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Principle of Low-temperature Fuel Cells Using an Ionic Membrane

Claude Lamy¹,²

¹Université de Montpellier, Institut Européen des Membranes, UMR CNRS no 5635, 2 Place Eugène Bataillon, CC 047, 34095 Montpellier Cedex, France
²Université de Nantes, Groupe de Recherches HySPÀC, CNRS GDR 3652, 2 rue de la Houssinière, 44322 Nantes Cedex 3, France

1.1 Introduction

A technology-oriented civilization needs more and more energy, particularly the emerging and developing countries. Fossil resources, such as coal, natural gas, and hydrocarbons, are the main primary sources of energy, but they are limited in size and volume and may be exhausted in coming few decades. Moreover, they are the main contributors to carbon dioxide (CO₂) emission that is the principal component of the greenhouse effect. An alternative approach is to use hydrogen (H₂) either to feed fuel cells in power plants, electric vehicles, and electrical devices or to store the intermittent energy (solar, photovoltaic, wind energy, etc.). This approach will strongly limit the production of greenhouse gases (GHGs), depending on the primary sources used for H₂ production since it is not a primary source. Among the renewable energy sources, such as hydroelectric power, wind, solar, and tidal power, the production of H₂ by water (H₂O) electrolysis is the most efficient process, leading to high-purity H₂, which is suitable to feed a low-temperature fuel cell (LTFC), such as a proton exchange membrane fuel cell (PEMFC) or an alkaline fuel cell (AFC) [1–5].

In this context, many investigations were carried out on the development of fuel cells fed either with pure H₂ [3–5] or with other fuels, for example, liquid fuels such as methanol (CH₃OH) [6,7] or ethanol (C₂H₅OH) [5,8]. In particular H₂/O₂ (air) fuel cells, such as PEMFCs, working at relatively low temperatures (ranging from ambient to 70–80 °C), are becoming a mature technology for powering electrical vehicles with an autonomy range approaching 600 km without H₂ refueling or for stationary power plants with relatively good electrical efficiencies (40–55%) depending on the applications and working conditions.

On the other hand, the direct alcohol fuel cell (DAFC), fed with CH₃OH [7] or C₂H₅OH [8], directly converts the chemical energy of alcohol combustion with O₂ into electrical energy. Such devices are particularly suitable for portable electronics, either to recharge their lithium battery or to power them directly. These fuel cells can work either with an acidic electrolyte, such as a proton exchange...
membrane (PEM), or with a solid alkaline electrolyte, for example, an anion exchange membrane (AEM) in a solid alkaline membrane fuel cell (SAMFC) of similar structure to that of a PEMFC.

In this chapter, we will present the working principle of LTFCs based on the PEM technology, either fed with H₂ (pure H₂ or reformate gases) or with a low-weight alcohol (CH₃OH or C₂H₅OH). Then, we will discuss the electrical energy efficiency either under equilibrium conditions (j = 0) or under working conditions at a current density (j), the variation of which with the electrode potential (E), that is, the fuel cell characteristics E(j), will be established from a theoretical analysis of the reaction kinetics. Finally, two typical examples of LTFCs under development and commercialization will be given, the first one concerning the direct methanol fuel cell (DMFC) for portable electronics and the second one the H₂/air PEMFC for the electrical vehicle.

1.2 Thermodynamic Data and Theoretical Energy Efficiency under Equilibrium (j = 0)

An elementary fuel cell directly converts the chemical energy of combustion with O₂ of a given fuel (H₂, natural gas, hydrocarbons, kerosene, alcohols, etc.) into electricity (i.e., the Gibbs energy change, −ΔGᵢ) [6,9–11]. Electrons liberated at the anode (negative pole of the cell) by the electrooxidation of the fuel pass through the external circuit and produce an electrical energy, Wₑ = nFΔGᵢ, where Eₑ is the cell voltage, n the number of electrons involved in the overall electrochemical reaction, and F = 96 485 C the Faraday constant (i.e., the electric charge of one electron mole), and reach the cathode (positive pole), where they reduce O₂ (either pure or from air). Inside the fuel cell, the electrical current is transported by migration and diffusion of the electrolyte ions (H⁺, OH⁻, O₂⁻, and CO₂⁻).

1.2.1 Hydrogen/oxygen Fuel Cell

The electrochemical reactions involved in the elementary processes of a H₂/O₂ fuel cell under acidic environment, for example, in a PEMFC (Figure 1.1) are the electrooxidation of H₂ at the anode:

\[
H₂ \rightarrow 2H^+ + 2e^- \quad E^0_1 = 0.000 \text{ V versus SHE} \quad (1.1)
\]

and the electroreduction of O₂ at the cathode:

\[
1/2O₂ + 2H^+ + 2e^- \rightarrow H₂O \quad E^0_2 = 1.229 \text{ V versus SHE} \quad (1.2)
\]

where \( E^0_i = -\Delta G^0_i/(nF) \) is the electrode potential versus the standard hydrogen electrode (SHE) as reference, and \( \Delta G^0_i \) is the Gibbs energy change involved in the electrochemical reaction. \( \Delta G^0_i < 0 \) since the reactions involved are spontaneous for producing energy.

Similarly, in a fuel cell working in alkaline medium (e.g., an AFC or a SAMFC), the following electrochemical reactions do occur:
In the fuel cell, the electrical balance corresponds to the complete combustion of the fuel in the presence of \( \text{O}_2 \) as follows:

\[
\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}
\]  

(1.5)

where the thermodynamic data associated with this reaction, under standard conditions \((T = 25 \, \text{°C}, \, p = 1 \, \text{bar}, \, \text{and liquid H}_2\text{O})\), have the opposite sign to those of \( \text{H}_2\text{O} \) decomposition:

\[
\Delta H^0 = -285.8 \, \text{kJ mol}^{-1} \, \text{of H}_2 \quad \text{and} \quad \Delta G^0 = -237.2 \, \text{kJ mol}^{-1} \, \text{of H}_2
\]

However, the thermodynamic data to consider \((\Delta H, \Delta G)\) are those at the working temperature of the device, for example, between 280 and 350 K for the PEMFC and 280–400 K for the AFC (see Table 1.1, where the negative values of the thermodynamic data concern the formation of \( \text{H}_2\text{O} \), which is a spontaneous process).

The equilibrium cell voltage \((E_{eq})\) can thus be evaluated from the Nernst potential at each electrode:

\[
E_{eq} = E_2 - E_1 = -\Delta G_r/nF = -\Delta G^0/2F + (RT/2F)\ln\left(\frac{p_{\text{H}_2}p_{\text{O}_2}}{p_{\text{H}_2\text{O}}^2}\right)
\]

\[
E_{eq} = E^0 + (RT/2F)\ln\left(\frac{p_{\text{H}_2}p_{\text{O}_2}}{p_{\text{H}_2\text{O}}^2}\right)
\]

with \(E^0 = -\Delta G^0/2F\) the standard cell voltage, that is, \(E^0 = E_2^0 - E_1^0 = 1.229 \, \text{V} \) at 25 °C, and \(p_{\text{H}_2}, \, p_{\text{O}_2}, \, \text{and} \, p_{\text{H}_2\text{O}}\) the partial pressures of \( \text{H}_2, \, \text{O}_2, \, \text{and} \, \text{H}_2\text{O} \), respectively. Therefore, by increasing the pressure of reactants \((\text{H}_2 \, \text{and} \, \text{O}_2)\) and decreasing the pressure of the product \((\text{H}_2\text{O})\), one can increase the cell voltage.

The variation of \(E_{eq}\) with \(T\) is contained mainly in the entropic term, that is, \(\Delta S^0 = nF \left(\frac{dE^0}{dT}\right)\), which is the temperature coefficient of the fuel cell. Thus, assuming that \(\Delta H\) and \(\Delta S\) are nearly independent of temperature (see Table 1.1), one may calculate \(E_{eq}\) as follows:

\[
E_{eq}(T) = -\Delta G_r/nF = -(\Delta H - T \Delta S)/nF = 1.481 - 0.000846 \, T \quad \text{(in V)}
\]

for \( \text{H}_2\text{O} \) in the liquid state at 25 °C \((\Delta H^0 = -285.8 \, \text{kJ mol}^{-1} \, \text{and} \, \Delta S^0 = -163.3 \, \text{J mol}^{-1} \, \text{K}^{-1})\).
For H$_2$O in the gaseous state at 25 °C ($\Delta H = 241.8$ kJ mol$^{-1}$ and $\Delta S = 44.42$ J mol$^{-1}$ K$^{-1}$), one obtains the following:

$$E_{eq}(T) = 1.253 - 0.000230 T \quad \text{(in V)}$$

In summary, $E_{eq}$ may be expressed as a function of temperature and pressure (liquid state) by

$$E_{eq}(T, P) = 1.481 - 0.000846 T + 0.0000431 T \ln\{p_{H_2}(p_{O_2})^{1/2}/p_{H_2O}\} \quad \text{in V}$$

or

$$E_{eq}(T, P) = 1481 - 0.846 T + 0.0431 T \ln\{p_{H_2}(p_{O_2})^{1/2}/p_{H_2O}\} \quad \text{in mV}$$

In the gaseous state (e.g., at $T = 400$ K with $\Delta H = 242.8$ kJ mol$^{-1}$ and $\Delta S = 47.37$ J mol$^{-1}$ K$^{-1}$), $E_{eq}$ can be calculated by the following expressions:

$$E_{eq}(T, P) = 1.258 - 0.000245 T + 0.0000431 T \ln\{p_{H_2}(p_{O_2})^{1/2}/p_{H_2O}\} \quad \text{in V}$$

or

$$E_{eq}(T, P) = 1258 - 0.245 T + 0.0431 T \ln\{p_{H_2}(p_{O_2})^{1/2}/p_{H_2O}\} \quad \text{in mV}$$

A fuel cell working under reversible thermodynamic conditions (i.e., at equilibrium with $j = 0$) does not follow Carnot’s theorem, which controls the energy efficiency of an internal combustion engine (ICE), so the theoretical energy efficiency of an elementary cell, $\varepsilon_{cell}^{rev}$, defined as the ratio of the electrical energy produced
(\(W_e = nFE_{cell} = -\Delta G_i\)) to the chemical energy of combustion (\(-\Delta H\)), that is,
\[
\varepsilon_{cell}^{rev} = \frac{-\Delta G}{-\Delta H} = \frac{\Delta G}{\Delta H} = (\Delta H - T\Delta S)/\Delta H = 1 - T(\Delta S/\Delta H) = 1 + T\Delta S/(-\Delta H)
\]
(1.8)

which can be very high (if \(T|\Delta S| \ll |\Delta H|\)).

