If the world wants sustainable development for all its denizens, it needs must restrict reliance on fossil energies, in favor of such energies as are least polluting and resource-hungry. Renewable energies, and nuclear power, are the only solutions affording adequate prospects in this respect.

# Energies for **today** and **tomorrow**



The Olkiluoto (Finland) site, showing, in the foreground (computer-generated imagery), the first European third-generation nuclear reactor (EPR), to be built by Framatome–ANP (Areva Group) and Siemens (for the conventional section), as forerunner to the initial series model, to be built by French electricity utility EDF at Flamanville (Manche département). In the background, the two second-generation reactors operated by TVO may be seen.

Whether one considers the slope of the curve for the rise in global temperature, due to greenhouse gases (see Box B, *The greenhouse effect and*  $CO_2$ ), the timeframe for fossil energy reserves (see Table 1), or the growth in world energy demand, it is becoming urgent, after Kyoto and the emerging awareness this evidenced in 1997, to develop those energy sources that are more environmentally friendly, and sparing in natural resources. Concurrently, consumption must be optimized, so that a given service may be obtained for the minimum amount of energy.

#### An inexorably rising demand

Energy consumption can but rise, for two reasons: one being accelerated population increase, which should reach the 8 billion mark by 2050, the other being the fact that developing countries may only improve their living standards through a major increase in their energy consumption. Out of 6 billion denizens of our planet, 2 billion have no access to electricity. Mean yearly electricity consumption stands at 2,000 kWh per capita,

coal <sup>(1)</sup>	346
lignite (+ sub-bituminous) <sup>(1)</sup>	155
oil <sup>(1)</sup>	156.7
natural gas <sup>(1)</sup>	158.2
bitumen (oil shale + bituminous sands) + extra-heavy oil <sup>[2]</sup>	500
methane hydrates <sup>(2)</sup>	2,800-6,900,000 <sup>[4]</sup>
uranium (in slow-neutron reactors) <sup>[3]</sup>	39 <sup>(5)</sup>
uranium (in fast-neutron reactors) <sup>(3)</sup>	1,967 <sup>(5)</sup>

Table 1.

Orders of magnitude for energy resources, in billion tonnes oil equivalent (Gtoe). [Sources: [1] BP, Statistical Review of World Energy 2004; [2] WEC, Survey of Energy Resources, 2001; [3] NEA-IAEA, Uranium 2001: Resources, Production and Demand ("Red Book"), 2001.] [4] Of these reserves, a small part would be actually recoverable, this being evaluated as amounting to 180,000 Gtoe, according to the WEC survey; [5] 1 tonne uranium = 10,000 toe in a slow-neutron reactor, 500,000 toe in a fast-neutron reactor.

however this involves huge disparities. Less than 10% of the world's population consume over 7,000 kWh/year, whereas 64% use less than 1,000 kWh/year. A French citizen consumes, on average, slightly more than 8,000 kWh per capita, per year. Now infant mortality rises as energy consumption drops: it increases by a



factor 70, for the lower energy figures, and life expectancy declines abruptly when power use falls below 1,600 kWh/year. While such situations are not solely due to energy underconsumption, the latter does reflect the poverty experienced by part of humankind: 2.8 billion humans live with less than €2 a day.

World energy consumption rose by a factor 10 between the beginning and the end of the 20th century, this going hand in hand with a major improvement in living standards. In France, wealth per capita thus rose by a factor 4 over 50 years, from 1950 to 2000, when it had only risen by a factor 2.3 over the period 1400–1820, i.e. more than 400 years.

Such massive use of energy enabled advances, reflected, e.g., by notably increased longevity. Whereas in the late 17th century life expectancy for a Frenchman stood at less than 30 years, this had risen to 50 years or so by the beginning of the 20th century, and over 75 years by the first years of the 21st century.

#### Exhaustible and renewable energy sources

Nonrenewable energy sources (coal, oil, natural gas, uranium) become exhausted even as they are extracted, by contrast to hydro energy, solar energy, wind energy, **biomass**..., which will remain available for another 5 billion years or so, until our planet is engulfed by our star, the Sun. Now world energy consumption-just as electricity generation-is largely dependent on fossil energies (oil, **natural gas**, and coal), these accounting for 85% of primary energy (see Box A, The many states of energy). Gas has become particularly competitive, with advances in gas turbines, and "combined cycle" technology, enabling sharp reductions in cost per kilowatt-hour, 70% of this, however, still being accounted for by the gas supply itself, this precluding stable prices being secured for any extended period.

