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Advanced Power Generation Technologies: Fuel Cells

Farshid Zabihian and Alan S. Fung
Ryerson University,
Toronto, Ontario,
Canada

1. Introduction

Dependency of the current sophisticated society and the standard of living on energy infrastructure development is going to continue in the future. According to the World Energy Outlook published by the International Energy Agency (IEA), the world's total electricity consumption will double between 2003 and 2030, growing at an average rate of 2.7% per year (IEA, 2006). Conventionally, the majority of electricity is generated by thermal fossil fuel power stations. However, global climate change and natural resource pollution as well as decline of fossil fuel resources cause significant worldwide concerns about the current trend in energy system development.

As a result of the aforementioned issues, sustainability considerations should be involved in all major energy development plans around the world. There are various definitions for sustainability. Probably the simplest one is that sustainable activities are the activities that help the existing generation to meet their needs without destroying the ability of future generations to meet theirs.

The IEA stated that global energy-related CO_2 emission would increase by 55% between 2003 and 2030 (IEA, 2006). This shows that conventional power plants using current technologies cannot address current environmental constraints. Therefore, they should be replaced by new and more environmentally benign technologies.

Ultimately, renewable energies are environmentally friendly candidates for sustainable electricity generation. But their applications have been limited by some major drawbacks, such as availability, reliability, and cost, at least in the short- and mid-term future. According to IEA, the share of renewable electrical energy in the world will experience a slight decrease from 23% in 2003 to 22% in 2030. On the other hand, the same report predicted that the share of fossil fuels as energy supplies for electricity generation would remain constant at nearly 65%. Global energy-related greenhouse gas (GHG) emissions would increase by 1.7% per year and would reach 40 Gt in 2030, a 54% increase over the 2004 level (IEA, 2006; Gale, 2002; Bauer, 2005).

Thus, both fossil and non-fossil forms of energy will be needed in the foreseeable future to meet global energy demand. That is why IEA has commented that "numerous technology solutions offer substantial CO_2-reduction potentials, including renewable energies, more efficient power generation, fossil-fuel use with CO_2 capture and storage, nuclear fission,

fusion energy, hydrogen, biofuels, fuel cells and efficient energy end use. No single technology can meet this challenge by itself. Different regions and countries will require different combinations of technologies to best serve their needs and best exploit their indigenous resources. The energy systems of tomorrow will rely on a mix of different advanced, clean, efficient technologies for energy supply and use" (IEA, 2003a, p. 5).

Fuel cells are a promising technology for electricity generation with high efficiency and minimal environmental impacts. The idea is to directly convert fuel chemical energy to electrical and thermal energy via electrochemical reactions. This section outlines the basic operation of a fuel cell and its essential components as well as the main subsystems of fuel cell plants. It also provides a brief overview of the different types of fuel cells and their applications. Then, the solid oxide fuel cell (SOFC), as a main candidate for stationary power generation, is investigated in detail. Also, some advanced power generation technologies that can be potentially integrated into SOFCs to form hybrid systems are explained. Finally, SOFC and hybrid SOFC cycle computer modeling are presented.

2. Introduction to fuel cells

Fuel cells are a very interesting alternative for conventional power generation technologies because of their high efficiency and very low environmental effects. In conventional power generation systems, fuel is to be combusted to generate heat and then heat is converted to mechanical energy before it can be used to produce electrical energy. The maximum efficiency that a thermal engine can achieve is when it operates at the Carnot cycle. The efficiency of this cycle is related to the ratio of the heat source and sink absolute temperatures. On the other hand, fuel cell operation is based on electrochemical reactions and not fuel combustion. Bypassing this conversion of chemical energy to thermal and then mechanical energy enables fuel cells to achieve efficiency potentially much higher than that of conventional power generation technologies.

A fuel cell can be considered as a "cross-over" of a battery and a thermal engine. It resembles an engine because theoretically it can operate as long as fuel is fed to it. However, similar to a battery, its operation is based on electrochemical reactions. This combination provides significant advantages for fuel cells. On the other hand, batteries are energy storage devices and when their chemical energy is depleted, they need to be replaced or recharged, whereas fuel cells can generate electricity continuously. Actually, in principle, a fuel cell resembles an instantly rechargeable battery. Mench (2008) explained the differences between a fuel cell and a battery based on the thermodynamic definition of a closed system and control volume. According to his description, a battery is a thermodynamically closed system, whereas a fuel cell is a thermodynamically control volume, and fuel and oxidizer can flow across the system's boundaries.

The main advantages of fuel cells can be summarized as follows. It should be noted that this list is not exhaustive and just enumerates general attributes of all types of fuel cells.

Direct energy conversion (no combustion): Most fuel cell attributes stem from direct electrochemical power generation. In conventional power plants, most irreversibilities, more than 30%, take place in the combustion process (Campanari & Macchi, 1998).

Potential for high efficiency: Stand alone fuel cell electrical efficiency is in the range of 40% to 60%, based on the lower heating value (LHV) (Young, 2007). For hybrid and cogeneration fuel cell systems, efficiency of around 70% (LHV) and higher than 80% have been predicted, respectively (EG&G Services, 2004; Larminie & Dicks, 2003).

Lower pollution: Fuel cells can generate electricity with very low amounts of pollutants, such as GHG, NO_x, and SO_x. This is due primarily to their high efficiency. Also, since there is no combustion in the power generation process, the emissions associated with combustion are eliminated. Moreover, since most fuel cells should be operated on desulfurized fuels, they do not emit any SO_x.

Scalability: The unique characteristic of fuel cells is that their high efficiency and other attributes are nearly unaffected by the size of the plant. That means fuel cells are scalable to all sizes with, more or less, the same high efficiency, low emissions and costs. In addition, modular installations of fuel cells can help them to match load and increase their reliability (EG&G Services, 2004).

No moving parts in the energy converter: A fuel cell generates electricity by the movement of mobile ions and electrons. Therefore, there are no moving parts in the fuel cell itself. However, some compressors and/or fans are required to supply oxidizer and fuel to the system.

Quiet operation: Due to minimal moving parts, fuel cells can be operated with minimal noises and vibrations. This is very important for some applications such as residential distributed electricity generation.

Fuel flexibility: The ideal fuel for a fuel cell is hydrogen. If fueled by hydrogen, there are no emissions by the fuel cell and the only emissions are for hydrogen generation. However, fuel cells can operate on a wide range of fuels, from conventional fuels, such as natural gas, petroleum, and coal, to renewable fuels, like biogas and ethanol, to landfill gas. This fuel flexibility can provide smoother transition to future power generation infrastructures. Fuel cells can operate, directly or indirectly, based on the fossil fuel, until renewable hydrogen is available commercially. In other words, fuel cells are power generators of today and tomorrow.

Easier carbon capture: In the fuel cell operation, fuel and air streams are not mixed, making CO_2 capture easier and less energy intensive.

Possibility for water production: If pure hydrogen and oxygen are used as a fuel and oxidizer, respectively, the only products of the fuel cell operation are electricity, heat, and potable water.

Hybrid systems and cogeneration: Most fuel cells, especially high operating temperature ones, can be used in hybrid systems to produce further electricity and/or in cogeneration systems to produce heating and/or cooling as well as electricity.

Moreover, at least some types of fuel cells have demonstrated the following characteristics: fast response to load changes, unattended operation, good off-design load operation, reliability, and high availability.

All these attributes and characteristics make fuel cells ideal candidates for some major applications. However, before this commercialization can be realized, some significant improvements are required. The most important barrier is cost. In order to reduce the cost of fuel cells, new construction methods and materials must be developed. Mass production and the economy of scale can reduce cost significantly, but some mass markets have to be in place to support it. Also for each application, suitable durability, endurance, reliability, longevity, specific power, and power density need to be achieved, especially for high temperature fuel cells. This includes transient operation and operation in extreme ambient conditions. In addition, the performance of the balance of plant (ancillary system) should be improved to meet the technical and economic requirements of fuel cell systems. Other obstacles to overcome can be enumerated as follows: lack of familiarity of markets with fuel cell technology (especially the power generation industry) and the lack of hydrogen production, storage, and distribution infrastructure for hydrogen fueled fuel cells.

Fuel cell technology is highly multidisciplinary and its development requires engagement and embrace most of the engineering fields, from electrochemistry to manufacturing and from thermodynamic to material science and control, and is experiencing a tremendous growth. For instance, it has been shown that the number of registered patents related to fuel cells has increased exponentially in the United States in recent years (Mench, 2008). However, any claim regarding the future of fuel cells should be considered cautiously, because a quick review of literature over the past few decades shows that fuel cells have always been seen, and still are being seen, to be a few years away from commercialization.

3. Fuel cell basic operation

Since the operation of fuel cell is, in principle, a reverse of the operation of an electrolyzer, the electrolysis process will be briefly explained. Electrolysis is a process to separate substances into their elements by means of the passage of a direct electric current. This process requires three main components: an electrolyte and two electrodes. The external source of direct electric current is supplied to electrodes, where electrons are removed from or added to atoms to generate ions. The electrolyte provides a site to carry mobile ions. Negatively-charged ions (anions) lose electrons at the anode and positively-charged ions (cations) receive electrons at the cathode to become an uncharged atom separated from the electrolyte.

The same principle is true for fuel cells, but the objective is to combine substances to generate electricity. Actually, the concept of fuel cells was discovered when water electrolysis was reversed. In a fuel cell, the reductant (fuel) flows across the anode and is oxidized by removal of electrons. Similarly the oxidant (usually oxygen from air) flows across the cathode, where it is reduced by gaining electrons. Then either positively-charged or negatively-charged ions, depending on the fuel cell type, flow through the electrolyte to participate in electrochemical reactions. The excessive electrons in the anode and lack of electrons in the cathode generate the desired product of the system, electricity. Fig. 1 illustrates a sketch of the basic operation of a typical fuel cell fueled by hydrogen and oxygen. The exact reactions in the electrodes and the type of ions transferred through the electrolyte depend on the fuel cell type and the type of inlet fuel.
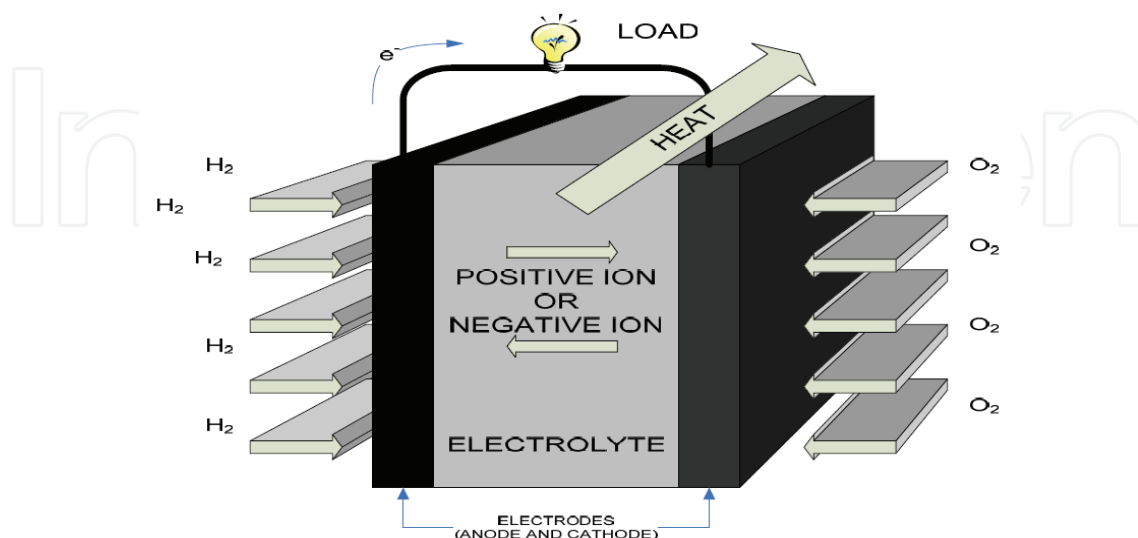

Fig. 1. Sketch of the basic operation of a typical fuel cell fueled by hydrogen and oxygen (Suther, 2006)

4. Fuel cell components

As noted earlier, every fuel cell requires an electrolyte, two electrodes, and interconnections. In order for a material to be suitable for these components, it should have high mechanical strength and thermal conductivity. Furthermore, it should be chemically stable in air and/or fuel as well as with other cell components at operating temperature and during the fabrication. Also, for overall mechanical strength of the fuel cell, the thermal expansion of all components must match. These are the minimum general requirements of fuel cell components. This section provides a brief discussion of the tasks of these components and required characteristics of candidate materials.