In the case of a \(H_2/O_2\) fuel cell working at 25°C, the energy efficiency of an elementary cell will be \(\varepsilon_0^{cell} = \Delta G^0/\Delta H^0 = 237.17/285.83 = 0.829 \approx 83\%\), if \(\Delta H\) is taken with \(H_2O\) in the liquid state (standard conditions), that is, \(\Delta H\) is the high heating value (\(\Delta H_{HHV}\)). But the heat of \(H_2O\) condensation \(\Delta Q_{cond} = \Delta H_{HHV} - \Delta H_{LHV} = 285.8 - 241.8 = 44\ kJ\ mol^{-1}\) (where \(\Delta H_{LHV}\) is the low heating value = 241.8 kJ mol\(^{-1}\) – see Table 1.1) is not useful for producing electrical energy, so a more realistic energy efficiency will be \(\varepsilon^{rev}_{cell} = \Delta G/\Delta H = 228.6/241.8 = 0.945 \approx 95\%\) using the thermodynamic data of \(H_2O\) formation under the gaseous state at 25°C (Table 1.1).

On the other hand, using the Gibbs energy change \(\Delta G^0\), given in Table 1.1, allows us to evaluate the specific energy \(W_s\) of \(H_2\) (expressed in kWh kg\(^{-1}\)) as follows:
\[
W_s = \frac{W_e}{3600 M} = \left(\frac{-\Delta G^0}{3600 M}\right)
\]
(1.9)

with \(M = 0.002\) kg the molecular mass of \(H_2\). This gives
\[
W_s = \frac{237.2 \times 10^3}{3600 \times 0.002} = 32.94\ kWh\ kg^{-1} \approx 33\ kWh\ kg^{-1}
\]
which is a very high value when not taking into account the weight of the \(H_2\) tank.

### 1.2.2 Direct Alcohol Fuel Cell

The DAFC directly converts the Gibbs energy of combustion of an alcohol into electricity, without a fuel processor. This greatly simplifies the system, reducing its volume and cost [12,13]. Important developments of DAFCs are due to the use of a PEM as electrolyte, instead of a liquid acid electrolyte, as previously done.

The electrical energy \(W_e = nFE_{cell} = -\Delta G_i\) is related to the Gibbs energy change, \(\Delta G_i\), of the oxidation reaction of an alcohol with \(O_2\). The overall combustion reaction of a monoalcohol \(C_xH_yO\) leading to \(H_2O\) and \(CO_2\), that is,
\[
C_xH_yO + \left(x + \frac{y}{4} - \frac{1}{2}\right)O_2 \rightarrow x CO_2 + \frac{y}{2}H_2O
\]
(1.10)

involves the participation of \(H_2O\) or of its adsorbed residue (\(OH_{ads}\)) provided by the cathodic reaction (electroreduction of dioxygen).

The electrochemical oxidation of a monoalcohol in acid medium to reject the \(CO_2\) produced can thus be written as follows:
\[
C_xH_yO + (2x - 1)H_2O \rightarrow x CO_2 + n H^+ + n e^-
\]
(1.11)

with \(n = 4x + y - 2\). Such an anodic reaction is very complicated from a kinetics point of view since it involves multielectron transfers and the presence of different adsorbed intermediates and several reaction products and by-products (see Section 3.3.4 in Chapter 3). However, from the thermodynamic data it is easy...
to calculate the standard equilibrium potential, $E_{eq}^0$, the theoretical efficiency and the energy density under standard conditions.

According to reaction (1.11), the standard Gibbs energy change, $\Delta G_{i}^0$, allowing to calculate the standard anode potential $E_{1}^0 = -\Delta G_{1}^0/nF$, can be evaluated from the standard energy of the formation $\Delta G_{i}^{f}$ of reactant $(i)$:

$$-\Delta G_{1}^0 = x\Delta G_{CO_{2}}^{f} - \Delta G_{C_{2}H_{5}O}^{f} - (2x - 1)\Delta G_{H_{2}O}^{f}$$  \hspace{1cm} (1.12)

In the cathodic compartment, the electroreduction of $O_2$ does occur as follows:

$$1/2 \text{O}_2 + 2 \text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O}$$  \hspace{1cm} (1.13)

with $\Delta G_{2}^0 = \Delta G_{H_{2}O}^{f} = -237.2 \text{ kJ mol}^{-1}$, leading to a standard cathodic potential $E_{2}^0$:

$$E_{2}^0 = -\frac{\Delta G_{2}^0}{2F} = \frac{237.2 \times 10^{3}}{2 \times 96485} = 1.229 \text{ V versus SHE}$$  \hspace{1cm} (1.14)

The standard Gibbs energy change, $\Delta G_{r}^0$, of the overall reaction (1.10) can be evaluated as follows:

$$\Delta G_{r}^0 = \left(2x + \frac{y}{2} - 1\right)\Delta G_{2}^0 - \Delta G_{1}^0 = x\Delta G_{CO_{2}}^{f} + \frac{y}{2}\Delta G_{H_{2}O}^{f} - \Delta G_{C_{2}H_{5}O}^{f},$$  \hspace{1cm} (1.15)

leading to $E_{eq}^0$ under standard conditions:

$$E_{eq}^0 = -\frac{\Delta G_{r}^0}{nF} = -\left(\frac{\Delta G_{2}^0}{2F} - \frac{\Delta G_{1}^0}{nF}\right) = E_{2}^0 - E_{1}^0$$  \hspace{1cm} (1.16)

Then, it is possible to evaluate the specific energy $W_s$ in kWh kg$^{-1}$, using equation (1.9) where $M$ is the molecular mass of the alcohol, and knowing the enthalpy of formation $\Delta H_{i}^{f}$ from the thermodynamic data, one may calculate $\Delta H_{r}^{0}$:

$$\Delta H_{r}^{0} = \left(2x + \frac{y}{2} - 1\right)\Delta H_{2}^{0} - \Delta H_{1}^{0} = x\Delta H_{CO_{2}}^{f} + \frac{y}{2}\Delta H_{H_{2}O}^{f} - \Delta H_{C_{2}H_{5}O}^{f}$$  \hspace{1cm} (1.17)

and the reversible energy efficiency under standard conditions $\varepsilon_{cell}^0 = (\Delta G_{r}^{0}/\Delta H_{r}^{0})$.

For example, for CH$_3$OH and C$_2$H$_5$OH, the electrochemical oxidation reactions and the standard anode potentials are, respectively, as follows:

CH$_3$OH + H$_2$O $\rightarrow$ CO$_2$ + 6 H$^+$ + 6 e$^-$  \hspace{1cm} $E_{cell}^{0 \text{ MeOH}} = 0.016 \text{ V versus SHE}$  \hspace{1cm} (1.18)

CH$_3$CH$_2$OH + 3 H$_2$O $\rightarrow$ 2 CO$_2$ + 12 H$^+$ + 12 e$^-$  \hspace{1cm} $E_{cell}^{0 \text{ EtOH}} = 0.084 \text{ V versus SHE}$  \hspace{1cm} (1.19)

This corresponds to the overall combustion reaction of these alcohols in O$_2$:

CH$_3$OH + 3/2 O$_2$ $\rightarrow$ CO$_2$ + 2 H$_2$O  \hspace{1cm} (1.20)

CH$_3$CH$_2$OH + 3 O$_2$ $\rightarrow$ 2 CO$_2$ + 3 H$_2$O  \hspace{1cm} (1.21)

with the thermodynamic data under standard conditions (see Table 1.2). The corresponding $E_{eq}^0$ are the following:
For higher alcohols, such as \( n \)-propanol, for example, the following calculations can be made:

\[
\begin{align*}
\Delta G_1^0 &= 3 \Delta G_{CO_2}^f - \Delta G_{C_3H_7OH}^f - 5 \Delta G_{H_2O}^f = -3 \times 394.4 + 168.4 + 5 \times 237.1 = 171 \text{ kJ mol}^{-1} \\
\text{so that } E_1^0 &= -\frac{\Delta G_1^0}{18F} = \frac{171 \times 10^3}{18 \times 96485} = 0.098 \text{ V versus SHE}
\end{align*}
\]

and

\[
\begin{align*}
C_3H_7OH + 9/2 O_2 &\rightarrow 3 CO_2 + 4 H_2O \\
\Delta G_r^0 &= 9\Delta G_2^0 - \Delta G_1^0 = 3\Delta G_{CO_2}^f + 4\Delta G_{H_2O}^f - \Delta G_{C_3H_7OH}^f \\
&= -3 \times 394.4 - 4 \times 237.1 + 168.4 = -1963 \text{ kJ mol}^{-1}
\end{align*}
\]

\( E_{eq}^0 \) under standard conditions is thus

\[
E_{eq}^0 = -\frac{\Delta G_r^0}{18F} = \frac{1963 \times 10^3}{18 \times 96485} = \frac{237.1 \times 10^3}{2 \times 96485} = \frac{171 \times 10^3}{18 \times 96485} = 1.229 - 0.098 = 1.131 \text{ V}
\]

and the specific energy is

\[
W_s = \frac{1963 \times 10^3}{3600 \times 0.060} = 9.09 \text{ kWh kg}^{-1}
\]

The enthalpy change of reaction (1.23) is

\[
\Delta H_r^0 = -3 \times 395.5 - 4 \times 285.8 + 302.6 = -2027 \text{ kJ mol}^{-1}
\]

so the reversible energy efficiency under standard condition is

\[
\epsilon_{cell}^0 = \frac{\Delta G_r^0}{\Delta H_r^0} = \frac{1963}{2027} = 0.968 \approx 97\%
\]