#### Finite reserves and the greenhouse effect

Massive use of fossil energies means our planet is faced with two major issues – increased greenhouse



Unit 1 of the new Dunkerque 6 combined-cycle power station French gas utility GDF is planning to put on stream in 2005, close to the Arcelor steel plant. This is the first large gas-turbine, combined-cycle installation to be built in France, with an electricity generation capacity of 2 x 400 MWe.

	low assumption	high assumption <sup>(1)</sup>
coal	860	1,290
natural gas	480	780
hydro energy	4	18
nuclear energy	8	59
wind energy	11	75
photovoltaic solar	30	280
biomass	0	116

(1) The high assumption corresponds: for coal, to a poorquality grade, and fairly lengthy transport; for natural gas, to  $CH_4$  losses over long distances (this is case in Russia); for hydro energy, to generation of  $CH_4$  during reservoir filling; for nuclear energy, to enrichment achieved by means of coalgenerated electricity (this is the case in the United States); for wind energy and photovoltaic solar energy, to use of natural gas-generated electricity to complement intermittent production; for biomass, to lack of reforestation.

#### Table 2.

CO<sub>2</sub> equivalent content per kilowatt-hour generated (in g).

effect, over the relatively short term, and exhausted reserves, in the long term – which may not altogether be separated. It is indeed the carbon atoms, extracted in the form of natural gas, oil, or coal, that result in the inexorable production of **carbon dioxide** (CO<sub>2</sub>), the sources with the highest **hydrogen** content being those that emit the least CO<sub>2</sub> (see Table 2).

We are going through a period of abundant energy, energy prices remaining below what would be required, if we took a responsible attitude with respect to natural resources and future generations. By the latter half of the 21st century, natural gas and oil will become scarcer, and more expensive. In the longer term, their use will have to be restricted to nobler purposes than combustion, such as the requirements of the chemical industry. For coal, reserves should last several centuries. As regards nuclear energy, resources may be counted in terms of tens of thousands of years, if "fast"-neutron reactors are used, these allowing nearly all the fuel's energy to be extracted, whereas the timeframe would be of the same order as for hydrocarbons, for "slow"neutron reactors, these only using 0.5-1% of the energy. It may one day be economic to use other sources of uranium, such as sea water, or turn to thorium, which is even more abundant than uranium. The advantage of nuclear power is the small contribution from the cost of natural uranium to overall cost per kilowatt-hour. A rise in the price of natural uranium by a factor 10 would result in an increase of less than 40% in the price per kilowatt-hour, whereas this would rise by a factor 7 in the natural gas case.

In the longer term, **thermonuclear fusion** could supply energy for thousands of years, if deuterium-tritium (D–T) fusion is used, or for the entire lifespan of the Earth, should humankind some day achieve mastery of deuterium-deuterium fusion. Still a long way from being mastered in industrial terms, D–T fusion is being targeted by intensive research efforts, under the aegis of the Euratom–CEA Association, and preparations for the ITER international program. Finally, global **methane hydrate** reserves, greater than the combined reserves of coal, oil and gas, may become usable in the future.

#### Renewable, though not competitive yet

Renewed interest is being shown in renewable energies, these being, at first blush, inexhaustible, and less detrimental to the environment than fossil energies. Such energies are those that were used from the time humans mastered fire, probably some 500,000 years ago, right up to the Industrial Revolution, less than 200 years ago. Since the latter, their share in energy use has greatly declined. Their major advantage? Negligible contribution to increases in greenhouse effect. Their disadvantages? They are diffuse, not constantly available, and, for the most part, not yet competitive in the majority of conditions. Hydro energy, allowing as it does cheap electricity to be obtained, provided costly investments are made, is the only one to see widespread use. This may occasion disamenities, or adverse environmental effects, <sup>(1)</sup> or even accidents. Was it not the breaching of the Morvi Dam, in 1979, in India, that resulted in 5,000 fatalities? In France, two accidents, at Le Bouvet in 1895, and Malpasset in 1959, caused 100 and 421 deaths respectively.

Standing as the prime source of electricity in France in 1960 (56%), hydropower only accounted for 12% in 2000. The price per kilowatt–hour it allows remains particularly low, nevertheless, since the capital outlay has been made. Hydropower can look to a high potential in Asia, South America, and in the former Soviet Union. Hydropower also covers tidal power, wave power (1 watt per square meter), and, affording a potential a hundred times greater, highly expensive ocean thermal power.

Most renewable energies and fossil fuels originate in the Sun's energy. Solar energy in the broadest sense covers all forms of energy involved in the Earth's atmospheric machinery: solar energy proper, wind energy, hydro energy, **photosynthesis**, and wave energy. It includes neither tidal energy, this being due to the Moon's motions, nor geothermal energy, this deriving essentially from the Earth's **radioactivity**, and amounting to 0.06 watt per square meter (some 3,500 times weaker than the solar flux). The Earth receives from the Sun 170,000 **TW** total power: more than 2,500 times – over the sole continental landmasses – world electricity consumption! However, if renewable energies are "free," their recovery is anything but free!

