



Why hydrogen?

Why go for hydrogen? A number of responses to that question stem, in equal measures, from overoptimism or overpessimism. As is often the case in such debates, truth lies somewhere in between these two extremes. This corresponds to the outcome of large-scale, long-term trends: the explosion in energy demand, exhaustion of fossil resources, and global warming due to a runaway greenhouse effect.



Cryogenic stages of the Ariane 5 space launcher being welded at Cryospace [ESC-A upper stage in the foreground, EPC main stage behind]. Space propulsion, while quantitatively limited, represents an initial industrial use of hydrogen as an energy carrier.

When dealing with the issue of **hydrogen** utilization, some media are wont to convey equally outrageously optimistic, and excessively pessimistic responses. Among the former may be ranged claims that hydrogen is a clean, high-performance **fuel**, universally available and useable, and that all that is required is to go for wholesale utilization, even wondering the while why the notion has not occurred earlier. Among the latter are such as make the point that this hydrogen has to be generated, since it does not occur naturally, and this production is energy-intensive, accruing no benefit in term of the environmental balance, and even makes for added complexity in systems drawing on it.

The “proper response” needs must be based on two facts, noted by serious surveys of energy prospects. The first is that, while **fossil** resources will still meet, in 2050, over 60% ⁽¹⁾ of world energy requirements (as against 85% currently), the latter will have more than doubled by that time! Complementing the presently existing supply can only be achieved through **renewable energies**, and nuclear energy. The second fact is that resulting **CO₂** emissions will by then greatly exceed the concentration threshold of 550 **ppmv**, ⁽²⁾ beyond which

(1) According to the Royal Dutch–Shell survey (2001): *Energy Needs, Choices and Possibilities. Scenarios to 2050* (www.shell.com).

(2) Current levels stand at 370 ppmv.

mean atmospheric temperature will rise by values that are environmentally unacceptable.

The only solution that can be entertained, to resolve this apparent contradiction, is to restrict **CO₂** emissions from fossil energies through **sequestration**. Which is to say that fossil fuel is to undergo transformation, extracting its carbon atoms which, once turned into **CO₂**, are to be stored in large geological reservoirs, such as depleted oil and gas fields or worked-out coal mines (see *CO₂ sequestration in underground geological reservoirs?* p. 20). The residue from this transformation – generally known as **reforming** – is **synthesis gas**, which is still a fuel. When purified, this yields pure hydrogen, this being a new **energy carrier**, a substitute for the **hydrocarbons** it is directly derived from, shorn however of carbon atoms, which are unavoidably transformed into **CO₂** over their life cycle.

The relevance of hydrogen, however, is not restricted to the sole enhancement of fossil fuels, but extends equally to other forms of **primary energy**. Indeed, such alternative energy sources are of two types. These either directly yield electricity (**photovoltaics**, wind power, geothermal power), which may be used immediately, or be transformed into hydrogen (through **electrolysis**) to be stored, or utilized in other systems, be they mobile (transportation) or stationary (industrial); or they yield hydrogen directly (**thermochemistry**) or indirectly (**biomass** transformation).

Manifest qualities

The hydrogen atom occurs, in the form of water molecules, with great abundance on Earth. It has the most energetic molecule: 120 MJ/kg, i.e. 2.2 the value for natural gas (see Table). Hydrogen has an energy content of 39.4 kWh/kg, whereas coal, according to the form it comes in, is bracketed in the 7.8–8.7 kWh/kg range, i.e. some 5 times less per unit mass. It is neither a pollutant, nor toxic, and its combustion in air yields only water. It is the lightest of gases, this being a positive factor as regards safety (high diffusion speed in air). Aside from so-called “confined” conditions (i.e. enclosed with a quantity of air in a closed space), hydrogen is less hazardous than natural gas (see *Hydrogen safety: a fail-safe technology as the key to social acceptance* p. 96). Hydrogen transport (in particular by means of pipelines) and storage (pressurized or in liquid form) are easily effected. Production may be carried out through a variety of methods (see *How is hydrogen to be produced?* p. 31), and it forms the ideal fuel for **fuel cell**, and the most efficient means for the conversion of chemical energy into electric energy (see the section devoted to *Energy converters* p. 64).

