1

THE WORKING PRINCIPLES OF A FUEL CELL

1.1 THERMODYNAMIC ASPECTS

1.1.1 Limitations of the Carnot Cycle

Up to the middle of the twentieth century, all human energy needs have been satisfied by natural fuels: coal, oil, natural gas, wood, and a few others. The thermal energy Q_{react} set free upon combustion (a chemical reaction of oxidation by oxygen) of natural fuels is called the *reaction enthalpy* or *lower heat value* (LHV): "lower" because the heat of condensation of water vapor as one of the reaction products is usually disregarded. A large part of this thermal energy serves to produce mechanical energy in heat engines (e.g., steam turbines, various types of internal combustion engines).

According to one of the most important laws of nature, the *second law of thermodynamics*, the conversion of thermal to mechanical energy W_m is always attended by the loss of a considerable part of the thermal energy. For a heat engine working along a Carnot cycle within the temperature interval defined by an upper limit T_2 and a lower limit T_1, the highest possible efficiency, $\eta_{\text{theor}} \equiv W_m/Q_{\text{react}}$, is given by

$$\eta_{\text{theor}} = \frac{T_2 - T_1}{T_2} \tag{1.1}$$

Fuel Cells: Problems and Solutions, Second Edition. Vladimir S. Bagotsky.

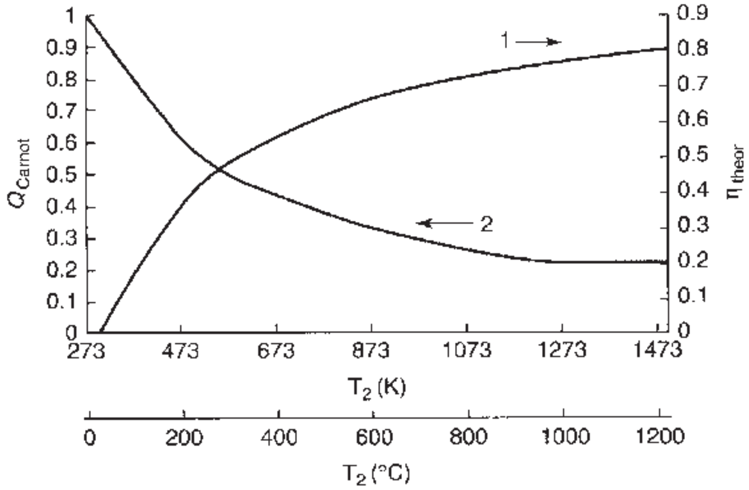

Figure 1.1 Limitations of the Carnot cycle. Theoretical efficiency η_{theor} (1) and the Carnot heat Q_{Carnot} (2) as functions of the upper operating temperature T_2 of the heat engine at a lower temperature T_1 of 298 K (25°C).

T_2 and T_1 being the temperatures (in kelvin) of the working fluid entering into and leaving the heat engine, respectively. The Carnot heat Q_{Carnot} (or *irretrievable heat*), for thermodynamic reasons known as the *Carnot-cycle limitations* is given by $Q_{\mathrm{Carnot}} = (T_1/T_2)Q_{\mathrm{react}}$. There is no way to reduce this loss. For a steam engine operating with superheated steam of 350°C ($T_2 = 623$ K) and release of the exhausted steam into a medium having an ambient temperature of 25° C($T_1 = 298$K), the maximum efficiency according to equation (1.1) is about 50%, so half of the thermal energy is irretrievably lost. As a matter of fact, the efficiency that can be realized in practice is even lower because of various other types of thermal losses Q_{loss} (e.g., heat transfer out of the engine, friction of moving parts); the total losses ($Q_{\mathrm{exh}} = Q_{\mathrm{Carnot}} + Q_{\mathrm{loss}}$) are even higher. The efficiency η_{theor} can be raised by working with a higher value of T_2 (Figure 1.1), but losses due to nonideal heat transfer will also increase.

In part, the mechanical energy produced in heat engines is used, in turn, to produce electrical energy in the generators of stationary and mobile power plants. This additional step of converting mechanical into electrical energy involves additional energy losses, but these could be as low as 1 to 2% in a large modern generator. Thus, for a modern thermal power generating plant, a total efficiency η_{total} of about 40% is regarded as a good performance figure.

1.1.2 Electrochemical Energy Conversion

Until about 1850, the only source of electrical energy was the galvanic cell, the prototype of modern storage and throwaway batteries. In such cells, an electric current is produced through a chemical reaction involving an oxidizing agent and a reducing agent, which are sometimes quite expensive. In mercury primary cells, the current is generated through an overall reaction between mercuric oxide (HgO) and metallic zinc (Zn). In the cell, this *redox* (reducing and oxidizing) *reaction* occurs via an electrochemical mechanism that is fundamentally different from ordinary chemical mechanisms. In fact, in a reaction following chemical mechanisms, the reducing agent (here, Zn) reacts directly with the oxidizing agent (here, HgO):

$$\mathrm{Zn} + \mathrm{HgO} \rightarrow \mathrm{ZnO} + \mathrm{Hg} \tag{1.2}$$

the reaction involving a change in the valence states of the metals:

$$\mathrm{Zn} + \mathrm{Hg}^{2+} \rightarrow \mathrm{Zn}^{2+} + \mathrm{Hg} \tag{1.2a}$$

or electron transfer from Zn to Hg (the oxygen simply changing partners). If one were to mix zinc and mercuric oxides as powders in a reaction vessel and cause them to react, the electron transfers between the reacting particles would occur chaotically throughout the space taken up by the reactants, and no electron flow in any particular direction would be observed from the outside. For this reason, all of the chemical energy set free by the reaction would be evolved in the form of heat.