Solar energy in the narrow sense may be used directly (thermal energy), or transformed into electricity (**photovoltaics**). The outstanding issue? A cost per kilowatt–hour, for grid-connected systems, that is still ten times higher than that achieved with gas or nuclear power. With stand-alone systems, it is more expensive still (around €1.50/kWh, since batteries are required to store energy for nighttime use). Highly advantageous as it is for remote sites (savings on connection costs), it is not suited to heavy power supply requirements. Achieving major cost reductions for photovoltaic cells will require technological break-throughs, such as fabrication of mineral or organic thin films, an avenue being explored, in particular, by a collaboration bringing together CEA and CNRS.

Wind energy, corresponding to the transformation into mechanical energy of 1% of the energy received by the Earth, is taking off, however the generated kilowatt-hour still bears a price tag 2-4 times higher than for nuclear or gas. A wind-turbine yields power that is proportional to the cube of wind speed. A 750-kW installation, delivering this power output for a 15-m/s wind (force 7), only delivers some 30 kW under a 5-m/s wind (force 3), and... zero output on windless days: a well-ventilated site may yield 20-30% of installed power. Wind-turbines may be sited offshore, where winds are stronger, and more regular. Their disadvantages (footprint, visual and acoustic disamenities) are more widely known than the advantages, such as the screen or hedge effect, which is a boon to agriculture.

Biomass provides a useful means of storing solar energy, which is diffuse and intermittent, however this is achieved with low efficiency: 1% or less in temperate regions. Plants consume carbon dioxide, compensating to some extent for the CO<sub>2</sub> released by combustion. For wood, for instance, CO<sub>2</sub> balance is 7-12 times lower than for natural gas. However, there is a need to improve biomass combustion methods at low energy densities: CEA and IFP are working on this issue. As for other sources, it is essential to draw up an overall balance, before considering efficiency: for instance, 1 liter of fossil hydrocarbon fuel equivalent is required for production of 1.5 liter bioethanol, or 12 liters rape methyl ester. However, it is feasible to make better use of byproducts. Finally, even though the aim is first and foremost their destruction, reduction or inerting, wastes may provide an auxiliary energy source (at best 1% of consumption in France, for domestic waste).

#### Transportation: a hard case

Oil, nowadays, is irreplaceable in transportation, for which it covers 95% of r e q u i r e m e n t s . Energy consumption in this sector accounts, in France, for one quarter of total consumption,

and is rising faster than the latter. Current technology may not be retained much longer, owing to the contribution it makes to the greenhouse effect (one car releases into the atmosphere about 1 tonne  $CO_2$  for every 5,000 km traveled), and the growing scarcity and rising prices of fossil energies.

For automobiles, one likely evolution is the **hybrid vehicle**, powered by both a heat engine and an electric motor, coupled to a battery. In the longer term, hydrogen may be used, with **fuel cells**. Major technical and economic barriers still remain, however, that need to be resolved, and CEA is actively addressing these issues (see Chapter I). For instance, clean hydrogen, as generated by **electrolysis**, is 3 times more expensive than hydrogen produced from natural gas. At the same time, fuel cells for personal vehicles are some one hundred times more expensive than a heat engine of comparable performance.

Christian Occhipinti/Renaul

Hybrid vehicle of the Scenic type, built by Renault, powered by both a heat engine and electric batteries. This formula represents a likely step in the evolution to automobiles powered, in the longer term, by hydrogen-fed fuel cells.

<sup>(1)</sup> One should point out, among its benefits, the regulation of river networks.



#### Hydrogen, an energy carrier for the future

Hydrogen could establish itself as a new **energy carrier**, complementing electricity and heat. CEA, aware as it is of these prospects, is raising its research efforts in this area, as in that of fuel cells, which could find many applications in transportation and in the **stationary** domain, as a source of heat and electricity, or for portable applications, to power devices "on the move" (mobile telephones, computers, gardening tools, camping equipment...).

Electricity requirements, together with those related to hydrogen production (by water electrolysis, for instance), will involve considerable amounts of energy. A rational solution would be to use nuclear power, which in no way augments the greenhouse effect, to generate a major part of this. To generate, by electrolysis, the hydrogen needed to run as many vehicles as are currently used would require, in France, 450 TWh per year, i.e. approximately the quantity of electricity consumed at present. This corresponds to the output from some sixty 1,000-MWe nuclear reactors, or 300,000 750-kW wind-turbines. To bring forward high-efficiency, clean generation processes is one of the goals set for the work being carried out in this area by CEA.

#### Nuclear power of the future

Aside from its highly competitive price, especially in off-peak hours (less than 3 euro cents per kilowatt–hour), and the independence it secures, nuclear power generates a major part of the added value involved in the user country. Hence, in the context of sustainable development, its contribution should remain significant.

