

Hydrogen production by water photolysis?

Could one imagine seeing some day rooftop solar collectors generating hydrogen and oxygen, rather than hot water? This scenario could well become a reality, building on solutions that advances in the field of photoelectrochemical water splitting by sunlight are now making possible.

Photoelectrochemical (PEC) cells, illuminated by sunlight, have the ability to split water into hydrogen and oxygen. Such cells use photoactive electrodes, immersed in an aqueous electrolyte or water. In their simplest form, they may be described as integrated, or monolithic, photovoltaic-electrolytic devices. A wide range of PEC and photo-catalysis processes having the capability to split water are being investigated around the world.

Still at the fundamental research stage

Intrinsically simple though they be, the scientific and developmental aspects of materials for hydrogen-evolving PEC cells are still at the preliminary, if fascinating, stage of fundamental research.

Four main steps are involved in the photoelectrochemical water-splitting process. The first one is the generation of an electronic charge at the surface of the photo-anode subjected to solar radiation, yielding electron-hole pairs. The second step consists in oxidation of water by the holes at the photoanode, yielding molecules of oxygen (O_2). The third step is that of the transport of hydrogen ions (H^+) and electrons, from the photoanode to the cathode, by way respectively of the electrolyte and of the electric connection (the cathode may be a light-induced photocathode). Finally, reduction of the H^+ at the cathode by the electrons yields hydrogen molecules (H_2).

The choice of *n*-type semiconductor material for the photoanode is crucial for PEC cells, and involves two criteria: existence of a “perfect” bandgap, and ability

to preclude recombination of charge carriers. Minimum theoretical energy for the photon that must be absorbed by a “perfect” photoanode is 1.23 electronvolts (eV). This is the minimum theoretical value for the electromotive force (EMF) required by PEC cells to split the water molecule.

Conceptually, three main approaches are currently being investigated around the world, with regard to photoelectrochemical water splitting (photolysis). These involve, respectively, single-photoelectrode systems, two-photoelectrode systems, and hybrid photoelectrode-photovoltaic systems.

As a subvariant of PEC water splitting, photocatalytic splitting uses a light-induced photocatalyst, hosting at its surface both processes, water oxidation and reduction. The resulting gaseous mixtures of hydrogen and oxygen present practical drawbacks, by comparison with the physically-separated gases cogenerated by PEC systems.

A range of materials under investigation

Titanium dioxide (TiO_2) is the most widely investigated photoelectrode material. In the form of rutile crystals, this was successfully tested in PEC cells by Honda and Fujishima by the early 1970s. ⁽¹⁾ As reported in an overview edited by the author of this paper, ⁽²⁾ howe-

(1) A. Fujishima and K. Honda, *Nature* 1972, 238, 37.

(2) A. Luzzi (ed.), *Photoelectrolytic Production of Hydrogen*, Final Report of Annex 14, International Energy Agency Hydrogen Implementing Agreement (www.ieahia.org), 2004.

