Onboard storage of hydrogen

Three pathways are currently emerging for onboard hydrogen storage - this being one of the challenges set by use of hydrogen as an energy carrier: liquid storage at low temperature, gaseous storage under pressure, and solid storage. CEA is working particularly on the latter two, innovative paths.

C. Gardin/PSA Peugeot Citroën

High-pressure hydrogen tank rack of the prototype TaxiPac fuel-cell vehicle, based on a Peugeot Partner chassis, as shown in 2001.

Aside from manufacturing and cost issues, storage stands at the core of the three issues arising from **hydrogen** utilization on board a vehicle. Deployment of a distribution network will require, first of all, the emergence of a standardized storage method. Levels of safety, reliability and ease of use, for hydrogen-powered vehicles, will then have to prove equal to those for current internal-combustion engine vehicles. Finally, hydrogen storage, more fraught with difficulty and less efficient as it is, compared to storage of conventional **hydrocarbon fuels**, will ultimately have to enable travel ranges similar to those of current vehicles.
On the other hand, the techno-economic goals set for onboard hydrogen storage are essentially based on vehicular constraints (available space, weight allowed, desired costs…), rather than on the capabilities and limitations of the various technologies involved.

The three modes to be considered

At the present time, hydrogen storage modes on board a vehicle fall into three types to be considered. Storage in liquid form at 20 K (- 253 °C) at a pressure of 10 **bars** (1 MPa) allows useful volumetric and gravimetric densities to be achieved, however this requires tanks with extensive thermal insulation, to minimize evaporation.
Storage on substrates, in absorbed form, in particular on **metal hydrides**, exhibits very attractive volumetric density, but very low gravimetric density. Moreover, the kinetics, temperature and **cycling** pressure remain, along with other issues, among the difficult points yet to be mastered.
Storage in compressed form (currently at 350 bars, i.e. 35 MPa), finally, allows a satisfactory gravimetric density to be achieved, with **composite** tanks. Volumetric storage density remains poor: pressure of 700 bars (70 MPa) is an inescapable requisite, if this technology is to become competitive.

Demanding technical targets

The technical targets, as proposed by the United States Department of Energy (DOE) (see Table), are the same

for all potential storage paths (metal or **chemical hydrides**, liquid, compressed gaseous, carbon structures), however each path does have its specific features. According to DOE, gravimetric storage capacity should rise from 4.5% (i.e. 1.5 **kWh**/kg) in 2005 to 6% (2 kWh/kg) in 2010, on to 9% (3 kWh/kg) in 2015, entailing a gain by a factor close to 2. Volumetric storage capacity should be multiplied by a factor of about 2.25, taking into account the volume allowed for the tank. Reduction of system total cost, by a factor 3 (from $6/kWh to $2/kWh over the period 2005-15), takes on board series production - this probably not being sufficient, by itself, to achieve this target(see Figure 1). Allowable loss rate for tanks is set at 1 gram hydrogen per hour per kilogram stored (1 cm^3 gas at normal temperature and pressure per tank liter per hour) in 2005.

What is a tank?

Computations, for hydrogen, of gravimetric and volumetric storage capacities, as also of cost, depend on the definition given of a tank. Should this include, in the case of cryogenic storage, for instance, the heat exchanger? Are pressure relief devices and valves part of a pressure tank? What of the metallic container of metal hydrides? And so on. To allow evaluation and comparison of systems hailing from vastly different technologies, a common definition of hydrogen tanks was adopted, by analogy with gasoline tanks.
Obviously, taking in all of the peripherals required for filling, fastening, safety, etc., only leads to making the technical targets for onboard storage even more demanding. Indeed, manufacturers further call for a travel range of around 500 km, with reference to established expectations for internal-combustion engine vehicles.

