CHAPTER 1
INTRODUCTION

1.1 Fuel cell: an emerging power technology

Fuel cells have attracted considerable interest during recent years. Fuel cell based power system is an emerging and efficient energy conversion system with flexible fuel utilization and very low pollutant emissions. Unlike in conventional power systems, where fuel needs to be combusted to generate heat which gets transformed into mechanical work for electrical output, a fuel cell power system avoids direct fuel combustion and converts the fuel chemical energy directly to electrical energy through an electrochemical kinetic process. Efficiency of a fuel cell system is not subject to the limitations of Carnot cycle as in the case of a conventional heat engine.

There are various types of fuel cell; the classification mainly depends upon the type of electrolytes, fuels and catalysts they use and their operating conditions. These are also factors that decide the suitable field of applications of a given type of fuel cell. Fuel cells are mainly classified as follows:

**Alkaline Fuel Cells (AFCs):** These fuel cells use a solution of potassium hydroxide in water as the electrolyte. The electro-chemical reactions in AFCs occur at a faster rate and these were widely used in the U.S. space program. However, the problem with AFC is that it is susceptible to poisoning by CO\(_2\) and even a small amount of CO\(_2\) in the air drastically reduces the cell performance and durability due to carbonate formation.

**Proton Exchange Membrane Fuel Cells (PEMFCs):** PEMFCs use a solid polymer as electrolyte and porous carbon containing platinum or platinum alloy catalyst as electrodes. It operates at 80–100°C and delivers high power density at lower weight and volume as compared with other fuel cells. So, they are basically suitable for passenger vehicles, such as cars and buses. However, PEMFCs are intolerant to CO and the low operating temperature creates a water-handling problem with the reaction product H\(_2\)O. If liquid methanol is used as an oxidizer directly in the PEMFCs, then they are referred to as direct methanol fuel cells (DMFCs).

**Phosphoric Acid Fuel Cells (PAFCs):** PAFCs have a corrosive liquid phosphoric acid electrolyte and porous carbon electrodes containing a platinum catalyst. They are
operated at high temperature about 220°C and therefore it can be used as a small combined heat and power plants. PAFCs are more tolerant of impurities in fossil fuels that have been reformed into hydrogen than PEM cells, which are easily "poisoned" by carbon monoxide. They require much higher loadings of expensive platinum catalyst so they are more expensive than other fuel cell.

**Molten Carbonate Fuel Cells (MCFCs):** MCFCs are high-temperature fuel cells that use an electrolyte composed of a molten carbonate salt mixture suspended in a porous, chemically inert ceramic lithium aluminum oxide matrix and they operate at high temperatures of 650°C. Molten carbonate fuel cells (MCFCs) are currently being developed for natural gas and coal-based power plants for electrical utility, industrial, and military applications. Due to high operating temperature, current MCFC technology is not durable for long period of working time.

**Solid Oxide Fuel Cells (SOFCs):** SOFCs use a hard, non-porous ceramic compound as the electrolyte and operate at 850–1000°C. For power generation, high temperature operation is viewed as a distinct advantage because of the possibility of powering a gas turbine with the SOFC exhaust.

Among the various types of fuel cell, the solid oxide fuel cells (SOFCs) have better potential to achieve higher efficiency for electricity production. SOFC is suitable for both large power plants and small cogeneration unit [1]. SOFCs provide significant environmental benefits with low level of CO, CO$_2$, HC, NOx and SOx emissions. Its high operating temperature allows direct internal reforming of fuels and thereby reduces system complexity involved with low-temperature power plants which require hydrogen generation in an additional process step [2]. One of the most notable advantages with SOFC is that it can be integrated with bottoming cycles to generate further power from high temperature exhaust stream. However, higher manufacturing and material cost is a factor, hence continuous effort is being made simultaneously in order to lower the operating temperature from ~1000°C to ≤ 800°C for improving its system economy, reliability and to reduce high polarization losses [3].

### 1.2 SOFC technology

The characteristic features of SOFC are its solid-state construction and high-temperature operation. Combination of these two features offer a number of benefits
such as high oxide-ion conductivity, better energy conversion efficiency due to high rate of reaction kinetics, internal reforming, fuel flexibility, flexibility in cell and stack designs, manufacturing processes, and power plant sizes [4, 5].

1.2.1 SOFC components

A single cell SOFC is mainly composed of two electrodes (the anode and the cathode), and a solid electrolyte. To produce more power, practical SOFC elements are assembled into a stack in which cell assemblies; each including an anode, an electrolyte and a cathode are stacked with interconnecting plates between them that connect the anode of one cell to the cathode of the next cell in the stack. The function of the anode is to distribute the fuel equally over its whole surface and also to supply the electrons to the cathode via an external circuit. The cathode distributes the air borne oxygen equally over its surface and collects the electrons back from the external circuit. The electrolyte transports the ionic charge between the electrodes and prevents the direct flow of electrons from the anode to the cathode. The interconnecting plates connect the anode and the cathode of two neighboring cell in the fuel cell stack. It also conducts electrons between the electrodes, cells and the external circuit and hence high electrical conductivity of interconnecting material is an important requirement. Sealants are used in certain SOFC designs to form a gas tight seal to prevent leakage of gases from the fuel cell interior to outside and also from one chamber to the other. Leaks may occur due to fracture of the brittle material under severe thermal stresses, cracking caused by mismatched coefficients of thermal expansion and also during thermal cycling of the components.