### Table 1.2

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>( \Delta G_1^0 ) (kJ mol(^{-1}))</th>
<th>( E_1^0 ) (V) versus SHE</th>
<th>( \Delta G_r^0 ) (kJ mol(^{-1}))</th>
<th>( E_{cell}^0 ) (V)</th>
<th>( W_s ) (kWh kg(^{-1}))</th>
<th>( \Delta H_r^0 ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3)OH</td>
<td>-9.3</td>
<td>0.016</td>
<td>-702</td>
<td>1.213</td>
<td>6.09</td>
<td>-726</td>
</tr>
<tr>
<td>C(_2)H(_5)OH</td>
<td>-97.3</td>
<td>0.084</td>
<td>-1326</td>
<td>1.145</td>
<td>8.00</td>
<td>-1367</td>
</tr>
<tr>
<td>C(_3)H(_7)OH</td>
<td>-171</td>
<td>0.098</td>
<td>-1963</td>
<td>1.131</td>
<td>9.09</td>
<td>-2027</td>
</tr>
<tr>
<td>CH(_3)OH–(\text{CHOH}–\text{CH}_2\text{OH})</td>
<td>-409</td>
<td>0.177</td>
<td>-2436</td>
<td>1.052</td>
<td>9.14</td>
<td>-2676</td>
</tr>
<tr>
<td>CH(_2)OH–(\text{CHOH}–\text{CH}_2\text{OH})</td>
<td>-25.5</td>
<td>0.026</td>
<td>-1160</td>
<td>1.203</td>
<td>5.20</td>
<td>-1189</td>
</tr>
<tr>
<td>CH(_2)OH–(\text{CHOH}–\text{CH}_2\text{OH})</td>
<td>1</td>
<td>-0.001</td>
<td>-1661</td>
<td>1.230</td>
<td>5.02</td>
<td>-1650</td>
</tr>
</tbody>
</table>
For all the alcohols listed in Table 1.2, $E_0^{\text{cell}}$ varies from 1.23 to 1.05 V, which is very similar to that of a H$_2$/O$_2$ fuel cell ($E_0^{\text{cell}} = 1.229$ V). The energy density varies from 0.5 to 1 of that of gasoline (which is around 10–11 kWh kg$^{-1}$); therefore, these compounds are good alternative fuels to hydrocarbons. Furthermore, the reversible energy efficiency $E_0^{\text{cell}}$ is close to 1, while that of the H$_2$/O$_2$ fuel cell is 0.83 at 25 °C (standard conditions).

1.3 Electrocatalysis and the Rate of Electrochemical Reactions

However, under working conditions, the practical electric efficiency of a fuel cell depends on the current density $j$ that is delivered by the cell and is lower than that of the equilibrium reversible efficiency (at $j = 0$). This is due to the irreversibility of the electrochemical reactions involved at the electrodes, leading to overpotentials $\eta_a$ at the anode, $\eta_c$ at the cathode, so the working $E_{\text{cell}}$ becomes (taking into account the ohmic losses $R_e j$ coming from the cell resistance $R_e$)

$$E_{\text{cell}}(j) = E_0^{\text{eq}}(j = 0) - (|\eta_a| + |\eta_c| + R_e j)$$  \hspace{1cm} (1.24)

where the overpotentials $\eta_i$ are defined as the deviation of the working electrode potential $E_i(j)$ from the equilibrium potential $E_i^{\text{eq}}(0)$ \cite{14–16}; that is, $\eta_i = E_i(j) - E_i^{\text{eq}}(0)$.

For the H$_2$ electrode, $\eta_a$ is very small and can be approximated by a linear relationship with $j$, that is, $\eta_a = R_t j$, where $R_t$ is the charge transfer resistance (see Section 1.3.1). But for the alcohol oxidation, $\eta_a$ is at least 0.3–0.4 V for a reasonable $j$ value (100 mA cm$^{-2}$), so $E_{\text{cell}}$, including an overpotential $\eta_c = -0.3$ to $-0.4$ V for the cathodic reaction, will be on the order of 0.4–0.6 V, and the voltage efficiency will be $\varepsilon_E = E_{\text{cell}}(j)/E_0^{\text{eq}} = (0.4/1.2 = 0.33)$ to $(0.6/1.2 = 0.50)$, under operating conditions. Such a drawback of the direct alcohol fuel cell can be removed only by improving the kinetics of the electrooxidation of the fuel. This needs to have a relative good knowledge of the reaction mechanisms, particularly of the rate determining step, and to search for electrode materials (Pt-X binary and Pt-X-Y ternary electrocatalysts) with improved catalytic properties (see Chapter 3, Section 3.3.4).

From Eq. (1.24), it follows that the increase in the practical fuel cell efficiency $\varepsilon_{\text{cell}}$ can be achieved by increasing the voltage efficiency $\varepsilon_E = E_{\text{cell}}(j)/E_0^{\text{eq}}$ and the Faradaic efficiency $\varepsilon_F = n_{\text{exp}}/n_{\text{th}}$, the reversible efficiency, $\varepsilon_{\text{rev}}^{\text{cell}}$, being fixed by the thermodynamic data under the working conditions (temperature and pressure) (see Eq. (1.38).

For a given electrochemical system, the increase in voltage efficiency is directly related to the decrease in overpotentials of the oxygen reduction reaction (ORR), $|\eta_c|$, and alcohol oxidation reaction, $\eta_a$, which needs to enhance the activity of the catalysts at low potentials and low temperatures, whereas the increase in Faradaic efficiency is related to the ability of the catalyst to oxidize completely, or not, the fuel into CO$_2$, that is, it is related to the selectivity of the catalyst. Indeed, in the case of C$_2$H$_5$OH, for example, acetaldehyde and acetic acid are formed at the anode \cite{17},
which corresponds to a number of electrons involved, 2 and 4, respectively, against 12 for the complete oxidation of C\textsubscript{2}H\textsubscript{5}OH to CO\textsubscript{2}. The enhancement of both these efficiencies is a challenge in electrocatalysis.

In the following section, we will evaluate the different overvoltages involved in an elementary fuel cell and establish the electrical characteristics $E_{\text{cell}}(j)$ of the cell.

### 1.3.1 Establishment of the Butler–Volmer Law (Charge Transfer Overpotential)

For a given electrochemical reaction $A + n \, e^- \leftrightarrow B$, which involves the transfer of $n$ electrons at the electrode–electrolyte interface, the equilibrium potential (at $j = 0$), called the electrode potential, is given by the Nernst law as follows:

$$E^{A/B}_{\text{eq}} = E^{A/B}_0 + \frac{RT}{nF} \ln \frac{a_A}{a_B}$$

(1.25)

where $E^{A/B}_0$ is the standard electrode potential versus SHE (whose potential is zero at 25 °C by definition), and $a_i$ the activity of reactant $(i)$. As soon as the electrode potential takes a value $E^{A/B}_{\text{eq}}$ different from the equilibrium potential, $E^{A/B}_{\text{eq}}$, an electrical current of intensity $I$ passes through the interface, whose magnitude depends on the deviation $\eta = E^{A/B}_{\text{eq}} - E^{A/B}_{\text{eq}}$ from the equilibrium potential. $\eta$, which is called the overpotential, is positive for an oxidation reaction (anodic reaction $B \rightarrow A + n \, e^-$) and negative for a reduction reaction (cathodic reaction $A + n \, e^- \rightarrow B$). The current intensity $I$ is proportional to the rate of reaction $(r)$, that is, $I = nFr$. For a heterogeneous reaction, $r$ is proportional to the surface area $S$ of the interface, so the kinetics of electrochemical reactions is better defined by the intrinsic rate $r_i = r/S$ and the current density $j = I/S = nFr_i$.

The electrical characteristics $j(E)$ can then be obtained by introducing the exponential behavior of the rate constant (Arrhenius law) with the electrochemical activation energy, $\Delta G^\pm = \Delta G_0^+ - \alpha nFE$, which comprises two terms: the first one ($\Delta G_0^+$) is the chemical activation energy and the second one ($\alpha nFE$) is the electrical component of the activation energy. The latter is a fraction $\alpha (0 \leq \alpha \leq 1)$ of the total electric energy, $nFE$, coming from the applied electrode potential $E$, where $\alpha$ is called the charge transfer coefficient. The chemical activation energy can be decreased by a factor $K$ coming from the presence of a catalytic material in the electrode structure, so electrocatalysis can be defined as the activation of electrochemical reactions both by the electrode potential and by the electrode material (Figure 1.2).

In the theory of absolute reaction rate, one obtains for a first-order electrochemical reaction, the rate of which is proportional to the concentration $c_i$ of reactant $(i)$ [18],

$$r_a = k_a(E, T)S c_\text{B}^{\text{elec}} = k_0^0 S c_\text{B}^{\text{elec}} \exp(-\Delta G_a^+/RT) \quad \text{with } \Delta G_a^+ = \Delta G_a^+ - (1 - \alpha) nFE$$

$$r_c = k_c(E, T)S c_\text{A}^{\text{elec}} = k_0^0 S c_\text{A}^{\text{elec}} \exp(-\Delta G_c^+/RT) \quad \text{with } \Delta G_c^+ = \Delta G_c^+ + \alpha nFE$$

where $c_i^{\text{elec}}$ is the concentration of reactant $(i)$ at the electrode surface and $\alpha$ is the charge transfer coefficient ($0 < \alpha < 1$), that is, the fraction of the electrical energy that activates the reduction reaction ($A \rightarrow B$), and $(1 - \alpha) nFE$ activating the oxidation reaction ($B \rightarrow A$). Thus, $I = nF(r_a - r_c)$ so that $j = I/S$, that is, the current
intensity $I$ divided by the electrode surface area $S$, is given by

$$j = I/S = nF[k_c^0 \epsilon_c \exp(-\Delta G_c^+ / RT)](1 - \alpha)nFE/RT]$$

where the indices “$a$” or “$c$” stands for the anodic or cathodic reaction, respectively, and $k_i$ are the corresponding rate constant.

