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Technical, environmental and exergetic aspects of hydrogen energy systems

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Abstract

In this paper, a number of technical, environmental and exergetic aspects of hydrogen and hydrogen energy systems (particularly fuel cells) and their applications are discussed from an energy point of view. In addition, exergy concept is introduced for hydrogen energy systems and exergetic aspects are discussed through two illustrative examples which show a potential usefulness of exergy in hydrogen energy systems. © 2002 International Association for Hydrogen Energy. Published by Elsevier Science Ltd. All rights reserved.

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1. Introduction

Energy is a key element of the interactions between nature and society and is considered a key input for economic development. Environmental issues span a continuously growing range of pollutants, hazards and eco-system degradation factors that affect areas ranging from local through regional to global. Some of these concerns arise from observable, chronic effects on, for instance, human health, while others stem from actual or perceived environmental risks such as possible accidental releases of hazardous materials. Many environmental issues are caused by or relate to the production, transformation and use of energy, for example, acid rain, stratospheric ozone depletion and global climate change [1].

The impact of energy resource utilization on the environment and the achievement of increased resource-utilization efficiency are best addressed by considering exergy. The exergy of an energy form or a substance is a measure of its usefulness or quality or potential to cause change and provide the basis for an effective measure of the potential of

a substance or energy form to impact the environment. It is important to mention that in practice a thorough understanding of exergy and the insights it can provide into the efficiency, environmental impact and sustainability of energy systems, are required for the engineer or scientist working in the area of energy systems and the environment. During the past decade, the need to understand the linkages between exergy and energy, and environmental impact has become increasingly significant [2,3].

Hydrogen is one of the most promising energy carriers for the future. It is an energy-efficient, low-polluting fuel. When hydrogen is used in a fuel cell to generate electricity or is combusted with air, the only products are water and a small amount of NO_x . Hydrogen is renewable and found in many compounds such as water, fossil fuels, and biomass. Hydrogen typically makes up about 6% by weight of dry biomass. Using biomass for energy results in lower emissions than using fossil fuels. CO_2 is continuously recycled as biomass in the form of trees and other plants that use it to regenerate, and lower emissions of sulfur and NO_x can be expected when converting woody biomass in comparison to coal. To obtain hydrogen from biomass, pyrolysis or gasification must be applied, which typically produces a gas containing 20% hydrogen by volume, which can be further

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Nomenclature

h	specific enthalpy, kJ/kg
i	current, A
I	irreversibility (rate of exergy destruction), kW
\dot{m}	mass flow rate, kg/s
\dot{Q}	heat transfer rate, kW
P	pressure, kPa
s	specific entropy, kJ/kg K
T	temperature, K
v	voltage, V
\dot{W}	power, kW
x	mole fraction

Greek letters

ε	specific exergy, kJ/kg
μ	chemical exergy

Subscripts and superscripts

ch	chemical
e	exit
fc	fuel cell
g	gas
i	inlet
in	inlet
net	net
out	out
th	thermochemical
0	reference environment, ambient, surroundings

steam-reformed to make higher-purity streams for various fuel cells. The challenge is to overcome the economic barriers that current technology presents for converting biomass to hydrogen for use in clean, efficient energy conversion devices [4].

Hydrogen that is manufactured from renewable resources and used in fuel cells can provide sustainable energy to power electric vehicles. The total system, including distribution, refueling and on-board storage of hydrogen may prove superior to batteries recharged with grid power. A hydrogen-powered electric vehicle may offer a market entry for hydrogen and renewable resources in transportation. Attractive transitional applications of hydrogen include use in combustion engine vehicles and production from natural gas. In either case, the environmental and energy policy consequences are significantly less than continued use of oil-derived fuels in conventional combustion engine vehicles.

Fuel cells, which employ hydrogen to produce electricity, can be used to power a wide variety of applications. This is especially true in transportation, where there are several options for providing hydrogen for the fuel cells.

- One option for obtaining the hydrogen is to use an on-board reformer to extract it from the gasoline in our gas tanks. (Reformers break down hydrogen–carbon bonds to produce a mixed gas from which pure hydrogen is derived.) This approach could also be applied to other hydrocarbons.
- A second option is to use methanol as the hydrogen carrier. Methanol is easier to reform than gasoline and can be produced from natural gas, solid fossil fuels, or renewable biomass resources.
- A third option is to develop a fuel cell that uses methanol directly, eliminating the need for a separate reformer.

Instead, a catalyst on the fuel–cell membrane would chemically break the methanol into hydrogen and carbon dioxide [4].

- A fourth option is to produce the hydrogen at central locations and then store it on board the vehicle as a gas, as a cryogenic liquid, or in a solid. With this option, the hydrogen could be produced via steam reforming of natural gas, via pyrolysis or gasification of biomass or fossil fuels, or via electrolysis of water.

To date, the principal niche application for power generation with fuel cells has been in spacecraft. Recently, however, there has been increased interest in their application for both stationary and mobile power generation. This interest has been motivated by the fuel cells' high efficiency, even in small-scale installations, and their low waste emissions. Recent legislative initiatives in California, USA aimed at mandating the introduction of zero-emission vehicles, and the failings of other technologies (e.g., the limited range and long refueling times of battery-powered vehicles) have further promoted the investigation of fuel cells in mobile applications [5].

The primary objective of the present paper is to discuss technical, environmental and exergetic aspects of hydrogen and hydrogen energy systems. In order to highlight the importance of the exergy analysis, some illustrative examples are also presented.

2. Environmental issues

During the past two decades the risk and reality of environmental degradation have become more apparent. Growing evidence of environmental problems is due to a combination of several factors since the environmental

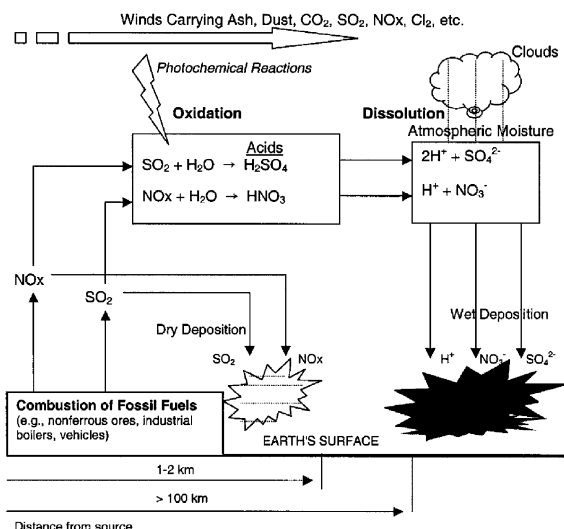


Fig. 1. Illustration of the formation, transport, and impact of acid precipitation [6].

impact of human activities has grown dramatically because of the sheer increase of world population, consumption, industrial activity, etc. Throughout the 1970s most environmental analysis and legal control instruments concentrated on conventional pollutants such as SO_2 , NO_x , particulates, and CO . Recently, environmental concern has extended to the control of micro- or hazardous air pollutants, which are usually toxic chemical substances and harmful in small doses, as well as to that of globally significant pollutants such as CO_2 . Aside from advances in environmental science, developments in industrial processes and structures have led to new environmental problems.

Three major areas of environmental problems are the acid precipitation, the stratospheric ozone depletion, and the global climate change. Thus, we will introduce these three issues in brief.

2.1. Acid rain

Acid rain (or acid precipitation) is a form of pollution depletion in which pollutants produced by the combustion of fossil fuels, particularly from both stationary and mobile sources such as smelters for nonferrous ores, industrial boilers, and transportation vehicles, are transported over great distances through the atmosphere and deposited via precipitation on the earth on ecosystems that are exceedingly vulnerable to damage from excessive acidity. This acid rain deposition was found to be mainly attributable to emissions of SO_2 and NO_x [1] and such gases react with water and oxygen in the atmosphere and result in acids such as sulfuric and nitric acids (Fig. 1). It is therefore obvious that

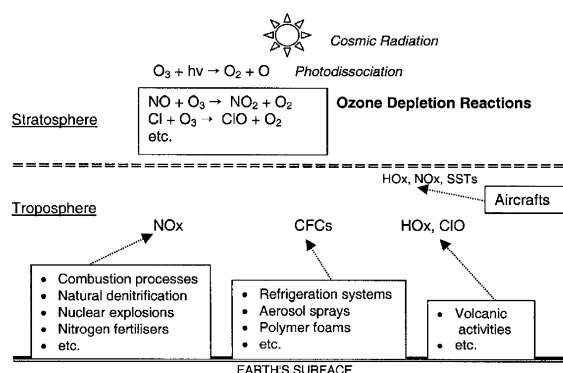


Fig. 2. Illustration of sources of natural and anthropogenic ozone depleters [6].

the solution to the issue of acid rain deposition requires an appropriate control of the pollutants such as SO_2 and NO_x .

The pollutants have caused only local concerns related to health in the past. However, as awareness of their contributions to the regional and transboundary problem of acid precipitation has grown, attention has begun also focusing on other substances such as volatile organic compounds (VOCs), chlorides, ozone and trace metals that may participate in the complex set of chemical transformations in the atmosphere resulting in acid precipitation and the formation of other regional air pollutants. There are a number of major evidences to show the damages of acid precipitation as follows [6]:

- acidification of lakes, streams and ground waters,
- toxicity to plants from excessive acid concentration,
- resulting in damage to fish and aquatic life,
- damage to forests and agricultural crops
- deterioration of materials, e.g., buildings, metal structures and fabrics, and
- influence of sulfate aerosols on physical and optical properties of clouds.

2.2. Stratospheric ozone depletion

Stratospheric ozone depletion is well known that the ozone present in the stratosphere, roughly between altitudes of 12 and 25 km, plays a natural, equilibrium-maintaining role for the earth, through absorption of ultraviolet (UV) radiation (240–320 nm) and absorption of infrared radiation [6]. A global environmental problem is the distortion and regional depletion of the stratospheric ozone layer which has been shown to be caused by the emissions of CFCs, halons (chlorinated and brominated organic compounds) and NO_x (Fig. 2). Ozone depletion in the stratosphere can lead to increased levels of damaging ultraviolet radiation reaching the ground, causing increased rates of skin cancer, eye damage and other harm to many biological species.

