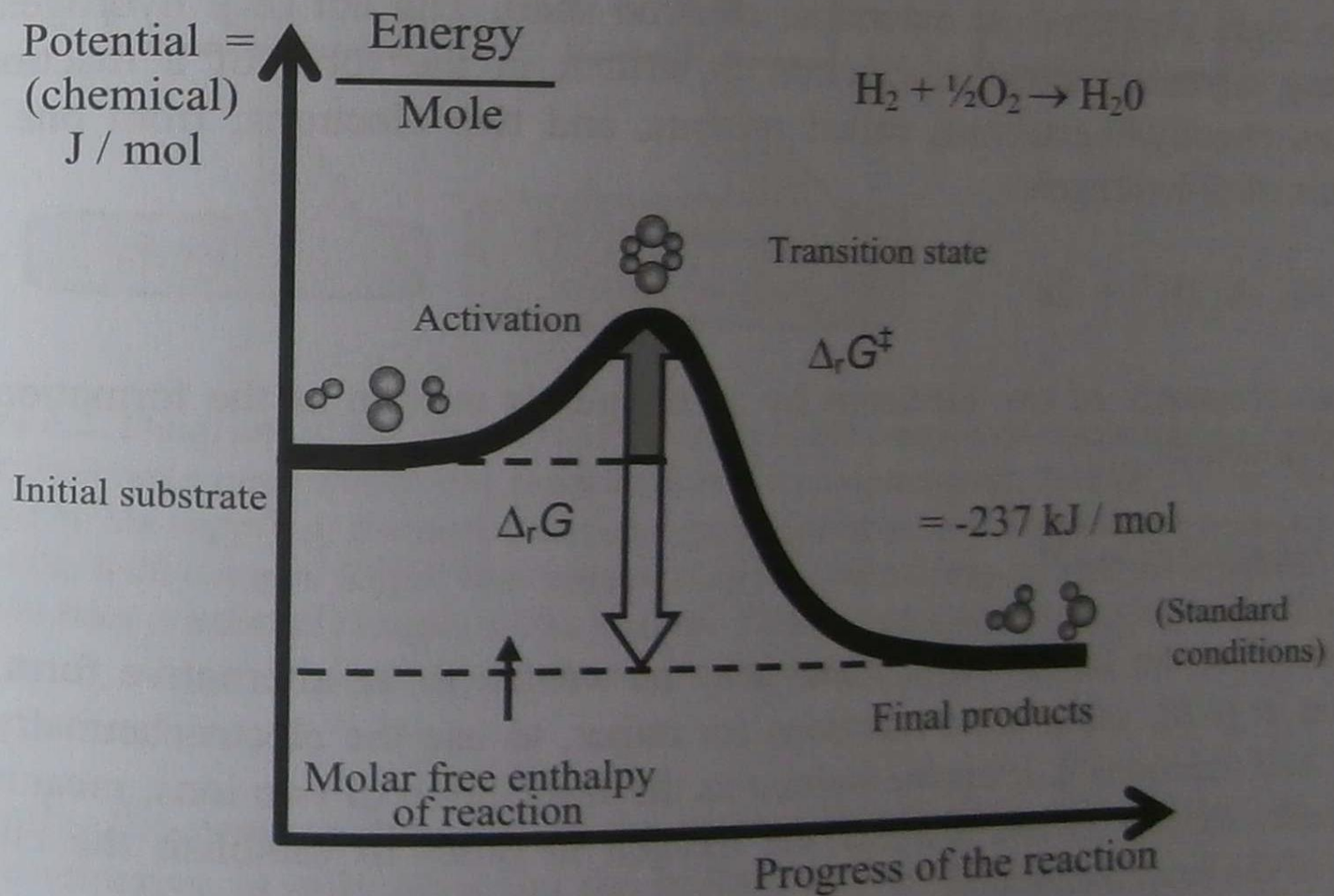


Chemical reagents that are continuously replaceable are known as *fuels* or *combustives* depending on their role in the reaction, as we shall see later on. Therefore, the fuel cell is a primary battery whose reagents are renewable during use. The primary/secondary distinction continues to be important for systems with renewable reagents, although these are rarely used for secondary batteries. A fuel cell functions in only one direction, that of converting chemical energy into electrical energy, whereas a *fuel accumulator* can function in both directions. Technologically speaking, this latter system is made up of two devices that can function independently: a fuel cell and an electrolyzer (the name given to a device that converts electrical energy to chemical energy). Table 6.1 lists the four categories that are founded in the criteria of rechargeability and renewability of reagents.

Process	Non-renewable fuel	Renewable fuel
Non-rechargeable	Primary battery	Fuel cell
Rechargeable	Accumulator (secondary battery)	Fuel cell + electrolyzer



**Figure 6.1.** Evolution of molar energy, the chemical potential, during the reaction to form water

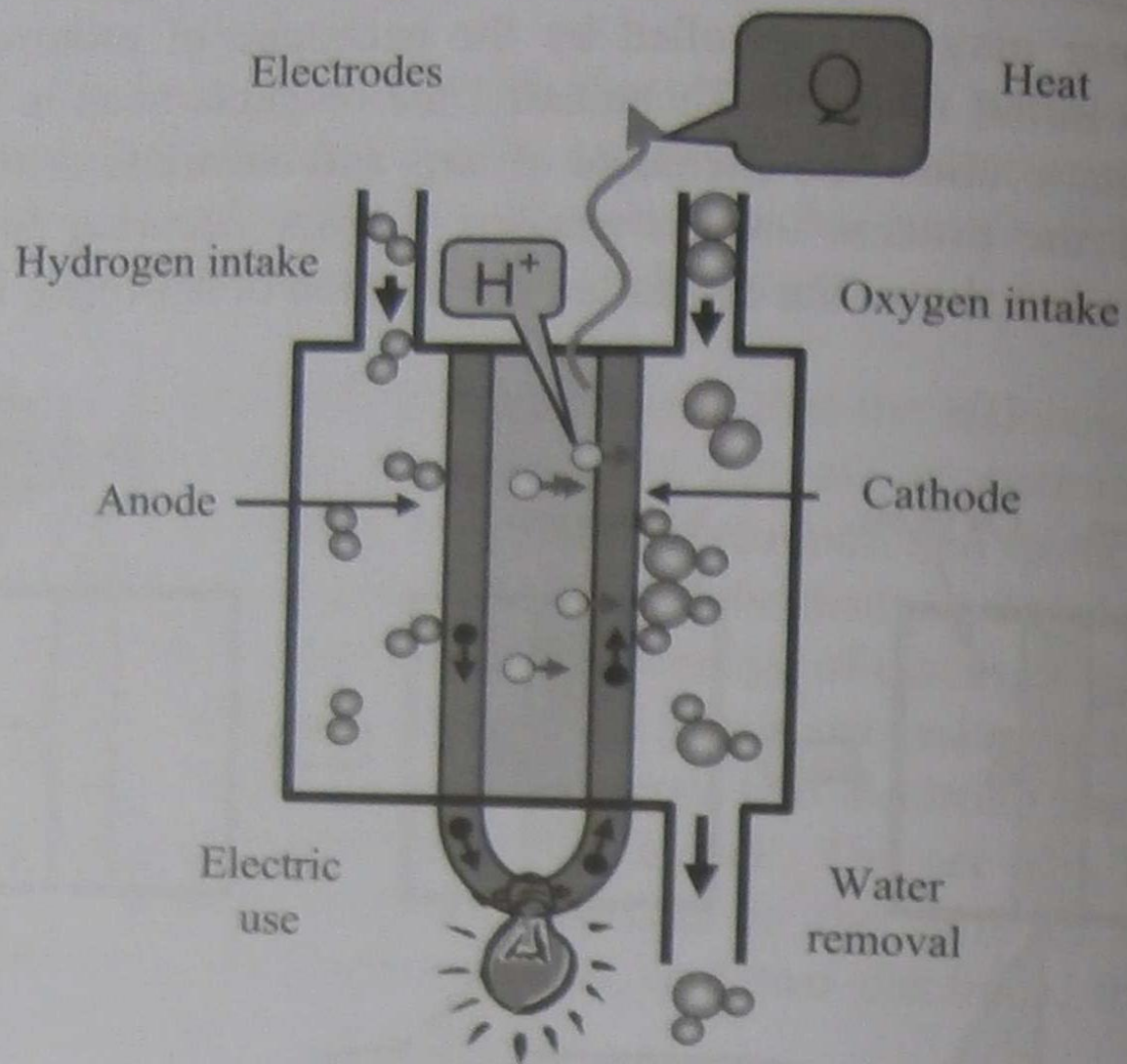
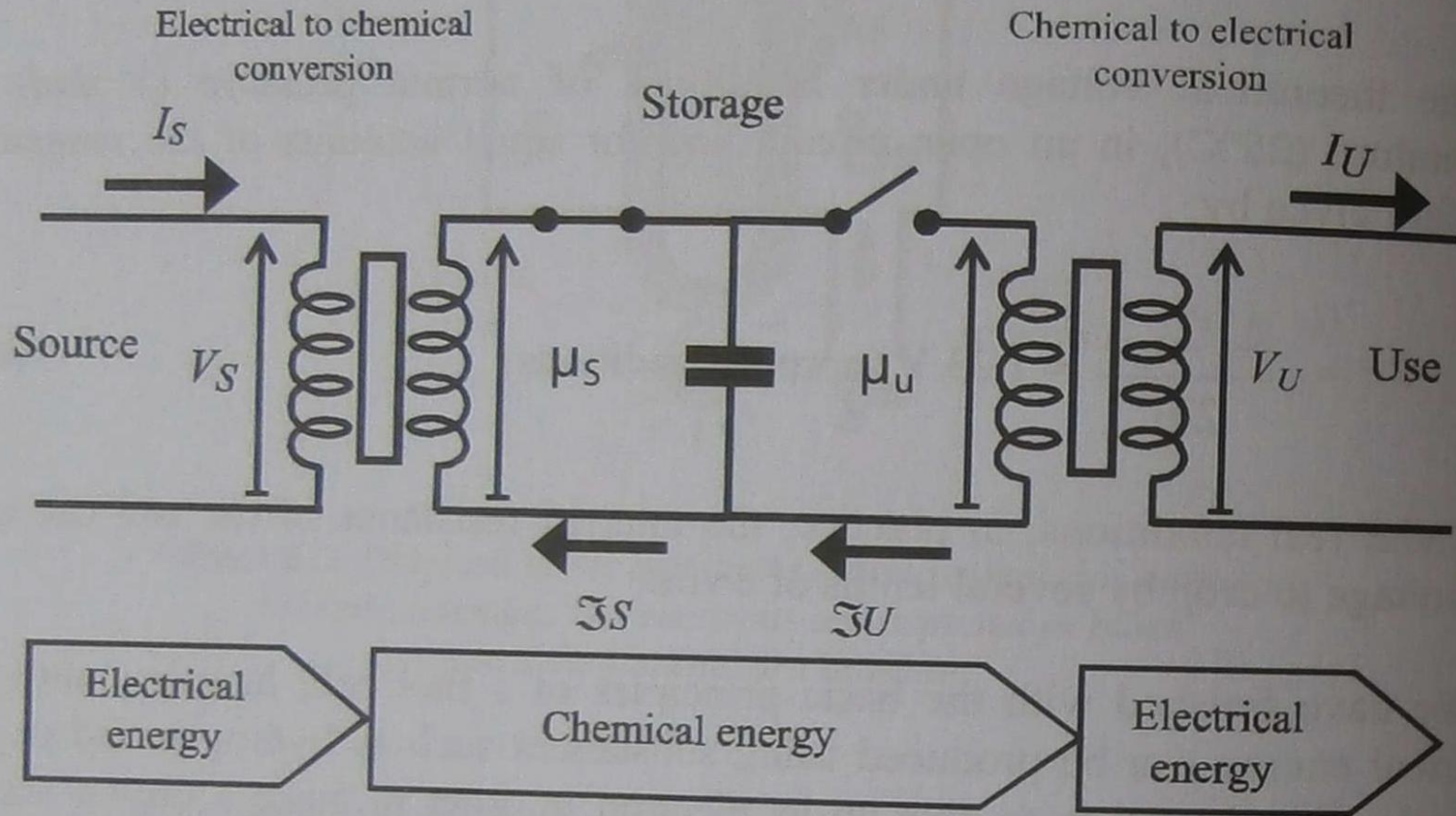


