input and output. It is capable of modulating real and reactive power in response to voltage and frequency changes on the grid. Van herle et al. [87] performed the energy balance analysis on a SOFC fed by biogas combined with a small gas engine and heat system. Petruzzi et al. [88] developed a numerical model for SOFC. This SOFC is being developed as an auxiliary power unit (APU) for luxury car conveniences. The model simulated the thermal-electrochemical behavior in all conditions that may occur during operation. Padullés et al. [35] created a simulation model of a SOFC-based power plant for use in a particularly well-known commercial power system simulation package.

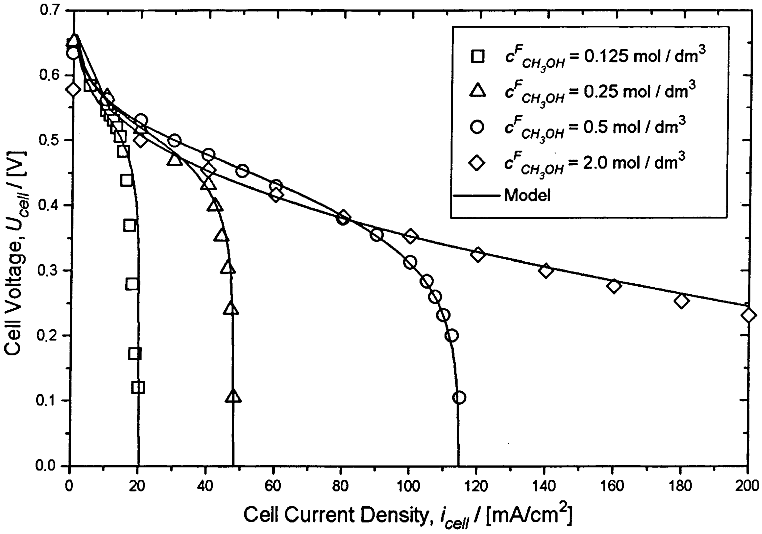

Fig. 13. Experimental and simulated steady-state current–voltage curves of DMFC for different methanol feed concentration ($T = 70$ °C, $V^F = 1.36$ mL/min, $P_a = 0.1$ MPa, $P_c = 0.3$ MPa) [79].

Many investigators studied issues of the chemical equilibrium for a SOFC with internal reforming and shift reactions (in cases where methane, biogas or natural gas are used as the fuel). Chen et al. [89] developed a mechanistic model for oxygen reduction at the YSZ/LSM interface. This micro-model considers some forms of polarization and establishes interrelationships among the transport phenomena, electrochemical process and the microstructure of the composite cathode. Li et al. [90] evaluated the performance of a single tubular SOFC. Fuel gas from a pre-reformer is considered to contain H_2, CO, CO_2, H_2O (vapor), and CH_4. The reforming and shift reactions in the cell are incorporated. Walters et al. [91] developed a plug-flow model for fuel (natural gas surrogate) within the anode channels. The model considers elementary gas-phase chemical kinetics of fuel pyrolysis and oxidation, as well as the limiting case of local chemical equilibrium. Guo et al. [92] studied the effect of the various operating parameters on the performance of oxidative coupling of methane. The two mathematical models based on well-mixed flow or plug flow were also used to describe the behavior of SOFCs.

The losses of electric potential in the operation of a SOFC were intensively studied, including activation polarization, ohmic loss, and the losses due to mass transport resistance. Tanner and Virkar [93] quantitatively examined the dependence of total SOFC stack resistance as a function of interconnect contact spacing, interconnect contact area, cathode thickness, electrolyte thickness, anode thickness, and transport properties associated with each region and interfaces (charge transfer resistance). The closed form analytical expressions were derived using a ladder network approach. Fukunaga et al. [94] investigated the relationship between overpotential and the three-phase boundary (TPB) length through experimental study and a mathematical model. They observed that the effective thickness of (TPB) length was less than 20 μm. Limiting behavior and optimization of cermet SOFC electrodes were discussed on the basis of an analytical model [95].

Modeling heat transfer in a SOFC is more tractable due to the absence of liquid phases. Iwata et al. [11] report the strong dependence of the temperature profile on the current density profile in their model of a SOFC. These studies demonstrate a correspondence between power density and temperature.

The coupled processes of flow, heat/mass transfer, chemical reaction, and electrochemistry are analyzed by numerical methods. Haynes and Wepfer [96] developed a thermal transport model for tubular SOFCs and concluded that radiation is a primary heat transfer mechanism between the air supply pipe and the cell. Larrain et al. [97] used a parameter estimation method to determine parameters for a thermal and simple kinetic model, which is applied to a small SOFC (20 cm^2 square cell of anode supported electrolyte with 1 cm^2 active area). Khaleel et al. [98] combined a commercial finite element analysis code, MARC®, with an in-house developed electrochemical (EC) module to simulate planar-type SOFCs. The EC module calculates the current density distribution, heat generation, and fuel and oxidant species concentration, taking the temperature profile provided by MARC. MARC performs flow and thermal analysis based on the initial and boundary thermal and flow conditions and the heat generation calculated by the EC module. Costamagna [34] analyzed the operating conditions of a rectangular planar SOFC with integrated air pre-heater. The idea of this fuel cell system is to reduce the cost of the expensive external air pre-heater by applying lower air flow rates together with lower inlet temperature. Boersma and Sammes [99] presented an analytical form for the gas-flow distribution in a planar SOFC stack under the assumption of the stack being viewed as a network of hydraulic resistances. Neophytides [100] developed a two-dimensional non-steady-state heterogeneous model to investigate the electrochemical oxidation of H_2 in SOFCs' monolithic arrangements, operating under forced periodic reversal of the flow.