1.2.2 SOFC component materials

1.2.2.1 Electrolyte

Although a variety of materials are used for solid non-porous electrolytes, the most common and widely used electrolyte for SOFC is the yttria-stabilised zirconia (Y$_2$O$_3$-stabilized ZrO$_2$) or YSZ. YSZ exhibits purely oxygen ionic conduction and no electronic conduction. Cerium oxide doped with samarium (SDC), gadolinium (GDC) or cerium gadolinium oxide (CGO), yttrium doped Ceria (YDC), Cerium doped with calcium (CDC), Lanthanum gallate ceramic that include lanthanum strontium gallium magnesium (LSGM), Bismuth yttrium oxide (BYO), Barium Cerate (BCN), Strontium
Cerate (SYC) are some other oxide based ceramic electrolyte used in SOFC [7]. Scandia stabilized zirconia (ScSZ) is another important material that shows higher ion conductivity, long term and better stability in oxidizing and reducing environment than YSZ. However, these are not readily available and involve higher cost [6, 8]. GDC or CGO shows higher conductivity than YSZ and ScSZ at low temperature and hence bear great potential for application in SOFC in the intermediate temperature range. However, GDC shows mechanical instability, lower ionic conductivity at low oxygen concentration. Lower availability and higher cost is also another problem with gadolinium. LSGM is another potential candidate with high ion conductivity at low temperature. However, lower mechanical and phase stability, gallium (Ga) evaporation at low-oxygen partial pressure, incompatibility with nickel oxide (NiO) at the anode, lower availability and higher price of Ga are its main limitations [8]

1.2.2.2 Anode

SOFC anodes are fabricated by dissolving NiO in the electrolyte material (YSZ, GDC or SDC) in which NiO finally reduces to metallic nickel. This helps in better sintering of the metal particles and provides a thermal expansion coefficient comparable to those of the other cell materials. The most common anode material is the porous Ni-YSZ cermet, in which nickel provides the electronic conductivity and YSZ provides the oxygen-ion conduction. NiO/YSZ anode material is used when YSZ is the electrolyte material. Similarly, NiO/SDC and NiO/GDC anode materials are used with ceria-based electrolyte materials. Morphological degradation from sintering, carbon deposition that destroys the catalytic activity of Ni-YSZ, poisoning from sulfur impurities in the fuel are some major problem for Ni-YSZ. Cu-YSZ could be a good alternative for Ni-YSZ because Cu does not catalyze the C-C bond of carbon deposition and it is more tolerant to sulfur impurities than Ni-YSZ. However, stability is a major concern for this material. Strontium titanate (SrTiO₃) which is chemically stable can be another choice. Electrical conductivity of such material could be enhanced by doping with tri or pentavalent oxides such as La³⁺, Y³⁺ or Nb⁵⁺ [8]. However, if SrTiO₃ anode is used with perovskite based electrolyte such as LSGM, then diffusion of gallium or magnesium from LSGM electrolyte to SrTiO₃ anode may create problem.
1.2.2.3 Cathode

In a fuel cell, the cathodic processes are usually complex with many intermediate process steps in series and parallel combinations. Strontium (Sr)-doped lanthanum manganite (LaMnO3) or LSM is the most common cathode material used in SOFC. Strontium is used as a doping material to enhance its electronic conductivity; however, its ion conductivity is relatively low. LSM offer similar thermal expansion coefficient with that of YSZ. Sometimes, there may be reaction between YSZ electrolyte and LSM cathode resulting in formation of La2Zr2O7 and/or SrZrO3 which can be avoided by using ceria-based interlayer between the two. Lanthanum calcium manganite, LaCaMnO3 (LCM) is another cathode material that offers good performance at high SOFC operating temperature above 800°C and excellent thermal expansion match with YSZ. Some other perovskite-structured ceramic materials that are suitable for low temperature operation (600–800°C) are Lanthanum strontium ferrite (LSF), Lanthanum strontium cobaltite (LSC), Lanthanum strontium cobaltite ferrite (LSMF), Samarium strontium cobaltite (SSC), Lanthanum calcium cobaltite ferrite (LCCF), Praseodymium strontium manganite (PSM), and Praseodymium strontium manganite ferrite (PSMF). Composites of perovskite electrode materials (LSM, LSF, or PSMF) with electrolyte materials (YSZ, SDC or GDC) are being considered to improve electrode performance at lower temperatures. Use of electrolyte and cathode material in composite form increases sites of active volume available for electrochemical reactions. Currently, major research emphasis has been laid on developing higher performance cathodes incorporating modifications such as (i) use of composites of LSM with YSZ electrolyte (ii) use of mixed ionic-electronic conducting oxide such as La1-xSrxC01-yFe3O3-δ (LSCF) (iii) impregnation techniques by depositing nano-dimensional catalyst in the cathode structure [3] by adding ionic conduction, improvement in the design of the three phase (air bound oxygen, the solid electrolyte and the cathode) boundary region and reducing cathode polarization losses have been the prime objectives of all these modifications. Shao et al. [9] made use of perovskite oxide based Ba0.5Sr0.5–C0.0,8Fe0.2O3-δ (BSCF) as cathode material in a thin-film doped ceria fuel cell and observed high power density at reduced temperature. Wei et al. [10] investigating cobalt-free perovskite oxide, Ba0.5Sr0.5Zn0.3Fe0.8O3-δ (BSZF) cathode found that it was superior to LSM and comparable to LSCF electrode. They recommended use of BSZF cathode with doped ceria electrolytes for intermediate temperature SOFCs.
1.2.2.4 Interconnects

