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Fuel processing for low-temperature and high-temperature fuel cells
Challenges, and opportunities for sustainable development in the 21st century

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Abstract

This review paper first discusses the needs for fundamental changes in the energy system for major efficiency improvements in terms of global resource limitation and sustainable development. Major improvement in energy efficiency of electric power plants and transportation vehicles is needed to enable the world to meet the energy demands at lower rate of energy consumption with corresponding reduction in pollutant and CO_2 emissions. A brief overview will then be given on principle and advantages of different types of low-temperature and high-temperature fuel cells. Fuel cells are intrinsically much more energy-efficient, and could achieve as high as 70–80% system efficiency (including heat utilization) in electric power plants using solid oxide fuel cells (SOFC, versus the current efficiency of 30–37% via combustion), and 40–50% efficiency for transportation using proton-exchange membrane fuel cells (PEMFC) or solid oxide fuel cells (versus the current efficiency of 20–35% with internal combustion (IC) engines). The technical discussions will focus on fuel processing for fuel cell applications in the 21st century. The strategies and options of fuel processors depend on the type of fuel cells and applications. Among the low-temperature fuel cells, proton-exchange membrane fuel cells require H_2 as the fuel and thus nearly CO-free and sulfur-free gas feed must be produced from fuel processor. High-temperature fuel cells such as solid oxide fuel cells can use both CO and H_2 as fuel, and thus fuel processing can be achieved in less steps. Hydrocarbon fuels and alcohol fuels can both be used as fuels for reforming on-site or on-board. Alcohol fuels have the advantages of being ultra-clean and sulfur-free and can be reformed at lower temperatures, but hydrocarbon fuels have the advantages of existing infrastructure of production and distribution and higher energy density. Further research and development on fuel processing are necessary for improved energy efficiency and reduced size of fuel processor. More effective ways for on-site or on-board deep removal of sulfur before and after fuel reforming, and more energy-efficient and stable catalysts and processes for reforming hydrocarbon fuels are necessary for both high-temperature and low-temperature fuel cells. In addition, more active and robust (non-pyrophoric) catalysts for water–gas-shift (WGS) reactions, more selective and active catalysts for preferential CO oxidation at lower temperature, more CO-tolerant anode catalysts would contribute significantly to development and implementation of low-temperature fuel cells, particularly proton-exchange membrane fuel cells. In addition, more work is required in the area of electrode catalysis

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and high-temperature membrane development related to fuel processing including tolerance to certain components in reformate, especially CO and sulfur species.

Keywords: Fuel processing; Reforming; Sulfur removal; Water–gas-shift; H_2; Fuel cell; Catalyst; Catalysis; Energy efficiency; Sustainable development

1. Introduction

As the world moved into the first decade of the 21st century, a global view is due for energy consumption in the last century and the situations around energy supply and demand of energy and fuels in the future. The world of the 20th century is characterized by growth. Table 1 shows the changes in worldwide energy use in the 20th century, including consumption of different forms of energy in million tonnes of oil equivalent (MTOE), world population, and per capita energy consumption comparing the years 1900 and 1997, which are based on recent statistical data [1–3]. The rapid development in industrial and transportation sectors and improvements in living standards among residential sectors correspond to the dramatic growth in energy consumption from 911 MTOE in 1900 to 9647 MTOE in 1997. This is also due in part to the rapid increase in population from 1762 million in 1900 to 5847 million in 1997, as can be seen from Table 1.

Table 1
Worldwide energy use in million tonnes of oil equivalent (MTOE), world population and per capita energy consumption in the 20th century

Energy source	1900		1997	
	MTOE	%	MTOE	%
Petroleum	18	2	2940	30
Natural gas	9	1	2173	23
Coal	501	55	2122	22
Nuclear	0	0	579	6
Renewable	383	42	1833	19
Total	911	100	9647	100
Population (million)	1762		5847	
Per capita energy use (TOE)	0.517		1.649	
Global CO_2 emission (MMTC)[a]	534		6601	
Per capita CO_2 emission (MTC)	0.30		1.13	
Atmospheric CO_2 (ppmv)[b]	295		364	
Life expectancy (years)[c]	47		76	

[a] Global CO_2 emissions from fossil fuel burning, cement manufacture, and gas flaring; expressed in million metric tonnes of carbon (MMTC).

[b] Global atmospheric CO_2 concentrations expressed in parts per million by volume (ppmv).

[c] Life expectancy is based on the statistical record in the US [2,3].

Table 1 also shows the data on combined global CO_2 emissions from fossil fuel burning, cement manufacture, and gas flaring expressed in million metric tonnes of carbon (MMTC) in 1990 and 1997 [4]. It is clear from Table 1 that global CO_2 emissions increased over 10 times, from 534 MMTC in 1900 to 6601 MMTC in 1997, in proportion with the dramatic increase in worldwide consumption of fossil energy. The emissions of enormously large amounts of gases from combustion into the atmosphere has caused a rise in global concentrations of greenhouse gases, particularly CO_2. Table 1 also includes data on the global atmospheric concentrations of greenhouse gas CO_2 in 1900 and in 1997, where the 1900 data was determined by measuring ancient air occluded in ice core samples [5], and that for 1997 was from actual measurement of atmospheric CO_2 in Mauna Loa, Hawaii [6]. The increase in atmospheric concentrations of CO_2 has been clearly established and can be attributed largely to increased consumption of fossil fuels by combustion. To control greenhouse gas emissions in the world, several types of approaches will be necessary, including major improvement in energy efficiency, the use of carbon-less (or carbon-free) energy, and the sequestration of carbon such as CO_2 storage in geologic formations.

2. Sustainable development of energy

2.1. *Supply-side challenge of energy balance*

Fig. 1 shows the energy supply and demand (in quadrillion Btu) in the US in 1998 [7]. The existing

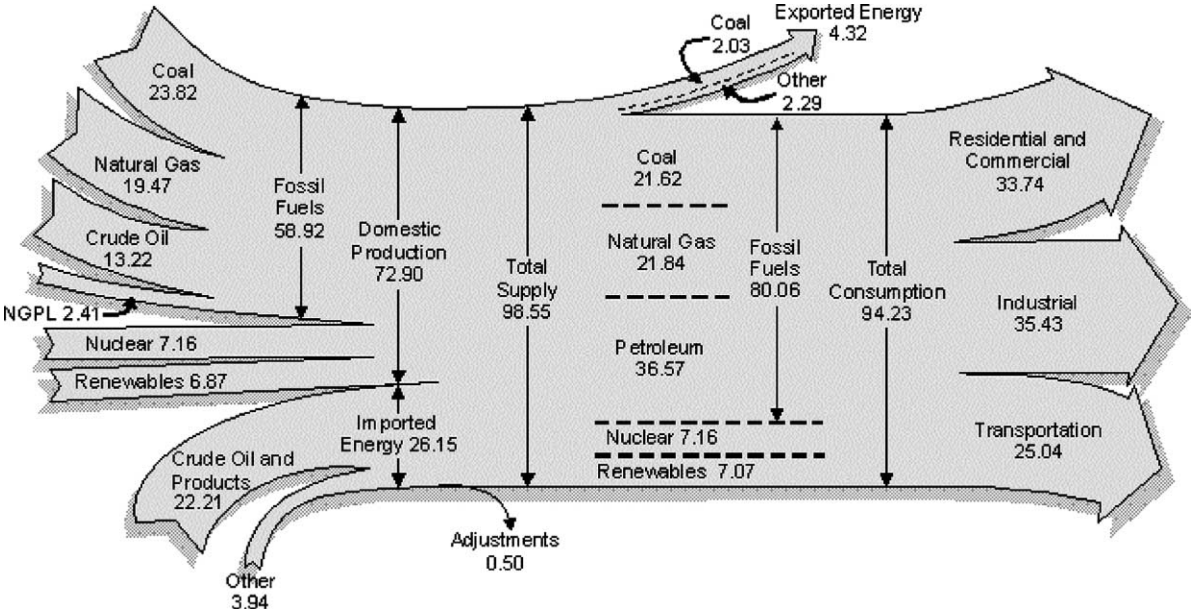


Fig. 1. Energy flow (quadrillion Btu) in the US in 1998 [7].

energy system in the US and in the world today is largely based on combustion of fossil fuels—petroleum, natural gas, and coal—in stationary and mobile devices. It is clear from Fig. 1 that petroleum, natural gas, and coal are the three largest sources of primary energy consumption in the US. Renewable energies are important but small parts (6.87%) of the US energy flow, although they have potential to grow.

Fig. 2 illustrates the energy input and the output of electricity (in quadrillion Btu) from power plants in the US in 1998 [7]. As is well known, electricity is the most convenient form of energy in industry and in daily life. The electric power plants are the largest consumers of coal. Great progress has been made in the electric power industry with respect to pollution control and generation technology with certain improvements in energy efficiency. What is not apparent in the energy supply–demand pictures is the following. The energy input into electric power plants represents 36.9% of the total primary energy supply in the US, but the majority of the energy input into the electric power plants, over 65%, is lost and wasted as conversion loss in the process, as can be seen from Fig. 2 for the electricity flow in the US including electric utilities and non-utility power producers. The same trend of conversion loss is also applicable for the fuels used in transportation, which represents 25.4% of the total primary energy consumption. This energy waste is largely due to the thermodynamic limitations of heat engine operations dictated by the maximum efficiency of the Carnot cycle.

How much more fossil energy resources are there? The known worldwide reserves of petroleum (1033.2 billion barrels in 1999) [8] would be consumed in about 39 years, based on the current annual consumption of petroleum (26.88 billion barrels in 1998). On the same basis, the known natural gas reserves in the world (5141.6 trillion cubic feet in 1999) would last for 63 years at the current annual consumption level (82.19 trillion cubic feet in 1998) [8]. While new exploration and production technologies will expand the oil and gas resources, two experts in oil industry, Campbell and Laherrere [9], have indicated that global production of conventional oil will begin to decline sooner than most people think and they have compellingly alluded to the end of cheap oil early in this century. Worldwide coal production and consumption in 1998 were 5042.7 and 5013.5 million short tonnes, respectively [7]. The known world recoverable coal reserves in 1999 are 1087.19 billion short tonnes [8],

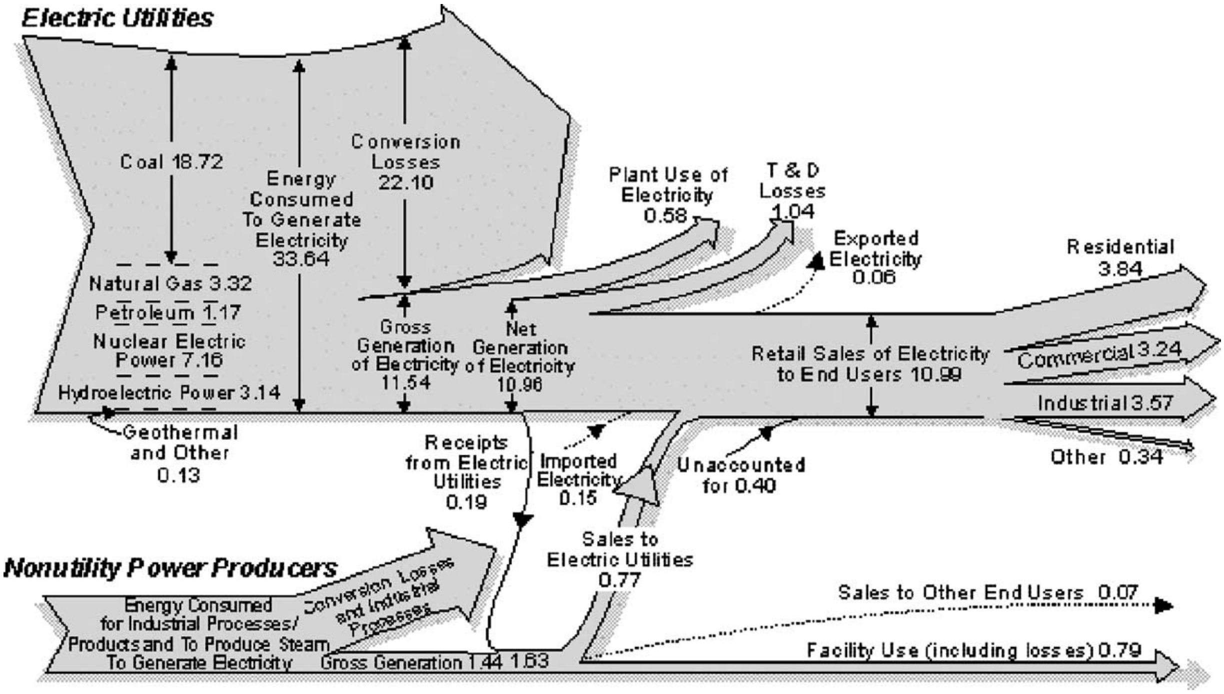


Fig. 2. Electricity flow (quadrillion Btu) in the US in 1998 [7].

which is over 215 times the world consumption level in 1998. Thus, coal has great potential as a future source of primary energy, although environmental pressures may militate against expanded markets for coal as an energy source. However, even coal resources are limited. Prof. George Olah, the winner of Nobel Prize in chemistry in 1994, pointed out in 1991 that “Oil and gas resources under the most optimistic scenarios won’t last much longer than through the next century. Coal reserves are more abundant, but are also limited. . . . I suggest we should worry much more about our limited and diminishing fossil resources” [10]. In this context, it is important to recognize the limitations of non-renewable hydrocarbon resources in the world.