To reduce the resistivity of the electrolyte, development has focused on reducing its thickness and finding new ion conductors. Dotelli et al. [101] used a digital image-based modeling procedure to simulate the electrical behavior of the composite electrolyte. They converted two-phase polyhedral microstructures into a random electric network by using the Voronoi tessellation technique. The real and imaginary part of the electric network impedance was computed by the transfer matrix method. Chan et al. [102] developed a mathematical model describing the distribution of the concentrations of electrons and electron holes and potential along the thickness of electrolyte. The effect of temperature on the resistance of the anode, cathode, electrolyte and interconnector is presented in Fig. 14a–d [102]. Chour et al. [103] fabricated bi-layer electrolyte structures by depositing YSZ films on doped ceria discs in a low-pressure MOCVD reactor. They also developed a model analysis of the kinetic data to provide insight into the nature of the hydrolysis-assisted pyrolytic deposition reactions.

3.4. Commercial fuel cell packages

Haraldsson and Wipke [104] reviewed a few commercial fuel cell models and additional software modules, e.g., Emmeskay, ADVISOR™ 2002 from the National Renewable Energy Laboratory, General Computational Toolkit (GCTool) from Argonne National Laboratory, the fuel cell modules in Easy 5 from Ricardo and FEMLAB from COMSOL. They also discussed two fuel cell models in more detail: the Virginia Tech model and the Royal Institute of Technology model. In this section, we will review three commercial models that were recently made available: two modules from FLUENT, Inc., a model CFD-ACE+ initially from Computational Fluid Dynamic Research Corporation (was sold to ESI group in February 2004) and fuel cell modules from CD-adapco Group.

FLUENT released the hydrogen PEMFC models in February 2004. This 3-D computational model for PEMFC has multi-physics capabilities, which include solving transport equations for flow, energy, species and electro-potentials in the computational domain that includes gas channels, porous gas diffusion layers, reacting catalyst layers and the membrane. The numerical model is also capable of simulating other physical effects encountered in PEMFC operations such as contact resistance, joule heating, time varying operating conditions, etc. Most recently Fluent also released SOFC module developed under SEGA project in 2004.

CFD-ACE+ can model PEMFCs, SOFCs and DMFCs. The model fully integrates the fundamental physics of fuel cells: flow, heat transfer, mass transfer, current transfer and electrochemistry in porous media, and thermal stress. User defined functions are not required for fuel cell modeling in this commercial numerical package. All functionality is fully controllable through an advanced graphical user interface that provides an ideal environment for the fuel cell designer to conceptualize, analyze and optimize the fundamental fuel cell components and systems.

CD-adapco has developed two expert system tools for fuel cell design. The first one is *es-pemfc*, a pre-and post-processing tool for simulation and analysis of PEMFCs. Solutions are calculated with University of South Carolina's electrochemistry subroutines and the STAR-CD, which is a control volume technique based CFD solver from CD-adapco. Typical PEMFC issues that can be simulated and analyzed using *es-pemfc* include: current density, overpotential, water management and temperature distribution. The second one is *es-sofc*, which works with the STAR-CD and electrochemistry subroutines developed at Pacific Northwest National Laboratory. Typical issues that can be handled by *es-sofc* include correcting the distributions of fuel and oxidant to the stack, mitigation of excessive thermal gradients along with temperature prediction for calculation of thermally induced stresses, and manifold flow passage optimization.

3.5. Unresolved issues in fuel cell modeling

In the past decade, numerical modeling of PEMFCs and SOFCs has received much attention. Many multi-physics models have been successfully developed that provide important tools for engineering design and optimization. Numerical fuel cell models can be improved with continued work in six areas.

The first one is numerical modeling of two-phase flows and cathode flooding phenomena. All the existing publications in the open literature are based on the theory that liquid transport in GDL is driven by the capillary saturation. The accuracy of this approximation requires further investigation. In addition, the calculated liquid saturation inside GDL from these numerical models could only reach a maximum value of 10%, resulting in negligible flooding effects [105–107]. Recent experimental observation shows that liquid water emerging

