The onboard reformer: a transitional solution?

One of the main uses under consideration for hydrogen lies in automotive transportation. To ease the transition to the fuel-cell powered electric vehicle, why not fit the vehicle with a mini-reforming unit? An idea mooted by some manufacturers, such as Renault.

In 1998, the European Automobile Manufacturers Association (ACEA) made the commitment to achieve a reduction of 25% in **CO_2** emissions by 2008, relative to the level prevailing in 1995. Electric vehicles, particularly **fuel-cell** powered vehicles, are seen as a promising solution to achieve this goal. However, one question is left standing: what of the **fuel**?

While **hydrogen** is seen as an **energy carrier** of the future, a number of problems must be addressed before it can be found on the road (distribution grid, means of storage, process safety). In order to cater for this transitional period, which may extend over several decades, onboard **reforming** appears as an attractive half-way stage. However, the performance of such hydrogen generators needs must be consonant with automotive constraints: high efficiency, rapid transient response (start up, power acceleration or deceleration), low cost, compactness, safety, and materials recyclability.

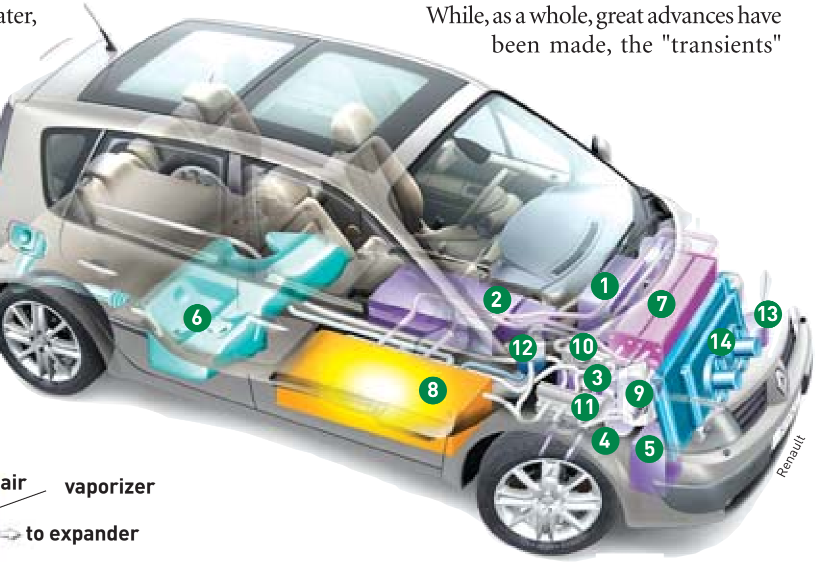
Over a few years, huge advances have been made in this area. Whereas at the end of the 1990s the volume of a complete reformer system would be close to one cubic meter, nowadays the most compact systems, with the capacity to power a vehicle of the Scénic II type, are no larger than 50-100 liters.

To generate fuel-cell grade hydrogen (CO content of under 100 **ppm**), the chosen fuel (**ethanol**, gasoline, **GtL**…) must undergo a number of chemical reactions. The first of these is reforming. In the presence of air and/or water, the fuel molecules are "broken up" to yield a mixture of hydrogen (30-35%), carbon monoxide and carbon dioxide (10-15% each). To lower CO content, three steps are required. Two water shift reactions and one preferential oxidation step result in CO content reduction, from 10-15% down to less than 100 ppm. These chemical reactions are relatively slow, and would require large reactors, incompatible with an automotive application. Use of **catalysts** allows reaction rates to be raised, and hence reactor size to be drastically cut down.

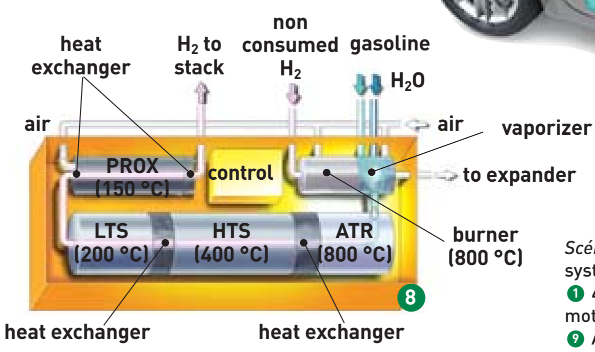
To arrive at a compact, high-efficiency system, heat exchanges must be particularly well thought out. The various reactions involved occur at temperatures ranging from 800 °C to 200 °C. A reduction in heat losses will allow a consequent improvement in reformer system efficiency. Currently, the best systems achieve efficiencies higher than 80%.

