An Introduction to Fuel Cells and Related Transport Phenomena

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In recent years, the development and commercialization of fuel cell systems for primary or auxiliary power for stationary, portable, and automotive systems has rapidly accelerated. In this paper, a basic introduction to fuel cell system components, operation, and related transport phenomena is presented. The advantages and limitations, state of development, and technical issues for three types of systems that are the subject of a majority of contemporary fuel cell research is given. Specifically, the hydrogen-fed polymer electrolyte membrane fuel cell (H₂ PEMFC), the direct methanol fuel cell (DMFC), and the solid oxide fuel cell (SOFC) are described.

Keywords: fuel cells, direct methanol, hydrogen, solid oxide, polymer electrolyte membrane, transport phenomena

INTRODUCTION

In 1839, William Grove conducted the first known demonstration of the fuel cell. It operated with separate platinum electrodes in oxygen and hydrogen submerged in a dilute sulfuric acid
electrolyte solution, essentially reversing a water electrolysis reaction. High temperature solid oxide fuel cells (SOFC) began with Nernst’s 1899 discovery of the still-used yttria-stabilized zirconia solid-state ionic conductor (Nernst, [1899]), although little additional practical development occurred until the 1960’s. Low temperature polymer electrolyte membrane (PEM) fuel cells were first developed by General Electric in the 1960’s for NASA’s Gemini space program. Both PEM and solid oxide fuel cell systems made slow progress until recently. Fueled by technology advances allowing greatly enhanced performance, continuing environmental concern, and a need to develop future power systems that are independent of petroleum fuel stock, interest in all types of fuel cell systems for stationary, automotive, and portable power applications is now very high. In all of these applications, there is a need for reduced system cost, high reliability, and acceptable performance. While the performance of many systems has made the greatest strides, there is still much work to be done.

The fuel cell is a unique and fascinating system. For optimal performance and design, accurate system modeling for prediction of performance as a function of the myriad of possible operating conditions and transients is needed, but such modeling requires an understanding of all relevant phenomena. Although the fundamentals of operation are couched in basic electrochemistry, advances in all areas are made in such a rapid fashion that it is nearly impossible for one researcher to be fully cognizant of all aspects of the state of the art. In order to make strides in the three primary needs of high performance, low cost, and high reliability, one must possess a basic understanding of the principles of electrochemistry, materials and manufacturing, and heat and mass transfer. Because of this highly interdisciplinary nature of fuel cell systems, many successful research programs are built around a team approach involving investigators from complementary disciplines.
The future of power generation will almost certainly include fuel cell systems. The purpose of this article is to provide an overview of the advantages, limitations, and technical challenges of contemporary hydrogen polymer electrolyte membrane, direct methanol, and solid oxide fuel cell technology, with emphasis on critical transport phenomena occurring in these systems.

The basic advantages common to all fuel cell systems are as follows:

1) Potential for a high operating efficiency (up to 50-70%), that is not a strong function of system size.

2) Zero or near-zero greenhouse emissions, with level of pollution reduction depending on the particular fuel cell system and fuel option.

3) No moving parts, except pumps or compressors, thus providing stealthy, vibration-free, and highly reliable operation.

4) A highly scaleable design.

5) Multiple choices of potential fuel feedstocks, from renewable ethanol to biomass hydrogen production.

6) A nearly instantaneous recharge capability compared to batteries.

Before successful market penetration can occur, however, the following limitations common to all fuel cell systems must be overcome:

1) Alternative materials and construction methods must be developed to reduce fuel cell system cost to be competitive with the automotive combustion engine (presently priced at about $20/kW), and stationary power systems (presently priced up to $1,000/kW). The cost of the catalyst no longer dominates the price of most fuel cell systems. Manufacturing and mass production technology is now a key component to the commercial viability of fuel cell systems.
2) Fuel storage and delivery technology must be advanced if pure hydrogen is to be used.

3) Fuel reformation technology must be advanced if a hydrocarbon fuel is to be used for hydrogen production.

4) Transformation from laboratory to practical systems must occur, with reliable lifetime performance. Due to catalyst degradation and electrolyte poisoning, the performance of every fuel cell gradually decreases over time. For an automotive system, the desired time to retain rated performance is about 4000+ hours (equivalent to 100,000 miles at 25 mph), and 40,000+ hours for stationary power systems.

**Fuel Cell Efficiency**

Because a fuel cell directly converts chemical energy into electrical energy, the maximum theoretical efficiency is not bound by the Carnot cycle, and can be shown as in Hamann et al. [1998]:

\[
\eta_{\text{max}} = 1 - \frac{T \Delta S}{\Delta H}
\]  

Values calculated from Eq. (1) range from 60-90%. As an example, a hydrogen fuel cell with water vapor as product has a maximum possible operating efficiency of 80% at an operating temperature of 100 °C, and 60% at 1000°C. In practice, however, higher temperature operation results in reduced activation polarization, and the difference in actual operating efficiency with temperature is less significant. In practice, a 100 kW system operated by Dutch and Danish utilities has already demonstrated an operating efficiency of 46% (LHV) over more than 3700 hours of operation, according to Yamamoto [2000]. Combined fuel cell/bottoming cycle and cogeneration plants promise operational efficiencies as high as 80%, with very low pollution.

Another major advantage of fuel cells compared to heat engines is that efficiency is not a major function of device size, so that high efficiency power for portable electronics can be
realized, whereas small scale heat engines can only reach system efficiencies of 10-15%. While advanced automotive direct injection heat engine efficiencies can achieve 28%, with little hope of significant future gains, future fuel cell systems can realistically achieve nearly 40%.

**Basic Fuel Cell Operation**

Figure 1 shows a generalized schematic of a fuel cell. The drawing is not to scale because it represents a generalized fuel cell system. Electrochemical reactions for the anode and cathode are shown for a hydrogen-fed polymer electrolyte membrane fuel cell (H$_2$ PEMFC), a direct methanol fuel cell (DMFC), and a solid oxide fuel cell (SOFC). Liquid or gas-phase fuel and oxidizer streams enter through flow channels, separated by the electrolyte/electrode assembly. Reactants are transported by diffusion and/or convection to the catalyzed electrode surfaces, where electrochemical reactions take place. In PEM fuel cells (these include H$_2$ and DMFC), transport to the electrode takes place through an electrically conductive carbon paper or carbon cloth backing layer, which covers the electrolyte on both sides. These backing layers (typical porosity 0.3-0.8) serve the dual purpose of transporting reactants and products to and from the electrode and electrons to and from the bipolar plates to the reaction site. An electrochemical oxidation reaction at the anode produces electrons that flow through the bipolar plate/cell interconnect to the external circuit, while the ions pass through the electrolyte to the opposing electrode. The electrons return from the external circuit to participate in the electrochemical reduction reaction at the cathode.

**Performance Characterization**

The single cell combination shown in Figure 1 provides a voltage dependent on operating conditions such as temperature, applied load and fuel/oxidant flow rates. Figure 2 is an illustration of a polarization curve for a fuel cell. The polarization curve, which represents the
cell voltage behavior against operating current density, is the standard measure of performance for fuel cell systems. Due to losses resulting from undesired species crossover from one electrode through the electrolyte and internal currents, the actual open circuit voltage is below the theoretical value. Besides this, there are three major classifications of losses that result in a drop from the open circuit voltage: 1) activation polarization, 2) ohmic polarization, and 3) concentration polarization. The operating voltage of a fuel cell can be represented as the departure from ideal voltage caused by these polarizations:

\[ V_{\text{cell}} = E - \eta_{a,a} - \eta_{a,c} - \eta_{r} - \eta_{m,a} - \eta_{m,c} \]  

where \( E \) is the open circuit potential of the cell, and \( \eta_{a}, \eta_{r}, \text{ and } \eta_{m} \) represent activation, ohmic (resistive) and mass concentration polarization. Activation and concentration polarization occurs at both anode and cathode locations, while the resistive polarization represents ohmic losses throughout the fuel cell.