Performances still requiring improvement

Bearing in mind hydrogen's heating value (see Why hydrogen? - Table), some 5 kg hydrogen must be stored to achieve such a range, depending on vehicle weight, motive power, and design. According to the timeline set out by DOE (see above), this results in the following specifications for future tanks: weight of 111 kg, overall volume of 139 liters, and refueling time of 10 minutes, for a cost of $1,000 (€830) by 2005. By 2015, weight must be reduced by half (55.6 kg), volume by a factor 2.25 (62 L), and refueling time by 4, for a total cost divided by 3.
In terms of storage capacities (complete systems), no technology currently meets the targets set by DOE for 2015.
While tank gravimetric and volumetric storage capacities require improvement, manufacturing costs require reductions by a factor in the bracket 3-10. However, it is advisable to include the cost of refueling, when comparing storage costs. Indeed, even though a cryogenic tank appears to be less expensive than a **high-pressure** tank, hydrogen liquefaction costs are probably higher

storage parameter	2005	2010	2015
usable specific energy (kWh/kg)	1.5	2	3
usable energy density (kWh/kg)	1.2	1.5	2.7
cost ($/kWh)	6	4	2
cycle life (cycles, 1/4 tank to full)	500	1,000	1,500
refueling rate (kg H_2/min)	0.5	1.5	2
loss of usable hydrogen (grams)	1	0.1	0.05
gravimetric capacity (specific energy)	1.5 kWh/kg 0.045 kg H_2/kg	2.0 kWh/kg 0.045 kg H_2/kg	3.0 kWh/kg 0.045 kg H_2/kg
system weight	111 kg	83 kg	55.6 kg
volumetric capacity (energy density)	1,2 kWh/L 0.036 kg H_2/L	1.5 kWh/L 0.045 kg H_2/L	2.7 kWh/L 0.081 kg H_2/L
system volume	139 l	111 l	62 l
storage system cost	6 $/kWh	4 $/kWh	2 $/kWh
system cost	1 000 $	666 $	333 $
refueling rate	0.5 kg H_2/min	1.5 kg H_2/min	2/0 kg H_2/min
refueling time	10 min	3.3 min	2.5 min

Table.
DOE technical targets for onboard hydrogen storage (top), and for tanks holding 5 kg hydrogen (bottom). (Source: United States Department of Energy, Hydrogen, Fuel Cells and Infrastructure Technologies [HFCIT] Program: Multi-Year Research, Development and Demonstration Plan, 3 June 2003.)

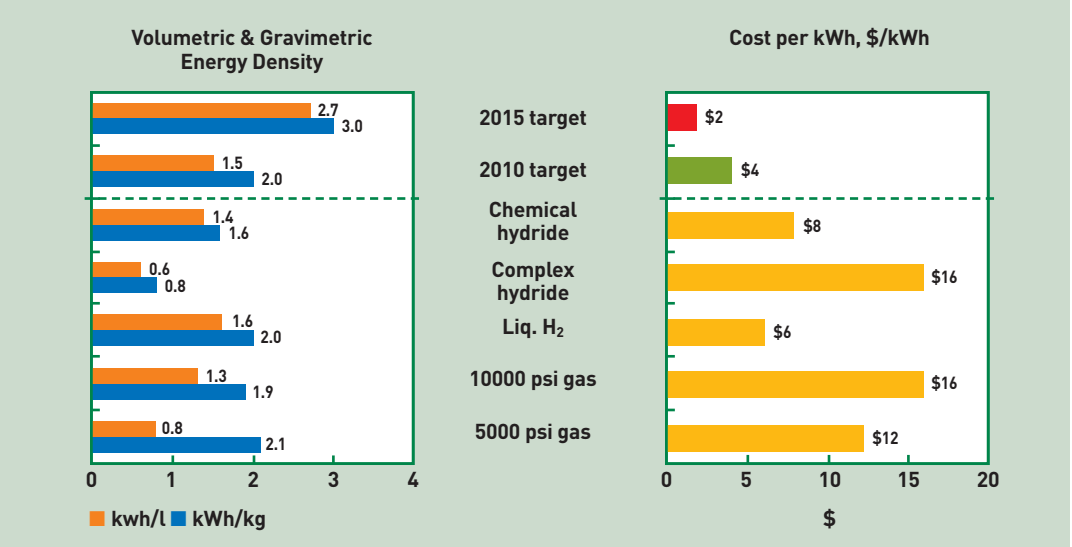


Figure 1.
Performance readings for the various types of hydrogen storage tanks, in terms of volumetric and gravimetric energy density (left), and cost per kilowatt-hour (right; €1 ≈ $1.2).
(Source: JoAnn Milliken [DOE] et al., "Hydrogen storage", US DOE HFCIT Program: 2004 Annual Program Review Proceedings, May 2004.)