2.2. Sustainable development of energy

Can the world sustain itself by continuously using the existing energy system based on combustion of fossil resources in the 21st century? Petroleum, natural gas and coal are important fossil hydrocarbon resources that are non-renewable. Sustainable development may have different meanings to different people, but a respected definition from the report “Our Common Future” [11], is as follows: “Sustainable development is development that meets the needs of the present without compromising the ability of future generations to meet their own needs” [12]. Sustainable development of the energy system focuses on improving the quality of life for all of the Earth’s citizens by developing highly efficient energy devices and utilization systems that are cleaner and more environmentally friendly. This requires meeting the needs of the current population with a balanced clean energy mix while minimizing unintentional consequences caused by increases in atmospheric concentrations of greenhouse gases due to a rapid rise in global consumption of carbon-based energy. Ultimately, human society should identify and establish innovative ways to satisfy the needs for energy and chemical feedstocks without increasing the consumption of natural resources beyond the capacity of the globe to supply them indefinitely. Sustainable development requires an understanding that inaction has consequences and that we must find innovative ways to change institutional structures and influence individual behavior [12]. Sustainable development is not a new idea since many cultures over the course of human history have recognized the need for harmony between the environment, society and economy. What is new is an articulation of these ideas in the context of a global industrial and information society [12].

2.3. Vision for efficient utilization of hydrocarbon resources

Fig. 3 presents a vision on directions and important issues in research on effective and comprehensive utilization of hydrocarbon resources that are non-renewable. It has been developed by the author for directing future research in our laboratory on clean fuels, chemicals, and catalysis. There are three fundamental elements in this vision: fuel uses, non-fuel uses, and environmental issues of energy and resources. This is a personal view reflecting my judgments and prejudices for future directions. It is helpful to us for seeing future directions and for promoting responsible and sustainable development in research on energy and fuels for the 21st century. Fundamentally, all fossil hydrocarbon resources are non-renewable and precious gifts from nature, and thus it is important to explore more effective and efficient ways of comprehensive utilization of all the fossil energy resources for sustainable development. The new processes and new energy systems should be much more energy-efficient, and also more environmentally benign.

Considering sustainable development seriously today is about being proactive and about taking responsible actions. The principle applies to all the nations in the world, but countries at different stages of economic development can take different but sustainable strategies. As indicated in “The Human Development Report” by the United Nations, “Developing countries face a fundamental choice [13]. They can mimic the industrial countries and go through a development phase that is dirty and wasteful and creates an enormous legacy of pollution. Or they can leapfrog over some of the steps followed by industrial countries and incorporate efficient technologies [13]. It is therefore very important for “the present in the world” to make major efforts towards more efficient, responsible, comprehensive and environmentally benign use of the valuable fossil hydrocarbon resources, towards sustainable development.

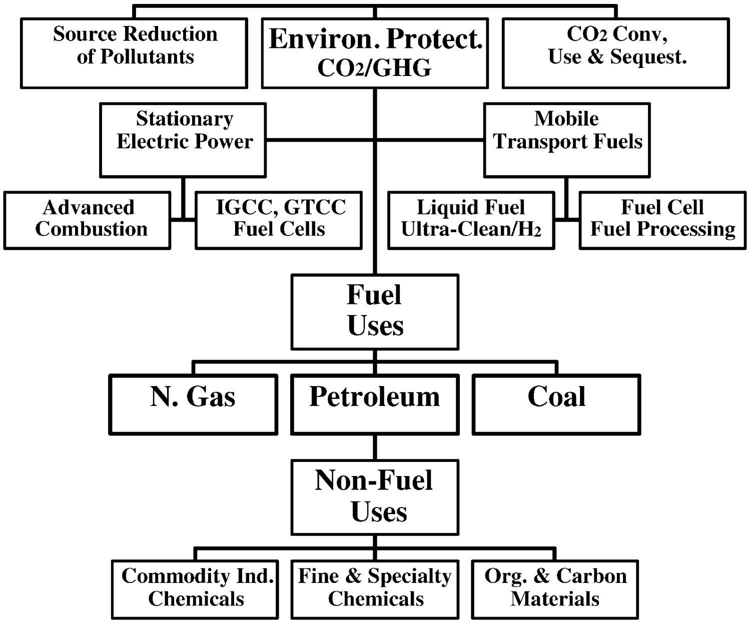


Fig. 3. A personal vision for research towards comprehensive and effective utilization of hydrocarbon resources in the 21st century.

Does the world really need new conversion devices in addition to internal combustion (IC) engines and heat engines for energy system? The fundamental answer to this question is yes, because the efficiencies of existing energy systems are not satisfactory since over 60% of the energy input is simply wasted in most power plants and in most vehicles for transportation. From an environmental standpoint, many of the existing processes in energy and chemical industries that rely on post-use clean-up to meet environmental regulations should be replaced by more benign processes that do not generate pollution at the source. For example, the current power plants use post-combustion SO_x and NO_x reduction system, but the future system should preferably eliminate or minimize SO_x and NO_x formation at the source. The current diesel fuels contain polycyclic sulfur and aromatic compounds that form SO_x and soot upon combustion in the diesel engines that would require exhaust gas treatment. In the future, ultra-clean fuels could be made at the source, the refinery, which will eliminate or minimize such pollutants before the fuel use in either current engines or future vehicles that may be based on fuel cells. Fuel cells are promising candidates as truly energy-efficient conversion devices [14].

3. Principle and advantages of fuel cells

3.1. Concept of fuel cell

The principle of fuel cell was first discovered in 1839 by Sir William R. Grove, a British jurist and physicist, who used hydrogen and oxygen as fuels catalyzed on platinum electrodes [15,16]. A fuel cell is defined as an electrochemical device in which the chemical energy stored in a fuel is converted directly into electricity. A fuel cell consists of an electrolyte material which is sandwiched in between two thin electrodes (porous anode and cathode). Specifically, a fuel cell consists of an anode—to which a fuel, commonly hydrogen, is supplied—and a cathode—to which an oxidant, commonly oxygen, is supplied. The oxygen needed by a fuel cell is generally supplied by feeding air. The two electrodes of a fuel cell are separated by an ion-conducting electrolyte. All fuel cells have the same basic operating principle. An input fuel is catalytically reacted (electrons removed from the fuel elements) in the fuel cell to create an electric current. The input fuel passes over the anode (negatively charged electrode) where it catalytically splits into electrons and ions, and oxygen passes over the cathode (positively charged electrode). The electrons go through an external circuit to serve an electric load while the ions move through the electrolyte toward the oppositely charged electrode. At the electrode, ions combine to create by-products, primarily water and CO_2. Depending on the input fuel and electrolyte, different chemical reactions will occur.

The main product of fuel cell operation is the DC electricity produced from the flow of electrons from the anode to the cathode. The amount of current available to the external circuit depends on the chemical activity and amount of the substances supplied as fuels and the loss of power inside the fuel cell stack. The current-producing process continues for as long as there is a supply of reactants because the electrodes and electrolyte of a fuel cell are designed to remain unchanged by the chemical reactions. Most individual fuel cells are small in size and produce between 0.5 and 0.9 V of DC electricity. Combination of several or many individual cells in a "stack" configuration is necessary for producing the higher voltages more commonly found in low and medium voltage distribution systems. The stack is the main component of the power section in a fuel cell power plant. The by-products of fuel cell operation are heat, water in the form of steam or liquid water, and CO_2 in the case of hydrocarbon fuel.

3.2. Efficiency of fuel cell

A simplified way to illustrate the efficiency of energy conversion devices is to examine the theoretical maximum efficiency [14]. The efficiency limit for heat engines such as steam and gas turbines is defined by Carnot cycle as maximum efficiency $= (T_1 - T_2)/T_1$, where T_1 is the maximum temperature of fluid in a heat engine, and T_2 is the temperature at which heated fluid is released. All the temperatures are in Kelvin ($K = 273 +$ degree Celsius), and therefore the lower temperature T_2 value is never small (usually >290 K). For a steam turbine operating at 400 °C, with the water exhausted through a condenser at 50 °C, the Carnot efficiency limit is $(673-323)/673 = 0.52 = 52\%$. (The steam is usually generated by boiler based on fossil fuel combustion, and so the heat transfer efficiency is also an issue in overall conversion.) For fuel cells, the situation is very different. Fuel cell operation is a chemical process, such as hydrogen oxidation to produce water, and thus involves the changes in enthalpy or heat (ΔH) and changes in Gibbs free energy (ΔG). It is the change in Gibbs free energy of formation that is converted to electrical energy [14]. The Gibbs free energy is related to the fuel cell voltage via $\Delta G = -nF\Delta U_0$, where n is the number of electrons involved in the reaction, F the Faraday constant, and ΔU_0 is the voltage of the cell for thermodynamic equilibrium in the absence of a current flow which can be derived by $\Delta U_0 = (-\Delta G)/(nF)$ [17]. For the case of H_2–O_2 fuel cell, the equilibrium cell voltage is 1.23 V corresponding to the ΔG of −237 kJ/mol for the overall reaction ($H_2+(1/2)\,O_2 = H_2O$) at standard conditions (25 °C).

The maximum efficiency for fuel cell can be directly calculated based on ΔG and ΔH as maximum fuel cell efficiency $= \Delta G/(-\Delta H)$. The ΔH value for the reaction is different depending on whether the product water is in vapor or in liquid state. If the water is in liquid state, then $(-\Delta H)$ is higher due to release of heat of condensation. The higher value is called higher heating value (HHV), and the lower value is called lower heating value (LHV). If this information is not given, then it is likely that the LHV has been used because this will give a higher efficiency value [14].

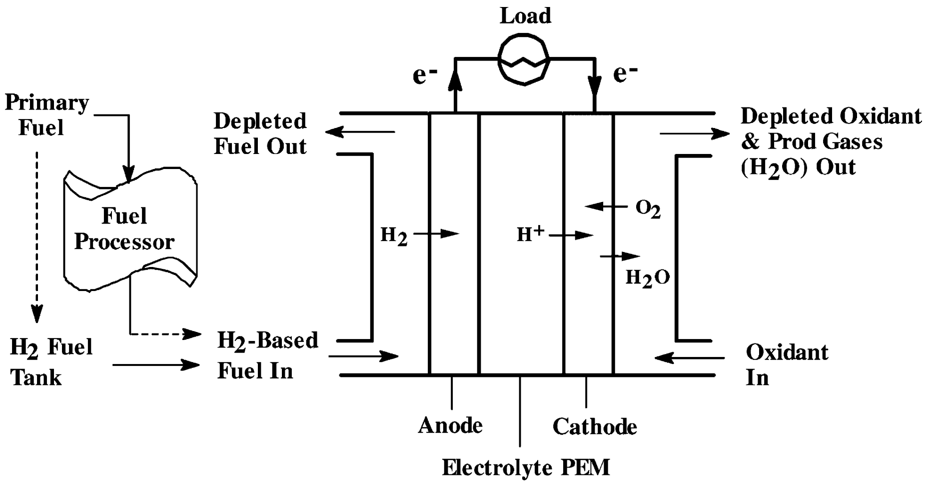
3.3. Types of fuel cells

On the basis of the electrolyte employed, there are five types of fuel cells. They differ in the composition of the electrolyte and are in different stages of development. They are alkaline fuel cells (AFC), phosphoric acid fuel cells (PAFC), proton-exchange membrane fuel cells (PEMFC), molten carbonate fuel cells (MCFC), and solid oxide fuel cells (SOFC). In all types there are separate reactions at the anode and the cathode, and charged ions move through the electrolyte, while electrons move round an external circuit. Another common feature is that the electrodes must be porous, because the gasses must be in contact with the electrode and the electrolyte at the same time.

Table 2 lists the main features of the four main types of fuel cells summarized based on various recent publications [14,18–21]. Each of them has advantages and disadvantages relative to each other. Different types of fuel cells are briefly discussed below, which will pave the ground for further discussions on fuel processing for fuel cell applications. Detailed description on these fuel cells can be found in comprehensive references [14,20].

Table 2
Types of fuel cells and their features

Features	Fuel cell type			
Name	Polymer electrolyte	Phosphoric acid	Molten carbonate	Solid oxide
Electrolyte	Ion exchange membrane	Phosphoric acid	Alkali carbonates mixture	Yttria-stabilized zirconia
Operating temperature (°C)	70–90	180–220	650–700	800–1000
Charge carrier	H^+	H^+	CO_3^{2-}	O^{2-}
Electrolyte state	Solid	Immobilized liquid	Immobilized liquid	Solid
Cell hardware	Carbon- or metal-based	Graphite-based	Stainless steel	Ceramic
Catalyst, anode	Platinum (Pt)	Platinum (Pt)	Nickel (Ni)	Nickel (Ni)
Fuels for cell	H_2	H_2	Reformate or CO/H_2	Reformate or CO/H_2 or CH_4
Reforming	External or direct MeOH	External	External or internal	External or internal, or direct CH_4
Feed for fuel processor	MeOH, natural gas, LPG, gasoline, diesel, jet fuel	Natural gas, MeOH, gasoline, diesel, jet fuel	Gas from coal or biomass, natural gas, gasoline, diesel, jet fuel	Gas from coal or biomass, natural gas, gasoline, diesel, jet fuel
Oxidant for cell	O_2/air	O_2/air	CO_2/O_2/air	O_2/air
Co-generation heat	None	Low quality	High	High
Cell efficiency (% LHV)	40–50	40–50	50–60	50–60



Anode (Fuel) Reaction: $H_2 = 2\,H^+ + 2\,e^-$

Cathode (oxidant) Reaction: $1/2\,O_2 + 2\,H^+ + 2\,e^- = H_2O$

Total Reaction: $H_2 + 1/2\,O_2 = H_2O$

Scheme 1. Concept of proton-exchange membrane fuel cell (PEMFC) system using on-board or on-site fuel processor, or on-board H_2 fuel tank.

