

Storage of photovoltaic electricity

If they are to be used in remote locations, photovoltaic systems, as is the case for any other intermittent energy, require an electricity storage system, allowing energy to be fed back on demand. Lead-acid batteries, owing to their low cost and simplicity of use, are currently the most widely used devices. Extending their durability, through investigation of corrosion and aging mechanisms, and seeking new storage paths number among the major research directions being pursued.



Roland Bourguet/Ademe

Fire-prevention watchtower, powered by photovoltaics, in the Bouches-du-Rhône département, southern France. One of the goals of research on photovoltaic electricity storage is to achieve battery durability matching that of the modules themselves.

Stand-alone photovoltaic generators require an electricity storage system, if they are to deliver a quasi-continuous energy supply, regardless of insolation sequences. Depending on applications, this energy supply is to be ensured, e.g. for periods of two to three days, for some small-scale household systems, or up to a fortnight for technical applications, such as marine lights. Such diverse applications make use of batteries involving a variety of technologies, to ensure service is guaranteed. Of these technologies, lead-acid batteries, though they have been known for more than a hundred years, do provide, currently, the best answer, in terms of price and durability. Some locations, involving particularly stringent operating requirements, and harsh climate conditions, may be fitted with nickel-cadmium batteries, however their cost, which is prohibitive, does not allow widespread utilization of this solution.

Experiments are being carried out, in some Northern European countries (Germany, Finland), on use of fuel cells as generators, associated to conventional storage devices. In this case, storage is effected by hydrogen reserves, generated by hydrolyzers, powered by

photovoltaic generators. This form of interseasonal storage exhibits no self-discharge. Were prices competitive enough to compensate for the currently low efficiency afforded by this technology, it would provide a means of resolving, for our latitudes, the issues arising from variations in electricity output, between summer and winter.

Lead-acid batteries: currently the most suitable

Stand-alone systems use flat-plate lead-acid batteries, of the starter type, for installations having an installed peak power close to a hundred watts or so. Larger installations tend to use tubular-plate batteries, which are better suited to daily cycling, involving, however, a cost per stored kilowatt-hour that is higher by a factor 1.5-2. This type of battery is used in installations with capacities ranging from several hundred peak watts to several peak kilowatts, and for all technical applications, owing to considerations of reliability, and safety (television and telecommunications radiowave repeater stations, marine lights). "Sealed" (valve-regulated) lead-



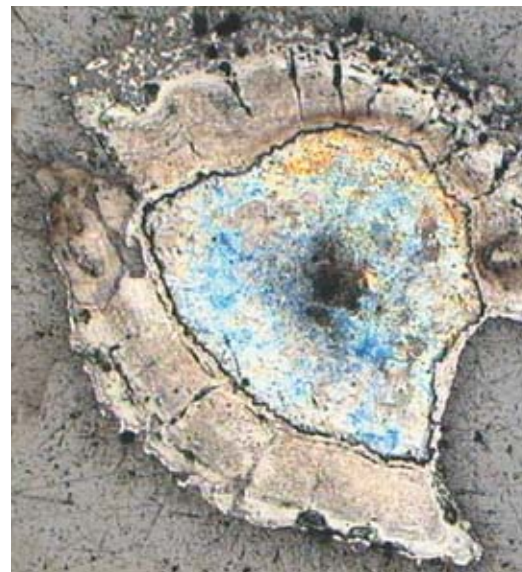
acid batteries are used mainly in demanding environments, allowing only infrequent maintenance, such as power for marine beacons, or installations in confined spaces.

Improving durability

Storage, in a photovoltaic system, accounts for a far from negligible contribution to overall operating costs, owing to successive replacements, over the system's lifetime. Indeed, depending on lead-acid battery technology and utilization, battery longevity may range from 2 to 12 years. Moreover, overall storage cost is not subject to any downward trend, matching that achieved for the other components of photovoltaic systems. One current goal is to double the durability of inexpensive batteries, to 6 years, and extend to 15 years that for industrial batteries of the **stationary**, tubular positive plate type. For that purpose, research directions, in work carried out in collaboration with manufacturers (Exide, in particular), are addressing design of new products, better suited to the requirements of photovoltaic applications.