Electrolyte: The electrolyte is the most important component of a fuel cell. The properties, operating conditions, and potential applications of each type of fuel cell are dictated by the electrolyte. The functions of the electrolyte, which in turn determine its characteristics, can be enumerated as follows:

- To transfer ionic charges between electrodes;
- To block direct transformation of electrons from the anode to the cathode so that the electric current conducts through an external load;
- To prevent physical mixing of the reductant and oxidant streams.

Electrodes: The electrodes should be able to perform the following functions:

- To provide a surface for electrochemical reactions;
- To supply reactant streams to the site of electrochemical reactions and distribute the streams over the cells as equally as possible;
- To collect and carry away electrons from the anode, and supply and distribute electrons to the cathode (which requires a good electrical conductor);
- To collect and carry away electrochemical reaction products from the site of the reactions.

In order for a substance to be able to perform the tasks mentioned above, it should typically be porous and electrically conductive and have sufficient electro-catalytic activity. Using porous materials for electrodes also significantly increases the contact between the electrode, the electrolyte, and streams. For low temperature fuel cells, few expensive materials can provide the required electro-catalytic activity. Therefore, to reduce the cost of the fuel cell, a small amount of these materials are deposited to the interface of the electrodes and electrolyte. However, for high temperature fuel cells, relatively inexpensive materials can provide sufficient electro-catalytic activity and the electrodes can be manufactured out of such.

Interconnections: The main purpose of interconnections in fuel cells is to conduct electrons from or to the electrodes. These electrons can be transferred either between the cells or between cells and the external circuit. Depending on the type of fuel cell and its configuration, interconnections may have other tasks as well. For instance, in a flat plate design, the interconnections separate the oxidizer and fuel by providing flow channels for streams in the anode and cathode. The material of the interconnections must have high electric conductivity and low ionic conductivity. Both properties are essential for an efficient interconnection.

5. Configuration of fuel cells

Although current and power output of a fuel cell, to some extent, can be controlled by its size and reactants flow rate, the voltage of electricity that can be generated by a single fuel

cell unit is limited to a theoretical maximum of about 1.2 V at 298 K and 0.9 V at 1273 K for hydrogen oxidation (Campanari & Macchi, 1998). This is due to the limited electrochemical potential of the reacting agents. Since actual operating voltage is generally lower than 1 V, several fuel cell units should be connected to generate a considerable amount of electricity. The combination of fuel cells is known as a fuel cell stack and gives fuel cells size flexibility. The fuel cell stacking is one of the reasons for the development of various fuel cell configurations, which are the subject of the rest of this subsection.

The configuration of a fuel cell is an important parameter in the fuel cell design that determines the shape of components, stacking of the fuel cell, and the system supporting mechanism. The common configuration of fuel cells can be categorized into two main groups: the planar and the tubular configurations. At the beginning of fuel cell development, there was monolithic design as well but due to its high fabrication costs, its development was not pursued (Singhal, 2000b).

Planar fuel cells: In this design, the fuel cell's flat plate electrolyte and electrodes are located parallel to each other and the individual cells are connected in series (bipolar plates). The planar fuel cells enjoy high power density and their fabrication is simpler. But their structural integrity and sealing at high operating temperatures are serious challenges.

In order to distribute air and fuel evenly within each cell, flow channels can be integrated into the interconnections. Also, there are two more functions for the interconnections:

• To separate fuel and oxidant of two adjacent unit cells;
• To provide electrical connection between adjacent unit cells.

In terms of the flow direction of the reductant and oxidant, there are three common configurations:

• Co-flow: Two streams are parallel and in the same direction;
• Counter-flow: Two streams are parallel and in opposite directions;
• Cross-flow: Two streams are perpendicular.

Also, manifolds are required to distribute fresh air and fuel between cells and collect depleted streams from cells. These manifolds can be either external or integrated in the fuel cell stack design. Further information and illustration about various configurations of fuel cells can be found in Larminie and Dicks (2003).

In solid state electrolyte fuel cells, in order to provide mechanical strength for a planar cell, each cell should be self-supported or supported by an external support. In a self-supported cell, either the electrodes or electrolyte should be thick enough to support other components. The three types of self-supported fuel cells are electrolyte supported, anode supported, and cathode supported. The problem with electrolyte supported cells is the high ionic resistance in the electrolyte due to its greater thickness, requiring a high operating temperature of the system. In electrode supported cells, due to their thinner electrolyte and lower ionic resistance, the operating temperature can be reduced significantly. Alternatively, cells can be externally supported by the interconnections, which results in stronger structure and thinner cell components, but cell support requirements may impose some limitations in flow channel design. Recently, anode supported fuel cells have been receiving the most attention due to their better thermal and electrical conductivity, mechanical strength, and minimal chemical interaction with the electrolyte (Singhal, 2002).

Tubular fuel cells: In this design, a whole cell is in the form of a tube, the cathode being the inner layer, and the electrolyte and anode are deposited on top of the cathode. Since this configuration is mainly used in solid oxide fuel cells, the detailed description of the design will be presented in subsection 12.

6. Balance of plant

The balance of plant (BoP) is a significant portion of a fuel cell system's weight, volume, and cost. The fuel processor is required to provide fuel in proper conditions for the fuel cell and increase the fuel flexibility of the system. Also, the generated electricity in the fuel cell cannot be directly used by end users and has to be adjusted to meet the load requirements. The inlet fuel type, system application, and operating conditions can affect the type and configuration of the balance of plant. The BoP can include all or some of the following subsystems:

• Feed stream conditioning: the fuel preparation and storage; and the fuel and oxidant supply (compressors or blowers as well as filters);
• Thermal management equipment (to manage the fuel cell stack temperature);
• Water management;
• Electric power conditioning (to convert variable DC fuel cell output to usable electricity);
• Residual fuel recirculation and/or consumption (due to a lower than 100% fuel utilization factor in fuel cells, residual fuel should be recycled or combusted before being discharged to the environment);
• Start-up equipment (to initiate start of components and preheating of the system);
• Cooling subsystem;
• Control subsystem.

Some of these subsystems will be discussed in more detail in subsection 15.

7. Fuel cell classification

Fuel cells can be classified based on various parameters. The most popular categorization is based on the type of electrolyte. The electrolyte can be either solid or liquid with the operating temperatures ranging from 80°C to over 1000°C. According to this classification fuel cells can be categorized into five groups;

1. Polymer electrolyte fuel cell (PEFC);
2. Alkaline fuel cell (AFC);
3. Phosphoric acid fuel cell (PAFC);
4. Molten carbonate fuel cell (MCFC); and
5. Solid oxide fuel cell (SOFC).

Fuel cells can also be grouped based on the charge of ions that are carried between the electrodes. In some fuel cells, positive ions move from the anode to the cathode to produce water and heat by reacting with oxygen (such as PEFC and PAFC). In others, however, negative ions move from the cathode to the anode (such as AFC, MCFC, and SOFC). Some fuel cells are classified by their fuel. The most important and well know fuel cells in this categorization are direct methanol fuel cells (DMFC) and direct carbon fuel cells (DCFC). For instance, the DCFC is a concept of which solid carbon is used directly in a SOFC, MCFC, or AFC with exceptionally high efficiency, due to the thermodynamics of the reactions.

As noted, the type of electrolyte determines the operating temperature of a fuel cell, which in turn dictates the material for other components. Different operating temperatures provide characteristics for each type of fuel cell, making them suitable for various applications.

Low temperature fuel cells: The low operating temperature of this type of fuel cells, usually lower than 200°C, including PEFC, AFC, and PAFC, provides them with some advantages, most important of which are faster start-up and usually higher efficiency. However, the low temperature fuel cells require expensive electro-catalysts (mostly platinum). Therefore, they

should be fueled with hydrogen with high purity (with some exceptions, such as DMFC), since some fuel gases, like carbon monoxide, can poison platinum.

High temperature fuel cells: The operating temperature of high temperature fuel cells, SOFC and MCFC, is between 500°C and 1000°C. Unlike low temperature fuel cells, they can operate with less expensive electro-catalysts and require minimal processing of conventional fuels. Some fuel components, like CO and CH_4, not only do not poison the fuel cell, but also can be internally reformed to produce hydrogen rich streams or even directly participate in the electrochemical reactions. The high temperature fuel cells are particularly suitable for stationary power generation, although they have been proposed for other applications as well. In addition, the high temperature exhaust stream of this type of fuel cells contains a considerable amount of energy, which can be used to generate further power and/or thermal energy by integrating bottoming cycle, such as a gas turbine or a waste heat recovery subsystem.

The following sections present a brief introduction to different types of fuel cells based on the type of the cell's electrolyte.

7.1 Polymer electrolyte fuel cell (PEFC)

The electrolyte in this type of fuel cell is an acidic solid proton exchange membrane (PEM), such as perfluorinated sulfonic acid polymer, which is an excellent positive ion conductor. Due to a restriction in the operating temperature of the membrane, the fuel cell operates at a low temperature, typically between 60°C and 100°C. Sometimes the PEFC are called proton exchange membrane fuel cells or polymer electrolyte membrane fuel cells (PEMFC) or solid polymer electrolyte fuel cells (SPEFC).

Both anode and cathode electrodes are made of porous carbon with impregnated platinum as electro-catalyst. Interconnections can be made of carbon or metals. The PEFC can be directly fueled either by hydrogen or methanol. For other fuels, however, an extensive fuel reforming is essential because the anode can be easily poisoned by CO (even with a concentration of as low as 10 ppm (Young, 2007)), sulfurs, and ammonia. A critical point in the PEFC design and operation is water management to provide sufficient water to hydrate membranes and avoid their flooding. Low operating temperature, high current density, low start-up time, compactness, and light weight make this type of fuel cell an ideal candidate for transportation applications. These attributes also suit other applications, such as stationary, combined heat and power cogeneration (CHP), and portable applications.

The main challenges for commercialization of PEFC are water management, thermal management, fuel processing, and durability in severe ambient conditions. The amount of required platinum as electro-catalysts has been reduced significantly in the past two decades, from 28 mg/cm² to 0.2 mg/cm² (Larminie & Dicks, 2003).

A specific type of PEFCs is direct methanol (CH_3OH) fuel cells (DMFC). This fuel cell, which is sometimes called a direct alcohol fuel cell (DAFC), is a PEFC directly fed by methanol or other alcohols. Due to its simplicity and compactness, the main application for DMFC is in portable application to replace lithium ion batteries.

7.2 Alkaline fuel cell (AFC)

In AFCs, the electrolyte is a corrosive mixture of potassium hydroxide (KOH) in water. The concentration of the mixture determines the operating temperature of the fuel cell. For low operating temperature (less than 120°C), low concentration of the mixture (between 35 and

50 wt%) is required, whereas a concentration of 85 wt% is more suitable for high operating temperature (around 250°C). The electrodes are metallic and usually an asbestos matrix is required to retain the liquid electrolyte. The AFCs' flexible choice of electro-catalyst (from nickel and metal oxides to noble metals) is one of their advantages. The development of AFCs began in the 1960s and resulted in their application in the Apollo Space missions to generate electricity and water. The system's performance with hydrogen as fuel and oxygen as oxidizer was remarkable. However, the system can be strongly poisoned by carbon monoxide and carbon dioxide, which prevent the system from operating with air and conventional fuels. Due to this problem, their development has nearly been ceased.

7.3 Phosphoric acid fuel cell (PAFC)

The electrolyte of PAFC is corrosive 100% concentrated phosphoric acid, and the electrodes are mainly made of porous carbon and graphite. In order for phosphoric acid to exhibit satisfactory ionic conductance, an operating temperature of above 150°C is required. In PAFC, similar to PEFC, protons are the charge carriers in the electrolyte, and platinum is used as an electro-catalyst for both the anode and the cathode. Thus, the electrochemical reactions in PAFCs are the same as PEFCs, but they occur at a higher temperature. This type of fuel cell can tolerate temperatures up to 220°C due to the stable nature of phosphoric acid (unlike other acids). This relatively high operating temperature reduces the sensitivity of these fuel cells to CO poisoning, while common construction materials can still be used in the balance of plant construction. However, the corrosive nature of the electrolyte necessitates application of special material in the fuel cell stack construction. The water and thermal management are relatively easy in the PAFC. Other major technical challenges are slow start-up, loss of the electrolyte, and expensive electro-catalyst. PAFC is one of the few fuel cells that are currently commercially available, especially for stationary applications. However, their development suffered a slowdown due to their high costs (Young, 2007).