3.3.1. *Proton-exchange membrane fuel cell*

The PEMFC uses a solid polymer membrane as its electrolyte (Scheme 1). This membrane is an electronic insulator, but an excellent conductor of protons (hydrogen cations). The ion-exchange membrane used to date is fluorinated sulfonic acid polymer such as Nafion resin manufactured by Du Pont, which consist of a fluorocarbon polymer backbone, similar to Teflon, to which are attached sulfonic acid groups. The acid molecules are fixed to the polymer and cannot “leak” out, but the protons on these acid groups are free to migrate through the membrane. The solid electrolyte exhibits excellent resistance to gas cross-over [20]. With the solid polymer electrolyte, electrolyte loss is not an issue with regard to stack life. Typically the anode and cathode catalysts consist of one or more precious metals, particularly platinum (Pt) supported on carbon. Because of the limitation on the temperature imposed by the polymer and water balance, the operating temperature of PEMFC is less than 120 °C, usually between 70 and 90 °C.

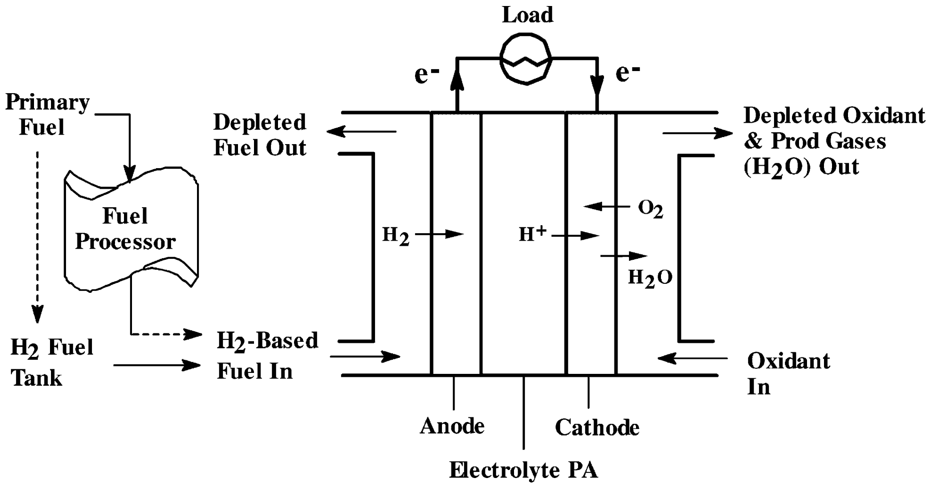
PEMFC system, also called solid polymer fuel cell (SPFC), was first developed by General Electric in the US in the 1960s for use by NASA on their first manned space vehicle Germini spacecraft [14]. However, the water management problem in the electrolyte was judged to be too difficult to manage reliably and for Apollo vehicles NASA selected the “rival” alkali fuel cell; General Electric did not pursue commercial development of PEMFC [14]. Today PEMFC is widely considered to be a most promising fuel cell system that has widespread applications. The significant advances in PEMFC in the 1980s and early 1990s were due largely to major development efforts by Ballard Power Systems of Vancouver, Canada, and Los Alamos National Laboratory in the US [14]. The developments on solid polymer fuel cells at Ballard have been summarized by Prater [22]. PEMFC performance has improved over the last several years. Current densities of 850 A/ft^2 are achieved at 0.7 V per cell with hydrogen and oxygen at 65 psi, and over 500 A/ft^2 is obtained with air at the same pressure [18]. The PEMFC technology is primarily suited for residential/commercial (business) and transportation applications [21]. PEMFC offers an order of magnitude higher power density than any other fuel cell system, with the exception of the advanced aerospace AFC, which has comparable performance [18]. The use of a solid polymer electrolyte eliminates the corrosion and safety concerns associated with liquid electrolyte fuel cells. Its low operating temperature provides instant start-up and requires no thermal shielding to protect personnel. Recent advances in performance and design offer the possibility of lower cost than any other fuel cell system [18].

In addition to pure hydrogen, the PEMFC can also operate on reformed hydrocarbon fuels without removal of the by-product CO_2. However, the anode catalyst is sensitive to CO, partly because PEMFC operates at low temperatures. The traces of CO produced during the reforming process must be converted to CO_2 by a catalytic process such as selective oxidation process before the fuel gas enters the fuel cell. Higher loadings of Pt catalysts than those used in PAFCs are required in both the anode and the cathode of PEMFC [20]. CO must be reduced to <10 ppm, and the CO removal is typically a catalytic process which can be integrated into a fuel processing system. Water management is critical for PEMFC; the fuel cell must operate under conditions where the by-product water does not evaporate faster than it is produced because the membrane must be hydrated [20].

3.3.2. Phosphoric acid fuel cell

The PAFC uses liquid, concentrated phosphoric acid as the electrolyte (Scheme 2). The phosphoric acid is usually contained in a Teflon bonded silicon carbide matrix. The small pore structure of this matrix preferentially keeps the acid in place through capillary action. Some acid may be entrained in the fuel or oxidant streams and addition of acid may be required after many hours of operation. Platinum supported on porous carbon is used on both the anode (for the fuel) and cathode (for the oxidant) sides of the electrolyte. PAFC operates at 180–220 °C, typically around 200 °C. The relative stability of concentrated phosphoric acid is high compared to other common acids, which enables PAFC operation at the high end of the acid temperature range of up to 220 °C [20]. In addition, the use of concentrated acid of nearly 100% minimizes the water vapor pressure and therefore water management in PAFC is not difficult, unlike PEMFC.

PAFC power plant designs can achieve 40–45% fuel-to-electricity conversion efficiencies on a lower heating value basis (LHV) [23]. PAFC has a power density of 160–175 W/ft^2 of active cell area [18]. Turnkey 200 kW plants are now available and have been installed at more than 70 sites in the United States, Europe, and Japan [21]. Operating at about 200 °C (400 °F), the PAFC plant also produces heat for domestic hot water and space heating. PAFC is the most mature fuel cell technology in terms of system development and is already in the first stages of commercialization. It has been under development for more than 20 years and has received a total worldwide



Scheme 2. Concept of phosphoric acid fuel cell (PAFC) system using on-board or on-site fuel processor.

investment in the development and demonstration of the technology in excess of \$ 500 million [18]. The PAFC was selected for substantial development a number of years ago because of the belief that, among the low-temperature fuel cells, it was the only technology which showed relative tolerance for reformed hydrocarbon fuels and thus could have widespread applicability in the near term [18].

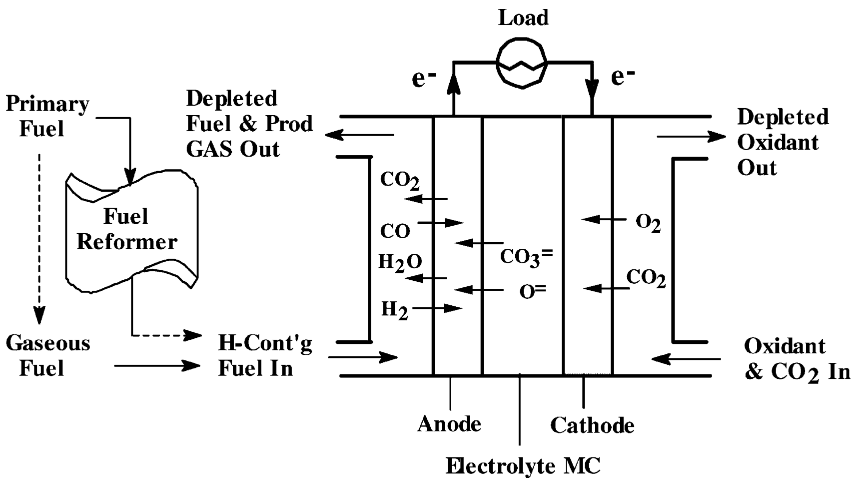
3.3.3. *Alkaline fuel cell*

AFC uses aqueous solution of potassium hydroxide (KOH) as its electrolyte. The electrolyte is retained in a solid matrix (usually asbestos), and a wide range of electrocatalysts can be used, including nickel, metal oxides, spinels, and noble metals electrode [20]. The operating temperatures of AFC can be higher than PAFC by using concentrated KOH (85%) for high-temperature AFC at up to 250 °C, or lower by using less concentrated KOH (35–50%) for low-temperature AFC at $<120\,^{\circ}C$. The fuel supply for AFC is limited to hydrogen; CO is a poison; and CO_2 reacts with KOH to form K_2CO_3, thus changing the electrolyte [20].

AFC concept has been described since 1902 in a US patent but they were not demonstrated till the 1940s and 1950s by Francis T. Bacon at Cambridge, England [14]. Since 1960s AFC has been used in space applications that took man to the moon with the Apollo missions [14]. However, the requirement of pure H_2 and the sensitivity to CO_2 appear to be among the major factors limiting the widespread application of AFC. The alkaline fuel cell is being phased out in the US where its only use has been in space vehicles [20]. However, it should be noted that AFC has its advantages of being simple in design and less expensive (electrolyte materials), and may have some applications where its disadvantages (require pure H_2, sensitive to CO_2) are not an issue such as with regenerative fuel cells involving water [14].

3.3.4. *Molten carbonate fuel cell*

The MCFC uses a molten carbonate salt mixture as its electrolyte (Scheme 3). The composition of the electrolyte varies, but usually consists of lithium carbonate and potassium carbonate (Li_2CO_3–K_2CO_3). At the operating temperature of about 650 °C (1200 °F), the salt mixture is liquid and a good ionic conductor. The electrolyte is suspended in a porous, insulating and chemically inert ceramic ($LiA1O_2$) matrix [18]. At the high operating temperatures in MCFCs, noble metals are not required for electrodes; nickel (Ni) or its alloy with chromium (Cr) or aluminum (Al) can be used as anode, and nickel oxide (NiO) as cathode [20]. The cell performance is sensitive to operating temperature. A change in cell temperature from 1200 °F (650 °C) to 1110 °F (600 °C) results in a drop in cell voltage of almost 15% [18]. The reduction in cell voltage is due to increased ionic



Scheme 3. Concept of molten carbonate fuel cell (MCFC) using on-site external fuel reformer. The external reformer can be integrated to the fuel cell chamber directly or indirectly because of the sufficiently high operating temperatures of MCFC.

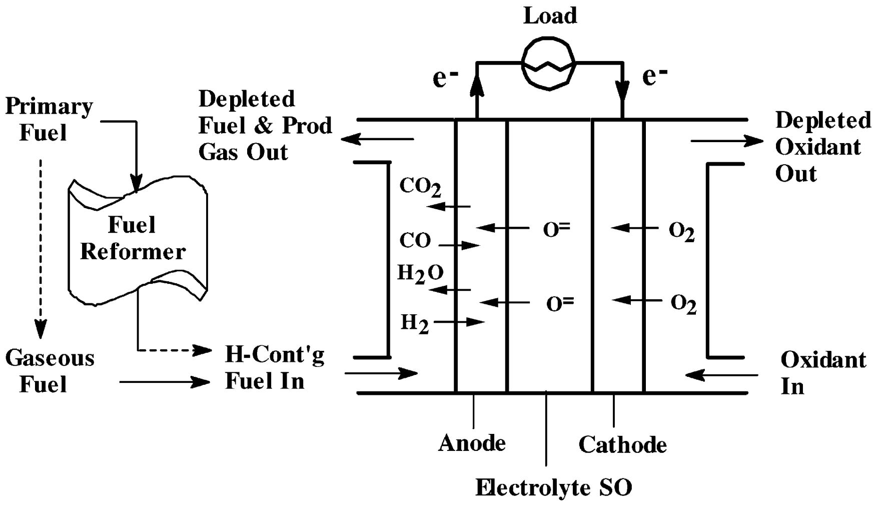
and electrical resistance and a reduction in electrode kinetics.

MCFCs evolved from work in the 1960s aimed at producing a fuel cell which would operate directly on coal [18]. While direct operation on coal seems less likely today, operation on coal-derived fuel gases or natural gas is viable. MCFCs are now being tested in full-scale demonstration plants and thus offer higher fuel-to-electricity efficiencies, approaching 50–60% (LHV) fuel-to-electricity efficiencies [23]. Because MCFCs operate at higher temperatures, around 650 °C (1200 °F), they are candidates for combined-cycle applications, in which the exhaust heat is used to generate additional electricity. When the waste heat is used, total thermal efficiencies can approach 85% [21]. The disadvantages of MCFC are that the electrolyte is corrosive and mobile, and a source of CO_2 is required at the cathode to form the carbonate ion [20].