Activation polarization, which dominates losses at low current density, is the voltage overpotential required to overcome the activation energy of the electrochemical reaction on the catalytic surface, and is thus heuristically similar to the activation energy of purely chemical reactions. Activation polarization is a measure of the catalyst effectiveness at a given temperature, and is thus primarily a material science and electrode manufacturing issue. This type of overpotential can be represented by the Tafel equation at each electrode, as described by Bard and Faulkner [1980]:

\[ \eta_{a,a} + \eta_{a,c} = \frac{RT}{nF\alpha} \ln \left( \frac{i}{i_o} \right)_a + \frac{RT}{nF\alpha} \ln \left( \frac{i}{i_o} \right)_c \]  

where \( \alpha \) is the charge transfer coefficient and can be different between anode and cathode, and represents the portion of the electrical energy applied that is used to change the rate of
electrochemical reaction. In this case, \( n \) is the number of exchange electrons per mole of reactant, and \( F \) is Faraday’s constant. A detailed list of all other symbols used can be found in the Nomenclature. The exchange current density, \( i_o \), represents the activity of the electrode for a particular reaction at equilibrium. In hydrogen PEM fuel cells, the anode \( i_o \) for hydrogen oxidation is so high, relative to the cathode \( i_o \) for oxygen reduction, that the anode contribution to this polarization is often neglected. On the contrary, direct methanol fuel cells suffer significant activation polarization losses at both electrodes. For SOFCs, the operating temperatures are so high that there are very low activation polarization losses. It appears from Eq. (3) that activation polarization should increase linearly with temperature. However, \( i_o \) is a function of the kinetic rate constant of reaction which is commonly modeled with an Arrhenius form, and thus \( i_o \) is an exponentially increasing function of temperature (Bard and Faulkner [1980]). Therefore, the net effect of increasing temperature is to decrease activation polarization. Accordingly, an effect of an increase in temperature would be to decrease the voltage drop within the activation polarization region shown in Fig. 2.

At increased current densities, a primarily linear region is evident on the polarization curve. In this region, reduction in voltage is dominated by internal ohmic losses (\( \eta_r \)) through the fuel cell that can be represented as:

\[
\eta_r = i \left( \sum r_k \right)
\]  

(4)

where each \( r_k \) value is the area-specific resistance of individual cell components, including the ionic resistance of the electrolyte, and the electric resistance of bipolar plates, cell interconnects, contact resistance between mating parts and any other cell components through which electrons flow. With proper cell design, ohmic polarization is typically dominated by electrolyte conductivity. Electrolyte conductivity is primarily a function of water content and temperature in PEM fuel cells, and operating temperature in SOFCs, thus water transport is an especially
important issue in PEM fuel cell design. Even a slight reduction in ohmic losses through advanced materials, thinner electrolytes, or optimal temperature/water distribution can significantly improve fuel cell performance and power density.

At very high current densities, mass transport limitation of fuel or oxidizer to the corresponding electrode causes a sharp decline in the output voltage. This is referred to as concentration polarization. This region of the polarization curve is solely a mass transport related phenomenon, and creative means of facilitating species transport to the electrode surface can result in greatly improved performance at high current density and fuel utilization conditions. The Damköler number ($Da$) is a dimensionless parameter that is the ratio of the characteristic electrochemical reaction rate to the rate of mass transport to the reaction surface. In the limiting case of infinite kinetics (high Damköler number), one can derive an expression for $\eta_m$ based on the Tafel expression as:

$$\eta_m = -\frac{RT}{nF} \ln\left(1 - \frac{i}{i_l}\right)$$

(5)

where $i_l$ is the limiting current density, and represents the maximum current produced when the surface concentration of reactant is reduced to zero at the reaction site. In reality, however, the assumption of a completely mass-transfer limiting case is rarely valid because there is a concentration dependence in the activation kinetics of reaction that affects activation polarization as well. In addition, the Tafel expression is not appropriate near equilibrium conditions and another function must be used. Near equilibrium and in cases of mixed kinetic/mass transfer limitation, a Butler-Volmer expression can be applied to express the resulting current density with a concentration dependence of the reactants (see, for example Um et al. [2000a]), although no explicit expression for $\eta_m$ can be written.
The appropriate mass flow rate of reactants is determined by several factors relating to
several requirements such as the minimum requirement for electrochemical reaction, maintaining
proper water balance and thermal management. In various situations, water management
concerns may dictate the need for increased flow rate, for example. However, the minimum flow
requirements for all fuel cells are determined by the requirements of the electrochemical
reaction. An expression for the molar flow rate of species required for electrochemical reaction
can be shown as:

\[ \dot{n}_{\text{reactant}} = \frac{iA}{nF} \]  \hspace{1cm} (6)

where \( i \) and \( A \) represent the current density and total electrode area, respectively. The
stoichiometric ratio for an electrode reaction is defined as the ratio of reactant provided to that
needed for the electrochemical reaction of interest. For example, consider a \( \text{H}_2 \) PEMFC stack
with 20 plates, an active area of 100 cm\(^2\) per plate, operating at a current density of 1 A/cm\(^2\).
This gives a total active area of 2000 cm\(^2\). For the anode reaction, \( n = 2 \), and one can easily
determine the minimum required flow rate of hydrogen from Eq. (6). If this minimum rate is
doubled, then the anode stoichiometric ratio, \( \xi_{\text{a}} \), is 2. On the cathode side, \( n = 4 \) (see Fig. 1) and
the required molar oxygen flow rate is simply half of the hydrogen molar flow rate. Since air
instead of pure oxygen is typically used, the resulting value must be converted into an air flow
rate. Considering Eq. (6), useful expressions can be developed for the required mass flow rates
as a function of fuel cell electrical power and operating conditions. For example, for the DMFC
cathode and anode, it can be shown that:

\[ \dot{m}_{\text{air}} = 3.56 \times 10^{-4} \frac{P_{\text{stack}}}{V_{\text{cell}}} \xi_{c} \quad \text{and} \quad \dot{m}_{\text{fuel solution}} = 1.71 \times 10^{-3} \frac{P_{\text{stack}}}{V_{\text{cell}}M_{\text{F}}} \xi_{\text{a}} \]  \hspace{1cm} (7)
where $P_{\text{stack}}$ is the fuel cell stack electrical power output, $V_{\text{cell}}$ is the operating cell voltage, $Mol$ is the fuel solution molarity, and other terms can be found in the Nomenclature section. These useful expressions can be used to approximate the flow requirements for any sized system. For example, a 2 kW DMFC stack operating at an average of 0.4 V per plate and a stoichiometry of 3 will require approximately 5.34 g/s of air. Similar expressions can be written for other fuel cell systems.

**Description of Materials**

Table 1 lists species and component materials commonly used in fuel cell systems, as well as some other general information. The electrolyte functions to transport ions created by reaction at one electrode to the other. In PEM fuel cell systems, the proton is transported through the electrolyte, whereas in SOFC systems, the $O^{2-}$ ion is transferred. The electrolyte can be a solid ionic conductive polymer (PEM fuel cells), liquid acid or base (alkaline and phosphoric acid) or ceramic material, such as yttria-stabilized zirconia (SOFC). It is always desirable to reduce electrolyte thickness to reduce internal ohmic losses. However, the electrolyte must also be relatively impermeable to fuel and oxidizer to minimize reactant crossover, stable in oxidizing and reducing environments over time, and maintain structural integrity at operating conditions. Permeability of the electrolyte to the reactants results in mixed potentials at the electrodes, reducing performance, and possibly degrading the catalyst. The requirements for the electrode include low activation losses, long-term stability, and acceptable ionic/electronic conductivity. In low temperature PEMFC systems, the catalyst material most frequently used is platinum, or platinum/ruthenium, while high temperature SOFC systems (with greatly reduced activation polarization) utilize much cheaper catalyst materials such as nickel.
The bipolar plate/cell interconnect must satisfy several requirements: impermeability to reactants, chemical stability in oxidizing and reducing environments, high electrical conductivity, and the ability to be produced as thin, low cost, and light weight components. In contrast to PEM fuel cells, the connection between the anode and cathode between cells in a SOFC stack is commonly referred to as the interconnect, rather than the bipolar plate. This is because the inter-cell electrical connection and flow field are not necessarily the same component, depending on the particular SOFC design. In the case of the higher-temperature SOFC system, the interconnect material must also have similar thermal expansion coefficients as other cell components to avoid excessive local stress distributions during cell operation and manufacture. Many different materials have been used for bipolar plate/cell interconnect material. Laboratory and prototype materials have primarily focused on satisfying the basic physical property requirements to permit high-performance testing. PEM fuel cells have generally utilized expensive, individually machined graphite or even gold-plated stainless steel flowfields for prototype and small-scale laboratory engines, although future mass production bipolar plates are likely to utilize an injection molding process of polymer doped with a conducting phase.