All-polymer 3-liter tank developed under the aegis of the Physe Program.

Pressure storage

To improve the performance of high-pressure hydrogen storage, research workers are mainly focusing on two areas: enhanced-performance tank structural and inside-liner materials, and more economical fabrication.

High-pressure tanks are classified into four categories. "Type I" tanks are all-metal tanks, while "type II" tanks are metal tanks wrapped with filament windings (usually glass fiber) around the cylindrical part. "Type III" tanks are made of **composite** materials (initially fiberglass, and increasingly carbon fiber), with a metal liner (i.e. the inside facing, acting as H_2 barrier) - initially aluminum, lately in steel. "Type IV" tanks are composite tanks (mainly carbon fiber) with a **polymer** liner (mostly **thermoplastic** polymers, of the polyethylene or polyamide type).

Limitations of metal tanks

In the mid-1970s, investigations of steel embrittlement highlighted the limitations, in terms of life span, of employing metal tanks for the storage of **hydrogen**. Moreover, the excessive weight of type I and type II tanks precludes their being considered for onboard purposes. In line with practice in North America, French regulations have allowed, since the mid-1990s, the type approval and commercialization of non-metallic (very) high-pressure devices using composite materials. Such high-pressure tanks may vary as regards constituent materials, design type, and fabrication processes.
High-pressure (350-bar, then 700-bar) tank storage of hydrogen is unavoidable, if required energy densities (1.2 kWh/L in 2005) are to be achieved. However, while compression to 700 bars only uses 10% energy (5% to 350 bars), compression beyond 350 bars is less efficient (25% loss of storage capacity, compared with compression of a perfect gas). (1)

(1) Don Fraser (Dynetek Industries), "*Solutions for hydrogen storage and distribution*", The PEI Wind-Hydrogen Symposium, June 2003.

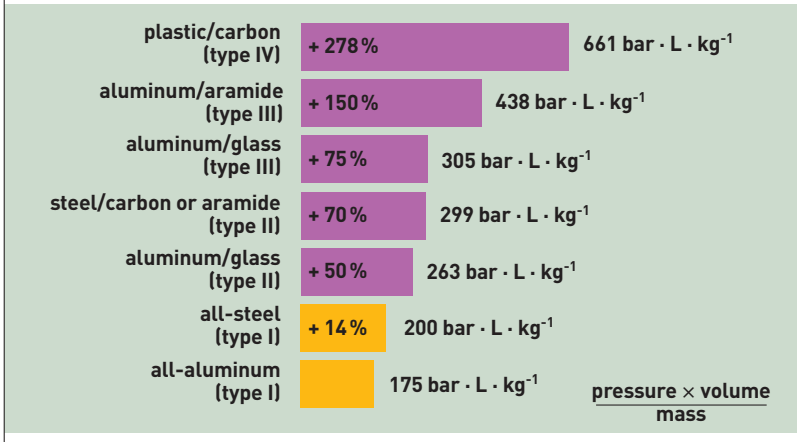


Figure 2.
Comparative analysis of the performance factor (pressure × volume/mass) of various tank types. (2)

Lightness of composite tanks

The prime advantage of composite (type III and type IV) tanks is their lightness. Comparison of mass per unit volume shows a composite tank exhibits mass lower by 25-75% than that of a steel tank having the same volume. (2) Likewise, a carbon-fiber tank fitted with a plastic liner enables a 4% mass gain, compared to a similar, aluminum-lined tank. Comparing the performance factor (the ratio of the product working pressure ´ volume, over mass) for various types of pressure tanks (see Figure 2) leads to the same finding: type III or IV composite tanks are the inescapable requisite for onboard storage of hydrogen, if the technical target demands are to be met.