7.4 Molten carbonate fuel cell (MCFC)

In MCFC, the electrolyte is usually a corrosive mixture of molten alkali carbonates retained in a porous ceramic matrix, which can conduct negative ions ($CO_3^=$) at high temperature (about 600°C to 700°C). The electrodes are commonly made of nickel and nickel oxide and due to sufficient activity of the electrodes, there is no need for noble metal as an electro-catalyst. Due to their high operating temperature, MCFCs have relatively large size, weight, and slow start-up. Thus, they are more suited for stationary and marine applications. In fact, commercial MCFCs are available in the market for stationary applications and several multi-megawatt demonstration power stations were installed. Because of the high operating temperature, CO is not harmful for system operation, but along with other conventional fuels, can be internally reformed to provide a hydrogen rich stream for the anode. MCFCs also can be combined with a bottoming cycle to make use of waste exhaust heat to generate further power and/or heat. The corrosive nature of the electrolyte, loss of the electrolyte, and low power density are the main challenges for this type of fuel cell. Moreover, the system requires a CO_2 injection to the cathode to produce carbonate ions, which increase system complexity and cost.

7.5 Solid oxide fuel cell (SOFC)

In SOFCs, the electrolyte is a solid ceramic (nonporous metal oxide), which demonstrates sufficient ionic conduction for oxygen ions at a high operating temperature, between 500°C

and 1000°C. The electro-catalyst is non-noble metal or other less expensive material, and the electrolyte, cathode, and anode are typically made of Y_2O_3-stabilized ZrO_2, Sr-doped $LaMnO_3$, and Ni-ZrO_2 cermet, respectively.

Major technical challenges are relatively expensive construction material, long start-up time, durability, and sealing of the cells. These problems can be intensified at higher temperatures. That is why lower operating temperature is desired, and there have been numerous studies to reduce the operating temperature even as low as around 500°C by using a thinner electrolyte. Stationary power generation, mobile power, and auxiliary power for vehicles are considered as potential applications of SOFCs. Similar to MCFC, SOFC can be integrated to bottoming cycles or heat and power cogeneration plants to increase the overall efficiency of the plant, up to 70% (Calise et al., 2006). A detailed review of the SOFC will be presented in subsection 10.

8. Application of fuel cells

There are many potential applications for fuel cells. However, in order to recognize the specific fuel cell type for each application, the attribute of the desired system should match the specifications required for particular applications. Most likely, it is not possible to find a system that perfectly satisfies all preferences for an application; therefore, the parameters should be ranked based on their priorities. The desired attributes can be one or several of the following characteristics: cost, efficiency, durability, power density, simplicity, rapid start-up, compactness, robustness, etc. This list is not exhaustive, and for every application other parameters may be added. In the following section, the main potential applications of fuel cells will be investigated.

Stationary and distributed power generation: For the stationary electricity generation, the main desired characteristics are high efficiency and long lifetime. Therefore, compactness, simplicity, and weight are not major constraints for this application. Their power generation capacity ranges from a few hundred kW to several MW for the following potential applications:

- Residential power generation;
- On-site industrial electricity generation;
- Backup power supply;
- Combined heat and power cogeneration (CHP);
- Continuous and uninterrupted electricity production.

Fuel cells are particularly suitable for distributed power generation, because the capital costs and efficiency are almost unaffected by the plant size. This means the cost of generated electricity for small power generation plants is close to that of the larger ones and is relatively insensitive to scale. With a well developed natural gas distribution network in urban and industrial regions, this characteristic provides a unique opportunity for residential and industrial on-site and distributed power generation. Fuel cells' modular nature can help them to match demand load specifications. In addition, high efficiency at partial loads, low air pollution, and quiet operation are other important positive attributes of fuel cells, especially for residential applications. Also, coal gasifier requirements closely match the high temperature fuel cell operational conditions. Thus, an integrated system can be developed to use inexpensive coal to generate electricity with high efficiency.

Transportation applications: Due to their high efficiency and low emissions, applications of fuel cells, especially PEFCs, to power light- and heavy-duty vehicles have been a very

attractive concept. There have been tremendous investments to develop such vehicles, and hundreds of demonstration vehicles are in different stages of development and tests; however, technical and economic constraints and lack of hydrogen infrastructure slow down the progress in this field. The successful introduction of hybrid electric and combustion engine cars and more recently plug-in electric cars has intensified the competition. It seems that the application of fuel cells as the primary power source of vehicles could not be realized, and utilization of fuel cells as a backup power source for plug-in electric cars is more probable.

Portable applications: In this application, DMFCs are employed for powering portable devices, such as laptop computers and cell phones. This is most likely the first application in which fuel cells can be utilized. This is due to the comparable cost of current fuel cells and lithium ion batteries and uninterrupted operation of fuel cell powered devices with replaceable fuel cartridges.

Other applications: Fuel cells are potential candidates wherever electricity is required; however, some applications fit the characteristics of fuel cells more closely. A few of these niche applications are auxiliary power units (APUs) for vehicles, electricity storage by regenerative (reversible) fuel cells, space applications, and military applications. Moreover, some innovative applications have been proposed in the literature.

9. Comparison of fuel cells

Table 1 summarizes the characteristics of various types of fuel cells, including the suitable material for different components, operating temperature, and potential applications.

Fuel cells were invented in the 19th century; however, it took more than a century before the first operational fuel cell was made. Over the past two decades, there have been tremendous R&D activities and dramatic improvements in this field. As noted in Table 1, most types of fuel cells, especially SOFC and MCFC, can be used for stationary power generation. For this work, SOFC will be further investigated for power generation application, which reflects the present level of interests in the field.

10. Solid oxide fuel cells

In the 1890s, Walther Nernst, a German scientist, was the first to observe the ion conductivity of stabilized zirconia at high temperature. His observation was used to build the first SOFC in the 1930s. The SOFC's actual development started in the 1950s, which gave SOFC the longest continuous development period among different types of fuel cells. An excellent historical and technical review of SOFCs can be found in Singhal & Kendall (2006), and also in Williams et al. (2006) and Singhal (2002). Moreover, Dokiya (2002) studied materials and fabrication technologies deployed for manufacturing of different cell components, investigated the performance of the fuel cells manufactured using these materials, and reviewed efforts to reduce fuel cell costs.

As noted in the previous section, among different types of fuel cells, high temperature fuel cells, SOFC and MCFC, are very attractive for stationary power generation. Because of high operating temperature, their application can lead to some advantages such as:

- ability to incorporate bottoming cycles to generate further power and/or thermal energy;
- co-production of hydrogen and electricity (Williams et al., 2006);

	PEFC	AFC	PAFC	MCFC	SOFC
Electrolyte material	Acidic solid proton exchange membrane	Potassium hydroxide (KOH)	Phosphoric acid	Molten alkali carbonates	Ceramic
Electrode material	Porous carbon	Metals	Porous carbon or graphite	Nickel or nickel oxide	Ceramic
Catalyst material	Platinum	Nickel, metal oxides, or noble metals	Platinum	Electrode material	Electrode material
Interconnections material	Carbon or metals	Metal	Graphite	Nickel or stainless steel	Nickel, ceramic, or stainless steel
Prime cell components	Carbon	Carbon	Graphite	Stainless steel	Ceramic
Mobile ion	H^+	OH^-	H^+	$CO_3^=$	$O^=$
Operating temperature	60°C to 100°C	50°C to 220°C	200°C to 220°C	600°C to 700°C	500°C to 1000°C
Electrolyte poisons	CO	CO, CH_4, CO_2, H_2S	CO, H_2S	H_2S	H_2S
Internal fuel reforming	No	No	No	Yes	Yes
Applications	Vehicles, mobile, small CHPs (DMFC: portable electronic systems)	Space vehicles	Medium-scale stationary and CHPs	Medium- and large-scale stationary, hybrid, and CHPs	All sizes of stationary stand alone and hybrid systems, CHPs, and APUs

Table 1. Summary of the characteristics of various types of fuel cells

- ability to reform hydrocarbons, including pipeline and liquefied natural gas, diesel, biogas, gasoline, coal syngas, etc., which results in fuel flexibility;
- capability to consume CO as fuel;
- no need for noble metal as electro-catalysts due to high reaction rates.

And in the case of SOFC:

- high oxide-ion conductivity;
- high energy conversion efficiency due to high rate of reaction kinetics;
- solid electrolyte and existence of only solid and gas phases resulting in:
  - simplicity in concept;
  - ability to be cast into various forms and configurations (that is why a wide range of cell and stack geometries have been proposed for SOFC);
  - accurate and appropriate design of the reaction sites;
  - no electrolyte management constraints.

Stationary and distributed power generation and auxiliary power units (APUs) for vehicles are the main potential applications of SOFCs, the latter being most likely the first real

market for such. However, before power generation with SOFCs can be commercialized, some technical challenges should be addressed, including the cost of materials and manufacturing, system life, thermal cycling, limited power density, mismatch of thermal expansion coefficient of different components and sealing problem in planar configuration, materials selection at high temperature especially metal interconnections (Williams et al., 2006), and corrosion in some components.

In the following sections, SOFC components, stack configurations, and balance of plant will be briefly introduced.

11. SOFC components

Fig. 2 illustrates the schematic of a typical planar SOFC, including its components and flow paths. Similar to other fuel cells, a SOFC can be broken down into four main components: the electrolyte, anode, cathode, and interconnections.
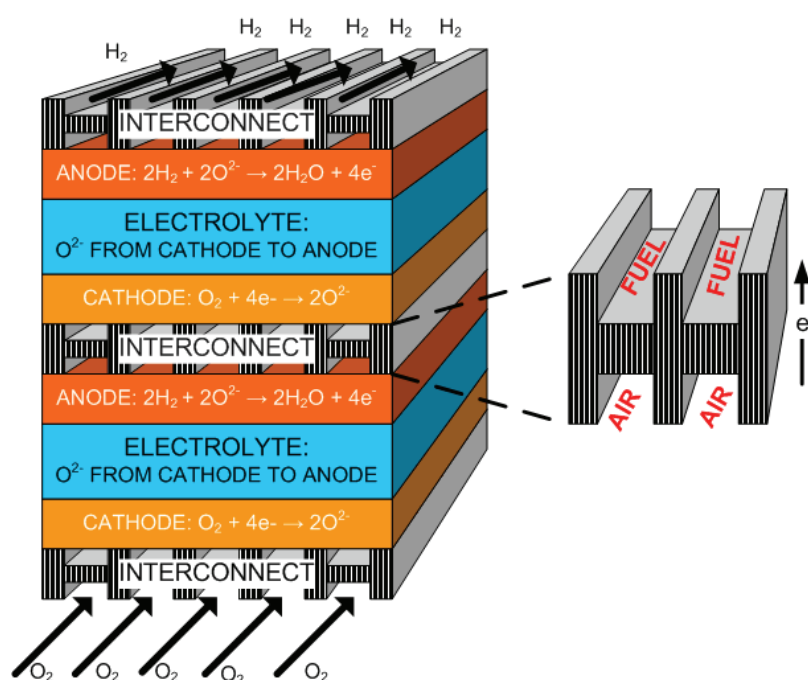
Fig. 2. Schematic of a typical planar SOFC (Suther et al., 2010)

In SOFCs, oxygen is reduced and gains electrons to produce free negatively charged oxygen ions. The electrons required for oxygen reduction are provided from the anode and via external electric load. The oxygen ions immigrate across the oxide-ion conducting electrolyte to the anode. In the anode, the negative ions participate in reactions with fuel to generate steam or carbon dioxide. The actual electrochemical reactions and the products depend on the reductant agents: hydrogen, carbon monoxide, or even methane (these reactions are presented in Fig. 2 for hydrogen as fuel). The reactions in the anode release electrons, which in turn are collected and transferred by the interconnections to generate external electric current.

The electrolyte of SOFC must have high ionic conductivity for the oxygen negative ions as well as low electrical conductivity. Several electrolytes have been proposed for SOFCs, which can be grouped in two categories based on their molecular structure: fluorite-structured and perovskite-structured. All these materials show sufficient ionic conductivity at high temperature, and that is the reason for the high operating temperature of SOFCs.

The oxygen ions conduction in fluorite-structured materials is due to oxide ion vacancies and interstitial oxide ions. Zirconia- and ceria-based materials are the two most common fluorite-structured electrolytes. In order for zirconia to exhibit sufficient ionic activity at reasonable temperature, it should be doped with other substances, such as yttria and scandia. Both yttria-stabilized zirconia (YSZ) and scandia-stabilized zirconia (SSZ) have been used as electrolytes for SOFCs, the former being the most favored. The ceria-based electrolytes, with many different dopants, have been proposed and utilized mainly for low temperature SOFCs.

Perovskites are compounds of the form ABO_3, (A and B are cations with very different sizes) and few of such structure materials have an ionic conduction property. The most common perovskite compound suitable for the electrolyte in SOFCs is $LaAlO_3$.

Among many compounds which have been investigated for use as electrolytes in SOFC, zirconia-based compounds are still the most suitable ones due to their stability, low electric conductivity, and high ion conductivity above 800°C (Singhal & Kendall, 2002).

For electrodes, the material should be highly catalytic for the specific reaction at the particular electrode and good electrical conductor. Also, they should not react with electrolyte material during not only the fuel cell operation, but also manufacturing process, and have thermal expansion coefficient close to the other components.

