MODULE 4:

Fuel Cell Technology

College of the Desert

Revision 0, December 2001

XCELLSiS
The Fuel Cell Engine Company

BALLARD

FTA
Federal Transit Administration

COLLEGE OF THE DESERT
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Valley Transportation Authority

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MODULE 4: FUEL CELL ENGINE TECHNOLOGY

CONTENTS

OBJECTIVES

At the completion of this module, the technician will understand the:

- advantages and disadvantages of fuel cells over conventional means of power production
- principles upon which fuel cells work
- operating principles and chemical reactions of different types of fuel cells
- comparative advantages and disadvantages of different kinds of fuel cells
- detailed construction of PEM fuel cells and fuel cell stacks
- effect of various parameters on PEM fuel cell performance

MODULE 4: FUEL CELL ENGINE TECHNOLOGY

Key Points & Notes

4.1 Fuel Cell Technology Use

4.1.1 History

The developments leading to an operational fuel cell can be traced back to the early 1800's with Sir William Grove recognized as the discoverer in 1839. Throughout the remainder of the century, scientists attempted to develop fuel cells using various fuels and electrolytes. Further work in the first half of the 20th century served as the foundation for systems eventually used in the Gemini and Apollo space flights. However, it was not until 1959 that Francis T. Bacon successfully demonstrated the first fully operational fuel cell.

Proton exchange membrane fuel cells were first used by NASA in the 1960's as part of the Gemini space program, and were used on seven missions. Those fuel cells used pure oxygen and hydrogen as the reactant gases and were small-scale, expensive and not commercially viable. NASA's interest pushed further development, as did the energy crisis in 1973. Since then, fuel cell research has continued unabated and fuel cells have been used successfully in a wide variety of applications.


Courtesy of Ballard Power Systems, Inc.

5 kW Fuel Cell System at NASA


Courtesy of Ballard Power Systems, Inc.

Figure 4-1 Various Proton Exchange Membrane Fuel Cell Stacks

4.1.2 Advantages of Fuel Cells

Fuel cell systems are usually compared to internal combustion engines and batteries and offer unique advantages and disadvantages with respect to them.

Fuel cell systems offer the following advantages:

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- Fuel cell systems operate without pollution when run on pure hydrogen, the only by-products being pure water and heat. When run on hydrogen-rich reformate gas mixtures, some harmful emissions result although they are less than those emitted by an internal combustion engine using conventional fossil fuels. To be fair, internal combustion engines that combust lean mixtures of hydrogen and air also result in extremely low pollution levels that derive mainly from the incidental burning of lubricating oil.
- Fuel cell systems operate at higher thermodynamic efficiency than heat engines. Heat engines, such as internal combustion engines and turbines, convert chemical energy into heat by way of combustion and use that heat to do useful work. The optimum (or "Carnot") thermodynamic efficiency of a heat engine is known to be:

$$\text{Efficiency}_{\text{MAX}} = 1 - \frac{T_2}{T_1}$$

Where:

T_1 = Absolute temperature of inlet (hot) gas (in $^{\circ}$R or K)

T_2 = Absolute temperature of outlet (cold) gas (in $^{\circ}$R or K)

This formula indicates that the higher the temperature of the hot gas entering the engine and the lower the temperature of the cold outlet gas after expansion, the higher the thermodynamic efficiency. Thus, in theory, the upper temperature can be raised an arbitrary amount in order to achieve any desired efficiency, since the outlet temperature cannot be lower than ambient.

However, in a real heat engine the upper temperature is limited by material considerations. Furthermore, in an internal combustion engine, the inlet temperature is the operating temperature of the engine, which is very much lower than the ignition temperature.

Since fuel cells do not use combustion, their efficiency is not linked to their maximum operating temperature. As a result, the efficiency of the power conversion step (the actual electrochemical reaction as opposed to the actual combustion reaction) can be significantly higher. The electrochemical reaction efficiency is not the same as overall system efficiency as discussed in Section 4.1.2. The efficiency characteristics of fuel cells compared with other electric power generating systems are shown in Figure 4-2.

Key Points & Notes

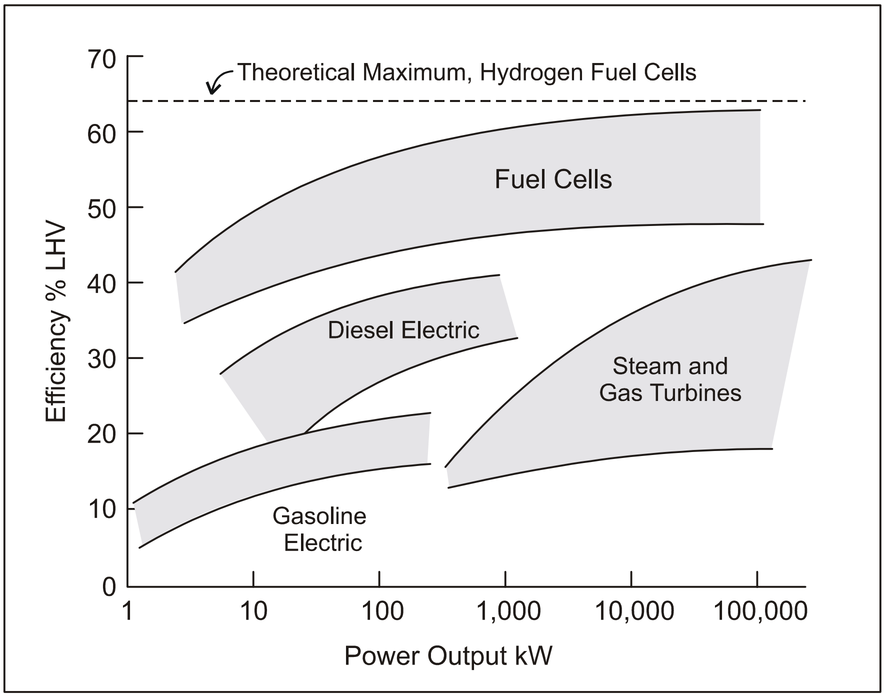


Figure 4-2 Power Generating Systems Efficiency Comparison

- In addition to having higher specific thermal efficiency than heat engines, fuel cells also exhibit higher part-load efficiency and do not display a sharp drop in efficiency as the powerplant size decreases. Heat engines operate with highest efficiency when run at their design speed and exhibit a rapid decrease in efficiency at part load.

  Fuel cells, like batteries, exhibit higher efficiency at part load than at full load and with less variation over the entire operating range. Fuel cells are modular in construction with consistent efficiency regardless of size. Reformers, however, perform less efficiently at part load so that overall system efficiency suffers when used in conjunction with fuel cells.

- Fuel cells exhibit good load-following characteristics. Fuel cells, like batteries, are solid state devices that react chemically and instantly to changes in load. Fuel cell systems, however, are comprised of predominantly mechanical devices each of which has its own response time to changes in load demand.

  Nonetheless, fuel cell systems that operate on pure hydrogen tend to have excellent overall response. Fuel cell systems that operate on reformate using an on-board reformer, however, can be sluggish, particularly if steam reforming techniques are used.

- When used as an electrical energy generating device, fuel cells require fewer energy transformations than those associated with a heat engine. When used as a mechanical energy generating device, fuel cells require an equal number of conversions, although the specific transformations are different.

  Every energy transformation has an associate energy loss so that the fewer transformations there are, the better the efficiency. Thus fuel cells are more ideally suited to applications that require electrical energy as the end product, rather than mechanical energy. Comparative energy transformations for fuel cells, batteries and heat engines are shown in Figure 4-3.

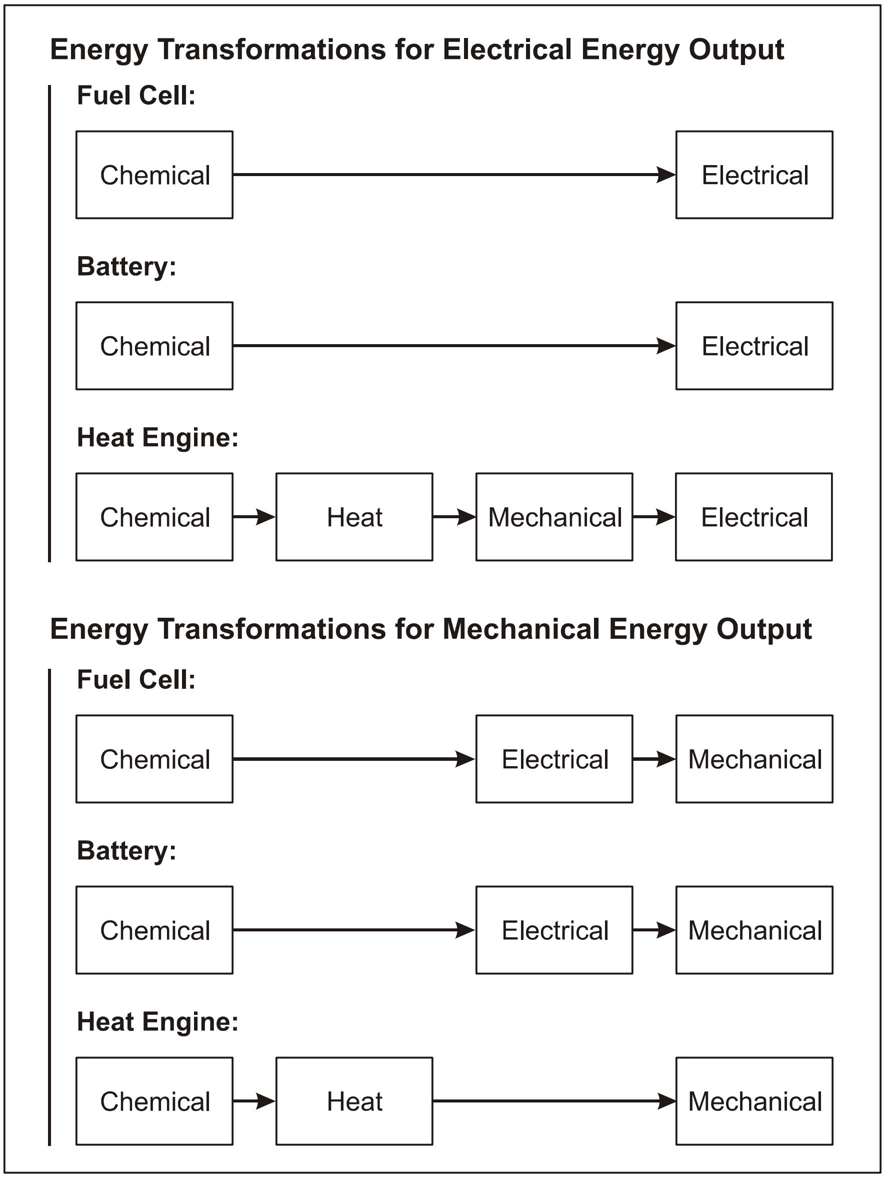


Figure 4-3 Comparative Energy Transformations

Key Points & Notes

- Fuel cell systems suitable for automotive applications operate at low temperatures (typically less than 212 °F/100 °C). This is an advantage in that the fuel cells require little warmup time, high temperature hazards are reduced, and the thermodynamic efficiency of the electrochemical reaction is inherently better. This is a disadvantage in that medium-grade waste heat is harder to expel (especially in hot climates) so that cooling systems must be larger, and the electrochemical reaction proceeds more slowly than at high temperatures. Reformers used in conjunction with fuel cells operate at high temperatures and therefore may require prolonged warmup periods.
- Fuel cell systems can be used in co-generation applications. In addition to electrical power, fuel cells generate pure hot water and medium-grade heat, both of which can potentially be used in association with domestic or industrial applications. When this is done, the overall efficiency of the combined systems increases.
- Fuel cell systems do not require tuning.
- Fuel cell systems do not require recharging. Rather, fuel cell systems must be re-fueled, which is faster than charging a battery and can provide greater range depending on the size of the storage tank.

4.1.3 Disadvantages of Fuel Cells

Fuel cell systems suffer the following disadvantages:

- Ironically, hydrogen which is of such benefit environmentally when used in a fuel cell, is also its greatest liability in that it is difficult to manufacture and store. Current manufacturing processes are expensive and energy intensive, and often derive ultimately from fossil fuels. An effective hydrogen infrastructure has yet to be established.

  Gaseous hydrogen storage systems are large and heavy to accommodate the low volumetric energy density of hydrogen. Liquid hydrogen storage systems are much smaller and lighter, but must operate at cryogenic temperatures. Alternatively, if hydrogen is stored as a hydrocarbon or alcohol and released on demand by way of an on-board reformer, the storage and handling issues simplify, but some of the environmental benefits are lost.
- Fuel cells require relatively pure fuel, free of specific contaminants. These contaminants include sulfur and carbon compounds, and residual liquid fuels (depending on the type of fuel cell) that can deactivate the fuel cell cata-

Key Points & Notes

lyst effectively destroying its ability to operate. None of these contaminants inhibit combustion in an internal combustion engine.

- Fuel cells suitable for automotive applications typically require the use of a platinum catalyst to promote the power generation reaction. Platinum is a rare metal and is very expensive.
- Fuel cells must not freeze with water inside. Fuel cells generate pure water during the power generating reaction and most fuel cells suitable for automotive applications use wet reactant gases. Any residual water within the fuel cells can cause irreversible expansion damage if permitted to freeze. During operation, fuel cell systems generate sufficient heat to prevent freezing over normal ambient temperatures, but when shut down in cold weather the fuel cells must be kept warm or the residual water must be removed before freezing. This normally entails bringing the vehicle into a heated facility or the use of a localized hot air heating device.
- Fuel cells that use proton exchange membranes must not dry out during use and must remain moist during storage. Attempts to start or operate these fuel cells under dry conditions can lead to membrane damage.
- Fuel cells require complex support and control systems. Fuel cells themselves are solid state devices, but the systems required to support fuel cell operation are not. Of particular note is the requirement for compressed air; this necessitates a high-speed compressor that imposes a large parasitic load on the overall system. System complexity increases significantly when the fuel cells are operated in conjunction with an on-board reformer.
- Fuel cell systems are heavy. Fuel cells themselves are not excessively heavy, but the combined weight of the fuel cells, their support systems and their fuel storage is presently greater than for a comparable internal combustion engine system. Systems that include an on-board reformer are heavier still. Fuel cell systems are generally lighter than comparable battery systems even though the battery systems require less support equipment. System weight will likely continue to decrease as the technology develops. Despite their weight, existing fuel cell prototype vehicles have shown that systems can be made sufficiently compact for automotive use.
- Fuel cells are an emerging technology. As with any new technology, reductions in cost, weight and size concur-

rent with increases in reliability and lifetime remain primary engineering goals.