*At equilibrium $\eta_i = 0$ and $r_i = r_c$, so that $j_a = j_c = j_0$, $E = E_{eq}$ and $c_i^{elec} = c_i^0$, where $c_i^0$ is the bulk concentration of reactant ($i$). This gives

$$j_0 = nFk_i^0 \epsilon_i \exp(-\Delta G_i^+ / RT)exp[(1 - \alpha)nFE_{eq}/RT]$$

leading to $j_0 = nFk_i^0 \epsilon_i \exp(-\Delta G_i^+ / RT)exp(-\alpha nF E_{eq}/RT)$.

$j_0$ is called the exchange current density and $k_i^0$ the standard rate constant. Then,

$$E_{eq}^{A/B} = E_{eq}^A + RT/nF \ln(\frac{\epsilon_A^{0}}{\epsilon_B^{0}}) = E_{0}^{A/B} + RT/nF \ln(K_{eq})$$

where the activity of reactant ($i$) has been replaced by its concentration $c_i$, $K_{eq}$ is the equilibrium constant of reaction $A + n e^- \leftrightarrow B$ and $E_{eq}^{A/B} = \exp(-\Delta G_i^0 / RT)$ is the standard electrode potential, with $\Delta G_i^0 = \Delta G_i^{+0} - \Delta G_i^{-0}$ the Gibbs energy of reaction.

This corresponds to the Nernst law.

*Out of equilibrium $j = j_0 + j_0$ and dividing $j$ by $j_0$ one obtains

$$j(\eta) = j_0 [(\epsilon_B^{elec} / \epsilon_B^{0}) \exp(nFE/RT) - (\epsilon_A^{elec} / \epsilon_A^{0}) \exp(-nFE/RT)]$$

\[ (1.26) \]

or $j(\eta) = j_0 \exp[(1 - \alpha)nFE/RT] - \exp(-\alpha nFE/RT)]$

when assuming no mass transfer limitation, that is, $c_i^{elec} = c_i^0$.

This is the Butler–Volmer law with $\eta = E - E_{eq}$ the overpotential and $j_0$ the exchange current density.

The expression of the Butler–Volmer law can be simplified in some limiting cases:

i) For $|\eta| \ll RT/nF \approx 25.7/n \text{ mV at } 25 \degree C$ then $j(\eta) = j_0 (nFE/RT) \eta = \eta/R_t$
or

\[ \eta = R_t j \text{ with } R_t = RT/(nFj_0) \text{ the charge transfer resistance.} \]  

(1.27)

This is the Ohm’s law.

ii) For \( \eta \gg RT/nF \) then \( j(\eta) = j_0 \exp\{(1 - \alpha) (nF/RT) \eta\} \) or \( \eta = RT/\{\{1 - \alpha\} nF\} \) \( \text{Ln} \) \( (j/j_0) \) (with \( j > 0 \)),

and for \( \eta \ll -RT/nF, \) then \( j(\eta) = -j_0 \exp\{-\alpha(nF/RT) \eta\} \) or \( \eta = -RT/(\alpha nF) \) \( \text{Ln} \) \( (-j/j_0) \) (with \( j < 0 \)),

that is,

\[ \eta = a + b_1 \log_{10}|j| \]  

(1.28)

This is the Tafel law with the Tafel slopes \( b_1 = 2.3 \, RT/(\alpha nF) \) in V dec\(^{-1}\) \( \approx 59/\) (\( \alpha, n \)) mV at 25 °C and \( \alpha_t = \alpha_a \) for an oxidation reaction and \( \alpha_t = \alpha_c \) for a reduction reaction. For a simple electrochemical reaction \( \alpha_a + \alpha_c = 1 \).

iii) For the hydrogen oxidation reaction (HOR) \( j_0 \) is very high \( (j_0 \approx 1 \, mA \, cm^{-2}) \) so that the reaction is reversible and the Ohm’s law does apply; therefore, a linear relationship between \( \eta \) and \( j \) is obtained, that is, \( j(\eta) = \eta/R_t \).

iv) For the ORR \( j_0 \) is small \( (j_0 \approx 1 \, \mu A \, cm^{-2}) \) so that the reaction is irreversible (one may neglect the reverse reaction, i.e., H\(_2\)O oxidation) and one may write:

\[ j(\eta) = -j_0 \exp\{-\alpha_c(nF/RT) \eta\} \text{ or } \eta_{\text{act}}^c = -RT/(\alpha_c nF) \text{Ln}(j/j_0) \]

where \( \eta_{\text{act}}^c \) is the activation overpotential for an irreversible reaction, such as the ORR or the alcohol oxidation reaction (AOR), with \( j_0 \) given by

\[ j_0 = nFk_a^0 c_b^0 \exp\{-(\Delta G_a^{0+} / RT)\} \exp(\alpha_a nF E_{eq}/RT) = nFk_c^0 c_{\lambda}^0 \exp\{-(\Delta G_c^{0+} / RT)\} \exp(\alpha_c nF E_{eq}/RT) \]  

(1.29)

with \( \alpha_a, \alpha_c \) the charge transfer coefficients for the anodic or the cathodic reaction, respectively. \( \alpha_c = 1 - \alpha_a \) usually for an elementary electrochemical reaction.

This last equation contains the two essential activation terms met in electrocatalysis: (i) an exponential function of the electrode potential \( E \) and (ii) an exponential function of the chemical activation energy \( \Delta G_{\text{act}}^0 \). By modifying the nature and structure of the electrode material, one may decrease \( \Delta G_{\text{act}}^0 \) by a given amount \( K \) (see Figure 1.2), thus increasing \( j_0 \) as the result of the catalytic properties of the electrode. This leads to an increase in the reaction rate \( r_t \) that is, of \( j = nFr_t \).

### 1.3.2 Mass Transfer Limitations (Concentration Overpotential)

The reaction kinetics can be controlled by mass transfer (diffusion, migration, and convection) of the reacting species inside the electrolytic phase, so the limiting current density \( (j_l) \) is proportional to the mass flux density \( J_l \) of species \( (i) \): \( j_l = |z_i|FJ_l \) with \( J_l = (1/S) \{\Delta N_i/\Delta t\} = c_i \, v_i \) (where \( z_i \) is the algebraic ionic charge of species \( i \), \( \Delta N_i \) the number of moles exchanged, \( v_i \) the geometric velocity, and \( S \) the electrode surface area).

\( J_i \) can be expressed by the Nernst–Planck equation:

\[ J_i = -D_i c_i \nabla \phi_i + c_i \mu_i^{\text{ext}} = -D_i \nabla c_i - z_i F \frac{c_i \nabla \phi}{RT} + c_i \mu_i^{\text{ext}} \]  

(1.30)
with \(D_i\) the diffusion coefficient of species \((i)\), \(\mu_i = \mu_i + z_i F \varphi\) its electrochemical potential, and \(\varphi\) the electrode potential, that is, the difference of inner potential at the electrode–electrolyte interface.

In the following, we will neglect the contribution of the convection current \(j_i^{cv} = |z_i| F c_i \vec{v}^{cv}\) and of the migration current \(j_i^{m} = |z_i| F \mu_i c_i \vec{E} = |z_i| \lambda_i c_i \vec{E} = \chi_i \vec{E}\) where \(\lambda_i = F c_i u_i\) is the molar conductivity with \(u_i = \mu_i / (RT)\) the electric mobility, \(\chi_i = |z_i| \lambda_i c_i\) the ionic conductivity, and \(\vec{E} = \vec{\nabla} \varphi\) the electrical field [19].

Thus, we will consider only the diffusion process (Fick’s laws) of species \((i)\):

\[
\frac{\partial j_i^d}{\partial t} = -D_i \nabla c_i \quad \text{(Fick’s 1st law)} \quad \text{and} \quad j_i^d = |z_i| F j_i^d
\]

\[
\frac{\partial c_i}{\partial t} = -\text{div} j_i^d = D_i \Delta c_i \quad \text{(Fick’s 2nd law)} \approx \text{mass conservation}
\]

(1.31)

The resolution of Fick’s equations in the approximation of a semi-infinite linear diffusion, under steady-state conditions, leads to the following relations:

\[
\begin{align*}
    j_i^d &= -D_i \frac{\partial c_i(x, t)}{\partial x}, \quad \frac{\partial c_i(x, t)}{\partial t} = 0 \quad \text{and} \quad j_i^d = \pm |z_i| F D_i \frac{\partial c_i(x, t)}{\partial x}_{x=0} \\
    \frac{\partial c_i(x, t)}{\partial t} &= D_i \frac{\partial^2 c_i(x, t)}{\partial x^2} = 0 \quad \text{giving} \quad \frac{\partial c_i}{\partial x} = \frac{c_{io} - c_i(0)}{\delta}, \quad \text{and} \\
    c_i(x) &= \left(\frac{\partial c_i}{\partial x}\right)_{x=0} x + c_i(0) = \frac{c_{io} - c_i(0)}{\delta} x + c_i(0) \quad (0 \leq x \leq \delta)
\end{align*}
\]

where \(\delta\) is the thickness of the diffusion layer, \(c_i(0)\) the concentration at the electrode surface, and \(c_{io}\) the bulk concentration of reactant \((i)\) (Figure 1.3). For the electrochemical reaction, \(A_i^{+} + ne^- \rightarrow B_i^{n}\), the rate of which is controlled only by diffusion, \(j\) can be written as follows:

\[
|\vec{j}| = |\vec{j}_i^d| = n F D_i (|c_{io} - c_i(0)|/\delta), \text{ with } n = z_A - z_B \quad \text{(charge conservation)}
\]

For high rate, that is, high current densities, all the reacting species arriving at the electrode surface are immediately consumed, that is, \(c_i(0) \rightarrow 0\), and their activity (concentration) becomes 0. Thus, the concentration gradient reaches a maximum value, leading to the following expression of the limiting current density \(j_{li}\):

\[
j_{li} = n F D_i c_{io}/\delta
\]

(1.32)

with \(D_i\) (in \(m^2\ s^{-1}\) or \(cm^2\ s^{-1}\)) the diffusion coefficient of species \((i)\), \(c_{io}\) its concentration in the bulk of electrolyte, and \(\delta\) the thickness of the diffusion layer (in the approximation of a semi-infinite linear diffusion).