Acceptance far from granted

The very lightness of hydrogen entails an energy density (per unit volume) that is less favorable, as regards transport and storage in the gaseous form, than for **natural gas** (by a factor 4 at 200 bars, for instance). Hydrogen's flammability and explosion limits, in air, are higher than those for natural gas, by a factor 5 or so (see Table in *Hydrogen safety*). Thermal, high-temperature combustion of hydrogen, in the presence of air, yields **nitrogen oxides**. Seen as a hazardous gas, hydrogen's public image is poor, and acceptability is thus still far from being achieved.



P. Legros/Photobrique PSA

Trials of the HydroGen prototype, based on a Peugeot Partner, were, at the beginning of this decade, a major milestone on the way to production of a fuel-cell powered vehicle, fed in this case with compressed hydrogen. CEA is working in association with the PSA-Citroën Group on this development.

Large-scale R&D programs under way

The choice of hydrogen as the energy carrier of the future is nowadays almost unanimously endorsed by the scientific and business communities and political leaders, whether in the French context (**PACo Program**, **CNRT Pile à combustible** [Fuel Cell National Technology Research Center], see p. 4) or that of the European Union (6th EU Framework Program, Hydrogen and Fuel Cell Technology Platform), or around the

properties	numerical value
atomic mass	1.0079
individual gas constant	4,124.5 J/kg·K
LHV (lower heating value)	33.33 kWh/kg, 3.00 kWh/Nm ³ (gasoline: ≈ 12.0 kWh/kg, 8.8 kWh/l) (natural gas: 10.6–13.1 kWh/kg, 8.8–10.4 kWh/Nm ³) The energy carried in 1 Nm ³ hydrogen is equivalent that of 0.34 liter of gasoline; 1 kg hydrogen is equivalent to 2.75 kg gasoline 10,800 kJ/Nm ³
HHV (takes in the energy in water vapor)	39.41 kWh/kg, 3.55 kWh/Nm ³ 12,770 kJ/Nm ³
gas density at 273 K	0.0899 kg/Nm ³ (natural gas: 0.6512 kg/Nm ³)
specific heat (Cp at 273 K)	14,199 J/kg·K
boiling temperature (at 1,013 mbar)	20.268 K

Table.
Some physical and physical-chemical characteristics of molecular hydrogen.

world (United States, Japan, Canada...). While there is general recognition that some barriers do remain, all are confident that research workers will be able to overcome these in the medium term. Thus, all industrialized nations have launched major research, development and demonstration programs, covering the entire vertical chain, from hydrogen production to utilization, as well as cross-cutting areas such as safety, security, standards and regulations, training, and social-cultural impacts.

The most attractive candidate

Within a few years, a more industrial stage will come into view. Embarking on it will be as much a matter of political will as of technological maturity. “Overoptimists” and “overpessimists” alike will then withdraw from their positions. The former, by agreeing that hydrogen has never laid claim to providing a universal answer to every energy situation: some carriers will stay in use, such as electricity, while others (liquid fuels generated from biomass, for instance) will rise. The latter, by taking stock of the fact that the requisite of sequestration of CO₂ from fossil energies, as well as the rise of alternative energies, will have put on the map a new energy carrier: hydrogen is unquestionably the most attractive of candidates.

> **Thierry Alleau**
French Hydrogen Association
Paris

Prototype demonstrator aeroplane designed by Boeing for trials of fuel cell utilization for aviation. This modification of a motor-glider from Austrian manufacturer Diamond Aircraft Industries was carried out by the US planemaker's Spanish research center, with contributions from a number of European manufacturers. First flight is scheduled for the end of 2004 or early 2005.



FOR FURTHER INFORMATION:

“L'hydrogène, carburant de demain?”, L'Actualité chimique, special issue, December 2001.

A The many states of energy

“Nothing 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).

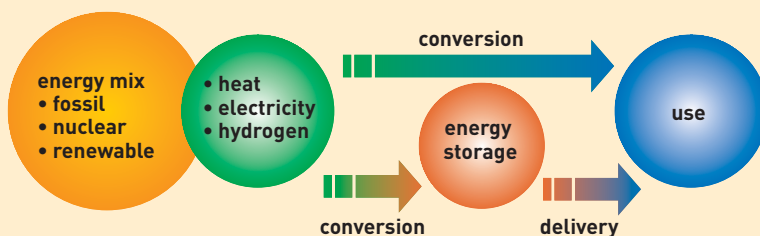


Figure 1. The energy scheme.