When an electrochemical mechanism is realized, then in the present example, electrons are torn away from the zinc at *one* electrode by making zinc dissolve in an aqueous medium:

$$\mathrm{Zn} - 2\mathrm{e}^- + 2\mathrm{OH}^- \rightarrow \mathrm{ZnO} + \mathrm{H_2O} \tag{1.3}$$

or, essentially,

$$\mathrm{Zn} - 2\mathrm{e}^- \rightarrow \mathrm{Zn}^{2+} \tag{1.3a}$$

and are added to mercuric oxide (HgO or Hg^{2+}) at *the other* electrode, by making the mercury deposit onto the electrode:

$$\mathrm{HgO} + 2\mathrm{e}^- + \mathrm{H_2O} \rightarrow \mathrm{Hg} + 2\mathrm{OH}^- \tag{1.4}$$

or, essentially,

$$\mathrm{Hg}^{2+} + 2\mathrm{e}^- \rightarrow \mathrm{Hg} \tag{1.4a}$$

the overall reaction occurring spatially separately at two different electrodes contacting the (aqueous) medium or electrolyte. Reaction (1.3) is zinc oxidation occurring as the anodic reaction at the anode. Reaction (1.4) is mercury reduction occurring as the cathodic reaction at the cathode. These two electrode reactions taken together yield the same products as those in chemical reaction (1.2).

Reactions (1.3) and (1.4) will actually proceed only when the two electrodes are connected outside the cell containing them. Electrons then flow from the zinc anode (the negative pole of the cell) to the mercuric oxide cathode (the positive pole). The cell is said to undergo *discharge* while producing current. Within the cell, the hydroxyl ions (OH^-) produced by reaction (1.4) at the cathode are transferred (migrate) to the anode, where they participate in reaction (1.3). The ions and electrons together yield a closed electrical circuit.

Of the total thermal energy of these two processes, Q_{react} [the *reaction enthalpy* $(-\Delta H)$], a certain part [called the *Gibbs reaction energy* $(-\Delta G)$] is set free as electrical energy W_e (the energy of the current flowing in the external part of the cell circuit). The remaining part of the reaction energy is evolved as heat, called the latent heat of reaction Q_{lat} [or reaction entropy $(-T\Delta S)$] (the latent heat in electrochemical reactions is analogous to the Carnot heat in heat engines):

$$Q_{\text{react}} = W_e + Q_{\text{lat}} \tag{1.5}$$

In summary, in the electrochemical mechanism, a large part of the chemical energy is converted directly into electrical energy without passing through thermal and mechanical energy forms. For this reason, and since the value of Q_{lat} usually (if not always) is small compared to the value of Q_{react}, the highest possible theoretical efficiency of this conversion mode,

$$\eta_{\text{theor}} = \frac{Q_{\text{react}} - Q_{\text{lat}}}{Q_{\text{react}}} \tag{1.6}$$

is free of Carnot cycle limitations and may approach unity i.e., 100%).* Even in this case, of course, different losses Q_{loss} have the effect that the practical efficiency is lower than the theoretical maximum, yet the efficiency will always be higher than that attained with a heat engine. The heat effectively exhausted in the electrochemical mechanism is the sum of the two components mentioned: $Q_{\text{exh}} = Q_{\text{lat}} + Q_{\text{loss}}$.

Toward the end of the nineteenth century, after the invention of the electric generator in 1864, thermal power plants were built in large numbers, and grid power gradually displaced the galvanic cells and storage batteries that had been used for work in laboratories and even for simple domestic devices. However, in 1894, a German physical chemist, Wilhelm Ostwald, formulated the idea that the electrochemical mechanism be used instead for the combustion (chemical oxidation) of natural types of fuel, such as those used in thermal power plants, since in this case the reaction will bypass the intermediate stage of heat generation. This would be cold combustion, the conversion of chemical energy of a

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*For certain reactions, Q_{lat} is actually negative, implying that latent heat is absorbed by the system from the surrounding medium rather than being given off into the surrounding medium. In this case, the theoretical efficiency may even have values higher than 100%.

fuel to electrical energy not being subject to Carnot cycle limitations. A device to perform this direct energy conversion was named a *fuel cell*.

The electrochemical mechanism of cold combustion in fuel cells has analogies in living beings. In fact, the conversion of the chemical energy of food by humans and other living beings into mechanical energy (e.g., blood circulation, muscle activity) also bypasses the intermediate stage of thermal energy. The physiological mechanism of this energy conversion includes stages of an electrochemical nature. The average daily output of mechanical energy by a human body is equivalent to an electrical energy of a few tens of watthours.

The work and teachings of Ostwald were the beginning of a huge research effort in the field of fuel cells.

1.2 SCHEMATIC LAYOUT OF FUEL CELL UNITS

1.2.1 An Individual Fuel Cell

Fuel cells, like batteries, are a variety of galvanic cells, devices in which two or more *electrodes* (electronic conductors) are in contact with an *electrolyte* (the ionic conductor). Another variety of galvanic cells are *electrolyzers*, where electric current is used to generate chemicals in a process that is the opposite of that occurring in fuel cells, involving the conversion of electrical to chemical energy.

In the simplest case, a fuel cell consists of two metallic (e.g., platinum) electrodes dipping into an electrolyte solution (Figure 1.2). In an operating fuel cell,

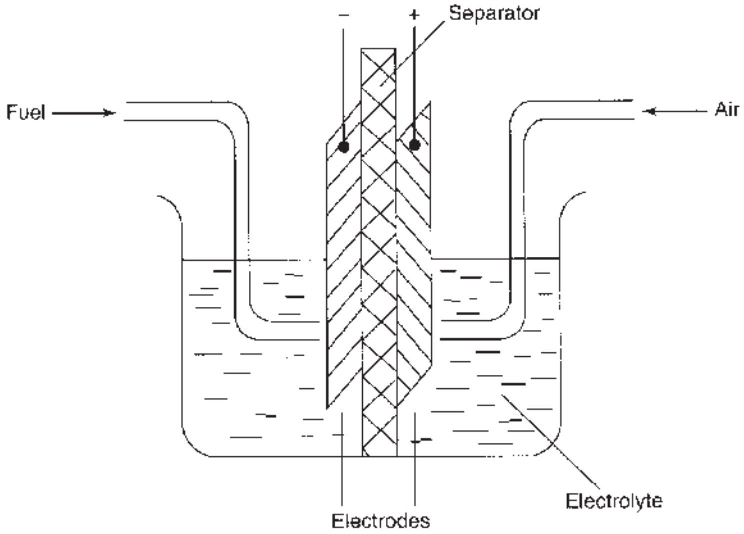

Figure 1.2 Schematic of an individual fuel cell.