By doing the ratio of \(j\) with \(j_{li}\) one may obtain the following:

\[
|\vec{j}|/j_{li} = (|c_{io} - c_i(0)|/c_{io}) = 1 - c_i(0)/c_{io} = 1 - p_i(0)/p_{io}
\]

\[Figure 1.3\] Concentration profiles of the reacting species for a semi-infinite linear diffusion under steady-state conditions.
The surface concentration \( c_i(0) \) (or partial pressure \( p_i(0) \) for gaseous species) will be given by

\[
\frac{c_i(0)}{c_{io}} = \frac{p_i(0)}{p_{io}} = 1 - \frac{|j|}{j_{li}} \quad (1.33)
\]

For a very fast transfer reaction (\( j_0 \to \infty \)), only limited by mass transfer, the Nernst equation does apply at the electrode surface, leading to concentration overpotentials (assuming the same diffusion coefficients for both species A and B):

\[
E_{eq} = E^0_{A/B} + \frac{RT}{nF} \ln\left(\frac{c_A(0)}{c_Ao}/\frac{c_B(0)}{c_Bo}\right)
= E_{1/2} + \frac{RT}{nF} \ln\left(\frac{|j|}{j_{li}}/j_{la} - j\right)
\]

This is the equation of a polarographic wave, with \( E_{1/2} \) the half-wave potential (Figure 1.4).

Thus,

\[
\eta_{la}^{\text{conc}} = \frac{RT}{n_AF} \ln\left(\frac{c_B(0)}{c_Bo}\right) = \frac{RT}{n_AF} \ln\left(1 - \frac{|j|}{j_{li}}\right) \quad \text{at the anode}
\]

\[
\eta_{lc}^{\text{conc}} = \frac{RT}{n_cF} \ln\left(\frac{c_A(0)}{c_Ao}\right) = \frac{RT}{n_cF} \ln\left(1 - \frac{|j|}{j_{lc}}\right) \quad \text{at the cathode}
\]

where \( \eta_{li}^{\text{conc}} \) is the concentration overpotential (mass transfer limitation). For \( |j| \ll j_{li} \) these equations lead to \( \eta_{li}^{\text{conc}} \approx R_d j \) with \( R_d = RT/(n_i F j_{li}) \) the diffusion resistance.

### 1.3.3 Cell Voltage versus Current Density Curves

The electrical characteristics \( E_{\text{cell}}(j) \) can then be obtained by taking into account the different overpotentials (charge transfer overpotentials, mass transfer overpotentials, etc.) and the ohmic losses due to \( R_e \).
For the unit cell, the voltage of the cell $E_{\text{cell}}(j)$ is the difference between the positive electrode potential $E_+^+(j)$ and the negative electrode potential $E_-^-(j)$:

$$E_{\text{cell}}(j) = E_+^+(j) - E_-^-(j) - R_e j = E_{\text{cell}}^\text{rev}(j = 0) - (\eta_a + |\eta_c| + R_e j)$$  \hspace{1cm} (1.36)

where $E_{\text{cell}}^\text{rev}(j = 0)$ is the cell voltage under the reversible conditions ($j = 0$) at temperature $T$ and pressure $p$, $R_e$ is the specific resistance of the cell (electrolyte + interfacial resistance), and $\eta_a$ and $\eta_c$ are, respectively, the charge transfer and concentration overpotentials ($\eta_a > 0$ for anodic reactions and $\eta_c < 0$ for cathodic reactions).

$E_{\text{cell}}$ versus $j$ characteristics of the fuel cell, taking into account charge transfer overpotentials, concentration overpotentials, and ohmic drop, can thus be written as follows:

$$E_{\text{cell}}(j) = E_+^+(j) - E_-^-(j) - R_e |j| = E_{\text{eq}} - (|\eta_a^\text{act}(j)| + |\eta_a^\text{conc}(j)| + |\eta_c^\text{act}(j)| + |\eta_c^\text{conc}(j)|) - R_e |j|$$

By replacing each contribution of charge transfer and concentration overpotentials by their expressions, one obtains

$$E_{\text{cell}}(j) = E_{\text{cell}}^\text{rev} - \frac{RT}{\alpha n F} \ln \left( \frac{j^2}{j_{0a} \times j_{0c}} \right) - \frac{RT}{n F} \ln \left( \frac{1 - |j|/j_{0a}}{1 - |j|/j_{0c}} \right) - R_e |j|$$  \hspace{1cm} (1.37)

Using this last equation, the different contributions to energy losses are illustrated in Figure 1.5 for different $j_0$ in $A \text{ cm}^{-2}$ (charge transfer overpotential), cell resistance $R_e$ in $\Omega \text{ cm}^{-2}$ (ohmic losses), and $j_l$ in $A \text{ cm}^{-2}$ (mass transfer

![Image](image-url)

**Figure 1.5** Theoretical cell voltage versus current density $E_{\text{cell}}(j)$ curves for a PEMFC: influence of the catalytic properties of electrodes (effect of $j_0$ on the charge transfer overvoltage), of the membrane specific resistance (effect of $R_e$ on the ohmic losses), and of the mass transfer of reactants (effect of $j_l$ on the mass transfer overvoltage).
overpotential). The effect of each energy loss on $j$ at a given $E_{\text{cell}}$ of 0.7 V, that is, on the power density ($P$) of the cell, is shown for each curve, increasing from $P_0 = 0.175 \text{ W cm}^{-2}$ for the worse parameters of the membrane–electrode assembly (MEA) to $P = 1.05 \text{ W cm}^{-2}$ under optimized conditions leading to a sixfold increase in the electric performance of the cell.

1.3.4 Energy Efficiency under Working Conditions ($j \neq 0$)

1.3.4.1 Hydrogen/oxygen Fuel Cell

The electrical energy efficiency of a fuel cell system under working conditions ($j \neq 0$) at temperature $T$ can be defined as the ratio of the electrical energy produced ($W_e = n_{\text{exp}}FE_{\text{cell}} = -\Delta G^0_T$) to the total energy used, that is, the chemical energy of combustion ($-\Delta H_T \approx -\Delta H^0$ since $|\Delta H|$ does not vary very much with temperature for H$_2$O in the gaseous state – see Table 1.1):

$$\varepsilon_{\text{cell}} = \frac{\Delta G^0_T}{|\Delta H_T|} \approx \frac{\Delta G_T}{\Delta H^0}$$

The overall energy efficiency of the fuel cell ($\varepsilon_{\text{cell}}$) thus becomes

$$\varepsilon_{\text{cell}} = \frac{W_e}{(-\Delta H^0)} = \frac{n_{\text{exp}} \times F \times E_{\text{cell}}(j)}{(-\Delta H^0)} = \frac{n_{\text{th}}FE_{\text{eq}}^0}{(-\Delta H^0)} \times \frac{E_{\text{cell}}(j)}{E_{\text{eq}}^0} \times \frac{n_{\text{exp}}}{n_{\text{th}}} = \varepsilon_{\text{cell}} \times \varepsilon_E \times \varepsilon_F$$

(1.38)

where $\varepsilon_E = E_{\text{cell}}(j)/E_{\text{eq}}^0$ is the voltage efficiency referred to standard conditions and $\varepsilon_F = n_{\text{exp}}/n_{\text{th}}$ is the Faradaic efficiency, that is, the ratio between the number of electrons $n_{\text{exp}}$ effectively exchanged in the overall reaction and the theoretical number of electrons $n_{\text{th}}$ exchanged for a complete oxidation of the fuel (leading to H$_2$O for hydrogen and to H$_2$O + CO$_2$ for a carbonaceous fuel). $\varepsilon_F \approx 1$ for H$_2$ oxidation but $\varepsilon_F = 4/6 = 0.67$ for the oxidation of CH$_3$OH stopping at the formation of formic acid (four exchanged electrons instead of six electrons for complete oxidation to CO$_2$ – see [20]). $\varepsilon_F$ depends also on the fuel utilization (stoichiometric ratio).

For the PEM H$_2$/O$_2$ fuel cell, the working $E_{\text{cell}}$ at 25°C is typically 0.72 V at 1 A cm$^{-2}$ [21], which leads to

$$\varepsilon_E = \frac{E_{\text{cell}}(j)}{E_{\text{cell}}(j = 0)} = 1 - \frac{|\eta_a(j) + |\eta_c(j)| + R_e |j|)}{E_{\text{eq}}^0} = \frac{0.72}{1.229} = 0.586 \approx 59\%$$

The overall energy efficiency of a H$_2$/O$_2$ fuel cell working at 25°C and 0.72 V with $j = 1$ A cm$^{-2}$ is then (see Table 1.1)

$$\varepsilon_{\text{cell}}^{H_2/O_2} = \varepsilon_{\text{cell}}^{\text{rev}} \times \varepsilon_E \times \varepsilon_F = 0.829 \times 0.586 \times 1 = 0.486 \approx 49\%$$

with the HHV

or

$$\varepsilon_{\text{cell}}^{H_2/O_2} = \varepsilon_{\text{cell}}^{\text{rev}} \times \varepsilon_E \times \varepsilon_F = 0.945 \times 0.586 \times 1 = 0.554 \approx 55\%$$

with the LHV.

1.3.4.2 Direct Ethanol Fuel Cell

The overall combustion reaction of C$_2$H$_5$OH into O$_2$ (see reaction (1.21)) corresponds to the following thermodynamic data, under standard conditions
$\Delta G^0 = -1326 \text{ kJ mol}^{-1}; \Delta H^0 = -1367 \text{ kJ mol}^{-1}$ of C$_2$H$_5$OH.