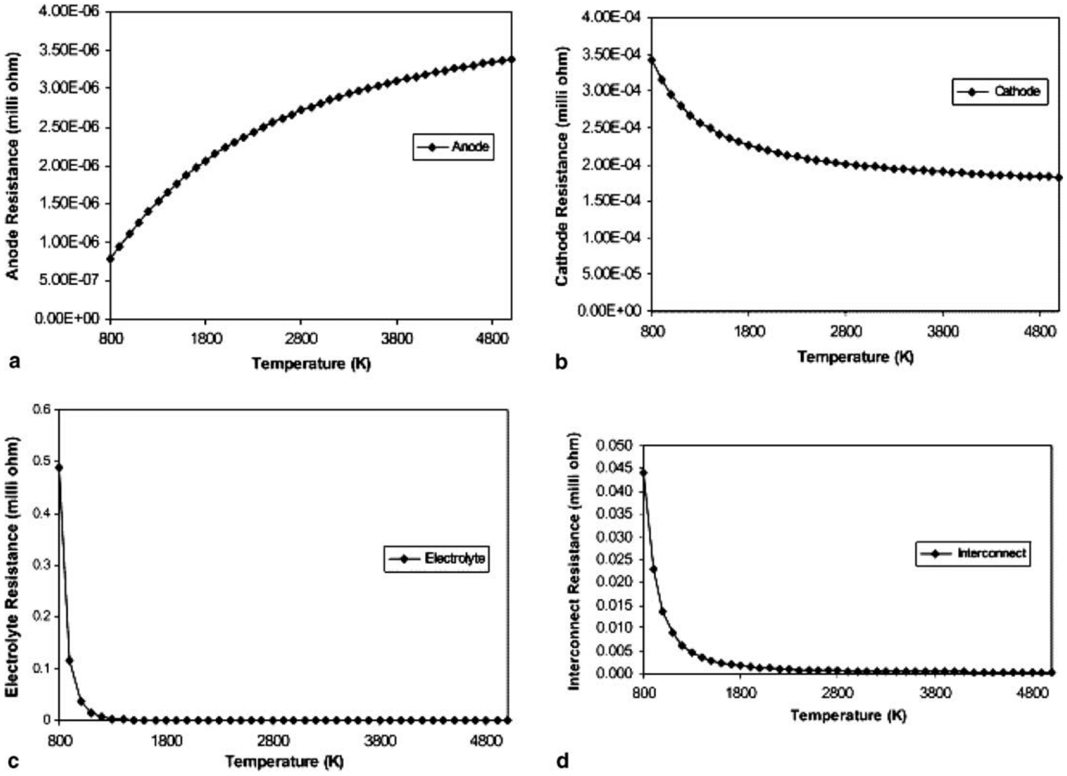

Fig. 14. Effect of temperature on: (a) anode ohmic resistance; (b) cathode ohmic resistance; (c) electrolyte ionic resistance; and (d) interconnector ohmic resistance [102].

from the GDL in the form of small droplets covering the GDL and channel interface [108,109]. These experimental data clearly indicate that a new liquid coverage submodel is needed and could dramatically improve the accuracy of existing numerical models. An initial step has been taken toward this direction [110]. It should be noted that the same issue applies to DMFC modeling. For liquid feed DMFC modeling, current models assume no phase change in water and methanol.

The second area involves the physical properties, such as exchange current density or membrane water content, on which all models rely and which are critically important to model accuracy. In the formulations for activation polarization, the exchange current density is a parameter that relates to the catalyst of the electrochemical reaction. However, the data appearing in the literature are not identical and well explained. Therefore, further study for activation polarization is important for modeling and simulations. At present, most models rely on estimated values for many of the required physical properties mainly because property data are evaluated under a limited set of conditions that may be differ from the conditions of a given model. Each of these estimations carries with it a degree of uncertainty that affects model accuracy. In fact, there is so much uncertainty in the physical properties that it is impossible for a given model to accurately simulate the performance of an actual fuel cell over a range of operating conditions. In general, when modelers validate a model, they do so by adjusting estimated physical property values until the model results come into agreement with experimental results from a fuel cell test. In this manner it is possible to "tune" the model into agreement with any set of test data. However, if the test and simulation conditions are changed (by changing average cell temperature, for example) and the model is not "retuned", the two sets of results will almost certainly disagree.

Some of the specific physical properties for which additional data are needed are listed below:

(1) Hydrogen and oxygen solubility and diffusion coefficients within Nafion and other ion conducting polymers are a function of temperature, polymer hydration level, and gas pressure.
(2) Kinetic parameters such as the exchange current density and charge transfer coefficient for both the oxygen reduction and hydrogen oxidation reactions as a function of temperature, polymer hydration level, and reactant concentration.

(3) Physical characteristics of the catalyst layer such as porosity, tortuosity, and agglomerate size/composition.
(4) Anything having to do with the manner in which liquid water is transported within the cell—for capillary flow, this may amount to determining a relationship between the capillary pressure and liquid water saturation level in the pores of measuring the contact angle within the porous media.

Having these data would certainly lead to an increase in the accuracy of existing numerical models.

The third area where fuel cell modeling can be improved is in the development of focused submodels, aimed at specific transport processes/phenomena that are too complex (computationally large) to explicitly include as part of a general comprehensive model. After all, in many cases the physical properties on which most current models rely are nothing more than a convenient way to describe, on a macroscopic level, something that occurs on a microscopic level. By modeling individual transport processes, it is possible to gain a far greater and more fundamental understanding of fuel cell operation than would be possible through the use of macroscopic models alone. Moreover, any insight gained using focused submodels would be transferable to more general comprehensive models.

