Solar Power Storage using Hydrogen: an e-lab experiment

Solar-Hydrogen conversion unit and Pulsed Electrolysis Experiment

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Abstract: The work in this thesis aims to automate an experimental setup which simulates the acquisition of solar power, converts it into hydrogen and later usage of the hydrogen to generate electric power. The generation and conversion of the Hydrogen was done using proton exchange membrane (PEM) cells. The automation of the setup was done through control and data acquisition of C routines, which were implemented using microcontrollers.

Some parallel testing was done regarding hydrogen generation through PEM water electrolysis, when a pulsed DC regime was applied. The frequency, power and the shape of the signal applied were varied. In none of the tests has the electrolyser's efficiency been higher than that at constant DC conditions.

I. INTRODUCTION

The ability to store electric energy is one of the most important aspects in electricity markets.
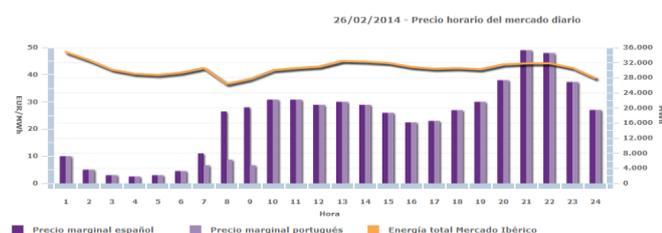

Figure 1 Energy pricing in the Iberian market [1]

The plot in Fig. 1 shows the energy price for Portugal and Spain during the same day. The most noticeable occurrence in the energy market is the great difference between the off-peak hours (02:00 – 06:00) and the remaining, which peak at around the 22nd hour.

In this difference lies the opportunity for energy storage. By using a buffer able to transport the less valuable energy of certain hours and sell it at a higher price, the power supply better fits the demand and should overtime provide profit.

Various energy storage methods exist. The main methods can be divided by their capacity:

- Large-scale energy storage (GW): reversible hydro (pumped storage), thermal storage.

- Storage in grids (MW): batteries; capacitors and superconducting coils; flywheels.

- At an end user level (kW): batteries, superconducting coils, flywheels. *[1]*

The work in this thesis intends to build a small system, from energy source to consumer application, using hydrogen to buffer energy for a given time period. Although there are various kinds of power storage systems, electricity still has to be imported at peak hours, so the opportunity to use alternatives is present.
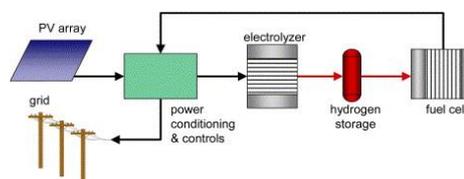

Figure 2 Structure of the experiment

In Fig. 2, it's depicted an idealization of the power system, able to provide electricity to the grid only when required.

The main reason why these systems are not functioning is because the marginal costs of producing energy are still too high. Even the most efficient branches of the hydrogen technologies are still waiting on scientific advances, tied mainly with the high costs associated with the materials used and their short lifetime. Until the overall robustness of these systems increases, these applications will be mainly prototypical and not meant for real world use.

To illustrate the principles behind energy storage using hydrogen, a small scale experiment was developed. In order to deal with time varying energetic needs, the experimental setup is able to: generate a variable luminous stimulus; convert said

stimulus to electric power; produce and store hydrogen; use the hydrogen to power a load able to produce visible work.
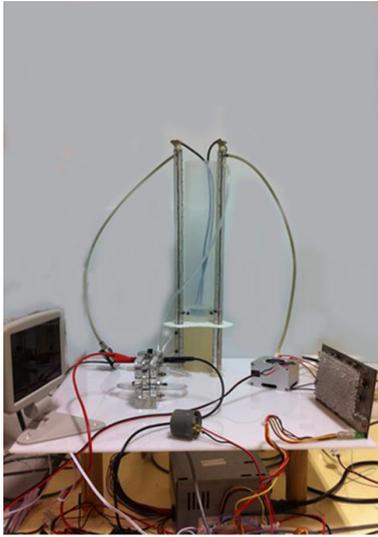
II. EXPERIMENTAL SETUP

Figure 3 Experimental setup

LED AND PV PANEL

Because the intent of the experiment was to simulate a supply powered by the sun, the size of the light source and the associated PV panel was reduced. This way, the response of the power source and PV cell was maintained, but scaled to a more manageable dimension.