Key Points & Notes

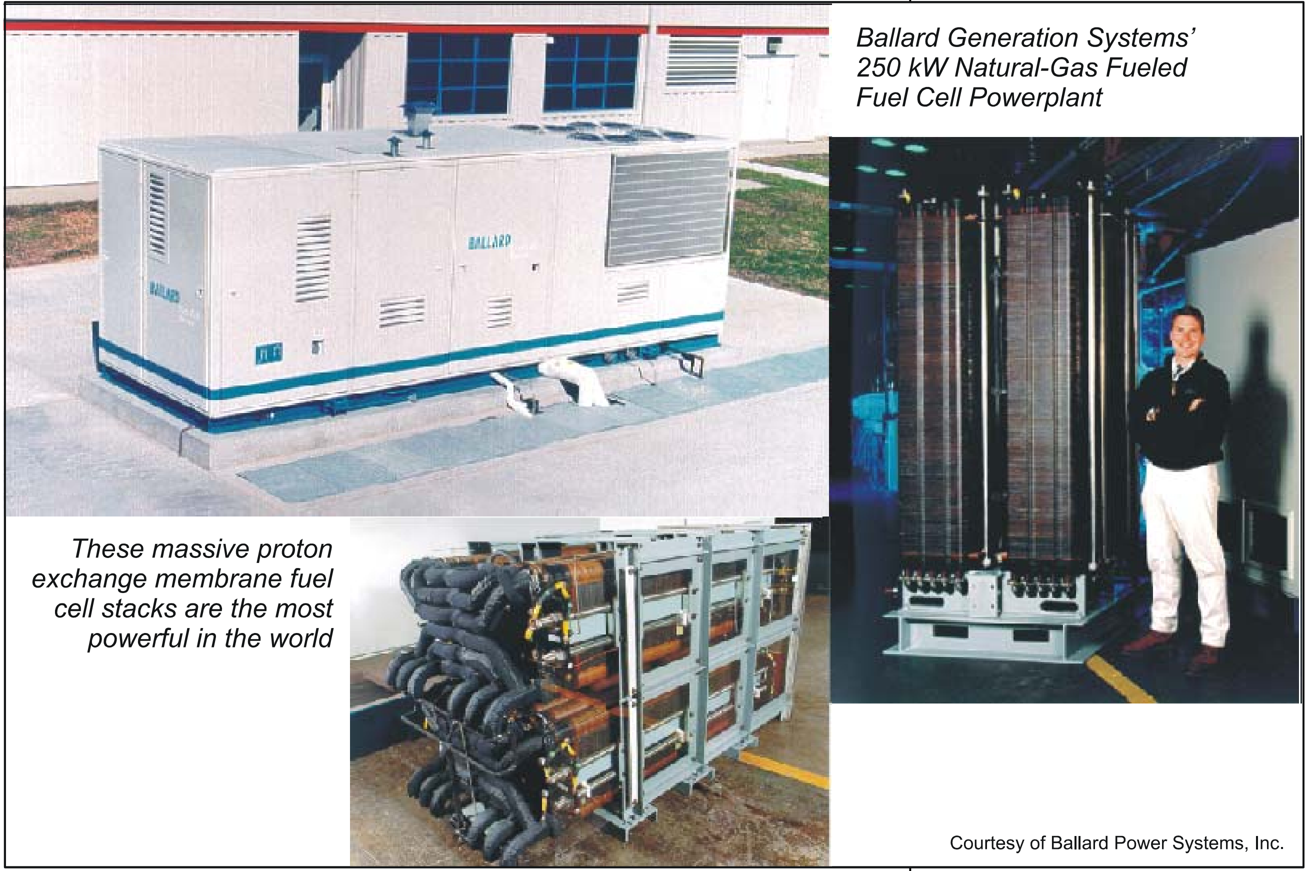
4.1.4 Applications

Fuel cells are inherently modular and therefore lend themselves to a wide range of applications, from large stationary powerplants to small portable power packs.

Stationary Powerplants

Stationary powerplant applications have been demonstrated in a number of pilot projects using a variety of fuel cell technologies over the past decades. The largest powerplant to date is the Ballard Generation Systems 250 kW natural gas fueled proton exchange membrane fuel cell powerplant currently operating at a number of sites worldwide. Although 250 kW is a small amount of power compared to conventionally powered generating stations, it is adequate to service isolated neighborhoods or to provide emergency backup power to critical facilities, such as hospitals.

Stationary powerplants are obvious candidates for operation using conventional fuels, such as natural gas, which can be piped to the powerplant and reformed on site. Overall size and warmup time are less critical issues than in smaller, mobile applications. In addition to the high operating efficiency, low emissions and good transient response characteristic of fuel cell systems, stationary applications also produce copious amounts of hot water and waste heat that can be used directly in the surrounding community, further increasing the overall system effectiveness.



Ballard Generation Systems' 250 kW Natural-Gas Fueled Fuel Cell Powerplant

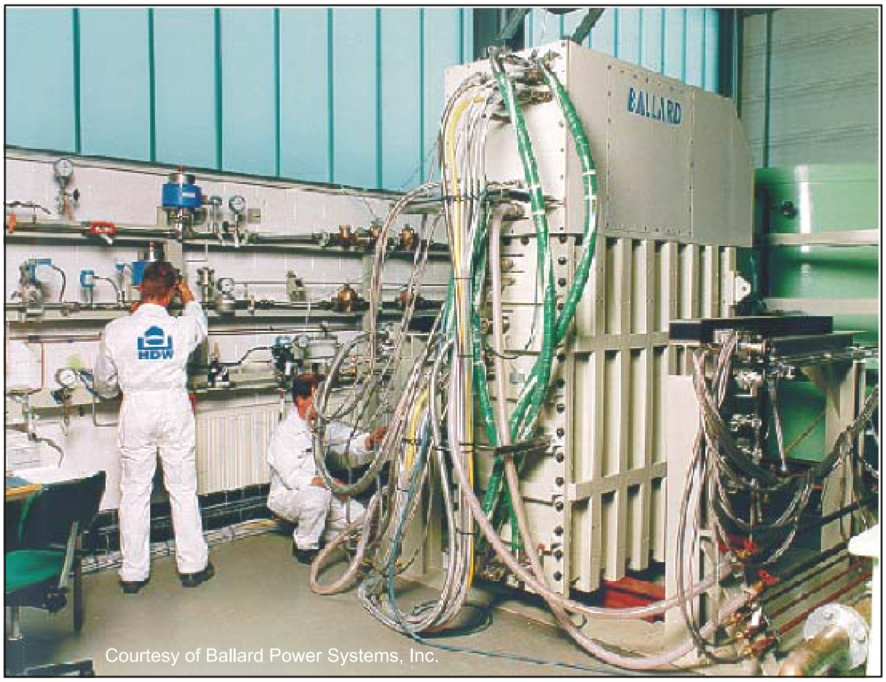
These massive proton exchange membrane fuel cell stacks are the most powerful in the world

Courtesy of Ballard Power Systems, Inc.

Figure 4-4 250 kW Stationary Fuel Cell Powerplant

Submarines

Fuel cells systems are attractive for military submarine applications due to their low noise and infrared signatures. In many ways, fuel cells are a logical replacement for the banks of batteries currently used to power many submarines. As with stationary powerplants, hot product water can be used for on-board domestic purposes. Prototype systems using pure reactants and on-board reformers have been demonstrated in recent years.



Courtesy of Ballard Power Systems, Inc.

Figure 4-5 Submarine Fuel Cell Powerplant

Key Points & Notes

This 80 kW powerplant was built by Ballard Power Systems for German submarine manufacturer Howaldtswerke-Deutsche Werft AD and operates using pure hydrogen and oxygen.

Buses

Buses are the most commercially advanced of all fuel cell applications to date. Successful demonstration programs have been carried out by XCELLSiS Fuel Cell Engines, Inc., with the introduction of three buses each in Vancouver, BC and Chicago, IL into revenue service for a period of two years, and a year-long field trial program in Palm Springs, CA. In the near future, additional buses will enter service throughout Europe and in other areas of the world. All of these buses use pure hydrogen stored as a high-pressure gas; other demonstration vehicles have used liquid fuels and incorporate on-board reformer systems.

Buses are a logical starting point for the introduction of fuel cell technology into the transportation sector for several reasons: they offer a reasonably large platform for system components and fuel storage, they can be fueled at a central fueling station, and they are regularly maintained by trained personnel.

Phase 1 Bus (1993)

Phase 2 Bus (1995)

Phase 3 Bus (1998). A fleet of six of these buses was put into revenue service in Vancouver and Chicago for 2 years.

Phase 4 Bus (2000). This bus endured desert conditions during a 1 year field trial in Palm Springs.

Courtesy of XCELLSIS Fuel Cell Engines, Inc.

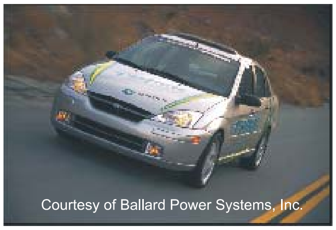
Figure 4-6 XCELLSiS Fuel Cell Bus Prototypes

Cars

Key Points & Notes

Cars represent the ultimate market for fuel cell manufacturers due to the quantities involved worldwide. While cars provide the major stimulus for fuel cell development, as they are a major contributor to air pollution, they also pose some of the greatest challenges to commercialization. These challenges include their relatively small size, the vast fueling infrastructure required, and the inconsistent maintenance habits of the public at large. In addition, performance and reliability expectations are high, while cost expectations are low.

Many major car companies are engaged in automotive fuel cell programs including Daimler-Chrysler, Ford, General Motors, Nissan, Mazda, Subaru, Toyota, Honda and Hyundai. Some of these companies have built prototype vehicles using fuel cells with or without auxiliary batteries, and fueled using either pure (gaseous or liquid) hydrogen or reformate.


Courtesy of Ballard Power Systems, Inc.

Ford TH!NK 2000 Fuel Cell Car


Courtesy of Ballard Power Systems, Inc.

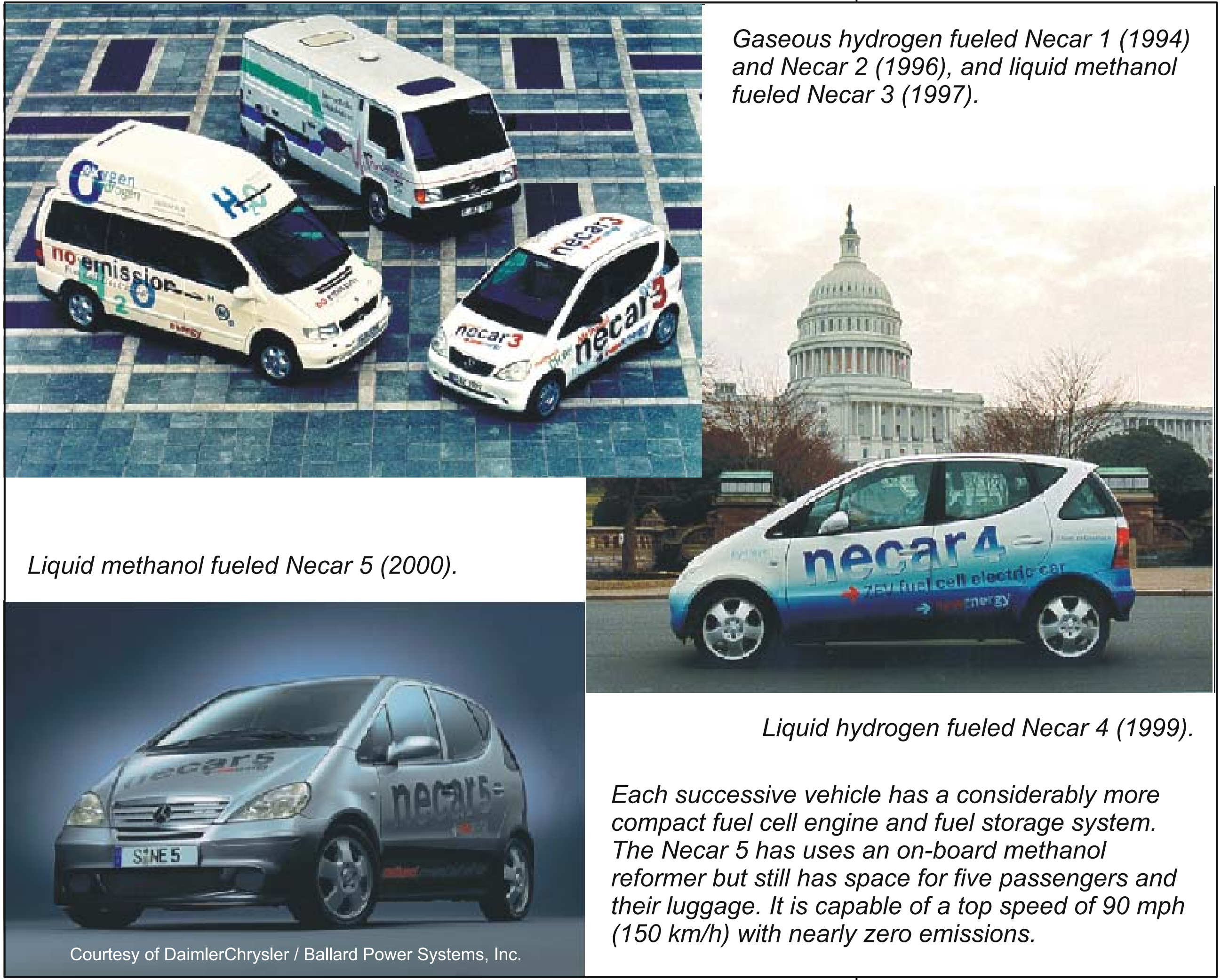
Nissan Fuel Cell Vehicle


Courtesy of Ballard Power Systems, Inc.

Honda Fuel Cell Vehicle

Lack of an existing hydrogen infrastructure is a serious deterrent to automotive fuel cell use. To this end, many current prototypes use an on-board reformer with methanol as the preferred fuel, although gasoline systems are also under investigation. Although this alleviates some of the fuel availability and storage problems, it increases the amount of hardware that must be installed in the vehicle (thereby increasing cost and complexity), and introduces control and performance problems associated with reformers. Of course, use of a reformer does not completely eliminate harmful emissions, and does little or nothing to reduce dependence on fossil fuels.

Some automotive manufacturers have made commitments to introduce fuel cell vehicles to the market in the early years of the first decade of this century. It is likely that these vehicles will make their debut within fleet operations so that fueling and maintenance issues can be minimized.



Gaseous hydrogen fueled Necar 1 (1994) and Necar 2 (1996), and liquid methanol fueled Necar 3 (1997).

Liquid methanol fueled Necar 5 (2000).

Liquid hydrogen fueled Necar 4 (1999).

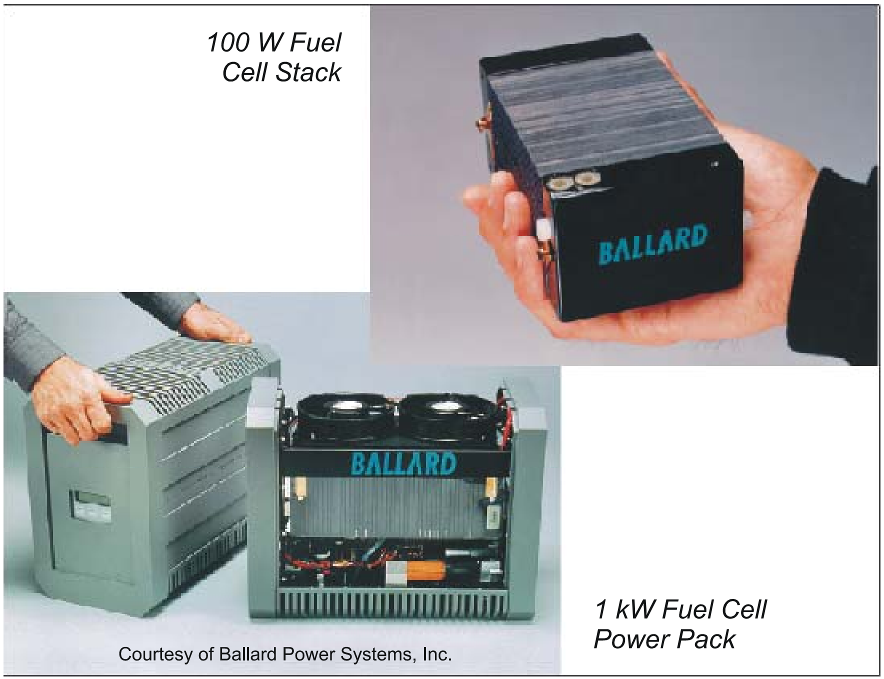
Each successive vehicle has a considerably more compact fuel cell engine and fuel storage system. The Necar 5 has uses an on-board methanol reformer but still has space for five passengers and their luggage. It is capable of a top speed of 90 mph (150 km/h) with nearly zero emissions.