Nuclear power in the future will need to meet five conditions, including that of a generation price per kilowatt–hour lower than, or equal to, other energy sources. It will have to be safer still, even though most earlier-generation pathways exhibit quite good safety levels, and generate more energy for the same amount of fuel. It must generate less waste, especially less longlived waste <sup>(2)</sup> and have the ability to burn part of the fuel used in older reactors, and not be amenable to military use.

#### Energy savings: "negawatts"

No less important is achieving best use of what energy is generated. Device optimization, relying on numeri-





Among the new energy sources for which technical, and most crucially economic, feasibility has yet to be demonstrated, may be numbered wave energy, which has been targeted, since 2003, by an experiment conducted in the Nissum Bredning Fjord, Denmark, under the aegis of the Wave Dragon Program.

cal simulation and programmed, smart systems, allows the same service to be obtained for less energy. Much remains to be done in the area of energy savings, where CEA has already gained experience of long standing. Microelectronics provides the best example of reductions in power consumption (and price), combined with an astounding increase in performance. Lower consumption contributes to the generation of negawatts (unconsumed watts), involving no reduction in the service provided, or in comfort levels.

#### Part of the energy future

CEA has made a strong contribution to the deployment of the nuclear pathway currently providing 78% of electricity, in France, at a price that will remain stable for a long time yet. Banking on the various areas of expertise it has grown, the organization embarked, very early on, on research in such areas as energy system optimization, or photovoltaics. It is contributing to investigations aimed at bringing down the presently excessive costs for renewable energies. It is strengthening its drive for the development of new energy carriers and energy converters, with work on hydrogen production and storage, on fuel cells, to achieve significant cost reductions and improved reliability, and on batteries, to secure improved capacity and durability, together with research on technologies allowing lower energy consumption. The pages that follow place in context the investigations carried out, outside of the nuclear domain, to achieve some of the breakthroughs required, and prepare part of the energy future.

#### > Christian Ngô

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(2) Such waste remains wholly localized, whereas greenhouse gas pollution is global. It should further be noted that even a coal-fired thermal power station, under normal operating conditions, involves radioactive releases well above those from a nuclear power station. On average, a coal-fired power station emits as much radioactivity into the atmosphere as 100 nuclear power stations.

Artist's impression of the Solar Tower project mooted by EnviroMission, which should involve a 1-km high shaft soaring above the Australian desert in 2008. At its base, 32 turbines will be entrained by an updraft generated by the temperature differential between the ambient atmosphere and air heated, by greenhouse effect, under transparent panels set close to the ground. Construction is scheduled to be initiated in 2005.

### A The many states of energy

othing lost, nothing created," as Lavoisier, the father of modern chemistry, wrote in his day. This motto, true as it is of chemical species, applies equally to energy. Indeed, energy is a multifarious entity, which may transform into highly diverse aspects. However, the primary energies that may be directly accessed in nature are limited in number: such are fossil energies (coal, oil, natural gas), nuclear energy, and renewable energies (hydro energy, biomass energy, solar energy, wind energy, geothermal energy, tidal energy). These primary energies are the constituents of what is known as the primary energy mix (see Figure 1).

tion carries a cost: a more or less extensive portion of the energy involved is dissipated in the form of unusable heat (through friction in a mechanical system, for instance). In the case of a present-generation nuclear power station, the electric energy generated only amounts to one third of the nuclear energy initially contained in the fuel.

Of course, matters would be altogether too simple, however, if energy could be consumed as and when it is generated, on the very site where it is produced. In very many cases, energyconsuming sites may be far removed from the production site, production and concomitant demand, moreover,



Figure 1. The energy scheme.

For most applications, energy must be **converted** to make it compatible with the use under consideration. Of course, nature, highly ingenious as it is, devised the very first energy converters, namely living beings. Plants, through photosynthesis, effect the conversion of radiant light energy into chemical energy. The human body itself allows, in particular, the conversion of chemical energy into mechanical energy, by way of the muscular system. Subsequently, humans went on to invent large numbers of converters (see Figure 2). The first such converter, chronologically, is guite simply fire, converting chemical energy (combustion) into light, and heat. Of more recent origin, a television set carries out conversion of electricity into light energy (pictures) and mechanical energy (sounds). In fact, many energy systems involve a combination of a number of converters, as e.g. a nuclear power station, effecting as it does the conversion of nuclear energy into thermal energy (reactor), then into mechanical energy (turbine), finally through to electric energy (alternator). Unfortunately, the second principle of thermodynamics tells us that any energy transformanot always being matched (as with photovoltaic electricity in nighttime, for instance). Sound energy management thus requires deployment both of an energy distribution network, and of energy storage capabilities. Energy transport is effected by means of an energy carrier. Currently, the two main such carriers are electricity, and heat. Tomorrow, however, a new carrier may become dominant: hydrogen, this being converted into electricity and heat by means of fuel cells.