Ceramics and alloy metals are most common materials for interconnects. Amongst the ceramic materials, the calcium doped lanthanum chromite (LaCrO$_3$) and YCrO$_3$ compound are the mostly used. Typical dopants such as strontium or calcium are used to increase the conductivity. Ceramic interconnects offer high electronic conductivity, show better stability with other cell components. However, the ceramics materials are costly component for the SOFC. Metallic interconnects include the chromium based alloys and ferritic steels with high electrical conductivity and thermal conductivity [8]. They are also capable of withstanding high thermal stresses. Chromium based alloys are costly and therefore the ferritic stainless steels are preferred over them [7]. LaCrO$_3$ coated metallic interconnects are also being developed basically to prevent metal oxidation and corrosion during SOFC operation. However, the problems with the metallic interconnects are the electrical connection with the ceramic electrodes, thermal expansion mismatch, oxide scale formation on metallic surface, cathode poisoning and long term instability during cell lifetime.

1.2.2.5 Sealants

Usually materials used for sealants are glass or composites of glass and ceramic, however, they are brittle. Therefore, metals, metal-ceramic and ceramic-ceramic composites are also used as sealants. Sealants can be used either as rigid or compressive seals. In rigid seals, no load is applied while the compressive seals are subjected to load during operation. The most common rigid seals for SOFCs are glass or glass-ceramic materials which can operate for long duration without any significant degradation. Alkaline earth based glasses are also used for SOFC applications [11]. Coefficient of thermal expansion of most rigid glass seals is lower than YSZ electrolytes; hence barium and calcium are added to induce high thermal expansion. Barium containing glass-ceramics (BaO-MgO-SiO$_2$ and BaO-ZnO-SiO$_2$) have shown to be the most promising compositions as they have relatively large coefficients of thermal expansion [8]. Metallic braze materials such as silver and gold are also common as rigid seals. They have lower stiffness compared to ceramics and therefore, can accommodate both the thermal and mechanical stresses. However, wetting of the ceramic by the braze metal is a serious problem which however can be overcome by addition of titanium and metal oxide mixture. On the other hand, compressive seals are not rigidly fixed to the other SOFC
components, hence exact matching of thermal expansion is not a prime requirement. The compressive seals are basically metal gaskets made of ductile metals such as gold or silver, super alloys and mica based materials. Gold and silver do not form solid oxides in air and seals made of such materials are not degraded by formation of an oxide scale. Two common mica type materials used for SOFC sealants are muscovite (KAl₂(AlSi₃O₁₀)(F,OH)₂) and phlogopite (KMg₃(AlSi₃O₁₀)(OH)₂) [11]. Between these two, phlogopite is preferred as it has higher coefficient of thermal expansion than muscovite. In mica based seals, the leakage is possible at the interface between the mica and the metal or the ceramic. Compliant layer of metal or glass can be used at the surface of the mica layer to improve the seal. Moreover, mica powder can also be put in the gaps of corrugated metal seals to prevent any kind of leakage.

1.2.3 SOFC design

The common SOFC design configuration can be categorized into two main groups: the tubular and the planar design configuration. Each of the design has different cell configurations, either self-supporting or external supporting. Some other design configurations such as monolithic, segmented-cell in-series or integrated planar SOFC (IP–SOFC), flat tube, micro-tubular, micro-flat tube SOFC designs have also been proposed and developed [4].

Self-supporting configurations of a single cell as shown in Fig. 1.1 include the electrolyte-supported, the anode-supported and the cathode-supported fuel cells where the electrolyte, anode and the cathode respectively provide the structural support to the fuel cell as the thickest layer. Electrolyte supported cells offer high ionic resistance due to its greater thickness and requires high operating temperature. On the other hand, ionic resistance in electrode supported cells is low due to thinner electrolyte and hence, operating temperature reduces significantly. Anode supported SOFCs are preferred due to their better thermal and electrical conductivity, higher mechanical strength, and minimal chemical interaction with the electrolyte [12]. In the external-supporting configuration, the cells are supported externally by the interconnections or a porous substrate. These also provide greater structural strength and thinner cell components, but cell support requirements may impose some limitations in flow channel design.
In the tubular design (Fig. 1.2), the layers of electrodes and the electrolyte are rolled in the form of a tube. In most of the tubular designs, a tube made of LSM functions as cathode as well as mechanical support (Cathode supported). Electrolyte and anode layers are formed on the outside of the tube [4]. Fuel flows outside the tube supplying \( \text{H}_2 \) to the anode, while air enters at the open end, flows axially along the central tube and then returns over the inner surface of the cathode. Siemens Westinghouse has been the pioneer in developing and manufacturing tubular SOFC design. Leakage of gases is not a problem in tubular design; however, tubular SOFCs have low power density due to longer current path and thus offer higher electrical resistance [12]. Fabrication cost is high and due to relatively high thickness of the electrolyte, their operating temperature is relatively higher.