Courtesy of DaimlerChrysler / Ballard Power Systems, Inc.

Figure 4-7 Daimler-Chrysler Necar Fuel Cell Vehicle Prototypes

Portable Power Systems

Portable fuel cell systems can potentially be used in many applications that currently rely on batteries. Commercial units that provide up to 1.2 kW (4100 Btuh) of electrical power are now available.



Courtesy of Ballard Power Systems, Inc.

Figure 4-8 Portable Fuel Cell Systems

4.2 Principle of Operation

Key Points & Notes

A fuel cell is an energy conversion device that converts the chemical energy of a fuel directly into electricity without any intermediate thermal or mechanical processes.

Energy is released whenever a fuel reacts chemically with the oxygen in air. In an internal combustion engine, the reaction occurs *combustively* and the energy is released in the form of heat, some of which can be used to do useful work by pushing a piston. In a fuel cell, the reaction occurs *electrochemically* and the energy is released as a combination of low-voltage DC electrical energy and heat. The electrical energy can be used to do useful work directly while the heat is either wasted or used for other purposes.

In *galvanic* (or "voltaic") cells, electrochemical reactions form the basis in which chemical energy is converted into electrical energy. A fuel cell of any type is a galvanic cell, as is a battery. In contrast, in *electrolytic* cells, electrical energy is converted into chemical energy, such as in an electrolyzer or electroplater.

A basic feature of fuel cells is that the electric current load determines the consumption rate of hydrogen and oxygen. In an actual systems application, a variety of electrical loads may be applied to the fuel cell.

4.2.1 Galvanic Cells

In principle, all galvanic cells consist of two electrodes — an anode and a cathode — and an electrolyte. The anode, or negative (fuel) electrode, is made of a substance that is readily *oxidized* (releases electrons). The cathode, or positive (oxidant) electrode, is made of a substance that is readily *reduced* (accepts electrons). When used together, the anode and cathode are two halves of a spontaneous *oxidation-reduction* reaction. In other words, the anode and cathode are at a high energy state and wish to combine to achieve a lower energy state.

For a chemical reaction to occur, the reactive elements must be in contact with each other so that electrons can be exchanged and bonds formed. If the anode and cathode are in direct contact, a reaction can occur where their surfaces touch. No useful work results as the electrons pass between the electrodes directly; all of the energy of reaction manifests itself as heat.

In order to take advantage of the available electrical energy, the electrodes must be separated in such a way that elec-

The term cathode always applies to the electrode at which reduction (a gain of electrons) takes place and the term anode always applies to the electrode at which oxidation (a loss of electrons) takes place. Thus, during operation of a fuel cell, the cathode is electrically positive and the anode is negative. During the opposite reaction of electrolysis, the cathode is electrically negative and the anode is positive. Electrons flow spontaneously from an electrically negative terminal to an electrically positive terminal.

trons can flow from the anode to the cathode through an external load while still being in some form of contact to enable the reaction to proceed. To achieve this, the anode and cathode are separated by an electrolyte.

An electrolyte is a substance that conducts *ions*. An ion is an atom or group of atoms that has acquired an electrical charge through the loss or gain of one or more electrons. Ions with a positive charge have lost one or more electrons and are known as positive ions or “cations”. Ions with a negative charge have gained one or more electrons and are known as negative ions or “anions”.

For example, when table salt (NaCl) is dissolved in water, it dissociates into a sodium cation (Na^+) and a chlorine anion (Cl^-). When an ion moves through an electrolyte, the charge moves with it. Thus, ionic movement imparts a form of conductivity to the electrolyte. Consequently salty water is more conductive than fresh water.

Although an electrolyte conducts *ions*, it does not conduct *electricity*. Electricity is the flow of free electrons such as through a metal. If the electrolyte were to conduct electricity in addition to ions, the anode and cathode would be short-circuited just as if they were in full contact. It is this duality of ionic conduction and electrical insulation that allows electrolytes to form the essential basis of all practical galvanic cells.

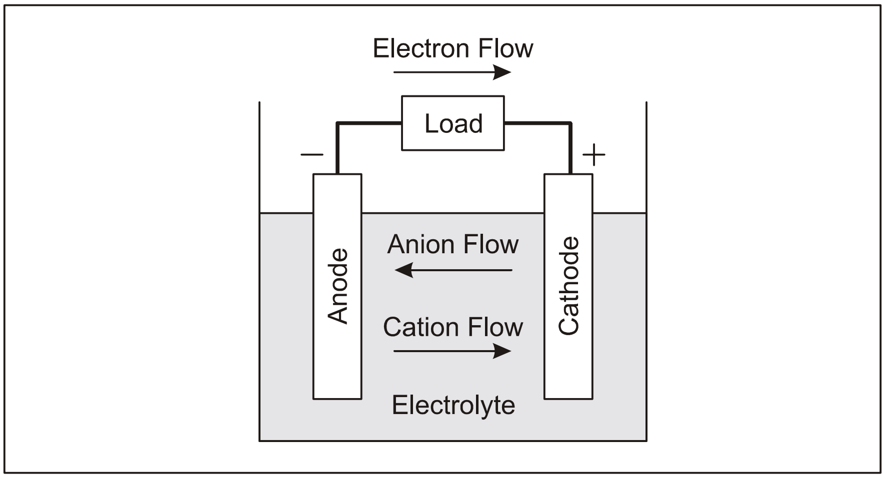


Figure 4-9 Galvanic Cell Operation

In practice, the anode material dissolves into the electrolyte forming positively charged cations and leaves behind a corresponding buildup of free electrons within the anode itself. This buildup of electrons manifests itself as a negative charge. Conversely, the cathode material has a tendency to attract positive cations that originate from either the anode (with which it reacts) or from the substance of the electrolyte itself.

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The accumulation of cations on the cathode manifests itself as a positive charge. Thus, an electrical potential exists between the cathode and the anode since the former is positively charged with respect to the latter. However, this is a static situation since the charge only builds up to a point beyond which there is insufficient chemical attraction to generate additional ions. This charge can be measured as the *open-circuit voltage* (OCV) and is a property of the chosen electrode materials and to some extent on cell temperature.

The chemical reaction between the anode and cathode cannot move to completion as long as the electrons remain trapped within the anode. These electrons are essential to the formation of the final reaction product and to the release of the reaction energy. In order to release the electrons, the electrical circuit between the two electrodes must be completed through an external flow path. If the external flow path includes a load, the electrons do useful work on their way to the cathode.

Once the anode and cathode are connected, the surplus electrons from the anode flow into the cathode, completing the chemical reaction. As the cathode loses its electron excess and therefore its negative charge, more cathode ions dissolve to produce a new excess of electrons. As the cathode gains electrons and loses its positive charge, more positive cations are attracted to the cathode.

In short, electrons flow from the anode to the cathode by way of the external load and then join the positively charged ions that migrate through the electrolyte. This flow continues until the anode is consumed, the electrolyte is unable to furnish further cations, or the load path is removed. The rate of reaction is set by the size of the load.

Overall, the net chemical change that occurs within a galvanic cell is the result of the individual reactions at the anode and the cathode, which always remain balanced in such a way that the same number of electrons are gained and lost. As the reaction completes, a reaction product compound is formed at the cathode. The reaction product depends on the chemical composition of the electrodes and can be a gas, a liquid or a solid. This product compound must be removed as it would otherwise block the reaction sites and thereby impede further reaction.

Practical galvanic cell designs often include a porous barrier between the anode and cathode. This barrier is permeable to the electrolyte but slows the ion flow and provides mechanical separation between the electrodes.

Key Points & Notes

The electrolyte is the heart of every galvanic cell. Different types of electrolytes account for fundamentally different designs of both batteries and fuel cells. Electrolytes may be liquids or solids and typically include salt, acid or alkali compounds. Regardless of their composition, electrolytes must have good ionic conductivity while being electrically non-conductive, must be non-reactive with the electrode materials, and exhibit little change in properties with changes in temperatures.

4.2.2 Fuel Cells

In a fuel cell, the fuel and the oxidant gases themselves comprise the anode and cathode respectively. Thus, the physical structure of a fuel cell is one where the gases are directed through flow channels to either side of the electrolyte. The electrolyte is the distinguishing feature between different types of fuel cells. Different electrolytes conduct different specific ions.

Electrolytes can be liquid or solid; some operate at high temperature, and some at low temperature. Low-temperature fuel cells tend to require a noble metal catalyst, typically platinum, to encourage the electrode reactions whereas high-temperature fuel cells do not. Most fuel cells suitable for automotive applications use a low temperature solid electrolyte that conducts hydrogen ions as shown in Figure 4-10.

In principle, a fuel cell can operate using a variety of fuels and oxidants. Hydrogen has long been recognized as the most effective fuel for practical fuel cell use since it has higher electrochemical reactivity than other fuels, such as hydrocarbons or alcohols. Even fuel cells that operate directly on fuels other than hydrogen tend to first decompose into hydrogen and other elements before the reaction takes place. Oxygen is the obvious choice of oxidant due to its high reactivity and its abundance in air.

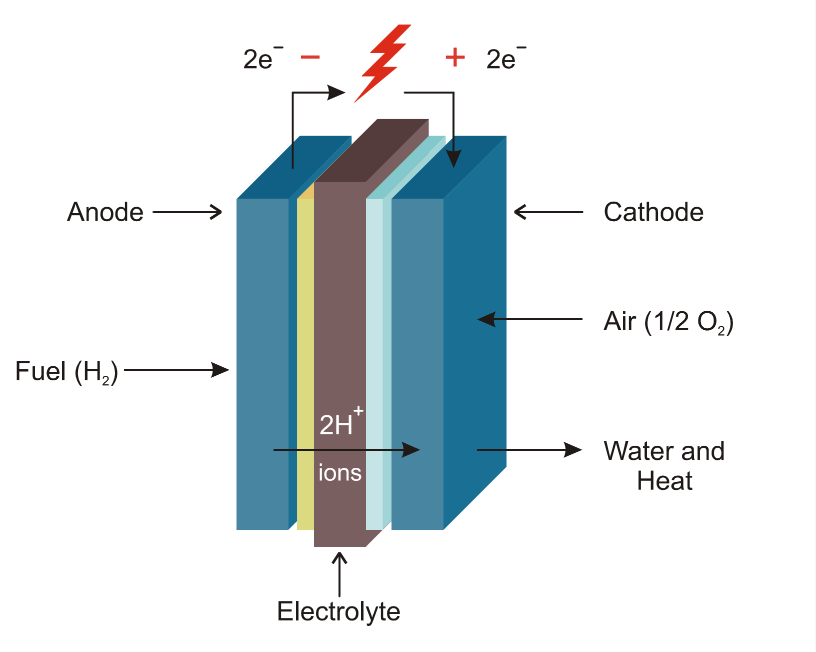


Figure 4-10 Generic Hydrogen Fuel Cell Operation

Key Points & Notes

Comparison of Fuel Cells with Batteries

Fuel cells and batteries are both galvanic cells and therefore have many similarities. Both fuel cells and batteries consist of an anode and a cathode in contact with an electrolyte. Both devices generate electrical energy by converting chemical energy from a high energy state to a lower energy state using an electrochemical reaction.

These reactions occur at the anode and cathode with electron transfer forced through an external load in order to complete the reaction. Individual cells of both batteries and fuel cells generate only small DC voltages, which are then combined in series to achieve substantial voltage and power capacities.

Fuel cells differ from batteries in the nature of their anode and cathode. In a battery, the anode and cathode are metals; zinc or lithium is typically used for the anode and metallic oxides for the cathode. In a fuel cell, the anode and cathode are composed of gases often in contact with a platinum catalyst to promote the power generating reaction. Hydrogen or a hydrogen-rich gas mixture is typically used as the anode and oxygen or air as the cathode.

Fuel cells also differ from batteries in the fundamental method in which the chemical reactants are stored. In a battery, the anode and cathode form an integral part of the battery structure and are consumed during use. Thus, a battery can only operate until these materials are fully consumed after which it must either be replaced or recharged, depending on the nature of the materials.

Key Points & Notes

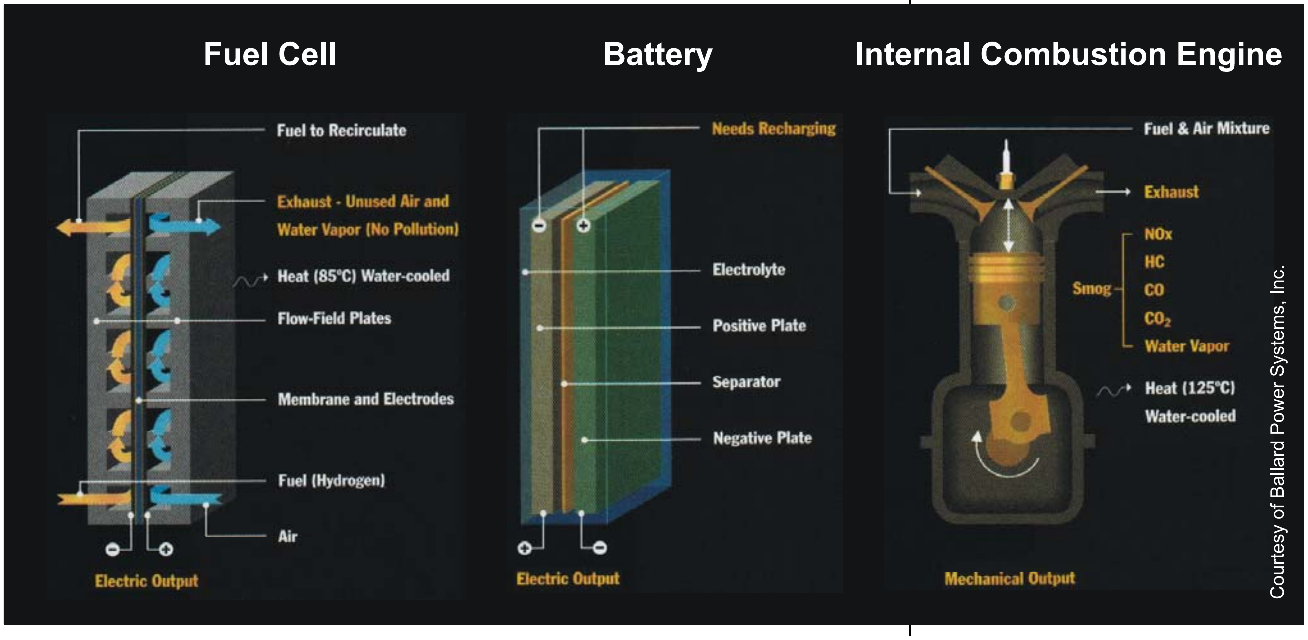
In a fuel cell, the chemical reactants are supplied from an external source so that its materials of construction are never consumed and do not need to be recharged. A fuel cell continues to operate as long as reactants are supplied and the reaction products are removed.