To simulate the sun, a panel of red, green and blue LEDs was used, which enabled, to a certain extent, the creation of various colors. This array was controlled by the user of the experiment.

PEM ELECTROLYSER

The device used to generate hydrogen is a proton exchange membrane electrolyser.

The relation between the power provided to the electrolyser and the amount of hydrogen it can produce is, at a first approach, related through the Faraday's Law of electrolysis: the production rate of hydrogen is proportional to the current provided to the electrolyser.

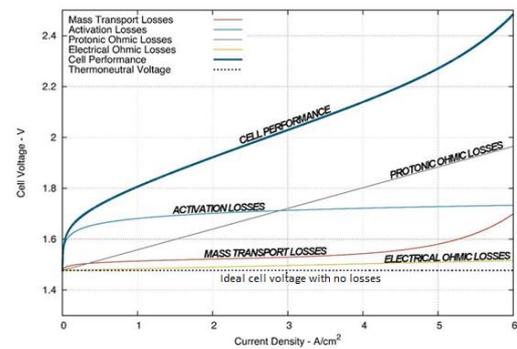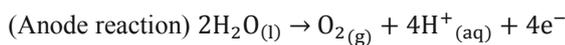The ideal chemical equations of the electrodes' reactions are as follow:

$$\text{(Anode reaction) } 2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-$$

$$\text{(Cathode reaction) } 2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$$

Figure 4 PEM electrolyser losses

There are three distinct regions in the representation of the stack performance, which are related to three main kinds of overpotentials:

Activation losses: these losses are related primarily to the type of catalyst, along with the active area and the support stability.

These are given by:

$$V_{act} = \frac{R.T}{2.\alpha.F}.\ln(\frac{I}{I_0})$$

(R is the ideal gas constant; T is the temperature; α the charge transfer coefficient; I0 is the exchange current between both electrodes)

Ohmic losses: mainly due to protonic ohmic losses, which are tied with the conduction of the protons across the membrane, and to a smaller degree with electron conduction losses. These losses are directly proportional to the membrane thickness and conductivity and to the materials used in the catalyst and separator plates.

$$v = ri$$

(v are the ohmic losses; r is the ohmic resistance; I is the current)

Mass Transport losses: these losses are associated with the conflict generated by the departure of oxygen from and water access to the anode. It is clear that these losses occur mainly at high oxygen production rates and consequently at high current densities.

$$V_{mt} = \frac{R.T}{2.F}.\ln(1 - (\frac{I}{I_l}))$$

(V_{mt} are the mass transport losses, R is the ideal gas constant; T is the temperature; I_l is the limiting current)

Some of the factors that maximize the efficiency are: increasing the temperature and pressure at which the device is working at; increasing the concentration of platinum or whatever catalyst is being used, so as to increase the active area for reactions to occur; geometry of the stack – distance and orientation of both electrodes; and detachment of oxygen bubbles from electrode.
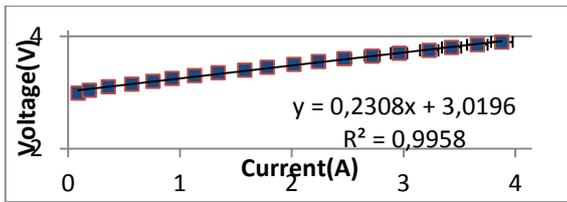
Figure 5 Electrolyser V-I characteristic

The chart shows $y = 0{,}2308x + 3{,}0196$ and $R^2 = 0{,}9958$.

STORAGE, VALVES AND VOLUME MEASUREMENTS

To measure the amount of hydrogen and oxygen produced, a sensor had to be constructed. Since the volume of the gases is proportional to the height of the water inside the gases' containers, the sensor detected variations in the height.

