

## Chapter 2

# Fuel Cells Operating and Structural Features of MCFCs and SOFCs

### 2.1 Introduction

The current movement toward environmentally friendlier and more efficient power production has caused an increased interest in alternative fuels and power sources [1]. Fuel cells are one of the older energy conversion technologies, but only within the last decade have they been extensively studied for commercial use. The reliance upon the combustion of fossil fuels has resulted in severe air pollution, and extensive mining of the world's oil resources. In addition to being hazardous to the health of many species (including our own), the pollution is indirectly causing the atmosphere of the world to change (global warming). This global warming trend will become worse due to an increase in the combustion of fossil fuels for electricity because of the large increase in world population. In addition to health and environmental concerns, the world's fossil fuel reserves are decreasing rapidly [2]. The world needs a power source that has low pollutant emissions, is energy efficient, and has an unlimited supply of fuel for a growing world population. Fuel cells have been identified as one of the most promising technologies to accomplish these goals.

Many other alternative energy technologies have been researched and developed [1, 3]. These include solar, wind, hydroelectric power, bioenergy, geothermal energy, and many others. Each of these alternative energy sources have their advantages and disadvantages, and are in varying stages of development. In addition, most of these energy technologies cannot be used for transportation or portable electronics. Other portable power technologies, such as batteries and supercapacitors also are not suitable for transportation technologies, military applications, and the long-term needs of future electronics. The ideal option for a wide variety of applications is using a hydrogen fuel cell combined with solar or hydroelectric power. Compared to other fuels, hydrogen does not produce any carbon monoxide or other pollutants. When it is fed into a fuel cell, the only by-products are oxygen and heat. The oxygen is recombined with hydrogen to form water when power is needed [4, 5].

Fuel cells can utilize a variety of fuels to generate power—from hydrogen, methanol, and fossil fuels to biomass-derived materials. Using fossil fuels to generate hydrogen is regarded as an intermediate method of producing hydrogen, methane, methanol, or ethanol for utilization in a fuel cell before the hydrogen infrastructure has been set up. Fuels can also be derived from many sources of biomass, including methane from municipal wastes, sewage sludge, forestry residues, landfill sites, and agricultural and animal waste [6–8].

Fuel cells can also help provide electricity by working with large power plants to become more decentralized and increase efficiency [7]. Most electricity produced by large fossil fuel burning power plants is distributed through high voltage transmission wires over long distances. These power plants seem to be highly efficient because of their large size; however, a 7 to 8 % electric energy loss in Europe, and a 10 % energy loss in the United States occur during long-distance transmission [9]. One of the main issues with these transmission lines is that they do not function properly all the time. It would be safer for the population if electricity generation did not occur in several large plants, but is generated where the energy is needed. Fuel cells can be used wherever energy is required without the use of large transmission lines.

Fossil fuels are limited in supply, and are located in select regions throughout the world. This leads to regional conflicts and wars which threaten peace. The limited supply and large demand drives up the cost of fossil fuels tremendously.

Other types of alternative energy technology such as fuel cells can last indefinitely when nonfossil fuel-based hydrogen is used.

### **2.1.1 Fuel Cells**

Fuel cells are energy conversion devices that continuously transform the chemical energy of a fuel and an oxidant into electrical energy. The fuel and oxidant gases lick the anode and cathode and are continuously fed promoting the oxidation reaction of fuel and oxidant gas reduction. Fuel cells will continue to generate electricity as long as both fuel and oxidant are available [6, 10, 11].

There are different types of fuel cells, showing a flexibility that could replace most of the devices for the production of electricity covering outputs ranging from a few W to several MW [6, 12].

A first classification distinguishes cells in high temperature (HT) up to 1100 °C, used in stationary systems for cogeneration processes, aerospace and marine applications, and low temperature (LT), from 60 to 120 °C, for low-cost portable devices and automobiles.

Power can be provided by fossil fuels, coal, biogas, and biomass (for PAFC, PEMFC, MCFC, SOFC), alcohol (DMFC), and hydrogen (PEMFC and AF).

A further classification of FCs is based on the electrolyte. In PEMFC and DMFC the electrolyte is a polymeric material with cation exchange capacity; Alkaline FCs (AFCs) have a KOH solution as electrolyte; MCFCs have electrolyte

based on molten carbonate of lithium and potassium; SOFC is based on phosphoric acid.

The FCs are often presented as the solution to the problem of the future production of electricity and for transport vehicles.

Indeed, this technology presents several advantages:

- low emissions, but depend on the fuel used, especially as regards the release of NO<sub>x</sub>, CO, and particulate
- high energy efficiency, especially when compared to those of thermal machines
- weak noise
- different operating temperatures
- modular construction, so by putting in series or in parallel several elementary units you are covering the power range required
- more simple construction, and thus greater reliability and easier maintenance [10, 13].

These advantages justify the strong interest, particularly from many automotive companies, to develop the technology based on fuel cells for automotive [14, 15].

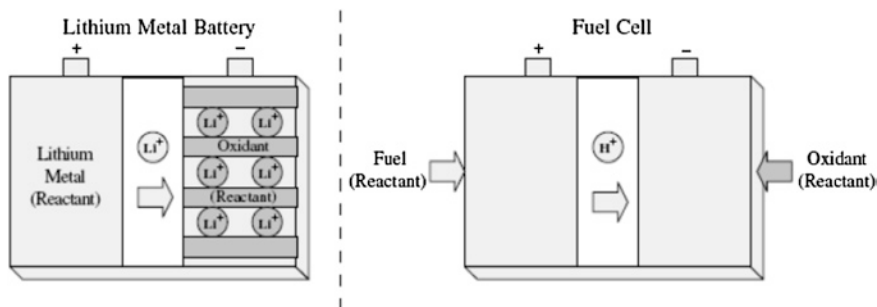
Nevertheless, there are some problems to be solved in order that fuel cells can be competitive and penetrate the market:

- the cost, due to the high value components
- the weight and volume, especially in the automotives
- the length of life, still very low (a few thousand hours for cars, about 40,000 for stationary systems)
- thermal management, for the large amount of heat exchange with an operative cooling system [16–19].

### ***2.1.2 Comparison with Batteries***

A fuel cell has many similar characteristics with batteries, but also differs in many respects. Both are electrochemical devices that produce energy directly from an electrochemical reaction between the fuel and the oxidant. The battery is an energy storage device. The maximum energy available is determined by the amount of chemical reactant stored in the battery itself. A battery has the fuel and oxidant reactants built into itself (onboard storage), in addition to being an energy conversion device. In a secondary battery, recharging regenerates the reactants. This involves putting energy into the battery from an external source. The fuel cell is an energy conversion device that theoretically has the capability of producing electrical energy for as long as the fuel and oxidant are supplied to the electrodes [11]. Figure 2.1 shows a comparison of a fuel cell and battery.

The lifetime of a primary battery is limited because when the amount of chemical reactants stored in a battery runs out, the battery stops producing electricity. In addition, when a battery is not being used, a very slow electrochemical reaction



**Fig. 2.1** Comparison of a fuel cell and a battery [11]

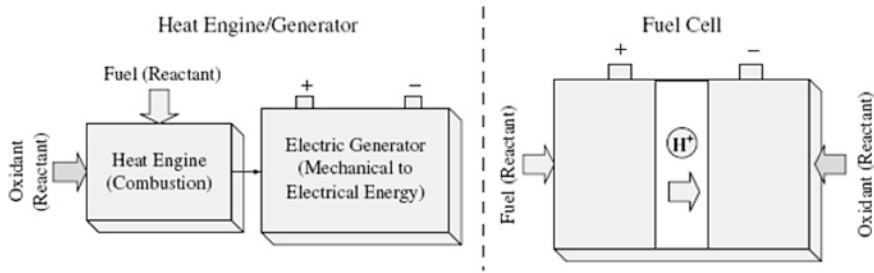
takes place that limits the lifetime of the battery. The electrode of a battery is also used in the process; therefore, the lifetime of the battery is dependent on the lifetime of the electrode. In comparison, a fuel cell is an energy conversion device where the reactants are supplied. The fuels are stored outside the fuel cell. A fuel cell can supply electrical energy as long as fuel and oxidant are supplied. The amount of energy that can be produced is theoretically unlimited as long as the fuel and oxidant are supplied. Also, no leakage occurs in a fuel cell, and no corrosion of cell components occurs when the system is not in use [11, 13, 19].

### 2.1.3 Comparison with Heat Engine

A heat engine converts chemical energy into electric energy like fuel cells, but through intermediate steps. The chemical energy is first converted into thermal energy through combustion, then thermal energy is converted into mechanical energy by the heat engine, and finally the mechanical energy is converted into electric energy by an electric generator.

This multistep energy process requires several devices in order to obtain electricity. The maximum efficiency is limited by Carnot's law because the conversion process is based upon a heat engine, which operates between a low and a high temperature [11, 13, 19]. The process also involves moving parts, which implies that they wear over time. Regular maintenance of moving components is required for proper operation of the mechanical components. Figure 2.2 shows a comparison between a fuel cell and a heat engine/electrical generator.

Since fuel cells are free of moving parts during operation, they can work reliably and with less noise. This results in lower maintenance costs, which make them especially advantageous for space and underwater missions. Electrochemical processes in fuel cells are not governed by Carnot's law, therefore high operating temperatures are not necessary for achieving high efficiency. In addition, the efficiency of fuel cells is not strongly dependent on operating power. It is their



**Fig. 2.2** Comparison of a fuel cell to a heat generator [11]

inherent high efficiency that makes fuel cells an attractive option for a wide range of applications, including road vehicle power sources, distributed electricity and heat production, and portable systems [11, 13, 19].

## 2.2 Sectors of Applications

Conventional power generation relies upon fossil fuels, which produce a significant amount of pollutants, and there is a limited supply. Many alternative energy approaches have been proposed, such as bio fuel, hydroelectric power, batteries, wind, solar, bioenergy, and geothermal energy [1]. All of these sources can provide energy, but every method has advantages and disadvantages. Fuel cells are needed because they provide electric power in applications that are currently energy limited. For example, one of the most annoying things about a laptop computer is that the battery gives out after a couple of hours.

Each market needs fuel cells for varying reasons described as follows:

- **Portable sector**

In coming years, portable devices, such as laptops, cell phones, video recorders, and others, will need greater amounts of power for longer periods of time. Fuel cells are very scalable and have easy recharging capabilities compared to batteries. Cell phone technology is advancing rapidly, but the limiting factor for the new technology is the power. More power is required to provide consumers with all of the functions in devices they require and want. The military also has a need for long-term portable power for new soldier's equipment. In addition, fuel cells operate silently, and have low heat signatures, which are clear advantages for the military [20–24].

- **Stationary sector**

Stationary fuel cells can produce enough electricity and heat to power an entire house or business, which can result in significant savings. These fuel cells may even make enough power to sell some of it back to the grid. Fuel cells can also power residences and businesses where no electricity is available. Sometimes

it can be extremely expensive for a house not on the grid to have the grid connected to it. Fuel cells are also more reliable than other commercial generators used to power houses and businesses. This can benefit many companies, given how much money they can lose if the power goes down for even a short time [25–29].

- Transportation sector

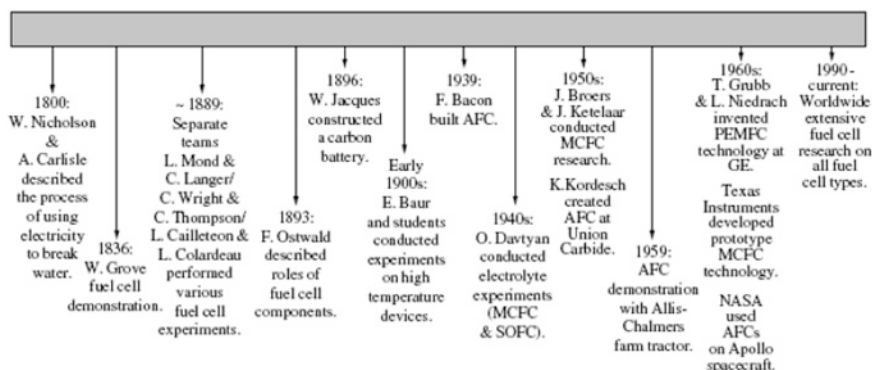
Many factors are contributing to the fuel cell push in the automotive market. The availability of fossil fuels is limited, and due to this, an inevitable price increase will occur. In addition, legislation is becoming stricter about controlling environmental emissions in many countries all over the world. One of the new pieces of legislation that will help introduce the fuel cell automobile market in the United States is the Californian zero emission vehicle (ZEV) mandate, which requires that a certain number of vehicles be sold annually in California. Fuel cell vehicles also have the ability to be more fuel efficient than vehicles powered by other fuels. This power technology allows a new range of power use in small two-wheeled and four-wheeled vehicles, boats, scooters, unmanned vehicles, and other utility vehicles [30–34].

## 2.3 History of Fuel Cells

Fuel cells have been known to science for about 150 years. They were minimally explored in the 1800 s and extensively researched in the second half of the twentieth century. Initial design concepts for fuel cells were explored in 1800, and William Grove is credited with inventing the first fuel cell in 1839 [11, 13, 35]. Various fuel cell theories were contemplated throughout the nineteenth century, and these concepts were studied for their practical uses during the twentieth century. Extensive fuel cell research was started by NASA in the 1960s, and much has been done since then [36]. During the last decade, fuel cells were extensively researched, and are finally nearing commercialization. A summary of fuel cell history is shown in Fig. 2.3.

In 1800, William Nicholson and Anthony Carlisle described the process of using electricity to break water into hydrogen and oxygen. William Grove is credited with the first-known demonstration of the fuel cell in 1839. Grove saw notes from Nicholson and Carlisle and thought he might “recompose water” by combining electrodes in a series circuit, and soon accomplished this with a device called a “gas battery.” It operated with separate platinum electrodes in oxygen and hydrogen submerged in a dilute sulphuric acid electrolyte solution. The sealed containers contained water and gases, and it was observed that the water level rose in both tubes as the current flowed. The Grove cell, as it came to be called, used a platinum electrode immersed in nitric acid and a zinc electrode in zinc sulfate to generate about 12 A of current at about 1.8 V.

Friedrich Wilhelm Ostwald (1853–1932), one of the founders of physical chemistry, provided a large portion of the theoretical understanding of how fuel



**Fig. 2.3** Main milestones in the history of fuel cells [36]

cells operate. In 1893, Ostwald experimentally determined the roles of many fuel cell components.

Ludwig Mond (1839–1909) was a chemist who spent most of his career developing soda manufacturing and nickel refining. In 1889, Mond and his assistant Carl Langer performed numerous experiments using a coal-derived gas. They used electrodes made of thin, perforated platinum, and had many difficulties with liquid electrolytes. They achieved 6 A per square foot (the area of the electrode) at 0.73 V.

Charles R. Alder Wright (1844–1894) and C. Thompson developed a similar fuel cell around the same time. They had difficulties in preventing gases from leaking from one chamber to another. This and other causes prevented the battery from reaching voltages as high as 1 volt. They felt that if they had more funding, they could create a better, robust cell that could provide adequate electricity for many applications.

The French team of Louis Paul Cailleteau (1832–1913) and Louis Joseph Colardeau came to a similar conclusion, but thought the process was not practical due to needing precious metals. In addition, many papers were published during this time saying that coal was so inexpensive that a new system with a higher efficiency would not decrease the price of electricity drastically.

William W. Jacques (1855–1932), an electrical engineer and chemist, did not pay attention to these critiques, and startled the scientific world by constructing a carbon battery in 1896. Air was injected into an alkali electrolyte to react with a carbon electrode. He thought he was achieving an efficiency of 82 %, but actually obtained only an 8 % efficiency.

Emil Baur (1873–1944) of Switzerland and several of his students conducted many experiments on different types of fuel cells during the early 1900s. His work included high-temperature devices, and a unit that used a solid electrolyte of clay and metal oxides.