3.3.5. *Solid oxide fuel cell*

SOFC uses a ceramic, solid-phase electrolyte (Scheme 4) which reduces corrosion considerations and eliminates the electrolyte management problems associated with the liquid electrolyte fuel cells. To achieve adequate ionic conductivity in such a ceramic, however, the system must operate at high temperatures in the range of 650–1000 °C, typically around 800–1000 °C (1830 °F) in the current technology. The preferred electrolyte material, dense yttria (Y_2O_3)-stabilized zirconia (ZrO_2), is an excellent conductor of negatively charged oxygen (oxide) ions at high temperatures. The SOFC is a solid state device and shares certain properties and fabrication techniques with semiconductor devices [18]. The anode of SOFC is typically a porous nickel–zirconia (Ni–ZrO_2) cermet (cermet is the ceramic–metal composite) or cobalt–zirconia (Co–ZrO_2) cermet, while the cathode is typically magnesium (Mg)-doped lanthanum manganate or strontium (Sr)-doped lanthanum manganate $LaMnO_3$ [18,20].

At the operating temperature of 800–1000 °C, internal reforming of most hydrocarbon fuels should be possible, and the waste heat from such a device would be easily utilized by conventional thermal



Anode (Fuel) Reaction: $H_2 + O^{=} \rightarrow H_2O + 2\,e^-$

$CO + O^{=} \rightarrow CO_2 + 2\,e^-$

Cathode (Oxidant) Reaction: $O_2 + 2\,e^- \rightarrow 2\,O^{=}$

Total Reaction: $H_2 + CO + O_2 \rightarrow H_2O + CO_2$

Scheme 4. Concept of solid oxide fuel cell (SOFC) system using on-site or on-board external reformer of primary fuel (natural gas, gasoline, diesel, jet fuel, alcohol fuels, bio-fuels, etc.). The external reformer can be integrated to the fuel cell chamber directly or indirectly because of the higher operating temperatures of SOFC.

electricity generating plants to yield excellent fuel efficiency. On the other hand, the high operating temperature of SOFC has its own drawbacks due to the demand and thermal stressing on the materials including the sealants and the longer start-up time [20]. Because the electrolyte is solid, the cell can be cast into various shapes such as tubular, planar, or monolithic [20]. SOFCs are currently being demonstrated in a 160 kW plant [21]. They are considered to be state-of-the-art fuel cell technology for electric power plants and offer the stability and reliability of all-solid-state ceramic construction. Operation up to 1000 °C (1830 °F) allows more flexibility in the choice of fuels and can produce better performance in combined-cycle applications [21]. Adjusting air and fuel flows allows the SOFC to easily follow changing load requirements. Like MCFCs, SOFCs can approach 50–60% (LHV) electrical efficiency, and 85% (LHV) total thermal efficiency [21].

3.4. *Advantages of fuel cells compared to conventional devices*

In general, all the fuel cells operate without combusting fuel and with few moving parts, and thus they are very attractive from both energy and environmental standpoints. A fuel cell can be two to three times more efficient than an IC engine in converting fuel to electricity [24]. A fuel cell resembles an electric battery in that both produce a direct current by using an electrochemical process. A battery contains only a limited amount of fuel material and oxidant, which are depleted with use. Unlike a battery, a fuel cell does not run down or require recharging; it operates as long as the fuel and an oxidizer are supplied continuously from outside the cell.

The general advantages of fuel cells are reflected by the following desirable characteristics: (1) high energy conversion efficiency; (2) extremely low emissions of pollutants; (3) extremely low noise or acoustical pollution; (4) effective reduction of greenhouse gas (CO_2) formation at the source compared to low-efficiency devices; and (5) process simplicity for conversion of chemical energy to electrical energy. Depending on the specific types of fuel cells, other advantages may include fuel flexibility and existing infrastructure of hydrocarbon fuel supplies; co-generation capability; modular design for mass production; relatively rapid load response.

Therefore, fuel cells have great potential to penetrate into markets for both stationary power plants (for industrial, commercial, and residential home applications) and mobile power plants for transportation by cars, buses, trucks, trains and ships, as well as man-portable micro-generators. As indicated by US DOE, fuel cells have emerged in the last decade as one of the most promising new technologies for meeting the US energy needs well into the 21st century for power generation [21,25], and for transportation [26,27]. Unlike power plants that use combustion technologies, fuel cell plants that generate electricity and usable heat can be built in a wide range of sizes—from 200 kW units suitable for powering commercial buildings, to 100 MW plants that can add base-load capacity to utility power plants [21].

The disadvantages or challenges to be overcome include the following factors. The costs of fuel cells are still considerably higher than conventional power plants per kW. The fuel hydrogen is not readily available and thus on-site or on-board H_2 production via reforming is necessary. There are no readily available and affordable ways for on-board or on-site desulfurization of hydrocarbon fuels and this presents a challenge for using hydrocarbon fuels [28,29]. The efficiency of fuel processing affects the over system efficiency.

4. Fuel processing for fuel cell applications

4.1. *Fuel options for fuel cells*

Fig. 4 illustrates the general concepts of processing gaseous, liquid, and solid fuels for fuel cell applications. For a conventional combustion system, a wide range of gaseous, liquid and solid fuels may be used, while hydrogen, reformate (hydrogen-rich gas from fuel reforming), and methanol are the primary fuels available for current fuel cells. The sulfur compounds in hydrocarbon fuels poison the catalysts in fuel processor and fuel cells and must be removed. Syngas can be generated from reforming. Reformate (syngas and other components such as steam and carbon dioxide) can be used as the fuel for high-temperature fuel cells such as SOFC and MCFC, for which the

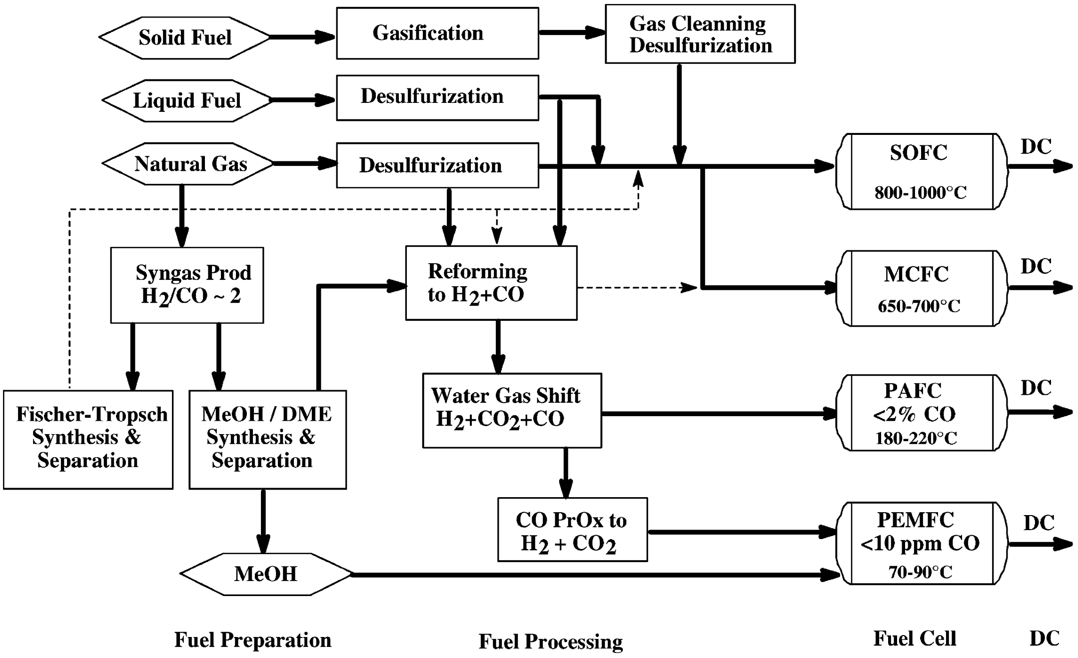


Fig. 4. The concepts and steps for fuel processing of gaseous, liquid and solid fuels for high-temperature and low-temperature fuel cell applications.

solid or liquid or gaseous fuels need to be reformulated. Hydrogen is the real fuel for low-temperature fuel cells such as PEMFC and PAFC, which can be obtained by fuel reformulation on-site for stationary applications or on-board for automotive applications. When natural gas or other hydrocarbon fuel is used in a PAFC system, the reformate must be processed by water–gas-shift (WGS) reaction. A PAFC can tolerate about 1–2% CO [20]. When used in a PEMFC, the product gas from water–gas-shift must be further processed to reduce CO to <10 ppm. Synthetic ultra-clean fuels can be made by Fischer–Tropsch synthesis [30] or methanol synthesis using the synthesis gas produced from natural gas or from coal gasification, as shown in Fig. 4, but the synthetic cleanness is obtained at the expense of extra cost for the extra conversion and processing steps.

Hohlein et al. [31] made a critical assessment of power trains for automobiles with fuel cell systems and different fuels including alcohols, ether and hydrocarbon fuels, and they indicated that hydrogen as PEFC fuel has to be produced on-board. H_2 can be obtained by catalytic steam reforming of methanol [32] and ethanol [33,34]. Methanol can also be used for direct electrochemical conversion to H_2 using direct methanol fuel cell (DMFC). Synthetic methanol has the advantage of being ultra-clean and easy to reform at lower temperatures. On the other hand, lower energy density and lack of infrastructure for methanol distribution and environmental concerns are some drawbacks for methanol. The advantages of existing infrastructures of worldwide production and distribution of natural gas, gasoline, diesel and jet fuels have led to active research on hydrocarbon-based fuel processors. Therefore, hydrogen production by processing conventional hydrocarbon fuels is considered by many researchers to be a promising approach [35–37].

It is increasingly recognized that the fuel processing subsystem can have a major impact on overall fuel cell system costs, particularly as ongoing research and development efforts result in reduction of the basic cost structure of stacks which currently dominate system costs [38]. The general processing schemes for syngas and H_2 production through steam reforming of hydrocarbons have been discussed by Gunardson [39], Rostrup-Nielsen [40] and Armor [41] for stationary

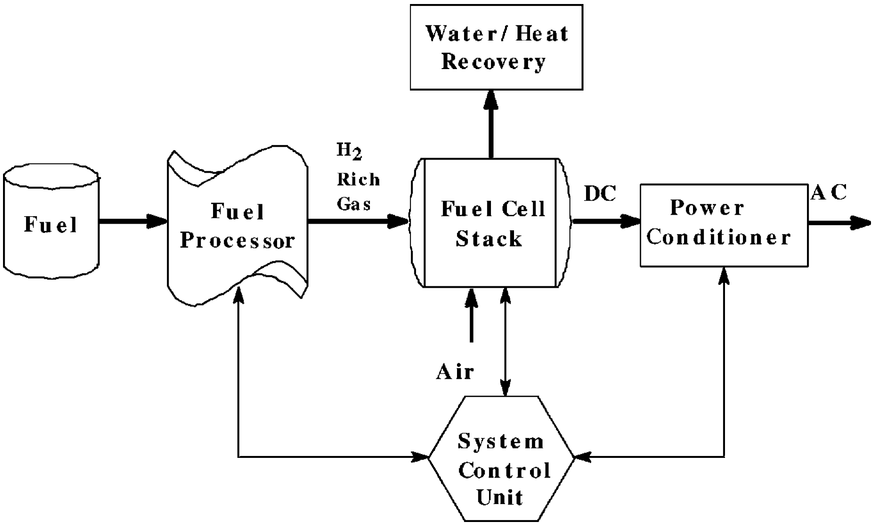


Fig. 5. The components of fuel cell systems for electric power plants.

H_2 plants in the gas industry, and by Clarke et al. [42], Dicks [43], and Privette [44] for fuel cell applications.

4.2. Fuel cells for electric power plants

Fig. 5 shows the components of fuel cell systems for electric power plants. Fuel cell systems can be grouped into three sections: fuel processor, generator (fuel cell stack), and power conditioner (DC/AC inverter). In the fuel processor, a fuel such as natural gas or gasoline is processed in several steps to produce hydrogen. The hydrogen-rich fuel and oxygen (air) are then fed into the generator section to produce DC electricity and reusable heat. The generator section includes a fuel cell stack which is a series of electrode plates interconnected to produce the required quantity of electrical power. The output DC electricity from fuel cell is then converted to AC electricity in the power conditioning section where it also reduces voltage spikes and harmonic distortions. The power conditioner can also regulate the voltage and current output from the fuel cells to accommodate variations in load requirements [45].