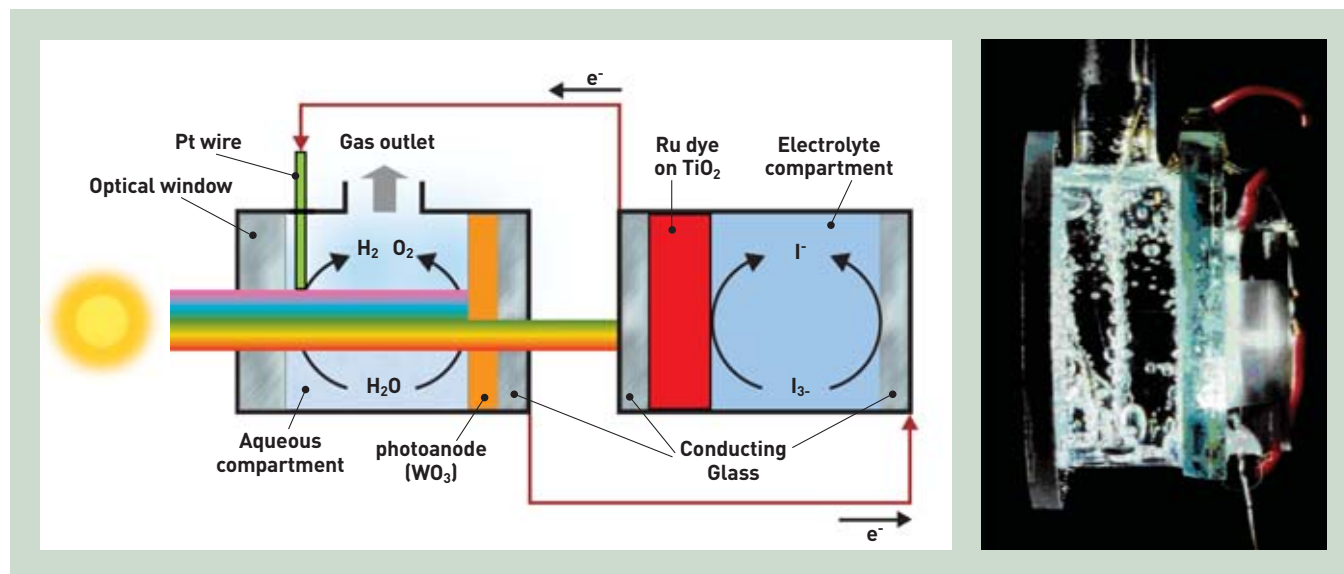
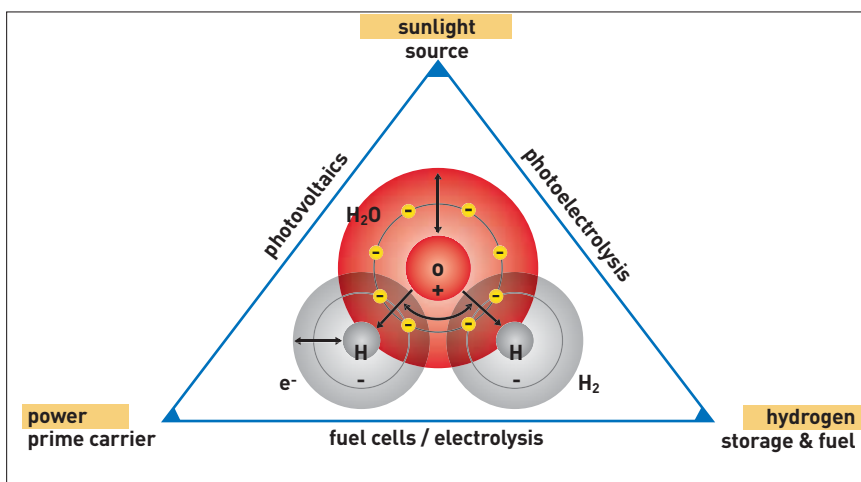


Figure 1. Schematics of a two-step photoelectrochemical (PEC) cell, based on mesoscopic semiconductor films (WO_3 for the photoanode, platinum as cathode metal, and a TiO_2 dye-sensitized solar cell for bias voltage), for visible-light water splitting. Solar-hydrogen conversion efficiency of 4.5% was demonstrated. [Source: Swiss Federal Institute of Technology [École polytechnique fédérale de Lausanne: EPFL] and Geneva University.]



Figure 2. A possible future “post-fossil-fuel energy triangle,” based on solar energy, would have for key energy carriers electricity and hydrogen. Photovoltaics, fuel cells and photoelectrochemical cells would be the associated enabling technologies. (Source: Andreas Luzzi.)



ver, more recent efforts have broadened the field of investigations to include use of alternative n-type semiconductor materials, exhibiting a lower bandgap energy for the photoanode, more specifically tungsten trioxide (WO_3) and, quite recently, hematite (Fe_2O_3). Since the PEC cell photovoltage applied to each of these photoanode materials is lower than 1.23 eV, a bias voltage is required if water splitting is to be effected. A two-photon “tandem-cell” PEC device, featuring a WO_3 photoanode and TiO_2 dye-sensitized photocell (DSC) connected in series, has been tested on a laboratory scale (see Figure 1).

“Valence” semiconductors such as gallium arsenide (AsGa) are being investigated as alternative photoelectrode materials, to substitute for oxide materials, owing to their favorable energy band. While they exhibit instability in aqueous environments, experimental PEC cells have achieved solar-hydrogen conversion efficiencies approaching 20%, an indication of the potential of such systems.

Indium- (In), niobium- (Nb) or tantalum- (Ta) based single-particle, mixed-oxide semiconductor photocatalyst powders are being developed. They exhibit fast hydrogen and oxygen response under visible-light irradiation, which is encouraging as regards applications in aqueous suspensions (“hydrogen ponds,” for instance).