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 quite 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 transformation 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, energy-consuming sites may be far removed from the production site, production

and concomitant demand, moreover, not 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.

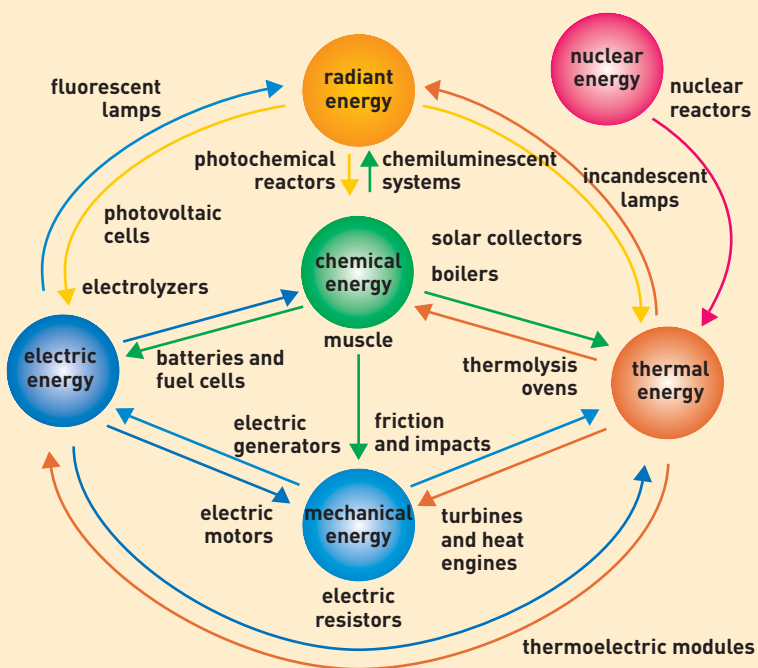
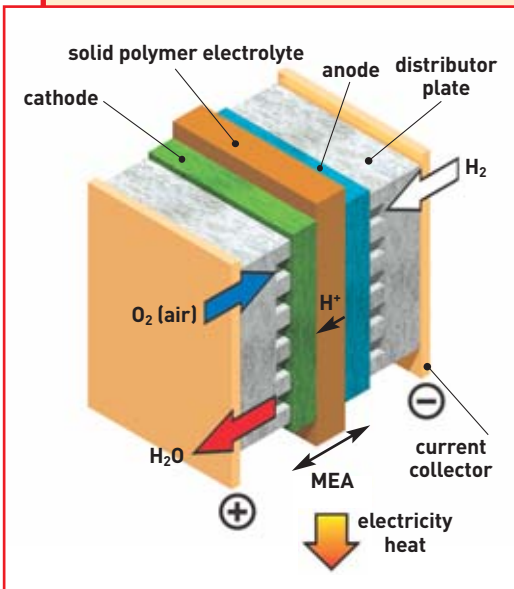


Figure 2. Conversions of the six main forms of energy, with a few examples of energy converters.

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.

The 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 **oxidation-reduction** 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^+) 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: $2 H^+ + 1/2 O_2 + 2 e^- \rightarrow H_2O$. 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/cm². 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

Storage 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,⁽¹⁾ 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,

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 cadmium (nickel-cadmium storage 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 ([see Box on Operating principle of a lithium storage battery](#)). 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

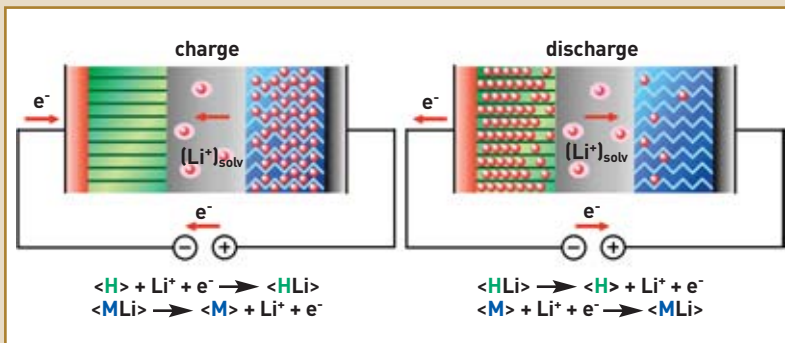
densities of 70–80 Wh/kg to be achieved. The second pathway had already been targeted by research around the late 1970s, with a view to finding electrochemical couples exhibiting better performance than the lead-acid or nickel-cadmium storage batteries used up to that point. Initial models were thus designed around a metallic-lithium-based 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.