Fig. 6 illustrates different paths of electricity generation from hydrocarbon-based solid, liquid and gaseous fuels by conventional technologies and new technologies based on fuel cells. As shown in Figs. 1 and 2 [7], a large amount of primary energy is consumed

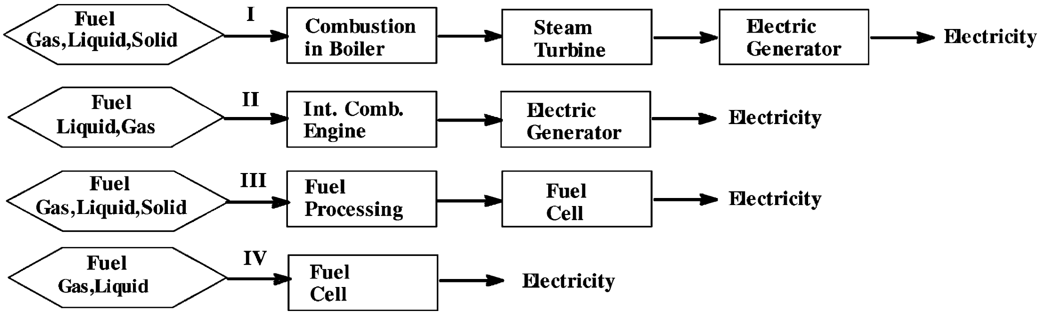


Fig. 6. Different paths of electricity generation from hydrocarbon-based solid, liquid and gaseous fuels.

for electricity generation, and most of this electric power is generated via path I in Fig. 6 for fossil fuel-based power plants, and later half of path I for nuclear power plants. The efficiencies of the current electric power plants are about 30–37% in the US. Path III is the electricity generation based on fuel cells including fuel processing, which is expected be more efficient than path I. Ideally, direct electricity generation based on path IV shown in Fig. 6 would be the most efficient.

Fuel cells have potential to double the efficiency of fossil fuel-based electric power generation, with a resultant slashing of CO_2 emissions [21,25]. The goals for the 21st century fuel cells program of the US DOE include development of solid state fuel cells with installed cost approaching $ 400 per kW (from current fuel cell cost of about $ 4000 per kW) and efficiencies up to 80% (LHV) by 2015, and applications include those in distributed power, central station power, and transportation [23,25]. Solid oxide fuel cells and molten carbonate fuel cells are promising for stationary applications such as electric power plants. Gasification of coal or other carbon-based fuels can be coupled to solid oxide-based or molten carbonate-based fuel cells for more efficient power generation. An extensive review on development of fuel cell technologies in the US, Europe and Japan up to 1995 has been published by Appleby [46] with emphasis on systems, economics and commercialization of fuel cells for stationary power generation.

4.3. Fuel cells for transportation

Currently, the typical overall fuel efficiency of gasoline-powered cars is only around 12%, and the overall fuel efficiency of diesel-powered vehicles are better, at around 15% [47]. These numbers, however, indicate that the majority of the energy is wasted. Therefore, new powering mechanisms (that are more efficient and clean) are also being explored by many auto manufacturers. Fundamentally, the theoretical upper limit of efficiency in the current IC engines is set by a thermodynamic (Carnot) cycle based on combustion, and this must be overcome by using different conversion devices. Fuel cells hold tremendous potential in this direction [48]. Fuel cell-powered cars are expected to be two to three times more efficient than the gasoline and diesel engines [153]. There is a great potential for the widespread applications and there is a fundamental need in view of sustainable development.

The consumption of transportation fuels is increasing worldwide. The total US consumption of petroleum products reached an all-time high of 18.68 million barrels per day (MBPD) in 1998. Of the petroleum consumed, 8.20 MBPD was used as motor gasoline, 3.44 MBPD as distillate fuels (including diesel fuels and industrial fuels), 1.57 MBPD as jet fuels, 0.82 MBPD as residual fuel oil, and 1.93 MBPD as liquefied petroleum gas (LPG), and 2.72 MBPD for other uses [7]. Among the distillate fuels, about 2.2 MBPD of diesel fuel is consumed in the US road transportation market [49]. Due to the high demand and low domestic production in the US, crude oil and petroleum products were imported at the all-time high rate of 10.4 MBPD in 1998, while exports measured only 0.9 MBPD [7]. Between 1985 and 1998, the rate of net importation of crude oil and refinery products more than doubled from 4.3 to 9.5 MBPD [7], largely as a result of increasing demand for transportation fuels in the US. The demand for diesel fuels is increasing faster than the demand for other refined petroleum products and at the same time diesel fuel is being reformulated [50]. According to a recent analysis, diesel fuel demand is expected to increase significantly in the early part of the 21st century and both the US and Europe will be increasingly short of this product [51]. While the world will continue to rely on liquid fuels for transportation in the foreseeable future, the way the world uses liquid fuels in the future—sometime in the 21st century—may be significantly different from today.

PEM-based fuel cells seem to be promising for energy-efficient transportation in the 21st century. The power density that can be achieved with PEMFC is roughly a factor of 10 greater than that observed for the other fuel cell systems which represents a great potential for a significant reduction in stack size and cost over that possible for other systems [18]. The PEMFC typically operates at 70 °C (160 °F) to 85 °C (185 °F). About 50% of maximum power is available immediately at room temperature. Full operating power is available within about 3 min under normal conditions. The low temperature of operation also reduces or eliminates the need for thermal insulation to protect personnel or other equipment [18]. There is also hope for using SOFC for automotive applications using hydrocarbon fuels.

The transportation fuel cell program of the US DOE has been introduced in an overview by Milliken [27]. There is a cooperative research program called Partnership for a New Generation of Vehicles (PNGV) between the US federal government and the auto manufacturers including Daimler Chrysler, Ford Motor, and General Motors [52]. The review by Chalk et al. [53] described the status of the PNGV program and the key role and technical accomplishments of the DOE program on transportation fuel cells. A recent NRC report summarized the progress and the current status of fuel processor for automotive applications [52]. The PNGV program for automotive fuel cell applications aimed at creating an 80 miles per gallon PEMFC-powered car [53]. Fuel cells have potential to double the efficiency of energy utilization for transportation, and as an example, the transportation fuel cell program of US DOE has year 2004 target efficiencies up to 48% for gasoline-based vehicles [27]. In January 2002, the US government announced a new program called Freedom CAR (CAR stands for Cooperative Automotive Research), which replaces the PNGV program [54,55]. The strategic objective of Freedom CAR seems to be directed at developing hydrogen-based fuel cells to power the cars of future [55].

In March 1999, Daimler Chrysler AG unveiled its newest fuel cell vehicle, Necar 4 (new electric car). This is the first time fuel cell system was mounted in the floor of the car. H_2 is the fuel for the fuel cell, and Necar 4 is powered by liquid hydrogen. Recently, Necar 5 has been announced by Daimler Chrysler, which uses the on-board methanol reformer for the fuel cell car; the first long-range fuel cell car test drive was conducted on Necar 5 in May 2002 starting from Sacramento in CA to Washington, DC for a driving distance of about 3000 miles [154]. In April 1999, a large number of companies and California state agencies formed the “California Fuel Cell Partnership” to advance further automotive fuel cell technology. The partnership plans to place 50 fuel cell cars and buses on the road between 2000 and 2003. Ogden et al. [56] made a comparison of hydrogen, methanol and gasoline as fuels for fuel cell vehicles, and discussed their implications for vehicle design and infrastructure development.

4.4. Fuel cells for residential and commercial sectors

While centralized electric utilities will continue to be the major generators of electricity in the near future, there are application markets where small fuel cells can serve as convenient generators for residential homes and commercial buildings. The general advantages for such applications include high energy efficiency, low noise, low emissions of pollutants, and low greenhouse gas emissions. For this type of applications using PEMFC, however, catalytic fuel processing should consider non-pyrophoric catalysts for the water–gas-shift reaction, as indicated recently [57]. The general principle of fuel processing is the same for most applications, and the fuel processor typically include the components of fuel reforming, water–gas-shift, and CO clean-up. The fuels, however, would preferably be those that have existing infrastructure in the distribution network such as natural gas [36]. For residential applications, in addition to natural gas, propane gas or LPG is also a potential fuel for on-site reforming for fuel cells [58].

4.5. Fuel cells as portable power sources

So far, the direct methanol fuel cell is the only option as the portable fuel cell. This type of fuel cell uses direct electrochemical oxidation of methanol without fuel reforming. Recently, research efforts have begun on developing miniaturized liquid hydrocarbon-based fuel processor as well as micro-reformer using methanol for micro-fuel cells, for use as man-portable electrical power sources. The advantage of liquid hydrocarbons is the higher energy density compared to methanol for micro-fuel processor development, which should preferably have at least an order of magnitude longer time of effective use without fuel replacement, as compared to batteries.

5. Challenges and opportunities for fuel processing research

The concepts and steps of fuel processing are illustrated in Fig. 4. There are challenges and opportunities for research and development on fuel processing for fuel cells. The progress in commercial development of fuel cells is faster than many people have predicted a few years ago. Fuel cells have become more promising and increasingly more important in the past few years, perhaps due to a combination of several factors [21,24–27,59–61,155] that stimulate investment in this area: (1) more stringent environmental regulations on controls of pollutant emissions such as EPA Tier II and California ZEV; (2) deregulation of electric power industry and the potential market for distributed generation; (3) intrinsically higher energy efficiency and environmentally friendly nature of fuel cells; (4) advances and successful demonstration of the technology by leading fuel cell companies (such as Ballard Power Systems Inc. in Canada, International Fuel Cells, Siemens Westinghouse, and the Fuel Cell Energy) and financially powerful alliances between fuel cell companies and large auto manufacturers (such as Daimler-Benz, Ford, General Motors and Toyota Motors) and various organizations including US DOE, US DOD, and NEDO in Japan; (5) potential to reduce CO_2 emissions while meeting the energy demands; (6) the potential to double the fuel efficiency in electric power plants by SOFC and MCFC and the potential to triple the fuel efficiency for transportation by PEMFC and SOFC development. Based on the report from Arthur D. Little Inc. in 1998, there are fuel processor technology paths which manufacturing cost analyses indicate are consistent with fuel processor subsystem costs of under $ 150 per kW in stationary applications and $ 30 per kW in transport applications [38].

Table 3 summarizes the general fuel requirements of fuel cells and impacts of gas components on five different types of fuel cells [14,20,62]. Table 4 lists some of the performance targets for stationary and transport fuel cell applications according to the US DOE [23,25,27]. The US DOE is supporting research and development to address some of the biggest remaining challenges, which include fuel processing and lowering the cost of transportation fuel cell systems [26,27], and the development of more advanced fuel cell systems such as 21st century fuel cells with efficiency up to 70–80% [23,25].

Fig. 7 shows the steps and current options for on-site and on-board processing to produce H_2 for low-temperature fuel cells such as PEMFC and PAFC. For catalytic research, needs and opportunities exist in several aspects in the area of fuel processing and electrode catalysis related to fuel processing, which involve one or more of the following aspects: catalytic materials development and application, process development, reactor development, system development, sensor and modeling development.

Gasoline, diesel fuels and jet fuels as well as natural gas are potential candidate fuels that all have existing infrastructure of manufacture and distribution, for hydrogen production for fuel cell applications either for stationary or mobile devices. Alcohol fuels such as methanol are among the candidate fuels. The reforming of alcohols can be done at lower temperatures. The processing sequence of hydrogen production from hydrocarbon fuels may involve several steps including fuel deep desulfurization, reforming (partial oxidation, steam reforming, autothermal reforming), water–gas-shift (high-temperature shift, low-temperature shift), CO clean-up (by either preferential CO oxidation or CO methanation), followed by feeding into fuel cells or feeding after some gas separation depending on the needs of purity of

Table 3
The fuel requirements of fuel cells and impacts of gas components

Species	PEMFC	AFC	PAFC	MCFC	SOFC
Operating temperature (°C)	70–90	70–200	180–220	650–700	800–1000
H_2	Fuel	Fuel	Fuel	Fuel	Fuel
CO	Poison (>10 ppm)	Poison	Poison (>0.5%)	Fuel[a]	Fuel[a]
CH_4	Diluent	Diluent	Diluent	Diluent[a,b]	Diluent[a,b]
CO_2 and H_2O	Diluent	Poison[c]	Diluent	Diluent	Diluent
Sulfur (as H_2S and COS)	Poison (>0.1 ppm)	Unknown	Poison (>50 ppm)	Poison (>0.5 ppm)	Poison (>1 ppm)

[a] CO can react with H_2O to produce H_2 and CO_2 by shift reaction; CH_4 reacts with H_2O to form H_2 and CO faster than reacting as a fuel at the electrode.

[b] A fuel in the external or internal reforming MCFC and SOFC.

[c] CO_2 is a poison for AFC which more or less rules out its use with reformed fuels. Sources [14,20,62].

Table 4
Performance targets for stationary and transport fuel cell applications

Program and application	Parameters	Target values
Second generation fuel cell for stationary applications[a,b]	Efficiency (% LHV)	50–60
	Cost ($ per kW)	1000–1500
	Target year	2003
21st century fuel cell for stationary applications[a,b]	Efficiency (% LHV)	70–80
	Cost ($ per kW)	400
	Target year	2015
Transportation[c] targets in Partnership for New Generation Vehicle (PNGV) Program	50 kW gasoline fuel processor	
	Energy efficiency (%)	80
	Power density (W/l)	750
	Specific power (W/kg)	750
	CO tolerance (ppm)	10 (CO); 0 (sulfur)
	Emissions	<EPA Tier II
	Start to full power (min)	0.5
	Life time (h)	>5000
	Cost ($ per kW)	10
	50 kW reformate fuel cell subsystem	
	Efficiency	60% at 25% peak power
	Platinum loading (g Pt per kW)	0.2
	Start to full power (min)	0.5
	Cost ($ per kW)	40
	Power density (W/l)	500
	CO tolerance (ppm)	100 (CO)
	Life time (h)	>5000
	Target year	2004
	50 kW gasoline-based fuel cell system by 2004	
	Energy efficiency	48% at 25% peak power
	Specific power (W/kg)	300
	Start-up to full power (min)	0.5
	Transient response (s)	1
	Cost ($ per kW)	50

[a] [23].
[b] [25].
[c] [27].