O.K. Davtyan of the Soviet Union did many experiments to increase the conductivity and mechanical strength of the electrolyte in the 1940s. Many of the designs did not yield the desired results, but Davtyan's and Baur's work contributed to the necessary preliminary research for today's current molten carbonate and solid oxide fuel cell devices [11, 13, 35].

## 2.4 Fuel Cells Fundamentals

To understand and quantify fuel cell performance, one must begin with the thermodynamic description of the fuel cell [36]. A fuel cell continuously produces electrical work and waste heat. The fuel cell can generate electricity continuously since it is an open system. The fuel cell is operated continuously for a given time period,  $\Delta t$ , during which reactants (fuel and oxidant) are added and products removed to maintain an electrical potential. If current is allowed to flow, a difference in electrical potential (also known as electrochemical overpotential) is maintained at the electrode interface through which charge transfer can occur. Charge carriers migrate across the cell when there is nonequilibrium between the electrical and chemical potentials across the cell. The movement occurs from a higher to lower potential energy. Thus, the chemical affinity or change in Gibbs free energy of reaction drives an electric current. The change in Gibbs free energy of reaction is available at any instant to perform electrical work.

The Gibbs free energy,  $G$ , is defined to be [13, 36, 37]

$$G = E + PV - TS \quad (2.1)$$

where  $P$  = pressure,  $V$  = volume,  $T$  = temperature,  $E$  = energy, and  $S$  = entropy.

At constant pressure and temperature (usual conditions of an electrochemical reaction), the change in the Gibbs free energy for a reaction,  $\Delta G$  (J/mole) is

$$\Delta G = \Delta E + P\Delta V - T\Delta S \quad (2.2)$$

From the first law of thermodynamics, assuming the fuel cell is operated reversibly,

$$\Delta E = q + w = q + w_{\text{electrical}} - P\Delta V \quad (2.3)$$

where  $q$  = heat and  $w$  = work (J/mole). Thus, equating terms and simplifying,

$$\Delta G = q + w_{\text{electrical}} - T\Delta S \quad (2.4)$$

Again, assuming reversible operation of the fuel cell,

$$q = q_{\text{reversible}} = T\Delta S \quad (2.5)$$

Thus,

$$\Delta G = w_{\text{electrical}} \quad (2.6)$$



The change in Gibbs free energy of reaction (J/mole) is referenced to the amount of fuel. The electrical work (J) in an open system operated continuously over a given time period,  $\Delta t$ , where reactants (mole/s) are added and products removed to maintain the electrical potential are given for hydrogen–oxygen reaction by

$$m_{H_2} \Delta G \Delta t = m_{H_2} w_{\text{electrical}} \Delta t = W_{\text{electrical}} \quad (2.7)$$

where  $m_{H_2}$  = flow rate of hydrogen for the  $H_2/O_2$  reaction (mole/s) and  $\Delta t$  = operation time (s).

The average rate of work generation during the time interval,  $\Delta t$ , is the power (J/s).

One can mathematically demonstrate that for any direct anodic oxidation reaction for any fuel cell or hybrid system containing any fuel cell at any operating temperature and any pressure, the reversible work,  $w_{\text{electrical}}$ , (J/mole) is equal to the change in Gibbs free energy of reaction at the standard state (STP),  $\Delta G^\circ$  [38, 39].

This reversible work is regarded as the maximum work. For the case of direct oxidation of hydrogen, one has

$$W_{\text{rev}} = m_{H_2\text{inlet}} w_{\text{rev}} = m_{H_2\text{inlet}} \Delta G^\circ \Delta t \quad (2.8)$$

where  $m_{H_2\text{inlet}}$  = flow rate of hydrogen fuel into system.

Inerts and/or water are added to or are present in a reformat with the hydrogen entering the system.

Exergy is a measure of heat quality or capability to do work. Exergetic efficiency,  $\zeta$ , is the ratio of actual electrical work and the reversible work:

$$\zeta = W_{\text{electrical}}/W_{\text{rev}} \quad (2.9)$$

Using Eq. (2.8), the actual or observed electrical work for direct oxidation of hydrogen, a fuel cell is given by

$$m_{H_2\text{utilized}} \Delta G_{\text{act}} \Delta t = W_{\text{electrical}} \quad (2.10)$$

where  $\Delta G_{\text{act}}$  = actual change in Gibbs free energy of reaction associated with the electrical work, J/mole,  $m_{H_2\text{utilized}}$  = flow rate of hydrogen utilized by fuel cell (moles/s) ( $m_{H_2\text{utilized}}$  equals the amount in the fuel cell anode inlet;  $m_{H_2\text{anode inlet}}$  minus the amount in the anode outlet;  $m_{H_2\text{anode outlet}}$ ).

For reforming done prior to the system,  $m_{H_2\text{inlet}} = m_{H_2\text{anode inlet}}$ . Thus, from Eqs. (2.8), (2.9), and (2.10)

$$\zeta = (m_{H_2\text{utilized}} \Delta G_{\text{act}} \Delta t) / (m_{H_2\text{inlet}} \Delta G^\circ \Delta t) = \mu_F \Delta G_{\text{act}} / \Delta G^\circ \quad (2.11)$$

where fuel utilization ( $\mu_F$ ) is

$$\mu_F = m_{H_2\text{utilized}} / m_{H_2\text{inlet}} \quad (2.12)$$

Using Eq. (2.8) for the reversible work, one can calculate the maximum thermal efficiency (maximum work for given energy input) of a fuel cell or fuel cell hybrid (fuel cell and heat engine) system for the  $H_2$  oxidation reaction, where  $\Delta H^\circ$  is

the reaction enthalpy for hydrogen direct oxidation (J/mole) at STP and where the inlet hydrogen is completely utilized in the fuel cell:

$$\eta_{th \max} = \Delta G^\circ / \Delta H^\circ \quad (2.13)$$

For the  $H_2$  oxidation reaction,  $\eta_{th \max}$  equals 0.83 (HHV) and 0.945 (LHV). One can also define a fuel cell intrinsic thermal efficiency at any temperature  $\eta_{int}(T)$  by  $\Delta G_{th}(T) / \Delta H^\circ$ . One can also define for the fuel cell an intrinsic exergetic efficiency at any temperature [38, 40]:

$$\zeta_{int}(T) = \Delta G_{th}(T) / \Delta G^\circ \quad (2.14)$$

$\Delta G_{th}(T)$  is defined as the free energy of the reaction, here the  $H_2$  oxidation reaction, at temperature,  $T$ , for unit concentrations of products and reactants.  $\Delta G_{th}(T)$  is associated with  $E^\circ(T)$ .  $\Delta G^\circ$  at STP with unit species concentrations is associated with  $E^\circ$ .

The actual thermal efficiency of the fuel cell is defined as the ratio of the work output to energy input, so we have

$$\eta = m_{H_2 \text{ utilized}} \Delta G_{act} \Delta t / (m_{H_2 \text{ inlet}} \Delta H^\circ \Delta t) = \mu_F \Delta G_{act} / \Delta H^\circ \quad (2.15)$$

It can be shown from Eqs. (2.11), (2.13), (2.14), and (2.15) that

$$\eta = \mu_F \Delta G_{act} / \Delta H^\circ = \eta_{int}(T) \zeta / \zeta_{int}(T) = \zeta \eta_{th \max} \quad (2.16)$$

If one knows the reversible work which is a function of fuel, system components, and system structure, one can separate thermal efficiency into an exergetic component and a fuel component.

Exergetic performance is determined by fuel cell performance which ultimately means fuel cell voltage. The link between the macroscopic thermodynamic parameters and fuel cell voltage can be developed as follows:

The  $W$  electrical is also defined electrically as

$$W_{\text{electrical}} = -nFE \quad (2.17)$$

where

$n$  = mole,

$F$  = Faraday's constant (J/mole/volt),

$E$  = fuel cell voltage (volt)

In general, from Eqs. (2.7), (2.10), and (2.17)

$$m_{H_2} \Delta G \Delta t = W_{\text{electrical}} = -nFE \quad (2.18)$$

Since for the  $H_2$  direct oxidation reaction,

$$2 m_{H_2} \Delta t = n \quad (2.19)$$

then, in general

$$\Delta G = -2FE \quad (2.20)$$

Specifically, using Eq. (2.20),

$$\Delta G_{ac} = -2FE \quad (2.21)$$

and

$$\Delta G^\circ = -2FE^\circ \quad (2.22)$$

so

$$\zeta = m_{H2utilized} \Delta G_{act} \Delta t / (m_{H2inlet} \Delta G^\circ \Delta t) = \mu_F (-2FE \Delta t) / (-2FE^\circ \Delta t) = \mu_F E / E^\circ \quad (2.23)$$

One of the central, steady-state fuel cell performance equations is thus given by

$$\zeta = \mu_F E / E^\circ \quad (2.24)$$

and combining with Eq. (2.16), one has

$$\eta = \zeta \eta_{th \max} = \eta_{th \max} \mu_F E / E^\circ \quad (2.25)$$

Exergetic efficiency and thermal efficiency are actually time-dependent functions describing the performance of the fuel cell at any time  $t$ .

These can be written as

$$\zeta(t) = \mu_F(t) E(t) / E^\circ \quad (2.26)$$

and

$$\eta(t) = \zeta(t) \eta_{th \max} = \eta_{th \max} \mu_F(t) E(t) / E^\circ \quad (2.27)$$

$DR_\zeta(t)$ , the exergetic efficiency rate of change, is a natural and instantaneous measure of the change in fuel cell performance occurring at any time  $t$ :

$$\partial(\zeta(t))/\partial t = DR_\zeta(t) \quad (2.28)$$

It can be seen from Eqs. (2.26) and (2.27) that the rate of change in exergetic efficiency and rate of change of thermal efficiency are directly proportional.

Equation (2.28) is the second central equation for fuel cell performance since it is an equation that can be used in the assessment of degradation, generally defined as the change of area-specific resistance (ASR) with time [41].

### 2.4.1 Fuel Cell Operations

Fuel cells can be operated in a variety of modes, including constant fuel utilization, constant fuel flow rate, constant voltage, constant current, etc. For the case of constant  $m_F$  and constant  $E$ , from Eq. (2.28),  $DR_\zeta(t) = 0$ , in which case the fuel cell is operating at constant exergetic efficiency. This mode of operation is achieved by lowering the current by lowering the hydrogen flow rate as the fuel cell degrades. As can be seen from Eqs. (2.26) and (2.27), to operate at constant exergetic efficiency is to operate at constant thermal efficiency.

However, efficiency is not the only important performance measure. As the current is lowered at constant voltage operation, the fuel cell power density is decreasing. Below a certain level of power or power density, given by

$$P(t) = E(t) J(t) \quad (2.29)$$

It is no longer economical to operate a fuel cell or fuel cell system. Power is the third central equation for fuel cell performance. General expressions can be derived for fuel cell performance involving the variables  $E$ ,  $J$ ,  $mF$ , pressure, and fuel flow rate to explore the full envelope of fuel cell operation.

The actual fuel cell potential is decreased from its full potential, the Nernst potential, because of irreversible losses. Multiple phenomena contribute to irreversible losses in an actual fuel cell. For the hydrogen oxidation reaction, the functionality of fuel cell voltage,  $E$ , is typically given by [42–44]

$$E(T) = E_N(T) - LJ/A\sigma - R_{ohmic}J - \eta_{act}^a - \eta_{act}^c - \eta_{conc}^a - \eta_{conc}^c \quad (2.30)$$

$$E_N(T) = E_{H_2/O_2rxn}^o(T) + RT/2F \ln \left( P_{H_2(a)} P_{O_2(c)}^{1/2} / P_{H_2O(a)} \right) = \text{Nernst voltage} \quad (2.31)$$

where

- $F$  = Faraday's constant,
- $J$  = appropriate current (amperes/cm<sup>2</sup>),
- $s$  = electrolyte charge carrier conductivity (S/cm),
- $L$  = electrolyte thickness (cm),
- $A$  = fuel cell active area (cm<sup>2</sup>),
- $\eta_{act}^a$  = activation polarization for the anode,
- $\eta_{act}^c$  = activation polarization for the cathode,
- $\eta_{conc}^a$  = concentration polarization for the anode,
- $\eta_{conc}^c$  = concentration polarization for the anode,
- $R_{ohmic}$  = series ohmic resistance of all nonelectrolyte fuel cell components including interconnect, interlayers, and contact layers,
- $E_{H_2/O_2rxn}^o(T)$  = voltage at unit concentrations for  $H_2/O_2$  reaction at temperature  $T$ .

The six negative terms on the RHS of Eq. (2.30) are the usual definition of ASR. The comprehensive functionality of  $E$  and the more general definition of ASR have recently been developed for solid-state fuel cells with dense, mixed, ionic–electronic conducting electrolytes using the Wagner mass transfer model (MTM) [41, 45, 46]:

$$E = E_{MTM} \left( 1 - (J_O^- - J_{ext}) / J_O^- \right) - L J_O^- / A \sigma_O^- - R_{ohmic} J - \eta_{act}^a - \eta_{act}^c - \eta_{conc}^a - \eta_{leakage} \quad (2.32)$$

where

$R_{\text{ohmic}}$  = series ohmic resistance of all nonelectrolyte fuel cell components, including interconnect, interlayers, and contact layers, which is multiplied by the appropriate current,  $J$ , for each type

$J_{\text{O}^-}$ ,  $J_e$ , and  $J_{\text{ext}}$  are the current terms from the Wagner MTM,  $(J_{\text{O}^-} - J_{\text{ext}})/J_{\text{O}^-}$  = the shorting ratio,

$\eta_{\text{leakage}}$  = fuel leakage polarization,  $E_{\text{MTM}}$  (anode–electrolyte interface to cathode–electrolyte interface) is the reversible voltage in the Wagner MTM model

The comprehensive model for solid-state fuel cells incorporates not only the typical definition of ASR, but also electronic shorting, leakage, and other current loss mechanisms. The first term on the RHS of Eq. (2.32) is not an ASR term.

A general ASR definition for solid-state fuel cells can be defined as follows:

$$\text{ASR} = R_{\text{ionic}} + R_{\text{ohmic}} + (\eta_{\text{act}}^a + \eta_{\text{act}}^c + \eta_{\text{conc}}^a + \eta_{\text{conc}}^c)/J_{\text{O}^-} + R_{\text{leakage}} \quad (2.33)$$

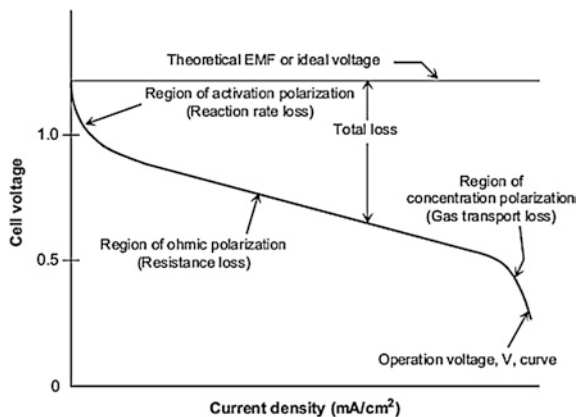
where  $R_{\text{ionic}} = L/A\sigma_o$  = ionic resistance of electrolyte and  $R_{\text{leakage}} = \eta_{\text{leakage}}/J_{\text{leakage}}$  = resistance attributed to fuel leakage.

This definition of ASR is very general. However when generalized, ASR and rate of change of ASR are not broad enough concepts to describe all the phenomena affecting fuel cell performance, such as electronic shorting.

The goal of a fuel cell should be to maximize exergetic or thermal efficiency and to minimize degradation while producing as much power as possible. These three goals can be achieved by improving the fuel cell design (more conductive electrolyte, better electrocatalysts, improvement in electrode structures, thinner cell components, etc.) [10] and/or by adjusting the operating conditions (e.g., higher temperature, higher gas pressure, and change in gas composition to lower the contaminant concentration).