Comparison of Fuel Cells with Internal Combustion Engines

Fuel cells and internal combustion engines share similarities of form. Both fuel cells and internal combustion engines use gaseous fuel, drawn from an external fuel storage system. Both systems use hydrogen-rich fuel. Fuel cells use pure hydrogen or a reformate gas mixture. Internal combustion engines typically use hydrogen-containing fossil fuels directly, although they could be configured to operate using pure hydrogen.

Both systems use compressed air as the oxidant; in a fuel cell engine the air is compressed by an external compressor. In an internal combustion engine, the air is compressed internally through piston action. Both systems require cooling, although engines operate at higher temperatures than fuel cells.

In some respects, fuel cells and internal combustion engines are fundamentally different. Fuel cells react the fuel and oxidant electrochemically whereas internal combustion engines react the fuel and oxidant combustively. Internal combustion engines are mechanical devices that generate mechanical energy while fuel cells are solid state devices that generate electrical energy (although the systems used to support fuel cell operation are not solid state).



Courtesy of Ballard Power Systems, Inc.

Figure 4-11 Fuel Cell, Battery and Internal Combustion Engine Comparisons

Pollution is related to the fuel composition and the reaction temperature. Fuel cell engines operating on pure hydrogen produce no harmful emissions; those that operate on hydrogen-rich reformate produce some harmful emissions depending on the nature of the process. Internal combustion engines operating on pure hydrogen can be designed to produce almost zero harmful emissions; those that run on conventional fuels produce significantly more pollution.

4.3 Types of Fuel Cells

Key Points & Notes

Types of fuel cells differ primarily by the type of electrolyte they employ. The type of electrolyte, in turn, determines the operating temperature, which varies widely between types.

High-temperature fuel cells operate at greater than 1100 °F (600 °C). These high temperatures permit the spontaneous internal reforming of light hydrocarbon fuels — such as methane — into hydrogen and carbon in the presence of water. This reaction occurs at the anode over a nickel catalyst provided that adequate heat is always available. This is essentially a steam reforming process (see Section 2.1.2.2).

Internal reforming eliminates the need for a separate fuel processor, and can use fuels other than pure hydrogen. These significant advantages lead to an increase in overall efficiency by as much as 15%. During the electrochemical reaction that follows, the fuel cell draws on the chemical energy released during the reaction between hydrogen and oxygen to form water, and the reaction between carbon monoxide and oxygen to form carbon dioxide.

High-temperature fuel cells also generate high-grade waste heat, which can be used in downstream processes for co-generation purposes.

High-temperature fuel cells react easily and efficiently without an expensive noble metal catalyst, such as platinum. On the other hand, the amount of energy released by the electrochemical reaction degrades as the reaction temperature increases.

High-temperature fuel cells suffer from severe materials problems. Few materials can work for extended periods without degradation within a chemical environment at high temperature. Furthermore, high-temperature operation does not lend itself easily to large-scale operations and is not suitable where quick startup is required. As a result, current high-temperature fuel cells applications have focused on stationary powerplants where the efficiencies of internal reforming and co-generative capabilities outweigh the disadvantages of material breakdown and slow startup.

The most prominent high-temperature fuel cells are:

- molten carbonate
- solid oxide

Low-temperature fuel cells typically operate below 480 °F (250 °C). These low temperatures do not permit internal reforming, and therefore require an external source of hydrogen. On the other hand, they exhibit quick startup, suffer fewer materials problems and are easier to handle in vehicle applications.

The most prominent low-temperature fuel cells are:

- alkaline
- phosphoric acid
- proton exchange membrane (or solid polymer)

4.3.1 Molten Carbonate Fuel Cells

Molten carbonate fuel cells use an electrolyte that conducts carbonate (CO_3^{2-}) ions from the cathode to the anode. This is the opposite of many other types of fuel cells, which conduct hydrogen ions from the anode to the cathode.

The electrolyte is composed of a molten mixture of lithium and potassium carbonates. This mixture is retained by capillary forces within a ceramic support matrix of lithium aluminate. At the fuel cell operating temperature, the electrolyte structure is a thick paste, and the paste provides gas seals at the cell edges.

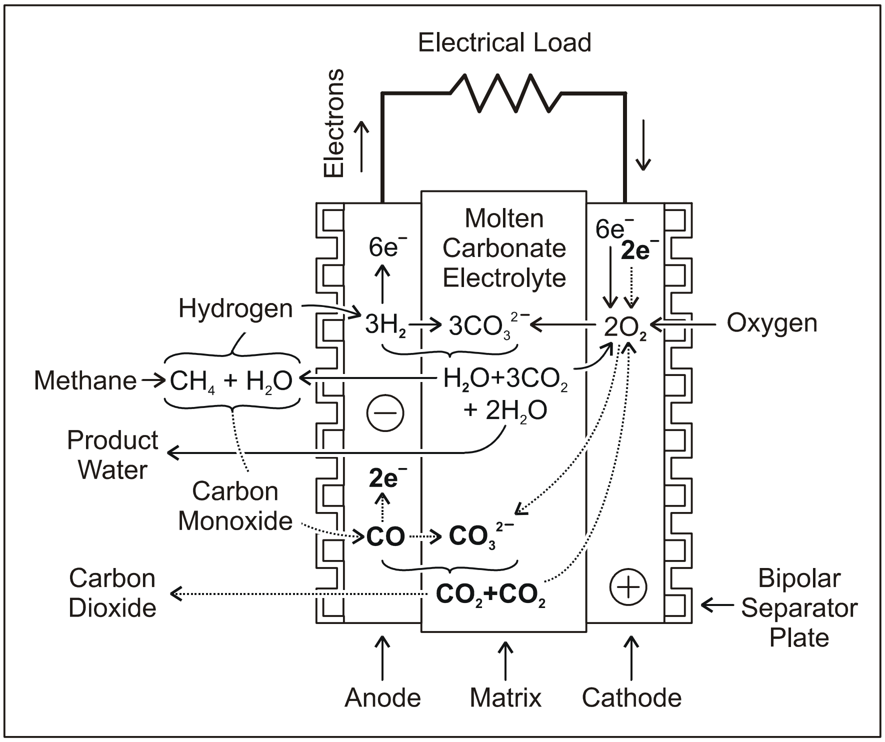


Figure 4-12 Molten Carbonate Fuel Cell

Key Points & Notes

Molten carbonate fuel cells operate at about 1200 °F (650°C) and a pressure of 15 to 150 psig (1 to 10 barg). Each cell can produce up to between 0.7 and 1.0 VDC.

Advantages and Disadvantages

The advantages of molten carbonate fuel cells are that they:

- support spontaneous internal reforming of light hydrocarbon fuels
- generate high-grade waste heat
- have fast reaction kinetics (react quickly)
- have high efficiency
- do not need noble metal catalysts

The disadvantages are that they:

- require the development of suitable materials that are resistant to corrosion, are dimensionally stable, have high endurance and lend themselves to fabrication.

  Corrosion is a particular problem and can cause nickel oxide from the cathode to dissolve into the electrolyte, loss of electrolyte, deterioration of separator plates, and dehydration or flooding of the electrodes. All of these corrosion effects result in a decline in performance, limit cell life, and can culminate in cell failure. Use of a platinum catalyst overcomes some of these problems, but eliminates an important cost-saving advantage.

  Dimensional instability can cause electrode deformation that alters the active surface area and may cause loss of contact and high resistances between components.
- have a high intolerance to sulfur. The anode in particular cannot tolerate more than 1-5 ppm of sulfur compounds (primarily H_2S and COS) in the fuel gas without suffering a significant performance loss.
- have a liquid electrolyte, which introduces liquid handling problems
- require a considerable warmup period

Reaction

Molten carbonate fuel cells can operate using pure hydrogen or light hydrocarbon fuels. When a hydrocarbon, such as methane, is introduced to the anode in the presence of water, it absorbs heat and undergoes a steam reforming reaction:

$CH_4 + H_2O \Rightarrow 3H_2 + CO$

When using other light hydrocarbon fuels, the number of hydrogen and carbon monoxide molecules may change but in principle the same products result.

The reactions at the anode are:

(1) $3H_2 + 3CO_3^{2-} \Rightarrow 3H_2O + 3CO_2 + 6e^-$	This is the hydrogen reaction and occurs regardless of fuel
(2) $CO + CO_3^{2-} \Rightarrow 2CO_2 + 2e^-$	This is the carbon monoxide reaction and occurs only when using a hydrocarbon fuel

The reaction at the cathode is:

(1) $2O_2 + 4CO_2 + 8e^- \Rightarrow 4CO_3^{2-}$	This is the oxygen reaction and occurs regardless of fuel

The CO_3^{2-} ion is drawn through the electrolyte from the cathode to the anode by the reactive attraction of hydrogen and carbon monoxide to oxygen, while electrons are forced through an external circuit from the anode to the cathode.

Combining the anode and cathode reactions, the overall cell reactions are:

(1) $2H_2 + O_2 \Rightarrow 2H_2O$	This is the hydrogen reaction and occurs regardless of fuel
(2) $CO + \frac{1}{2}O_2 \Rightarrow CO_2$	This is the carbon monoxide reaction and occurs only when using a hydrocarbon fuel

Thus, the fuel cell produces water, regardless of fuel, and carbon dioxide if using a hydrocarbon fuel. Both product water and carbon dioxide must be continually removed from the cathode to facilitate further reaction.

4.3.2 Solid Oxide Fuel Cells

Solid oxide fuel cells use an electrolyte that conducts oxide (O^{2-}) ions from the cathode to the anode. This is the opposite of most types of fuel cells, which conduct hydrogen ions from the anode to the cathode.

The electrolyte is composed of a solid oxide, usually zirconia (stabilized with other rare earth element oxides like yttrium), and takes the form of a ceramic.

Solid oxide fuel cells are built like computer chips through sequential deposition of various layers of material. Common configurations include tubular and flat (planar) designs. The designs differ in the extent of dissipative losses within cells, in the manner of sealing between the fuel and oxidant channels, and in the manner that cell-to-cell electrical connections are made in a stack of cells. Metals such as nickel and cobalt can be used as electrode materials.

Solid oxide fuel cells operate at about 1830 °F (1000 °C) and a pressure of 15 psig (1 barg). Each cell can produce between 0.8 and 1.0 VDC.

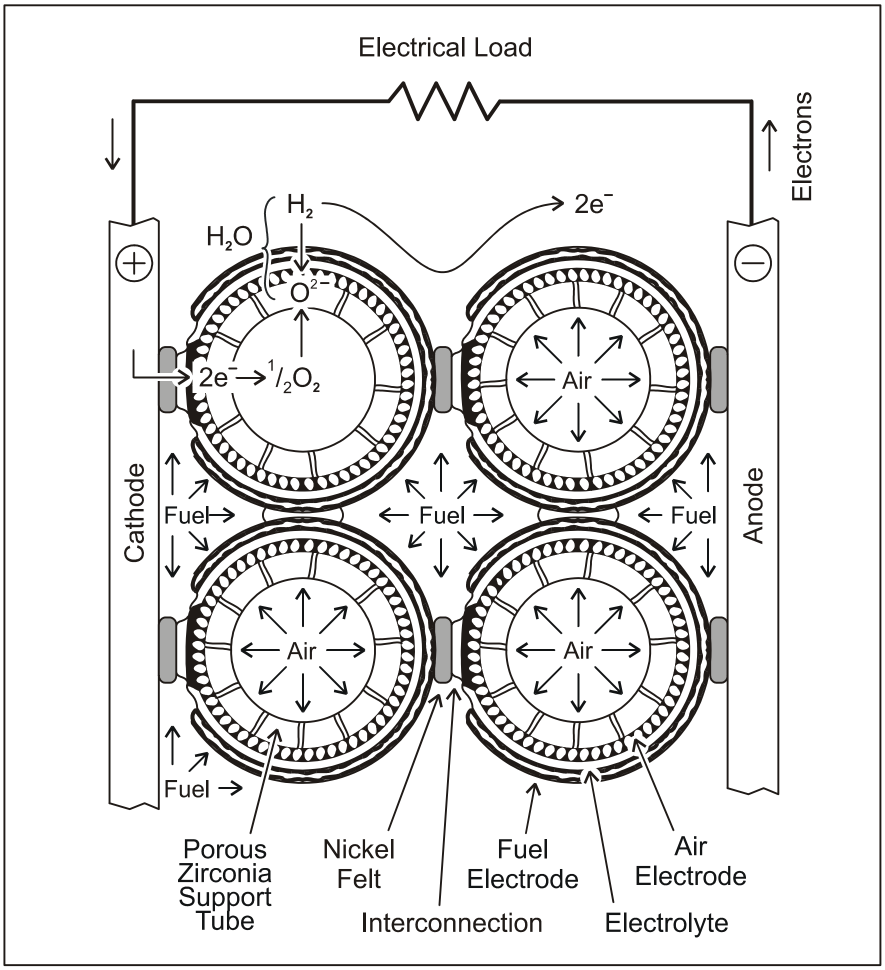


Figure 4-13 Solid Oxide Fuel Cell (Tubular Design)

Advantages and Disadvantages

The advantages of solid oxide fuel cells are that they:

- support spontaneous internal reforming of hydrocarbon fuels.

  Since oxide ions — rather than hydrogen ions — travel through the electrolyte, the fuel cells can in principle be used to oxidize any gaseous fuel.

Key Points & Notes

- operate equally well using wet or dry fuels
- generate high-grade waste heat
- have fast reaction kinetics
- have very high efficiency
- can operate at higher current densities than molten carbonate fuel cells
- have a solid electrolyte, avoiding problems associated with handling liquids
- can be fabricated in a variety of self-supporting shapes and configurations
- do not need noble metal catalysts

The disadvantages are that they:

- require the development of suitable materials that have the required conductivity, remain solid at high temperatures, are chemically compatible with other cell components, are dimensionally stable, have high endurance and lend themselves to fabrication.

  Few materials can operate at high temperatures and remain solid over long periods of time. Furthermore, the selected materials must be dense to prevent mixing of the fuel and oxidant gases, and must have closely matched thermal expansion characteristics to avoid delamination and cracking during thermal cycles.
- have a moderate intolerance to sulfur

  Solid oxide fuel cells are more tolerant to sulfur compounds than are molten carbonate fuel cells, but overall levels must still be limited to 50 ppm. This increased sulfur tolerance makes these fuel cells attractive for heavy fuels. Excess sulfur in the fuel decreases performance.
- do not yet have practical fabrication processes
- the technology is not yet mature

Reaction

Solid oxide fuel cells can operate using pure hydrogen or hydrocarbon fuels, just like molten carbonate fuel cells. This results in an inlet fuel stream comprised of hydrogen with or without carbon monoxide.

The reactions at the anode are:

(1) $H_2 + O^{2-} \Rightarrow H_2O + 2e^-$	This is the hydrogen reaction and occurs regardless of fuel
(2) $CO + O^{2-} \Rightarrow CO_2 + 2e^-$	This is the carbon monoxide reaction and occurs only when using a hydrocarbon fuel

The reaction at the cathode is:

(1) $\frac{1}{2}O_2 + 2e^- \Rightarrow O^{2-}$	This is the oxygen reaction and occurs regardless of fuel

The O^{2-} ion is drawn through the electrolyte from the cathode to the anode by the reactive attraction of hydrogen and carbon monoxide to oxygen, while electrons are forced through an external circuit from the anode to the cathode. Since the ions move from the cathode to the anode, this is the opposite of most types of fuel cells, the reaction products accumulate at the anode rather than the cathode.

