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Michael Muller
Technological University Dublin

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PRODUCTION AND STORAGE OF HYDROGEN

Michael Müller
Dipl.-Ing. Elektrotechnik (FH)

Master of Philosophy (MPhil)

School of Electrical Engineering Systems
Faculty of Engineering
Dublin Institute of Technology

Supervisors:

Professor Dr.-Ing. Heinz Schmidt-Walter
University of Applied Sciences Darmstadt

Professor Dr. Eugene Coyle
Dublin Institute of Technology

Professor Dr. James P. Hamilton
University of Wisconsin-Platteville

October 2009

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Signature Michael
Candidate
Date 19-01-10

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List of Symbols and Abbrevations

AC	alternating current
Cl	chlorine
CSV	comma-separated-values
DC	direct current
H	hydrogen atom
H_2	hydrogen molecule
KOH	potassium hydroxide
$LaNi_5$	lanthanum nickel five
$Li-ion$	Lithium-ion
max	maximum
min	minimum
Na	sodium
nc	normally closed
NI	National Instruments
$NiMH$	Nickel-metal hydride cell
O_2	oxygen molecule
OH^-	hydroxide
PEM	proton exchange membrane
$r.h.$	relative humidity
SiO_2	silicon dioxide
SO_3^-	sulfur trioxide
$TiFe$	titanium iron

A	ampere
A	surface area
a	year
Ah	ampere hour
α	charge transfer coefficient
As	ampere second
$barg$	bar gauge
$^\circ C$	degree celcius
C	capacity
cm	centimeter
cm^2	square centimeter
e	elementary charge $1.602 \cdot 10^{-19}$As

η	efficiency
F	force
f	degree of freedom
ΔG	Gibbs free energy
g	gram
ΔH	enthalpy
h	height
I	current
I_0	exchange current
j	current density
J	joule
K	kelvin
k	Boltzmann constant $1.381 \cdot 10^{-23}$
K^+	potassium ion
kg	kilogram
kJ	kilo joule
kW	kilowatt
kWh	hours
l	length
m	metre
m	mass
m^3	cubic metre
M_{H_2O}	Molar Mass of water $M_{H_2O} = 18.01528\ \mathrm{g/mol}$
$mbar$	millibar
min	minute
ml	millilitre
mm	millimetre
mol	mole
μs	microsecond
mWs	milli watt second
n	number
N_A	Avogadro constant $N_A = 6.023 \cdot 10^{23}\ \mathrm{1/mol}$
Nm	Newton metre
Ω	omega
π	pi
p	pressure
ppm	parts per million
$ppmv$	parts per million related to volume

Q	electrical charge
r	radius
R	resistance
R	ideal gas constant $R = 8.31447\ ^{\mathrm{J}}/_{\mathrm{molK}}$
r_0	vaporisation heat
ΔS	entropy
s	second
σ	sigma
s	thickness
S	Siemens
T	temperature
U	internal energy
V	Voltage
ΔV	volume change
W	Watt
W	Work

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1 Abstract

The Faculty of Electrical Engineering and Information Technology at the University of Applied Science in Darmstadt runs several hydrogen-related experiments at their fuel cell laboratory. In cooperation with the Dublin Institute of Technology (DIT), a new project was started in 2007.

The aim of this project was to develop an energy storage system, which would work with hydrogen as a high quality energy storage. This system was developed for using the electricity of solar panels in order to run an electrolyser. Hydrogen is produced and afterwards stored in an adequate storage tank. Once the hydrogen has been stored, it can be used by a fuel cell to produce electricity again, anytime energy is needed. The main difficulty of this project consists in storing the maximum amount of hydrogen with the minium loss of the energy needed for the periphery (cleaning, drying, storing).

This master's thesis was supervised by Prof. Dr. Heinz Schmidt-Walter, Prof. Dr. James Hamilton and Prof. Dr. Eugene Coyle and comprises the development and realisation of such an energy storage system.

2 Introduction to Electrolysis

2.1 History

> *In Greek 'Electrolysis' means "releasing by means of electricity". Nowadays, it is definied as "the process of chemical decomposition by the action of electricity". [1]*

Hydrogen was first discovered in the 16th century by Bombast von Hohenheim (1493-1540), better known as Paracelsus. In experiments with metals and acids, he gained a combustible gas. In 1766, it was Henry Cavendish (1731-1810) who found out that water results from the combustion of that gas. He recognised that hydrogen is a component of water and therefore water cannot be an element. The expression "Hydrogenium" (Greek:"to create water") was coined by Antoine Lavoisier (1743-1810). He was the first to realise that water is a chemical compound of oxygen and hydrogen.

At the beginning of the 18th century, Allesandro Volta invented a preliminary model of today's known battery. The "voltaic pile" consisted of many layers of copper and zinc plates, which were placed in series. These galvanic cells were separated by paperboard or leather, which were soaked in electrolyte. Current could be obtained from the voltaic pile through its electrodes. As the first significant battery of modern time, the voltaic pile was the foundation for the discovery of electrolysis. Already in the same year, Anthony Carlisle (1768-1842) and William Nicholson (1753-1815) reformed the first tests for splitting water using electrolysis. They placed both poles of a battery in water and discovered that hydrogen and oxygen bubbled up where the electrodes had been positioned .

Electrolysis was not only to be used for the splitting of water. In 1807 and 1808, Humphry Davy (1778-1829) used Volta's invention to produce hitherto unknown elements: sodium, potassium, barium, calcium and magnesium. Michael Faraday (1791-1867) continued the work of Davy and eventually created the terms electrolysis, electrolyte, electrode (Greek: "way of electricity"), anode (Greek: "going up") and cathode (Greek: "going down").

In 1832, Michael Faraday made the case for the fundamental laws of electrolysis, which are today known as the Faraday's laws of electrolysis.

Julius Tafel (1862-1918) published the first dissertation[1] about the function of the cathodic hydrogen production at the beginning of the 19th century. Since then, and especially in the 1930s, great efforts were made to clarify the procedure of electrolytical water splitting.

> *"To understand hydrogen is to understand all of physics"* [2]

2.2 Today's electrolysers

Continuous improvements in the 19th century turned electrolysis into a technically mature process. Today, there are electrolysers which produce hydrogen up to 760 $\mathrm{Nm^3/h}$,[3] which correspond to 2230 kW of electrical power. Because such large electrolysers need a high amount of water and electricity, they are often built near dams in order to save costs.

The first electrolysers all worked with a fluid electrolyte and so, they were called "alkaline electrolysers". Today, a second electrolyser technology has been established. The so-called "proton exchange membrane electrolysers" (PEM), which use a solid membrane instead of a fluid electrolyte.

2.2.1 Alkaline electrolysers

Alkaline electrolysers use a fluid electrolyte to transport ions between cathode and anode. The electrolyte usually consists of a 25% potassium hydroxide solution (KOH). There are two different kinds of alkaline electrolysers.

Atmospheric electrolysers

Atmospheric electrolysers, as the name implies, function under atmospheric pressure (1013 mbar). The usual gas purity of this kind of electrolysers is about 99.8 - 99.9%. They are able to produce a maximum of hydrogen of 485 $\mathrm{Nm^3/h}$. Due to their easy handling and their less expensive cost, atmospheric electrolysers are the most common.

---

[1] J.Tafel, "Über die Polarisation bei kathodischer Wasserstoffentwicklung"

[2] Viktor Weisskopf (1908-2002)

[3] $\mathrm{Nm^3/h}$ stands for standard m^3 i.e Norm m^3

Pressure electrolysers

Pressure electrolysers usually function with a pressure up to 40 barg. At a production rate of 760 $^{Nm^3}/_{h}$ they can produce far more hydrogen than the atmospheric electrolysers. Disadvantageous, on the other hand, are the more complex handling as well as the higher costs. If a higher pressure is needed, or less room is available, pressure electrolysers are a more efficient alternative for producing hydrogen than an inefficient compressor.

manufacturer	country	web address
ELT Elektrolyse	Germany	http://www.elektrolyse.de
Norsk Hydro ASA	Norway	http://www.hydro.com/en
The Electrolyser Cooperation	Canada	http://www.electrolyzercorp.com
Wasserelektrolyse Hydrotechnik	Germany	http://www.ht-hydrotechnik.de

Table 2.1: Manufacturers of alkaline electrolysis systems

2.2.2 Proton exchange membrane electrolysers

The PEM electrolysers are quite a new technology. They use a solid membrane instead of a liquid electrolyte to transport ions. This is an enormous advantage because no acid solution necessary, just water and electricity, making it much easier to handle. Another advantage lies in a higher gas quality compared to alkaline electrolysis. On the other hand, material costs are higher for PEM electrolysers.

Nowadays, PEM electrolysis systems cover the low production capacity range. There are electrolysers that can produce up to 30 $^{Nm^3}/_{h}$. Compared to alkaline electrolysers, this is quite a low production rate. In the future, it is likely that both systems will be commonly used. Alkaline electrolysers will be responsible for high production rates while PEM electrolysers will operate at a low production level.

manufacturer	country	web address
Giner, Inc.	USA	http://www.ginerinc.com
Proton Energy	USA	http://www.protonenergy.com
Sylatech GmbH	Germany	http://www.sylatech.de
H Tec GmbH	Germany	http://www.h-tec.com

Table 2.2: Manufacturers of PEM electrolysis systems

It is said that the efficiency of commercially available PEM electrolysers is lower than that of the advanced alkaline technique. However, efficiencies up to 93% have been reported and thus the potential for further improvement is expected to be high.

2.3 Ways to produce hydrogen

Because electricity is not cheap, electrolysis is not the common way to produce hydrogen. Worldwide, 45 billion kg of hydrogen are produced, from which only 2% comes from the production through electrolysis. Figure 2.1 shows that steam reforming through hydrocarbons (coal, mineral oil and natural gas) is the main source for the production of hydrogen.

The hydrogen production by thermolysis is not included in Figure 2.1. Thermolysis is defined as a chemical reaction when a substance breaks up into at least two other ones through heating. This method needs temperatures up to 4000°C for the dissociation. Usually, a catalyst is used to lower the reaction temperature, but temperatures between 800 and 1000°C are still necessary. Because of the high energy input needed to reach the necessary temperatures, this is not a common method to produce hydrogen.

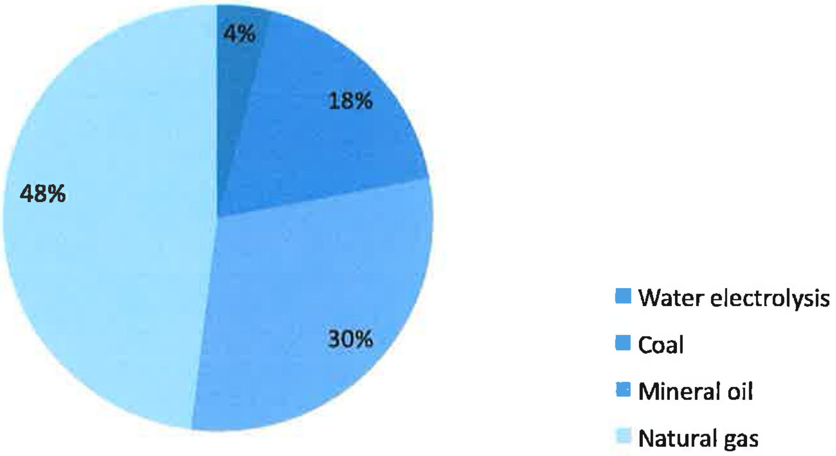


Figure 2.1: Worldwide production of hydrogen

2.4 Current and future applications of hydrogen

One could think that, in the future, the main use of hydrogen will be related to fuel cells. However, only 1% of today's hydrogen production is used as fuel (rocket fuel, fuel cells).

As shown in Figure 2.2, the main part of the hydrogen production is used to produce ammoniac, which in turn, will be used for fertilizers and explosives. The second largest consumer of hydrogen is the petrochemical industry, which uses it to clean hydrocarbons through synthesis. The best example of this is the production of fuel for vehicles. Production of methanol also plays a part in the improvement of fuel. Through methanol, the fuel increases its octane index which reduces the knocking susceptibility.

4% of the hydrogen production is used for extractive metallurgy. The section "Miscellaneous" includes, among others, the food industry (e.g.: fat hardening).

How could applications of hydrogen vary in future? Little change is expected in the production of ammoniac. Assuming that hydrogen really could replace mineral oil as fuel, this would lead to enormous changes. Most of the petrochemical industry and methanol production would not be necessary anymore. Hydrogen production would have to be increased drastically to cover the worldwide demand for fuel and would mainly be used as fuel instead of using it for obtaining ammoniac. It could take decades before such a change occurs. Therefore it is much more interesting to look into applications of hydrogen that are possible today.

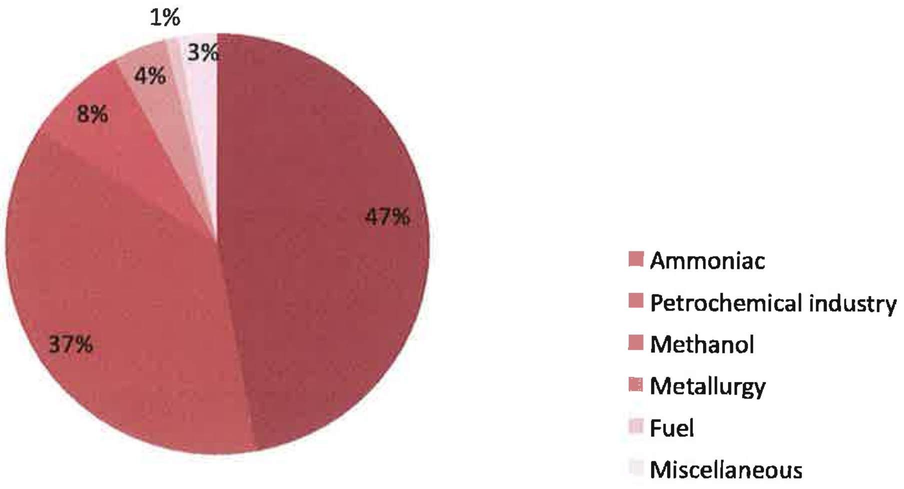


Figure 2.2: Worldwide applications of hydrogen

2.4.1 Stand alone energy system

A stand alone energy system for supplying energy to the users who have no connection to the power grid is needed. Wind power or solar cell systems are state-of-the-art technology for the production of energy. Rechargeable batteries (mostly car batteries) are still used for storing energy. High performance batteries are expensive and usually have a short life cycle. A good example is the life cycle of mobile phone batteries. After 2 years, it is recommended to buy a new battery or even a new phone. Hydrogen can be an alternative solution because its capacity does not decrease at all. Once hydrogen has been stored, it can be kept like that for a long time without losing any of its energy.

Figure 2.3 shows a possible scheme of an energy storage system with hydrogen. During the day, solar cells produce electricity which is used to produce hydrogen. Then, whenever electricity is required (mostly in the evening), a fuel cell can transform the chemical energy of the hydrogen into electrical energy. Hydrogen has the big advantage that it can store far more energy than batteries if the same volume is considered. If the adequate storage system is used, a high amount of energy can be stored. For example, a 300 bar pressure tank with a capacity of 50 l can store 44 kWh of electrical energy. This is the amount of energy an average 3-person family needs in 4 1/2 days.

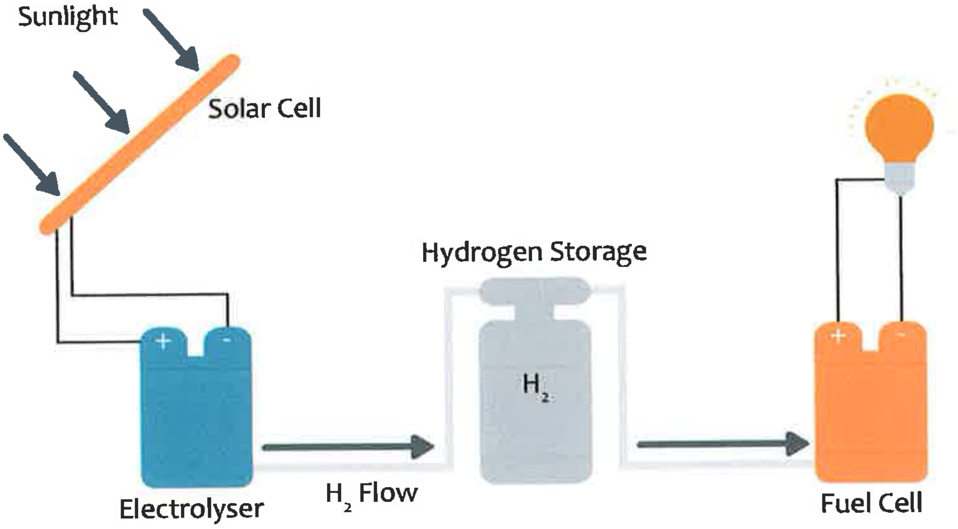


Figure 2.3: Stand alone energy system based on hydrogen

2.4.2 Hydrogen for marine purposes

In some areas of Europe it is not allowed to use combustion engines in boats, therefore electric motors are more commonly used. The batteries on these motors are not very powerful and their low capacity does not allow them to run for longer periods of time. Fuel cell technology offers a good alternative to the common battery. A fuel cell system installed on a boat gives an environmentally friendly and efficient option to move on the water. For example, using an engine with an output of 2000 W and a 50 l metal hydride storage container, would make it possible to run the engine continuously for 24 hours. The storage could be recharged overnight, for example, at a refill station at any harbour.

3 Electrolysis

Hydrogen is a high quality energy carrier, which can be used to store a large amount of energy. Unfortunately pure hydrogen is not available in the nature. It cannot be flowed like oil. Therefore, it must be produced. Electrolysis is one possibility to produce hydrogen. As already mentioned in previous chapters, there are two different kinds of electrolysers; alkaline and PEM electrolysers. The alkaline electrolysers use a liquid electrolyte, while a solid one is used by the PEM electrolysers.

The overall reaction for the splitting of water is:

$$H_2O \rightarrow 1H_2 + \frac{1}{2}O_2 \tag{3.1}$$

There are some specific differences between the alkaline and the PEM electrolysers.

3.1 Basics of alkaline electrolysis

The process of water splitting takes place in an environment of potassium hydroxide solution (KOH) with a concentration level of 20 to 40% (usually 25%). Two electrodes are placed in the KOH solution: a negatively charged cathode and a positively charged anode. Water molecules near the cathode set protons free, which combine with electrons provided by the cathode. Hydrogen molecules and also OH^- ions are formed (Equation 3.2).

$$4H_2O + 4e^- \rightarrow 4OH^- + 2H_2 \uparrow \tag{3.2}$$

The OH ions migrate through the diaphragm to the anode, where they form water and oxygen.

$$4OH^- \rightarrow 2H_2O + O_2 \uparrow + 4e^- \tag{3.3}$$

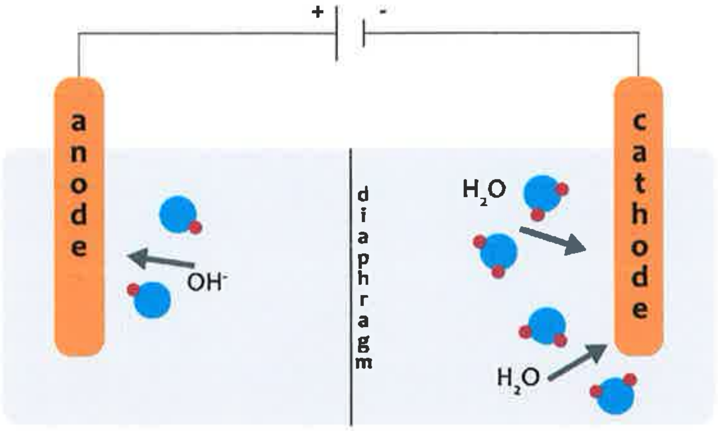


Figure 3.1: Scheme of alkaline electrolysis

Both reactions can be summarised into one: Equation 3.4.

$$4H_2O + 4e^- + 4OH^- \rightarrow 2H_2O + 4OH^- + 2H_2 \uparrow + O_2 \uparrow + 4e^- \qquad (3.4)$$

A simplification of equation 3.4 leads to equation 3.5.

$$2H_2O \rightarrow 2H_2 \uparrow + O_2 \uparrow \qquad (3.5)$$

3.1.1 Concentration of potassium hydroxide solution (EloFlux)

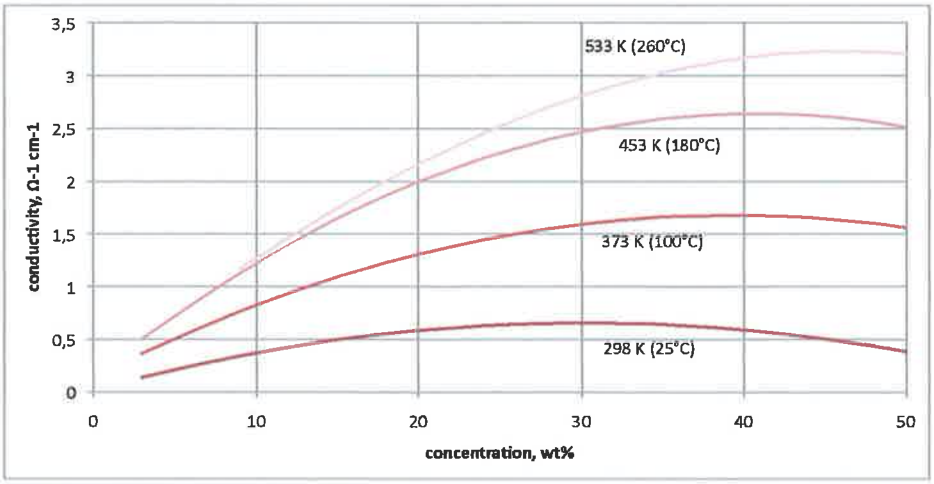


Figure 3.2: Conductivity of potassium hydroxide solution

Potassium hydroxide solution is a base which improves the conductivity in an electrolyser cell. The KOH solution dissociates OH^- and K^+ ions. Conductivity is improved by the OH^- ions while very little ohmic resistance remains.

At room temperature, ohmic resistance is at its lowest concentration level (between 25 and 30%) (Figure 3.2). Higher temperatures lead to an additional decrease in ohmic resistance.

3.1.2 Construction of an alkaline electrolyser

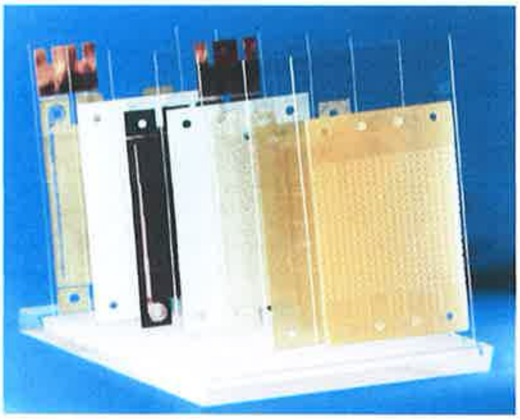


Figure 3.3: Layers of an EloFlux electrolyser [6]

Components in details
(from left to right)

1. O_2 electrode
2. separator
3. H_2 electrode
4. separator
5. electrolyte distributor
6. labyrinth layer
7. end plate

The EloFlux electrolyser was originally engineered by the German company Varta. Both oxygen and hydrogen electrodes (Fig. 3.3 (1, 3)) consist of a nickel grid on which a layer of catalyst material is applied. The material for the catalyst is mostly made of Raney nickel and some parts of PTFE. The plastic makes it easier to apply the catalyst to the grid.

The first separator (Fig. 3.3 (2)) consists of plastic. Its main function is to separate the electrodes from each other. Furthermore, it must be permeable to OH^- ions and has to be impermeable to hydrogen and oxygen to prevent the formation of explosive oxyhydrogen. This separator is called an active separator because the OH ions can permeate it. There is a passive separator next to the hydrogen electrode, through which KOH flows in and out. The electrolyte distributor and the labyrinth layer 3.3 (1, 3)) homogeneously distribute the KOH on the surface of the hydrogen electrode.

3.2 Basics of PEM electrolysis

In contrast to the alkaline electrolysis, a liquid electrolyte is not necessary for the PEM electrolysis. The transportation of the ions is managed by the proton exchange membrane, which is a solid electrolyte consisting of carbon chains and sulphonate (SO3^{-}). The sulphonate combines with the protons which allows the protons to travel through the membrane from the anode to the cathode. The membrane of a PEM electrolyser needs to be wet with pure water in order to work effectively. It is important for the membrane to be wet, since the electrodes would burn holes in a dry membrane destroying it. The water flows due to the gravity into the electrolyser to the anode, where the protons dissolve themselves from the oxygen atoms and oxygen (O_2) rises. The protons permeate the wet membrane in order to get to the cathode and combine with electrons to form hydrogen. (H_2) (Equation 3.4).

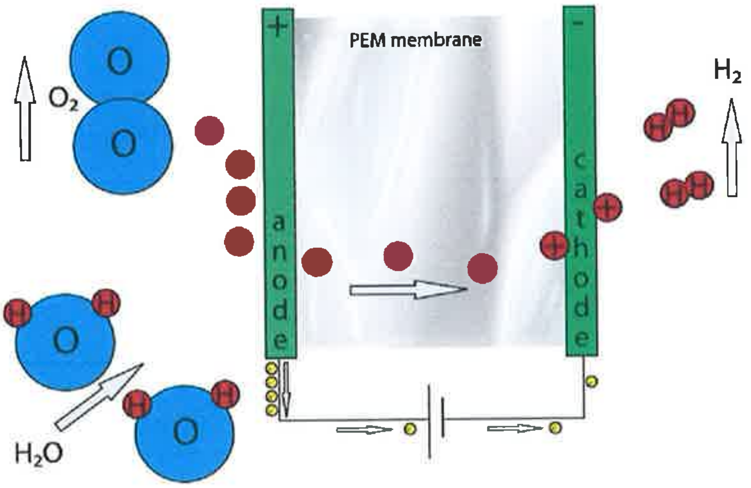


Figure 3.4: Scheme of PEM electrolysis

The overall reaction for the PEM electrolysis is:

$$H_2O \rightarrow H_2 \uparrow + \frac{1}{2}O_2 \uparrow \qquad (3.6)$$

The overall reaction can be split into two half-reactions, which take place at the anode and the cathode, respectively.

Anode (oxygen electrode):

$$2H_2O \rightarrow O_2 \uparrow + 4H^+ + 4e^- \qquad (3.7)$$

Cathode (hydrogen electrode):

$$4H^+ + 4e^- \rightarrow 2H_2 \uparrow \tag{3.8}$$

Overall reaction:

$$2H_2O + 4H^+ + 4e^- \rightarrow O_2 \uparrow + 4H^+ + 4e^- + 2H_2 \uparrow \tag{3.9}$$

A simplification of equation 3.9 results in equation 3.10.

$$2H_2O \rightarrow 2H_2 \uparrow + O_2 \uparrow \tag{3.10}$$

3.2.1 Construction of a PEM electrolyser

The construction of a PEM electrolyser is easier than that of an alkaline electrolyser. Since there is no potassium hydroxide solution in this system, components do not need to be resistant against it. A PEM electrolyser produced by Sylatech GmbH consists of five main parts:

1. holding plate
2. cathode
3. proton exchange membrane
4. anode
5. holding plate

A holding plate made of stainless steel on each side of the electrolyser fixes the electrodes and the membrane. The anode consists of titanium, while the cathode is an alloy of graphite, titanium and stainless steel. Water can flow into the electrolyser through a hole drilled at the bottom of the anode.

The membrane separates the anode from the cathode, functioning as electrolyte and separator at the same time. Protons are able to permeate the membrane, while oxygen and electrons are unable to pass through it. There is almost no space between the membrane and the electrodes in order to keep the ohmic voltage losses in the electrolyser low. Notches in the anode and the cathode let the gases rise out of the electrolyser.

The electrolysers of Sylatech GmbH have a special design. They are able to pressurise the hydrogen side of the electrolyser up to 11 bar without pressurising the oxygen side. This has 3 large advantages:

1. It is possible to pressurise the hydrogen in order to store it more efficiently (without using a compressor).
2. It is not necessary to control the differential pressure, since the pressure is just on the hydrogen side.
3. The water can flow depressurised to the anode and no pump is necessary to get the water into the electrolyser.

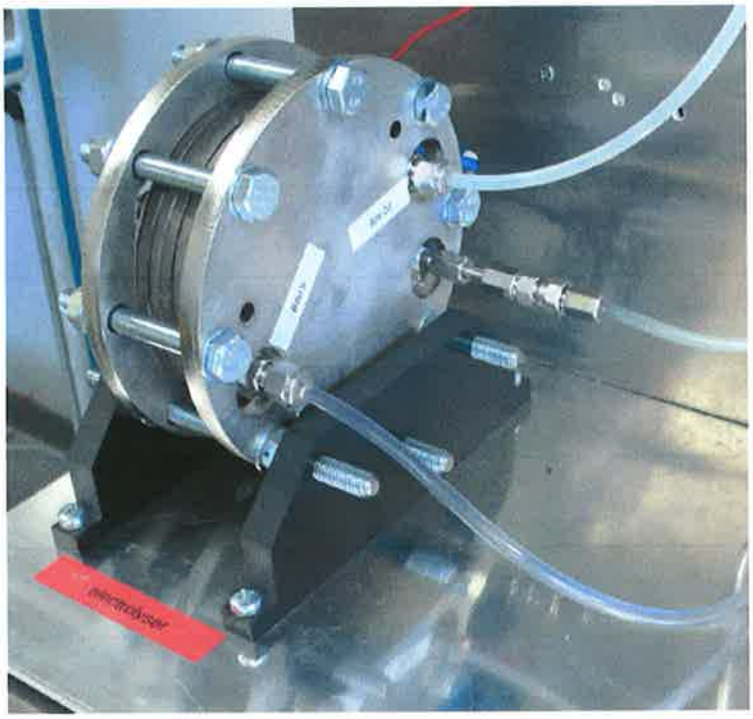


Figure 3.5: Electrolyser by Sylatech GmbH

Data sheet PEM electrolyser

company	Sylatech GmbH
max. power	250 W
max. current	30 A
max. hydrogen production	42 $^l/_h$
pressure	1...21 bar
surface area	66 cm^2
anode material	titanium
cathode material	titanium, stainless steel, graphite
cost	sponsored by Sylatech GmbH

3.3 Comparison between PEM and alkaline electrolysis

Alkaline and PEM electrolysers, both have their advantages and disadvantages. Alkaline electrolysers have been used in the industries for 80 years and are technically mature. Their efficiency usually lies between 80 to 90% and their production rate ranges from 1 to 760 $^{m^3}\!/\!_h$. PEM electrolysers, on the contrary, are quite a new technology. Efficiencies up to 90% are also possible, but the level is usually between 70 and 80%. The maximum production rate of a PEM electrolyser is at 30 $^{m^3}\!/\!_h$ much lower than that of an alkaline electrolyser. More common are electrolysers with a production rate of less than 1 $^{m^3}\!/\!_h$. The absence of potassium hydroxide solution makes the handling of the electrolyser much simpler. Since the PEM electrolysers are easier to handle and have a low production rate, they are often used in laboratories. These are also the reasons why a PEM electrolyser is used in this project.

3.4 Hydrogen production rate

The hydrogen production rate is directly related to the current which flows through the electrolyser. Therefore, the theoretical hydrogen production can be calculated using the current. The electrical charge (Q) of 1 hydrogen molecule is the elementary charge (e) multiplied by 2, since there are 2 hydrogen atoms in 1 hydrogen molecule.

$$Q = 2 \cdot e \tag{3.11}$$

If the energy of 1 mol hydrogen needs to be calculated, the elementary charge must be multiplied by the number of elements which are in 1 mol, which is called the Avogadro constant (N_A).

$$\begin{aligned} Q &= n \cdot N_A \cdot e && (3.12) \\ &= 2 \cdot 6.022 \cdot 10^{23}\ \mathrm{mol}^{-1} \cdot 1.602 \cdot 10^{-19}\ \mathrm{As} && (3.13) \\ &= 192970.7\ ^{\mathrm{As}}\!/\!_{\mathrm{mol}} && (3.14) \\ &= 53.6\ ^{\mathrm{Ah}}\!/\!_{\mathrm{mol}} && (3.15) \end{aligned}$$

According to equation 3.15, 53.6 Ah are necessary to produce 1 mol hydrogen. The multiplicative inverse of equation 3.15 is therefore the hydrogen production per ampere and hour.

$$\frac{1}{Q} = \frac{1}{53.6\ ^{\mathrm{Ah}}\!/\!_{\mathrm{mol}}} = 0.01865\ ^{\mathrm{mol}}\!/\!_{\mathrm{Ah}} \tag{3.16}$$

A more common nomenclature for production rates would be a value in litres instead of mol. At standard conditions 1 mol hydrogen has a volume of 22.414 Nl.

$$0.01865\ \mathrm{mol/Ah} \cdot 22.414\ \mathrm{Nl/mol} = 0.418\ \mathrm{Nl/Ah} \tag{3.17}$$

According to equation 3.17, 0.418 Nl are produced in 1 hour at 1 ampere. At 20 ampere, for example, the production rate is 8.36 Nl/h. This is the production rate of a 1-cell electrolyser. A 5-cell electrolyser has a maximum production rate of 41.8 Nl/h.

$$8.36\ \mathrm{Nl/h} \cdot 5 = 41.8\ \mathrm{Nl/h} \tag{3.18}$$

3.4.1 Energy amount in hydrogen

The minimum voltage V_{H_2} necessary for the electrolysis is 1.23 V (see chapter 5). This is also the maximum voltage a fuel cell can provide when reacting with hydrogen. A multiplication of the electrical charge Q by the voltage V_{H_2} results in the energy contained in 1 mol hydrogen.

$$W = Q \cdot V_{H_2} = 192970.7\ \mathrm{As/mol} \cdot 1.23\ \mathrm{V} = 237.35\ \mathrm{kWs/mol} \tag{3.19}$$

If the energy amount is denoted in kWh, this corresponds to 0.0659 kWh/mol.

$$W_{H_2-mol} = \frac{237.35\ \mathrm{kWs/mol}}{3600\ \mathrm{s/h}} = 0.0659\ \mathrm{kWh/mol} \tag{3.20}$$

In order to have a clearer overview of the energy amount in hydrogen, the following calculations show the hydrogen's energy amount for 1 litre, for 1 m^3, for 50 litres at 200 bar and for 1kg.

$$W_{H_2-1l} = \frac{0.0659\ \mathrm{kWh/mol} \cdot 1\ \mathrm{l}}{22.414\ \mathrm{l/mol}} = 0.00294\ \mathrm{kWh} \tag{3.21}$$

$$W_{H_2-1m^3} = 0.00294\ \mathrm{kWh} \cdot 1000 = 2.94\ \mathrm{kWh} \tag{3.22}$$

$$W_{H_2-50l-200bar} = 0.00294\ \mathrm{kWh/l\ bar} \cdot 50\ \mathrm{l} \cdot 200 bar = 29.4\ \mathrm{kWh} \tag{3.23}$$

1 mol hydrogen has a weight of 2.01588 g/mol. This information makes it possible to calculate the energy amount of hydrogen per kg.

$$W_{H_2-1kg} = \frac{0.0659\ \mathrm{kWh/mol}}{2.01588\ \mathrm{g/mol}} = 0.03269\ \mathrm{kWh/g} \tag{3.24}$$

$$= 0.03269\ \mathrm{kWh/g} \cdot 1000 = 32.69\ \mathrm{kWh/kg} \tag{3.25}$$

According to equation 3.25, 1 kg of hydrogen contains an energy amount of 32.69 kWh.

3.5 Consumption of water

Water is the chemical precursor of electrolysis. The question is, how much water is necessary to produce a specific amount of hydrogen? The equation for producing 1 mol hydrogen is the following:

$$1 \text{ mol } H_2O \rightarrow 1 \text{ mol } H_2 + 0.5 \text{ mol } O_2 \tag{3.26}$$

1 mol water has a weight of 18.01528 g, while the weight of 1 mol hydrogen is 2.01588 g. Hence, 18 g of water result in about 2 g of hydrogen.

$$18.01528 \text{ g } H_2O \rightarrow 2.01588 \text{ g } H_2 \tag{3.27}$$

An extrapolation to 1 kg hydrogen helps to have a better understanding of how much water is necessary for the electrolyisis.

$$\begin{align} 18.01528 \text{ g } H_2O &\rightarrow 2.01588 \text{ g } H_2 \tag{3.28}\\ 8.9367 \text{ g } H_2O &\rightarrow 1 \text{ g } H_2 \tag{3.29}\\ 8.9367 \text{ kg } H_2O &\rightarrow 1000 \text{ g } H_2 \tag{3.30} \end{align}$$

According to equation 3.30, 8.9 kg of water are necessary to produce 1 kg of hydrogen. Usually, water is measured in litres and 1 kg of water is equivalent to about 1 litre of water. Hence, in order to produce 1 kg of hydrogen, 8.9 litre of water are necessary.

4 Experimental rig

The aim of this project is to build an energy storage system which is able to produce and store hydrogen. This is the idea which needs to be realised. Besides the theoretical thoughts, it is necessary to make an experimental rig in order to test the theory. In the beginning, there was an electrolyser which was connected to a power and water supply, this produced hydrogen gas. The rig has been changed and improved many times and the final result of this development process is explained in this chapter.

4.1 Experimental rig requirements

The requirements for the experimental rig can be divided into two categories: function requirements and material requirements. The category "function requirements" itemises what the experimental rig should be able to do, while the category "material requirements" describes which materials are necessary.

Function requirements

- production of hydrogen with an electrolyser
- drying of hydrogen without losing extra energy
- storage of hydrogen in a metal hydride container
- measurements in order to verify the correct functioning
- combination of the electrolyser with solar cells

Material requirements

The electrolyser produces up to 11 bar of pressure in order to store the hydrogen in a metal hydride container. Since the electrolyser is the first part in the hydrogen pipeline, all other parts which are installed between the hydrogen storage container and the electrolyser must be able to withstand the pressure of 11 bar.

Hydrogen is the smallest of all elements and is therefore very volatile. Because of its small size, it leaks very easily through the smallest of gaps. In order to prevent the hydrogen from leaking out of the system, every part of the experimental rig must be well sealed.