As shown in Fig. 2.4, the activation polarization (reaction rate loss) is significant at lower current densities [10, 11]. At this point, electronic barriers must be overcome prior to ion and current flow. Ohmic polarization (resistance loss)

**Fig. 2.4** Typical current voltage performance [10]



changes directly with current, increasing over the entire range of current because cell resistance remains essentially constant. Concentration polarization (gas transport loss) occurs over the entire range of current density, but they become significant at high limiting currents where it becomes difficult to provide enough reactant flow to the cell reaction sites.

Changing the cell operating parameters (pressure and temperature) can have an advantageous or a disadvantageous impact on fuel cell performance and compromises in the operating parameters are essential to meet the application requirements of lower system cost and acceptable cell life [10, 11].

## 2.5 Characteristics and Features

Fuel cells have many inherent advantages over conventional combustion-based systems, making them one of the strongest candidates to be the energy conversion device of the future (Fig. 2.5). They also have some inherent disadvantages that require further research and development to overcome them.

### 2.5.1 High Efficiency

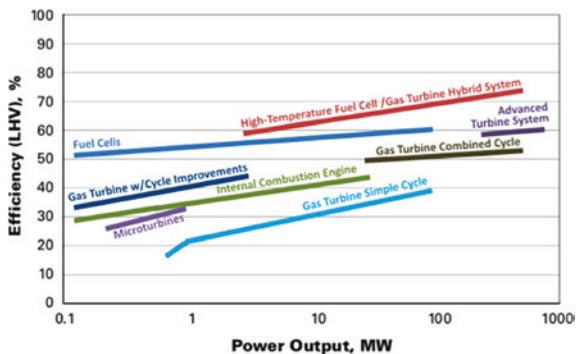
The amount of heat that could be converted to useful work in a heat engine is limited by the ideal reversible Carnot efficiency, given by the following equation:

$$\eta_{\text{Carnot}} = (T_i - T_e)/T_i \quad (2.34)$$

where  $T_i$  is the absolute temperature at the engine inlet and  $T_e$  is the absolute temperature at the engine exit. However, a fuel cell is not limited by the Carnot efficiency since a fuel cell is an electrochemical device that undergoes isothermal oxidation instead of combustion oxidation. The maximum conversion efficiency of a fuel cell is bounded by the chemical energy content of the fuel and is found by

$$\eta_{\text{rev}} = \Delta G_f / \Delta H_f \quad (2.35)$$

**Fig. 2.5** Efficiency comparison between fuel cells and other energy conversion devices with respect to system size [6]



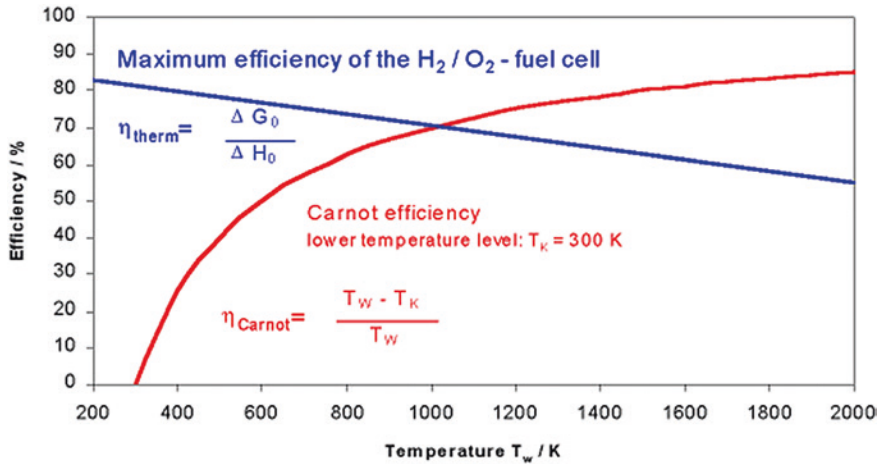


Fig. 2.6 Thermodynamic efficiency for fuel cells and Carnot efficiency for heat engines [11]

where  $\Delta G_f$  is the change in Gibbs free energy of formation during the reactions and  $\Delta H_f$  is the change in the enthalpy of formation (using lower heating value (LHV) or higher heating value (HHV)) [10, 11, 13].

Figure 2.6 illustrates the thermodynamic efficiency for fuel cells and Carnot efficiency for heat engines [11]. In light vehicles, for instance, the efficiency of a fuel cell-powered car is nearly twice the efficiency of an internal combustion engine-powered car. The fact that the number of energy transformations that occur within a fuel cell stack is less than that of any combustion-based device, when the required output is electricity, plays a significant role. This is because losses are associated with each energy transformation process; thus, the overall efficiency of a system generally decreases as the number of energy transformations increases.

### 2.5.2 Reduced Harmful Emissions

The only products from a fuel cell stack fuelled by hydrogen are water, heat, and DC electricity. And with the exception of controllable  $\text{NO}_x$  emissions from high-temperature fuel cells, a hydrogen fuel cell stack is emission-free. However, the clean nature of a fuel cell depends on the production path of its fuel.

For instance, the products of a complete fuel cell system that includes a fuel reformation stage include green house emissions (e.g.,  $\text{CO}$  and  $\text{CO}_2$ ). When the hydrogen supplied to the fuel cell is pure (i.e., not reformation-based hydrogen which is always contaminated with  $\text{CO}_x$ ), the durability and reliability of the fuel cell significantly improve in comparison to when we run the fuel cell on reformation-based hydrogen. This is one of the most important advantages of fuel cells in comparison to heat engines, i.e., fuel cells are inherently clean energy converters that ideally

run on pure hydrogen. This fact is actually pressingly driving researchers and the industry to develop efficient and renewable-based hydrogen generation technologies based on clean water electrolysis to replace the conventional reformation-based ones. Systems that integrate renewable-based hydrogen generation with fuel cells are genuinely clean energy generation and conversion systems that resemble what the energy industry is striving to achieve. It is worth mentioning that when we take into consideration the emissions from the fossil fuel reformation process, some heat engine systems appear to be less polluting than fuel cell systems [47, 48]. For non-renewable energy-based water electrolysis, the emissions and energy used for the electrolysis process make it more harmful to the environment than conventional combustion heat engines. Moreover, it is economically unfeasible since any fossil energy used for hydrogen production is going to be always more than the energy content of hydrogen. According to the studies by Argonne National Laboratory [49], 3,000,000–3,500,000 BTUs of fossil energy are used for the production of 1,000,000 BTUs of hydrogen through fossil energy-based water electrolysis. This only stresses the significance of the aforementioned conclusions regarding using renewable-based water electrolysis for hydrogen production [50].

### ***2.5.3 Modularity***

Fuel cells have excellent modularity. In principle, changing the number of cells-per-stack and/or stacks-per-system allows us to control the power output of any fuel cell system. Unlike combustion-based devices, a fuel cell's efficiency does not vary much with system size or load factor. In fact, as opposed to conventional power plants, fuel cells have higher efficiencies at part loads compared to full loads. This would prove advantageous in large-scale fuel cell systems that would normally run on part load instead of full load. Additionally, the high modularity of fuel cells means that smaller fuel cell systems have similar efficiencies to larger systems. This feature greatly facilitates the future integration of fuel cells (and hydrogen systems in general) in small-scale distributed generation systems, which hold a great potential in the power generation industry. It is worth noting, however, that reformation processors are not as modular as fuel cell stacks. This presents another reason to shift to renewable-based hydrogen production technology.

### ***2.5.4 Prompt Load Following***

Fuel cell systems generally have very good dynamic load following characteristics [51, 52]. This is partially due to the prompt nature of the electrochemical reactions that occur within a fuel cell. Again, when the fuel cell system includes a fuel reformation stage, the load following ability of the system noticeably decreases as a result of the slower nature of the reformation process.



### ***2.5.5 Static Nature***

Due to its electrochemical nature, a fuel cell stack is a static silent device. This is a very important feature that promotes the use of fuel cells for auxiliary power and distributed generation applications in addition to portable applications that require silent operation. The fact that a fuel cell system has very few dynamic parts (and hence, almost no vibrations) makes fuel cells design, manufacturing, assembly, operation, and analysis simpler than that of heat engines. Nevertheless, for fuel cell systems that use compressors instead of blowers for the oxidant supply, noise levels can noticeably increase. As such, fuel cell designers tend to avoid using compressors due to their high parasitic load, noise production, cost, weight, volume, and complexity relative to fans and blowers. The static nature of a fuel cell also reflects on its low maintenance requirements in comparison to competing technologies such as heat engines, wind turbines, and concentrated solar power plants.

### ***2.5.6 Range of Applications and Fuel Flexibility***

Fuel cells have diverse applications ranging from micro-fuel cells with less than 1 W power outputs to multi-MW prime power generation plants. This is attributed to their modularity, static nature, and variety of fuel cell types. This qualifies fuel cells to replace batteries used in consumer electronics and auxiliary vehicular power. These same properties also qualify a fuel cell to replace heat engines used in transportation and power generation. Fuel cells are also highly integrable to most renewable power generation technologies. Fuel cells that operate on low-temperature ranges require short warm-up times, which is important for portable and emergency power applications.

While for fuel cells that operate on medium-to-high temperature ranges, utilization of waste heat both increases the overall efficiency of the system and provides an additional form of power output useful for domestic hot water and space heating residential applications or CHP industrial-level applications. Fuels for a reformation-based fuel cell system include methanol, methane, and hydrocarbons such as natural gas and propane. These fuels are converted into hydrogen through a fuel reformation process. Alternatively, direct alcohol fuel cells (e.g., direct methanol fuel cells) can run directly on an alcohol. And even though fuel cells run best on hydrogen generated from water electrolysis, a fuel cell system with natural gas reformation also possesses favorable features to conventional technologies [13].

Fuel cells have been rapidly developing during the past 20 years due to the revived interest in them that started during the 1990s. However, they are still not at the widespread-commercialization stage due to many technical and sociopolitical factors, with cost and durability being the main hurdles that prevent fuel cells from becoming economically competitive in the energy market. The main challenges are detailed as follows:

### ***2.5.7 High Cost***

Fuel cells are expensive. Experts estimate that the cost-per-kW generated using fuel cells has to drop by a factor of 10 for fuel cells to enter the energy market [16, 18]. Three main reasons behind the current high cost of fuel cell stacks are: the dependence on platinum-based catalysts, delicate membrane fabrication techniques, and the coating and plate material of bipolar plates [17]. While from a system-level perspective, the BoP components such as fuel supply and storage subsystems, pumps, blowers, power and control electronics, and compressors constitute about half the cost of a typical complete fuel cell system. More specifically, whether renewable or hydrocarbon based, the current hydrogen production BoP equipment are far from being cost-effective. Technological advances in contaminant removal for hydrocarbon-based technologies are essential if the cost of fuel cell systems is to meet planned targets. Nevertheless, if fuel cells successfully enter the mass production stage, their costs are expected to significantly drop and become consumer affordable due to the fact that manufacturing and assembly of fuel cells is generally less demanding than typical competing technologies, such as heat engines.

### ***2.5.8 Low Durability***

The durability of fuel cells needs to be increased by about five times the current rates (e.g., at least 60,000 h for the stationary distributed generation sector) in order for fuel cells to present a long-term reliable alternative to the current power generation technologies available in the market. The degradation mechanisms and failure modes within the fuel cell components and the mitigation measures that could be taken to prevent failure need to be examined and tested. Contamination mechanisms in fuel cells due to air pollutants and fuel impurities need to be carefully addressed to resolve the fuel cell durability issue.

### ***2.5.9 Hydrogen Infrastructure***

One of the biggest challenges that face fuel cells commercialization is the fact that we are still producing 96 % of the world's hydrogen from hydrocarbon reformation processes [53]. Producing hydrogen from fossil fuels (mainly natural gas) and then using it in fuel cells is economically disadvantageous since the cost-per-kWh delivered from hydrogen generated from a fossil fuel is higher

than the cost-per-kWh if we were to directly use the fossil fuel. Thus, promoting renewable-based hydrogen is the only viable solution to help the shift from a fossil-based economy to a renewable-based, hydrogen-facilitated economy. Moreover, development of hydrogen storage mechanisms that provide high energy density per mass and volume whilst maintaining a reasonable cost is the second half of the hydrogen infrastructure dilemma. Any widely adopted hydrogen storage technology will have to be completely safe since hydrogen is a very light and highly flammable fuel that could easily leak from a regular container. Metal- and chemical hydride storage technologies are proving to be safer and more efficient options than the traditional compressed gaseous and liquid hydrogen mechanisms. However, more research and development are needed to reduce the relatively high cost of the hydride storage technologies and to further improve their properties.

### ***2.5.10 Water Balance***

Water transport within a fuel cell is a function of water entering with inlet streams, water generated by the cathodic reaction, water migration from one component to another, and water exiting with exit streams. Generally speaking, a successful water management strategy would keep the membrane well hydrated without causing water accumulation and blockage in any part of the MEA or flow fields. As such, maintaining this delicate water balance inside a PEMFC over different operation conditions and load requirements is a major technical difficulty the scientific community is required to fully address [54]. Flooding of the membrane; water accumulation in the pores and channels of the GDL and flow fields; dryness of the membrane; freezing of residual water inside the fuel cell; dependence between thermal, gases, and water management; and humidity of the feeding gases are all subtle and interdependent facets in the water management of a PEMFC. Improper water management within a PEMFC leads to both performance loss and durability degradations [54, 55] as a result of permanent membrane damage, low membrane ionic conductivity, nonhomogeneous current density distribution, delamination of components, and reactants starvation. As such, water management strategies range from direct water injection to reactant gases recirculation. The performance evaluation of a water management technique could be accomplished using empirical liquid water visualization or micro- and macroscale numerical simulation [44]. Nonetheless, fundamental understanding and comprehensive models of water transport phenomena within a fuel cell are highly needed in order to develop optimized component designs, residual water removal methods, and MEA materials according to application requirements and operation conditions [56].

### 2.5.11 Parasitic Load

The parasitic load required to run the auxiliary BoP components reduces the overall efficiency of the system. This is clearly evident when the power required to run auxiliary components such as air compressors, coolant pumps, hydrogen circulation pumps, etc., is included in the efficiency calculations. Additionally, the weight and size of fuel cell systems will need to be reduced in order for fuel cells to become compatible with onboard transportation applications and small-scale portable applications.

### 2.5.12 Codes, Standards, Safety, and Public Awareness

The lack of internationally accepted codes and standards for hydrogen systems in general and fuel cells in particular has a negative reflection on the public's acceptance of hydrogen power solutions. Government officials, policy makers, business leaders, and decision makers would feel more reassured about supporting early stage hydrogen power projects if general best practices and consistent safety standards in the design, installation, operation, maintenance, and handling of hydrogen equipment were established. The general public needs to be convinced that hydrogen is similar to conventional fuels in certain aspects and different in other aspects. But overall, hydrogen does not pose a safety issue if properly handled and regulated, just like any other conventional fuel. Codes and standards for hydrogen systems could be made available by the continuous collection of more real-world data and initiation of more trial projects and lab experiments, a process that could be regulated by a professional society or a government initiative (in the US, the Safety, Codes, and Standards subprogram of the Department of Energy Hydrogen and Fuel Cells Program is attempting to take this vital role) [10]. In Table 2.1 the main properties of different fuel cells are reported.