Finally, if energy is to be available at all times, it is essential that there should be the ability to store it: to "get it in a can," so to speak. Such **storage** may take a variety of forms. Energy may be stored in **mechanical** form (*potential energy*, in the case of the water reservoir of a hydroelectric dam, or *kinetic energy*, in the case of a flywheel), or in **thermal** (hot-water tank), **chemical** (gasoline tank, primary and **storage batteries**), or even magnetic (**superconducting** coil) form.

Energy management is thus a complex, involved craft, combining production, transformation, transport, and storage. In the current context of energy debate, it is becoming increasingly apparent that, tomorrow, energy networks will grow in size and number, in accordance with a multimodal approach (concurrent management of a number of networks combining diversified energy sources). New energy technologies are thus bound to play an essential part in these developments.



### The greenhouse effect and CO<sub>2</sub>

he Sun's energy reaching the ground warms the Earth, and transforms into infrared radiation. Just like the panes of a greenhouse - hence the name given to this mechanism - some of the gases present in the atmosphere trap part of this radiation, tending to warm the planet. Thus, in terms of power, the Earth receives, on average, slightly less than 240 watts/m<sup>2</sup>. Without the greenhouse effect, mean temperature on Earth would stand at - 18 °C, and very little water would be present in liquid form. This effect thus has a beneficial influence, since it allows our planet to experience a mean temperature of 15 °C.

However, from the beginning of the industrial era, i.e. for more than a hundred years, humans have been releasing into the atmosphere gases (carbon dioxide, methane, nitrogen oxides, etc.) that artificially augment the greenhouse effect. Since 1750, this increase, with respect to "well-mixed" gases, has amounted to 2.43 W/m<sup>2</sup>. Contributing as it does an "additional radiative forcing" of 1.46 W/m<sup>2</sup>, carbon dioxide  $(CO_2)$ accounts for more than half of this "additional greenhouse effect," well ahead of methane (0.48 W/m<sup>2</sup>), halocarbons (chlorofluorocarbons [CFCs], hydrochlorofluorocarbons [HCFCs], and hydrofluorocarbons [HFCs]), accounting for 0.34 W/m<sup>2</sup>, and nitrogen dioxide (0.15 W/m<sup>2</sup>). Further, the ozone in the troposphere exhibits a *positive* radiative forcing of 0.35 W/m<sup>2</sup> (however, it is estimated that depletion of the stratospheric ozone layer observed between 1979 and 2000 has resulted in a negative radiative forcing, of 0.15 W/m<sup>2</sup>).

This addition to the natural greenhouse effect (155 W/m<sup>2</sup>) is small, correspon-

ding to an increase of about 1%. Nevertheless, it is practically certain that this has contributed to the rise in mean temperature, for our planet, of about 0.5 °C, observed over the 20th century (see Figure 1). If nothing is done to curb these emissions, carbon dioxide concentration in the atmosphere (see Figure 2) could double by 2100. From current world consumption <sup>(1)</sup> of **fossil** fuels (7,700 **Mtoe**), the mass of CO<sub>2</sub> currently produced may easily be computed: 20 billion tonnes per year!

This could result in a substantial increase in the greenhouse effect, causing, through nonlinear amplifying effects,

 European Community,
Directorate General for Energy (DG XVII),
"Conventional Wisdom" scenario (*European* Energy to 2020: A scenario approach, 1996).

8) ·····).

profound alterations in climate. Most models predict that doubling the present carbon dioxide concentration would result, by the end of the 21st century, in a rise in temperature of some 2–3 °C. Some models even yield a bracket of 1.5–4.5°C, meaning dramatic consequences could be foreseen for the environment, such as a substantially rising sea level.

Such figures may seem small, entailing only minor consequences for the climate; that, however, is not the case. To understand this point, one should bear in mind that during the "little ice age," from 1450 to 1880, mean temperature only fell, in France, by 1 °C, on average. Some 6,000–8,000 years ago, as Western Europe experienced a war-



### The greenhouse effect and CO<sub>2</sub>



#### Figure 2.

Evolution of atmospheric CO2 concentration since 1980, as measured on a daily basis by the automatic stations of the Climate and Environmental Science Laboratory (LSCE: Laboratorie des sciences du climat et de l'environnement), since 1981 on Amsterdam Island (Indian Ocean), and since 1992 at Mace Head, on the western coast of Ireland.

