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HIGH-CAPACITY HYDROGEN-BASED GREEN-ENERGY STORAGE SOLUTIONS FOR THE GRID BALANCING

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Abstract

One of the current main challenges in green-power storage and smart grids is the lack of effective solutions for accommodating the unbalance between renewable energy sources, that offer intermittent electricity supply, and a variable electricity demand. Energy management systems have to be foreseen for the near future, while they still represent a major challenge. Integrating intermittent renewable energy sources, by safe and cost-effective energy storage systems based on solid state hydrogen is today achievable thanks to recently some technology breakthroughs. Optimized solid storage method made of magnesium-based hydrides guarantees a very rapid absorption and desorption kinetics. Coupled with electrolyzer technology, high-capacity storage of green-hydrogen is therefore practicable. Besides these aspects, magnesium has been emerging as environmentally friend energy storage method to sustain integration, monitoring and control of large quantity of GWh from high capacity renewable generation in the EU.

Introduction

Renewable Energy Sources (RES), such as Wind and Solar Energy, biomass, and hydropower have been relatively highly costly, but advances over the past few decades have made some renewable resources much more price-competitive. While the Organisation for Economic Co-operation and Development (OECD) countries' global primary energy demand is expected to show only a slightly grow with respect to other countries worldwide (with an overall 36% increase by 2035), their demand for RES will show a relatively large increase, thus calling for appropriate solutions with a systematic approach.

The problems of climate change, air pollution and energy insecurity requires a large scale conversion to clean, perpetual, and reliable energy at low cost together with an increase in energy efficiency. That is why, for the next future, RES will enter more and more the current mainstream, also consistently with EU strategic policies and initiatives in the energy segment (such as the European Electricity Grid Initiative (EEGI), the European Strategic Energy Technology (SET) Plan, etc.).

To this purpose the European Strategic Energy Technology (SET) Plan has identified fuel cells and hydrogen among the technologies needed for Europe to achieve the targets for 2020 as well as to achieve the long-term vision for 2050 towards decarbonisation.

A possible scheme for the future evolution of the energy distribution usually refers to the so-called SMART GRID that consists widely in the intelligent (i.e. dual side communication) integration of systems for distributed generation, centralized renewable power generation, non-renewable but cleaner centralized power generation for RES peaks stabilizing and information from the users' side to efficiently manage - in real-time - electricity peripheral flows in order to avoid mismatching between demand side (users) and supply side (power production). All these features seek to build IT framework to overcome constraints due to "passive" architecture of current grid. Peaks loads efficient management is crucial for give chance to further increase for share of power generation via-renewable sources.

One other important issue the International Energy Agency (IEA) identified as key is energy storage.

Energy storage is considered one of the promising means both to feed the grid by RES and also to balance the grid energy flow according to the demand needs. It is also clear that advanced storage solutions, of course coupled with other infrastructures and technology initiatives (such as the ones above mentioned on Smart Grids) can power off-grid utilities, such as a green mobility system with electric vehicles, that are powered by stored electricity once the grid can feed exclusively the requested demand.

Energy storage is therefore one of the most promising solution to support the development and usage of RES, as well as introduce other benefits as it enables:

- to capture surplus renewable energy, that cannot be utilized by the grid due to low load demand or transmission constraints;
- to provide supplementary or backup power in correspondence of RES reduction or absence;
- to effectively alleviate power quality issues (e.g. interferences arising from the connection of wind turbines to the grid), thus improving the electrical quality of the RES power output.

Existing technologies for energy storage

Electricity storage systems can be categorized as mechanical, electromagnetic and electrochemical storage devices. Various technologies are at varying stages of technological maturity and they usually are exploited by their storage capacity (stored energy per mass or volume), or energy density, power (energy output per time), storage period (how long the energy should be stored) and size. Many of these key parameters actually can vary over a huge scale: from latent heat storage to prevent laptops from getting too hot (stored energy in the range of a few Wh) to the heat and cold thermal underground storage system underneath the German Reichstag in Berlin (stored energy in the range of some GWh).

Generally, energy density, power and energy ratings are essential criteria for any surveying process and synthetic selection maps have been developed to support selection. In Figure 1, currently electricity storage technologies are mapped over power and energy dimensioning basic features.

Together with above energy storage solutions today available, the "hydrogen battery" method is based on hydrogen energy storage (HES) route that consists in storing electricity into form of hydrogen (a high density energy carrier) produced by no-emission water electrolysis process powered by excess of electricity from RES. In Table I, some basic features of storage technologies are reported, as alternative solutions to HES systems.

