POLITECNICO DI TORINO

Corso di Laurea Magistrale
in Ingegneria Energetica e Nucleare

Tesi di Laurea Magistrale

Technical and economic analysis of state-of-the-art electrolytic systems for hydrogen production

Relatore
prof. Massimo Santarelli

Candidato
Karen Bosio

Corelatori
Giulio Buffo
Luca Piantelli

Anno Accademico 2020/2021

Alla mia famiglia, il bene più prezioso che ho, e a tutte le persone che mi sono state accanto in questo percorso.

Contents

Abstract

At a time when decarbonization constitutes an issue of global relevance, hydrogen is seen as one of the most promising solutions. To date, around 96% of hydrogen is produced from fossil fuels, in processes like steam methane reforming (SMR) or coal gasification, while only the remaining 4% is produced in cleaner ways like thermochemical cycles and, especially, water electrolysis. This last method is based on water splitting into hydrogen and oxygen through chemical reactions driven by electrical energy or solar energy in the case of photoelectrolysis. Nowadays, the main types of water electrolysers, distinguished on the base of the electrolyte used, are essentially three: alkaline water electrolyser (AWE), proton exchange membrane electrolyser (PEM) and solid oxide electrolysis cell (SOEC). While the first two technologies are classified as low temperature electrolysers, operating between 60 °C and 80 °C, SOECs perform a high temperature electrolysis ranging between 800 °C and 1000 °C. Alkaline electrolysers constitute the oldest and more mature technologies and, together with PEM devices, are the most diffused, while SOECs are still in a research and development phase.

The thesis mainly focuses on the description of water electrolysers, concentrating in particular on a technical and economic analysis of alkaline and PEM technologies. From the comparison of various electrolysers produced by different suppliers, it emerged that both alkaline and PEM electrolysers can satisfy a wide range of hydrogen demands, varying from values lower than 1 Nm^3/h of hydrogen up to typically 4000 Nm^3/h, with sizes, in terms of input power, going from 1 kW (or even less) up to around 10 MW. With the same hydrogen flow rate produced, PEM electrolysers usually present higher values of electrical power requirements, which translate into greater specific energy consumptions, expressed as the electrical power required per unit of hydrogen flow rate. AWEs are usually characterized by specific energies comprised between 3.8 kWh/Nm^3 and 6.0 kWh/Nm^3, while the typical range of PEM technologies is 4.5 – 6.0 kWh/Nm^3. Even if the upper extreme is the same in both cases, it is exceeded more times by PEM electrolysers rather than alkaline ones. Anyway, PEM electrolysers are able to tolerate higher pressures (up to 350 bar) compared to alkaline technologies, leading to the possibility of avoiding the expense for a hydrogen compressor.

Under the economic point of view, the state of greater development of alkaline electrolysers, together with the possibility of using cheaper materials for the catalysts, results in typically lower investment costs. Indeed, actual values ordinarily reported in several literature articles correspond to 700 – 1700 €/kW for alkaline systems and 1000 – 1500 €/kW for PEM systems. Then, since the operational lifetime of the plants is about 20 years, while the stacks maximum

operational lifetime is generally 80000 hours, they need to be replaced, at a typical cost of 340 €/kW for alkaline electrolysers and 420 €/kW for PEM devices.

1. Introduction

1.1. Towards a global decarbonization

Nowadays, one of the global major issues is represented by the greenhouse effect, a natural temperature regulation process according to which radiation emitted by a planet provided of atmosphere, like the Earth, warms the planet's surface. This is due to the greenhouse gases present in the atmosphere: they permit the entrance of solar radiation, hindering, instead, the exit of the infrared radiation re-emitted by the planet. This is a phenomenon which, normally, allows to maintain thermal conditions suitable for birth and maintenance of terrestrial life. However, when the atmosphere contains an excessive quantity of greenhouse gases, the global temperature reaches levels higher than the normal ones. As a consequence, the conditions on the Earth are no more optimal for the living beings. Examples of related issues are excessive melting of the glaciers with annexed rise of the sea level and extreme meteorological phenomena, all increasing risk of flooding (especially for coastal areas). The higher temperature causes also dryness and a high fire risk. Moreover, health consequences on the population deriving from heat waves have to be considered.

Almost three-quarters of greenhouse gas emissions are constituted by carbon dioxide. A percentage equal to 80% of these emissions derives from energy-related processes, so fossil fuels (e.g., oil, coal, natural gas) combustion, and industrial sectors such as steel or chemical ones. The remaining quantity comes principally from land use.

During the last century, greenhouse gas emissions related to fossil fuels caused an increase of 1°C of the average global temperature and a further increase would lead to very damaging climate changes.

The only way to avoid this is the decarbonization of the global economy in a relatively short time frame, made through an energy transformation which must be initiated now. Anyway, since such a global transformation is difficult and expensive, a compromise between the simultaneous economic growth and CO_2 emissions reduction has to be established.

In addition, beside a not negligible global economic effort, the adoption of several policies is necessary. Success, thus, depends on the quantity of resources committed and on the policies quality and their implementation speed. Moreover, in order to obtain the maximum result international co-ordination and co-operation are necessary, selecting the appropriate energy transformation pathway for each regional circumstance.

Regarding the policies, two main documents aimed at decarbonisation are the **Kyoto Protocol** and the **Paris Agreement**. The Kyoto Protocol is an international treaty regarding the global warming. It has been signed on 11 December 1997 under the agreement of 180 Countries (number that increased during the successive years) and entered into force on 16 February 2005. In principle, it contained the imperative to reduce, during the period 2008-2012, emissions of CO_2 and other greenhouse gases by at least 8.65% with respect to 1990. Subsequently, the final term has been extended from 2012 to 2020, with the addition of further restrictions on greenhouse gases emissions.

The Paris Agreement, subscribed in 2015, is an accordance within the United Nations Framework Convention on Climate Change (UNFCCC), regarding the reduction of greenhouse gas emissions and finance starting from 2020. The objective is the containment of the increase of the average global temperature under the 2°C limit with respect to pre-industrial levels, even if it has been established that, in order to substantially reduce risks and effects related to climate changes, the temperature increment must be limited to 1.5 °C. Each Country involved in the agreement established its future efforts to reduce national emissions. All these efforts, which include mitigation and adaptation actions, are reported in the *Nationally determined contributions (NDCs)*, which are the heart of the Paris Agreement. Anyway, according to following studies, such as the International Renewable Energy Agency (IRENA) one, present NDCs do not allow to meet climate goals. The abatement of annual energy-related CO_2 emissions, from now until 2050, needed to respect the temperature limit assessed by the Paris Agreement, should be more than 70% (3.8% per year). This means that the world should shift from 34 Gt of CO_2 emitted today to 10 Gt in 2050. A percentage equal to 75% of the required reductions can be provided by a large-scale shift to renewable energy and electrification of transport, heat and hydrogen production. The previous value can arrive to 90% by including measures regarding energy efficiency enhancement. However, during the last five years, not only carbon dioxide emissions did not reduce, but they annually increased by 1.3%, so it is really necessary to accelerate the decarbonization process.

The International Renewable Energy Agency mentioned above, in its latest *Global Renewables Outlook (2020)*, has provided a technically and economically feasible pathway to decarbonise the energy sector by using low-carbon technologies with the final aim of observing the temperature target of the Paris Agreement. For this purpose, different scenarios have been analysed:

- The **“Planned Energy Scenario (PES)”** provides a perspective of energy system developments based on current energy plans and other planned targets, including the

Nationally Determined Contributions of the Paris Agreement. According to this scenario, energy-related CO_2 emissions should increase until 2030 and then go down to a level lower than today by 2050. This would, probably, result in a global temperature rise of 2.5 °C in the second half of the century. Thus, the PES is in disaccord with the Paris Agreement objectives.

- The **"Transforming Energy Scenario (TES)"** contains an ambitious but realistic energy transformation mainly based on improved energy efficiency and renewable energy sources, whose share in the total final energy consumption is expected to be around 28% in 2030 (compared to the 17% of 2017). At a sectorial level, buildings will have the highest share of renewable energy, followed by industries and transport. Projects of this scenario would allow to respect the 1.5 °C limit within the current century (making the TES an acceptable scenario), since the required reduction of 70% of energy-related CO_2 emissions by 2050 can be achieved. In 2050, the remaining 9.5 Gt of energy-related CO_2 emissions can be partly reduced in the following ways:
    - For the power sector, by full deployment of zero-carbon electricity sources: renewable energy coupled with storage or with the use of hydrogen. In addition, carbon capture and storage systems (CCS) combined with existing natural gas plants can have a role, even if limited.
    - The building sector can be fully decarbonised by employing electricity coming from renewable sources or hydrogen.

The two mentioned approaches will result in 6.7 Gt of residual energy-related CO_2 emissions, coming from industry and transport sectors.

- The **"Deeper Decarbonisation Perspective (DDP)"** is not a real scenario, but an enhancement of technology options of the Transforming Energy Scenario, together with structural and behavioural changes. In fact, the DDP shows how to reduce to zero remaining CO_2 emissions from the TES by 2050 or, at least, 2060. Renewable energy, including green hydrogen (electrolytic-grade hydrogen, produced with electricity coming from renewable sources), provides 60% of the reduction, while 37% comes from energy efficiency and the remaining 3% derives from carbon capture, utilisation and storage (CCUS) and nuclear.
- The **"Baseline Energy Scenario (BES)"** exploits policies already in place at the time of the Paris Agreement, with the addition of some more recent views on energy development. This scenario expects an annual rate of 0.7% of emissions increase, resulting in a temperature rise of 3 °C by the end of the century. This perspective makes the BES even more unacceptable than the Planned Energy Scenario.

At the end of the analysis, it came out that the Transforming Energy Scenario is the most promising one.

A further analysis of it highlighted that the reduction of carbon emissions is not the only advantage that the energy transformation will bring in 2050. Indeed, other considerable aspects need to be mentioned:

- Improved energy security: the big dependence of many countries from import of fossil fuels can be reduced by employing renewable energy local generation.
- Full energy access: renewable energy technologies can be installed in rural areas not yet connected to electricity grid, thus bringing rural electrification.
- Three types of job effects: creation, substitution and transformation. Experts knowledge on today's gas plants, for example, can be employed in wind turbines installation. Anyway, the energy transition will also lead to the loss of those jobs related to fossil fuels that cannot be reconverted or replaced.
- Falling energy costs: between 2010 and 2019, the global weighted average levelized cost of electricity (LCOE) fell by 82% for solar PV, while electricity produced by onshore wind reduced its cost by 45%.
- Improved air quality and so economic gain: air pollution is a major problem for public health. The use of clean renewable energy sources will reduce ill health and, so, health costs.

Moreover, a simulation of the Transforming Energy Scenario revealed that, following the pathway by which it is characterised, in 2050 there will be no great flexibility issues bringing to unserved energy in any region and curtailments of intermittent wind and solar power will be limited. The main options to achieve good flexibility and low curtailment are the following ones: electric vehicles (combined with smart charging systems), hydrogen production using electrolysis and battery storage.

Pratically, at a global level, the decarbonization process can follow two different approaches:

- the **"net-zero" emissions approach**, involving a total balance of CO_2 emissions by means of reforestation and afforestation actions and carbon capture and storage systems (it is like an union of TES and DDP);
- the **"zero" emissions approach**, concerning a null CO_2 emission.

Since the first option is simpler than the second one, it is the most considered. The best way to reach the objective is based on the combination of low-cost renewable energy (mainly wind, solar PV and hydropower) technologies and electrification, when possible, of the end-use applications. In addition, cleaner fuels, such as hydrogen and biomethane, can substitute traditional fossil fuels for both transport and industrial sectors. Furthermore, an increase of the productive systems energy efficiency can be considerably helpful. Such improvement represents the capability of a physical system to consume less energy, compared to another one, with the aim of satisfying the same kind of demand, resulting, for those sectors still using fossil fuels, in minor CO_2 emissions.

1.1.1. Decarbonization at a European level

The European Union is focusing on problems related to climate changes since many years ago. An important initiative, introduced with the Directive 2003/87/CE, is the **European Union Emissions Trading Scheme (EU ETS).** It is a mechanism of exchange of quotes (European Union Allowances – EUA) of greenhouse gases emissions put in practice from 1 January 2005 and used by the European Union in order to obtain a CO_2 emissions reduction mainly in the industrial and aviation sectors. In particular, the directive is applied to:

- electric power plants;
- high-energy intensity[1] industrial sectors;
- aircrafts;
- emissions of:
    - carbon dioxide
    - nitrous oxide
    - perfluorocarbons
    - methane
    - hydrofluorocarbons
    - sulphur hexafluoride.

Such mechanism is named "cap&trade" because it fixes a maximum quantity (cap) of allowed emissions over the European territory and, from this value, derives a number of "quotes" (1 ton CO_2 eq. = 1 quote) that can be purchased or sold in a dedicated market (trade). Equivalent carbon dioxide (CO_2 eq.) is a measure of the impact on global warming given by a certain amount of a greenhouse gas in the atmosphere, compared to the same quantity of carbon dioxide. This value is calculated by multiplying the mass of the examined greenhouse gas by its

---

[1] Energy intensity represents an economic measure of the energetic efficiency of the economic system of a Country. It is calculated as unit of energy divided by unit of gross domestic product.

Global Warming Potential, an index which reveals the contribution of the associated gas to the greenhouse effect with respect to the one of the carbon dioxide. Typically, the comparison is made within a time span of 100 years.

All industrial operators must compensate, on an annual basis, their own emissions with a corresponding quantity of quotes. Polluters that need to increase their emissions have to buy a corresponding number of quotes from other operators. These latters are those who don't reach their allowed limit of emission, so they can sell the remaining quantity as quotes.

The total number of available quotes (cap) annually decreases because of the imposed CO_2 emissions reduction. Such decrement has been equal to 1.74% per year between 2013 and 2020 and will be of 2.2% starting from 2021.

The European Union Emission Trading Scheme is developed in four phases, going from 2005 until 2030. Each new phase improves the previous one by modifying or adding characteristic points:

1. Phase 1 (2005-2007)

   The first phase, going from 2005 to 2007, took into account CO_2 emissions from power generators and energy-intensive industries, contemplating a penalty of 40 € per tonne for non-compliance.

2. Phase 2 (2008-2012)

   The second phase coincided with the first commitment period of the Kyoto protocol and introduced the following news:

   - the cap on allowances was decreased by 5.6% compared to 2005;
   - the penalty for non-compliance was increased to 100 € per tonne;
   - the aviation sector was brought into the EU ETS on 1 January 2012.

3. Phase 3 (2013-2020)

   The third (and actual) phase is characterised by:

   - a single, EU-wide cap on emissions in place of the previous system of national caps;
   - more sectors and gases included;

- 300 million allowances set aside in the New Entrants Reserve to fund the deployment of innovative, renewable energy technologies and carbon capture and storage through the NER 300 programme[2].

4. Phase 4 (2021-2030)
   The future fourth phase will provide an increase in the pace of the annual reduction in allowances to 2.2% as of 2021 and a help, through funding mechanisms, given to industry and power sectors to meet innovation and investment challenges of the low-carbon transition. This last stage will follow the content of the Directive 2018/410/UE, which modifies the 2003/87/CE one with the purpose of sustaining a more efficient emissions reduction under an economic point of view, promoting investments in favour of low-carbon emissions.

In addition to the just described "cap&trade" mechanism, a series of policies, constituting the European Green Deal will be established by the European Commission with the final purpose of reaching climate neutrality[3] on the European territory by 2050, respecting the 1.5 °C limit of the Paris agreement. Together with these initiatives, there will be a plan oriented towards 50% (and also 55%) reduction of greenhouse gases emissions by 2030, with respect to 1990 levels. Each existing climate law will be revised and new ones will be introduced, mainly about buildings, agriculture and innovation. This process, financed with public and private funds, is necessary to reach a European Union with a null climate impact, solving the actual problems related to:

1. Energy
   Since the electrical energy production and use represent more than 75% of greenhouse gas emissions, a decarbonisation of the energy sector, with the aim of obtaining null net emissions by 2050, is particularly important. The roads to reach this goal are the improvement of the energy efficiency of the technologies and an energy sector mainly based on renewable sources.

2. Buildings

---

[2] The NER 300 programme is a funding programme which makes available €2 billion for innovative low-carbon technology, focusing on the demonstration of environmentally friendly safe Carbon Capture and Storage (CCS) and innovative renewable energy technologies on a commercial scale within the EU.

[3] The expression "climate neutrality" implies the minimization of CO_2 emissions and the managing of the remaining part with protection measures. In other words, it means to create a balance between emission and absorption of CO_2 from the atmosphere.

Around 40% of consumed energy belongs to the buildings sector: policies regarding buildings renovation will help people in the reduction of the energy necessity, leading to lower expenditures.

3. Industry
   In order to obtain a minor energetic consumption, industry needs a decarbonisation, above all, in those sectors which are highly energy intensive, such as steel and concrete ones. Moreover, it can increase its percentage of recycle materials, which today is around 12%.

4. Mobility
   Transport constitutes approximately 25% of greenhouse gases emissions, hence new types of mobility technologies, such as electrically or hydrogen feed ones, will be necessary for climate purposes.

1.2. Hydrogen as a solution

Hydrogen represents one of the main solutions applicable to the decarbonisation process, looking for the carbon neutrality by 2050. It is appreciated for its wide range of applications, mainly in industrial, mobility, buildings and power sectors. It can act as a fuel or as an energy carrier and storage for seasonal variations, helping in balancing the fluctuations of the energy demand and better exploiting the intermittent renewable energy sources. Since hydrogen does not produce greenhouse gases emission, it is also particularly convenient in those situations where it is difficult to achieve decarbonisation by means of electrification or it can replace fossil fuels in some carbon intensive industrial processes (chemical or steel sectors). According to IRENA's latest studies, in order to respect the objective of the Paris agreement, hydrogen will need to cover around 8% of the global energy consumption (compared to the current less than 2%), thus, it has a priority role in the European Green Deal. Nevertheless, hydrogen still has to face some challenges in order to be used to its full potential, such as the immature infrastructure development, critical investments, public perception of safety and the need of a new policies. Regarding this last necessity, on 8 July 2020 in Brussels, the European Commission presented the **Strategy for Energy System Integration**, which describes how the combination between hydrogen, renewable electricity and renewable and low-carbon fuels will favour the process towards a climate neutral European Union. Such strategy is complemented by the **European Clean Hydrogen Alliance**, that represents a collaboration, launched on the same day, between public authorities, industry and civil society aimed to the development of an investment agenda and concrete projects.

1.2.1. Three types of hydrogen

In nature, hydrogen only exists in chemically bound form. Thus, specific processes of production are needed. They can involve fossil fuels or renewable energy sources. Today, three "colours" of hydrogen are distinguished, based on greenhouse gas emission coming from production processes: grey, blue and green. **Grey hydrogen** is produced by thermochemical conversion of fossil fuels (mainly coal gasification and natural gas reforming) without a CO_2 capture system, with a resulting annual release of 70-100 million tonnes of CO_2 in the European Union. Even if most of the hydrogen produced today belongs to this category, in order to achieve the established climate targets, different and cleaner means of production are necessary.

Blue hydrogen is a low-carbon gas produced with the same processes of the previous one, but capturing almost 90% of the emitted CO_2 and then storing it. Old plants producing grey hydrogen can be retrofitted by adding a CCS system, in order to shift their production to blue hydrogen. In addition, captured CO_2 can be used to produce fuels, feedstocks and construction materials (CCU), which represent a permanent storage of CO_2. Blue hydrogen will have to replace grey hydrogen in order to dull the high carbon footprint of fossil fuels. The European Union has a geological storage potential for CO_2 of around 104 Gt, that, despite a possible reduction to 77 Gt by some legislative and regulatory limitations, is not a constraining factor for the production of blue hydrogen, whose market could grow at a relatively fast pace. Anyway, despite the advantages of blue hydrogen with respect to grey hydrogen, it remains the fact that not all the emissions are captured. This will result in a constraint for this type of hydrogen if engineering efforts will not bring the level of the technologies to a 100% capture by 2050. If so, there will be the necessity of compensate any remaining emissions.