Readings on Amsterdam Island (shown in green), well away from any direct perturbation of human origin, essentially evidence the constant rise in concentration. The Mace Head site basically measures oceanic atmosphere (under normal conditions, westerly winds: blue). When wind conditions are reversed, the site receives a continental atmosphere, showing a strong excess in CO<sup>2</sup> (red plots), compared to oceanic atmosphere. Over the mean rise in CO<sub>2</sub> concentration is superimposed a marked seasonal modulation, due to plant vegetative cycle (chlorophyll photosynthesis), plants being CO<sub>2</sub> emitters in winter, and CO<sub>2</sub> absorbers in summer.

mer spell, with a mean temperature 2-3 °C higher than it is today, the Sahara was not a desert, but a region of abundant rainfalls. It is not so much the rise in temperature that gives cause for concern, as its rapid variation (in the course of one century). The large variations previously observed in nature all occurred over much longer timescales, for those at least of a global character. Thus, the last glaciation lasted 100,000 years, and the corresponding deglaciation took 10,000 years. The rapid variation we are currently experiencing may induce major, unexpected perturbations in the climate and the ecosystem, which will not always have time to adapt.

#### From Rio to Kyoto: the major conferences on the global environment

The evolution of the global environment has led to major conferences being organized, starting in the closing decade of the 20th century.

At the Earth Summit, held in **Rio de** Janeiro (June 1992), the United Nations Framework Convention on Climate Change was signed, this setting the goal of a stabilization of greenhouse gas emissions (this convention came into force on 21 March 1994).

At the Kyoto Conference (December 1997), the protocol was signed providing for a global reduction in emissions of such gases, by an average 5.2% in the period 2008–2012, compared to 1990 levels, for **OECD** countries and Eastern European countries (including Russia). Reduction targets for the European Union and France are set at 8% and 0% respectively. The ways and means to meet these targets were debated, unsuccessfully, in November 2000 at The Hague. Subsequent conferences, held in Marrakech (2001), Johannesburg (Earth Summit held in August-September 2002), New Delhi (October 2002), Moscow (September-October 2003), and Milan (December 2003) had still not enabled, by 2004, this Kyoto Protocol to be brought into force, until Russia finally decided to ratify the document, at last allowing this enforcement in February 2005.

Under the impetus provided by the United Nations Environment Program (UNEP), the issues raised by substances that deplete the ozone layer in the atmosphere were addressed in Vienna (1985), and most importantly in Montreal (1987), where the protocol was signed, imposing a reduction in production and use



National University of Ireland

The Mace Head monitoring station, Ireland.

of chlorofluorocarbons (CFCs). This protocol was specified by amendments adopted in London (1990), imposing a ban on CFCs from 1 January 2000, and extending controls to other compounds (including HCFCs), Copenhagen (1992), Montreal (1997), and Beijing (1999).

### C How does a fuel cell work?



Operating principle of the fuel cell: the example of the proton-exchange membrane fuel cell. MEA stands for membrane-electrode assembly.

he fuel cell is based on a principle discovered quite some time ago, since it was in 1839 that Sir William Grove constructed the first electrochemical cell working with hydrogen as its fuel, thus demonstrating the ability to generate electric current through direct conversion of the fuel's chemical energy. Since the fuel cell has the special characteristic of using two gases - hydrogen  $H_2$  and oxygen  $O_2$  - as its electrochemical couple, the oxidationreduction reactions occurring inside the fuel cell are particularly simple. The reaction takes place inside a structure (the basic electrochemical cell). consisting essentially in two electrodes (the anode and cathode), separated by an electrolyte, i.e. a material that lets ions through. The electrodes employ catalysts, to activate, on the one side, the hydrogen oxidation reaction, and, on the other, the oxygen reduction reaction.

In the case of an acid-electrolyte cell (or proton exchange membrane fuel cell), the hydrogen at the anode is dissociated into protons (or hydrogen ions H<sup>+</sup>) and electrons, in accordance with the oxidation reaction:  $H_2 \rightarrow 2 H^+ + 2 e^-$ . At the cathode. the oxygen, the electrons and the protons recombine to yield water:  $2 \text{ H}^+ + 1/2 \text{ O}_2 + 2 \text{ e}^- \rightarrow \text{H}_2\text{O}$ . The principle of the fuel cell is thus the converse of that of water electrolysis. The thermodynamic potential for such an electrochemical cell, consequently, stands at around 1.23 volt (V). However, in practice, the cell exhibits a voltage of about 0.6 V for current densities of 0.6-0.8 A/cm<sup>2</sup>. The efficiency of such a fuel cell is thus equal to about 50%, the energy dissipated naturally being so dissipated in the form of heat.

### E Storage batteries, cells and batteries: constantly improving performance

Ctorage batteries – also known as accumulators, or secondary batteries – and batteries – so-called primary batteries - are electrochemical systems used to store energy. They deliver, in the form of electric energy, expressed in watt-hours (Wh), the chemical energy generated by electrochemical reactions. These reactions are set in train inside a basic cell, between two electrodes plunged in an electrolyte, when a load, an electric motor, for instance, is connected to its terminals. Storage batteries are based on reversible electrochemical systems. They are rechargeable, by contrast to (primary) batteries, which are not. The term "battery" may further be used more specifically to denote an assembly of basic cells (whether rechargeable or not).