In early stages of SOFC development, noble metals, such as platinum and gold, were used for the anode and cathode. However, due to high cost as well as physical and chemical instability of these precious metals, they were replaced with other less expensive materials with more desirable properties. The most common material for anode is cermet of nickel and YSZ and for cathode are lanthanum-based perovskite materials such as Sr- or Ca-doped $LaMnO_3$ (Singhal, 2002). Because of some undesirable characteristics of these materials, such as sensitivity to some contaminants, mismatch of thermal expansion coefficient with other cell components, poor activity for direct electrochemical reactions of hydrocarbons, and potential carbon formation (EG&G Services, 2004), the research of finding better options for the electrodes is ongoing.

For interconnections, at high temperature SOFCs perovskite-based materials, such as Ca- or Sr-doped $LaCrO_3$ and at lower temperature SOFCs inexpensive metallic alloys are very common (Singhal, 2002). It should be noted that the requirements of interconnections are the most severe among SOFC components, because they are exposed to both air and fuel (Singhal, 2000b).

12. Configurations of SOFCs

Due to the solid state electrolyte in SOFCs, there are fewer limitations in their design. That is why wide range of cell and stack geometries have been proposed for SOFCs. As noted earlier, the configuration of SOFCs can be categorized into two main groups: the flat plate and the tubular configurations.

Tubular fuel cells were specifically designed for SOFC and most progress in SOFC design has been achieved for this type (Singhal, 2000b). This design solved the sealing problem and provides excellent mechanical integrity for the stack. In this design, the electrodes and electrolyte are in the form of different layers on a tube. In earlier designs, these layers were deposited over a cylindrical tube that did not participate in the electrochemical process (Bevc, 1997). But in current designs, the tube is made of lanthanum manganite and functions as the cathode as well as mechanical support (Singhal & Kendall, 2002). In any case, for

operation of this type of SOFC, fuel is passed outside the tube, while air is passed inside the inner cathode tube. Siemens Westinghouse has been historically the pioneer in the tubular SOFC design and manufacturing since 1984 (Singhal, 2000a). The latest development in this design is flat-tube design, which is less expensive and has higher power density (Young, 2007). This design is similar to tubular design only with flattened tubes which incorporates ribs inside the cell. The ribs reduce the current path, like a bridge for electrons, decreasing the cell internal resistance. They can also help to reduce the thickness of cathode and its overpotential (Singhal, 2000a). Another innovative design, developed by Rolls-Royce and called integrated-planar SOFC (IP-SOFC), is a combination of the two aforementioned designs. This type of SOFC enjoys the lower fabrication cost of the planar SOFC and thermal-mechanical strength of the tubular SOFC (Young, 2007).

However, the tubular SOFCs suffer both low specific power density (W/cm^2) and volumetric power density (W/cm^3) due to longer current path and thus higher electrical resistance (Singhal, 2002). Also, their fabrication cost is high, and there is not much potential to reduce this cost. Last but not least, due to the relatively high thickness of the electrolyte, their operating temperature is high. These problems are partially solved in planar SOFCs. They can achieve high power density. Their manufacturing cost is relatively lower due to the possibility of using a boarder set of materials, and can be significantly reduced by mass production and the economy of scale. Also, the electrode-supported planar SOFCs can be made of very thin electrolyte, which means they can operate at lower temperature (as low as 500°C). This is very important for some applications such as APUs for vehicles. Furthermore, lower operating temperature results in simpler BoP, easier thermal management, less degradation of the components, and faster start-up and cool down. However, the temperature gradient and heat cycles as well as slight mismatch in thermal expansion coefficient between cell components can cause huge thermal stress, as high as several tens of MPa (Yakabe et al., 2001), which makes the sealing of the stack more challenging.

For the tubular SOFC, a power density of about 0.3 W/cm^2 with degradation rate of less than 0.1% per 1000 hours of operation and fuel utilization factor of about 85% and for the planar SOFC a power density of about 2 W/cm^2 with fuel utilization factor of about 95% has been reported (Singhal, 2002, 2000a; Williams et al., 2006).

13. Hybrid SOFC cycles

As mentioned earlier, one of the advantages of high temperature fuel cells is their capability to be integrated to a bottoming cycle, so that exhaust thermal energy can be used to generate further useful energy in the form of electricity and/or heat. Singhal (2000a) reported that due to higher efficiency and availability as well as low maintenance costs, the hybrid SOFC plants could compete with conventional power generation systems. In a fuel cell hybrid cycle, both SOFC and MCFC can be utilized in the fuel cell stack, but the focus of this work is only on SOFC hybrid cycles, which reflects current trend in the field.

The high temperature of SOFC products provides very good potential for hybrid SOFC systems, especially for distributed generation (DG). The outlet temperature of SOFCs perfectly matches the requirement of modern gas turbines (Calise et al., 2007). Rajashekara (2005) classified the hybrid fuel cell systems as Type-1 and Type-2 systems. They are mainly suited for combined cycles power generation and backup or peak shaving power systems, respectively. An example of Type–1 hybrid systems is hybrid fuel cell and gas turbine (GT)

cycle, where high temperature of fuel cell off-gas is used in GT to increase the efficiency of combined system. Another example of this type of combined cycle is designs that combine different fuel cell technologies. Examples of Type–2 hybrid systems are designs that combine a fuel cell with wind or solar power generation systems which integrate the operating characteristics of the individual units such as their availability of power.

By definition, proposed by Winkler et al. (2006), any combination of a fuel cell and a heat engine can be considered as fuel cell hybrid system. Therefore, a hybrid cycle can be any combination of SOFC and gas turbine, steam and gas turbine combined cycle power plant (CCPP), steam turbine, coal integrated gasification (IG), integrated gasification combined cycle (IGCC), and application in combined cooling and/or heating, and power (CCHP/CHP) cycles. These power cycles are investigated later in subsection 14.

The operating pressure of SOFC affects the types of bottoming cycle that can be integrated into the system. In Type–1 hybrid systems, if the fuel cell is operated at atmospheric pressure, the exhaust gases can be passed through series of heat exchangers to generate hot water and/or low pressure steam for industrial applications (Riensche & Fedders, 1993) or high pressure steam for a Rankine power cycle. The latter scheme was proposed as early as 1990 (Dunbar et al., 1990). The fuel cell may also be operated at elevated pressure. In this case, the pressurized hot combustion gases exiting combustor at the bottom of SOFC can be used to drive a gas turbine with or without a bottoming steam cycle. This scheme was proposed in 1991 (Donitz et al., 1991).

Among various hybrid schemes proposed for pressurized fuel cells, probably SOFC-GT hybrid cycles are the most popular systems being studied theoretically and the only one being studied experimentally. There are two main designs to combine SOFC and GT. The difference between these designs is how they extract heat from fuel cell exhaust. In the first design, fuel cell off-gas directly passes through GT. That means the gas turbine combustor is replaced by the fuel cell stack. But in the second scheme, the fuel cell off-gas passes through a high temperature recuperator, which, in fact, replaces the combustor of the gas turbine cycle (Roberts et al., 2006). From operational point of view, these designs are distinguished by the operating pressure of the fuel cell. Their operating pressure is equal to operating pressure of the gas turbine and slightly above atmospheric pressure, respectively. It should be mentioned that in all cases a steam cycle (Campanari & Macchi, 1998) and CHP plants can be integrated into the hybrid system to recover more energy from exhaust.

So far, to the authors' best knowledge, there have been three proof-of-concept and demonstration SOFC-GT power plants installed in the world. Siemens Westinghouse claimed that it successfully demonstrated its pressurized SOFC-GT hybrid system and has two units, a 220 kW at the University of California, Irvine and a 300 kW unit in Pittsburgh (Veyo et al. 2002a). Also, in 2006 Mitsubishi Heavy Industries, Ltd. (MHI, Japan) claimed that it succeeded in verification testing of a 75 kW SOFC-Micro gas turbine (MGT) hybrid cycle (http://www.mhi.co.jp/en/news/sec1/200608041128.html). These experiences prove the possibility of integrating SOFC and gas turbine. However, they showed that this integration was not necessarily straightforward, and finding a GT with operational condition close to SOFC exhaust condition and coupling them could be extremely challenging (Calise et al., 2007).

The advanced cycles that can be used as bottoming cycle for SOFCs are briefly explained in the following subsection.

14. Advanced power generation cycles

Power cycles are thermodynamic cycles of which their objective is to generate power. The power cycles can be categorized based on several characteristics from thermodynamic point of view:

Gas and vapor cycles: In this categorization the cycles are distinguished based on the phase of the working fluid of the cycle. If the working fluid phase remains unchanged (gaseous phase), it is called gas cycle. On the other hand, in a vapor cycle, the working fluid can be in both gaseous and liquid forms in different parts of the cycle.

Open and closed cycles: If working fluid is recycled and returned to its initial condition, the cycle is called closed cycle. But in an open system, in each cycle, the working fluid is discharged to the surrounding and replaced by a fresh feed. The open system is mechanically, but not thermodynamically, a cycle.

Internal and external combustion engines: Unlike previous cases, this categorization is based on the source of heat and not the cycle's working fluid. In internal combustion cycles, the required heat for the cycle is provided from combustion of fuel in the system, as in gas turbines. But in external combustion engines, the heat should be transferred from an external source, as in steam cycles.

It should be noted that there are power generation cycles that do not fit into some of these categorizations, such as fuel cells. In this subsection, some basic and advanced power generation systems, namely gas turbines, steam cycles, combined cycles, and integrated gasification combined cycles as well as some technologies to improve performance of the cycles, such as gas turbine inlet air cooling and CO_2 capture and storage technologies are briefly introduced. In this section, there is not enough space to explain the thermodynamic principles of the cycles, so it is advisable that readers review these topics in a basic thermodynamic book.

14.1 Carnot cycle

The Carnot cycle is the most efficient and simplest thermodynamic cycle. It consists of two isentropic (and adiabatic) and two isothermal processes. Fig. 3 shows the temperature-entropy diagram of a Carnot cycle (blue dashed line) that operates between a heat source and sink with temperatures of 1572 K and 293 K, respectively. All processes are reversible and cycle efficiency can be estimated by following equation:

$$\eta = 1 - \frac{T_L}{T_H} \tag{1}$$

where T_H and T_L are the absolute temperatures of heat source and sink, respectively. For the cycle in Fig. 3, this efficiency is about 81%.

14.2 Gas turbine

A gas turbine theoretically operates based on a Brayton cycle. However, real gas turbines are usually operated based on an open cycle and consist of three main components: compressor, combustor, and gas turbine. Fig. 4 shows a schematic of basic gas turbine components in a simple gas turbine cycle model developed in Aspen Plus®. The temperature-entropy diagram of this simple GT cycle is shown in Fig. 3 (gray solid line). In this cycle, air flow rate = 145 kg/sec, fuel (natural gas) flow rate = 2.7 kg/s, compressor

pressure ratio=34, efficiency = 36.8 % (based on lower heating value), and efficiency = 33.2 % (based on higher heating value).
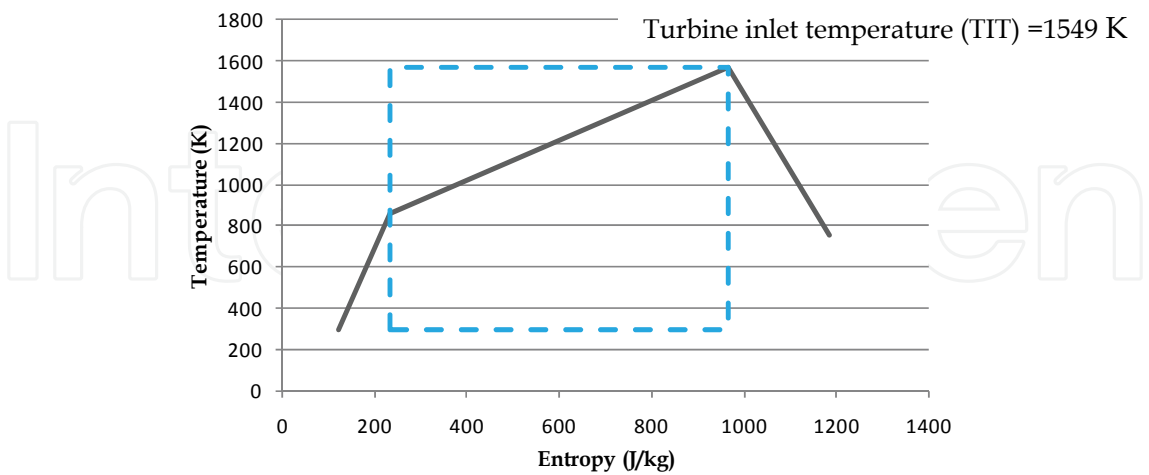