**Table 2.1** Summary of the main advantages and disadvantages of fuel cells [6]

Advantages	Disadvantages
Less/no pollution	Immature hydrogen infrastructure
Higher thermodynamic efficiency	Sensitivity to contaminants
Higher part-load efficiency	Expensive platinum catalysts
Modularity and scalability	Delicate thermal and water management
Excellent load response	Dependence on hydrocarbons reforming
Fewer energy transformation	Complex and expensive BoP components
Quiet and static	Long-term durability and stability issues
Water and cogeneration applications	Hydrogen safety concerns
Fuel flexibility	High investment cost-per-W
Wide range of applications	Relatively large system size weight

### 2.5.13 Types

Fuel cells can be designed in various ways including many geometries, planar, tubular, radial, etc., and using many fuels and electrolyte charge carriers. Distinction of fuel cell types begins with the type of electrolyte used in the cells, the charge carrier, and the operating temperature. Low-temperature fuel cells (PEFC, AFC, and PAFC) require noble metal electrocatalysts to achieve practical reaction rates at the anode and cathode, and  $H_2$  is the only acceptable fuel for the PEMFC. With high-temperature fuel cells (MCFC and SOFC), the requirements for catalysis are relaxed, and the number of potential fuels expands. (Other types of fuel cells are not addressed here, such as biological and enzymatic fuel cells.) For example, carbon monoxide “poisons” a noble metal anode catalyst such as platinum in low-temperature fuel cells, but it competes with  $H_2$  as a reactant in high-temperature fuel cells where non-noble metal catalysts such as nickel can be used.

The operating temperature and required useful life of a fuel cell dictate the physicochemical and thermomechanical properties of materials used in the cell components (e.g., electrolyte, electrodes, and interconnect) [10].

Aqueous electrolytes are limited to temperatures of  $>200^\circ C$  because of their high water vapor pressure and/or rapid degradation at higher temperatures. The operating temperature also determines the type of fuel that can be used in a fuel cell. The low-temperature fuel cells with aqueous electrolytes are, in most practical applications, restricted to  $H_2$  as a fuel. In high-temperature fuel cells, CO and even  $CH_4$  can be used because of the inherently rapid electrode kinetics and the lesser need for high catalytic activity at high temperature.

Table 2.2 summarizes the main differences between the most common fuel cell types.

**Table 2.2** Comparison of FCs with their performance parameters [6]

Fuel cell	Cell voltage	Start-up time	Power density ( $W/m^2$ )	Temperature ( $^\circ C$ )
PEMFC	0.7–0.8	Seconds	3.8–6.5	60–100
AFC	1.0	Seconds	1.0	100–250
PAFC	1.0	Few minutes	0.8–1.9	150–250
MCFC	0.7–1.0	Few minutes	1.5–2.6	500–700
SOFC	0.8–1.0	Few minutes	0–0.15	700–1000
DMFC	0.2–0.4	Few seconds	1.0–2.0	60–200
DCFC	0.7–1.0	Few minutes	0.5–1.0	650–800
DFAFC	0.6–1.0	Seconds	0.5–1.2	60–100
DBFC	0.6–1.0	Seconds	0.5–1.2	70–100

## 2.6 Fuel Cells Types

### 2.6.1 Proton Exchange Membrane Fuel Cell (PEMFC)

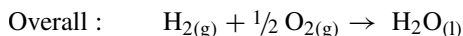
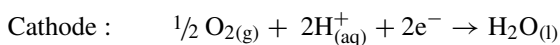
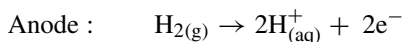
Proton exchange membrane fuel cells (PEMFC) are believed to be the best type of fuel cell as the vehicular power source to eventually replace the gasoline and diesel internal combustion engines. PEMFCs are currently being developed and demonstrated for systems ranging from 1 W to 2 kW.

PEM fuel cells use a solid polymer membrane (a thin plastic film) as the electrolyte. The standard electrolyte material currently used in PEM fuel cells is a fully fluorinated Teflon-based material produced by DuPont for space applications in the 1960s. The DuPont electrolytes have the generic brand name Nafion, and the types used most frequently are 113, 115, and 117 [13, 57–62, 68]. The Nafion membranes are fully fluorinated polymers that have very high chemical and thermal stability. This polymer is permeable to protons when it is saturated with water, but it does not conduct electrons.

The fuel for the PEMFC is hydrogen and the charge carrier is the hydrogen ion (proton).

The best catalyst for both the anode and cathode is platinum. This catalyst was used at a content of 28 mg/cm<sup>2</sup> of Pt. Due to the high cost of Pt in recent years the usage has been reduced to around 0.2 mg/cm<sup>2</sup>, yet with power increasing [13]. Platinum is dispersed on porous and conductive material, such as carbon cloth or carbon paper. PTEF will often be added also, because it is hydrophobic and so will expel the product water to the surface from where it can evaporate [13, 63–68].

At the anode, the hydrogen molecule is split into hydrogen ions (protons) and electrons. The hydrogen ions permeate across the electrolyte to the cathode while the electrons flow through an external circuit and produce electric power. Oxygen, usually in the form of air, is supplied to the cathode and combines with the electrons and the hydrogen ions to produce water. The reactions at the electrodes are as follows:



Compared to other types of fuel cells, PEMFCs generate more power for a given volume or weight of fuel cell [57–62]. This high-power density characteristic makes them compact and lightweight. In addition, the operating temperature is less than 100 °C, which allows rapid start-up. These traits and the ability to rapidly change power output are some of the characteristics that make the PEMFC the top candidate for automotive power applications [57–62].

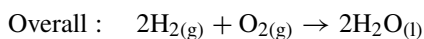
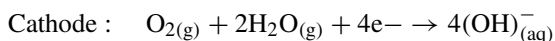
Other advantages result from the electrolyte being a solid material, compared to a liquid. The sealing of the anode and cathode gases is simpler with a solid electrolyte, and therefore, less expensive to manufacture. The solid electrolyte is also more immune to difficulties with orientation and has less problems with corrosion, compared to many of the other electrolytes, thus leading to a longer cell and stack life.

One of the disadvantages of the PEMFC for some applications is that the operating temperature is low. Temperatures near 100 °C are not high enough to perform useful cogeneration. Also, since the electrolyte is required to be saturated with water to operate optimally, careful control of the moisture of the anode and cathode streams is important.

### 2.6.2 Alkaline Fuel Cell (AFC)

Alkaline fuel cells (AFCs) have been used by NASA on space missions and can achieve power-generating efficiencies of up to 70 % [13, 69–72]. The operating temperature of these cells range between room temperature to 250 °C. The electrolyte is aqueous solution of alkaline potassium hydroxide (30–75 w %) soaked in a matrix [13]. (This is advantageous because the cathode reaction is faster in the alkaline electrolyte, which means higher performance).

Several companies are examining ways to reduce costs and improve operating flexibility. AFCs typically have a cell output from 300 W to 5 kW [71]. The chemical reactions that occur in this cell are as follows:



Another advantage of AFCs are the materials such as the electrolyte and catalyst used are low cost [69, 70]. The catalyst layer can use either platinum or nonprecious metal catalysts such as nickel [72–75]. Successful achieving of very active and porous form of a metal which has been used for alkaline fuel cells from the 1960s to the present, is the use of Raney metals. These are prepared by mixing the active metal (Ni) with an inactive metal, usually aluminum. The mixture is then treated with a strong alkali that dissolves out the aluminum. This leads a porous material, with very high surface area [13]. A disadvantage of AFCs is that pure hydrogen and oxygen have to be fed into the fuel cell because it cannot tolerate the small amount of carbon dioxide from the atmosphere.

Over time, carbon dioxide degrades the KOH electrolyte which can lead to significant issues. Two commonly used solutions are refreshing the KOH electrolyte or carbon dioxide scrubbers. Due to these limitations, AFCs are not used for many power applications.

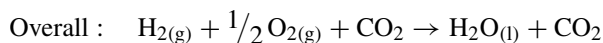
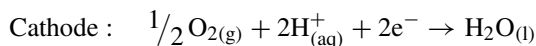
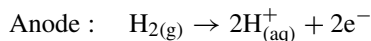
### 2.6.3 Phosphoric Acid Fuel Cells (PAFC)

PAFCs are very efficient fuel cells, generating electricity at more than 50 % efficiency [13]. About 85 % of the steam produced by the PAFC is used for cogeneration. This efficiency may be compared to about 35 % for the utility power grid in the United States. As with the PEMFC Pt or Pt alloys are used as catalysts at both electrodes [76]. The electrolyte is inorganic acid, concentrated phosphoric acid (100 %) which will conduct protons [77–79]. Operating temperatures are in the range of 150–220 °C. At lower temperatures, PAFC is a poor ionic conductor, and carbon monoxide (CO) poisoning of the platinum catalyst in the anode can become severe [76, 80, 81].

Two main advantages of the phosphoric acid fuel cell include a cogeneration efficiency of nearly 85 % and its ability to use impure hydrogen as fuel. PAFCs can tolerate a carbon monoxide concentration of about 1.5 % which increases the number of fuel types that can be used. Disadvantages of PAFCs include their use of platinum as a catalyst (like most other fuel cells) and their large size and weight. PAFCs also generate low current and power comparable to other types of fuel cells [13].

Phosphoric acid fuel cells are the most mature fuel cell technology. The commercialization of these cells was brought about through the Department of Energy (DOE) and ONSI (which is now United Technologies Company (UTC) Fuel Cells) and organizational linkages with Gas Research Institute (GRI), electronic utilities, energy service companies, and user groups.

The chemical reactions for PAFCs are as follows:



### 2.6.4 Direct Methanol Fuel Cells (DMFC)

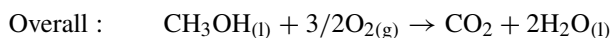
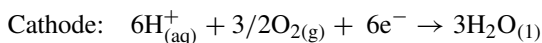
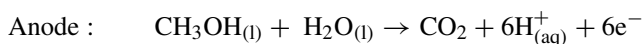
A Direct Methanol Fuel Cell (DMFC) works creating an electric potential by the reaction between methanol and oxygen, specifically it produces electricity through an electrochemical process without combustion and without the need for a reformer system for the fuel [82].

The electric potential is created using a polymeric membrane that is selective to certain chemical molecules, in this case the membrane allows the passage of  $\text{H}^{+}$  ions (proton conductivity). On one side of the membrane, an aqueous solution of methanol with  $\text{CH}_3\text{OH}$  concentration of around 1 M (3w%) is feed to the anode



catalyst where the catalytic decomposition of methanol molecules producing  $\text{CO}_2$  and  $\text{H}_2$  is oxidized to  $\text{H}^+$  ions at the anode [13]. The protons produced can migrate to the cathode of the cell through the membrane where the electrons produced to the anode, passing through an external circuit, reduce the oxygen that is plugged in, allowing the formation of water.

The reactions occurring in the DMFC are as follows:



Because none of the methanol oxidation reaction proceeds as readily as the oxidation of hydrogen, there are considerable activation overvoltages at the fuel anode, as well as at the cathode in the DMFC. This is the main cause for the lower performance. Much work has been done to develop suitable catalysts for the anode of the DMFC. It is usually used as mixture of Pt and Ru in equal proportions. Other bimetal catalysts have been tried but this 50:50 Pt/Ru combination seems to guarantee the best performances [13, 82–84]. The cathode reaction in the DMFC is the same as that for the hydrogen fuel cells with acid electrolyte, so the same catalyst is used. There is no advantage in using the more expensive Pt/Ru bimetal catalyst used on the anode [13, 82–84].

The research and development of novel proton exchange membranes (PEMs) is known to be one of the most challenging issues regarding the direct methanol fuel cell technology [85–87]. The PEM is usually designated as the heart of the DMFC, and should ideally combine high proton conductivity (electrolyte properties) with low permeability toward DMFC species. Additionally, it should have a very high chemical and thermal stability in order to enable the DMFC operation at up to 150 °C. For this reason, a variety of PEMs have been developed by various researchers using different preparation methods [85, 88].

The different companies producing polymer electrolyte membranes have their specific patents. However, a common theme is the use a sulphonated fluoropolymers, usually fluoroethylene. The most well known and well established of these is Nafion (®Dupont), which has been developed through several variants since 1960s.

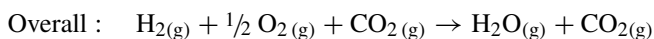
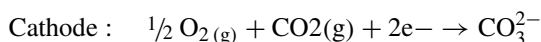
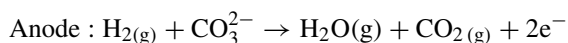
### 2.6.5 Molten Carbonate Fuel Cell (MCFC)

The electrolyte in the molten carbonate fuel cell uses a liquid solution of lithium, sodium, and/or potassium carbonates, soaked in a matrix. MCFCs have high fuel-to-electricity efficiencies ranging from 60 to 85 % with cogeneration, and operate

at about 620–660 °C [89–91]. The high operating temperature is an advantage because it enables a higher efficiency and the flexibility to use more types of fuels and inexpensive catalysts. This high operating temperature is needed to achieve sufficient conductivity of the electrolyte [13, 89, 90].

Molten carbonate fuel cells can use hydrogen, carbon monoxide, natural gas, propane, landfill gas, marine diesel, and coal gasification products as the fuel. MCFCs producing 10 kW to 2 MW MCFCs have been tested with a variety of fuels and are primarily targeted to electric utility applications. MCFCs for stationary applications have been successfully demonstrated in several locations throughout the world.

The reactions at the anode, cathode, and the overall reaction for the MCFC are



The high operative temperatures and the electrolyte chemistry can be responsible of some issues. The high temperature requires significant time to reach operating conditions and responds slowly to changing power demands. These characteristics make MCFCs more suitable for constant power applications. The carbonate electrolyte can also cause electrode corrosion problems [92, 93]. Furthermore, since  $\text{CO}_2$  is consumed at the anode and transferred to the cathode, introduction of  $\text{CO}_2$  and its control in air stream becomes an issue for achieving optimum performance that is not present in any other fuel cell [13].

The history of Molten Carbonate Fuel Cell (MCFC) can be traced back to the late nineteenth century when W.W. Jacques had produced his carbon–air fuel cell, a device for producing “electricity from coal.” This device used an electrolyte of molten potassium hydroxide at 400–500 °C in an iron pot [94]. Jacques suggested to replace molten alkali electrolytes with molten salts such as carbonates, silicates, and borates.

By the 1930s Davtayan proposed a baked mixture of 43 % calcined  $\text{Na}_2\text{CO}_3$ , 27 % monazite sand (a mixture of rare earth oxides), 20 %  $\text{WO}_3$ , and 10 % soda glass [95]. By treatment at 850 °C a mixture containing  $\text{Na}_3\text{PO}_4$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_2\text{WO}_4$ ,  $\text{Na}_2\text{SiO}_3$ , and oxides of  $\text{CeO}_2$ ,  $\text{La}_2\text{O}_3$ , and  $\text{ThO}_2$  was obtained [95]. The mixture was constituted by a porous framework of high-melting rare earth oxides in which was constrained a eutectic mixture of molten carbonates, phosphates, tungstates, and silicates. The eutectic mixture provided the means of ionic conduction.

The works of Broers and Ketelaar [95] established that molten carbonates as the preferred electrolyte for carbon containing fuels, since other molten salts tested were decomposed by steam produced at the anode of the fuel cell. Broers and Ketelaar [95] proposed a mixture of lithium, sodium, and/or potassium carbonates

impregnated into a porous disk of magnesium oxide. Using carbonates there was no problem in replacing  $\text{CO}_2$  at the cathode, which was effectively transferred through the molten electrolyte to the anode.

There was a general decline in interest in MCFCs during the 1970s but by the mid-1980s R&D the interest for MCFC has grown mainly in Japan and Europe [13, 95].

In recent years, MCFC development has been focused mainly on large-scale stationary and marine applications, where the relatively large size and weight of the MCFC and slow start-up time are not a problem. Molten carbonate fuel cells are under development for use with a wide range of conventional and renewable fuels.

The modern MCFC system has a high efficiency typically above 50 % and very low emissions. Since it operates at high temperature (about 650 °C) it can be used for cogeneration, combined heat and power, and distributed electricity generation. Most applications have so far been for stationary plants in hospitals, hotels, and resorts where the fuel is natural gas. The MCFC has been demonstrated to run on propane, coal gas, and anaerobic digester gas [90, 94, 96, 97]. Plants have been published for integrated coal gasifier/MCFC systems.