A storage battery, whichever technology is implemented, is essentially defined by three quantities. Its gravimetric (or volumetric) energy density, expressed in watt-hours per kilogram (Wh/kg) (or in watt-hours per liter [Wh/l]), corresponds to the amount of energy stored per unit mass (or per unit volume) of battery. Its gravimetric power density, expressed in watts per kilogram (W/kg), measures the amount of power (electric energy delivered per unit time) a unit mass of battery can deliver. Its cyclability, expressed as a number of cycles, <sup>[1]</sup> characterizes storage battery life, i.e. the number of times the battery can deliver an energy level higher than 80% of its nominal energy; this quantity is the one most frequently considered for portable applications.

Up to the late 1980s, the two main technologies prevalent on the market were lead-acid storage batteries (for vehicle start-up, backup power for telephone exchanges...), and nickel-cadmium storage batteries (portable tools, toys,

(1) One cycle includes one charge and one discharge.

emergency lighting...). Lead-acid technology, more widely referred to as lead-acid batteries, or lead batteries, is also denoted as lead-acid systems. Indeed, the chemical reactions employed involve lead oxide, forming the positive electrode (improperly termed the cathode), and lead from the negative electrode (anode), both plunged in a sulfuric acid solution forming the electrolyte. These reactions tend to convert the lead and lead oxide into lead sulfate, further yielding water. To recharge the battery, these reactions must be reversed, through circulation of a forced current. The disadvantages found with lead-acid technology (weight, fragility, use of a corrosive liquid) resulted in the development of alkaline storage batteries, of higher capacity (amount of energy delivered during discharge), yielding however a lower electromotive force (potential difference between the system's terminals, under open circuit conditions). Electrodes for these systems are either based on nickel and cad-(nickel-cadmium storage mium batteries), or nickel oxide and zinc (nickel-zinc storage batteries), or silver oxide coupled to zinc, cadmium, or iron (silver-oxide storage batteries). All these technologies use a potassium hydroxide solution as electrolyte. Lead-acid technologies, as indeed alkaline batteries, are characterized by high reliability, however gravimetric energy densities remain low (30 Wh/kg for lead-acid, 50 Wh/kg for nickel-cadmium).

In the early 1990s, with the growth in the portable device market, two new technological pathways emerged: nickel-metal hydride storage batteries, and lithium storage batteries (<u>see Box on</u> <u>Operating principle of a lithium storage</u> <u>battery</u>). The first-mentioned pathway, involving a nickel-based positive electrode and a negative electrode – made of a hydrogen-absorbing alloy – plunged in a concentrated potassium hydroxide solution, allowed gravimetric energy

densities of 70-80 Wh/kg to be achieved. The second pathway had already been targeted by research around the late 1970s, with a view to finding electrochemical couples exhibiting better performance than the lead-acid or nickel-cadmium storage batteries used up to that point. Initial models were thus designed around a metallic-lithiumbased negative electrode (lithium-metal pathway). However, that technology was faced with issues arising from poor reconstitution of the lithium negative electrode, over successive charging operations. As a result, around the early 1990s, research was initiated on a new. carbon-based type of negative electrode, this serving as a lithium-insertion compound. The lithium-ion pathway was born. Japanese manufacturers soon made their mark as leaders in the field. Already in business as portable device manufacturers, they saw the energy source as numbering among the strategic components for such devices. Thus it was that Sony, not initially involved in battery manufacture, decided, in the 1980s, to devote considerable resources to advance the technology, and make it suitable for industrialization. In February 1992, Sony announced, to general stupefaction, the immediate launching of industrial production of lithium-ion storage batteries. These early storage batteries exhibited limited performance (90 Wh/kg). Since then, these batteries have seen notable improvement (from 160 Wh/kg to over 180 Wh/kg in 2004), owing, on the one hand, to the technological advances made (reduction in the unproductive fraction of battery weight and volume), and, on the other, to optimization of materials performance. Gravimetric energy densities of over 200 Wh/kg are expected around 2005.