The fourth area in fuel cell modeling is water transport through the polymer electrolyte membrane. A majority of numerical models in the open literature have adopted the view of Springer et al. [111] in which the membrane is treated as a homogeneous solvent. Water transport through the membrane in diffusion mechanism, and water diffusivity has been experimentally determined. However, once the membrane is in contact with liquid water, pore-like structures are formed, and the membrane should be treated as a porous media for liquid water transport. A physical description and mathematical model have recently been proposed by Weber et al. [75,113], which could serve as a good starting point. But much more fundamental research is required to fully understand this intricate phenomenon.

The fifth area is in SOFC modeling with the absence of a comprehensive approach capable of fully coupling fluid flows, species transport, heat transfer, and electrochemical kinetics. The fuels for SOFCs might have hydrocarbons that can be reformed internally. The modeling for cell performance is thus complicated by the coupled electrochemical, reforming and shift reactions. For high temperature SOFCs, internal reforming and shift reactions attain chemical equilibrium rather fast. However, for intermediate temperature SOFCs, which are currently very promising due to the development of electrolyte materials, the reaction kinetics for the reforming reaction requires intensive studies. In addition to the above-mentioned capability, since hydrocarbon fuel is a prime choice of SOFC energy systems, a numerical model should be able to simulate the chemical reaction processes inside the pre-reformer and internal reformer before becoming a practical tool for design and optimization. To achieve this modeling capability, a complete integration of transport phenomena, electrochemical kinetics, and large-scale high-performance computational techniques is required.

The sixth area is related to stack modeling capability. Most heat transfer problems occur at stack level rather than a single cell. In order to model a stack, CFD models need to have a robust solution algorithm specifically for stack, combined with parallel computing. To our knowledge, no such detailed model has been published in the open literature.

4. Conclusions

Fuel cell technology promises to be a highly efficient and environmental-friendly power source with broad applications, including transportation and both portable and stationary power generation. Although tremendous progress in fuel cell stack and system development has been made in past decades, fuel cells are still relatively far from being fully commercialized. Numerous technical challenges remain, such as performance, cost, system issues, and choice of fuel. Thermal management plays an important role in fuel cell design and optimization from single cells to the system level. Manufacturing and operational costs can be reduced by optimizing the efficiency of fuel cells through detailed analysis of heat and mass transport phenomena taking place within the stack and system.

This paper has revealed challenges and opportunities of thermal management issues related to low temperature fuel cells and high temperature fuel cells. Thermal management is closely related to water management in PEM fuel cells, where water is used for both humidification of reactant gases and cooling purposes. Thermal management is also a key tool for system energy balance design. This is particularly true for fuel cell systems that include a reformer, which increases the system complexity dramatically. Heat transfer in auxiliary components such as heat exchangers, blowers, burners, etc., also needs careful consideration and implementation.

The high operating temperature imposes stringent requirements both on SOFC design and on defining operating conditions. The key to thermal management of SOFC stacks is to satisfy the high temperature reaction requirement but avoid steep temperature gradients. A better understanding of thermal management issues of fuel cell systems will enable the system's designer to select a cogeneration turbine, to estimate the size of the auxiliary equipment (pumps, compressor, heat exchangers, etc.), and to estimate the optimal set of stack operating conditions for a higher efficiency and long-term operation.

This paper also provides an overview of fuel cell models developed in the past few years. Though the literature shows that many researchers have focused on development of viable fuel cell models, a number of unresolved issues demand more intensive research. The advanced two-phase models for fuel cell application are needed for better understanding of the behavior of heat and mass transfer issues in flow channel. For example for PEMFC modeling, two-phase flow in the cathode gas channel is not modeled at present, despite the importance of flooding. Because of the simplicity and reasonable performance within a certain range of applications, the Darcy model has been used for the majority of existing studies on mass flow in porous electrodes. It has been found that the Darcy model has some limitations, and the second phase should be taken into account when massive bubbles are produced. The loss due to contact resistance is a significant factor in fuel cell operation, and future fuel cell models should address the numerical modeling of contact resistance loss. More accurate models on internal reforming chemistry is needed for SOFC modeling. Advanced stack and system level modeling combined with parallel computing is also required for improved stack and system performance.

References

[1] R.K. Ahluwalia, E.D. Doss, R. Kumar, Performance of high-temperature polymer electrolyte fuel cell systems, J. Power Sources 117 (2003) 45–60.

[2] Y. Cao, Z. Guo, Performance evaluation of an energy recovery system for fuel reforming of PEM fuel cell power plants, J. Power Sources 109 (2002) 287–293.

[3] J. Larminie, A. Dicks, Fuel Cell Systems Explained, John Wiley, 2002.

[4] R. Hahn, M. Krumm, H. Reichl, Thermal management of portable micro fuel cell stacks, in: 19th IEEE SEMI-THERM Symposium, 2003.

[5] S. Um, C.Y. Wang, Three-dimensional analysis of transport and electrochemical reactions in polymer electrolyte fuel cells, J. Power Sources 125 (2004) 40–51.

[6] P.R. Margiott, US Patent No. 6365291, 2002.

[7] R.D. Breault, US Patent No. 6548200, 2003.