### 2.6.5.1 Components of the Molten Carbonate Fuel Cells

#### Materials

The heart of the molten carbonate fuel cell (MCFC) is the electrolyte, which is an ion-conducting molten salt [13, 90, 95, 96, 98–100]. This is typically a mixture of two or three alkali metal lithium, potassium, or sodium carbonates. The mixture is solid at room temperature but about 400 °C and above it becomes molten and is able to conduct carbonate ( $\text{CO}_3^{2-}$ ) ions. The molten carbonate in an MCFC is constrained within a porous solid material named electrolyte matrix. An important feature of the electrolyte matrix is the chemical stability toward the molten salt that penetrates in the matrix framework and many efforts have been done in the last 20–30 years for the development of new materials [89, 94]. Alumina can be used as an MCFC matrix since it can be obtained by simple coprecipitation from an aqueous solution of aluminum nitrate, and can be made into a thin sheet. The so obtained  $\gamma$ -alumina, changes phase to more stable  $\alpha$ -form at high temperatures (1200 °C). For this reason the long-term stability of the matrix could be an issue and has been investigated [101–105]. In particular lithium from the electrolyte will react over time with the alumina to form lithium aluminate ( $\text{LiAlO}_2$ ), which also exists in two interchangeable  $\alpha$  and  $\gamma$  phases: above 700 °C,  $\gamma$ - $\text{LiAlO}_2$  appears to be the more stable form, at 600–650 °C, the  $\alpha$  form is more stable. The industry is directed to the use of  $\alpha$ - $\text{LiAlO}_2$  for long-term stability [13].

The powdered matrix material is mixed with a binder to obtain sheets of 100–300 mm thickness. The carbonate electrolyte is also manufactured as similar thin sheets: cells are usually made by a sandwich of electrolyte and matrix sheets.

The stacks are assembled by building up layers of cells inserting current collectors and separator plates between one cell and the next. Once the cell or stack is assembled and mechanically clamped together, it is slowly heated up to above the melting temperature of the electrolyte. Once the electrolyte melts, it penetrates into the pores of the matrix.

Materials of anode and cathode of the MCFC are typically porous nickel and nickel oxide, respectively, in form of thin sheets [95].

### Electrolyte

State-of-the-art MCFC electrolytes contain typically 60 wt% carbonate constrained in a matrix of 40 wt% Li–AlO<sub>2</sub>. The  $\alpha$  form of Li–AlO<sub>2</sub> is the most stable in the MCFC electrolyte at low temperatures and is used in the form of fibers of 0.1 mm diameter. Other materials (e.g., larger size particles of Li–AlO<sub>2</sub>) may be added and many details are proprietary [99, 100].

The ohmic resistance of the MCFC electrolyte has an important and large effect on the operating voltage compared with most other fuel cells. Under typical MCFC operating conditions, it has been established that the electrolyte matrix contributes some 70 % of the ohmic losses. There is a direct relationship between the thickness of the electrolyte layer and the ionic conductivity. The thinner the electrolyte, the lower the ohmic resistance, and electrolyte matrices 0.2–0.5 mm in thickness can give better performances. However thicker materials are more stable, so low resistance and long-term stability must be optimized. For the MCFCs the typical power density at 650 °C is 0.16 Wcm<sup>2</sup> [13, 92, 93, 95, 106, 107].

It has been found that for the carbonates, a eutectic mixture of lithium and potassium carbonates

Li<sub>2</sub>CO<sub>3</sub>–K<sub>2</sub>CO<sub>3</sub> (62:38 mol%) is good for atmospheric pressure operation, whereas the lithium and sodium carbonate mixture Li<sub>2</sub>CO<sub>3</sub>–Na<sub>2</sub>CO<sub>3</sub> (60:40 mol%) is better for improved cathode stability when the cell is operated at elevated pressure [13, 95, 108–110].

An important difference between MCFC and other fuel cells is the conditioning of the electrolyte that is carried out once the stack is assembled. Layers of electrodes, electrolyte and matrix, and the various nonporous components are assembled together, and the stack is heated slowly. As the carbonate reaches its melt temperature (over 450 °C), it is absorbed into the ceramic matrix. This process can lead to some shrinkage of the components, and it is needed to pay attention to the mechanical design of the stack. An MCFC stack typically takes 14 h or more to reach the operating temperature. Another important aspect is that every time the MCFC stack is heated and cooled through the electrolyte melt temperature, stresses are set up, which can lead to cracking of the electrolyte matrix and permanent cell damage caused by fuel crossover. Thermal cycling of MCFC stacks

is therefore best avoided and MCFC systems are ideally suited to applications that need a continuous power supply.

### Anode

Because the anode reaction is relatively fast at MCFC temperatures, a high surface area anode catalyst is not required [13, 95, 111–114]. State-of-the-art anodes are made of a sintered Ni–Cr/Ni–Al alloy with a thickness of 0.4–0.8 mm and porosity of 55–75 %. Fabrication is carried out usually by tape casting a slurry of the powdered material, which is subsequently sintered. Chromium is added to the basic nickel component to reduce the nickel sintering that could give rise to a decay in the MCFC, performances. However, chromium can react with lithium of the electrolyte causing some loss of electrolyte. Addition of aluminum can improve both creep resistance in the anode and electrolyte loss due to the formation of  $\text{LiAlO}_2$  within the nickel particles. Ni–Cr/Ni–Al alloy are well established materials for the anodes, however nowadays the research is addressed to obtain new and less expensive materials. Moreover many efforts are addressed toward sulfur resistance materials such as  $\text{LiFeO}_2$ .

### Cathode

One of the major problems with the MCFC is that the state-of-the-art nickel oxide cathode material shows a weak, but significant, solubility in molten carbonates [13, 95, 114–119]. Through dissolution, some  $\text{Ni}^{2+}$  ions are formed in the electrolyte and diffuse toward the anode, leading to precipitation of metallic nickel dendrites. This precipitation can cause internal short circuits with subsequent loss of power. It has been reported [13] that solubility is reduced if the more basic, carbonates are used in the electrolyte. The addition of some alkaline earth oxides ( $\text{CaO}$ ,  $\text{SrO}$ , and  $\text{BaO}$ ) to the electrolyte has also been found to be beneficial [13].

With state-of-the-art nickel oxide cathodes, nickel dissolution can be minimized by (1) using a basic carbonate, (2) operating at atmospheric pressure and keeping the  $\text{CO}_2$  partial pressure in the cathode compartment low, and (3) using a relatively thick electrolyte matrix to increase the  $\text{Ni}^{2+}$  diffusion path. By these means, cell lifetimes of 40,000 h have been demonstrated under atmospheric pressure conditions. For operation at higher pressure, alternative cathode materials such as  $\text{LiCoO}_2$  have been investigated. This has a dissolution rate in molten carbonate an order of magnitude lower than that of  $\text{NiO}$  at atmospheric pressure. Dissolution of  $\text{LiCoO}_2$  also shows a lower dependency on the partial pressure of  $\text{CO}_2$  than  $\text{NiO}$ .

### 2.6.5.2 Cell Configuration

MCFC can have different configurations depending on the flows of fuel and oxidant streams. Fuel and oxidant that flow on opposite sides of each cell can be flowing in the same direction from inlet to outlet (coflow), in opposite directions (counterflow), or at  $90^\circ$  to each other (crossflow) [13, 95, 114, 120–124].

If the gases supplied to the cells are connected manifold externally to the stack, then the crossflow configuration is the only option and gas inlets and outlets for the fuel and oxidant can be located on the four sides of the stack. Figure 2.7 shows the cross-flow configuration adopted by CFC Solutions.

Cross-flow has many advantages: it allows a homogeneous reactant distribution to the cell, a uniform fuel utilization over the cell, a low pressure drops through the gas channels. Moreover, simple and less expensive separator plates than other configurations can be employed.

However, the significant disadvantages of large temperature profiles across the face of the electrodes and gas leakage and migration (ion pumping) of the electrolyte must be taken into account [123, 124].

If internal manifolding is applied, then coflow or counterflow can be configured [13, 123, 124]. With coflow, the concentrations of reactants on both sides of the cells are highest at the inlet and decrease toward the outlet. Concentrations of products increase toward each outlet. Coflow produces a larger temperature gradient across the cell than counterflow, especially when internal reforming is applied. With internal reforming, counterflow is normally the best option and results in the best distribution of current density and temperature throughout the cell.

The operating temperature of the MCFC of around  $650^\circ\text{C}$  provides ideal opportunities from a system design perspective. At these temperatures with a suitable catalyst, internal reforming can be carried out. Most available fuels, such as

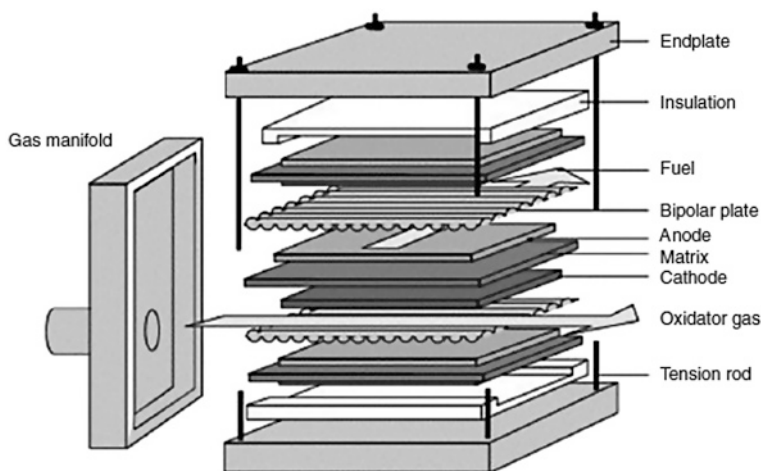
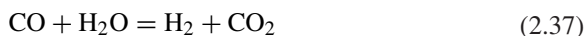


Fig. 2.7 Configuration of MCFC [13]

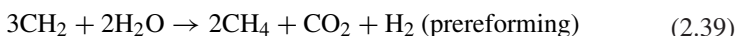
natural gas, liquefied petroleum gas, and biogases, need to be reformed to a hydrogen-rich gas for the fuel cell. This can be done external to the cell or stack but by carrying out the endothermic reforming reactions inside the MCFC (internal reforming), advantage is taken of the reaction to provide cell or stack cooling [13, 95, 114].

### 2.6.5.3 Steam Reforming

Methane reforming Eq. (2.36) is the simplest example of steam reforming (SR). This reaction is endothermic at MCFC temperatures and over an active solid catalyst the product of the reaction in a conventional reforming reactor is dictated by the equilibrium of Eq. (2.36) and the water–gas shift (WGS) reaction Eq. (2.37). This means that the product gas from a reformer depends only by the inlet steam/methane ratio (or more generally steam/carbon ratio) and the reaction temperature and pressure. Similar reaction can be written for other hydrocarbons such as natural gas, naphtha, purified gasoline, and diesel. In the case of reforming oxygenates such as ethanol [125, 126], the situation is in some way more complex, as other side reactions can occur. With simple hydrocarbons, like as methane, the formation of carbon by pyrolysis of the hydrocarbon or decomposition of carbon monoxide via the Boudouard reaction Eq. (2.38) is the only unwanted product.



In the MCFC carbon formation can be avoided by carrying out some degree of prereforming externally to the fuel cell stack. Prereforming consists of vaporizing the fuel and passing this with steam over a suitable catalyst. It converts high-molecular-weight hydrocarbons to methane, thereby reducing the risk that they pyrolyze or decompose to carbon in the MCFC stack [13, 127]. Moreover, in this way some hydrogen is present at the inlet of the fuel cell. If excess steam is used carbon monoxide decomposition is avoided due the Boudouard equilibrium. A hydrocarbon fuel such as diesel may be represented by the empirical formula  $\text{CH}_2$  and prereforming of this fuel may be represented as



Prereforming is usually carried out at modest temperatures (i.e., 320 °C) over a supported nickel catalyst in an adiabatic reactor [13].

Any fuel, including gases produced by the gasification of coal, wood waste, or other organic waste or biogas from digesters, that is fed to either the anode compartment directly or to an external reformer or prereformer must contain low sulfur to avoid poisoning of the reforming or prereforming catalyst [128].

### 2.6.5.4 MCFC Internal Reforming and Steam Reforming Catalyst

One of the advantages of the MCFC over low-temperature fuel cells is the ability to internally convert fuels such as methane or natural gas directly into hydrogen via internal steam reforming [127, 129–132]. The reforming reaction is endothermic, therefore by cooling the stack can reduce the heat that is removed out of the stack in the cathode exhaust stream. So the flow of air to the cathode (which normally provides the cooling for the stack) can be reduced. In this way the  $\text{CO}_2$  partial pressure through the cathode compartment is raised, leading to a higher cell voltage, moreover it reduces the parasitic electrical load on the system related the cathode air compressor. For these reasons an internal reforming MCFC system has a higher efficiency than an external reforming system.

There are two approaches to internal reforming. Indirect internal reforming (IIR): the reforming reaction takes place in channels or compartments within the stack that are adjacent to the anode compartments, the heat generated in the cell is transferred to the reforming channels, and the product from the reforming is fed to the anode channels.

In direct internal reforming (DIR) the reforming reaction is carried out on the fuel cell anode itself (or as close to it as possible); in this way hydrogen produced by reforming is immediately consumed by the electrochemical cell reaction allowing to shift the equilibrium of the reforming and WGS reactions to the right as product is consumed by the electrochemical reaction [13, 95, 133–135]. The DIR approach is best carried out at low pressures with catalyst inside the anode compartment close to the anode of the cell.

In the IIR configuration, commercial reforming catalyst (e.g., nickel/alumina) exhibits little deactivation because the cell temperature is generally much lower than in a conventional reforming plant (usually above 800 °C) [13, 136–139]. The stability of a DIR catalyst, however, is strongly affected by the anode environment. Conventional catalysts decay usually via two mechanisms—sintering of the metal particles or support leading to a loss of catalytic surface area, or poisoning of catalyst active sites by sulfur [13, 128].

Carbonate retention has been the biggest issue for MCFC developers. There are two mechanisms for loss of carbonate from the cells, namely, creepage and loss by vapor phase transport [140, 141].

Steam reforming of ethanol has been demonstrated in the MCFC and proceeds rather differently to the reforming of hydrocarbons [125, 126]. Rinaldi et al. [121] studied ethanol reforming over supported metal catalyst (nickel on doped magnesium oxide). They concluded that acetaldehyde is the main unwanted product. Further catalyst optimization may improve the selectivity in the MCFC.

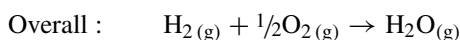
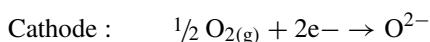
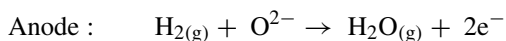
Some tests have been carried out recently with catalysts of titanium dioxide promoted with lanthanum or samarium oxides [13].



### 2.6.6 Solid Oxide Fuel Cell (SOFC)

The SOFC is a complete solid-state device that uses an oxide ion-conducting ceramic material as the electrolyte. The electrolyte is a nonporous solid, such as  $\text{Y}_2\text{O}_3$  stabilized  $\text{ZrO}_2$  with conductivity-based oxygen ions [122, 128, 142–144]. Yttria-stabilized zirconia (YSZ) is the most commonly used material for the electrolyte. It was first used as a fuel cell electrolyte by Baur and Preis in 1937 [145]. The anode is usually made of a Co- $\text{ZrO}_2$  or Ni- $\text{ZrO}_2$  cement [13, 95, 146, 147], while the cathode is made of Sr-doped  $\text{LaMnO}_3$  (LSM) [13, 148–150].

The anode, cathode, and overall cell reactions are



SOFCs efficiency is lower than MCMF although the operating temperature (850–1000 °C) is higher. The high operating temperatures imply that precious metal electrocatalysts are not needed, hence reducing the cost of cell components; it is also possible to use carbon-based fuels directly, removing the need for external reformers, further reducing the cost [13]. The high operating temperature of SOFC enables relatively inexpensive electrode materials to be used. Moreover, SOFC has high tolerance to impurities due to the catalytic properties of the nickel anode catalyst unlike PEMFC. The conductivity of the fuel cell materials increases with temperature [151, 152]. The dominant losses in SOFCs is mainly due to the ohmic resistance losses, thus increasing the temperature enhances the SOFC efficiency. Noticeable interest to develop electrolytes that are able to operate at lower temperatures is ongoing for several reasons: lowering the operating temperature would reduce the costs and improve cell lifetime [153].