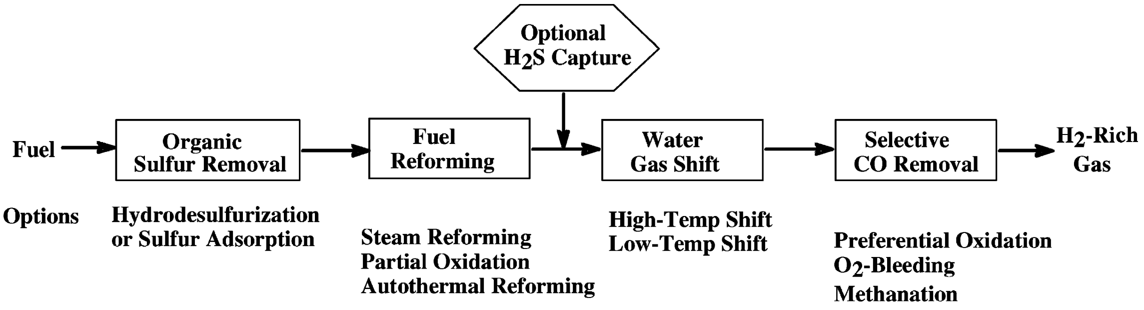


Fig. 7. Steps and current options for on-site and on-board processing liquid and gaseous hydrocarbon fuels and alcohol fuels to produce H_2-rich gas for low-temperature fuel cells (PEMFC).

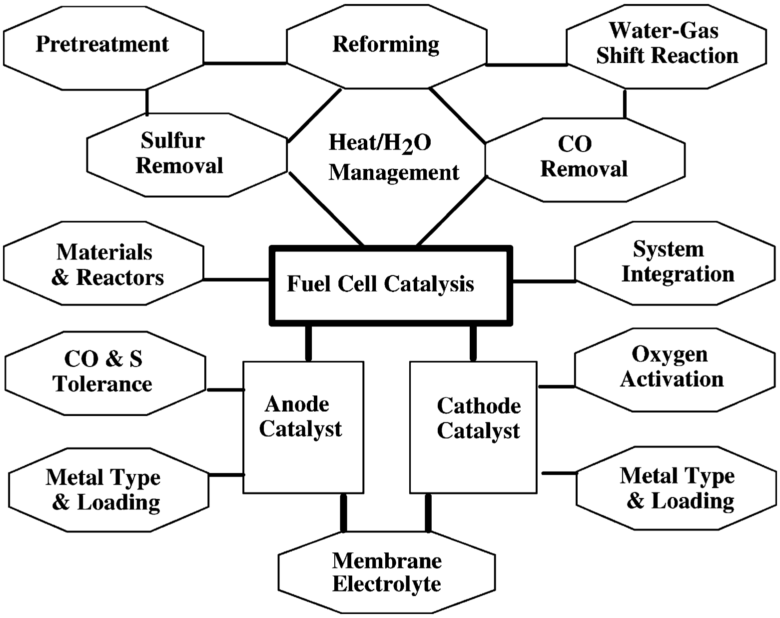


Fig. 8. Some key issues for research and development on fuel processor for fuel cells.

hydrogen and the impacts of impurities for the specific applications.

Based on the studies reported in literature and conducted in our laboratory, some key issues can be summarized, as shown in Fig. 8, for fuel processing for fuel cells. Based on a preliminary analysis of current situations, it appears necessary for further research to develop (1) effective ways for ultra-deep removal of sulfur from hydrocarbon fuels before reforming; (2) more energy-efficient and compact processors for on-site or on-board fuel reforming; (3) more effective removal of inorganic sulfur (H_2S) after fuel reforming; (4) non-pyrophoric, and more active catalysts for water–gas-shift reactions at medium and low temperatures; (5) highly selective and active catalysts for preferential oxidation of CO to enable maximum production of H_2; (6) high-performance electrode catalysts such as CO-tolerant electrodes with lower costs or lower loading of precious metals, and suitable proton-exchange membranes at higher (than current) temperatures for PEMFC. Several of the above issues are further elaborated below.

It should be noted that by using fuel processing for hydrogen production in multiple steps, the net efficiency of the fuel cell system is reduced, and its efficiency advantage is consequently reduced, although such an indirect fuel cell system would still display a significant efficiency advantage. In this context, it is important to develop highly efficient and compact fuel processor for fuel cell applications. While this review focuses on fuel processing, there are other important aspects of fuel cell system such as computational and experimental fluid dynamics [63,64].

5.1. Sulfur removal from hydrocarbon fuels before/after reforming

For conventional transportation fuels used in IC engines, catalytic research on clean fuels involve the following three aspects: (1) fuel processing for improved performance, (2) fuel refining for meeting environmental regulations such as deep removal of sulfur and reduction of aromatics, and (3) pollution control using the exhaust gas treatment system. For fuel cell applications, ultra-clean fuels are needed [28,62], and thus most of the recent discussions in literature on desulfurization of conventional refinery streams to make clean fuels [65–67] also apply to the fuels for fuel cells. Deep hydrodesulfurization of diesel fuels has been discussed in several recent reviews [68–70]. New types of catalysts for conventional hydrodesulfurization of diesel fuels [71] and jet fuels [72] and low-temperature hydrotreating [73] as well as a new integrated system [152] are being explored in our laboratory for deep removal of sulfur from diesel and jet fuels.

However, even with the so-called ultra-low sulfur clean fuels which only contain <30 ppmw sulfur in gasoline and <15 ppmw sulfur in diesel fuels that would meet the EPA Tier II specifications for year 2006, the sulfur contents are still too high for fuel cell applications [28,29]. Some treatments for the sulfur removal is still necessary either before the fuel reforming, with possibly additional polishing for H_2S removal [74] after reforming before the reformate flows to the water–gas-shift reactor which also serves to protect PEMFC anode catalyst from sulfur poisoning [29,62]. This will be especially necessary for using petroleum-based gasoline, diesel fuels and jet fuels, because they will inevitably contain sulfur species, mostly in the two-ring to three-ring polycyclic structures [75,76]. Different approaches for treating sulfur may be needed as a part of the fuel processor system [62,77].

A recent study explored the selective adsorption for removing sulfur (SARS) as a new process for on-site or on-board removal of organic sulfur species from hydrocarbon fuels for fuel cell systems [78,79]. It is advantageous to use the selective adsorption for sulfur removal from fuels before the reformer for fuel cells, since this approach can be used at ambient temperatures without using hydrogen [29,62,78]. As indicated by Bellows of International Fuel Cells [77], sulfur is a severe poison for catalysts in fuel processors for fuel cells, especially downstream of reformer; some developers are using sulfur traps before or after the reformer, but “other developers ignore sulfur removal and simply assume that when fuel cells are commercialized the refineries will produce sulfur-free or ultra-low-sulfur fuels” [77]. The selective adsorption [78] can be applied as organic sulfur trap for sulfur removal from fuels before the reformer for fuel cells on-board or on-site, and it may be applied in a periodically replaceable form such as a cartridge. Further improvement in adsorption capacity is desired.

Reformate from autothermal reforming of hydrocarbon fuels such as gasoline, diesel and jet fuels may contain H_2S at ppm levels, which can deactivate the catalysts for subsequent processing such as water–gas-shift and also poison the anode catalysts based on platinum. On-site or on-board sulfur removal from such reformate may be necessary. Some recent studies examined solid adsorbent such as ZnO to capture H_2S from reformate before it enters the water–gas-shift reactor [20,44,80,81]. The pre-desulfurization of sulfur-containing liquid fuels is also used prior to the catalytic autothermal in the multi-fuel processor being developed by McDermott Technology [82]. Capturing the organic sulfur with solid adsorbent by SARS before fuel reforming is an alternative approach [28,29,79] to conventional hydrodesulfurization. Any organic sulfur species will be converted to H_2S during reforming which produces a reducing atmosphere due to H_2-rich gas. For H_2S capture using ZnO, the morphology of ZnO in the adsorbent is important for effective sulfur removal [74]. More effective adsorbent materials for either organic sulfur or H_2S would be needed for more efficient deep sulfur removal for fuel cell applications.

5.2. Fuel reforming for PEMFC and PAFC

Various fuel cell systems and general fuel reforming methods have been reviewed by Larminie and Dicks [14], Hirschenhofer [20]. Privette [44], and Farrauto and Heck [59] have indicated recently that the proton-exchange membrane fuel cell will be a major focus for research in catalytic fuel processing to make hydrogen from hydrocarbons. PEMFC require hydrogen but not necessarily pure H_2 as the fuel. PEMFC is sensitive to CO because CO poisons the precious metal in the anode at the PEMFC operating temperature. Hydrogen from on-site or on-board fuel processing is an important part of most PEM-based fuel cell systems. The fuel processor converts the hydrocarbon or alcohol fuels into hydrogen-rich gas in several steps. There are three common methods of processing hydrocarbon fuels to create the hydrogen required by the fuel cells. They are steam reforming, partial oxidation, and autothermal reforming or oxidative steam reforming, and the fuels include alcohols and hydrocarbons.

The following equations represent the possible reactions in different processing steps involving three representative fuels: natural gas (CH_4) and liquefied propane gas (LPG) for stationary applications, and liquid hydrocarbon fuels (C_mH_n) and methanol (MeOH) and other alcohols for mobile applications.

Most reactions (Eqs. (1)–(10) and (15)–(17)) require specific catalysts and process conditions in the current system. Some reactions (Eqs. (11)–(14) and (18)) are undesirable but may occur under certain conditions. Trimm and Onsan [83] published a review for on-board fuel conversion and concluded that a combination of oxidation and steam reforming or direct partial oxidation are the most promising processes.

- *Steam reforming*

$$CH_4 + H_2O = CO + 3H_2 \tag{1}$$

$$C_mH_n + mH_2O = mCO + (m + (\tfrac{1}{2})n)H_2 \tag{2}$$

$$CH_3OH + H_2O = CO_2 + 3H_2 \tag{3}$$

- *Partial oxidation*

$$CH_4 + O_2 = CO + 2H_2 \tag{4}$$

$$C_mH_n + (\tfrac{1}{2})mO_2 = mCO + (\tfrac{1}{2})nH_2 \tag{5}$$

$$CH_3OH + \tfrac{1}{2}O_2 = CO_2 + 2H_2 \tag{6}$$

$$CH_3OH = CO + 2H_2 \tag{7}$$

- *Autothermal reforming*

$$CH_4 + \tfrac{1}{2}H_2O + \tfrac{1}{2}O_2 = CO + \tfrac{5}{2}H_2 \tag{8}$$

$$\begin{aligned} &C_mH_n + (\tfrac{1}{2})mH_2O + (\tfrac{1}{4})mO_2 \\ &\quad = mCO + ((\tfrac{1}{2})m + (\tfrac{1}{2})n)H_2 \end{aligned} \tag{9}$$

$$CH_3OH + \tfrac{1}{2}H_2O + \tfrac{1}{4}O_2 = CO_2 + 2.5H_2 \tag{10}$$

- *Carbon formation*

$$CH_4 = C + 2H_2 \tag{11}$$

$$C_mH_n = xC + C_{m-x}H_{n-2x} + xH_2 \tag{12}$$

$$2CO = C + CO_2 \tag{13}$$

$$CO + H_2 = C + H_2O \tag{14}$$

- *Water–gas-shift*

$$CO + H_2O = CO_2 + H_2 \tag{15}$$

$$CO_2 + H_2 = CO + H_2O \quad \text{(RWGS)} \tag{16}$$

- *CO oxidation*

$$CO + O_2 = CO_2 \tag{17}$$

$$H_2 + O_2 = H_2O \tag{18}$$

5.2.1. *Reforming of alcohol fuels*

Production of H_2 from alcohol fuels can be achieved by steam reforming of methanol [84,85] and ethanol [33,35,86]. Peppley et al. [87] have reported on the reaction network for steam reforming of methanol on $Cu/ZnO/Al_2O_3$. Their experimental results showed that, in order to explain the complete range of observed product compositions, one need to include rate expressions for all three reactions (methanol–steam reforming, water–gas-shift and methanol decomposition) in the kinetic analysis. The same group has reported on surface mechanisms for steam reforming of methanol over $Cu/ZnO/Al_2O_3$ catalysts, which account for all three of the possible overall reactions: methanol and steam reacting directly to form H_2 and CO_2, methanol decomposition to H_2 and CO and the water–gas-shift reaction [88]. For practical application, Wiese et al. [89] reported on methanol steam reforming in a fuel cell drive system. Peters et al. [90] reported their study on a methanol reformer concept and they considered the particular impact of dynamics and long-term stability for use in a fuel cell-powered passenger car.