Combining the anode and cathode reactions, the overall cell reactions are:

(1) $H_2 + \frac{1}{2}O_2 \Rightarrow H_2O$	This is the hydrogen reaction and occurs regardless of fuel
(2) $CO + \frac{1}{2}O_2 \Rightarrow CO_2$	This is the carbon monoxide reaction and occurs only when using a hydrocarbon fuel

Thus, the fuel cell produces water — regardless of fuel — and carbon dioxide if using a hydrocarbon fuel. Both product water and carbon dioxide must be continually removed from the cathode to facilitate further reaction.

4.3.3 Alkaline Fuel Cells

Alkaline fuel cells use an electrolyte that conducts hydroxyl (OH^-) ions from the cathode to the anode. This is opposite to many other types of fuel cells that conduct hydrogen ions from the anode to the cathode.

The electrolyte is typically composed of a molten alkaline mixture such as potassium hydroxide (KOH). The electrolyte can be mobile or immobile.

Mobile alkaline electrolyte fuel cells use a fluid electrolyte that continuously circulates between the electrodes. The product water and waste heat dilute and heat the liquid electrolyte but are removed from the cell as the electrolyte circulates.

Key Points & Notes

Immobile alkaline electrolyte fuel cells use an electrolyte that consists of a thick paste retained by capillary forces within a porous support matrix such as asbestos. The paste itself provides gas seals at the cell edges. Product water evaporates into the source hydrogen gas stream at the anode from which it is subsequently condensed. The waste heat is removed by way of a circulating coolant.

Alkaline fuel cells operate at about 150 to 430 °F (65 to 220 °C) and a pressure of about 15 psig (1 barg). Each cell can produce up to between 1.1 and 1.2 VDC.

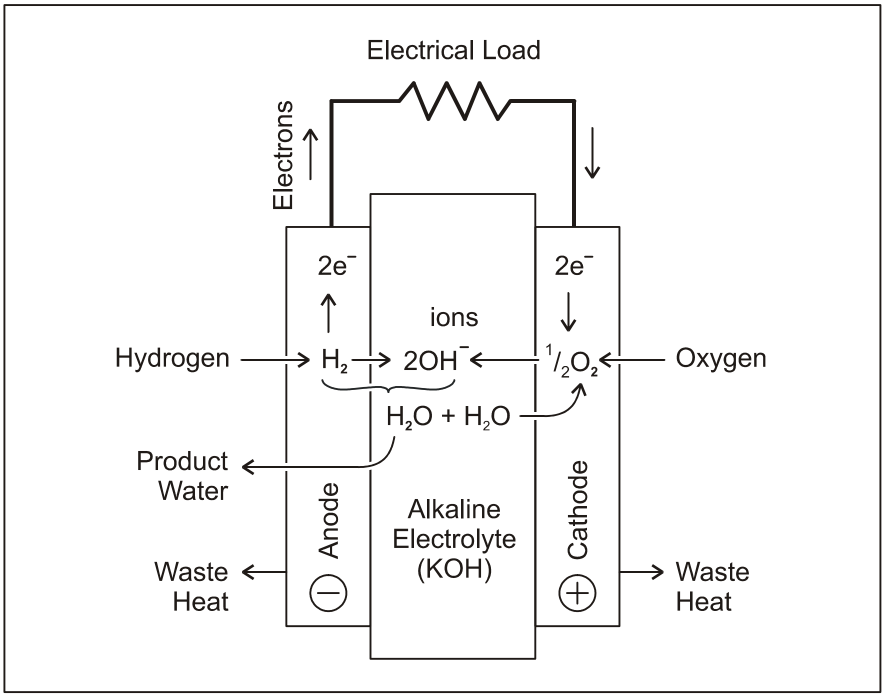


Figure 4-14 Alkaline Fuel Cell

Advantages and Disadvantages

The advantages of alkaline fuel cells are that they:

- operate at low temperature
- have fast startup times (50% rated power at ambient temperature)
- have high efficiency
- need little or no expensive platinum catalyst
- have minimal corrosion
- have relative ease of operation
- have low weight and volume

Key Points & Notes

The disadvantages are that they:

- are extremely intolerant to CO_2 (about 350 ppm maximum) and somewhat intolerant of CO

  This is a serious disadvantage and limits both the type of oxidant and fuel that can be used in an alkaline fuel cell. The oxidant must be either pure oxygen or air that has been scrubbed free of carbon dioxide. The fuel must be pure hydrogen due to the presence of carbon oxides in reformate.
- have a liquid electrolyte, introducing liquid handling problems
- require complex water management
- have a relatively short lifetime

Reaction

Alkaline fuel cells must operate using pure hydrogen free of carbon oxides.

The reactions at the anode are:

(1) $H_2 + 2K^+ + 2OH^- \Rightarrow 2K + 2H_2O$

(2) $2K \Rightarrow 2K^+ + 2e^-$

The reactions at the cathode are:

(1) $\frac{1}{2}O_2 + H_2O \Rightarrow 2OH$

(2) $2OH + 2e^- \Rightarrow 2OH^-$

The OH^- ion is drawn through the electrolyte from the cathode to the anode by the reactive attraction of hydrogen to oxygen, while electrons are forced through an external circuit from the anode to the cathode.

Combining the anode and cathode reactions, the overall cell reactions are:

(1) $H_2 + 2OH^- \Rightarrow 2H_2O + 2e^-$

(2) $\frac{1}{2}O_2 + H_2O + 2e^- \Rightarrow 2OH^-$

Thus, the fuel cell produces water that either evaporates into the source hydrogen stream (in an immobile system) or is flushed out of the cells along with the electrolyte (in a mobile system). This water must be continually removed to facilitate further reaction.

4.3.4 Phosphoric Acid Fuel Cells

Phosphoric acid fuel cells use an electrolyte that conducts hydrogen ions (H+) from the anode to the cathode. As its name implies, the electrolyte is composed of liquid phosphoric acid within a silicon carbide matrix material. (Some acid fuel cells use a sulfuric acid electrolyte.)

Phosphoric acid fuel cells operate at about 300 to 400 °F (150 to 205 °C) and a pressure of about 15 psig (1 barg). Each cell can produce up to about 1.1 VDC.

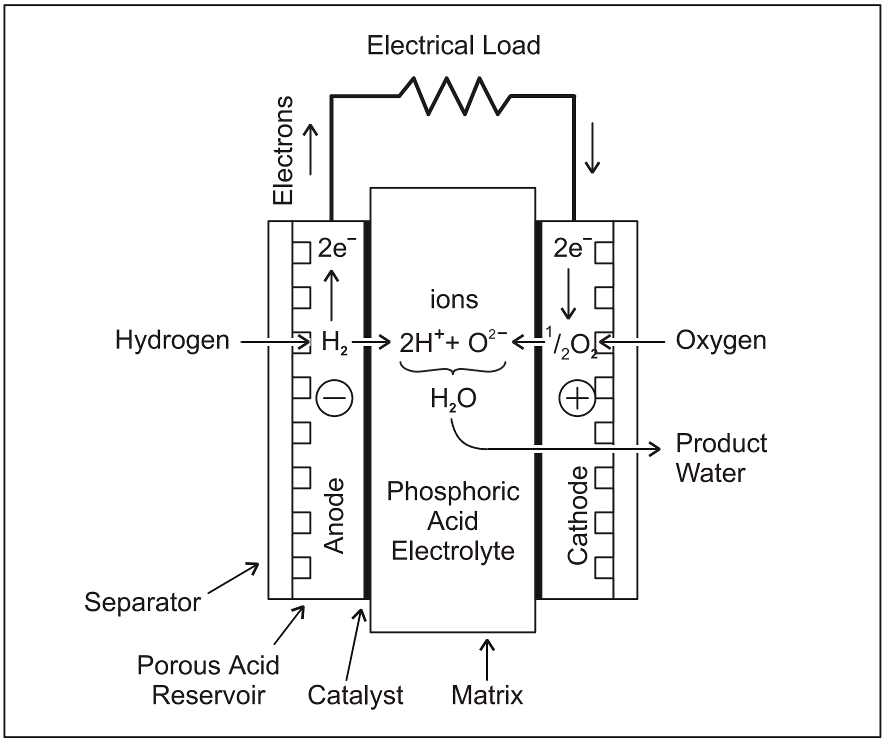


Figure 4-15 Phosphoric Acid Fuel Cell

Advantages and Disadvantages

The advantages of phosphoric acid fuel cells are that they:

- are tolerant of carbon dioxide (up to 30%). As a result, phosphoric acid fuel cells can use unscrubbed air as oxidant, and reformate as fuel.
- operate at low temperature, but at higher temperatures than other low-temperature fuel cells. Thus, they produce higher grade waste heat that can potentially be used in co-generation applications.
- have stable electrolyte characteristics with low volatility even at operating temperatures as high as 392 °F (200°C)

Key Points & Notes

A new form of acid fuel cell currently under development uses a solid acid electrolyte. These cells are made of compounds such as $CsHSO_4$ *and operate at temperatures up to 480 ºF (250 ºC) with open circuit voltages of 1.11 V. These cells offer the advantages of operation without humidity, moderate carbon monoxide tolerance, and support auto-reforming of methanol. They suffer from disadvantages of sulfur degradation, high ductility at temperatures above 257 ºF (125 ºC), and water solubility. Practical manufacturing techniques have not yet been developed.*

The disadvantages are that they:

- can tolerate only about 2% carbon monoxide
- can tolerate only about 50 ppm of total sulfur compounds
- use a corrosive liquid electrolyte at moderate temperatures, resulting in material corrosion problems
- have a liquid electrolyte, introducing liquid handling problems. The electrolyte slowly evaporates over time.
- allow product water to enter and dilute the electrolyte
- are large and heavy
- cannot auto-reform hydrocarbon fuels
- have to be warmed up before they are operated or be continuously maintained at their operating temperature

Reaction

Phosphoric acid fuel cells react hydrogen with oxygen.

The reactions at the anode are:

(1) $H_2 \Rightarrow 2H^+ + 2e^-$

The reaction at the cathode is:

(1) $\frac{1}{2}O_2 + 2e^- + 2H^+ \Rightarrow H_2O$

The H^+ ion is drawn through the electrolyte from the anode to the cathode by the reactive attraction of hydrogen to oxygen, while electrons are forced through an external circuit. Combining the anode and cathode reactions, the overall cell reaction is:

(1) $H_2 + \frac{1}{2}O_2 \Rightarrow H_2O$

Thus, the fuel cell produces water that accumulates at the cathode. This product water must be continually removed to facilitate further reaction.

4.3.5 Proton Exchange Membrane (PEM) Fuel Cells

Proton exchange membrane (PEM) (or “solid polymer”) fuel cells use an electrolyte that conducts hydrogen ions (H+) from the anode to the cathode. The electrolyte is composed of a solid polymer film that consists of a form of acidified Teflon.

PEM fuel cells typically operate at 160 to 195 °F (70 to 90 °C) and a pressure of 15 to 30 psig (1 to 2 barg). Each cell can produce up to about 1.1 VDC.

PEM fuel cells are currently the most promising type of fuel cell for automotive use and have been used in the majority of prototypes built to date. As a result, the remainder of this course will focus exclusively on PEM fuel cells.

Key Points & Notes

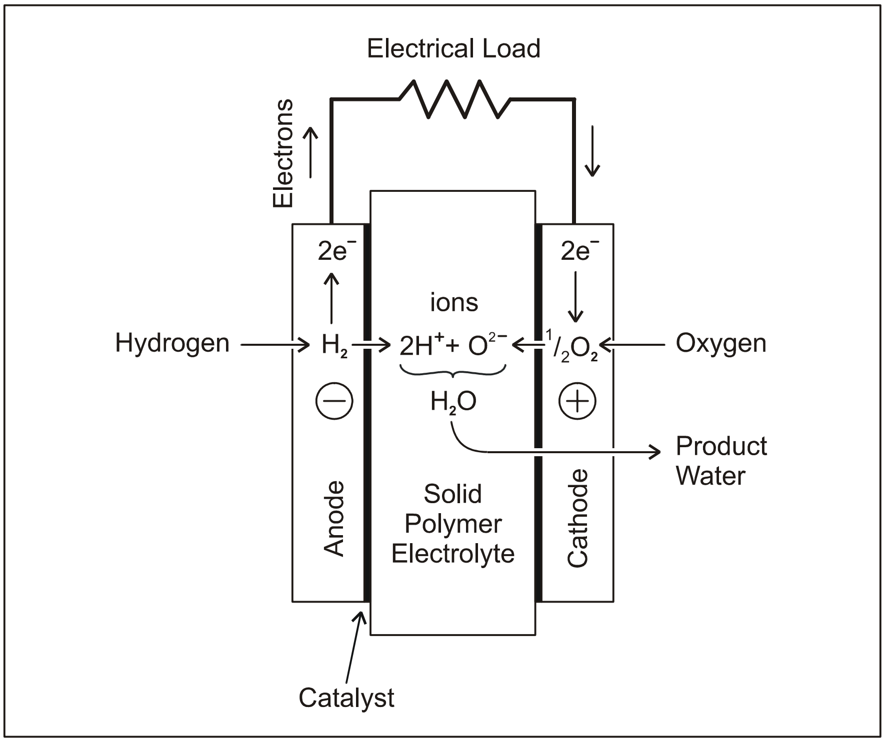


Figure 4-16 PEM Fuel Cell

Advantages and Disadvantages

The advantages of PEM fuel cells are that they:

- are tolerant of carbon dioxide. As a result, PEM fuel cells can use unscrubbed air as oxidant, and reformate as fuel.
- operate at low temperatures. This simplifies materials issues, provides for quick startup and increases safety.
- use a solid, dry electrolyte. This eliminates liquid handling, electrolyte migration and electrolyte replenishment problems.
- use a non-corrosive electrolyte. Pure water operation minimizes corrosion problems and improves safety.
- have high voltage, current and power density
- operate at low pressure which increases safety
- have good tolerance to differential reactant gas pressures
- are compact and rugged
- have relatively simple mechanical design
- use stable materials of construction

The disadvantages are that they:

- can tolerate only about 50 ppm carbon monoxide
- can tolerate only a few ppm of total sulfur compounds
- need reactant gas humidification

  Humidification is energy intensive and increases the complexity of the system. The use of water to humidify the gases limits the operating temperature of the fuel cell to less than water's boiling point and therefore decreases the potential for co-generation applications.
- use an expensive platinum catalyst
- use an expensive membrane that is difficult to work with

Key Points & Notes

Reaction

PEM fuel cells react hydrogen with oxygen.

The reactions at the anode are:

(1) $H_2 \Rightarrow 2H^+ + 2e^-$

The reaction at the cathode is:

(1) $\frac{1}{2}O_2 + 2e^- + 2H^+ \Rightarrow H_2O$

The H^+ ion is drawn through the electrolyte from the anode to the cathode by the reactive attraction of hydrogen to oxygen, while electrons are forced through an external circuit. Combining the anode and cathode reactions, the overall cell reaction is:

(1) $H_2 + \frac{1}{2}O_2 \Rightarrow H_2O$

Thus, the fuel cell produces water that accumulates at the cathode. This product water must be continually removed to facilitate further reaction.

Direct Methanol PEM Fuel Cells

PEM fuel cells can also run using methanol fuel directly, rather than hydrogen. Although the energy released during this reaction is less than when using pure hydrogen, it results in a much simpler fuel storage system and circumvents the need to produce hydrogen.