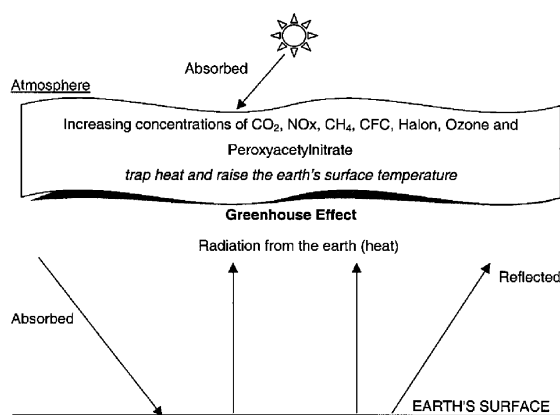


Fig. 3. Illustration of greenhouse effect [6].

Energy- and non-energy-related activities are only partially (directly or indirectly) responsible for the emissions which lead to stratospheric ozone depletion. CFCs, which are used in air conditioning and refrigerating equipment as refrigerants and in foam insulation as blowing agents, and NO_x emissions which are produced by the fossil fuel and biomass combustion processes, the natural denitrification, the nitrogen fertilizers, and the aircrafts play the most significant role in ozone depletion.

2.3. Greenhouse effect

Greenhouse effect (or global climate change) is known as a rise in the earth's temperature as a result of emissions of greenhouse gases. Although the term *greenhouse effect* has generally been used for the role of the whole atmosphere (mainly water vapor and clouds) in keeping the surface of the earth warm, it has been increasingly associated with the contribution of CO_2 (currently, it is estimated that CO_2 contributes about 50% to the anthropogenic greenhouse effect). However, several other gases such as CH_4 , CFCs, halons, N_2O , ozone and peroxyacetylnitrate (so-called: *greenhouse gases*) produced by the industrial and domestic activities can also contribute to this effect, resulting in an increase in the earth's temperature (Fig. 3).

Potentially, the most important environmental problem relating to energy utilization is the greenhouse effect, also known as the global warming. Increasing atmospheric concentrations of greenhouse gases are increasing the manner in which these gases trap heat radiated from the earth's surface, thereby raising the surface temperature of the earth. The earth's surface temperature has increased by about 1°C over the last century, and as a consequence sea level is estimated to have risen by perhaps 20 cm. Such changes can have wide-ranging effects on human activities all over the world.

Recently, a large number of potential solutions to these environmental problems associated with the harmful pollu-

tant emissions have been worked out, including:

- hydrogen energy,
- renewable energy technologies,
- energy conservation, leading to efficient energy utilization,
- cogeneration and district heating,
- energy storage technologies,
- alternative energy dimensions for transport,
- energy source switching from fossil fuels to environmentally benign energy forms,
- coal cleaning technologies,
- process change and sectoral shiftment,
- acceleration of forestation,
- carbon or fuel taxes,
- materials substitution,
- promoting public transport,
- changing life styles,
- increasing public awareness.

Of these potential solutions, we will discuss the most important ones, in particular, hydrogen energy, in the following section.

3. Comparison of possible fuels

Since we need to manufacture a fuel for the post-fossil fuel era, we are in a position to select the best possible fuel. There are many candidates, such as synthetic gasoline, synthetic natural gas (methane), methanol, ethanol and hydrogen. The fuel of choice must satisfy the following conditions [7]:

- It must be a convenient fuel for transportation.
- It must be versatile or convert with ease to other energy forms at the user end.
- It must have high utilization efficiency.
- It must be safe to use.

In addition, the resulting energy system must be environmentally compatible and economical.

Veziroglu and Barbir [8] also pointed out that hydrogen is the best fuel, particularly for transportation based on the following criteria: versatility, utilization efficiency and safety.

4. Hydrogen

Unlike most other fuels, hydrogen cannot be produced directly by digging a mine or drilling a well. It must be extracted chemically from hydrogen-rich materials such as natural gas, water, coal, or plant matter. Accounting for the energy required for the extraction process is critical in evaluating any hydrogen use option. The current hydrogen production techniques include steam reforming of natural gas, cleanup of industrial by-product gases, and electrolysis of water. A number of other technologies are being studied,

particularly in developed countries, including several that produce hydrogen from water or biomass using solar or other renewable energy.

At present, fuel hydrogen is mostly distributed in tankers as a cryogenic liquid. Expanded use would probably be the mean distribution in pipelines as a gas, but few hydrogen pipelines now exist and any large-scale distribution system would also require techniques for bulk storage.

In the USA today, the only major non-experimental user of hydrogen as a fuel is the space program, for propulsion and as an on-board source of electricity. Aircraft applications have been widely studied, particularly for supersonic and hypersonic planes. Cars, trucks, and buses can burn pure hydrogen in an internal combustion engine, use it in a fuel cell to drive an electric motor, or burn a hydrogen-containing mixture to reduce the environmentally harmful emissions from another fuel [9].

The idea of using hydrogen as a fuel has been around for many years. As early as 1874, a character in Jules Verne's novel *The Mysterious Island* suggested that when fossil fuel supplies run out, hydrogen "will furnish an inexhaustible source of heat and light". So far, however, this idea has generated much research but little commercial application.

In the USA, a serious hydrogen commercialization plan is underway and is one major tool needed to implement the U.S. National Hydrogen Association (NHA) mission statement: "...to foster the development of technologies and their utilization in industrial and commercial applications and promote the transition role of hydrogen in the energy field". The hydrogen commercialization plan is a living document to be revised and expanded over the coming years as more and better information becomes available about new technologies and the growing market for hydrogen energy systems. The primary objective of the plan is to obtain commitments from both industry and government to begin implementing the hydrogen energy industry. Such joint commitment will require an economically and technically feasible road map on how to get from here to there. Industry must be convinced that it can eventually make a return on investments in hydrogen technology. Government should be convinced that its investments will leverage larger societal benefits in the form of reduced health costs, reduced oil imports, and improved international competitiveness over time. In short, the hydrogen commercialization plan should point to a credible benefit/cost ratio for all participants. In summary, the plan will be used to [10]:

- identify unique niche market opportunities where hydrogen is economical now, or nearly so, with growth potential toward longer-term goals;
- convince appropriate companies, both members and non-members of the NHA, to make investments in hydrogen development, demonstration, and commercialization projects, with industry paying an increasing share of the cost as each technology approaches market viability;
- convince government decision makers to provide steadily increasing support for hydrogen and fuel cell development programs in the near-term, with the realization that these technologies will eventually become economically viable on a broad scale without any government support;
- help guide hydrogen energy investment choices by government agencies in the industrialized world, including choices by the U.S. Department of Energy;
- help convince other key players (such as state and local officials, building inspectors, the insurance industry, the investment industry, and the public at large) that the hydrogen energy industry is safe, economical, and sustainable; and
- encourage other companies and organizations to join the NHA.

The above commercialization plan begins by identifying the most likely early markets for hydrogen as an energy carrier, and sets realistic near-term and mid-term goals for selected market penetration. The plan outlines the major barriers to achieving those goals and recommends activities to capitalize on the incentives and overcome the market barriers.

5. Technical aspects of hydrogen energy

5.1. Hydrogen energy production

Although hydrogen is the universe's most abundant element, it is present in the atmosphere only in concentrations of less than one part per million. Most of the Earth's hydrogen is bound up in chemical compounds. Hydrogen for large-scale use should therefore be extracted from a source such as water, coal, natural gas, or plant matter. It cannot simply be produced from a mine or a well. Since considerable energy is consumed in the extraction process, hydrogen should properly be considered an energy carrier rather than an energy source; the energy released when it is finally used is just the energy that was invested in its original manufacture (minus any losses). Recognizing this fact is of critical importance. Any analysis of how hydrogen is to be used must also consider how the hydrogen is to be produced. A variety of alternative hydrogen energy production technologies are available in practice, including [9]:

- *Steam reforming.* Steam reforming is a chemical process that makes hydrogen from a mixture of water and a hydrocarbon feedstock, usually a fossil fuel. The most common feedstock is natural gas, consisting primarily of methane. When steam and methane are combined at high pressure and temperature, a chemical reaction converts them into hydrogen and carbon dioxide. The energy content of the hydrogen produced is actually higher than that of the natural gas consumed, but considerable energy is required to operate the reformer, so the net conversion efficiency

is typically only about 65%. Hydrogen produced by this technique can cost as little as 65 ¢/kg.

- *Off-gas cleanup.* After steam reforming, the next most common source of hydrogen at present is the cleanup of industrial off-gases. Numerous industries give off high concentrations of hydrogen in their waste streams petroleum refineries, blast furnaces, and some chemical plants, for example. Collecting and purifying these gases is often cost-effective, with costs typically ranging between 80 and 120 ¢/kg. Most off-gas hydrogen is used on-site by the industry that produces it, so although off-gas cleanup is an important feature of today's market, it seems unlikely that it could be expanded enough to meet the increased demand that would result from widespread use of hydrogen as a fuel.
- *Electrolysis.* Electrolysis means passing an electrical current through water to split individual water molecules into their constituent hydrogen and oxygen. Energy losses during this process are relatively modest: 65% energy efficiency is common, and state-of-the-art large electrolyzers can be 80–85% efficient. Electrolysis has captured considerable attention, even though it accounts for only a small fraction of current hydrogen production, because it is a clean process and water is abundant. At present, however, the technique is only used at relatively small plants, with a cost of 2.40–3.60 \$/kg of hydrogen produced. This high cost is expected to limit electrolysis to niche markets in the near and mid-term. In the long term, could electrolysis become more competitive? At present, natural gas reforming is more than 3 times more energy efficient than electrolysis if fossil-source electricity is used.
- *Photoprocess.* Photoprocesses use the energy and other special properties of light (usually sunlight) to produce hydrogen from either water or biomass. There are three broad categories of photoprocess. Photobiological techniques are based on the photosynthesis cycle used by plants and by some bacteria and algae. The efficiency of photobiological hydrogen production is only 1–5%, but researchers hope to increase it to 10% or more. Photochemical processes mimic natural photosynthesis using synthetic molecules. This technique is only about 0.1% efficient now, but could in principle be much improved. Photoelectrochemical techniques use layers of semiconductor material separated by water. When exposed to light, the semiconductor layers produce an electrical voltage that splits the water into hydrogen and oxygen. The best prototypes yet demonstrated in the laboratory are about 13% efficient, but the maximum theoretical efficiency is believed to be more than 35%. It has been estimated that an efficiency in the field of 10–15% might be economical, but such estimates depend strongly on projections of equipment costs. Note that since all these photoprocesses use light as their primary energy source, their efficiencies should not be used directly in cost comparisons with processes that use hydrocarbon fuels or electricity.