[8] J.C. Amphlett, B.A. Peppley, E. Halliop, A. Sadiq, The effect of anode flow characteristics and temperature on the performance of a direct methanol fuel cell, J. Power Sources 96 (2001) 204–213.

[9] H. Dohle, H. Schmitz, T. Bewer, J. Mergel, D. Stolten, Development of a compact 500 W class direct methanol fuel cell stack, J. Power Sources 106 (2002) 313–322.

[10] H. Dohle, J. Mergel, H. Scharmann, H. Schmitz, Development of an air-breathing 50 W direct methanol fuel cell stack, Electrochem. Soc. Proc. (2001) 208–220.

[11] M. Iwata, T. Hikosaka, M. Morita, T. Iwanari, K. Ito, K. Onda, Y. Esaki, Y. Sakaki, S. Nagata, Performance analysis of planar-type unit SOFC considering current and temperature distributions, Solid State Ionics 132 (2000) 297–308.

[12] T.A. Trabold, Minichannels in polymer electrolyte membrane fuel cells, Heat Transfer Eng. 26 (3) (2005) 3–12.

[13] J.M. Moore, J.B. Lakeman, G.O. Mepsted, Development of a PEM fuel cell powered portable field generator for the dismounted soldier, J. Power Sources 106 (2002) 16–20.

[14] D.E. Curtin, R.D. Lousenberg, T.J. Henry, P.C. Tangeman, M.E. Tisack, Advanced materials for improved PEMFC performance and life, J. Power Sources 131 (2004) 41–48.

[15] S. Takahisa, T. Takumi, M. Yu, K. Masaya, H. Naoki, K. Atsushi, US Patent No. 6607856 B2, 2003.

[16] Z. Siroma, N. Fujiwara, T. Ioroi, S. Yamazaki, K. Yasuda, Y. Miyazaki, Dissolution of Nafion® membrane and recast Nafion film in mixtures of methanol and water, J. Power Sources 126 (2004) 41–45.

[17] S.D. Knights, K.M. Colbow, J. St-Pierre, D.P. Wilkinson, Aging mechanisms and lifetime of PEFC and DMFC, J. Power Sources 127 (2004) 127–134.

[18] R. Mohtadi, W.-k. Lee, J.W. Van Zee, Assessing durability of cathodes exposed to common air impurities, J. Power Sources 138 (2004) 216–225.

[19] Y.L. Liu, S. Primdahl, M. Mogensen, Effects of impurities on microstructure in Ni/YSZ-YSZ half-cells for SOFC, Solid State Ionics 161 (2001) 1–10.

[20] C.M. Finnerty, R.M. Ormerod, Internal reforming over nickel/zirconia anodes in SOFCs operating on methane: influence of anode formulation, pre-treatment and operating conditions, J. Power Sources 86 (2000) 390–394.

[21] S.J.A. Livermore, J.W. Cotton, R.M. Ormerod, Fuel reforming and electrical performance studies in intermediate temperature ceria-gadolinia-based SOFCs, J. Power Sources 86 (2000) 411–416.

[22] S.K. Mazumder, Acharya, C.L. Haynes, R. Williams, M.R. von Spakovsky Jr., D.J. Nelson, D.F. Rancruel, J. Hartvigsen, R.S. Gemmen, Solid-oxide-fuel-cell performance and durability: resolution of the effects of power-conditioning systems and application loads, IEEE Trans. Power Electron. 19 (5) (2004).

[23] J.S. Yi, D. Yang, R.D. Breault, A.P. Grasso, G.W. Scheffler, US Patent No. 6794077 B2, 2004.

[24] M.E. Gorman, D.L. Maricle, C.A. Reiser, J.C. Trocciola, L.L. Van Dine, US Patent No. 6723461, 2004.

[25] C. Reiser, US Patent No. 5700595, 1997.

[26] A.P. Meyer, G.W. Scheffler P.R. Margiott, US Patent No. 5503944, 1996.

[27] W.S. Wheat, M.A. Meltser, D.A. Masten, US Patent No. 6727013, 2004.

[28] T.F. Fuller, D.J. Wheeler, US Patent No. 6103401, 2000.

[29] J.A. Rock, L.B. Plant, US Patent No. 6358638, 2002.

[30] C.A. Reiser, US Patent No. 6777115, 2004.

[31] Fuel Cell Handbook, sixth ed., EG&G Technical Services, Inc., Science Applications International Corporation, 2002.

[32] S. Veyo, Westinghouse SOFC field unit status, in: Proceeding of the Fuel Cells '97 Review Meeting,

Westinghouse Science & Technology Center, August 26–28, 1997, Morgantown, WV.

[33] W. Winkler, H. Lorenz, The design of stationary and mobile solid oxide fuel cell-gas turbine systems, J. Power Sources 105 (2002) 222–227.

[34] P. Costamagna, The benefit of solid oxide fuel cells with integrated air pre-heater, J. Power Sources 69 (1997) 1–9.

[35] J. Padullés, G.W. Ault, J.R. McDonald, An integrated SOFC plant dynamic model for power systems simulation, J. Power Sources 86 (2000) 495–500.

[36] J. Palsson, A. Selimovic, L. Sjunnesson, Combined solid oxide fuel cell and gas turbine systems for efficient power and heat generation, J. Power Sources 86 (2000) 442–448.