the negative electrode, the anode, produces electrons by “burning” a fuel. The positive electrode, the cathode, absorbs electrons in reducing an oxidizing agent. The fuel and the oxidizing agent are each supplied to its electrode. It is important at this point to create conditions that exclude direct mixing of the reactants or that supply to the “wrong” electrode. In these two undesirable cases, direct chemical interaction of the reactants would begin and would yield thermal energy, lowering or stopping the production of electrical energy completely.

So as to exclude accidental contact between anode and cathode (which would produce an internal short of the cell), an electronically insulating porous separator (holding an electrolyte solution that supports current transport by ions) is often placed into the gap between these electrodes. A solid ionically conducting electrolyte may serve at once as a separator. In any case, the cell circuit continues to be closed.

For work by the fuel cell to continue, provisions must be made to realize a continuous supply of reactant to each electrode and continuous withdrawal of reaction products from the electrodes, as well as removal and/or utilization of the heat being evolved.

1.2.2 Fuel Cell Stacks

As a rule, any individual fuel cell has a low working voltage of less than 1 V. Most users need a much higher voltage: for example, 6, 12, or 24 V or more. In a real fuel cell plant, therefore, the appropriate number of individual cells is connected in series, forming *stacks* (*batteries*).[*] A common design is the *filter-press design* of stacks built up of bipolar electrodes, one side of such electrodes working as the anode of one cell and the other side working as the cathode of the neighboring cell (Figure 1.3). The active (catalytic) layers of each of these electrodes face the separator, whose pores are filled with an electrolyte solution. A bipolar fuel cell electrode is generally built up from two separate electrodes, their backs resting on opposite sides of a separating plate known as the *bipolar plate*. These plates are electronically conducting and function as cell walls and intercell connectors (i.e., the current between neighboring cells merely crosses this plate, which forms a thin wall that has negligible resistance). This implies considerable savings in the size and mass of the stack. The bipolar plates alternate with electrolyte compartments, and both must be carefully sealed along the periphery to prevent electrolyte overflow and provide reliable separation of the electrolyte in neighboring compartments. The stacks formed from the bipolar plates (with their electrodes) and the electrolyte compartments (with their separators) are compressed and tightened with the aid of end plates and tie bolts. Sealing is achieved with the aid of gaskets compressed when tightening the assembly. After sealing, the compartments are filled with electrolyte via manifolds and special narrow channels in the gaskets or electrode edges. Gaseous reactants are supplied to the electrodes via manifolds and grooves in the bipolar plates.

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[*] A dc–dc transformer could be used to produce higher output voltage, but would introduce efficiency loss.

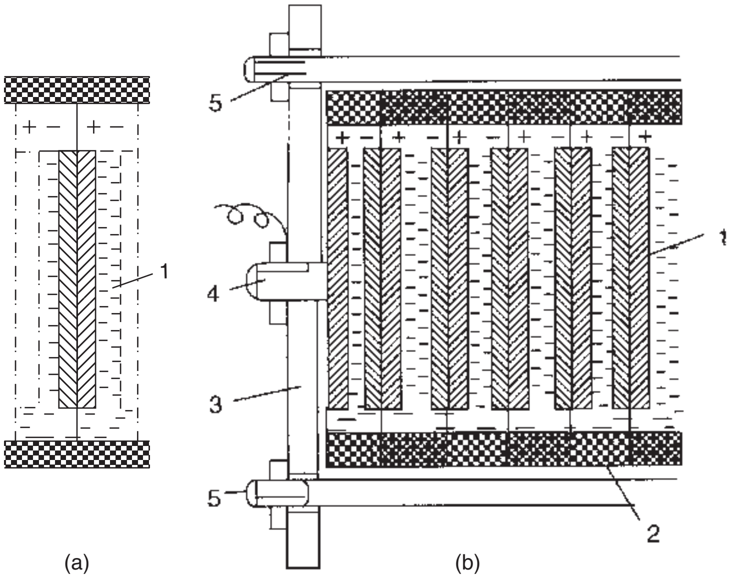

Figure 1.3 Fuel cell components: (a) bipolar electrode; (b) filter-press battery: 1, bipolar electrode; 2, gaskets; 3, end plate; 4, positive current collector; 5, tie bolts.

1.2.3 Power Plants Based on Fuel Cells

The heart of any fuel cell power plant (electrochemical generator or direct energy converter) is one or a number of stacks built up from individual fuel cells. Such plants include a number of auxiliary devices needed to secure stable, uninterrupted working of the stacks. The number or type of these devices depends on the fuel cell type in the stacks and the intended use of the plant. Below we list the basic components and devices. An overall layout of a fuel cell power plant is presented in Figure 1.4.