Figure 6.3. Diagram of the principles behind a fuel cell based on proton exchange. The electrons are depicted in black and the protons are in white

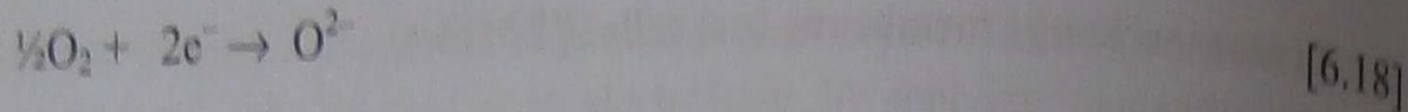




**Figure 6.4.** Equivalent circuit for a conversion device that stores electrical energy in chemical form using an electrolyzer (left) and a fuel cell (right). The interrupter positions corresponds to the storage function

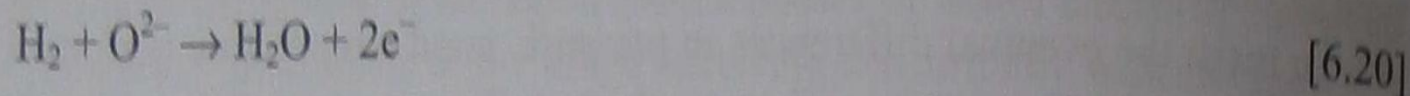
## 6.5. The solid oxide fuel cell (SOFC)

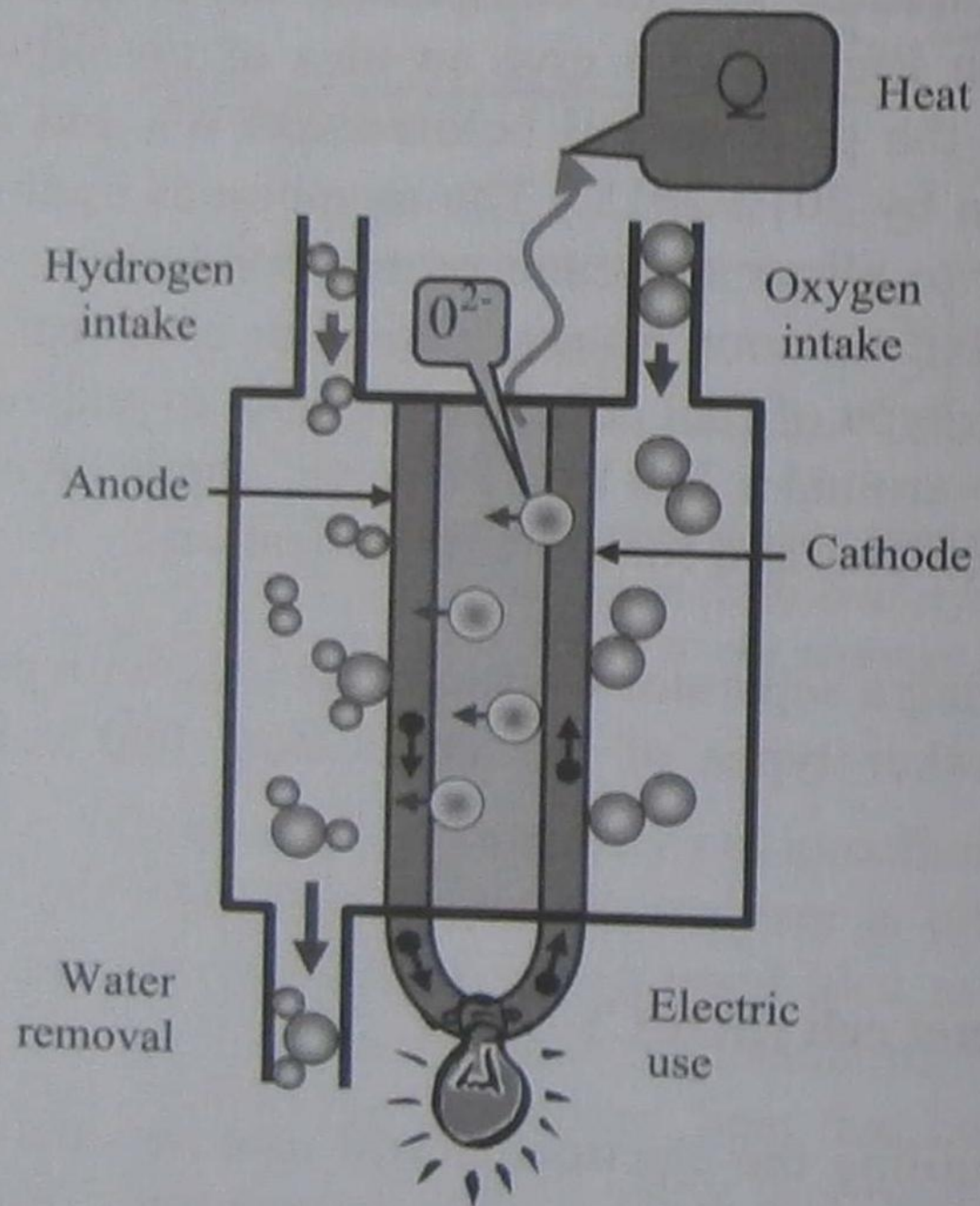
When we were detailing the electrochemical reactions that govern the formation of water, we had mentioned that the two partial reactions of oxidation of hydrogen [6.9] and of reduction of oxygen [6.10] and the reaction for water formation [6.11] that we repeat here:



could be combined in several ways, and therefore that the reaction [6.12] on which a PEMFC is based was not the only way in which to control the combustion.

For example, combining reactions [6.17] and [6.19] instead of [6.18] and [6.19] gives:







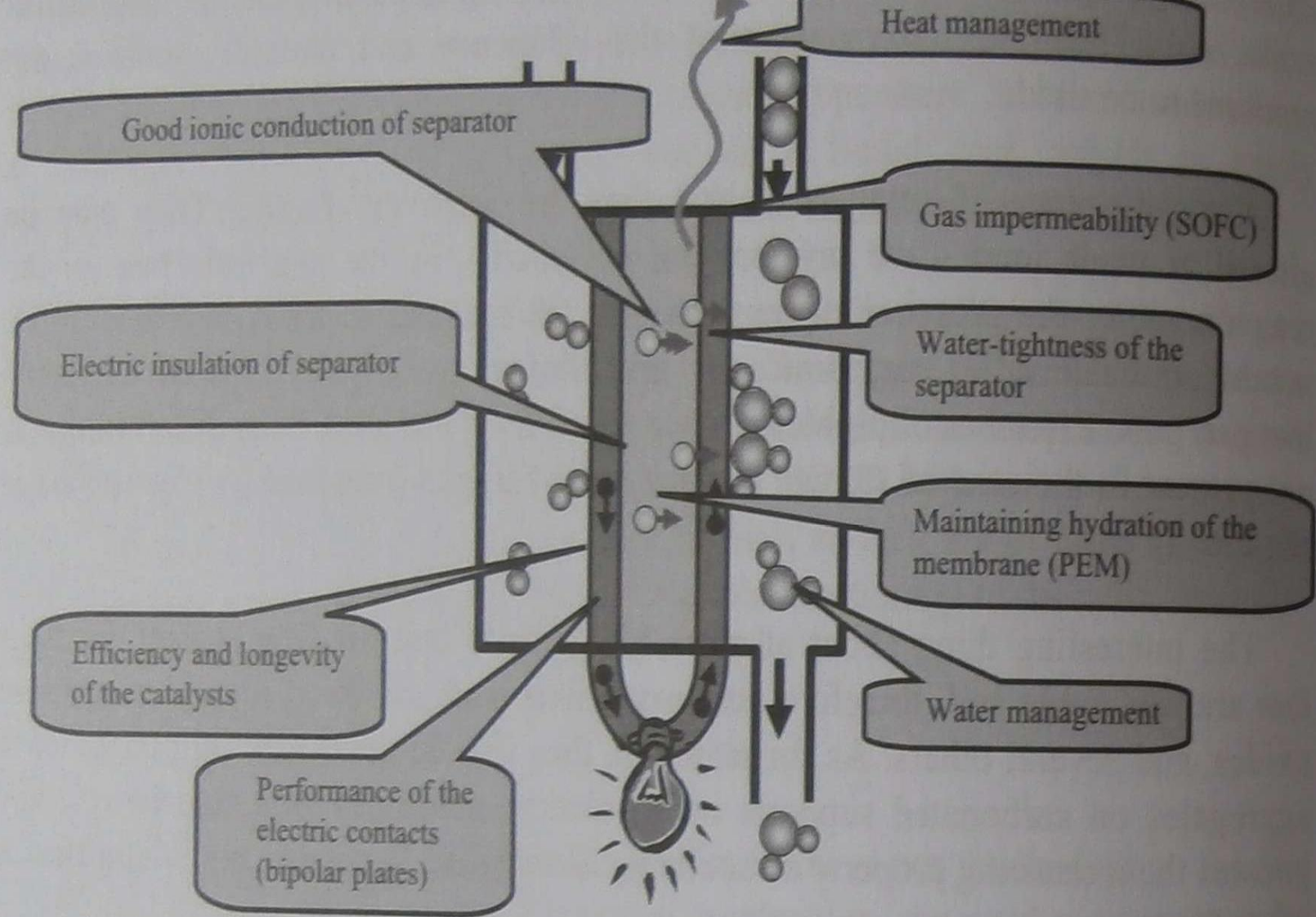


Figure 6.8. *The critical points in fuel cell technology (outside of cost issues)*