Photoprocesses are a major component of current hydrogen research programs.

- *Thermochemical process.* This process uses heat to split water into hydrogen and oxygen. The conceptually simplest version of this technique is direct thermal conversion, i.e. heating water to extreme temperatures, perhaps 3400 K. Owing to the high temperatures required, however, direct thermal conversion is as yet impractical outside the laboratory. Chemical reactions can be employed to reduce the required temperature. Various alternatives have been studied, often involving complex multistep processes. Hybrid techniques that incorporate electrolysis into one or more of the reaction steps are under investigation. There has been little recent work available on thermochemical techniques.
- *Radiolysis.* This process is the splitting of water molecules by collisions with high-energy particles produced in a nuclear reactor. Since the hydrogen and oxygen atoms thus produced quickly recombine to produce water again, radiolysis would probably be only about 1% efficient. Most experts agree that radiolysis is less promising than other techniques.
- *Solar hydrogen.* In this original and simplest form of hydrogen energy production, the solar hydrogen scenario envisions producing electricity from sunlight using photovoltaic cells, electrolyzing water to produce hydrogen, and substituting this hydrogen for the oil and other fossil fuels in general use today. The term is now often used more broadly to include electrolysis based on other renewable sources of electricity, such as wind. This idea has received considerable attention largely because of the environmental benefits of using hydrogen instead of fossil fuels. It also addresses two barriers to the ultimate achievement of large-scale use of solar energy: that solar electricity cannot be used directly for non-electric applications, such as combustion engines, and that electricity is difficult and expensive to store.
- *Partial oxidation of hydrocarbons.* Hydrogen may be formed from the noncatalytic partial oxidation (i.e., gasification) of hydrocarbons such as residual oil. Any hydrocarbon feedstock that can be compressed or pumped may be used in this technology. However, the overall efficiency of the process (50%) is less than that for SMR (65–75%) and pure oxygen is required [11]. Two commercial technologies for this conversion are available: the Texaco gasification process and the Shell gasification process [12].

There are also some other hydrogen production technologies, such as:

- thermal decomposition of hydrocarbon fuels,
- thermocatalytic CO₂-free production of hydrogen from hydrocarbon fuels,
- superadiabatic decomposition of hydrogen sulfide,

- autothermal reforming (combining partial oxidation and steam reforming),
- sorption enhanced reaction process (SERP),
- production of hydrogen from biomass-derived liquids,
- photoelectrochemical hydrogen production,
- biological H_2 from fuel gases and from H_2O ,
- two-phase photobiological algal H_2 -production system,
- H_2 production from glucose-6-phosphate.

Most of the above listed methods are at developmental stage.

5.2. Hydrogen storage

5.2.1. Bulk storage in distribution system

It is expected that any large-scale hydrogen distribution system should address the problem of bulk storage, to provide a buffer between production facilities and fluctuations in demand. Low-cost and efficient bulk storage techniques are a major research goal. One can store hydrogen as either a gas or a liquid. The most widely studied options for storing gaseous hydrogen are underground caverns and depleted underground natural gas formations. Although hydrogen is more prone to leak than most other gases, leakage is shown not to be a problem for these techniques. For example, town gas (a mixture containing hydrogen) has been stored successfully in a cavern in France, and helium, which is even more leak-prone than hydrogen, has been stored in a depleted natural gas field near Amarillo, Texas. The energy consumed in pumping gas in and out of such storage facilities may be significant, however. Above-ground storage tanks at high pressure are another option.

A certain amount of gaseous storage can be achieved by allowing modest pressure changes in the distribution pipeline system. In the case of natural gas, this technique is used to help manage transient demand fluctuations, such as the morning and evening peaks in residential demand in urban areas. Though the same technique might be useful for hydrogen, its potential is limited, particularly if the hydrogen is to be produced from intermittent sources such as solar or wind.

Storage in liquid form uses tanks similar to those used for liquid hydrogen distribution. For example, Kennedy Space Center uses a 3217 m³ sphere near the launch pad, and can transfer fuel from this tank to the space shuttle at up to 38 m³ per minute. Storage at liquefier plants is in vacuum-insulated spherical tanks that usually hold about 1514 m³ [9]. The energy required for liquefaction may not be a barrier if the hydrogen is to be transported as a liquid anyway, or if the end-use application requires its fuel to be in liquid form.

5.2.2. Hydrogen storage in end use

The difficulty of onboard storage is the main barrier to fueling vehicles with hydrogen. Because it is a gas, hydrogen at room temperature and pressure takes up about 3000 times more space than an energy equivalent amount of gasoline. This obviously means that compression, liquefaction, or

some other technique is essential for a practical vehicle. So far, storage requirements tend to severely limit range. During the past two decades, several techniques have been studied to overcome this problem. The four main contenders are compressed gas, cryogenic liquid, metal hydride, and carbon adsorption. Of these, the first two appear most promising for the short-term. Metal hydrides are also relatively mature, but require further R&D to be competitive. Carbon adsorption is not yet a mature technique, but it appears very promising if R&D goals can be met. Glass microspheres and onboard partial oxidation reactors are currently under investigation, but as yet are “insufficiently characterized for evaluation at the systems level”. It is likely that different techniques will turn out to be most appropriate for different applications (buses are less size-sensitive than cars, for example) [9].

- Compressed gaseous hydrogen storage is at room temperature in a high-strength pressure tank. Including the weight of the tank, compressed gas storage holds about 1–7% hydrogen by weight, depending on the type of tank used. Lighter, stronger tanks, capable of holding more hydrogen with less weight, are more expensive. Compressing the hydrogen gas at the filling station requires about 20% as much energy as is contained in the fuel.
- Cryogenic liquid storage is at 20 K in a heavily insulated tank at ordinary atmospheric pressure. As a liquid, hydrogen contains almost 3 times more energy than an equal weight of gasoline, and takes up only about 2.7 times as much space for an equal energy content. Including the tank and insulation, this technique can hold as much as 16% hydrogen by weight. Furthermore, liquefaction at the filling station requires about 40% as much energy as is contained in the fuel. Another disadvantage is the so-called “dormancy problem”: despite the insulation, some heat leaks into the tank, eventually boiling off the hydrogen. A “cryopressure” system stores liquid hydrogen in a pressure vessel like that used for compressed gaseous storage, allowing containment of the boiled-off gas. This helps with dormancy, but increases weight and size.
- Metal hydride systems store hydrogen in the interatomic spaces of a granular metal. Various metals can be used. The hydrogen is released by heating. Metal hydride systems are reliable and compact, but can be heavy and expensive. Varieties now under development can store about 7% hydrogen by weight. Unlike the compressed gas and cryogenic liquid techniques, metal hydrides require little or no “overhead” energy when refueling. They do require energy to release the fuel, however. For low-temperature varieties this energy may be available as waste heat from the fuel cell or engine. For high-temperature varieties, which tend to be the less expensive ones, as much as half of the vehicle’s energy consumption may go to releasing the fuel from the metal.
- The carbon adsorption technique stores hydrogen under pressure on the surface of highly porous superactivated graphite. Some varieties are cooled, others operate at room

temperature. Current systems store as much as 4% hydrogen by weight. It is hoped to increase this efficiency to about 8%, even for the room temperature variety. Carbon adsorption is very similar to compressed gas storage except that the pressure tank is filled with graphite; the graphite adds some weight but allows more hydrogen to be stored at the same pressure and tank size.

- Glass microspheres are small, hollow, glass micro-balloons whose diameters vary from about 25 to 500 μm , and whose wall thicknesses are about 1 μm . They can be used in large beds to store hydrogen at high pressures. The microspheres are filled with hydrogen gas at temperatures of 200–400°C. The high temperature makes the glass walls permeable, and the gas fills the spheres. Once the glass is cooled to room temperature, the hydrogen is trapped inside the spheres. The hydrogen can be released as needed by heating the spheres. The spheres can also be crushed to release hydrogen. This option precludes sphere recycling, but is desirable for applications where weight is important.
- Onboard partial oxidation reactor is a concept proposed to help bring about a transition from conventional automobiles to cars powered by hydrogen fuel cells. First, a shift would be made from the internal combustion engine to the fuel cell using a conventional hydrocarbon fuel such as gasoline or diesel coupled to an on-board partial oxidation process and a water gas shift reaction process. The partial oxidation process yields 30% hydrogen gas directly and 20% carbon monoxide. Then, the carbon monoxide is chemically reacted with steam to produce additional hydrogen and carbon dioxide gas, which is readily usable by a hydrogen fuel cell. This fossil-to-hydrogen fuel system would be used as a “bridge” until R&D yields a commercially ready advanced hydrogen storage system or a suitable hydrogen carrier.
- Other techniques are still in the early stages of development. One uses powdered iron and water. At high temperatures these react to produce rust and hydrogen. Other methods are similar to the metal hydride option, but substitute certain liquid hydrocarbons (also known as “recyclable liquid carriers”) or other chemicals for the metal.

5.3. Safety

Hydrogen is intrinsically no more dangerous than many other fuels. Its different characteristics require different safety equipment and procedures, but all fuels have some potential for accidents; if they did not burn, they would not be much use as a fuel. Hydrogen is already routinely and safely used worldwide in the petroleum and chemical industries and elsewhere. It was also routinely used in the USA as a fuel (a component of “town gas”) before natural gas became widely available. Town gas is still used in some countries. Moreover, hydrogen ranks between propane and methane (natural gas) in safety.

The physical properties of hydrogen make its safety characteristics rather different from those of other fuels. Its low density means that it tends to rise and disperse into the atmosphere in the event of a leak, rather than remaining in a “puddle” near the ground. This increases safety in well-ventilated applications. Its low density also means that a hydrogen explosion releases less energy in a given volume than an explosion of other fuels, and compared to gasoline or natural gas, hydrogen requires much higher concentrations in the air to produce an explosion rather than just a flame. Furthermore, hydrogen’s low ignition temperature and flammability over a wide range of concentrations make leaks a significant fire hazard, especially in confined spaces such as a garage. Because it is clear and odorless, leaking hydrogen is also more likely to go undetected than a leak of gasoline or most other fuels. Even the flame of burning hydrogen is invisible. Techniques of leak detection have been and continue to be an R&D priority. A simple approach is to add an odorant like that added to natural gas, or possibly a colorant, or both. Any addition may detract somewhat from the environmental cleanliness inherent to pure hydrogen, however, and additives would need to be chosen with care to avoid destroying other important features. For example, contaminants may reduce the efficiency and/or lifetime of a fuel cell.