Due to the high pressure and the volatileness of hydrogen, plastic valves or pipelines are not an option. A material which is able to withstand high pressure and prevent the hydrogen from leaking is stainless steel. (Useable types of stainless steel are: 1.4571, 1.4301, 1.4541.) Therefore, all tubes and almost all parts which come into contact with hydrogen are made of stainless steel. The diameter of the tubes is 6 mm, while the wall thickness is 1 mm. Hence, the inside diameter of the tube is 4 mm. The disadvantages of using stainless steel as the main material are the high material costs and the expense of forming the tubes. They must be bent and cut very precisely, which require a remarkable expenditure of time. Since stainless steel is very expensive and complex to handle, plastic tubes and fittings have been used for the water and oxygen circuit.

In order to seal the fittings, the threads are covered with thread-seal tape made of PTFE-TEFLON®, which seals the minute gaps in the thread.

4.2 Setup of the experimental rig

Three substances take part in the electrolysis: water, oxygen and hydrogen. Figure 4.1 shows the simplified connection diagram of the three fluids. Light blue shows the water circuit, dark grey shows the oxygen circuit and light grey shows the hydrogen circuit. Also, one can see that the power supply is provided by solar cells. A DC/DC converter transforms the voltage to a capable level for the electrolyser. A fuel cell could be connected to the outlet, in order to transform the chemical bond energy in hydrogen into electrical energy.

4.2.1 Power supply

Solar cells on the roof of the laboratory in Darmstadt produce electrical energy for the electrolyser. Four solar panels, with an overall area of six square metres, produce about 660 kWh of energy per year. The photovoltaic setup was designed by Julian Salvatore, a student of the Hochschule Darmstadt. It was designed for a 200 W electrolyser [10]. The maximum power of the solar cells is higher than the maximum power of the electrolyser. This allows the electrolyser to operate even

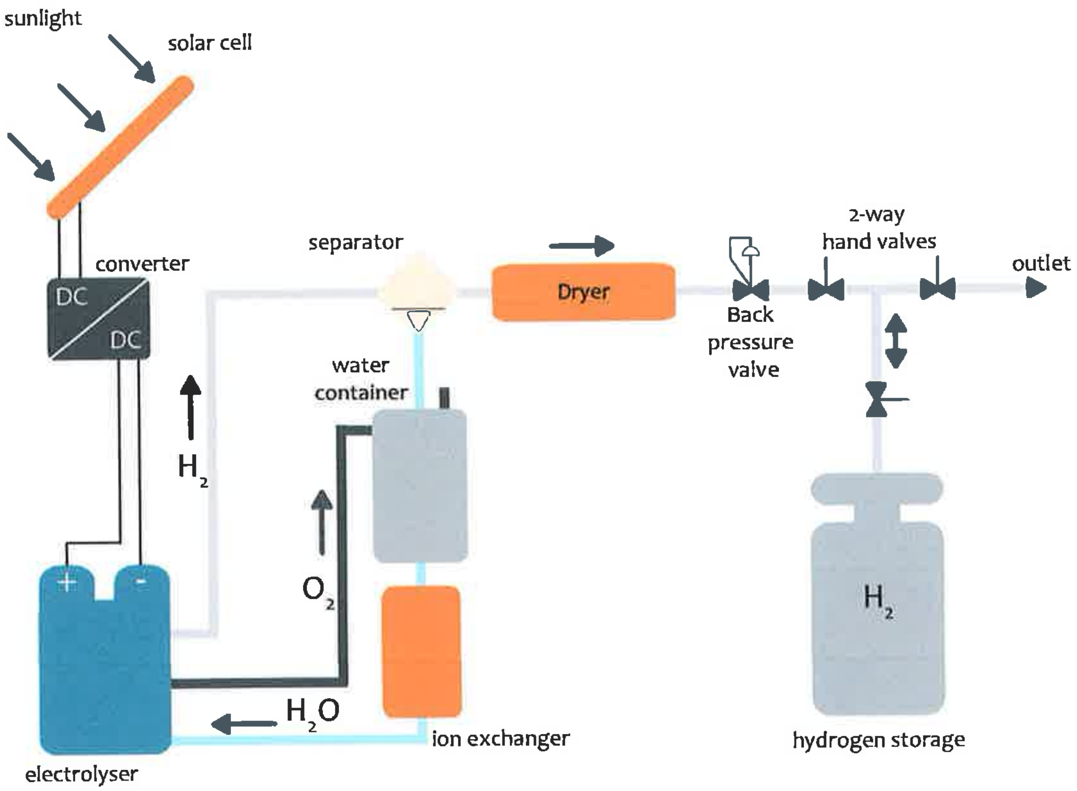


Figure 4.1: Connection diagram of the fluids

when the sun partially obscured. As a consequence, not all of the energy which is provided by the solar cells is used to produce hydrogen. On sunny days, the solar cells produce more energy than the electrolyser can handle. A buffer battery can prevent this waste of energy. Therefore, an improved converter must be built, which is a task for the future. In this project, it proceeds on the assumption that all of the energy from the solar cells is used by the electrolyser. The solar cells provide around 660 kWh of energy per year. At 70% efficiency, the electrolyser transforms 460 kWh into hydrogen. This results in a hydrogen production of 14.1 kg per year.

Data sheet of solar cells

brand name	RA 160 M
company	Ralos
number of solar cells	4
surface area	5.9 m^2
max. power	640 W
energy amount	660 $^{kWh}/_{a}$
max. voltage	43 V
cost	sponsored

Figure 4.2: Solar cells by Ralos

Since the voltage of the solar cells is too high for the electrolyser, it must be transformed by a converter. Daniel Schumacher, another student of the Hochschule Darmstadt, built a maximum power point tracker in combination with a buck converter. The maximum power point tracker locates the maximum power point of the solar cells, which is the point when current and voltage are at their maximum (figure 4.3). The buck converter uses the maximum power point in order to transform the voltage to an adequate level. The regulation of the buck converter ensures that the electrolyser always receives a maximum current, since the hydrogen production is directly related to the current (see section 3.4).

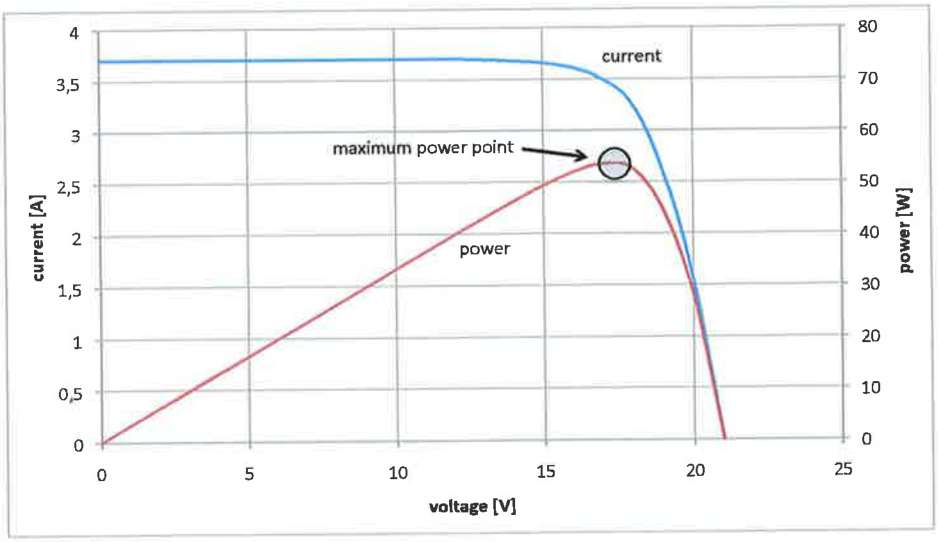


Figure 4.3: Example for the maximum power point of a solar cell

During this project, several tests with the electrolyser where a constant current was necessary have been made. Since the power of the solar cells is related to solar radiation, they cannot provide a constant current or voltage. Therefore, a laboratory power supply of the company Elektro-Automatik has been installed parallel to the solar converter. Its voltage and current can be adjusted manually and it can be used instead of the solar converter. Therefore, the cables which connect the solar converter with the electrolyser must be plugged-in the power supply unit.

Besides the power supply for the electrolyser, an auxiliary power supply for the measuring and steering devices is necessary. This supply is provided by the AC power grid. In order to make the system self-sufficient, a battery would be necessary. This battery could be charged by a fuel cell connected to the hydrogen outlet. Also, the power consumption of the measuring and steering devices must be reduced. A suggested design for a power supply using a battery is explained in chapter 9.

The power grid provides a voltage of 230 V AC. A power supply unit connected

Figure 4.4: Power supply by EA [12]

Data sheet of laboratory power supply

brand name	EA-PS 3016-20 B
company	EA Elektro-Automatik
supply voltage	230 V AC
output voltage	0..16 V
output current	0..20 A
dimensions	240 x 120 x 300 mm
weight	10 kg
temperature	0..40°C
cost	300 Euro

to the power grid transforms the 230 V into 24 V, which is the maximum required voltage by the measuring and steering devices. There are two exceptions which are not connected to the 24 V power supply:
-the conductivity meter, which needs a power supply of 230 V
-the heat mat used for the regeneration of silica gel, which needs a voltage of 12 V

The wiring diagrams for the different voltage levels are attached in appendix B.3.

4.2.2 Water circuit

Water is the chemical precursor of the electrolysis. In order to produce 1 kg of hydrogen, 8.9 litres of water are necessary (see section 3.5). According to the installed power of the solar cells, the electrolyser transforms about 125 litres into hydrogen and oxygen per year. A plastic container with a capacity of 1 litre is mounted above the electrolyser, so that the gravity makes the water flow into the electrolyser.

In order to prevent the water container from emptying, the water refill has been automated. If the 1 litre container reaches a low level, water is pumped from a larger 30-litre container into the 1 litre container. The 30-litre container is placed at the bottom of the experimental rig and needs to be refilled manually after three months.

An ion exchanger is installed between the water container and the electrolyser, which extracts foreign ions from the water, since these ions reduce the efficiency of the electrolyser (see section 5.2.2).

Ion exchanger

The ion exchanger used in this project is the SG-700 from SG Water GmbH.

Figure 4.5: Ion exchanger by SG Water GmbH

Data sheet of ion exchanger

brand name	SG 700
company	SG Water GmbH
dimension	ø 170 x 370 mm
weight	7 kg
capacity at 300 $^{\mu S}/_{cm}$	700 l
cost	430 Euro

Ion exchange is the exchange of unwanted ions for wanted ions. In this project, the water for the electrolysis must be cleaned before it flows into the electrolyser and therefore the ion exchanger is installed. The ion exchanger is a canister filled with cation and anion exchange resin. These exchange resins contain OH^- and H^+ ions (figure 4.6).

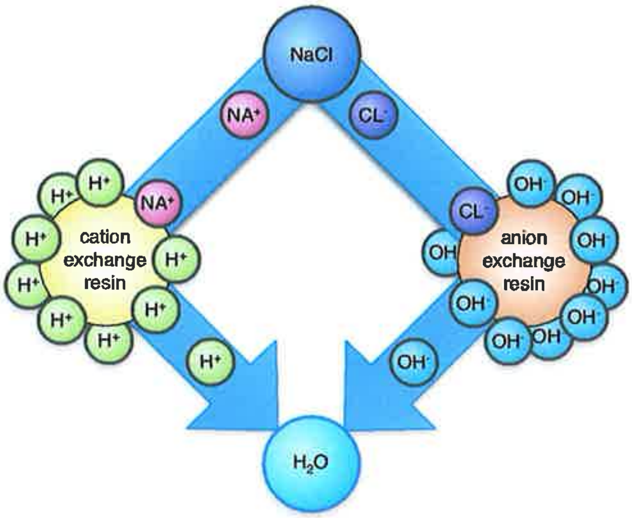


Figure 4.6: The principle of ion exchange

The cation exchange resin contains protons and exchanges positively charged ions in the water with protons. On the contrary, the anion exchange resin contains OH^- ions and exchanges these with the negative charged ions in the water. After the ion exchange, the protons merge with the OH^- ions which results in water as the by-product of the exchange. This process reduces the conductivity of water down to 0.05 $^{\mu S}/_{cm}$.

The life cycle of the ion exchanger is strongly related to the water quality. By using distilled water, the ion exchanger can work for over 20 years, while the use of ground water reduces the life cycle drastically. In Darmstadt, for example, the water conductivity is about 600 $^{\mu S}/_{cm}$ which results in a life cycle of less than 3 years (table 4.1). In this project, only distilled water is used which results in a life cycle that is longer than 20 years. Taking into account, the long life cycle of the current ion exchanger, it seems that a smaller ion exchanger would also be adequate. This is correct, but the SG-700 is the smallest ion exchanger in the product range of SG Water GmbH.

water type	**distilled water**	**drinking water**	**rainwater**	**ground water**	**Darmstadt**
σ [$^{\mu S}/_{cm}$]	5	40	60-100	100 - 2500	600
life cycle [years]	> 20	> 20	20 - 15	15 - 0.5	2.7

Table 4.1: Life cycle of the ion exchanger

If the resin is fully saturated, it is necessary to exchange it. The cost for the regeneration of the resin is 20 Euro.

Water refill

In average the solar cells produce 1.8 kWh of energy per day. Since the efficiency of the electrolyser is about 70%, 1.26 kWh are transferred into about 19 mol of hydrogen. According to equation 3.26, 19 mol of water are necessary to produce this amount of hydrogen. This means that the process needs about 345 ml of water per day.

Data sheet of pump

brand name	NF 10
company	KNF
flow rate	0.1 $^{l}/_{min}$
suction head	max. 10 mWs
weight	70 g
material	PP, EPDM
voltage supply	24 V
power rating	3.4 W
cost	237 Euro

Figure 4.7: Pump by KNF [14]

If 345 ml of water per day are required, a container with a volume of 1 litre would be empty in less than 3 days. Since it is very time consuming to refill the container every 3 days, its refilling has been automated. As already mentioned, a larger container with a capacity of 30 litres is installed at the bottom of the setup. This one is connected with the 1 litre container through a mini pump.

Inside of the 1 litre container, a liquid level switch is installed which monitors its water level. A contact (S1) at the bottom of the container activates when the water level runs low. This starts the mini pump which pumps water from the 30-litre container into the 1 litre container. Another contact (S2) at the top of the 1 litre container causes the mini pump to stop. This refill process takes about 10 minutes. Since the large container can also empty, there is also a liquid level switch (S3) at the bottom of this container, which shuts down the electrolyser. In order to continue the hydrogen production, the 30-litre container must be refilled with water manually. Figure 4.8 shows the wiring diagram for the automated water refill system.

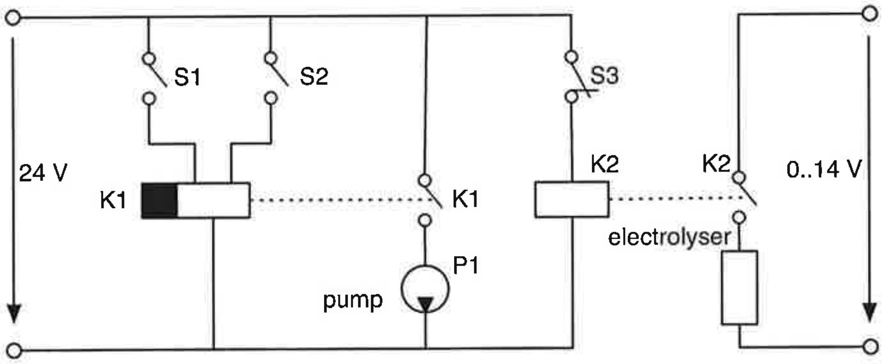


Figure 4.8: Wiring diagram of the water refill

4.2.3 Oxygen circuit

The oxygen is a byproduct of the electrolysis and is not stored. For the recombination of hydrogen and oxygen in a fuel cell, the oxygen which is contained in air can be used. Hence, the oxygen produced just spreads out into the air. When the oxygen leaves the electrolyser, it carries some water droplets with it. In order to prevent the loss of this, the oxygen output is connected to the top of the 1 litre water container. The water droplets fall back into the container and the oxygen rises up into the air.

4.2.4 Hydrogen circuit

Hydrogen is the energy carrier which will be stored in a metal hydride container. It is produced in an electrolyser from Sylatech GmbH. This electrolyser has five cells and can produce about 40 litres of hydrogen per hour. In order to store the hydrogen, it must be dried and pressurised. This is not as simple as depicted in figure 4.1 and the actual setup is more complex. In practice, the hydrogen must also be released in order to use it in a fuel cell, safety units must be installed in order to prevent damage to the experimental rig and the dryer must be regenerated from time to time. All the parts which are necessary to put these terms into practice are explained in this section and also depicted in figure 4.9. As one can see, beside the normal hydrogen storage circuit, another circuit for the regeneration of the dryer is necessary.

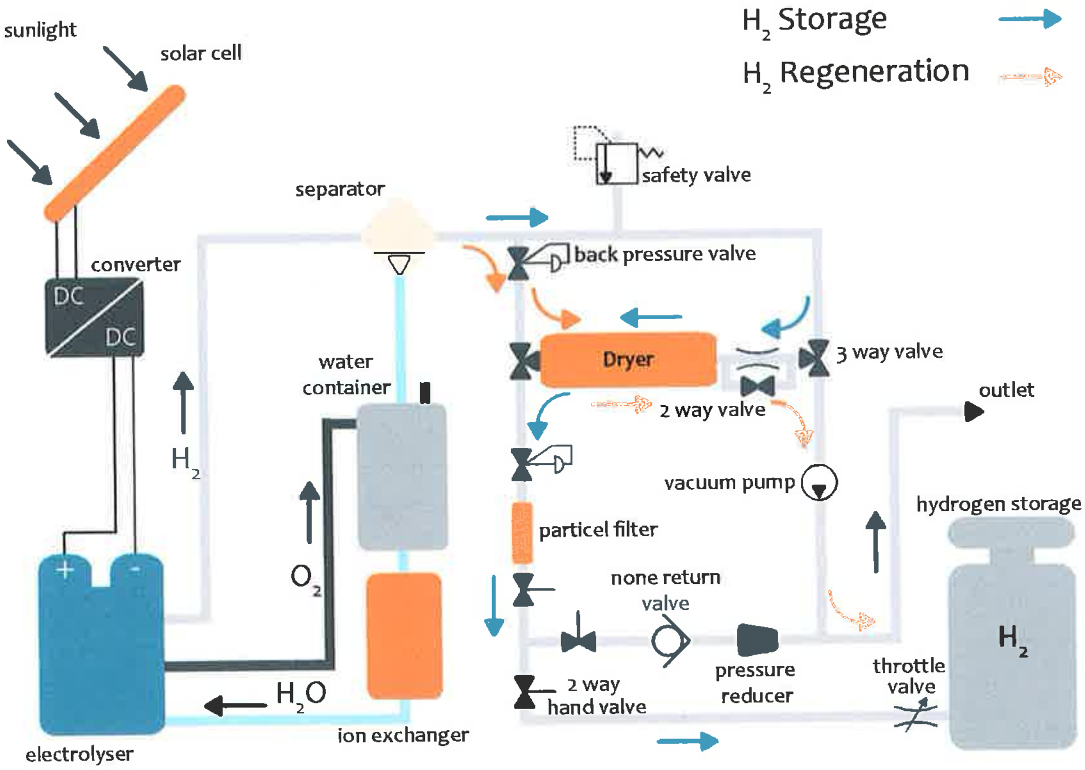


Figure 4.9: Detailed connection diagram of the fluids

Like the oxygen, the hydrogen also contains some water droplets. These water droplets get separated in a separator from M&C Tech Group (figure 4.10), which is made of stainless steel, is capable of whitstanding a pressure of up to 19 bar and is also approved for hydrogen. The hydrogen and the water droplets flow into the separator and the droplets gravitate to the bottom of the separator. At the bottom, the droplets are collected until the water reaches a certain level. This triggers a valve at the bottom, which opens.Since the separator is installed above the water container, the water flows into the container. The hydrogen, on the other hand, leaves the separator through the top.

Data sheet separator

brand name	ADS-SS
company	M&C Tech Group
capacity	160 l/h
pressure	1..19 bar
weight	0.8 kg
temperature	0..200°C
material	stainless steel
cost	390

Figure 4.10: Separator by M&C Tech [15]

After the separator, a cross union is installed. One route of the union leads to the regeneration circuit for the silica gel, where the saturated silica gel is regenerated in a hydrogen dryer (see current section below). Another outlet of the cross union is connected to a safety relief valve from Wittgas (figure 4.11). This safety valve is adjusted to 13 bar. If the pressure reaches this level, the safety valve opens and releases hydrogen until a pressure lower than 13 bar is achieved.

Data sheet safety relief valve

brand name	SV 805
company	Wittgas
relieve pressure	12 bar
flow rate	159 l/h
weight	260 g
temperature	-60..160°C
material	brass
cost	80 Euro

Figure 4.11: Safety relief valve by Wittgas [16]

The last outlet is the hydrogen's normal storage route. The gas passes through two valves which are installed in order switch between the storage and the regeneration process. The dryer is mounted at the output from the second valve. It consist of stainless steel and is filled with silica gel which adsorbs the water vapour from the hydrogen. After the hydrogen has passed through the dryer, it is dry enough in order to be stored in the metal hydride container. (For more information see chapter 6).

Figure 4.12: Dryer by Landefeld [17]

Data sheet dryer

brand name	BHL 0,1/16 ES
company	Landefeld
pressure	1..17 bar
dimensions	ø 40 x 132 mm
volume	0.1 l
silica gel capacity	70 g
capacity H_2O	21 g
life cycle	15 days
temperature	0...200 °C
material	stainless steel
cost	70 Euro

When the hydrogen leaves the dryer it reaches the back pressure valve made by the Parker Hannifin Corporation. This valve can be manually adjusted to a certain pressure level. In order to store hydrogen in the metal hydride container, the valve is adjusted to 11 bar, which means that it will not open until a pressure of 11 bar is achieved. This has two advantages: Firstly, the water vapour in the hydrogen gas is reduced due to the pressure and secondly, the required pressure level to store the hydrogen is achieved.

Data sheet back pressure valve

brand name	ABP 1
company	Parker
pressure	1..18.2 bar
dimension	ø 51 x 125 mm
weight	1 kg
temperature	-40..204°C
material	stainless steel, Teflon
cost	325 Euro

Figure 4.13: Back pressure valve by Parker [18]

After the back pressure valve a particle filter is installed, which filters small particles out of the system in order to protect the metal hydride storage. Particles or debris can pass through the non-return valve without a significant drop in the pressure. This is important if the electrolyser has to run at atmospheric pressure, which can be necessary for tests.

Figure 4.16: Non-return valve by Wittgas [16]

Data sheet non-return valve

brand name	R 53
company	Wittgas
flow rate	20 l/min
pressure	1..26 bar
dimension	ø 25 x 78 mm
weight	190 g
temperature	200°C
material	brass
pressure drop	< 30 mbar
cost	42 Euro

The last part of the hydrogen circuit is a pressure reducer from Landefeld GmbH. This part is installed in order to reduce the pressure and allow the connection of a fuel cell to the outlet. 11 bar of pressure would destroy a fuel cell, but with the pressure reducer it is possible to reduce the pressure to 1 - 2 bar, allowing the connection of a fuel cell.

Data sheet pressure reducer

brand name	DR 00-16
company	Landefeld
flow rate	340 l/min
pressure	1..16 bar
weight	200 g
temperature	0..50°C
material	brass
cost	25 Euro

Figure 4.17: Pressure reducer by Landefeld [17]

This kind of construction makes it possible to store the hydrogen directly into a fuel cell or to use the stored hydrogen in the fuel cell. A parallel use of the stored and produced hydrogen in a fuel cell is also possible.

Besides the normal hydrogen circuit, there is also the regeneration circuit (figure 4.9). The two 3-way valves activates when the regeneration process for the silica gel starts. A LabView program which monitors the measurements in the setup, checks the concentration of water present in the hydrogen. If the concentration of water rises above 150 ppmv, LabView sets the switch to regeneration mode. When the regeneration mode has started, the hydrogen flows through a different route (see figure 4.9). First, the hydrogen reaches another back pressure valve, which is necessary to produce a pressure in the pipeline, in order to reduce the humidity in the gas. Afterwards, the hydrogen flows backwards through the dryer, which is covered with a heater mat. Combined with the following vacuum pump, the relative humidity in the dryer gets reduced to around 0.5%. The large discrepancy in water concentration between the silica gel and the surrounding hydrogen gas, makes the silica gel release its water molecules, which leads to the regeneration of the silica gel. After leaving the dryer, the wet hydrogen gas passes through the vacuum pump and can be used in a fuel cell.

Figure 4.18: Vacuum pump by KNF [14]

Data sheet vacuum pump

brand name	N 86 KNDC B
company	KNF
power	5 W
flow rate	6 $^{l}/_{min}$
pressure	0.1..2.4 bar
weight	0.56 kg
material	Ryton, EPDM, FPM
cost	237 Euro

4.3 Measuring and steering devices

The monitoring of the experimental rig is very important since it is necessary to check that it functions correctly and also to analyse measurements that are recorded. Therefore the whole setup is equipped with different sensors which measure the following values: voltage, current, temperature of the electrolyser, pressure, humidity, conductivity of the water and the rate flow. All the sensors are connected to a measurement card, which is connected to a computer. The monitoring and processing of the measured values are realised through a software called LabView. With

LabView it is also possible to send signals, which is important in order to start the regeneration process.

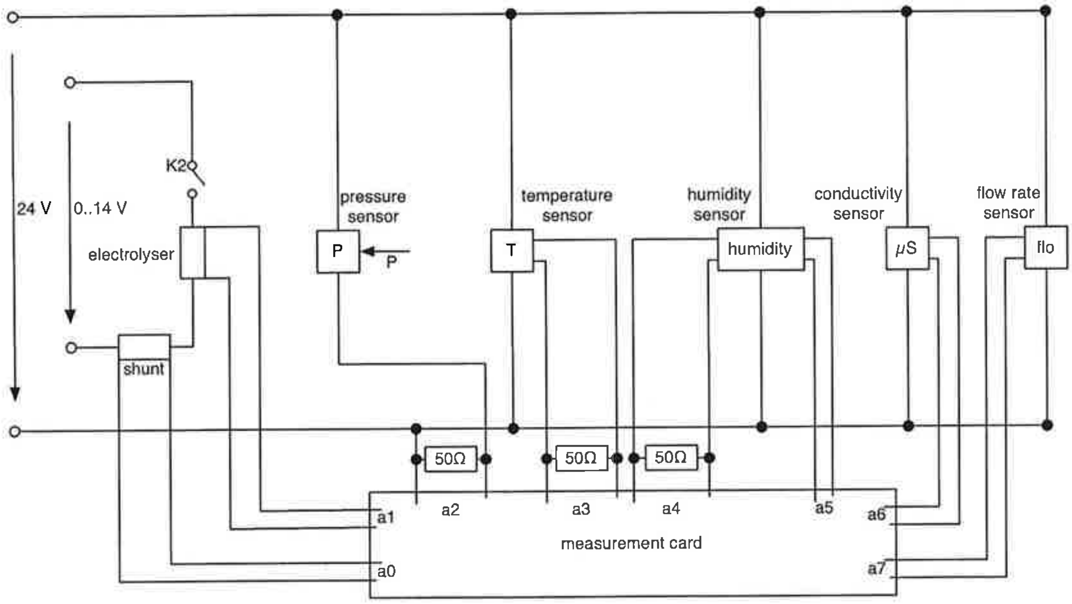


Figure 4.19: Wiring diagram of the measurement

Figure 4.19 shows the wiring diagram for the measuring of the experimental rig. Overall, eight signals are sent to the measurement card, which measures their voltage signals. Four sensors use a current as signal output. These signals must be measured with a precision resistance device called a shunt, in order to obtain a voltage value.

4.3.1 Measurement card

The measurement card "NI PCI 6025E" is the interface between the electrical signals sent by the sensors and the computer which processes and displays the signals. Eight analog input signals can be measured, and two analog output channels make it possible to send signals. Each channel is able to send or read a maximum of 10 Volts.

In order to connect the sensors to the measurement card, a connector block is installed between the sensors and the measurement card in the computer. The connector block is connected to the measurement card by a data cable, while the sensors are connected to the strip terminal on the connector block.

Figure 4.20: Measurement card by NI [21]

Data sheet measurement card

brand name	NI PCI 6025E
company	National Instruments
analog input channels	8
analog output channels	2
digital input channels	8
digital output channels	32
voltage range	-10..10 V
accuracy	0.106 mV
sample rate	200 $^{kS}/_{s}$
cost	in stock (1168 Euro)

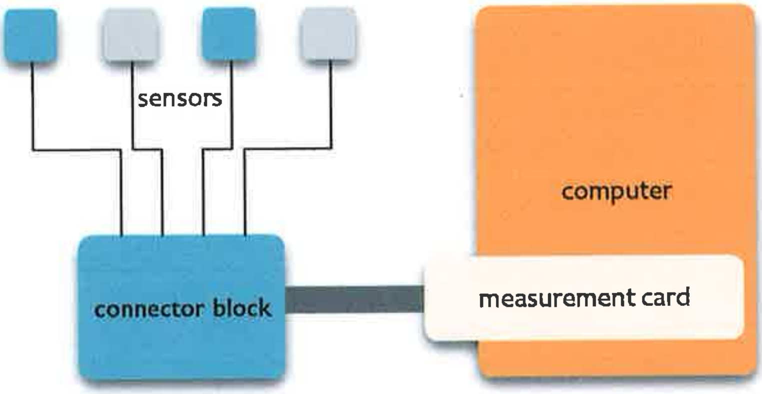


Figure 4.21: Interfaces of the measurement

4.3.2 Voltage and current

The efficiency and the losses of the electrolyser are calculated by the voltage and the current. Hence, these two measurements must be obtained. In order to measure the voltage, the electrodes are simply connected to the measurement card. Since the maximum voltage value of the five cells in the electrolyser is not higher than 10 V, it is not necessary to install a transformer, which would transform the measured voltage to a value lower than 10 V.

A shunt helps to measure the current. The current flows through the shunt and an ohmic voltage drop occurs which is measured by the measurement card. The resistance of the shunt is 3.96 mΩ which results in an ohmic drop of 3.96 mV at a current of 1 A. In order to calculate the current from the measured voltage, the voltage must be divided by 0.00396 Ω.

$$I = \frac{U}{0.00396\ \Omega} \tag{4.1}$$

4.3.3 Pressure

Pressure is necessary to reduce the humidity and to store the hydrogen. One electrical sensor and four manometers monitor the pressure. While the electrical sensor is installed near to the electrolyser, the manometers are installed in different places on the experimental rig.

Figure 4.22: Pressure sensor by Gems Sensors [22]

Data sheet pressure sensor

brand name	1000BGB
company	Gems Sensors & Controls
power supply	10..35 V
power	0.5 W
output	4..20 mA
pressure	1..17 bar
weight	60 g
material	stainless steel
cost	98 Euro

The electrical sensor sends a current of between 4 and 20 mA to the measurement card, where a 50 Ω precision resistor is installed. Due to the resistance, a voltage drop occurs which is measured by the measurement card and monitored by the computer. The four manometers act as a quick control for the user. One manometer is installed after the dryer as a additional point of meter reading. A second manometer is mounted at the metal hydride storage in order to check its fill level. The third manometer is connected to the pressure reducer and displays the pressure after being reduced. The fourth is the vacuum manometer, which is installed near to the vacuum pump. It serves to control the vacuum being created by the vacuum pump.

4.3.4 Temperature

Temperature has an influence on the efficiency of the electrolyser. Therefore a resistance thermometer known as PT100 is installed at the cathode of the electrolyser. PT100 sensors are made of platinum, consisting of an extremely thin layer of the noble metal applied to a substrate. Their resistance is related to the temperature. An increase in temperature will lead to an almost linearly increase of the resistance.

At 0°C, the resistance of the sensor is 100 Ω, while at 100°C, the resistance is increased to 138.5 Ω. In order to measure the change in resistance, a constant current with a maximum value of around 1 mA is sent through the resistor and the voltage is measured. A higher current would result in an increase in temperature in the PT100 sensor due to ohmic losses which occur in form of heat. The voltage drop at a current of 1 mA and a temperature of 0°C is 0.1 V. This voltage drop is influenced by the resistance of the cable which connects the PT100 sensor and the voltmeter.

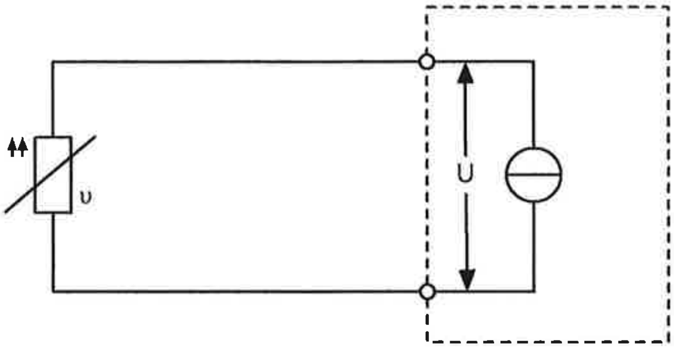


Figure 4.23: Circuit for the measuring of the resistance thermometer

In order to reduce the influence of the cable to a minimum, it should be as short as possible. Often this is not possible. Therefore, a measuring transducer can be used, which is installed near the PT100 sensor. The transducer measures the voltage drop and sends a current of between 4 and 20 mA to the measurement card. This has two advantages. First, the 24 V power supply can be connected to the transducer and a current supply for a constant current is not necessary. Second, the measurement output signal is a current and can therefore be transported over longer distances, since current signals are unaffected by electromagnetic interference and voltage losses due to the resistivity. Figure 4.24 shows the wiring diagram for the measurement by using a measuring transducer.

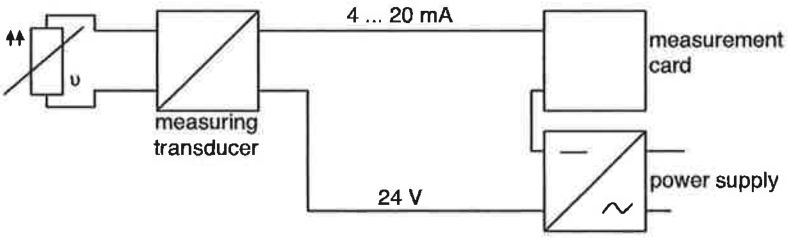


Figure 4.24: Wiring diagram for monitoring the resistance thermometer by using a transducer

The measuring transducer used in this project is the Jumo dTRANS 03.

Figure 4.25: Measuring transducer by Jumo [41]

Data sheet measuring transducer

brand name	dTRANS T03
company	Jumo GmbH
supply voltage	7.5...30 V
output current	4..20 mA
temperature range	0..100°C
cost	47.50 Euro

4.3.5 Conductivity of water

An ion exchanger reduces the conductivity of the water before it flows into the electrolyser. A conductivity meter measures the quality of the deionized water. It comes with the ion exchanger and is installed on its top. The water passes through the ion exchanger and the conductivity meter before it reaches the electrolyser. The conductivity meter has an analogue display. It is not meant to be connected to a measurement card. In order to make the device capable of connecting to the measurement card, two cables have been connected to the circuit points of the analogue display. So it is possible to send a signal from the conductivity meter to the measurement card and a voltage can be read. However, it is not known how the voltage is related to the conductivity. In order to obtain a relation between the voltage and the conductivity, a test was made, where the conductivity was increased and the voltage was measured.

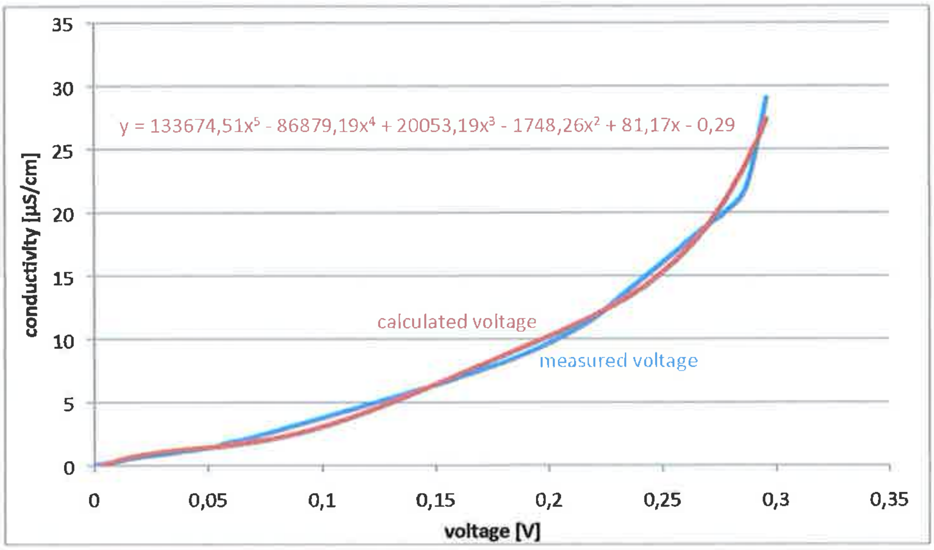


Figure 4.26: Testing in order to obtain the relation between conductivity and voltage

In Microsoft Excel it is possible to show a trend line alongside the measured values. Additionally, the formula for the trend line can be displayed. The measurement of the voltage which is related to the conductivity is shown in figure 4.26. As one can see, the formula for the trend line of this measurement is:

$$133674.51\ x^5 - 86879.19\ x^4 + 20053.19\ x^3 - 1748.26\ x^2 + 81.17\ x - 0.29 \qquad (4.2)$$

This formula is used in LabView to convert the measured voltage into the calculated conductivity.

The conductivity meter used for the measuring is the P2/30 from SG Water GmbH. According to its data sheet, it is possible to measure conductivities of up to 30 $^{\mu S}/_{cm}$. The range of the analogue display is only able to show a maximum of 30 $^{\mu S}/_{cm}$. Since the display range is not limited in LabView by an analogue display, it is possible to receive and display values higher than 30 $^{\mu S}/_{cm}$. However, since the measuring device is not designed for higher values, measuring results above 30 $^{\mu S}/_{cm}$ can only be taken as an approximation.

Figure 4.27: Conductivity meter by SG Water [13]

Data sheet conductivity meter

brand name	P2/30
company	SG Water GmbH
supply voltage	230 V
metering range	0.1...30 $^{\mu S}/_{cm}$
temperature range	0..30°C
cost	part of ion-exchanger

4.3.6 Humidity

Humidity in hydrogen gas is a major problem when storing hydrogen in a metal hydride container. In order to remove the humidity, the hydrogen gas passes through a dryer. Afterwards, the hydrogen gas should have a gas purity of 99.99%, which means that only 0.01% water molecules should be in the gas (More information in chapter 6). Usually the humidity is measured in dew points (°C). A humidity of 0.01% equates to a dew point of -42°C, which is a really small value. In contrast, the dew point in the atmosphere is usually about 12-16°C. Hence, the measuring device must be very precise. Additionally, it must be able to measure the humidity in hydrogen at a pressure of 11 bar. A measurement device which is able to measure these small humidities in hydrogen at 11 bar, is the dew point and temperature transmitter DMT340 from Vaisala.