**Description of a Fuel Cell Stack**

A single cell can be made to achieve whatever current and power is required, simply by scaling up the size of the active electrode area. However, the output voltage of a single H₂ PEMFC, DMFC, or SOFC is less than 1 V for realistic operating conditions. Therefore, for most applications and for compact design, a fuel cell stack of several individual cells connected in series is used. Figure 3 shows the 1 kW, 20 cell H₂ PEMFC stack at the Penn State Electrochemical Engine Center (ECEC). Other components necessary for fuel cell system
operation are shown, such as compressors for reactant species flow, an electronic control system, and a fuel storage and delivery system (in this case compressed hydrogen). For the H₂ PEM fuel cell, separate humidification and cooling systems are also needed to ensure proper membrane content and adequate removal of waste heat, so that system temperature remains below Nafion® perfluorinated membrane material limits of around 120 °C. A battery is used to power pumps during the start-up transient. For the DMFC, a liquid pump is required to deliver anode flow. In a SOFC, a pre-heating system is needed to raise cell temperatures during cold start-ups. This is typically accomplished with a combustion chamber that burns fuel and oxidizer gases. In all commercial fuel cells, provision must be made for effluent recovery. Fuel utilization efficiency is not 100% due to concentration polarization limitation on performance, so that unused hydrogen in the case of SOFC and H₂ PEMFC, or liquid and vapor-phase methanol in the case of DMFC, must be actively recycled, utilized, or converted prior to exhaust to the environment. Potential schemes include the use of condensers, recyclers, secondary burners, or catalytic converters.

**Hydrogen Fuel Storage**

Presently, the problem of hydrogen storage and delivery is a roadblock to mass commercialization of fuel cells for automotive and stationary applications. Hydrogen storage and delivery on a mass scale is a long-term issue. While now nearly universally accepted, the future conversion to a “hydrogen economy” will be extremely costly and will take decades to complete. Prior to this, it is likely that local hydrogen generation plants will be built in select locations such as California, where initial demand and government subsidy would be high. There are several possibilities for hydrogen storage in the immediate future, including utilization
of compressed hydrogen, liquefied hydrogen, storage in a metal hydride, and storage in a hydrocarbon until release through a reformation process.

Compressed hydrogen is considered by many as the best future on-board storage technology for portable and automotive applications. In the past, 24.8 MPa (3600 psig) metal tanks have been used, although higher pressure, 34 MPa (5000 psig) light-weight polycarbonate tanks are now in use. Several prototype vehicles utilize compressed hydrogen. This method has the drawbacks of difficult market acceptance, safety, and low energy storage density of 31 g/L at 34 MPa.

Liquefied hydrogen has a higher storage density of 71 g/L, and has been the storage and delivery method of choice for large industrial-scale quantities. However, the liquefaction process is highly energy intensive, there is a health concern with consumers handling a cryogenic fluid, and fuel evaporation rates can be as high as 1-2% per day, even with heavy insulation. Besides the high relative cost, a major problem with this form of storage is that hydrogen venting of hydrogen gas will necessarily occur, causing safety concerns. While acceptable for demonstration purposes, liquefied hydrogen is not a likely future storage technology for portable or automotive applications.

Another potential storage medium is metal hydrides. Hydrogen can bond with certain metal compounds as a metal hydride, releasing hydrogen when heated. Conventional hydride technology allows 1-2 weight percent of H\textsubscript{2} stored in the metal. For a 600 km drive, a 460-920 kg fuel system would be required with conventional hydrides, an impractical weight for automotive applications. Some small devices can benefit from the convenience of hydride use, such as computers or cell phones. If higher storage percentages can be reached in operating systems, hydride technology could become the dominant mechanism of hydrogen storage.
Before this becomes a viable solution, however, it must be demonstrated that problems with refueling time, product cycle life, cost, and sensitivity to impurities have been overcome.

Hydrogen can also be produced in large quantities at relatively high efficiency by hydrocarbon reformation. The three main types of reformation are steam reforming, partial oxidative reforming (POX) and autothermal reformation. In all three schemes, operation is at a low enough temperature so that nitrous oxide (NOx) formation is negligible. Endothermic steam reforming is a mature, effective, and relatively inexpensive technology for light hydrocarbons. Steam reformation utilizes the water-gas shift reaction and a catalytic bed to convert a hydrocarbon, CO and steam to CO\textsubscript{2} and H\textsubscript{2}. H\textsubscript{2} conversion efficiencies of steam reforming are around 80%.

High temperature (~800-1300 °C) POX reformation occurs via partial combustion of hydrocarbons to form hydrogen and carbon monoxide. Several companies are actively studying compact POX reformers with advanced catalysts for reduced temperature operation. Advantages of this process are that it is exothermic and responsive to varying loads, can handle heavier hydrocarbons, and does not require a catalyst bed or a source of steam. However, since the output has a high fraction of CO and low H\textsubscript{2} conversion efficiencies of ~50%, additional tailoring (via water-gas-shift reaction) is needed for use in PEM systems intolerant of CO. Without additional tailoring, however, POX reformation is well suited for the CO-tolerant high temperature SOFC systems.

Autothermal reforming essentially combines aspects of both POX and steam reforming, utilizing the exothermic heat release of combustion to balance the endothermic steam reformation process. Fuel and oxidant with steam is provided to the fuel processor, which consists of a combustor and a catalytic bed. The advantage of this system is that it is more
responsive to unsteady load than steam reformation, and has higher hydrogen conversion efficiency than POX reformation.

The temperature at which a particular fuel is reformed has a tremendous impact on its potential use in different fuel cell systems. For example, one reason methanol is an attractive option for PEM fuel cells is that it reforms at around 200-300°C, just above the operating temperature of the fuel cell. Alternatively, an automotive PEM fuel cell utilizing hydrogen reformed from gasoline is less attractive, because the high (~800°C) reformation temperature of gasoline necessitates a large heat exchanger to dump thermal energy from the reformer, reducing efficiency. Alternatively, the obvious thermal matching between gasoline or diesel fuel reformation and SOFC operating temperature makes this choice of fuels attractive in SOFC applications.

Although reformation technology is receiving intense interest, it is believed that ultimately hydrocarbon reformation for hydrogen production will not provide a permanent energy solution. Instead, hydrogen production from solar, nuclear, biomass, or other renewable sources will be used. In the near term, however, hydrocarbon reformation represents a viable conduit between the present petroleum and a future hydrogen-based fuel economy. In the near term, unless other technologies such as metal hydrides or nanotube hydrogen storage have real breakthroughs, it is expected that reformed hydrocarbons will play a major role in future fuel cell systems.

THE HYDROGEN PEM FUEL CELL

The hydrogen polymer electrolyte membrane fuel cell (H₂ PEMFC) has received the most attention in recent years, primarily because of its relatively high performance, rapidly advancing technology, and system simplicity. The H₂ PEMFC is fueled either by pure hydrogen, or from a diluted hydrogen mixture generated from a hydrocarbon reformation process. Incredible
progress has been made in H\textsubscript{2} PEMFC technology since the early 1990’s. Perhaps the most advanced H\textsubscript{2} PEMFC full-size stack design has a power density of 1.3 kW/L (Budd [2000]). However, improvements are made so rapidly that future increases in power density are expected.

Though first developed in the 1960’s for the U.S. Gemini Space Program, H\textsubscript{2} PEMFCs were soon replaced by alkaline fuel cells during the Apollo and subsequent space programs due to water management difficulties (Larminie and Dicks [2000]). As a testament to the increased performance and reliability of PEMFC systems, NASA is committed to using H\textsubscript{2} PEM fuel cells in future shuttle applications (Warshay and Prokopius [1990]).