While, as a whole, great advances have been made, the "transients"

Reformer system developed by Nuvera Fuel Cells, world specialists in multi-fuel reforming and fuel cells, a firm in which Renault has taken up, in May 2004, a 10% holding.



Scénic II vehicle fitted with a fuel cell and a complete onboard gasoline reformer system.
❶ 42-V battery and voltage converter ❷ Power battery ❸ Inverter ❹ Electric motor ❺ 15-kW converter ❻ Gasoline tank ❼ Fuel cell ❽ Gasoline reformer ❾ Air filter ❿ Compressed-air cooler ⓫ Turbine-compressor unit ⓬ Pure-water condenser ⓭ Electric water pump ⓮ Radiator-fan unit.



gasoline processor

aspect and cost are the two major issues the thrust of research will be addressing in the years to come. To obtain a system that is competitive with conventional vehicles, the reformer system should be able to "start" in under 30 seconds, and it should not cost more than €700. The latter figure is still well outside what can be claimed for the best current systems, prototypes costing hundreds of thousands of euros.

With several years' activity already, directed to reduction of vehicle **greenhouse-effect gas** emissions and fuel consumption, Renault is intensifying its effort in the field of fuel cells. Capitalizing on the expertise gained in the research programs carried out in the years 1992-2002, the manufacturer is complementing its know-how with that from companies acknowledged as leaders in this field. Since 1999, Renault and Nissan have been working in synergy on development of the "fuel-cell" vehicle, the former company focusing on the onboard gasoline reforming path, the latter on a vehicle with direct hydrogen feed.

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Production by water electrolysis

Water electrolysis is nowadays an expensive hydrogen production process, used on an industrial basis in facilities of several megawatts capacity to generate high-purity hydrogen, when low-cost electricity is available. This process could experience definite growth, both in terms of small facilities using renewable energies, or implemented on a large scale, drawing on the resources of high-temperature nuclear reactors.

Terje S. Knudsen

Electrolyser for hydrogen generation, designed by Hydro Electrolysers.

Water **electrolysis** is, together with **steam reforming** or **hydrocarbon** gasification, one of the main processes available for **hydrogen** production, even though such production of hydrogen only accounts, at present, for a negligible fraction - about 1% - of world output. This process is used on an industrial basis in facilities of several **megawatts** capacity, to generate high-purity hydrogen, when low-cost or surplus electricity is available, as is the case around the Aswan Dam, in Egypt.

A simple concept

The splitting of water by electrolysis may be expressed in the overall form: H_2O ® $H_2 + 1/2\ O_2$, with a reaction **enthalpy** of 285 kJ/mole (at 298 K and 1 bar). The amount of electric energy to be supplied depends on this reaction enthalpy, on reaction **entropy**, and on temperature ($\Delta H = \Delta G + T\,\Delta S$, where ΔH stands for reaction enthalpy, ΔG for electric energy, and ΔS for reaction entropy). The theoretical voltage required for splitting at 298 K is 1.481 V. Typically, cell voltage in industrial facilities lies in the range 1.7-2.1 V.

Required water supply for an electrolyser is 0.8 L/**Nm³** hydrogen, close in practice to 1 L/Nm^3. The water used must be as pure as possible, in order to prevent formation of scale deposits and **electrode** corrosion processes.