The structure of the height sensor is basically an implementation of the astable circuit of the IC ne555 – the 555 timer puts out a continuous stream of rectangular pulses at specific frequencies.
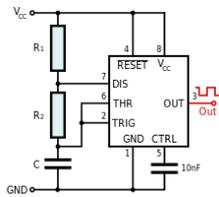

Figure 6 Astable circuit

Because the output frequency of the circuit is dependent on the parameters of passive components, the containers served as capacitors by adding a small copper conductor placed in the middle and a nickeled net on its surface at a ground voltage.
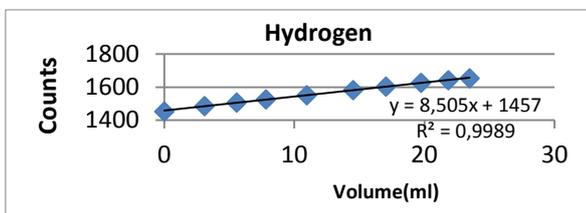

Figure 7 Calibration of the height for the hydrogen column

The chart titled "Hydrogen" shows $y = 8{,}505x + 1457$ and $R^2 = 0{,}9989$.

PEM FUEL CELL

The conversion of hydrogen to electricity using a PEM fuel cell is, to an extent, the reverse of what happens in the electrolyser.
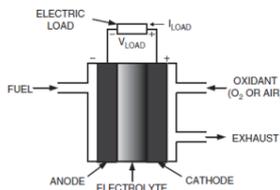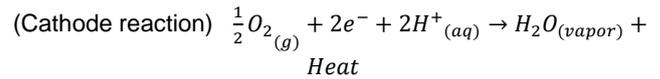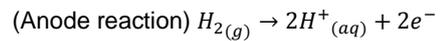

Figure 8 PEM fuel cells schematic

(Anode reaction) $H_{2\,(g)} \rightarrow 2H^+_{\ (aq)} + 2e^-$

(Cathode reaction) $\frac{1}{2}O_{2\,(g)} + 2e^- + 2H^+_{\ (aq)} \rightarrow H_2O_{(vapor)} + Heat$

As one can see, in the anode, when the flow of hydrogen molecules is faced with the MEA – similar to the one found in the cathode of the PEM electrolyser – it's catalytically split into protons and electrons. The flux of electrons can be used to power a load, while travelling to the cathode of the cell.

In the cathode, the reaction is completed contingent on three conditions: In the same location there must be the catalyst – to conduct the returning electrons – molecular oxygen and the protons transported through the membrane. If this takes place, water in vapor state is formed and thermal energy is released.

One can divide the operation of fuel cell in three areas, just like the electrolyser.

Activation losses: these are pronounced in the low current region but exist through all the regions. In this region electronic barriers must be overcome before the current and protonic flow. The activation polarization can be represented as

$$V_{act} = \frac{R.T}{2.a.F}.\ln(\frac{I}{I_0}) \text{ (3.22)}$$

(α the charge transfer coefficient, F the Faraday constant, I the current density, and I0 the exchange current density)

Activation polarization is due to the speed of the electrochemical reactions at the electrode surface, where the species are oxidized or reduced in a fuel cell reaction.

Ohmic losses: these losses can be represented as:

$$v = ri \text{ (3.23)}$$

The origin of ohmic polarization comes from the resistance to the flow of ions in the electrolyte and flux of electrons through the electrodes and the external electrical circuit resistance. The dominant ohmic loss is in the electrolyte, which is reduced by decreasing the electrode separation, enhancing the ionic conductivity of the electrolyte and by modification of the electrolyte properties.

Concentration losses: these occur over the entire range of current density, but these become prominent at high limiting currents where it becomes limited for the oxygen flow to reach the fuel cell reaction sites, as well as for the water formed to exit the anodic side of the MEA. These mass transfer losses can be represented as:

$$V_{mt} = \frac{R.T}{2.F}.\ln(1 - (\frac{I}{I_l})) \text{ (3.24)}$$

(I_l is the limiting current density)

III. ELECTRONICS AND CONTROL

The electronics in the experimental setup can be divided in two areas: firstly there was the power conversion. This step dealt with the proper energetic supply of the LED panel, electrolyser and test load – converting the fuel cell power output. Secondly, there was the data acquisition and control, which was done using a microcontroller and encompasses signal filtering, amplification, reduction…