[37] S.M. Scheifers, D.H. Klosterman, M.K. Chason, K.W. Wyatt, US Patent No. 572322, 1998.

[38] J. Pavio, J. Bostaph, A. Fisher, J. Hallmark, B.J. Mylan, C. Xie, LTCC fuel cell system for portable wireless electronics, Adv. Microelectron. 29 (5) (2002).

[39] M. Broussely, G. Archdale, Li-ion batteries and portable power source prospects for the next 5–10 years, J. Power Sources 136 (2004) 386–394.

[40] A. Cisar, Monopolar DMFC fuel cells for portable applications, in: The Knowledge Foundation's 4th Annual International Symposium-Small Fuel Cells for Portable Power Applications, April 21–23, 2002, Wyndham Washington, Washington, DC, USA.

[41] H. Chang, Technical and commercial issues of DMFC: 5 W for mobile devices and 100 W for portable power, in: 5th Annual International Symposium—Small Fuel Cells for Portable Power Applications, May 7–9, 2003, Hyatt Regency, New Orleans, LA, USA.

[42] J. Hallmark, Portable reformed methanol-to-hydrogen fuel cells: system design, tradeoffs and results, in: Small Fuel Cells for Portable Applications, fifth ed., The Knowledge Press, Brookline, MA, 2004.

[43] E. Bostic, N. Sifer, C. Bolton, U. Ritter, T. Dubois, The US army foreign comparative test fuel cell program, J. Power Sources 137 (2004) 76–79.

[44] S. Gottesfeld, US Patent No. 6686081 B2, 2004.

[45] S. Gottesfeld, Comparative evaluation of direct methanol fuel cells portable power sources: state of the art and projections, in: Small Fuel Cells for Portable Applications, fifth ed., The Knowledge Press, Brookline, MA, 2004.

[46] J. Hallmark, A reformed hydrogen fuel cell system for portable power applications, in: The Knowledge Foundation's 5th Annual International Symposium—Small Fuel Cells for Portable Power Applications, May 7–9, 2003, Hyatt Regency, New Orleans, LA, USA.

[47] R.G. Hockaday, Small diffusion driven fuel cells, in: The Knowledge Foundation's 5th Annual International Symposium—Small Fuel Cells for Portable Power Applications, May 7–9, 2003, Hyatt Regency, New Orleans, LA, USA.

[48] J. Pavio, Performance and design of a reformed hydrogen fuel cell system, in: 2003 Fuel Cell Seminar, November 3–7, 2003, Miami Beach, FL, USA.

[49] H.Y. Kim, Proton exchange membrane with nano-sized proton conductor for DMFC's, in: Small Fuel Cells for Portable Applications, fifth ed., The Knowledge Press, Brookline, MA, 2004.

[50] M. Yonetsu, M. Takashita, H. Sumino, US Patent No. 6506513, 2003.

[51] Z. Guo, Y. Cao, A passive fuel delivery system for portable direct methanol fuel cells, J. Power Sources 132 (2004) 86–91.

[52] Z. Guo, Y. Cao, Experimental studies of biliquid capillary siphons, Chem. Eng. Sci. 60 (10) (2005) 2621–2626.

[53] S. Ha, B. Adams, R.I. Masel, A miniature air breathing direct formic acid fuel cell, J. Power Sources 128 (2004) 119–124.

[54] T. Chen, C.S. Barton, G. Binyamin, Z.Q. Gao, Y.C. Zhang, H.H. Kim, A. Heller, A miniature biofuel cell, J. Am. Chem. Soc. 123 (2001) 8630–8631.

[55] B.E. Logan, C. Murano, K. Scott, N.D. Gray, M.I. Head, Electricity generation from cysteine in a microbial fuel cell, Water Res. 39 (5) (2005) 942–952.

[56] G.T.R. Palmore, H.H. Kim, Electro-enzymatic reduction of dioxygen to water in the cathode compartment of a biofuel cell, J. Electroanal. Chem. 464 (1999) 110–117.

[57] G.T.R. Palmore, Bioelectric power generation, Trends Biotechnol. 22 (3) (2004) 99–100.

[58] C. Xie, J. Bostaph, J. Pavio, Development of a 2 W direct methanol fuel cell power source, J. Power Sources 136 (2004) 55–65.

[59] Y. Zhu, S. Ha, R.I. Masel, High power density formic acid fuel cells, J. Power Sources 130 (2004) 8–14.

[60] Y. Zhu, Z. Khan, R.I. Masel, The behavior of palladium catalysts in direct formic acid fuel cells, J. Power Sources 139 (2005) 15–20.

[61] W. Viestich, A. Lamm, H.A. Gasteiger (Eds.), Handbook of Fuel Cells: Fundamentals, Technology, and Applications, John Wiley, 2003.

[62] P.T. Nguyen, T. Berning, N. Djilali, Computational model of a PEM fuel cell with serpentine gas flow channels, J. Power Sources 130 (2004) 149–157.

[63] P.W. Li, L. Schaefer, Q.M. Wang, T. Zhang, M.K. Chyu, Multi-gas transportation and electrochemical performance of a polymer electrolyte fuel cell with complex flow channels, J. Power Sources 115 (2003) 90–100.