In the planar design, a single cell is configured as flat plates (rectangular, square and circular), the two electrodes and the electrolyte are located parallel to each other and the individual cells are connected in electrical series (bipolar plates) in the planar design (Fig. 1.3). The schematic of the planar design is shown in Fig. 1.3. In contrast to tubular design, the planar fuel cell is less expensive; it’s manufacturing and fabrication cost is relatively lower due to the use of low cost materials. It also offers high power density [13]. Electrode-supported planar SOFCs can be made of thin electrolyte and thus can operate at lower temperature (as low as 500°C). Lower operating temperature results in faster start-up, lower thermal stress and longer life of the cell components. However,
structural integrity and leakage at high operating temperature are some of the major problems with planar SOFC.

Fig. 1.2: Tubular design [12]

Fig. 1.3: Planar design with fuel and air in cross-flow [12]

The monolithic design developed during the initial stages of fuel cell development consists of its components made in the form of a corrugated structure of either in co-flow or cross-flow arrangements [4]. Further development of this design was not pursued due to its higher fabrication cost and greater ionic resistance [6].

The integrated-planar solid oxide fuel cell (IP–SOFC) developed in Rolls-Royce Strategic Research Centre combines the advantages of the tubular and the planar designs and thus has the advantage of higher thermo-mechanical strength of the former and lower fabrication cost of the latter [13-16]. The concept of an IP–SOFC is based on a segmented in series design, with an array of cells supported by a flat/tubular porous support tube (porous substrate configuration) or fitted one into the other to form a tubular self-supporting structure (electrolyte-supported) [4]. Fuel is introduced through the centre of the support tube, while the oxidant flows at the outside of the support tube. The Rolls-Royce IP–SOFC concept is a bundle of glass sealed ceramic modules as shown in Fig. 1.4. The outermost cathode layer is supplied with O₂ from the air flow and the anode is printed directly onto the module surface and receives H₂ from the internal fuel channels.

Flat tube design (Fig. 1.5) has been developed to increase thermal stability by combining tubular and planar cell structures. These are relatively cheaper and have higher power density [13, 17]. The flattened tubes incorporate ribs inside the cell which
reduce the current path and thus decreases the cell internal resistance. The ribs in the plates also help reducing the thickness of cathode and it’s over potential [18, 19, 20].

Fig. 1.4: Integrated planar SOFC design [13]

Fig. 1.5: Flat-tube design [13]

Kendall was the pioneer in the development of micro-tubular SOFC during 1992-1993 [21]. For tubular cells, the power density is inversely proportional to the cell diameter hence smaller the diameter, better is the performance [22]. Thus tubes which are on the scale of millimeters in micro-tubular SOFC results in higher power density. These also have the advantage of short start-up times [22, 23]. They are more resistant to thermal degradation during cycling and sealing requirements are usually less compared to the planar fuel cells. However, fitting of interconnects creates problem during manufacturing and assembling of micro-tubular SOFC stacks. Comprehensive review discussing performance of individual MT–SOFC cell, progress in MT SOFC stack design and current research activities are summarized in references [23, 24, 25]. Extrusion is the mostly used method for fabrication of MT–SOFCs which together with co-extrusion helps in fabricating multilayer tubes with better matching of thermal
expansion coefficients of the materials. This further reduces cracking on thermal cycling and thus improves properties and the structural strength.

SOFC stacks are also available in co-flow, counter-flow and cross-flow configurations. Details about various stack designs and flow configurations are available in [1, 7, 26]. The flow configuration has significant effects on temperature and current distributions within the stack. Various flow patterns such as Z-flow, serpentine flow, radial flow, and spiral flow can also be implemented within a given flow configuration especially in the planar design. These are done mainly (i) to obtain uniform gas distribution (ii) to promote heat and mass transfer in the fuel cell. Design optimization of fuel cell stack is possible through variations in flow configuration and pattern. Manifolds which are required to distribute and collect the flow streams between the cells can be either external or integrated in the fuel cell stack design.