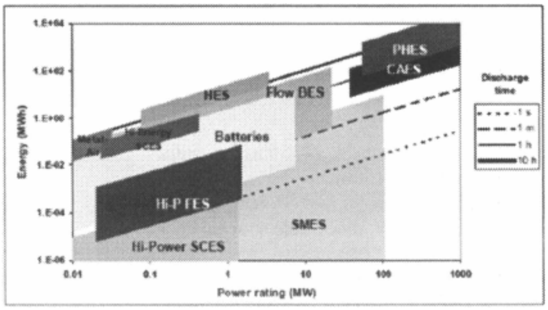

Figure 1 - Map of current available electricity storage technologies on energy vs. power comparison diagram (Source: Gonzales, 2004).

Table I – Main features, principles and drawbacks of the storage methods mapped in Figure 1.9, with the exception of HES.

Technologies	Main features, advantages and drawbacks
Compressed air energy storage (CAES)	Utilizes off-peak electricity to compress air that is then stored in an airtight reservoir (typically an underground geological formation such as a salt or limestone cavern) thus releasing it from the reservoir to run it through a gas-fired combustion turbine. Main advantage of this method is a high efficiency around 70% (Robyns, 2005), technology maturity and high power and energy capacity[1], but low energy density, in the order of 12 kWh/m³ (Multon, 2003).
Pumped hydro energy storage (PHES)	Utilizes off-peak electricity to pump water from a lower reservoir into a higher reservoir then producing electricity by releasing the potential energy stored in elevated water through turbines (in the same manner as conventional hydro facilities). As CAES, PHES have a high conversion efficiency of about 65–80% (Multon, 2003), meanwhile, as for the large energy storage capacity of CAES, the main shortcoming of this technology is the need for a site with different water elevations.
Flywheel energy storage (FES)	Store kinetic energy in a rotating mass with minimized friction losses to improve efficiency. They have a great cycling capacity (a few 10,000 to a few 100,000 cycles) . While the instantaneous efficiency is around of 85%, the main drawback is an overall efficiency that would drop to 78% by progressively release of kinetic energy to after 5 h, and 45% after one day. For a long-term storage, this type of apparatus is therefore not foreseeable.
Batteries	Conventional chemical storage achieved through accumulators (lead–acid, nickel–cadmium, etc.) are high energy densities (up to 150 and 2000Wh/kg for lithium), while they have relatively low durability for large-amplitude cycling (a few 100 to a few 1000 cycles).
Flow batteries (Flow BES)	A two-electrolyte system in which the chemical compounds used for energy storage are in liquid state, in solution with the electrolyte. They have a relative high efficiency about 75% (Couffin, 2004–2005) and want to overcome the limitations of standard battery system in which the electrochemical reactions create solid compounds that are stored directly on the electrodes on which they form. They are at development stage; in 2003 Regenesys Technologies (UK) developed a system with a storage capacity of 15MW /120MWh.
Superconducting magnetic energy storage (SMES)	Stores energy in the magnetic field created by the flow of direct current in a coil of cryogenically cooled, superconducting material. Great instantaneous efficiency, near 95% (Anzano 1989) and a fast response time (under 100 ms). Major shortcomings represented by the refrigeration system and necessity for massive storage (5000–10,000MWh) of very large coils (several 100m in diameter) to generate enormous electromagnetic forces. Underground installation is foresee to limit infrastructure costs.
Super-Capacitors Energy Storage (SCES)	Store energy in the form of an electric field between two electrodes. Generally very durable (8–10 years), with very high efficiency around 95%, drawbacks are represented by a very high self-discharge around 5% per day and the low energy density 3–5 W·h/kg, against 30-40 W·h/kg for a lead acid battery.

Water electrolysis provide water decomposition when a direct current is passed between two electrodes immersed in water separated by a non-electrical conducting aqueous or solid electrolyte to transport ions and completing the circuit. Ideally, 39 kWh of electricity and 8.9 liters of water are required to produce 1 kg of hydrogen at 25 °C and 1 atmosphere pressure.

The energy efficiency of commercial water electrolyzer widely ranges from 50 to 70%, and it strongly depends also on how much system is efficient as external current density that feeds cell stack varies due to the variability and intermittency of RES power production.

As efficiency of the hydrogen generation system is one major drawback if compared with conventional battery, a very important key-point is that water electrolysis systems are cleaner in energy generation, modular as they can be easily grouped to produce hydrogen over wide scales ranging from few kilowatts to hundreds of megawatts and furthermore today commercial electrolyzers are capable of quick response to fluctuant electricity that is typically produced by intermittent and fluctuant wind turbines.