[64] H.T. Liu, T.H. Zhou, Fuel cell performance augmentation: mass transfer enhancement, J. Enhanced Heat Transfer 10 (3) (2003) 257–274.

[65] H. Meng, C.Y. Wang, Large-scale simulation of polymer electrolyte fuel cells by parallel computing, Chem. Eng. Sci. 59 (2004) 3331–3343.

[66] T. Mennola, M. Noponen, M. Aronniemi, T. Hottinen, M. Mikkola, O. Himanen, P. Lund, Mass transport in the cathode of a free-breathing polymer electrolyte membrane fuel cell, J. Appl. Electrochem. 33 (2003) 979–987.

[67] Y.M. Ferng, Y.C. Tzang, B.S. Pei, C.C. Sun, A. Su, Analytical and experimental investigations of a proton exchange membrane fuel cell, Int. J. Hydrogen Energy 29 (2004) 381–391.

[68] N.P. Siegel, M.W. Ellis, D.J. Nelson, M.R. von Spakovsky, A two-dimensional computational model of a PEMFC with liquid water transport, J. Power Sources 128 (2004) 173–184.

[69] D. Natarajan, T.V. Nguyen, A two-dimensional two-phase multicomponent transient model for the cathode of a proton exchange membrane fuel cell using conventional

gas distributors, J. Electrochem. Soc. 148 (12) (2001) A1324–A1335.

[70] T. Berning, N. Djilali, A 3D multiphase multicomponent model of the cathode and anode of a PEM fuel cell, J. Electrochem. Soc. 150 (12) (2003) A1589–A1598.

[71] S. Jemei, D. Hissel, M.C. Péra, J.M. Kauffmann, On-board fuel cell power supply modeling on the basis of neural network methodology, J. Power Sources 124 (2003) 479–486.

[72] W.Y. Lee, G.G. Park, T.H. Yang, Y.G. Yoon, C.S. Kim, Empirical modeling of polymer electrolyte membrane fuel cell performance using artificial neural networks, Int. J. Hydrogen Energy 29 (9) (2004) 961–966.

[73] J.H. Nam, M. Kaviany, Effective diffusivity and water-saturation distribution in single- and two-layer PEMFC diffusion medium, Int. J. Heat Mass Transfer 46 (2003) 4595–4611.

[74] P.W. Li, T. Zhang, Q.M. Wang, L. Schaefer, M.K. Chyu, The performance of PEM fuel cells fed with oxygen through the free convection mode, J. Power Sources 114 (2003) 63–69.

[75] A.Z. Weber, J. Newman, Transport in polymer electrolyte membranes III. Model validation in a simple fuel-cell model, J. Electrochem. Soc. 151 (2004) A326–A339.

[76] H. Meng, C.Y. Wang, Electron transport in PEMFCs, J. Electrochem. Soc. 151 (3) (2004) A358–A367.

[77] P. Argyropoulos, K. Scott, W.M. Taama, One-dimensional thermal model for direct methanol fuel cell stacks, Part I. Model development, J. Power Sources 126 (1999) 169–193.

[78] A.A. Kulikovsky, Two-dimensional numerical modeling of a direct methanol fuel cell, J. Appl. Electrochem. 30 (2000) 1005–1014.

[79] K. Sundmacher, T. Schultz, S. Zhou, K. Scott, M. Ginkel, E.D. Gilles, Dynamics of the direct methanol fuel cell (DMFC): experiments and model-based analysis, Chem. Eng. Sci. 56 (2001) 333–341.

[80] K.T. Jeng, C.W. Chen, Modeling and simulation of a direct methanol fuel cell anode, J. Power Sources 112 (2002) 367–375.

[81] A.A. Kulikovsky, Analytical model of the anode side of the DMFC: the effect of non-Tafel kinetics on cell performance, Electrochem. Communicat. 5 (2003) 530–538.

[82] B.L. García, V.A. Sethuraman, J.W. Weidner, R.E. White, R. Dougal, Mathematical model of a direct methanol fuel cell, J. Fuel Cell Sci. Technol. 1 (2004) 43–48.

[83] P. Argyropoulos, K. Scott, A.K. Shukla, C. Jackson, A semi-empirical model of the direct methanol fuel cell performance, Part I. Model development and verification, J. Power Sources 123 (2003) 190–199.

[84] Z.H. Wang, C.Y. Wang, Mathematical modeling of liquid-feed direct methanol fuel cells, in: Electrochemical Society Proceedings 2001-4, 2001, pp. 286–319.

[85] S.H. Chan, X.J. Chen, K.A. Khor, An electrolyte model for ceramic oxygen generator and solid oxide fuel cell, J. Power Sources 111 (2002) 320–328.

[86] F. Jurado, Modeling SOFC plants on the distribution system using identification algorithms, J. Power Sources 129 (2004) 205–215.

[87] J. Van herle, F. Maréchal, S. Leuenberger, D. Favrat, Energy balance model of a SOFC cogenerator operated with biogas, J. Power Sources 118 (2003) 375–383.