Figure 4.28: Dew point transmitter by Vaisala [24]

Data sheet dew point transmitter

brand name	DMT340
company	Vaisala
supply voltage	0...35 V
voltage output	0...1 V, 0...5 V, 0...10 V
current output	0...20 mA, 4...20 mA
dew point range	-70...80°C
cost	2170 Euro

This consists of two parts: a transmitter with a display for the results and a sensor which measures the humidity. The transmitter's body is mounted at a clearly visible spot on the setup, while the sensor is installed in a sampling cell after the dryer. The sampling cell is made of stainless steel and has three vents: an inlet and an outlet for the hydrogen gas and an inlet for the sensor. This construction allows the sensor to be placed directly in the hydrogen stream for an optimum measurement.

As already mentioned, the results of the measurements are displayed on the transmitter. Altogether, three values are displayed: dew point [°C], volume concentration [ppmv] and mixing ratio[g/kg].

dew point The relative humidity in the air is related to the temperature. Usually it is about 40 to 50%. If the temperature decreases and the absolute humidity stays the same, the relative humidity will increase. At a specific point, the relative humidity will reach 100%. This point is called the dew point and it provides the information at which temperature the water in the air will condense. For example, a relative humidity of 40% at 25°C has a dew point of 10.47°C. If the temperature drops below 10.47°C, the water in the carrier gas will condense. As a result one can say that the gas is dry when it has a low dew point, since then the absolute humidity in the gas is low.

volume concentration The volume concentration is measured in parts per million in relation to volume. It is the amount of a given substance in a total amount of 1,000,000. The units of both substances must be the same. For example, 1 ml per 1 m^3. In order to reach a gas purity of 99.99%, the volume concentration must be lower than 100 ppmv.

mixing ratio The mixing ratio is the mass of water per mass of dry gas. Usually, it is measured in g per kg. At a dew point of -42°C and a pressure of 11 bar, the mixing ratio is 0.006 g/kg. Since the mixing ratio is very low at low dew points and high pressure, it is not suitable to measure the dehumidified hydrogen.

Besides monitoring the measured values, the transmitter is also able to graphically display the humidity over the last three hours.

Figure 4.29: Measurement values of DMT340

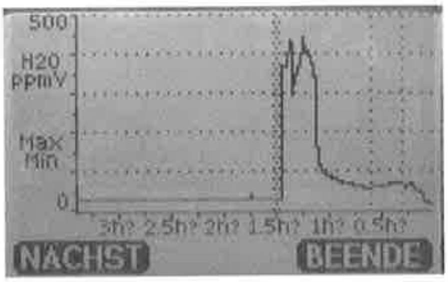


Figure 4.30: Graph of measured values for the last 3 hours

Fortunately, it is possible to send the measurement results to the measurement card. The DMT340 has two analog outputs. It also has a very useful feature which makes it possible to choose the type and range of the output signal. One can choose between voltage and current output. The range of the voltage outputs available are: 0 to 1 V, 0 to 5 V and 0 to 10 V, while the range of current available is 0 to 20 mA and 4 to 20 mA. In the menu of the transmitter, it is possible to choose which signal should be sent from the outputs. Since the volume concentration and the dew point are more accurate than the mixing ratio, these two signals have been chosen to be sent to the measurement card. The dew point signal uses 0 to 1 V, while the signal for the volume concentration uses 4 to 20 mA.

The reason for sending two different signals is the following: it is easier to send a voltage signal, but this signal is strongly influenced by electromagnetic interferences. On the other hand, by sending a current signal, an additional precision resistance is necessary to measure the current. However, the current is not influenced by electromagnetic interference or by an ohmic voltage drop. Since the value for the volume concentration is almost zero, few factors can change the measured value drastically. Therefore, the output signal used for the volume concentration is a current signal.

4.3.7 Flow rate

The theoretical amount of hydrogen produced can be calculated by using the current, since the amount of hydrogen produced is proportional to the current. A mass flow meter measures the hydrogen flow and can verify the amount of hydrogen produced. If the theoretical and the measured values are not equal, than there is a leak in the system. This can either be a leak at a fitting, or a leak in the membrane of the electrolyser. If there is a leak at a fitting, the sealing must be improved or renewed. In the case of a leak in the membrane, the electrolyser must be sent to the manufacturer and the membrane must be exchanged. Damage to the membrane can be caused by too much pressure or a dry membrane. A wet membrane is necessary, since the electrodes would burn holes in the membrane if it was dry.

A mass flow meter able to measure hydrogen is the D-5110 from Manger + Wittmann. The measuring device operates on the principle of heat transfer. In a heated capillary tube, the temperature difference ΔT between input and output is measured. This temperature difference is related to the heat quantity absorbed by the gas flow. The relation between gas flow (ϕ_m) and temperature difference is shown in equation 4.3. K is a constant and C_p is the specific heat capacity of hydrogen.

$$\Delta T = K \cdot C_p \cdot \phi_m \tag{4.3}$$

The mass flow meter is installed after the pressure reducer. At this point the pressure is just a little higher than atmospheric pressure, which reduces the stress on the materials of the mass flow meter. Therefore, the mass flow meter does not need to be able to withstand a high pressure, which reduces its cost.

Figure 4.31: Mass flow meter by Manger+Wittmann [60]

Data sheet mass flow meter

brand name	D-5110
company	Manger+Wittmann
supply voltage	24 V
output signal	0...5 V
flow rate	0.25...5 l/min
temperature range	0..70°C
pressure range	0...10 bar
cost	in stock (600 Euro)

4.3.8 Valves

The valves in the experimental rig are installed in order to switch between normal mode and regeneration mode. Three electromagnetic valves are mounted in the hydrogen circuit. Two of them are 3-way valves and one is a 2-way valve. They are specifically designed to be used with hydrogen, which guarantees that they are leak-proof. A disadvantage of the valves is that they need a constant power supply to stay open, which costs energy. Bistable valves would be better, since they just need a short impulse to activate. However, bistable valves designed for hydrogen are not available. Due to the importance of the valves being leak-proof, the option of a constant power supply was favored. The supply for the valves comes from the power grid. In the future, if the system needs to run self-sufficiently, bistables valves that are compatible with hydrogen needs to be tested and installed. As figure 4.1 shows, the 3-way valves change the course of the hydrogen flow and the hydrogen passes backwards through the dryer.

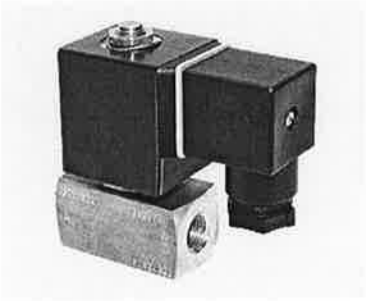


Figure 4.32: 3-way valve by GSR [26]

Data sheet electromagnetic valves

brand name 3-way	G075
brand name 2-way	G052
company	GSR Ventiltechnik
supply voltage 3-way	18.5 W
supply voltage 2-way	11 W
pressure	0...12 bar
voltage supply	24 V
materiel	brass
cost of 3 valves	172 Euro

The dryer and a throttle are installed between both 3-way valves. A 2-way valve is also mounted parallel to the throttle valve. The throttle valve regulates the difference in pressure when switching to regeneration mode. Before switching, the pressure in the tubes is about 11 bar, while the pressure at the vacuum pump is 1 bar. If no throttle valve was installed, a pressure of 11 bar would push against the vacuum pump and would break it. The throttle valve reduces the flow rate and the hydrogen flows slowly to the vacuum pump. So the pump has time to generate a vacuum without being damaged. When the vacuum is generated, the 2-way valve installed in parallel to the throttle valve opens and the throttle valve is bridged. Without this bridge, the vacuum pump cannot create an adequate vacuum in the dryer. The 2-way valve is controlled by LabView.

The same process starts when switching back to normal mode. The throttle valve reduces the flow rate which occurs due the pressure difference. This protects the electrolyser, since abrupt changes in pressure could damage the membrane.

Besides the electromagnetic valves, there are three ball valves installed which can only be adjusted by hand (see figure 4.1). They are necessary to do different tests and to switch between the storage of hydrogen and its release. If they are adjusted

Figure 4.33: Throttle valve by Landefeld [17]

Data sheet throttle valve

brand name	DV 14 ES
company	Landefeld
flow rate	0...640 l/min
temperature range	-20..180°C
pressure range	0...13 bar
material	stainless steel
cost	124 Euro

in order to release the hydrogen, the hydrogen will flow out into the air since there is no fuel cell connected to the outlet.

4.3.9 LabView

LabView is a graphical programming environment, which communicates with the measurement card. It can read out measured values and also send steering values. All electrically measured values are displayed with the LabView software on a computer.

LabView has three different software components: the connection block, the block diagram and the front panel. In the connection block the input signals are connected to virtual channels in LabView. These virtual channels can be used in the block diagram to read out the signal. The block diagram is the programming area of LabView. Here, the input signals which come from the measurement card are read out and processed in order to monitor the real values on the display. The processing of the signals starts with the measuring of 100 values for each channel, which are used to calculate their average values. This method prevents wrong monitoring due to short-term measurement errors. Since the sampling rate of the measurement card is 200,000 samples per second, the generation of the average values takes just a split second. After the calculation of the average values, the modified input signals are scaled to their real value, which is shown in table 4.2.

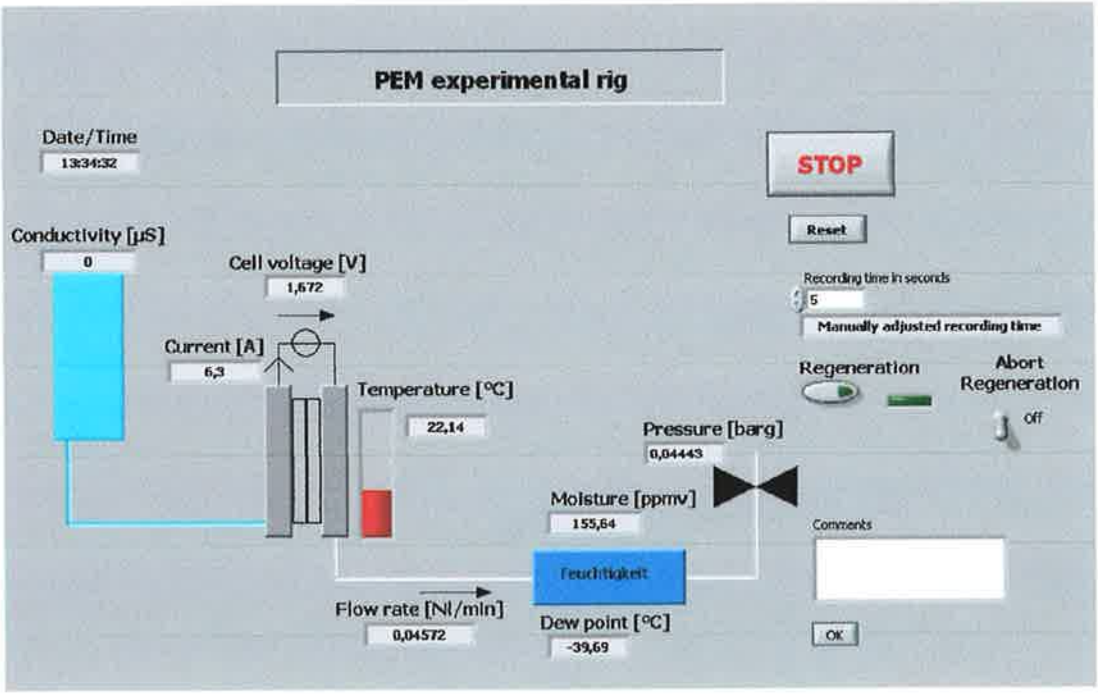
After the values have been read out and scaled, they are written to an array. This array can either be stored manually, or automatically once a day in a so called csv-file. CSV is the abbreviation for Comma-Separated Values. In fact, the csv-file is a text file which has stored all values like in a table. Instead of lines, the csv-file uses tabs and line breaks to separate the values. The great advantage of using this kind of file is its small memory size and also, that it is very easy to import it to

measurand	input signal	scale factor	real and displayed value
cell voltage	0...10 V	1	0...10 V
current	0...80 mV	252.52	0...20 A
pressure	4...20 mA	$1000 \cdot I - 4$	0...16 bar
temperature	4...20 mA	$6250 \cdot I - 25$	0...100 °C
conductivity	0...0.3 V	eqn in fig: 4.26	0...30 $^{\mu S}/_{cm}$
dew point	0...1 V	$120 \cdot V - 60$	-60...60 °C
volume conc.	4...20 mA	$3125000 \cdot I - 12500$	0...50000 ppmv
flow rate	0...5 V	1	0...5 $^{l}/_{min}$

Table 4.2: Processing of measured values in LabView

Microsoft Excel. In addition to the 8 input signals, date, time and user comments are also stored in the csv-file.

Besides being stored in an external file, the values are also monitored directly on the display of the computer. The visualisation is made on the front panel, the last of the three components of LabView. On the front panel, measured values can be displayed, steering data can be entered, and it is possible to design the panel individually. Figure 4.34 shows the front panel designed for this project.


PEM experimental rig

Date/Time: 13:34:32

Conductivity [µS]: 0

Cell voltage [V]: 1,672

Current [A]: 6,3

Temperature [°C]: 22,14

Pressure [barg]: 0,04443

Moisture [ppmv]: 155,64

Flow rate [Nl/min]: 0,04572

Dew point [°C]: -39,69

Recording time in seconds: 5

Manually adjusted recording time

Abort Regeneration: Off

Figure 4.34: Front panel in LabView

As one can see, the experimental rig is graphically depicted on the front panel. The separate measurement stations are arranged as they are in the reality and the measured values are placed near to their measurement stations. Below the reset button, the user can manually enter the time intervals for when the measurement values should be recorded. If no time is written in the field, a standard interval of 30 seconds is used. On the right-hand side of the panel there is a button and a switch to control the regeneration of the silica gel. The latter is the main switch for the regeneration process. If it is turned off, regeneration will not start. If it is turned on, the automatic humidity detection is activated. When the volume concentration of water rises higher than 150 ppmv, the regeneration process will start automatically. Additionally, it is possible to press the button to start the regeneration , but only when the switch is turned on.

A box on the lower right corner can be used for comments, which are recorded in the aforementioned array. This array is also displayed on the front panel, but is only visible by scrolling down (Figure 4.35). In this table all values recorded since the start of the measuring are listed. The table can be reset by pushing the reset button. Below the table, there is a graph depicting the relation between voltage and time.

time	T PEM [°C]	voltage [V]	current [A]	conduc.[uS]	humidity [ppmv]	dew point [°C]	pressure [barg]	flow rate [l/min]	comment
20:06:43	21,38	0,120	0,01	0,13	169	-39,0	-0,00	0,00	
20:06:48	21,38	0,120	0,01	0,13	157	-39,0	0,01	0,00	
20:06:53	21,39	0,120	0,01	0,13	168	-39,0	0,01	0,00	Start
20:06:58	21,41	0,120	0,01	0,13	169	-39,0	0,01	0,00	
20:07:03	21,43	0,120	0,02	0,13	156	-38,9	0,01	0,00	
20:07:08	21,43	0,120	0,01	0,13	179	-39,0	0,01	0,00	
20:07:13	21,40	0,120	0,02	0,13	169	-39,0	0,00	0,00	
20:07:18	21,43	0,120	0,02	0,13	172	-39,0	0,00	0,00	
20:07:23	21,39	0,120	0,01	0,13	171	-39,0	-0,00	0,00	

Figure 4.35: Table and graph of measured values on front panel

4.4 Possibilities to use the produced energy

The energy amount produced by the solar cells is about 660 $^{\mathrm{kWh}}/_{\mathrm{a}}$. Losses related to the production of hydrogen reduces the maximum storable amount to 460 $^{\mathrm{kWh}}/_{\mathrm{a}}$. The solar cells have been dimensioned with the intention to constantly provide the electrolyser with energy. The primary aim of this project was to realise a stand alone system which produces hydrogen with the energy of a solar cell system. It was only secondary to focus on how to use the produced energy. In this section, the possibilities of using the produced energy are examined from 2 different perspectives.

1. In which basic conditions can the produced energy be used?
2. What are the possibilities to use the stored energy in the metal hydride container (2 kWh)?

4.4.1 In which basic conditions can the produced energy be used?

The possibilities of using the produced energy is strongly related to the energy consumption of the used electronic devices. Energy efficient electronic devices can of course operate for a longer time than uneconomic devices. With regards to a stand-alone system, it is absolutely necessary to use electronic devices, which are energy efficient since the available energy amount is limited. Table 4.3 provides an overview of electronic devices which are used at home, their power consumption and their energy consumption per year for a one person household.

The values in table 4.3 are estimated for energy efficient devices and a thrifty use of them. As one can see, it is possible to live with about 600 kWh per year. For this estimation it has been assumed that propane gas is used for cooking and warm water is provided by a solar heating system. If the baking oven would also operate with propane gas, the necessary energy amount per year would be reduced to about 460 kWh. According to this value, the installed solar cells would suffice to provide enough energy for a one person household using energy efficient electronic devices.

A problem with running some of the electronic devices is their high power consumption. An electronic iron or a washing machine require a power of about 2000 W. The power a metal hydride storage can provide, is related to the hydrogen flow rate that it is able to deliver. The installed metal hydride storage is only able to deliver a flow rate of about 2.3 $^{\mathrm{Nl}}/_{\mathrm{min}}$, which is equivalent to a power of about 400 W. Hence, in order to provide a constant power of 2000 W, 5 metal hydride storages would

electric device	power [W]	energy per year [kWh/a]
energy saving lamp	3 x 15	45
fridge	200	84
laptop	50	55
tv	45	40
stereo	35	40
vacuum cleaner	1000	26
mobile charger	4	1.5
printer	13	0.5
toaster	1000	20
water boiler	1500	30
washing machine	2000	90
electric iron	2000	20
coffee machine	800	15
oven	1500	110
Overall		**577**

Table 4.3: Estimation of the energy consumption of electronic devices for a one person household (References: [29], [30], [31], [50])

have to operate parallel. The cost for one metal hydride is about 1300 Euro. Furthermore, the fuel cell must be also able to transform the high amount of hydrogen into electrical energy. The company Heliocentris sells fuel cell stacks with a power of 2100 W for a price of 20.000 Euro. Hence, if the experimental rig is supposed to provide a power of 2000 W, the cost would increase drastically. Consequently, in order to prevent these additional purchases, the use of electronic devices with a high power consumption should be avoided. For example, instead of using a vacuum cleaner, a broom could be used.

Instead using the stand-alone system throughout the whole year, a good possibility is to use it in summer holiday homes. Often, these houses are in warm and sunny areas, which has several advantages. Firstly, more energy is produced, due to the increased hours of sunshine. Secondly, the house is only used in the summer time which decreases the necessary energy amount per year. A solar heating system could provide warm water for showering and since the house is just temporarily used, the electrical energy of the stand alone system build in this project may also suffice to provide enough energy for cooking. Therefore the use of propane gas would not be necessary.

4.4.2 What are the possibilities to use the stored energy in the metal hydride container (2 kWh)?

Currently, only 1 metal hydride container is installed. This one can store hydrogen equivalent to an energy amount of 2 kWh. The question is, what can be operated with these 2 kWh. According to table 4.3, 577 kWh are consumed by one person per year. At one day, this is an energy consumption of 1.58 kWh. Hence, without sunshine, the metal hydride container would be empty in less than two days. In order to increase the time of the usage of the electronic devices, a larger or additional metal hydride container must be installed. In order to use the electronic devices at least for three days, the metal hydride container must be able to store hydrogen equivalent to 5 kWh. An adequate metal hydride container is listed in chapter 9.

Another problem by using only a 2 kWh metal hydride storage is its filling. It can not be guaranteed to store all the energy which is produced by the solar cells. The solar cells produce an average energy amount of 1.25 kWh per day. Accordingly, the metal hydride storage will be full in about two days, which is another reason to increase the storable amount of hydrogen.

From a different perspective, using only the small powered electronic devices, would increase their time of usage. If only the electronic devices below a power of 500 W of table 4.3 are being used, this would result in a necessary energy amount of 0.73 kWh per day.

$$\frac{(45+84+55+40+40+1.5+0.5)\ \mathrm{Wh/day}}{365\ \text{days}} = 0.73kWh \tag{4.4}$$

An energy consumption of 0.73 kWh per day, would enable the metal hydride container to provide electrical energy for almost three days. Hence, if only small powered electronic devices like tv, stereo, refrigerator or lamps are being used, a metal hydride container, whit a storage capacity of 2 kWh is sufficient.

4.5 Cost

Building a new experimental rig is a cost intensive process. In this regard, the usage of hydrogen was a significant factor for the high costs of this project, since almost all parts have to be resistant to hydrogen and must be able to withstand a pressure of 11 bar. This section provides an overview of the costs of all parts that have been mounted in the experimental rig. Such parts, which have been previously installed, and then got exchanged with improved or different parts are not listed. There are also some parts which have been sponsored by their manufacturer. These are also listed, but in most cases their price could only be estimated.

The costs are separated into three different categories: Electronic and measuring devices, connections parts and build up, functional parts.

4.5.1 Electronic and measuring devices

The control and the measurement of the setup has been managed with separate electronic devices. Also the cabling and the power supply are included in this field. The following table lists all installed parts, which fall into this category.

device	name	cost [Euro]
24 V power supply	Puls ML70.100	83
12 V power supply	Puls ML30.102	67
laboratory power supply	EA-PS 3016-20 B	300
solar cells	Ralos - RA 160 M	sponsored (4000)
water pump	KNF - NF10	237
dew point transmitter	Vaisala - DMT 340	2170
cabling, switches, etc.	various	100
mass flow meter	Manger + Wittmann - D-5110	in stock (600)
vacuum pump	KNF - N86 KNDC B	237
measurement card	NI PCI 6025	in stock (1100)
pressure sensor	Gems - 1000 BGB	98
heater mate	RS components	29
measuring transducer	Jumo - dTRANS T03	48
PT100 sensors	various	85
electromagnetic valves	GSR - G052 + G075	172
computer	-	in stock (200)
Overall (incl. sponsored)		3626 (9526)

Table 4.4: Cost for electronic and measuring devices

4.5.2 Connection parts and build up

This cost field lists the cost for the framework, the tubes and the fittings. The framework is a mobile table with a rear panel. It is manufactured by the workshop of the Hochschule Darmstadt and consist mainly of aluminum. On this table all the measurement devices, filters and connection parts are mounted. The connection parts, tubes and fittings are manufactured by the german company Serto GmbH. Since these parts are in contact with pressurised hydrogen, they consist of stainless steel.

device	**company - name**	**cost [Euro]**
stainless steel tubes	Serto - SO 51521-6	50
fittings	Serto - various	330
valves	Serto - various	135
table	Isel - various	in stock
screws, nuts, etc.	various	20
miscellaneous	various	50
Overall		585

Table 4.5: Cost for connection parts and build up

4.5.3 Functional parts

The functional parts are those parts which have a major task in the experimental rig, like the dryer or the metal hydride storage.

device	**company - name**	**cost [Euro]**
electrolyser	Sylatech	sponsored (7000)
water separator	M&C Tech Group - ADS-SS	390
ion exchanger	SG water GmbH - SG700	430
back pressure valves	Parker - ABP 1	325
dryer	Landefeld - BHL 0,1/16 ES	70
silica gel	Carl Roth - silica gel 2.5 kg	45
particle filter	Pure Gas Products - GSP37	230
safety relief valve	Wittgas - SV 805	80
metal hydride storage	H Bank - HB-SC-0660-N-L	2200
non return valve	Wittgas - R 53	42
pressure reducer	Landefeld - DR 00-16	25
Overall		3837 (10837)

Table 4.6: Cost for connection parts and build up

4.5.4 Summary cost

The sum of these three cost fields results in an overall cost of about 8,050 Euro. Furthermore, if the sponsored and already existing parts are also included in this calculation the overall costs increase to about 21,000 Euro. Hence, the supporting companies contributed greatly in reducing the costs of the rig. So far, the cost for a fuel cell which is supposed to be connected to the rig in the future, is not included in the calculations either. In order to build a market-ready product, there are of course possibilities to reduce the costs. The high accuracy of the measurement devices is not necessary and the mass production of this system would also lower the price. When ordered in large quantities, the cost for the electrolyser and the metal hydride storage clearly be lower. Also, it might be possible to use different connection parts, since the ones from Serto GmbH are of high quality but, thus, come at a high price. In the future, further research on ways to save cost could greatly contribute to making the rig market ready.

5 Efficiency

The efficiency is the percentage of the total energy output obtained from the total energy input, in other words, the difference between input power and output power. The total input power of an electrolyser results from multiplying the input voltage by the input current. The total output power is the hydrogen value, which can be expressed as a power where 1 $\mathrm{m^3/h}$ = 2.94 kW. The losses which occur are the difference between input power and output power. When constructing an energy storage system it is necessary to calculate this value.

The current chapter deals with the energy necessary for the electrolysis and explains the factors which influence the electrolyser's efficiency.

5.1 Minimum required energy for electrolysis

In order to split water into hydrogen and oxygen, a certain amount of electrical energy is necessary. This energy amount is known as the Gibbs free energy (ΔG). It is the minimum electrical energy necessary for the electrolysis.

$$\Delta G = \Delta H - T \cdot \Delta S \tag{5.1}$$

As equation 5.1 shows, the Gibbs free energy is the difference between the enthalpy of water (ΔH) minus the product of entropy (ΔS) and temperature (T). The enthalpy is the thermodynamic potential of water. In order to split water into hydrogen and oxygen, energy equal to the amount of the enthalpy must be applied. Since the environment has also its own internal energy, some of the necessary energy can be provided by the environment. This amount of heat energy is equal to the entropy multiplied by the environmental temperature.

The following values for enthalpy and entropy are for standard conditions
($T = 25°\mathrm{C}\ (298.15\ \mathrm{K}), p = 1.01325\ \mathrm{bar}$):

$$\Delta H = 285.83\ \mathrm{kJ/mol} \tag{5.2}$$

$$\Delta S = 162.63 \ {}^{\mathrm{J}}/_{\mathrm{mol\ K}} \tag{5.3}$$

$$\Delta S \cdot T = 162.63 \ {}^{\mathrm{J}}/_{\mathrm{mol\ K}} \cdot 298.15 \ \mathrm{K} = 48.49 \ {}^{\mathrm{kJ}}/_{\mathrm{mol}} \tag{5.4}$$

Hence, the result for the Gibbs free energy is:

$$\Delta G = 285.83 \ {}^{\mathrm{kJ}}/_{\mathrm{mol}} - 48.49 \ {}^{\mathrm{kJ}}/_{\mathrm{mol}} = 237.34 \ {}^{\mathrm{kJ}}/_{\mathrm{mol}} \tag{5.5}$$

Michael Faraday was the first scientist who researched the efficiency of the electrolysis. He published the Faraday's laws of electrolysis in 1834.

> **Faraday's 1st Law of electrolysis:** The mass of a substance altered at an electrode during electrolysis is directly proportional to the quantity of electricity transferred at that electrode.

According to Faraday's 1st law, there is no loss of electricity during the electrolysis. Every electron combines with a proton to form a hydrogen atom. Hence, the efficiency of the electrolysis is only related to the voltage.

$$\eta = \frac{V_0 \cdot I}{V_{real} \cdot I} = \frac{V_0}{V_{real}} \tag{5.6}$$

1 hydrogen molecule consists of two hydrogen atoms ($n = 2$). 1 mol hydrogen consists of $6.022 \cdot 10^{23}\ {}^{1}/_{\mathrm{mol}} \cdot 2$ particles, which is the Avogadro constant multiplied by the number of atoms in that molecule. In order to produce 1 mol of hydrogen the electrical charge Q is necessary, which is the following:

$$Q = n \cdot N_A \cdot e = 2 \cdot 6.022 \cdot 10^{23}\ \mathrm{mol}^{-1} \cdot 1.602 \cdot 10^{-19}\ \mathrm{As} \tag{5.7}$$

e is the elementary charge of one electron. The electrical charge of 1 mol is therefore the elementary charge of 1 hydrogen molecule multiplied by the Avagadro constant. The multiplication of the Avagadro constant and the elementary charge is also known as the Faraday constant ($F = N_A \cdot e = 96485.34\ {}^{\mathrm{C}}/_{\mathrm{mol}}$). The minimum energy required for the electrolysis is $237.34\ {}^{\mathrm{kJ}}/_{\mathrm{mol}}$. In order to obtain the minimum voltage (V_0), the Gibbs free energy must be divided by the electrical charge of 1 mol hydrogen.

$$V_0 = \frac{\Delta G}{n \cdot N_A \cdot e} \tag{5.8}$$

$$V_0 = \frac{\Delta G}{n \cdot F} \tag{5.9}$$

$$= \frac{237.34 \ {}^{\mathrm{kJ}}/_{\mathrm{mol}}}{2 \cdot 96485.34 \ {}^{\mathrm{As}}/_{\mathrm{mol}}} \tag{5.10}$$

$$= 1.23 \text{ V} \tag{5.11}$$

5.1.1 Influence of temperature on the energy needed for electrolysis

According to equation 5.11, the minimum ideal voltage needed for electrolysis is 1.23 V. This result is valid for standard conditions. At a different temperature or pressure range, the necessary energy for the electrolysis changes due to the variation in the water's internal energy (U). The sum of the internal energy of water and the energy which is necessary for the expansion of the gas ($p \cdot \Delta V$) is known as the enthalpy.

$$\Delta H = \Delta U + p \cdot \Delta V \tag{5.12}$$

Change of the water's internal energy

At standard conditions the internal energy of water is:

$$U_0 = -282.1 \ {}^{\mathrm{kJ}}/_{\mathrm{mol}} \tag{5.13}$$

The internal energy of chemical elements at their most stable state (H_2, O_2, He, Li...) is 0 ${}^{\mathrm{kJ}}/_{\mathrm{mol}}$ per definition. Since both hydrogen and oxygen are among these elements, the difference between the internal energy of water and the internal energy of the two gases is:

$$\Delta U_0 = 282.1 \ {}^{\mathrm{kJ}}/_{\mathrm{mol}} \tag{5.14}$$

If there is a change in temperature, the internal energy of water will also change. A higher temperature results in a higher internal energy, while a lower temperature results in lower internal energy. The relation between the water's internal energy and the temperature can be calculated as shown in equation 5.15.

$$\Delta U(T) = \Delta U_0 - \Delta U_T \cdot N_A \tag{5.15}$$

ΔU_T is the change in internal energy, which is the difference between the internal energy at standard conditions (ΔU_0) and the internal energy which is related to the temperature ($U(T)$). In order to obtain a relation between the change in internal energy and the amount of water which changes its temperature, ΔU_T is multiplied by the Avogadro constant (N_A). The exact calculation of ΔU_T is shown in equation 5.16:

$$\Delta U_T \cdot N_A = \frac{3}{2} \cdot f \cdot k \cdot \Delta T \cdot N_A \tag{5.16}$$

f is the degree of freedom which, in the case of water, is 6. k is the Boltzmann constant with a value of $1.308065 \cdot 10^{-23}$ J/K and ΔT is the temperature difference to 25°C.

$$\Delta T = T_{new} - T_0 \tag{5.17}$$

A multiplication of the Boltzmann constant by the Avogadro constant results in the ideal gas constant ($R = 8.314$ J/mol K), which changes equation 5.16 to equation 5.19. Hence, equation 5.15 changes as well and results in equation 5.20:

$$R = k \cdot N_A \tag{5.18}$$

$$\Delta U_{Tmol} = \frac{3}{2} \cdot f \cdot R \cdot \Delta T \tag{5.19}$$

$$\Delta U(T) = \Delta U_0 - \Delta U_{Tmol} \tag{5.20}$$

An example calculation with temperature increase of 30 K is shown in the following equation:

$$U(T) = 282.1\ \mathrm{kJ/mol} - \frac{3}{2} \cdot 6 \cdot 8.314\ \mathrm{J/mol\ K} \cdot 30\ \mathrm{K} \tag{5.21}$$

$$= 282.1\ \mathrm{kJ/mol} - 2.24\ \mathrm{kJ/mol} \tag{5.22}$$

$$= 279.86\ \mathrm{kJ/mol} \tag{5.23}$$

According to the result in equation 5.23, an increase of 30 K results in a change of 2.24 kJ in the water's internal energy.

Energy for the expansion of the produced gases

The calculation for the change of the water's internal energy is completed. Hence, the first part of equation 5.12 is known. In order to calculate the total value of the enthalpy, it is necessary to know how much work needs to be expended for the expansion of the gases.

$$W = p \cdot \Delta V \tag{5.24}$$

The pressure is constant (p = 101325 Pa), while the volume change (ΔV) is the difference between final state and initial state.

$$\Delta V = V_{end} - V_{start} \tag{5.25}$$

The volume of condensed fluids is much smaller than the volume of a gas. Due to the large volume difference between fluid water and expanded gas, the volume of the water has very little influence on the result and can be disregarded. Hence, the volume change is the same as the final volume.

$$\Delta V = V_{end} \tag{5.26}$$

The work for the gas expansion is graphically depicted in figure 5.1.

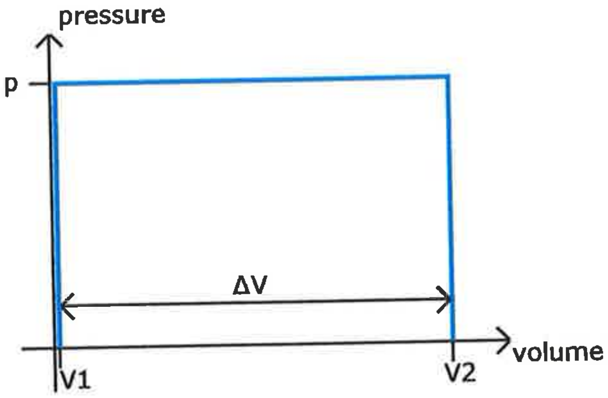


Figure 5.1: Required energy for the expansion of the produced gases

In order to calculate the volume of gas, the ideal gas law can be used.

$$\Delta V = \frac{nRT}{p} \tag{5.27}$$

R is the ideal gas constant; T is the temperature of the gas; p is the pressure of the gas and n is the number of mol which are produced. The electrolysis of water results in 1 mol H_2 and 0.5 mol O_2. Overall this is a gas production of 1.5 mol.

$$1n_{H_2O} = 1n_{H_2} + \frac{1}{2}n_{O_2} \tag{5.28}$$

The unit of the enthalpy and the internal energy is $^{kJ}/_{mol}$, while kJ is the unit of volume change. The volume change must be divided by n in order to include it in an equation with the enthalpy and the internal energy. The factor 1.5 stays on the right side of the equation, since the unit is kJ per 1 mol.

$$\begin{aligned} \Delta V_{mol} &= \frac{\Delta V}{n} && (5.29) \\ &= \frac{RT}{p} \cdot 1.5 && (5.30) \end{aligned}$$

Now that all unknown factors have been eliminated, it is possible to calculate the work per mol, as shown in equation 5.33.

$$W_{mol} = p \cdot \Delta V_{mol} \tag{5.31}$$

$$= p \cdot \frac{RT}{p} \cdot 1.5 \tag{5.32}$$

$$= RT \cdot 1.5 \tag{5.33}$$

The following example calculates the work at a temperature of 328.15 K (55°C).

$$W_{mol} = RT \cdot 1.5 \tag{5.34}$$

$$= 8.314\ {}^{\mathrm{J}}/_{\mathrm{mol\ K}} \cdot 328.15\ \mathrm{K} \cdot 1.5 \tag{5.35}$$

$$= 4.09\ {}^{\mathrm{kJ}}/_{\mathrm{mol}} \tag{5.36}$$

Having obtained the values for the internal energy of water and the energy for the expansion of the gases, the enthalpy can be calculated for different temperatures.

$$\Delta H = \Delta U_0 - \Delta U_{Tmol} + p \cdot \Delta V \tag{5.37}$$

$$\Delta H = \Delta U_0 - \frac{3}{2} \cdot f \cdot R \cdot \Delta T + RT \cdot 1.5 \tag{5.38}$$

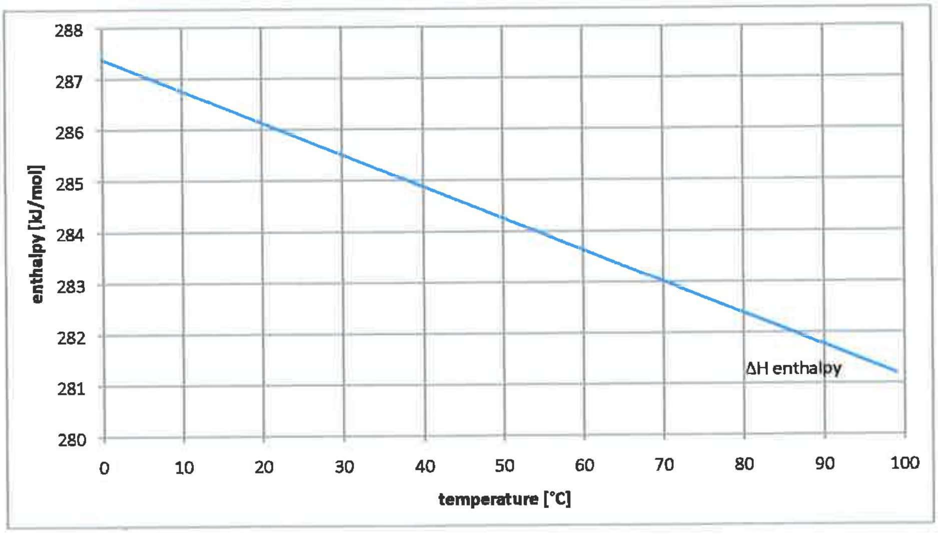


Figure 5.2: Enthalpy in relation to the temperature

Figure 5.2 shows that the enthalpy decreases with an increasing temperature. Due to the higher temperature, the water is closer to the boiling point less energy is necessary to reach the gaseous state.