An electrolysis cell comprises two electrodes (the **anode** and the **cathode**, these being electron conductors), connected to a direct-current generator, and an **electrolyte** (an **ion**-rich conducting medium). In conventional low-temperature electrolysis, the electrolyte, as a rule, is an aqueous alkaline solution (potassium hydroxide, for industrial electrolysis), or a **proton**-exchange **polymer** membrane (low-capacity electrolysis). In the

manufacturer	technology	capacity (Nm³/h)	pressure (bar)	cell energy efficiency (% LHV) [1]	overall energy efficiency (% LHV) [2]	electricity requirements (kWh/Nm³)
Giovanola	alkaline	20-500	1	77	60	5
Giovanola	alkaline	20-500	33	77	63.8	4.7
Hydro	alkaline	100-400	-	87	-	-
Vandenborre Technologies	membrane (inorganic)	10-60	1-8	91	62-65	4.6-4.8
Proton Energy Systems	membrane (polymer)	1-10	13	90	50-68	4.4-6
Stuart Energy	alkaline	10-36	-	-	51	5.9

(1) Cell energy efficiency: energy in the H_2 generated/electric energy supplied.

(2) System energy efficiency: energy in the H_2 generated/electric energy consumed by the system.

Table. Characteristics of a number of commercial electrolysers. Overall system energy efficiency figures take into account the electricity consumption of auxiliary equipment associated to the electrolysis module itself.


C. Etievant/École polytechnique

Prototype solid-polymer-membrane electrolyser for hydrogen and oxygen generation, developed in collaboration with the French École polytechnique.

case of advanced electrolysis, where water is in the form of steam, the electrolyte is a ceramic membrane, an O^{2-} ion transporter (see High-temperature electrolysis). In what follows, this paper will consider low-temperature electrolysis.

Current developments and economic aspects

Over the past ten years, many companies have developed low-output electrolysers (0-100 Nm^3/h hydrogen) for certain industrial applications (in the sectors of electronics, the agricultural and food industry, metal treatment, ceramics…). In some cases, indeed, electrolysis turns out to be a safer and more economical solution than hydrogen delivery by truck.


Stuart Energy

Hydrogen dispenser module fed by an electrolysis unit.

The Table provides a few examples, and shows the characteristics of commercially available small- and medium-capacity electrolysers. Hydrogen production costs from electrolysis can be arrived at from the capital cost for the electrolyser, operating and maintenance costs, electricity costs and rate of availability. Depending on the technology adopted and on capacity, production costs lie in the $11-50/GJ (€9-41/GJ) range.

Prospects

Hydrogen production by water electrolysis is one of the technological options being considered for onsite production of hydrogen for the supply of small fleets of fuel-cell powered vehicles (using electricity from the grid, or generated from renewable energies). About one third of currently operated or planned hydrogen fueling stations feature an electrolyser (i.e. about 20 stations).

Small-capacity hydrogen generation by electrolysis exhibits, at matching capacity, a higher level of technological maturity than conventional production technologies from hydrocarbons. A research and development effort is still required, however, if optimized systems are to be developed. Novel "mini-electrolyser" concepts are being investigated, for "home" hydrogen production, to supply personal vehicles. The environmental impact of electrolysis, in terms of CO_2 emissions, is zero, provided the electricity used is of renewable or nuclear provenance.

For higher-capacity production, high-temperature electrolysis is also being considered (this having the potential to be associated to high-temperature nuclear reactors). This technology allows water splitting to be effected with a better energy efficiency than with low-temperature electrolysis. Indeed, the higher the temperature, the lower the electric energy requirement to be met.

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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).

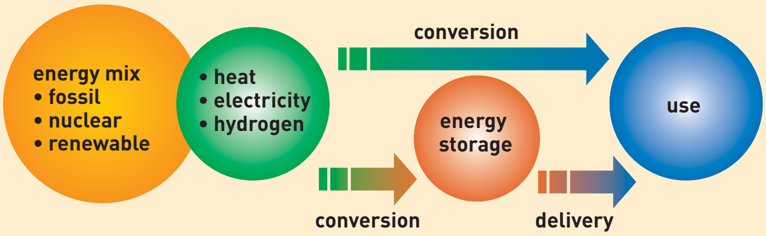


Figure 1.
The energy scheme.

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.