As with most fuels, the fire and explosion hazards discussed above are the main safety concerns. In some situations, there may be other safety issues, for example in applications that involve hydrogen storage under high pressure or at extreme low temperatures. These problems can be minimized with proper equipment design and operating procedures, however, and are generally agreed to be of less concern than hydrogen’s flammability.

5.4. Economics of hydrogen energy

Hydrogen is currently more expensive than other fuel options, so it is likely to play a major role in the economy only in the long term, if technology improvements succeed in bringing down costs. Higher prices for fossil fuels would not necessarily make hydrogen more cost-competitive in the short term. Since fossil fuels are currently the main source of heat, feedstock, and electricity for hydrogen production plants, rising prices for gas, oil, or coal would also drive up the price of hydrogen. Since hydrogen can be produced in many different ways, from many different sources, most hydrogen-related international commerce is likely to be not of fuel but of technology: plant components, engineering services, construction know-how, and so on. These areas could potentially represent new export markets.

6. Environmental aspects of hydrogen energy

The use of hydrogen as a fuel is inherently very clean. Hydrogen consumed by either combustion or a fuel cell

produces only water as an end product. The high temperatures involved in combustion may stimulate some NO_x production from nitrogen and oxygen in the air, but this problem is familiar from other fuels and can be controlled. Unlike other fuels, hydrogen contains no other pollutant-producing elements, so it has no potential to produce SO_2 , CO , CO_2 , volatile organic chemicals, etc.

The environmental consequences of hydrogen production should also be considered, however. As mentioned above, production from fossil fuel feedstocks by steam reforming leads to carbon dioxide emissions greater than those from simply using the feedstock itself as a fuel. Steam reformers should also somehow dispose of feedstock impurities such as sulfur. Electrolysis is responsible for the emissions of whatever power plants are used to generate the needed electricity. Production of hydrogen from sustainably harvested biomass, solar energy, or other renewable sources might considerably reduce production emissions, but (as described above) these techniques are not yet fully developed.

The U.S. Department of Energy (has examined the full-cycle environmental effects of various scenarios for hydrogen production and use. It concludes that “substantial emissions can be generated when hydrogen is produced from certain energy sources”, namely fossil fuels. Thus, the technique of hydrogen production remains crucial.

7. Fuel cells as hydrogen energy systems

Fuel cells power generation is not a new idea. The principle was discovered over 160 years ago by a Welsh judge, Sir William Grove. Until recently, their use was confined to the laboratory and to space applications where they provide electricity, heat and water, and have done so since the 1960s when they were chosen over riskier, less reliable options. But the technology was immature and far too expensive for terrestrial applications.

Recently, interest in fuel cells has increased sharply and progress towards commercialization has accelerated. Today, practical fuel cell systems are becoming available and are expected to take a growing share of the markets for automotive power and generation equipment once costs fall to competitive levels.

On 26 July 1996 the London Financial Times stated that “... recent progress in cutting the costs and improving the performance of fuel cells has been so rapid that there really does seem to be a good prospect of the technology going into mass production as a clean energy source in the next century, both for moving vehicles and for stationary power generation”. Since then the pace of development has further accelerated.

Commercialization is being driven by four major challenges that fuel cells are uniquely able to address [13]:

- Build-up of carbon dioxide and other greenhouse gases is leading to global warming with unpredictable but potentially catastrophic consequences.

- When fossil fuels burn, they emit a cocktail of toxic pollutants that damage the environment and people's health.
- World oil production will decline in the next 10–20 years and dependence on a few energy-rich nations will significantly increase. Energy security and price will be threatened.
- Deregulation of the electricity supply industry is changing the market. New companies are entering the market offering energy services based on distributed on-site power generation. This segment of the energy market is likely to grow rapidly and utilities will have to adapt to the opportunity and challenge.

The market for automotive power and stationary generation conversion equipment is the largest market for capital equipment in the world. Fuel cells and fuel-cell-powered vehicles will be an economic growth leader in the coming decades securing high-quality employment for many thousands of people.

7.1. Utilization of fuel cells

Fuel cell technology is clean, quiet and flexible one and is already beginning to serve humanity in a variety of useful ways. But production volume is low and costs are too high. Public support is needed to help generate initial demand to break this cycle.

Fleet vehicles, in particular urban transit buses, represent an early entry route into the transportation market. This is due to several factors: conventional buses are significant sources of noxious emissions in urban areas; central fuelling depots will facilitate the use of hydrogen; and, fuel cell buses are expected to have lower maintenance and operating costs.

Several fuel cell buses have been demonstrated in public transport systems, particularly in the USA. An event of special significance occurred on 16 March 1998, when fare-paying passengers in Chicago boarded the world's first fuel cell bus to enter revenue service. Compressed hydrogen fuels the engine, providing a range of about 250 miles. The bus has equivalent performance to a conventional diesel without the growling engine and unhealthy emissions.

Hydrogen fuel cell buses are now sufficiently technically advanced to enter the market but extensive field demonstration and fleet testing is required to prove performance and build confidence in the technology.

Light-duty automotive applications are by far the largest market opportunity available to fuel cell technology and have been the focus of intense development effort. All major automakers now have fuel cell vehicle programs. Most have either launched prototype cars or announced their intention to do so. Some examples are as follows. A major milestone was achieved on 17 March 1999 with the launch of a prototype fuel cell car, based on the sub-compact Mercedes A-class. Described as the first viable fuel cell car, Necar IV demonstrated that fuel cell technology had advanced to the point where it met the high performance and compact size

needed for automobile propulsion (the complete fuel cell engine and components are all contained in the double-skinned floor). The car's energy efficiency is reported to be close to double that of the diesel version. Liquid hydrogen tanks provide a range of 280 miles.

Recently, Daimler–Chrysler has indicated that the technology has the possibility to be maintenance free and that mass-produced fuel cell cars are expected in 2004. GM, Ford, Toyota, Nissan and Honda have already targeted similar dates.

7.2. Benefits of fuel cells

Fuel cells are considerably efficient power producers and create electricity in one simple step, with no moving parts and (at least in the case of PEMFC) at a very low temperature. (Compare this to the combustion process employed by traditional power plants: a fuel is burned at high temperature to create heat, the heat energy is then converted to mechanical energy and that mechanical energy is finally converted into electricity.)

Since fuel cells do not combust fossil fuels, they are known as clean power producers, they emit none of the acid rain or smog producing pollutants that are the inevitable by-product of burning coal or oil or natural gas.

Furthermore, fuel cells provide a range of critical benefits that no other single power technology can match [13].

- *A fuel cell converts the chemical energy of hydrogen and oxygen directly to produce water, electricity, and heat.* They are therefore inherently clean and efficient and are uniquely able to address the issues of environmental degradation and energy security. They are also safe, quiet and very reliable.
- *Fed with pure hydrogen, they produce zero emissions of carbon dioxide, oxides of nitrogen or any other pollutant.* Even if fed with fossil fuels as a source of hydrogen, noxious emissions are orders of magnitude below those for conventional equipment.
- *They offer significant improvements in energy efficiency* as they remove the intermediate step of combustion and mechanical devices such as turbines and pistons. Unlike conventional systems, they operate at high efficiency at part load. Also, unlike conventional plants, their high efficiency is not compromised by small sizes. High efficiency saves fuel and reduces CO₂ emissions.
- *Fuel cell power plants have demonstrated unprecedented reliability and durability* that is significantly better than conventional equipment. The absence of combustion and moving parts means that fuel cells can run continuously for long periods before servicing and they are far less prone to breakdown.
- *They promote energy security and will assist the transition to renewable energy sources.* Fuel cells can use hydrogen derived from a variety of sources, including

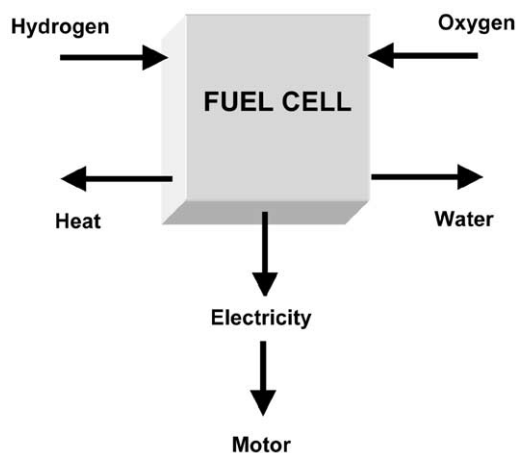


Fig. 4. Operation of a fuel cell, converting hydrogen and oxygen (from the air) into electricity, water and heat.

natural gas and coal, and renewables such as biomass or, through electrolysis, wind and solar energy.

- *Fuel cells offer utilities the opportunity to provide customers with an added value energy service* that is not subject to the same competitive or regulatory pressures as exist for conventional electric supply and will be able to do so at overall lower cost.

7.3. Principle of fuel cell operation

In principle, a fuel cell operates like a battery. Unlike a battery, it does not run down or require recharging, and produces energy in the form of electricity and heat as long as fuel is supplied. The fuel cell converts chemical energy directly into electricity without combustion by combining oxygen from the air with hydrogen gas. It produces electricity as long as fuel, in the form of hydrogen, is supplied. The only by-products are water and heat (Fig. 4). No pollutants are produced if pure hydrogen is used. However, very low levels of nitrogen oxides are emitted, but usually in the undetectable range. The carbon dioxide emissions which come out from the electrochemical conversion are relatively low because of high efficiency, and are in concentrated form, facilitating capture hydrogen can be produced from water using renewable solar, wind, hydro or geothermal energy. Hydrogen also can be extracted from anything that contains hydrocarbons, including gasoline, natural gas, biomass, landfill gas, methanol, ethanol, methane and coal-based gas.

7.4. Types of fuel cells

Fuel cells sound are an efficient, nonpolluting power source that produce no noise and have no moving parts. But such cells not only exist, they have been providing electricity on spacecraft since the 1960s. In more down-to-earth applications, they could be used as electricity-generating

plants or as a power source for nearly exhaust-free automobiles. The main sticking point is the high cost of manufacturing the devices, which has largely limited them to a handful of exotic applications. Now falling prices and new technologies suggest that the fuel cell's day may finally have arrived. In fuel cells, like in batteries, silent reactions produce an electric current. Unlike batteries, however, fuel cells are almost endlessly rechargeable. The cells run on hydrogen, which reacts with oxygen from the air in such a way that a voltage is generated between two electrodes; the reactions occur in a chemical mediator known as an electrolyte. (Some designs consume hydrogen directly; others start with natural gas that is converted to hydrogen before entering the cell.) Compared with conventional fossil-fuel power sources, fuel cells are exceptionally clean and efficient. Practically their only waste product is water; natural gas-fueled cells do produce some carbon dioxide as well, though less than would be created if the fuel were burned.