1.2.4 SOFC operation

1.2.4.1 Fuel reforming

Most of the SOFCs use natural gas, producer gas or biogas as primary fuels which need to be converted to hydrogen in a process called reforming. Methane (CH$_4$) is the major constituent in all these gaseous fuels. In SOFC system analysis, it is commonly assumed that H$_2$ is produced by CH$_4$ and CO reacting with H$_2$O at equilibrium through steam reforming and water gas shift reactions respectively. The reaction mechanisms are as follows.

\[
CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad (1.1) \text{ Reforming reaction}
\]

\[
CO + H_2O \leftrightarrow CO_2 + H_2 \quad (1.2) \text{ Shifting reaction}
\]

This fuel reforming process can be performed either in a separate chemical reactor (external reforming) or internally within the fuel cell (internal reforming) [18]. In case of external steam reforming, it requires heat from an external source, while in case of internal reforming; the heat required for the endothermic reforming reactions is supplied by the exothermic electrochemical reactions within the cell.
### 1.2.4.2 Working principle

The hydrogen (H₂) produced by steam reforming is fed into the anode and air bound oxygen enters the cathode. In the cathode, oxygen diffuses through the electrode and reaches the electrode/electrolyte interface, where the oxygen is electrochemically transformed into oxygen ions by consuming the electrons transported through the external circuit. The solid ceramic electrolyte in a SOFC conducts only the oxygen ions and do not conduct electron, hence the electrons flow via the external circuit from the anode to the cathode. The oxygen ion is transported through the electrolyte to the anode side. At the anode, diffused H₂ reacts with the oxygen ions producing water and releasing electrons along with electrical energy and heat. This is shown schematically in Fig. 1.6.

![Diagram of SOFC cell](image)

**Fig. 1.6: Working principle of SOFC cell [7]**

### 1.2.4.3 Electrochemical reaction

The electrochemical reactions that occur at the anode and cathode of the SOFC are:

- At the anode: \[ H_2 + O^{2-} \rightarrow H_2O + 2e^- \] (1.3)

- At the cathode: \[ \frac{1}{2}O_2 + 2e^- \rightarrow O^{2-} \] (1.4)

The overall electrochemical cell reaction: \[ H_2 + \frac{1}{2}O_2 \rightarrow H_2O \] (1.5)
Most fuel cells generate electrical power from direct oxidation of \( \text{H}_2 \) as shown in the above exothermic electrochemical reaction. Under certain conditions, the SOFC anode may support the direct electrochemical oxidation of CO and hydrocarbon fuel usually at the entrance of the fuel cell [27]. These are described as follows:

**Reaction mechanism for CO:**

At the anode: \( \text{CO} + \text{O}^{2-} \rightarrow \text{CO}_2 + 2e^- \)  
(1.6)

At the cathode: \( \frac{1}{2} \text{O}_2 + 2e^- \rightarrow \text{O}^{2-} \)  
(1.7)

The overall reaction: \( \text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2 \)  
(1.8)

**Reaction mechanism for hydrocarbon fuel [22]:**

At the anode: \( C_xH_y + (2x + 0.5y)\text{O}^{2-} \rightarrow x\text{CO}_2 + (0.5y)\text{H}_2\text{O} + (4x + y)e^- \)  
(1.9)

At the cathode: \( (x + 0.25y)\text{O}_2 + (4x + y)e^- \rightarrow (2x + 0.5y)\text{O}^{2-} \)  
(1.10)

The overall reaction: \( C_xH_y + (x + 0.25y)\text{O}_2 \rightarrow x\text{CO}_2 + (0.5y)\text{H}_2\text{O} \)  
(1.11)

The key issue in the direct oxidation of hydrocarbons at the Ni/YSZ anode is carbon deposition [4].

**1.2.4.4 The Gibbs and the Nernst Potential**

The electrochemical work in a fuel cell, the work done by movement of electrons through an electric potential difference, \( E \) across the electrodes is denoted by

\[
W_e = n_eFE
\]

(1.12)

Where \( F \) is the Faraday’s constant, and \( n_e \) is the number of electrons transferred per molecule of fuel utilized. The change in Gibbs energy is equal to the negative of the electrochemical work [1] i.e.

\[
\Delta G = -n_eFE
\]

(1.13)
Applying the same substitution to the standard Gibbs free energy change ($\Delta G^0$), we obtain the standard Gibbs potential, $E^0$ which is also called the ideal open-circuit voltage of a fuel cell (the equilibrium condition in which no current is being drawn from the cell).

$$E^0 = -\frac{\Delta G^0}{n_e F}$$  \hspace{1cm} (1.14)

$\Delta G^0$ is a function of the SOFC operating temperature and corresponds to the standard reference pressure $p^0 = 1$ atmosphere.

For a hydrogen–oxygen fuel cell electrochemical reaction [Equation (1.5)] occurring at constant temperature ($T$) and pressure ($p$), the change in the Gibbs energy can be simplified to

$$\Delta G = \Delta G^0 + RT \ln \frac{p_{H,O}}{p_{H_2} p_{O_2}^{1/2}} + \left[ \frac{1}{2} RT \ln p_0 \right]$$  \hspace{1cm} (1.15a)

At standard reference pressure of 1 atm., the term within bracket will vanish. Further simplification gives:

$$-n_e F E = -n_e F E^0 + RT \ln \frac{p_{H,O}}{p_{H_2} p_{O_2}^{1/2}}$$  \hspace{1cm} (1.15b)

$$E = E^0 - \frac{RT}{n_e F} \ln \frac{p_{H,O}}{p_{H_2} p_{O_2}^{1/2}}$$  \hspace{1cm} (1.15c)

$$E = \frac{-\Delta G^0}{n_e F} - \frac{RT}{n_e F} \ln \frac{p_{H,O}}{p_{H_2} p_{O_2}^{1/2}}$$  \hspace{1cm} (1.15d)