In a direct methanol PEM fuel cell, the cells are supplied with a liquid mixture of methanol and water at the anode, and air at the cathode. At 266 °F (130 °C), a noble catalyst immediately decomposes the methanol according to the reaction:

$$CH_3OH + H_2O \Rightarrow 6H^+ + CO_2 + 6e^-$$

Key Points & Notes

Oxygen, from the air, ionizes and reacts with the hydrogen to form water:

$$^3/_2O_2 + 6e^- + 6H^+ \Rightarrow H_2O$$

Combining the anode and cathode reactions, the overall cell reaction results in pure water and carbon dioxide. This technology is still in its infancy, but holds great promise for the future.

4.4 PEM Fuel Cell Stack Construction

Key Points & Notes

Individual fuel cells have an maximum output voltage on the order of 1 VDC. Substantial voltages and power outputs are obtained by connecting many cells electrically in series to form a fuel cell stack, much like a loaf of sliced bread. Different designs of fuel cell stacks use fuel cells of varying dimensions and in varying quantities.

Physically, each fuel cell consists of a membrane electrode assembly (MEA), which consists of the anode, cathode, electrolyte and catalyst, sandwiched between two flow field plates made of graphite. The plates channel the fuel and air to opposite sides of the MEA. The MEA and flow field plates are presented in greater detail in the next section.

Coolant is used to regulate the fuel cell reaction temperature. To facilitate this, cooling plates are placed between each fuel cell. These cooling plates channel the coolant past the fuel cells to absorb or supply heat as required. Seals between the graphite plates ensure that the oxidant, fuel and coolant streams never mix within the fuel cells.

Electrical endplates are placed at either end of the series of flow field plates. These endplates are connected to the terminals from which the output power is extracted, and typically include the fluid and gas interface connections. The entire sequence of plates is held together by a series of tie rods or other mechanical means.

Practical fuel cell design focuses on achieving a high power output per area of membrane, scaling the active membrane area to a useful size, and making the overall stack suitably compact for its intended use. Critical areas of concern are seals, flow field pattern tolerances and cell alignment. As with any commercial product, the resulting design must be reliable, manufacturable, economically viable and have a significant operating life.

Flow Field Plate

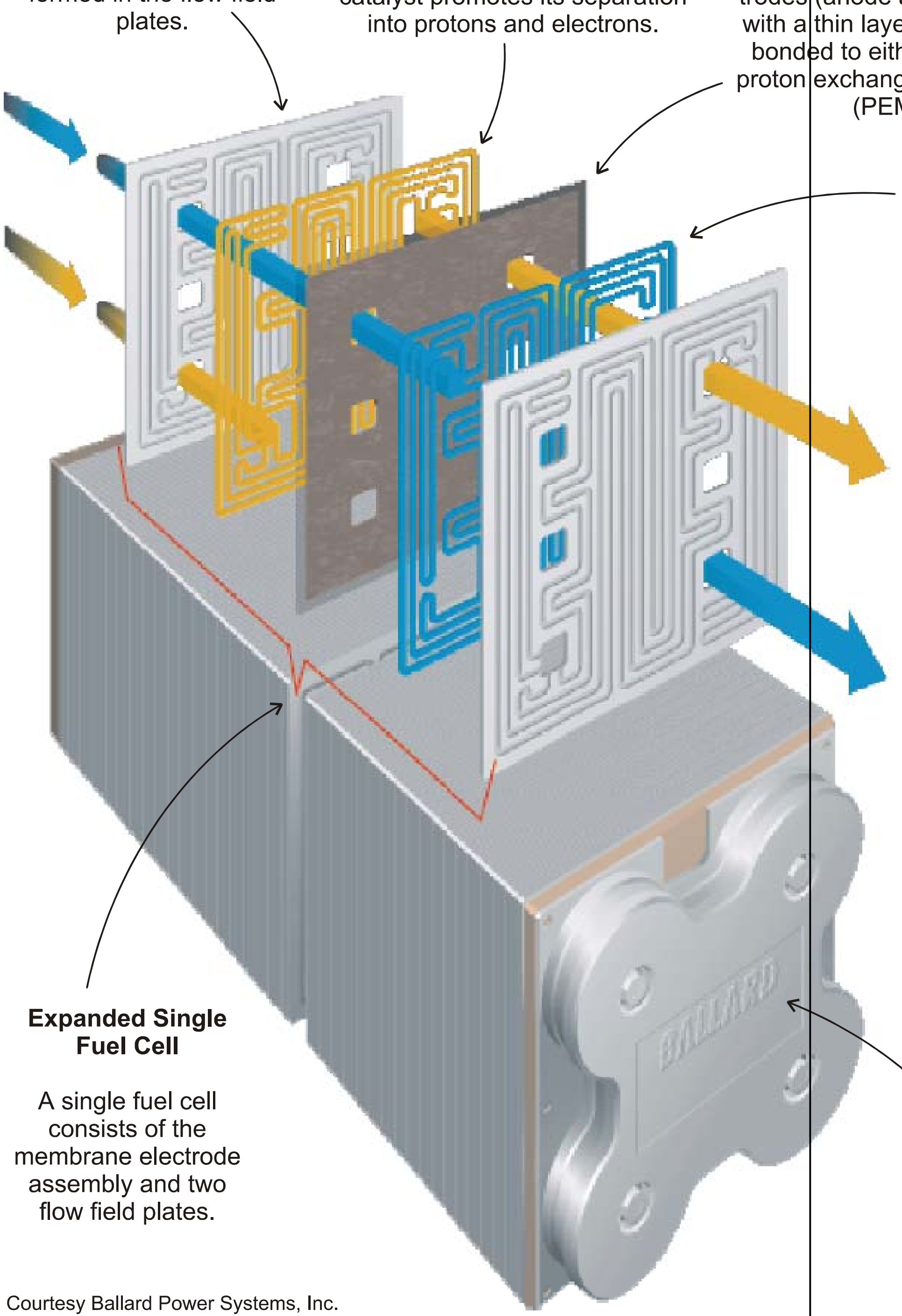
Gases (hydrogen and air) are supplied to the electrodes through channels formed in the flow field plates.

Hydrogen

Hydrogen flows through channels in the flow field plates to the anode where the platinum catalyst promotes its separation into protons and electrons.

Membrane Electrode Assembly

Each membrane electrode assembly consists of electrodes (anode and cathode) with a thin layer of catalyst, bonded to either side of a proton exchange membrane (PEM).



Air

Air flows through channels in the flow field plates to the cathode. Oxygen in the air attracts the hydrogen protons through the PEM. The air stream also removes the water created as a by-product of the electrochemical process.

Expanded Single Fuel Cell

A single fuel cell consists of the membrane electrode assembly and two flow field plates.

Completed Fuel Cell Stack

Single fuel cells are combined into a fuel cell stack to produce the desired level of electrical power.

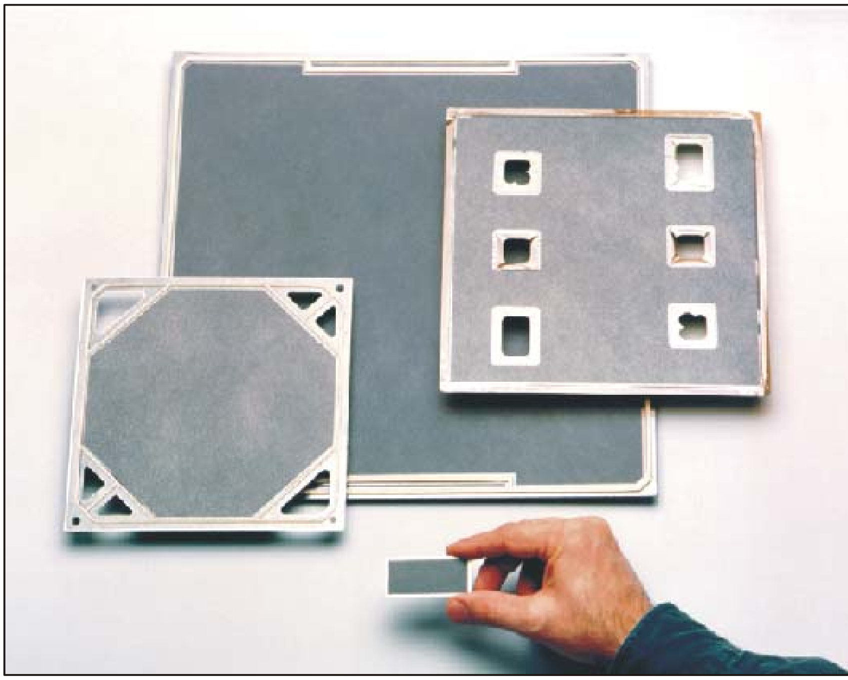
Courtesy Ballard Power Systems, Inc.

Figure 4-17 Basic PEM Fuel Cell Stack Arrangement

4.4.1 Membrane Electrode Assembly (MEA)

Key Points & Notes

The MEA is the heart of the fuel cell. The MEA consists of a solid polymer electrolyte membrane sandwiched between two porous carbon electrodes. A platinum catalyst is integrated between the membrane and the electrodes. The electrode assemblies often include integral seals where they contact adjacent components.



Courtesy of Ballard Power Systems, Inc.

Figure 4-18 PEM Membrane Electrode Assemblies

Electrodes

The electrodes provide the interface between the reactant gases and electrolyte. As such they must allow wet gas permeation, provide a reaction surface where they contact the electrolyte, be conductive to the free electrons that flow from anode to cathode, and be constructed of compatible materials. Carbon fiber paper is typically used for this purpose since it is porous, hydrophobic (non-wettable), conductive and non-corrosive. The electrode material is very thin to maximize gas and water transport.

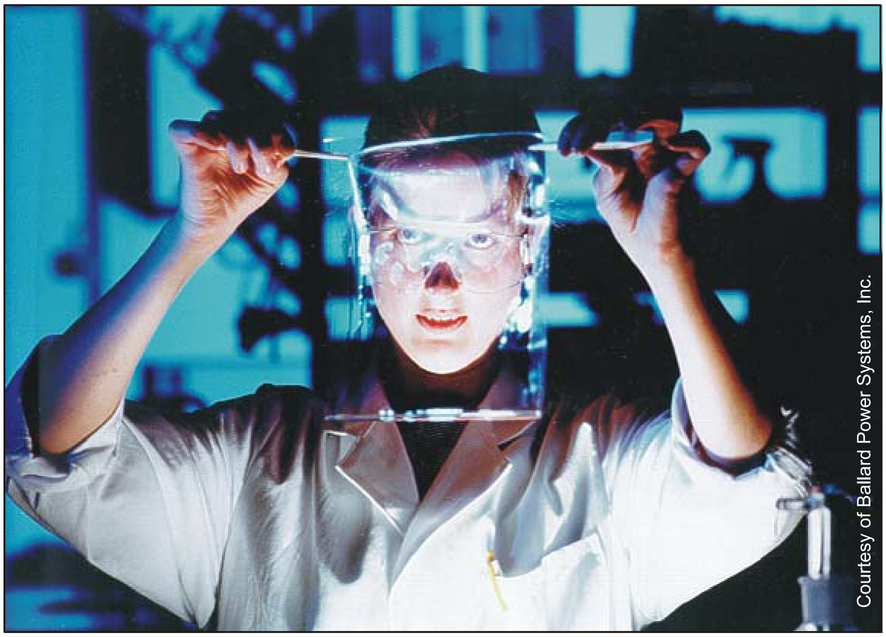
A catalyst is added to the surface of each electrode where it contacts the electrolyte in order to increase the rate at which the chemical reaction occurs. A catalyst promotes a chemical reaction by providing ready reaction sites but is not consumed in the process. Platinum is typically used for this purpose due to its high electro-catalytic activity, stability and electrical conductivity. Platinum is very expensive, so the amount used (known as the catalyst loading) is a significant factor in the cost of a fuel cell. Fuel cell designers strive to minimize the amount of platinum used while maintaining good cell performance.

Electrolyte

The solid polymer electrolyte is the ultimate distinguishing characteristic of a PEM fuel cell.

The electrolyte is a thin membrane of a plastic-like film that ranges in thickness from 50 to 175 ③m (microns). These membranes are composed of perfluorosulfonic acids, which are Teflon-like fluorocarbon polymers that have side chains ending in sulfonic acid groups ($–SO_3^{2-}$). Thus, PEM fuel cells ultimately use an acidic electrolyte just like phosphoric acid fuel cells.

All acidic solid polymer electrolytes require the presence of water molecules for hydrogen ion conductivity since hydrogen ions move together with water molecules during the ion exchange reaction. The ratio of water to hydrogen ions for effective conductivity is typically about 3:1. For this reason, the gases in contact with the membrane must be saturated with water for effective fuel cell operation.



Courtesy of Ballard Power Systems, Inc.

Figure 4-19 A Solid Electrolyte Membrane For Ballard's PEM Fuel Cells

At the molecular level, the polymer has a tubular structure in which the sulfonic acid groups are on the inner surface of the tubes. These groups provide the hydrophilic (readily wettable] conduits for conduction. The outer parts of the tubes are hydrophobic fluorinated material. The tubular structures shrink and rearrange as the water content decreases. As these tubes contract during dehydration, the conductivity drops sharply resulting in higher contact resistance between the membrane and the electrode. This can lead to cracks or holes in the membrane.

A number of commercial membranes are available such as Nafion, produced by Dupont, and others by the Dow Chemical Company. In addition, fuel cell manufacturers like Ballard Power Systems have developed their own proprietary membranes.

All electrolytes must perform the fundamental functions of being a proton conductor, an electron insulator and a gas separator. In addition, manufacturers strive to produce membranes that have reasonable mechanical strength, dimensional stability (resistance to swelling), high ionic conductivity, low equivalent weight (the weight of polymer relative to the number of acid sites), and that are easily manufacturable. To some extent, mechanical and dimensional stability of the polymer is provided through its integration into a membrane electrode assembly which adds a supporting structure.

4.4.2 Flow Field Plates

The flow field plates channel fuel and oxidant to opposite sides of the MEA.

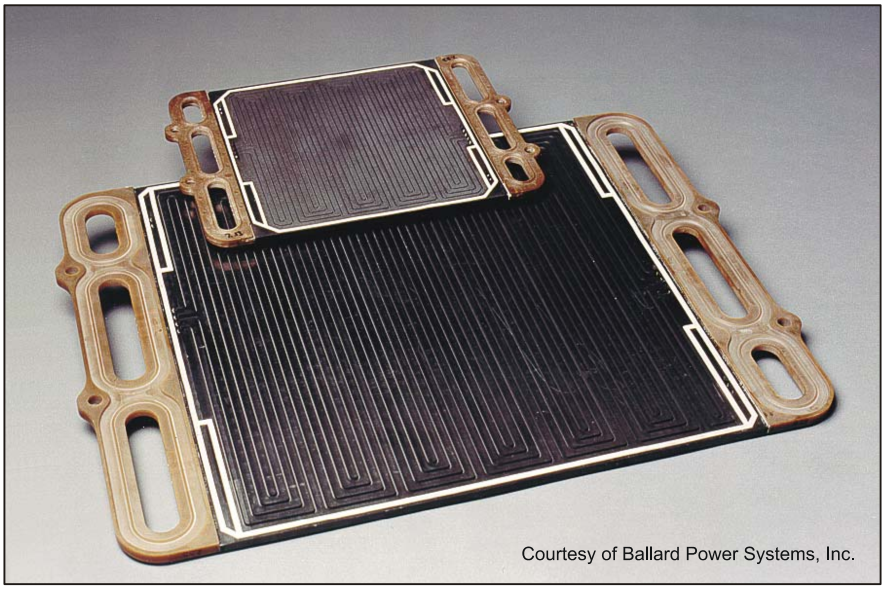
Each flow field plate contains a single gas channel of serpentine design that maximizes gas contact with the MEA. The specific shape of the gas channels is critical for uniform power generation, stable cell performance and correct product water management. Different flow field plate designs are tailored to various fuel cell applications.