1. *Reactant storage containers*. These containers include gas cylinders, recipients, vessels with petroleum products, cryogenic vessels for refrigerated gases, and gas-absorbing materials among others.
2. *Fuel conversion devices*. These devices have as their purpose (a) the reforming of hydrocarbons, yielding technical hydrogen; (b) the gasification of coal, yielding water gas (syngas); or (c) the chemical extraction of the reactants from other substances, including devices for reactant purification, devices to eliminate harmful contaminants, and devices to separate particular reactants from mixtures. These are considered in greater detail in Chapter 11.
3. *Devices for thermal management*. In most cases, the working temperature is distinctly above ambient temperature. In these cases the working temperature is maintained by exhaust (Q_{exh}) of the heat evolved during fuel cell

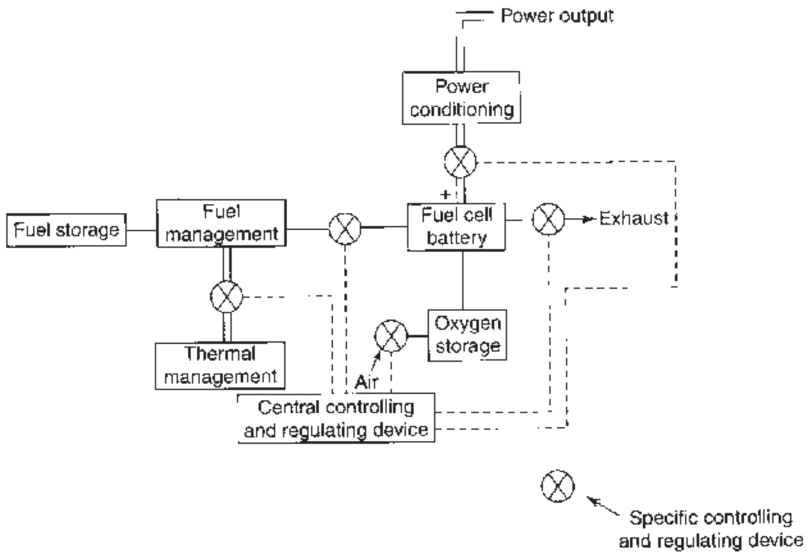

Figure 1.4 Overall schematic of a power plant.

operation. A cooling system must be provided when excess heat is evolved in fuel cell stacks. Difficulties arise when starting up the plant while its temperature is below the working temperature (such as after interruptions). In these cases, external heating of the fuel cell stack must be made possible. In certain cases, sufficient heat may be generated in the stack by shorting with a low-resistance load, where heating is begun at a low current and leads to a larger current producing more heat, and so on, until the working temperature is attained.

4. *Regulating and monitoring devices*. These devices have as their purpose (a) securing an uninterrupted reactant supply at the required rate and amount, (b) securing product removal (where applicable, with a view to their further utilization), (c) securing the removal of excess heat and maintaining the correct thermal mode, and (d) maintaining other operating fuel cell parameters needed in continuous operation.
5. *Power conditioning devices*. These devices include voltage converters, dc–ac converters, and electricity meters, among others.
6. *Internal electrical energy needs*. Many of the devices listed include components working with electric power (e.g., pumps for gas supply or heat-transfer fluid circulation, electronic regulating and monitoring devices). As a rule, the power needed for these devices is derived from the fuel cell plant itself. This leads to a certain decrease in the power level available to consumers. In most cases these needs are not very significant. In certain cases, such as when starting up a cold plant, heating using an external power supply may be required.

1.3 TYPES OF FUEL CELLS

Different attributes can be used to distinguish fuel cells:

1. *Reactant type*. As a fuel (a reducing agent), fuel cells can use hydrogen, methanol, methane, carbon monoxide (CO), and other organic substances, as well as some inorganic reducing agents [e.g., hydrogen sulfide (H_2S), hydrazine (N_2H_4)]. As the oxidizing agent, fuel cells can use pure oxygen, air oxygen, hydrogen peroxide (H_2O_2), and chlorine. Versions with other, exotic reactants have also been proposed.
2. *Electrolyte type*. Apart from the common liquid electrolytes (i.e., aqueous solutions of acids, alkalies, and salts; molten salts), fuel cells often use solid electrolytes (i.e., ionically conducting organic polymers, inorganic oxide compounds). Solid electrolytes reduce the danger of leakage of liquids from the cell (which may lead to corrosive interactions with the construction materials and also to shorts, owing to contact between electrolyte portions in different cells of a battery). Solid electrolytes also serve as separators, keeping reactants from reaching the wrong electrode space.
3. *Working temperature*. One distinguishes low-temperature fuel cells, those having a working temperature of no more than 120 to 150°C; intermediate-temperature fuel cells, 150 to 250°C; and high-temperature fuel cells, over 650°C. Low-temperature fuel cells include membrane-type fuel cells as well as most alkaline fuel cells. Intermediate-temperature fuel cells are those with phosphoric acid electrolyte as well as alkaline cells of the Bacon type. High-temperature fuel cells include fuel cells with molten carbonate (working temperature 600 to 700°C) and solid-oxide fuel cells (working temperature above 900°C). In recent years, interim-temperature fuel cells with a working temperature in the range 200 to 650°C have been introduced. These include certain varieties of solid-oxide fuel cells developed more recently. The temperature ranges are stated conditionally.

1.4 LAYOUT OF A REAL FUEL CELL: THE HYDROGEN–OXYGEN FUEL CELL WITH LIQUID ELECTROLYTE

At present, most fuel cells use either pure oxygen or air oxygen as the oxidizing agent. The most common reducing agents are either pure hydrogen or technical hydrogen produced by steam reforming or with the water gas shift reaction from coal, natural gas, petroleum products, or other organic compounds. As an example of a real fuel cell we consider the special features of a hydrogen–oxygen fuel cell with an aqueous acid electrolyte. Special features of other types of fuel cells are described in later sections.

1.4.1 Gas Electrodes

In a hydrogen–oxygen fuel cell with liquid electrolyte, the reactants are gases. Under these conditions, porous gas-diffusion electrodes are used in the cells. These electrodes (Figure 1.5) are in contact with a gas compartment (on their back side) and with the electrolyte (on their front side, facing the other electrode). A porous electrode offers a far higher true working surface area and thus a much lower true current density (current per unit surface area of the electrode). Such an electrode consists of a metal- or carbon-based screen or plate serving as the body or frame, a current collector, and support for active layers containing a highly dispersed catalyst for the electrode reaction. The pores of this layer are filled in part with the liquid electrolyte and in part with the reactant gas. The reaction itself occurs at the walls of these pores along the three-phase boundaries between the solid catalyst, the gaseous reactant, and the liquid electrolyte.