Finally, **green hydrogen** is produced via electrolysis, exploiting electricity from renewable resources, such as solar PV, wind or hydropower. This is carbon neutral hydrogen, since no CO_2 emissions take place, fact that makes it a perfect substitute of grey hydrogen. In addition, such kind of production allows to storage the excess of renewable electricity in a useful form.

Concerning the costs, to date, the most convenient is still grey hydrogen, with a production cost of 1.5 €/kg, while estimated costs for blue hydrogen and green hydrogen are, respectively, 2 €/kg and 2.5-5.5 €/kg. Anyway, the cost of both renewable electricity sources and electrolysis technologies is going down quickly, so the possibility of producing electrolytic-grade hydrogen becomes more and more promising. For example, during the last ten years, electrolyzers have reduced their cost by 60% and it is expected to be halved, with respect to today, in 2030. Thus, even if today green hydrogen is still too expensive (in fact, only less than 1% of produced hydrogen is green), thanks to the costs decrement, it will be cheaper than blue hydrogen within the next 5 to 15 years. In the meantime, anyway, blue hydrogen can have an important role in accelerating climate mitigation in the short and medium term, enabling to rapidly reduce emissions due to current grey hydrogen production.

1.2.2. Optimised gas scenario and minimal gas scenario

A confirmation of the convenience of hydrogen for the decarbonization process is find also in different studies. One of these, recent and notable, is that published in February 2018 (and updated in 2019) by the Gas for Climate consortium[4]. Such analysis, carried out by Ecofys[5] (now part of Navigant[6]), aims to find the most optimal use of renewable and low-carbon gas, produced in Europe from surplus renewable power, with the objective of achieving a net-zero emissions Europe by 2050 and the requirement of maintaining the Europe's energy supply reliable, secure and competitive. It is defined as renewable gas the one produced exploiting renewable sources, such as biomethane and green hydrogen. Low-carbon gas, instead, includes blue hydrogen and natural gas combined with CCS or CCU, whose production involves small quantities of uncaptured CO_2. The study is based on the comparison between the energy system costs of a "with gas" scenario and a "no gas" scenario: the optimal one is chosen on the basis of the resulting economic saving. The first situation, also called *optimised gas scenario*, allows the renewable and low-carbon gas to be used to its full potential. It is taken

---

[4] Gas for Climate consortium is a group composed by ten European gas transport companies (Enagás, Energinet, Fluxys, Gasunie, GRTgaz, ONTRAS, Open Grid Europe, Snam, Swedegas and Teréga) and two renewable gas industry associations (Consorzio Italiano Biogas and European Biogas Association). The consortium aims to reach net-zero greenhouse gas emissions in EU by 2050 using renewable and low-carbon gas through the existing gas infrastructure, in order to obtain the maximum economic benefits.

[5] Ecofys is a global consultancy which conducts studies about sustainable energy for everyone, developing solutions aimed to help its client in the transition towards a cleaner energy.

[6] Navigant is a company offering management consultancy to business in the energy and other industries.

into account the existence of a gas infrastructure to transport biomethane and centrally produced hydrogen, which can be also mixed together. This way of transporting hydrogen is convenient because it not only avoids additional costs for compression and liquefaction (needed, instead, for a transport by truck, rail or ship), but it also allows the reuse of the existing gas infrastructure, preventing possible decommissioning costs. The second scenario (*minimal gas scenario*) limits the usage of renewable and low-carbon gas to those sectors where no alternatives are available. Hydrogen is considered totally produced on site, giving a significant increase of industrial electricity demand. Moreover, this scenario has additional costs with respect to the other one, due to the fact that biomass is necessary when the electrification is unable to cover the residual load.

The study focuses on the application of different technologies in the following main sectors:

1. Buildings

   When referring to buildings, their heating is the center of the study: it is done considering both heating pumps and a certain share of district heating. In the "optimised gas" scenario, heat pumps are hybrid (electric heat pumps integrated with a gas heating system), while the "minimal gas" scenario only sees the application of completely electric heat pumps. The second case requires higher insulation levels, additional electricity distribution networks and expensive peak electricity generation, leading to a higher cost.

2. Industry

   The study considers the three main energy-intensive industries with high emissions levels: iron and steel, ammonia and methanol, cement and lime production. In this sector, both the scenarios include a role for gas partly because no alternatives are possible and also gas is inherent to the production process.

3. Transport

   For the mobility sector, the "optimised gas" scenario considers hydrogen and bio natural gas, while the "minimal gas" scenario only includes electricity and advanced biofuels. It is important to notice that, in any case, in order to reach the target of a net-zero emissions Europe, a full decarbonization of the transport sector is necessary.

4. Power

Power generation in the "optimised gas" scenario is done using both gas-fired power plants, fed with hydrogen and biomethane, and biomass-fired power plants. These last ones represent, instead, the only possible option for the "minimal gas" scenario.

As a conclusion, the study found that the best scenario is the "optimised gas" one: carrying on a decarbonization process including a role for renewable gas results in a saving of around €217 billion per year, compared to the "minimal gas" scenario.

Moreover, it came out that Europe has a large potential in the production of renewable electricity from wind, solar PV and hydropower, which, in addition to helping the decarbonization process, assures an increase of security and stability of the European energy system, thanks to a reduction of the energy dependency from import. Anyway, there is a discrepancy between electrical energy demand and supply because both constantly change. The demand change is due to the end users' behaviour and activities, while the variation in the supply, when done with renewable energy sources, is due to the modification of the weather conditions. Thus, it is necessary to cover demand peaks: today this function is performed by coal-, oil- and gas-fired plants, but, in a low-carbon future, such flexibility has to be given by cleaner options, such as stored hydrogen.

Finally, regarding the transports, it is emerged that some sectors, such as aviation and shipping, despite the usage of bio-based fuels, will be very hard to decarbonise by 2050. Thus, in order to reach the goal of net-zero emissions, negative emissions in other sectors are needed.

1.2.3. Hydrogen storage

A big issue, for each one of the three types of hydrogen, is the storage methodology. Hydrogen can be stored in the following forms:

- gaseous;
- liquid;
- solid (solid matrix).

When it is stored in a **gaseous** state, it is a compressed gas contained in hollow cylinders composed by three layers. The most internal layer, in contact with hydrogen is made up of a polymeric or glassy material. Here, metals must be avoided because their mechanical properties would be degraded by the hydrogen absorption (embrittlement phenomenon). The layer in the middle is an elycoidal wrapping, necessary to assure mechanical strength to the storage device. It can be in stainless steel or aluminum: on the basis of the material used, the cylinder weight and the mass fraction of stored hydrogen change. When using stainless steel, hydrogen stored constitute 4% of total mass, while, in the other case, it is the 6%. Finally, the external layer is metallic, in order to tolerate mechanical stresses.

This storage mechanism is not the optimal one because the hydrogen density is quite low, compared with the one of the other storage forms: for example, even at a pressure of 700 bar, the gaseous hydrogen density is 57.47 kg/m^3, while it is 71 kg/m^3 for liquid hydrogen and 180 kg/m^3 for hydrogen stored in a solid matrix.

The second storage option, the **liquid** one, needs very low temperatures, since, at the pressure of 1 bar, the hydrogen boiling point is 21 K. In order to maintain such a temperature level, the storage technology is constituted by an insulated double cylinder with low-emissivity materials and void between the two layers. When storing hydrogen as a liquid, it has to be payed attention to the transformation of orto-H_2 (with parallel spin of protons) into para- H_2 (with anti-parallel spin of protons). In Normal Temperature and Pressure (NTP) conditions (20 °C, 1 bar), the molar fractions of orto-H_2 and para-H_2 are, respectively, 75% and 25%. At the temperature of 21 K, instead, there is the spontaneous transformation of orto-H_2 into para-H_2, resulting in 98% of para-H_2 and 2% of orto-H_2. Such process is slow and exothermic: the heat released causes the evaporation of part of the liquid hydrogen, dangerously increasing the pressure inside the cylinder. Thus, in order to avoid arriving to the boiling point with the composition of the gaseous form (fact that would favour the spontaneous conversion), the transformation has to be catalytically forced during the liquefaction process.

Finally, the third storage solution is a chemi- (creation of chemical bonds) and physi- (there is not creation of chemical bonds) sorption process in a **solid** matrix, at a typical pressure of 10 bar (safer compared to the pressure of compressed gaseous hydrogen, around 200 bar).There are vessels containing powders able to reversibly absorb hydrogen, creating some metal hydrides by gas dispersion in interstitial sites of the metal crystal lattice. In this case, hydrogen molecules are forced to be closer than in the liquid form, so the density is higher. The best solution from the density point of view is the hydride MgH_2, leading to 180 kg/m^3. Anyway, also metals such as nickel, titanium and vanadium are used: like manganese, they are heavy metals, so their weight constitutes around 98% of the total, while the remaining 2% is represented by the hydrogen. Metals are placed in the bottom part of the vessel: the volume above is empty and enables a uniform distribution of hydrogen on the metals.

The absorption process is exothermic (heat has to be removed) and thermodynamically effective at low temperature, while the desorption is endothermic (heat has to be supplied) and thermodynamically effective at high temperature. Thanks to its endothermicity, the desorption process is intrinsically safe. It is a thermal diffusion which starts at the edges of the cylinder and slowly continues towards the center: in order to enhance its speed, the thermal conductivity of the powders needs to be maximized by adding aluminum sheets and also tubes for the passage of a hot liquid can be inserted. For what concerning the absorption procedure, initially, hydrogen is injected, increasing the pressure until a certain level: in this phase hydrogen concentration increases, but it is still low and a solid phase α, in which hydrogen is dissolved into the metals, starts creating. When both pressure and concentration of hydrogen reach an adequate level, its atoms interact with each other and a solid phase β starts nucleating and grow, coexisting with the other phase until a hydrogen concentration of 90% (after which only the phase β remains) is achieved. During the coexistence of the two phases, in an ideal situation, at constant temperature (T_{eq}) and pressure (p_{eq}), there is the process of formation of metal hydrides (chemi-sorption), until the maximum reversible concentration of hydrogen (90%) is reached. From this moment, hydrogen is still injected, with a pressure increase, but this is simply a physical phenomenon. Regarding the desorption, instead, the inverse process has to be done, with a higher pressure. Both processes, in the phase with constant temperature and pressure, are governed by the following Van't Hoff equation:

$$ln\left(p_{eq}\right) = \frac{\Delta H}{R} \cdot \frac{1}{T_{eq}} - \frac{\Delta S}{R}$$

where:

- ΔH and ΔS are, respectively, the enthalpy and entropy variations of the processes;
- R is the gas constant;
- p_{eq} and T_{eq} are, respectively, the equilibrium pressure and temperature.

In reality, absorption and desorption are not at constant temperature and pressure, but there is a hysteresis. As a result, at a given temperature, the absorption process is at higher pressure compared to both the Van't Hoff case and the desorption, which has a lower pressure with respect to the ideal case. This results in a lower efficiency when using these devices.

1.2.4. A roadmap for the European Union

The European Commission, on 8 July 2020, in its Communication regarding "A hydrogen strategy for a climate-neutral Europe", divided the decarbonisation process, from 2020 to 2050, into three phases:

1. The **first phase (2020-2024)** has as objective the installation of at least 6 GW of electrolyzers in the EU for the production of 1 million tonnes of renewable hydrogen. This will help in both decarbonising existing hydrogen production and incentivizing hydrogen in some end-use applications, such as industrial processes and heavy-duty transport, for which refuelling stations must be installed. For this phase, electrolyzers arriving to 100 MW of power are needed: they can be installed close to demand centres (on-site production) and fed by local renewable electricity sources. Beside the electrolyzers' installation, also the transformation of grey hydrogen production plants into blue hydrogen production ones is contemplated. The investments needed in this phase will be organized by the European Clean Hydrogen Alliance.
2. During the **second phase (2025-2030)**, the electrolyzers installed power has to reach a value of at least 40 GW, in order to produce, in the EU, up to 10 million tonnes of renewable hydrogen, which, at that time, should have become cost-competitive with other forms of hydrogen production. Part of this hydrogen will be produced in remote areas or islands and will be able to provide heating to residential and commercial buildings. Moreover, an EU-wide infrastructure will be necessary to transport renewable hydrogen produced in Member State with higher potential of renewable electricity towards demand centres in other European Countries, creating, by 2030, a competitive EU hydrogen market, whose security can be assured by exchanges based on euro. For this purpose, the existing gas grid will be useful (its repurposing will enable a cost-effective energy transition), together with the installation of hydrogen storage facilities. In an initial transition phase towards the replacement of natural gas with hydrogen, the two can be blended in the pipelines (with hydrogen limited to a certain percentage). However, this solution decreases the value of hydrogen and changes the quality of the gas, affecting the design of end-user applications. Moreover, if Member States will accept different levels of blending, the European internal market will fragment. Again, some policies will be necessary in order to increase the hydrogen demand in sectors like steel-making and transport ones. In these years, green hydrogen should start assuring flexibility to the electricity system, being produced when a surplus of renewable electricity is present and used to produce electrical power (e.g. in fuel cells) when there is demand of it. Finally, the retrofitting of fossil-based hydrogen production plants, started in the previous phase, will continue.
3. Lastly, in the **third phase (2031-2050)**, the maturity of the technologies for the production of renewable hydrogen should be reached, assuring their use in aviation, shipping, commercial and industrial buildings and all those hard-to-decarbonise

sectors where other alternatives are not so feasible. This will require that around a quarter of the renewable electricity produced will be for green hydrogen production, thus a large increase of its generation will be needed.

For the objectives set in the three phases, research and innovation efforts are needed on the sides of hydrogen generation, distribution and storage and end-use applications. For what concerning the generation, more efficient and cost-effective electrolyzers, in the range of gigawatts, are needed. In addition, the annual production of electrolyzers, today below 1 GW per year, is still too low and needs to be incentivized increasing the hydrogen demand. This can be done under the condition of the availability of a valid energy infrastructure connecting supply and demand. Such connection includes both pipelines and other ways of transport, like trucks or ships. Finally, an increment of the hydrogen demand can be obtained also promoting its use in sectors such as the industry and transport ones. Nevertheless, further studies need to be carried out about the full life-cycle greenhouse gas emissions of hydrogen technologies in order to evaluate their environmental impacts.

Moreover, the increasing diffusion of hydrogen demand within Europe will be favourable not only for a decarbonisation process of the Member States, but also for other Countries, such as African ones, which are near to Europe and have an abundant renewable potential, useful for the supply of cost-competitive renewable hydrogen to the EU. Cooperation between the EU and these Countries will create a way to promote their clean energy transition and sustainable development.

2. Technical analysis of the main types of electrolysers

2.1. Technologies for water splitting reaction

Hydrogen production, as already introduced, can follow different pathways, one of which is the following water splitting reaction:

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

It is a nonspontaneous transformation over a wide range of temperature and pressure values. Such thermal dissociation, in fact, at the pressure of 1 bar, becomes spontaneous only with at least 2200 °C, that, to date, is a temperature hardly tolerable by most of the available materials. Moreover, an energy expenditure is needed in order to successfully separate the resulting H_2/O_2 gas mixture.

A valid alternative to the reactors for water thermal dissociation is represented by the electrolyzers, whose related process, the electrolysis, was applied for the first time in 1789 by Jan Rudolph Deiman and Adriaan Paets van Troostwijk with electric sparks and gold wires. Electrolysis devices are convenient technologies, since some of them can split water in near ambient temperature (NAT) conditions and, moreover, hydrogen and oxygen are produced in different compartments, meaning that no further separation is needed. Electrolyzers belong to the group of the electrochemical cells, a class of devices able to directly convert electrical energy into chemical energy (electrolytic cells) or vice versa (galvanic cells) by means of reduction and oxidation reactions. In the case of the electrolytic cells, the electrochemical reactions developing inside them are non-spontaneous, so they need to be forced by means of an external electrical input (DC power), that, for the production of green hydrogen has to be provided by renewable energy sources (wind, photovoltaic or hydroelectric).

Examples of electrolytic cells are, indeed, electrolyzers and closed batteries in recharge, while batteries in discharge and fuel cells belong to the galvanic cells group.

2.2. Electrolysers

2.2.1. General features

Electrolyzers are devices composed by three main elements: two electrodes (**anode** and **cathode**) and an **electrolyte** which separates them. Anode and cathode are the cell compartments in which, respectively, oxidation and reduction take place. They are connected by means of an external electric circuit which conducts the electrons produced by the anodic oxidation towards the cathode. In order to enhance the kinetic of the electrochemical reactions, catalyst materials in the electrodes compartments are needed. They are chemical species which reduce the activation energy of the chemical processes, that is the minimum energy necessary to start the chemical reaction. In other words, it is the energy needed in order to create the activated complex, a particular configuration of transition considered as the moment of rupture of the reactants' chemical bonds with subsequent creation of new bonds in order to generate the products. In particular, a catalyst is a material usually solid, which takes part to the chemical reaction, but it is not modified by it. A well-performing electrode contains several small grains of catalyst distributed over its surface. Such a configuration is better than one having few big grains because many more points are available for the electrochemical reactions.

Regarding the electrolyte, its function is the conduction of ions generated by oxidation-reduction processes (positive ions move from the anode to the cathode, while negative ions do the opposite). Oxidation and reduction are the half-reactions that compose the total chemical reaction of interest. While they change on the base of the material of the electrolyte, the global transformation remains the same.

Typically, the electrochemical cells are connected in series, creating a stack: each single cell is separated by the adjacent one by an interconnector, also called *bipolar plate* because on one side it is in contact with the anode (positive polarization) of one cell and on the opposite side with the cathode (negative polarization) of another cell. At each of the two extremes of the stack an end plate is placed. Such stack configuration enables the obtainment of the desired exiting gas production rate. This parameter is numerically evaluated by means of the following Faraday law (for a single electrochemical cell), according to which the molar flow of a chemical species (reactant or product) $\dot{n}_i$ is directly proportional to the electrical current I exchanged between the electrodes:

$$\dot{n}_i = \frac{I}{Z_i \cdot F} \quad \left[\frac{mol}{s}\right]$$

The denominator contains the product between the Faraday number F, which, with a value of 96487 C mol^{-1}, represents the electric charge associated to 1 mole of electrons and the charge number of the chemical species considered, Z_i. The last parameter expresses the quantity of electrons delivered or recombined during the chemical reaction involving the considered chemical species. In the case of water, hydrogen and oxygen, the three values are:

- $Z_i = 2$ for a water molecule (H_2O);
- $Z_i = 2$ for a hydrogen molecule (H_2);
- $Z_i = 4$ for an oxygen molecule (O_2).

The previous equation can be rewritten in terms of mass, simply multiplying by the molar mass of the chemical species of interest, $\overline{M}_i$:

$$G_i = \frac{I}{Z_i \cdot F} \cdot \overline{M}_i \quad \left[\frac{g}{s}\right]$$

Multiplying, then, by the number of cells in series, n_c, the total mass flow rate of the i-th chemical species associated to the whole stack is obtained:

$$G_i = \frac{I}{Z_i \cdot F} \cdot \overline{M}_i \cdot n_c \quad \left[\frac{g}{s}\right]$$

2.2.2. Principle of operation and performance of the electrolysers

The electrolysis process is an electrochemical phenomenon based on the imposition of a voltage gradient (cell voltage) between the electrodes of the cell, which enables the oxido-reduction reactions of the chemical species to take place. During the operation of the electrolyzers, the main parameters to control are: current density, cell voltage, temperature and pressure of operation. An increase of the current density means a higher production of the chemical species of interest, but also a greater electrical energy expenditure. The cell voltage, together with the specific energy, represents the main parameter to describe the performance of the electrolytic cells. Typically, the **cell voltage** is evaluated with the polarization curve, which shows its trend with respect to the variation of the electrical current density, given by the electrical current needed per unit of conduction surface of the cell. Such voltage is the algebraic sum of the *open circuit voltage* (between the electrodes) and three *overvoltages*, due to three different types of transport phenomena.