The type of fuel cell is typically distinguished by the electrolyte that is utilized and can be classified into two main categories, based on their operating temperatures, such as low-temperature fuel cells (e.g., 60–250°C) and high-temperature fuel cells (e.g., 600–1000°C). Low-temperature fuel cells have made significant progress in transportation applications due to their quick start times, compact volume and lower weight compared to high-temperature fuel cells. The common types of low-temperature fuel cells are proton exchange membrane fuel cells, phosphoric acid fuel cells, alkaline fuel cells, unitized regenerative fuel cells, direct methanol fuel cells. The high-temperature fuel cells are more efficient than low-temperature ones in generating electrical energy. Also, they provide high-temperature waste heat which is a benefit in stationary cogeneration applications, but presents a problem for transportation applications. Two common ones are molten carbonate fuel cells and solid oxide electrolyte fuel cells. All these are explained below:

(a) *Phosphoric acid fuel cells (PAFCs)*. PAFCs are the most mature fuel cell technology and are commercially available now in sizes ranging from 200 kW to 11 MW. This type of fuel cell has been operating successfully in Japan for several years. Current phosphoric-acid fuel cell design has an electrical conversion efficiency of 41%. Major improvements await in the areas of capital cost reduction, stack life extension, and operation/management cost reduction.

Fig. 5 exhibits a PAFC designed and constructed by ONSI Corporation in Windsor, CN. Seventy-four of these units, each the size of a minivan, are now in operation, often in locations such as hospitals and remote hotels where grid power is expensive and reliability is worth a premium.

PAFCs use liquid phosphoric-acid as an electrolyte. At the anode, hydrogen gas is ionized to produce hydrogen ions and electrons. The electrons travel from anode to cathode through an external circuit. Hydrogen ions travel to the cathode through the electrolyte. At the cathode, oxygen reacts with the hydrogen ions and the electrons to form water.



Fig. 5. A commercial ONSI PAFC [4].

Phosphoric acid-based cells tend to be heavy, which makes them less than ideal for use in vehicles. Other companies are developing cells that are specifically designed for that purpose.

(b) *Molten carbonate fuel cells (MCFCs)*. MCFCs are a type of direct fuel cell that eliminates external fuel processors. Methane (the main ingredient of natural gas) and steam are converted into a hydrogen-rich gas in the reforming anode or in a reforming chamber, which are part of the fuel cell stack. The fuel cell stack comprises two porous electrodes in contact with a molten salt of lithium–potassium carbonate (LiKCO_3). It operates at approximately 650°C. At the cathode, O_2 and CO_2 are converted into carbonate ions. The electrolyte allows carbonate ions to migrate to the anode. At the anode, hydrogen reacts with carbonate ions to form water and CO_2 , and two electrons are released. Connecting the two electrodes through an external circuit completes the flow of electrons to generate DC electricity. MCFC plants can achieve an electric efficiency of 50%, which is considerably higher than that of a PAFC plant.

Fig. 6 shows a MCFC system compatible with coal-gasified fuel, and is suited for large-sized applications. There are plans to develop a 1000 kW class power generation system by 1997 [14,15]. Improvement of the performance, extension of the service life and reduction of the cost will be the priority themes for future development programs, including:

- Development of stacks: in connection with the external reforming type fuel cell, a 1000 kW stack will be developed. Small cells will be operated for the study of service life and so on. As for the internal reforming type fuel cell, a cell will be improved and operated.
- Development of balance of plant and plant system: development of the 1000 kW class power generation system will be carried out.
- Support study: technological development of stack materials and development for compatibility with coal-gasified fuel will be carried out.

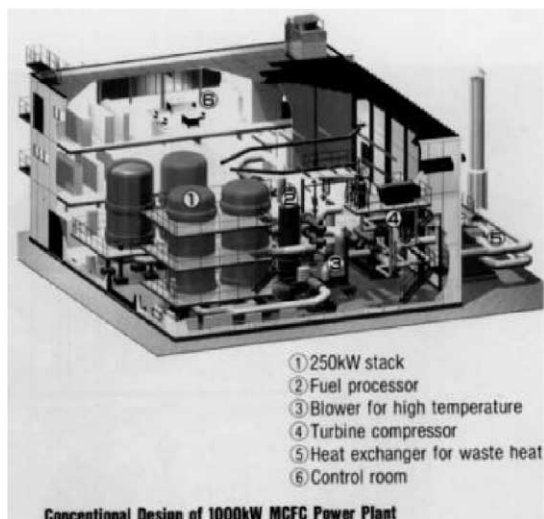


Fig. 6. An MCFC power plant [7].

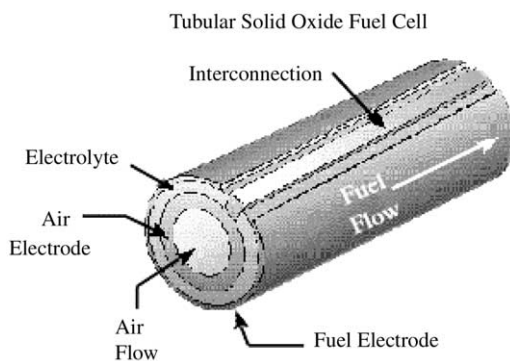


Fig. 7. Zirconia ceramic tubes are the key to Westinghouse Electric's design for a solid oxide fuel cell. Each tube (right) is made up of multiple ceramic layers bonded together. Multiple tubes can be linked (left) to form power modules that can be combined to build small generators or larger power plants [14].

(c) *Solid oxide electrolyte fuel cells (SOFCs)*. SOFCs utilize a solid oxide, usually doped zirconia, as the electrolyte (see Fig. 7). It operates at atmospheric or elevated pressures at a temperature of approximately 1000°C . At this temperature, the electrolyte material becomes sufficiently conductive to oxide ions. The temperature of exhaust gases from the cells is $500\text{--}850^{\circ}\text{C}$ (a temperature which is attractive for cogeneration applications or for use in bottoming cycles for all-electric power plants) [14].

The SOFC conducts oxygen ions (O_2) from an air electrode (cathode), where they are formed, through a solid electrolyte to a fuel electrode (anode). There, they react with CO and H_2 contained in the fuel gas to deliver electrons and produce electricity. Reformation of natural gas or other fuels containing hydrocarbons can be accomplished within

the generator, thus eliminating the need for an external reformer. Individual cells are bundled into an array of series-parallel electrically connected cells forming a semi-rigid structure that comprises the basic generator building block.

There are several features of SOFC technology that make it very attractive for utility and industrial applications. One is high tolerance to fuel contaminants. The high temperature of the reaction does not require expensive catalysts and permits direct fuel processing in the fuel cells. The solid oxide electrolyte is very stable. Because no liquid phases are present in the electrolyte, many of the problems associated with electrode flooding, electrolyte migration, and catalyst wetting are avoided. Cell components of the solid oxide electrolyte fuel cell can be fabricated into a variety of self-supporting shapes and configurations that may not be feasible with fuel cells employing liquid electrolytes.

Analyses and operations of experimental units have shown that an SOFC plant can achieve an electric efficiency of 50%. SOFC technology also has very low emissions. Because sulfur is removed from the fuel, no SO_x is emitted. The gas-impermeable electrolyte does not allow nitrogen to pass from the air electrode to the fuel electrode, hence, the fuel is oxidized in a nitrogen-free environment, averting the formation of NO_x . The temperatures of exhaust gases are not high; this also helps reduce NO_x . NO_x emissions measured at the testing plant have been fewer than 0.5 ppm [14].

(d) *Proton exchange membrane fuel cells (PEMFCs)*. These cells (membrane or solid polymer) operate at relatively low temperatures (about 90°C), have high power density, can vary their output quickly to meet shifts in power demand, and are suited for applications, particularly for automobiles (where quick startup is required). According to the U.S. Department of Energy, "they are the primary candidates for light-duty vehicles, for buildings, and potentially for much smaller applications such as replacements for rechargeable batteries". The proton exchange membrane is a thin plastic sheet that allows hydrogen ions to pass through it. The membrane is coated on both sides with highly dispersed metal alloy particles (mostly platinum) that are active catalysts. Hydrogen is fed to the anode side of the fuel cell where the catalyst encourages the hydrogen atoms to release electrons and become hydrogen ions (protons). The electrons travel in the form of an electric current that can be utilized before it returns to the cathode side of the fuel cell where oxygen has been fed. Moreover, the protons diffuse through the membrane to the cathode, where the hydrogen atom is recombined and reacted with oxygen to produce water, thus completing the overall process.

Ballard Power Systems in Vancouver, B.C., has for several years been developing a lightweight PEMFC. Fig. 8 shows a hydrogen PEMFC power system, which was developed as an early version of Ballard's fuel cell system (for details, see Refs. [16,17]). In place of phosphoric acid, PEM cells employ a thin polymer membrane as their electrolyte. By mid-1997, Ballard is planning to launch pilot fleets of a

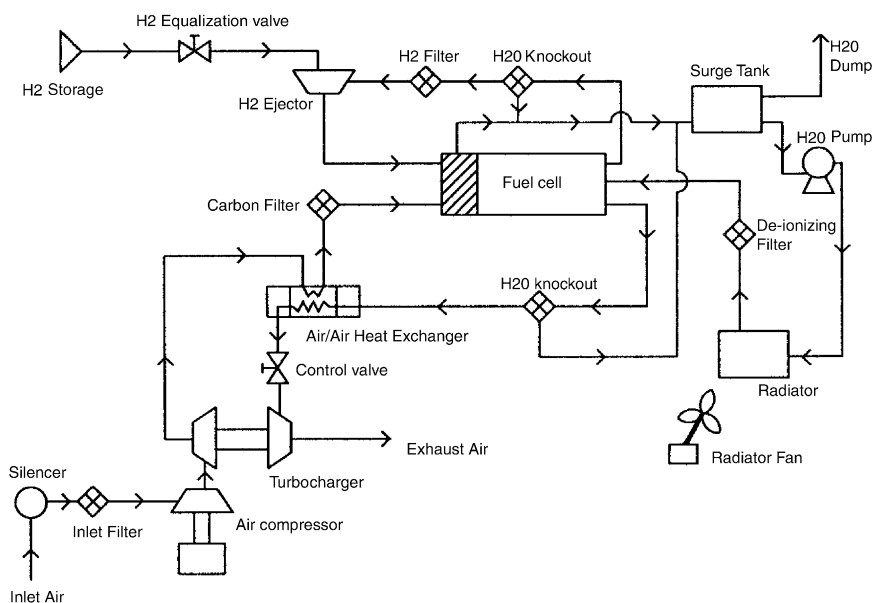


Fig. 8. A schematic of PEMFC system [17].

fuel cell-powered passenger bus in Vancouver and Chicago. The U.S. Department of Transportation is also developing fuel-cell buses.