**H\textsubscript{2} PEMFC Performance**

Modern H\textsubscript{2} PEM fuel cells operate at 60-100ºC. The anode and cathode catalyst is typically ~2 nm sized platinum powder supported on significantly larger size carbon particles with a platinum loading of ~ 0.2 mg/cm\textsuperscript{2}. This represents a major breakthrough in required catalyst loading from the 28 mg/cm\textsuperscript{2} of the original 1960’s H\textsubscript{2} PEMFC. As a result, the catalyst is no longer the dominating factor in fuel cell cost. A typical performance curve for a H\textsubscript{2} PEMFC is shown in Fig. 4. Most stacks operate around 0.6 V per cell, in order to maintain a balance between system power density and efficiency losses leading to cooling requirements. There is always a desire to operate at higher voltages, because of increased efficiency and reduced flow requirements. However, power density typically peaks below 0.6 V, so there is a size tradeoff for high voltage operation. Although power density can be higher, operation at lower voltage results in increased waste heat that needs to be removed from the cell to prevent PEM dehydration and overheating. In addition, according to Eq. (7), operation at reduced voltage requires additional flow of anode and cathode species, and increased associated parasitic pumping losses. Anode and cathode stoichiometry requirements are low, with typical values of 2
or less for the cathode and even lower values for the anode. Although older designs utilized humidified anode and cathode flows, modern designs require only a humidified anode flow to maintain a proper water balance in the PEM.

**Technical Issues of the H₂ PEMFC**

Active research areas for the H₂ PEMFC include: 1) increasing PEM CO tolerance, 2) optimizing thermal and water management, 3) design of the membrane electrode assembly (MEA), 4) optimizing flowfield design, and 5) reducing component cost. If reformed hydrocarbons are used as fuel, perhaps the greatest potential area for advance is in CO tolerance. Carbon monoxide gas has an affinity for platinum, thereby blocking site access to hydrogen and reducing performance. Although performance can be regained after poisoning if CO is removed from the fuel stream, H₂ PEMFC output is greatly degraded with CO contamination in the fuel stream at levels as low as 10 ppm (Springer et al. [2001]). Addition of CO scrubbing equipment to reformation systems to achieve this low level of contamination greatly increases fuel cell system cost, size and complexity. Depending on the size of the system, the CO scrubber can even be larger than the fuel cell stack itself. Another technique for possible CO removal from fuel streams, in levels up to around 1000 ppm, is bleeding a small percentage of air or oxygen in with the fuel flow to promote oxidation of the CO (Stumper et al. [1998]). However, careful control of the oxygen must be maintained to prevent loss of performance from hydrogen oxidation with excess oxygen.

Identification of catalysts capable of withstanding high levels of CO, while maintaining low activation polarization for hydrogen oxidation would greatly benefit H₂ PEMFC development. Attempts are also being made to develop electrolyte materials capable of withstanding higher temperatures. This would permit decreased catalyst loading, reduced cooling system
requirements, reduced activation polarization, and higher CO tolerance in the fuel stream due to decreased CO sticking coefficient.

In the H\textsubscript{2} PEMFC, thermal management is also a major issue. The energy that is released by electrochemical reaction is split between electrical and thermal components. The waste heat rate can be as much as 60\% or more of the output and is roughly equal to the current density \(i\) multiplied by the departure from actual open circuit voltage:

\[
P_{\text{waste}} = niA(V_{oc} - V_{cell})
\]

where \(n\) is the number of cells in series in the stack, \(V_{cell}\) is the cell operating voltage and \(V_{oc}\) is the theoretical open circuit voltage and can be calculated from basic thermodynamic data, e.g. Newman [1991]. Waste heat must be properly managed with cooling channels in the stack, which take up space and require parasitic pumping losses. The choice of coolant is based on the necessary properties of high specific heat, non-conductive, non-corrosive, sufficient boiling/freezing points for operation in all environments, and low viscosity. As an approximation, the required mass flow rate of coolant for a desired maximum coolant temperature rise, can be written as:

\[
\dot{m}C_p\Delta T = P_{\text{waste}} = niA(V_{oc} - V_{cell})
\]

This assumes all of the waste heat is removed by the coolant flow. Note that smaller systems can be air cooled, while larger systems must use a liquid coolant, with higher specific heat. Laboratory systems typically use deionized water, although practical systems exposed to the environment must use a lower freezing point solution. Equation (9) is valid for all fuel cell systems.

Water management and humidification is another major issue in H\textsubscript{2} PEMFC performance. Depending on operating conditions, a membrane can have a highly non-homogeneous water (and
therefore ionic conductivity) distribution. The membrane beneath a long channel may be dried by hot inlet flow, ideally saturated near the middle of the cell, and experiencing flooding near the exit. It is difficult in practice to maintain an ideal water distribution throughout the length of the cell. Advanced modeling of two-phase flow and transport in PEM fuel cells has been treated by Wang et al. [2001].

Water transport through the electrolyte occurs by diffusion, electro-osmotic drag, and hydraulic permeation resulting from a pressure difference across the anode and cathode. Diffusion through the electrolyte can be represented with Fick’s law, and appropriate expressions relating to diffusion coefficients for Nafion® can be found in several references, e.g. Motupally et al. [2000]. Electro-osmotic drag of water through Nafion® membranes has been recently studied by Ren and Gottesfeld [2001]. A water drag coefficient ($\lambda_{\text{drag}}$) of 1-5 H$_2$O/H$^+$ was shown for a fully hydrated Nafion® 117 membrane. The drag coefficient was shown to be a nearly linearly increasing function of temperature from 20-120°C. Hydraulic permeation of water through the membrane is typically small for H$_2$ PEMFCs due to the low pressure differences between the two sides. At the cathode surface, the oxygen reduction reaction shown in Fig. 1 will result in water production proportional to the current density. Considering the cathodic water reduction reaction, and combining the different forms of water transport through the membrane, the molar water transport and creation at the cathode can be shown as:

$$j_{H_2O} = -D \frac{\Delta C_{c-a}}{\Delta x} + \frac{iA}{F} \left(\lambda_{\text{drag}} + 0.5\right) - \frac{aK}{l} \Delta P$$

(10)

At a typical operating temperature of 70°C, $\lambda_{\text{drag}}$ was determined by Ren and Gottesfeld [2001] to be around 3, or 86% of the current-dependent transport. Since the reduction and electro-osmotic drag result in water transport and generation at the cathode surface, the flux of water by diffusion can be either from or to the anode surface, depending on flow and humidity conditions.
Membrane performance suffers without sufficient water, because PEM ionic conductivity is directly related to the degree of water content and temperature, as correlated by Springer et al. [1991]. Alternatively, excessive water at the cathode can cause flooding i.e., liquid water accumulation at the cathode surface that prevents oxygen access to the reaction sites. Flooding is most likely near the cathode exit under high current density, high humidification, low temperature, and low flow rate conditions. However, in most H₂ PEMFC systems, drying is more of a concern than flooding, and an external humidifier is needed. The maximum mass flow rate of water that can be removed from the fuel cell by gas flow can be shown by letting the exit relative humidity, $\phi$, go to 1 in the following expression:

$$\dot{n}_{H_2O, removed} = \dot{n}_{others} \left( \frac{P_{g,sat} \phi}{P - P_{g,sat} \phi} \right)$$  \hspace{1cm} (11)$$

where $\dot{n}_{others}$ is the molar flow rate of all other species in the flow besides water vapor, and $P$ is the total pressure. Note that the consumption of oxygen at the cathode will result in a decrease in $\dot{n}_{others}$ along the flow path that can be non-negligible, depending on stoichiometry and species. For air with a stoichiometry of 2, the total oxygen consumed would be around 10% of the total flow, reducing the molar flow rate of water vapor capable of being removed by the incoming flow by this percentage. Clearly, flow stoichiometry and temperature dominate the water removal process, considering saturation vapor pressure varies in a nearly exponential way with temperature. The inlet relative humidity also should affect the ability of the flow to remove water, however this effect is typically quite small. This is a result of the vast difference between typical ambient temperature and operating temperature $P_{g,sat}$ values. For example, even fully saturated inlet flow drawn from an ambient air source at 20°C ($P_{g,sat} = 2.338$ kPa) contains only 5% of the water required for saturation in a fuel cell operating at 80 °C ($P_{g,sat} = 47.39$ kPa).
Flowfield Design in H\textsubscript{2} PEM Fuel Cells

In PEM fuel cells, flow conditions are typically laminar, with Re numbers on the order of 100-1000. In general, the flowfield should be designed to minimize pressure drop (reducing parasitic pump requirements), while providing adequate and evenly distributed mass transfer through the carbon diffusion layer to the catalyst surface for reaction. Reduction in performance of scale-up versions of laboratory fuel cells is common, and is mainly a result of non-homogeneous species distribution. In H\textsubscript{2} PEM fuel cells, the reaction is typically limited by the cathode kinetics. There is typically a nearly negligible anode activation polarization unless the inlet flow of hydrogen is greatly diluted. As described by Gottesfeld [1997], at a current density of 1 A/cm\textsuperscript{2}, a 0.4 –0.5 V voltage loss is required to overcome cathode activation polarization losses, while a loss of only 20-30 mV results at the hydrogen anode for the same current density. Since air is generally used as the oxidizer, significant cathode concentration polarization can also exist without adequate flow rates and properly designed flow fields. Three basic channel configurations of 1) serpentine, 2) parallel, and 3) interdigitated flow have been used in PEM fuel cells, although some small-scale fuel cells do not use a flow field and rely on diffusion processes from the environment.