This gives a standard electromotive force (e.m.f.) at equilibrium:

$$E^0_{eq} = \frac{-\Delta G^0}{nF} = \frac{1326 \times 10^3}{12 \times 96485} = E_2^0 - E_1^0 = 1.145 \text{ V}$$

with $n = 12$ the number of electrons exchanged per molecule for complete oxidation to CO$_2$ – see reaction (1.19). The corresponding electrical energy, $W_{el} = nF E^0_{eq} = -\Delta G^0$, leads to a mass energy density $W_e = -\Delta G^0/(3600M) = 8.00 \text{ kWh kg}^{-1}$, where $M = 0.046 \text{ kg}$ is the molecular weight of C$_2$H$_5$OH.

The theoretical energy efficiency of a direct ethanol fuel cell (DEFC), under reversible standard conditions, defined as the ratio between the electrical energy produced ($-\Delta G^0$) and the heat of combustion ($-\Delta H^0$) at constant pressure, is (see Eq. (1.8)) as follows:

$$\epsilon_{rev} = \frac{-\Delta G^0}{-\Delta H^0} = \frac{1326}{1367} = 0.969 \approx 97\%$$

But under working conditions, at a given $j$, $E_{cell}(j)$ is lower than $E^0_{eq}$ (see Eq. (1.24)), so the practical energy efficiency, for a DEFC working at 0.5 V and 100 mA cm$^{-2}$ with complete oxidation to CO$_2$, would be (see Eq. (1.38)) as follows:

$$\epsilon_{C_2H_5OH/O_2} = \epsilon_{cell} \times \epsilon_E \times \epsilon_F = 0.969 \times 0.437 \times 1 = 0.423 \approx 42\%$$

since $\epsilon_E = (E_{cell}(j)/E^0_{eq}) = (0.5/1.145) = 0.437$ and $\epsilon_F = (n_{exp}/n_{th}) = 1$ for complete oxidation to CO$_2$. This is quite similar to that of the best thermal engine (diesel engine). However, if the reaction process stops at the acetic acid stage, which involves the transfer of 4 electrons (instead of 12 for complete oxidation), the efficiency will be reduced by two-thirds, reaching only 14%.

An additional problem arises from C$_2$H$_5$OH crossover through the PEM. It results that the platinum (Pt) cathode experiences a mixed potential, since both the ORR and the C$_2$H$_5$OH oxidation take place at the same electrode. The cathode potential is thus lower, leading to a further decrease in $E_{cell}$ and a decrease in $\epsilon_E$.

### 1.4 Influence of the Properties of the PEMFC Components (Electrode Catalyst Structure, Membrane Resistance, and Mass Transfer Limitations) on the Polarization Curves

In the $E(j)$ characteristics given in Figure 1.5, one may distinguish three zones associated with the main energy losses encountered in a PEMFC, each corresponding to the influence of the characteristics of the components of the MEA: catalytic properties of the electrodes, specific resistance of the membrane, and mass transfer in the electrode structure [21]. Thus, these three key points will determine the energy efficiency and the specific power of the elementary fuel cell: in these theoretical examples, an improvement in each component of the cell will increase the power density from 0.175 to 1.05 W cm$^{-2}$, that is, an increase by a
factor of 6. As a consequence for the fuel cell systems, the weight and volume will be decreased by a similar factor, for a given power of the system, and presumably the overall cost will be similarly diminished. The improvement in the components of the elementary fuel cell has a direct effect on the system technology and therefore on the overall cost.

1.4.1 Influence of the Catalytic Properties of Electrodes

The effect of the nature of the catalytic layer is particularly visible at the beginning of the $E(j)$ characteristics (low current densities) and corresponds to the charge transfer polarization, that is, the activation overpotentials due to a relatively low electron transfer rate at the electrode–electrolyte interface. This comes mainly from the ORR whose $j_0$ is much smaller than that of the HOR. An increase in $j_0$ from $10^{-8}$ to $10^{-6}$ A cm$^{-2}$ leads to an increase in $j$ (at 0.7 V) from 0.4 to 0.9 A cm$^{-2}$, that is, an increase in the energy efficiency and in the power density by 3.6 times compared to the initial curve (Figure 1.6).

Similar behavior is encountered in the electrooxidation of alcohols, whose kinetics is rather slow, which needs active catalysts to increase $j_0$ and thus $j$ at a given $E_{cell}$, as shown in Figure 1.7 for a DEFC [8].

1.4.2 Influence of the Membrane-specific Resistance

The $E$ versus $j$ linear part of the $E(j)$ characteristics corresponds to ohmic losses $R_e |j|$ resulting from $R_e$ due to the electrolyte and interface resistances. A decrease

![Figure 1.6 Influence of the catalytic properties of electrodes ($j_0 = 10^{-8}$ or $10^{-6}$ A cm$^{-2}$) on the $E_{cell}$ versus $j$ characteristics $E(j)$. Source: Lamy 2011 [21]. Reproduced with permission of Elsevier.](image)
Specific resistance \( R_e \) from 0.3 to 0.15 \( \Omega \text{ cm}^2 \) leads to an increase in \( j \) (at 0.7 V) from 0.25 to 0.4 A cm\(^{-2}\), that is, an increase in the energy efficiency and in the power density by 1.6 times (see Figure 1.5). This was experimentally observed by Ballard Power Systems when comparing the behavior of Nafion® and Dow® membranes, which are sulfonated perfluorinated membranes (Figure 1.8) [22].

1.4.3 Influence of the Mass Transfer Limitations

The effect of the structure of the gas diffusion layer (GDL) controls \( j_l \) associated with mass transfer limitations for the reactive species and reaction products to and/or from the electrode active sites. An increase in \( j_l \) from 1.4 to 2.2 A cm\(^{-2}\) leads to a further increase in \( j \) (at 0.7 V) from 0.9 to 1.5 A cm\(^{-2}\), that is, an increase

![Figure 1.7](image.png)

**Figure 1.7** Fuel cell characteristics of a DEFC recorded at 110 °C: (a) polarization curves; (b) power density curves. Influence of the nature of the Pt-based catalyst (30% loading loading on XC72 carbon powder) containing tin (Sn), ruthenium (Ru), or molybdenum (Mo). Anode catalyst: 1.5 mg cm\(^{-2}\); cathode catalyst: 2 mg cm\(^{-2}\) (40% Pt/XC72 E-TEK; membrane: Nafion® 117; C\(_2\)H\(_5\)OH concentration: 1 M. (Reproduced with permission from Ref. [8]. Copyright 2009 Wiley-VCH.)

![Figure 1.8](image.png)

**Figure 1.8** \( E(j) \) characteristics of an elementary PEMFC with different membranes: ▲ Dow (\( e = 125 \mu \text{m} \)); ○ Nafion® 115 (\( e = 125 \mu \text{m} \)); △ Nafion® 117 (\( e = 175 \mu \text{m} \)).
in the energy efficiency and in the power density by six times compared to the initial curve with $j_0 = 10^{-8} \text{ A cm}^{-2}$, $R_e = 0.30 \Omega \text{ cm}^2$ and $j_l = 1.2 \text{ A cm}^{-2}$ (Figure 1.5). This was experimentally observed for three different GDLs of different composition at the air cathode: a microporous layer (MPL), coated with 30 wt.% fluorinated ethylene propylene (FEP), and two other FEP-impregnated layers with 30 and 10 wt.% FEP, respectively (Figure 1.9) [23].

1.5 Representative Examples of Low-temperature Fuel Cells

Several review papers on fuel cells and their different applications have been recently published. For example, Sharaf and Orhan presented many possible applications of the different kinds of fuel cells, particularly for portable electronics and the electric vehicle [24], whereas Wang et al. focused their paper on PEMFCs, their technology, and applications mainly for the electric vehicle [25]. Li and Faghri did a review of DMFC stacks for recharging Li-ion batteries for portable equipments and on portable fuel cell systems for soldiers [26]. On the other hand, many review papers on PEMFCs for the electrical vehicle can be found in recent publications [27–29].

1.5.1 Direct Methanol Fuel Cell for Portable Electronics

The electrocatalytic oxidation of CH$_3$OH has gained much interest over a number of years because it is the simplest alcohol which can be completely oxidized to CO$_2$ in a DMFC [6,7,30], thus providing the maximum energy densities (6.1 kWh kg$^{-1}$ or 4.8 kWh dm$^{-3}$). The great advantage of a DMFC is that CH$_3$OH is a liquid fuel, thus more easily handled and stored than H$_2$. Moreover, CH$_3$OH is produced in large quantities from natural gas by steam methane reforming (SMR) at a low cost (~0.2 US dollar per liter), making it a key product in the chemical industry. Its toxicity is relatively low and its boiling point (~65 °C) makes it liquid for most
The development of PEM led to great simplification of DMFC by avoiding a fuel processor that must provide a reformate gas with a low concentration of carbon monoxide (CO) (<10 ppm, otherwise it may strongly poison the catalysts used in the Pt-based anode). Due to system simplicity, DMFCs are particularly efficient power sources for portable electronics (cell phones, laptop computers, cam recorders, etc.) and for small-size applications (micropower sources, power sources for the soldier, propulsion of small devices such as golf carts, drones, etc.).

A DMFC consists of two electrodes, a catalytic CH$_3$OH anode, and a catalytic O$_2$ cathode, separated by an ionic conductor, preferably an acid electrolyte, for rejecting the CO$_2$ produced. Great progress was made by feeding CH$_3$OH directly to the anodic compartment of a PEMFC, in which the protonic membrane, for example, Nafion$^\circledR$, plays the role both of an acidic medium and of a separator between the two electrode compartments (Figure 1.10). This technology has the added advantage of thin elementary cells and hence of compact stacks.