The main configurations of SOFC are tubular, bipolar, and a planar, this last being developed more recently [13, 154–156]. SOFCs can operate at a high enough temperature to incorporate an internal fuel reformer that uses heat from the fuel cell. The recycled steam and a catalyst can convert the natural gas directly into a hydrogen-rich fuel. The waste heat allows the development of cogenerative processes enhancing energy efficiency to very attractive levels.

Power-generating efficiencies could reach 60 to 85 % with cogeneration [13, 128, 142–144, 146–150, 154–158]. Tubular SOFC technology has produced as much as 220 kW [154, 155]. Japan has two 25-kW units online, and a 100 kW plant is being tested in Europe [6, 159]. SOFCs coupled with small gas turbines are high-efficiency systems that have a combined rating in the range of 250 kW to 25 MW, and are expected to fit into grid support or industrial onsite generation markets [6, 13, 159].

### 2.6.6.1 Components of the Solid Oxide Fuel Cells

#### Electrolyte

In an SOFC the electrolyte is exposed to both oxidizing (air side) and reducing species (fuel side) at high temperatures. Several properties of the SOFC electrolyte are required: (1) Sufficient ionic conductivity (the electronic conductivity of the electrolyte must be sufficiently low in order to provide a high energy conversion efficiency); also the oxide ion conductivity must be high to minimize the ohmic loss. (2) Dense structure, in order to produce maximum electrochemical performance. (3) Stability since the electrolyte is exposed to the air and the fuel at elevated temperatures. This requires that the thermal expansion coefficients must match at the interfaces.

Typical electrolyte materials for SOFCs are oxides with low valence element substitutions, sometimes named acceptor dopants [13, 95] which create oxygen vacancies through charge compensation. For SOFC applications, there are various materials that have been explored as electrolyte, yttria-doped zirconia (YSZ) and gadolinium-doped ceria (GDC) are the most common materials used for the oxide-conducting electrolyte. Above 800 °C, YSZ becomes a conductor of oxygen ions ( $O^{2-}$ ); zirconia-based SOFC operates between 800 and 1100 °C. The ionic conductivity of YSZ is  $0.02 \text{ S m}^{-1}$  at 800 °C and  $0.1 \text{ S cm}^{-1}$  at 1000 °C. A thin electrolyte (25–50  $\mu\text{m}$ ) ensures that the contribution of electrolyte to the ohmic loss in the SOFC is kept to a minimum.

#### Zirconium oxide-based electrolyte (YSZ)

Yttria-doped zirconia (YSZ) is stable under reducing and oxidizing conditions. It is a pure ionic conductor, completely nonreactive with anode and cathode at operating and production temperatures. Above 800 °C, YSZ becomes a conductor of oxygen ions ( $O^{2-}$ ) and typically operates at 800–1100 °C. The ionic conductivity of YSZ is  $0.02 \text{ S m}^{-1}$  at 800 °C and  $0.1 \text{ S cm}^{-1}$  at 1000 °C. A thin electrolyte (25–50  $\mu\text{m}$ ) ensures that the contribution of electrolyte to the ohmic loss in the SOFC is kept to a minimum. Its thermal expansion has to be close to other fuel cell components and it must be gas tight to prevent direct combination of fuel and oxidant. Pure zirconia is not used, as its ionic conductivity is too low for fuel cell use [160].

#### Cerium oxide-based electrolyte

Doped cerium dioxide materials are candidates for the electrolyte for cell operation at  $T \leq 600 \text{ °C}$ , because of their higher oxide ion conductivity ( $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ :  $0.025 \text{ O}^{-1} \text{ cm}^{-1}$  at 600 °C) compared to YSZ ( $<0.005 \text{ } \Omega^{-1} \text{ cm}^{-1}$ ). Gadolinium- or samarium-doped cerium dioxide provides the highest ionic conductivity in cerium dioxide-based materials owing to similar ionic radii of  $\text{Gd}^{3+}$ / $\text{Sm}^{3+}$  and  $\text{Ce}^{4+}$ . The main issue of doped cerium dioxide is the onset of electronic

conduction in reducing conditions at  $T \geq 650\text{ }^{\circ}\text{C}$  owing to the reduction of  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$  to compensate the formation of oxygen vacancies [13].

### Perovskite electrolytes

The perovskite structure ( $\text{ABO}_3$ ) offers an opportunity for a material scientist to selectively substitute either the A or the B ion by introducing isovalent or aliovalent cations. The compound  $(\text{La}, \text{Sr})(\text{Mg}, \text{Ga})\text{O}_3$  (LSMG) has been developed as an oxide ion conductor. The use of LSMG is attractive because it has reasonable oxide ion conductivity and is compatible with a variety of cathodes, in particular the highly active ones. Other interesting materials, such as  $\text{Bi}_4\text{V}_2\text{O}_{11}$  (BIMEVOX (bismuth metal vanadium oxide)), have also been mentioned in the literature.

### Cathode

The cathode electrode operates in an oxidizing environment of air at  $1000\text{ }^{\circ}\text{C}$ . The cathode electrode is a porous structure that allows mass transport of reactants and products.

Materials suitable for an SOFC cathode have to satisfy the following requirements: high electronic conductivity; stability in oxidizing atmospheres at high temperature; thermal expansion match with other cell components; compatibility and minimum reactivity with different cell components; sufficient porosity to allow transport of the fuel gas to the electrolyte/electrode interface [148–150].

LSM,  $(\text{La}_{0.84}\text{Sr}_{0.16})\text{MnO}_3$ , a p-type semiconductor, is most commonly used for the cathode material. Although adequate for most SOFCs, other materials may be used, particularly attractive being p-type conducting perovskite structures that exhibit mixed ionic and electronic conductivity [13]. The advantages of using mixed conducting oxides become apparent in cells operating at around  $650\text{ }^{\circ}\text{C}$ . As well as the perovskites, lanthanum strontium ferrite, lanthanum strontium cobaltite, are proposed in literature [13, 160–162].

$\text{LaMnO}_3$  can react with the YSZ electrolyte at high temperature producing insulating phases of lanthanum zirconate [13].

### Anode

The key requirements for the anode are high conductivity, stability in reducing atmospheres, and sufficient porosity to allow good mass transport. The most common anode for SOFCs is the Ni/YSZ cermet. Ni is chosen among other components because of its high electronic conductivity and stability under reducing conditions. Moreover, Ni activates both direct oxidation and steam reforming. The use of YSZ has multiple purposes: to inhibit sintering of the nickel [160, 161], to guarantee thermal expansion coefficient (TEC) comparable with other fuel cell components (mainly the electrolyte), and to increase the triple phase boundary

(TPB) [163, 164]. The anode porosity (20–40 %) ensures good mass transport and improves the triple boundary by allowing  $O^{2-}$  ion movement within the anode electrode [13, 160]. A small amount of ceria is added to the anode cermet to improve ohmic polarization loss at the interface between the anode and the electrolyte. This also improves the tolerance of the anodes to temperature cycling and redox changes within the anode gas [13, 160].

The TPB is a key area and it is important to increase this surface area since in this point the oxygen ions and the hydrogen gas are brought together to react at the surface of the nickel site [160, 165–167].

### 2.6.6.2 Fuel Reforming

The high operational temperature of SOFCs has two benefits: high efficiency and fuel flexibility. The high operating temperature allows the production of high-quality off-gases, which can be used for cogeneration processes [122, 154–156, 168], or to heat the reformer for endothermic steam reforming reactions, or even to fire a secondary gas turbine. Therefore, SOFCs have a high electrical efficiency, higher than other fuel cells [13, 95]. Moreover, a variety of fuels can be reformed within the cell stack (internal reforming) or through a separate fuel reformer (external reforming). This flexibility allows use of fuels such as biogas [169], liquid hydrocarbon fuels, and landfill gas. These fuels can be reformed to a mixture of hydrogen and carbon monoxide.

In the internal reforming arrangement, two configurations are employed: the direct internal reforming (DIR), and indirect internal reforming (IIR).

In the DIR the fuel reforming occurs directly on the fuel cell anode where the fuel is converted into a hydrogen-rich mixture directly inside the anode compartment: electrochemical reaction and fuel reforming reactions simultaneously take place at the anode. This is a simple and very efficient design and involves low capital costs. However, some issue must be taken into account: the anode compartment must be equipped with a proper catalyst for the steam reforming; carbon deposition is favored due to the larger content of fuel at the anode side; temperature distribution should not be homogeneous due to cooling caused by the endothermic reaction [170–175].

The problems of DIR can be in some way overcome by the indirect internal reforming (IIR) configuration. IIR uses a separate fuel reforming catalyst that is integrated within the SOFC stack upstream of the anode side, and typically utilizes heat and water from the SOFC stack. Therefore, in this case only a thermal coupling between the reformer and the SOFC stack exists. Obviously, the IIR configuration results in a higher system complexity and in higher capital costs [127, 133].

IIR should not be as efficient as DIR, however it allows a more stable cell performance. Since the external reformer is physically separated from the fuel cell stack it can be operated at different pressures and temperatures if necessary. This is of particular importance because in this way it is possible to eliminate the problem of carbon deposition via fuel decomposition that deactivates the anode [13, 133, 168, 169].

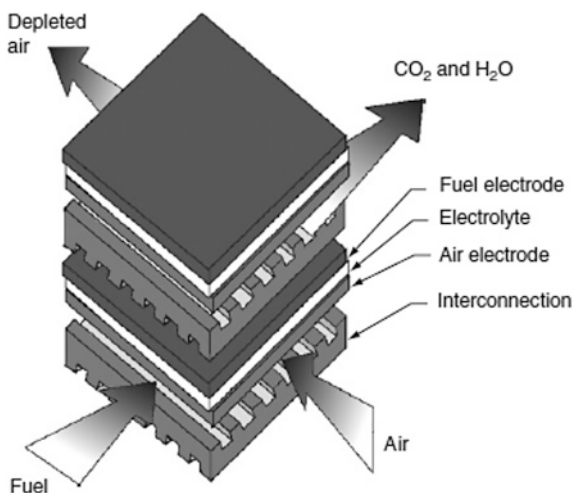
### 2.6.6.3 Solid Oxide Fuel Cell Configurations

The most common SOFC designs are planar and tubular, and their many variants.

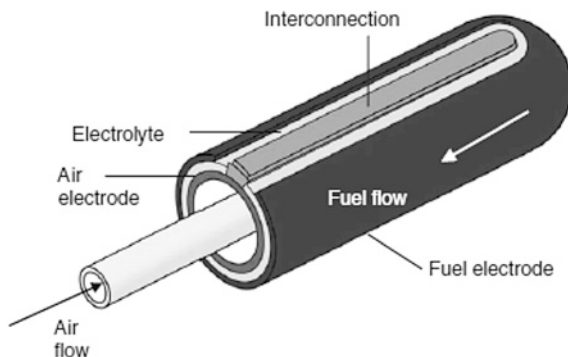
In the planar SOFC, cell components are thin and flat plates electrically connected in series. A generic schematic of a planar SOFC design is shown in Fig. 2.8 [176]. The planar cells can be electrolyte supported, electrode supported, or metal supported. For instance, the cell may be in the form of a circular disk fed with fuel from the central axis, or it may be in the form of a square plate fed from the edges. Planar designs offer several potential advantages, including simpler and less expensive manufacturing processes and higher power densities, than tubular cells. However, planar designs need high-temperature gas-tight seals between the components in the SOFC stack; but these still remain a challenging area for the successful commercialization of planar SOFCs [177, 178]. The electrochemical performance is highly dependent on cell materials, electrode microstructures, and cell geometric parameters. The cell was optimized with an anode of thickness 0.5 mm and porosity ~57 %. The anode interlayer was ~20 mm. The electrolyte was ~8 mm and cathode interlayer ~20 mm. The flow rates of humidified hydrogen and air were 300 and 550 mL min<sup>-1</sup>, respectively. The maximum power density obtained is about 1.8 Wcm<sup>2</sup> at 800 °C [179–181].

In the tubular SOFC design, components are flat tubes and joined together to give higher power density and easily printable surfaces for depositing the electrode layers. It may be of a large diameter (>15 mm), or a microtubular cells with a smaller diameter (<5 mm) [44, 179, 182]. Figure 2.9 illustrates a tubular SOFC in which the oxidant (air or oxygen) is introduced through an alumina injector tube positioned inside the cell. The oxidant is discharged near the closed end of the cell and flows through the annular space formed by the cell and the coaxial injector tube. The fuel flows on the outside of the cell from the closed end and is electrochemically oxidized while flowing to the open end of the cell generating

**Fig. 2.8** Planar SOFC design [176]



**Fig. 2.9** Tubular SOFC design [176]



electricity. Part of the fuel is recirculated in the fuel stream and the rest combusted to preheat the incoming air and/or fuel. The exhaust gas from the fuel cell is at 600–900 °C depending on the operating conditions. The single biggest advantage of tubular cells over planar cells is that they do not require any high-temperature seals to isolate the oxidant from the fuel, and this leads to very stable performance of tubular cell stacks over long periods of time (several years). However, their areal power density is much lower (about  $0.2 \text{ Wcm}^{-2}$ ) compared to planar cells, and manufacturing costs are high [183–185].

A single planar or tubular SOFC generally produces a low voltage and power and the connection into a stack is needed in order to give higher power. Electrochemical performance, structural and mechanical integrity gas manifold and ease of fabrication are important targets for the improvements of cell performances [176, 186].