Figure 5 (a) illustrates a continuous serpentine path flow field. The flow path is continuous from start to finish. An advantage of the serpentine flow path is that any obstruction in the path, such as a water droplet, will not block all activity downstream of the obstruction. In an obstructed serpentine channel, the reactant gas is forced to bypass the channel by flowing under the current collecting rib, through the porous backing layer, and emerges in an adjacent channel. The bypass flow can then diffuse back toward the location of the obstruction, so that the net effect of the obstruction will be an increased pressure drop, but no loss of active area.
Conversely, in a parallel configuration, as shown in Fig. 5 (b), an obstruction in one channel results in flow redistribution among the remaining channels and a dead zone downstream of the blockage. This dead zone will become deprived of reactant, and hence be inactive.

The disadvantages of serpentine flow include a higher pressure drop than parallel flow, and the fact that reactant is depleted through the length of the channel, so that adequate species must be provided to avoid excessive concentration polarization losses. Parallel flow channels require less mass flow per channel for an equivalent stoichiometry and provide more uniform species distribution and reduced pressure drop. Since the hydrogen reaction is typically not rate limiting, and water blockage in the humidified anode can occur, a serpentine arrangement is typically used for the anode in smaller PEM fuel cells. As the active area of cells gets very large, however, often a combined parallel/serpentine arrangement is utilized.

A third type of flowfield design, referred to as interdigitated, can be traced back to work by Ledjef et al. [1993], and Wilson et al. [1995]. In the interdigitated design, the ends of the flowfield channels are blocked, so that flow is forced through the porous backing layer under the current collecting rib and into the adjacent channel, as shown in Fig. 6. This type of flow field has the major advantage of transporting flow directly to the catalyst reaction surface by forced convection, rather than solely by diffusion, as in the conventional design. This can reduce concentration polarization at high power load conditions, where the reactant species is being quickly consumed. Performance of an H₂ PEMFC with an interdigitated cathode has recently been modeled and is discussed by Um and Wang [2000b]. Another benefit of this design is enhanced water removal from flooded catalyst sites, and increased usage of active area located under current collecting ribs, depending on backing layer porosity and species diffusivity. The main drawback of this design is the increased pressure drop and possible wear on the electrode.
In the cathode, concentration polarization losses occur readily, water accumulation that can lead to flooding can occur, and some unused active area below rib shoulders can exist. Therefore, the interdigitated flowfield design is ideally suited for the cathode in an H₂ PEMFC when operated under low stoichiometric ratio or high current density conditions.

**Reactant Bypass**

In serpentine flow paths, the flow can result in a relatively high pressure drop. In addition, reactant consumption can lead to additional pressure drop. If not designed properly, some flow channels with a high local pressure may be adjacent to channels with low pressure. In this case, resultant pressure mismatch can lead to reactant bypass, a phenomenon of *undesired* reactant penetration through the backing layer, underneath a current collecting rib, and into another flow channel. This is similar conceptually to interdigitated flow, only no intentional channel blockage exists, and bypass is not desired. This can lead to drastically reduced performance for a diluted fuel or oxidizer flow stream, as active area downstream of the bypass location will be starved of reactant. This type of phenomenon has been modeled using the computational fluid dynamics model of Um and Wang [2000b]. The predicted streamtraces of a test case with a serpentine path with a 180° turn are shown in Fig. 7, and show significant hydrogen bypass underneath the current collecting rib, for the conditions chosen.

The fraction of flow that is bypassed under the backing layer is controlled by the ratio of the pressure drop of the flow through the channel to the pressure drop through the backing layer. If the pressure drop through the backing layer to the bypass emergence point is low, relative to the pressure drop through the channel to the same bypass emergence point, significant bypass can occur.
Assuming laminar flow, the pressure drop through the channel a distance \( L \) from the bypass location to the bypass emergence point can be derived from laminar flow theory (White [1999]):

\[
\Delta P_{\text{flow path}} = \frac{32L \mu V}{d_n^3} \quad (12)
\]

where \( V \) is the channel bulk flow velocity. An estimate of the pressure drop through the porous backing layer can be estimated with Darcy’s law (Vafai and Hadim [2000]):

\[
\Delta P_{\text{Backing}} = \frac{U_{\text{ave}} \cdot \mu}{\kappa} \cdot \Delta S \quad (13)
\]

where \( \rho \) is the density of the fluid, \( U_{\text{ave}} \) is the bulk average velocity through the porous medium, \( \Delta S \) is the porous medium thickness in the direction of flow (equivalent to the current collecting rib shoulder width), and \( \kappa \) is the permeability of the backing layer. The backing layer permeability is a highly non-linear function of porosity, and can be shown by the Kozeny-Carman relation (Vafai and Hadim [2000]):

\[
\kappa = \frac{\varepsilon^3 d_s^2}{180(1-\varepsilon)^2} \quad (14)
\]

where \( \varepsilon \) is the porosity of the porous medium and \( d_s \) is the diameter of the theoretical spherical particles the medium is modeled to consist of. A dimensionless parameter termed the bypass ratio (BPR) can be defined as the ratio of pressure drop through the channel to the backing layer:

\[
\text{BPR} = \frac{32L \nu \kappa}{d_n^2 U_{\text{ave}} \Delta S} \quad (15)
\]

Obviously, the channel bulk flow velocity and the average bypass velocity, \( U_{\text{ave}} \) will be related, but the basic physics can be understood with this relationship. If BPR is much greater than unity, significant bypass should occur, if BPR is much less than unity, significant bypass can be avoided. However, this concept has yet to be verified experimentally. It is interesting to
note that in Eq. (15), channel pressure, flow viscosity, and temperature should have little or no effect, while the hydraulic diameter, channel length, current collecting rib thickness, and backing layer permeability are the key physical parameters. Hydraulic diameter $d_h$ and $\kappa$ dominate as a result of their non-linear relationship to BPR. Therefore, backing layer compression to reduce effective porosity under by current collecting ribs is also a major factor in avoidance of reactant bypass.

**THE DIRECT METHANOL FUEL CELL**

The liquid-fed direct methanol fuel cell (DMFC) has received enormous interest recently because DMFC systems require less ancillary equipment and are therefore much more simplified compared to an H$_2$ PEMFC. Note that fuel cells that utilize reformed methanol are referred to as indirect methanol fuel cells. Some direct methanol fuel cells also utilize fuel heated above the methanol solution boiling point of ~95°C at 1 atm; these are referred to as vapor-fed direct methanol fuel cells. Because of system simplicity, a majority of methanol fuel cell research has been focused on liquid-fed DMFC development. Figure 8 shows a 50 cm$^2$ active area, highly instrumented, transparent DMFC designed and built by the Penn State Electrochemical Engine Center. While both H$_2$ PEMFC and DMFC utilize polymer electrolyte membranes, and both transfer hydrogen protons through the electrolyte, the DMFC feeds a solution of methanol and water (typically 0.5-2 molar) to the anode, where it is internally reformed by the catalyst. The additional complexities of the low temperature internal reformation prevent the DMFC from obtaining the same level of fuel cell power density as the H$_2$ PEMFC under the same conditions. For the DMFC, both anode and cathode activation polarizations are significant and are the same order of magnitude. However, reduced performance compared to the H$_2$ PEMFC is tolerable in light of other advantages of the DMFC, namely:
1) Because the anode flow is mostly liquid, there is no need for a separate cooling or humidification subsystem, as in the H₂ PEMFC.