The electrochemical oxidation of CH$_3$OH occurs on the anode electrocatalyst (e.g., dispersed Pt-based catalysts), which constitutes the negative pole of the cell:

\[
\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6 \text{H}^+ + 6 \text{e}^- \quad \text{in acid electrolytes} \quad (1.18)
\]

\[
\text{CH}_3\text{OH} + 8 \text{OH}^- \rightarrow \text{CO}_3^{2-} + 6 \text{H}_2\text{O} + 6 \text{e}^- \quad \text{in alkaline electrolytes} \quad (1.39)
\]

whereas the electrochemical reduction of O$_2$ occurs at the cathode (also containing a Pt-based catalyst) that constitutes the positive pole of the cell:

\[
\frac{1}{2} \text{O}_2 + 2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2\text{O} \quad \text{in acid electrolytes} \quad (1.13)
\]

\[
\frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2 \text{e}^- \rightarrow 2 \text{OH}^- \quad \text{in alkaline electrolytes} \quad (1.40)
\]

![Figure 1.10 Schematic diagram of a DMFC based on a PEM. Source: Lamy 2014 [20]. Reproduced with permission of Springer.](image-url)
The overall reaction corresponds thus to the catalytic combustion of CH₃OH into O₂:

\[
\text{CH}_3\text{OH} + \frac{3}{2} \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O} \quad \text{in acid electrolytes} \quad (1.20)
\]

\[
\text{CH}_3\text{OH} + \frac{3}{2} \text{O}_2 + 2 \text{OH}^- \rightarrow \text{CO}_3^{2-} + 3 \text{H}_2\text{O} \quad \text{in alkaline electrolytes} \quad (1.41)
\]

One main advantage of such a power source is the direct transformation of the chemical energy of CH₃OH combustion into electrical energy, thus avoiding a low energy efficiency given by the Carnot’s theorem for thermal engines. Hence, \( E_{\text{cell}}^{\text{rev}} \) can be calculated from the Gibbs energy change, \( \Delta G_r \), associated with the total combustion reaction of CH₃OH (reaction (1.20)), by the following equation:

\[
\Delta G_r + nF E_{\text{cell}}^{\text{rev}} = 0 \quad \text{leading to} \quad E_{\text{cell}}^{\text{rev}} > 0
\]

since \( \Delta G_r < 0 \) (spontaneous reaction)

where \( n = 6 \) is the number of Faradays (per mole of CH₃OH) involved in the half-cell reaction (1.18) or (1.39).

Under standard conditions (25 °C), the enthalpy change \( \Delta H^0 \) for reaction (1.20), is \(-726\) kJ mol\(^{-1}\) of CH₃OH, and the Gibbs energy change \( \Delta G^0 \) is \(-702\) kJ mol\(^{-1}\) of CH₃OH (see Table 1.2). This corresponds to a standard reversible cell voltage \( (E_{\text{cell}}^0) \) as given by the following equation:

\[
E_{\text{cell}}^0 = E_c^0 - E_a^0 = -\frac{\Delta G^0}{nF} = \frac{702 \times 10^3}{6 \times 96485} = 1.213 \text{ V}
\]

where \( E_c^0, E_a^0 \), the standard potentials of each electrode versus SHE used as a reference electrode, are defined as the difference of the inner potential at each electrode–electrolyte interface.

The main features of the DMFC are its high specific energy \( (W_s) \) and high volume energy density \( (W_{sl}) \), the values of which are calculated as follows:

\[
W_s = \frac{(-\Delta G^0)}{3600 \times M} = \frac{702 \times 10^3}{3600 \times 0.032} = 6.09 \text{ kWh kg}^{-1}
\]

and \( W_{sl} = W_s \times \rho = 4.82 \text{ kWh dm}^{-3} \), where \( M = 0.032\) kg is the molar weight of CH₃OH and \( \rho = 0.7914 \text{ kg dm}^{-3} \) its density.

Under standard reversible conditions (25 °C), the energy efficiency is very high:

\[
\varepsilon_{\text{cell}}^{\text{rev}} = \frac{W_e}{(-\Delta H^0)} = \frac{nFE_{\text{cell}}^0}{(-\Delta H^0)} = \frac{\Delta G^0}{\Delta H^0} = \frac{702}{726} = 0.967 \approx 97\%
\]

It is much higher than that of a H₂/O₂ fuel cell (i.e., 83%) under standard conditions. However, under usual operating conditions, at a given \( j \), the electrode potentials deviate from their equilibrium values due to large overpotentials, \( \eta \), at both electrodes (Figure 1.11):

\[
\eta_a = E_a(j) - E_a^0 \geq 0 \quad \text{at the CH₃OH anode}
\]

\[
\eta_c = E_c(j) - E_c^0 \leq 0 \quad \text{at the O₂ cathode}
\]
This results from a slow kinetics of both CH\textsubscript{3}OH oxidation and ORR. An additional loss is due to $R_e$ (arising mainly from the proton conducting membrane). $E_{\text{cell}}$ under working conditions is thus

$$E_{\text{cell}}(j) = E_c(j) - E_a(j) - R_e j = E_{\text{cell}}(0) - (\eta_c + \eta_a + R_e j) \leq E_{\text{cell}}(0)$$  \hspace{1cm} (1.36)

so the energy efficiency will be decreased proportionally to the voltage efficiency $\varepsilon_E$.

For a DMFC working at 200 mA cm\textsuperscript{-2} and 0.5 V (e.g., with a Pt-Ru anode), this ratio will be

$$\varepsilon_E = 0.5/1.21 = 0.413 = 41.3\%$$

and the overall efficiency of the fuel cell will be (see Eq. (1.38))

$$\varepsilon_{\text{MeOH}} = \varepsilon_{\text{cell}} \times \varepsilon_E \times \varepsilon_F = 0.967 \times 0.413 \times 1 = 0.399 \approx 40\%$$

assuming a Faradaic efficiency of 100%, that is, the total oxidation of CH\textsubscript{3}OH. This is acceptable for an autonomous power source oxidizing CH\textsubscript{3}OH completely to CO\textsubscript{2} and giving the theoretical number of Faradays $n_{\text{th}} = 6$ F per mole of CH\textsubscript{3}OH – see reaction (1.18) or (1.39). However, under some operating conditions CH\textsubscript{3}OH oxidation to CO\textsubscript{2} is not complete, so a Faradaic efficiency is introduced, $\varepsilon_F = n_{\text{exp}}/n_{\text{th}}$, where $n_{\text{exp}}$ is the number of Faraday effectively exchanged in the half-cell reaction.

Therefore, the overall efficiency $\varepsilon_{\text{cell}} = \varepsilon_{\text{cell}}^{\text{rev}} \times \varepsilon_E \times \varepsilon_F$ may be dramatically decreased, for example, if the electrooxidation stops at the formaldehyde stage:

$$\text{CH}_3\text{OH} \rightarrow \text{HCHO} + 2\,\text{H}^+ + 2\,\text{e}^- \hspace{1cm} (n_{\text{exp}} = 2)$$

or at the formic acid stage:

$$\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{HCOOH} + 4\,\text{H}_\text{aq}^+ + 4\text{e}^- \hspace{1cm} (n_{\text{exp}} = 4)$$
Thus leading, respectively, to a Faradaic efficiency:

\[ \varepsilon_F = \frac{n_{\text{exp}}}{n_{\text{th}}} = \frac{2}{6} = 0.333 \]

or

\[ \varepsilon_F = \frac{n_{\text{exp}}}{n_{\text{th}}} = \frac{4}{6} = 0.667 \]

and, respectively, to an overall energy efficiency:

\[ \varepsilon_{\text{MeOH cell}} = \varepsilon_{\text{cell}}^{\text{rev}} \times \varepsilon_E \times \varepsilon_F = 0.967 \times 0.413 \times 0.333 = 0.133 \approx 13\% \]

or

\[ \varepsilon_{\text{MeOH cell}} = \varepsilon_{\text{cell}}^{\text{rev}} \times \varepsilon_E \times \varepsilon_F = 0.967 \times 0.413 \times 0.667 = 0.266 \approx 27\% \]

The electrical characteristic of a DMFC depends strongly on the nature and structure of the anode catalysts. Pt-Ru nanoparticle catalysts dispersed on an electron conductive substrate, such as Vulcan XC-72R carbon powder, give the best results. The bimetallic composition is particularly important and the optimum atomic composition corresponds to 20% Ru versus 80% Pt, that is, an atomic ratio of Pt:Ru close to 4:1, as discussed in Section 3.3.4.1 of Chapter 3. This is illustrated in Figure 1.12 [31].

DMFC systems are, therefore, competitive with energy density on the order of 400 Wh kg\(^{-1}\) or 500–800 Wh l\(^{-1}\), which is two–three times greater than that of a Li-ion battery [26]. DMFC systems have been developed by several companies all around the world: Toshiba, Sony, Panasonic, Sharp, Hitachi in Japan; Samsung in South Korea; Jet Propulsion Laboratory, MTI Microfuel Cells, Oorja Protonics, Relion in USA; ZSW, Julich Center, Smart Fuel Cells, Baltic Fuel Cells in Germany;

![Figure 1.12 E(j) and P(j) curves of a single DMFC with Pt-Ru/C electrodes of different Pt-Ru atomic ratios. Anode loading: 2 mg cm\(^{-2}\) Pt-Ru/C; membrane: Nafion\textsuperscript{®} 117; cathode loading: 2 mg cm\(^{-2}\) Pt/C; [MeOH] = 2 M, 2 ml min\(^{-1}\), \(p_{\text{MeOH}} = 2\) bar; \(T_{\text{cell}} = 110^\circ\text{C}\); \(O_2 = 120\) ml min\(^{-1}\), \(p_{O_2} = 2.5\) bar; \(T_{\text{MeOH}} = T_{O_2} = 95^\circ\text{C}\). Source: Coutanceau 2004 [31]. Reproduced with permission of Springer.](attachment:image.png)
CMR Fuel Cells Limited in UK; and Cellera Technologies in Israel. They can be used as small power sources, mainly for portable electronics (cell phone, notebook PC, music player, electric tools, soldier equipment, etc.) with liquid CH$_3$OH stored either in a small cartridge or in a small tank. In most of these technologies, the DMFC provides power for recharging a Li-ion battery, thus extending greatly its autonomy and allowing a quick recharge of the system by refilling the tank with fresh CH$_3$OH.