Regarding with modularity capabilities, power scale can be thought as unlimited, as a capillary distribution of these systems connected to the grid can build an infinite power capacity (Figure 2).

Storage System	Typical Output Rating (Megawatt)	Typical Storage Rating (Megawatt hours)	Physical Linkage Reqd.
Pumped Hydro	100	500- 10000	Yes
CAES	25	200	No
Battery	10	100	Yes
Hydrogen	10	Unlimited	No

Figure 2 – Summary of power and energy storage rating of HES compared with great capacity alternative energy storage technology (Price, 2000).

Behavior of water electrolyzer based HES in presence of high intermittent power source

Experiences have been performed by 2004 to provide information about potential operation of alkaline commercial water electrolyzer HySTAT® by Hydrogenics under emulated intermittent conditions generated from actual wind speed data [1]. In this test research a period of 14 h of a typical day with good wind conditions in the Sierra del Perdon's wind farm (Navarra region, Spain) was selected.

The evolution with time of the wind speed during this period and the electric power output expected the specific wind turbine used according to its power curve are reported in the Figure 2.

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[1] The first storage station using an underground compressed air reservoir has been in operation since November 1978 in Huntorf, near Bremen, Germany, while a larger installation has been set set in 1991 in MacIntosh, Alabama, (http://www.caes.net/mcintosh.html) began to deliver 100MW of power for 226 h, compressing ambient air and storing it at a pressure between 40 and 70 bars in a 2,555,000-m3 cavern, 700m deep in the ground.

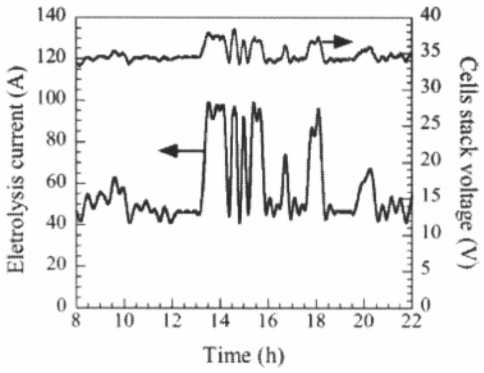

Figure 2- Evolution with time of the electrolysis current in a Hydrogenic HySTAT: total voltage established in the electrolyzer cell stack as a result of the passage of the electrolysis current (source: [1]).

The fast response of the stack voltage shown in Figure 2 demonstrated that electrolysis cell stack voltage readily matches a highly varying electric current-time profile, suggesting an essentially ohmic behavior governed by the internal resistances associated to the electrolyte and cells components. During test campaign electrolyzer worked reliably and at high efficiency, as it ranged 74-83% basing on the stack voltage. The hydrogen produced was at high purity as oxygen contents was always below 0.2 vol %.

The hydrogen produced by electrolyzer can be therefore stored to be released and used "on-demand" by various (also combined) user systems:

- an advanced modified turbine for power generation, advanced hydrogen fuelled turbines for power generation;
- a fuel cell stack to produce directly green-electricity, that functions in a "reverse mode" of the water electrolyzer, thus recombining hydrogen with oxygen to produce electricity and waste heat and pure water;
- as a green-fuel for either Fuel Cell vehicles or modified internal combustion engine vehicles;
- introducing this green-hydrogen by hydrogen merchants, thus providing an alternative to conventional hydrogen, normally produced by Steam Methane Reforming, SMR, at high carbon footprint.

Electricity storage technologies for the RES integrating purposes

Conventional network operation of distribution network, at least in some regions of Europe, is actually based on a "fit and forget" approach. This means that verifications are performed during the connection phase and the connection schemas adopted ensures any reasonable behavior of network users is allowed.

From a technical point of view, however, it would be possible to increase the amount of distributed generation points connected to the grid where RES plants could contribute to voltage regulation and to provide ancillary services.

An appropriately sized storage device would reduce uncertainties in the capability of the system of self-regulating, thus allowing a further increase of RES units connectable to the grid. As stated, the various storage technologies have a number of features, such as efficiency, size, dynamic behavior, etc. which are all relevant in the selection of the most suitable system for a particular application or set of applications.

Hydrogen-based energy storage systems deploy the highest energy density; thanks to high modularity, they are of unlimited storage capacity, but, conversely, when the storage pathway is completed by a fuel cell system for the back conversion of the electricity the round-trip efficiency[2] of the system is low (around 30%).