## 6.10. Conclusion: the storage application

We have already mentioned a few points about fuel cells in relation to storage, and we recall these here briefly:

- linking an electrolyzer and a fuel cell forms a realistic device, the fuel accumulator;
- usage and storage may occur concurrently (unlike for a purely electrochemical accumulator);
- the heat released by the cell can be supplied to the electrolyzer (high temperature), which increases the overall efficiency (without this it would be around 25%);

conversion of the



We will now list a few characteristics that favor the fuel accumulator:

- storage does not have mass or volume constraints, nor are there restrictions on the mobility or the range, which exist for an onboard battery, and this leads to cheaper and easier realization;
- storage capacity is much higher than for an accumulator battery, for a comparable cost. It is only limited by the hydrogen reservoir;
- coupling with other sources of hydrogen production (bio-sources for example) gives flexibility;
- respect for the environment and durable development are facilitated.

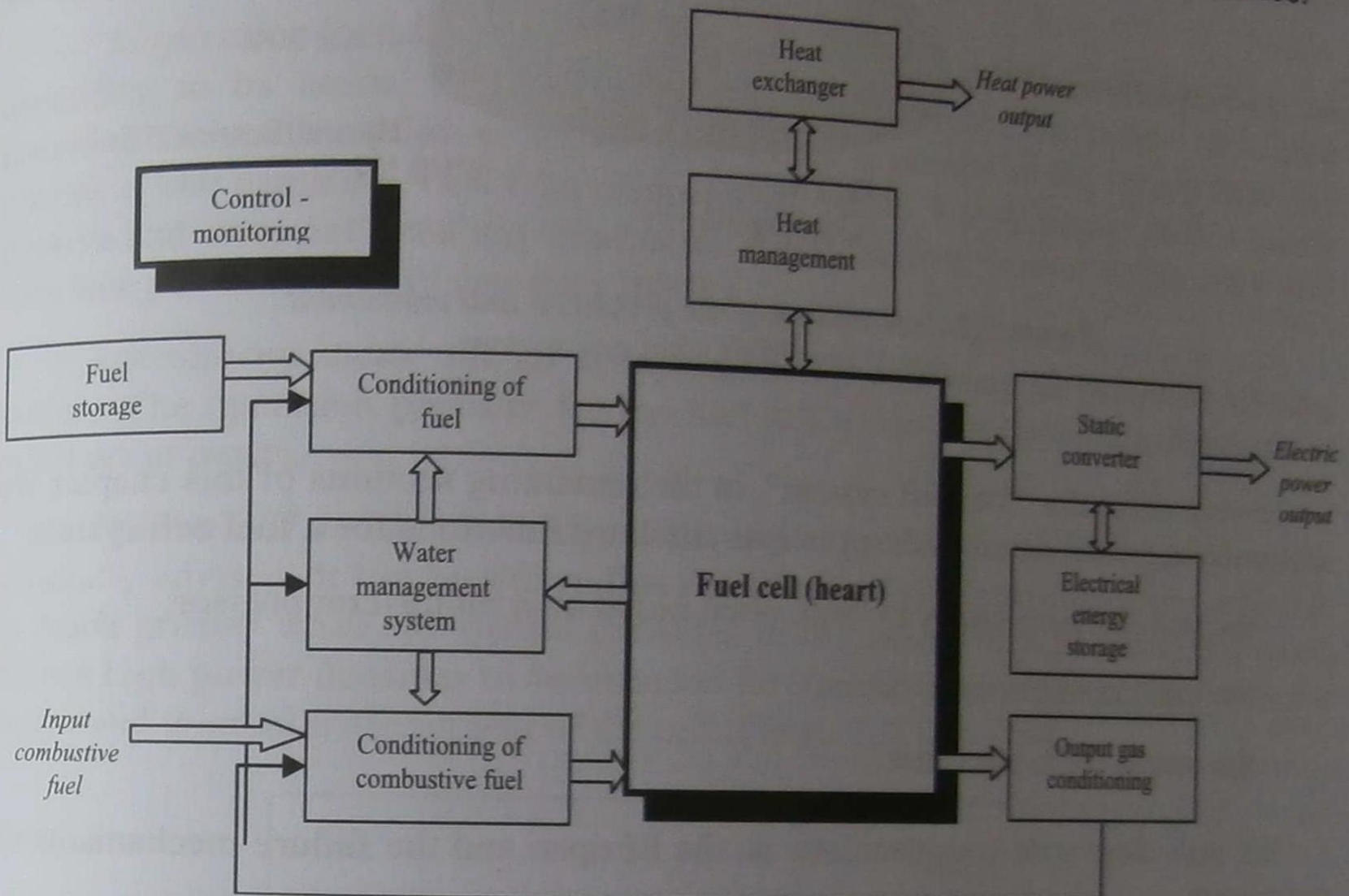


Referring to Figure 7.1, the fuel for the fuel cell must first of all be produced (especially if this is a hydrogen fuel – hydrogen being the most common compound on earth, but almost non-existent in its natural state) and stored. Then it is conditioned, in terms of pressure, temperature, rate of flow, and hygrometry, before being placed in the anode compartment of the fuel cell. The combustive must be conditioned in the same way, before being placed in the cathode compartment. Moreover, for each of the two gaseous circuits, we can recover the water produced within the heart of the cell by the electrochemical reaction, and carried by the exhaust gases of the fuel cell, in order to use this water to humidify the gases entering the cell. In certain cases and for certain modes of function, this leads to a system that is self-sufficient for water.

In addition, as the electrochemical reaction that takes place within the cell is exothermic, it is necessary to use a dedicated cooling circuit, with a liquid coolant, as soon as the cell's power becomes significant (typically above a kilowatt). Regulation of this cooling circuit aims to keep the temperature within the cell at roughly nominal conditions, as specified by the supplier of the cell. Of course, the cooling circuit controller must be coupled with the controller for the hygrometry of the entering gases, as the evolution of these two variables is, by their nature, coupled.







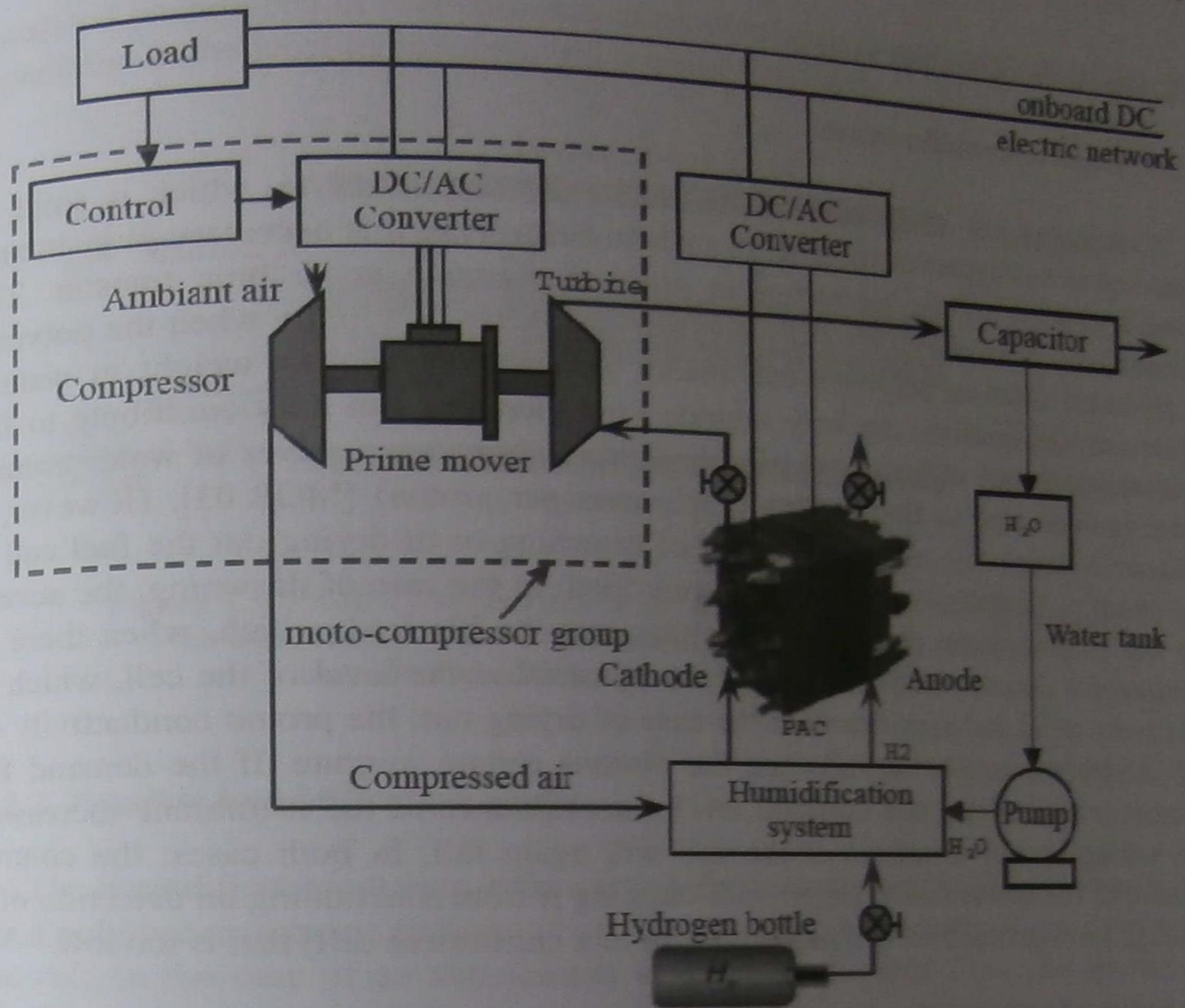
**Figure 7.1. Fuel cell system**

Having defined a “fuel cell system”, in the remaining sections of this chapter we will provide greater detail of the principal auxiliary functions for a fuel cell system:

- the air (oxidizer) supply system, often based on a motor-compressor;
- the gas humidification system;
- the output static converter.