Equation (1.15d) is referred to as Nernst equation. The second term in Equation (1.15d) is a function of the partial pressures of the reactants and the product. Therefore, diluting of $H_2$ and $O_2$ will reduce their mole fraction and the partial pressures lowering the cell voltage. $H_2$ may be diluted by gas mixture of CO, CO2, H2O and CH4 formed during fuel reforming. Similarly, $O_2$ in the air stream contain N2 which reduces its partial pressure. However, reduction in Nernst potential due to dilution of the reacting species could somewhat be offset by operating the SOFC at higher pressure.
1.3 SOFC hybrid cycles

SOFCs provide very good opportunity for hybrid systems especially for distributed generation. Any combination of SOFC and a heat engine can be considered as hybrid SOFC system [28]. In a hybrid SOFC system, the heat energy of the SOFC off-gas is used to generate additional electricity in a heat engine [26], which could be either a gas turbine (GT) or a steam turbine (ST) or both. Accordingly, the hybrid system can be any combination of SOFC–GT, SOFC–ST and SOFC–GT–ST combined cycle (CC) depending on the cycle that is used to form the hybrid system. SOFCs produce electricity and heat using primary fuels such as natural gas, biogas, producer gas made by gasification of coal and woody biomass. Therefore, hybrid SOFC system can also be available in combination of integrated gasification (IG), and integrated gasification combined cycle (IGCC). SOFCs also find applications in combined cooling and/or heating, and power (CCHP/CHP) cycles.

In both the SOFC–ST and SOFC–GT–ST cycle (also referred to as SOFC–CC), steam is generated in a heat recovery steam generator (HRSG) which is then supplied to the ST cycle for further power generation. IG–SOFC systems have more fuel flexibility and would be feasible for countries like India and China where large reserves of coal of different grades are available. SOFC integration with coal gasification in a combined cycle (IG–SOFC–CC) has been reported by many authors [28-31]. Use of syngas produced from biomass gasification as fuel for SOFC is also gaining importance and is bound to draw significant attention from the scientific community [32]. Such systems would be vital for generation of renewable and sustainable electric energy in the near future. Review on all these hybrid cycles separately is provided in the next chapter (chapter-2).

1.3.1 Hybrid SOFC–GT systems

The hybrid SOFC–GT system can be designed for SOFC operation either at ambient pressure (ambient pressure system) or at elevated pressure (pressurized system). In a pressurized system as shown in Fig. 1.7, the high pressure air from the compressor is fed to the cathode whereas in an ambient pressure system, the fuel cell cathode is fed with the gas turbine exhaust gases plus some ambient air bypassing the air compressor. Pressurized SOFC–GT systems have been developed and operated [33]. Although, the pressurized system is compact and has the advantage of higher cell performance, but still
some critical design and operational problems exist, such as more complex system design, high pressure gradients between anode and cathode, difficulty in matching SOFC and GT with the pressurized system etc. In ambient pressure system, the GT pressure is uncoupled from the cell pressure and hence the GT pressure can be selected over a wide range. The schematic of the ambient system is shown in Fig. 1.8. At elevated pressure, SOFC produces more power due to higher cell voltage which increases with increasing GT pressure ratio in pressurized system. In the ambient pressure system however, cell voltage is not affected by the GT pressure ratio and it remains constant. Therefore, the overall system efficiency is higher for the pressurized system than the ambient. This is because, the turbine inlet temperature (TIT) and the net GT power output increases with the increase in pressure. For high pressure ratio, the ambient system is not very feasible because the TIT would be low and the efficiency also will be lower than that of the standalone SOFC system [33]. Further, the range of available design parameters will be less due to the limit on the recuperator temperature.

Fig. 1.7: Pressurized SOFC–GT system [33]
There can be either direct or indirect integration of SOFC into a GT power cycle. The direct and indirect SOFC–GT systems are shown in Fig. 1.9 and Fig. 1.10 respectively. When the SOFC is directly integrated with the GT, the fuel cell stack is placed ahead of an afterburner where the residual fuel is burnt and the gases leaving the burner is expanded in the GT. Additional fuel can also be supplied in the afterburner in order to increase the GT inlet temperature. In case of indirect integration, the fuel cell off-gas passes through a heat exchanger and the air from the compressor is heated before it enters the combustor of the GT cycle. In the indirect SOFC–GT hybrid system, the SOFC can be operated at atmospheric pressure which reduces the sealing requirement, however, in such situation the heat exchanger needs to be operated at very high temperatures and pressure differences.
Both direct and indirect hybrid SOFC–GT systems are efficient than the state of the art recuperative GT system. Indirect hybrid systems are however less efficient than the direct ones. Electrical efficiencies in the range of 50-70% are possible even at low pressure ratios for the indirect and direct hybrid SOFC–GT systems respectively [34, 35]. In the direct system, system efficiency increases rapidly with pressure ratio initially and then changes in an asymptotic manner and becomes independent of pressure ratio at higher pressure. However in an indirect system, the shape of the efficiency vs. pressure ratio curves is similar to the efficiency curve of a conventional recuperative GT system where the efficiency first increases with pressure ratio and then reaches an maximum at a given pressure ratio followed by a decrease thereafter with pressure ratio. This is discussed in detail in [27, 35]. Generally, in a hybrid SOFC–GT system most of the power is produced by the SOFC and amount of power produced by the GT is less compared to SOFC power. The SOFC in an average produces three to five times more power than the GT in case of both direct and indirect integration [35].