[88] L. Petruzzi, S. Cocchi, F. Fineschi, A global thermo-electrochemical model for SOFC systems design and engineering, J. Power Sources 118 (2003) 96–107.

[89] X.J. Chen, S.H. Chan, K.A. Khor, Simulation of a composite cathode in solid oxide fuel cells, Electrochim. Acta 49 (2004) 1851–1861.

[90] P.W. Li, L. Schaefer, M.K. Chyu, A numerical model coupling the heat and gas species transport processes in a tubular SOFC, ASME J. Heat Transfer 126 (2004) 219–229.

[91] K.M. Walters, A.M. Dean, H.Y. Zhu, R.J. Kee, Homogeneous kinetics and equilibrium predictions of coking propensity in the anode channels of direct oxidation solid-oxide fuel cells using dry natural gas, J. Power Sources 123 (2003) 182–189.

[92] X.M. Guo, H. Kus, C.B. Ching, Simulation of a solid oxide fuel cell for oxidative coupling of methane, Catal. Today 50 (1999) 109–116.

[93] C. Tanner, A.V. Virkar, A simple model for interconnect design of planar solid oxide fuel cells, J. Power Sources 113 (2003) 44–56.

[94] H. Fukunaga, M. Ihara, K. Sakaki, K. Yamada, The relationship between overpotential and the three phase boundary length, Solid State Ionics 86–88 (1996) 1179–1185.

[95] P. Costamagna, P. Costa, E. Arato, Some more considerations on the optimization of cermet solid oxide fuel cell electrodes, Electrochim. Acta 43 (8) (1998) 967–972.

[96] C. Haynes, W. Wepfer, Characterizing heat transfer within a commercial-grade tubular solid oxide fuel cell for enhanced thermal management, Int. J. Hydrogen Energy 26 (2001) 369–379.

[97] D. Larrain, J. Van herle, F. Maréchal, D. Favrat, Thermal modeling of a small anode supported solid oxide fuel cell, J. Power Sources 118 (2003) 367–374.

[98] M.A. Khaleel, Z. Lin, P. Singh, W. Surdoval, D. Collin, A finite element analysis modeling tool for solid oxide fuel cell development: coupled electrochemistry, thermal and flow analysis in MARC®, J. Power Sources 130 (2004) 136–148.

[99] R.J. Boersma, N.M. Sammes, Computational analysis of the gas-flow distribution in solid oxide fuel cell stacks, J. Power Sources 63 (1996) 215–219.

[100] S.G. Neophytides, The reversed flow operation of a crossflow solid oxide fuel cell monolith, Chem. Eng. Sci. 54 (1999) 4603–4613.

[101] G. Dotelli, I.N. Sora, C. Schmid, C.M. Mari, Composite materials as electrolytes for solid oxide fuel cells: simulation of microstructure and electrical properties, Solid State Ionics 152–153 (2002) 509–515.

[102] S.H. Chan, F.C. Low, O.L. Ding, Energy and exergy analysis of simple solid-oxide fuel-cell power systems, J. Power Sources 103 (2002) 188–200.

[103] K.W. Chour, J. Chen, R. Xu, Metal-organic vapor deposition of YSZ electrolyte layers for solid oxide fuel cell applications, Thin Solid Films 304 (1997) 106–112.

[104] K. Haraldsson, K. Wipke, Evaluating PEM fuel cell system models, J. Power Sources 126 (2004) 88–97.

[105] Z.H. Wang, C.Y. Wang, K.S. Chen, Two-phase flow and transport in the air cathode of proton exchange membrane fuel cells, J. Power Sources 94 (2001) 40–50.

[106] L. You, H. Liu, A two phase flow and transport model for the cathode of PEM fuel cells, Int. J. Heat Mass Transfer 45 (2002) 2277–2287.

[107] S. Mazumder, J.V. Cole, Rigorous 3-D mathematical modeling of PEM fuel cells, Part II. Model predictions with liquid water transport, J. Electrochem. Soc. 150 (11) (2003) A1510–A1517.

[108] K. Tûber, D. Pócza, C. Hebling, Visualization of water buildup in the cathode of a transparent PEM fuel cell, J. Power Sources 124 (2003) 403–414.

[109] X.G. Yang, F.Y. Zhang, A.L. Lubawy, C.Y. Wang, Visualization of liquid water transport in a polymer electrolyte fuel cell, Electrochem. Solid-State Lett. 7 (2004) A408–A411.

[110] H. Meng, X.G. Yang, K. Kinoshita, C.Y. Wang, Interfacial droplet phenomena in PEM fuel cells—modeling and visualization, in: Proceedings of 206th ECS Meeting Abstracts, Honolulu, Hawaii, October 3–8, 2004.

[111] T.E. Springer, T.A. Zawodzinski, S. Gottesfeld, Polymer electrolyte fuel cell model, J. Electrochem. Soc. 138 (1991) 2334–2342.

[112] V. Gurau, H. Liu, S. Kakac, A two dimensional model for proton exchange fuel cells, AIChE. J. 44 (11) (1998) 2410–2422.

[113] A.Z. Weber, J. Newman, Transport in polymer electrolyte membranes I. Physical model, J. Electrochem. Soc. 150 (7) (2003) A1008–A1015.