The conversion of the AC signal from the grid to the LED panel (DC) was done using the following rectifying circuit.
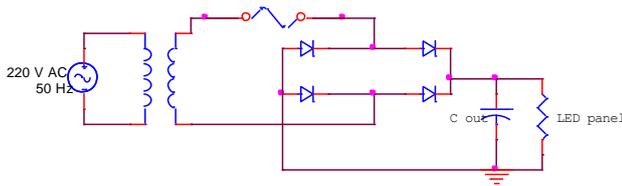

Figure 9 Full wave rectifier schematic

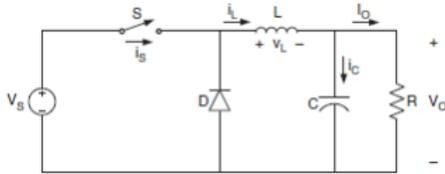The remaining devices required DC/DC conversion which was done using a buck converter.

Figure 10 Buck converter schematic

The operating principle behind this circuit is to circuit is to alternate the state of the inductor and filter the resulting output in order to achieve a steady DC voltage. In this application the current that goes through the inductor never falls to zero. This is called the continuous operation mode.

When the circuit's switch is on, the inductor's induced voltage increases linearly up to the voltage of the source, while the current is forming a magnetic field in the inductor.

When the switch is not conducting, the voltage induced by the collapsing magnetic field decreases. During this period, current is conducted through the diode, from the ground.

By controlling the switch with a square wave, the inductor voltage will be proportional to the Duty Cycle and will be triangular in shape. Obviously, as this process is done at a greater rate (higher switching frequency) the amplitude of the AC component of the signal is lowered.

The components chosen to build this circuit were very important. When the energy is finite, like in the fuel cell case, the losses must be avoided. So the choice of transistors and diode was of paramount importance.

DATA ACQUISITION AND CONTROL

The acquisition of signals by the microcontroller was prepared by transforming the input signal in its amplitude (5V max) and its quality (removing noise wherever possible).

This was done using a second order filter with an amplification band, with the corresponding Bode diagrams, shown in the following figure.
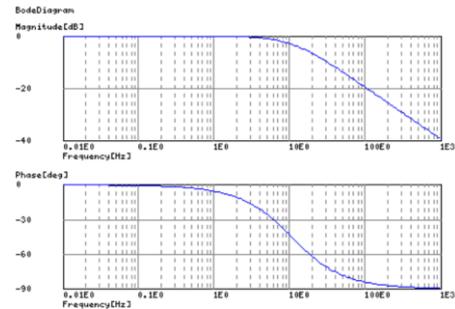

Figure 11 Bode Diagrams for the filters

The control of the components was done implementing a PID controller.

- To control the power supplied to the electrolyser, based on the amount of power the PV panel is at, by measuring the voltage drop across a resistor; the output of the controller will change the duty cycle of the buck converter that controls the power supplied to the device.
- To ensure the fuel cells' voltage never goes too low. By keeping track of the overall voltage in the stack, the PID routine is activated if said voltage goes below 0.3 V (in average), and keeps it at that setpoint. When the duty cycle is lower than 0.03, the PWMs are switched off and no more power can be drained from the PEM stack.

One of the main issues with the PID controllers was to adequately find the constants for the control, with a fairly high dt in each update (in order not to interfere with the communications with the e-lab platform).

CIRCUIT TESTING AND PCB DESIGN

The testing of these circuits was found to be one of the main issues. The circuits were not overly complicated, however, the currents at which the devices operated made prototypes hard to construct.

In low current circuits, usually the use of test boards is sufficient, however in this case, it was not possible due to excessive noise and energy dissipation due to poor contact.

In addition, the grounding between the power circuits and the control circuits was often tricky. The ground from the power circuit was very noisy and would corrupt the integrity of the logical circuitry if some preventive measurements weren't taken.

In particular, the design of the PCB tried to: maximize the distance between the high current components and the microcontroller; minimize the loop areas in the switched circuits; connect the grounding in just one point; …

III. FUEL CELL STACK RECOVERY

During the course of the preparation of the devices required for the experiment an extensive amount of time was spent on the study of the recovery of the fuel cell stacks.