This last point is illustrated in Figures 1.13 and 1.14 showing a Toshiba DMFC of 5 W to recharge a Li-ion battery for a cell phone [32] and a LG Chemical DMFC of 25 W to power a laptop computer [26]. Eight unit cells, each having 9 cm$^2$ of active surface area, are connected in series [32] in order to raise the output voltage to 2.5–3.9 V, which is the typical voltage range for most cell phone applications.

Finally to favor the commercial issue of DMFC, new low-cost components have to be developed, particularly catalysts with a lower amount of platinum group metals (PGMs) or even with no noble metals, and high-temperature-resistant membranes of lower cost than Naion$^{	ext{®}}$ and of higher protonic conductivity and stability to operate the DMFC at higher temperatures (150–200 °C), which may increase the power density through thermal activation of the reaction kinetics.
1.5.2 Hydrogen/air PEMFC for the Electrical Vehicle

An elementary PEMFC comprises several elements and components: the MEA, the flow-field plate (bipolar plate (BP), which also ensures electric contact with the next cell and evacuation of excess heat), gaskets to ensure tightness to reactants, and end plates (Figure 1.15).

The MEA consists of a thin (10–200 μm) solid polymer electrolyte (a protonic membrane, such as Nafion®) on both sides of which are pasted the electrode structures (fuel anode and O₂ cathode) (Figure 1.16). The electrode structure comprises several layers: a first layer made of carbon paper (or cloth) to strengthen...
the structure, on which are coated the GDLs, and then the catalyst layer (CL), directly in contact with the protonic membrane [10].

The PEM, which is a solid polymer electrolyte, plays a key role in the PEMFC. It allows the electrical current to pass through it thanks to its $\mathrm{H^+}$ ionic conductivity and prevents any electronic current through it in order that electrons are obliged to circulate in the external electric circuit to produce the electric energy corresponding to the combustion reaction of the fuel; it must avoid any gas leakage between the anodic and the cathodic compartments, so that no chemical combination between $\mathrm{H_2}$ and $\mathrm{O_2}$ is directly allowed; it must be stable mechanically, thermally (up to 150 °C in order to increase the working temperature of the cell) and chemically; and finally, its lifetime must be sufficient for practical applications (e.g., >2000 h for transportation power trains or >40 000 h for stationary power plant).

Using a Naion® 212 membrane (50 μm thickness) and optimized Pt/C electrodes, one obtains good electrical characteristics with power density greater than 1.2 W cm$^{-2}$ [21] (Figure 1.17).

A single cell delivers a cell voltage between 0.5 and 0.9 V (instead of $E_{\text{eq}}^{\text{cell}} = 1.23$ V under standard equilibrium conditions), depending on the working conditions and $j$, so many elementary cells, electrically connected by the bipolar plates, are assembled together in a filter press configuration (in series and/or in parallel) to reach the nominal voltage (such as 48 V for electric vehicles) and the power needed for a given application. Such fuel cell stacks are able to power an electric vehicle, for example, the FCveloCity® fuel cell stacks (developed by Ballard Power Systems) that can deliver electric power from 4 to 21 kW [33] (Figure 1.18).

The actually developed PEMFC have a Naion® membrane, which partially fulfills these requirements, since its thermal stability is limited to 100 °C and its protonic conductivity strongly decreases at higher temperatures because of its dehydration. On the other hand, it is not completely tight to liquid fuels (such as alcohols). This is as important as the membrane is thin (a few 10 μm). Furthermore,
its actual cost is still too high (about € 400 per m$^2$), so its use in a PEMFC for a low-cost passenger electric car is still a challenge.

One of the main problems of low temperatures (20–90 °C) PEMFCs is the relatively low kinetics rate of the electrochemical reactions involved, for example, ORR at the cathode and fuel (pure H$_2$ or H$_2$ from a reformate gas) oxidation at the anode. Pt-based catalysts are actually the only efficient catalysts used in commercial PEMFCs, but PGM loading of the electrode is still too high, particularly at the O$_2$ electrode, leading to a large part of the MEA cost. Another problem, particularly crucial for the electric vehicle, is the relatively low working temperature (70–90 °C), which prevents efficient exhaust of the excess heat generated by the power fuel cell. Therefore, new membranes, such as polybenzimidazole [34], are investigated with improved stability and conductivity at higher temperatures (up to 150 °C). For power fuel cells, the increase in temperature will increase the rate of the electrochemical reactions occurring at both electrodes, that is, $j$ at a given $E_{\text{cell}}$ and the specific power. Furthermore, thermal management and heat utilization will be improved, particularly for residential applications with heat cogeneration, and for large-scale applications to exhaust excess heat.

Fuel supply is usually from liquid H$_2$ or pressurized gaseous H$_2$ (between 350 and 700 bars). For other fuels, such as natural gas, CH$_3$OH, and so on, a fuel processor is needed, which includes a reformer, water gas shift reactors, and purification reactors (in order to decrease – a few tens of parts per million – the amount of CO to an acceptable level, which would otherwise poison the Pt-based catalysts). This equipment is still heavy and bulky and limits the dynamic response of the fuel cell stack, particularly for the electric vehicle in some urban driving cycle. In addition, the nature of other auxiliary equipment depends greatly on the stack characteristics and targeted applications (Figure 1.19):

- Air compressor, the characteristics of which are related to the differential pressure supported by the PEM
- Humidifiers for the reacting gases with controlled humidification conditions
- Preheating of gases to avoid any condensation phenomena
- H$_2$ recirculation, purging system of the anode compartment
- Cooling system for MEAs
- Control valves of pressure and/or gas flows
- DC/DC or DC/AC electric converters
The system control must ensure correct working of the system, not only under steady-state conditions but also during power transients. All the elementary cells must be controlled (measurement of $E_{\text{cell}}$ of each elementary cell, if possible) and the purging system must be activated in case of technical incident.

The electrical energy efficiency of such a device is very high, reaching 55% under usual operating conditions ($T = 70$ °C, $p = 2$ to 3 bars). This is at least two–three times more than the energy efficiency of an ICE, so the PEMFC stacks are very attractive sources for the electric vehicle [24]. Moreover, the thickness of an elementary cell is rather small (on the order of a few millimeters), so PEMFC stacks of 10–100 kW, consisting of a few hundred elementary cells in series (Figure 1.20), are very compact leading to high power density (3.1 kW kg$^{-1}$ or 2.5 kW dm$^{-3}$ for the stack) and about 1 kW per kg or per liter for the entire system (fuel cell stack with its auxiliary components), fitting easily under the hood of the car.

Therefore, PEMFCs provide power trains to car manufacturers for their electrical vehicles with near-zero harmful emissions without having to compromise the efficiency of the vehicle’s propulsion system. Due to their inherent advantages, such as static operation, fuel flexibility, modularity, dynamic response, low operation temperatures, and low maintenance requirements, fuel cells become an ideal alternative to the actual ICEs, provided that durability, low cost, H$_2$ infrastructure, and technical targets are met on schedule. Japan, for example, plans to deploy 2 million fuel cell electric vehicles (FCEVs) with 1000 hydrogen refueling stations by 2025 [24]. Many car manufacturers (General Motors, Toyota, Mazda, Daimler AG, Volvo, Volkswagen, Honda, Hyundai, Nissan, etc.) have

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**Figure 1.19** Detailed scheme of a PEMFC system with its auxiliary and control equipment. (Reproduced with permission from Ref. [21]. Copyright 2011 Elsevier.)
demonstrated the feasibility of electrical vehicles equipped with a fuel cell stack to power the main propulsion system (Figure 1.21). Some of them have begun the commercialization of FCEVs, such as the ix35 [35] of Hyundai (Korea) at the beginning of 2013 in Denmark and Sweden, and the Toyota Mirai at the end of 2015 in Japan and California.

As an example, the Toyota Mirai (Figure 1.22) is a five-seat compact car equipped with a 114 kW PEMFC stack (volumetric specific power of 3.1 kW dm$^{-3}$), allowing a maximum speed of 175 kmph, a nickel metal hydride battery and two fuel tanks with a total of 1221 of compressed H$_2$ at 700 bars (weight storage density of 5.7%) providing an autonomy close to 600 km [36].

In Europe, Daimler AG is ready to commercialize its B-Class with a fuel cell stack of 100 kW and a Li-ion battery of 1.4 kWh leading to a maximum speed of

Figure 1.20 Fuel cell stack of 80 kW for transportation applications.

Figure 1.21 Some examples of FCEVs ready to be commercialized.
170 kmph and autonomy of about 400 km with a H$_2$ tank of 3.7 kg at 700 bars (Figure 1.23) [37].

1.6 Conclusions and Outlook

The actual development of LT PEMFCs fed either with H$_2$ or with a liquid fuel, such as an alcohol (CH$_3$OH, C$_2$H$_5$OH, etc.), gives us new opportunities to improve our environment, by providing electric power sources with good energy efficiency (40–55%) and near zero emissions of pollutants (except for the production of H$_2$ from carbon-containing fossil fuel, for example, by SMR).

The H$_2$/O$_2$ (air) PEMFC is nearly mature to power the electric vehicle and automakers are quite ready to commercialize such cars, provided hydrogen refueling stations are put in place everywhere. This is the responsibility of federal and local governments, for example, California in the United States, to promulgate the corresponding laws in order to improve the air quality of large cities (e.g., Los Angeles) by preventing any emissions of deleterious gases (NO$_x$, SO$_x$, etc.) or GHGs (i.e., CO$_2$) produced by ICE cars still consuming fossil fuels.

On the other hand, small DAFCs, particularly the DMFCs, are developing rapidly for powering portable electronics, either to recharge their lithium battery
or to supply power directly to them, due to their ease of fuel refueling and greater autonomy compared to the lithium batteries.

Further progress in the development of LT PEMFCs, either the $\text{H}_2/\text{O}_2$ PEMFC or the DAFC (DMFC or DEFC), depends on the investigation of improved or new electrocatalysts, particularly for the ORR and the AOR, which is still a challenge for scientists and engineers working in the field of electrocatalysis.

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