For efficient operation of the electrode, it is important to secure a uniform distribution of reaction sites throughout the porous electrode. With pores that have hydrophilic walls, walls well wetted by the aqueous electrolyte solution, the risk of flooding the electrode—or of complete displacement of gas from the pore space—exists. There are two possibilities for preventing this flooding of the electrode:

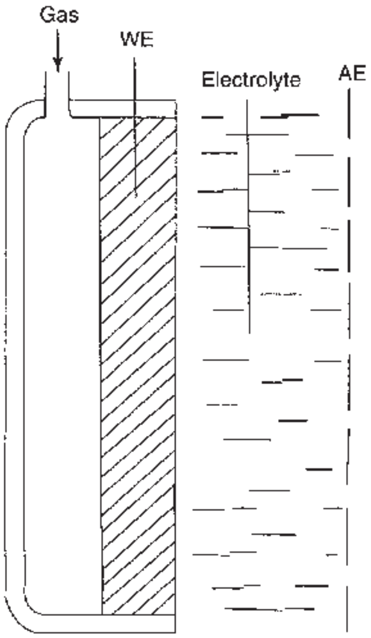

Figure 1.5 Schematic of a gas-diffusion electrode. WE, working electrode; AE, auxiliary electrode.

1. The electrode is made partly hydrophobic by adding water-repelling material. Here it is important to maintain an optimum degree of hydrophobicity. When there is an excess of hydrophobic material, the aqueous solution will be displaced from the pore space.
2. The porous electrode is left hydrophilic, but from the side of the gas compartment the gas is supplied with a certain excess pressure so that the liquid electrolyte is displaced in part from the pore space. To prevent gas bubbles from breaking through the porous electrode (and reaching the counterelectrode), the front side of the electrode that is in contact with the electrolyte is covered with a hydrophilic blocking layer having fine pores with a capillary pressure too high to be overcome by the gas, so that the electrolyte cannot be displaced from this layer. Here it is important to select an excess gas pressure that is sufficient to partially fill the active layer with gas, but insufficient to overcome ("break through") the blocking layer.

1.4.2 Electrochemical Reactions

A reaction of the type (1.3) occurs at the (negative) hydrogen electrode, or anode:

$$2H_2 \rightarrow 4H^+ + 4e^- \tag{1.7}$$

while a reaction of type (1.4) occurs at the (positive) oxygen electrode, or cathode*:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{1.8}$$

The hydrogen ions being formed in the electrolyte layer next to the anode in reaction (1.7) are transferred through the electrolyte toward the cathode, where they undergo reaction (1.8). In this way a closed electrical circuit is obtained. In the electrolyte, a (positive) electrical current flows from the anode to the cathode; in the external circuit it flows in the opposite direction, from the cathode terminal to the anode terminal. The overall chemical reaction producing the current is

$$2H_2 + O_2 \rightarrow 2H_2O \tag{1.9}$$

which means that by reaction of 2 mol of hydrogen and 1 mol of oxygen (at atmospheric pressure and a temperature of 25°C, 1 mol of gas takes up a volume of 24.2 L), 2 mol of water (36 g) is formed as the final reaction product.

The thermal energy Q_{react} (or reaction enthalpy $-\Delta H$) set free in reaction (1.9) when this occurs as a direct chemical reaction amounts to 285.8 kJ/mol.

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*Sometimes the opposite definition is encountered, where the anode is the positive pole of a galvanic cell and the cathode is the negative pole. This definition is valid for electrolyzers but not for fuel cells and other electrochemical power sources, the direction of current in the latter being the opposite of that in electrolyzers.

The Gibbs free energy $-\Delta G$ of the reaction amounts to 237.1 kJ/mol. This value corresponds to the maximum electrical energy $W_e^{\max}$ that could theoretically be gained from the reaction when following the electrochemical mechanism. This means that the maximum attainable thermodynamic efficiency η_{therm} of energy conversion in this reaction is 83%.

For practical purposes it is convenient to state these energy values in electron volts (1 eV $= n \cdot 96.43$ kJ/mol, where n is the number of electrons taking part in the reaction per mole of reactant, in this case per mole of hydrogen). In these units, the enthalpy of this reaction (with $n = 2$ per mole) is 1.482 eV and the Gibbs free energy is 1.229 eV. In the following, the heat of reaction expressed in electron volts is denoted as q_{react}.

1.4.3 Electrode Potentials

At each electrode in contact with an electrolyte, a defined value of electrode potential E is set up. It can only be measured relative to the potential of another electrode. By convention, in electrochemistry the potential of any given electrode is referred to the potential of the *standard hydrogen electrode* (SHE), which in turn, by convention, is taken as zero. A practical realization of the SHE is that of an electrode made of platinized platinum dipping into an acid solution whose mean ionic activity of the hydrogen ions is unity, washed by gaseous hydrogen at a pressure of 1 bar.

In our example, the potential $E_{\text{h.e.}}$ of the hydrogen electrode, to which, according to reaction (1.7), electrons are transferred from the hydrogen molecule, is more negative than the potential $E_{\text{o.e.}}$ of the oxygen electrode, which, according to reaction (1.8), gives off electrons to an oxygen molecule.

The potentials of electrodes can be equilibrium or reversible, or nonequilibrium or irreversible. An electrode's equilibrium potential (denoted E^0 below) reflects the thermodynamic properties of the electrode reaction occurring at it (thermodynamic potential). The hydrogen electrode is an example of an electrode at which the equilibrium potential is established. When supplying hydrogen to the gas-diffusion electrode mentioned above, a value of electrode potential $E^0_{\text{h.e.}}$ is established at it (when it is in contact with the appropriate electrolyte) that corresponds to the thermodynamic parameters of reaction (1.7). On the SHE scale, this value is close to zero (depending on the pH value of the solution, it differs insignificantly from the potential of the SHE itself).