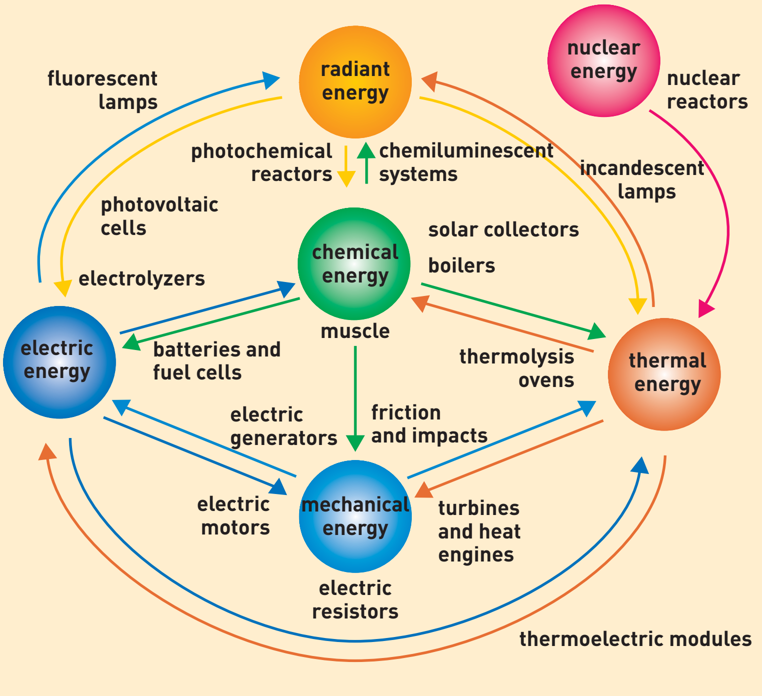
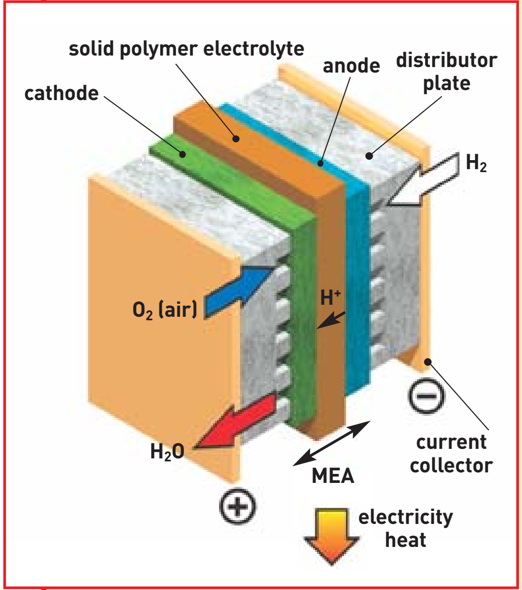


Figure 2.
Conversions of the six main forms of energy, with a few examples of energy converters.

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 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/cm^2. 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.

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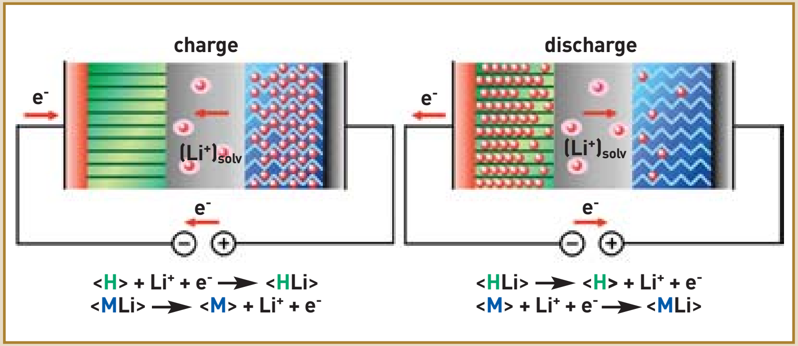
(1) One cycle includes one charge and one discharge.

Operating principle of a lithium storage battery



$$\langle H\rangle + Li^+ + e^- \longrightarrow \langle HLi\rangle \qquad \langle HLi\rangle \longrightarrow \langle H\rangle + Li^+ + e^-$$

$$\langle MLi\rangle \longrightarrow \langle M\rangle + Li^+ + e^- \qquad \langle M\rangle + Li^+ + e^- \longrightarrow \langle MLi\rangle$$

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.