### 1.3.2 Hybrid SOFC–ST systems

Hybrid SOFC–ST system is relatively simple compared to SOFC–GT system; however, its efficiency is low [36]. SOFC–ST hybrid systems are suitable for SOFC operating at intermediate and low temperature [37]. Efforts are being made to develop
low temperature SOFC to reduce SOFC manufacturing cost, so combination of SOFC–ST hybrid system in that case would be more attractive than the SOFC–GT systems [37].

The schematic of a typical SOFC–ST power cycle is shown in Fig. 1.11 [38]. In a hybrid SOFC–ST system, the exhaust heat of the product stream from the SOFC and the afterburner (combustor) is utilized to produce steam in an HRSG at high pressure for driving the ST of the bottoming vapor power cycle. In this particular schematic, the heated exhaust stream provides the heat required to preheat and reform the fuel (methane) into hydrogen which then goes into the SOFC anode. The steam required for fuel reforming is derived through partial anode gas recycling. Similarly, a part of the depleted air from the SOFC cathode is recycled and mixed with the main air stream to raise the temperature of the incoming air. If compared with the SOFC system alone, the overall efficiency of the hybrid system increases when the SOFC is integrated with bottoming ST cycle. Some other possible SOFC–ST configurations have also been investigated and discussed in articles [37, 39]. Like in a SOFC–GT system, in this system also the SOFC produces more power and the power output from the bottoming ST plant is relatively less.
1.3.3 Hybrid SOFC–GT–ST cycles

This hybrid system (Fig. 1.12) is similar to the SOFC–GT system but additionally at the bottom of the GT, an ST cycle is incorporated. The SOFC produces electricity directly from the fuel through electro-chemical reaction while the GT cycle produces mechanical power through expansion of combustion gases which is later converted to electrical power through use of electric generator. The exhaust heat of the GT leaving gases is further utilized to produce steam in the HRSG that drives the ST for further power generation in the ST cycle.
Fig. 1.12: A hybrid SOFC–GT–ST system [38]

1.4 Thermodynamic analysis of SOFC hybrid cycles

Exergy analysis is a powerful thermodynamic tool for assessing and improving the efficiency of processes, energy conversion devices and thermal systems. Exergy analysis based on second law of thermodynamics can be applied to design, evaluate, optimize and improve any energy system. In studies related to energy analysis of hybrid SOFC power systems, mainly the systems’ efficiency and power are evaluated under different operating and design conditions. Evaluation of some features of energy resource utilization is not possible through energy analysis alone as it deals with only the quantity of energy and completely ignores the qualitative aspect of it. It is the second law which deals with the quality of energy and provides the framework for evaluating the irreversible losses occurring in various system components. Irreversibility contribution of each individual component can be found out and knowing the exergy destruction in each individual component, it is possible to find ways and means for improvement of
system operations through exergy analysis. Moreover performing energy and exergy analyses together is a better approach of performance assessment and determination of steps towards improvement as it gives a complete depiction of system characteristics.

Often energy and exergy analyses are performed to evaluate the thermodynamic performance of SOFC hybrid GT/ST/GT–ST power cycles [27, 35, 40-57]. New hybrid configurations (involving SOFC) are proposed and thermodynamic modeling is done to evaluate the system’s energetic and exergetic performance mostly under steady state conditions. In Ref. [51] however, attempt has been made to analyze hybrid SOFC–GT system dynamics through development of thermodynamic model under dynamic conditions. Performance of hybrid SOFC–GT power systems have also been evaluated in off design (part load) conditions [58, 59]. With the help of thermodynamic modeling one can predict the overall performance of the SOFC hybrid power system. In many cases, parametric analysis is also performed to evaluate the effect of operating parameters on the energetic and exergetic system performance of hybrid SOFC systems.