Because steam reforming is an endothermic reaction, one processing approach is to create nearly autothermal system by incorporating oxidation into steam reforming, as in the case of hydrocarbon fuel reforming. There are several recent reports on oxidative steam reforming of methanol [32,91–93,156]. Johnson Matthey has recently developed the HotSpot^{TM} methanol processor which combines the steam reforming with catalytic partial oxidation in a single catalyst bed [156], followed by CO removal for on-board hydrogen generation [94]. Reitz et al. [32,92] reported some recent results on steam reforming of methanol over CuO/ZnO under oxidizing conditions. Recently, Velu et al. [93] reported on oxidative steam reforming of methanol over CuZnAl(Zr)-oxide catalysts for the selective production of hydrogen for fuel cells. Fierro [91] presented an overview on both partial oxidation and steam reforming involved in the oxidative steam reforming of methanol for the selective production of hydrogen. Fierro [91] covered studies on activity and effects of operating conditions as well as some mechanistic and kinetic aspects on oxidative steam reforming and partial oxidation of methanol over Cu/ZnO and Pd/ZnO catalysts. Steam reforming and oxidative steam reforming of alcohol are easier than that of a hydrocarbon, but water–gas-shift is still necessary for CO removal in general.

5.2.2. Reforming of hydrocarbon fuels

One of the recent focus areas is fuel processing for H_2 production from hydrocarbon fuels such as gasoline and diesel fuels for transportation as well as natural gas for stationary applications using low-temperature fuel cells, particularly PEMFC [35–37]. In addition to low cost, transport applications require a fuel processor that is compact and can start rapidly. The fuel processing subsystem for PEMFC, which is the focus of transport applications, includes the reforming, water–gas-shift, and deep CO removal [38].

There are two types of metals as candidate catalysts for reforming. The first is non-precious metal (base metal), and the second is precious metal (noble metal) catalyst. Typical base metal catalyst is nickel (Ni) supported on Al_2O_3, with or without alkali promoters. Typical precious metal that has been widely studied is platinum (Pt). While Al_2O_3 is still the widely used support material, various new support materials are being studied. Methods for hydrocarbon reformation include steam reforming, partial oxidation, and autothermal reforming. Steam reforming is widely used in industry for making H_2 and syngas [39–41]. Steam reforming generally give higher H_2/CO ratios (=3) compared to partial oxidation for a given feed, but steam reforming is endothermic and thus requires external heating. Direct partial oxidation (POX) of CH_4 to produce syngas [95,96] and partial combustion of CH_4 for energy-efficient autothermal syngas production [97] are being explored. Liquid fuel can be reformed by partial oxidation; all the commercial partial oxidation reactors employ non-catalytic partial oxidation of the feed stream by oxygen in the presence of steam with flame temperatures of about 1300–1500 °C [20]. These reactions are important but the catalytic partial oxidation is more difficult to control. The major operating problems in catalytic partial oxidation include the over-heating or hot spots due to the exothermic nature of the reactions, and coking problem.

Consequently, coupling the partial oxidation with endothermic steam reforming could lead to a more efficient catalytic autothermal reforming. Many papers and reviews have been published in the recent past on syngas production using autothermal reforming as a part of gas-to-liquids (GTL) research and development efforts worldwide, although such studies were directed for stationary syngas production [30,97–100]. Trimm and Onsan [83] reported that indirect partial oxidation, which involves combustion of part of the fuel to produce sufficient heat to drive the endothermic steam reforming reaction, is the preferred process for on-board reforming of all fuels including methanol, methane, propane and octane.

The principle of autothermal reforming is applicable to both stationary syngas or H_2 plants and mobile fuel processors. However, non-catalytic POX or non-catalytic combustion, is not suitable for on-board autothermal reforming for fuel cells for mobile applications which prefer compact fuel processors where all the individual steps including reforming, water–gas-shift and CO clean-up are carried out inside one enclosure. Some technical issues for H_2 production by reforming of hydrocarbon fuels for PEMFC have been discussed by Bellows [101] and Krumpelt [102]. Several studies have been presented at recent conferences, including fuel processing research at Epyx [103], fuel-flexible processing system at Hydrogen Burner Technology [81], compact fuel processor for fuel cell vehicles being developed jointly by McDermott Technology and Catalytica [82], fuel processors for small-scale stationary PEMFC systems at Northwest Power Systems [104], and reformate gas processing at Los Alamos National Laboratory [105]. Epyx Corp. (a subsidiary of Arthur D. Little) in the US merged with De Nora Fuel Cells in Italy to form a new company called Nuvera Fuel Cells in April 2000, which will produce fuel cell systems for applications in the stationary power and transportation markets.

Reformation of liquid or gaseous fuels may become an important process for hydrogen production for on-site stationary fuel cell or on-board mobile fuel cell applications, until the direct electrochemical conversion of fuels (or other more efficient conversion routes) become practically feasible. Consequently, there are considerable research interests and commercial developments in hydrocarbon-based fuel processing for transportation [31,38] using gasoline [157] or diesel fuel [158]. Fuel processing studies at US national laboratories have been presented at a recent conference. For example, studies reported by Argonne National Laboratory include catalytic autothermal reforming [106], alternative water–gas-shift catalysts

[57], effects of fuel contaminants on reforming catalyst performance and durability [107], integrated fuel processor development for PEMFC-based vehicle applications [108], and sulfur removal from reformate [80]. Studies presented by Los Alamos National Laboratory include fuel processing with emphasis on the effects of fuel and fuel constituents on fuel processor performance and catalyst durability [109], and CO clean-up development by preferential oxidation (PrOx) [110]. Researchers from Pacific Northwest National Laboratory reported a compact fuel reforming reactor system based on micro-channel fuel processing [111].

Chalk et al. [26] discussed the challenges for fuel cells in transport applications. Fuel processing for H_2 production by on-board reforming of hydrocarbon fuels for cars and trucks may become important in the early part of next century. It is expected that in the near future a significant fraction of newer vehicles may be hybrid vehicles which use conventional fuels as well as the existing fuel handling and distribution system. An example is a fuel cell vehicle that uses conventional hydrocarbon fuels and performs on-board steam reforming to convert the hydrocarbon fuels into hydrogen and carbon monoxide, followed by the water–gas-shift and preferential oxidation to convert CO and water into H_2 and CO_2. In this case, clean hydrocarbon fuels that are extremely low in sulfur and aromatics will be needed. As the new technologies develop further and gain widespread acceptance, vehicles that do not use conventional fuels may penetrate more into road transportation.

A new approach for fuel reforming is to use H_2-selective membrane. The use of supported palladium membrane reactor for steam reforming has also been reported by Kikuchi [112] for membrane development and by Lin and Rei [113] for process development. Kikuchi [112] and Kikuchi et al. [114] have created a composite membrane consisting of thin palladium layer deposited on the outer surface of porous ceramics. By using electroless-plating, the palladium layer could completely cover the surface, so that only hydrogen could permeate through the membrane with a 100% selectivity, and such membrane has been incorporated in a steam reformer being developed by Tokyo Gas and Mitsubishi Heavy Industries for the PEMFC system [112]. In a related study, Prabhu and Oyama [115] reported on the preparation and application of hydrogen-selective ceramic membranes for CO_2 reforming of methane.

The work on catalytic fuel reforming in our laboratory is directed towards energy-efficient oxidative steam reforming in carbon-free regions for hydrocarbon fuels as well as methanol for stationary and mobile applications. This is based on our prior work and on-going study for reforming of natural gas to produce syngas and H_2 under various conditions including high-pressure regime [29,65,75,116–119]. There are also fundamentally interesting issues and concepts in literature on hydrocarbon reforming such as oxygen spillover. Based on the report by Maillet et al. [120], oxygen species (OH, O) can be transferred from a Rh/Al_2O_3 catalyst to pure oxides such as ceria, and OH groups stored on the support migrate to the metal particles where the reaction with CH_x fragments from the activation of C_3H_8 (feed molecule) can occur. Rostrup-Nielsen and Alstrup [121] reported that the rates of steam reforming and hydrogenolysis are closely correlated indicating common rate-controlling steps.

It should also be noted that hydrogen production itself is an important subject. In addition to fuel cells, hydrogen production, storage and transportation have other potential applications as a clean energy, as a reactant for chemical processing such as hydrogenation, as well as for fuel processing such as hydrodesulfurization for making ultra-clean fuels. One could also envision some new developments that could result in high-capacity materials for safe storage and transportation of hydrogen that could also be released readily in a safe manner.

5.3. *Carbon formation during reforming*

Carbon formation is a problem in reforming of hydrocarbon fuels in the stationary syngas plants [122], particularly for hydrocarbon fuels with two or more carbon atoms in the main chain. The same problem can occur also during fuel reforming for fuel cell applications. For example, Sone et al. [159] recently reported on carbon deposition in fuel cell system. Partial oxidation, steam reforming and autothermal reforming can be used for converting liquid hydrocarbon fuels such as gasoline, jet fuel, and diesel fuels into synthesis gas, followed by water–gas-shift reaction and preferential CO oxidation to produce H_2-rich gas for use in fuel cells. Heavier hydrocarbons in the jet fuels and diesel fuels can form carbon deposits even at relatively lower temperatures such as 450 °C due to fuel pyrolysis [123,124]. More aromatic fuels such as diesel fuels will have a higher tendency of carbon formation.

It is important to clarify the carbon-free conditions and to design effective reforming processes for stable and selective synthesis gas production, which also depend on the type and nature of catalysts. Computational analysis can be carried out to predict the thermodynamically carbon-free region of reforming operations, as has been shown for natural gas reforming under various conditions in our laboratory [116,117]. This is a complicated problem, because there are regions of reaction conditions with certain catalysts where thermodynamics predict no carbon formation but on some catalyst surface carbon is formed. The problem of carbon formation during reforming is also being studied in our laboratory using a tapered element oscillating microscope [118,125].

The high risk of carbon formation problem in steam reforming of liquid hydrocarbons (naphtha) and the importance of using a pre-reformer for reforming of liquid hydrocarbons have been discussed by Rostrup-Nielsen et al. [126]. There are two ways to suppress carbon formation, one is by changing process conditions such as steam/carbon ratio, and the other is by using carbon-resistant catalysts. Higher steam/carbon ratio is useful for minimizing carbon formation, but the use of more steam also increases energy cost. Modification of Ni catalyst by using Mg is beneficial for decreasing carbon formation, and the possible reasons are inhibition of dehydrogenation of adsorbed CH_x species, and enhanced steam adsorption [126]. Another approach is to use noble metal catalyst. It has been reported that the whisker carbon, which is frequently observed on Ni catalyst, does not form on noble metals because these metals do not dissolve carbon [126]. It is well known that essentially all hydrocarbon feeds contain sulfur at different concentrations, and sulfur is the main force for deactivation of pre-reforming and reforming catalysts [126].

5.4. *Catalytic water–gas-shift*

WGS is one of the major steps for H_2 production from gaseous, liquid and solid hydrocarbons or alcohols. WGS is already commercially practiced in the gas industry for syngas and H_2 production, for which the state-of-the-art has been summarized by Gunardson [39] and Armor [41]. For PEM-based fuel cell applications, CO is a poison to the Pt-based anode catalyst and thus deep removal of CO to the ppm level is necessary. On the other hand, the activity of existing commercial WGS catalysts is generally low, and as a result, the largest fraction of the reactor volume is occupied by the WGS part of the fuel processor for H_2 production. Development of more active catalysts would be necessary for a more efficient WGS step in the fuel processing train. Examples of some recent studies are mentioned below.

Thompson and coworkers have recently found that molybdenum carbide catalysts are more active than a commercial Cu-Zn-Al shift catalyst for the water–gas-shift reaction at 220–295 °C under atmospheric pressure [160]. They also noted that Mo_2C did not catalyze the methanation reaction, and is a promising candidate for new water–gas-shift catalyst. Li et al. [127] reported on a low-temperature water–gas-shift reaction over Cu- and Ni-loaded cerium oxide catalysts. Tabakova et al. [128] examined supported gold catalysts on various supports for the WGS reaction, and they concluded that the catalytic activity of the gold/metal oxide catalysts depends strongly not only on the dispersion of the gold particles but also on the state and the structure of the supports. Recently, Utaka et al. [129] made an attempt on CO removal by an oxygen-assisted water–gas-shift reaction over supported Cu catalysts. Cu/Al_2O_3-ZnO demonstrated an excellent activity for catalytic removal of CO by oxygen-assisted WGSR, and the equilibrium concentration obtained from thermodynamic data indicates that the reaction is desirable at lower temperatures [129]. New ways of catalyst preparation could lead to more active or more selective catalysts, and this is applicable to but not limited to WGS reaction. Shen and Song [130] reports a new method to prepare highly active Cu-ZnO-Al_2O_3 catalyst that can minimize CO formation and is active at lower temperature. Chandler et al. [131] reported on the preparation and characterization of supported bimetallic Pt-Au and Pt-Cu catalysts from bimetallic molecular precursors.

From the reactor engineering side, Tonkovich et al. [132] reported on a different approach to water–gas-shift using micro-channel reactors. Micro-channel reactors reduce heat and mass transport limitations for reactions, and thus facilitate exploiting fast intrinsic reaction kinetics, i.e. high effectiveness factors [132].