The **open circuit voltage** is the minimum (theoretical) value of voltage of the curve, corresponding to a null current density. It depends on the temperature and pressure of the electrochemical reaction and is calculated by means of the following Nernst equation:

$$E = \frac{\Delta \bar{g}_{reaction}(T, p)}{Z_F \cdot F}$$

At the numerator, $\Delta \bar{g}_{reaction}(T, p)$ represents the variation of the molar Gibbs free energy of the total reaction, at its pressure and temperature values.

The previous formula ca be rewritten highlighting the dependence of the open circuit voltage on the chemistry of the reaction (species of reactants and products) and its thermodynamics (temperature and pressure). In this case, the variation of the molar Gibbs free energy of the reaction depends no more on the operating pressure, but on a reference pressure p_0. If the chemical species involved in the electrochemical reaction can be considered as ideal gases, the Nernst equation has the following form:

$$E = \frac{\Delta \bar{g}_{reaction}(T, p_0)}{Z_F \cdot F} + \frac{R \cdot T}{Z_F \cdot F} \cdot ln\left(\frac{\prod_P \left(\frac{p_i}{p_0}\right)^{\nu_i}}{\prod_R \left(\frac{p_i}{p_0}\right)^{\nu_i}}\right)$$

The dependence of the open circuit voltage on reactants and products is expressed by means of the product between the ratios of the partial pressure p_i of each chemical species with respect to the reference pressure, each of them elevated to the stoichiometric coefficient ν_i of the molecule in the reaction. Finally, the parameter R is the gas constant.

The variables which influence the open circuit voltage are the operating temperature and the partial pressure of reactants and products. In order to decrease this voltage value and, thus, the electrical energy expenditure, an increment of reactants' partial pressure is positive as well as a decrement of products' partial pressure. For what concerning the temperature, instead, its increase produces both an increment of the second addend of the sum and a reduction of $\Delta\bar{g}_{reaction}(T, p_0)$. The combination of the two variations leads to a global decrease of the open circuit voltage.

If, instead, the chemical species considered are not ideal gases, the Nernst equation can be generalized as follows, in function of their concentration *C_i*:

$$E = \frac{\Delta\bar{g}_{reaction}(T, p_0)}{Z_F \cdot F} + \frac{R \cdot T}{Z_F \cdot F} \cdot ln\left(\frac{\prod_P {C_i}^{\nu_i}}{\prod_R {C_i}^{\nu_i}}\right)$$

For what concerns the **overvoltages**, they correspond to an additional voltage to the theoretical one, required to overcome the resistances due to: activation of the electrochemical reactions (*activation overvoltage*), the charge (electrons and, mostly, ions) transport through the external circuit and the electrolyte (*ohmic overvoltage*) and mass transport of the molecules inside the electrodes at high current densities (*diffusion overvoltage*).

The activation of the electrochemical reactions requires an initial potential, correlated, thus, with the charge transfer occurring during oxidation and reduction transformations. Since the electrochemical reactions occur in both the electrodes, each of them gives its own contribution to the **activation overvoltage**. For both the anode and the cathode, it is calculated as:

$$\eta_{act} = \frac{R \cdot T}{n_{RDS} \cdot \beta \cdot F} \cdot sinh^{-1}\left(\frac{I}{2 \cdot I_0}\right) = \frac{R \cdot T}{n_{RDS} \cdot \beta \cdot F} \cdot sinh^{-1}\left(\frac{i}{2 \cdot i_0}\right)$$

where:

- R is the gas constant;
- T is the operating temperature of the cell;
- n_{RDS} is the number of electrons exchanged in the rate determining step, that is the slowest transformation among the ones composing the mechanism of reaction (set of reactions that, together, lead to the global one);
- β is the symmetry factor, used to quantify the modification in the molar enthalpy of reactants and products, due to the presence, in an electrochemical reaction, of an electric field;
- F is the Faraday constant;

- I (i) is the current (current density) exchanged between the electrodes;
- I_0 (i_0) is the exchanged current (exchanged current density), which, characteristic of a given reaction associated to a particular electrode, expresses its capability of transferring charges during operation. Quantity, quality and distribution of catalyst material on the electrode influences, together with the operating temperature, the current I_0. An increase of all the mentioned parameters leads to an increase of the exchanged current and, thus, to a decrease of the activation overvoltage.

The **ohmic overvoltage** is correlated to charge (ions and electrons) conduction within the cell. The electronic conductivity and the ionic conductivity values are, respectively, more or less 10^7 Ω^{-1} m^{-1} and 10 Ω^{-1} m^{-1}. Hence, even if the length of the electrons' pathway, from the anode to the cathode, is greater than the one of the ions across the electrolyte, the ion conductivity represents the limiting factor which gives the largest contribution to the ohmic overvoltage. Such value is calculated starting from the first Ohm's law, which states that, in a conductor, the difference of potential (η_{ohm}) between two points is directly proportional to current I across them, with the electrical resistance R as constant of proportionality:

$$\eta_{ohm} = R \cdot I$$

Then the definition of current density and the second Ohm's law, according to which the electrical resistance R of a conductor is directly proportional to its resistivity ρ and length L and inversely proportional to its cross section S, are applied to the previous formula:

$$\eta_{ohm} = R \cdot I = \rho \cdot \frac{L}{S} \cdot i \cdot S = (\rho \cdot L) \cdot i$$

The final equation giving the ohmic overvoltage is, thus, the following one:

$$\eta_{ohm} = ASR \cdot i$$

where the product between the resistivity and length of the conductor constitutes the Area Specific Resistance (ASR).

In order to reduce the negative effect given by the low ionic conductivity, the thickness of the electrolyte needs to be reduced as much as possible, without an excessive loss of mechanical strength of the cell.

Finally, the **diffusion overvoltage** is generated, at high current densities, by the excessive slowness of mass transport of the molecules within the electrodes. It is important to observe that the electrochemical reactions take place only in specific sites of the electrodes: these are the Three Phase Boundary (TPB) sites. They are constituted by a catalyst grain surrounded by three different phases:

- a pore phase, necessary for the adsorption of molecules on the surface of the catalyst grain;
- an ionic phase, necessary for the conduction of ions;
- an electronic phase, necessary for the conduction of the electrons.

The mass transport of reactants follows a diffusion model from a bulk concentration (C_{bulk}) to a well-ordered concentration on the TPB points (C_{cat}).

Most of these sites are close to the electrolyte, so, at high values of current density, the pathway of molecules coming from the bulk situation can require too much time to provide the necessary amount of electrons in the external circuit.

The voltage increase due to the described phenomenon can be taken into account with the general form of Nernst equation:

$$E = \frac{\Delta \bar{g}_{reaction}(T, p_0)}{Z_F \cdot F} + \frac{R \cdot T}{Z_F \cdot F} \cdot ln\left(\frac{\prod_P C_i^{\nu_i}}{\prod_R C_i^{\nu_i}}\right)$$

where C_i represents the concentration value of reactants and products on the catalyst grains. It is easy to see that, reducing the concentration of reactants, the open circuit voltage undergoes an increase.

Since the diffusion overvoltage can be considered in the previous equation, differently from the other two, which are real, it is only fictitious. This means that, there are two alternatives in writing the cell voltage equation:

1. considering the concentration C_{cat} in Nernst equation:

$$V_c = E(C_{cat}) + \eta_{act}(i) + \eta_{ohm}(i)$$

2. considering the concentration C_{bulk} in Nernst equation:

$$V_c = E(C_{bulk}) + \eta_{act}(i) + \eta_{ohm}(i) + \eta_{diff}(i)$$

In order to go from a measured concentration C_{bulk} to a calculated concentration C_{cat}, a diffusion model is needed. The most used is the Fick's law

$$\dot{n} = S \cdot D^{eff} \cdot \nabla c$$

according to which the molar flow $\dot{n}$ of a diffused chemical species is directly proportional to the surface of diffusion S, to the effective diffusion coefficient D^{eff} and to the concentration gradient ∇c between the bulk and well-ordered conditions. Considering the diffusion of molecules prevailing only along the x-axis, the model can be rewritten as:

$$\frac{\dot{n}}{S} = D^{eff} \cdot \frac{dC}{dx} = D^{eff} \cdot \frac{C_{bulk} - C_{cat}}{t}$$

where *t* is the length of the diffusion pathway.

Considering, now, the definition of the current density and the Faraday law, the following equation comes out:

$$i = \frac{I}{S} = \frac{\dot{n}}{S} \cdot Z \cdot F$$

By substituting it in the diffusion model a relation between the electrical phenomena and the mass transport is found:

$$i = Z \cdot F \cdot D^{eff} \cdot \frac{C_{bulk} - C_{cat}}{t} \qquad (1)$$

It is possible to define a limit situation in which the concentration C_{cat} goes to zero, arriving to the limiting current density of a single electrode:

$$i_l = Z \cdot F \cdot D^{eff} \cdot \frac{C_{bulk}}{t} \qquad (2)$$

This is the maximum value of current exchanged by an electrode and it will be contained in the equation for the calculation of the diffusion overvoltage, deriving from the difference of concentration:

$$\eta_{diff} = \left(\frac{R \cdot T}{Z \cdot F} \cdot \ln(C_{cat}) - \frac{R \cdot T}{Z \cdot F} \cdot \ln(C_{bulk}) \right) = \frac{R \cdot T}{Z \cdot F} \cdot \ln \frac{C_{cat}}{C_{bulk}}$$

By substituting the equations (1) and (2), the final equation of the diffusion overvoltage (for a single electrode) is obtained:

$$\eta_{diff} = \left| \frac{R \cdot T}{Z \cdot F} \cdot \ln \left(1 - \frac{i}{i_l} \right) \right|$$

Finally, the resulting equation of the cell voltage (considering C_{bulk} in the Nernst equation) is:

$$V_c = E(C_{bulk}) + \eta_{act}(i) + \eta_{ohm}(i) + \eta_{diff}(i)$$

$$= \frac{\Delta \bar{g}_{reaction}(T, p_0)}{Z_F \cdot F} + \frac{R \cdot T}{Z_F \cdot F} \cdot ln \left(\frac{\prod_P C_i^{\nu_i}}{\prod_R C_i^{\nu_i}} \right) + \frac{R \cdot T}{n_{RDS,an} \cdot \beta \cdot F} \cdot sinh^{-1} \left(\frac{i}{2 \cdot i_{0,an}} \right)$$

$$+ \frac{R \cdot T}{n_{RDS,cath} \cdot \beta \cdot F} \cdot sinh^{-1} \left(\frac{i}{2 \cdot i_{0,cath}} \right) + ASR \cdot i + \left| \frac{R \cdot T}{Z \cdot F} \cdot \ln \left(1 - \frac{i}{i_{l,an}} \right) \right|$$

$$+\left|\frac{R \cdot T}{Z \cdot F} \cdot \ln\left(1 - \frac{i}{i_{l,cat}}\right)\right|$$

Considering the water splitting reaction, under the hypothesis of ideal gas, the polarization equation can be rewritten as:

$$V_c = \frac{\Delta \bar{g}_{reaction}(T, p_0)}{2 \cdot F} + \frac{R \cdot T}{2 \cdot F} \cdot ln\left(\frac{p_{H_2} \cdot p_{O_2}^{0.5}}{p_{H_2O}}\right) + \frac{R \cdot T}{n_{RDS,an} \cdot \beta \cdot F} \cdot sinh^{-1}\left(\frac{i}{2 \cdot i_{0,an}}\right)$$

$$+ \frac{R \cdot T}{n_{RDS,cath} \cdot \beta \cdot F} \cdot sinh^{-1}\left(\frac{i}{2 \cdot i_{0,cath}}\right) + ASR \cdot i + \left|\frac{R \cdot T}{2 \cdot F} \cdot \ln\left(1 - \frac{i}{i_{l,an}}\right)\right|$$

$$+\left|\frac{R \cdot T}{4 \cdot F} \cdot \ln\left(1 - \frac{i}{i_{l,cath}}\right)\right|$$

A temperature increment globally reduces both the open circuit voltage and the additional voltage required to overcome the resistances due to the transport phenomena. This means that electrolyzers working at elevated temperature will require a lower electrical input, as showed in Figure 1, which reports two polarization curves for alkaline electrolyzers at two different temperature levels.

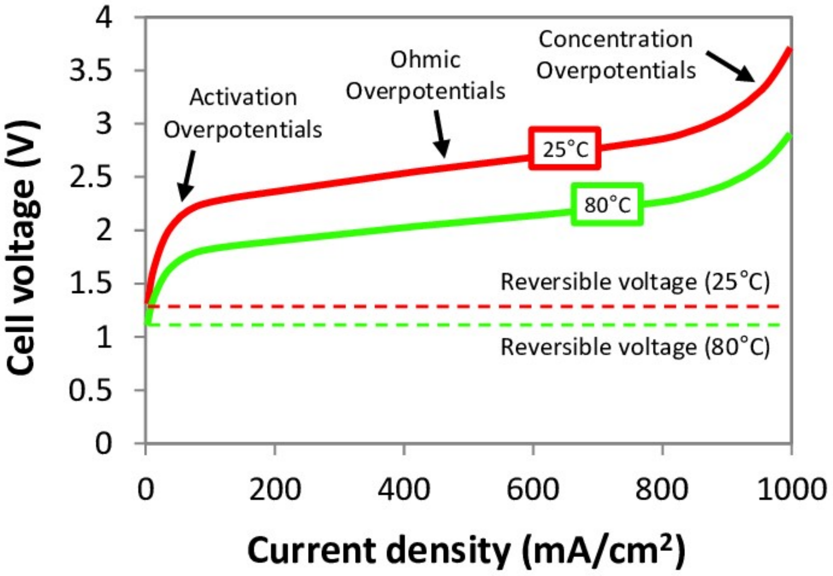

Figure 1 – Polarization curves for alkaline electrolysers with different temperature levels

As previously introduced, the second parameter useful to estimate the performance of an electrolyzer is the **specific energy**. It is the electric energy required to produce 1 Nm^3 of the product of interest (hydrogen in the case of water electrolysis), so it is directly proportional to the cell voltage. Being the ratio between the energy spent and the volume of gas (hydrogen) produced, it can be written as:

$$E_{sp} = \frac{n_c \cdot V_c \cdot I \cdot 10^{-3}\ [kW]}{\left(\frac{I}{2 \cdot F} \cdot n_c\right)\left[\frac{mol}{s}\right] \cdot V_m \left[\frac{Nm^3}{mol}\right] \cdot 3600\ \left[\frac{s}{h}\right]} \quad \left[\frac{kWh}{Nm^3}\right]$$

where:

- At the numerator, n_c, V_c, I are, respectively: the number of cells in series belonging to the stack, the cell voltage and the electric current. Their product gives the electric power supplied to the stack.
- At the denominator, the product between the terms of the Faraday law (for the hydrogen), the number of cells in series and the molar volume V_m gives the volumetric flow rate of hydrogen.

Considering that, for a gas, the molar volume V_m is equal to:

$$V_m = 22.4 \left[\frac{l}{mol}\right] = 0.0224 \left[\frac{Nm^3}{mol}\right]$$

the equation of the specific energy for the hydrogen production becomes:

$$E_{sp} = 2.44 \cdot V_c \left[\frac{kWh}{Nm^3}\right]$$

Considering the cell voltage equal to the open circuit one, the limit value (theoretical minimum) of the specific energy is found.

2.2.3. Thermal management

The electrochemical cells (both galvanic and electrolytic), beside the electric power, exchange also thermal power with the external environment, in an endothermic or exothermic way. Such heat flux must be managed in order to maintain at a fixed value the operating temperature of the devices.

The exchanged thermal power is constituted by two contributions:

1. Heat related to the electrochemical reactions, so to the thermodynamics (molar entropy variation of the reaction) of the process. The exchanged thermal power can be written as follows:

$$\Phi_{reaction} = T \cdot \Delta\bar{S}_{reaction} \cdot \dot{n}_R \quad [W]$$

where:

- T is the operating temperature of the electrochemical cell;
- $\Delta\bar{S}_{reaction}$ is the molar entropy variation of the global reaction;
- $\dot{n}_R$ is the molar flow of reactants.

This heat flux can be positive, if the process is endothermic (entropy positive variation), or negative, in the exothermic case (entropy negative variation).

2. Heat related to transport processes: it is due to the irreversibilities (Φ_{irr}) generated. This kind of heat flux, calculated as the product between the electrical current and the overvoltages summation, is always positive, but in such a way that it is produced by the electrochemical cell. This means that it is an exothermic heat flux.

For what concerning the electrolyzers, the reaction heat (the first one) is positive, so endothermic: the reactions need a supply of heat. By its combination with the heat due to transport processes, the total heat flux exchanged by the electrolytic cell is obtained:

$$\Phi_c = \Phi_{reaction} - \Phi_{irr} = \left(\frac{\Delta\bar{h}_{reaction}}{Z \cdot F} - V_c\right) \cdot I$$

where:

- $\Delta\bar{h}_{reaction}$ is the molar enthalpy variation of the reaction, positive for the electrolyzers;
- Z and F are, respectively, the charge number and the Faraday constant;
- V_c is the cell voltage;
- I is the electrical current.

Starting from the previous equation, three situations can take place:

1. Endothermic electrolyzer

$$V_c < \frac{\Delta\bar{h}_{reaction}}{Z \cdot F} \quad and \quad \Phi_c > 0$$

At low currents, the heat required by the device in order to carry out the electrochemical reactions is greater than the one produced by the irreversibilities. This means that a supply of heat is necessary and part of it can come directly from the cell itself, while the remaining from the external.

2. Exothermic electrolyzer

$$V_c > \frac{\Delta \bar{h}_{reaction}}{Z \cdot F} \quad and \quad \Phi_c < 0$$

This is the most common case, obtainable at high current values. The heat produced by transport phenomena exceeds the one required by the reactions, so the electrolyzers needs a heat removal.

3. Adiabatic electrolyzer

$$V_c = \frac{\Delta \bar{h}_{reaction}}{Z \cdot F} \quad and \quad \Phi_c = 0$$

This is the ideal operating situation, in which the cell requires neither subtraction nor supply of heat. The cell voltage, in this case, is named *thermoneutral voltage (*V_{TN}).

2.2.4. Water electrolysers

To date, on the base of the kind of electrolyte, three main types of water electrolyzers have been developed:

1. **Alkaline water electrolyzer (AWE)**
   Utilized at a market level, it is the classical electrolyzer, with a power level going from 1 kW to 100 MW (for modular devices).
2. **Proton exchange membrane electrolyzer (PEM)**
   It is used at a semi-market level and needs an electrical power comprised between 110 W and 20 MW.
3. **Solid oxide electrolyzer (SOEC)**
   It is at a prototype level, with a power between 1 kW and 200 kW.

The first two technologies work in near ambient temperature (NAT) conditions, so usually between 60 and 80 °C, whereas SOECs operate with high temperature levels, around 800-1000 °C. Regarding the thermal management, alkaline and PEM electrolyzers are typically exothermic devices, with a need of heat removal, while solid oxide technologies require a heat supply, since they operate in endothermicity. Beside these three technologies, also a fourth one has to be mentioned: the **molten carbonate electrolyzer (MCE)**, a high temperature device which, anyway, is at an earlier stage of development with respect to SOECs.