An example of an electrode having a nonequilibrium value of potential is the oxygen electrode. The thermodynamic value of potential $E^0_{\text{o.e.}}$ of an oxygen electrode at which reaction (1.8) takes place is 1.229 V (relative to the SHE). When supplying oxygen to a gas-diffusion electrode, the potential actually established at it is 0.8 to 1.0 V, that is, 0.3 to 0.4 V less (less positive) than the thermodynamic value.

The degree to which electrode potentials are nonequilibrium values depends on the relative rates of the underlying electrode reactions. Under comparable conditions, the rate of reaction (1.8), cathodic oxygen reduction, is 10 orders of magnitude lower than that of reaction (1.7), anodic hydrogen oxidation.

In electrochemistry, reaction rates usually are characterized by values of the exchange current density i^0, in units of mA/cm^2, representing (equal values of) current density of the forward and reverse reactions at the equilibrium potential when the net reaction rate or current is zero.

The reaction rates themselves depend strongly on the conditions under which the reactions are conducted. Cathodic oxygen reduction, more particularly, which at temperatures below 150°C is far from equilibrium, comes closer to the equilibrium state as the temperature is raised.

The reasons that the real value of the electrode potential of the oxygen electrode is far from the thermodynamic value, and why cathodic oxygen reduction is so slow at low temperatures, are not clear so far, despite the large number of studies that have been undertaken to examine it.

1.4.4 Voltage of an Individual Fuel Cell

As stated earlier, the electrode potential of the oxygen electrode is more positive than that of the hydrogen electrode, the potential difference existing between them being the *voltage U* of the fuel cell:

$$U = E_{\text{o.e.}} - E_{\text{h.e.}} \tag{1.10}$$

When the two electrodes are linked by an external electrical circuit, electrons flow from the hydrogen to the oxygen electrode through the circuit, which is equivalent to (positive) electrical current flowing in the opposite direction. The fuel cell operates in a *discharge mode*, in the sense of reactions (1.7) and (1.8) taking place continuously as long as reactants are supplied.

The thermodynamic value of voltage (i.e., the difference between the thermodynamic values of the electrode potentials) has been termed the cell's *electromotive force* (EMF), which in the following is designated as $\mathscr{E}^0(\mathscr{E}^0 = E^0_{\text{o.e.}} - E^0_{\text{h.e.}})$. The EMF of the hydrogen–oxygen fuel cell (in units of volts) corresponds numerically to the Gibbs free energy of the current-producing reaction (1.9) (in units of electron volts) [i.e., $\mathscr{E}^0(= W_e) = 1.229$ V].

The practical value of the voltage of an idle cell is called the *open-circuit voltage* (OCV) U_0 of this cell. For a hydrogen–oxygen fuel cell, the OCV is lower than $\mathscr{E}^0$, owing to the lack of equilibrium of the oxygen electrode. Depending as well on technical factors, it is 0.85 to 1.05 V.

The working voltage of an operating fuel cell U_i is even lower because of the internal ohmic resistance of the cell and the shift of potential of the electrodes occurring when current flows, also called *electrode polarization*, and caused by

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The term *discharge* ought to be seen as being related to a *consumption* of the reactants, which in a fuel cell are extraneous to the electrodes but in an ordinary battery are the electrodes themselves.

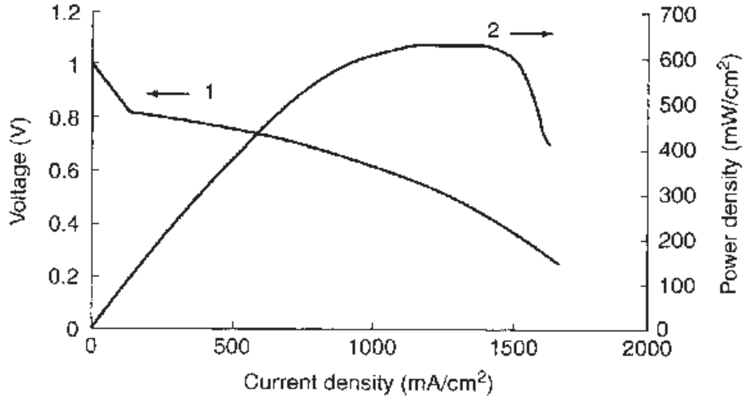

Figure 1.6 Typical current–voltage curve, and discharge power as a function of current load.

slowness or lack of reversibility of the electrode reactions. The effects of polarization can be made smaller by the use of suitable catalysts applied to the electrode surface that accelerate the electrode reactions.

The voltage of a working cell will be lower the higher the current I that is drawn (the higher the current density $i = I/S$ at the electrode's working surface area S). The current–voltage relation is a cell characteristic, as shown in Figure 1.6. Sometimes this relation can be expressed by the simplified linear equation

$$U_i = U_0 - IR_{\text{app}} \tag{1.11}$$

where the apparent internal resistance R_{app} is conditionally regarded as constant. This is a rather rough approximation, since R_{app} includes not only the cell's internal ohmic resistance but also components associated with polarization of the electrodes. These components are a complex function of current density and other factors. Often, the U_i versus I relation is S-shaped. Sometimes it is more convenient to describe the relation in the coordinates of U_i versus ln I. At moderately high values of the current, the voltage of an individual hydrogen–oxygen fuel cell, U_i, is about 0.7 V.