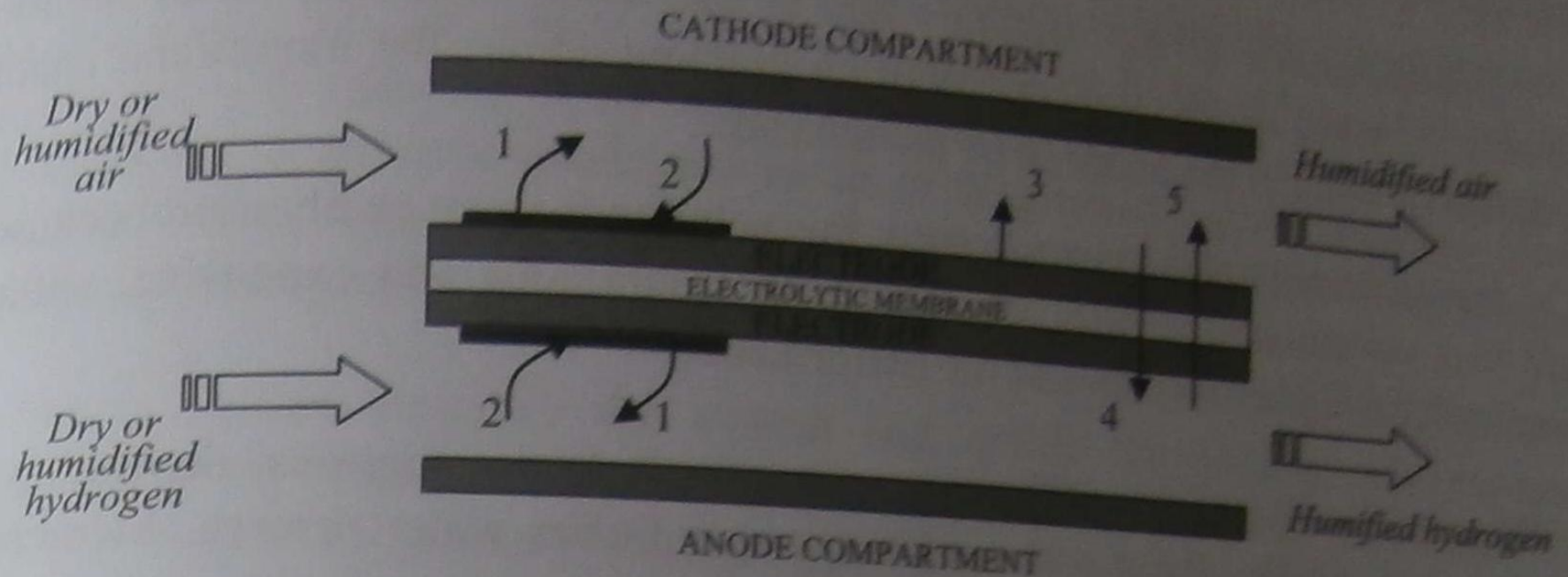
We will close with considerations on the lifespan and the failure mechanisms of the system.





**Figure 7.4.** Diagram of the principles behind a PEMFC using a compressor linked to an expansion turbine that regulates the air entering [TEK 04]





**Figure 7.5.** PEMFC: water cycle in the heart of the cell. 1-2: evaporation-condensation of water on the walls; 3: production of water from the cathode side; 4: diffusion; 5: electro-osmosis

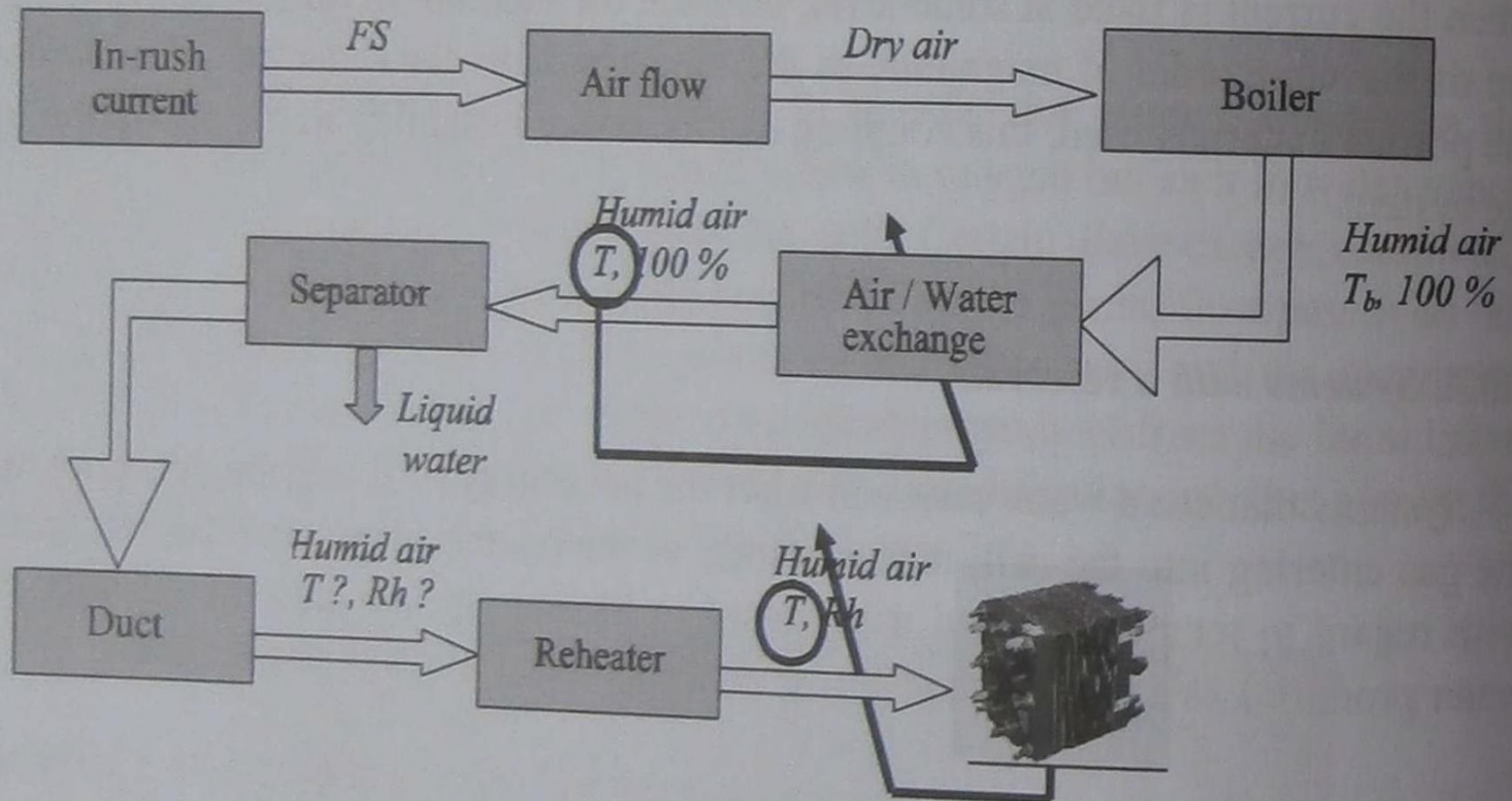


Figure 7.7. Principles behind the operation of a distiller humidification system permitting the dew point and the temperature of the airflow to be fixed

A *battery of accumulators*, is a grouping together of several identical accumulators, using series or parallel mounting.

The *capacity* is the amount of electricity, usually evaluated in ampere-hours (Ah), which a charged accumulator can release during the discharge period.

The capacity of an element is a function of the discharge regime. The nominal capacity of a battery is generally given for a discharge regime of 10 hours ( $C/10$ ):

- for a higher discharge regime ( $I > C/10$ ) the capacity is reduced.
- for a lower discharge regime ( $I < C/10$ ) the capacity is increased.

The discharge current, in amperes, is evaluated in fractions of the capacity expressed in ampere-hours (for example,  $C/100$ ).

*Example:* an accumulator of 100 Ah at  $C/10$  can supply a current of 10 A over 10 hours. Its capacity will be reduced to 80 Ah for a discharge regime with  $I = C/5$  whereas the capacity could be increased to 140 Ah for a discharge regime with  $I = C/100 = 1$  A.