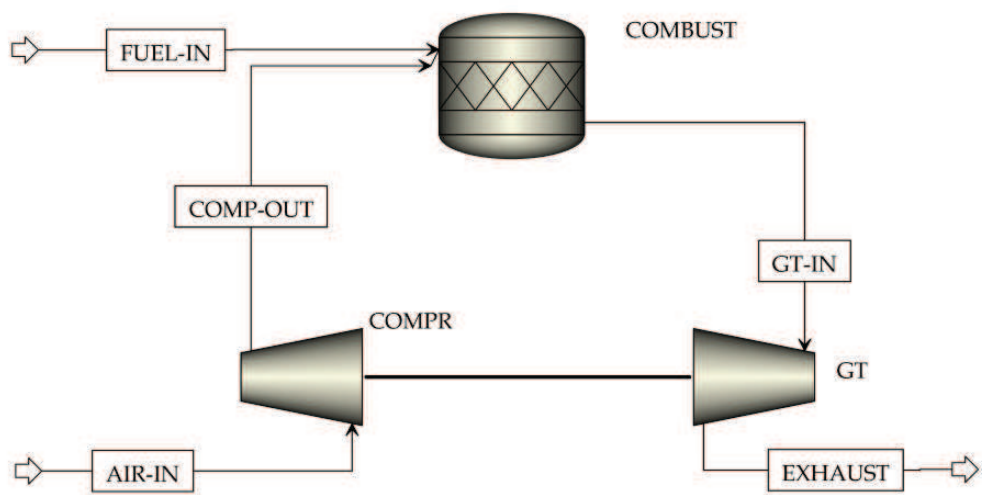Fig. 3. T-S diagram of a Carnot cycle and a gas turbine cycle

Fig. 4. Schematic of a simple gas turbine cycle in Aspen Plus®

The turbine inlet temperature is an important parameter for GT design and operation, because it is the highest temperature throughout a specific gas turbine. The turbine inlet temperature (TIT) is limited by turbine blade material and the maximum permitted NO_x emission.

Gas turbines have been used in power generation industry for more than a century due to their low capital cost and short installation time. Also the short start-up and shut-down time of gas turbines make them a suitable option for peak load operation. Due to their widespread utilization, their technology is mature and very well developed.

Despite their wide application, there are two main problems in using simple gas turbines for power generation. First, the exhaust temperature of GTs is very high, which means high-grade energy is wasted and results in low efficiency of the system. Second, the output and efficiency of GTs and other cycles based on gas turbines strongly depend on ambient temperature and are reduced with higher ambient temperature. These two issues will be investigated in the following subsections (14.3 and 14.4).

14.3 Combined cycle power plant (CCPP)

In order to improve efficiency of GTs, combining the gas turbine with a steam cycle is a suitable option. A schematic diagram of a steam cycle, working based on the Rankine cycle, is illustrated in Fig. 5.
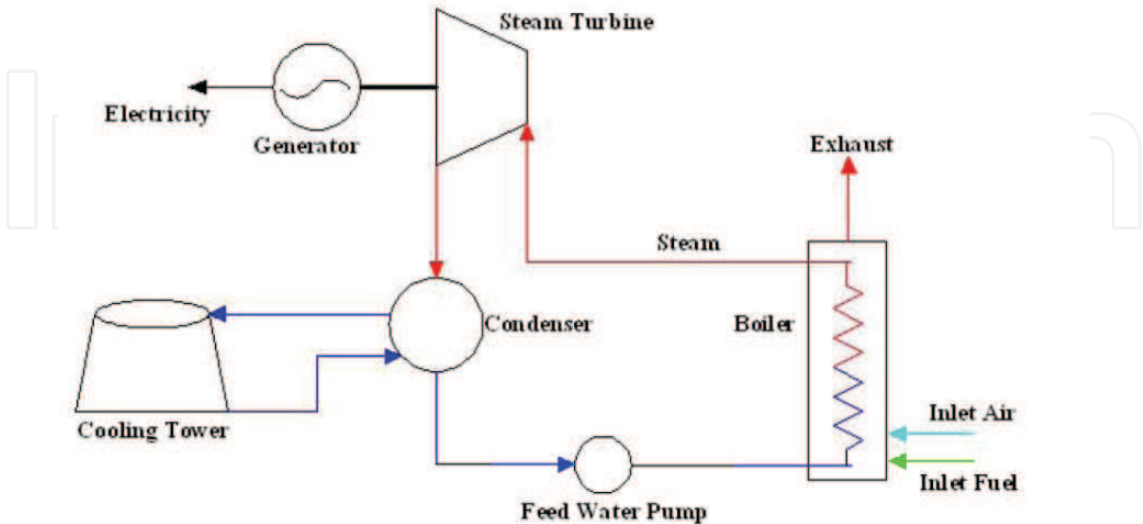

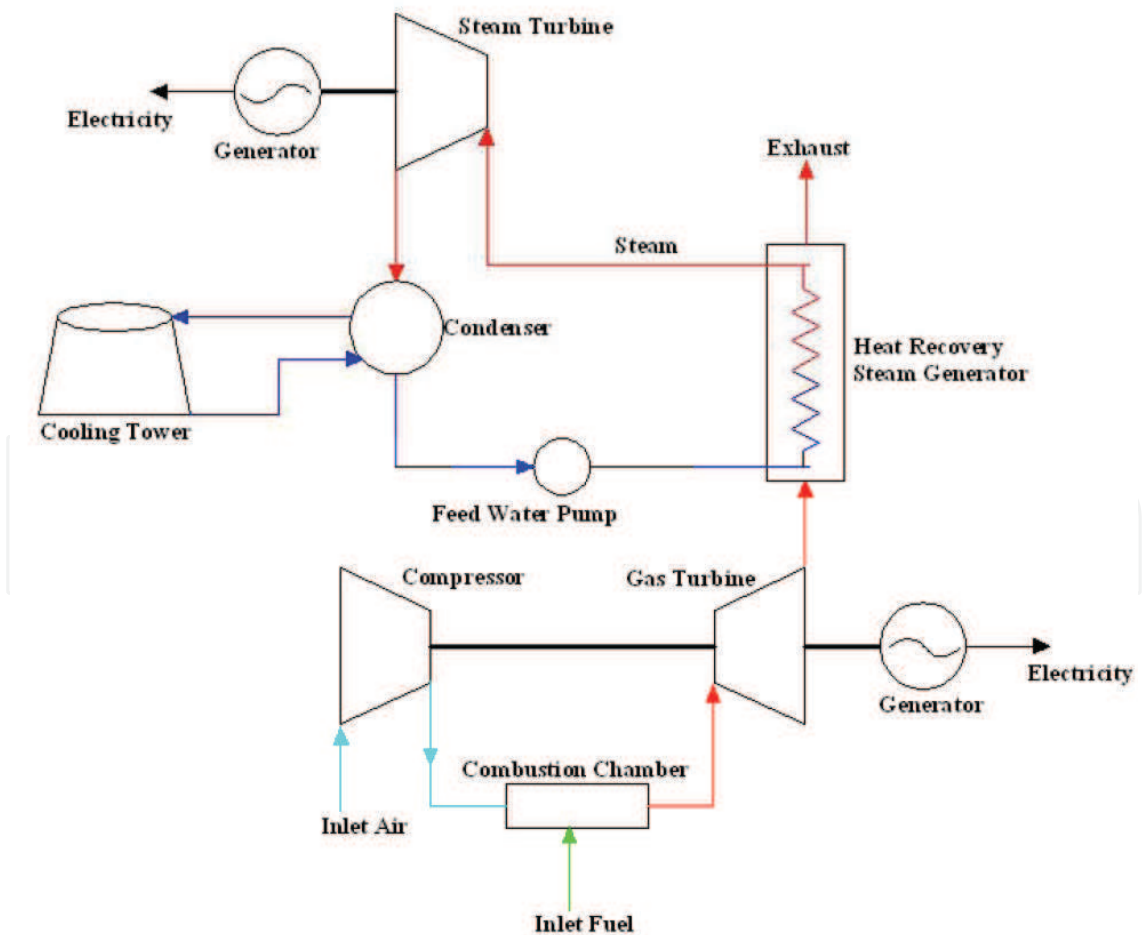Fig. 5. Schematic of a simple steam power generation (Rankine) cycle

Fig. 6. Schematic of a simple combined cycle power plant

In a combined cycle power plant, high temperature exhaust stream of the gas turbine is used to generate required steam for the steam cycle in a heat recovery steam generator (HRSG). This is possible because the inlet temperature to the turbine in a gas turbine, higher than 1400 °C for modern GTs, is much higher than that for steam turbine, around 600 °C. A unit of CCPP consists of several GTs, usually two or three, a heat recovery steam generator, and a single steam cycle (Fig. 6). Very high efficiency, above 60%, has been reported for recent modern CCPPs (Cengel & Boles, 1998).

HRSG can be designed with or without additional firing. Additional firing is used to increase the inlet temperature of HRSG and as a result the output power of steam cycle; although the overall efficiency of the cycle reduces. In earlier CCPPs, this configuration was very common due to low temperature of the GT exhaust. However, due to simplicity of construction and the higher temperature of the exhaust stream of modern GTs, CCPP with no additional firing in HRSG, where all fuel is combusted in the GT cycle, is more common nowadays. In CCPP without additional firing, the efficiency and power output of the bottoming steam cycle is limited by the temperature and flow rate of gas turbine off-gas and the temperature of the exhaust stream at the stack. The stack temperature is bounded by the exhaust stream dew point to prevent acid corrosions.

Based on the HRSG arrangement, CCPP can be single-, two-, or three-pressure cycle. In the simplest configuration, the single-pressure cycle, HRSG can consist of either an economizer, an evaporator, and a superheater or an once-through boiler to generate steam with one pressure. The disadvantage of this configuration is its poor waste heat recovery efficiency. To improve this efficiency, a multi-pressure HRSG can be used to produce steam with
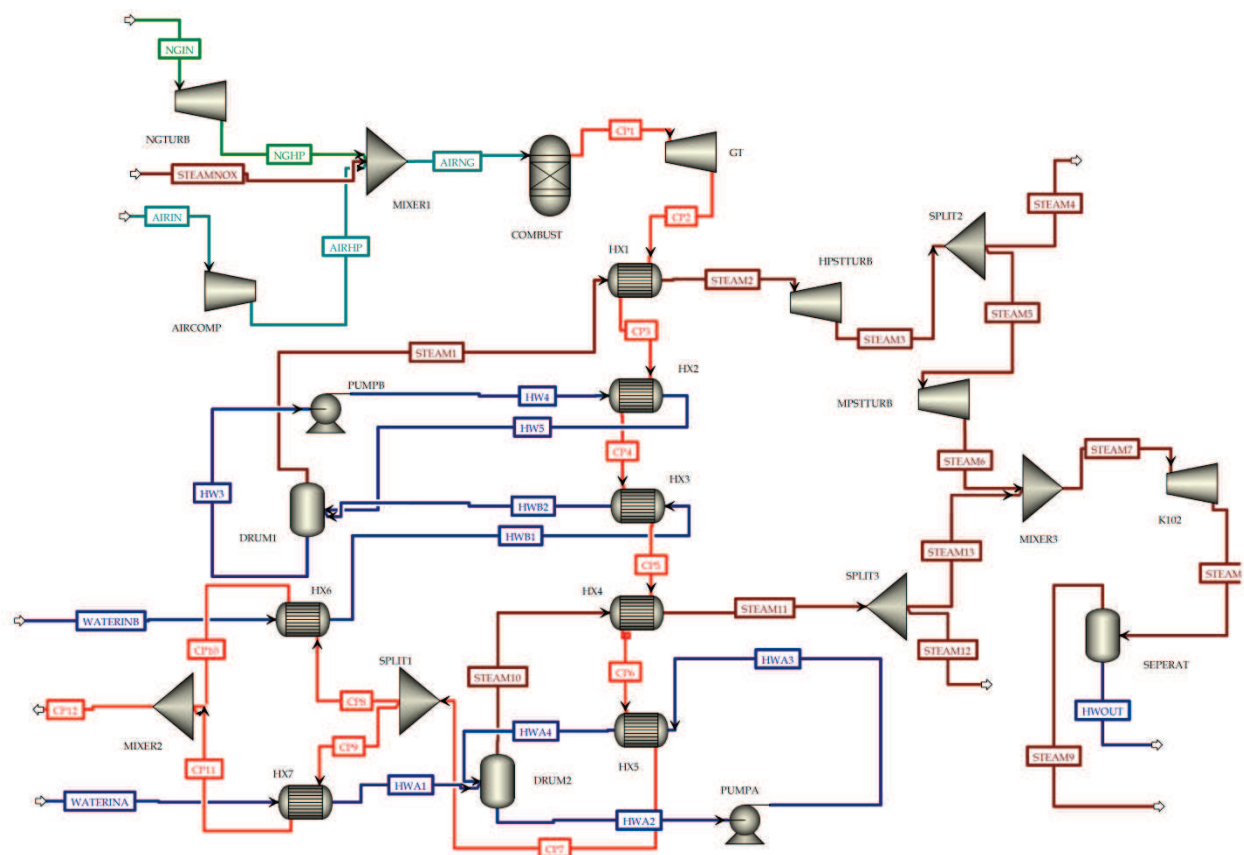

Fig. 7. Schematic of an Aspen Plus® model of a two-pressure CCPP

different pressures. These multiple-pressure steams can drive high and low-pressure (and possibly medium-pressure) steam turbines with much higher efficiency. Fig. 7 illustrates an Aspen Plus® model of a two-pressure CCPP.