Initially, the fuel cell used in the remote controlled experiment exhibited clear signs of being in far from ideal conditions – in particular, it could not provide significant current to power

even a light load. Because of this, two spare cells in the laboratory were considered as replacements. Because these cells shown signs of being merely dehydrated, though trial and error, the following recovery procedure was found:

1. Hydrate the membrane by filling the stack with water.

2. Still filled with water, the stack is submitted during a period of around 12 hours to a temperature of 80ºC.

3. Remove the remaining water with a low pressure nitrogen flow (or another inert gas).

4. Provide the cells with hydrogen and relatively high currents (drain currents which leave the short circuit voltage slightly above the threshold mentioned above) for short amounts of time (6 seconds).

5. Increase the current drained if the short circuit voltage increases.

6. Repeat step 5 until an equilibrium is achieved.

The plots in the following figure show the evolution of the voltage, current, resistance and power for one of the stacks recovered.
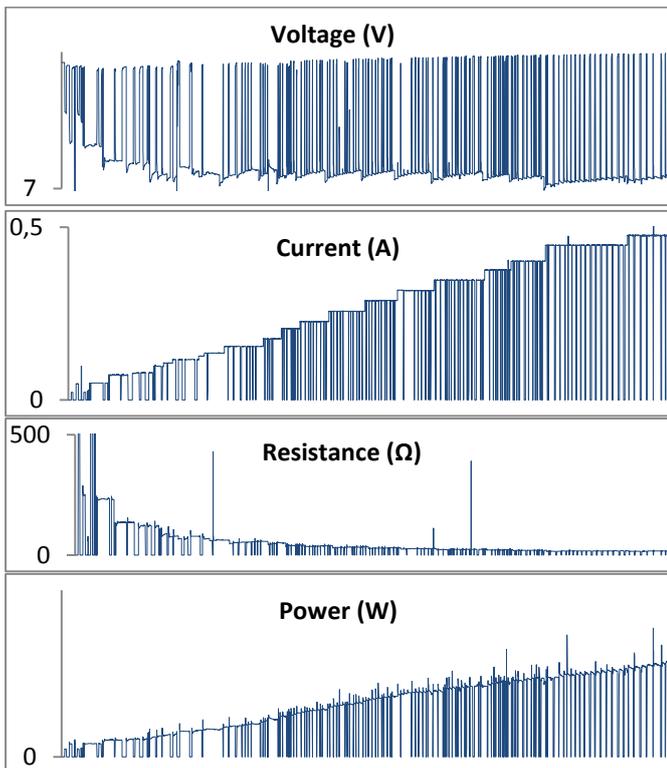

Figure 12 Evolution of the various electric variables overtime

As can be seen, the overall power keeps increasing as these steps are operated and the internal resistance of the cell decreases immensely.

IV. E-LAB

E-lab is a remote controlled laboratory which enables the control and acquisition of data from various experiments.

The interaction between a user and the platform that controls the experiment is done using the Internet and typically shares the following structure: Choice of what experiment to select; Selection of the parameters relevant to the experiment; Real time video streaming; Presentation of data acquired in tables and scatters.

The experiments that compose e-lab are found in IST's Alameda Campus. Such setups require that a computer running the corresponding driver, a java program designed to link the hardware and the user.
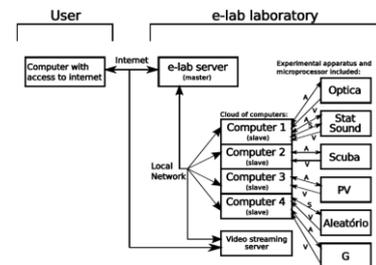

Figure 13 e-lab experiment structure [2]

As one can see, the structure of the system can be divided in three sections, each with a need to translate the instructions to the other: firstly there is the bridging between the commands of the user, coded in java, to the e-lab server. This is done using the xml file; secondly, the bridge between the computer driving the experiment and the hardware, which is done with the ReC generic driver communication protocols.
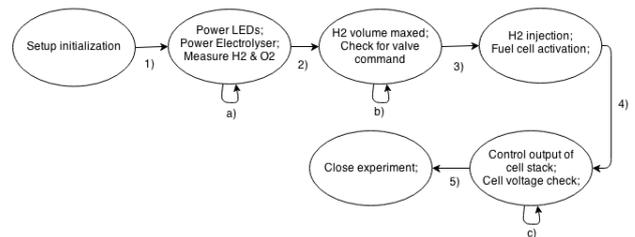

Figure 14 Diagram of the states of the experiment

In the figure shown above, it can be seen a simplified relation of the main tasks the hardware performs.