Energy provided by the environment

The energy necessary for the electrolysis is a mixture of electrical energy and heat energy provided by the environment. At higher temperatures, less electrical energy is necessary and at lower temperatures, more electrical energy is required. This amount of heat energy (Q) is equal to the temperature (T) multiplied by the entropy change (ΔS).

$$Q = T \cdot \Delta S \tag{5.39}$$

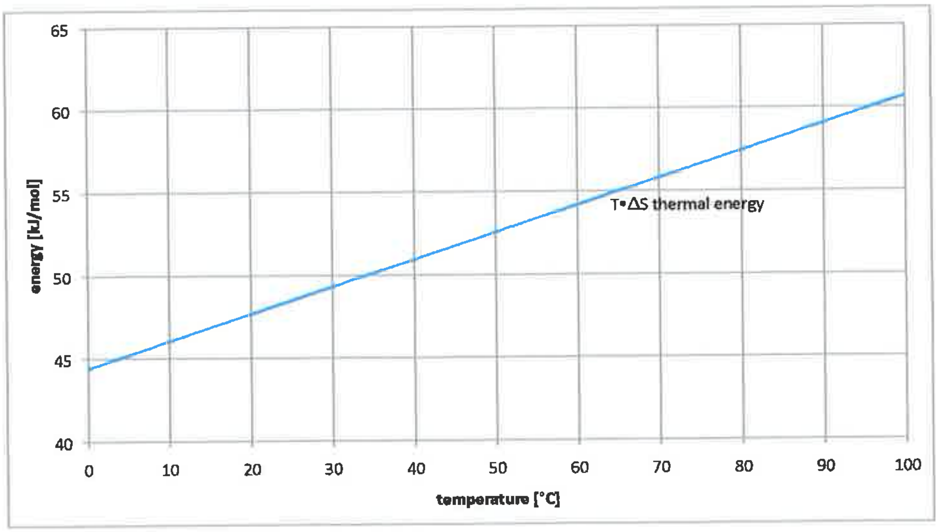


Figure 5.3: Heat energy for the electrolysis which is provided by the environment

For standard conditions the heat energy is $Q = 48.49\ ^{\mathrm{kJ}}/_{\mathrm{mol}}$. At higher temperatures, more heat energy is available for the electrolysis (Figure 5.3). A temperature increase of 30 Kelvin, results in a heat energy of $53.37\ ^{\mathrm{kJ}}/_{\mathrm{mol}}$.

$$Q = (298.15\ \mathrm{K} + 30\ \mathrm{K}) \cdot 162.63\ ^{\mathrm{kJ}}/_{\mathrm{mol\ K}} = 53.37\ ^{\mathrm{kJ}}/_{\mathrm{mol}} \tag{5.40}$$

Summary of the temperature's influence on electrolysis

Having calculated the enthalpy ΔH, as well as the thermal energy $\Delta S \cdot T$, the Gibbs free energy can be calculated for different temperatures. Diagram 5.4 shows the thermal energy, the Gibbs free energy and the thermal energy in relation to the temperature.

As already mentioned, the enthalpy decreases with increasing temperature. The thermal energy of the environment, on the contrary, increases proportionally to the

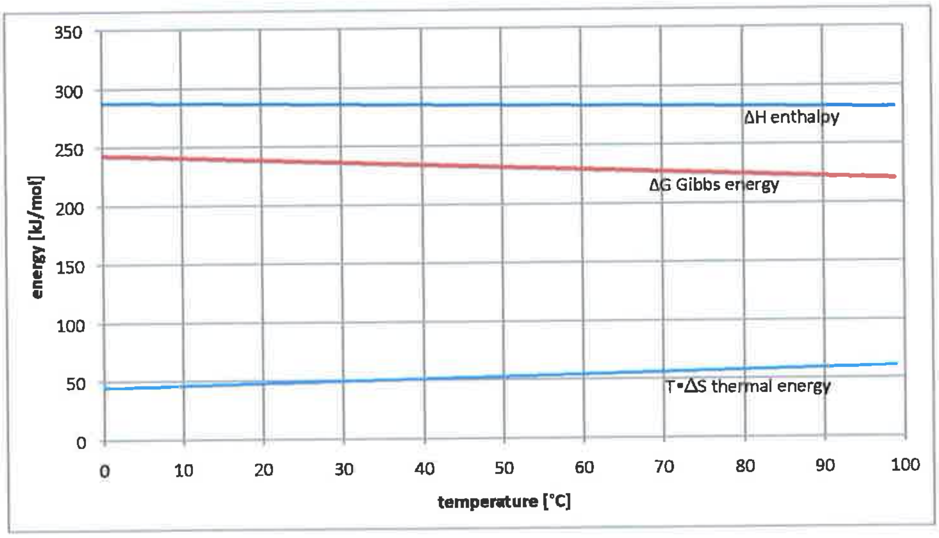


Figure 5.4: Entropy, Gibbs energy and enthalpy in relation to the temperature

temperature. Hence, at higher temperatures more energy is provided by the environment and less energy is necessary to split the water. The Gibbs free energy is the result subtracting the thermal energy from the enthalpy and represents the electrical energy which is necessary for the electrolysis. As figure 5.4 shows, less electrical energy is necessary if the process of electrolysis runs at higher temperatures.

A temperature increase of one Kelvin results in an energy change of 225 $^{\mathrm{J}}/_{\mathrm{mol}}$ (equation 5.41) which is equivalent to a voltage change of 1.2 mV (equation 5.42).

$$\Delta G(T) - \Delta G(T+1) = 225\ ^{\mathrm{J}}/_{\mathrm{mol\ K}} \tag{5.41}$$

$$\frac{\Delta G(T)}{2F} - \frac{\Delta G(T+1)}{2F} = 1.2\ ^{\mathrm{mV}}/_{\mathrm{K}} \tag{5.42}$$

5.1.2 Influence of pressure on the energy needed for electrolysis

In the previous section, the energy for the expansion of the gas has been calculated for a constant pressure. Since the electrolyser usually runs at a pressure of 11 bar, the work for the gas expansion at a higher pressure needs to be included into the calculation for gas expansion. The influence of an increased pressure results in an additional work for gas expansion. This changes equation 5.24 into equation 5.43:

$$W = p \cdot \Delta V + \int_{V2}^{V1} p(V)\ dV \tag{5.43}$$

$$= \quad RT \cdot 1.5 + \int_{V2}^{V1} \frac{nRT}{V} \, dV \tag{5.44}$$

Figure 5.5 exemplifies how much energy is necessary when using an increased pressure during the process of the electrolysis. As one can see, using a higher pressure

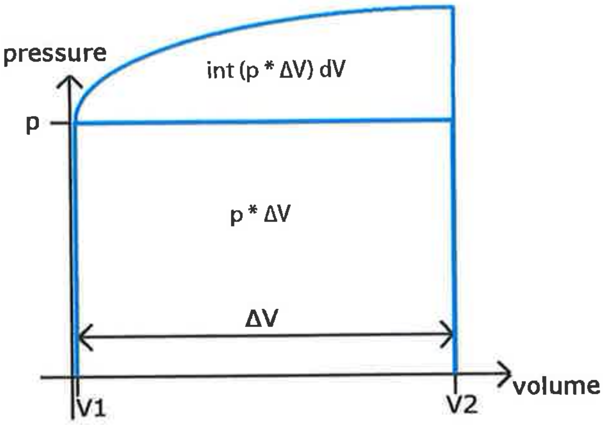


Figure 5.5: Energy for the expansion of the produced gases at various pressures

requires more energy for the expansion of gases. Besides the energy amount which is necessary at standard conditions ($p \cdot \Delta V$), additional energy is necessary to produce the higher pressure ($\int_{V2}^{V1} p(V) \, dV$). The sum of these two energy amounts results in the overall energy amount necessary for the expansion of gases at a higher pressure (equation 5.43). The resolution of this equation is shown in equation 5.45.

$$W = RT \cdot 1.5 + nRT \cdot ln \frac{p_2}{p_1} \tag{5.45}$$

The electrolysis of water results in the production of two gases. 1 mol H_2O is split into 1 mol H_2 and 0.5 mol O_2. The consideration of this fact requires an adaptation of equation 5.45.

$$W_{H_2O} = RT \cdot 1.5 + RT \cdot \left(\frac{1}{2} \cdot ln \frac{p_{O_2}}{p_0} + ln \frac{p_{H_2}}{p_0} \right) \tag{5.46}$$

p_{O_2} is the pressure of the oxygen gas, p_{H_2} is the pressure of the hydrogen gas and p_0 is the atmospheric pressure. Now, it is possible to calculate the energy required for the expansion of gases at different pressures and temperatures. Hence, the Gibbs free energy can be calculated completely.

$$\Delta G = U(T) + RT \cdot 1.5 + RT \cdot \left(\frac{1}{2} \cdot ln \frac{p_{O_2}}{p_0} + ln \frac{p_{H_2}}{p_0} \right) - T \cdot \Delta S \tag{5.47}$$

In order to translate the result into voltage, all factors are divided by $2F$.

$$V = \frac{U(T)}{2F} + \frac{RT \cdot 1.5}{2F} + \frac{RT}{2F} \cdot \left(\frac{1}{2} \cdot ln \frac{p_{O_2}}{p_0} + ln \frac{p_{H_2}}{p_0} \right) - \frac{T \cdot \Delta S}{2F} \tag{5.48}$$

Using this equation at a constant temperature of $T = 25$ °C, equation 5.48 can be rearranged into the Nernst equation.

$$V = \frac{\Delta G^\circ}{2F} + \frac{RT}{2F} \left(\frac{1}{2} \cdot ln \frac{p_{O_2}}{p_0} + ln \frac{p_{H_2}}{p_0} \right) \tag{5.49}$$

The Nernst equation is named after the German physical chemist Walther Nernst who first formulated the equation. This equation considers the influence of pressure on the energy required for electrolysis. However, the Nernst equation does not consider the influence of temperature on the enthalpy at non-standard conditions. Therefore, equation 5.48 will be used for the following calculations.

The construction of the electrolyser makes it possible to pressurise the electrolyser only on the hydrogen side, while the oxygen side is at atmospheric pressure and can therefore be eliminated from equation 5.48.

$$V = \frac{U(T)}{2F} + \frac{RT \cdot 1.5}{2F} - \frac{T \cdot \Delta S}{2F} + \frac{RT}{2F} \cdot ln \frac{p_{H_2}}{p_0} \tag{5.50}$$

The graphical representation of equation 5.50 is depicted in figure 5.6, which shows, as does figure 5.5, that more energy is necessary when the electrolyser operates at a higher pressure. Also, one can see that most of the energy is consumed at lower pressure levels. A further increase in pressure does not need so much energy. Due to the natural logarithm in equation 5.50, doubling the pressure always needs the same energy. Hence, a pressure increase from 1 to 2 bar needs the same energy as a pressure increase from 5 to 10 bar.

An increase in pressure from 1 to 11 bar, results in an additional energy expenditure of about 30.8 mV.

$$\begin{aligned}
V &= \frac{285.83\ {}^{\mathrm{kJ}}/_{\mathrm{mol}}}{2 \cdot 96485.34\ {}^{\mathrm{As}}/_{\mathrm{mol}}} - \frac{48.49\ {}^{\mathrm{kJ}}/_{\mathrm{mol}}}{2 \cdot 96485.34\ {}^{\mathrm{As}}/_{\mathrm{mol}}} && (5.51)\\
&\quad + \frac{8.314\ {}^{\mathrm{J}}/_{\mathrm{mol\ K}} \cdot 298.15\ \mathrm{K}}{2 \cdot 96485.34\ {}^{\mathrm{As}}/_{\mathrm{mol}}} \cdot ln \frac{11\ \mathrm{bar}}{1\ \mathrm{bar}} && (5.52)\\
&= 1.2608\ \mathrm{V} && (5.53)\\
\Delta V &= V - V_0 = 1.2608\ \mathrm{V} - 1.23\ \mathrm{V} = 0.0318 V && (5.54)
\end{aligned}$$

11 bar is the pressure which is necessary to store the hydrogen in a metal hydride

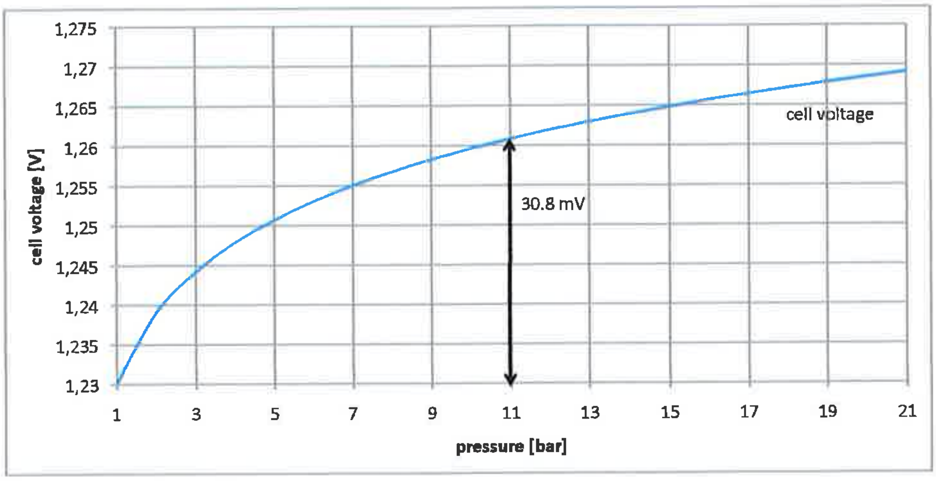


Figure 5.6: Influence of pressure on the cell voltage

storage. The loss in efficiency of about 2.5% is very low, compared to the energy which would be necessary if a compressor was used.

5.1.3 Summary of the minimum energy needed for electrolysis

Temperature and pressure both have an influence on the energy needed for electrolysis. While a high temperature improves the process of the electrolysis, a high pressure increases the necessary energy.

Since a high temperature increases the efficiency, the electrolyser is isolated in styrofoam. The insulation keeps the heat resulting from the ohmic losses near the electrolyser making it possible to use this for improving the efficiency.

In order to effectively store the hydrogen in a metal hydride storage, it is essential to use a higher pressure. The electrolyser used in this project can produce this pressure by itself in the process of the electrolysis. It is not necessary to use an external compressor. Additionally, the electrolyser pressurises the hydrogen very effectively. There are no moving parts which could cause losses. A compressor, on the contrary, has pistons and an engine, both of which are moving and therefore cannot be as effective as the electrolyser.

Figure 5.7 shows some examples for different pressure and temperature ranges.

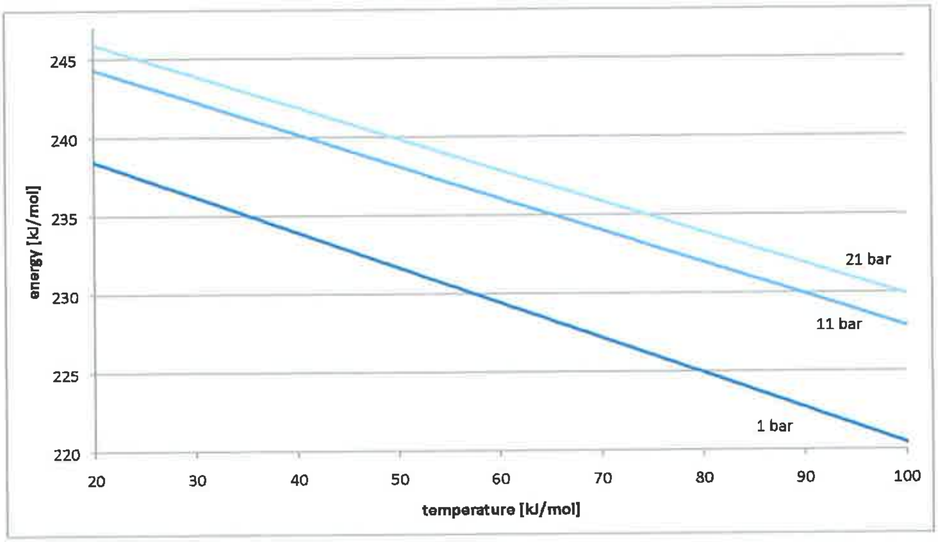


Figure 5.7: Influence of pressure and temperature on the Gibbs energy

5.2 Influence of current on the energy needed for electrolysis

The previous section has explained how much energy is necessary for electrolysis. Those calculations have not considered the influence of the electric current. From the view of an electrical engineer, one can say that only the open circuit voltage has been calculated. In fact, the current causes ohmic and activation losses, both of which have an influence on the efficiency of the electrolyser. This section explains how these losses occur and how great their influence is.

5.2.1 Activation losses

In order to start the splitting of water, the process of the electrolysis needs activation energy. This activation energy forces the hydrogen to split into electrons and protons. Additionally, the protons are forced to travel through the membrane. The activation energy is only necessary at the beginning of electrolysis, which means that the losses mostly occur at a low current. At a higher current, almost no losses occur due to the activation losses.

Activation losses ΔV_{act} lead to an increase of the necessary voltage of electrolysis. Hence, a more precise denotation would be: "activation voltage losses". The following equation, known as the "Tafel equation", shows how to calculate these losses.

$$\Delta V_{act} = \frac{RT}{n \cdot \alpha \cdot F} \cdot ln\frac{I}{I_0} \tag{5.55}$$

The ideal gas constant R, the temperature T, the number of electrons n and the Faraday constant F have been introduced in the previous chapter. The current I, which can be set manually or by the solar cells, is also known. The new elements in this equation are the charge transfer coefficient α and the exchange current I_0.

Charge transfer coefficient

The charge transfer coefficient is a value between 0 and 1 that shows how the electrical energy is distributed to the anode and cathode reaction. A value of almost 0 would mean that the reaction at the cathode was be very good, while the anode reaction was very poor. Looking at equation 5.55, it is clear that a low α would result in higher losses since it is placed in the denominator. This higher losses occur due to the speed of the anode reaction. If the anode reaction (which is the first and slower part of the reaction) does not provide enough protons and electrons, the cathode reaction will have no particles to react with, which would result results in higher losses. On the contrary, if the anode reaction operates at a maximum speed ($\alpha = 1$), the cathode reaction will also work faster and the losses would be lower.

Exchange current

An electrochemical cell always has a dynamic equilibrium. I_a is the current at the anode and I_c is the current at the cathode, which has the same absolute value as I_a, but flows in the opposite direction. These minimal currents flow without producing any losses and since they both have the same absolute value, they are denoted by I_0. Hence, I_0 is the maximum current which can flow before the activation voltage losses occur.

Determination of the charge transfer coefficient and the exchange current

The charge transfer coefficient and the exchange current are related to the catalyst of the electrolyser. Better catalysts would improve their values and would result in less activation voltage losses. The company Sylatech, who manufactured the electrolyser, provides no information about the charge transfer coefficient or the exchange current. Hence, they must be determined empirically.

In order to determine α and I_0, the activation voltage losses ΔV_{act} have been measured at small currents. The results of this measurement are shown in a diagram (fig. 5.8), in which the x-axis is the natural logarithm of the current density and the y-axis is the activation voltage loss.

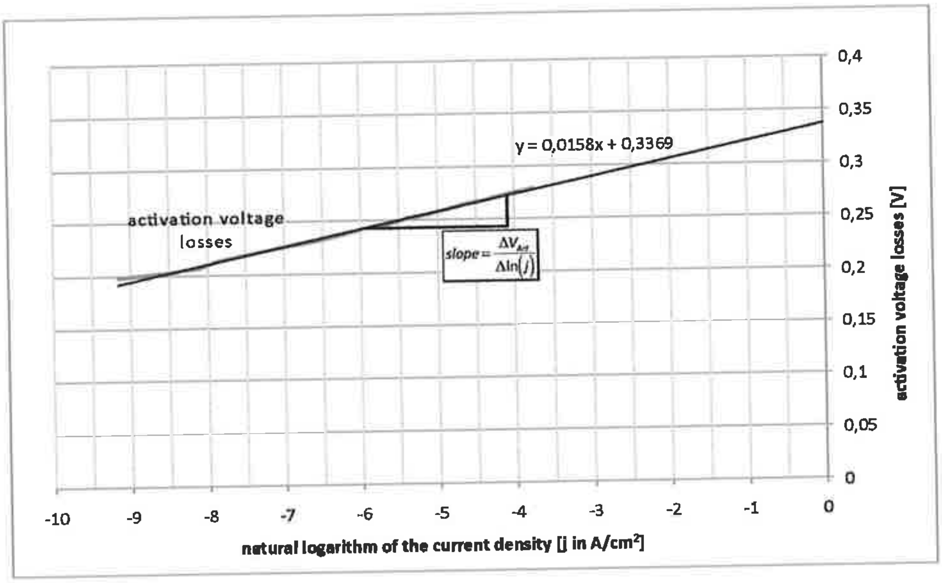


Figure 5.8: Activation voltage losses at small currents

The slope of the graph is the quotient of the y and the x-axis.

$$slope = \frac{\Delta y}{\Delta x} \tag{5.56}$$

In this case, the slope is the loss of activation voltage divided by the natural logarithm of the current density.

$$slope = \frac{\Delta V_{act}}{\Delta ln(j)} \tag{5.57}$$

The slope is also the first part of the Tafel-equation.

$$slope = \frac{RT}{n \cdot \alpha \cdot F} \tag{5.58}$$

Having obtained the slope, it is now possible to calculate the charge transfer coefficient.

$$\alpha = \frac{RT}{n \cdot slope \cdot F} \tag{5.59}$$

As shown in figure 5.8, the slope of the activation losses for this electrolyser is 0.0158 V. This value can be used to calculate the charge transfer coefficient.

$$\alpha = \frac{8.314\ {}^{\mathrm{J}}\!/_{\mathrm{mol\ K}} \cdot 298.15\ \mathrm{K}}{2 \cdot 0.0158\ \mathrm{V} \cdot 96485.3\ {}^{\mathrm{As}}\!/_{\mathrm{mol}}} = 0.813 \tag{5.60}$$

According to equation 5.60, the charge transfer coefficient is 0.813. The next step is to calculate the exchange current. In figure 5.8 the curve intercepts the y-axis at 0.3369 V. Consequently, the intercept point with the x-axis is -21.32. This results in the following exchange current density:

$$j = e^{-21.32}\ {}^{A}/_{cm^2} = 5.49 \cdot 10^{-10}\ {}^{A}/_{cm^2} \tag{5.61}$$

A multiplication by the size of the surface area, results in the exchange current.

$$5.49\ {}^{A}/_{cm^2} \cdot 10^{-10} \cdot 66.48\ cm^2 = 3.65 \cdot 10^{-8}\ A \tag{5.62}$$

Influence of activation losses on the efficiency

The charge transfer coefficient and the exchange current density are now known and the activation losses can be calculated for different current densities. Figure 5.9 shows the overvoltage due to activation voltage losses compared to the ideal voltage.

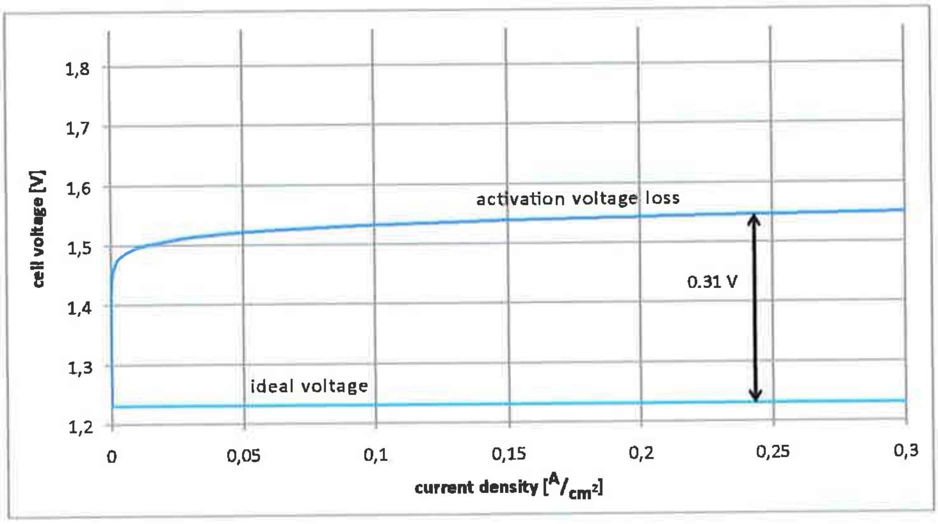


Figure 5.9: Activation voltage losses related to the current density

As one can see in figure 5.9, the activation voltage losses occur almost exclusively at the beginning of the electrolysis (low current). At a higher current, the losses are infinitesimal. A current density of 0.24 ${}^{A}/_{cm^2}$ (I =16A) results in an overvoltage of 0.31 V. This represents a loss in efficiency of about 20%. These losses can not be avoided. In order to reduce the activation voltage losses, the manufacturer would have to improve the material of the electrode. The user of the electrolyser can only give their advice as to what could be improved in the electrolyser.

5.2.2 Ohmic voltage drop

Electrical conductors always have ohmic losses when electrical charges are moving inside of them. These losses occur due to the ohmic law.

$$\Delta V = I \cdot R \tag{5.63}$$

The voltage drop is the result of multiplying the electrical charge by the resistance. There are two major types of electrical charges: ions and electrons. An electrolyser must transport both charge types. Electrons flow through the metallic conductor while positive charged ions (protons) flow from the anode to the cathode through the membrane. Transporting both charges produces an ohmic voltage drop, which must be compensated with an additional voltage supply. This additional voltage supply results in a decrease in efficiency. This section explains how to calculate the ohmic voltage drop and how great its influence is.

Electrical resistance

Electrical conductors have a specific cross section (A), length (l) and conductivity (σ). These three factors influence the dimension of the resistance.

$$R = \frac{l}{\sigma A} \tag{5.64}$$

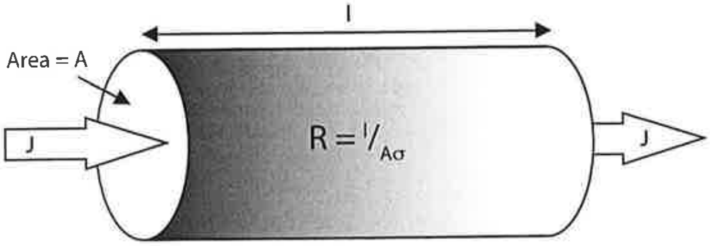


Figure 5.10: Charge transport along an uniform conductor

Since the electrolyser transports electrons and protons, the overall resistance consists of two separate resistances. The electrical conductor is the resistance which transports the electrons (R_{elec}), while the membrane is the resistance which transports the ions (R_{ionic}).

$$R_{\Omega} = R_{elec} + R_{ionic} \tag{5.65}$$

The resistance of the membrane is much higher than the resistance of the electrical conductor. In fact, the difference between both resistances is so large, that the electrical resistance can be disregarded. Hence, it is enough to calculate the ionic resistance in order to obtain the ohmic voltage drop.

According to equation 5.64, the distance between the anode and cathode should be as short as possible, while the surface of the electrodes and the conductivity of the membrane should be as large and as high as possible. The surface area of the electrolyser is $A = 6648\ \mathrm{mm}^2$ and the thickness of the membrane is $l = 0.12$ mm. Information about the conductivity of the membrane was not available from the manufacturer. Since the conductivity is not known, the resistance of the electrolyser must be measured. Therefore, the voltage and the current were measured making it possible to calculate the resistance (figure 5.11). In order to minimise the influence of the activation losses, the measurement was made at higher currents.

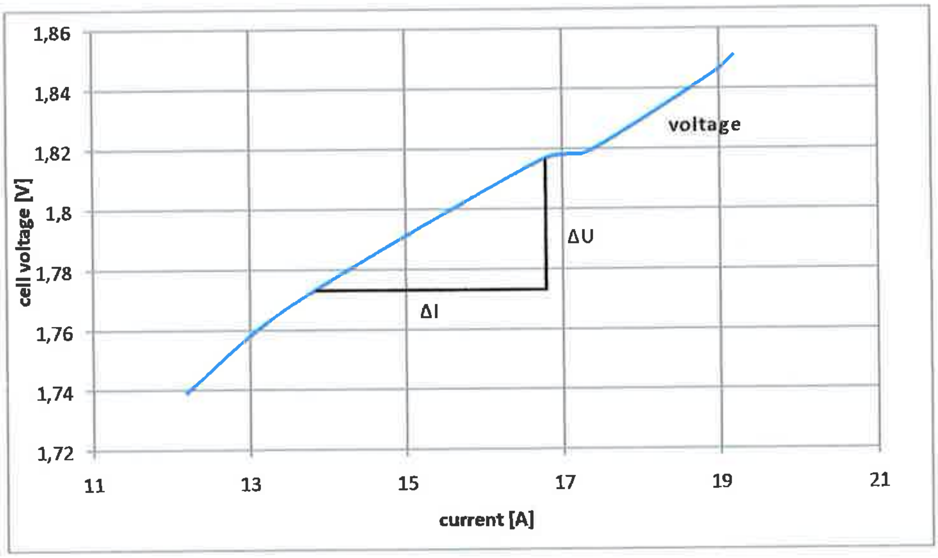


Figure 5.11: Measuring in order to obtain the resistance

As a result, the resistance is approximately $R = 0.015\ \Omega$. Since the resistance is now known, the conductivity of the membrane can be calculated.

$$\sigma = \frac{l}{A \cdot R} = \frac{0.12\ \mathrm{mm}}{6648\ \mathrm{mm}^2 \cdot 0.015\ \Omega} = 1.2\ \Omega^{-1}\mathrm{m}^{-1} \tag{5.66}$$

Influence of ohmic voltage drop on the efficiency

Having obtained the resistance value the ohmic voltage drop can be calculated for different currents (eqn. 5.63).

As one can see in figure 5.12, the ohmic voltage drop increases proportionally to the current. A current density of 0.24 A/cm^2 (I =16A) results in an ohmic voltage

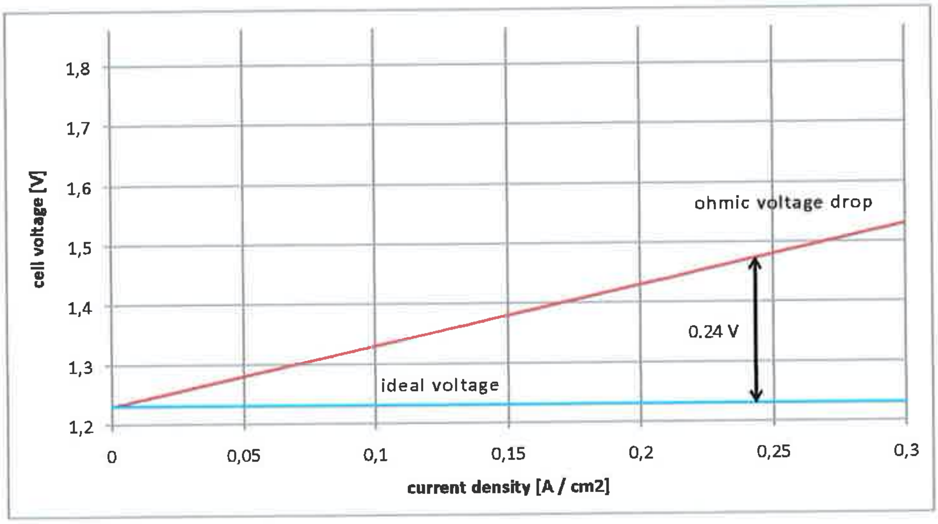


Figure 5.12: Ohmic voltage drop related to the current density

drop of about 0.24 V. This represents a loss in efficiency of about 20 %. In order to reduce the ohmic voltage drop it is necessary to improve the conductivity of the membrane or to decrease its thickness. Especially when the conductivity has a great influence on the efficiency, as the following section will explain.

Influence of water's conductivity on the ohmic voltage drop

An electrolyser needs water in order to split it into hydrogen and oxygen. Alkaline electrolysers use this water in combination with potassium hydroxide, which increases the conductivity of the water and allows the ions to flow between anode and cathode. On the contrary, a PEM electrolyser needs pure water since the conductivity which is necessary to transports ions is provided by the proton exchange membrane. The question is, how clean must that water be in order to guarantee an optimum efficiency and is tap water adequate enough? Or is it necessary to use distilled water? In the case of a PEM electrolyser, conductivity of the water means that ions are present in it which would in turn represent impurities for the electrolyser. A high conductivity implies that too many ions are present in the water. A low conductivity, on the contrary, implies that only few ions are in the water which means that the impurity of the water is very low. Actually, in order to optimise the conductivity of the membrane, the conductivity of the water should be zero. The reasons for that relation are explained in this section.

In a PEM electrolyser protons migrate from the anode to the cathode through the membrane. As already explained in the last section, the conductivity of the membrane influences the ohmic voltage drop of the electrolyser. However, this conductivity, is related to the hydrogen concentration. The membrane of the electrolyser consists basically of carbon chains and sulphonate ($SO3^-$). These $SO3^-$ ions join with the protons which makes the membrane able to transport protons from the anode to the cathode. If the proton concentration decreases, the conductivity of the membrane will also be worse. Foreign ions in the water form intermediate products with hydrogen, which reduces the concentration of protons and therefore the conductivity of the membrane. As already mentioned, this has an negative effect on the ohmic voltage drop and consequently also on the efficiency.

A measuring was made in order to analyse the influence of the water's conductivity. Contamination of the water occurs because of leaving the container open and not using the ion exchanger for cleaning it. Figure 5.13 shows the consequences of contaminated water on the ohmic voltage drop.

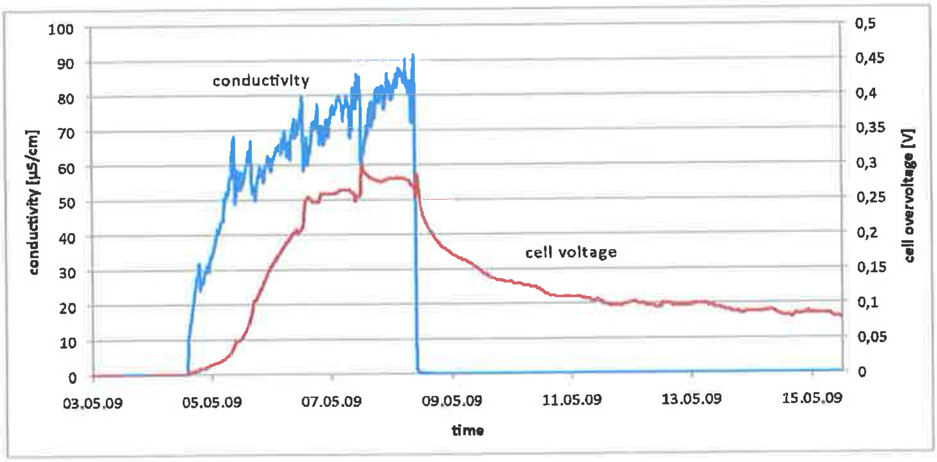


Figure 5.13: Influence of conductivity on the ohmic voltage drop

Increasing water conductivity results in a significant ohmic voltage drop. As figure 5.13 shows, an additional voltage supply of 0.3 V must be provided in order to compensate the ohmic voltage drop. This represents a loss in efficiency of about 20%. It is striking that the conductivity does not rise higher than 90 $^{\mu S}/_{cm}$. The reason for this is the limited range of the device used for measuring the water's conductivity which is only capable of measuring conductivities of up to 30 $^{\mu S}/_{cm}$. In fact, the real value is higher than 90 $^{\mu S}/_{cm}$. The result is not significantly affected by this measurement error, since the aim was to analyse if the water needs to be cleaned, which is precisely what this measurement establishes. Should this step be neglected, the efficiency will be significantly reduced.

5.2.3 Comparison: calculation and measuring

All values which have an influence on the efficiency have been calculated. As a next step, measurements were made in order to proof the obtained values.

Comparison: temperature

According to the calculations, an increasing temperature improves the efficiency. An increase in temperature of 1 Kelvin should reduce the necessary voltage for the electrolysis about 1.2 mV. The comparison between the measured and the calculated values is somehow difficult, since the calculated values do not involve the losses which occur due to the current. However, during the measurement, a current flows in order to make the influence of the temperature visible. Hence, the calculated absolute voltage cannot be compared to the actual absolute voltage since the voltage of the measured values includes the losses related to the current. In order to compare the calculated and the measured values, only the difference from the voltage at 25°C to the voltage at higher temperatures was measured (figure 5.14).

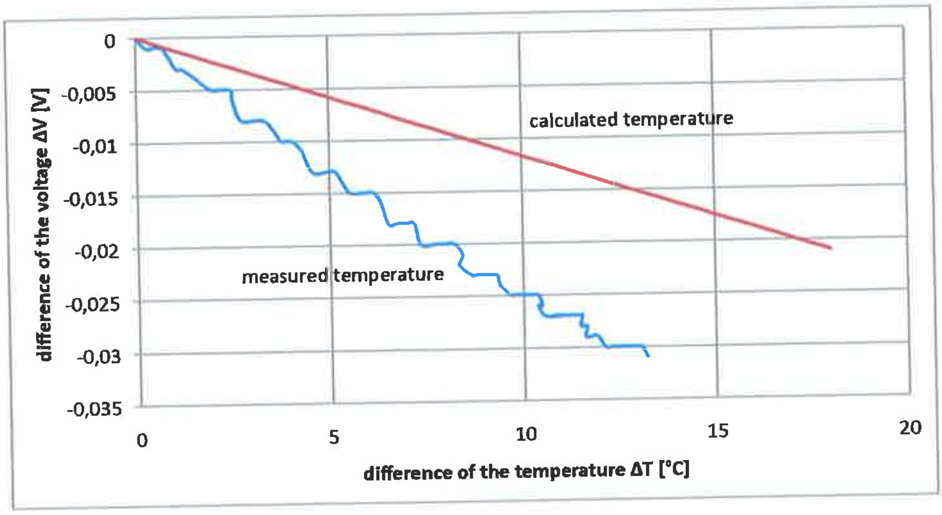


Figure 5.14: Comparison of the temperature's influence: measured and calculated

As one can see in figure 5.14, the calculated and the measured values differ from each other. Instead of a calculated voltage change of 1.2 $^{\mathrm{mV}}/_{\mathrm{K}}$, the voltage change is around 2.3 $^{\mathrm{mV}}/_{\mathrm{K}}$. This difference occurs due to the conductivity of the membrane. An increment in the temperature also increases the conductivity of the membrane. In combination with the thermal energy from the environment, this results in a voltage change of about 2.3 $^{\mathrm{mV}}/_{\mathrm{K}}$. Although the manufacturer of the electrolyser is aware of this effect, they could not provide any information on the relation between temperature and conductivity. According to the measurement results, an increase in temperature results in a change in voltage of about 1.1 $^{\mathrm{mV}}/_{\mathrm{K}}$.