2) Liquid fuel used in the anode results in lower parasitic pumping requirements compared to gas flow. In fact, several designs operate without any external parasitic losses, relying on natural forces such as capillary action, buoyancy, and diffusion to deliver reactants.

3) The highly dense liquid fuel stored at ambient pressure eliminates problems associated with reformation or on-board hydrogen storage.

As a result of the great reduction in system components and complexity, the DMFC total system power density may eventually be greater than that of the H₂ PEMFC. The lack of ancillary equipment makes the DMFC design ideal for portable electronics presently using batteries. In many such systems, there is a need to dissipate heat from electronics that can be facilitated by pre-heating the methanol solution, thus enhancing performance of the fuel cell at the same time.

Besides relatively low anodic activity, other disadvantages of the DMFC are related to use of methanol. Methanol is toxic; can spread rapidly into ground water; has a colorless flame; and is more corrosive than gasoline. In addition, it would be financially difficult to fuel providers for an intermediate switch to a methanol economy, only to be replaced by a hydrogen economy shortly thereafter. As a result of these potential drawbacks, there is a great debate in the fuel community over the future use of methanol for fuel cells.

**DMFC Performance**

It is very difficult to compare performance from different research groups, due to the fact that operating conditions and material properties are so different. Temperatures run from 50 to nearly 100°C, cathode pressures go from nearly ambient to 5 atmospheres of air or oxygen
(anode is generally at ambient pressure unless temperatures above boiling are used), catalyst loading and membrane assembly technique are also greatly varied. Several polarization curves generated at the Penn State Electrochemical Engine Center representing typical performance are shown in Fig. 9. Other designs, using different stoichiometries and temperatures have achieved very different results. Much greater performance has been achieved in higher temperature, pressure, and pure oxygen environments useful for niche applications, e.g. Baldauf and Preidel [1999]. Relatively poor performance is tolerated in smaller systems for portable electronics. The catalyst loading has a large effect on performance. Due to the fact that Pt-Ru is used as the anode catalyst to limit CO poisoning, a carbon-supported catalyst layer is typically too thick, and can result in unacceptable ohmic losses. It should be noted that catalyst application technology is highly varied and rapidly evolving, so that some groups have utilized a carbon supported loading (e.g. Aricò et al. [1999]) or different techniques as well.

**Technical Issues of the DMFC**

Although the DMFC is quite promising, four main technical issues affecting performance remain, including: 1) water management, 2) methanol crossover, 3) managing two-phase transport in the anode, and 4) high activation polarization losses and catalyst loading. While significant progress has been made by various groups to determine alternative catalysts, additional work is needed.

Although external humidification is typically not needed in the DMFC due to the liquid anode solution, prevention of cathode flooding is critical to ensure adequate performance. Flooding is more of a concern for DMFCs than H₂ PEM fuel cells. This is because, in addition to the terms shown in Eq. (10) for the H₂ PEMFC, there is water production at the cathode via methanol oxidation resulting from methanol crossover according to:
\[ \text{CH}_3\text{OH} + \frac{3}{2} \text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \]  \hspace{1cm} (16)

Therefore, 2 moles of water will be produced for every mole of methanol that crosses over to the cathode, as discussed in the following paragraph. In addition, due to the liquid solution in the anode, the direction of diffusion will always be from the anode to the cathode, until flooding occurs at the electrode. In this case, there is no water activity gradient, and diffusion through the electrolyte ceases. To prevent flooding, cathode airflow must be adequate to remove water at the rate that it arrives and is produced at the cathode surface. Therefore, typical cathode stoichiometries are significantly greater than that needed to supply adequate oxidant to the reaction site.

Another critical issue in the DMFC is methanol crossover from the anode to cathode. This is a result of diffusion, electro-osmotic drag, and hydraulic permeation from pressure gradients. Therefore, an expression for the methanol crossover through the membrane can be written similar to Eq. (10), with different transport properties. When crossover occurs, the mixed potential, caused by the anodic reaction on the cathode electrode, reduces cell output and the true stoichiometry of the cathode flow by consumption of oxygen outside the desired reduction reaction.

Methanol diffusion through PEMs has been studied extensively (e.g. Ren et al. [2000], Cruickshank and Scott [1998], and Tricoli et al. [2000]). Methanol diffusion rate estimations vary between groups, but in general are on the order of $10^{-7}$ to $10^{-6}$ cm$^2$/s for Nafion® under typical DMFC operating conditions. Electro-osmotic drag of methanol through Nafion® has also been studied extensively by various groups, with a measured drag coefficient about an order of magnitude less than that of water. Because of the hydraulic permeation effect, cathode pressures in the DMFC are typically higher than anode pressures. As cathode pressure is
increased, the resulting increase in voltage output that is not predicted from the Nernst relationship (see, e.g. Newman [1991]) is attributable to reduced crossover by hydraulic permeation effects. This effect has been modeled by Cruickshank and Scott [1998]. Of the three modes of methanol crossover, diffusion is dominant under normal conditions, especially at higher temperatures. This is because the methanol that crosses over to the cathode is electro-oxidized with oxygen. Since the driving potential for oxidation is so high at the cathode, the methanol that crosses over is almost instantly and completely converted, which sets up a sustained maximum activity gradient in methanol concentration across the electrolyte. Because of the nearly complete conversion to CO₂, crossover has been measured experimentally by determination of the CO₂ concentration in the cathode effluent.

In order to prevent crossover and greatly enhance DMFC performance, use of an electrolyte that effectively retards methanol crossover would prevent mixed potential losses and allow higher concentrations of fuel mixtures, thus reducing parasitic pumping loss and fuel storage requirements. In order to limit the dominant mode of diffusion crossover, the most common PEM used for DMFC application is Nafion® 117 (thickness of 178 µm), more than three times as thick as the Nafion® 112, typically used in the H₂ PEMFC. The increased thickness reduces crossover, but results in increased ohmic losses. Ongoing efforts are focused on the elimination or reduction of crossover by replacement of the Nafion® with alternative materials, or through flow field modification.

Several other transport-related issues are important to DMFC performance. The anode side is a two-phase system primarily consisting of methanol solution and product CO₂. The methanol must diffuse to the catalyst, while the reaction-generated CO₂ must diffuse outward from the catalyst. At high current densities, CO₂ can become a large volume fraction (>90%) in the anode
flowfield. CO₂ removal from the catalyst sites is critical to ensure availability of adequate surface area for methanol oxidation. Anode backing layers are typically partially coated in Teflon® to aid in CO₂ removal. In addition to CO₂ transport from the catalyst surface to the backing layer, CO₂ removal from the anode exit manifold is critical. Gas slugs can form that are larger than exit manifold openings, resulting in a significant pressure drop at this location (Argyropoulos et al. [1999]). As a result of the higher required anode pressure, increased methanol crossover to the cathode will occur, reducing performance. Thus, it is critical to ensure optimal CO₂ removal, both from the backing layer and from the flow channels.

Mench et al. [2001] examined gas bubble growth and ejection from the backing layer/flow channel interface region with video microscopy and observed discrete bubbles on the order of 0.1 to 0.5 mm evolving from various locations within the backing layer. Figure 10 shows several images of various bubbles attached to the anode backing layer. An increase in the current density immediately increased the frequency of bubble creation, but did not alter bubble size. CO₂ bubble removal from the anode backing layer was observed to occur by two mechanisms: 1) flow-induced removal and 2) large gas bubble coalescence. In addition, it was found that attached bubbles grew to larger sizes (1-5 mm) near the current collecting rib-backing layer interface, as a result of increased surface tension area. Therefore, the area with the greatest potential for methanol ‘starvation’ by CO₂ blockage appears to be the region near the ribs, where CO₂ bubbles tend to be removed less easily.