1) After the call for protocol 1, which includes the initialization of the setup and the input of the LED panel parameters (color and intensity) the experiment powers the LED panel which calls the electrolyser power control routine as well as it initializes the volume measurements. A check for the LED parameters is done in a), which enables the control of the H2 generation rate.

2) Once the maximum volume of H2 has been achieved, with b) the setup waits for the command for the electrovalve to release the hydrogen, and with it ends the first protocol.

3) As the fuel enters the cell stack, the routine to properly start the fuel cell starts. This includes the delay required to include the starting period of the cells and the closing of the electrovalves.

4) Once the stack is outputting usable power, the user has the ability to choose the percentage of the maximum power in c). In addition, that percentage is adjusted by a voltage sensor across the first 2 cells of the stack.

5) Once the output power reaches a minimum value, the valves are opened and the experiment ends.

It was also created an animation to introduce the user to the physical processes occurring. It shows the entire evolution of the major particles involved in the experiment.

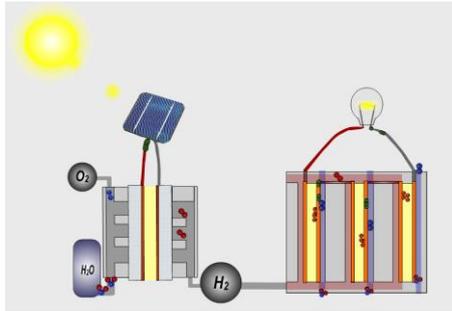In the following figure, a frame can be seen.

Figure 15 Experiment animation

V. PULSED ELECTROLYSIS

The motivation to study the efficiency of an electrolyser under a pulsed DC regime comes from two phenomena which occur at different scales.

Firstly there are mass transfer losses. These are related with the formation of oxygen at the anode of the electrolyser and the subsequent loss of active area for water to undergo electrolysis. Even though these losses are most prominent at higher current densities, they are present at all operating conditions of the electrolyser. Since the electrolyser worked in the ohmic region – which is by definition not greatly affected by other losses than those by conduction – no visible gain made should be made on the minimization of mass transfer losses.

Secondly there is the double layer effect.

The thickness of the layer is related to an increased potential. The minimization of the layer should bring a greater efficiency to the process, namely by reducing the amount of particles that form the layer. The double layer formed adds a capacitive signature to the electrolyser's transient response, which includes the electrostatic capacitance, responsible primarily for the existence of the double layer; and possibly an electrochemical (or Faradaic) capacitance, which occurs because of the electron charge transfer between the electrode and formed products (hydronium ions) at the cathode.
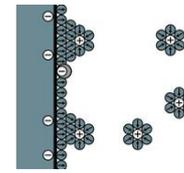

Figure 16 Pseudo capacitance caused by the ions in the cathode surface

In addition, there was literature claiming to have found high efficiencies using pulsed electrolysis. [3]

TESTS AND RESULTS

To determine whether the efficiency suffered positive changes, three main variables were studied.

The power provided to the electrolyser, when a pulsed signal was applied (duty cycle = 0.5); the frequency of the switched signal; and the duty cycle of the signal. The automation of these tasks allowed the collection of data which formed the plot in the following image.
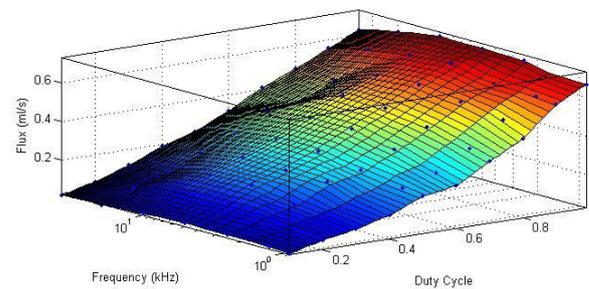

Figure 17 Frequency vs Duty cycle vs flow, at 4v

One can observe that the response is not linear, and never seems to surpass the DC efficiency.
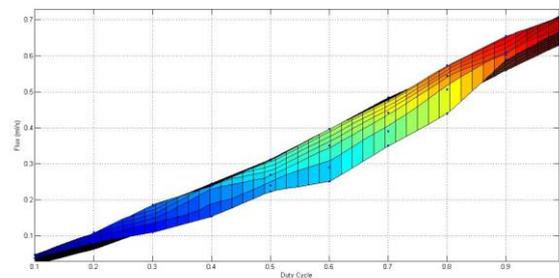

Figure 18 Profile of the previous plot: duty cycle vs flow

In the previous figure, it can be seen by converting the DC to watts (power = (duty cycle) x16), that the flow never reached the DC case.