Each plate must be electrically conductive so that the current released during the electrochemical reaction can flow from one cell to the next, and ultimately to the electrical endplates from which the stack power is drawn.

The plates are typically made of graphite into which the flow channels are either machined or pressed. Graphite is the preferred material due to its excellent conductivity, low contamination and relatively low cost.

Coolant plates, placed between each fuel cell, are of similar design and construction to the gas flow field plates. Coolant flow channels are designed for effective heat management.

Key Points & Notes



Courtesy of Ballard Power Systems, Inc.

Figure 4-20 PEM Flow Field Plates

Flow field and coolant plates incorporate gas and water ports used to distribute evenly the fuel, oxidant and coolant that enter and exit the stack. Seals between the graphite plates ensure that these flow streams do not mix.

Courtesy of Ballard Power Systems, Inc.

Figure 4-21 Assembling a PEM Fuel Cell Stack

4.4.3 Humidifiers

Humidification of the reactant gases is an important aspect of PEM fuel cell operation. Without adequate humidification, ion conduction cannot occur and fuel cell damage can result.

The amount of water that a gas can absorb is highly dependent on the humidification temperature — particularly at low pressure. Hotter gases can hold more water than colder gases.

Since the goal of humidification is to saturate the reactant gases with as much water as possible, the gases must be humidified at or near the fuel cell operating temperature (as set by the stack coolant temperature). If humidified at a lower temperature, the gas would no longer be saturated once it reached the operating temperature. If humidified at a higher temperature, some water would condense into the gas paths once it dropped to the operating temperature.

On some fuel cell stacks, humidifiers are integrated into the stack itself. On other fuel cell stacks, humidifiers are separate, external components.

Internal humidifiers consist of an additional series of graphite plates assembled into the fuel cell stack. This separates the stack into an active section, which contains the fuel cells, and an inactive section, which contains the humidifier plates. The humidification plates are similar to flow field plates and are used to channel gas and water to either side of a hydrophilic membrane. The water migrates across the membrane and saturates the adjacent gas. A variety of membranes are commercially available for this purpose.

Internal humidifiers draw water directly from the stack coolant stream and results in a simple, well integrated system with excellent temperature matching characteristics. However, this arrangement precludes the use of anything other than pure water as coolant. Pure water exacerbates cold weather starting problems as the cooling water would freeze. In addition, the combined stack/humidifier tends to be bulky and complicates service since both components must be repaired concurrently.

External humidifiers are most commonly of either a membrane or a contact design. Membrane humidifiers operate in the same fashion as internal humidifiers although they are packaged separately. Contact humidifiers operate by spraying humidification water onto a hot surface or into a chamber of high surface area through which one of the reactant

Key Points & Notes

gases flows. The water then evaporates directly into the gas causing it to saturate.

External humidifiers draw water either from the stack coolant stream or from a separate humidification water circuit. The advantages and disadvantages of drawing water from the coolant stream are the same as with an internal humidifier. When using a separate humidification water circuit, a stack coolant with superior low-temperature characteristics than water may be used, although the humidifier and stack temperature matching process becomes more complicated. Regardless of the water source, use of external humidifiers results in individual components that are less bulky and potentially more robust, especially on a contact design.

4.5 PEM Fuel Cell Performance

Key Points & Notes

Ballard's Mk900 fuel cell stack generates 80 kW of power from a volume of only 61 L when run on pure hydrogen.

Figure 4-22 Ballard's State-of-the-Art Mk900 PEM Fuel Cell Module

4.5.1 Efficiency

The efficiency of fuel cells is often touted as one of the primary benefits of the technology. Although this is true in principle, it is important to distinguish between *fuel cell stack* efficiency and *fuel cell system* efficiency.

Fuel Cell Stack Efficiency

Fuel cell stack efficiency is commonly taken to mean the actual efficiency of the electrochemical reaction. This efficiency can be derived as follows.

The amount of energy released when hydrogen and oxygen combine to form water according to the reaction $H_2 + \frac{1}{2}O_2 \Rightarrow H_2O$ is quantified as the "enthalpy of reaction" (ΔH°). This value is measured experimentally and depends on whether the water is formed as a gas or a liquid. For fuel cells, the water forms as a gas and the enthalpy of reaction is known to be:

$$\Delta H^\circ_{(gas)} = -230 \frac{\text{BTU}}{\text{mole}_{\text{Water}}} = -242 \frac{\text{kJ}}{\text{mole}_{\text{Water}}}$$

Where:

$\text{mole}_{\text{Water}} = 6.023 \times 10^{23}$ molecules of water

The negative sign denotes that the energy is released during the reaction, and not absorbed.

Key Points & Notes

This value of the enthalpy of reaction is only strictly correct at 77 °F (25 °C) and 1 atmosphere. The effect of temperature is more significant than pressure, and the amount of released energy decreases as the temperature goes up. This change in available energy only varies by a few percent within PEM fuel cell operating temperatures, but can be as much as 30% lower for high-temperature fuel cells. For this reason, high-temperature fuel cells are inherently less powerful than low-temperature fuel cells.

Unfortunately, not all of the enthalpy of reaction is available to do useful work. A portion of the enthalpy adds to the disorder of the universe in the form of entropy and is lost; the remainder is known as the "Gibbs free energy" (ΔG°). For gaseous water (at 77 °F/25 °C and 1 atmosphere) this is known to be:

$$\Delta G^\circ_{(gas)} = -217\,\frac{\text{BTU}}{\text{mole}_{\text{Water}}} = -229\,\frac{\text{kJ}}{\text{mole}_{\text{Water}}}$$

The voltage of each cell ($\mathcal{E}_{\text{Cell}}$) is related to the Gibbs free energy according to the equation:

$$\mathcal{E}_{\text{Cell}} = -\frac{\Delta G^\circ}{n\,\mathcal{F}}$$

Where:

n = Number of electrons involved in the reaction. This is most conveniently expressed as "mole of electrons" (or mole e^-) where each mole e^- is equal to 6.023×10^{23} electrons.

From the anode and cathode reactions ($H_2 \Rightarrow 2H^+ + 2e^-$ and $\frac{1}{2}O_2 + 2e^- + 2H^+ \Rightarrow H_2O$), two electrons are involved in the formation of each water molecule. Thus, n = 2 mole e^- for every 1 $\text{mole}_{\text{Water}}$ formed.

$\mathcal{F}$ = Faraday's constant, equal to 96,500 coulombs/mole e^-. Coulombs are a unit of electric charge.

Substituting values into the equation (using imperial units):

$$\mathcal{E}_{\text{Cell}} = -\frac{-217\,\cancel{\text{BTU}}}{\cancel{\text{mole}_{\text{Water}}}} \times \frac{1055.7\ \text{J}}{\cancel{\text{BTU}}} \times \frac{\cancel{\text{mole}_{\text{Water}}}}{2\,\cancel{\text{mole e}^-}} \times \frac{\cancel{\text{mole e}^-}}{96{,}500\ \text{coul}}$$

$$= \frac{1.187\ \text{J}}{\text{coul}} = 1.187\ \text{V}$$

The amount of hydrogen and oxygen consumed is directly related to the operating current:

- *$0.43\ in^3$ ($7.0\ cm^3$) of hydrogen are consumed per minute per ampere per cell*
- *$0.21\ in^3$ ($3.5\ cm^3$) of oxygen are consumed per minute per ampere per cell*

Actual gas flow rates may be higher depending on stoichiometry and dilution of the fuel and oxidant with non-reactive gases.

Similarly, using metric units:

$$\mathcal{E}_{\text{Cell}} = -\frac{-229\ \cancel{\text{kJ}}}{\cancel{\text{mole}_{\text{Water}}}} \times \frac{1000\ \text{J}}{\cancel{\text{kJ}}} \times \frac{\cancel{\text{mole}_{\text{Water}}}}{2\ \cancel{\text{mole e}^-}} \times \frac{\cancel{\text{mole e}^-}}{96{,}500\ \text{coul}}$$

$$= \frac{1.187\ \text{J}}{\text{coul}} = 1.187\ \text{V}$$

Thus each cell can generate a maximum theoretical voltage of 1.187 V (at 77 °F/25 °C and 1 atmosphere). The fuel cell efficiency is therefore simply the proportion of the actual voltage the cell produces with respect to this theoretical maximum:

$$\text{Efficiency}_{\text{Cell}} = \frac{V_{\text{Actual}}}{\mathcal{E}_{\text{Cell}}} \cong \frac{V_{\text{Actual}}}{1.2\ \text{V}}$$

For a real fuel cell, typical voltages are between 0.5 and 0.6 V at normal operating loads and can reach 1.1 V at open circuit conditions. The electrochemical efficiency is therefore typically between approximately 40 and 50% with open circuit conditions reaching 90%.

Fuel Cell System Efficiency

Fuel cell system efficiency relates to the overall performance of a fuel cell powerplant.

A fuel cell stack can only operate if provided with pressurized air and hydrogen and flushed with coolant. Practical fuel cell systems require additional equipment to regulate the gas and fluid streams, provide lubrication, operate auxiliary equipment, manage the electrical output and control the process. Some systems include reformers for fuel processing. All of this equipment introduces losses and reduces the total efficiency of the system from its theoretical ideal.

In order to make meaningful efficiency comparisons between fuel cell and other power generating systems, each powerplant must be defined in a similar way.

When comparing a fuel cell powerplant to an internal combustion engine for an automotive application, it is convenient to define each as a device that inputs fuel and air and delivers mechanical output power to a driveshaft. In either case, fuel is drawn from a tank in either gaseous or liquid form that has been stored after refining or other processing.

Both systems compress atmospheric air; the internal combustion engine uses piston action whereas the fuel cell powerplant uses an external compressor. The internal combustion engine delivers mechanical power to the driveshaft directly while the fuel cell powerplant uses an inverter and electric motor. Both systems reject waste heat to the ambient surroundings using a coolant pump, radiator and other heat management equipment. Both systems supply equal auxiliary vehicle loads.

The overall efficiency of an internal combustion engine is often quoted as between 15 and 25%. These values are representative of the output efficiency at the *wheels* of a vehicle; efficiencies at the *output of the flywheel* are more typically between 30 to 35% and even higher for diesel engines.

For a fuel cell powerplant operating on pure hydrogen, the comparable efficiency breakdown at the *output of the flywheel* is roughly as follows:

Fuel cell efficiency:	40 to 50%
Air compression:	85% (uses 15% of gross power)
Inverter efficiency:	95%
Electric motor efficiency:	97%

Multiplying each of these values together yields an overall system efficiency of roughly 31 to 39%.

For a fuel cell system that operates using a reformer, these efficiencies are further reduced by 65 to 75% (depending on the type of reformer) for an overall system efficiency of roughly 20 to 29%.

More difficult to quantify is the effect of overall system weight. Fuel cell systems (including fuel storage) are heavier than internal combustion engine systems of comparable power and range, and therefore use more power on an ongoing basis.

Batteries have electrochemical efficiencies comparable to fuel cells. When used as an automotive powerplant, battery systems also require an inverter and electric motor, although they do not require air compression, complex cooling equipment or reformers. Batteries as a means of power storage are heavier than fuel cells although this is offset somewhat by the elimination of other components.

When stepping back further, the source of fuel becomes an essential component of the overall efficiency. With an internal combustion engine, this usually involves refining hydrocarbon fuels. With a fuel cell, this involves producing hydrogen from fossil fuels or through water electrolysis, or the production of secondary fuels such as methanol for use with an on-board reformer. With a battery system, this involves a source of electrical power for charging.

Analysis of these factors is complex and depends on the source fuel, processing method, handling and transportation difficulty, and other factors such as the energy required to compress or liquefy the final fuel. In the end, these factors reduce the overall fuel cost although this cost may not take into account the cost associated with long-term damage of the environment.

4.5.2 Polarization Characteristics

In an ideal world, the theoretical optimum fuel cell voltage of 1.2 V would be realized at all operating currents. In reality fuel cells achieve their highest output voltage at open circuit (no load) conditions and the voltage drops off with increasing current draw. This is known as polarization and is represented by a polarization curve as shown in Figure 4-23.

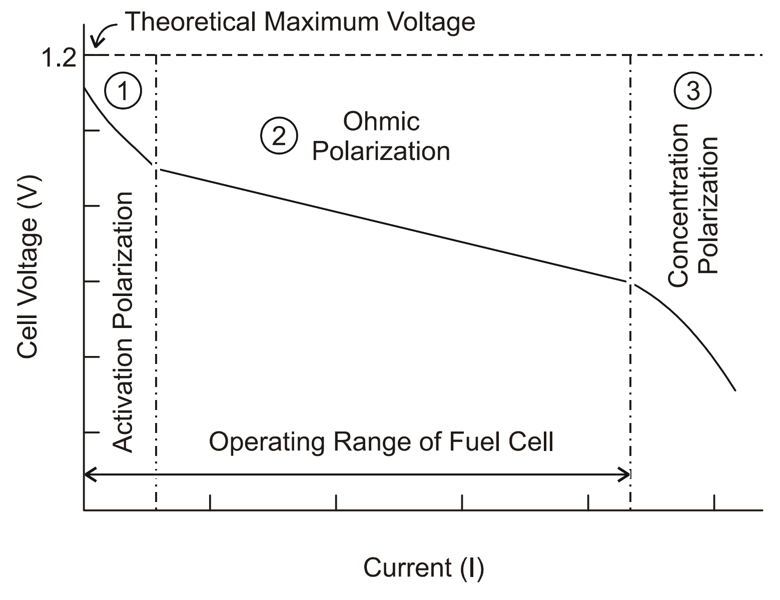


Figure 4-23 Typical PEM Fuel Cell Polarization Curve

The polarization curve characterizes the cell voltage as a function of current. The current, in turn, depends on the size of the electrical load placed across the fuel cell. In essence the polarization curve shows the electrochemical efficiency of the fuel cell at any operating current since the efficiency is the ratio of the actual cell voltage divided by the theoretical maximum of 1.2 V (see Section 4.5.1).

Fuel cell designers often use "current density" rather than current when characterizing fuel cell performance. Current density is calculated as the current divided by the active area of the fuel cell with units of A/cm^2. Current density indicates how effectively the MEA materials are being utilized; high current density indicates greater utilization than low current density.

Key Points & Notes

Batteries have polarization curves very much like fuel cells. Both batteries and fuel cells exhibit excellent partial load performance since the voltage increases as the load decreases. In contrast, internal combustion engines operate most efficiently at full load and exhibit a rapid decrease in efficiency at part load.

Polarization is caused by chemical and physical factors associated with various elements of the fuel cell. These factors limit the reaction processes when current is flowing. There are three basic regions affecting the overall polarization:

- activation polarization
- ohmic polarization (or resistance polarization)
- concentration polarization

The deviation of cell potential from ideal behavior is a direct result of the sum of these factors over the entire load range.

Activation Polarization

Activation polarization is related to the energy barrier that must be overcome to initiate a chemical reaction between reactants. At low current draw, the electron transfer rate is slow and a portion of the electrode voltage is lost in order to compensate for the lack of electro-catalytic activity.