2.2.4.1. Alkaline water electrolysers

The alkaline water electrolyzer is the oldest and more mature technology: it has been used by industries for over a century, becoming the cheapest option to produce hydrogen of electrolytic grade. Devices of this type range from really small hydrogen productions (lower than 1 Nm^3/h) to flow rates of around 4000 Nm^3/h, with an exiting pressure arriving to 35 bar. Thanks to the modularity, today, alkaline technologies arriving to the megawatt (MW) of electric power are available on the market. The alkaline environment of operation confers a long operational lifetime, arriving to 15 years for the stacks themselves and up to 20 years for the whole system (electrolyzers and auxiliary components). Such values of durability are the main reason motivating the research about AWEs. To date, three models of alkaline water electrolyzers are available: the traditional one, the zero-gap electrolyzer and the one operating at a medium temperature.

2.2.4.1.1. Traditional alkaline water electrolysers (gap-cells)

The traditional alkaline water electrolyzers, like the one reported in Figure 2, are characterized by a liquid electrolyte, composed of 30% by weight of potassium hydroxide (KOH) or sodium hydroxide (NaOH) dissolved into the remaining 70% of H_2O.

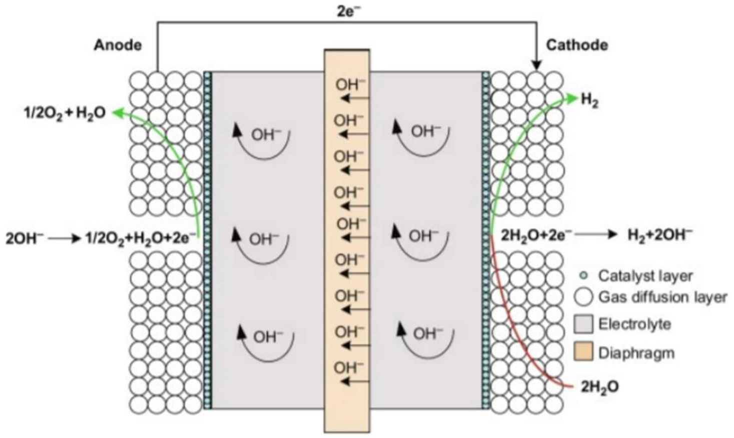

Figure 2 – Schematic of a traditional alkaline water electrolyser

Water is injected into the cathode, where it is reduced, releasing OH^- ions and hydrogen, according to the following reaction:

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2$$

Since water is injected in excess into the cell, part of it exits from the cathodic compartment mixed with the hydrogen. The produced ions are conducted across the electrolyte, towards the anode. Here, by means of the following oxidation reaction, electrons, oxygen and water are released:

$$2OH^- \rightarrow 2e^- + \frac{1}{2}O_2 + H_2O$$

The sum of the previous two half-reactions gives the water splitting reaction:

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

Both the electrodes are constituted by steel with nickel as electrocatalyst material. The application of nickel, which is a non-noble metal, as catalyst brings an advantage to alkaline water electrolyzers over the other technologies, thanks to its reduced cost, sufficiently high activity and corrosion resistance. The possibility of using nickel derives from the sufficiently high production rate of OH^- ions and the non-aggressive alkaline environment.

In order to avoid contact and recombination of exiting gas, a cell separator (diaphragm), theoretically permeable to ions but not to the exhausts, is interposed between the electrodes. Anyway, due to the porosity of the diaphragm, a non-negligible gas crossover between anode and cathode is present. This fact reduces the hydrogen purity and limits the operating pressure near to the atmospheric one because an increase of this parameter would cause a greater gas crossover. Initially, the separator was made of asbestos, then eliminated because of its dangerousness. Today, an example of solution is provided by inorganic ion-exchange type membranes (IMET) used by Cummins, which give a hydrogen purity greater than 99.999%.

The distance between the electrodes and the separator affects the ohmic losses. For a given current, there is an optimal value of this gap. If the real value is greater than the optimal one, ohmic losses are increased due to ions' longer pathway, incrementing also the potential demanded. This means that, for an optimized configuration, the electrode-diaphragm distance needs to be reduced. If, instead, the distance is lower than the optimal one, the produced gas remains confined nearby the electrode, producing a screening effect which results, again, in a need of higher potential. This last request of additional voltage can be reduced by means of an increased forced convection (circulation) of water, which removes bubbles from the electrodes surface. However, there is a limit value of water flow rate above which there are no relevant improvements. Moreover, even if forced convection improves the electrolysis efficiency, the global one is reduced because of the increased energy need to pump the flow.

Technical analysis of traditional alkaline electrolysers

In order to perform a technical analysis of the traditional alkaline water electrolyzers, the datasheets provided by the main suppliers have been analyzed. To date, most of AWEs manufactures are situated in Europe, followed by America and Asia. In particular, the suppliers are distributed as follows:

- Europe
    - GreenHydrogen.dk Aps (Denmark)
    - IHT Industrie Haute Technologie S.A. (Switzerland)
    - McPhy (France)
    - Nel (Norway)
    - Pure Energy Centre PEC (United Kingdom)
    - Thyssenkrupp Uhde Chlorine Engineers GmbH (Germany)
- America
    - Cummins (Ohio)
- Asia
    - Toshiba Energy Systems & Solutions Corporation (Japan)

As it emerged from the following analysis, there is a wide choice of traditional AWEs, ranging from the lowest hydrogen flow rates such as 0.4 Nm^3/h to the higher ones, like 4000 Nm^3/h. Some of the mentioned providers, like GreenHydrogen.dk Aps, Pure Energy Centre PEC and Cummins, focus on smaller size electrolysis devices (up to 90 Nm^3/h), while other ones such as IHT Industrie Haute Technologie S.A., Nel and Thyssenkrupp Uhde Chlorine Engineers GmbH produce electrolyzers of medium/large size (up to 4000 Nm^3/h). McPhy, instead, ranging between 0.4 Nm^3/h and 800 Nm^3/h, does not offer technologies with the biggest flow rates, but it is the most flexible supplier, suitable for very different hydrogen demands.

The choice of one electrolyzer rather than another obviously depends first of all on its purpose: for example, it can mainly be used to satisfy a certain hydrogen demand or as an energy storage. In the first case, the attention is primarily focused on the amount of hydrogen required, while in the second case the choice is based on the amount of electrical energy that is typically in excess. Then, a comparison among the other Key Performance Indicators of the suitable electrolyzers is necessary in order to find the optimal one.

In order to compare all the suppliers mentioned before, it was taken into consideration the first situation, so the analysis is based on the hydrogen flow rate produced by the electrolyzers. Since the range of possible hydrogen flow rates is particularly wide, in order to carry on a more accurate and orderly comparison four different sets of hydrogen flow rates were identified, with an increasing order of magnitude. Thus, on the basis of the technical specifications provided by the suppliers, their electrolysis devices were classified in four groups having the following ranges of hydrogen flows:

1. 0.4 – 10 Nm^3/h;
2. 10 – 90 Nm^3/h;
3. 100 – 970 Nm^3/h;
4. 2000 – 4000 Nm^3/h.

Then, the following Key Performance Indicators have been chosen as the most representative:

- **Electrical power consumption (kW)**, so the electrical input given to the electrolyzer in order to perform the electrochemical reaction;
- **Load/flow range (%)**, expressing how much the input power/hydrogen flow rate can vary with respect to the nominal value;
- **Electrolyzer specific energy consumption (kWh/Nm^3)**, so the electrical energy required to produce a single normal cubic meter of hydrogen or, in other words, the electrical power per unit of hydrogen flow rate produced;
- **Cell voltage (V)**, calculated using the equation previously introduced which relates it to the specific energy:

$$V_c = \frac{E_{sp}}{2.44} \ [V]$$

- **Electrolyzer conversion efficiency referred to the hydrogen Higher Heating Value (%)**, expressing the electrolyzer's ability to transform the received electrical power into chemical power:

$$\eta_{conversion} = \frac{\dot{m}_{H_2} \cdot HHV_{H_2}}{W_{el}}$$

  At the numerator there is the chemical power stored into hydrogen, calculated by means of the product between its flow rate $\dot{m}_{H_2}$ and its Higher Heating Value HHV_{H_2} (it is possible to perform the same calculation using the Lower Heating Value). The denominator contains the electrical power required as input by the electrolyzer.

- **Cold (off) start-up time (s, min),** so the time required for a start-up from an off-state;
- **Warm (stand-by) start-up time (s),** so the time required for a start-up from a stand-by state;
- **System operational lifetime (years)**, referring to the lifetime of the system composed by all the auxiliary components;
- **Stack operational lifetime (hours)**, indicating how often the stack needs to be replaced;
- **Electrolyzer/system footprint (m^2)**, so the free surface needed for the installation of the electrolyzer/system.

Anyway, it was not possible to obtain the complete set of indicators for all the suppliers, so it has to be taken into account that those identified as the most convenient basing on the available data, in reality could be overcome by others whose specifications were unavailable.

Range 0.4 – 10 Nm^3/h

The first range analyzed is that comprising the smallest electrolysers, producing between 0.4 Nm^3/h and 8.66 Nm^3/h.

Since one of the main inputs of water electrolysis process is the electrical power and the hydrogen flow represents the output of interest, a first consideration can be done about their correlation. The two following (Figures 3 and 4) show the increasing trend of the input electrical power according to the increment of the electrolysers productivity, in terms of both volumetric and mass hydrogen flow rate.

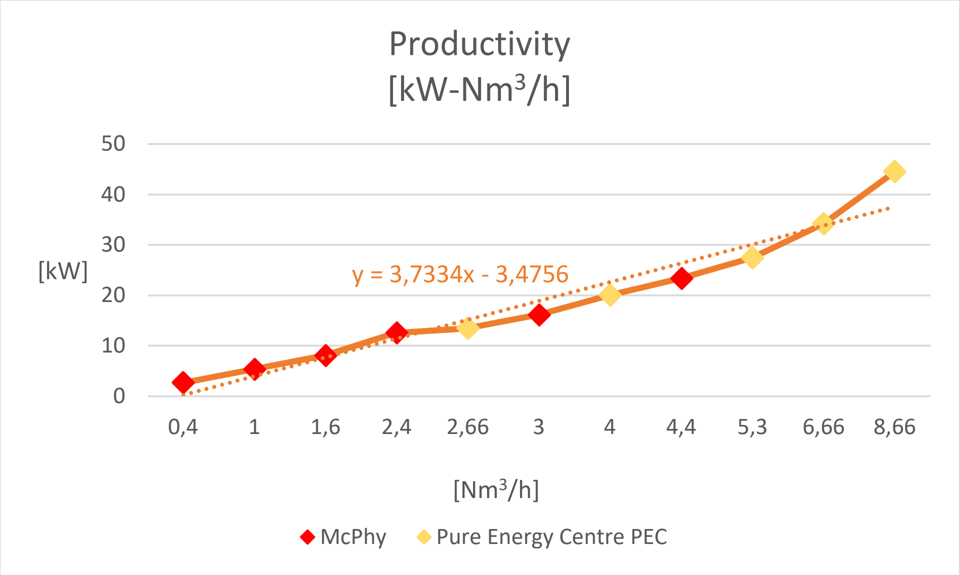

Figure 3 – Electrical input power of traditional AWEs as a function of the volumetric hydrogen production rate

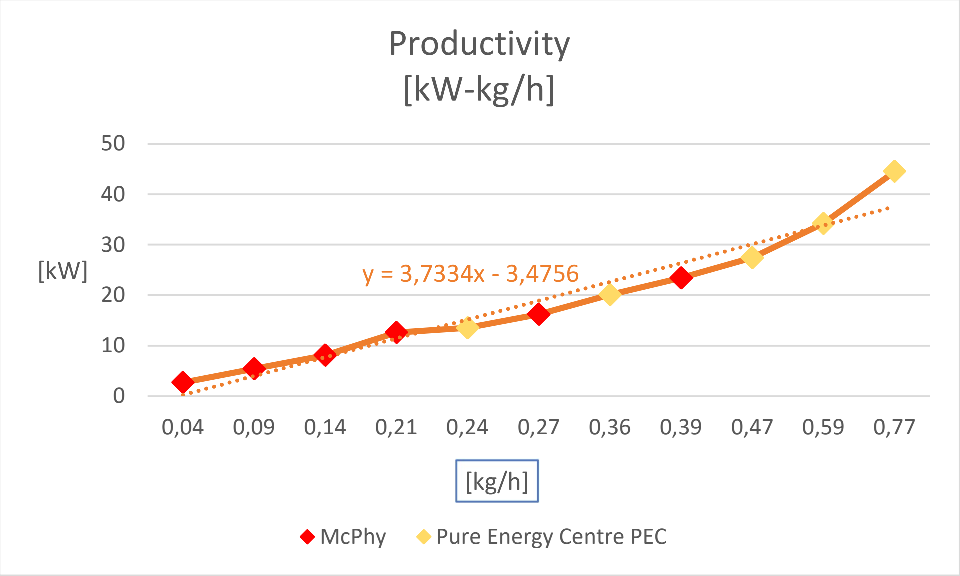

Figure 4 – Electrical input power of traditional AWEs as a function of the mass hydrogen production rate

The amount of required power grows following a fairly linear trend, as showed by the interpolating dashed line and its equation. The absence of peaks means that there are no technologies presenting an excessive request of power. In particular, electrolysers provided by Pure Energy Centre PEC, being almost always below the trend line, have in proportion smaller sizes compared to electrolysers of McPhy with lower levels of productivity. Moreover, it can be noted that while P electrolyser with its lower extreme of 2.4 Nm^3/h (0.21 kg/h) is located on the interpolating line, in the case of the upper extreme of 4.4 Nm^3/h (0.39 kg/h) goes below, thus, proportionally, the input power requirement decreases. Finally, according to the two previous figures it can be noted that for hydrogen demands lower than 2.66 Nm^3/h the only suitable supplier is McPhy.

Then, in order to compare technologies producing different amounts of hydrogen per hour, the electrolyser size alone is not a suitable indicator: instead, it is useful to consider it normalised to the hydrogen flow rate. In other words, the electrolyser specific energy consumption is a good means of comparison (Figures 5 and 6).

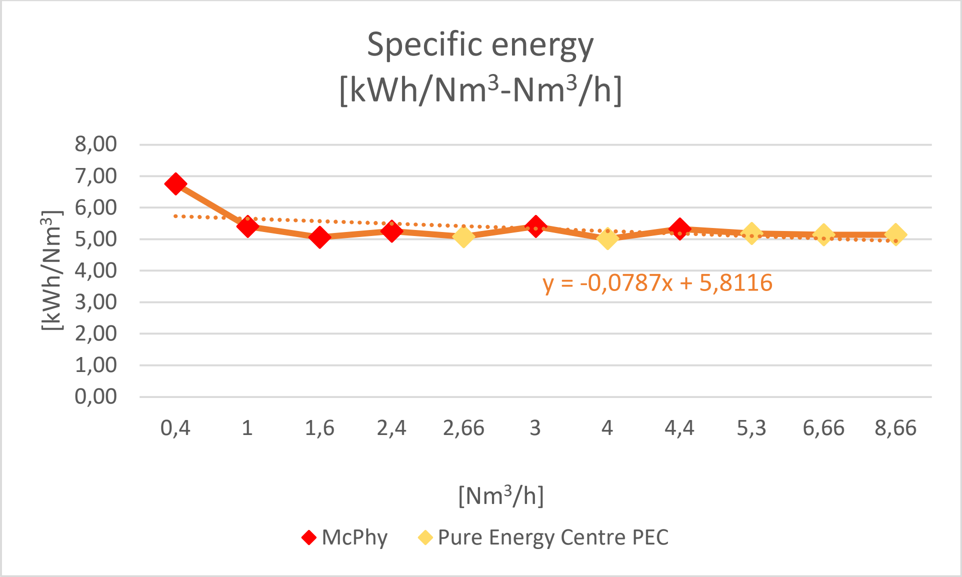

Figure 5 – Specific energy of traditional AWEs as a function of the volumetric hydrogen production rate

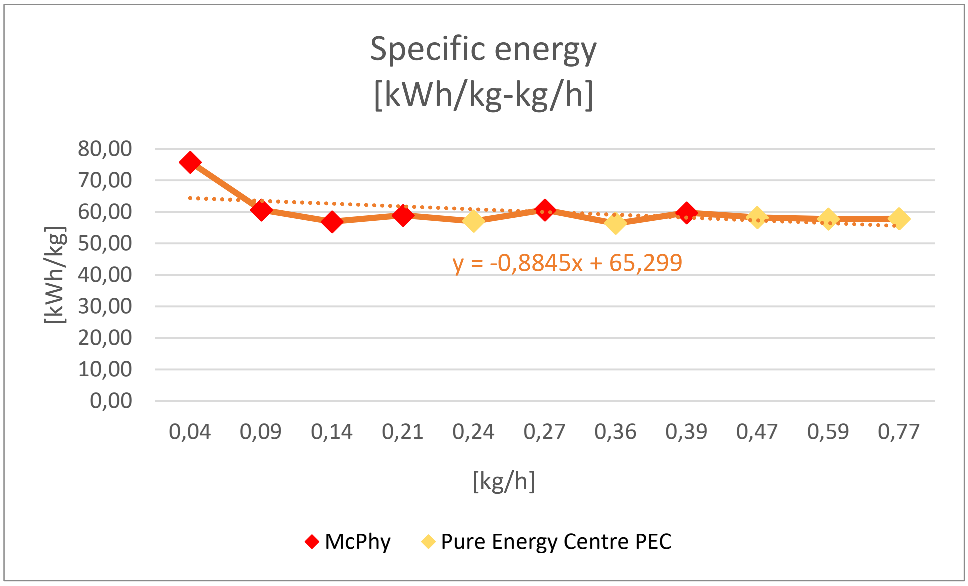

Figure 6 – Specific energy of traditional AWEs as a function of the mass hydrogen production rate

Under this aspect, the technologies of both providers are quite similar, except for the smallest McPhy device which requires 6.75 kWh/Nm^3 (75.84 kWh/kg), while all the other values are comprised between 5.02 kWh/Nm^3 (56.38 kWh/kg) and 5.40 kWh/Nm^3 (60.67 kWh/kg). Anyway, considering similar hydrogen flow rates it can be said that technologies produced by **Pure Energy Centre PEC** are those with lower specific energy consumptions. Indeed, while McPhy M electrolyser for 2.4 Nm^3/h needs 5.25 kWh/Nm^3, Pure Energy Centre PEC device requires 5.08 kWh/Nm^3 for a hydrogen production equal to 2.66 Nm^3/h. The same thing can be said in the case of 4 Nm^3/h for Pure Energy Centre PEC and 4.4 Nm^3/h for McPhy: in fact, the first device requires 5.05 kWh/Nm^3 while the second one 5.32 kWh/Nm^3. Moreover, from an overall point of view, it is present a little scale effect for which the specific energy consumption decreases as the hydrogen flow rate (and electrolysers size) increase.

Then, the same considerations done about the specific energy can be repeated for both the cell voltage and the electrolyser conversion efficiency. In fact, Baby McPhy electrolyser besides the highest specific energy consumption presents also the greatest cell voltage and the lowest conversion efficiency, respectively equal to 2.77 V and 52.0%. All other technologies remain, instead, in the ranges 2.06 – 2.21 V and 65.0 – 69.9%. Looking at the efficiency, Pure Energy Centre PEC technologies are those with the highest values, varying between 67.7% and 69.9%, while McPhy, aside from Baby, goes from 65.0% to 69.3%. However, the difference is so subtle that is negligible.

Finally, the last main Key Performance Indicator that can be taken into consideration is the footprint, that, depending on the supplier, can be referred to the electrolyser itself or to the whole system. In this case, the only data reported are those of Pure Energy Centre PEC (0.893 m^2, 1.11 m^2 and 1.9 m^2) and are referred to the whole system.

Range 10 – 90 Nm^3/h

Now, the description focuses on the second group of electrolysers, so those producing between 10 Nm^3/h and 90 Nm^3/h of hydrogen.