1.5 BASIC PARAMETERS OF FUEL CELLS

1.5.1 Operating Voltage

Fuel cell systems differ in the nature of the components selected, and thus in the nature of the current-producing chemical reaction. Each reaction is associated with a particular value of enthalpy and Gibbs free energy of the reaction, and thus also with a particular value of the heat of reaction Q_{reac} and of the thermodynamic EMF $\mathscr{E}^0$. Very important parameters of each fuel cell are its open-circuit voltage (OCV) U_0 and its discharge or operating voltage U_i as observed under given conditions (at a given discharge current). It had been shown in Section 1.4.1 that the OCV is lower than the EMF if the potential of at least one of the electrodes is a nonequilibrium potential. The difference between $\mathscr{E}$ and U_i depends on the nature of the reaction. Because of the cell's internal resistance and of electrode polarization during current flow, the discharge or operating voltage U_i is lower than the OCV, U_0. In different systems the influence of polarization of the electrodes is different; hence, the difference between U_0 and U_i also depends on the nature of the electrode reaction.

1.5.2 Discharge Current and Discharge Power

The discharge current of a fuel cell at any given voltage U_i across an external load with the resistance R_{ext} is determined by Ohm's law:

$$I = \frac{U_i}{R_{\mathrm{ext}}} \tag{1.12}$$

Since U_i in turn depends on the current, and writing Eq. (1.11) for the current, the expression for the current becomes

$$I = \frac{U_0}{R_{\mathrm{app}} + R_{\mathrm{ext}}} \tag{1.13}$$

During discharge of a fuel cell the power $P = U_i I$ is delivered, or using Eqs. (1.12) and (1.13), we obtain

$$P = \frac{U_i^2 R_{\mathrm{app}}}{(R_{\mathrm{app}} + R_{\mathrm{ext}})^2} \tag{1.14}$$

With increasing current (decreasing R_{ext}), the voltage decreases; hence, the power–current relation goes through a maximum (Figure 1.6, curve 2).

Neither the discharge current nor the power output are sole characteristics of a fuel cell, since both are determined by the external resistance (load) selected by the user. However, the maximum admissible discharge current I_{adm} and associated maximum power P_{adm} constitute important characteristics of all cell types. These performance characteristics place a critical lower bound U_{crit} on cell voltage; certain considerations (such as overheating) make it undesirable to operate at discharge currents above I_{adm} or cell voltages below U_{crit}. To a certain extent the choice of values for I_{adm} and U_{crit} is arbitrary. Thus, in short-duration (pulse) discharge, higher currents can be sustained than in long-term discharge.

For sustainable thermal conditions in an operating fuel cell, it will often be necessary for the discharge current not to fall below a certain lower admissible limit $I_{\mathrm{min,adm}}$. The range of admissible values of the discharge current and the ability of a cell to work with different loads are important characteristics of each fuel cell.

1.5.3 Operating Efficiency of a Fuel Cell

The operating efficiency of a fuel cell is its efficiency in transforming a fuel's chemical energy to electrical energy, or the ratio between the electrical energy produced and the chemical energy of oxidation of a fuel supplied, $\eta = W_e/Q_{\mathrm{react}}$. As a rule, the overall efficiency of fuel cells η_{total} is less than unity (less than 100%). A number of factors influence the overall efficiency.

Theoretical (Thermodynamic) Efficiency η_{therm}
The theoretical (thermodynamic efficiency was defined above by Eq. (1.6))

Voltage Efficiency η_V
The value of the voltage efficiency is given by

$$\eta_v = \frac{U_i}{\mathscr{E}^0} \tag{1.15}$$

where U_i is the real operating voltage of the fuel cell during discharge at a current density i and $\mathscr{E}^0$ is the value of the EMF for the given fuel cell type (i.e., the highest thermodynamically possible value of the cell voltage). For hydrogen–oxygen fuel cells the value of $\mathscr{E}^0$ at a temperature of 25°C is 1.229 V.

Efficiency of Reactant Utilization: The Coulombic Efficiency η_{Coul} ***(Often Called Faradaic Efficiency)***
Usually, not all of the mass or volume of the reactants supplied to a fuel cell stack is used for the current-producing reaction or production of electric charges (coulombs). External reasons for incomplete utilization include trivial leakage from different points in the stack. Intrinsic reasons include (1) diffusion of a reactant through the electrolyte (possibly a membrane) from "its own" to the opposite electrode, where it undergoes direct chemical reaction with the other reactant; (2) use of a reactant for certain auxiliary purposes, such as the circulation of (excess) oxygen serving to remove water vapor from parts of a membrane fuel cell and its subsequent venting to the ambient air; and (3) incomplete oxidation of individual organic fuel types: for example, an oxidation of part of methanol fuel to formic acid rather than to CO_2.

Design Efficiency η_{design}
Often, part of the electrical energy generated in a fuel cell is consumed for the (internal) needs of auxiliary equipment such as pumps supplying reactants and removing products, and devices for monitoring and controlling. The leakage of reactants mentioned above as a possibility also depends on design quality. If the

fuel cells making up an electric power plant work with a secondary fuel derived on site from a primary fuel (such as with hydrogen made by steam reforming), the efficiency of such processing must also be taken into account.

Overall Efficiency η_{total}
The overall efficiency of the power plant will depend on all of the following factors:

$$\eta_{\text{total}} = \eta_{\text{term}}\eta_{\text{volt}}\eta_{\text{Coul}}\eta_{\text{design}} \tag{1.16}$$

The overall efficiency is a very important parameter for fuel cell–based power plants, both the centralized plants of high capacity and the medium or small-capacity plants set up in large numbers in a distributed fashion. The basic goal of these setups is that of reducing the specific consumption of primary fuels for power generation.

1.5.4 Heat Generation

The amount of thermal energy liberated during operation of a fuel cell bears a direct relation to the value of the discharge operating voltage. When passing an electrical charge of λ_e coulombs, the total heat of reaction is given by $\lambda_e q_{\text{react}}$ joules (where the heat of reaction q_{react} is expressed in electron volts). The electrical energy produced is given by $\lambda_e U_i$ joules. The thermal energy produced will then be (in units of joules)

$$Q_{\text{exh}} = (q_{\text{react}} - U_i)\lambda_e \tag{1.17}$$

This includes both the latent heat Q_{lat} and all types of energy loss Q_{loss} incurred because of the efficiencies mentioned above being less than unity.