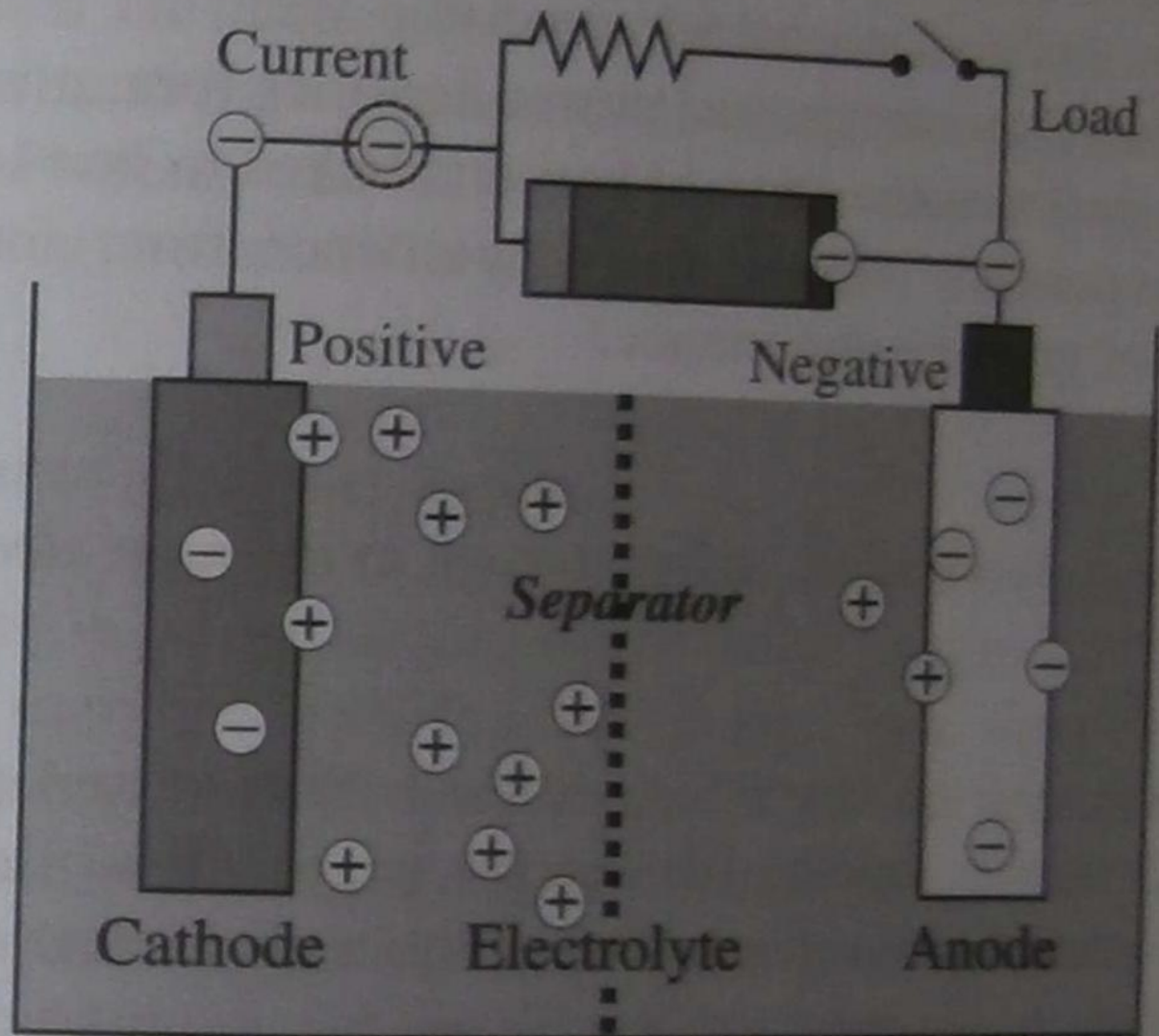


The capacity of an element is a function of its temperature: it varies according to variations in temperature.

The *faradic efficiency* is the ratio between the amount of electricity used during discharge,  $Q_D$ , and the amount of electricity supplied during charging,  $Q_C$ .  $\eta_q = Q_D/Q_C$ .

The *energy efficiency* is the ratio between the amount of energy discharged and the amount charged in Watt-hours. These efficiencies strongly depend on the technologies being considered and the conditions of charging and discharging applied. The energy efficiency is lower than the faradic efficiency because ampere-hours are not stored and released in the same way.

The *self-discharge level* of an accumulator represents the average relative loss of capacity per month in storage for a given temperature. Self-discharge is an internal characteristic of the technology used and is generally given for a temperature of 20°C.



**Figure 8.1.** *Diagram of the principle of operation of a secondary electrochemical cell (rechargeable)*

## 8.2. Applications

Electrochemical accumulators are electrical energy storage systems that are used as essential complements for traction applications (cars, scooters, etc.), as well as for renewable energy producing systems (solar, wind power, etc.).

These two types of applications, mobile and stationary, have different battery selection criteria. In addition to criteria associated with the cost, the lifespan (in cycles and on the shelf), the energy and power densities (per unit mass or volume), and the temperature performance, there are criteria linked to non-toxicity of systems, recyclability of components, as well as independence from foreign competition, which are currently of growing importance.





### 8.3.6. Redox

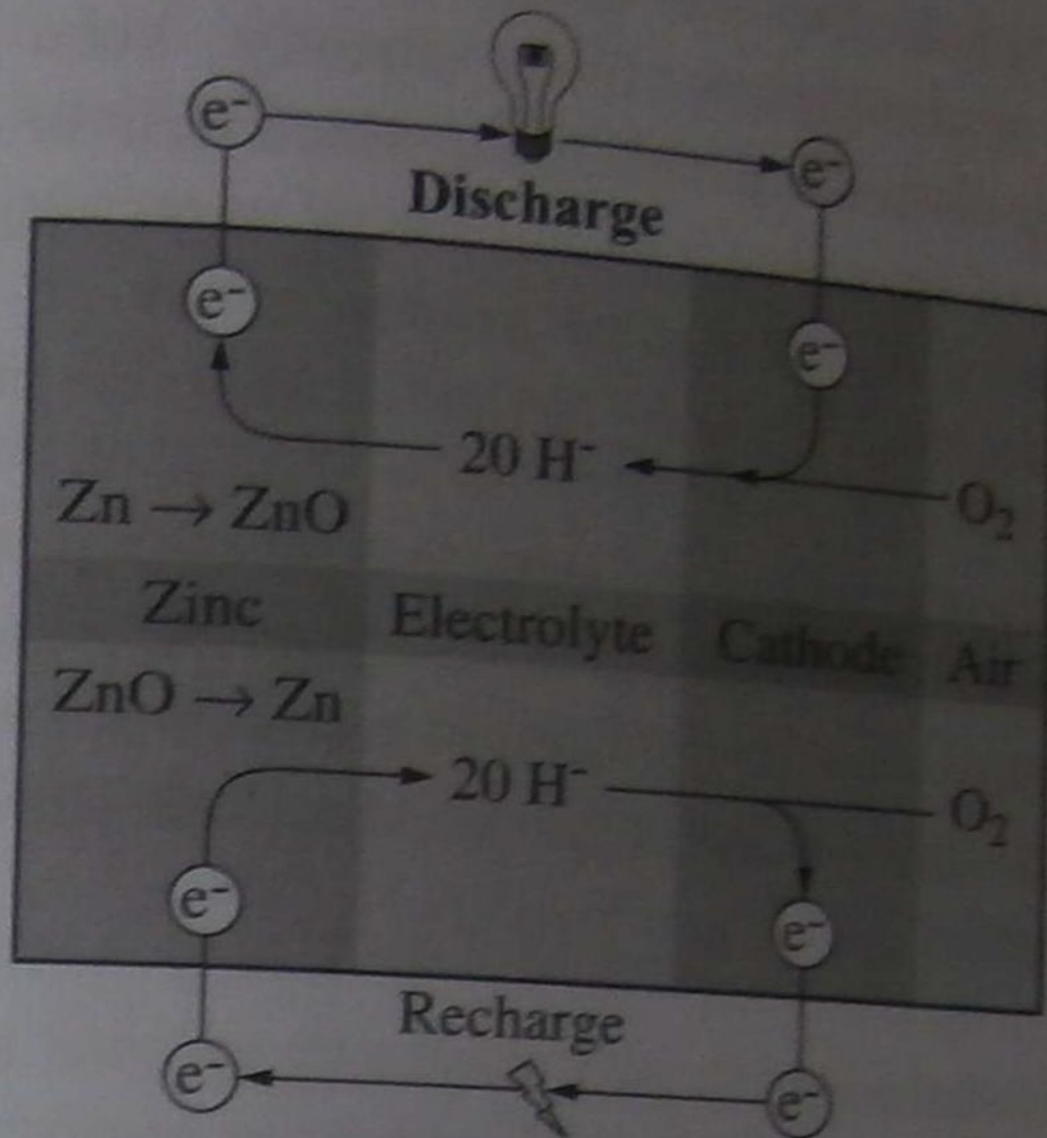
Redox batteries are batteries with electrolyte circulation in which the chemical compounds are in solution. Several associations with bromine can be envisaged: with zinc, sodium, and more recently, with sodium poly-sulfide. The electrochemical reaction across a membrane in the cell is reversible (charge and discharge). By using large reservoirs and coupling numerous cells, great quantities of energy can be stored and released. For example, Regenesys Technologies in England has made a storage system using this process in 2003, which has a range of 15-120 MW, but this technology is now dominated by electrochemistry that is entirely based on vanadium. The global efficiency of the storage is around 75%.



### 8.3.7. *The Zebra system*

The sodium-nickel chloride battery ( $\text{Na-NiCl}_2$ ), operates at high temperature ( $300^\circ\text{C}$ ) at a nominal voltage of 2.58 V per cell. The negative electrode is made of liquid sodium whereas the anode is a nickel chloride. The sodium is separated from the chloride by a ceramic electrolyte which allows sodium ions to pass during charging and discharging. The system thing is mounted in a metallic case which acts as a negative terminal. The battery can generate from 8.5 to 30 kWh with a specific energy of 85 Wh/kg for a power which varies from 72 to 130 W/kg depending on the cooling mode. Its lifespan is 1,000 cycles at 80% discharge. Still in the research and development stage, its operation at high temperature and the risks in case of breakage limit its large-scale use. However, this technology would be more secure than Na-S.