In this category, there is also another type of fuel cell, polymer electrolyte fuel cell (PEFC). The PEFC generally operates at 80°C which makes it ideal for small applications and allows reasonably inexpensive materials to be used. Unfortunately, such a low temperature is quite near the ambient temperature which hampers disposing of excess heat. A catalyst is also required to promote the chemical reaction at the low temperatures involved. Previously, the platinum catalysts used in the stack made this type of fuel cell expensive. New techniques for coating very thin layers of catalyst on the polymer electrolyte have reduced the cost of the catalyst to around \$150 per automobile.

The PEFC is particular in that only hydrogen fuel can be used in the cell. Hydrocarbon fuels must be reformed carefully. Even small amounts of CO in the cell can poison the catalyst permanently. If a reformer is used, this also requires a few minutes warm up time. Stored hydrogen must be used in the startup phase. Such problems make the PEFC running on stored hydrogen sound better. A larger manufacturing plant running continuously has a much better chance of supplying very pure hydrogen.

Larger than 1 kW PEFCs are generally pressurized to increase the chemical reaction at the low temperatures involved. Air compression to about 3 atm or higher must be used for the fuel cell to have a reasonable power density. On small systems this results in a substantial loss of efficiency. The air compressors also add considerable complexity to

the fuel cell. On automobiles and buses two air compressors are often used. One is a turbocharger and the second is a supercharger.

(e) *Unitized regenerative fuel cells (URFCs)*. If the fuel cell is designed to operate also in reverse as an electrolyzer, then electricity can be used to convert the water back into hydrogen and oxygen (Fig. 9). This dual-function system is known as a reversible or unitized regenerative fuel cell. Lighter than a separate electrolyzer and generator, a URFC is an excellent energy source in situations where weight is a concern.

Mitlitsky et al. [18,19] developed the 50-W prototype which is a single proton-exchange membrane cell (a polymer that passes protons) modified to operate reversibly as a URFC. It uses bifunctional electrodes (oxidation and reduction electrodes that reverse roles when switching from charge to discharge, as with a rechargeable battery) and cathode-feed electrolysis (water is fed from the hydrogen side of the cell). By November 1996, the prototype had operated for 1700 ten-min charge–discharge cycles, and degradation was less than a few percent at the highest current densities. Testing will continue in a variety of forms. Larger, more powerful prototypes are expected to increase the size of the membrane and by stacking multiple fuel cells. For use on Helios, a prototype will likely provide 2–5 kW running on a 24-h charge–discharge cycle.

In a 1994 study for automotive applications, Livermore and the Hamilton Standard Division of United Technologies studied URFCs and found that compared with battery-powered systems, the URFC is lighter and provides

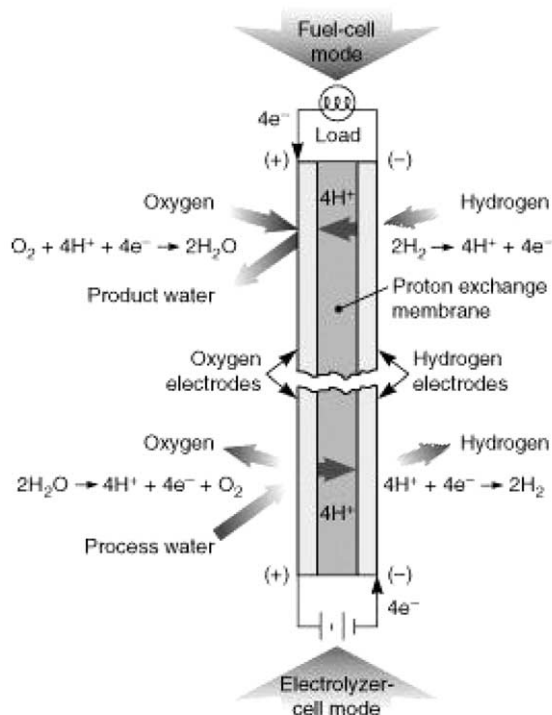


Fig. 9. Schematic illustration of the electrochemistry of a URFC [18,19]. In the fuel cell mode, a proton-exchange membrane combines oxygen and hydrogen to produce electricity and water. When the cell reverses operation to act as an electrolyzer, electricity and water are combined to produce oxygen and hydrogen.

a driving range comparable to gasoline-powered vehicles. Over the life of a vehicle, they found the URFC would be more cost effective because it does not require replacement.

In the electrolysis (charging) mode, electrical power from a residential or commercial charging station supplies energy to produce hydrogen by electrolyzing water. The URFC-powered car can also recoup hydrogen and oxygen when the driver brakes or descends a hill. This regenerative braking feature increases the vehicle's range by about 10% and could replenish a low-pressure (1.4 MPa) O_2 tank about the size of a football [16].

In the fuel-cell (discharge) mode, stored hydrogen is combined with air to generate electrical power. The URFC can also be supercharged by operating from an oxygen tank instead of atmospheric oxygen to accommodate peak power demands such as entering a freeway. Supercharging allows the driver to accelerate the vehicle at a rate comparable to that of a vehicle powered by an internal-combustion engine.

(f) *Alkaline fuel cells (AFCs)*. The alkaline hydrogen oxygen fuel cell, as shown in Fig. 10, is one of the oldest and most simple type of fuel cell. This is the type of fuel cell that has been used in space missions for some time. H_2 and O_2 are used as the fuel and oxidant. The electrodes are

made of porous carbon plates which are laced with a catalyst which is a substance that accelerates chemical reactions. The electrolyte is potassium hydroxide. At the anode, the hydrogen gas combines with hydroxide ions to produce water vapor. This reaction results in electrons that are left over. These electrons are forced out of the anode and produce the electric current. At the cathode, oxygen and water plus returning electrons from the circuit form hydroxide ions which are again recycled back to the anode. The basic core of the fuel cell consisting of the manifolds, anode, cathode and electrolyte is generally called the stack.

Long used by NASA on space missions, these cells can achieve power generating efficiencies of up to 70%. They use alkaline potassium hydroxide as the electrolyte. Until recently they were too costly for commercial applications, but several companies are examining ways to reduce costs and improve operating flexibility [20].

(g) *Direct methanol fuel cells (DMFCs)*. These fuel cells are similar to the PEMFCs in that they both use a polymer membrane as the electrolyte. However, in the DMFC, the anode catalyst itself draws the hydrogen from the liquid methanol, eliminating the need for a fuel reformer. Efficiencies of about 40% are expected with this type of fuel cell, which would typically operate at a temperature between 50°C and 90°C . Higher efficiencies are achieved at higher temperatures.

In summary, there are a number of different types of fuel cells which are being developed. The characteristics of each type are very different: operating temperature, available heat, tolerance to thermal cycling, power density, tolerance to fuel impurities, etc. These differences make each technology suitable for particular applications. They are also at very different stages of development. Some have not yet fully emerged from the laboratory. Table 1 shows the most common fuel cells and their operating temperature ranges and applications.

It is the view of the WFCC [13] that all these technologies could achieve significant market shares in competition with conventional alternatives. That is if they become technically mature on the one hand, and can be produced at costs required to be competitive for their particular application on the other. Table 2 provides a summary on the status of fuel cell technologies.

8. Exergetics

In a broader perspective (except for the zeroth and third law of thermodynamics), we can define the thermodynamics as a science of energy and exergy including a number of concepts of temperature, pressure, enthalpy, heat, work, energy, as well as entropy. Apparently, the first law of thermodynamics refers to the energy analysis which only identifies losses of work and potential improvements or the effective use of resources, e.g., in an adiabatic throttling process. However, the second law of thermodynamics, i.e.,

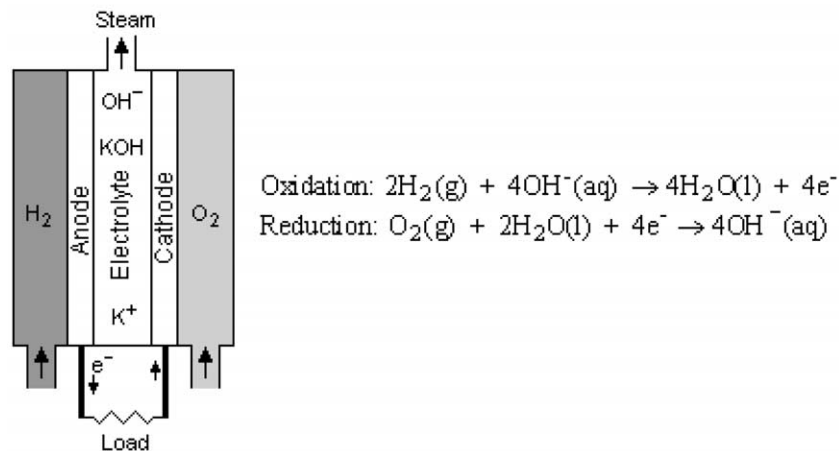


Fig. 10. Schematic of an AFC [9].

Table 1
Common fuel cells and their technical details^a

Type	Operation temperature range (°C)	Application
Solid oxide (SOFC)	500–1000	All sizes of CHP
Direct methanol (DMFC)	50–100	Buses, cars, appliances, small CHP
Polymer electrolyte (PEFC)	50–100	Buses, cars
Phosphoric acid (PAFC)	200	Medium CHP
Molten carbonate (MCFC)	600	Large CHP
Alkaline (AFC)	50–250	Space vehicles

^aSource: Wiens [21].

Table 2
Status of fuel cell technology development^a

Application	Commercial plant (available from) ^b	Fuel cell type ^c
• Commercial cogeneration (< 5 MW)	1996	Phosphoric acid (PAFC)
• Portable/backup power	1999	
• Automotive	2002	Proton exchange membrane (PEMFC)
• Commercial and residential cogeneration (< 500 kW)	2003	
• Distributed power/cogeneration	2005	
• Industrial cogeneration	2005	Molten carbonate (MCFC) and solid oxide (SOFC)
• Central generation	—	

^aSource: WFCC [13].