The advantages of plastic-liner tanks

Type IV composite, plastic-liner tanks are lighter, cheaper, and exhibit longer life spans (no creep fatigue) than aluminum-lined tanks. Advances are sought mainly with respect to the composite material (pressure-resisting) and liner (H_2 barrier), two of the three essential components of type IV tanks, the third being the collars allowing tank coupling.

Composite optimization and *liner* improvement

The carbon fiber going into the outer composite material alone accounts for 40% of the price of a composite, plastic-lined tank. Optimization is thus required, of design dimensions (burst pressure should be equal to 2.35 times working pressure) as of the filament winding, to obviate excessive tank weight, but also, most crucially, to keep final cost from rising out of hand, especially at 700 bars.
The other key point is development of thermoplastics that are effective as hydrogen barriers, to ensure maximum loss rate of 1 cm^3/L/h for the tank, and exhibiting good mechanical strength, at temperatures ranging from - 40 °C to + 85 °C. Further, fabrication technologies for such technical polymers should enable liners to be obtained for a broad range of volumes (1-150 liters) and thicknesses (1-10 mm), of uniform, consistent quality, exhibiting no residual stress, ensuring good interfacing with collars, and at low cost.

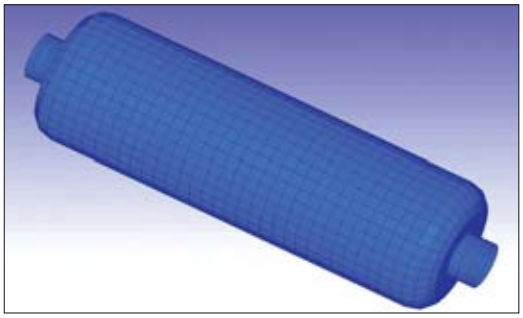
CEA's type IV tank roadmap

CEA initiated development of type IV tanks in 1998. The French Physe Program, endorsed by the **PACo Network** and funded by the French Ministry charged with industry, was launched in 2000, its goal being development of a 3-liter, 300-bar tank for small, portable electrical equipment applications. First-genera-

(2) Patricia Krawczak (École des mines, Douai, France), "*Réservoirs haute pression en composites*", Techniques de l'ingénieur, 2002.

tion liners developed for these prototypes were three-layer, EVOH- (ethylene-vinyl alcohol copolymer) based polymers, which are subject to patents. (3)
As part of the CEA-Air liquide collaboration, the French Polystock Program, also endorsed by the PACo Network and funded by the French Ministry in charge of industry, was launched at the end of 2002, its goal being development of a 22-liter, 350-bar tank for transportation applications. The second-generation liners are specific polyamides, under CEA and Air liquide patent, (4) for which the fabrication process is ten times faster than the present process.
The European StorHy Program (coming under the 6th Framework Program), initiated in March 2004 and bringing together nearly 40 partners, aims, among other goals, to develop pressure (type III and type IV), **cryogenic** or **metal-hydride** tanks for automotive applications. In the "Pressure Vessel" Subproject, CEA is charged with development of type IV, rotomolded-liner tanks of 48- and 150-liter capacity at 700 bars.
Several CEA centers are involved in this tank-related R&D effort. The CESTA (Centre d'études scientifiques et techniques d'Aquitaine: Aquitaine Scientific and Technological Research Center) and Le Ripault (Indre-et-Loir *département*) CEA centers are working on the design of the tanks and epoxy-resin impregnated carbon-fiber windings to achieve final performance optimization (weight, cost, and burst resistance). The Le Ripault Center is also developing the new technical thermoplastics, and new rotomolding processes for liner forming, in its plastics manufacturing, polymers and composites unit, while barrier performance of the technical thermoplastics is evaluated at the Grenoble and Valduc (Côte-d'Or *département*) centers.
Transfer to industrial production of the new generations of liners is leading to fabrication of complete prototype tanks, intended for numerous validation tests at CESTA (drop, fire, crash, gunfire penetration…), at Valduc (gas loss, hydrogen cycling), or at the facilities of various partners.
In all of these developments, CEA is working in collaboration with many partners, both academic or at engineering schools (ENSAM in Paris, ENSMA in Poitiers, INSA Lyons, Claude-Bernard University in Lyons, ICAM in Nantes…) and in industry (Air liquide, Ullit, Metroplast, Composites Aquitaine…), as well as all its European partners in the StorHy Program.