## References

1. Dincer I, Zamfirescu C (2014) Advanced power generation systems. In: Chapter 3—Fossil fuels and alternatives, 95–141
2. Shafiee S, Topal E (2009) When will fossil fuel reserves be diminished? *Energy Policy* 37:181–189
3. Abas N, Kalair A, Khan N (2015) Review of fossil fuels and future energy technologies. *Futures* 69:31–49
4. Ball M, Weeda M (2015) The hydrogen economy—Vision or reality? *Int J Hydrogen Energy* 40:7903–7919
5. Andrews J, Shabani B (2012) Where does hydrogen fit in a sustainable energy economy? *Procedia Eng* 49:15–25
6. Sharaf OZ, Orhan MF (2014) An overview of fuel cell technology: fundamentals and applications. *Renew Sustain Energy Rev* 32:810–853
7. Elmer T, Worall M, Wu S, Riffat SB (2015) Fuel cell technology for domestic built environment applications: state of-the-art review. *Renew Sustain Energy Rev* 42:913–931
8. Alves HJ, Bley C, Niklevicz RR, Pires Frigo E, Sato Frigo M, Coimbra-Araújo CH (2013) Overview of hydrogen production technologies from biogas and the applications in fuel cells. *Int J Hydrogen Energy* 38:5215–5225

9. The Department of Energy hydrogen and fuel cells program plan: an integrated strategic plan for the research, development, and demonstration of hydrogen and fuel cell technologies US Department of Energy (2011)
10. National Energy Technology Laboratory, U.S. Department of Energy Fuel Cell Handbook 7th ed. Morgantown, 1–35 (2005)
11. O'Hayre R, Cha SW, Colella W, Prinz FB (2006) Fuel cell fundamentals. Wiley, New York
12. Carter D, Ryan M, Wing J (2012) The fuel cell industry review 2012. Fuel Cell Today
13. Larminie J, Dicks A (2003) In: Fuel Cell Systems Explained, 2nd edn, Wiley
14. Park SY, Kim JW, Lee DH (2011) Development of a market penetration forecasting model for hydrogen fuel cell vehicles considering infrastructure and cost reduction effects. Energy Policy 39:3307–3315
15. Simons A, Bauer C (2015) A life-cycle perspective on automotive fuel cells. Appl Energy 157:884–896
16. Hellmana HL, van den Hoedb R (2007) Characterising fuel cell technology: challenges of the commercialisation process. Int J Hydrogen Energy 32:305–315
17. Wang J (2015) Barriers of scaling-up fuel cells: cost, durability and reliability. Energy 80:509–521
18. Lewis J (2014) Stationary fuel cells insights into commercialisation. Int J Hydrogen Energy 39:21896–21901
19. Xianguo L (2006) Principles of fuel cells. Taylor & Francis Group, New York
20. Cowey K, Green KJ, Mepsted GO, Reeve R (2004) Portable and military fuel cells. Curr Opin Solid State Mater Sci 8:367–371
21. Patil AS, Dubois TG, Sifer N, Bostic E, Gardner K, Quah M (2004) Portable fuel cell systems for America's army: technology transition to the field. J Power Sources 136:220–225
22. Wang Y, Chen KS, Mishler J, Cho SC, Adroher XC (2011) A review of polymer electrolyte membrane fuel cells: technology, applications, and needs on fundamental research. Appl Energy 88:981–1007
23. Breakthrough Technologies Institute Fuel cell technologies market report US Department of Energy (2011)
24. Abdullah MO, Yung VC, Anyi M, Othman AK, Hamid KBA, Tarawe J (2010) Review and comparison study of hybrid diesel/solar/hydro/fuel cell energy schemes for a rural ICT Telecenter. Energy 35:639–646
25. Bauen A, Hart D, Chase A (2003) Fuel cells for distributed generation in developing countries: an analysis. Int J Hydrog Energy 28:695–701
26. Munuswamy S, Nakamura K, Katta A (2011) Comparing the cost of electricity sourced from a fuel cell-based renewable energy system and the national grid to electrify a rural health centre in India: a case study. Renew Energy 36:2978–2983
27. Santarelli M (2004) Design and analysis of stand-alone hydrogen energy systems with different renewable sources. Int J Hydrog Energy 29:1571–1586
28. Kazempoor P, Dorer V, Weber A (2011) Modelling and evaluation of building integrated SOFC systems. Int J. Hydrog Energy 36:13241–13249
29. Alcaide F, Cabot PL, Brillas E (2006) Fuel cells for chemicals and energy cogeneration. J Power Sources 153:47–60
30. Agnolucci P (2007) Prospects of fuel cell auxiliary power units in the civil markets. Int J Hydrog Energy 32:4306–4318
31. Lutsey N, Brodrick CJ, Sperling D, Dwyer HA (2002) Markets for fuel cell auxiliary power units in vehicles: a preliminary assessment. Institute of Transportation Studies. UCD-ITS-RP-02-44
32. Hochgraf C (2009) Application: transportation: electric vehicles: fuel cells. In: Garche J (ed) Encyclopedia of electrochemical power sources. Elsevier, Amsterdam
33. Bradley TH, Moffitt BA, Mavris D, Parekh DE (2009) Applications: transportation: aviation: fuelcells. In Garche J (ed) Encyclopedia of Electrochemical Power Sources, Elsevier Amsterdam



34. Saxe M, Folkesson A, Alvfors P (2008) Energy system analysis of the fuel cell buses operated in the project: clean urban transport for Europe. *Energy* 33:689–711
35. Collecting the History of Fuel Cells (2006). <http://americanhistory.si.edu/fuelcells/index.htm>. Smithsonian Institution. Accessed 30 Oct 2015
36. Shekhawat D, Spivey JJ, Berry DA (2011) Fuel cells: technologies for fuel processing, Elsevier (2011)
37. Wark K (1977) Applied thermodynamics for engineers. McGraw-Hill, New York
38. Williams MC, Yamaji K, Yokokawa H, Fundamental thermodynamic studies of fuel cells using MALT2. *J Fuel Cell Sci Technol* 6:97–102 and 113–116 (2009)
39. Winkler W (2003) High temperature solid oxide fuel cells: fundamentals, design, and applications Thermodynamics. In: Singhal SC, Kendall K (eds) Oxford. Elsevier, UK, pp 53–82
40. Winkler W (1994) SOFC integrated power plants for natural gas. In: Proceedings of first European solid oxide fuel cell forum, Lucerne, Switzerland, 821–848, 3–7 Oct 1994
41. Williams M, Yamaji K, Horita T, Sakai N, Yokokawa H (2009) Exergetic studies of intermediate temperature, solid oxide fuel cell electrolytes. *J Electrochem Soc* 156:546–551
42. Virkar A, Williams MC, Singhal SC (2007) Concepts for ultrahigh power density solid oxide fuel cells In: Williams M, Krist K (eds) ECS Transactions, vol 5. pp 401–422
43. Virkar AV (2005) Theoretical analysis of the role of interfaces in transport through oxygen ion and electron conducting membranes. *J Power Sources* 147:8–31
44. Zhao, Virkar AV (2005) Dependence of polarization in anode-supported solid oxide fuel cells on various cell parameters. *J Power Sources* 141:79–95
45. Yokokawa H, Sakai N, Horita T, Yamaji K, Brito ME (2005) Electrolytes for solid-oxide fuel cells. *MRS Bull* 30(8):591–595
46. Choudhury NS, Patterson JW (1970) Steady-state chemical potential profiles in solid electrolytes. *J Electrochem Soc* 117:1384–1388
47. Space applications of hydrogen and fuel cells (2015) National Aeronautics and Space Administration. [http://www.nasa.gov/topics/technology/hydrogen/hydrogen\\_2009.html](http://www.nasa.gov/topics/technology/hydrogen/hydrogen_2009.html). Accessed 30 Oct 2015
48. Sheffield JW (2007) Assessment of hydrogen energy for sustainable development. In: Sheffield C (ed) Springer, Netherlands (2007)
49. Gaines LL, Elgowainy A, Wang MQ (2008) Full fuel-cycle comparison of forklift propulsion systems. In: Argonne National Laboratory. ANL/ESD/08-3
50. Wang M, Elgowainy A, Han J (2010) Life-cycle analysis of criteria pollutant emissions from stationary fuel cell systems. US Department of Energy Hydrogen and Fuel Cells Program AN012
51. El-Sharkh MY, Rahman A, Alam MS, Byrne PC, Sakla AA, Thomas T (2004) A dynamic model for a stand-alone PEM fuel cell power plant for residential applications. *J Power Sources* 138:199–204
52. Zhu Y, Tomsovic K (2002) Development of models for analyzing the load—following performance of microturbines and fuel cells. *Electr Power Syst Res* 62:1–11
53. Grimes CA, Varghese OK, Ranjan S (2008) Light, water, hydrogen: the solar generation of hydrogen by water photoelectrolysis. Springer, New York
54. Jiao K, Li X (2011) Water transport in polymer electrolyte membrane fuel cells. *Prog Energy Combust Sci* 37:221–291
55. Ous T, Arcoumanis C (2013) Degradation aspects of water formation and transport in proton exchange membrane fuel cell: a review. *J Power Sources* 240:558–582
56. Tsushima S, Hirai S (2011) In situ diagnostics for water transport in proton exchange membrane fuel cells. *Prog Energy Combust Sci* 37:204–220
57. Zhang Y, Li J, Ma L, Cai W, Cheng H (2015) Recent developments on alternative proton exchange membranes: strategies for systematic performance improvement. *Energy Technol* 3:675–691
58. Dubau L, Castanheira L, Maillard F, Chatenet M, Lottin O, Maranzana G, Dillet J, Lamibrac A, Perrin JC, Moukheiber E et al (2014) A review of PEM fuel cell durability:



- materials degradation, local heterogeneities of aging and possible mitigation strategies. *Wiley Interdisc Rev Energy Environ* 3:540–560
59. Banham D, Feng F, Furstenhaupt T, Pei K, Ye S, Birss V (2015) Novel mesoporous carbon supports for PEMFC catalysts. *Catalysts* 5:1046–1067
60. Anstrom JR (2014) Hydrogen as a fuel in transportation. *Energy* 63:499–524
61. Chirachanchar S, Pongan A, Jarumaneeroj C (2013) High temperature performance polymer electrolyte membranes. *Membr Process. Sustain. Growth* 247–287
62. Sim V, Han W, Poon HY, Lai YT, Yeung KL (2014) Confinement as a new architecture for self-humidifying proton-exchange membrane for PEMFC Abstracts of Papers. In: 248th ACS National Meeting & Exposition, San Francisco, CA, United States, 10–14 Aug 2014
63. Moilanen D E, Piletic IR, Fayer MD (2007) Dynamics of water in Nafion fuel cell membranes: the effects of confinement and structural changes on the hydrogen bonding network. In: NSTI Nanotech 2007, Nanotechnology Conference and Trade Show, Santa Clara, CA, United States, vol 4, pp 712–715 20–24 May 2007
64. Narayanan SR, Valdez TI, Firdosy S (2009) Analysis of the performance of Nafion-based hydrogen-oxygen fuel cells. *J Electrochem Soc* 156:B152–B159
65. Tian JH, Gao PF, Zhang ZY, Luo WH, Shan ZQ (2008) Preparation and performance evaluation of a Nafion-TiO<sub>2</sub> composite membrane for PEMFCs. *Int J Hydrogen Energy* 33:5686–5690
66. Tsai CH, Wang CC, Chang CY, Lin CH, Chen-Yang YW (2014) Enhancing performance of Nafion-based PEMFC by 1-D channel metal-organic frameworks as PEM filler. *Int J Hydrogen Energy* 39:15696–15705
67. Matolin V, Fiala R, Vaclavu M, Matolinova I (2014) Thin film catalysts for PEMFCs. In: Abstracts of Papers, 248th ACS National Meeting & Exposition, San Francisco, CA, United States. 2014 ENFL-211, pp 10–14 (2014)
68. Boyaci SFC, Isik-Gulsac I, Osman OO (2013) Analysis of the polymer composite bipolar plate properties on the performance of PEMFC (polymer electrolyte membrane fuel cells) by RSM (response surface methodology). *Energy* 55:1067–1075
69. Lin BYS, Kirk DW, Thorpe SJ (2006) Performance of alkaline fuel cells: a possible future energy system. *J Power Sources* 161:474–483
70. Aremo B, Adeoye MO, Obioh IB (2015) A simplified test station for alkaline fuel cell. *J Fuel Cell Sci Technol* 12:1–7
71. Fuel Cell Basics (2000). Fuel Cells. <http://www.fuelcells.org/basics/how.html>. Accessed 30 Oct 2015
72. Marino MG, Kreuer KD (2015) Alkaline stability of quaternary ammonium cations for alkaline fuel cell membranes and ionic liquids. *ChemSusChem* 8:513–523
73. Ishimoto T, Hamatake Y, Kazuno H, Kishida T, Koyama M (2015) Theoretical study of support effect of Au catalyst for glucose oxidation of alkaline fuel cell anode. *Appl Surf Sci* 324:76–81
74. Geng F, Zeng WM, Ma YL (2013) Preparation and characterization of foam-Ni deposit Pt and Pd catalysts for alkaline fuel cell. *Dianyan Jishu* 37:387–389
75. Aziznia, Oloman CW, Gyenge EL (2013) Platinum- and membrane-free swiss-roll mixed-reactant Alkaline Fuel cell. *ChemSusChem* 6:847–855
76. Fuller TF, Perry M, Reiser C (2006) Applying the lessons learned from PAFC to PEM fuel cells. *ECS Trans* 1:337–344
77. Fuller TF, Gallagher KG (2008) Phosphoric acid fuel cells. *Mater Fuel Cells* 209–247
78. Sammes N, Bove R, Stahl K (2004) Phosphoric acid fuel cells: fundamentals and applications. *Curr Opin Solid State Mater Sci* 8:372–378
79. Steele BCH (2001) Material science and engineering: the enabling technology for the commercialisation of fuel cell systems. *J. Mater Sci* 36:1053–1068
80. Antolini E, Salgado JRC, Gonzalez ER (2006) The stability of Pt-M (M = first row transition metal) alloy catalysts and its effect on the activity in low temperature fuel cells. *J Power Sources* 160:957–968

81. Stonehart P, Wheeler D (2005) Phosphoric acid fuel cells (PAFCs) for utilities: electrocatalyst crystallite design, carbon support, and matrix materials challenges. *Mod Aspects Electrochem* 38:373–424
82. Hogarth M, Hards G (1996) Direct methanol fuel cells: technological advances and further requirements. *Plat Met Rev* 40:150–159
83. Hamnett A, Kennedy BJ (1988) Bimetallic carbon supported anode for the direct methanol-air fuel cell. *Electrochim Acta* 33:1613–1618
84. Hamnett A (1997) Mechanism and electrocatalysis in the direct methanol fuel cell. *Catal Today* 38:445–457
85. Libby B, Smyrl WH, Cussler EL (2003) Polymer-Zeolite composite membranes for direct methanol fuel cells. *AIChE J* 49:991–1001
86. R. F. Service (2002) Fuel cells. Shrinking fuel cells promise power in your pocket. *Science* 296:1222–1224
87. Lu GQ, Wang CY, Yen TJ, Zang X (2004) Development and characterization of a silicon-based micro direct methanol fuel cell. *Electrochim Acta* 49:821
88. Li X, Roberts EPL, Holmes SM (2006) Evaluation of composite membranes for direct methanol fuel cells. *J Power Sources* 154:115–123
89. Tomczyk P (2006) MCFC versus other fuel cells—characteristics, technologies and prospects. *J Power Sources* 160(2006):858–862
90. Zhu XJ, Huang B (2012) Molten carbonate fuel cells. *Electrochem Technol Energy Storage Convers* 2:729–775
91. Rossi et al C (1999) In: *Proceedings of Micro Nanotechnology for Space Applications*, vol 1, Apr (1999)
92. Blomen L, Leo JMJ, Mugerwa M (1993) *Fuel cell systems*. Plenum Publishing, New York
93. Kunz HR (1987) Transport of electrolyte in molten carbonate fuel cells. *J Electrochem Soc* 134:195–113
94. Perry ML, Fuller TF (2002) A historical perspective of fuel cell technology in the 20th century. *J Electrochem Soc* 149:S59–S67
95. *Fuel Cell Technology Handbook* (2002) In: Hoogers G (ed), CRC Press
96. McPhail SJ, Hsieh PH, Selman JR (2013) Molten carbonate fuel cells. *Mater High-Temp Fuel Cells* 341–371
97. Chen B (2011) Research and development of fuel cell technology in China. In: *Asia-Pacific Power and Energy Engineering Conference*, Wuhan, China, (Pt. 1), 529–532, 25–28 Mar 2011
98. Mirahmadi A, Akbari H (2012) A noble method for molten carbonate fuel cells electrolyte manufacturing. *J Solid State Electrochem* 16:931–936
99. Maru HC, Pigeaud A, Chamberlin R, Wilemski G (1986) Electrolyte management in molten carbonate fuel cells. *Proc Electrochem Soc* 86:398–422
100. Ang PGP, Sammells AF (1980) Influence of electrolyte composition on electrode kinetics in the molten carbonate fuel cell. *J Electrochem Soc* 127:1287–1294
101. Albin V, Goux A, Ringuède A, Belair S, Lair V, Cassir M (2007) Screening and properties of new materials for MCFC application. *ECS Trans* 3:205–213
102. Park E, Hong M, Lee H, Kim M, Kim K (2005) A new candidate cathode material as (Co/Mg)-coated Ni powder for molten carbonate fuel cell. *J Power Sources* 143:84–92
103. Wijayasinghe A, Lagergren C, Bergman B (2003) New cathode materials for molten carbonate fuel cells. *Fuel Cells* 2:181–188
104. Fang B, Chen H (2001) A new candidate material for molten carbonate fuel cell cathodes. *J Electroanal Chem* 501:128–131
105. Nguyen HVP, Kang MG, Ham HC, Choi SH, Han J, Nam SW, Hong SA, Yoon SP (2014) A new cathode for reduced-temperature molten carbonate fuel cells” *J. Electrochem Soc* 161:F1458–F1467
106. Li S, Sun J (2010) Electrochemical performances of NANOCOFC in MCFC environments. *Int J Hydrogen Energy* 35:2980–2985