14.4 Augmentation of gas turbine power output

The power output and efficiency reduction with higher ambient temperature is a major problem for gas turbine-based cycles, especially in hot climate. Because the peak load in these areas is during summer hot days, and GT-based power plants cannot produce their maximum power output (rated power) when it is most needed. This issue has been intensified with the recent global climate change. The reason for this problem can be explained based on the fact that in a single-shaft gas turbine, the rotational speed of the shaft and as a result the volumetric flow rate of the air are constant. On the other hand, high ambient temperature reduces air density. These two facts, constant volumetric air flow rate and lower air density, cause air mass flow rate reduction with increased ambient temperature. This means lower power output from the gas turbine and higher power requirement in the compressor. Obviously, cooling the inlet air to the compressor can solve the problem. Several methods have been proposed and/or employed to decrease inlet air temperature to the cycle. Generally, these systems can be divided into two main groups: evaporative and non-evaporative systems.

14.4.1 Evaporative cooling

In this system, water evaporates in the inlet air stream to the compressor. The heat required for this phase change (the latent heat of evaporation) is achieved by cooling down the air. It should be noted that at constant ambient temperature, increase in relative humidity results in stream with lower density and higher specific heat, which usually the latter overcomes the former. The problem for evaporative systems is that once the air relative humidity reaches 100%, no extra water can be added to the air. Therefore, the cooling capacity of the system is limited by the relative humidity of the air. The evaporative systems are ideal for hot arid regions. The advantages of these systems are their low capital, operating, and maintenance costs, and quick installation. But their operational capacity is limited and highly affected by ambient wet bulb temperature. Also, they require relatively great amount of water, which is usually precious commodity in arid regions.

There are two main types of compressor inlet air evaporative cooling: media evaporative cooler and inlet fogging.

Media evaporative cooler: In this design, the compressor inlet air passes over a film of water in a carefully designed wetted media, such as honey-comb-like medium. This is the first technology employed for gas turbine inlet cooling. The system has the lowest cost among all cooling systems partially because it can operate with less treated water. The system also acts as air washer that cleans air, which in turn can increase the longevity of the gas turbine's filters. However, the water consumption of the system is high, because in each cycle, water is partially evaporated and the remaining water should be partially recycled, with proper control of its chemistry, and the rest should be rejected from the system as blow down. Another disadvantage of the system is that it cannot achieve very high air relative humidity and take advantage of full cooling capacity.

Inlet fogging: In this design, atomized demineralized water is sprayed in the compressor inlet air by high pressure (100 to 200 bar) nozzles, mostly impaction pin type. The GT inlet

temperature can be controlled by the amount of water sprayed into the stream. The fogging system can increase the air relative humidity to almost 100%. If more water is sprayed, the excessive water will carry over to the compressor in the form of water droplets. These droplets can provide intercooling for the compressor by evaporating while the air temperature increases due to compression. This latter system is called overspraying or wet compression.

Also there are other gas turbine power augmentation methods, such as injection of water or steam to combustion chamber. The main objective of most of this type of GT augmentation is NO_x emission control and reduction. However, due to increase in GT mass flow rate, higher output power can be achieved as well.

14.4.2 Mechanical refrigeration system cooling

Alternatively, mechanical refrigeration systems can be used to decrease gas turbine cycle inlet air temperature. These systems are not limited by ambient conditions and can reduce air temperature lower than that of evaporative systems. The refrigeration system can be either compressor chiller or absorption chiller. The former suffers from high operation cost due to high electricity consumption, and the latter suffers from high capital cost partially due to required waste heat recovery system.

In order to reduce the cost of electricity and take advantage of low night time tariff, thermal energy storage systems can be used. In these systems, ice or chilled water are generated during off-peak hours, usually in the night time, and then used to cool down inlet air in peak hours (Wang, 2007).

14.5 Integrated gasification combined cycle (IGCC)

Coal has been used as a fuel for power generation for a long time. This utilization has been mostly in steam power plants, where coal is combusted in a conventional boiler to produce steam for the power plant. These types of coal-fired power plants are mainly pulverized fuel-fired stations and fluidized bed combustion–based plants. The utilization of coal as fuel in GTs was possible only in externally or indirectly fired gas turbines, where coal is burned in an external combustor and then the heat was transferred to air via a heat exchanger to pass through the gas turbine. On the other hand, coal gasification is a well-developed technology to produce synthesis gas (syngas, mainly hydrogen and carbon monoxide) by gasifying coal with steam, oxygen, or air.

Integrated gasification combined cycle is the combination of coal gasification technology with a gas turbine and steam cycle to generate electricity. The advantages of the technology can be summarized as:

- Higher efficiency, around 40%, in comparison to other coal-fired power generation technologies (Ratafia-Brown et al., 2002);
- Feedstock flexibility, since coal, heavy petroleum products, petroleum coke, biomass, etc. can be used as inlet fuel to the system;
- Very low pollutant, such as CO_2, CO, NO_x, SO_x, emissions in comparison to other coal-fired power generation technologies. IGCCs can meet the requirements of the most strict air control regulations (Elseviers et al., 1996);
- Various potential products, such as electricity, high and low pressure steam, hot water, hydrogen, syngas fuel, other chemicals, sulphur by-products, even valuable solid wastes (Ratafia-Brown et al., 2002), can be generated;

- Capability to be adapted for repowering of old coal-fired power plants.

The main additional equipment in IGCC, compared to CCPP, is the gasifier and gas clean up components. In the gasifier, the inlet fuel is converted to high temperature and normally high pressure syngas. The reaction in the gasifier is endothermic, and the required heat can be supplied by fuel partial oxidation. The reactions and their attributes will be explained in the subsection 15.1. The pollutants, such as minerals, ash, slag, particulate, nitrogen, sulphur compounds, and gaseous mercury are then separated from syngas in different stages of gas clean up. Different carbon dioxide capture technologies can be used to significantly reduce greenhouse gas (GHG) emissions. These CO_2 capture technologies will be briefly explained in following subsections.

14.6 CO$_2$ capture and storage technologies

As noted in the introduction, power generation industry is responsible for the majority of GHG emissions from industrial activities. Thus, it is essential to try to reduce such in light of climate change and environmental concerns. One of the methods to achieve this goal is to increase efficiency in power generation, which has been a main topic of this section. Another method is the utilization of CO_2 capture and storage systems in power plants. Potentially, CO_2 capture technology has already existed for all of the aforementioned power generation technologies, although in most cases it has not been developed particularly for that system. For different types of power plants fueled by oil, natural gas, and coal, there are three main techniques that could be applied (Riahi et al., 2003; Metz et al., 2005):

- CO_2 capture after combustion (post-combustion);
- CO_2 capture after concentration of flue gas by using pure oxygen in boilers and furnaces (oxy-fuel power plant);
- CO_2 capture before combustion (pre-combustion).

These technologies will be explained in the following subsections.

14.6.1 CO$_2$ capture after combustion (post-combustion)

This method treats plants' flue gases to remove CO_2. This methodology can be easily applied in the near future. Post-combustion CO_2 capture in conventional power plants is currently too costly and energy consuming. Several methods to capture CO_2 from thermal power stations flue gas are as follows:

Solvent scrubbing systems: This method is suitable for CO_2 separation for low concentration of carbon dioxide (5 to 15% by volume) in a stream at low pressure. This low concentration of CO_2 and low pressure is very similar to condition in the flue gas of conventional power plants. In this method, the solution of amines is used as solvents to separate CO_2. Using this process, 90% of CO_2 in the flue gas can be captured. The separation process of carbon dioxide by chemical absorption consists of two steps:

- the absorption of CO_2 by chemical solvents at a low temperature (40 - 65 °C);
- the recovery of CO_2 from chemical solvents by using low temperature (100 – 150 °C) heat sources usually from power plants.

The details of the mechanisms of CO_2 absorption into an amine solution are quite complex (Danckwerts & Sharma, 1966; Versteeg et al., 1996). At present, a few coal- and gas-fired power plants utilize this technology to capture CO_2 (IEA, 2003b). However, scrubber-based systems require considerable capital investment as well as remarkable reduction in the overall plant efficiency.

Cryogenics: CO_2 can be separated from other gaseous compounds in the flue gas by cooling and condensation. This method is suitable for high concentration of CO_2 (more than 90%), and the technology is not applied to typical power generation plant exhaust stream. Obviously, a disadvantage of the process is that it requires a significant amount of energy.
Membranes: In this method, a separation membrane is used to allow one component to pass more speedily through the membrane. A range of membranes is available for this purpose in which all of them are complex and energy consuming with low degree of separation.
Adsorption: Some solids can separate CO_2 from gas mixtures. They are not yet considered to be applicable for power plant application because the capacity and CO_2 selectivity of adsorbents is not acceptable yet.
In practice, the most popular technology for CO_2 capture from power generation plants and other industries is the scrubber-based system.

14.6.2 CO_2 capture after concentration in the flue gas (oxy-fuel power plants)

As mentioned, the removal of CO_2 from the exhaust stream of power plants is very energy demanding. The oxy-fuel process is proposed to increase the CO_2 concentration in the flue gas by burning fuel with pure oxygen instead of air. If oxygen is used for combustion process, the exhaust stream will be mainly composed of CO_2 and steam. An air separation unit (ASU) is required to provide pure oxygen. Also, flue gas should be recycled to reduce temperature in the boiler. With this technology, a CO_2 concentration of above 90% is achievable which in turn lowering the energy requirement for the separation process. In order to reduce impurities in the off-gas, reduction of excess oxygen from 17% to 5% is proposed (Kather et al., 2007).

14.6.3 CO_2 capture before combustion (pre-combustion)

In this method, first fuel is gasified and then CO_2 is removed. The product fuel gas is almost pure hydrogen. This method is very attractive for the mid-term future in the hydrogen economy. There are different methods to produce hydrogen from decarbonization of fossil fuels, for instance, methane partial oxidation, methane steam reforming, and coal gasification, which will be explained in subsection 15.1. The latter is mostly being used in IGCC plants. In all these methods after preparation of hydrogen rich stream, CO_2 is usually removed by chemical absorption method. In all of the above processes, the incorporation of power plants and these systems is complex.

14.6.4 CO_2 liquefaction and sequestration

After CO_2 separation, it is stored as liquid. The liquefaction is implemented in various steps by compressing and cooling of the stream. This process is very energy intensive. The use of geologic formations, gas and oil underground fields, old coal seams, and deep-sea sediments, etc. is all possible methods for CO_2 sequestration. Further research and development is required to confirm suitability of which.

15. Balance of plant in hybrid SOFC systems

In previous section, the general BoP for fuel cell systems was briefly presented. In this subsection, some of these subsystems that are more important for hybrid SOFC systems' performance will be considered in more details. It should be noted that a great number of

configurations have been proposed in the literature for hybrid SOFC systems. These layouts have combined some of the following equipment: various SOFC stacks with different configurations, gas turbines, fuel and air compressors, heat exchangers, anode recirculation, water pump, heat recovery steam generators, pre-reformers, internal reformers, mixers, (catalytic) burners, bypasses, electric generators, invertors, etc.
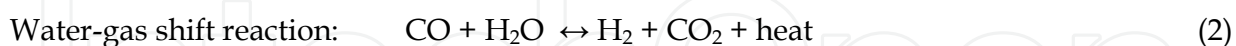
15.1 Fuel processing

Theoretically, every fluid that can be chemically oxidized can be used as a fuel in a fuel cell (Appleby & Foulkes, 1998). SOFCs can be directly fuelled by hydrogen. In this case, the fuel processing system is only hydrogen storage and handling system. For fuels other than hydrogen, generally the first step in fuel preparation process is removal of species, such as sulfur and ammonia, that can degrade fuel cell and/or auxiliary systems. Sometimes it is required to remove some components at the end of fuel processing, such as removal of CO in PEFC, but this is not the case for SOFCs. The fuel cleaning is a well-developed process and existing technologies can be employed for this purpose.