Comparison: pressure

As the calculations in section 5.1.2 show, more voltage is necessary when there is an increase in pressure. An increase of 1 to 11 bar should result in a necessary additional voltage of 30.8 mV. The comparison of the calculated and measured pressure is depicted in figure 5.15.

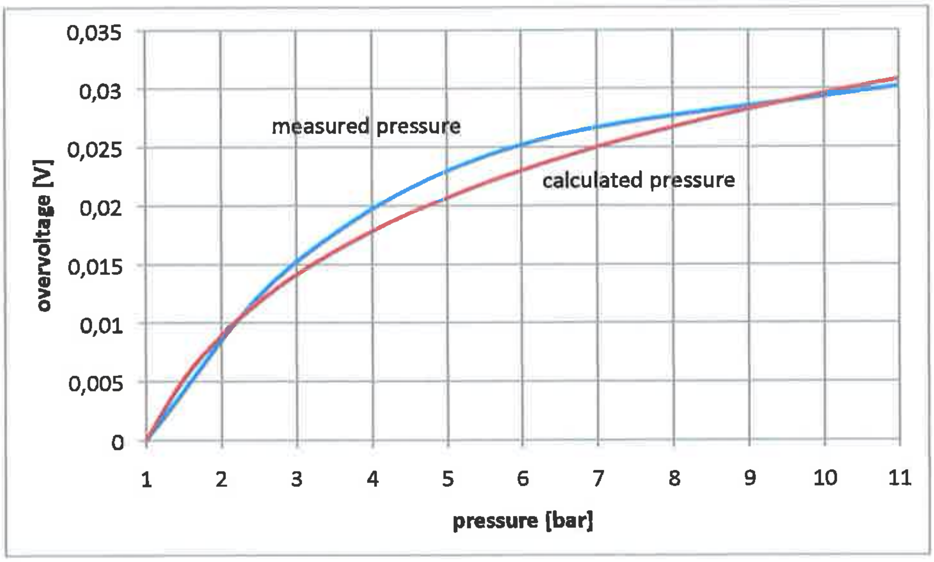


Figure 5.15: Comparison of the pressure's influence: measured and calculated

As figure 5.15 shows, the measured and the calculated values are almost identical. First, the voltage rises significantly and with a further increase of the pressure, the slope value for the voltage becomes lower. Hence, the calculations are correct.

Comparison: current

A current in the electrolyser causes activation voltage losses and an ohmic voltage drop. These losses are related to the architecture of the electrolyser.

Figure 5.16 shows the calculated activation voltage loss, the ohmic voltage drop and a combination of both losses. Beside it is the graph of the measured cell voltage. As one can see, the calculated and the measured values are almost the same, which leads to the conclusion that the calculations are correct.

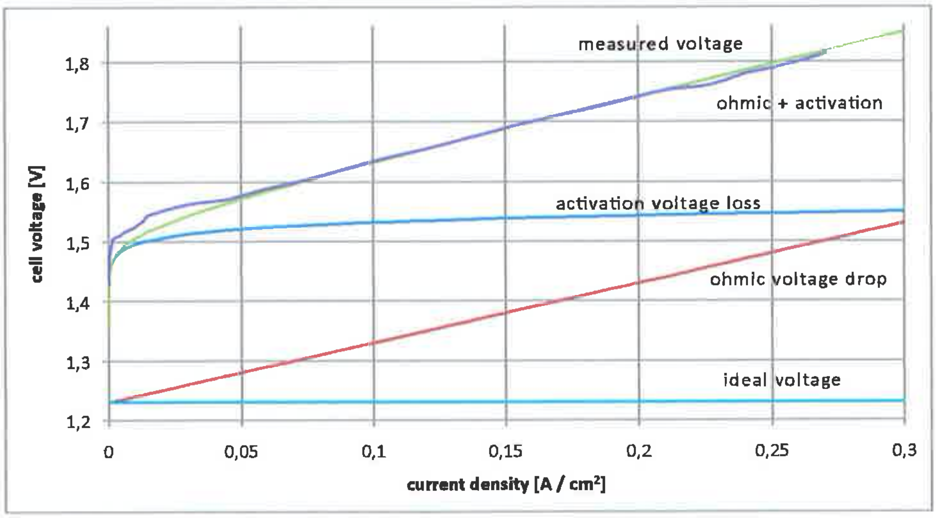


Figure 5.16: Comparison of the current's influence: measured and calculated

Figure 5.17 shows how the efficiency decreases with an increasing current.

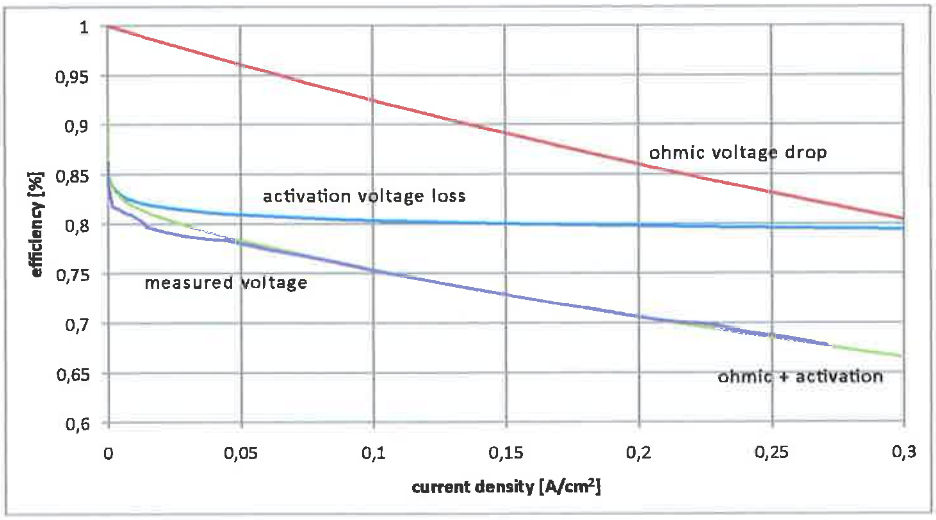


Figure 5.17: Comparison of the current's influence on the efficiency: measured and calculated

5.3 Summary of the influences on efficiency

Many factors have an impact on the efficiency of the electrolyser. Temperature, pressure, catalyst material, conductivity and thickness of the membrane, and the dimensions of the electrolyser affect the efficiency. A high temperature increases the efficiency and, in order to benefit from this, the electrolyser has been insulated with styrofoam. A high pressure decreases the efficiency, but since it is a very effective way to store the compressed hydrogen in a metal hydride storage, these losses are passable. The catalyst material in the membrane is responsible for the activation voltage loss. An improvement in the catalyst material would reduce the activation voltage losses significantly. An improvement in conductivity would have a considerable effect on the reduction of the ohmic voltage drop. A reduction of the thickness of the membrane would positively affect the ohmic voltage drop as well, but in order to achieve a high pressure inside the electrolyser, the membrane must be thick enough to withstand this pressure. If only atmospheric pressure was used, the membrane could be thinner, which would result in a higher conductivity and a lower ohmic voltage drop. Hence, if hydrogen has been pressurised, this does not only affect the work done on compression, but also indirectly influences the ohmic voltage drop. Nevertheless, the use of a thinner membrane which is not able to withstand 11 bar of pressure, would result in a completely different setup. The drying system would have to be modified since it uses the produced pressure. Also, a compressor would be necessary in order to store the hydrogen. If the design of the electrolyser was to be improved, it would be simpler to do it by increasing the surface area of the electrodes or by reducing the current.

All the aforementioned factors affect the efficiency, but only the effects of the temperature and pressure can be influenced by the user. In order to reduce the losses related to the current (thickness, conductivity, surface area), the user can only advise the manufacturer as to what can be improved in the electrolyser.

6 Drying

Hydrogen has a relative humidity of 100% when it is produced by an electrolyser. Depending on the temperature the amount of water vapour can be rather large. In order to store the hydrogen in a metal hydride container, it is necessary to separate this water from the hydrogen. This chapter shows the different drying options and explains why in this project, silica gel is the best choice for drying hydrogen.

6.1 Gas purity

Metal hydride containers are very sensitive to impurities. Oxygen, carbon dioxide, water vapour, etcetera, lead to a decrease in the adsorption capacity. A continuous contamination could damage and eventually destroy the metal hydride making it worthless to the user and impossible for more hydrogen to be absorbed. Only the manufacturer might be able to recycle some of the metal hydride to build a new storage tank.

A minimum gas purity of 99.99% (4.0) is necessary to guarantee a long life cycle. This corresponds to an impurity of 0.01%. It would be optimal if the gas purity was 99.999% (5.0), which would mean 0.001% impurities. The gas purity depends mainly on the electrolyser. Ideally, there should be no impurities except for water vapour. However, some impurities do exist:

Oxygen	$<$ 2ppm
Hydrocarbon	$<$ 1ppm
Water vapour	Depending on the drying method

The PEM electrolyser used in this project provides a very high hydrogen purity, which has two reasons. On the one hand, the electrolyte is a solid membrane instead of a liquid one as in the alkaline electrolyser, and on the other hand, the high pressure at the hydrogen side locks out impurities from the outside. In fact, the amount of oxygen and hydrocarbon is so small that these impurities can be disregarded, making water vapour the only significant impurity.

6.1.1 Calculation of gas purity

Rudolf Clausius and Emile Claperyon defined an equation for calculating the pressure of saturated vapour. Today, it is known as the Clausius-Claperyon equation (Eqn. 6.1). The saturated vapour pressure is a function only of temperature and indicates the maximum amount of water that can exist in the vapor state.

$$\ln\frac{p}{p_0} = \frac{r_0 M_{H_2O}}{RT_0}(1 - \frac{T_0}{T}) \tag{6.1}$$

For the calculation of the vapour pressure at a user-defined temperature, a reference value is necessary. 0.01 bar is common standard value (Table 6.1).

p_0 **[bar]**	T_0 **[°C]**	T **[K]**	r **[kJ/kg]**
0.01	6.98	280.13	2484.66

Table 6.1: Standard value of saturated vapour pressure

Generally, the dryness degree is determined by the dew point. In order to calculate the dew point at a gas purity of 4.0 or 5.0, the Clausius-Claperyon equation needs to be rearranged.

$$T = \frac{T_0}{1 - ln\frac{p}{p_0} \cdot \frac{RT_0}{r_0 M_{H_2O}}} \tag{6.2}$$

The partial vapour pressure at an atmospheric gas purity of 4.0 is $p = 1$ bar $\cdot\ (1 - 0.9999) = 1 \cdot 10^{-4}$ bar. By using equation 6.2, the dew point T can be obtained.

$$T = \frac{280.13\text{ K}}{1 - ln\frac{0.0001\text{ bar}}{0.01\text{ bar}} \cdot \frac{8.314\ \text{J/molK} \cdot 280.13\text{ K}}{18.01528\ \text{g/mol} \cdot 2484.66\ \text{kJ/kg}}} = 225.98\text{ K} \tag{6.3}$$

225.98 K is equal to -47.17°C, which is the dew point at a gas purity of 4.0 at atmospheric pressure. Therefore, if a gas purity of 4.0 is required, the dew point must be T= -47.17°C. This value will vary, if the gas pressure is increased from 1 bar to 11 bar: $p_{11bar} = 11$ bar $\cdot\ 0.0001 = 1.1 \cdot 10^{-3}$ bar

$$T = \frac{280.13\text{ K}}{1 - ln\frac{0.0011\text{ bar}}{0.01\text{ bar}} \cdot \frac{8.314\ \text{J/molK} \cdot 280.13\text{ K}}{18.01528\ \text{g/mol} \cdot 2484.66\ \text{kJ/kg}}} = 251.27\text{ K} \tag{6.4}$$

By using a gauge pressure of 11 bar, the dew point changes to T=-21.88°C. The gas purity is still 4.0, but because of the higher gas pressure, a lower dew point is necessary to reach this purity. Table 6.2 shows the coherency between pressure and gas purity for some significant values.

gas purity	3.0	4.0	5.0
1 bar	-22.99	-47.17	-67,09
11 bar	8,38	-21.88	-46,26

Table 6.2: Dewpoint T[°C] in dependence of pressure and gas purity

6.2 Method of gas drying

There are four main options for drying gas: cooling, increasing the pressure, chemical absorption and physical adsorption.

Cooling The amount of water a gas can contain is dependent on temperature. Decreasing temperature reduces the potential amount of water. The excess of water will turn to snow forcing the gas to dry.

Increasing pressure The effect of increasing the pressure is similar to the effect of cooling. Increasing the pressure also reduces the potential amount of water, but instead of turning to snow, the water vapour will condense to water droplets.

Chemical absorption In the process of chemical absorption, the gas flows through a solid or a liquid chemical substance (e.g. sulfuric acid). The H_2O molecules diffuse into the chemical substance and bond with it.

Physical adsorption In physical adsorption, wet gas passes through a desiccant and the water molecules accumulate on the surface of the adsorbent. This differs form the absorption, where the water is not chemically bonded, but just physically bonded with the surface of the desiccant. Hence this process is also called physisorption.

6.2.1 Drying requirements

The efficiency of a stand alone system is influenced by two factors. The first factor is the efficiency of the main applications (e.g. a transformer or an electrolyser). The second factor is the energy consumption of the periphery. Valves, dryer and other components need energy. The energy they use is not available for producing hydrogen. Therefore, the peripheral energy consumption should be as low as possible. For that purpose, the drying device should work at a low energy level. Furthermore, the drying device should be small-sized and easy to handle.

Cooling is an energy intensive process. A permanent energy supply is necessary to cool down the hydrogen. Although there are ways to support the cooling with a heat exchanger, the construction of such a system is very complex. Especially since the whole electrolyser system works with a pressure of 10 barg.

Chemical absorption does not need any energy while drying the hydrogen. Dew points far below the freezing point are possible. The problem of this method is the hazardous acid or base that is required. Several safety arrangements would be necessary in order to prevent any injuries to the user in case of a leak. Another problem would be the disposal of the hazardous byproduct.

Increasing the pressure usually requires energy, but if the pressure is obtained without using an energy intensive compressor, it is a simple and effective way to reduce moisture. In this case, the electrolyser produces a pressure of 10 barg by itself. By using the pressure, a dew point of -11°C can be reached. This is not the final required purity of 4.0, but it is the first step in the right direction.

The method of adsorption uses a desiccant to dry the carrier gas. Reachable dew points depend on the desiccant and are between -40°C and -80°C. Desiccants are the most widespread drying technology in the industry. They do not need any energy while drying, are cheap, easy to handle, non toxic and can be regenerated when saturated. The regeneration in turn, does need energy.

6.2.2 Desiccants

After having compared the pros and cons of the different drying methods, adsorption proves to be the best option for drying hydrogen. The three most common desiccants and their different attributes are listed in table 6.3.

All three desiccants are capable of drying hydrogen. They differ from each other in three fields: residual moisture, adsorption capacity and price. The residual moisture is measured in dew point. The lower their dew point, the lower is their residual moisture. The minimum dew points are between -62°C and -84°C, while the minimum dew point required for an atmospheric gas purity of 4.0 is -47°C. Since the dew points of all three desiccants fall within the aforementioned dew point range, the choice of which desiccant should be used does not depend on the dew point.

The adsorption capacity is the amount of adsorbed substance. For example, 100 g of a desiccant with an adsorption capacity of 10% are able to adsorb 10 g of water. In figure 6.1, the adsorption capacities of the three desiccants are depicted in relation to the relative humidity. As one can see, the adsorption capacity of

desiccant	**silica gel**	**activated alumina**	**molecular sieve**
diameter [mm]	1.5 - 3	3.2 - 6.4	1.5 - 5.0
cost [€/kg]	20	45	70
density [kg/m^3]	700 ±50	800 ±50	760 ±50
min. dew point [°C]	-62	-73	-84
enthalpy [J/mol]			
adsorption capacity at 40% r.h. [%]	21	13.5	22
adsorption capacity at 60% r.h. [%]	32	20	22
adsorption capacity at 100% r.h. [%]	40	40	22
regeneration temperature [°C]	120 - 175	160 - 210	200 - 300
special feature	Changes color from orange to white	-	-

Table 6.3: Comparison between desiccants

molecular sieve is almost independent from the relative humidity, but its maximum capacity is only 22%. The adsorption capacities of silica gel and activated alumina are very similar. Both increase with an increment of the relative humidity and their maximum adsorption capacity is around 40%. If hydrogen is produced, its relative humidity is around 100%. Therefore, in this project, silica gel and activated alumina are more adequate for the drying of hydrogen.

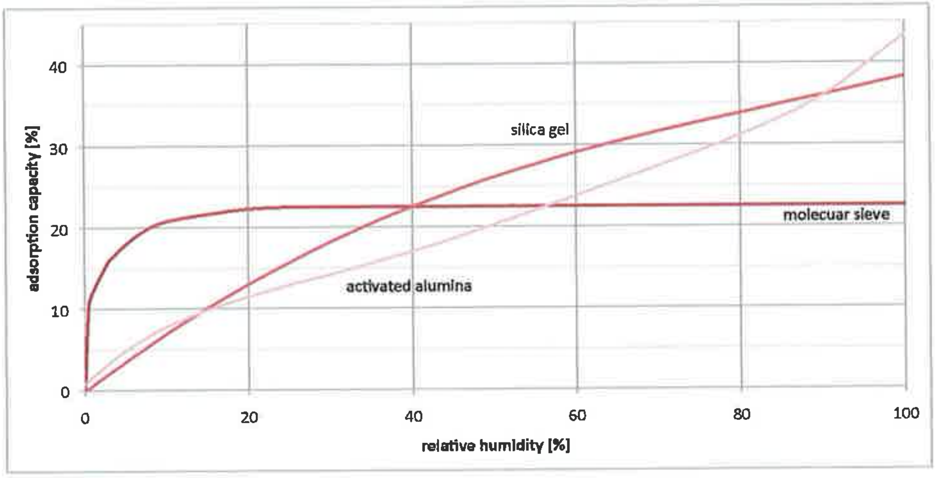


Figure 6.1: Capacity of desiccants [39]

Besides its high adsorption capacity, silica gel has the advantages of being the cheapest desiccant and of changing its colour when saturated. Therefore silica gel is the best choice of desiccant.

6.2.3 Silica gel

There are different types of silica gel. It is available as granulate or pearls in white or orange colour. The orange colour is an indicator (ferric ammonium sulphate) for the already adsorbed moisture. If the desiccant is saturated to 19%, the colour will change from orange to white. Granulate is porous, which involves the risk of contamination through dust. Therefore pearls are the best choice for drying hydrogen. Most producers are cautious and specify their silica gel to a minimum dew point of -40°C. It is presumed, however, that it can in fact reach a dew point of -62°C, as shown in table 6.3.

Figure 6.2: Orange and clear silica gel

Data sheet silica gel

brand name	Sorbsil® Chameleon®
company	Oker-Chemie GmbH
formula	$SiO_2 \cdot (H_2O)$
colour change	orange → white
max. adsorption cap.	50 %
diameter	1 - 3 mm
bulk density	700 $^{g}/_{l}$
dew point	-40 °C
max. reg. temperature	140°C
cost	22 Euro

The vapour pressure at a dew point of -40°C can be calculated by the Clausius-Claperyon equation. Table 6.4 shows the results for pressures of 1 bar and 11 bar.

pressure [bar]	**1**	**11**
partial pressure [bar]	$2.08062 \cdot 10^{-4}$	$2.08062 \cdot 10^{-4}$
gas purity [%]	99.979	99.998
gas purity [%]	3.7	4.8

Table 6.4: Gas purity at -40°C

6.3 Drying system

The hydrogen must pass through the desiccant to dry. For this purpose, an adsorption canister needs to be filled with silica gel. The following criteria should also be met:

- The canister should be capable of holding hydrogen

- The canister should be capable of withstanding pressures up to 10 barg
- The amount of silica gel in the canister must be useable for at least half a year or it must be possible to easily regenerate the silica gel
- Optional: The canister should be capable of withstanding temperatures up to 140°C, which are required for the regeneration of the silica gel

Since hydrogen is the smallest existing element, the adsorption canister needs to be well designed in order to prevent leaking.

10 barg are necessary to store the hydrogen in a metal hydride container and the adsorption canister must be able to withstand this pressure. A positive side effect is that the pressure helps to reduce the moisture.

Since the adsorption canister will always be completely filled up, the time it can be used will depend on its size and on the production rate of hydrogen. When deciding on the size of the adsorber, there are two possibilities. The size of the adsorber can either be large, so that regenerating or replacing the silica gel is not necessary more than once every six months, or the adsorber can be small, in which case, little energy is necessary to regenerate the silica gel. Replacing the silica gel when using a small container is out of the question since the process would be needed to often and the system would be contaminated with air every time.

Silica gel usually is regenerated at a temperature of about 140°C. Therefore it would be advantageous if the adsorption container could withstand this temperature.

Otherwise, the silica gel needs to be replaced. The problem with replacing the silica gel is that impurities (e.g. air) get into the adsorber. Hence, it would be necessary to run the system for some time in order to eliminate the impurities. The hydrogen produced during this time should not be stored since it would not be pure enough.

It is very difficult to find an adsorption container which fulfills all the aforementioned mentioned criteria. The main problem is that common containers are not capable of holding hydrogen and withstanding high pressure. This limits the choice extremely. However, there are two containers which are capable of holding hydrogen and of withstanding high pressure. The first container is the ALB-S-3 by the Pall Corporation which fulfills all criteria except for the resistance to high temperature. Its silica gel filling capacity is 2.6 kg. The second container that can be used is a small sized stainless steel container by Landefeld with a filling capacity of 70 g silica gel. It is even able to withstand a temperature of 140°C. Its data sheet is already listed in chapter 4.2.4.

Figure 6.3: Adsorber ALB-S-3

Data sheet large adsorber

brand name	ALB-S-3
company	Pall Corporation
pressure	1..11 bar
temperature	0...40°C
capacity silica gel	2.6 kg
body material	steel, borosilicate glass
dimension	373 x 150 x 133 mm
weight	11.5 kg
cost	1157 Euro

6.3.1 Functioning of the adsorber

Full saturation of silica gel through adsorption of water is reached at a specific point. The question here is if the ability of adsorbing water vapour is reduced when the silica gel is partly saturated. In order to be able to answer this question, it is necessary to understand the functioning of a silica gel adsorber.

Silica gel contained in an adsorber canister does not saturate homogeneously. The desiccant pearls at the front of the adsorber are saturated first, while the pearls at the back are fully unsaturated. The silica gel is saturated layer by layer, as described in figure 6.4. Once the last layer is saturated, the humidity in the system will increase rapidly. Before that, the hydrogen gas will be completely dry.

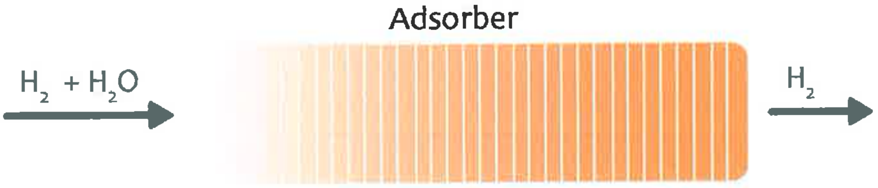


Figure 6.4: Scheme of an adsorber

The two tested adsorbers are able to contain 2.6 kg and 0.07 kg. The adsorption capacity of the silica gel depends on the relative humidity, as shown in table 6.3. At a relative humidity of 100% silica gel has an adsorption capacity of 40%. To offset variations, the following calculations have been made using a capacity value of 30%.

Large container

$$\begin{aligned} 30\% &\hat{=} 0.3 \cdot 2600\ \mathrm{g} \qquad (6.5)\\ &= 780\ \mathrm{g} \qquad (6.6) \end{aligned}$$

Small container

$$\begin{aligned} 30\% &\hat{=} 0.3 \cdot 70\ \mathrm{g} \qquad (6.7)\\ &= 21\ \mathrm{g} \qquad (6.8) \end{aligned}$$

At an adsorption capacity of 30%, the silica gel in the large container can adsorb 780g of water, while the small container is able to adsorb 21 g of water.

6.3.2 Production rate

The electrolyser receives its energy from the solar cells (see chapter 4.2.1) installed on the roof of building C15 at the University of Applied Sciences in Darmstadt. These solar cells are able to produce a total energy amount of approximately 660 kWh per year. Since the electrolyser usually works with an efficiency of around 70%, 460 kWh can be stored in the hydrogen. This amount of electrical energy is equivalent to a specific amount of hydrogen.

$$\begin{aligned} 1\ \mathrm{mol}\ H_2 &\hat{=} 2.01588\ \mathrm{g} \qquad (6.9)\\ 2.01588\ \mathrm{g} &\hat{=} 0.0659\ \mathrm{kWh} \qquad (6.10)\\ 14.1\ \mathrm{kg} &\hat{=} 461\ \mathrm{kWh} \qquad (6.11) \end{aligned}$$

In other words, the electrolyser produces 14.1 kg of hydrogen per year. The amount of water vapour which is mixed with the hydrogen gas depends on temperature and pressure. (Figure 6.5)

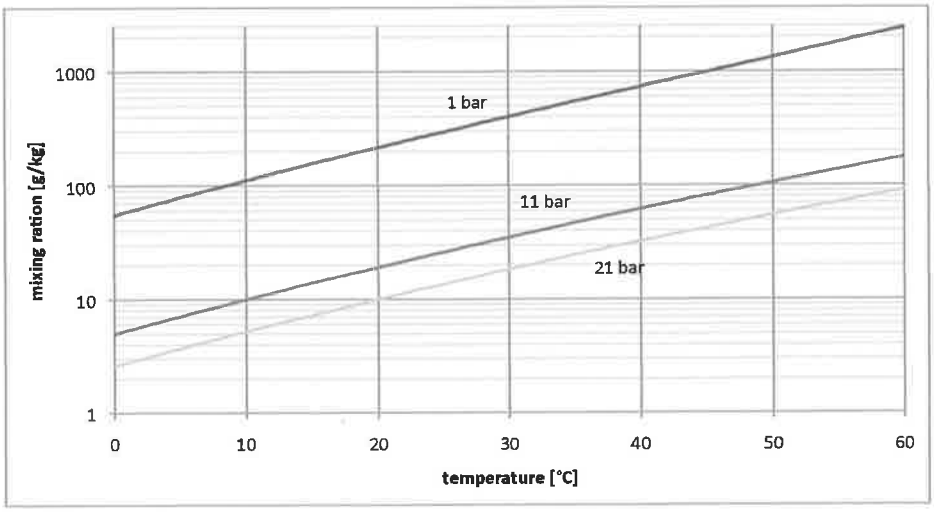


Figure 6.5: Mixing ratio in relation to temperature

Table 6.5 shows the amounts of water vapour at some significant temperature and pressure values. As one can see, increasing temperature leads to more water vapour in the hydrogen gas, while increasing pressure results in less water vapour. Especially the increase of pressure leads to a drastic decrease of humidity. For example, at 25°C, 1 kg of hydrogen contains 292.6 g of water at a pressure of 1 bar. An increase to 11 bar of pressure reduces the amount of water to 25.89 g. Hence, the pressure can be used as a first stage dryer.

pressure [bar]	**1**	**11**	**21**
20°C	214.1	19.1	10.0
25°C	292.6	25.8	13.5
30°C	396.3	34.6	18.1
35°C	532.8	45.9	24.0

Table 6.5: Mixing ratio [g/kg]

6.3.3 Life cycle of the adsorber

Losses in the electrolyser increase its heat, while the air from the environment cools down the electrolyser. This results in a temperature balance of about 30°C, in an environment with a temperature between 20 and 25°C. Under these conditions and a pressure of 11 bar, the maximum amount of water vapour is 34.62 g/kg. Since the production rate of hydrogen is 14.1 kg/a, the amount of water per year equals 488.14 g.

The large container holds 2.6 kg of silica gel, which can adsorb 780 g of water. Provided the aforementioned amounts of silica gel and water in combination with 11 bar of pressure at 30°C, the adsorber can operate for 1 year and 6 months before the silica gel needs to be replaced or regenerated. The small container, on the other hand, can adsorb 21 g of water, which results in a life cycle of 0.5 months. In table 6.6 are listed different life cycles of the adsorbers in relation to temperature and pressure.

	large adsorber			small adsorber		
pressure [bar]	**1**	**11**	**21**	**1**	**11**	**21**
20°C	3.1	35	67	0.08	0.9	1.8
25°C	2.3	26	49	0.06	0.7	1.3
30°C	1.7	**19**	37	0.05	**0.5**	1
35°C	1.3	14	28	0.03	0.4	0.7

Table 6.6: Life cycle of the adsorbers [months]

As one can clearly see, the reduced water vapour at higher pressure leads to an increase in both of the adsorbers life cycles.

6.4 Renewing of silica gel

When the silica gel is saturated, it is no longer able to dry the hydrogen gas. Hence, it needs to be replaced or regenerated.

6.4.1 Replacing the silica gel

In order to continue using the adsorber, replacing the silica gel is easier than regenerating it. Silica gel is a cheap desiccant and refilling the adsorber would have a cost of only around 50 Euro. However, there is a significant problem when replacing the desiccant. Opening the adsorption canister allows air to flow through it. This air contains impurities harmful to the metal hydride storage, such as oxygen, water vapour and carbon dioxide. The adsorber needs to run for a while in order to be free of all impurities again. The replacing of silica gel was tested by the manufacturer of the electrolyser. According to their data, 7 days after the replacing of the silica gel, there were still a few parts of oxygen in the system. If no hydrogen could be stored for 7 days, there would be a loss of about 6 kWh. In order to prevent this loss, it was decided to use the small adsorber container and to develop a system which regenerates the silica gel without coming into contact with the air from the environment.

6.4.2 Regeneration

Water vapour is bonded to the surface of the silica gel. In order to regenerate the silica gel, the water molecules must diffuse away from this surface.

If the gas surrounding the silica gel has a higher relative humidity than the gel, they will bond. In other words, the adsorbing system tries to reach an equilibrium between the water molecules in gaseous form and those which are adsorbed on the surface of the silica gel.

$$N_{(g)} + X \rightleftharpoons N_{(ADS)} \tag{6.12}$$

$N_{(g)}$ is the number of water molecules in gaseous form while $N_{(ADS)}$ is the number of adsorbed molecules. The free amount of space on the surface of the silica gel is represented by X.
Surface area, pressure and temperature have an effect on the equilibrium. High pressure, low temperature and a large surface would shift the equilibrium to the right side of the equation (more adsorbed water molecules). In contrast, the equilibrium would shift to the left side(more gaseous water molecules) at low pressure, high temperature and a small surface.

Since it is not possible to change the surface of the silica gel, either the temperature must increase or the pressure must decrease in order to regenerate the silica gel.

In industry, it is common to use high temperatures for the regeneration of silica gel. Usually, the silica gel is heated to 140°C. This reduces the relative humidity to 1.18%. Higher temperatures would increase the speed of regeneration, but would also partially damage the silica gel. The high temperature affects the surface by reducing its area. Nevertheless, after about 30 regeneration processes using a temperature of 140°C, the silica gel is no longer usable and needs to be replaced. Additionally, heating is an energy-intensive process and would need a very good insulation in order to reach the 140°C in the adsorber. For example, a measurement has shown that a mini oven requires about 230 W to reach and maintain a temperature of 140°C. A regeneration process of 6 hours would require an energy amount of 1.4 kWh, which is almost the same amount the solar cells produce on an average day.

A less energy-intensive process is the reduction of pressure. To reach the same relative humidity as in the process of heating, the pressure must be reduced from 11 bar to 130 mbar. In order to reduce the pressure to 130 mbar, a vacuum pump is necessary. A suitable pump is the N86KNDC B, produced by KNF Neuberger GmbH (see chapter 4). This pump has a maximum power of 16 W. Tests have shown that the usual energy consumption of the pump is about 5 W, which is over 40 times less than the oven would need.

Construction of the regeneration system

The aim of the regeneration system is to dry the silica gel and to dispose of the water vapour. Therefore, the silica gel needs a constant flow of dry hydrogen gas, which transports the H_2O molecules out of the adsorber. In order to dry the gas stream, a pressure of 11 bar needs to be produced in the first instance, followed by a reduction of the pressure to 150 mbar.

For the gas stream to be dry, it needs to be produced at a pressure of 11 bar before it is reduced to 150 mbar. The high pressure at the beginning reduces the absolute humidity, while the vacuum afterwards lowers the relative humidity. This results in a relative humidity of 1.4% at a temperature of 30°C.

Functioning of the regeneration system (figure 6.6):
The hydrogen gas that comes from the electrolyser is held back by the back pressure valve until a pressure of 11 bar is reached. Afterwards, the hydrogen passes through the back pressure valve. Due to the vacuum created by the vacuum pump, the pressure on the outlet side of the back pressure valve is 150 mbar. As a result, there is a constant hydrogen gas flow with a relative humidity of 1.4%, which flows backwards through the adsorber. Due to the gas flow, the silica gel dissolves its water molecules into the gas stream until it is dry again. In a final step, the wet hydrogen can be used in a fuel cell to recharge a battery.

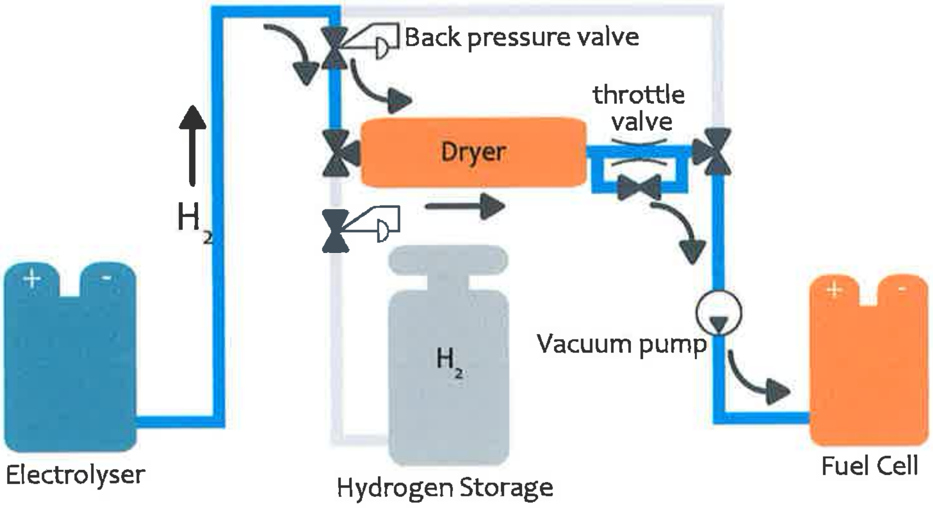


Figure 6.6: Regeneration of silica gel

Regeneration time

Surface area, temperature, relative humidity, mass of silica gel, mass of water vapour, pressure and a few other factors all influence the time of regeneration. Therefore, it is very difficult to calculate the time of regeneration, making it simpler and more accurate to just measure it. Hence, a test was made where the silica gel first was saturated and then regenerated. As a reference value, the manufacturer of the silica gel need between 4 and 12 hours to dry it. The adsorber container holds 70 g of silica gel and at an adsorption rate of 30%, the silica gel is able to adsorb 21 g of water. In order to saturate the silica gel faster, the drying process was carried out at atmospheric pressure, which increased the humidity in the hydrogen gas. The maximum production rate of hydrogen is 42 $^{\mathrm{l}}/_{\mathrm{h}}$ which is equivalent to 3.777 $^{\mathrm{g}}/_{\mathrm{h}}$.

$$
\begin{aligned}
22.414\ \mathrm{l} &\mathrel{\hat{=}} 2.01588\ \mathrm{g} && (6.13)\\
1\ \mathrm{l} &\mathrel{\hat{=}} 0.09\ \mathrm{g} && (6.14)\\
42\ \mathrm{l} &\mathrel{\hat{=}} 3.777\ \mathrm{g} && (6.15)
\end{aligned}
$$

At 25°C the humidity is about 300 $^{\mathrm{g}}/_{\mathrm{kg}}$, which results in a humidity of 1.133 $^{\mathrm{g}}/_{\mathrm{kg}}$ at a production rate of 3.777 $^{\mathrm{g}}/_{\mathrm{h}}$.

$$0.3 \cdot 3.777\ ^{\mathrm{g}}/_{\mathrm{h}} = 1.133\ ^{\mathrm{g}}/_{\mathrm{h}} \qquad (6.16)$$

Since the silica gel in the adsorber can adsorb 21 g of water, it takes about 18.5 hours until the silica gel is fully saturated.

$$\frac{21\ \mathrm{g}}{1.133\ ^{\mathrm{g}}/_{\mathrm{h}}} = 18.5\ \mathrm{h} \qquad (6.17)$$

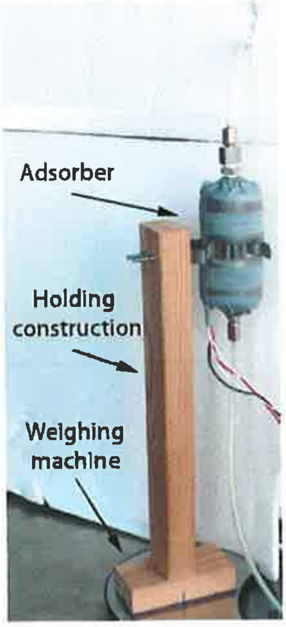


Figure 6.7: Construction in order to hold the adsorber upright

A weighing machine measured the degree of saturation. The adsorber filled with silica gel was weighed before and after the saturation. The point at which the silica gel was fully saturated was noted by the dew point transmitter. After the silica gel was fully saturated, the regeneration process started. In order to determine when the process was completed, the silica gel was weighed during its regeneration. Removing the adsorber from the experimental rig and installing it on a contraption which held it upright (figure 6.7), allowed for it to be weighed.

Flexible tubes can be connected to the adsorber while it stands on the weighing machine. Hence, it is always possible to measure the saturation rate of the silica gel during the regeneration process.