Major challenges to be met

The key challenges to be taken up, to advance innovation in the field of PEC cells and bring them to market, lie in materials science and systems technology. The most important of these challenges concern development of high-efficiency, corrosion-resistant photoelectrode materials and their transformation processes. No “ideal” water-splitting photoelectrode material (i.e. exhibiting the optimum bandgap of about 2 eV) being available on the market, novel materials must be devised. Combinatorial chemistry approaches offer, in this respect, potentials for fast tracking, to screen the required materials.

The greatest requirement for fundamental research concerns **doping** for bandgap shifting and surface chemistry modification, a research effort covering work on associated surface and bulk semiconducting properties (i.e. light absorption, electric potential barriers and interfacial charge transfers in

metal-semiconductor junctions, flat-band potential, etc.). Corrosion and photocorrosion resistance present further significant challenges which must be addressed, with most of the currently available options for promising materials.

From a systems integration point of view, and to optimize the techno-economic performance of PEC water-splitting systems, current matching between anode and cathode, and ohmic resistance minimization both deserve considerable attention, in terms of design and of materials engineering.

Towards a future “energy triangle”

Ultimately, in a “post-fossil-fuel” era, the Sun will reemerge as the overall driving force, with the ability to fully sustain life on Earth, most likely with electricity and hydrogen as key **energy carriers**. One may predict that these two carriers will define, in future years, an “energy triangle” building on the science, technology, and “sister” engineering components of photovoltaics, **fuel cells** and photoelectrochemical cells (see Figure 2).

Integrated PEC devices offer a great potential in terms of simplicity, thin-film-based mass production, applications for abundant, environmentally benign materials. They could thus enable cost reductions, compared to other sunlight-driven hydrogen production options.

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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).

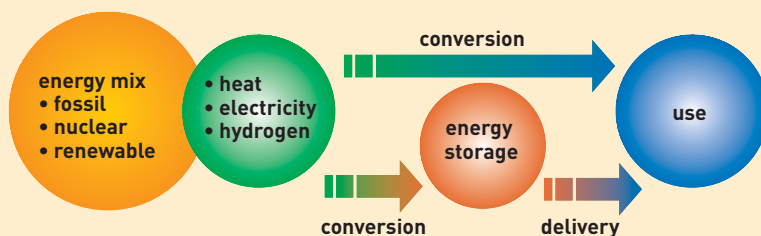


Figure 1. The energy scheme.

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.

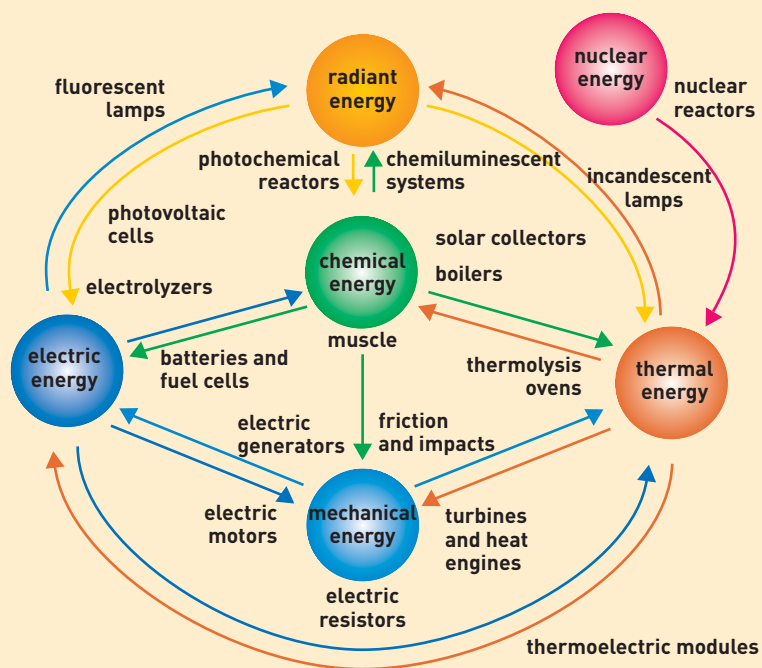
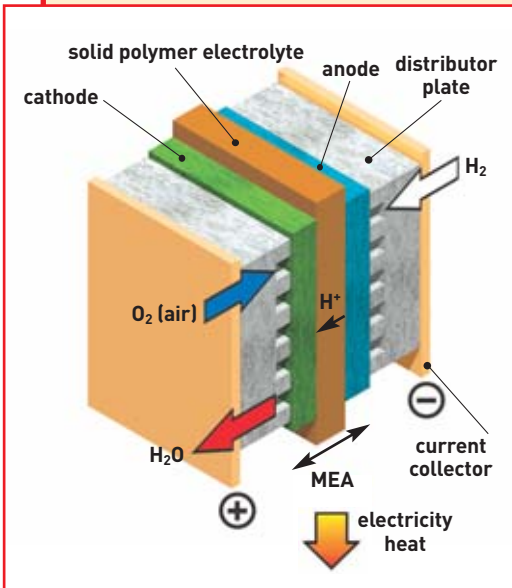