For this second grouping of electrolysers, as before, the variation of the required input power as a function of the productivity can be plotted in two graphs (Figures 7 and 8).

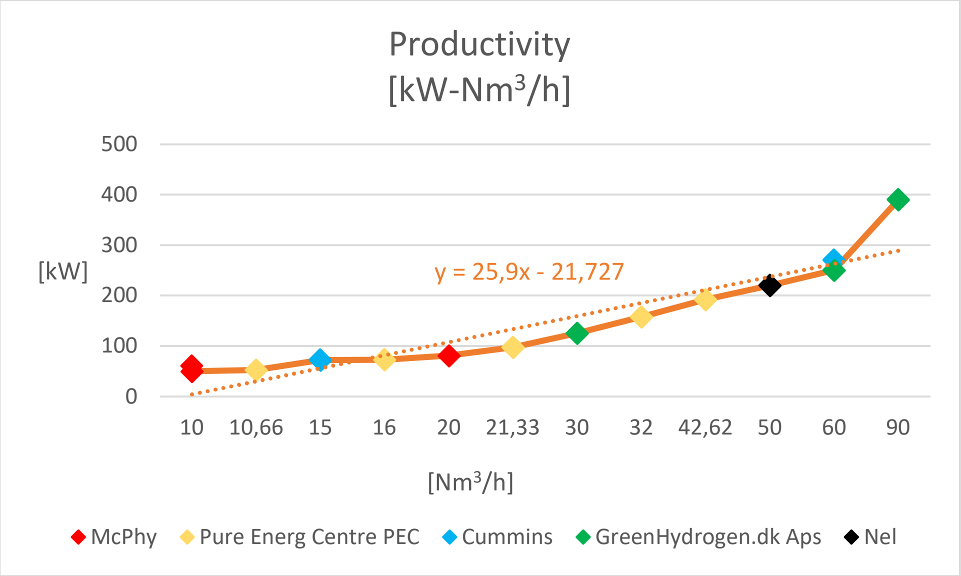

Figure 7 – Electrical input of traditional AWEs as a function of the volumetric hydrogen production rate

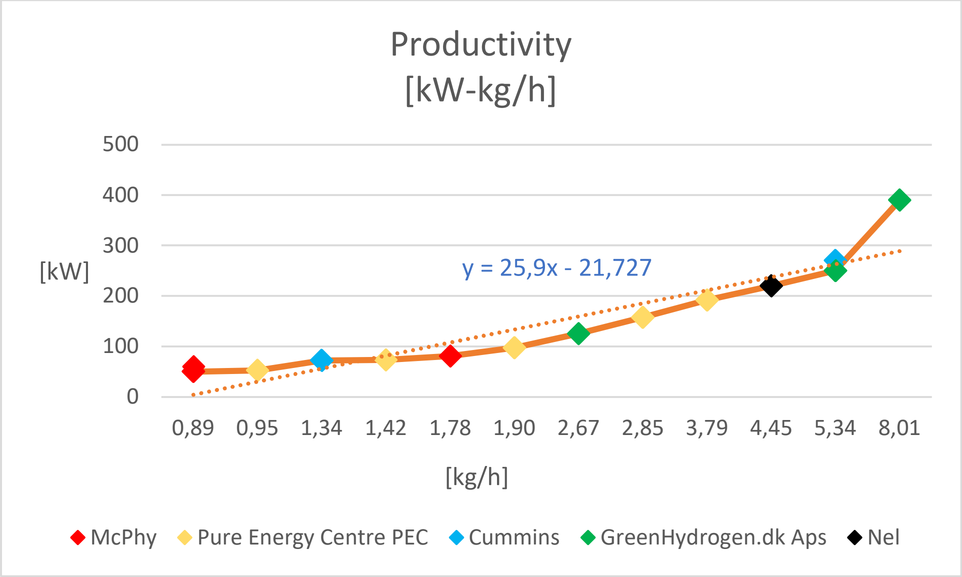

Figure 8 – Electrical input of traditional AWEs as a function of the mass hydrogen production rate

A first consideration that can be done regards the electrolysers characterised by a production of 10 Nm^3/h and 60 Nm^3/h. Indeed, for both the values there are two suitable technologies which have anyway different sizes. In the first case, the devices both belong to McPhy and correspond to McLyzer 10 – 30 (50 kW) and Piel H (60 kW), which is the electrolyser already inserted in the previous group, this time operating at the maximum production. The second couple includes GreenHydrogen.dk Aps A60, which with 250 kW has a smaller size with respect to Cummins HySTAT–60-10 (270 kW).

Globally, the sizes of this second group follow quite well the linear trend, except for the two smallest McPhy electrolysers (10 Nm^3/h) and the GreeHydrogen.dk Aps biggest one (90 Nm^3/h) which deviate more upward. These variations are due to two different factors. The first is that McPhy H electrolyser, requiring 60 kW for 10 Nm^3/h, has a greater size than the subsequent Pure Energy Centre PEC technology (52.2 kW for 10.66 Nm^3/h). The variation corresponding to 90 Nm^3/h is instead due to the greater gap between the penultimate and last value of hydrogen flow rate compared to the previous ones, which naturally leads to a larger increase of size. Thus, the size of this last technology cannot be considered excessive for its level of production. This is confirmed by the following graphs (Figures 9 and 10), showing the electrolyser specific energy as a function of the productivity. Indeed, among the two devices considered, only McPhy H electrolyser, with 6.00 kWh/Nm^3 (67.4 kWh/kg), differs from the general trend, while GreenHydrogen.dk Aps A90, characterised by 4.33 kWh/Nm^3 (48.69 kWh/kg), is located on the interpolating line.

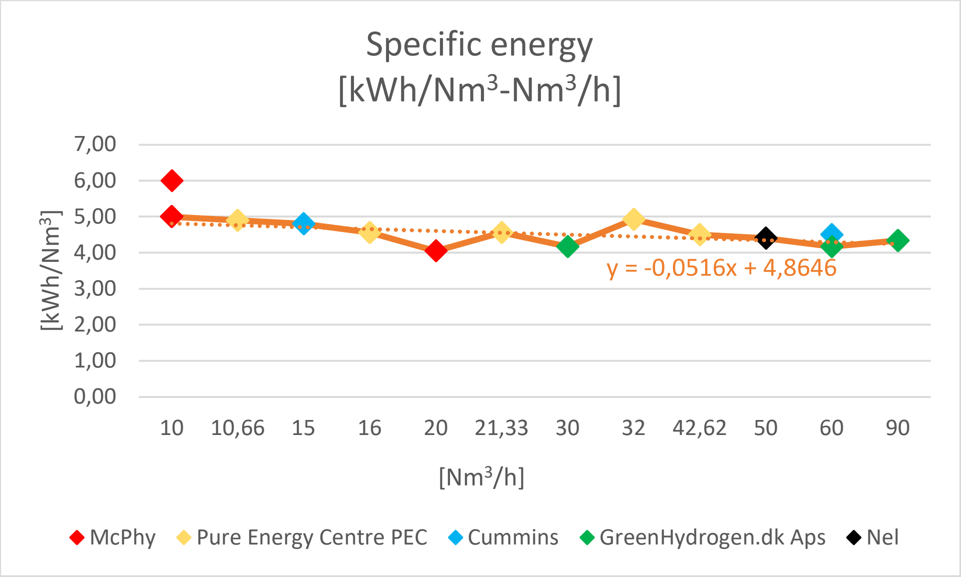

Figure 9 – Specific energy of traditional AWEs as a function of the volumetric hydrogen production rate

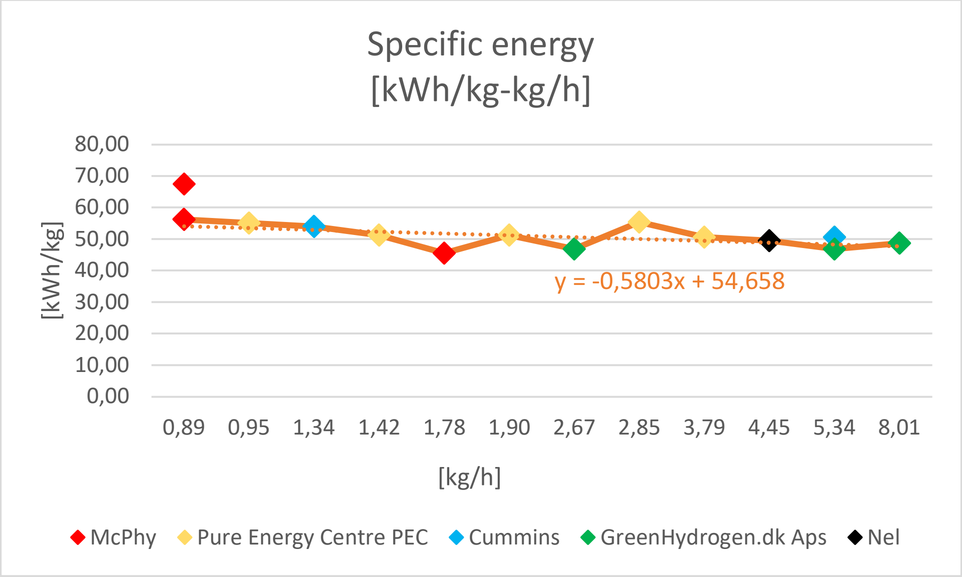

Figure 10 – Specific energy of traditional AWEs as a function of the mass hydrogen production rate

Generally, the specific energy of this group of electrolysers typically varies between 4.05 kWh/Nm^3 (45.5 kWh/kg) and 5.00 kWh/Nm^3 (56.2 kWh/kg), except for the mentioned McPhy H electrolyser. The linear decreasing trend, showing again the presence of the scale effect, is well approximated by almost all the devices, except for some technologies belonging to McPhy, Pure Energy Centre PEC and GreenHydrogen.dk Aps. Among these, McPhy McLyzer 20 -30 (20 Nm^3/h) and GreenHydrogen.dk Aps A30 (30 Nm^3/h) electrolysers, with respectively 4.05 kWh/Nm^3 and 4.17 kWh/Nm^3, being below the trend line, present a greater scale effect, with respect to their previous technologies, compared to the other cases. These two technologies, together with GreenHydrogen.dk Aps A60 electrolyser (4.17 kWh/Nm^3) present the lowest specific energies of the entire group, closely followed by GreenHydrogen.dk Aps A90 device with 4.33 kWh/Nm^3. McPhy Piel H electrolyser and Pure Energy Centre PEC technology for 32 Nm^3/h are, instead, located above the dashed line, showing an increase of specific energy consumption with respect to that expected. They, with respectively 6.00 kWh/Nm^3 and 4.92 kWh/Nm^3, together with McPhy McLyzer 10-30 (5.00 kWh/Nm^3), Pure Energy Centre PEC electrolyser for 10.66 Nm^3/h (4.90 kWh/Nm^3) and Cummins HySTAT-15-10 (4.80 kWh/Nm^3) show the highest specific energies. Finally, the same thing said in terms of size for the couples of technologies satisfying hydrogen demands of 10 Nm^3/h and 60 Nm^3/h can be repeated here, since for 10 Nm^3/h McPhy Piel H (6.00 kWh/Nm^3) has a greater specific consumption than McLyzer 10-30 (5.00 kWh/Nm^3) and for 60 Nm^3/h Cummins HySTAT-60-10 (4.50 kWh/Nm^3) is more energy-intensive than GreenHydrogen.dk Aps A60 (4.17 kWh/Nm^3).

As before, from the electrical consumption specifications, the operating voltage and the electrolyser conversion efficiency can be derived. Naturally, those technologies with the lowest specific energies present the lowest cell voltages and the highest conversion efficiencies. These are McPhy McLyzer 20-30 (1.66 V and 86.6%), GreenHydrogen.dk Aps A30, A60 (both with 1.71 V and 84.2%) and A90 (1.78 V and 80.9%).

GreenHydrogen.dk Aps is competitive also under the durability aspect, since it presents a system lifetime of 20 years and a stack operational lifetime longer than 80000 hours. These are both values corresponding to the typical maximum in the field of water electrolysis. In this group, also Cummins provides this kind of information, corresponding to 20 years and 80000 hours for the overall system and the stack respectively. Thus, the technologies of both the suppliers can be considered equivalent under the durability point of view.

Another good point of Cummins is then the operational window in terms of load of HySTAT 60-10, ranging from 10% to 100% of the nominal load, even if the other technology, HySTAT 15-10 has a much more restricted range (40 – 100%). Considering, instead, the operational window in terms of flow range, Nel and Pure Energy Centre PEC are almost similar, arriving, respectively, to 15% and 20% of the nominal hydrogen flow.

The remaining KPI that has to be considered in order to complete the comparison is the footprint, that, like in the previous description is referred to the entire system. The less demanding technologies, in terms of space, are those of GreenHydrogen.dk Aps, all three with a footprint of 1.98 m^2. However, also Pure Energy Centre PEC electrolysers have similar footprint, ranging from 1.9 m^2 to 4.42 m^2. Cummins and Nel, instead, require much larger surfaces, equal to 14.8 m^2 and 29.7 m^2 for the two Cummins electrolysers and 150 m^2 for that of Nel. This last value is due to the fact that Nel A150 electrolyser does not produce only 50 Nm^3/h of hydrogen, but it can arrive up to a production of 150 Nm^3/h.

In the end, comparing the electrolysers basing on similar hydrogen flow rates it can be said that:

- for hydrogen demands of lower than 20 Nm^3/h the optimal choice is constituted by **Pure Energy Centre PEC**;
- for hydrogen flow rates of 20 - 40 Nm^3/h the most performant technologies are those of **McPhy** and **GreenHydrogen.dk Aps**;
- for production levels greater than 60 Nm^3/h **GreenHydrogen.dk Aps** is again the most competitive supplier.

Range 100 – 970 Nm^3/h

The third group of electrolysers that has to be analysed is that ranging from 100 Nm^3/h to 970 Nm^3/h.

Like in the previous cases, the following two graphs (Figures 11 and 12) show that the input electrical power follows a quite linear increase with the productivity.

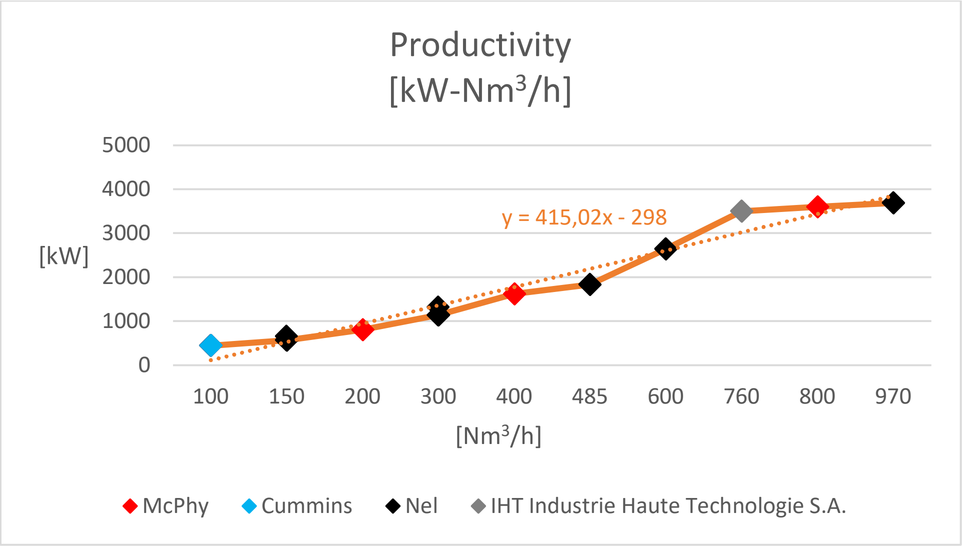

Figure 11 – Electrical input of traditional AWEs as a function of the volumetric hydrogen production rate

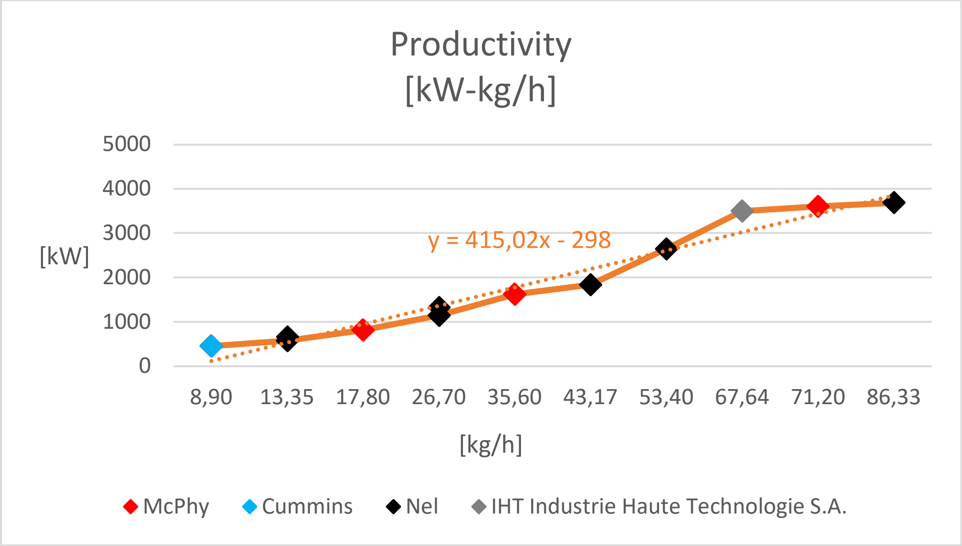

Figure 12 – Electrical input of traditional AWEs as a function of the mass hydrogen production rate

The major deviations with respect to the trend line can be attributed to McPhy, Cummins, Nel and IHT Industrie Haute Technologie S.A.. In particular, McPhy McLyzer 100-30 and Cummins HySTAT-100-10 electrolysers, with the same hydrogen production (100 Nm^3/h) and size are above the dashed line, like IHT Industrie Haute Technologie S.A. Type S-556 electrolyser (760 Nm^3/h). Nel A485 device, instead, when producing 485 Nm^3/h of hydrogen, goes more below the interpolating line with respect to other technologies. Concentrating on hydrogen demands equal to 150 Nm^3/h and 300 Nm^3/h, it can be noted that they can be satisfied by more than one Nel electrolyser. In particular A150 (50 – 150 Nm^3/h), AC150 (150 Nm^3/h) and A300 (150 - 300 Nm^3/h) in the first case and again A300 (150 - 300 Nm^3/h), AC300 (300 Nm^3/h) and A485 (300 – 485 Nm^3/h) in the second case. In this way, the customers have a wide range of choice, with smaller or larger hydrogen flow rates and the possibility of having a containerised solution (AC150 and AC300). However, depending on the technology, slightly different sizes correspond to the same hydrogen production. Indeed, for 150 Nm^3/h it is possible to have both 570 kW (A150) and 660 kW (AC150 and A300), while for 300 Nm^3/h the size can be 1140 kW (A300) or 1320 kW (AC300 and A485).

Looking at the previous graphs, it results evident that while both McPhy and Nel cover almost the entire range of hydrogen flow rates, Cummins is suitable only for nominal values of 100 Nm^3/h and IHT Industrie Haute Technologie S.A. only for 760 Nm^3/h.

Analysing then the electrolyser specific energy, whose trend is reported in the following graphs (Figures 13 and 14), it can be noted that this time there is no scale effect and all the values do not follow a real linear trend, indeed only the first two McPhy technologies are located on the interpolating line.