5.5. Deep removal of CO

For PAFC, the above-mentioned WGS is usually sufficient for producing H_2-rich fuel gas, because the anode catalyst in PAFC can tolerate about <2% CO. The anode catalyst for PEMFC is usually made of Pt/C, which is more sensitive to CO because PEMFC operates at lower temperatures at which CO can deactivate Pt metal. Usually, CO in the fuel must be reduced to <10 ppm. Even with Ru addition to modify Pt for improved CO tolerance by using Pt-Ru/C anode, CO in the H_2-rich gas should be reduced to <30 ppm. It is difficult for WGS to reach this level of CO reduction. Three processes can be used to further reduce CO in the feed, preferential or selective oxidation, methanation, and membrane separation [14]. In the PrOx, a small amount of air (usually about 2%) is added to the gas (fuel) stream from WGS, which then passes over a precious metal catalyst. This catalyst preferentially adsorbs CO, rather than H_2, where CO reacts with oxygen (from air). After water–gas-shift, selective oxidation of CO may be performed, preferably inside a compact unit [133]. Rohland and Plzak [134] reported on CO oxidation using Fe_2O_3-Au catalyst system and achieved relatively high oxidation rate at 1000 ppm CO and 5% “air bleed” at 80 °C that could enable a PEMFC-integrated CO oxidation. Dudfield et al. [135] reported on a modeling study for a CO-selective oxidation reactor for solid polymer fuel cell automotive applications.

Methanation is the hydrogenation of CO using the H_2 that is already present in the feed stream. Methanation reaction is the opposite of steam reforming of methane. The methanation approach avoids the oxygen addition, and thus avoids the process complication. The methane produced does not poison the electrode, and only act as a diluent. However, the disadvantage of the method is the consumption of hydrogen [14].

Membrane approach is generally designed for separation and purification. Membrane can be used for separating hydrogen from gas mixtures. Palladium membrane has been studied more extensively than other types of membranes for hydrogen separation, but it is still very expensive for use in fuel cell system [14]. If a membrane is used, then the selective removal of hydrogen in a membrane reactor enables the hydrogen production by steam reforming at lower reaction temperatures than conventional processes.

5.6. Fuel processing for SOFC and MCFC

For the low-temperature fuel cells (PEMFC and PAFC) using hydrocarbon fuels, in addition to fuel reforming, several steps of fuel processing are required to convert the CO because H_2 is a fuel but CO is not a fuel and CO can deactivate the anode catalyst. These add to the cost and complexity of the fuel processing system when compared to those needed for the high-temperature fuel cells (SOFC and MCFC). Therefore, another focus area is fuel processing for high-temperature fuel cells including SOFC and MCFC, which could use either internal reforming (since the internal temperature is high enough for fuel conversion) or external reforming, or both. The fuel reforming discussed above for PEMFC is also applicable to the external reformer for SOFC and MCFC, which could use steam reforming, or partial oxidation, or autothermal reforming. However, water–gas-shift reaction and preferential CO oxidation will not be necessary when SOFC and MCFC are used.

When hydrocarbon fuels are to be used, high-temperature fuel cells (SOFC and MCFC) have an efficiency advantage over the PEMFC at the system level. One of the major problems of fuel reforming at high temperatures is carbon formation, as already discussed in the previous section. Fuel reforming for SOFC or MCFC is an active research subject. For example, recently, Peters et al. [90] reported on pre-reforming of natural gas in SOFC systems. Finnerty et al. [136] described a SOFC system with integrated catalytic fuel processing. The higher temperature waste heat of these systems (in the case of the SOFC and MCFC) can be used to assist in the reforming of hydrocarbon fuels, to drive air compressors, and to produce steam for thermal electric generation or other thermal load [18].

The catalytic aspects for the internal fuel reforming have been discussed recently [42,43]. There are two approaches in internal reforming, direct internal reforming fuel cell where both fuel reformation and electrochemical reaction takes place in anode chamber, and indirect internal reforming fuel cell where the fuel reformation and electrochemical reaction takes place on the two sides of the wall for anode gas chamber. Fuel Cell Energy is developing an externally manifolded, internally reforming molten carbonate fuel cell [25] called the direct fuel cell or DFC [137]. They have completed a 4000 h, 250 kW stack test in Danbury, CT [25]. Because the fuel is reformed to hydrogen-rich gas internally in the stack, this design eliminates the external fuel processing unit required by PAFC and PEMFC. The advantages of internal reforming include: (1) separate equipment to process the fuel externally is eliminated; (2) equipment count is lower, leading to simpler operation and higher reliability; and (3) efficiency of the system is increased [20,137].

One of the problems with internal reforming is anode deactivation. Coe et al. [138] reported on a kinetic study for the removal of surface carbon formed by methane decomposition following high-temperature reforming on a nickel/zirconia SOFC anode using methods based on temperature-programmed oxidation. They observed that the addition of small quantities of lithium to the anode resulted in a significant lowering of the activation energy for surface carbon removal by about 50 kJ/mol [138].

External fuel reforming is also being explored for high-temperature fuel cells. The advantage of external reforming is the flexibility of fuel processor design which is not limited by fuel cell stack design [20]. In the case of using liquid fuels (gasoline, diesel, and jet fuel) and gaseous fuels (natural gas, propane gas), a catalytic reformer can be placed adjacent to the anode gas chamber. In the design with external reformer, the reformer can be operated at elevated pressures although the fuel cell stack may be operated under atmospheric pressure. The reformer and the fuel cell do not have a direct physical effect on each other, other than heat transfer. This is an advantage also because this design eliminate the problem of deactivation of electrode catalyst due to carbon formation via fuel decomposition, which may be an important concern in the internal reforming fuel cells. Cavallaro and Freni [139] have discussed the feasibility and the overall process economy of an integrated system of autothermal reformer (ATR) and MCFC. M-C Power is developing an internally manifolded, externally reforming molten carbonate fuel cell, and they have completed two 75 kW stack tests in California [25].

The advantage of external reforming is also important when considering the SOFC-type or MCFC-type fuel cell-based electric power plants using coal gasification. Production of gaseous fuel (syngas) from coal gasification requires solid-gas reactions and involves both ash/residue disposal and hot gas clean-up before its use in fuel cell stack. It is better for such a process to be carried out outside the fuel cell stack. Detailed discussions on coal gasification are available in literature [46]. For SOFC and MCFC, CO does not act as a poison and can be used directly as a fuel. The SOFC is also the most tolerant of any fuel cell type to sulfur. It can tolerate several orders of magnitude more sulfur than other fuel cells. However, the 900–1000 °C operating temperature of the SOFC requires a significant start-up time. The cell performance is very sensitive to operating temperature. A 10% drop in temperature results in ∼12% drop in cell performance due to the increase in internal resistance to the flow of oxygen ions [18].

For both internal and external reforming, the reaction process needs to be carried out in the thermodynamically carbon-free region using suitable steam/carbon ratios. Even in such a region catalyst may still suffer from deactivation due to carbon formation (and in the case of MCFC, contamination of catalyst surface by other metal compounds). The development of catalysts that resist coke formation and other deactivation would be desirable. Increasing steam/carbon ratios for the reforming could reduce carbon formation, but higher steam/carbon ratios also result in lower energy efficiency, because vaporization and heating of water consume significant amount of energy. In industrial steam reformer, steam/carbon ratios of around 3 are used, but much lower ratios would be desirable for fuel cell processors [29].

SOFC offers inherently high efficiency up to 60–70% in individual systems and up to 80% in staged or hybrid systems [140]. The development of SOFC has been mainly directed towards large-scale power generation with early commercial devices of 1–3 MW [61]. The high temperature of SOFC also demands that the system include significant thermal shielding to protect personnel and to retain heat. While such requirements are acceptable in a utility application, they are not consistent with the demands of most transportation applications nor do they lend themselves to small, portable or transportable applications

[18]. When the operating temperatures of SOFC can be lowered from 900–1000 to 600–800 °C with improved cell performance, SOFC would be more promising for both stationary and mobile applications. Siemens Westinghouse is developing tubular SOFC under the support of US DOE, and they have tested multiple tubular SOFC for 70,000 h [25]. A recent study involved thermodynamic model and parametric analysis of a tubular SOFC module [161]. Recent advances have made SOFC seem also promising for transport applications in addition to stationary applications [140]. SOFC can handle liquid fuels by on-board reforming relatively easily because of the high cell operating temperatures enabling reformation of hydrocarbon fuels such as gasoline and diesel fuels [140]. There are also on-going efforts for developing hybrid fuel cell/turbine systems, for which the fuel-to-electricity efficiency goal is 70% [25].

For MCFC, the need for CO_2 in the oxidant stream requires that CO_2 from the spent anode gas be collected and mixed with the incoming air stream. Before this can be done, any residual hydrogen in the spent fuel stream must be burned. Future systems may incorporate membrane separators to remove the hydrogen for recirculation back to the fuel stream [18].

5.7. *Electrode catalysis related to fuel processing*

Precious metals are used for electrode catalysts in low-temperature fuel cells such as PEMFC and PAFC. It is important to reduce the amount of precious metal loadings such as Pt by using effective techniques [141]. The anode catalysts for PEM-based fuel cells are generally based on Pt, which is active at the low operating temperature of PEMFC but is sensitive to CO poisoning. Progress has been made in improving CO tolerance of the anode catalysts [27], and one of the ways to increase CO resistance is to use Pt-Ru as anode catalyst. Paulus et al. [142] used organometallic compounds for preparing Pt–Ru alloy colloids as precursors for fuel cell catalysts. Some recent studies have been reported on the characteristics of platinum-based electrocatalysts and more CO-tolerant Pt catalysts for mobile PEMFC applications [143]. Understanding the key factors affecting CO tolerance of the metal and alloy catalysts and the development of more CO-tolerant anode metal or alloy catalysts can reduce the need for deep CO removal or even reduce the need for extremely high CO conversion by the less-efficient WGS. This can lead to higher fuel cell system efficiency. New ways of reducing the minimum loading of precious metals or the use of non-precious metals, if successful, will be beneficial to the cost reduction of fuel cell system. Electrocatalysis for direct methanol oxidation (without reforming) has some problems due to conflicting demands.

The anode catalysts for high-temperature direct internal reforming fuel cells (SOFC, MCFC) need to be active and more resistant to carbon formation involving hydrocarbon fuels. The chemical composition and nature of anode catalysts also affect carbon formation in addition to the internal reforming reaction conditions. There are recent reports on internal reforming on anode catalyst in SOFC. For example, Finnerty et al. [136] have conducted internal steam reforming of methane using nickel/zirconia fuel reforming anodes in SOFC and observed that addition of small quantities of molybdenum leads to a significant reduction in the amount of carbon deposited, whilst having little effect on the reforming activity or cell performance. Based on temperature-programmed oxidation, Finnerty et al. [136] found that three types of carbon are formed on the anodes of SOFC during high-temperature steam reforming of methane. They also observed that as current is drawn from the cell, increased methane conversion occurs together with reduced carbon deposition, through reaction via partial oxidation and oxidative coupling with the flux of oxygen ions through the solid electrolyte. Nakagawa et al. [144] studied the catalytic activity of Ni-YSZ-CeO_2 anode for the steam reforming of natural gas in a direct internal reforming SOFC.

5.8. *Direct oxidation of methanol and methane in fuel cells*

All of the above-mentioned fuel cells require some fuel reformation when the fuels are hydrocarbons or alcohols. As indicated already, fuel processing for reformulation also reduces the efficiency of the overall energy conversion. It should be mentioned that the concepts of direct fuel-electricity conversion without fuel reforming are being explored, although the details are beyond the scope of this paper on fuel processing. Two principal approaches are DMFC based on PEMFC, and direct methane fuel cell (DMeFC) or direct hydrocarbon fuel cell based on SOFC.

Direct methanol fuel cell operate at relatively low temperatures in the range of ambient temperature to 150 °C; it is promising for portable devices such as fuel cell for laptop computer and mobile telephone. Recent studies on direct methanol fuel cells and advances in this topic area have been summarized in several reviews [145–147]. The challenges include the development of more efficient anode and cathode catalysts, and the more effective membranes that resist methanol cross-over and can operate at higher temperatures.

Direct methane fuel cell based on SOFC requires much higher operating temperatures compared to direct methanol fuel cell. Direct electrochemical methane oxidation have been studied for some time. Further development of science and technology for SOFC could make it possible to directly use hydrocarbons such as CH_4 to generate electricity. More recent studies have been reported on direct electrochemical oxidation of hydrocarbons (beyond methane) in SOFC without fuel reforming [148–150]. These recent developments made direct oxidation based on SOFC more promising, but there are also major problems to be solved [151].

6. Concluding remarks

Development and utilization of more efficient energy conversion devices are necessary for sustainable and environmentally friendly development in the 21st century.

Fuel cells are fundamentally much more energy-efficient, and can achieve as high as 70–80% system efficiency in integrated units including heat utilization, because fuel cells are not limited by the maximum efficiency of heat engines or IC engines dictated by the Carnot cycle.

Hydrogen would be an ideal fuel for fuel cells but due to the lack of infrastructure for distribution and storage, processing of fuels is necessary for producing H_2 on-site for stationary applications or on-board for mobile applications.

Hydrocarbons and alcohols can both be used as fuels for reforming on-site or on-board. Hydrocarbon fuels have the advantages of existing infrastructure of production and distribution, while alcohol fuels can be reformed at substantially lower temperatures.

Further research and development are necessary on fuel processing for improved energy efficiency and size reduction, and on electrode catalysis related to fuel processing such as tolerance to CO and sulfur components in reformate. For example, more effective ways of deep removal of sulfur before and after reforming, energy-efficient and stable autothermal reforming catalyst and processing scheme, more active and non-pyrophoric catalysts for water–gas-shift, more CO-tolerant anode catalysts or membrane electrode operating at higher temperature would contribute significantly to implementation of low-temperature fuel cells, particularly proton-exchange membrane fuel cells.

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