Another transport issue is methanol vapor removal from anode effluent. On the anode side, gas slugs consisting mostly of CO₂ will also contain methanol vapor, which must be separated by filtering or condensation before release of the CO₂ to the environment.
THE SOLID OXIDE FUEL CELL

The solid oxide fuel cell (SOFC) represents a very different system from the PEM fuel cell. The solid-state, high-temperature (600-1000°C) SOFC system eliminates many of the technical challenges of the PEM fuel cell, although different limitations arise. In general, a SOFC system is well suited for applications where a high operating temperature and a longer startup transient are not a limitation, or high amounts of CO impurities are present. The main advantages of the SOFC system include:

1) Tolerance to CO, because it is oxidized as a fuel, eliminating one of the main drawbacks of the PEM fuel cell.

2) High operating temperature greatly reduces activation polarization and eliminates the need for expensive catalysts.

3) Potential for internal reformation of hydrocarbons.

4) Potential for high hybrid system efficiencies (~70%) utilizing a bottoming cycle or cogeneration, as described by Singhal [2000].

5) Tolerance to a variety of fuel stocks.

6) High-quality waste heat generated is ideal for a cogeneration system.

Technical Issues of the SOFC

Although problems of CO poisoning and precious metal loading are eliminated with the SOFC, unique limitations exist. Many difficulties with SOFC technology deal with manufacturing issues beyond the scope of this paper. For more details, an excellent text for SOFC systems was written by Minh and Takahashi [1995]. The high operating temperature of the SOFC requires a long startup duration, since commonly used electrolyte conductivity is very low until around 800°C is reached (Larminie and Dicks [2000]). This is a serious limitation for
SOFC use as a main propulsion system in automotive applications. Doshi et al. [1999] have shown feasibility of low temperature SOFC operation at 500 ºC using doped ceria (CeO₂) ceramic electrolytes. Lower temperature operation would allow use of cheaper metallic compounds for cell interconnects, reduced start-up time, increased reliability and reduced manufacturing costs. One of the major challenges in SOFC system design is the component materials, such as the cell interconnect and electrodes. Materials are needed that 1) satisfy the basic electrical and permeation requirements, and 2) have matched thermal expansion properties of other components, to avoid internal stress concentrations and damage during both manufacture and operation.

Despite the technical challenges, the SOFC system is a good potential match for many applications, including auxiliary power for automotive applications, and stationary cogeneration plants. As a result of the potential, continued development of various types of SOFC technology is expected.

**Performance and Materials**

There are several major differences between the SOFC and PEM fuel cell systems. First, the operating temperature of the SOFC is 600-1000 ºC, compared to only 90ºC for PEM fuel cells. This high temperature is required to ensure adequate ionic conductivity (of O²⁻) in the solid-phase ceramic electrolyte. In addition, high temperatures reduce activation polarization so much that cell losses are typically dominated by internal cell ohmic resistance through the electrolyte, electrodes, and cell interconnects. SOFC open circuit cell voltages of around 1 V are typical, and operating current densities can vary greatly depending on design. While the theoretical maximum efficiency of the SOFC is less than the H₂ PEMFC because of increased temperature, decreased activation polarization is extremely low, and operating efficiencies as high as 60%
have already been attained for a 220 kW cogeneration system described by Service [2000]. Another major difference between PEM and solid oxide fuel cells are the materials. In the SOFC system, a ceramic such as yttria (Y$_2$O$_3$) stabilized zirconia (ZrO$_2$) is used as the electrolyte. In contrast to PEM fuel cells, O$^{2-}$ ions are passed from the cathode to anode instead of H$^+$ ions from anode to cathode. Other cell components such as interconnects and bipolar plates are typically doped ceramic, cermet, or metallic compounds.

**SOFC Design Concepts**

To date, there are essentially four different basic designs for the SOFC system: the planar, seal-less tubular, monolithic, and segmented cell-in-series design. The planar configuration looks geometrically similar to the PEMFC systems described previously. The electrolyte (~ 25 - 250 µm thick) is formed by methods such as tape casting into a sheet, onto which electrodes (25-100 µm) are coated. Other methods are being actively researched to produce thin electrolyte layers by techniques such as chemical vapor deposition, sputtering, vapor jet deposition, and tape casting. The flow channel structure is used as support for the electrolyte, and a stacking arrangement, similar to that described for PEM fuel cells is used. Although this design is simple to manufacture and model, one of the major problems with it is difficulty sealing the flow fields at the edges of the fuel cell. Compressive, glass, cermet, and glass-ceramic seals have been used. Sealing is still a key issue in planar SOFC design, because it is difficult to maintain system integrity over the large thermal variation and reducing/oxidizing environment.

The second design, and probably the most advanced, is the seal-less tubular concept pioneered by Westinghouse (now Siemens-Westinghouse) in 1980. A schematic of the general design concept is shown in Fig. 11. Air is injected axially down the center of the fuel cell, which provides preheating of the air to operation temperatures before exposure to the cathode. The
oxidizer is provided at adequate flow rates to ensure negligible concentration polarization at the
cathode exit, to maintain desired cell temperature, and to provide adequate oxidizer for effluent
combustion with unused fuel. In many SOFC designs, a combustor is utilized to burn fuel and
oxidizer effluent, providing a source of heat for cogeneration during normal operation, and
enabling a more rapid start-up transient time. In addition, the combustor effectively eliminates
unwanted hydrogen or CO, which is especially high during start-up when fuel cell performance
is low. Anode-side hydrogen or CO fuel can be provided externally as in other fuel cells, or
internally, by anode-side reformation using recycled water vapor product from the anode
reaction and the water-gas-shift reaction. The major advantage of this design is that the difficult
high-temperature seals needed for other SOFC designs are eliminated. Tubular designs have
been tested in 100 kW atmospheric pressure and 250 kW pressurized demonstration systems
with little performance degradation with time (less than 0.1% per 1000 hour) and efficiencies of
46 and 57% (LHV), respectively (Singhal [2000]).

One drawback of this type of tubular design is the more complex and limited range of cell
fabrication methods (Singhal [2000]). Another drawback is high internal ohmic losses relative to
the planar design, due to the in-plane path that electrons must travel along the electrodes to and
from the cell interconnect. This design can also experience significant losses due to limited
oxygen transport through the porous (~35% porosity) structural support tube used to provide
rigidity to the assembly.

The monolithic and segmented cell-in-series designs are less developed, although
demonstration units have been constructed and operated. A schematic of the monolithic cell
design is shown in Fig. 12. In the early 1980s, the corrugated monolithic design was developed,
based on the advantage of high power density compared to other designs. Both co-flow and
crossflow designs have been built and tested in small demonstration units. The high power
density of the monolithic design is a result of the high active area exposed per volume and the
short ionic paths through the electrolyte, electrodes and interconnects. The primary disadvantage
of the monolithic SOFC design, preventing its continued development, is the complex
manufacturing process required to build the corrugated system.

The segmented-cell-in-series design has been successfully built and demonstrated in two
configurations: the bell-and-spigot and the banded configuration shown schematically in Figure
13. The bell-and-spigot configuration uses stacked segments with increased electrolyte thickness
for support. Ohmic losses are high because electron motion is along the plane of the electrodes
in both designs, requiring short individual segment lengths (~1-2 cm). The banded configuration
avoids some of the high ohmic losses of the bell-and-spigot configuration with a thinner
electrolyte, but suffers increased mass transport losses associated with the porous support
structure used. The main advantage of the segmented cell design is a higher operating efficiency
than larger-area single electrode configurations. That is, each cell in series with small active area
can produce a higher output in series than the equivalent total active area in a planar design,
because individual cells with favorable conditions can achieve a higher voltage when segmented,
that is not possible with a non-segmented design, where concentration polarization or local cold
spots reduce the entire active area voltage.