This was explained by the existence of the double layer effect. In fact, each time the electrolyser's supply was turned on, energy was spent building a layer of particles, and only then would the generation of hydrogen start.

So, in each switching cycle, there could be no improvement because it implies additional losses. In the case of working outside of the ohmic region, the savings in the mass transport losses could overturn this energetic balance.
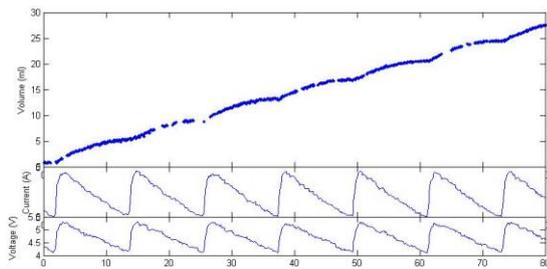
Figure 19 Hydrogen evolution with saw tooth signal

Additional tests were done, where the shape of the signal was changed, but the electrodes were never turned off. In this way, there would be no double layer building and the associated energetic costs. This seemed to achieve an efficiency equal to the DC case. It could present improvements when the electrolyser is forced to work outside the ohmic region.

VI. CONCLUSIONS

During the construction and tuning of the experimental setup, the greatest difficulty found was to have the apparatus functioning without the need of human supervision. The need for bigger pressure on the hydrogen fed to the cell stack is required to perform purges of excess water.

During the recovery of the fuel cell stacks found in the laboratory, it was found that the recovery of devices presenting very feeble performances is usually possible. The main issues holding back the stack are usually an overall lack of hydration and poor catalyst placement or an individual cell with severe damage, which needs to be excluded from the stack.

During the pulsed electrolysis tests, it was concluded that the electrolyser had fewer losses in the DC regime than all of the other tested conditions. This was explained by the existence of the double layer, which exhibited a capacitive behavior. The layer was formed when the potential was applied, using energy meant to electrolyze water in the gathering of ions. When the potential was discontinued, those charges were partially discarded the corresponding hydrogen could not be formed.

Observing the behavior of the electrolyser under the pulsed DC tests, one could conclude that the hydrogen production occurs

even when fed with non-uniform power sources, being able to receive high current densities, which makes it an ideal candidate to receive the variable output available from various renewable energy sources.

For systems including hydrogen technologies and dynamic applications, controllable power conversion seems to be a requirement – both for the electrolyser and fuel cell – because there is the possibility of matching the impedance between power and load, and thus minimize losses.

For efficiency purposes, the choices on the active devices in switched power conversion and circuit architecture are of paramount importance. The amount of losses generated by conduction and switching can be, using inadequate devices, superior to the energetic waste of hydrogen leakage.

Still regarding the switched converters, due the effects present during its operation – ground bounce, EMI… – the PCB design must be carefully planned, in particular when there are sensitive devices such as microcontrollers, which require stable supplies.

Finally, it would be interesting to have the application sending the data from each of the tests performed by the user of e-lab, to an external text file. Over time, valuable data would be gathered, showing the evolution of the PEM evolution until reaching failure, without any significant investment – only the disk space in the application server.

VII. REFERENCES

[1] [Cited 2013-2014]. Available from: http://www.ree.es/ .

[2] Henriques RB, Duarte AS, Fernandes H, Pereira T, Fortunato J, Pereira J. Generic protocol for hardware control @ e - lab. 1st Experiment@ International Conference; Gulbenkian, Lisbon, Portugal17-18 Nov, 2011.

[3] SHIMIZU N, HOTTA S, SEKIYA T, ODA O. A novel method of hydrogen generation by water electrolysis using an ultra-short-pulse power supply. Journal of Applied Electrochemistry. 2006(36):419-23.