(3) CEA patents FR/00.11072 and FR/00.11073 of 30 August 2000.
(4) CEA-Air liquide patent FR/04.51104 of 3 June 2004.



CEA

Finite-element modeling of a 22-liter flask developed for the Polystock Program (a photograph appears on the cover).

A. Gonin/CEA

Facility, installed at CEA's Le Ripault Center (Indre-et-Loire département), for the rotomolding of plastic liners for hydrogen-storage tanks. The mold rotates over 3 dimensions, inside an oven at 350 °C.

> Philippe Mazabraud
Military Applications Division
CEA Le Ripault Center

Hydrides

Solid storage of hydrogen refers as a rule to absorption or adsorption of hydrogen by a material. Some compounds, better known as hydrides, have the ability to absorb hydrogen in reversible fashion. There are further carbon materials exhibiting a capability for adsorption, i.e. to effect surface retention, of hydrogen. Technological breakthroughs are anticipated in this area.

The name **hydride** covers a wide variety of materials, which may be described as compounds featuring metal-**hydrogen** bonds. Hydrides may be divided into three groups, according to the nature of the metal-hydrogen bond: **ionic**, **covalent**, or **metallic**. The kind of bond depends on the host element's position in the periodic table. **Alkali** and **alkaline earth** metals yield hydrides featuring ion bonds exhibiting strong electrical polarity, contributing to making such compounds dense, and very stable. Metals on the right of group VIII form hydrides featuring covalent bonds, thus exhibiting low electrical **polarity**, poor stability and low density. Metals such as magnesium may yield hydrides featuring two type of bond: covalent and ionic. **Transition metals** yield hydrides featuring metallic bonds. These hydrides have been the object of many investigations with reference to hydrogen storage, as they are the only ones to act in reversible fashion.
Hydriding and dehydriding, for most metals, take place in accordance with a direct reaction of the metal with hydrogen: $M + x/2\ H_2 \rightarrow MH_x$.

Low pressures and compactness

Storage in the hydride form offers two main benefits: safety, since the pressures involved can be low (often

less than atmospheric pressure), and compactness, since metal hydrides exhibit high volumetric **absorption** capacities. For instance, 100 g palladium (i.e. 8.3 cm^3) allow storage of a quantity of hydrogen equivalent to the content of a 7-L tank holding hydrogen at atmospheric pressure. The main disadvantage of this type of storage medium is the low gravimetric absorption capacity exhibited by most hydrides. This, as a rule, has a value in the 0.5-2% bracket, well down on the 6% required for automotive applications. Moreover, the cost of hydrides is often prohibitive: over €20/kg. Two types of material currently look promising, in view of their characteristics (reversible absorption capacity, equilibrium pressure, sensitivity to impurities, and absorption/**desorption** kinetics; see Table): magnesium-based compounds (7% gravimetric capacity), and alanates (up to 5% gravimetric capacity).

Three promising families

Much research work is currently ongoing, to improve hydride absorption capacities and absorption/desorption kinetics, with a view to using such hydrides for buffer storage, for **fuel-cell** hydrogen supply. Research is currently being directed to three families of hydrides: certain AB alloy hydrides, magnesium-based materials, and alanates.

The hydrides of AB5 ($LaNi_5$), AB_2 ($ZrMn_2$), AB (TiFe) alloys are the best known among all hydride families. (1) However, recent research on TiFe, AB_2 and AB_5 alloys does not permit any technological breakthrough to be foreseen, that might lead to any notable improvement in their performance. Absorption capacities, for these alloys, remain limited (< 2% gravimetric capacity).