^bCommercial availability is defined as series production of complete system after extensive field-testing (> 20,000 h/multiple units) of early production prototypes.

^cPractical, full-scale systems have not been fully demonstrated, projected applications, sizes and availability are therefore speculative.

exergy analysis takes the entropy portion into consideration by including irreversibilities. During the past decade exergy-related studies have received tremendous amount of attention from various disciplines ranging from chemical engineering to mechanical engineering, from environmental engineering to ecology and so on. As a consequence of

this, recently, international exergy community has expanded greatly.

The exergy of a quantity of energy or a substance is a measure of its usefulness, quality or potential to cause change. Exergy appears to be an effective measure of the potential of a substance to impact the environment. In practice, the

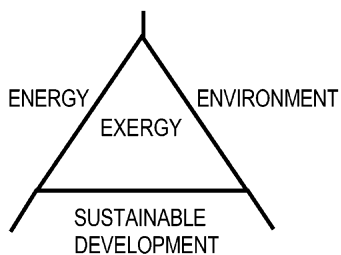


Fig. 11. The interdisciplinary triangle of exergy.

author feels that a thorough understanding of what exergy is, and how it provides insights into the efficiency and performance of energy systems, are required for the engineer or scientist working in the area of energy systems and the environment.

Here we also provide some key points to highlight the importance of the exergy and its utilization [2]: It is a primary tool in best addressing the impact of energy resource utilization on the environment.

- It is an effective method using the conservation of mass and conservation of energy principles together with the second law of thermodynamics for the design and analysis of energy systems.
- It is a suitable technique for furthering the goal of more efficient energy-resource use, for it enables the locations, types, and true magnitudes of wastes and losses to be determined.
- It is an efficient technique revealing whether or not and by how much it is possible to design more efficient energy systems by reducing the inefficiencies in existing systems.
- It is a key component in obtaining sustainable development.

Under these facts, we earlier introduced a new concept and defined exergy as a distinct discipline, because of its interdisciplinary character as the confluence of energy, environment and sustainable development (Fig. 11). Energy production, transformation, transport and use have important impacts on the earth's environment. Energy and environment policies increasingly play a prominent role in relating to a broad range of local, regional and global environmental concerns.

9. Exergy and energy

Exergy is defined as the maximum amount of work which can be produced by a system or a flow of matter or energy as it comes to equilibrium with a reference environment. Unlike energy, exergy is not subject to a conservation law (except for ideal, or reversible, processes). Rather exergy is consumed or destroyed, due to irreversibilities in any real process. The exergy consumption during a process is pro-

portional to the entropy created due to irreversibilities associated with the process. Here, Table 3 clearly compares the concepts of energy and exergy from different perspectives.

Exergy analysis is a method that uses the conservation of mass and conservation of energy principles together with the second law of thermodynamics for the analysis, design and improvement of energy and other systems. The exergy method is a useful tool for furthering the goal of more efficient energy-resource use, for it enables the locations, types, and true magnitudes of wastes and losses to be determined. In general, more meaningful efficiencies are evaluated with exergy analysis rather than energy analysis, since exergy efficiencies are always a measure of the approach to the ideal. Therefore, exergy analysis can reveal whether or not and by how much it is possible to design more efficient energy systems by reducing the inefficiencies in existing systems. Many engineers and scientists suggest that the thermodynamic performance of a process is best evaluated by performing an exergy analysis in addition to or in place of conventional energy analysis because exergy analysis appears to provide more insights and to be more useful in efficiency improvement efforts than energy analysis. Further discussions of exergy analysis for a large number of processes and systems are given elsewhere [22–44].

It is extremely important that for exergy analysis, the state of the reference environment, or the reference state, must be specified completely. This is commonly done by specifying the temperature, pressure and chemical composition of the reference environment. The results of exergy analyses, consequently, are relative to the specified reference environment, which in most applications is modelled after the actual local environment.

The exergy method of evaluating energy systems integrates the first and second laws of thermodynamics and particular environmental conditions. Exergy analysis has been discussed extensively elsewhere and applied to a wide variety of processes [22–44]. Exergy is defined as the maximum work that may be achieved by bringing a system into equilibrium with its environment. Every substance not in equilibrium with its environment has some quantity of exergy, while an object or system that is in equilibrium with its environment has, by definition, zero exergy since it has no ability to do work with respect to its environment.

10. Exergy analysis of fuel cell systems

A hydrogen fuel cell is a device that converts hydrogen and oxygen directly into electricity, water and waste heat while producing none of the noxious by-products typical of combustion processes. A single fuel cell is connected in series with other cells in a stack to provide a higher voltage. A basic hydrogen fuel cell power system is comprised of this stack together with the required ancillary components to provide the stack with the necessary reactants as well as to remove the wastes.

Table 3

The main differences between energy and exergy

Energy	Exergy
<ul style="list-style-type: none"> Is dependent on the parameters of matter or energy flow only, and independent of the environment parameters. Has the values different from zero (equal to mc^2 in accordance with Einstein's equation). Is guided by the first law of thermodynamics for all the processes. Is limited by the second law of thermodynamics for all processes (incl. reversible ones). Is motion or ability to produce motion. Is always conserved in a process, so can neither be destroyed or produced. Is a measure of quantity. 	<ul style="list-style-type: none"> Is dependent both on the parameters of matter or energy flow and on the environment parameters. Is equal to zero (in dead state by equilibrium with the environment). Is guided by the first law of thermodynamics for reversible processes only (in irreversible processes it is destroyed partly or completely). Is not limited for reversible processes due to the second law of thermodynamics. Is work or ability to produce work. Is always conserved in a reversible process, but is always consumed in an irreversible process. Is a measure of quantity and quality due to entropy.

The fuel cell stack, particularly for a PEMFC is the central component of the system — this is where the output power is generated and where the electrochemical reaction of hydrogen and oxygen takes place as follows:



It is important to mention that humidification cells for humidification of the inlet stream are used to prevent dehydration of the membranes in the fuel cell assembly.

An exergy analysis is similar to an energy analysis, but takes into account the quality of the energy as well as the quantity. Since it includes a consideration of entropy, exergy analysis allows a system to be analyzed more comprehensively by determining where in the system the exergy is destroyed by internal irreversibilities, and the causes of those irreversibilities.

The Second Law equations for the system under consideration were derived from a basic exergy balance. For any open system at steady state, an equation for the rate of exergy destruction is

$$I = \sum_i (1 - T_0/T_i) \dot{Q}_i - \dot{W}_{\text{net}} + \sum_{\text{in}} (\dot{m}\epsilon)_{\text{in}} - \sum_{\text{out}} (\dot{m}\epsilon)_{\text{out}}, \quad (2)$$

where \dot{Q}_i is the heat transfer rate crossing the system boundary at a constant temperature T_i . \dot{W}_{net} is the net work transfer rate (net power) crossing the system boundary. For a complete fuel cell system, the net work may be summation of the parasitic loads (works or energies) of various ancillary components (e.g., fuel cell, the water pump, the air compressor and the radiator fan).

The gross fuel cell stack power is

$$\dot{W}_{\text{fc}} = i v. \quad (3)$$

Here the exergy of particular flow in the above equation consists of two components in terms of thermomechanical exergy (ϵ^{tm}) and chemical exergy (ϵ^{ch}) for a given state as follows:

$$\epsilon^{\text{th}} = (h - h_0) - T_0(s - s_0), \quad (4)$$

where kinetic and potential energy effects are neglected.

$$\epsilon^{\text{ch}} = \sum_j x_j (\mu_{j0} - \mu_{j00}), \quad (5)$$

where x_j is the mole fraction of the species j in the flow, μ_{j0} is the chemical potential of species j in the flow evaluated at T_0 and P_0 , and μ_{j00} is the chemical potential of species j in the flow evaluated in the reference environment (or as if it exists in the reference environment). The chemical potential values for most materials can be found in a tabular form in some reference books (e.g., Kotas [32]).

10.1. For a PEMFC stack

In the case of the fuel cell stack (see Fig. 8), heat is transferred from the stack to the environment, and the work interaction is the gross power produced by the stack. Three mass streams flow in and out of the fuel cell: air, hydrogen, and water. For clarity, separate terms are included here to account for the water chemically produced that flows out of the fuel cell, and the chemical exergy of the hydrogen consumed by the reaction. Thus, the internal irreversibilities of the fuel cell can be written in an expanded form with an exergy balance as

$$I = (1 - T_0/T_{\text{fc}}) \dot{Q}_{\text{fc}} - \dot{W}_{\text{fc}} + \dot{m}_{\text{H}_2, \text{cons}} [(\epsilon_{\text{H}_2})_{\text{in}}]_{\text{fc}} - \dot{m}_{\text{H}_2\text{O}, \text{pr}} [(\epsilon_{\text{H}_2\text{O}})_{\text{out}}]_{\text{fc}} + [\dot{m}_{\text{air}} (\epsilon_{\text{in}} - \epsilon_{\text{out}})_{\text{air}}]_{\text{fc}} + [\dot{m}_{\text{H}_2, \text{recir}} (\epsilon_{\text{in}} - \epsilon_{\text{out}})_{\text{H}_2\text{O}, \text{recir}}]_{\text{fc}} + [\dot{m}_{\text{H}_2\text{O}, \text{recir}} (\epsilon_{\text{in}} - \epsilon_{\text{out}})_{\text{H}_2, \text{recir}}]_{\text{fc}}, \quad (6)$$

where the mass flow rate of the water used to humidify the air and hydrogen streams is assumed to be negligible, and the composition of the exhaust air from the fuel cell is assumed to be the same as that for the inlet air. This simplification will have only negligible effects on the exergy analysis results presented subsequently because the flow rate of humidification water is small and it is at near-environmental conditions (implying its specific exergy is small).

In calculating exergy flow rates for material flows, Eq. (4) was used to evaluate thermomechanical exergy and, if necessary, chemical exergy as given by Eq. (5) was then added on. Air and hydrogen were treated as ideal gases and water as an ideal liquid. The chemical exergy values for both air and water are negligible [17].