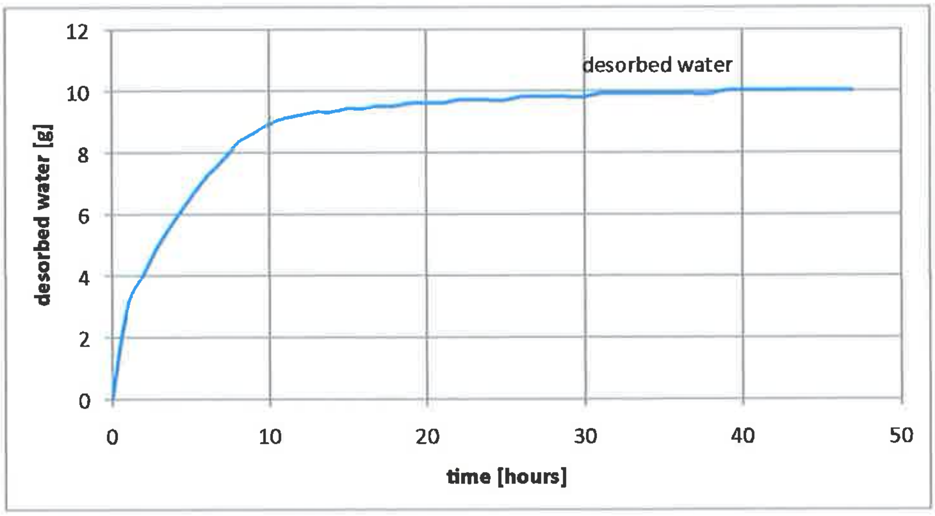


Figure 6.8: Regeneration of silica gel using vacuum
$T_U = 23°\text{C}$ - flow rate $= 0.34\ ^{\text{Nl}}/_{\text{min}}$

Figure 6.8 shows the regeneration process when using a vacuum pump. As one can see, at the beginning, the regeneration went well and the water in the silica gel was desorbed. After 10 hours, the process slowed and the regeneration continued at a slower pace. In other words, the vacuum created did not suffice to desorb all of the water out of the silica gel. The reason for this is the heat exchange property of silica gel: it heats up when adsorbing water, while it cools down when the water is desorbed. The problem is that the adsorption and desorption rates are related to the temperature. Low temperatures decrease the desorption rate, while the adsorption rate is decreased by high temperatures. Hence, for an optimal use, the temperature should be low when adsorbing, but high when desorbing. The same effect occurs in metal hydride containers when loaded or unloaded with hydrogen. (This process is explained in more detail in section 7.2.2)

As a consequence of the heat reduction during the desorption, the regeneration of silica gel needs an additional heat source apart from the vacuum. Heating the adsorber costs additional energy. In order to keep this energy cost low, the adsorber should be heated to a temperature not higher than 60°C. The heating is managed with the use of a heat mat which covers the adsorber. In order to keep the heat inside the adsorber, an insulating foam covers the adsorber.

The maximum power of the heat mat is 15 W, but the heat mat does not need to run all the time. A digital temperature indicator, named Jumo di eco, measures and displays the temperature with a PT100 sensor which is installed between the heat mat and the adsorber. If the temperature rises above 60.5°C, the temperature indicator shuts down the heat mat until its temperature drops below 59.5°C. Then the heat mat is switched on again. In order to estimate the heat mat's constant power, the turn-on and turn-off times were measured. In 363 seconds, the heat mat was on for 211 seconds, which means 58.1% of the time.

Data sheet of digital temperature indicator

brand name	Jumo di eco
company	Jumo
temperature range	-200...500°C
sampling rate	200 ms
installed relay	10 A
supply voltage	12...24 V
power supply	<3 W
cost	237 Euro

Figure 6.9: Jumo di eco - Jumo [41]

$$\frac{211 \text{ s}}{363 \text{ s}} = 0.581 \tag{6.18}$$

With a maximum power of 15 W, this results in a constant power of 8.7 W.

$$0.581 \cdot 15 \text{ W} = 8.7 \text{ W} \tag{6.19}$$

The positive effect being that the additional heat reduces the relative humidity of the gas stream. A pressure of 150 mbar in combination with a temperature of 60°C results in a relative humidity of 0.3%. Consequently, the gas will be drier than if only the vacuum pump is used.

The results of the regeneration process when using heat are shown in figure 6.10. As one can see, the time for the regeneration was reduced to 7 hours. With a constant power of 8.7 W for the heat mat and 5 W for the vacuum pump, an energy amount of 95.9 Wh was necessary for the regeneration process.

$$(5 \text{ W} + 8.7 \text{ W}) \cdot 7 \text{ h} = 95.9 \text{ Wh} \tag{6.20}$$

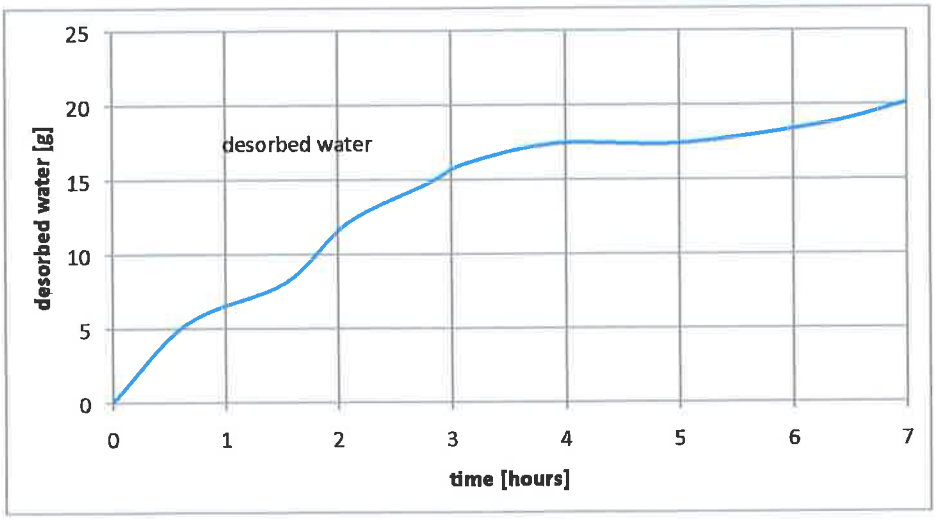


Figure 6.10: Regeneration of silica gel with vacuum and heat
$T_U = 60°\mathrm{C}$ - flow rate = $0.34\ {}^{\mathrm{Nl}}/_{\mathrm{min}}$

Since 24 regeneration processes are necessary in one year, the energy cost per year is of 1.8 kWh. At a production rate of 660 ${}^{\mathrm{kWh}}/_{\mathrm{year}}$, the loss is of 0.35 %.

$$24 \cdot 96\ \mathrm{Wh} = 2.3\ \mathrm{kWh} \tag{6.21}$$

$$\frac{100\%}{660\ \mathrm{kWh}} \cdot 2.3\ \mathrm{kWh} = 0.35\% \tag{6.22}$$

Considering this very small loss. Using heat and a vacuum in combination to regenerate the silica gel works very well. Due to the low temperature, the silica gel is not stressed and its life cycle can be expected to be long as a result of this regeneration method.

After the regeneration, the hydrogen has to pass through the dryer for about 15 minutes in order to eliminate the water molecules at the end of the adsorber. Since the adsorber is regenerated in reverse direction, there are a few water molecules at its end. Tests have shown, that after 15 minutes the hydrogen has again a gas purity of 4.0 or better. During these 15 minutes, the hydrogen must not be stored.

7 Storage

The advantage of using hydrogen as an energy carrier is the high volume-specific storage density. Depending on the method of storage, it is possible to store a large amount of energy. There are different options for the storage of hydrogen, which are described in the following chapter.

7.1 Storage options

There are three main options for the storage of hydrogen:
Compressed hydrogen, liquid hydrogen and solid state hydrogen adsorbers (metal hydrides).
Every method has its advantages and disadvantages. There are differences in the storage density, in the energy consumption for storing and in the complexity of the storage method. An ideal storage system should have a high storage density, should not require any energy for storing and should be easy to handle. However, such a system does not exist and one has to choose the best out of these three options. The current chapter explains the different storage methods and shows the reasons why in this project, metal hydrides are the best choice for storing hydrogen.

7.1.1 Storing hydrogen in liquid state

Hydrogen in liquid state has a very high storage density. 1.6 $^{\mathrm{kWh}}/_{\mathrm{l}}$ can be stored in a volume of 1 liter. For hydrogen to reach its liquid state, a temperature of -253°C is necessary, and in order to reach this temperature, the energy required to liquefy hydrogen consumes 30% of the stored chemical energy. Besides, it is very complex to reach and handle a temperature which is so close to the absolute zero point. The storage tank must be well insulated, otherwise the liquid hydrogen would increase its temperature and would become gaseous again reducing the storage capacity of the tank. The Linde Group invented a high tech cryogenic tank made of 40 layers of metal foil which help to keep the liquid hydrogen cool. Nevertheless, after several days, the storage tank becomes too warm to hold all of the liquid hydrogen. Some hydrogen needs to be released into the environment to keep the rest of the hydrogen cool. This amount of hydrogen is known as the boil-off gas.

Although liquid hydrogen has a very high storage density, the high energy amount and the complexity required for storing hydrogen are two significantly negative factors which make this storage technology unfeasible for this project.

7.1.2 Storing hydrogen in pressure tanks

Pressure tanks are the most common method for storing gas. The storage density depends on the pressure level. High pressure leads to a high storage density while low pressure results in a low storage density. Energy is required for pressurised hydrogen storage. For example, a 700 bar pressure tank with a storage density of 1.3 kWh/l, consumes the energy of 15% of the stored hydrogen. A storage tank of 350 bar has a storage density of about 0.75 kWh/l and needs a energy amount of about 12%. Hence, lower pressure needs less energy for storage, but has also a lower storage density.

A big advantage of the pressure technology is its simple handling. It is well known how to handle high pressure and how to fill gas in a storage tank by using a compressor. Nevertheless, energy is necessary to reach a good storage density. Without using a compressor, the pressure level provided by the electrolyser is of only 11 bar, at which the storage density is 40 times lower than the one reached with a metal hydride storage (Figure 7.1).

7.1.3 Storing hydrogen in metal hydrides

Storing hydrogen in metal hydrides is quite a new technology with a high volume specific storage density (1.2 kWh/l). The metal hydride consists of a porous metal alloy capable of adsorbing hydrogen. Some common metal hydrides which are stable at room temperature are lanthanum pentanickel (LaNi5) and titanium iron (TiFe). Since they consist of metal, these hydrides are quite heavy. Only 1.5 to 1.9 % of the weight of a full storage container corresponds to the stored hydrogen, while the other 98.1 to 98.5 % corresponds to the container's material. Nevertheless, in this project there is no need to move the storage tank, which means that the weight is not a disadvantage.

The metal hydride is placed in a pressure-resistant container made of stainless steel. Usually, a pressure between 11 to 16 bar is necessary to fill the container. Since the absorption of hydrogen is an exothermic reaction, heat develops from filling the container. In contrast, the temperature of the metal hydride decreases when extracting the hydrogen. The temperature between heating and cooling ranges from 70° to 0°C. Therefore, heat management is necessary. More details about heat management and about the influence of temperature on the pressure are explained in chapter 7.1.3.

7.1.4 Comparison between the storage options

Its high storage density at low pressure makes the metal hydride storage the best option for storing hydrogen. Figure 7.1 shows the relation between different storage methods and their storage densities. According to this table, liquid hydrogen has the highest storage density, followed by high pressure storage at 700 bar and metal hydride storage at 11 bar. While pressurised storage is strongly dependent on the pressure level, metal hydride storage needs a constant pressure of 11 bar and has a storage density of 1.2 kWh/l. Additionally, the metal hydride storage requires no additional energy. Hence, it is possible to store the same amount of hydrogen as in a 620 bar pressure bottle without the need for external energy.

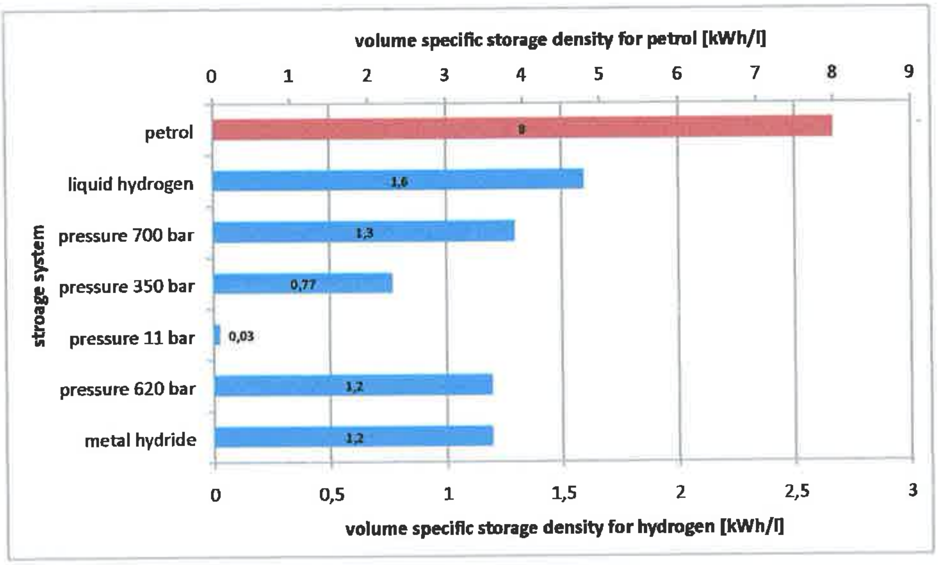


Figure 7.1: Storage density for different storage options

By comparing the degrees of complexity of the three previously mentioned methods for storing hydrogen, it is obvious that the liquefying of hydrogen is the most complex possibility. Metal hydride storages generate heat while absorbing hydrogen and they cool down while releasing hydrogen. Therefore, it is necessary to control the heat, which results in additional work. Pressurised hydrogen, in contrast to metal hydrides, does not require heat management. Neither does it need extremely low temperatures, as liquid hydrogen does. The hydrogen can simply be stored in a pressure bottle. However, if the only pressure used is the one provided by the electrolyser, the storage density will be quite low.

Petrol

In figure 7.1, one can see that there is a high discrepancy between the storage densities of petrol and hydrogen. It is well known that petrol is an energy storage substance with a high energy content. Its volume-specific storage density is five times higher than the density of liquid hydrogen. Nevertheless, petrol is a limited resource as well as harmful to the environment. Alternatives to petrol are necessary and, from a present day perspective, hydrogen seems to be the only alternative for replacing petrol as the most frequently used fuel.

7.2 Metal hydride storage

As already mentioned in section 7.1.3, metal alloys react with hydrogen and form solid metal-hydrogen compounds. The interaction between hydrogen and the metal alloys can be divided into two types: physical adsorption (physisorption) and chemisorption.

Far from the metal surface, hydrogen molecules and the metal alloys are in initial state. If hydrogen molecules come closer to the metal surface, attractive van der Waals forces occur and the hydrogen becomes atomic, which is called the physisorbed state. The hydrogen is now close to the metal surface, but not yet chemically bond to it. When closer to the surface, the hydrogen has to overcome an activation barrier. Once past this barrier, it can dissociate and then form a bond with the metal. As a result, hydrogen atoms share their electrons with the metal atoms and are then in chemisorbed state.

The mechanism of chemisorption can be divided into the following steps: hydrogen atoms diffuse randomly into the bulk metal, dissolve at interstitial sites and form a solid solution. This is the so-called alpha phase. The concentration (number of hydrogen atoms (H) over the number of metallic atoms(M)) is quite low: $H/M < 0.1$. When the hydrogen in alpha phase exceeds a certain limit, the alpha phase becomes saturated. The interactions between the hydrogen atoms increase and come into play. These increased interactions are explained by the fact that the host metal lattice is expanded by the hydrogenation. As a result, the nucleation of the more highly concentrated beta phase occurs. This is also called the hydride phase. Every metal-hydrogen compound can be called a hydride once the hydrogen atoms are in a solution phase and not randomly distributed. The transition from the alpha phase into the beta phase occurs without a significant increase of pressure, as shown in figure 7.2. The concentration in the beta phase is usually H/M = 1.

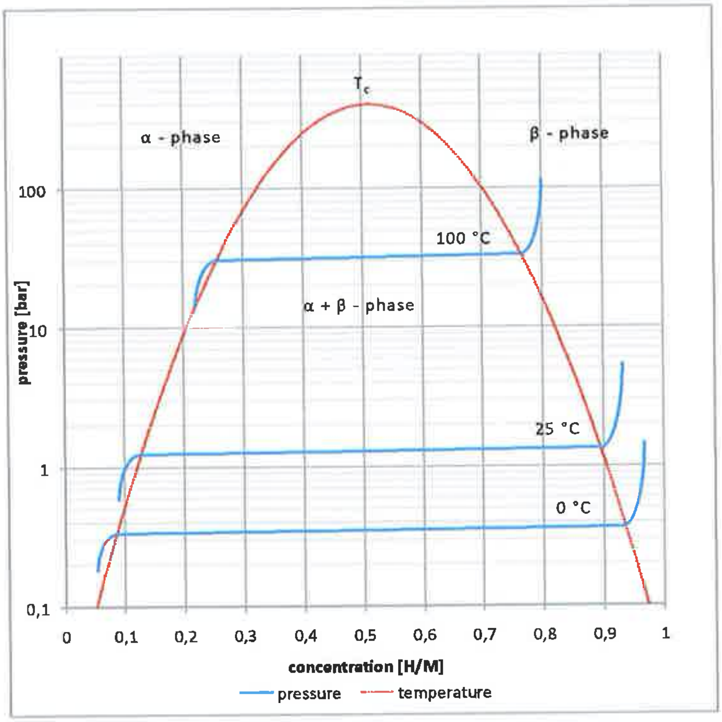


Figure 7.2: Pressure composition isotherms for hydrogen absorption
(H/M: number of hydrogen atoms over the number of metallic atoms)

New hydrogen gas streaming into the metal hydride must pass through the beta phase and then into a new alpha phase. Part of the hydrogen diffuses into the new alpha phase while the beta phase also grows. After the complete formation of the hydride phase, the hydrogen pressure rises sharply at a certain level of concentration.

7.2.1 Thermodynamics of metal hydride

As it has previously been mentioned in this chapter, filling the metal hydride with hydrogen leads to a rise in temperature. The reason for this heat increase is the exothermic process of absorption. The hydrogen absorbed by the metal hydride has a lower energy level than pure hydrogen; the difference between the energy levels is set free in form of heat. Figure 7.3 shows the Lennard-Jones potential of hydrogen approaching a metallic surface and graphically explains the development of the adsorbed hydrogen's energy. First, the hydrogen molecules are in gaseous state and are physisorbed on the surface of the metal. As one can see in figure 7.3, the energy level of hydrogen in its physisorbed state is slightly lower than that of pure hydrogen. Afterwards, when the physisorbed hydrogen transits into the chemisorption hydrogen state, very little energy is necessary (pressure) for the hydrogen to be chemisorbed. Since the energy level of the chemisorbed hydrogen is lower than of pure hydrogen, this difference in energy occurs in form of heat.

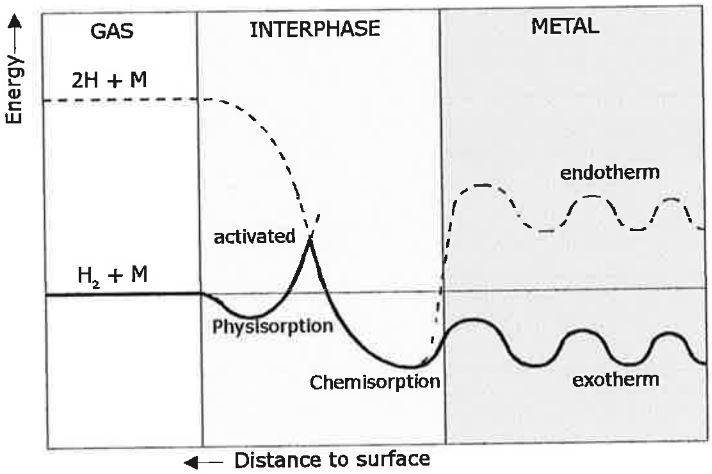


Figure 7.3: Lennard-Jones potential of hydrogen approaching a metallic surface

In order to compensate the increase in heat, it is necessary to manage the heat, for example, with a heat exchanger. Otherwise, the temperature would rise, leading to an increase in the equilibrium pressure which, in turn, would require more pressure to continue storing hydrogen.

7.2.2 Equilibrium pressure

The equilibrium pressure in a "hydrogen-metal hydride" system is the pressure level at which absorbed and pure hydrogen are in equilibrium. At this point, hydrogen will not diffuse into or out of the metal hydride. Since the equilibrium pressure is related to the temperature, an increase in the temperature would lead to an increase in the equilibrium pressure. This coherence is described by the van't Hoff's law.

$$ln\ p_{eq} = -\frac{\Delta H^\circ}{R\,T} + \frac{\Delta S^\circ}{R} \tag{7.1}$$

Figure 7.2 illustrates the equilibrium pressure for three different temperatures. As one can see, a higher temperature leads to an increase in the equilibrium pressure. The equilibrium pressure does not only depend on the temperature, but also on the enthalpy ΔH and the entropy ΔS of the transition from the alpha phase into the beta phase. Therefore, the material of the metal alloy is also a factor which influences the equilibrium pressure. There are many different metal alloys which can absorb hydrogen, but only few of them work at room temperature and at a pressure level below 11 bar. Table B.5 lists three alloys which can be used for storing hydrogen at room temperature.

Name	**Formula**	**ΔH [kJ/mol]**	**Δ S [kJ/mol]**
titanium-iron	TiFe	28.1	0.106
lanthanum pentanickel	$LaNi_5$	30.8	0.108
mischmetal nickel	$MmNi_5$	21.1	0.097

Table 7.1: Metal hydride properties [48]

These values can be used for the calculation of the equilibrium pressure in relation to the temperature. Figure 7.4 shows a curve for each metal hydride and also the pressure range of the electrolyser. Above the 11 bar line, it is not possible to fill the metal hydride with the given electrolyser. On the other hand, the hydrogen cannot be released at a pressure of less than 1 bar. Therefore, it is necessary to control the temperature of the metal hydride in order to stay within the pressure range. As one can see in figure 7.4, $MmNi_5$ reaches the 11 bar at 0°C. In order to fill the metal hydride, a higher pressure would be necessary. The use of this metal alloy would have the advantage of a high release flow rate since the minimum release temperature is far below 0°C and a heat exchange with the environment's temperature would not be a problem. Therefore, if a higher pressure were to be available, this would be a good option.

The other two metal alloys can be used within more adequate temperature - pressure ranges. $LaNi_5$ functions in a temperature range between 12 and 73°C and TiFe can be used between -8°C and 50°C. $LaNi_5$ is better for storing hydrogen, while TiFe can release hydrogen at a higher flow rate.

7.2.3 Flow rate

Due to the increase in heat in the metal hydride, it is not possible to fill or release the hydrogen at any flow rate. The flow rate is limited by the temperature range of the hydride, which is in turn, influenced by the method of cooling and heating. Since

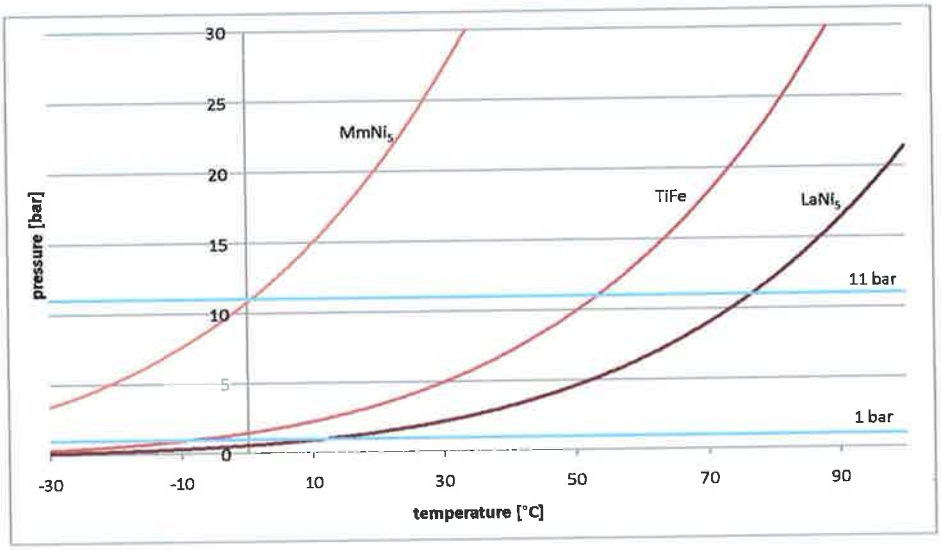


Figure 7.4: Equilibrium pressure in metal hydride

heat management should not need any additional energy, a passive heat exchanger should be used. An adequate heat exchanger can be a water bath, in which the capacity for cooling depends on the amount of water.

Filling the metal hydride

The heat increase of $LaNi_5$ is $\Delta H = 30.8\ ^{kJ}/_{mol}$. This means that if the metal hydride storage is filled with 1 mol of hydrogen, an energy amount of 30.8 kJ will come out free in form of heat. 1 mol of hydrogen is equivalent to 22.414 norm litres, which means that the flow rate is 22.414 $^{l}/_{h}$. A five-cell electrolyser can produce about 42 $^{l}/_{h}$ which is equivalent to about 1.9 mol of hydrogen per hour. Therefore, when using this electrolyser to store hydrogen in the metal hydride, the heat power is:

$$\dot{Q} = 30.8\ ^{kJ}/_{mol} \cdot 1.9\ ^{mol}/_{h} = 58.5\ ^{kJ}/_{h} = 16.25\ \mathrm{W} \tag{7.2}$$

The three different options for cooling the metal hydride container are: air convection, the use of a fan and a water bath. The cooling efficiency of a water bath is better than that of air convection, but air convection does not need additional infrastructure. The question is whether air convection can transport enough heat away from the metal hydride container or not.

The formula to calculate the change in temperature when filling the metal hydride is:

$$T = P \cdot R_{th} + \upsilon_{env} \tag{7.3}$$

T [°C] is the absolute temperature, R_{th} [K/w] is the thermal resistance, P [W] is the heat power of the metal hydride and υ_{env} [°C] is the temperature of the environment. Heat power and heat flow are the same.

$$P = \dot{Q} \tag{7.4}$$

The overall heat resistance consists of three to six separate resistances. The number of the heat resistances depends on the method of heat exchange. In order to calculate the heat resistance of air convection, three single heat resistances are necessary: the resistance of the metal alloy ($R_{th-LaNi_5}$), the metal hydride case ($R_{th-case}$) and the transition from the metal hydride case into air (R_{th-air})(Figure 7.5). Using a fan would require the same three separate resistances except that (R_{th-air}) would have to have a higher value because of the increased activity of the air.

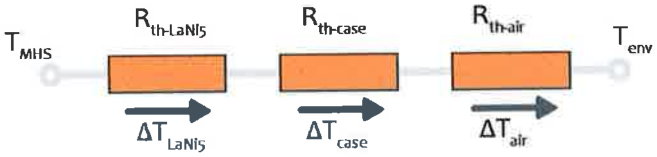


Figure 7.5: Heat resistance of the metal hydride system (T: temperature in °C)

Using a water bath requires six separate resistances: the metal alloy ($R_{th-LaNi_5}$), the metal hydride case ($R_{th-case}$), the transition from the metal hydride to water ($R_{th-case-H_2O}$), the transition from water to water container (R_{th-H_2O-con}), the water container (R_{th-con}) and the transition from water container to air ($R_{th-con-air}$) (Figure 7.6).

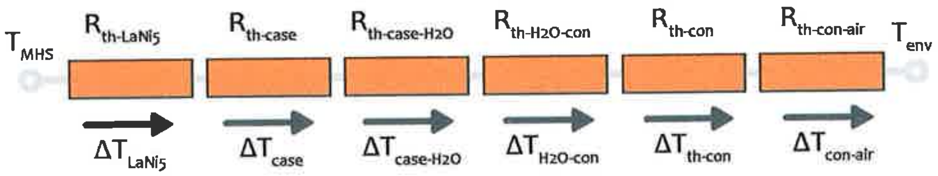


Figure 7.6: Heat resistance of the metal hydride system in a water container

The heat resistance of the MHS and that of the water container can be calculated from their heat conductivity, their chemical characteristics and their dimensions (equation 7.5). In order to calculate the heat resistance of air and water, the heat transfer coefficient (α [W/K m^2])[1] and the transition surface size (A [m^2]) are necessary (equation 7.6).

---

[1] Reference: [46]

$$R_{th-MHS} = \frac{1}{2 \cdot \pi \cdot l \cdot \lambda} \tag{7.5}$$

$$R_{th-H_2O} = \frac{1}{\alpha \cdot A} \tag{7.6}$$

The surface's size and the dimensions of the metal hydride influence the calculation of the heat resistance, any further calculations will apply the technical data of the metal hydride used in this project. The technical data of this $LaNi_5$ storage container is listed in chapter 4.

The overall heat resistance can be calculated by the addition of the separate heat resistances.

$$R_{th-total} = R_1 + R_2 + R_3 ... + R_n \tag{7.7}$$

Table 7.2 shows different heat resistances related to the three methods of heat exchange.

heat exchange method	**air convection**	**fan**	**water bath**
$R_{th-LaNi_5}$[K/W]	0.035	0.035	0.035
$R_{th-case}$[K/W]	0.001	0.001	0.001
R_{th-air}[K/W]	1.4	0.88	-
$R_{th-case-H_2O}$[K/W]	-	-	0.056
R_{th-H_2O-con}[K/W]	-	-	0.016
R_{th-con}[K/W]	-	-	0.021
$R_{th-con-air}$[K/W]	-	-	0.411
$\mathbf{R_{th-total}}$[K/W]	1.43	0.91	0.54

Table 7.2: Heat resistance of the storage system

A water bath's heat resistance depends on the amount of water and on the dimensions of the water container. In order to prevent the metal hydride from crossing its minimum or maximum temperature, the amount of water must have an adequate volume. Calculations have shown that 15 litres of water are enough to run the metal hydride storage constantly. In fact, these 15 litres are only necessary for the emptying of the storage tank at once.

Besides the calculated maximum temperature the metal hydride storage can achieve, it is necessary to know how fast the temperature increases when filling it. This temperature increase is related to the heat capacity. Every material has its own heat capacity which enables them to absorb a specific amount of heat energy. Therefore no material heats up abruptly. Instead, its temperature increases slowly, depending on its heat capacity and the heat power.

Using air convection as heat exchange method, results in two heat capacities: The heat capacity of the $LaNi_5$ alloy ($C_{th-LaNi_5}$) and the heat capacity of the stainless steel case ($C_{th-case}$). Graphically, the heat capacities are parallel connected to the heat resistances, as shown in figure 7.7. At the beginning of the heating process, the heat capacities are charged and then the resistance is heated up.

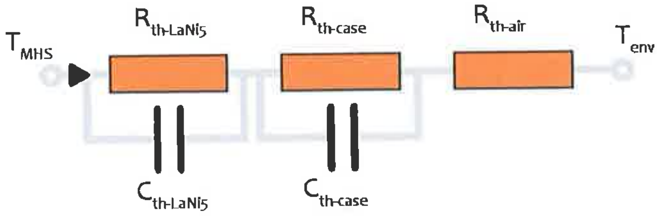


Figure 7.7: Heat capacity and heat resistance of the metal hydride system

In case of using a water bath, the heat capacity of water (C_{th-H_2O}) and of the water container (C_{th-con}) are also involved in the heating process (figure 7.8).

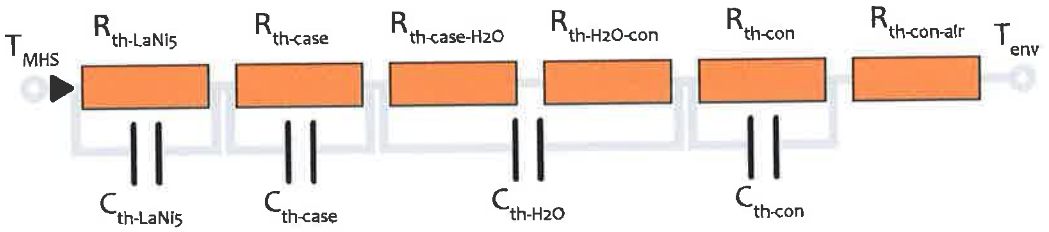


Figure 7.8: Heat capacity and heat resistance of the metal hydride system when using a water bath

The heat capacity (C_{th}) is related to the specific heat capacity (c_{th}) of the material and the material's weight (m). The specific heat capacities for water, air or stainless steel are well known and are listed in the book "Taschenbuch der Physik" [46]. On the contrary, the heat capacity of $LaNi_5$ must be calculated. As its name implies, the alloy $LaNi_5$ consists of one part lanthanum and five parts nickel. The specific heat capacities of lanthanum and nickel are the following:

$$c_{la} = 190\ {}^{J}/_{kgK} \quad (7.8)$$

$$c_{ni} = 440\ {}^{J}/_{kgK} \quad (7.9)$$

A combination of both elements results in a new heat capacity as shown in equation 7.11.

$$c_{LaNi_5} = \frac{1}{6} \cdot 190\ {}^{J}/_{kgK} + \frac{5}{6} \cdot 440\ {}^{J}/_{kgK} \quad (7.10)$$

$$= 398.33\ {}^{J}/_{kgK} \quad (7.11)$$

Having obtained the specific heat capacity, the absolute heat capacity can then be calculated through the multiplication of the specific heat capacity by the mass of the material.

$$C_{th} = c_{th} \cdot m \tag{7.12}$$

The overall heat capacity can be calculated by adding up each one of the heat capacities.

$$C_{th-total} = C_1 + C_2 + C_3 ... + C_n \tag{7.13}$$

Table 7.3, shows the heat capacities of the storage setup for the three different heat exchange methods.

heat exchange method	**air convection or fan**	**water bath**
$C_{th-LaNi_5}$ [K/W]	2171.9	2171.9
$C_{th-case}$ [K/W]	534.2	534.2
C_{th-H_2O} [K/W]	-	62993.4
R_{th-con} [K/W]	-	377.7
$\mathbf{C_{th-total}}$ [K/W]	2706.1	660772.2

Table 7.3: Heat capacities of the storage system

Having obtained the heat resistance and the heat capacity, the heat increase in relation to the time can be calculated. A multiplication of the total heat resistance by the total heat capacity results in the time constant τ.

$$R_{th-total} \cdot C_{th-total} = \tau \tag{7.14}$$

After 1 τ, 63.2 % of the end temperature has been achieved and after 5 τ, the temperature has been achieved almost completely (99.3 %) (figure 7.9) As already mentioned, the final temperature can be calculated using the heat power and the heat resistance (equation 7.3).

It is also possible to calculate the temperature directly in relation to the time.

$$T(t) = (T_{end} - T_u) \cdot (1 - e^{-\frac{\alpha \cdot A}{C_{th-total}}}) + T_u \tag{7.15}$$

T_{end} is the final temperature, T_u is the environmental temperature, α is the heat transfer coefficient of air (or displaced air, in case of a fan), A is the surface area of the metal hydride storage (or of the water container, in case of having used a water bath) and $C_{th-total}$ is the sum of all heat capacities.

Having obtained the heat capacity and the heat resistance, the heat curves for the filling and emptying of the metal hydride storage can be calculated. The filling rate

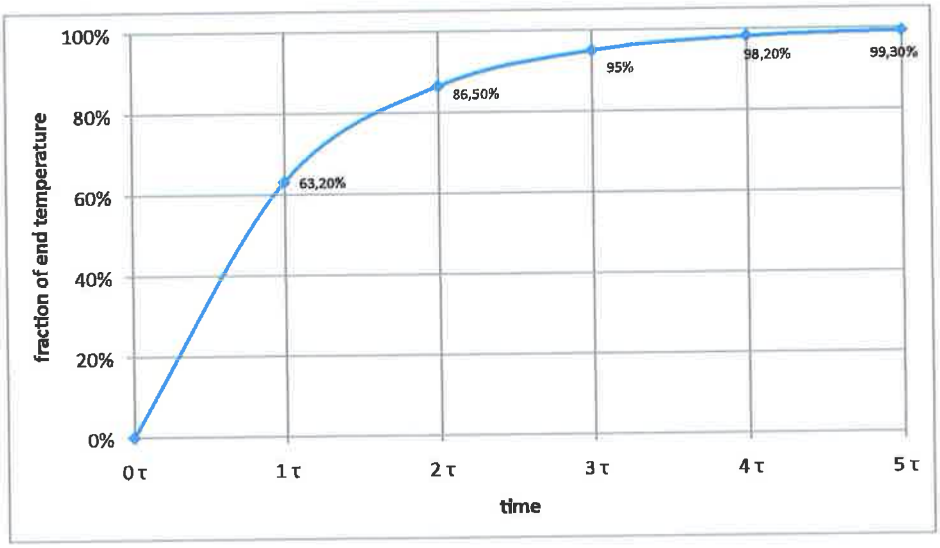


Figure 7.9: Temperature increase related to the time constant τ

is limited by the hydrogen output of the electrolyser, which is 42 $^{Nl}/_{min}$. According to equation 7.3, this results in a maximum temperature of 48°C when using air convection ($T_u = 25°C$). Figure 7.10 shows the three cooling methods and their temperature characteristics. As one can see, at a flow rate of 42 litres per hour, each of the three methods extracts enough heat from the metal hydride in order to keep it within the allowed temperature range ($T_{max} = 73$ °C).

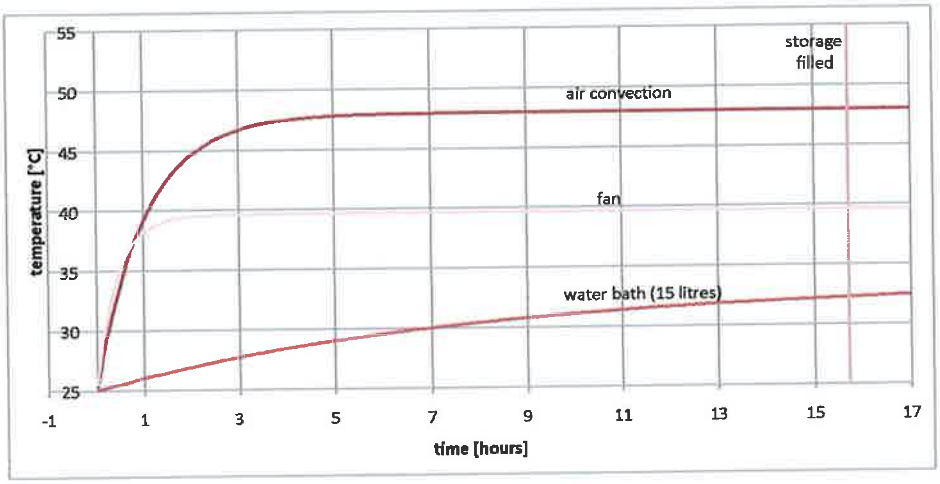


Figure 7.10: Filling of a $LaNi_5$ container at 42 $^{l}/_{h}$ and T_u= 25°C

Heat capacity and heat resistance can also be used in order to calculate the cooling down of the metal hydride storage, which is described in the following section.