Investigation of degradation mechanisms

A second research thrust is concerned with improvement of battery management systems. The point here is to preserve the battery, by making it operate in the least stressful state of charge domains, or, when meteorological conditions allow it, applying forced charging, to achieve recovery from the degradations generated. Such improvements thus require enhanced understanding of these degradations, as observed *in situ*. Work currently carried out at CEA/GENEC, under the aegis of contracts passed by **Ademe**, EDF, the **European Union**, and manufacturers (Total Énergie, BP Solar), is enabling identification, and investigation, of influential parameters, underlying degradation mechanisms. The damage found on batteries returned from field



CEA's characterization resources, at Cadarache, allow investigation of battery aging, particularly corrosion, evidenced here on a cross-section of a lead-acid battery positive **electrode**.

utilization results mainly from hard sulfation, loss of active matter cohesion, and, to a lesser extent, grid corrosion. To carry out these investigations, the laboratory can call on charge-discharge cycling, electrochemical investigation, and optical and chemical characterization resources. The understanding thus gained has allowed **modeling** of these mechanisms, and development of management algorithms, based on battery physical-chemical behavior, enabling enhanced service provision, and, in the longer term, extended durability for storage devices, by a factor 2.

Lithium-ion technology seen as promising

What are the coming challenges, regarding storage for such photovoltaic systems? Recent improvements in lithium-ion technology (*see [New paths in lithium storage batteries and battery electrolytes](#)*), together with the findings from the European INVESTIRE (Investigation on Storage Technologies for Intermittent Renewable Energies) thematic network, this being coordinated by GENEC, have confirmed the advantage of lithium-ion technology with respect to this application, owing to its specific characteristics: high energy efficiency, high longevity, no maintenance, reliability, predictability of behavior. With the cost of such storage batteries - this being the main limiting factor - currently experiencing a marked falling off (with a gain by a factor 4 over the past few years), this technology will be playing a growing role in years to come. Lithium-ion technology may well provide the means to achieve storage durability to match that of **photovoltaic modules**, i.e. 20-25 years.

> **Florence Mattera**

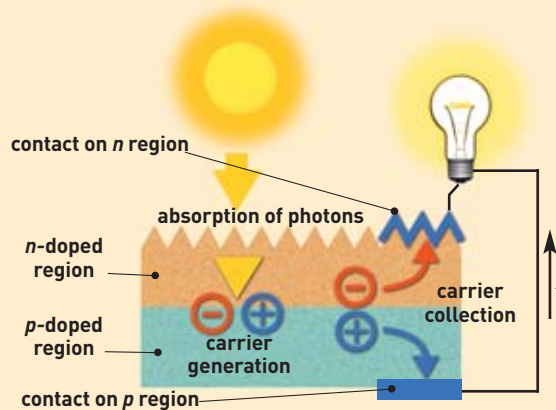
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Testing hall at Cadarache, where CEA is investigating behavior and optimization of batteries coupled to photovoltaic modules.

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 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 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.

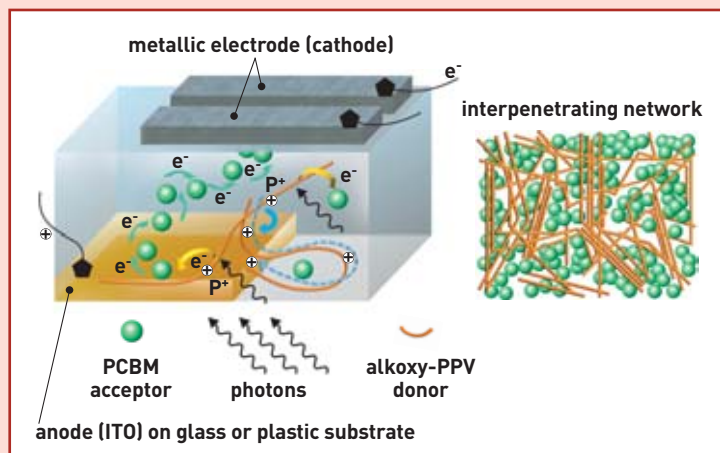


Figure from a presentation by S. Sariciffici (www.itiis.at)

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

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.

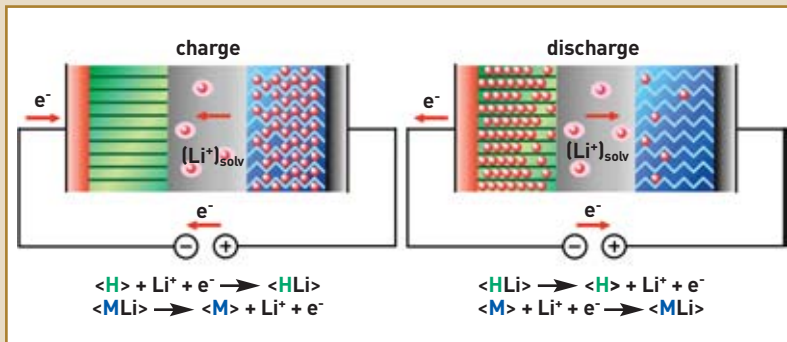
⁽¹⁾ One cycle includes one charge and one discharge.

Operating principle of a lithium storage battery

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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.