Here the exergy of the air into the system is zero since it is assumed to be at atmospheric conditions. The composition of air exiting the fuel cell is assumed to be the same as that of the environmental air, even though it is actually depleted in oxygen and rich in water vapor due to the chemical reaction occurring within the fuel cell. This compositional difference leads to the exhaust air having a small chemical exergy, which is assumed to be negligible.

10.2. Illustrative example 1

This example was taken from Cownden et al. [17] to highlight some significant exergetic aspects of fuel cells. Here are the details on the fuel cell studied [17]:

- The fuel cell is A Ballard MK5 solid polymer, or polymer electrolyte membrane fuel cell.
- The active cell area is 232.0 cm^2 .
- The specific chemical exergy of hydrogen is 235.2 kJ/kmol .
- The number of cells in the stack: 40.
- The fuel cell operating temperature: 75°C .
- The operating pressure of the fuel cell is varied linearly as a function of current density — from 1.3 atm at 0.11 amp/cm^2 to 3 atm at 1.08 amp/cm^2 . Below 0.11 amp/cm^2 , the operating pressure is equal to 1.3 atm, while above 1.08 amp/cm^2 , it is equal to 3 atm. The exergy analysis methodology was integrated into the existing hydrogen fuel cell performance model, and applied to the system with the fuel cell operating at current densities ranging from 0.054 to 1.29 amp/cm^2 .
- The environment consists of a gaseous mixture at 1 atm and 298.15 K , composed of 79% nitrogen and 21% oxygen, on a volume basis; and of liquid water at 298.15 K .

Cownden et al. [17] applied the model to one set of operating conditions, and the effect of varying the current density was studied. They made a number of assumptions

were made to simplify the analysis of the system, including:

- The fuel cell system is operating at steady state.
- A theoretical amount of hydrogen is required based on the current produced (using Faraday's constant). As well, a theoretical amount of oxygen can be calculated based on the required hydrogen. During operation, we assume that twice the theoretical amount of hydrogen and 1.75 times the theoretical amount of oxygen are supplied to the fuel cell.

10.2.1. Results

The exergy analysis of the solid polymer fuel cell system has led to a better understanding of the system. Some of the findings obtained from the exergy analysis are similar to the findings obtained from the first law analysis of the same system (e.g. the energy and exergy efficiencies for the overall system are similar), while others are markedly different (e.g. the locations and causes of the main energy losses are different than those for the main exergy losses). In particular, the exergy analysis has allowed for a more accurate and comprehensive quantification of the losses within the system. The main losses of exergy within the system are associated with exergy consumptions (or irreversibilities), and the great majority of exergy losses occur within the fuel cell stack. It is hoped that a more accurate fuel cell model that accounts for mass transport losses can be developed and incorporated into the overall system model so that the causes of the losses can be investigated in more detail, and a meaningful analysis of the effects of varying the operating parameters in the fuel cell system can be performed. The model with its exergy analysis capability is expected to provide a powerful tool for the design of fuel cell systems.

The specific results of the work of Cownden et al. [17] can be summarized as follows:

- The second law system efficiencies are very similar in magnitude to the first law efficiencies obtained from an energy analysis of the same system. It is expected, since the chemical exergy of hydrogen is very close to the lower heating value that was used in the first law analysis of the system.
- Most of the exergy entering the system either is consumed by internal irreversibilities or leaves the system with the product electricity.
- The largest irreversibilities in the system occur within the fuel cell itself. For example, at maximum net system power, 80% of the system irreversibilities occur within the fuel cell. This result is not surprising, since the fuel cell is the site of chemical reaction. The irreversibilities in the fuel cell of this model are due only to the activation overpotential, the ohmic losses within the fuel cell, and

the pressure drop of the reactant streams passing through the fuel cell.

- Further losses, due to concentration overpotential at the electrodes and other mass transport losses within the stack, are not accounted for here. Mass transport losses become particularly important in the high current density regime of the polarization curve, causing the fuel cell voltage to exponentially decrease to zero at the limiting current density.
- The substantial improvements can be made in the performance of the fuel cell system. In the fuel cell, which is the major source of irreversibilities, these could be reduced primarily by reducing the activation and ohmic overpotentials, and mass transport losses.

10.3. Some additional facts on exergy analysis of fuel cells

Here, we list some additional facts about exergy analysis of fuel cells which were summarized from the work of Standaert [45]:

- Exergy losses in high-temperature fuel cells are small.
- Overall efficiencies benefit seriously from a reduction in the amount of heat transferred in the system.
- Two fuel cells with different electrolyte, but with equal internal resistances and cell areas, may produce a different amount of power while converting the same amount of fuel and oxidant. These differences in power performances are expressed by the reversible efficiency. At a total fuel utilization of 80%, the reversible efficiency of an ER-MCFC equals 0.75 (based on a homogeneous oxidant flow of 70% air and 30% CO₂). Under the same operating conditions (except that pure air with 1% H₂O is supplied), the reversible efficiency of an ER-PCCFC equals 0.89. Hence, if both cells operate reversibly, the PCCFC generates $100 \times (89 - 75)/75 = 19\%$ more power than the MCFC. Consequently, the amount of reversibly generated heat by the MCFC will be relatively large, since both cells release the same amount of power plus heat. The relatively small heat production of a PCCFC is an extra advantage with respect to the overall system efficiency.
- Under the appropriate operating conditions, fuel cells based on the direct oxidation of alternative fuels (e.g. methanol, methane or carbon instead of hydrogen) may have a reversible efficiency larger than unity. Then heat is absorbed and converted into power simultaneously with the electrochemical conversion of fuel and oxidant. Of course, this happens without violating the second law or Carnot limitation. In principle, fuel cells are very suitable for the conversion of recovery heat from industrial processes.

10.4. Illustrative example 2

In this illustrative example, a comparative illustration of the exergy efficiencies of various types of fuel cells

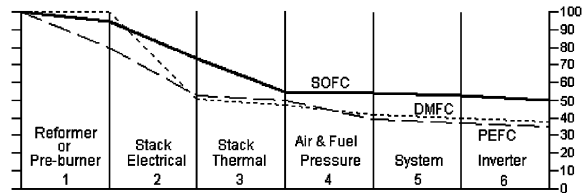


Fig. 12. Exergy efficiency diagram for proposed 30 kW AC power plants operating on hydrocarbon fuel [21].

which was taken from Wiens [21] is presented in Fig. 12. In the figure, the exergy efficiencies of three types of fuel cells are compared when operating on hydrocarbon fuel. The fuel cell process is divided into six subsystems. In each subsystem there are inefficiencies involved that reduce the exergy that is left in the system. In all cases, the electricity that is extracted is still considered to be part of the exergy of the system. It appears that the SOFC 30 kW system will have an efficiency of 1.4 times that of the PEFC and 1.3 times that of the DMFC. If Fig. 12 is examined in more detail, it is apparent that the SOFC is the most efficient largely because of the low reformer and air pressurization losses. This is because the SOFC can reform fuel inside the stack and utilize some of the stack waste thermal-energy. Because the PEFC operates at a lower temperature this is not possible. The SOFC does not need to operate at higher than ambient air pressure. It only uses a low-pressure blower to drive air through the cell. The PEFC runs at a high air pressure. In a small 30 kW power plant this pressure-energy cannot be readily recovered. The DMFC stack efficiency is very low, but because there are no reformer losses and less air pressurization and system losses, the final efficiency is still higher than the PEFC.

A more detailed breakdown of the three types of fuel cells is summarized in Table 4. In this table, for each fuel cell system there are three columns. The system efficiency shows how efficient each system is in retaining the exergy. The BEP is the amount of bound-energy produced which is equal to the loss of exergy. The ExO is the amount of exergy output that is passed on to the next subsystem.

It can be readily seen why the SOFC is the most desirable fuel cell of the three for ultimate efficiency in a fuel cell gas turbine power plant. Notice that after the electricity extraction process in the stack, there are still 82 units of exergy retained in the SOFC. The PEFC has only 51.5 units and the DMFC has only 46.8 units.

Not shown, however, is that the PEFC operating at ambient air pressure and using hydrogen as it is fuel would be the most efficient fuel cell without using a bottoming cycle such as a gas turbine. It would achieve 57% exergy efficiency, while the SOFC would be 53% and the DMFC would be 43%.

Table 4

Exergy efficiency of subsystems in 30 kW AC power plants operating on hydrocarbon fuel^a

Subsystem	SOFC			PEFC			DMFC		
	η_{ex} (%)	BEP (kW)	ExO (kW)	η_{ex} (%)	BEP (kW)	ExO (kW)	η_{ex} (%)	BEP (kW)	ExO (kW)
Hydrocarbon fuel	—	—	100.0	—	—	100.0	—	—	100.0
Reformer/burner	95.0	5.0	95.0	80.0	20.0	80.0	100.0	0.0	100.0
Stack electrical	86.0	14.0	82.0	64.0	28.5	51.5	47.0	53.2	46.8
Stack thermal	0.0	27.0	55.0	0.0	1.5	50.0	0.0	1.4	45.4
Pressurization	98.0	1.0	54.0	78.0	10.8	39.2	90.0	4.6	40.8
System	98.0	1.0	53.0	95.0	2.0	37.2	98.0	0.8	40.0
Inverter	94.0	3.0	50.0	94.0	2.2	35.0	94.0	2.5	37.5 ^b

^aSource: Wiens [21].^bAbbrev.: BEP, bound energy produced; ExO, exergy output; η_{ex} , exergy efficiency of the system (= Exergy output/exergy input).

11. Conclusions

The present study has discussed technical, environmental and exergetic aspects of hydrogen and hydrogen energy systems and presented some illustrative examples in order to highlight the importance of the exergy analysis of hydrogen energy systems. The following key concluding remarks can be drawn from this study:

- An enhanced understanding of the environmental problems relating to energy use presents a high-priority need and urgent challenge, both to allow the problems to be addressed and to ensure the potential solutions are beneficial for the economy and the energy and energy systems themselves.
- Hydrogen is one of the best alternatives as the most versatile fuel, the most efficient fuel and the safest fuel. Hydrogen energy systems, particularly fuel cells, found application in space exploration, opening new frontiers by virtue of their inherently clean, efficient, and reliable service. It is expected that fuel cells be widely used in a variety of applications ranging from transport vehicles to power generation industry.
- Exergy analysis is an effective method using the conservation of mass and conservation of energy principles together with the second law of thermodynamics that can be employed for the design and analysis of hydrogen energy systems. It is an efficient technique revealing whether or not and by how much it is possible to design more efficient energy systems by reducing the inefficiencies in existing systems.

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