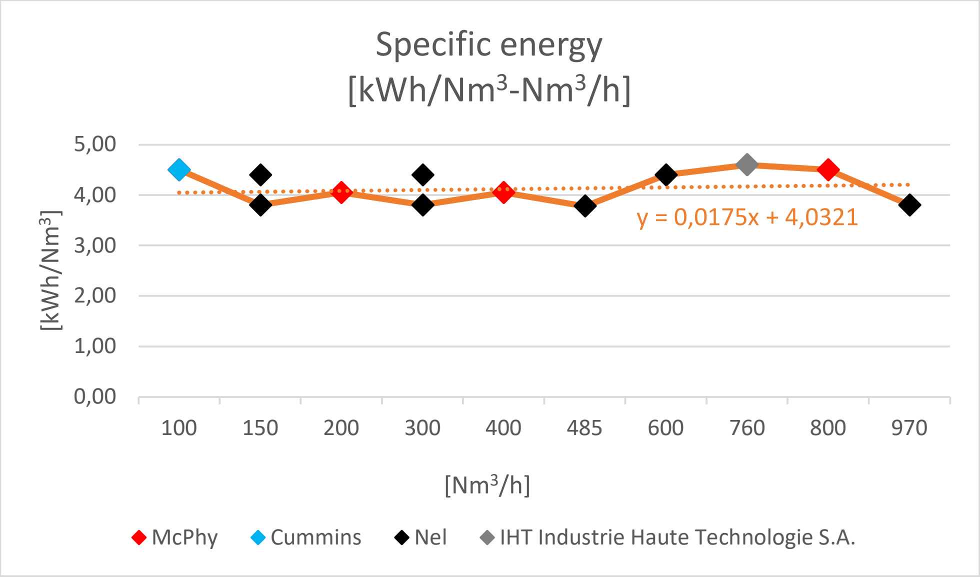

Figure 13 – Specific energy of traditional AWEs as a function of the volumetric hydrogen production rate

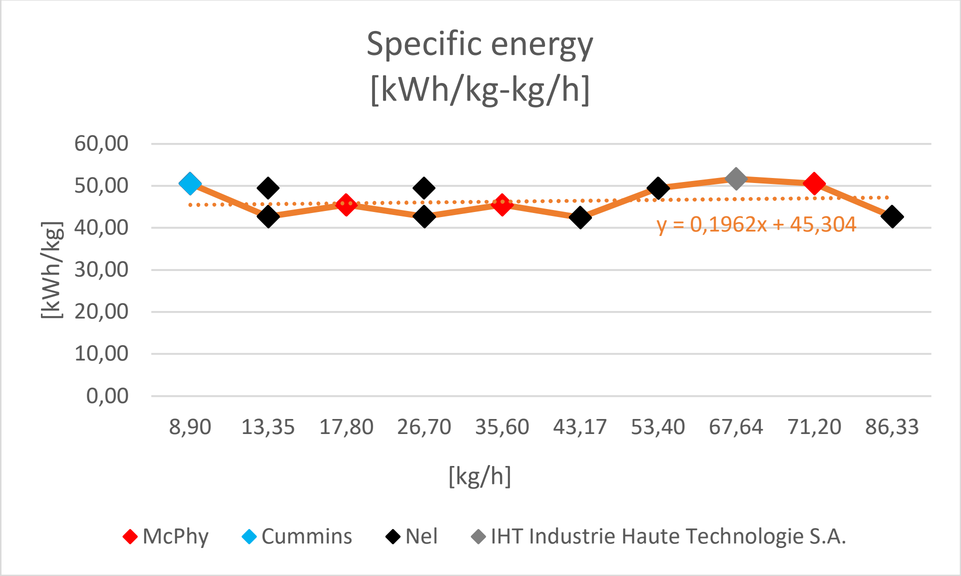

Figure 14 – Specific energy of traditional AWEs as a function of the mass hydrogen production rate

All the technologies located below the dashed line, so with lower specific energy compared to the expected value, belong to **Nel**. In particular, with the same hydrogen flow rate (150 Nm^3/h or 300 Nm^3/h), the electrolyser with the lower power requirement is located below the dashed line, while the other one has is above. Globally, the specific energies of this third group vary between a minimum of 3.8 kWh/Nm^3 (42.70 kWh/kg) for Nel to a maximum of 4.60 kWh/Nm^3 (51.69 kWh/kg) for IHT Industrie Haute Technologie S.A.. However, even if the value associated to IHT Industrie Haute Technologie S.A. is the maximum one, it is very similar to the highest consumptions of Nel technologies (4.40 kWh/Nm^3) and McPhy (4.50 kWh/Nm^3). Differently from before, where consumptions greater than 5 kWh/Nm^3 were frequent, especially in the first group, here all the values remain well below 5.0 kWh/Nm^3: this results in lower cell voltages and, especially, higher conversion efficiencies. Regarding the cell voltages, the lowest values (1.56 V) correspond to Nel technologies with 3.8 kWh/Nm^3 of specific energy, while the remaining values arrive up to 1.89 V (IHT Industrie Haute Technologie S.A.). Looking at the efficiencies, the best results are those of Nel, with 92.3%, followed by McPhy with 86.6%. The minimum efficiency is that of IHT Industrie Haute Technologie S.A., equal to 76.2%. All these two values are really high, especially the first one, considering the fact that typical maximum efficiencies are around 80%.

Under the dimensional aspect, the only available data are those of Nel and Cummins. Comparing Nel AC150 and Cummins HySTAT-100-10 electrolysers, which produce more or less the same amount of hydrogen per hour and are both supplied in containers, their footprints result really similar, varying from 26.1 m^2 to 34.8 m^2 (depending on the type of the container) for Nel and being equal to 29.7 m^2 for Cummins.

A final comment about this set of technologies involves the stack and system operational lifetimes: even if Cummins represents the typical maximum in terms of both stack and system operational lifetime (80000 hours and 20 years, respectively), IHT Industrie Haute Technologie S.A. is even better because its stacks need to be changed every 15 years (more than 131000 hours).

Range 2000 – 4000 Nm^3/h

Finally, the last subdivision, is going to be analysed. In this case, the amount of available data is not suitable to obtain a significant trend, however, as showed in the following graphs (Figures 15 and 16), the sizes of the electrolysers create really well a linear trend.

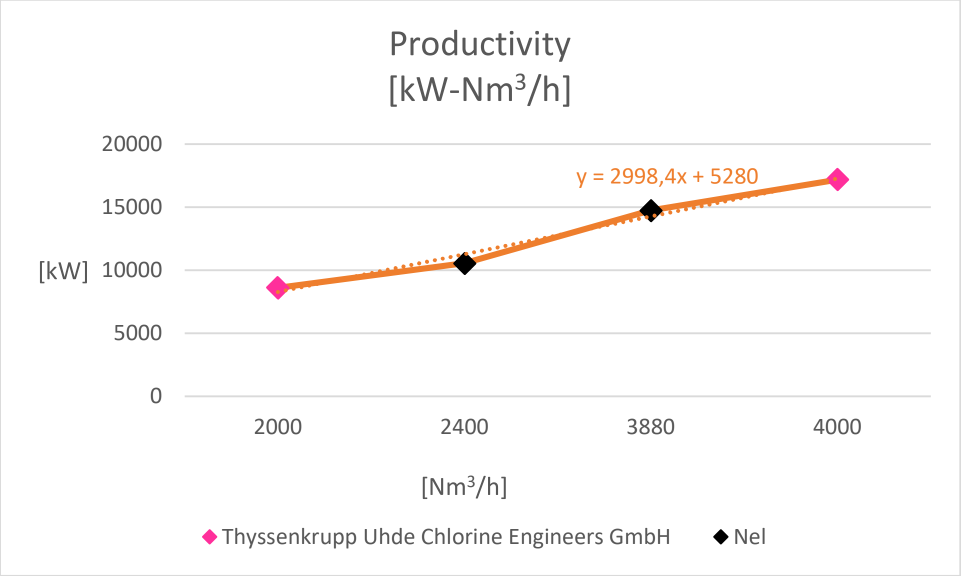

Figure 15 – Electrical input of traditional AWEs as a function of the volumetric hydrogen production rate

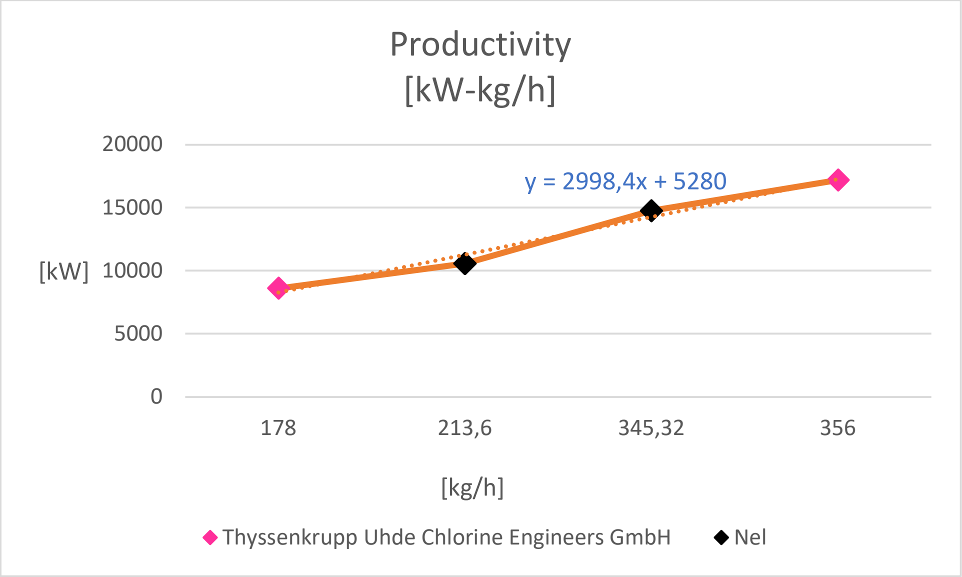

Figure 16 – Electrical input of traditional AWEs as a function of the mass hydrogen production rate

Considering then the specific energy consumption (Figures 17 and 18), the situation in terms of overall trend is different. In fact, while both **Thyssenkrupp Uhde Chlorine Engineers GmbH** technologies require 4.30 kWh/Nm^3 (48.31 kWh/kg), **Nel** electrolyser changes its specific consumption depending on the productivity. Assuming a scale effect, it consumes 4.40 kWh/Nm^3 (49.44 kWh/kg) in the case of the minor hydrogen flow rate (2400 Nm^3/h) and 3.8 kWh/Nm^3 (42.70 kWh/kg) for its maximum production (3880 Nm^3/h). This results in a global trend which is no more linear, but that shows anyway a global scale effect.

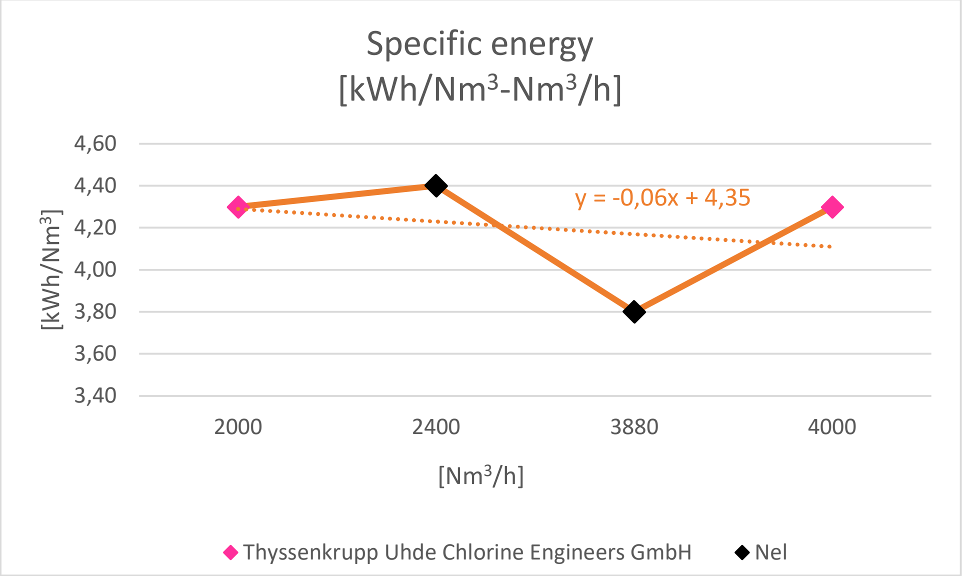

Figure 17 – Specific energy of traditional AWEs as a function of the volumetric hydrogen production rate

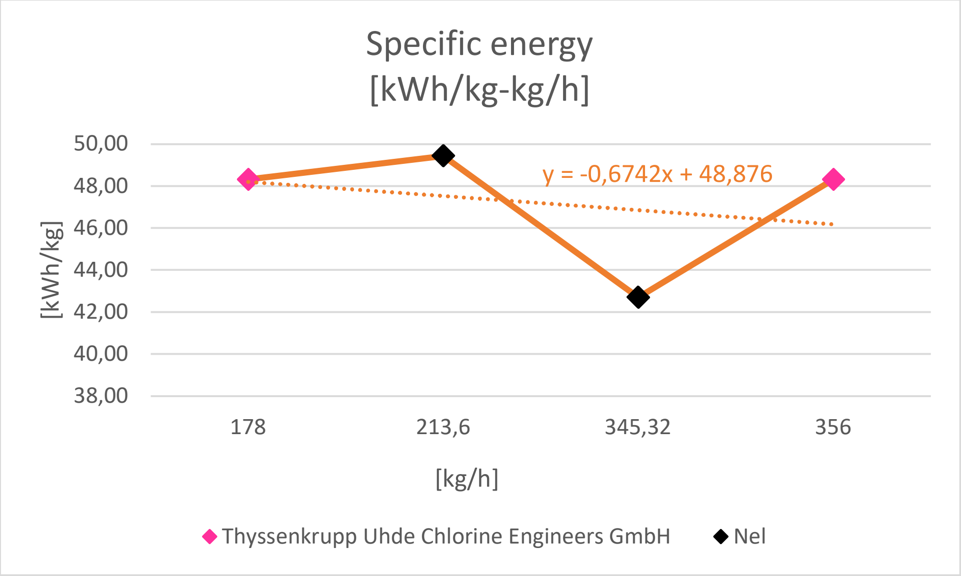

Figure 18 – Specific energy of traditional AWEs as a function of the mass hydrogen production rate

Comparing the three devices on the basis of a similar hydrogen production, it results that for around 2000 Nm^3/h the technologies provided by both the suppliers are almost equivalent, since their specific energy consumptions differ only for 0.1 kWh/Nm^3, whereas in the case of approximately 4000 Nm^3/h Nel electrolyser, with 3.8 kWh/Nm^3, is less energy intensive than the one produced by Thyssenkrupp Uhde Chlorine Engineers GmbH (4.3 kWh/Nm^3). The three values of specific energy consumption are among the lowest ones, considering all the four groups of alkaline electrolysers. In particular, 3.8 kWh/Nm^3 corresponds precisely to the minimum. Thus, the corresponding values of cell voltage and electrolyser conversion efficiency result, respectively, among the lowest and highest. In particular, Nel present a cell voltage of 1.80 V and an efficiency of 79.7% for a consumption of 4.40 kWh/Nm^3, while 1.56 V and 92.3% are associated to a specific energy of 3.8 kWh/Nm^3. Thyssenkrupp Uhde Chlorine Engineers GmbH technologies, having in both cases the same consumption, are characterised by 1.76 V and 81.6% of efficiency. The three efficiencies reported, varying from around 80% to more than 90%, are respectively equal or major than the typical maximum for alkaline water electrolysis. Moreover, both the suppliers offer good technologies under the flexibility point of view since Nel A3880 electrolyser has a flow range of 15 – 100%, while the two devices of Cummins have a load range of 10 – 100%.

Final comparison of traditional alkaline water electrolysers

At the end of the comparison, in order to summing up, it can be said that McPhy, Nel, Pure Energy Centre PEC and Cummins are the suppliers (especially the first two) covering the widest ranges of hydrogen production rates. In particular:

- Nel deals both with enough small hydrogen flow rates of 50 Nm^3/h and the largest ones, like 3880 Nm^3/h;
- McPhy, similarly to Nel, covers a range of hydrogen production going from the smallest value of 0.4 Nm^3/h to larger values of 800 Nm^3/h;
- Cummins deals with technologies of enough small size (15 – 100 Nm^3/h)
- Pure Energy Centre PEC focuses mainly on the smaller productions (2.66 – 42.62 Nm^3/).

Then, focusing on key performance indicators like electrolyser specific energy consumption, cell voltage and electrolyser efficiency (HHV), it was found that:

- For the set 0.4 – 8.66 Nm^3/h, globally, the best choice is **Pure Energy Centre PEC**, but for hydrogen demands lower than 2 Nm^3/h only **McPhy** is suitable, since Pure Energy Centre PEC does not produce such small technologies;
- For 10 – 90 Nm^3/h **McPhy**, **GreenHydrogen.dk Aps** and **Pure Energy Centre PEC** represent the most convenient suppliers;
- For 100 – 970 Nm^3/h **Nel** has been classified as the optimal option;
- For 2000 – 4000 Nm^3/h, Nel and Thyssenkrupp Uhde Chlorine Engineers GmbH are equivalent in the case of the lower extreme (with **Thyssenkrupp Uhde Chlorine Engineers GmbH** electrolyser consuming 0.1 kWh/Nm^3 less), while for 4000 Nm^3/h **Nel** is the most convenient supplier.

The following table (Table 1) reports the average value for the main key performance indicators utilized as a means of comparison.

Hydrogen flow rate [Nm^3/h]	**0.4 – 8.66**	**10 – 90**	**100 – 970**	**2000 – 4000**
Electrical power consumption [kW]	18.9	149	1714	12776
Flow range	20 – 100%	15 – 100% 20 – 100%	15 – 100%	15 – 100%
Load range	-	10 – 100% 25 – 100% 40 – 100%	5 – 100% 25 – 100%	10 – 100%
Electrolyser specific energy consumption [kWh/Nm^3]	5.34	4.63	4.20	4.20
Electrolyser specific energy consumption [kWh/kg]	59.99	52.04	47.17	47.19

Cell voltage [V]	2.19	1.90	1.72	1.72
Electrolyser conversion efficiency (HHV)	66.1%	76.4%	84.0%	83.8%
Cold start-up time*	-	-	-	-
Warm start-up time*	-	-	-	-
System operational lifetime* [years]	-	20	20	-
Stack operational lifetime* [hours]	-	≥ 80000	80000 - 131400	-
Footprint [m^2]	1.3	7.73	113 *	770 *

Table 1 – Average values of the main Key Performance Indicators

* The available data are too few to be averaged, so these values have been inserted in this table for completeness, but they were not considered in the following description.

Regarding the electrolyser size, it increases of one order of magnitude when the productivity does the same. Considering the whole set of devices analysed, thus from 0.4 Nm^3/h up to 4000 Nm^3/h, and plotting the overall size trend according to the hydrogen flow rate (Figures 19 and 20), it appears clear that it follows a linear trend, albeit with some fluctuations of course. This means that, among all the water alkaline electrolysers suppliers, none produces technologies with really low or high electrical requirements.