A SOFC can directly use conventional fuels, such as methane, in electrochemical reactions, at least theoretically. However, this is not currently feasible (Peters et al., 2000). Therefore, in order to increase fuel flexibility, a fuel cell system should be able to use commercially available fuels to produce hydrogen rich stream, a chemically preferred fuel for fuel cells.

At present, three fuel conversion technologies are commercially available, namely steam reforming, partial oxidation, and autothermal reforming.

15.1.1 Steam reforming

In this technique, the vaporized hydrocarbon fuel and superheated steam react to create hydrogen and carbon monoxide. To increase concentration of hydrogen, CO participates in the water-gas shift reaction, where carbon monoxide and steam react to create hydrogen and carbon dioxide. Stream reforming has the highest efficiency and hydrogen concentration at the product among various fuel preparation techniques. For methane, the steam reforming and water-gas shift reactions are as follows:

$$\text{Steam reforming reaction:} \quad CH_4 + H_2O + \text{heat} \leftrightarrow 3H_2 + CO \quad (1)$$

$$\text{Water-gas shift reaction:} \quad CO + H_2O \leftrightarrow H_2 + CO_2 + \text{heat} \quad (2)$$

For higher hydrocarbons, the steam-reforming reaction produces a stream of combination of hydrogen, methane, and carbon oxides. This reaction can be simplified in Equation 3 (total reaction including the steam reforming of generated methane but not water-gas shift reaction):

$$C_nH_m + SCRnH_2O \leftrightarrow nCO + (\tfrac{m}{2} + n)H_2 + (SCR - 1)nH_2O \quad (3)$$
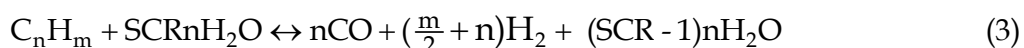
where n and m define the composition of the fuel and SCR represents the fraction of steam-to-carbon of the mixture.

Although the steam reforming reaction does not require catalyst, a catalyst can improve reaction efficiency at lower temperature. The steam reforming process is endothermic and the reaction is slow by nature; therefore, it needs large reactor. Also, this technology is not suitable for rapid start-up and its response to load change is slow.

The water-gas shift reaction is exothermic; however, the overall reaction, both steam reforming and water-gas shift simultaneous reactions, is endothermic. In a fuel cell system, the required heat can be provided from the electrochemical reactions in fuel cell (which can help to cool down the cell), or from a furnace that burns some of the inlet fuel, or the fuel effluent from the fuel cell. It has been shown that the heat generated in the electrochemical reactions is greater than heat required for steam reforming reaction and excessive heat is removed from fuel cell by exhaust streams. Ahmed and Forger (2000) reported that, under typical operating conditions, the rate of heat generation in the electrochemical reactions was about twice as the thermal energy consumption in steam reforming reaction.

In a steam reforming process, there is possibility of carbon formation by the following reactions (Van Herle et al., 2003):

$$CH_4 \leftrightarrow C + 2H_2 \tag{4}$$

$$2CO \leftrightarrow C + CO_2 \tag{5}$$

$$CO + H_2 \leftrightarrow C + H_2O \tag{6}$$
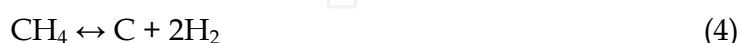
The carbon formation can be suppressed by providing sufficient steam. The steam-to-carbon molar ratio of higher than 2 is common to prevent soot formation and to force the reaction to completion (EG&G Services, 2004; Achenbach, 1994).

As Equations 1 and 2 show, these reactions require steam. This steam can be provided from an external water or steam source. In case of water, the water can be converted to steam in a heat recovery steam generator (HRSG) by recovering the waste heat of the system exhaust. Alternatively, the steam can be provided by recycling steam rich anode products. The mixing of the fuel and anode exhaust stream can be performed by means of an ejector. Obviously, during the start-up, the plant requires an external boiler that produces steam for the reactions.

15.1.2 Partial oxidation (POX)

Unlike the steam reforming reaction, the partial oxidation does not require any steam. In this process, the fuel is partially combusted with substoichiometric amount of air or oxygen:

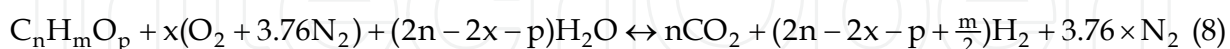$$CH_4 + \tfrac{1}{2}O_2 \leftrightarrow 2H_2 + CO + heat \tag{7}$$

Due to the exothermic fuel combustion, the temperature of the reaction is high, but can be reduced by steam injection during water-gas shift reaction. Since there is no need for indirect heat, the equipment is simpler, lighter, and smaller. Its response to load change is fast and start-up time is shorter. However, the concentration of hydrogen in the products is lower. There are different opinions regarding its efficiency. Some references, like EG&G Services (2004), reported higher efficiency for the partial oxidation process, but widely-held opinion is that the efficiency of steam reforming process is higher. Due to higher temperature of POX, most liquid fuels are reformed in POX reformers (Petruzzi et al., 2003). If air is used for the process (opposed to pure oxygen), nitrogen from air is introduced to the product, which reduces the partial pressure of hydrogen in the product stream and thus the fuel cell power output. In addition, since available heat from the fuel cell is not used in this system and the fuel is directly combusted for this purpose, the effectiveness of the system is lower.

15.1.3 Autothermal reforming

The autothermal reforming is a combination of steam reforming and partial oxidation reactions, where the heat generated by the latter reaction is consumed by the former reaction, resulting in a slightly exothermic reaction. The technique results in a simpler, smaller, and faster responding system than the steam reformer and in higher hydrogen concentration and lower temperature than partial oxidation processor.

A generic equation that covers all aforementioned techniques (the total reaction including water-gas shift reaction) can be summarized as follows (EG&G Services, 2004):

$$C_nH_mO_p + x(O_2 + 3.76N_2) + (2n - 2x - p)H_2O \leftrightarrow nCO_2 + (2n - 2x - p + \tfrac{m}{2})H_2 + 3.76 \times N_2 \quad (8)$$

For instance, for x=0, p=0, n=1, and m=4, this equation reduces to the steam reforming of methane (Equations 1 and 2).

The efficiency of a fuel processor can be defined based on Equation 9 (EG&G Services, 2004):

$$\text{Efficiency} = \frac{\text{LHV of anode fuel produced}}{\text{LHV of inlet fuel}} \quad (9)$$

Both steam reforming and partial oxidation can be utilized in SOFC plants. However, only a few experimental and modeling works, such as Finnerty et al. (2000) and Petruzzi et al. (2003), used POX and great majority of the SOFC systems in the literature applied the steam reformer. It is suggested that, for small units, where compactness is important, POX process is applied and for applications, where high efficiency is desired, steam reformer is used (Peters et al. 2002). Also, POX is used when the fuel cell is fueled with liquid fuel, for example, for auxiliary power units (APUs) in vehicles, where the system should use same fuel as the vehicle to avoid a second fuel tank (Petruzzi et al. 2003; Steffen et al., 2005).

In the high temperature fuel cells, the fuel, especially methane, can be internally reformed. Although a few SOFC systems with the external reformer have been reported in the literature (Harvey & Richter, 1994; Palsson et al., 2000; Massardo & Lubelli, 2000; Van Herle et al., 2003), due to the considerable benefits of internal reformers, most systems make use of this capability of high temperature fuel cells. The internal reforming of fuel can significantly decrease the system cost and increase its efficiency. Also, the endothermic internal steam reforming process can help to provide additional cooling for the cells, which otherwise should be provided by flowing excess air through the cathode. This can cause even distribution of hydrogen, which can potentially result in more even temperature distribution in the stack (Ahmed & Foger, 2000). However, the complete internal reforming can result in some problems, such as carbon formation in the anode and the exposure of stack to large temperature gradients as a result of the cooling effects of the endothermic reforming reaction (Peters et al., 2000). Existence of heavier hydrocarbons in natural gas, which at high temperatures have a tendency to produce unwanted materials, such as carbon, can intensify the problem. Therefore, to avoid aforementioned problems, it is suggested that the fuel cell system to be equipped with a compact pre-reformer (Peters et al., 2000, 2002; Ahmed & Foger, 2000; Calise et al., 2007; Dicks et al., 2000).

15.1.4 Internal reformer

As noted earlier, high operating temperature of SOFC can eliminate or at least minimize the fuel reforming process by internal reforming of the fuel. There are two designs for internal

reforming in SOFCs; direct internal reforming (DIR) and indirect internal reforming (IIR). The difference between these two techniques is the actual place that fuel reforming takes place. In DIR, the fuel is reformed while it flows over the catalyst particles in the anode. While in IIR, the reforming reactions take place over the paths close to the stack before the fuel reaches the anode. In both cases, the reformer is integrated to the stack and the heat required for the reforming reaction is provided by the electrochemical reactions in the fuel cell and some kind of catalyst, such as the nickel content, is required to promote the reforming reaction.

15.2 Combustor

The fuel cannot be completely consumed in a fuel cell and the fuel utilization factor of fuel cell is always less than 100%. Therefore, in order to avoid unnecessary air pollution and the loss of fuel energy, the remaining fuel should be burned before the SOFC exhaust can be discharged to the environment or a bottoming cycle. This can be done by combusting the anode exhaust with depleted air in the cathode outlet stream. The available fuels in the combustor are hydrogen and lower percentage of carbon monoxide and methane. The cathode air mass flow rate is much higher than the fuel flow rate in order to control stack temperature. Thus, there is enough air in the cathode outlet for the combustion process. The extra heat generated in the combustor can help improve the performance of bottoming cycle and/or heating inlet air as well as fuel to the fuel cell.

15.3 Heat exchangers

Heat exchangers are an important part of a hybrid fuel cell system. Although electrochemical reaction in fuel cell is highly exothermic, the inlet air and fuel should be preheated before they are fed to the fuel cell to prevent high temperature gradient and thermal stress in the stack.

16. Fuel cell modeling

Simulation and mathematical models are certainly helpful for the development of various power generation technologies; however, they are probably more important for fuel cell development. This is due to the complexity of fuel cells and systems based on them, and the difficulty in experimentally characterizing their internal operation. This complexity can be explained based on the fact that within the fuel cell, tightly coupled electrochemical reactions, electrical conduction, ionic conduction, and heat transfer take place simultaneously. That is why a comprehensive study of fuel cells requires a multidisciplinary approach. Modeling can help to understand what is really happening within the fuel cells (EG&G Services, 2004).

Understanding the internal physics and chemistry of fuel cells are often difficult. This is due to the great number of physical and chemical processes in the fuel cells, difficulty in independent controlling of the fuel cell parameters, and access limitations to inside of the fuel cells (Bove & Ubertini, 2006).

In addition, fuel cells simulation can help to focus experimental research and to improve accuracy of interpolations and extrapolations of the results. Furthermore, mathematical models can serve as valuable tools to design and optimize fuel cell systems. On the other hand, dynamic models can be used to design and test fuel cell systems' control algorithms.

Finally, models can be developed to evaluate whether characteristics of specific type of fuel cell can meet the requirements of an application and its cost-effectiveness (EG&G Services, 2004).

Due to its importance, in the past 2 decades, there has been tremendous progress on numerical and computational tools for fuel cells and energy systems based on them, and virtually unlimited number of papers has been published on fuel cells modeling and simulation. With this large amount of literature, it is very difficult to keep track of the development in the field. This problem can be intensified for new researchers as they can be easily overwhelmed by this sheer volume of resources. That is why there have been many review papers on the modeling of different types of fuel cells, especially for modeling and simulation of PEFC (Biyikoglu, 2005; Haraldsson & Wipke, 2004; Sousa & Gonzalez, 2005; Tao et al., 2006; Young, 2007; Wang, 2004), SOFC (Young, 2007; Wang, 2004; Kakac et al., 2007; Bove & Ubertini, 2006) and to a lesser extent MCFC (Baker, 1984).

As mentioned previously, although both SOFC and MCFC can be used in hybrid cycles, due to the cell reactions and the molten nature of the electrolyte and lower efficiency of MCFC (Song et al., 2005), vast majority of research in this field are in SOFC hybrid cycles. There have been some steady state (Massardo & Bosio, 2002; Iora & Campanari, 2007) and dynamic (Ghezel-Ayagh et al., 2004) modeling on the hybrid MCFC-GT cycles. However, the number of papers and diversity of such are not comparable with papers on the SOFC hybrid cycle modeling.

The complex nature of interaction between the already complicated fuel cell and bottoming cycle makes simulation and modeling an essential tool for researchers in this field. In the next section, the ways to categorize the modeling of SOFC hybrid cycles will be discussed.