On the other hand, thanking to varying deploying architectures today possible to develop, these energy storage systems could be really promising in near-term.

Economic viability of large storage system has to be evaluated taking into account these major requirements:

- working in combination with RES, especially fluctuant RES
- serving for secure balancing of the grid
- reducing curtailing and allowing progressive and potentially unlimited installation of RES.

Accordingly, the optimal choice should be driven mainly by these following important driving key-factors:

- The charge and discharge response to fluctuant electricity;
- The capital cost of the facility, including those ones of the RES plant (charging equipment, storage equipment, and discharge equipment);
- The O&M costs for the facility, including those ones of the RES plant;
- The transmission power costs;
- The power and energy rate;
- The power quality;
- Safety and security for the grid;
- The round-trip system efficiency;
- Reversibility of charge/discharge cycle;
- Modularity and easiness of upscale;
- The dispatchability;
- The flexibility and adaptability to future trends in the electric sector;
- Environmental sustainability and safe operation
- Possible synergies

At present time, very few storage systems can solve power peaks curtailment over a longer term (10-12 hours) of functioning.

Magnesium as key-solution for safe and viable hydrogen solid storage for saving power curtailing

Both commercial water electrolyzers and fuel cell stacks have the major advantages of an instantaneous response: a) any electricity variability that flows into the water electrolyzer is used for producing hydrogen; b) any request of electricity by downstream users (i.e. demand) is matched by flowing variable hydrogen flux into the fuel cell stack.

On the other hand the major drawbacks of the supply-chain water electrolyzer→hydrogen storage→fuel cell stack is represented by:

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[2] Round-trip efficiency is calculated throughout the first electricity conversion in hydrogen and the downstream back-conversion into electricity of hydrogen by use of fuel cell system.

- lost energy used during the storage phase, as hydrogen can be usually stored either as pressurized gas or liquefied cryogenically cooled to achieve adequate energy density;
- the low-efficiency of the fuel cell, that obviously affects the overall round-trip efficiency of the system: 70% for electrolyzer efficiency and not more than 50% for the fuel cell result generally in low round-trip efficiency of 35%.

On the other hand, one major advantage of using hydrogen is its high energy content, namely 39.4 kWh per kg of hydrogen[3]. But the actual energy density strongly depends on the storage methods used. Viability of the hydrogen storage systems are strictly related to the real capability of deploying a not expensive long-term safe storage of hydrogen.

The hydrogen produced can be stored in various forms: liquid (by cryogenic process, liquid hydrogen can be stored in tanks at 21.2 K at ambient pressure), compressed gas (high pressure gas cylinders usually operate at a maximum pressure of 20 MPa) or via solid–state methods. In any case the major objective of industrial hydrogen storage methods is reaching the highest volumetric density with full reversibility of hydrogen uptake and release. At ambient temperature and atmospheric pressure, 1 kg (equivalent to nominal 39 kWh) of the gas has a volume of 11 m^3. To increase hydrogen density in conventional storage methods it is necessary to spend energy either for compressing gas or lowering temperature for liquefying. With an un-conventional solid-state method, energy must be used to contrast repulsion deriving from the interaction of hydrogen with another material.

Generally speaking a solid-state hydrogen storage (HSS) method is intrinsically safe (no pressurized reactive hydrogen gas is present) and a long-term storage, since no boil-off problems can occur.

HSS into metals physically consists of diffusion of hydrogen into metal (absorption phase) that is finally bonded with host material forming stable metal hydrides. Therefore, hydrogen storage capability of metals is strongly influenced by the way this two-phase process develops. Hydrogen atoms[4] penetrate and diffuse into metal by preferential routes: they flow throughout grain boundaries, i.e. preferential pathways due to higher concentration of vacations. The host metal initially dissolves some hydrogen as a solid phase. As the hydrogen pressure together with the concentration of hydrogen in the metal is increased, interactions between hydrogen atoms become locally important, and nucleation and growth of the hydride phase can start. Therefore the "storing" phase develops by the formation of intermetallic compounds (interstitial hydrides, or complex metal hydrides) at any sites (interstitial sites present in crystal lattice host) available for hydrogen locating and bonding to metal element.

Further constraints that work against absorption phase are: a) the presence of oxide layers that spontaneously formed in air on metals and, b) such a "barrier effect" that impedes hydrogen atoms to more deeply penetrate inside bulk because top layers saturate. These represents actually physical (oxide layers) and chemical (saturated layers) barriers that can prevent a fully hydrogen absorption inside bulk material; these barriers are generally responsible of lower sorption kinetics and practical absorption rate (weight percentage of hydrogen absorbed into host metal) far from theoretical values.