107. Selman JR (2006) Molten-salt fuel cells-Technical and economic challenges. *J Power Sources* 160:852–857
108. Kaun TD, Schoeler A, Centeno CJ, Krumpelt M (1999) Improved MCFC performance with Li/Na/Ba/Ca carbonate electrolyte. *Proc Electrochem Soc* 99:219–227
109. Makkus RC, Sitters EF, Nammensma P, Huijsmans JPP (1997) MCFC electrolyte behavior; Li/K versus Li/Na carbonate. *Proc Electrochem Soc* 97:344–352
110. Ketelaar JAA (1987) Molten carbonate fuel cells. *From Fuel Cells Trends Res Appl [Proc. Workshop]* 161–72
111. Cigolotti V, McPhail S, Moreno A, Yoon SP, Han JH, Nam SW, Lim TH (2011) MCFC fed with biogas: Experimental investigation of sulphur poisoning using impedance spectroscopy. *Int J Hydrogen Energy* 36:10311–10318
112. Lee D, Kim J, Jo K (2011) A Study on In-Situ Sintering of Ni-10 wt % Cr Anode for MCFC. *J Electrochem Soc* 158:B500–B504
113. Devianto H, Yoon SP, Nam SW, Han J, Lim TH (2006) Study on ceria coating effect of H<sub>2</sub>S tolerance in the anode of molten carbonate fuel cell. *Stud Surf Sci Catal* 159:601–604
114. Hirschenhofer JH, Stauffer DB, Hengelman RR (1998) Fuel cell handbook 4th edn. Passons Co. for US Department of Energy
115. Melendez-Ceballos A, Albin V, Ringuede A, Fernandez-Valverde SM, Cassir M (2014) Electrochemical behavior of Mx-IOx (M = Ti, Ce and Co) ultra-thin protective layers for MCFC cathode. *Int J Hydrogen Energy* 39:12233–12241
116. Bozzini B, Maci S, Sgura I, Lo Presti R, Simonetti E (2011) Elisabetta Numerical modelling of MCFC cathode degradation in terms of morphological variations. *Int J Hydrogen Energy* 36:10403–10413
117. Matsuzawa K, Akinaga Y, Mitsushima S, Ota KI (2011) Solubilities of NiO and LaNiO<sub>3</sub> in Li/Na eutectic carbonate with rare-earth oxide. *J Power Sources* 196:5007–5011
118. Escudero MJ, Ringuede A, Cassir M, Gonzalez-Ayuso T, Daza L (2007) Porous nickel MCFC cathode coated by potentiostatically deposited cobalt oxide. *J Power Sources* 171:261–267
119. Matsuzawa K, Tazawa G, Matsuda Y, Ryoike H, Mitsushima S, Kamiya N, Ota KI (2006) Effect of rare earth addition to molten carbonate on the solubility of NiO. *Proc Electrochem Soc* 24:666–678
120. Sciaiovelli A, Verda V, Amelio C, Repetto C, Diaz G (2012) Performance improvement of a circular MCFC through optimal design of the fluid distribution system. *J Fuel Cell Sci Technol* 9:041011/1–041011/8
121. Rinaldi G, McLarty D, Brouwer J, Lanzini A, Santarelli M (2015) Study of CO<sub>2</sub> recovery in a carbonate fuel cell tri-generation plant. *J Power Sources* 284:16–26
122. Minutillo M, Perna A, Jannelli E (2014) SOFC and MCFC system level modeling for hybrid plants performance prediction. *Int J Hydrogen Energy* 39:21688–21699
123. Kim YJ, Chang IG, Lee TW, Chung MK (2010) Effects of relative gas flow direction in the anode and cathode on the performance characteristics of a Molten Carbonate Fuel Cell. *Fuel* 89:1019–1028
124. Law MC, Lee VC-C, Tay CL (2015) Dynamic behaviors of a molten carbonate fuel cell under a sudden shut-down scenario: the effects on temperature gradients. *Appl Therm Eng* 82:98–109
125. Zanchet D, Santos JBO, Damyanova S, Gallo JMR, Bueno JMC (2015) Toward Understanding Metal-Catalyzed Ethanol Reforming *ACS Catalysis* 5:3841–3863
126. Guerrero L, Castilla S, Cobo M (2014) Martha Advances in ethanol reforming for the production of hydrogen. *Quimica Nova* 37:850–856
127. Vatani A, Khazaeli A, Roshandel R, Panjeshahi MH (2013) Thermodynamic analysis of application of organic Rankine cycle for heat recovery from an integrated DIR-MCFC with pre-reformer. *Energy Convers Manag* 67:197–207
128. Vahc ZY, Jung CY, Yi SC (2014) Performance degradation of solid oxide fuel cells due to sulfur poisoning of the electrochemical reaction and internal reforming reaction. *Int J Hydrogen Energy* 39:17275–17283

129. Dimopoulos G G, Stefanatos IC, Kakalis NMP (2015) Exergy analysis and optimisation of a marine molten carbonate fuel cell system in simple and combined cycle configuration. *Energy Convers Manag* (2015). in press
130. Gharieh K, Jafari MA, Guo Q (2015) Investment in hydrogen tri-generation for wastewater treatment plants under uncertainties. *J Power Sources* 297:302–314
131. Zhang X, Liu H, Ni M, Chen J (2015) Performance evaluation and parametric optimum design of a syngas molten carbonate fuel cell and gas turbine hybrid system. *Renewable Energy* 80:407–414
132. Zhang J, Zhang X, Liu W, Liu H, Qiu J, Yeung KL (2014) A new alkali-resistant Ni/Al<sub>2</sub>O<sub>3</sub>-MSU-1 core-shell catalyst for methane steam reforming in a direct internal reforming molten carbonate fuel cell. *J Power Sources* 246:74–83
133. Moon HD, Lim TH, Lee HI (1999) Chemical poisoning of Ni/MgO catalyst by alkali carbonate vapor in the steam reforming reaction of DIR-MCFC. *Bull Korean Chem Soc* 20:1413–1417
134. Tanaka J, Sai ai A, Sakurada S, Nakajima T, Miyake Y, Saitoh T, Sasaki M, Yanaru H (1993) Design of 30 kW class DIR-MCFC system. *Proc Electrochem Soc* 93:37–47
135. Baker B, Burns D, Lee C, Maru H, Patel P (1981) Internal reforming for natural gas-fueled molten-carbonate fuel cells. Report 107. (90-6194-(13), GRI-80/0126; Order No. PB82-200676)
136. Kim H, Cho JH, Lee KS (2013) Detailed dynamic modeling of a molten carbonate fuel cell stack with indirect internal reformers. *Fuel Cells* 13:259–269
137. Pfafferoth M, Heidebrecht P, Sundmacher K, Wuertenberger U, Bednarz M (2008) Multiscale Simulation of the Indirect Internal Reforming Unit (IIR) in a Molten Carbonate Fuel Cell (MCFC). *Ind Eng Chem Res* 47:4332–4341
138. Freni S, Aquino M, Passalacqua E (1994) Molten carbonate fuel cell with indirect internal reforming. *J Power Sources* 52:41–47
139. Miyazaki M, Okada T, Ide H, Matsumoto S, Shinoki T, Ohtsuki J (1992) Development of an indirect internal reforming molten carbonate fuel cell stack. In: *Proceedings of the Intersociety Energy Conversion Engineering Conference*, 27th(3), vol 3, 287–3.292
140. Huijsmans JPP, Kraaij GJ, Makkus RC, Rietveld G, Sitters EF, Reijers HThJ (2000) An analysis of endurance issues for MCFC. *J Power Sources* 86:117–121
141. Williams MC, Maru HC (2006) Distributed generation—Molten carbonate fuel cells. *J Power Sources* 160:866–867
142. Coddet P, Liao HL, Coddet C (2014) A review on high power SOFC electrolyte layer manufacturing using thermal spray and physical vapour deposition technologies. *Adv Manufact* 2:212–221
143. Patakangas J, Ma Y, Jing Y, Lund P (2014) Review and analysis of characterization methods and ionic conductivities for low-temperature solid oxide fuel cells (LT-SOFC). *J Power Sources* 263:315–331
144. Zhu B (2009) Solid oxide fuel cell (SOFC) technical challenges and solutions from nano-aspects. *Int J Energy Res* 33:1126–1137
145. Ishihara S, Yamamoto T (2003) High temperature solid oxide fuel cells fundamentals, design and applications. In: Singhal SC, Kendal K (eds) Elsevier
146. Mukhopadhyay M, Mukhopadhyay J, Basu RN (2013) Functional anode materials for solid oxide fuel cell—a review. *Trans Indian Ceram Soc* 72:145–168
147. Tao SW, Cowin PI, Lan R (2012) Novel anode materials for solid oxide fuel cells. *Energy* 35:445–477
148. Grenier JC, Bassat JM, Mauvy F (2012) Novel cathodes for solid oxide fuel cells. *Energy* 35:402–444
149. Ding D, Li X, Lai SY, Gerdes K, Liu M (2014) Enhancing SOFC cathode performance by surface modification through infiltration. *Energy Environ Sci* 7:552–575
150. Backhaus-Ricoult M (2008) SOFC—a playground for solid state chemistry. *Solid State Sci* 10:670–688

151. Vielstich W (1970) In: *Fuel Cells, Modern Processes for the Electrochemical Production of Energy* Chichester, Wiley-Interscience, UK
152. Yamamoto O (2000) Solid oxide fuel cells: fundamental aspects and prospects. *Electrochim Acta* 45:2423–2435
153. Huijsmans JPP, van Berkel FPF, Christie GM (1998) Intermediate temperature SOFC—A promise for the 21st century. *J Power Sources* 71:107–110
154. Singh P, Minh NQ (2004) Solid oxide fuel cells: technology status. *Int J Appl Ceramic Technol* 1:5–15
155. Veyo SE, Vora SD, Lundberg WL, Litzinger KP (2003) Tubular SOFC hybrid power system status. ASME Turbo Expo: Power for Land, Sea & Air, Atlanta, GA, United States, 708–714, 16–19 June 2003
156. Hishinuma M, Kawashima T, Yasuda I, Matsuzuki Y, Ogasawara K (1995) Current status of planar SOFC development at Tokyo Gas. *Proc Electrochem Soc* 1:153–162
157. Singhal SC (2000) Advances in solid oxide fuel cell technology. *Solid State Ionics* 135:305–313
158. Winkler W, Lorenz H (2002) The design of stationary and mobile solid oxide fuel cell-gas turbine systems. *J Power Sources* 105:222–227
159. Horiuchi K (2013) Current status of national SOFC projects in Japan. *ECS Trans* 57:3–10
160. Jones FGE, Casting T (2005) Co-Firing and Electrical Characterisation of Novel Design Solid Oxide Fuel Cell SOFCROLL PhD thesis, University of St Andrews
161. Minh NQ (1993) Ceramic fuel-cells. *J. American Ceramic Soc* 76:563–588
162. Lee HM (2003) Electrochemical characteristics of  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  for solid oxide fuel cell. *Mater Chem Phys* 77:639–646
163. Tanner CW, Fung KZ, Virkar AV (1997) The effect of porous composite electrode structure on solid oxide fuel cell performance. 1. Theoretical analysis. *J Electrochem Soc* 144:21–30
164. Gorte RJ et al (2000) Anodes for direct oxidation of dry hydrocarbons in a solid-oxide fuel cell. *Adv Mater* 12:1465–1469
165. Ivers-Tiffée E, Weber A, Herbstritt D (2001) Materials and technologies for SOFC-components. *J Eur Ceram Soc* 21:1805–1811
166. Dees DW et al (1987) Conductivity of porous Ni/ZrO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub> cermets. *J Electrochem Soc* 134:2141–2146
167. Jiang SP, Callus PJ, Badwal SPS (2000) Fabrication and performance of Ni/3 mol% Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> cermet anodes for solid oxide fuel cells. *Solid State Ionics* 132:1–14
168. Buonomano A, Calise F, Dentice d'Accadia M, Palombo A, Vicidomini M (2015) Hybrid solid oxide fuel cells–gas turbine systems for combined heat and power: a review. *Appl Energy* 156:32–85
169. Doherty W, Reynolds A, Kennedy D (2015) Process simulation of biomass gasification integrated with a solid oxide fuel cell stack. *J Power Sources* 277:292–303
170. Zabihian FA (2009) A review on modeling of hybrid solid oxide fuel cell systems. *Int J Eng* 3:85–119
171. McPhail SJ, Aarva A, Devianto H, Bove R, Moreno A (2011) SOFC and MCFC: commonalities and opportunities for integrated research. *Int J Hydrogen Energy* 36:10337–45.9
172. Calise F, Dentice d'Accadia M, Vanoli L, von Spakovsky MR (2007) Full load synthesis/design optimization of a hybrid SOFC GT power plant. *Energy* 32:446–458
173. Zhang X, Chan SH, Li G, Ho HK, Li J, Feng Z (2010) A review of integration strategies for solid oxide fuel cells. *J Power Sources* 195:685–702
174. Calise F, Dentice d'Accadia M, Vanoli L, von Spakovsky MR (2006) Single-level optimization of a hybrid SOFC GT power plant. *J Power Sources* 159:1169–1185
175. Calise F, Ferruzzi G, Vanoli L (2009) Parametric exergy analysis of a tubular solid oxide fuel cell (SOFC) stack through finite-volume model. *Appl Energy* 86:2401–2410
176. Zhou XD, Singhal SC, *Fuel Cells—Solid Oxide Fuel Cells*, pp 1–16
177. Amarasinghe S, Ammala P, Aruliah S, Mizusaki J (2005) Solid Oxide Fuel Cells IX (SOFC-IX). In: Singhal SC (ed) *The Electrochemical Society, Inc*, 184–190

178. Singhal SC, Kendall K (2003) High temperature solid oxide fuel cells: fundamentals, design and applications. Elsevier, Oxford
179. Mukerjee S, Haltiner K, Kerr R et al (2007) Solid oxide fuel cell development: latest results. In: Eguchi K, Singhal SC, Yokokawa H, Mizusaki J (eds) Solid oxide fuel cells-X. The Electrochemical Society, New Jersey, pp 59–65
180. Brandon NP, Blake A, Corcoran D et al (2004) Development of metal supported solid oxide fuel cells for operation at 500–600 °C. *J Fuel Cell Sci Technol* 1:61–65
181. van Gerwen RJF (2003) High temperature solid oxide fuel cells, fundamentals, design and applications, systems and applications. In: Singhal SC, Kendall K (eds.) Elsevier, New York, 364–392
182. Atkinson A, Barnett S, Gorte RJ et al (2004) Advanced anodes for high-temperature fuel cells. *Nat Mater* 3:17–27
183. Suzuki M, Sogi T, Higaki K et al (2007) Development of SOFC residential cogeneration system at Osaka Gas and Kyocera. In: Eguchi K, Singhal SC, Yokokawa H, Mizusaki J (eds) Solid Oxide Fuel Cells-X, The Electrochemical Society, 27–30
184. Tanner CW, Fung KZ, Virkar AV (1997) The effect of porous composite electrode structure on solid oxide fuel cell performance: theoretical analysis. *J Electrochem Soc* 144:21–30
185. Vora SD (2007) Development of high power density seal-less SOFCs. In: Eguchi K, Singhal SC, Yokokawa H, Mizusaki J (eds) Solid oxide fuel cells-X. Electrochem Soc, New Jersey, pp 149–154
186. Stevenson JW, Singh P, Singhal SC (2005) The secrets of SOFC success. *Fuel Cell Rev* 2:15–21

Treatment of Biogas for Feeding High Temperature Fuel  
Cells

Removal of Harmful Compounds by Adsorption  
Processes

Turco, M.; Ausiello, A.; Micoli, L.

2016, XI, 166 p. 13 illus., 9 illus. in color., Hardcover

ISBN: 978-3-319-03214-6