### **Operating principle of a lithium storage battery**

During use, hence during discharge of the **storage battery**, lithium released by the **negative electrode** (<H>: host intercalation material) in ion form (Li<sup>+</sup>) migrates through the ion-conducting **electrolyte** to intercalate into the **positive electrode** active material (<MLi>: lithium-insertion compound of the metal oxide type). Every Li<sup>+</sup> ion passing through the storage battery's internal circuit is exactly compensated for by an **electron** passing through its external circuit, thus generating a current. The **gravimetric energy density** yielded by these reactions is

proportional both to the difference in potential between the two electrodes, and the quantity of lithium intercalating into the insertion material. It is further inversely proportional to system total mass. Now lithium is at the same time the lightest (molar atomic mass: 6.94 g), and the most highly **reducing** of metals: electrochemical systems using it may thus achieve voltages of 4 V, as against 1.5 V for other systems. This allows lithium batteries to deliver the highest gravimetric and volumetric energy densities (typically over 160 Wh/kg, and 400 Wh/l),



50% greater, on average, than those of conventional batteries. The operating principle of a lithium storage battery remains the same, whether a lithium-metal or carbon-based negative electrode is employed. In the latter case, the technological pathway is identified as lithium-ion, since lithium is never present in metal form in the battery, rather passing back and forth between the two lithium-insertion compounds contained in the positive and negative electrodes, at every charge or discharge of the battery.

### How does a photovoltaic solar cell work?

The photovoltaic effect used in solar cells allows direct conversion of light energy from the Sun's rays into electricity, by way of the generation, and transport inside a semiconductor material, of positive and negative electric charges, through the action of light. This material features two regions, one exhibiting an excess of electrons, the other an electron deficit, respectively referred to as *n*-type doped, and *p*-type doped. When

the former is brought into contact with the latter. excess electrons from the *n* material diffuse into the *p* material. The initially *n*-doped region becomes positively charged, and the initially pdoped region negatively charged. An electric field is thus set up between them, tending to force electrons back into the *n* region, and holes back into the *p* region. A junction (so-called *p*-*n* junction) has been set up. By placing metallic contacts on the *n* and *p* regions. a diode is obtained. When the junction is illuminated, photons having an energy equal to, or higher than, the width of the forbidden band, or **band gap**, yield their energy to the atoms, each photon causing an electron to move from the valence band to the conduction band. leaving behind it in turn a hole, also able to move around the material, thus



giving rise to an **electron-hole pair**. Should a load be positioned at the cell's terminals, electrons from the *n* region will migrate back to the holes in the *p* region, by way of the outside connection, giving rise to a potential difference: an electric current passes (see Figure).

The effect thus involves, basically, the material's semiconducting properties, and its doping, to improve conductivity. Silicon, now used in most cells, was selected for the presence of four valence electrons in its outermost shell (column IV of the Mendeleyev periodic table). In solid silicon, each atom - termed a tetravalent atom - is bound to four neighbors, and all electrons in the outermost shell participate in the bonds. Should a silicon atom be substituted for by an atom from column V

(a phosphorus atom, for instance), one of its five valence electrons is not involved in the bonds; as a result of thermal agitation, it soon moves to the conduction band, thus becoming free to move through the crystal, leaving behind it an immobile hole, bound to the doping atom. There is electron conduction, and the semiconductor is designated as an *n-type doped semiconductor*. If, on the other hand, a silicon atom is substituted for by an

atom from column III (boron, for instance), carrying three valence electrons, one electron is missing, if all bonds are to be maintained, and an electron may quickly move in to fill this gap, taking up the vacant orbital, as a result of thermal agitation. A hole thus arises in the valence band, contributing to conduction, and the semiconductor is said to be a *p-type doped semiconductor*. Atoms of elements such as boron or phosphorus are thus doping agents in silicon. Photovoltaic cells are assembled into **modules**.

Note: In *Organic photovoltaic cells: towards an all-polymer path...*, you will find the operating principle of organic photovoltaic cells (Box, p. 122).

## Operating principle of an organic photovoltaic cell

Following absorption of **photons** by the **polymer**, bound **electron-hole** pairs (excitons) are generated, subsequently undergoing dissociation. Owing to inherent limitations in organic materials (exciton lifetime, low charge mobility), only a small fraction of photon-generated electron-hole pairs effectively contribute to the photocurrent. One of the main ideas is to achieve volume distribution of the photogeneration sites, to enhance exciton dissociation. This approach is based on increasing junction surface area, through deployment of an interpenetrating network of the donoracceptor (D-A) type, effecting transport of holes (P<sup>+</sup>) to the anode (indium-tin oxide [ITO]), and of electrons (e<sup>-</sup>) to the metallic cathode (made e.g. of aluminum [Al]). While quantum separation efficiency, for photoinduced charges in systems associating a **semiconducting** polymer (of PPV or polythiophene type) with a fullerene derivative (PCBM), is thus close to unity, the challenge now is to restrict recombination and trapping processes limiting charge transport and collection at the electrodes, to improve overall device efficiency, this currently still being low (less than 5%). The rise of the pathway is also heavily dependent on mastery and understanding of cell aging mechanisms, but equally on mastery of thin-film technologies, to achieve protection of the device against atmospheric oxygen and water vapor.



The blue dotted line shows the trajectory of holes inside the material.