Among metals that are more attractive for hydrogen storage, magnesium is considered a key material since that it is the eighth most frequent element on the earth, it has a good reversible storage capacity, achieving theoretically the 7.6 wt.%, it is relatively inexpensive and it has very low density. On the other hand, Mg major drawback is its high desorption temperature of over 300 °C; the high stability of magnesium-hydrogen bond is the reason of such a high enthalpy of hydride formation that is responsible of high desorption temperatures and efficient heat management systems. During the absorption phase magnesium hydrides form with heat release, while the desorption phase host material needs to be heated up for the hydrogen realease. An efficient heat management systems is therefore required for industrial systems.

One possible route to produce Mg hydride reactions with lowered reaction enthalpy (i.e. low temperatures for uptake and release phases) is to add elements which exhibit lower enthalpies of formation. Mg_2Ni is an example of this class of materials, as the enthalpies of formation for the ternary hydride Mg_2NiH_4 and the Mg_2Ni is of the order of -67 $kJmol^{-1}$ per H_2, therefore lower than the -78 $kJmol^{-1}$ per H_2 that is enthalpy for the MgH_2 formation. Unfortunately this route reduces drastically the storage capacity and increases the density of the modified Mg-based material.

In last two decades further breakthroughs in hydrogen sorption kinetics have been achieved by pre-treating magnesium by high-energy ball milling operations (Schulz, 1995; Zaluska 1999). Ball milling applies severe plastic deformation to material for a high refining microstructure (i.e. dramatic increase of grain boundaries) that finally becomes more reactive to hydrogen diffusion.

During the last decade advancements in kinetics sorption of hydrogen in magnesium-based host materials have been done by selection of additives and nano-structuring techniques for increasing grain boundary density [2-10].

Exploiting economically viable solid-state hydrogen by magnesium-based storing solutions is possible if hydrogen kinetics sorption is rapid, the storage capacity can reach the theoretical value of 7.6 wt.% of hydrogen (corresponding at around 400 kWh/m^3) and heavy and expensive additives are limited.

A major breakthrough in magnesium storage is represented by proprietary patented manufacturing process of nanostructured magnesium-based material for hydrogen storage created by Mc Phy Energy (Mc Phy), a French company based in Grenoble. Cheaper magnesium-based nanostructured materials produced by Mc Phy are capable of hydrogen kinetics absorption that are industrially exploitable. The modularity concept exploited by Mc Phy is schematically represented in the Figure 4.

Basing on solid-state technology, the Mc Phy solution does not require hydrogen from the water electrolyzer unit to be compressed, as the pressure for starting hydrogen absorption is of the same level of the hydrogen pressure at the electrolyzer outlet. And pressure of hydrogen desorbed by the tank is similar to the level (around 2 bars) required for fuel cell stack, a costly and energy dissipative compressor is therefore eliminated. These solid storage system are highly efficient, since about 3-5% are the losses in absorption-desorption cycles due to that part of energy used to heat-up tank material for achieving desorption. Storage modules require less energy than liquid or compressed hydrogen

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[3] Energy content of 1 kg hydrogen (equivalent to 141.9 MJ) at Higher Heating Value (HHV).

[4] Molecular hydrogen is dissociated at the surface before absorption; two H atoms recombine to H_2 in the desorption process.

technologies, which generally use up to 33% of the hydrogen energy content for storage phase.

These storing systems are produced in modular sub-units that can be installed and grouped in parallel to increase system capacity. As hydrogen is stored in solid state, storage modules are furthermore safe to be transported as any non-hazardous goods.
Raw materials used in manufacturing do not generate any hazardous waste at the end of their life cycle, and they are fully recyclable.

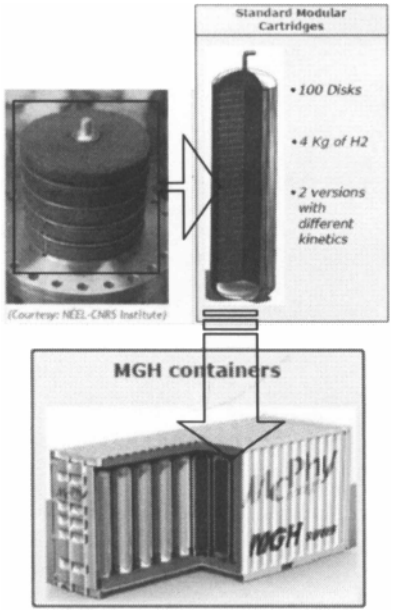


Figure 4 – Modularity concept realized by Mc Phy technology (courtesy of: Mc Phy Energy SA).