Emptying of the metal hydride

The amount of hydrogen that can get extracted from the metal hydride is equivalent to a specific amount of electrical power. One litre of hydrogen per minute equates to a power of 176 W. When using air convection, the metal hydride reaches the minimum temperature level ((T_{min} =12 °C) after about half an hour. If the hydrogen flow were not to be stopped at 12 °C, the metal hydride would decrease its temperature to -8 °C. The final temperature when using a fan would only be 4 °C, but the minimum temperature level would also be reached after approximately half an hour. On the other hand, using a 15-litre water bath as a heat exchanger leads to a temperature decrease of only 1 °C after half an hour. The final temperature of the emptied container is 16 °C. Table 7.4 shows the temperatures for each of the three heat exchange methods related to the hydrogen flow and the electrical power.

flow rate [$^{l}/_{\mathrm{min}}$]	**power** [W]	**emptying time** [h]	**temp. air convection** [°C]	**temp. water fan** [°C]	**temp. bath** [°C]
0.4	**71**	**27.5**	**11.9**	16.6	20.4
0.6	**106**	**18.3**	5.3	**12.5**	18.5
0.7	123	15.7	2	10.4	17.7
1	176	11	-7.8	4.1	15.9
2.3	**406**	**4.8**	-49.7	-23.1	**12.2**
3	529	3.7	-70.4	-37.7	11.3
6	1058	1.8	-137.5	-98.4	9.67
12	2117	0.9	-204.3	-195	8.8

Table 7.4: Emptying of the metal hydride storage: Temperature related to hydrogen flow

In order to reach adequate flow rates, using a water bath for heat exchanging is the only possibility for an efficient heat management. A water amount of 15 litres can manage the heat exchange for a constant hydrogen flow of 2.3 litres per minute, which equates to an energy output of 400 W. This power can constantly be produced until the storage container is empty. It is also possible to obtain more power in shorter time periods. For example, 2000 W can be obtained in a time period of 45 minutes, while 1000 W can be obtained in 1.5 hours. Figure 7.11 shows a flow rate of 6 $^{l}/_{\mathrm{min}}$ which equates to approximately 1000 W. As one can see, after 1 hour and 45 minutes, the end temperature would be about 10°C, which is below the minimum temperature. This means that the metal hydride cannot continuously provide this flow rate. It is possible to obtain 1000 W for 1.5 hours, but afterwards the temperature would fall below 12°C.

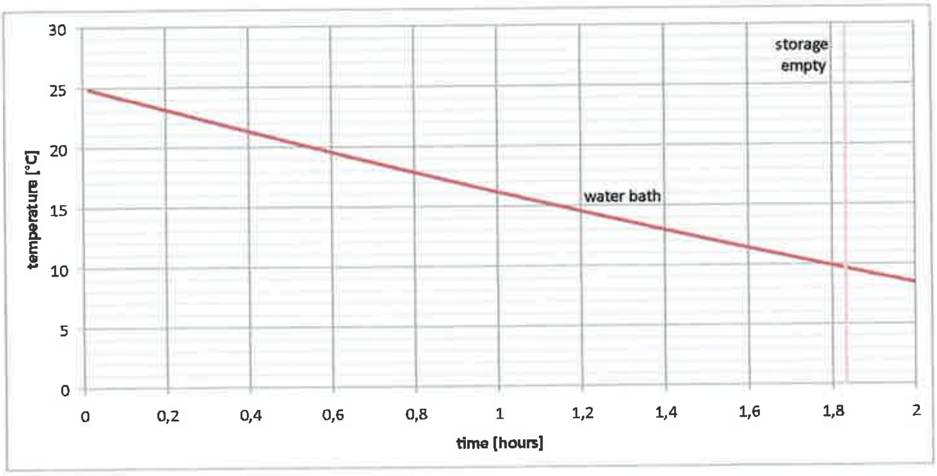


Figure 7.11: Emptying of the $LaNi_5$ container at 6 $^{l}/_{min}$ (1000 W) and $T_{environment} = 25°C$

7.2.4 Actual measured flow rate

In order to prove the previously mentioned theoretical results, the temperature was measured at constant flow rates while applying the three different methods of heat exchange. This test has been made for the emptying and the filling of the metal hydride storage. A PT100 sensor, installed on the surface of the metal hydride storage, measured the temperature and a constant flow rate was set using the throttle valve on the metal hydride storage. The flow rate of the hydrogen was measured by the mass flow meter from Manger + Wittmann. Applying a constant flow rate is somehow difficult, since the pressure of the metal hydride storage decreases during the emptying process. The throttle valve on the outlet of the metal hydride container regulates the flow rate, but this flow rate is related to the pressure on its inlet. Hence, if the pressure in the metal hydride decreases, the flow rate does too. In order to compensate the decrease in pressure, the throttle valve must be manually readjusted at different stages of the measurement in order to obtain a constant hydrogen flow.

Emptying the metal hydride

The emptying of the metal hydride storage was realised by applying a flow rate of 2 $^{Nl}/_{min}$. During the emptying, the temperature was measured by the PT100 sensor.

Air convection is the first of the three heat exchange methods which was tested. Therefore, no additional build up was necessary. As one can see in figure 7.12, the temperature decreases as expected during the process of emptying the metal hydride storage. At the beginning, the temperature decreases parallely to the calculated

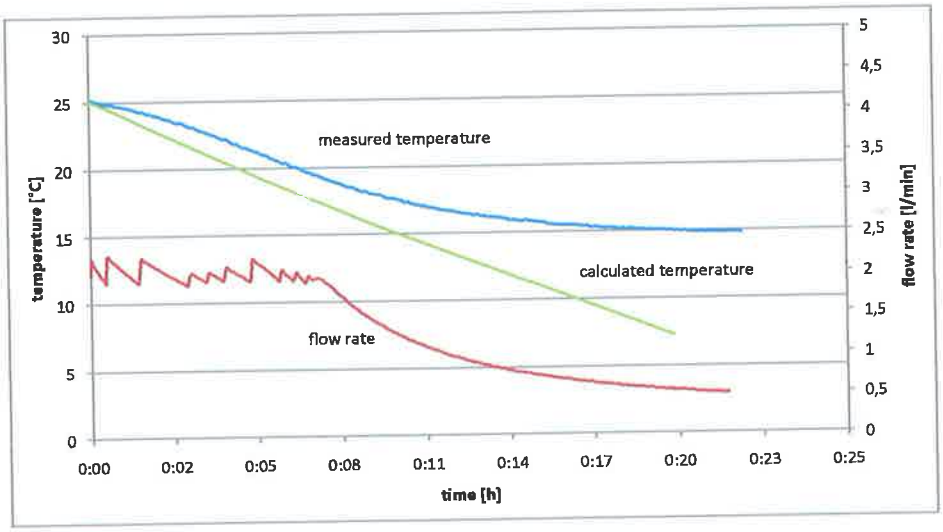


Figure 7.12: Emptying of the metal hydride storage using air convection

temperature. At about 19°C, the metal hydride storage was not able to provide the 2 $^{\mathrm{Nl}}/_{\mathrm{min}}$ anymore, which resulted in a decrease in the flow rate. The decrease in the flow rate is related to the equilibrium pressure of the metal hydride. If the equilibrium pressure comes too close to the atmospherical pressure, the difference in pressure between inside and outside of the metal hydride is not high enough for the metal hydride storage to keep providing 2 $^{\mathrm{Nl}}/_{\mathrm{min}}$. If the flow rate decreases, the temperature decrease is also lower than calculated at 2 $^{\mathrm{Nl}}/_{\mathrm{min}}$, as one can see in figure 7.12. Hence, apart from a slight beside a little discrepancy in temperature, the actual values are as expected.

The second method of heat exchange is the using of a fan, which is installed in front of the metal hydride storage and blows air against it. A fan with little power consumption was chosen in order to keep the influence on the experimental rig's efficiency low. The fan, manufactured by Sunon, has a power of 1.7 W and a volumetric flow of 61.2 $^{\mathrm{m}^3}/_{\mathrm{h}}$.

Data sheet of fan

brand name	KDE2408PKV1
company	Sunon
voltage supply	24 V
power	1.7 W
volumetric flow	61.2 $^{\mathrm{m}^3}/_{\mathrm{h}}$
cost [Euro]	13

Figure 7.13: Fan - Sunon [49]

The results of using a fan as heat exchange method are shown in figure 7.14. As one can see, the decrease in temperature starts with a significant drop, as it was the case when using air convection. In contrast to the latter, the temperature stabilises at about 17°C, which results in a higher flow rate. While the flow rate drops below 0.5 Nl/min after 22 minutes when using air convection, it is only slightly lower than 1Nl/min after 28 minutes in the case of using a fan. Nevertheless, the decrease in temperature was not as strong as expected, which could possibly result from imprecise calculations. It is very difficult to get a precise calculation when displaced air is used as a factor. The determination of the heat transfer coefficient, which is necessary for calculating the temperature-time curve, can only vaguely be calculated with values like wind speed and contact area of the moving wind. Therefore, it was expected to get a larger deviation between actual and calculated values. On the other hand, the assumption that a higher flow rate could be obtained was correct.

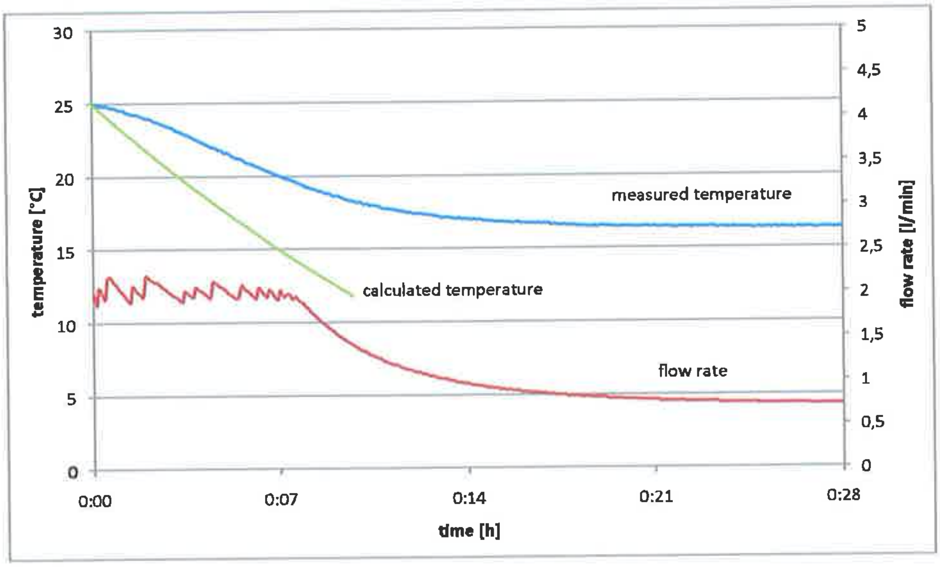


Figure 7.14: Emptying of the metal hydride storage when using a fan as heat exchange method

Placing the metal hydride storage in a water bath is the last heat exchange method. Therefore, the metal hydride storage has been placed in a water container filled with 15 litres of water. In order to prevent a displacement due to the evaporation of the water, a top cover seals the water container. The metal hydride storage and the water container were placed at the bottom of the setup.

As depicted in figure 7.15, using a water bath results in a huge increase in the flow rate. After two hours, it is still possible to obtain a flow rate of 2 Nl/min. The actual values closely match the calculations, and, as expected, it is possible to reach a constant flow rate of 2 Nl/min when a water bath with a volume of 15 litres.

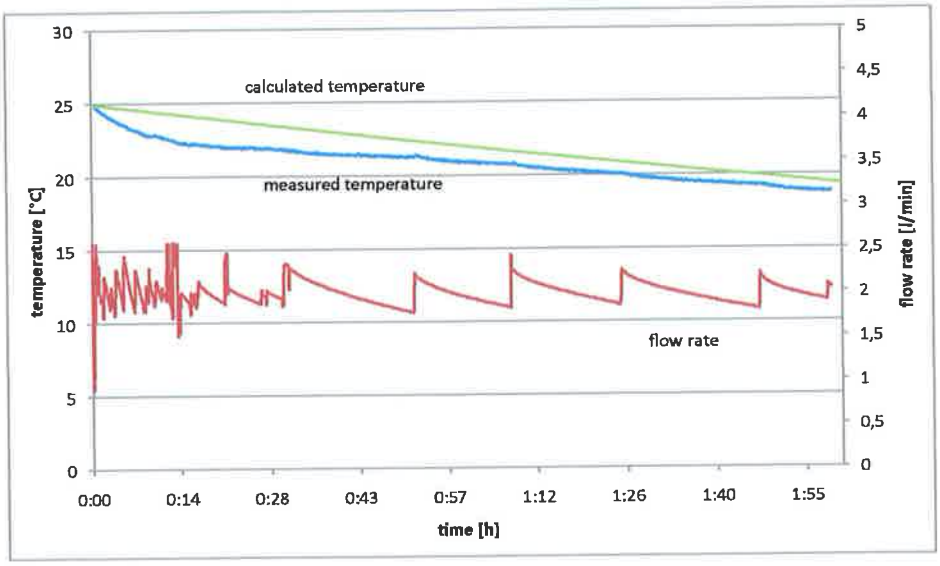


Figure 7.15: Emptying of the metal hydride storage when using a water bath as heat exchange method

Figure 7.16, shows a direct comparison between the three different heat exchange methods. They all were set at a flow rate of 2 Nl/min. In the case of air convection, the flow rates dropped below 1 Nl/min during the measurement. The same happened when a fan was used. Only the heat exchange method of using a water bath resulted in constant flow rate of 2 Nl/min. Hence, using a water bath is the only reasonable method in order to empty the metal hydride storage at adequate flow rates. Another enormous advantage of using this method is that no additional energy is necessary.

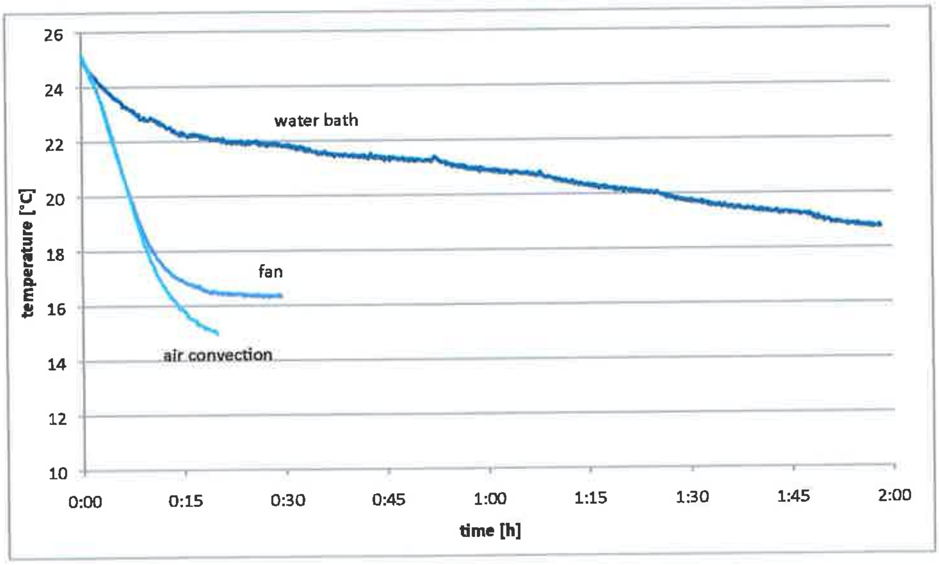


Figure 7.16: Emptying of the metal hydride storage using different heat exchange methods

Filling the metal hydride

The filling of the metal hydride was also tested. It was expected the that filling of the metal hydride storage should have been possible using each one of the three heat exchange methods, since the maximum filling rate is only of 0.7 $^{Nl}/_{min}$. The first heat exchange method to be tested was a water bath. The electrolyser runs with a current of 20 A, which results in the aforementioned maximum flow rate.

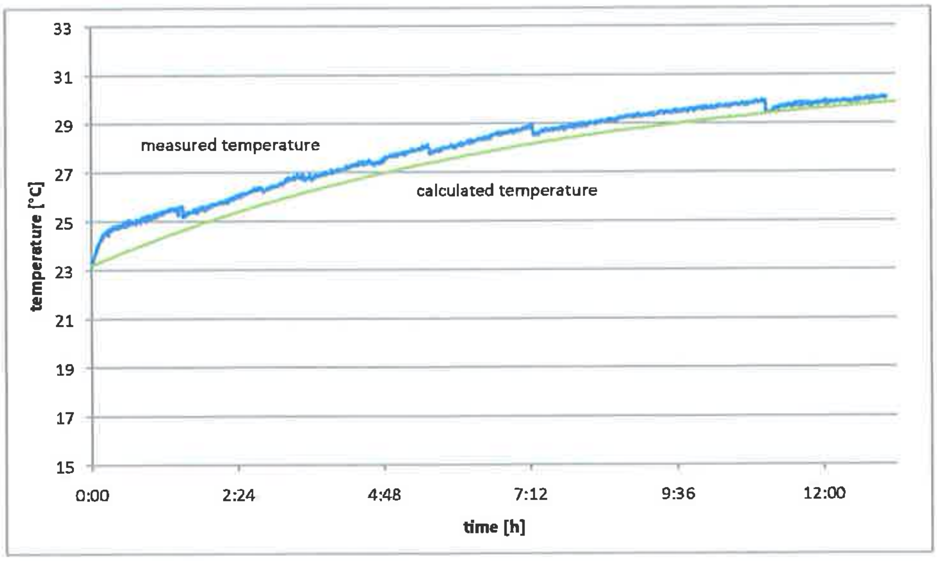


Figure 7.17: Filling of the metal hydride storage when using a water bath as heat exchange method

As depicted in figure 7.17, the filling of the metal hydride when using a water bath does not pose any difficulties. The temperature progression is similar to the calculated values and increases around 7°C in two hours. Since the temperature remains this low, it would be also possible to fill the metal hydride storage at a lower pressure. The equilibrium pressure at 35°C is around 2.5 bar. Hence, if the temperature remains below 35°C, it is also possible to fill the metal hydride at a pressure of 2.5 bar. Nevertheless, it still makes sense to use a pressure of 11 bar in order to reduce the humidity in the hydrogen before it flows through the dryer. Also, at 11 bar a small additional amount of hydrogen can be stored in the metal hydride container. The saturation of the LaNi5 alloy in the metal container is almost the same at 11 bar and 2.5 bar, if the temperature is below 35°C. However, the alloy does not fill the metal container completely. There are still some gaps within the alloy. These gaps can also be filled with hydrogen, and at 11 bar of pressure, more hydrogen can be stored than at 2.5 bar.

The final pressure also helps to recognise when the metal hydride container is full.

If the pressure inside of the container rises to the same level of the pressure used for filling it ant the temperature is low, the container will be completely full.

The a second heat exchange method, tested while filling the metal hydride storage was air convection. Like in the case of the water bath, a flow rate of 0.7 $^{Nl}/_{min}$ was set. As one can see in figure 7.18, the temperature increases almost as expected. First, there is a strong increase in the temperature before it settles down at 42 °C. The expected temperature was around 45°C and the actual results differed only slightly from the calculated values. The important conclusion is to have established that air convection can also be used for filling the metal hydride. The maximum temperature allowed for the filling process is 60°C and the maximum actual temperature was of 42°C. Since the temperature is higher than 35°C, it is not possible to fill the metal hydride at 2.5 bar as it was, using a water bath. Instead, a pressure around 11 bar must be used.

In contrast to using a water bath, it is not possible to theoretical fill the metal hydride at 2.5 bar. Instead a pressure of 11 bar is adequate.

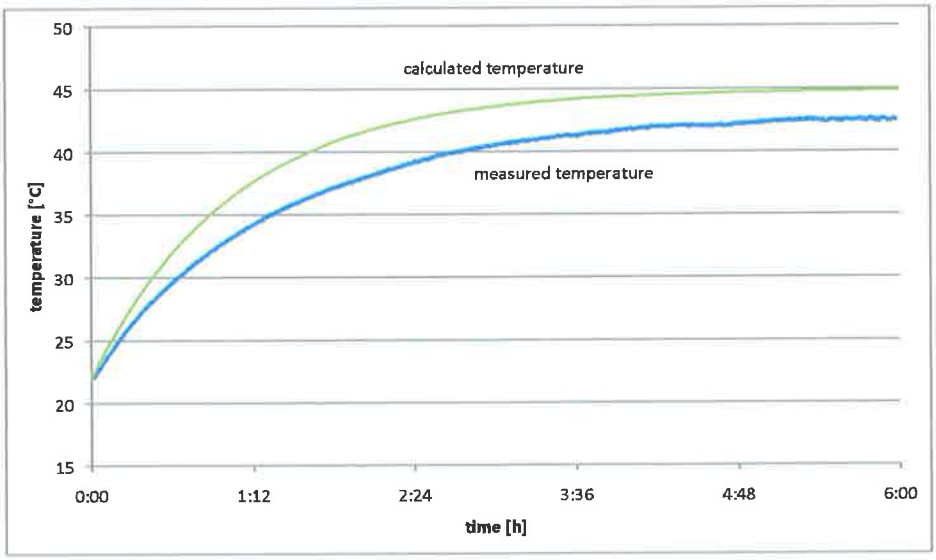


Figure 7.18: Filling of the metal hydride storage when using air convection as heat exchange method

Both tested heat exchange methods remain within the allowed temperature range. Hence, no additional heat exchange method is necessary for the filling of the metal hydride with the given electrolyser.

7.3 Alternative storage options

Metal hydride storage is a high tech solution for storing hydrogen. This technology is expensive and therefore, it might also be interesting to consider alternatives with a lower cost. Pressurised storage can be a cheaper option for the storing of hydrogen. Rechargeable batteries are a second possibility. The latter can be used to store the electrical energy directly.

7.3.1 Pressurised storage

Since the electrolyser is able to produce a pressure of 11 bar by itself, it is possible to store hydrogen at a low pressure level without the use of additional energy. The volume-specific storage density at this pressure level is about 40 times lower than the storage density of a metal hydride storage. Hence, this would require a larger storage container. If equal amounts of hydrogen were to be stored in an 11-bar pressurised container and in a metal hydride storage, the size of the pressurised container would have to be 40 times larger than that of the metal hydride storage.

The metal hydride container used in this project can store an amount of 660 Nl of hydrogen in a volume of 1.7 litres. In order to store the same amount of hydrogen, a pressurised container would need a volume of about 70 litres at a pressure level of 11 bar. Apart from the disadvantage of the increased size, an additional problem is that standard hydrogen containers for a pressure level as low as 11 bar and with a volume of 70 litres do not exist.

attributes	**pressure bottle**
max. pressure level	300 bar
volume including case	61.4 l
storage capacity at 1 bar	50 l
storage capacity at 11 bar	500 l
storage density	0.024 $^{\mathrm{kWh}}/_{\mathrm{l}}$
cost	300 Euro

Table 7.5: Data of a 300 bar pressure bottle

Standard containers are designed for a pressure level of 300 bar. In this project, a container able to withstand a pressure of 11 bar would suffice. Hydrogen containers for a pressure level of 11 bar are only available in 1 Nl. These containers are produced exclusively by Linde Gas and can only be used once. Since the size of these so-called Minican® containers is very small, they cannot be used for storing larger amounts of hydrogen. In order to store the same amount of hydrogen as in the metal hydride storage, the volume of the pressurised bottle must be of 50 to 70 Nl. Pressurised bottles in these sizes are only available for a pressure level of 300 bar. The disadvantages of using a 300 bar pressurised bottle are the increased size and the additional weight due to the bottle's thicker walls. A 300 bar pressurised bottle usually has a volume of 50 Nl. When using a storage pressure of 11 bar, it is possible to store about 500 Nl of hydrogen, which are equivalent to an energy amount of around 1.5 kWh. The cost of a 300 bar pressurised bottle with a volume of 50 litres is of around 300 Euro. Although the cost is lower compared to a metal hydride storage, the size is significantly larger. On the other hand, the method of storing hydrogen using pressure does not need any heat management and the pressurised bottle is not vulnerable to impurities. However, since a fuel cell needs a minimum gas purity of 99.9%, it is still necessary to dry the hydrogen using a silica gel dryer. For this setup, it is not possible to dry the hydrogen just with the help of pressure, since the necessary pressure level for reaching a gas purity of 99.9% is about 40 bar.

7.3.2 Energy storage using a rechargeable battery

When referring to energy storage, the possibility of storing energy in rechargeable batteries should also be mentioned. It is the easiest way to store electrical energy. A complex setup is not necessary in order to produce and store hydrogen. The electrical energy from the solar cells can be stored directly in a battery. The advantages and disadvantages of a battery storage system will be discussed later in this section. In order to evaluate these two energy storage systems, they will be compared in four different categories: complexity of the setup, storage density, life cycle and cost.

Complexity of the setup

In order to store the electrical energy of the solar cells in a battery, only a converter and a charge controller are necessary. There is no need of using a hydrogen dryer, neither of working with an increased pressure. Hence, the setup of a stand-alone system using a battery is far simpler than the setup using hydrogen.

Storage density

The volume-specific storage density of a battery is strongly related to the battery type. There are many different battery types available and the three most common are: lithium-ion, nickel-metal hydride and lead-acid batteries.

Lithium-ion (li-ion) batteries are very popular for portable electronics. Of all battery types, they have the highest volume-specific storage density as well as a very good energy-to-weight ratio. They are also growing in popularity for automotive and aerospace applications. However, since they tend to explode when misused, they are not yet widely spread in the automotive sector. Additionally, lithium-ion batteries lose 20% of their capacity every year.

Nickel-metal hydride (NiMH) batteries' only real advantage compared to the lithium-ion type is that they pose no risk of exploding due to misuse. They have a lower volume-specific storage density that lithium-ion batteries and their self-discharge rate is very high. They lose 5 to 10% of their stored energy on the first day, after which the self-discharge rate stabilises at 0.5 to 1% per day. Hence, this type of battery is not able to store the electrical energy for a long period of time and therefore, cannot be used in connection to a stand-alone solar system.

Lead-acid batteries are commonly used in automobiles. They are the oldest type of rechargeable batteries, have the lowest energy-to-weight ratio and a low energy-to-volume ratio. On the other hand, lead-acid batteries are able to supply high currents and are low priced, which makes them attractive for being used in motor vehicles. Lead-acid batteries are the only ones produced in larger dimensions, which gives them a higher energy storage capacity. Since lithium-ion batteries can explode and NiMH batteries have a high self-discharge rate, both types are only built in small sizes, making lead-acid batteries the only possible choice for storing larger amounts of electrical energy.

Efforts are being made to improve the safety of lithium-ion technology. Since lithium-ion batteries have the highest volume-specific storage density and have a three to four times better weight-specific density than lead-acid batteries, they will probably have a huge breakthrough not only in the automotive sector, but in all kinds of devices requiring a battery. Table 7.6 shows the attributes of the three different battery types mentioned above. As one can see, lithium-ion batteries are the most advanced available batteries.

Life cycle

The life cycle of a battery is strongly related to the environmental conditions. Batteries placed in a cold environment will have a longer life cycle than batteries placed in a warm environment. The life cycle of a battery is also related to the discharge rate of the battery. If a battery gets discharged to 20% of its capacity, this will have a negative effect on its life cycle, while batteries which get discharged only to 80%

battery type	**lithium-ion**	**NiMH**	**lead-acid**	***H_2 in MHS***
energy/size [Wh/l]	250 - 360	140 - 300	60 - 75	*1200*
energy/weight [Wh/kg]	100 - 160	30 - 80	30-40	*300*
power/weight [W/kg]	250 - 340 (1700 lab)	250 - 1000	180	*300*
self-discharge rate [%/month]	5 - 10	30	3 - 20	*0*
cycle durability (deep cycle)	1200	500 -1400	500 - 800 (1500)	*8000*
cost [Euro/Wh] (deep cycle)	2	0.8 - 1.1	0.07 - 0.13 (0.2 - 0.5)	*0.5 - 1.1*

Table 7.6: Different battery types

of their capacity will work for a longer time. Lead-acid batteries used in cars are not adequate for combining with solar cells. In a solar cell system, the batteries would often get significantly discharged. Car batteries are not designed for operating at high discharge rates. In combination with a solar cell system they would probably get damaged after one year. In order to reduce their discharge rates, a different type of lead-acid batteries was invented. The so called "deep cycle batteries" are able to withstand high discharge rates and can run for more cycles. The increased life cycle is possible due to thicker electrodes in the batteries. As a result, deep cycle batteries are heavier than ordinary lead-acid batteries, but since the battery is installed at a fixed place, this does not represent a problem.

Li-ion and NiMH batteries should not be discharged to less than 40% of their capacity. In the case of lead-acid batteries, this should not be less than 80%. Deep cycle batteries, on the contrary, are able to reach a discharge rate of about 20%.

Deep cycle lead-acid batteries, li-ion batteries and NiMH batteries all have similar life cycles (see table 7.6), with that of lead-acid batteries being clearly the shortest.

Cost

Lead-acid batteries are the cheapest available batteries, but they have the shortest life cycle and also the lowest volume-specific storage density. Li-ion batteries, on the contrary, are the most expensive, but also the most powerful batteries. NiMH batteries are slightly cheaper than li-ion batteries, while the price for deep cycle batteries ranges between li-ion and lead-acid batteries. The more powerful the battery is, the higher is the price. A li-ion battery with an energy capacity of about 2 kWh would cost about 4000 Euros while the cost for a deep cycle battery would be of around 600 Euros.

Batteries: conclusion

After having compared the different battery types, it is easy to conclude that none of them is ideal for being used in a stand-alone solar cell system. High performance li-ion batteries are expensive, while low-cost lead acid batteries do not have a good performance. Hence, there has to be a compromise between cost and performance. At present, deep cycle batteries seem to be the best solution storing electrical energy in a stand-alone solar cell system. They are able to withstand high discharge rates, have a low cost and a long life cycle. In the future, li-ion batteries could become more popular due to sinking costs and improved safety.

Best battery for a stand alone solar cell system

This section describes a battery which could be used in combination with a stand-alone solar cell system. The power.bloc is a deep cycle battery from the company Hoppecke GmbH. This battery has a capacity of around 2.5 kWh for a volume of 29.8 litres, which represents a volume-specific storage density of 0.08 $^{\mathrm{kWh}}/_{\mathrm{l}}$. Due to its 1400 charging cycles, the power.bloc has a life expectancy of three to six years.

attributes	Hoppecke power.bloc
capacity	2.5 kWh
volume	29.8 l
storage density	0.08 $^{\mathrm{kWh}}/_{\mathrm{l}}$
cycles	1400
life cycle	3 to 6 years
cost	500 Euro

Table 7.7: Data of Hoppecke's power.bloc

7.3.3 Comparison between storing energy in hydrogen or in batteries

Each one of these options for storing energy has its pros and cons. A system which uses batteries for the storage of energy has a less complex setup than one that uses hydrogen. The electrolyser, the water separator and the dryer are not necessary.

Instead, the battery can easily be charged with the electricity provided by the solar cells. Since it is not necessary to first produce hydrogen and then transform it back into electricity, the efficiency of a battery system can be higher than 90%. This battery is clearly more efficient than a hydrogen storage. However, these batteries need a lot of space due to their low volume-specific storage density. A deep cycle battery has a storage density eighteen times lower than a metal hydride storage. Also, batteries have a self-discharge rate, which is not the case in a hydrogen system. Once hydrogen is stored, it remains in the storage container and cannot be lost. Additionally, the metal hydride can be fully charged and discharged without being damaged. Another point in favour of hydrogen storage is the life cycle. A metal hydride storage can withstand over 8000 life cycles, whereas a battery needs to be replaced after only 1500 life cycles. As a result, the life cycle of a metal hydride storage is around five times longer than that of a battery. Finally, hydrogen can be easily refilled into portable containers. This can be advantages if the hydrogen is going to be used, for example, in a boat, or in combination with a small fuel cell for portable devices.

After having revised the pros and cons of the two systems, it can be concluded that both of them are adequate for being used in combination with solar cells. Batteries would probably have a slight advantage since they are currently available and can be installed immediately. However, the hydrogen option has the great advantage of its high volume-specific storage density. This technology is just beginning to be applied, therefore, hydrogen will probably play an important role in the storage of energy in the future.

8 Instruction manual

During the two years of this project, the experimental rig has grown and become more complex. Currently, it is capable of producing hydrogen, storing it, releasing it from the metal hydride storage, drying it and regenerating it. Some processes are automated and some must be done manually. This chapter explains how to use the experimental rig correctly and how to prevent any damage to it. In order to have a connection between this instruction manual and the real setup, the setup is labeled with name tags for each one of the installed units.

Figure 8.1: Experimental rig

8.1 Getting started

The first step is to check for any loose tubes, cables or fittings. The water container at the bottom should has an adequate water level. If not, it must be refilled with distilled water. Finally, before turning on the main switch, the switches of the solar converter and the power supply unit connected to grid must be turned off (figures 8.2 and 8.3).

Figure 8.2: Solar converter

Figure 8.3: Power supply

Once the visual check has been completed, the main switch on the left side of the setup can be turned on. This activates the power supply for the measuring and control devices as well as the power supply for the electrolyser. Since the power supply unit and the solar converter have been turned off, the electrolyser does not receive any electrical energy yet. In order to monitor the experimental rig, the computer must be switched on. The LabView program for the monitoring and control of the setup pops up automatically, but does not start right away. In order to start the program, the button in the upper left corner displaying a white arrow must be pushed. If the white arrow turns to black, the LabView program will be running. With the LabView program on, only the hand valves on the setup must be correctly adjusted before the electrolyser can be started. It is possible to select whether the electrolyser receives its energy from the solar cells or from the power grid.

8.1.1 Adjusting the hand valves

There are three hand valves installed on the setup (figures 8.4 and 8.5). At the beginning, the hand valves must be adjusted as follows:

(1): open - (2): open - (3): close

In this standard configuration, the hydrogen produced by the electrolyser flows to the outlet, while the metal hydride container is shut. Once the hand valves have

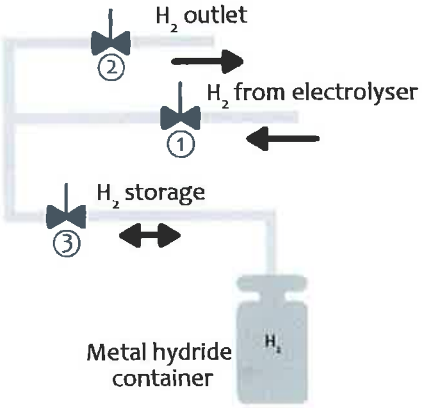


Figure 8.4: Graphic of the three adjustable hand valves

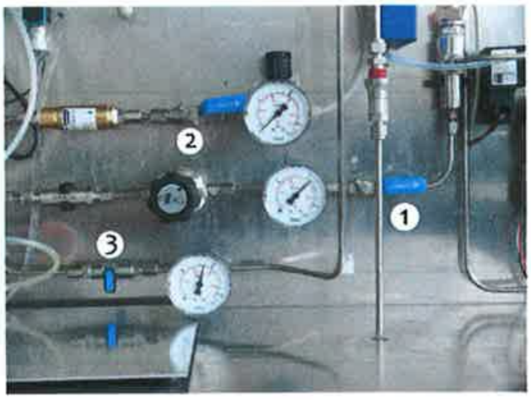


Figure 8.5: Picture of three adjustable hand valves

been correctly adjusted, the electrolyser can be started. At this point, the electrical energy can either be obtained from the solar cells or from the power grid.

8.1.2 Energy provided by the solar cells

In order to use the energy from the solar cells, the solar converter must be connected to the electrolyser. Therefore, the two large cables connected to the electrolyser must also be connected to the solar converter. If they are not already plugged-in, they must be disconnected from the power supply unit at the bottom of the setup and connected to the solar converter. As soon as they are connected, the power switch on the solar converter must be turned on. As a result, the electrolyser receives its energy from the solar cells.

When using this method in order to provide the electrolyser with energy, one should be aware that it is not possible to influence the amount of power the electrolyser will get. This amount depends only on how strongly the sun shines on the solar cells.

8.1.3 Energy provided by the power grid

A power supply unit able to receive energy from the power grid, is installed at the bottom of the setup. In order to use this power supply, it must be connected to the electrolyser. If the cables are not plugged-in, they must be disconnected from the solar converter and connected to the power supply.

In contrast to the solar converter, with this power supply it is possible to influence the amount of power the electrolyser will receive. There are four potentiometers at the front of the power supply unit in order to adjust the power (figure 8.3). The two on the left side are for adjusting the voltage, while the two on the right side are for adjusting the current. There are two potentiometers for each value since one is for the coarse tuning and the other for the fine tuning. The voltage potentiometers must be set to their maximum, while the current potentiometers must be set to zero. Once it has been properly set, the power supply unit can be turned on with the switch on the left side. Since the potentiometers for the current are set to zero, the electrolyser still not yet receive any energy. At the beginning, the current must be set to 1 A. After five minutes, the current can be increased to the required level. The power supply can be used at its maximum current (20 A), since the electrolyser is able to handle a current of up to 30 A.

8.2 Recording measurements

At this point, the electrolyser should be operating and the hydrogen should be flowing to outlet of the experimental rig. Next, the setup can be used to take measurements. Some of the measured values are shown directly on the setup, while most of them are displayed by the LabView program on the computer.