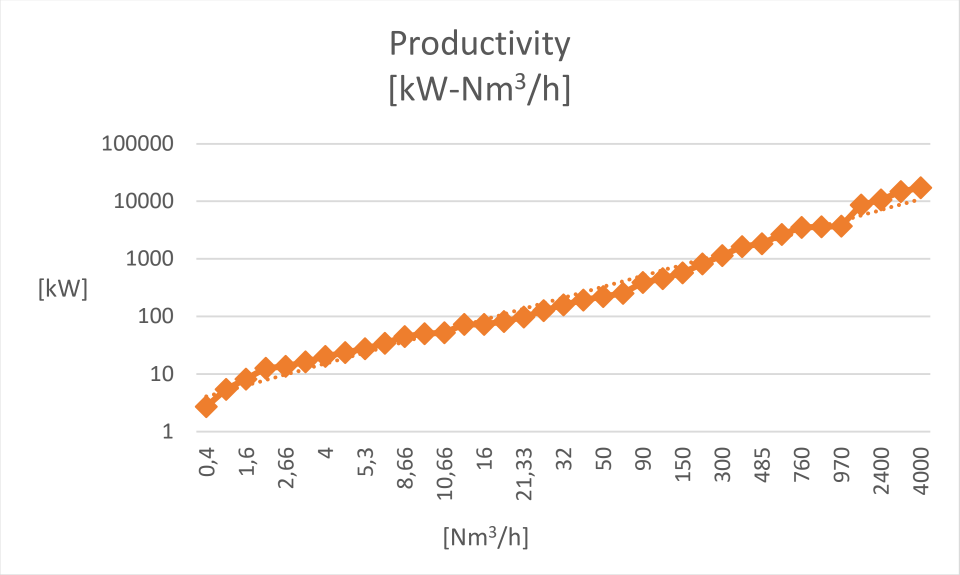

Figure 19 – Electrical input of traditional AWEs as a function of the volumetric hydrogen production rate

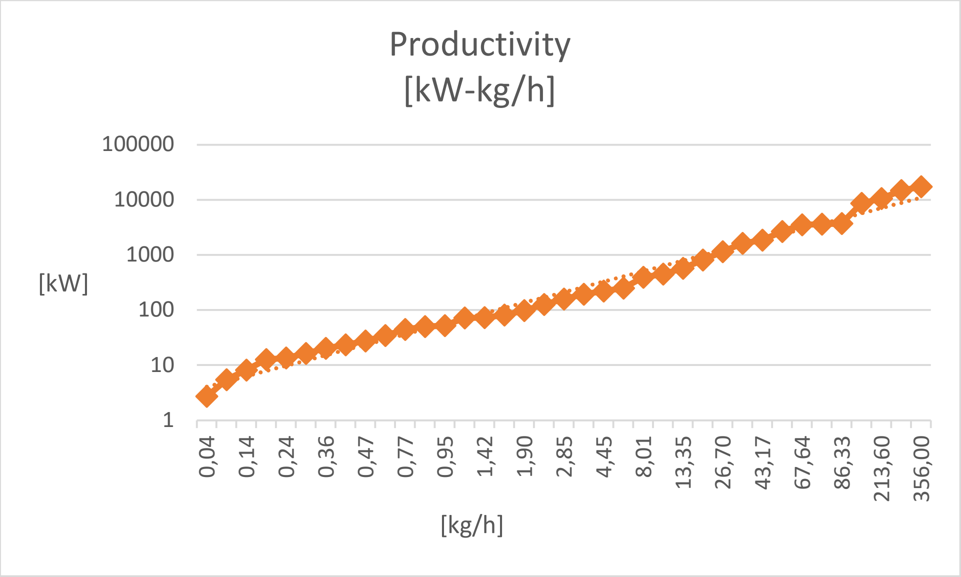

Figure 20 – Electrical input of traditional AWEs as a function of the mass hydrogen production rate

Considering then the second indicator, the flow range, it can be said that most of the electrolysers present a quite good flexibility, since many of them can arrive to 15 – 20% of the nominal hydrogen flow. Such flexibility is confirmed by the load range, even if some technologies have tighter operational windows.

In order to do a comparison with a common basis, the electrolyser specific energy consumption is again the most suitable indicator. While the technologies ranging from 10 Nm^3/h to 4000 Nm^3/h have roughly similar average specific consumptions, the smallest electrolysers are more energy intensive. In fact, the first group is characterised by an average specific consumption of 5.34 kW/Nm^3 (around 60 kWh/kg), the second one by 4.63 kWh/Nm^3 (52.04 kWh/kg) and the remaining two by 4.20 kWh/Nm^3 (47.2 kWh/kg). The values just mentioned highlight an overall scale effect, which is visible in the following graphs (Figures 21 and 22), reporting the electrolyser specific energy as a function of the productivity. Indeed, despite the presence of some oscillations, especially for hydrogen flows greater than 10 Nm^3/h, the interpolating line has a negative slope, indicating a decrement of the specific energy associated to an increment of the productivity and, thus of the electrolysers size.

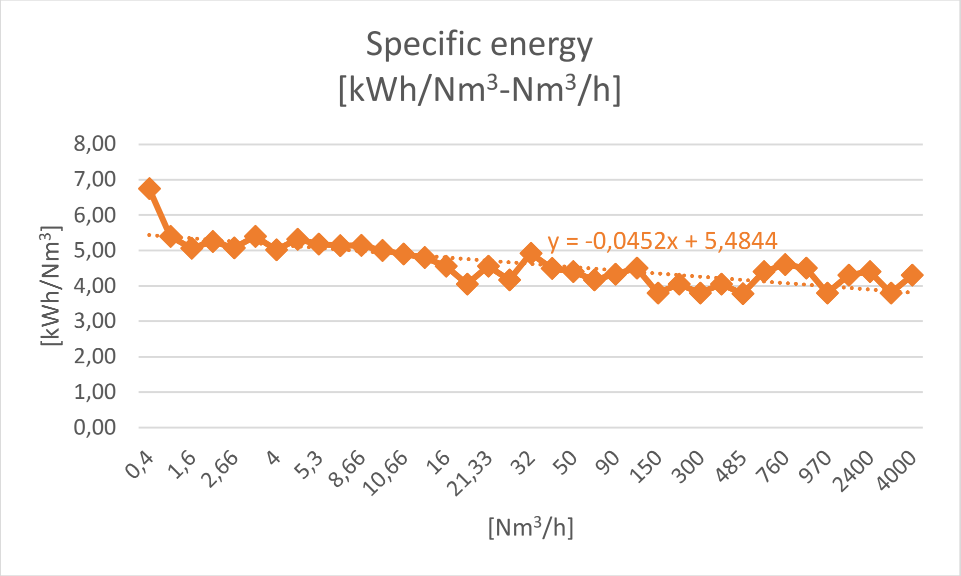

Figure 21 – Specific energy of traditional AWEs as a function of the volumetric hydrogen production rate

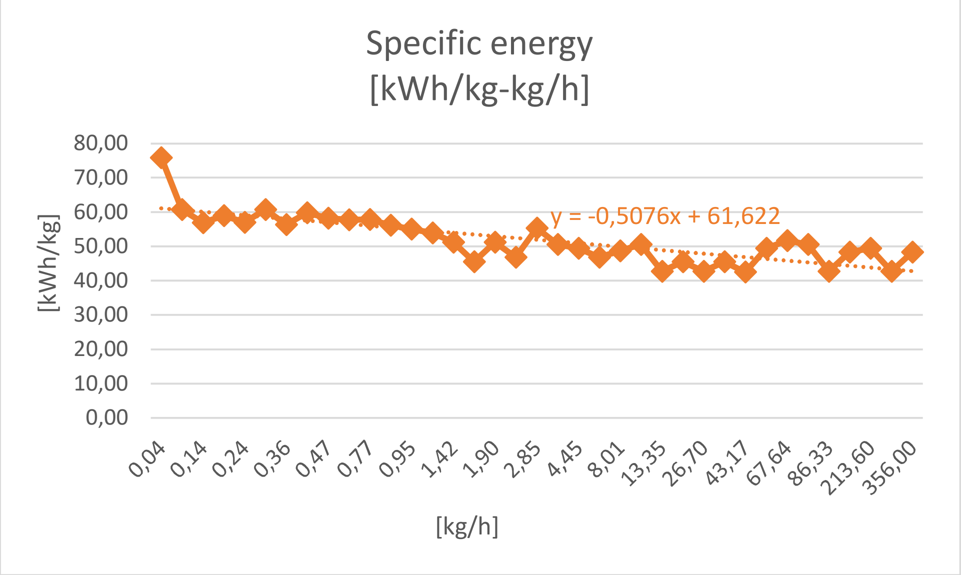

Figure 22 – Specific energy of traditional AWEs as a function of the mass hydrogen production rate

Once again, the considerations done on the specific consumptions directly reflect on the cell voltage and the electrolyser efficiency. In the case of the cell voltage, the difference is less evident, since the first group operates on average with 2.19 V, while the other three range between 1.72 – 1.90 V. The discrepancy appears clearer considering the electrolyser efficiency since from values equal to 76.4 – 84.0% of the last three sets, the average efficiency drops down to 66.1% for the smallest devices. While the first two values are satisfactory, being around to the classical maximum of 80%, the third one is closer to the typical minimum of 60 - 65%.

Finally, the footprint, as an average value is meaningful only for the second set of electrolysers, since in the other cases there were too few values to obtain a representative average.

The average values reported in Table 1 are useful to have an idea about the variation of the operating parameters of the electrolysers according to their productivity (and size), but, when analyzing an electrolyser from a technical point of view, the main indicators taken into account are: current density, electrolyser specific energy, cell voltage and conversion efficiency. The following table (Table 2) summarizes the values of the previous parameters typical for alkaline electrolysers. While most of them directly derive from the various datasheets, the current density is often not reported. However, it has been calculated in many occasions and its values are contained in literature articles.

	Minimum	**Maximum**
Current density [mA/cm^2]	200	500
Electrolyser specific energy consumption [kWh/Nm^3]	3.8	6.75
Cell voltage [V]	1.55	2.77
Electrolyser conversion efficiency (HHV)	52.0%	92.8%

Table 2 – Typical operating parameters of traditional alkaline water electrolysers

Typically, traditional alkaline water electrolysers operate with a current density going from 200 mA cm^{-2} to 500 mA cm^{-2} [2]. However, the maximum value often allowed is 450 mA cm^{-2} because, at too much elevated current densities, the exhausts of the reaction (hydrogen and oxygen), in the form of gas bubbles that flow upwards along the electrodes surface, create a continuous and nonconductive film of gas over the whole cathode and anode surfaces. The result is a screening effect which both increases the energy consumption, since it reduces the available area for the electrochemical reactions, and the probability of gas transport across the diaphragm. The values of specific energy reported in the datasheets go from a minimum of 3.8 kWh/Nm^3 to a maximum of 6.75 kWh/Nm^3, however, most of the values are comprised between approximately 4.00 kWh/Nm^3 and 5.40 kWh/Nm^3. The same can be said for the cell voltage: its entire range is between 1.55 V and 2.77 V, but in most of cases it arrives only to around 2.21 V. Finally, this reflects also on the electrolyser conversion efficiency: its lower extreme of 52.0% (belonging to the same electrolyser characterized by 6.75 kWh/Nm^3 and 2.77 V) is an isolated case and, at worst, the efficiency is around 65%. The upper extreme of the efficiency range is, instead, really high since the highest typical values are around 80%.

Electrolysis plant

Any type of electrolyser represents the core of the electrolysis plant, while the remaining parts are all the necessary auxiliary components. The typical plant for a traditional alkaline water electrolyser is that represented in Figure 23.

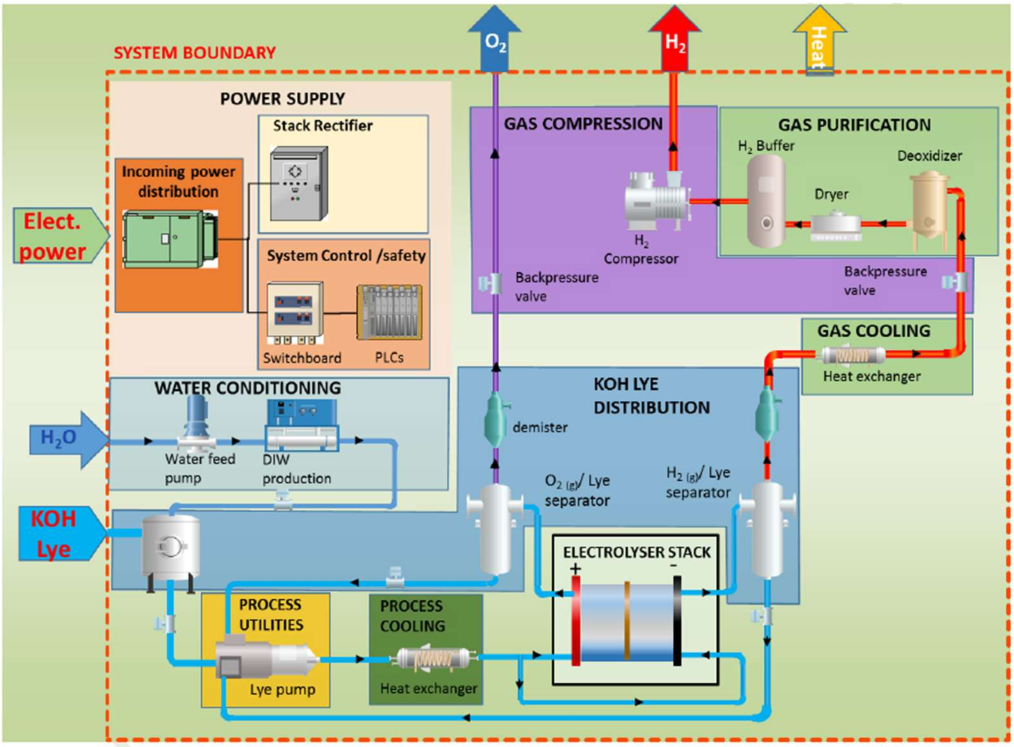

Figure 23 – Main components of a traditional alkaline water electrolysis system

In a water electrolysis plant, there is always a power supply section, containing a transformer, adjusting the electricity arriving from the grid to the electrolyser requirement, a rectifier, converting alternating current (AC) into direct current (DC), and a system control board, containing safety sensors, emergency shut down systems, process parameters gauges and a Programmable Logic Controller (PLC). Moreover, an Uninterruptible Power Supply (UPS) can be present in order to provide power to the electrolyser and auxiliary components when the main source fails.

Since water entering the electrolyser needs a certain level of purification in order to avoid a chemical contamination of the stack, a section for water treatment is necessary: typically, it is composed by a reverse osmosis system, sometimes together with a De-Ionized Water production unit (DIW). Then, only for traditional alkaline electrolysers, which use a KOH lye as liquid electrolyte, there is the need of a supply/recirculation system, constituted by a recirculation pump and a heat exchanger. The aim of the first component is to guarantee a continuous electrolyte flow inside the stack, while the second component is related to the thermal management. Subsequently, at both anodic and cathodic outlets two gas/lye separators are present: an oxygen/lye separator and a hydrogen/lye separator respectively, which effectuate an initial removal of residual electrolyte from the exiting gas streams. The separation can be then continued by means of demisters and scrubbers. The path of the hydrogen stream presents then three more stages: cooling, purification and compression. The purification process is made by two components: a de-oxygenation unit, to remove residual traces of oxygen due to crossover inside the electrolyser, and a gas dryer which removes residual moisture up to an acceptable remaining concentration. Lastly, the hydrogen pressure is brought to the desired level by an eventual compressor, which can be followed by a hydrogen storage system.

2.2.4.1.2. Anion exchange membrane cells (zero-gap cells)

In order to overcome the issues related to bubble effect and gas crossover, characteristic of traditional alkaline electrolysers, anion exchange membrane (AEM) electrolysers have been developed. They represent an alternative structure of alkaline electrolysers (operating with similar values of current density and temperature), that is the "zero-gap" cell, in which the porous electrodes are pressed against a membrane (as showed in Figure 24), which acts both as an electrolyte (transporting OH^- ions) and a barrier for electrons and gases produced by the electrochemical reactions.

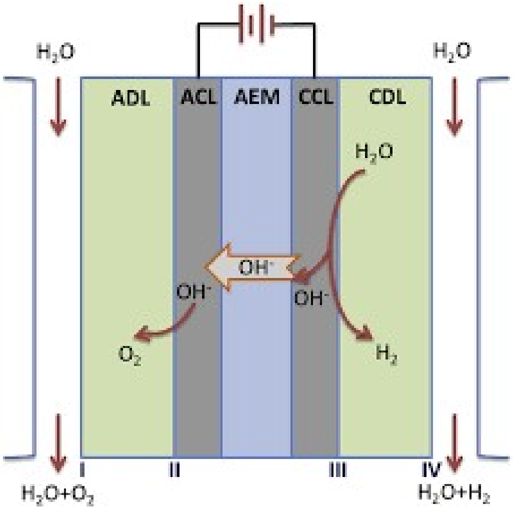

Figure 24 – Schematic of an anion exchange membrane electrolyser

As in the traditional alkaline water electrolysers, water reduction takes place in the cathode: the necessary water passes through the cathode diffusion layer (CDL) and arrives to the cathode catalyst layer (CCL), where it combines with the electrons produced by the anode and releases OH^- ions and hydrogen. OH^- ions migrate through the anion exchange membrane towards the anode catalyst layer (ACL). Here, they are oxidized, releasing electrons, water and oxygen. The last two products are finally removed through the anode diffusion layer (ADL) and the water can be recirculated towards the cathode.

The anion exchange membrane belongs to the group of the ion-exchange membranes: these are devices that transport only positive or negative ions, while they are impermeable to ions of the opposite sign and neutral molecules. In alkaline water electrolysers an anion exchange membrane is used for OH^- ions conduction. Such a system results more compact if compared to the previously described one, fact that brings to lower ohmic losses. Moreover, it is devoid of bubble effects, so that a less resistive and more stable cell is obtained.

Finally, the substitution of the diaphragm with the membrane, thanks to the reduced porosity, leads to a reduction of the crossover issue and to a mechanically stronger component. The benefit resulting from this latest characteristic is the tolerability of a differential pressure between anode and cathode and, thus, the possibility of having already pressurized hydrogen at the electrolyser exit. This is advantageous because in many cases, such as for mobility applications, hydrogen needs to be stored under pressure, but a compression after the electrolyser is costly, due to the high specific compression work, calculated as follows:

$$l_c = \frac{c_{p,H_2} \cdot T_{in} \cdot \left(\beta^{\frac{\gamma-1}{\gamma}} - 1\right)}{\eta_{is,c}}$$

where

- c_{p,H_2} is the hydrogen specific heat at constant pressure;
- T_{in} is the inlet temperature of the compressor;
- β is the pressure ratio of the compressor, so the ratio between the outlet and the inlet pressure values. For a constant outlet pressure, the increase of the inlet one, causes a decrement of the pressure ratio and so of the compression work. Thus, having pressurized hydrogen at the compressor inlet, reduces the expenditure for its feeding. Anyway, an increase of the hydrogen partial pressure involves also a rise of the open circuit voltage and, so, of the cell voltage required. The increase of the open circuit voltage is called *Nernstian effect*. It is easy to notice it in the following Nernst equation for ideal gases, rewritten for water electrolysis:

  $$E = \frac{\Delta \bar{g}_{reaction}(T, p_0)}{2 \cdot F} + \frac{R \cdot T}{2 \cdot F} \cdot ln\left(\frac{p_{H_2} \cdot p_{O_2}^{0.5}}{p_{H_2O}}\right)$$

  Hence, a compromise between the energy spent in the electrolyser and compressor feeding is necessary, obtaining an optimal value of exiting pressure of hydrogen from the electrolysis device and, finally, an optimal value of the parameter β. In traditional alkaline electrolysers, conversely, it is dangerous to operate under pressure because of the possible explosive gas mixtures that can be created due to the crossover, if the pressure difference is not well managed;

- γ is the ratio between the hydrogen specific heat at constant pressure and the one at constant volume;
- $\eta_{is,c}$ is the compression isentropic efficiency.

Still concerning the production of pressurized hydrogen, an alternative option with respect to the differential pressure is a pump collocated at the water entrance in the device. Such configuration, anyway, requires a further need of electrical energy for the pump feeding.

The AEM is made up of a polymer matrix backbone on which fixed cationic groups, needed for OH^- conduction, are concentrated. These positive ions, ordinarily NH_3^+, constitute the exchange functional group, whose choice is a crucial point during the design of the cells. Indeed, beside the requirement of a good performance in the ions' mobility, also a great chemical stability needs to be assured. This means that the cationic groups must not be excessively degraded by hydroxyl ion

(OH^-) attack.