The primary disadvantages of the segmented cell designs include the necessity for many
high-temperature gas tight seals, relatively high internal ohmic losses, and requirement for
manufacture of many segments for adequate power output. As a result of these disadvantages,
the majority of SOFC research is now focused on the seal-less and planar design concepts.
CONCLUDING REMARKS

The recent interest in various fuel cell systems including portable electronics, automotive and stationary power has resulted in increased understanding of the relevant mechanisms controlling performance, but each system has unique barriers which must be overcome. Future performance enhancements, environmental regulations and incentives, and increased conventional energy costs should provide ample financial impetus for continued research. In general, future fuel cell research will result in reduction in manufacturing and component cost, increased system longevity, and enhanced system modeling for use as a design optimization tool. In addition, high performance and longevity must be demonstrated in real world systems, as the transition from laboratory steady state operation to commercial product is made. The main goals specific to H₂ PEM fuel cell research include finding membrane-electrode assemblies with increased CO tolerance, better performance in dry conditions, and reduced catalyst loading. The major goals of DMFC research now include development of membrane electrode assemblies with enhanced anodic performance, reduced catalyst loading, optimized water management, and decreased methanol crossover. Finally, future SOFC research will likely result in performance increases through reduced internal component resistance and novel design, lower operating temperatures, and ease of manufacturing.
NOMENCLATURE

a constant modifying hydraulic permeability

A Area term, cm²

C molar concentration, mol/cm³

Cₚ specific heat, J/mole K

dₘ channel hydraulic diameter, cm

D Diffusion coefficient, cm²/s

E open circuit potential

F Faraday constant, charge on one mole of electrons, 96,487 As/mole electrons

g gravitational constant, 9.81 m/s²

H enthalpy, kJ/kg

i current density, A/cm²

iₒ exchange current density, A/cm²

iᵢ mass limited current density, A/cm²

j flux term, mol/s

K hydraulic permeability, cm²

l thickness of electrolyte, cm

L flow channel length, cm

Mol solution molarity, moles/liter

n electrons per mole oxidized or reduced

P pressure, Pa

r area specific resistance, Ω/cm²
R  gas constant, 8.314 J/mol·K
S  entropy, kJ/kg·K, or current collecting rib width, cm
T  temperature, K
U  reactant crossover bulk velocity, cm/s
V  potential, V, or bulk channel velocity, cm/s

**Greek letters**

α  charge transfer coefficient
ε  backing layer porosity
φ  relative humidity, unitless
η  fuel cell electrical energy conversion efficiency, or polarization
κ  backing layer gas-phase permeability, cm²
λ_{drag}  electro-osmotic drag coefficient, mol/mol H⁺ transferred through electrolyte
μ  viscosity, g/cm·s
ξ  stoichiometric flow ratio

**Subscripts**
a  activation or anode
air  air
ave  average
backing  backing layer
c  cathode
cell  fuel cell
g, sat  at saturation conditions
m  mass transport

max  maximum

oc  open circuit

others  all other components in flow

r  resistive

st  fuel cell stack

w  waste
FIGURE 1 Generalized schematic of a single fuel cell.

Anode Reaction:
- **H₂ PEM:** \( H₂ \rightarrow 2H^+ + 2e^- \)
- **DMFC:** \( CH₃OH + H₂O \rightarrow CO₂+ 6H^+ + 6e^- \)
- **SOFC:** \( H₂ + O^2- \rightarrow H₂O+2e^- ; \)
  \( CO + O^2- \rightarrow CO₂ + 2e^- \)

Cathode Reaction:
- **H₂ PEM:** \( O₂ + 4e^- +4H^+ \rightarrow 2H₂O \)
- **DMFC:** \( 6H^+ + 6e^- + 3/2O₂ \rightarrow 6H₂O \)
- **SOFC:** \( 1/2O₂ + 2e^- \rightarrow 2O^3- \)
FIGURE 2 Generalized polarization curve for a fuel cell showing regions dominated by various types of losses.
FIGURE 3 The 1 kW, 20 cell H₂ PEMFC stack at the Penn State Electrochemical Engine Center.
FIGURE 4 Typical polarization curve for hydrogen PEM fuel cell. Active area: 50 cm$^2$, cathode stoichiometry: 2, anode stoichiometry: 1.2, cathode pressure: 0.122 MPa, anode pressure: 0.101 MPa, temperature: 60 °C.
FIGURE 5 Schematic of (a) serpentine, and (b) parallel flow field design.
FIGURE 7  Simulated streamtraces of unintentional hydrogen bypass in the anode channel of a hydrogen PEM fuel cell with $180^\circ$ turn in a serpentine flow channel.
FIGURE 6  Schematic of the interdigitated flow field design used in PEM fuel cells.
FIGURE 8 A 50cm², highly instrumented, transparent direct methanol fuel cell (DMFC) at the Penn State Electrochemical Engine Center.
FIGURE 9 Several DMFC polarization curves taken at the Penn State Electrochemical Engine Center, showing typical performance. Active area: 50 cm$^2$, fuel solution molarity: 1.0 M, cathode pressure: 0.205 MPa, anode pressure: 0.101 MPa, cathode flow rate: 2100 mL/min, anode flow rate: 14 mL/min, catalyst loading: 4 mg/cm$^2$. 
FIGURE 10 Pictures of anode-side CO\textsubscript{2} bubbles (a) emergence from the backing layer with small-size (b) emergence from the backing layer with larger-size and (c) large sized accumulation attached to a current collecting rib.
FIGURE 11 Schematic of seal-less tubular SOFC design from Minh and Takahashi [1995].
FIGURE 12  Schematic of the monolithic SOFC design from Minh and Takahashi [1995].
FIGURE 13 Schematic of the segmented cell-in-series design: (a) banded and (b) bell-and-spigot configuration (from Minh and Takahashi [1995]).
Table 1. Fuel cell system basic data.

<table>
<thead>
<tr>
<th>Fuel Cell System</th>
<th>H₂ PEMFC</th>
<th>DMFC PEM</th>
<th>SOFC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel</td>
<td>H₂</td>
<td>CH₃OH and H₂O</td>
<td>CO, H₂</td>
</tr>
<tr>
<td>Oxidizer</td>
<td>O₂</td>
<td>O₂</td>
<td>O₂</td>
</tr>
<tr>
<td>Most common electrolyte</td>
<td>Perflourosulfonic acid membrane (e.g. Nafion® by DuPont)</td>
<td>Perflourosulfonic acid membrane (e.g. Nafion® by DuPont)</td>
<td>Yttria stabilized zirconia (YSZ)</td>
</tr>
<tr>
<td>Electrolyte thickness</td>
<td>~ 50-175 µm</td>
<td>~ 50-175 µm</td>
<td>~ 25-250 µm</td>
</tr>
<tr>
<td>Ion transferred</td>
<td>H⁺</td>
<td>H⁺</td>
<td>O²⁻</td>
</tr>
<tr>
<td>Most common anode catalyst</td>
<td>Carbon supported Pt or Pt/Ru</td>
<td>Unsupported Pt/Ru</td>
<td>Nickel/YSZ</td>
</tr>
<tr>
<td>Anode catalyst layer thickness</td>
<td>~ 10 – 30 µm</td>
<td>~ 10 – 30 µm</td>
<td>~ 25-150 µm</td>
</tr>
<tr>
<td>Most common cathode catalyst</td>
<td>Carbon supported Pt</td>
<td>Carbon supported Pt</td>
<td>Sr-doped LaMnO₃</td>
</tr>
<tr>
<td>Cathode catalyst layer thickness</td>
<td>~ 10 – 30 µm</td>
<td>~ 10 – 30 µm</td>
<td>~ 25-150 µm</td>
</tr>
<tr>
<td>Bipolar plate/interconnect material</td>
<td>Graphite, titanium, stainless steel, and doped polymers</td>
<td>Graphite, titanium, stainless steel, and doped polymers</td>
<td>Doped LaCrO₃, YCrO₃, Iconel alloys</td>
</tr>
<tr>
<td>Operating temperature</td>
<td>60-100 °C</td>
<td>60-100 °C</td>
<td>600-100 °C</td>
</tr>
<tr>
<td>Operating pressure (atm)</td>
<td>1-3</td>
<td>1 (anode) 1-3 (cathode)</td>
<td>1*</td>
</tr>
<tr>
<td>Major contaminants</td>
<td>CO &lt; 100 ppm, sulfur, dust</td>
<td>CO &lt; 100 ppm, sulfur, dust</td>
<td>&lt; 100 ppm sulfur</td>
</tr>
<tr>
<td>Maximum fuel cell efficiency</td>
<td>~ 80%</td>
<td>~ 80%</td>
<td>~ 62%</td>
</tr>
<tr>
<td>Primary applications</td>
<td>Stationary, portable, and vehicular</td>
<td>Portable electronics or as an APU</td>
<td>Stationary and distributed power, or as an APU</td>
</tr>
</tbody>
</table>

* Combined systems with gas turbines are operated with increased operating pressure
REFERENCES