8.2.1 Measured values displayed directly on the setup

Overall, there are four analog manometers installed in the setup which measure and display different pressures. The first manometer measures the pressure of the electrolyser; the second measures the pressure of the metal hydride container; the third measures the pressure at the outlet behind the pressure reducer and the last manometer measures the vacuum pressure for the regeneration. In order to recognise the separate manometers, they are labeled as shown in table 8.1.

manometer	measured value	label name
1	pressure of electrolyser	electrolyser
2	pressure of metal hydride container	metal hydride
3	pressure at the outlet	outlet
4	vacuum pressure for regeneration	vacuum

Table 8.1: Different manometers installed on the experimental rig

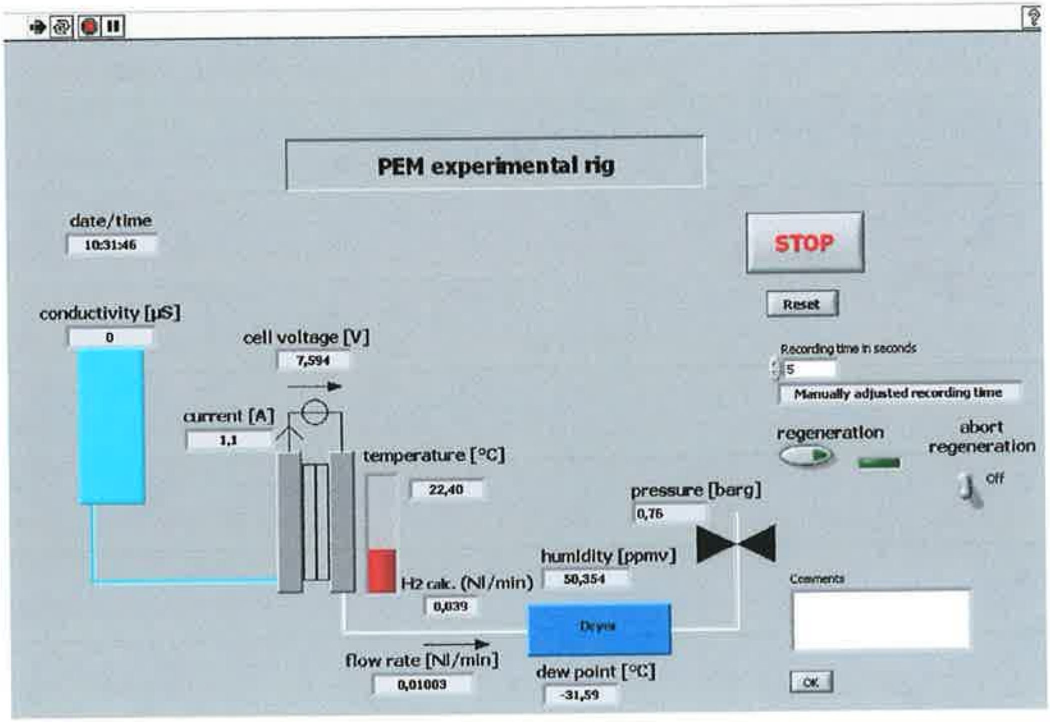
The dew point transmitter in the upper left corner of the experimental rig displays the dew point, the water volume's concentration and the mixing ratio of the hydrogen gas. Each of these values can be used to measure the humidity in the hydrogen gas.

Since the mixing ratio is to small when measuring a gas purity of 4.0 or higher, only the signals of dew point and volume concentration are sent to the measurement card for their values to be displayed on the setup as well as in LabView. There are so many possibilities for using the dew point transmitter, that it would take too long to explain them all in this document. They can be found in the dew point transmitter's instruction manual.

A temperature measurement device, which is usually turned off, is installed on the right side, in the middle section. Only when the regeneration of the silica gel starts, it turns on in order to display and control the temperature of the dryer. The maximum temperature should not be higher than 61°C.

8.2.2 Measured values displayed in LabView

The LabView program monitors all important values and regulates the regeneration of the silica gel. As shown in figure 8.6, the measured values are displayed on a graphic of the experimental rig, while the control elements are placed at the right side of the display. By scrolling down, one can see all measured values listed in a table. Below this table, a curve of the relation between voltage and time is shown.



date/time 10:31:46
conductivity [µS] 0
cell voltage [V] 7,594
current [A] 1,1
temperature [°C] 22,40
H2 calc. (Nl/min) 0,039
flow rate [Nl/min] 0,01003
pressure [barg] 0,76
humidity [ppmv] 50,354
dew point [°C] -31,59
Recording time in seconds 5
Manually adjusted recording time
Comments

Figure 8.6: LabView interface

As already mentioned, the control elements are placed on the right side in LabView. The following enumeration describes each one of the control elements starting from the top.

- The "STOP" button stops the measurement. If the measurement should continue, the white arrow in the upper left corner must be pressed.
- The "Reset" button clears the table. This table can be viewed by scrolling down the screen.
- The intervals for recording the values can be entered in the white field "Recording time in seconds". If negative values or no values at all are entered, the program will use a standard recording time of 30 seconds.
- The regeneration button and switch are for the control of the dryer's regeneration. The button on the left side activates the regeneration process manually. The main switch for the regeneration is on the right side. If this switch is turned off, the regeneration will not start. Neither manually nor automatically.
- The comment field allows the user to type in comments during the measurements. After typing in the comment, the "OK" button must be pushed. This transfers the comment to the table with the measurement results and also to the data-file in which the results are saved.

The LabView program automatically saves all measurement results. If the "STOP" or "Reset" buttons are activated, the results will also be saved in an external csv-file. All measured values are saved in a folder named "measurement results" located on the desktop. Each file is named after the current date (year-month-day).

8.3 Different options for using the experimental rig

The experimental rig can be used in different operation modes. The user can decide which mode to use. Overall, there are six possibilities using the experimental rig:

1. Hydrogen is produced with energy from the solar cells
2. Hydrogen is produced with energy from the power grid
3. The produced hydrogen flows to the outlet
4. The produced hydrogen is stored in the metal hydride

5. The silica gel gets regenerated
6. The stored hydrogen flows to the outlet

For the first five possibilities, the electrolyser must receive electrical energy, while for the last possibility, the electrolyser must remain offline. In order to pipe the hydrogen in the correct direction, the hand valves installed on the setup must be adjusted correctly.

Which energy source can be used for the electrolyser has already been explained in sections 8.1.2 and 8.1.3. If the valves are set to their standard configuration, the hydrogen flows to the outlet as described in point 3. In the next step, it can be decided between storing the hydrogen, regenerating the silica gel or using the stored hydrogen.

8.3.1 Storage of hydrogen

In order to store hydrogen in the metal hydride container, there are some points to beconsidered. Before starting the storage process, the pressure must have a level of 10 barg. Additionally, the produced hydrogen must be dry enough, which means that its humidity, measured in volume concentration, must be lower than 100 ppmv. If the concentration is above this value, the hydrogen must not be stored in the metal hydride. In order to reduce the humidity, the hydrogen has to flow through the outlet for a while, since the latter transports water molecules to the outside. If this does not help and the humidity does increase further, the silica gel must be regenerated. If no regeneration is necessary - the hydrogen is dry enough and a pressure of 10 barg has been achieved -, the hand valves can be adjusted in order to pipe the hydrogen into the metal hydride container.

Initiate storage of hydrogen: Close valve 2 -> Open valve 3 -> (Valve 1 stays open) (figure 8.4)

In order to stop the process of filling the metal hydride container, the valves must be adjusted in the opposite sequence.

Stop storage of hydrogen: Close valve 3 -> Open valve 2 -> (Valve 1 stays open)

The sequence is very important. If valves 2 and 3 are opened at the same time, the hydrogen from the metal hydride will flow out into the air.

It is also possible that the metal hydride container is already full and the valves are still adjusted for the process of filling it. In this case, the safety relief valve will open at a pressure of 12 barg. This can be recognised if the valve fizzles. If this happens, the regeneration must be stopped in order to pipe the hydrogen through the normal outlet.

8.3.2 Regenerating of the silica gel

Normally, the regeneration of the silica gel is automated. If the humidity rises above 150 ppmv, LabView will initiate the regeneration process, which works fully automated for 7 hours. After this time, the regeneration is completed. However another fifteen minutes are required before the hydrogen is completely dry again, since the water molecules in the dryer's outlet must be released outside.

It may be required to start the regeneration process manually, even if the humidity is lower than 150 ppmv. This is also possible with LabView. On the LabView's interface, the switch on the right side must be turned on and the regeneration button next to the switch must be pushed in order to start the regeneration. By pressing the regeneration button, the valves activate and the dryer will become heated. By pressing the same button again, the regeneration process stops.

8.3.3 Using the stored hydrogen

Once the hydrogen has been stored, it can be released. Opening the metal hydride container, releases the hydrogen through the outlet. Ideally, a fuel cell is connected to the outlet so that the hydrogen is not wasted. In order to start the releasing process, the electrolyser must be shut off and the valves must be adjusted as follows:

Releasing of hydrogen:
Close valve 1 -> Close pressure reducer-> Open valve 3 -> (Valve 2 stays open) (figure 8.4)

Since the pressure reducer is closed, the hydrogen cannot flow out yet. In order to release the hydrogen, the pressure reducer must carefully be opened. The LabView program should be used to check the flow rate. By opening the pressure reducer, the flow rate will increase. If no fuel cell is connected to the outlet, the hydrogen may rush through the tubes even if the pressure reducer is just slightly open. It has to be emphasised: opening the pressure reducer must be done very carefully!

Since the flow rate which can be provided by the metal hydride container is related to the heat exchange method, the container should always be placed in a water bath.

For low flow rates up to 0.3 $^{\mathrm{Nl}}/_{\mathrm{h}}$, air convection is also sufficient as a heat exchange method. For flow rates above 0.3 $^{\mathrm{Nl}}/_{\mathrm{h}}$, a water bath is necessary.

In order to stop the release of hydrogen, valve 3 must be closed.

8.4 Summary

This instruction manual has provided an overview about how to use the experimental rig. Since there a different possibilities for using the experimental rig, a flow chart in appendix A provides an overview of the entire manual.

8.5 Sources of error

This chapter explains some common problems, their cause and how they can be solved.

problem	**possible cause**	**solution**
the electrolyser does not operate	the cables are not connected	connect cables to power supply
	the main switch is not turned on	turn on main switch on
	the water container is empty	refill container
the hydrogen flow is not displayed	hydrogen did not reach mass flow meter	opens valve 1 and 2 and pressure reducer
the MHS does not provide any hydrogen flow	the MHS is empty	fill MHS
	the MHS is too cold	wait a few minutes heat MHS
the pump on the wall make strange noises	the pump is refilling water into the small container	wait until refilling process is over
the hydrogen gets not dry	the silica gel is saturated	start regeneration with LabView

Table 8.2: Source of errors

9 Future directions

The construction of an experimental rig is always the beginning of something new. Tests are run and the setup of the experimental rig evolves step by step. Positive and negative influences on the test object are being researched. Every so often, new problems occur and new solution processes must be found. This is a continuous development process and there is always something that can be improved. This chapter explains what can be done next in order to improve the experimental rig of this project.

9.1 Stand alone system

Two different electric circuits are installed at the experimental rig. One circuit provides the electrolyser with energy. It starts at the solar cells and ends at the electrolyser. The second circuit is a 24 V circuit for the measurement and control of the setup. Currently, the power supply for the electronic control is provided by the power grid. In the future, the electronic control shall also receive its energy from the solar cells. For this to occur, two requirements must be met. First, the energy consumption of the electronic control must be minimized and second, an additional battery for the power supply of the measurement and control devices must be installed.

9.1.1 Minimizing of the energy consumption

Most of the electric devices which monitor the experimental rig need electrical energy, while operating. There are passive devices for the measurement and several active ones for the control. The measurement devices only need little energy. Altogether, their power consumption is less than 2 W. For the control devices, on the contrary, significantly more energy is necessary. The first device is a heat mat, which covers the dryer and is necessary, such that it cannot be removed. The second and more interesting devices are the electromagnetic valves, which are installed in order to switch between regeneration and normal mode. There are two 3-way valves and one 2-way valve. Each of the 3-way valves need a power of 18.5 W, while the 2-way valve needs 11 W. Altogether, this is a power consumption of 48 W, which is merely used to keep the electromagnetic valves open. If the valve just would need energy, when switching like an ordinary hand valve, this could save a lot of energy. Such valves are available and are called pulse valves. These type of valves are not very common and therefore it is difficult to find adequate ones, since they also must be able to handle hydrogen and a pressure of 11 bar. A company who manufactures such valves is Officine di Esino Lario (ODE). Before their valves can be used in this context, it should be checked whether the valves can handle hydrogen at high pressure. If so, they can be exchanged with the valves installed at the experimental rig. If not, more research must be done to find adequate pulse valves.

Another large energy consumer is the computer, which monitors measured values and sends control signals for the regeneration of the silica gel. Should the electrolyser work without a connection to the power grid, using a computer is no longer an option. Another solution must then be found in order to monitor the experimental rig. A programmable micro controller might be a solution.

9.1.2 Battery as a power supply unit for the measuring and steering devices

In order to guarantee a continues monitoring of the experimental rig, a battery needs to be installed, which provides the electrical energy for the measurement and control devices. Based on the assumption that the installed valves get exchanged by pulse valves, the usual power consumption is approximately 2 W. During the process of refilling the water from the large canister at the bottom into the small canister at the top, the power consumption increases from 2 to 5 W. This process takes 10 minutes and needs to be done 10 times a month. An additional process that consumes electricity is the regeneration of the silica gel. With the vacuum pump requiring 5 W and the heat mate consuming 8.7 W, the additional power necessary for the regeneration process amounts to 13.7 W. The regeneration process takes about 7 hours and is necessary twise a month. Hence, in one month the following energy is consumed by the monitoring and control devices:

$$W_{measuring} = 2\ \mathrm{W} \cdot 1\ \mathrm{h} \cdot 24\ ^{\mathrm{h}}/_{\mathrm{day}} \cdot 30\ ^{\mathrm{days}}/_{\mathrm{month}} = 1440\ ^{\mathrm{Wh}}/_{\mathrm{month}} \tag{9.1}$$

$$W_{waterrefill} = 5\ \mathrm{W} \cdot \frac{1}{6}\ \mathrm{h} \cdot 10\ ^{1}/_{\mathrm{month}} = 8.33\ ^{\mathrm{Wh}}/_{\mathrm{month}} \tag{9.2}$$

$$W_{regeneration} = 13.7\ \text{W} \cdot 7\ \text{h} \cdot 2\ {}^{1}/_{\text{month}} = 191.8\ {}^{\text{Wh}}/_{\text{month}} \tag{9.3}$$

$$W_{tot} = 1440\ {}^{\text{Wh}}/_{\text{month}} + 8.33\ {}^{\text{Wh}}/_{\text{month}} + 191.8\ {}^{\text{Wh}}/_{\text{month}} \tag{9.4}$$

$$= 1640.33\ {}^{\text{Wh}}/_{\text{month}} \tag{9.5}$$

As one can see in equation 9.4, most of the energy is necessary for running the measurement devices. Although the measurement devices have the lowest power consumption, over a long period of time, they need more energy than the refilling of water or the regeneration of silica gel. Hence, the power consumption of the measurement devices should be reduced in order to increase the efficiency of the experimental rig. Nevertheless, if a battery shall provide the energy for the monitoring and control of the setup, it must have an adequate energy amount. The maximum demand for energy, within a 24 hour period amounts to 144.73 Wh. This value includes the regeneration of the silica gel and the refilling of the water. If only the monitoring devices are switched on, the necessary energy per day is 48 Wh. In order to guarantee a correct functioning, a battery shall be able to provide enough energy for one entire day. An adequate model is the "solar dryfit S12/17 G5" with an energy amount of 204 Wh.

Data sheet of battery

brand name	solar dryfit S12/17 G5
company	Exide
voltage	12 V
energy amount	204 Wh
battery type	gel battery
weight	6.1 kg
dimensions	181 x 76 x 167 mm
cost	100 Euro

Figure 9.1: Solar dryfit - Exide [58]

In order to charge this battery, there are two possibilities. It could either be charged directly from the solar cells or the hydrogen could be used in a fuel cell which could generate electrical energy for the battery. In both cases, a power electronic would be necessary to transform the voltage to an adequate level.

9.1.3 Fuel cell

In this project, hydrogen is used as an energy storage. In order to receive electrical energy from the hydrogen, a fuel cell is necessary. Connected to the outlet of the setup, a fuel cell can produce electrical energy, which can either be used to run electrical devices or to charge a battery. Depending on the possible flow rates, the maximum power of the fuel cell should be about 500 W.

$$1\ \mathrm{l}\ H_2 \ \widehat{=}\ 2.94\ \mathrm{Wh} \tag{9.6}$$

$$1\ {}^{\mathrm{l}}/_{\mathrm{min}} \ \widehat{=}\ 2.94\ {}^{\mathrm{Wh}}/_{\mathrm{min}} = 176.4\ \mathrm{W} \tag{9.7}$$

$$\frac{500\ \mathrm{W}}{176.4\ \mathrm{W}} = 2.83 \tag{9.8}$$

$$500\ \mathrm{W} \ \widehat{=}\ 1 \cdot 2.83\ {}^{\mathrm{l}}/_{\mathrm{min}} \tag{9.9}$$

The necessary flow rate in order to achieve a power of 500 W is 2.83 litres. For a short period of time, the metal hydride storage can provide this hydrogen flow. A fuel cell system, which can provide a power of 500 W is the FC 42 Double Stack. With a maximum power of 720 W, this system is adequate for the use in the experimental rig.

Figure 9.2: FC 42 Double Stack Schunk [59]

Data sheet fuel cell stack

brand name	FC 42
company	Schnuk Bahn- und Industrietechnik GmbH
voltage output	24 V
power output	700 W
cooling medium	water, glycol
temperature range	5..50 °C
dimensions	130 x 108 x 190 mm
weight	4 kg
cost	6700 Euro

The advantage of using this fuel cell stack is their simple handling and their compact design. They can be operated with air or oxygen as reactant gas and the cooling can be realised with tap water instead of deionized water.

9.2 Automatic control of the setup

The setup is mainly controlled by the LabView program, but there are still some hand valves installed, which must get adjusted manually. In order to fully automate the experimental rig, the setup must get modified at some points.

9.2.1 Flow controller

The hydrogen's flow rate produced thus electrolysis is related to the current of the electrolyser. When releasing hydrogen from the metal hydride storage on the other hand, the flow rate must be adjusted manually by a throttle valve. The mass flow meter measures the flow rate and the user must adjust the throttle valve in order to reach the required hydrogen flow. By releasing the hydrogen, the metal hydride storage cools down and the pressure in the storage container decreases, which influences the flow rate. If the flow rate should be constant, the throttle valve must be readjusted by hand during the emptying process. This method of releasing hydrogen, thus, requires a constant attention of the user. In order to automate the emptying process, it is necessary to exchange the mass flow meter with a flow controller. A flow controller receives an electrical signal in order to regulate the amount of gas which passes through it. A possible flow controller is the model D-6211 of Manger + Wittmann. It can regulate the hydrogen flow from 0.25 to 5 $^{l}/_{\mathrm{min}}$. With this device, no further manual adjustments are necessary to release the hydrogen from the metal hydride storage.

Figure 9.3: Flow controller
Manger+Wittmann [60]

Data sheet mass flow meter

brand name	D-6211
company	Manger+Wittmann
power supply	24 V
input signal	0...5 V
output signal	0...5 V
flow rate	0.25...5 $^{l}/_{\mathrm{min}}$
temperature range	0..70 °C
pressure range	0...4 bar
cost	-

9.2.2 Automatic switch between storage and release

Currently, the produced hydrogen can either flow into the metal hydride storage or get released out in the air. To choose between these two possibilities, three hand valves need to be switched, which are installed near a T union (figure 9.4-left). In the future, this shall be done automatically, controlled by the LabView program. Therefore, a 3-way valve must be installed which replaces the three hand valves (figure 9.4-right). This new valve shall be controlled by the LabView program. In normal mode, the produced hydrogen shall be stored in the metal hydride storage. If the pressure rises above 12 bar, the LabView program shall recognize this and switch

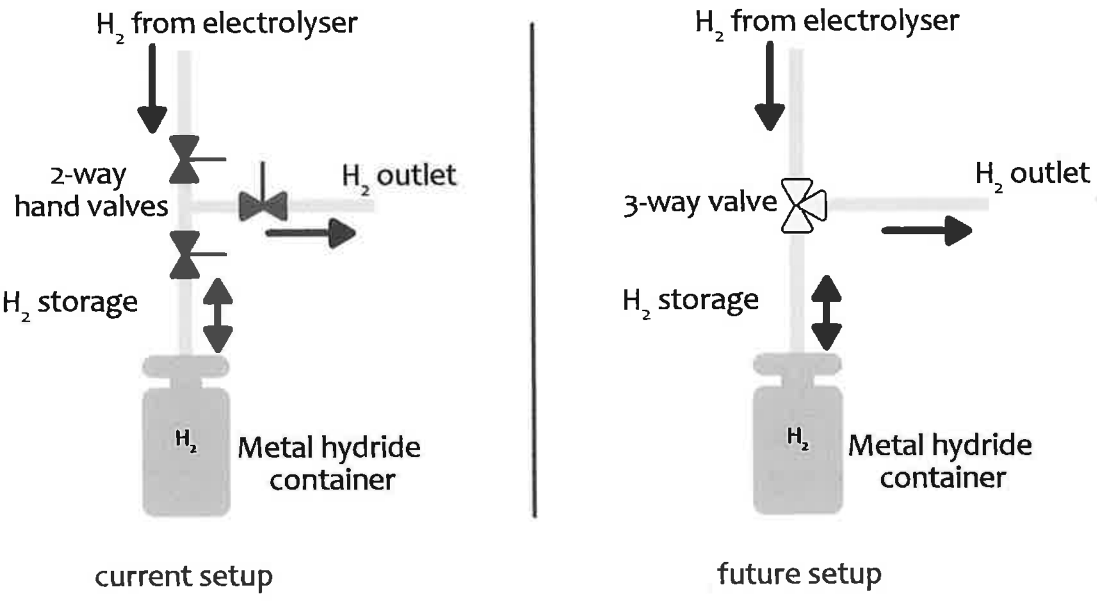


Figure 9.4: Current and future setup in order to automate the filling and release process

the 3-way valve, which directs the hydrogen to the outlet. If a fuel cell is connected to the outlet, the hydrogen can be used to produce electrical energy. Otherwise, the hydrogen flows out in the air. Beside the automatic pressure detection, the user must be able to manually switch between normal mode and release mode in the LabView program. It should be possible to turn of the electrolyser and release the hydrogen in the metal hydride storage by pressing a button in LabView. The hydrogen flow rate shall be controlled by the previously mentioned flow controller.

9.3 Energy storage

The storage of energy is the essential element in this project. In order to optimize the energy storage, all of the electrical energy produced by the solar cells should get stored effectively. In this regard, the metal hydride storage can be improved or a buffer battery can be installed, in order to buffer energy when more electrical energy is produced than the electrolyser can handle.

9.3.1 Buffer battery

The maximum power of the installed solar cells is higher than the maximum power of the electrolyser. Hence, if the solar cells operate at their maximum, the electrolyser is not able to transform all the energy into hydrogen. Consequently, a part of the electrical energy is wasted. In order to prevent losing this energy, a buffer battery could be installed which is able to store the excess energy.

Stefan Geidel, a student of the Hochschule Darmstadt, who is currently working on, already did some research on how to use the excess energy of the solar cells. He ascertained that the solar charge controller Steca Solarix is able to provide energy for the electrolyser and can charge a battery at the same time. This charge controller can provide a constant current of 10 A for the electrolyser and a maximum of 20 A for the charging of a battery. If the current from the solar cells falls below 10 A, the electrolyser receives its energy from the battery. In other words, the electrolyser can run for a while, even after dark. This has two advantages: None, of the energy from the sun gets wasted and the efficiency of the electrolyser is higher since it only operates with a maximum of 10 A.

Data sheet of solar charge controller

brand name	Solarix MPPT 2010
company	Steca Elektronik
supply voltage	15...100 V
load current	10 A
charging current	20 A
charging voltage	13.9 V
efficiency	98 %
dimensions	187 x 153 x 68 mm
cost	sponsored by Steca

Figure 9.5: Solar charge controller Steca Elektronik [61]

At the time of completion of this master's thesis, initial estimations of Stefan Geidel have shown that a battery of 72 Ah is sufficient to buffer the whole excess energy of one day. If the battery is fully charged at the end of the day, the electrolyser can operate for another 9 and a half hours, since its power consumption at a current of 10 A is about 90 W.

$$12\ \text{V} \cdot 72\ \text{Ah} = 864\ \text{Wh} \tag{9.10}$$

$$\frac{864\ \text{Wh}}{90\ \text{W}} = 9.6\ \text{h} \tag{9.11}$$

9.3.2 Hydrogen storage

The installed metal hydride storage can store hydrogen equivalent to an amount of energy of about 2 kWh. If no hydrogen is extracted, the storage will be full within about 2 days. If more energy shall be stored, either a larger or an additional metal hydride are necessary. The metal hydride used in this rig, was very expensive (2200 Euro). Meanwhile, new and cheaper metal hydride storages have become available. The company ECD Ovonics offers a metal hydride storage for about 1300 Euro, which can store hydrogen equivalent to 2.6 kWh.

Figure 9.6: Metal hydride storage ECD Ovonics [62]

Data sheet mass metal hydride storage

brand name	HS900
company	ECD Ovonics
storage capacity	900 l
energy capacity	2.6 kWh
dimensions	ø 90 x 425 mm
volume	2.4 l
weight	7 kg
temperature	0...54 °C
material body	aluminum
material alloy	TiFe
cost	1300 Euro

Besides the cheaper price and the higher hydrogen capacity, the new metal hydride storage is also able to release hydrogen even at low temperatures around 0°C, whereas the actual metal hydride is only able to operate down to 15°C. Due to the lower temperature, the flow rate of the new metal hydride can be higher and less water is necessary for the heat exchange. Hence, if a new metal hydride storage is necessary, the model of ECD Ovonics is the best choice. It is available at the german company Heliocentris Fuel Cells AG.

10 Conclusion

Pure hydrogen is a high quality energy storage. The aim of this project was to develop and build a system able to produce hydrogen through solar energy and afterwards store it in an adequate hydrogen storage. In order to benefit from the solar energy, solar cells were mounted on the roof of the university's laboratory in Darmstadt, where the project was based. An electrolyser produced the required hydrogen by using the electricity from the solar cells. Afterwards, the pressurised hydrogen passed through a dryer before being stored in a metal hydride container. When required, the hydrogen was released from the metal hydride container, for example, in a fuel cell. The entire process was monitored by a LabView program connected to separate sensors on the experimental rig.

The project has ultimately covered many different topics. It began with the production of electrical energy, was followed by the physical adsorption of water, and ended with the chemical absorption of hydrogen in the metal hydride container. Especially the process of drying the hydrogen turned out to be very complex. A drying method had to be found, which operated with the minimum possible amount of energy and which prevented impurities from entering the system. In the end, using silica gel was the best solution and regenerating it kept the system free of impurities. The storage of hydrogen, on the other hand did not pose major difficulties. The experimental results corresponded to the theoretical calculations and demonstrated that a metal hydride storage is the best option for effectively storing a large amount of hydrogen.

The overall efficiency proved to be a disadvantage when using hydrogen as an energy storage. A system which first transforms electrical energy into hydrogen and then transforms this hydrogen back into electrical energy involves significant losses. In the end, only around 50% of the produced electricity can be used in electrical devices. Due to the high losses, the use of a battery system, which has a higher efficiency, could be a viable alternative. Nevertheless, the use of hydrogen in certain areas can be an important advantage. For example, in holiday homes, where a large amount of energy is required within a short period of time. The hydrogen storages could be charged during the absence of guests and could then be used when required.

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A Instruction manual diagram

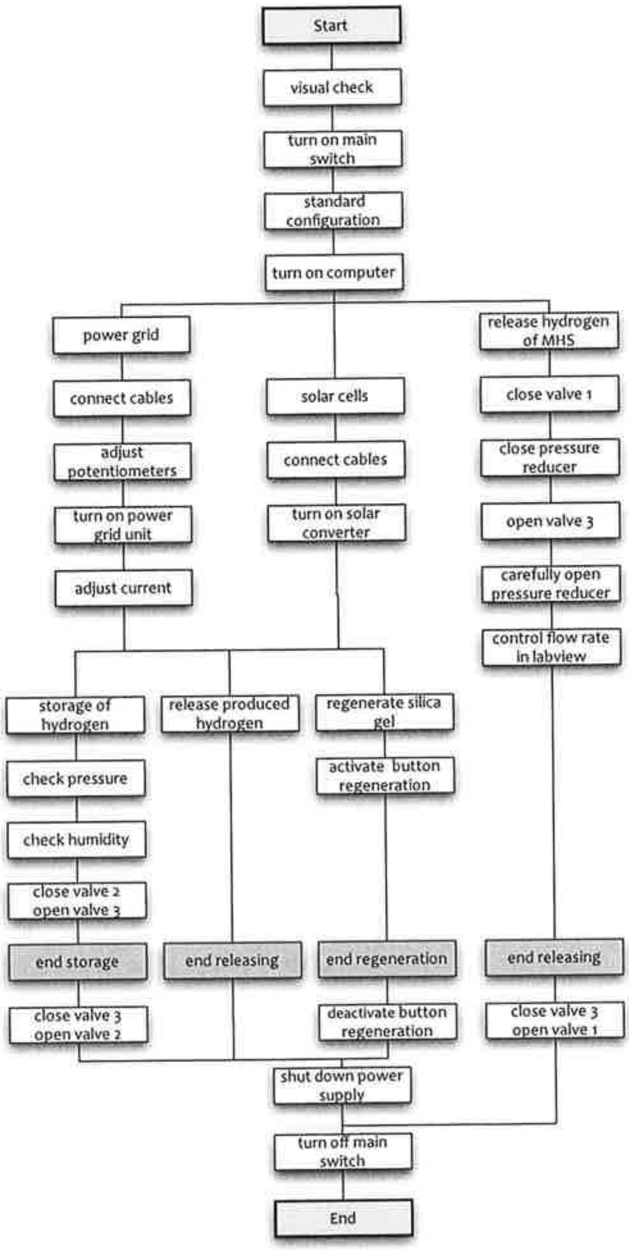


Figure A.1: Diagram: instruction manual

B Wiring diagrams

B.1 Solar cells wiring diagram

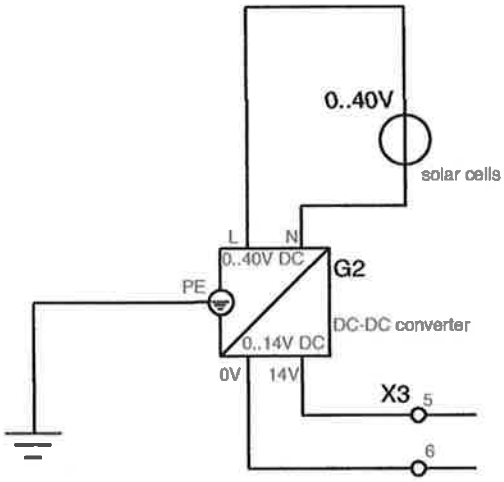


Figure B.1: diagram of how to use the experimental rig

B.2 230V - wiring diagram

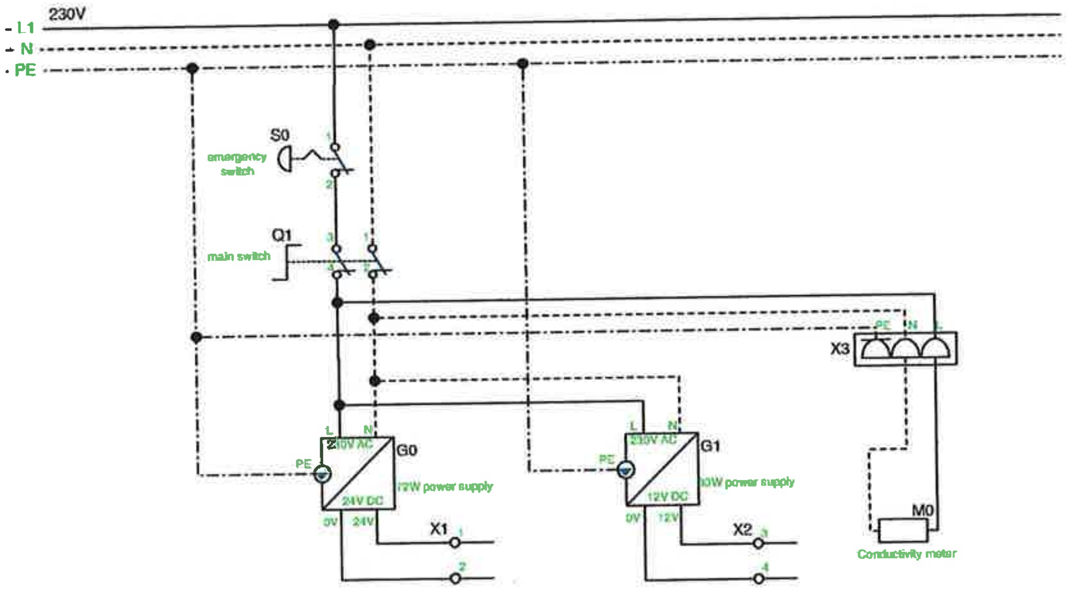
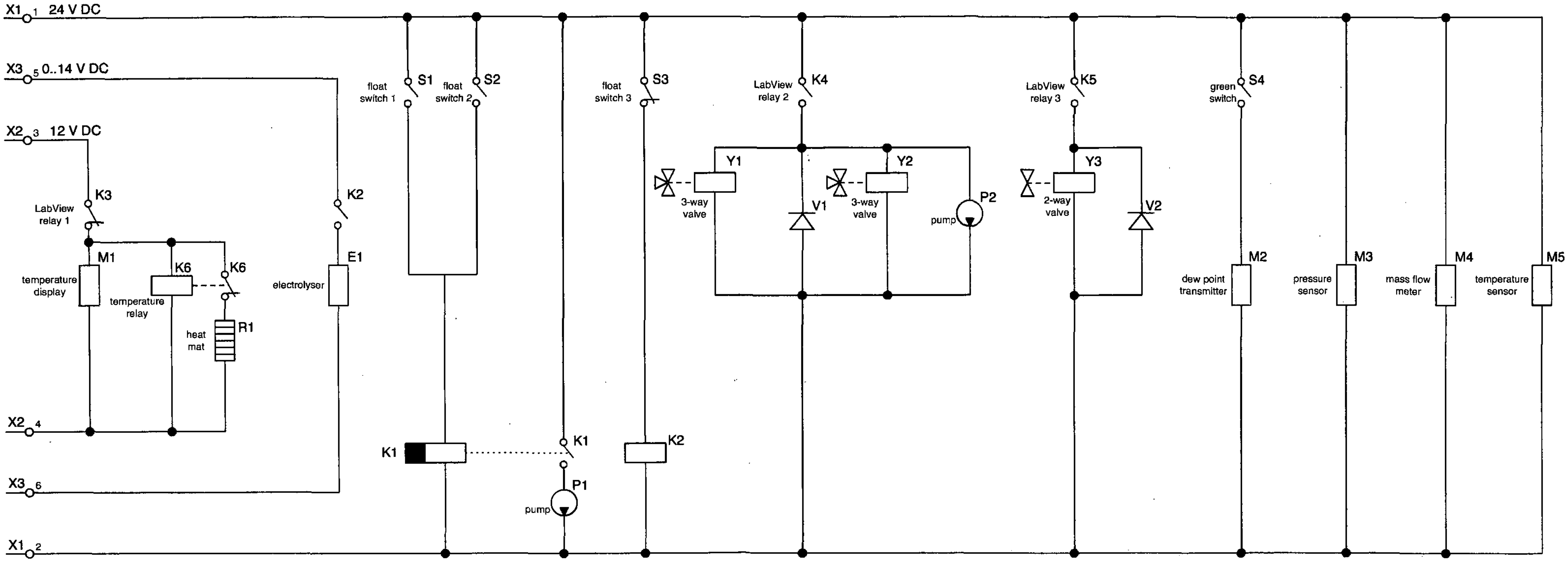


Figure B.2: 230V wiring diagram

B.3 24V - wiring diagram


X1 1 24 V DC
X3 5 0..14 V DC
X2 3 12 V DC
K3
LabView relay 1
M1
temperature display
K6
temperature relay
K6
R1
heat mat
X2 4
X3 6
K2
E1
electrolyser
float switch 1
S1
float switch 2
S2
K1
K1
P1
pump
float switch 3
S3
K2
LabView relay 2
K4
Y1
3-way valve
V1
Y2
3-way valve
P2
pump
LabView relay 3
K5
Y3
2-way valve
V2
green switch
S4
M2
dew point transmitter
M3
pressure sensor
M4
mass flow meter
M5
temperature sensor
X1 2

B.4 5V - wiring diagram

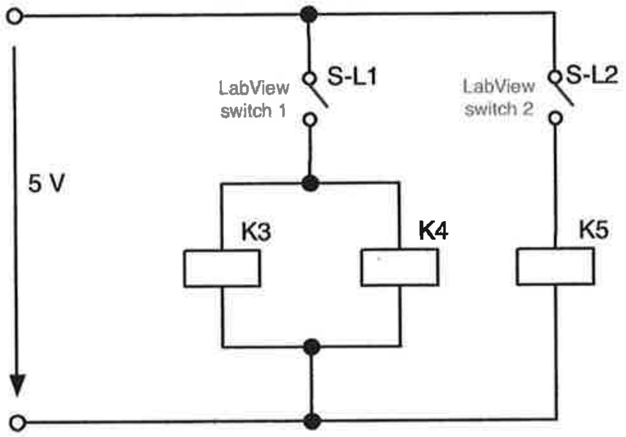


Figure B.3: diagram of how to use the experimental rig

B.5 Electrical parts list

code	part	manufacturer	brand name
E1	electrolyser	Sylatech	HE 500
G0	power supply	Puls	Puls ML70.100
G1	power supply	Puls	Puls ML30.102
G2	solar power supply	own production	-
K1	bistable relay	Finder	RALD24W-K
K2	power relay	Finder	65.31/24V
K3	power relay	Finder	34.51/5V
K4	power relay	Finder	34.51/5V
K5	power relay	Finder	34.51/5V
K6	temperature relay	Jumo	Jumo di eco
M0	conductivity meter	SG Water	P2/30
M1	temperature display	Jumo	Jumo di eco
M2	dew point transmitter	Vaisala	DMT 340
M3	pressure sensor	Gems Sensors	1000 BGB
M4	mass flow meter	Manger+Wittmann	D-5110
M5	temperature sensor	RS	PT100
P1	water pump	KNF	NF10
P2	vacuum pump	KNF	N86 KNDC B
Q1	main switch	Moeller	T0-2-1/E+EZ-P1/SOND
R1	heat mate	RS	245-562
S0	emergency switch	Moeller	FAK
S1	float switch	Cynergy3	RSF66A25B125
S2	float switch	Cynergy3	RSF74Y100RN
S3	float switch	Cynergy3	RSF74Y100RN
S4	rocker switch green	Acrolectric	C6053AL
V1	recovery diode	RS	484-3283
V2	recovery diode	RS	484-3283
Y1	3-way valve	GSR	G052
Y2	3-way valve	GSR	G052
Y3	2-way valve	GSR	G075

List of Publications

3 November 2008	7th Research day, University of Applied Sciences, Darmstadt, Germany; Poster presentation: Hydrogen production and storage
1 March 2009	Querschnitt, Darmstadt, Germany; Article: Wasserstofferzeugung und Speicherung