For hydrogen–oxygen fuel cells, $q_{\text{react}} = 1.48$ eV. With a discharge voltage of $U_i = 0.75$ V, heat generation amounts to $0.73\lambda_e$ joules, which is close to the value of electrical energy produced. Also, η_{volt} can be seen to be about 0.6 at this discharge voltage.

1.5.5 Ways of Comparing Fuel Cell Parameters

Often, a need arises to compare electrical and other characteristics of fuel cells that differ in their nature or size, or to compare fuel cell–based power generators with others. This is most readily achieved when using reduced or normalized parameters.

A convenient measure for the relative rates of current-producing reactions of fuel cells of a given type but differing in size is by using the current density, that is, the current per unit surface area S of the electrodes: $i = I/S$ (the units: mA/cm^2). The power density $p_s = P/S$ (the units: mW/cm^2) is a convenient measure of the relative efficiency of different varieties of fuel cells.

For users of fuel cells, important performance figures are the values of power density referred to unit mass M: $p_m = P/M$ (the units: W/kg) or unit volume V: $p_v = P/V$ (the units: W/L), and also the energy densities per unit mass (in Wh/kg) or unit volume (in Wh/L), both including the reactant supply. The power density is usually reported merely by referring to the mass or volume of the fuel cell battery itself but not to those of the power plant as a whole, since the mass and volume of reactants, including their storage containers, depend on the projected operating time of the plant. The energy density is usually reported for the power plant as a whole.

For stationary fuel cell–based power plants, the most important parameter is the energy conversion efficiency, inasmuch as this will define the fuel consumption per unit of electric power generated. For portable and other mobile power plants, the most important parameters are the power density and the energy density, inasmuch as they reflect the mass and volume of the mobile plant.

1.5.6 Lifetime

Theoretically, a fuel cell should work indefinitely, that is, as long as reactants are supplied and the reaction products and heat generated are duly removed. In practice, however, the operating efficiency of a fuel cell decreases somewhat in the long run. This is seen from a gradual decrease in the discharge or operating voltage occurring in time at any given value of the discharge or operating current. The rate of decrease depends on many factors: the type of current load (i.e., constant, variable, pulsed), observation of all operating rules, conditions of storage between assembly and use, and so on. It is usually stated in μW/h. If for a cell operated under constant load, the lifetime may be stated in hours, a better criterion for the lifetime of cells operated under a variable load is the total of energy generated, in Wh, while the rate of decrease of the voltage would then be given in μV/Wh.

The major reason for this efficiency drop is a drop in activity of the catalysts used to accelerate the electrode reactions. This activity drop may be due to:

- Spontaneous recrystallization of the highly disperse catalyst, its gradual dissolution in the electrolyte, or deposition of contaminants (inhibitors or catalytic poisons) on its surface
- A drop in ionic conductivity of the electrolyte: for example, of the polymer membrane in proton-exchange membrane and direct methanol fuel cells and that is caused by its gradual oxidative destruction
- The corrosion of different structural parts of fuel cells, leading to partial destruction and/or the formation of corrosion products that lower the activity of the electrodes, particularly in high-temperature fuel cells
- A loss of sealing of the cells: for example, because of aging of packings, so that it becomes possible for reactants to reach the “wrong” electrode

The rate of drop of fuel cell efficiency depends strongly on the mode and conditions of use. Periodic interruptions and temperature changes of idle cells from their operating temperature to ambient temperature and back when reconnected may have ill effects, and sometimes the documentation mentions an admissible number of load or temperature cycles. On relatively rare occasions, a fuel cell may suddenly fail, its voltage falling to almost zero. This type of failure is usually caused by an internal short that could occur when electrolyte leaks out through defective packing or when metal dendrites form and grow between electrodes.

It should be pointed out that since fuel cell problems are relatively new, few statistical data are available from which to judge the expected lifetime of different types of fuel cells under different operating conditions. The largest research effort goes into finding reasons for the gradual efficiency drop of fuel cells and finding possibilities to make it less important.

1.5.7 Special Operating Features

Transient Response

A fuel cell power plant is usually operated with variable loads, including the periodic connection and disconnection of different power consumers. This leads to periodic changes in the load resistance R_{ext} and the discharge or operating current. Any such act gives rise to a transient state where one parameter (e.g., current) changes and other parameters (e.g., heat removal) have to accommodate to the new conditions. For normal operation of fuel cell power plants, it is important that the time spent under transient operating conditions be as short as possible.

Startup

Problems often arise at the startup of a new cell stack after its manufacture and storage, or in repeated startup after a long idle period. Usually, the operating temperature of a fuel cell stack is higher than ambient or warehouse. If external heating is not possible, it may be possible, as pointed out in Section 1.2.3, to begin heating the battery on its own with a small discharge current and to raise its temperature gradually. An important criterion for a power plant is the time from switching on to full power.

The Effects of Climate

Any power plant should be operative over a wide range of temperatures and humidities of the surroundings. In most countries the temperature bracket needed reaches from -20 to $+\ 50^\circ$C. For countries with a cold climate, such as Russia and Canada, operation should be guaranteed down to -40°C.

Reliability and Convenient Manipulation

Power plants on the basis of fuel cell batteries constitute rather complex setups, including different operating, monitoring, and regulating units. The uninterrupted operation of these power plants depends largely on the smooth work of all these units. Their work should be governed by a single controlling unit or “brain.” The work of operators running the plant should be minimized and reduced to that of “pushing buttons.” The plant should also be sufficiently foolproof, in order not to react overly strongly to operator faults. Mobile plants for portable devices or transport applications should be compact and mechanically sturdy.

REFERENCE

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