**Figure 8.4.** *Diagram of a metal-air battery*  
(source ESA Technology website)



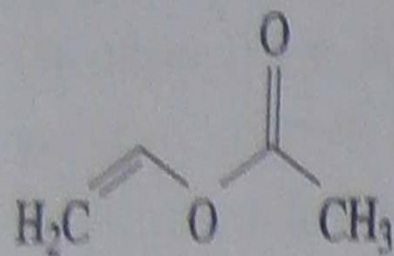
Technology	Specific energy density (Wh/kg)	Energy density per unit volume (Wh/L)	Voltage of an element (V)	Charge time (h)	Peak power (W/kg)	Number of cycles (ch./dch.)	Self-discharge per month (%)	Operating temp (°C)
Lead acid	30-50	75-120	2	6-12	700	400-1,200	5	-20 to 60
Ni-Cd	45-80	80-150	1.2	1-2	?	2,000	>20	-40 to 60
Ni-MH	60-120	220-330	1.2	2-4	900	1,500	>30	-20 to 60
Li-ion	100-200	300-550	3.7	2-4	1,500	500-1,000	<10	-20 to 65
Li-ion polymer	100-130		3.7	2-4	250	200-500	<10	0 to 60
Na-NiCl <sub>2</sub> (ZEBRA)	120	180	2.6	Unknown	200	800	>100 (12%/j)	Unknown
Ni-Zn	70-80	120-140	1.65	Unknown	1,000	>1,000	>20	Unknown

Table 8.1. Battery technology specifications

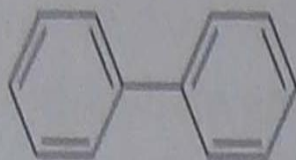
Techno.	Lead acid	Ni-Cd	Ni-MH	Li-ion	Li-ion polymer	Zebra	Ni-Zn
Cost comparison (2004)	\$25 (6 V)	\$50 (7.2 V)	\$60 (7.2 V)	\$100 (7.2 V)	\$100 (7.2 V)	Unknown	Unknown
Cost per cycle (2004)	\$0.10	\$0.04	\$0.12	\$0.14	\$0.29	Unknown	Unknown

Table 8.2. Battery technology costs

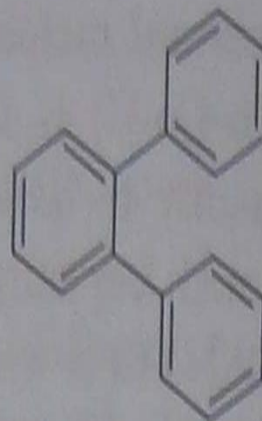




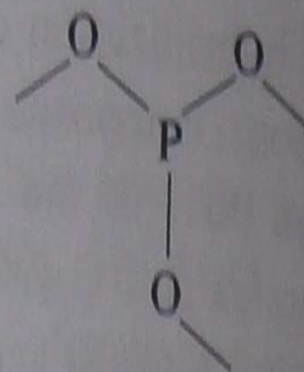
a) Vinyl acetate



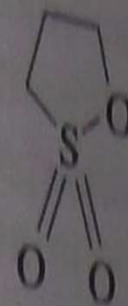
b) Biphenyl



c) o-terphenyl



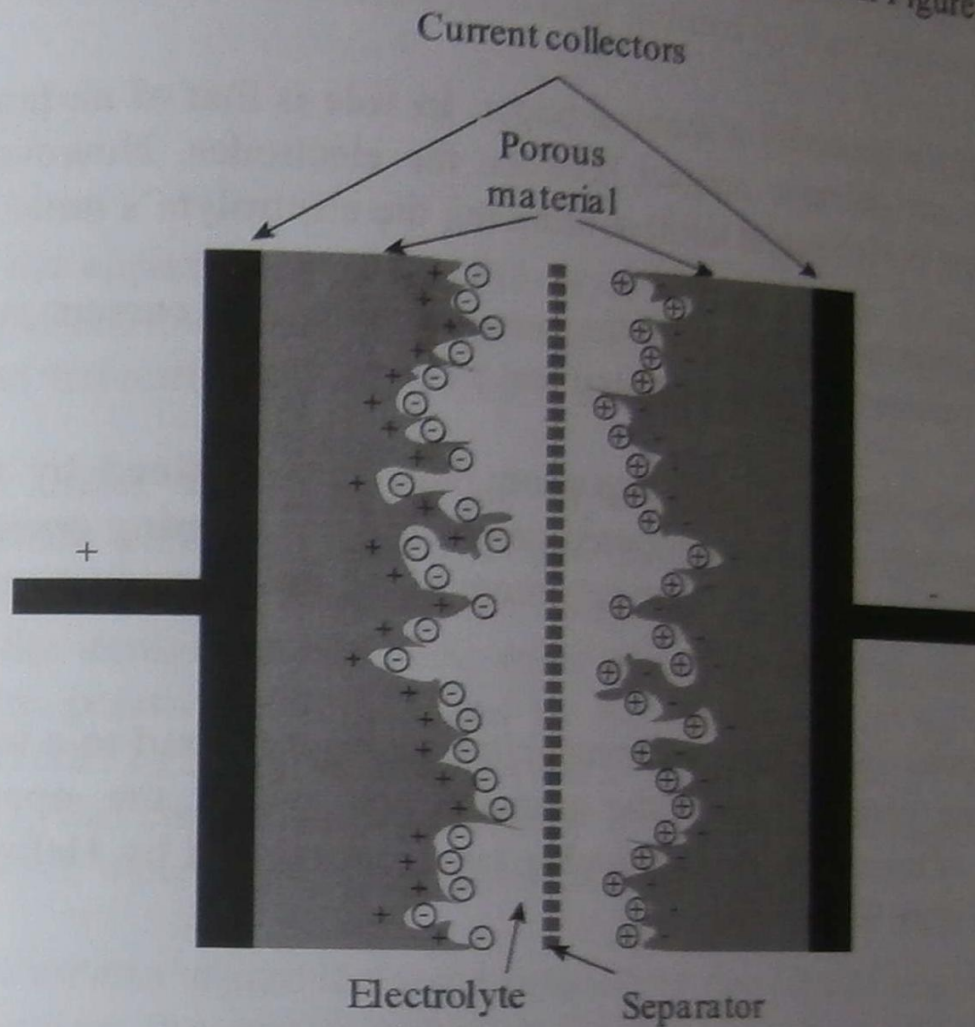
d) trimethyl phosphite



e) γ-sultone

**Figure 8.6.** Foreseeable additive families  
for high-voltage electrolytes





**Figure 9.1.** *Principles of operation for a supercapacitor*

A supercapacitor consists of two electrodes that are galvanically isolated by a separator, which is soaked in an electrolyte.

The two electrodes are created by deposition of a porous material on a metallic film. The metallic film is generally aluminum, whereas charcoal (activated charcoal) is chosen as the porous material. When the component is charged, the charges are stored at the interface between the porous material and the electrolyte. The use of activated charcoal enables charge to be stored on a significant active surface while offering a good electric conductivity.

The function of the electrolyte is to ensure the mobility of the ions it contains towards the electrodes. The anions should be able to progress freely towards the positive electrode, whereas the cations should be able to progress freely towards the



negative electrode. The electrolyte may be solid, but is generally liquid. The choice of the electrolyte is the result of a compromise between the voltage performance and the ionic conductivity. Minimization of the latter leads to a choice of electrolytes that have low dissociation voltages (1 V). In order to avoid oxido-reduction mechanisms, which would lead to irreversible mechanisms during the charge and discharge phases, the operating voltages of the supercapacitor must be limited (from 2.5 to 3 V).

The separator is generally a sheet of paper. Its role is that of an insulator, which should prevent any galvanic contact between the electrodes. However, it must be able to be soaked in electrolyte without reducing the electrolyte's ionic conductivity.

Two principal parameters lead to the energy density of a current supercapacitor: the maximum voltage that can be applied and its capacitance.



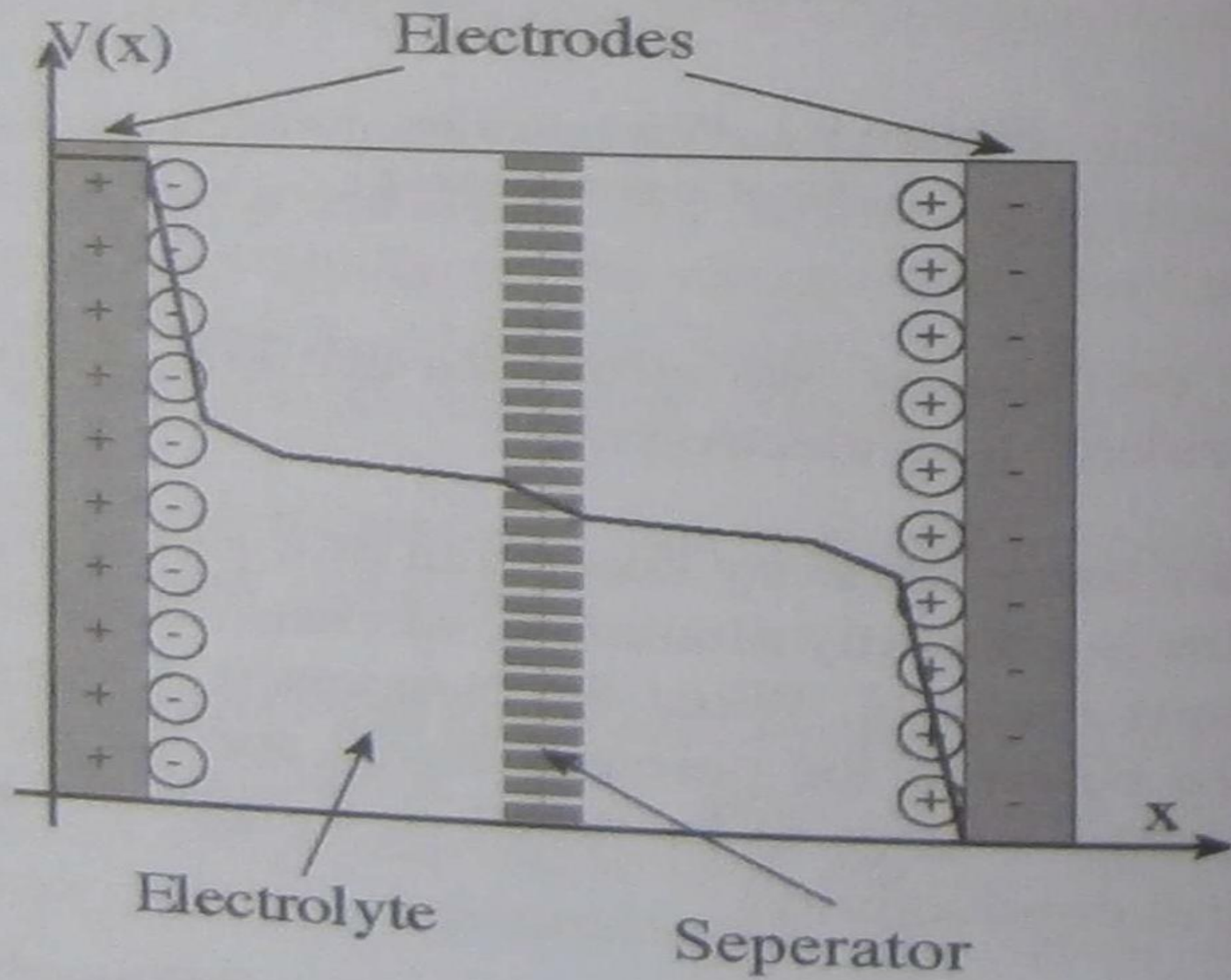


Figure 9.2. Electric double-layer capacitor

$$C_{dc} = \epsilon \frac{A}{d}$$

[9.1]

where  $C_{dc}$  is the capacitance of a double-layer (on the positive or negative electrode side),  $\epsilon$  is a dielectric constant,  $A$  is the effective surface of the electrodes, and  $d$  is the equivalent dielectric value for a traditional capacitor.