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

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^+) 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^+ 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

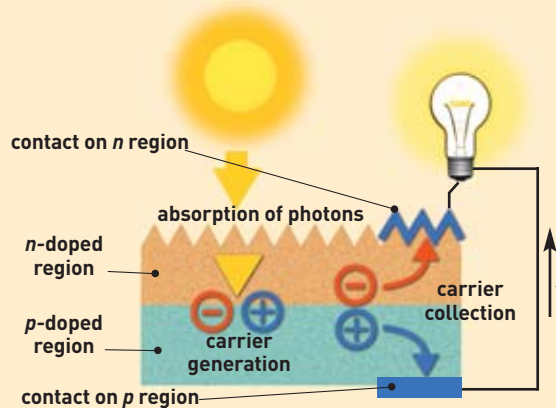
proportional both to the difference in potential between the two electrodes, and the quantity of lithium intercalating into the insertion material. It is further inversely proportional to system total mass. Now lithium is at the same time the lightest (molar atomic mass: 6.94 g), and the most highly **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.

D 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 *p*-doped 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 Mendeleev 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 donor-acceptor (D-A) type, effecting transport of holes (P^+) to the **anode** (indium-tin oxide [ITO]), and of electrons (e^-) 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.

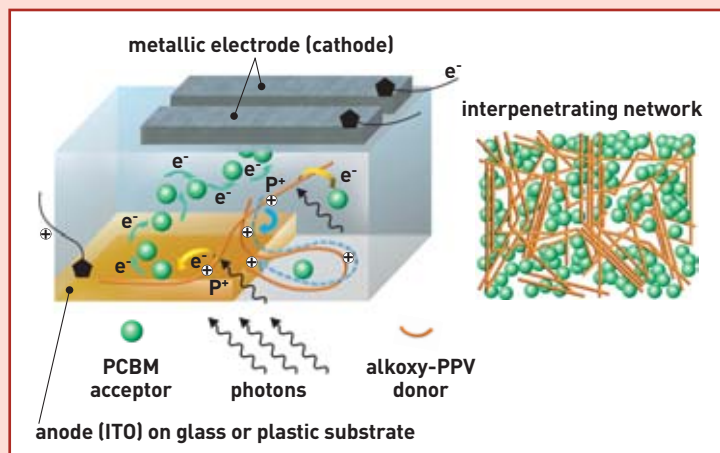


Figure from a presentation by S. Sariciffici (www.itos.at)

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

	hydrogen H ₂	propane C ₃ H ₈	natural gas (methane CH ₄)	gasoline (fumes)
molecular mass (g/mol)	2	44	16	
density (atmospheric conditions) (kg/m ³)	0.08	1.87	0.7	
heating value (lower) (kJ/g)	120	46	50	44,5
flammability domain limits in air (vol%)	4.0 – 75.0	2.1 – 9.5	5.3 – 15.0	1.0 – 7.6
minimum ignition energy (mJ, for a stoichiometric mixture at ambient pressure and temperature)	0.02	0.26	0.29	0.24
autoignition temperature (°C)	585	487	540	228 – 501
flame temperature (°C)	2,045		1,875	2,200
detonation limits (vol%)	13 – 65		6.3 – 13.5	1.1 – 3.3
combustion rate in air (in atmospheric conditions) (cm/s) [laminar flame speed]	265 – 325	30 – 40	40	
explosive energy (kg TNT/m ³)	2.02	20.3	7.03	44.24
diffusion coefficient in air (cm ² /s)	0.61		0.16	0.05
flame speed in air (cm/s)	260		37	
detonation velocity in air (km/s)	2		1.8	

Table.

Comparative properties of hydrogen, propane, methane, and gasoline fumes
(source: HyWeb, INERIS and AFH₂).