Figure 2. Conversions of the six main forms of energy, with a few examples of energy converters.

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 H₂ and oxygen O₂ - 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: $\text{H}_2 \rightarrow 2 \text{H}^+ + 2 \text{e}^-$. 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/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

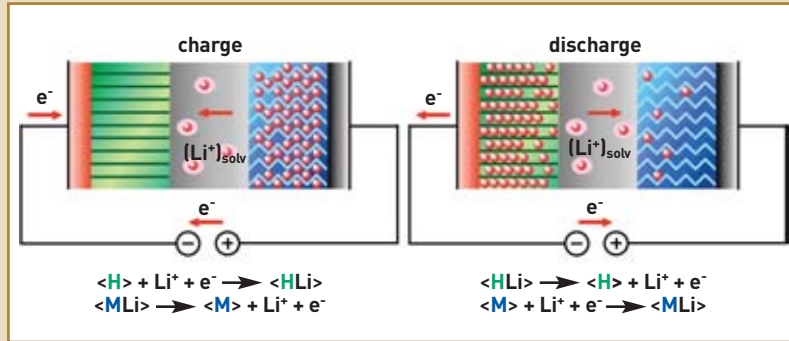
densities of 70–80 Wh/kg to be achieved. The second pathway had already been targeted by research around the late 1970s, with a view to finding electrochemical couples exhibiting better performance than the lead-acid or nickel-cadmium storage batteries used up to that point. Initial models were thus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

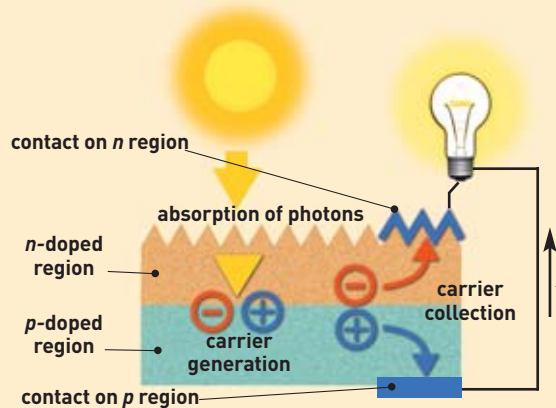
proportional both to the difference in potential between the two electrodes, and the quantity of lithium intercalating into the insertion material. It is further inversely proportional to system total mass. Now lithium is at the same time the lightest (molar atomic mass: 6.94 g), and the most highly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

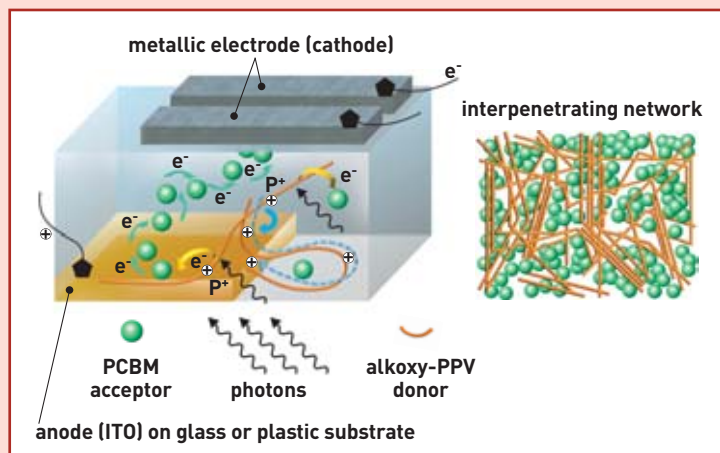


Figure from a presentation by S. Sariciffici (www.itos.at)

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