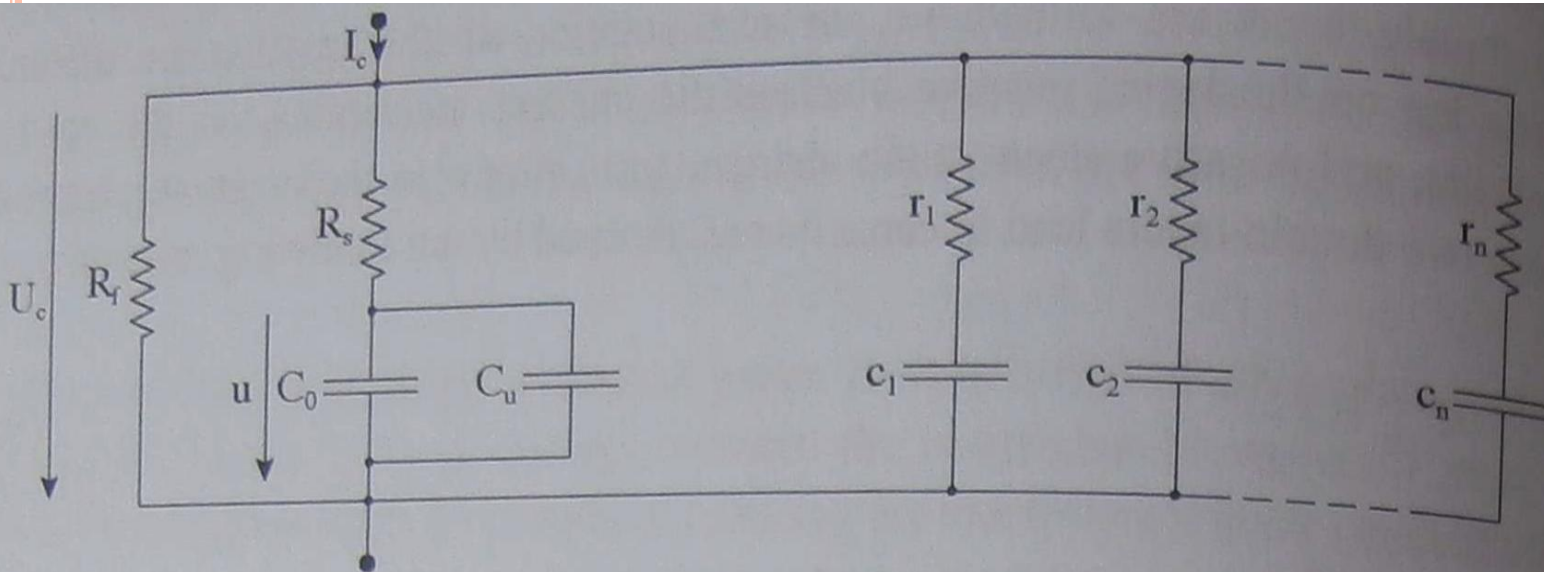


Figure 9.3. Electric model of a supercapacitor

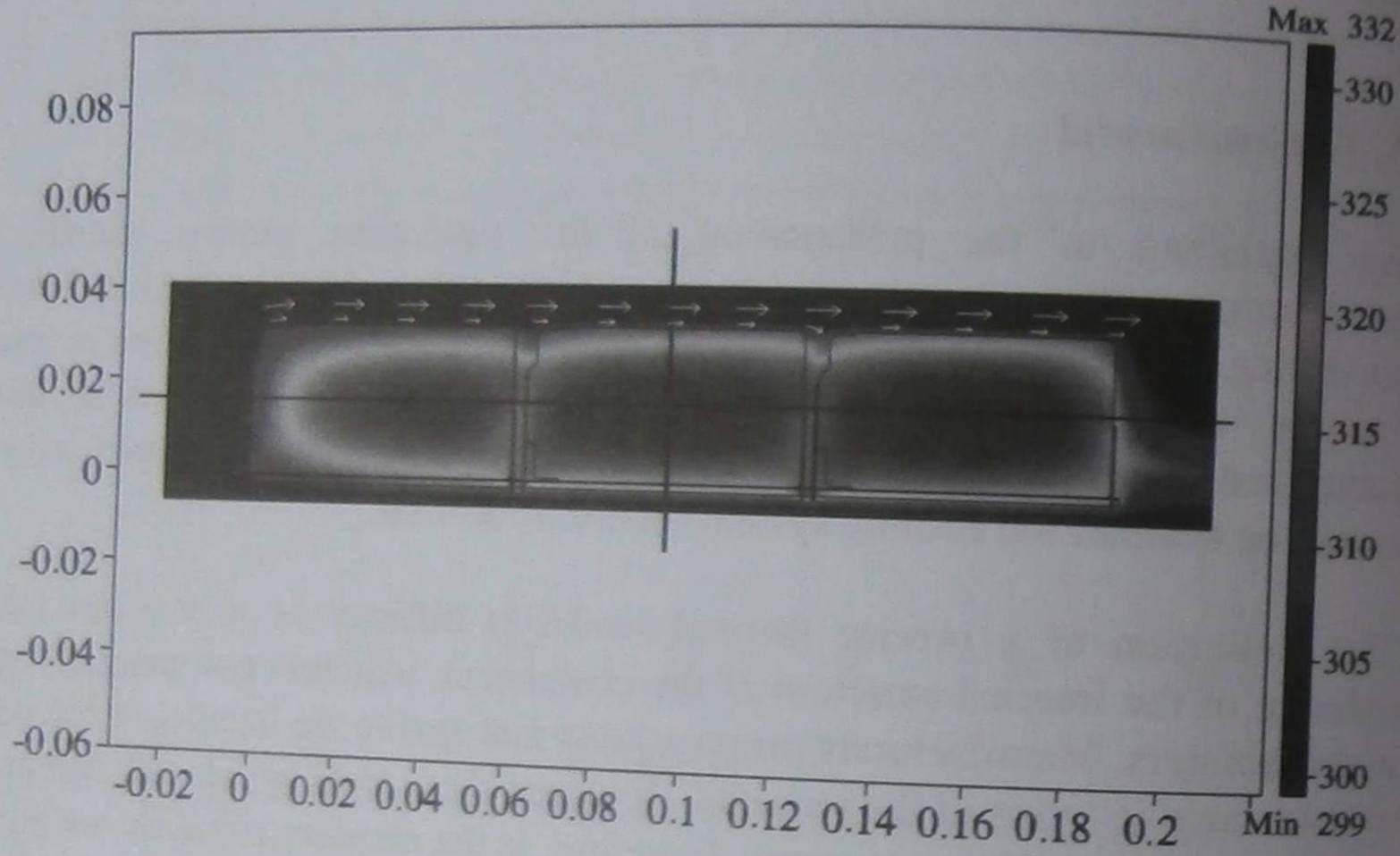
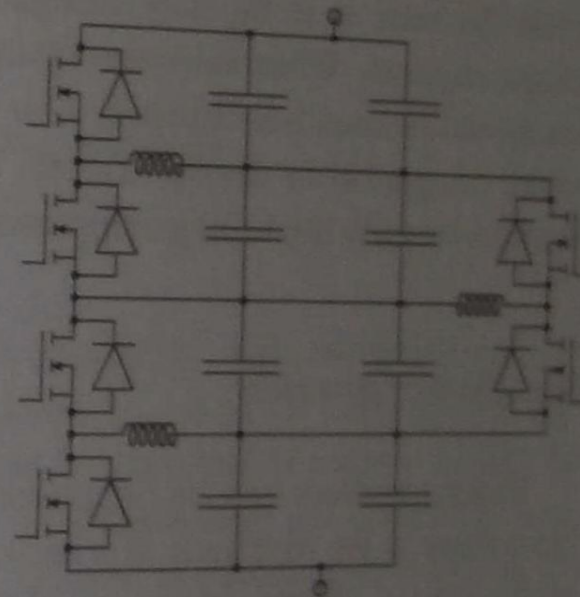
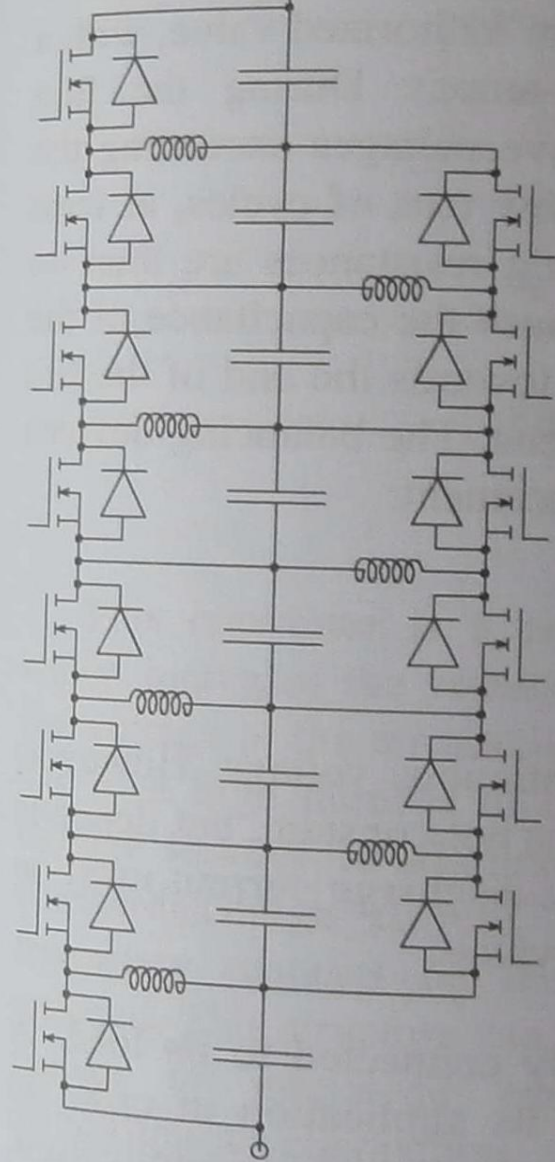


Figure 9.5. Thermal model of a supercapacitor

$$W_M = \frac{1}{2} C U_M^2$$

$$W_u = W_M \left( 1 - \left( \frac{d}{100} \right)^2 \right)$$





**Figure 9.8.** *Balancing voltages*

### 9.5.2. *Supercapacitors used as principal source*

The number of applications for which supercapacitors are used as the principal source is low due to their energy density. Nevertheless, we can cite two key applications.