Dynamic behavior of the WE coupled with Hydrogen Solid Storage system

HSS needs to be optimally coupled with the WE, the upstream unit to assure high dynamic storage capability in transient and dynamic phase. This fact implies that HSS has to be capable to accept (absorb) in real time hydrogen at any rate that is produced by water electrolyzer that can function at varying conditions depending on external fluctuant electricity produced by RES.
For that, dynamic behavior of the HSS module has been extensively tested coupled with WE module that had to respond to an intermittent power source.
At CEA (Commissariat à l'Energie Atomique et aux énergies alternatives) facilities in Grenoble, a complete test campaign has been performed on a fully instrumented system constituted by a Mc Phy solid-state hydrogen storage tank, upstream coupled with a water electrolyzer and downstream connected to a fuel cell (figure 5). Extensive test campaign have done in order to analyze and optimize response of the system when connected with varying and fluctuant renewable source. Specifically the WE was directly linked to solar panel source emulator. Storage capability (i.e. sizing capacity for absorbing variable quantity of hydrogen) has been pointed out (figure 6).

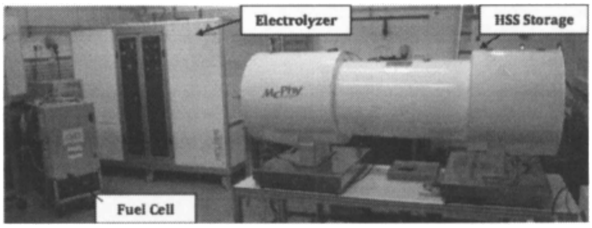
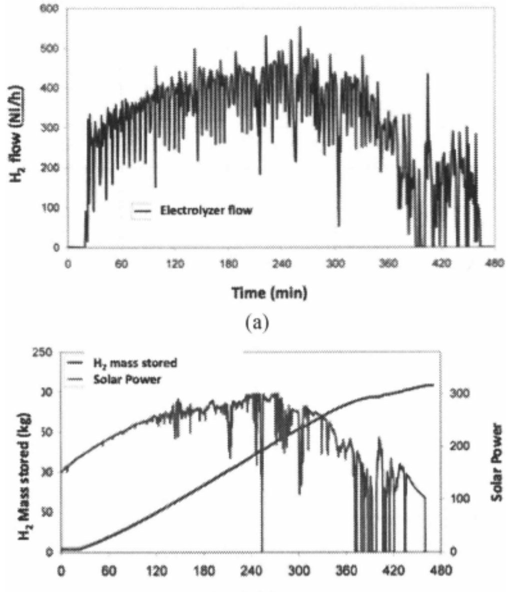


Figure 5- Test bench facility set at CEA premises.

A load power profile had been modeled in order to feed electrolyzer simulating electricity production of a common solar farm over 8 hours of functioning, sunny in the morning and cloudy in the afternoon. A total 200 grams of hydrogen have been produced by the electrolyzer and constantly absorbed by McPhy tank in 8 hours.



(a)

(b)

Figure 6 – Dynamic behavior diagrams showing: a) hydrogen flow produced by water electrolyzer fed by electricity produced by solar panels; b) hydrogen produced and stored in HSS module .

test results, water electrolyzer shown fully capability of accepting power variations from RES. Most important conclusions from test campaign were: a) electricity variations from power source feeding electrolyzer had no effects on hydrogen production; b) HSS module was well dimensioned to absorb all the hydrogen produced by water electrolyzer and it serves water electrolyzer unit in a fully stable mode.

Conclusions

Hydrogen storage via solid state (hydrides) is becoming a new challenge for magnesium based materials. Modular products commercially available are capable of sorption kinetics suitable to be coupled with up to date water electrolyzer technology.

Advancements have been done in the water electrolyzer technology specifically related to efficiency of such systems when they work at varying operating conditions, as high variable current density that is typical of intermittent and fluctuant wind sources. Behind this improvements, energy storage can be realized by new generation of hydrogen storage systems. New advancements in magnesium-based materials for hydrogen storage is leading to rapid improvements for high capacity "hydrogen batteries". Novel hydrogen solid storage modular units are suitable to be coupled with rapid and efficient electrolyzers to serve highly intermittent RES.

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