1.5. Inverse analysis

The inverse problem consists in using the results of a direct/forward problem to estimate the values of unknown parameters that characterize a given system under consideration. It is called so because in inverse problem, it is assumed that the end results are known and inversely the parameters affecting the end results are calculated and as such, it is the inverse of the forward problem. In the direct/forward problem, the end results (outputs) are calculated based on input parameters and accordingly the values of the input parameters can be changed to investigate their effects on system performance. Such parametric analysis gives a fair idea about the performance variation of the system with the changing values of the input parameters. In an inverse analysis on the other hand, the parameters are assumed unknown and unknown parameters are estimated against the known values of the system performance parameters. Therefore, the inverse problems are more object oriented and sometimes depending upon the nature of the problem, multiple combinations of parameters are obtained from inverse analysis that satisfy a given particular objective function/set of objective functions. This is one special characteristic of inverse analysis that makes it completely different from the direct/forward problem. The fact that a multiple set of parameters satisfy the same objective function/functions can be shown only through inverse analysis and not possible
through conventional parametric analysis. Inverse analysis however cannot be performed without formulating the forward model and hence it is done by coupling of one with the other. Inverse model, in combination with the forward model offers lot of flexibility at the designer’s hand in selecting the most suitable combination of parameters satisfying a given set of objective functions. Hence, the inverse problems play an important role in obtaining parameter values that can’t be directly observed otherwise from the forward analysis.

Inverse techniques are often used for resolving complex engineering problems. It is an efficient mathematical tool which can be used for estimating operating and design parameters of a given system. The only disadvantage is that they are computationally expensive and mathematically more challenging compared to their forward counterpart [60,61].

1.6 Motivation and Research Objectives

SOFC is undoubtedly an efficient energy conversion system. Manufacturing SOFC through development of low cost component materials with proper design configuration that reduces fabrication cost and improves system performance are the key challenges in SOFC design. SOFC integration with conventional GT and ST based power systems and also with the combined GT–ST power cycle has been viewed as the most promising power plant of the future. Lot of researches has been done particularly with thermodynamic modeling and simulation of the hybrid SOFC–GT power systems. There are direct/indirect and ambient/pressurized hybrid SOFC–GT systems. Direct pressurized system is a better choice due to higher overall system efficiency. Again there are configurations that consider either complete fuel reforming internally within the fuel cell or external fuel reforming partially in a pre-reformer (PR) and the remaining fuel reforming inside the fuel cell. Internal reforming is simple, economic and efficient. It provides additional cooling for the SOFC stack. But due to inherent problems of entrance region local sub-cooling, inhomogeneous temperature distributions, thermal stress and anode carbon deposition complete internal reforming is sometimes avoided and partial reforming is done in the external reformer. The heat source for the external reformer could be either a HRSG or the recycled anode gas stream, but it would still require a steam generator for starting purpose in case of external reforming with anode gas recycling. So a hybrid SOFC–GT plant configuration with HRSG and ST plant would be
vital for use in the combined cycle mode. In so far as SOFC integrated ST and combined GT–ST cycles are considered, not much works on thermodynamic modeling and performance evaluation of hybrid SOFC–ST and SOFC–GT–ST configuration are available. Therefore, this research is carried out with the following objectives.

(i) Propose a new SOFC integrated CC power system configuration with a single pressure bottoming ST cycle with provision for fuel and air preheating, additional fuel burning and steam extraction from the ST for fuel reforming in the PR.

(ii) Develop thermodynamic model and perform energy and exergy based parametric analysis of the above mentioned SOFC integrated combined GT–ST power cycle.

(iii) Estimate operating parameters of the proposed SOFC–GT–ST (single pressure ST cycle) power cycle through inverse analysis

(iv) Develop thermodynamic model for simulation of another novel SOFC–GT–ST configuration with dual and triple pressure reheat bottoming ST cycle to predict its energetic and exergetic system performance.

(v) Perform a comparative performance analysis, both in terms of energy and exergy, for the SOFC integrated combined power cycles with three different bottoming ST cycles viz. the triple pressure reheat, dual pressure reheat and single pressure ST cycle.

1.7 Chapter wise organization of the thesis

The thesis consists of six chapters. The present chapter provides the introduction along with motivation and research objectives. The remaining chapters are organized as follows:

- Chapter 2 describes the literature review and scope of the present work. This chapter presents a detail review on previous studies related to SOFC integrated advanced power cycles. The scope of the present research work is highlighted at the end.
• Chapter 3 describes the energy and exergy based thermodynamic modeling and performance analysis of the proposed SOFC–GT–ST CC power plant. A parametric analysis is presented to show the effect of important operating parameters on performance of the hybrid system. Furthermore, performance comparison is provided for two cases of fuel and air recuperation with one preceding the other.

• Chapter 4 presents the inverse analysis of the SOFC–GT–ST CC power system. Where, a differential evolution (DE) based optimization method is used for simultaneous estimation of six unknown system operating parameters. The system’s net power, total irreversibility, energy and exergy efficiencies are taken as objective functions for the inverse analysis. The DE algorithm is described and estimated parameters are discussed.

• In Chapter 5, another SOFC–GT–ST CC power system is proposed with triple pressure reheat cycle in the bottoming ST plant. Detailed thermodynamic modeling of the triple pressure reheat ST cycle is presented and performance variation is provided as a function of compressor pressure ratio (CPR). Further, thermodynamic modeling of two other systems with dual pressure reheat and single pressure ST cycles are presented. Performance comparison is provided among the three systems under identical conditions.

• Chapter 6 summarizes the important observations and conclusions made from this research study. The possible scope of future research on SOFC integrated power cycles and multigeneration systems is also suggested at the end.
Bibliography