Magnesium (in doped form) or magnesium-based alloys exhibit high absorption capacities (≥5% gravimetric capacity). Charging and desorption kinetics are very rapid, owing to recent discoveries. The main issue with this type of compound remains the excessively high hydrogen-desorption temperature. Moreover, investigation of these alloys has only got underway fairly recently. Kinetic and thermodynamic properties for larger bulks are as yet unknown. Finally, their utilization entails demanding constraints: scrupulously inerted glove boxes throughout fabrication, since these materials are pyrophoric. (2) A technological breakthrough may be achieved fairly quickly, since many investigations are presently addressing the behavior of such hydrides, when used in large amounts.

Metal hydrides (excluding transition metals) form the third family arousing interest. The most interesting compounds, in this respect, are alanates (e.g.: $NaAlH_4$), which have been subjected to investigation for some five years. These compounds exhibit a gravimetric capacity of about 5%. Hydrogen-desorption temperature remains high, and rehydriding still requires high pressure and temperature conditions. Further, just as for magnesium, absorption/desorption kinetics for these compounds is as yet unknown, when they are used in large amounts. Finally, handling of such materials is quite tricky, owing to their pyrophoric character. Despite such disadvantages, these hydrides appear promising, insofar as research work is only beginning.

Coming demonstrators

The various hydride families exhibit diverse characteristics. The hydride can thus be selected according to the application: stationary, or mobile. Storage in the hydride form thus provides high modularity, and may be used, in the short term, for stationary applications (lanthanum-nickel hydrides…), or mobile applications, in the longer term (magnesium hydride and alanates). Programs designed for the testing of demonstrators holding 10 kg of hydride are currently under way at CEA. These will be used subsequently, being connected to a fuel cell, to supply power to a research center. Utilization of hydrides as a storage medium thus yields a good safety level and high modularity, particularly for stationary applications.

> Isabelle Moysan
Military Applications Division
CEA Valduc Center

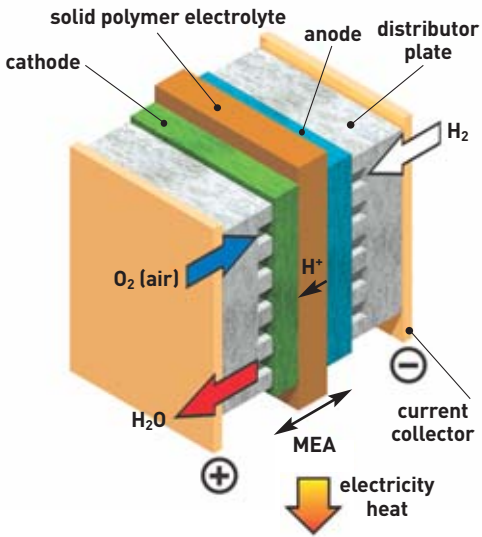
(1) Where A stands for a **rare earth** or a **transition metal**, and B for a transition metal.

(2) Pyrophoric: combusting spontaneously when coming into contact with air.

family property	lanthanum-nickel hydride	zirconium-manganese hydride	titanium-iron hydride	magnesium hydride Mg + c + v (5%at) by mechanical synthesis at 300 °C under 4 bars H_2	alanates ($NaAlH_4$)
reversible capacity	1.28%	0.9%	1.5%	7%	4-5%
desorption pressure at 25 °C	1.8 bar	0.001 bar	4.1 bars		desorption at 220 °C
temperature for 1 bar	12 °C	167 °C	- 8 °C	300 °C for 0.15 bar	
activation	easy	moderate	difficult	easy	hydrogenation at 150 °C under 170 bars
impurities	not very sensitive up to 500 ppm	fairly sensitive	sensitive	sensitive	sensitive
synthesis	fairly easy	difficult	difficult	difficult	difficult
kinetics	rapid	rapid	average	rapid	slow

Table.
Main characteristics of various hydride families.

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.

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