16.1 SOFC hybrid systems modeling categorization

Haraldsson and Wipke (2004) summarized the key features of the fuel cells models as follows:

- modeling approach (theoretical or semi-empirical);
- model state (steady state or transient);
- system boundary (atomic/molecular, cell, stack, or system);
- spatial dimension (zero to three dimensions);
- complexity/details (electrochemical, thermodynamic, or fluid dynamic relationships);
- speed, accuracy, and flexibility;
- source code (open or proprietary);
- graphical representation of model;
- library of models, components, and thermodynamic properties;
- validation.

Although they provided the above list for PEFC, it could equally be applicable for SOFC modeling. They described the approach of a model as being either theoretical (mechanistic) or semi-empirical. The mechanistic models are based upon electrochemical, thermodynamic, and fluid dynamic relationships, whereas the semi-empirical models use experimental data to predict system behaviors. The state of the model, either steady state or transient, shows whether the model can simulate system only at single operating condition or it can be used in dynamic conditions, including start-up, shut-down, and load changes too. Spatial dimension of a model can be zero to three dimensions. Zero-dimension models only consider current-voltage (I-V) curves. On the other hand, mechanistic approaches address

governing laws, including mass, momentum, and energy balances, and the electrochemical reactions and need the explicit treatment of geometry (Beausoleil-Morrison et al., 2004).

Singhal and Kendall (2006) categorized the resolution of SOFC models in four levels: atomic/molecular, cell, stack, and system. As Singhal and Kendall pointed out, "the appropriate level of modeling resolution and approach depended upon the objectives of the modeling exercise". For instance, the recommended approach for IEA Annex 42, model specifications for a fuel cell cogeneration device, is system level approach. It is because the Annex 42 cogeneration models include the models of associated plant components, such as hot-water storage, peak-load boilers and heaters, pumps, fans, and heat exchangers. In addition, the systems models should be able to couple to the building models. These models simulate the building to predict its thermal and electrical demands (Beausoleil-Morrison et al., 2004).

On the other hand, the models can be categorized based on their SOFC type rather than modeling approach. For instance,

- Fuel cell type:
    - Planar;
    - Tubular;
    - Monolithic (MSOFC);
    - Integrated Planar (IP-SOFC);
- Cell and stack design (anode-, cathode-, electrolyte-supported and co-, cross-, and counter- flow types)
- Temperature level:
    - Low temperature (LT-SOFC, 500–650 °C);
    - Intermediate temperature (IT-SOFC, 650–800 °C);
    - High temperature (HT-SOFC, 800–1000 °C);
- Fuel reforming type:
    - External steam reforming;
    - Internal steam reforming;
    - Partial oxidation (POX);
- Anode recirculation;
- Fuel type.

They can even be categorized by the cycles, such as GT, CCPP, IGCC, and CHP, that are used to form hybrid system with SOFC. Alternatively, the purpose of modeling such as parametric sensitivity analysis, optimization, exergy analysis, economical analysis, configuration analysis, feasibility studies, partial load and transient conditions analysis can be considered for categorizing SOFC hybrid models.

16.2 Modeling steps

Before starting modeling of a hybrid system, it is very important to define the purpose of desired model and then determine the key features of the model. The best modeling approach and the characteristics of the model are dependent on the application. Although this is a vital step, there is high tendency to be overlooked. After finalizing these criteria, details of the model can be identified (Haraldsson & Wipke, 2004).

Similar to modeling of other thermal systems, the first step in the modeling of a SOFC hybrid system is to understand the system and translate it into mathematical equations and statements. The common steps for model development are as follows:

- specifying a control volume around desired system;
- writing general laws (including conservation of mass, energy, and momentum; second law of thermodynamics; charge balance; and so on);
- specifying boundary and initial conditions;
- solving governing equations by considering boundary and initial conditions (analytical or numerical solution);
- validating the model.

Unlike the actual fuel cell operation which is three dimensional and time dependent, fuel cell simulation can be simplified to a steady state, 2-D, 1-D, or 0-D problem by proper assumptions, based on the application of the modeling. Many of the SOFC hybrid system simulations in the open literature are 0-D models. In this type of modeling, series of mathematical formulations are utilized to define output variables based on input ones. In this approach, fuel cell is treated as a dimensionless box and that is why some authors referred it as box modeling. Despite the large numbers of assumptions and simplifications in this method, it is useful to analyze the effects of various operational parameters on the cycles' overall performance, perform sensitivity analysis, and compare different configurations. When the objective of modeling is to investigate the inner working of SOFC, 0-D approach is not appropriate. However, for hybrid SOFC system simulation, where emphasis is placed on the interaction of fuel cell and the rest of the system and how fuel cell can affect the overall performance of the system, this approach can be suitable. In this level of system modeling, there are a variety of assumptions and simplifications. For instance, Winkler et al. (2006) developed a hybrid fuel cell cycle model and assumed that the fuel cell was operated reversibly, representing any fuel cell type, and the heat engine was a Carnot cycle, representing any heat engine.

Different software and programming languages have been used in hybrid SOFC system simulation. Since there is no commercially available model for SOFC stack, all modelers should prepare their own model with appropriate details and assumptions. Therefore, from this point of view, what differentiates models is how they simulate the other components of the system. Generally, they can be divided into two categories. In the first approach, whole models can be developed in programming languages such as Fortran or high level software such as MATLAB/Simulink® platform to solve governing equations of the system. In the second approach, the modelers can take advantage of commercial software such as Aspen Plus® to model conventional components of the cycle.

Due to the nature of numerical modeling, its results should be used carefully. In every modeling, the physical realities of the system should be translated into mathematical equations and solution of these equations is used to express behavior of the system. In case of fuel cells, the physical realities are extremely complex and some of which are completely unknown. Therefore, in order to extract these governing equations, high level of assumptions and simplifications should be considered which in turn introduce inaccuracy to the final results. This means fuel cell models are a "simplified representation of real physics" and even with appropriate validation, accuracy of their results cannot be guaranteed (Bove & Ubertini, 2006). For instance, one should be aware of the possible problems that can arise when local equations are considered as global. Bove et al. (2005) highlighted such problem in their paper. They described the main problem of using 0-D approach for modeling was the negligence of variation in the fuel, air, and exhaust gas compositions through the fuel

cell. As a result of this problem, when the inlet, outlet, or an average value of the gas composition was used in the modeling, different results could be obtained. In particular, it was shown that it was impossible to evaluate effects of fuel utilization variation through the fuel cell when inlet gas composition was considered. On the other hand, considering output streams composition could result in underestimating cell voltage and power output.

However, Magistri et al. (2004) studied simplified versus detailed SOFC models and how this affected the predictions of the design-point performance of the hybrid systems. They emphasized the usefulness of the simplified model for hybrid system design and off-design analysis and detailed model for complete description of the SOFC internal behavior.

Judkoff and Neymark (1995) classified the sources of simulation errors into three groups (these were provided for building simulation programs, but they were equally applicable to SOFC hybrid system simulation):

- Errors introduced due to assumptions and simplifications;
- Errors or inaccuracies in solving mathematical equations;
- Coding errors.

They also proposed a pragmatic, three-step approach to identify these errors. In the first approach, comparative testing, the results of the model should be compared with the results of other models for the same problem with similar initial and boundary conditions. If the results of the models match with acceptable error, it means the implementations are acceptable. However, this does not guarantee the correctness of the results because they all can be incorrect. In the second approach, analytical validation, the results of the model for a simple case are compared with the results of available analytical solution. Finally, in empirical validation, the results of the simulation are compared with real data from the actual system under laboratory or field conditions.

Finally, the validation of a model is important because a model must be validated to be a credible tool. Appropriate data are needed for validation. With limited resources, this can be difficult because most data cannot be found in the open literature. Although performance data from an entire hybrid power generation systems are usually proprietary and are not available in the literature, this information from a single system is easier to find. Therefore, a way to resolve the problem of limited performance data is to develop and validate well-defined subsystem models, and then integrate them to have a complete model of a large hybrid power generation system.

16.3 A detailed example of SOFC-GT hybrid cycle

The purpose of this section is to explain the general steps discussed earlier in the context of a real modeling example (Suther et al., 2010). A steady state thermodynamic model of a hybrid SOFC-GT cycle is developed using the commercial process simulation software, Aspen Plus®. Aspen Plus® is a computerized process simulation tool that can be used for realistic steady state simulation of thermodynamic cycles. In this software, built-in and user-defined models can be connected with material, work, and heat streams to form a model of an actual system. The user-defined models can be created using Fortran, Aspen Custom Modeler®, or Microsoft Excel®. There are various physical property models that can be selected for the flow sheet calculations (Aspentech, 2010). One of the inherent characteristics of Aspen Plus® is its sequential modular approach to modeling. That means each

component, either built-in or user-defined models, is treated independently and calculation results for each block are considered the input for the next block (Bove et al., 2005).

The hybrid cycle model incorporated a 0-D macro level SOFC model. As noted earlier, there is no built-in SOFC model available in this software. Therefore, first, the 0-D model of a SOFC stack was developed using Fortran programming language as user-defined model in Aspen Plus®. Therefore, the model consisted of two main parts; the cycle model with various equipments and the SOFC model. The cycle model included all required system equipment such as fuel reformer, compressors, combustor, heat exchangers, mixing chambers, pump, and the fuel cell stack which were linked together with material and energy streams. The SOFC stack model was developed using fundamental equations of thermodynamics, chemical reactions, and electrochemistry. For chemical reactions, it was assumed that three reactions taking place within the SOFC: reaction of H_2 with O_2 forming H_2O, methane steam reforming reaction, and water-gas shift reaction. The electrochemical calculations were used to estimate the power output of the SOFC. In order to estimate actual operating voltage of the SOFC, the open-circuit voltage was first calculated, and then the three overpotentials (losses), namely the activation, ohmic, and concentration losses were deducted. The thermodynamics equations were also applied to estimate the heat output from the stack and the outlet temperature.

The model constants were determined by using the data from Siemens-Westinghouse SOFC systems (Veyo et al., 2002a, 2002b) as well as considering the ranges available in the literature. As a last step for stack modeling, the model was validated using experimental data from Siemens-Westinghouse SOFC (Veyo et al., 2002a, 2002b). After integrating all equipment, it was possible to investigate two configurations with the same model: with the anode exhaust recirculation and with the heat recovery steam generator, both for maintaining the steam-to-carbon ratio of the reformer. The model was used to carry out parametric study (Suther et al., 2010).

17. Conclusion

The power generation industry is responsible for significant portion of industrial GHG and other emissions. Thus, sustainability considerations should be involved in all major energy development plans around the world. Fuel cells are an interesting alternative for conventional power generation technologies because of their high efficiency and low environmental effects. Their operation is based on the electrochemical reactions (and not combustion) of fuel and air. They can directly convert the chemical energy of many types of fuels to electrical energy. Scalability, quiet operation, easier carbon capture, and possible water production are some of their attributes. Based on the type of electrolyte, fuel cells can be categorized into five groups: polymer electrolyte fuel cell (PEFC), alkaline fuel cell (AFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC), and solid oxide fuel cell (SOFC). Each type of fuel cells is suitable for certain application. Stationary and distributed power generation, transportation, and portable applications are the main candidates for fuel cell utilization. Among these fuel cells, due to their high operating temperature, solid oxide fuel cells are specially suited for stationary electricity generation. They can internally reform some of hydrocarbon fuels and do not need noble metals as electro-catalysts. Also a bottoming cycle, such as gas turbine, steam and gas turbine combined cycle power plant (CCPP), steam turbine, coal integrated gasification, integrated gasification combined cycle (IGCC), and combined cooling and/or heating, and power

(CCHP/CHP) cycles, can be integrated to the SOFC to generate further power and/or thermal energy and increase the system efficiency. Energetic and/or environmental performance of these bottoming cycles can be improved by some methods, such as augmentation of gas turbine power output and CO_2 capture and storage technologies. However, some technical challenges, such as the cost of materials and manufacturing, system life, thermal cycling, limited power density, mismatch of thermal expansion coefficient of different components, sealing problem, materials selection at high temperature especially metal interconnections, and corrosion in some components, should be addressed before SOFCs can be commercialized. The stand alone and hybrid SOFC cycle modeling is an important tool for their developments, due to their complexity and difficulties in conducting experiments on the fuel cell.

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Paths to Sustainable Energy

Edited by Dr Artie Ng

The world's reliance on existing sources of energy and their associated detrimental impacts on the environment- whether related to poor air or water quality or scarcity, impacts on sensitive ecosystems and forests and land use - have been well documented and articulated over the last three decades. What is needed by the world is a set of credible energy solutions that would lead us to a balance between economic growth and a sustainable environment. This book provides an open platform to establish and share knowledge developed by scholars, scientists and engineers from all over the world about various viable paths to a future of sustainable energy. It has collected a number of intellectually stimulating articles that address issues ranging from public policy formulation to technological innovations for enhancing the development of sustainable energy systems. It will appeal to stakeholders seeking guidance to pursue the paths to sustainable energy.

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