The first application is linked to the starting-up of internal combustion engines. For this type of application, energy needs are not important, so supercapacitors are adapted to answer instantaneous power supply needs of start-up. In addition, the high number of cycles characterizing supercapacitors is compatible with the lifespan of a thermal motor, which is an undeniable asset compared with batteries of accumulators, especially if we take into account the savings in terms of maintenance [SCH 00].

The second application is linked to supply of security functions, where it is necessary to supply a system during a short time, in case of a short general power-cut. We can list security supplies dedicated to computers, whose autonomy must at least allow the correct switching off of the computers. Generally, the autonomy sought is of the order of a minute to tens of minutes. The advantage of using supercapacitors instead of batteries resides in their lifespan, in the absence of maintenance operations, and in their rapid recharging when the principal power source is once again active.



### 9.5.3. Hybrid systems

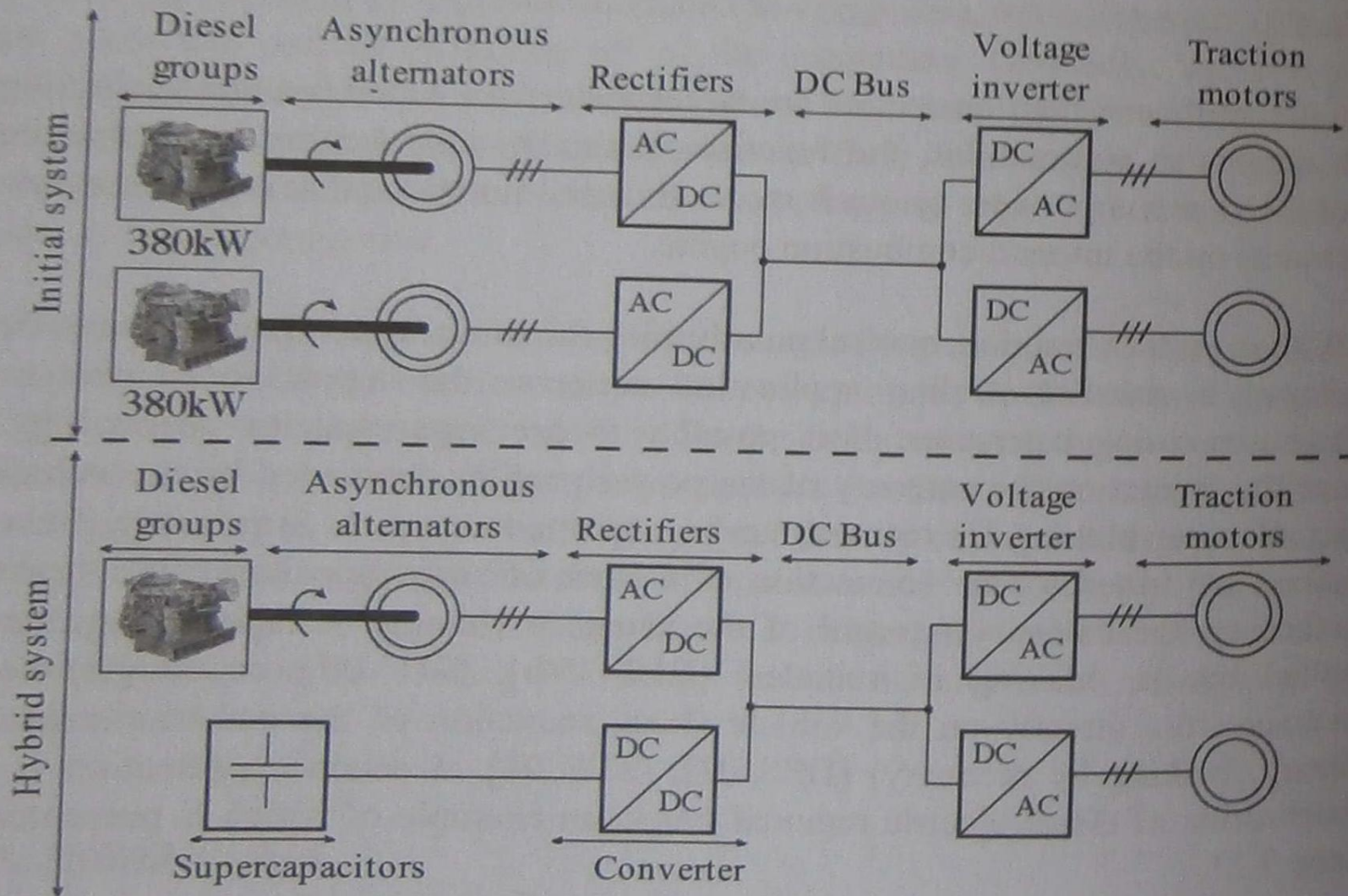
The power supply to hybrid systems is split in two, each of the sources supplying the application in a complementary manner. In the ideal case, the sources are associated in such a way so that each one is in its nominal usage range.

The hybridization of a system with the help of supercapacitors as a secondary source covers a very wide spectrum of applications.

In the low-power range, supercapacitors are associated with batteries in devices, such as a camera or camcorder, in order to increase the lifespan of the batteries by reducing the restrictions that are applied to them.

As to applications with power in the order of tens of kilowatts, replacement of some of the braking resistances used in elevators by supercapacitors is being considered. The objective is to cover a wide range of the energy and power needs of the elevator using supercapacitors, and to reduce the impact on the supply network of the up/down cycles of the elevator, which leads to discontinuous power profiles [RUF 02].

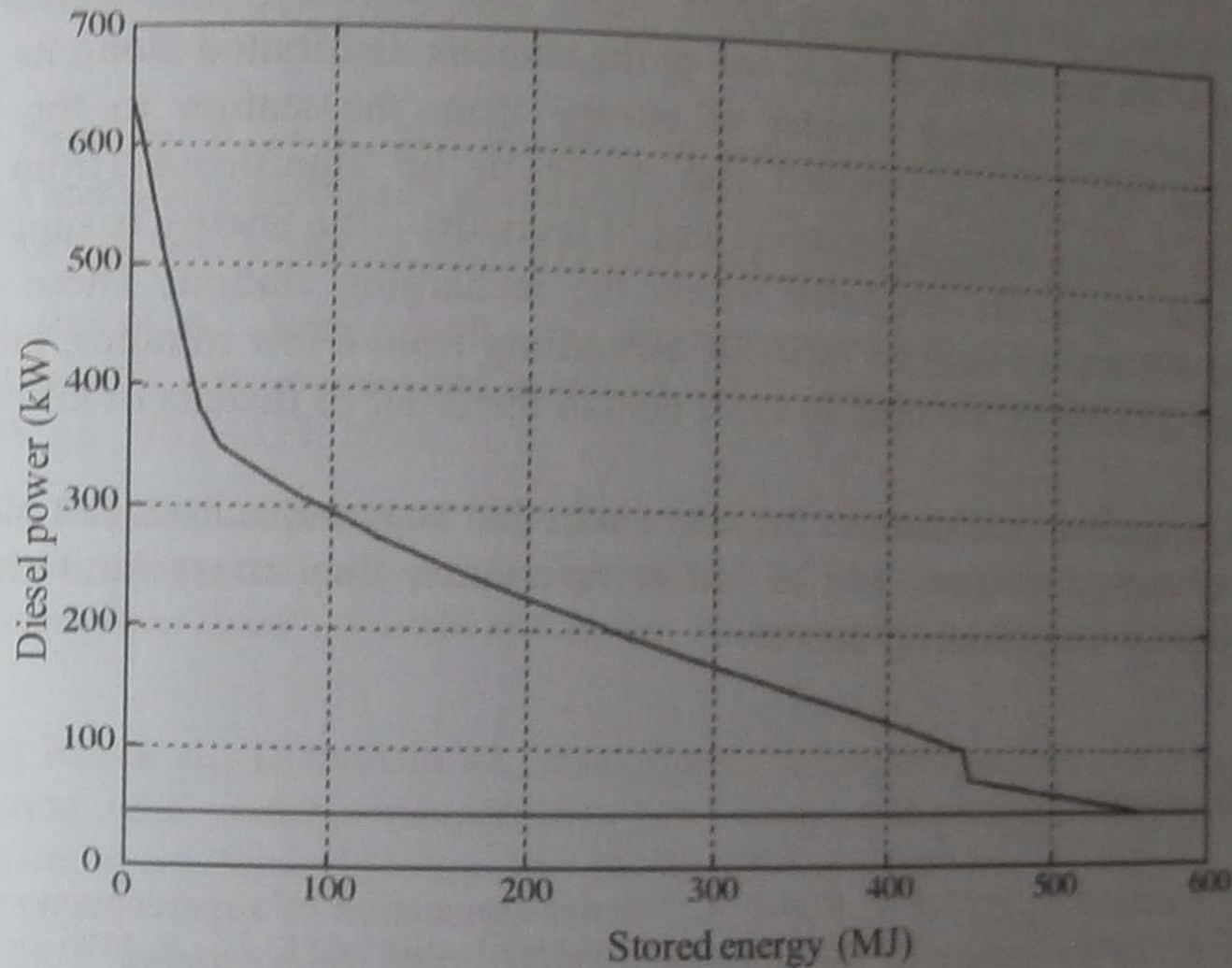




b) From the initial system towards its hybridization

**Figure 9.11.** Hybrid vehicle – sizing of the diesel generator

The evaluation of how much energy to store in supercapacitors in order to satisfy these criteria is given in Figure 9.12, and shows its direct influence on the diesel power that must be installed.



**Figure 9.12.** *Impact of storage on the diesel power installed*