Ohmic Polarization

Ohmic polarization (or "resistance polarization") occurs due to resistive losses in the cell. These resistive losses occur within the electrolyte (ionic), in the electrodes (electronic and ionic), and in the terminal connections in the cell (electronic). Since the stack plates and electrolyte obey Ohm's law ($V=IR$), the amount of voltage lost in order to force conduction varies linearly throughout this region.

Concentration Polarization

Concentration polarization results when the electrode reactions are hindered by mass transfer effects. In this region, the reactants become consumed at greater rates than they can be supplied while the product accumulates at a greater rate than it can be removed. Ultimately these effects inhibit further reaction altogether and the cell voltage drops to zero.

4.5.3 Power Characteristics

Electrical power is the product of its voltage and current ($P=VI$). Since a fuel cell's polarization curve indicates the relationship between voltage and current at all operating conditions, it can be used to derive a corresponding power curve. At any point along the curve the instantaneous power is represented graphically as the rectangular area that just touches the curve. A typical power curve is shown in Figure 4-24.

Maximum power occurs at approximately 0.5 to 0.6 V, which corresponds to relatively high current. At the peak point, the internal resistance of the cell is equal to the electrical resistance of the external circuit. However, since efficiency drops with increasing voltage, there is a tradeoff between high power and high efficiency. Fuel cell system designers must select the desired operating range according to whether efficiency or power is paramount for the given application. It is never desirable to operate in the range beyond where the power curve drops off.

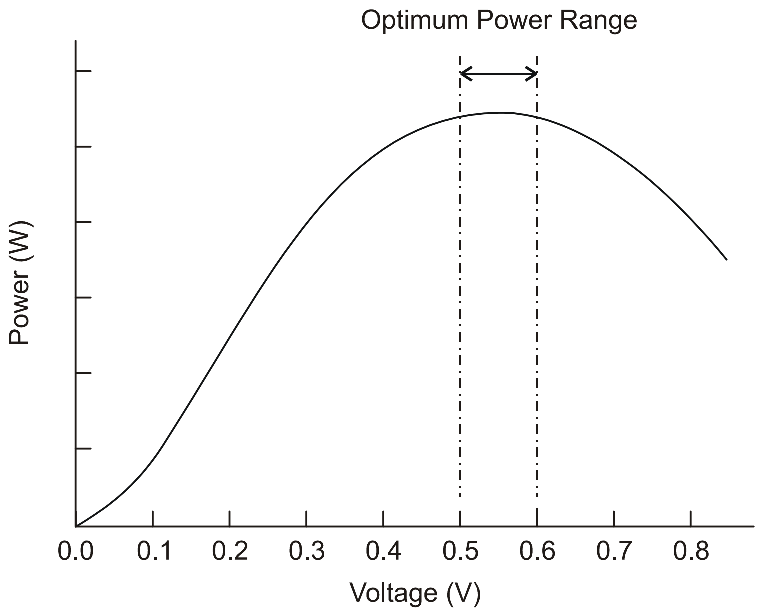


Figure 4-24 Typical PEM Fuel Cell Power Curve

4.5.4 Temperature and Pressure Effects

The shape of a polarization curve depends on the operating temperature and pressure of the stack. In general, a family of polarization curves can be drawn that characterize the stack performance over its entire operating envelope.

Fuel cell designers assess the overall effectiveness of a fuel cell stack in terms of its volumetric power density. This is calculated as its maximum power divided by its physical volume with units of W/L. High power density indicates that much power is being drawn from a small unit. Power density for state-of-the-art PEM fuel cells exceeds 1350 W/L; a decade ago power density was on the order of 90 W/L

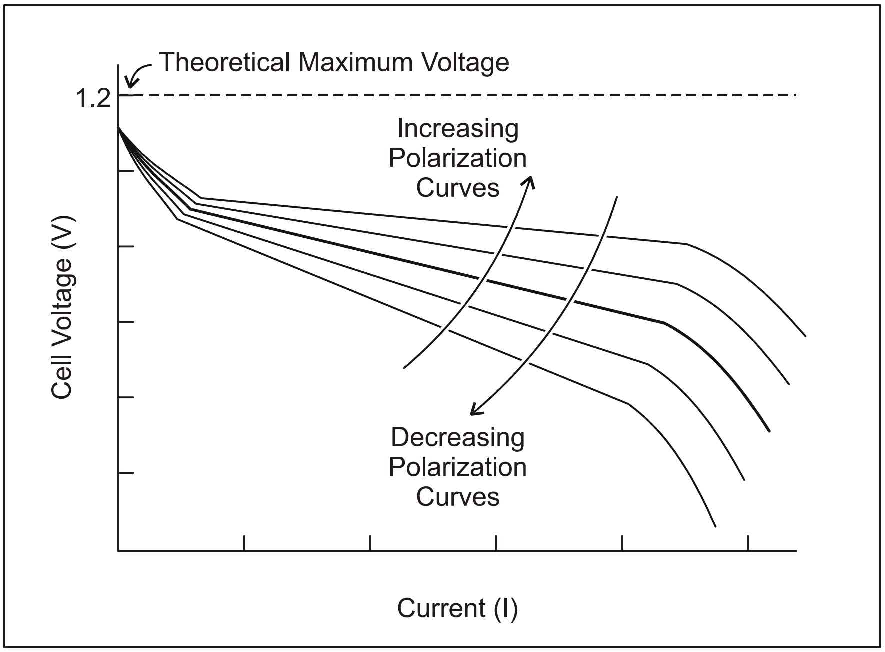


Figure 4-25 Polarization Curve Variations

In general, any parameter variation that causes the polarization curve to go up is beneficial since this results in greater power and higher electrochemical efficiency. The converse is also true.

Pressure

Fuel cell polarization curves typically increase with increasing operating pressure. Conversely, the polarization curves decrease with decreasing operating pressure.

The reason for this is that the rate of the chemical reaction is proportional to the partial pressures of the hydrogen and the oxygen. (Each gas within a gas mixture contributes a partial pressure, the sum of which makes up the total pressure.) Thus, the effect of increased pressure is most prominent when using a dilute oxidant (like air) or a dilute fuel (like reformate). In essence, higher pressures help to force the hydrogen and oxygen into contact with the electrolyte. This sensitivity to pressure is greater at high currents.

Although an increase in pressure promotes the electrochemical reaction, it introduces other problems. Fuel cell stack flow field plates work better at low pressure since they exhibit smaller flow-induced pressure losses. Fuel cell seals operate under additional stress. Additional air compression is required, which absorbs more of the gross power. Other system components must be re-designed accordingly; some components must increase in size and cost.

Key Points & Notes

Fuel cell polarization curves tend to drop as the fuel cells age.

Use of a pure fuel (like hydrogen) or oxidant (like oxygen) increases stack polarization curves. This effect is essentially one of partial pressure: when no other gases are present, all of the available pressure helps force the hydrogen and oxygen into contact with the electrolyte and none is lost pressurizing other gases.

Key Points & Notes

Ultimately, increases in pressure achieve diminishing returns when considering both stack efficiency and overall system consequences. Because of these factors, PEM fuel cells are typically operated at pressures no greater than a few atmospheres.

Temperature

Fuel cell polarization curves increase with increasing operating temperature. Conversely, the polarization curves decrease with decreasing operating temperature.

The reason for this is that higher temperatures improve mass transfer within the fuel cells and results in a net decrease in cell resistance (as the temperature increases, the electronic conduction in metals decreases but the ionic conduction in the electrolyte increases). Together, these effects improve the reaction rate.

The accumulation of product water within the oxidant stream effectively limits operating temperatures to below 212 °F (100 °C). At this temperature, the water boils and the resulting steam severely reduces the partial pressure of the oxygen. This, in turn, drastically reduces cell performance due to oxygen starvation. This can damage the fuel cells and reduce their life.

To some extent, higher temperatures can be achieved by operating at higher pressures since this increases the water boiling point accordingly. However, this effect is slight at the practical PEM fuel cell operating pressures.

The net effect is that fuel cell voltage increases with temperature until the temperature approaches the boiling point of water at which point the voltage begins to decline. The optimum temperature occurs near 175 °F (80 °C) where the two effects balance each other as shown in Figure 4-26. Typically operating temperatures are 158 to 194 °F (70 to 90 °C).

Key Points & Notes

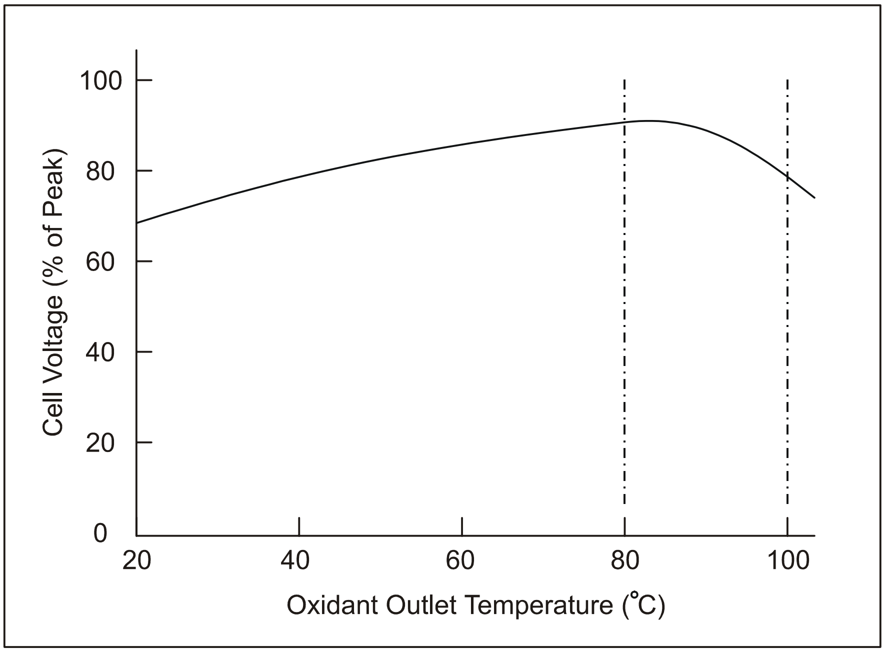


Figure 4-26 Effect of Temperature on Fuel Cell Voltage

As with high pressure operation, operation at elevated temperatures affects all system components, some of which must be re-designed accordingly.

4.5.5 Stoichiometry Effects

Fuel cell polarization curves increase with increasing reactant gas stoichiometry. Conversely, the polarization curves decrease with decreasing reactant gas stoichiometry.

The reason for this is that higher stoichiometry increases the chance that sufficient numbers of hydrogen and oxygen molecules interact with the electrolyte. Insufficient stoichiometry deprives (or “starves”) the fuel cell stack of sufficient reactants and may cause permanent damage.

The stoichiometric ratio provides a fundamental method of comparing the gas utilization of different energy conversion devices. For example, steam plants typically run at an air stoichiometric ratio of about 4.0 and diesel electric generators typically run at a ratio of about 7.0.

Stoichiometry is the ratio of the amount of gas present relative to the amount of that gas that is needed to exactly complete the reaction. This is much like the definition of specific gravity where densities are indicated relative to a reference substance. Thus, a stoichiometric ratio of 1.0 provides exactly the correct number of gas molecules to theoretically complete the reaction. Stoichiometric ratios greater than 1.0 provide excess gas and ratios less than 1.0 provide insufficient gas. A stoichiometric ratio of 2.0 provides exactly twice the number of gas molecules as required.

As gas stream stoichiometric ratio increases, the resulting fuel cell voltage approaches its terminal voltage asymptotically as shown in Figure 4-27. Practical fuel cell stacks are

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typically operated at a hydrogen stoichiometric ratio of 1.4 and an air stoichiometric ratio of 2.0 at rated load; additional gas provides little additional benefit. Higher stoichiometric ratios are required when operating at low power.

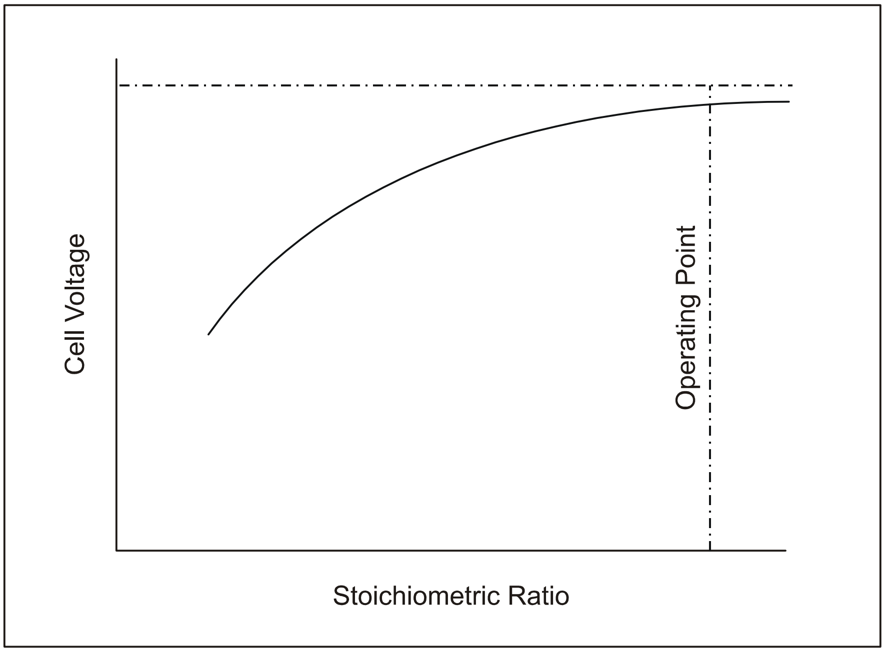

Figure 4-27 Effect of Stoichiometry on Fuel Cell Voltage

4.5.6 Humidity Effects

Sufficient gas stream humidification is essential to PEM fuel cell operation since water molecules move with the hydrogen ions during the ion exchange reaction.

Insufficient humidification water dehydrates the membrane and can lead to cracks or holes in the membrane. This results in a chemical short circuit, local gas mixing, hot spots, and the possibility of fire.

Conversely, excess humidification water leads to condensation and flooding within the flow field plates. This, in turn, can result in a phenomenon known as cell reversal where the affected cells produce a zero or negative voltage. If a large enough negative voltage occurs, the affected fuel cells start to act like an electrolyzer. This produces a lot of heat and can potentially destroy the cell. Cell monitoring systems are typically installed to detect cell reversal before cell damage occurs.

Humidity is typically measured as “relative humidity”; relative since it depends on the pressure and temperature of the gas. When a gas has absorbed as much water as it is physi-

Key Points & Notes

cally able to at a given pressure and temperature, it is said to be saturated and has a relatively humidity of 100%. If that saturated gas then becomes hotter (without the addition of more water), the relative humidity drops. (Every degree Celsius increase in temperature drops the relative humidity by approximately 4%.) If the gas cools, some of the water condenses and the gas remains saturated at the new temperature.

Fuel cells are typically operated at or near saturated conditions at the fuel cell operating temperature (as set by the stack coolant temperature). This provides the maximum amount of water possible while preventing flooding.

The use of water for humidification purposes effectively limits fuel operating and storage temperature to between 32 and 212 °F (0 and 100 °C). Outside of these limits, the water freezes and boils respectively.

A further consideration is that the humidifier water must remain non-conductive. Failure to do so causes short circuits and corrosion currents within the fuel cell stack. Water becomes conductive as it absorbs ions from its surroundings. To eliminate these ions, the water must continuously flow through a de-ionizing filter.