During AEM cells operation, an important parameter to control is the ionic conductivity of the membrane, given by the following equation:

$$\sigma = \frac{l}{R_b \cdot A}$$

Constants l and A are, respectively, the thickness and known area of the membrane, while R_b is its resistance to the passage of ions. Thus, ionic conductivity is inversely proportional to this last parameter, which depends on the mobility of ions inside the membrane matrix and the charge density. The latter corresponds to the concentration of charged groups in the membrane, determined by the ion exchange capacity (IEC), so the number of moles of cationic groups per unit of mass of dry polymer, and the swelling of the membrane. It is necessary to pay attention to the IEC because, if on one side a higher IEC results in a higher number of charged groups (so a higher charge density), on the other hand it induces an increased swelling of the membrane (so a lower charge density), due to water uptake into the membrane caused by ion exchange groups, which increases with the temperature. Concerning the ion mobility, it is influenced by the operating temperature and the nature of fixed charges in the polymer, so by their interactions with mobile ions. It also depends on the nature of mobile ions and the water content in the matrix.

The ions are transferred across the membrane by means of Grotthuss mechanism, diffusion, migration and convection. It is thought that Grotthuss mechanism is the prevailing one, even if further studies are needed in order to reach a confirmation. This conduction process is implemented with the presence of water within the membrane. Water content, lower than in traditional AWEs (resulting in less corrosion problems), must not be in excess in order to avoid a degradation of mechanical stability. In such transport mechanism, the negative charge of OH^- interacts with the positive one of water hydrogen atoms becoming a hydrated anion which diffuses through a hydrogen-bonded network of water molecules exploiting the formation and cleavage of hydrogen bonds. A problem that has been noticed concerns the fact that the hydroxyl anions have a stable solvation shell (overall volume constituted by the ion and solvent molecules around it) that reorganize the solvent (water) molecules, perturbing the hydrogen bond network. The described phenomenon leads to a decrease in ionic conductivity of the membrane.

The polymer matrix, which can be homogeneous or heterogeneous, assures to the cell thermal and mechanical stability. The homogeneous matrix has been the first to be implemented, but heterogeneous matrices are less expensive and thicker, so mechanically stronger. Anyway, their heterogeneity makes them less conductive. In order to further enhance the mechanical stability of these materials (both homogeneous and heterogeneous), it is possible to incorporate an inert support.

Even if the anion exchange membrane devices totally or partially solve the problems of bubble effect and gas crossover, they present some other problems. An example is the degradation suffered by the membrane due to nucleophilic attack, which leads to a decrease of the ionic conductivity. In chemistry, a nucleophile is a species that, when involved in a reaction, donates an electronic doublet to another species (electrophile), creating a bond with it. Examples of nucleophiles can be anions or neutral molecules with unshared electronic doublets: they interact with electron-poor species (positive charge), creating unstable intermediate species. In the AWE cells, this phenomenon is carried on by the reaction between water molecules and NH_3^+ ions, which brings to a modification of such cations and, thus, a decrease of the ionic conductivity of the membrane.

Regarding the operating pressure, instead, if it reaches too high values, hydrogen and oxygen are not able to leave the electrodes, causing the blockage of the active sites.

Finally, when working with AEM electrolysers (especially during experimental set ups) a lot of care should be taken to avoid the entrance of air because OH^- may react with CO_2 from air and convert into carbonate or bicarbonate ions with a relatively fast process, causing again the decrease of the ionic conductivity.

In conclusion, AEM technology for hydrogen production is cheaper and more stable than the traditional alkaline one, but further developments in the fields of power efficiency, membrane stability and ease of handling are necessary.

In order to report some real operating parameters of this kind of technologies, some data coming from literature ([1] and those of the electrolyser EL 2.1 provided by Enapter, a supplier with offices both in Europe (Germany, Italy, Russia) and Asia (Thailand), are shown below (Table 3). EL 2.1 is suitable for really small hydrogen flow rates, equal to 0.5 Nm^3/h, so it can be compared to McPhy Baby traditional alkaline.

	Literature	**Enapter (EL 2.1)**	**McPhy (Baby)**
Hydrogen production rate [Nm^3/h]	0.25 – 1	0.5	0.4
Electrical power consumption [kW]	1.3 – 4.8	2.4	2.7
Flow range	-	60 – 100%	-
Electrolyser specific energy consumption [kWh/Nm^3]	4.8 – 5.2	4.8	6.75
Cell voltage [V]	-	1.97	2.77
Electrolyser conversion efficiency (HHV)	-	73.8%	52.0%
Cold (off) start-up time [min]	-	30	-
Warm (stand-by) start-up time [min]	-	20	-
System operational lifetime [years]	-	20	-
Stack operational lifetime [hours]	-	30000	-
Footprint [m^2]	-	0.306	-

Table 3 – Operating parameters of Enapter EL 2.1 AEM electrolyser and McPhy Baby traditional alkaline electrolyser

As it appears clear looking at Table 3, the technology provided by Enapter presents parameters perfectly matching with those reported by literature, which indicates also a current density of 200 – 500 mA cm^{-2}, thus equal to that of traditional alkaline electrolysers. Comparing the two electrolysers, it is evident that EL 2.1 is much more convenient than Baby. In particular, an electrolyser specific energy consumption of 4.8 kWh/Nm^3 is much lower than one of 6.75 kWh/Nm^3 and results in 1.97 V of cell voltage and 73.8% of efficiency, which are both values contained in the typical ranges of the traditional alkaline electrolysers reported in Table 2. Moreover, also the system operational lifetime and the footprint represent two advantageous parameters for Enapter EL 2.1 electrolyser, since the first corresponds to the typical maximum identified for traditional alkaline electrolysers and the other reflects the average footprint for hydrogen flow rates of 0.4 – 8.66 Nm^3/h. Regarding the two start-up times, they are the only values available from the datasheets for the alkaline water electrolysers, so it is not possible to do a comparison in this field. Anyway, a publication of IRENA [27], shows that in 2017 the warm and cold start-up times for alkaline electrolysers were, respectively, 1 minute and 10 minute. Even if these values are lower than those of EL 2.1 electrolyser, they are however particularly high if compared to the ones of PEM electrolysers that described in the following paragraphs.

Electrolysis plant

The overall plant containing an AEM electrolyser (Figure 25) is clearly similar to that of a traditional alkaline electrolyser, except for some variations.

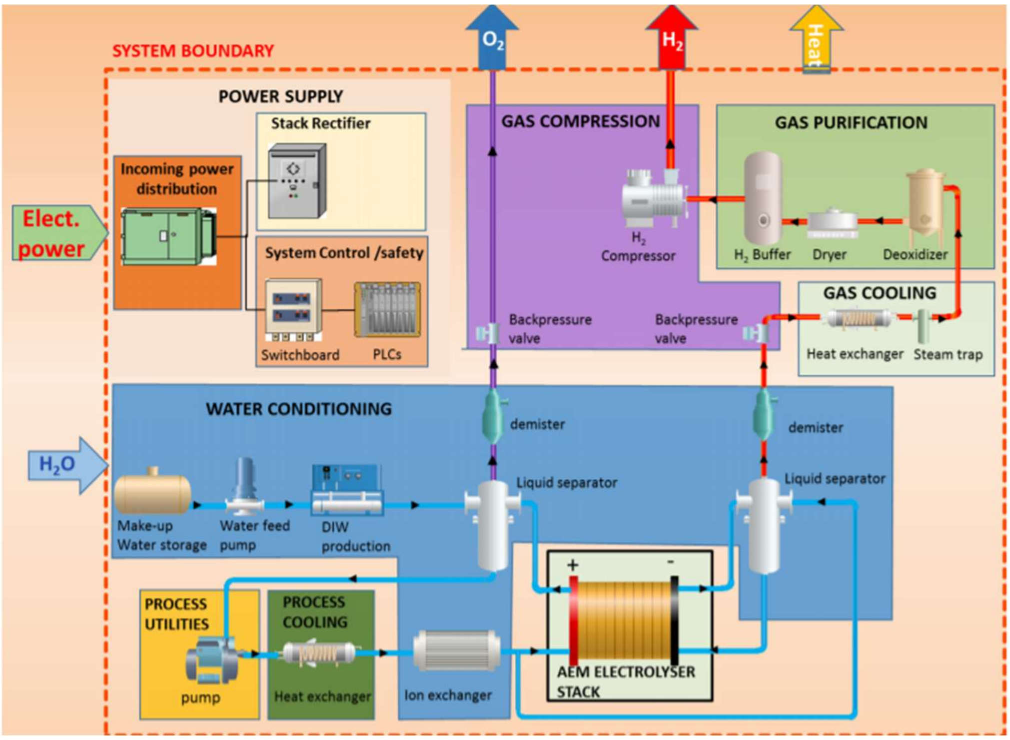

Figure 25 - Main components of an AEM water electrolysis system

In the case of the traditional alkaline electrolysers, the pump and the heat exchanger upstream of the electrolyser were needed for the supply and recirculation of KOH lye, while in the case of AEM electrolysers these components are crossed by a water stream. The liquid water entering the plant is used not only for the electrochemical reaction inside the electrolyser, but it is useful also for its thermal management, so, it needs a heat exchanger to remove heat extracted from the electrolyser and recirculation pumps, enabling its continuous flow. These last components, together with other devices such as pressure and temperature sensors, flow meters and gas detectors, constitute the process utilities. With respect to the case of traditional alkaline electrolyser, the gas/lye separators are substituted by two liquid separators which divide hydrogen and oxygen from the residual liquid water needed for the electrochemical reaction and thermal management.

2.2.4.1.3. Alkaline water electrolysers at medium temperature

The alkaline water electrolysers operating at a medium temperature constitute an alternative configuration, still under research, of the zero-gap cells. The higher temperature levels, approximately equal to 250 °C, favour the kinetic of the electrochemical reactions. Such temperature value can be reached thanks to the particular structure of the electrolyte. It is a porous separator with immobilized KOH/H_2O melt: the higher boiling point of concentrated KOH (aq) allows to avoid the evaporation of the liquid electrolyte. The porosity, anyway, increments the tortuosity of the ions' pathway, which causes a reduction of the ionic conductivity.

The electrodes, called "gas diffusion electrodes" (GDEs), are porous and pressed on the electrolyte surface. Their porosity is necessary because, at such temperature levels, water is sent in steam phase. The cathodic compartment is made of Inconel (a family of nickel-chromium-based superalloys, with high mechanical strength and resistance to corrosion) foam, while, in the anode side, there is a silver-plated nickel foam.

Since the injected water has to be maintained in steam phase, the operating pressure must be kept under control. If it is too high, water vapor can condense, causing the dilution of the electrolyte, flooding of the electrodes and circuit disconnection. The optimal pressure value, for a typical temperature of 250 °C, is 42 bar.

One positive aspect of this kind of electrolysers is again the elimination of bubbles formation, thus no resistive film is created on the electrodes surface.

Moreover, since metal foams constituting the electrodes are not so precious materials and they are also largely used in industrial processes, the expenditure for them is not very high, even if a bit more than the materials of traditional AWEs because they need to tolerate higher temperatures and pressures. Anyway, this higher expenditure is compensated by the fact that these latter systems are much smaller, if compared with the others at the same production rate.

Finally, operating at a pressure greater than the atmospheric one, the following cost for hydrogen pressurization is reduced, too.

2.2.4.2. Proton exchange membrane electrolysers

Proton exchange membrane (or polymeric electrolyte membrane) electrolysers constitute the second main group of water electrolysis devices. Since they operate, like the alkaline technologies, at a temperature between 60°C and 80°C, so below the water boiling point, no risk of water evaporation is present and, thus, water is pumped in a liquid phase. As represented in Figure 26, its entrance is from the anodic side, but since PEM electrolysers are exothermic devices, water is needed also in the cathodic compartment in order to remove the excess of heat produced by the process.

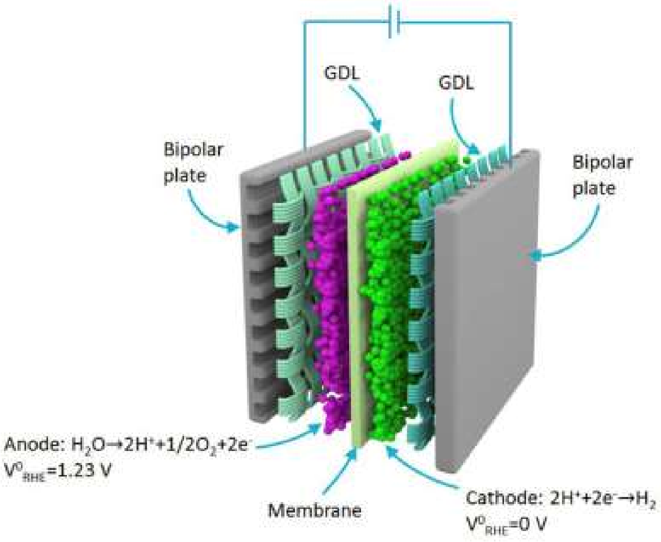

Figure 26 - Schematic of a PEM water electrolyser

The peculiar characteristic is the electrolyte: it is a proton-conducting polymeric membrane, which, together with the electrodes, both porous carbon papers, creates the membrane electrode assembly (MEA). The MEA is contained between two bipolar plates (interconnectors), whose roles are the transport of water necessary for both reaction and cooling purposes and the removal of product gases. Differently from the alkaline electrolyte, in this case positive ions are conducted from the anode to the cathode. As highlighted by the following reactions, they are H^+ cations deriving from the anodic oxygen evolution reaction (OER) and going to participate to the cathodic hydrogen evolution reaction (HER):

$$Anode\ (OER):\ H_2O \rightarrow 2H^+ + 2e^- + \frac{1}{2}\,O_2$$

$$Cathode\ (HER):\ 2H^+ + 2e^- \rightarrow\ H_2$$

$$Total:\ H_2O \rightarrow H_2 + \frac{1}{2}\,O_2$$

The OER corresponds to water oxidation, a transformation releasing, beside H^+ ions, also electrons and oxygen. The HER, instead, represents the ions H^+ reduction, whose product is the hydrogen. The resulting global reaction, as for the alkaline water electrolysers, is the splitting of water into hydrogen and oxygen.

In order to enhance the kinetic of both the half-reactions, again a catalyst material is needed: it is in the form of a porous layer coated directly onto the membrane surface or onto each of the two porous gas diffusion layers (GDL) which allow a better distribution of reactant and products.

The most used catalyst material is platinum: it can be applied on both the electrodes or only in the cathodic compartment. In this latter case, iridium is used for the anode. Both the mentioned materials are precious metals: they are necessary in PEM electrolysers because of their tolerance towards the acidic (corrosive) environment in which they operate. This reflects in higher costs, compared to alkaline water electrolysers.

For what concerning the membrane, the most used is called **Nafion®**: it is a homogeneous polymeric ion-selective membrane produced starting from hydrophobic polytetrafluoroethylene PTFE (Teflon), a chain of carbon atoms, each bonded with two fluorine atoms, $(CF_2)_n$. The strong bond established between fluorine and carbon atoms confers to Teflon a good chemical stability. In order to obtain Nafion®, Teflon is modified with the addition of lateral chains, like that showed in Figure 27, sulfonated at the end with a $-SO_3H$ group, whose main characteristic is its hydrophilicity.

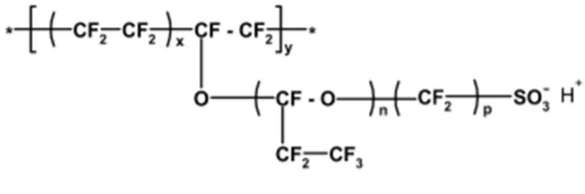

Figure 27 – Structural formula of Nafion

The lateral chains with the hydrophilic functional groups are arranged in spherical domains in order to minimize the system energy. Since HSO_3 groups are hydrophylic, in presence of water molecules, these will be attracted in the center of the spheres, producing a swelling of such domains. A sufficient swelling leads to the formation of interconnections between the single spheres, as showed in Figure 28.

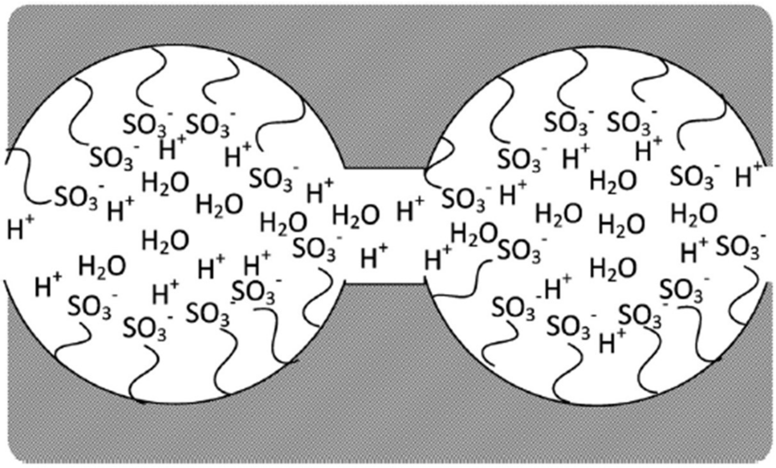

Figure 28 – Interconnected spherical domains in a Nafion membrane

The channels composed by the spherical domains and their interconnections constitute, in the end, water channels (H_2O clusters) which are able to conduct ions H^+ with a good ionic conductivity. The conduction takes place by means of the Grotthuss mechanism (Figure 29): the ion H^+ creates a bond with a water molecule, which becomes hydronium (H_3O^+). Then a hydrogen atom of H_3O^+ forms a hydrogen bond with the oxygen of a second water molecule and breaks that with the first one. As a consequence, the second water molecule turns into hydronium. This mechanism continues until the ion H^+, which in this case is a hydrated ion, arrives to the cathode and, since it is guided by the presence of water, in order to maintain a good ionic conductivity Nafion membrane needs an adequate humidification. This is the reason of the operating temperature of PEM electrolysers: it must be kept under the water boiling point (100°C at 1 bar) in order to maintain water in a liquid phase.

A possible solution to overcome the problem of poor ionic conductivity of Nafion under low humidity conditions is a hybrid approach which consists in modifying the membrane using inorganic materials. They can be hygroscopic (if exposed to air, they absorb its humidity) or ionic conductors able to preserve their conductivity even under low humidity conditions.

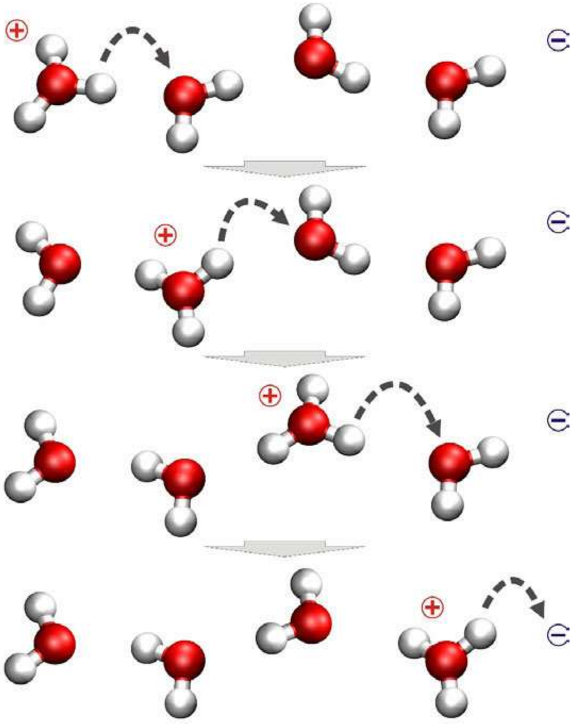

Figure 29 – Grotthuss mechanism

When designing a proton exchange membrane, a key dimension is its thickness because it affects both the ohmic losses and the membrane permeability, among which a compromise is needed. The membrane thickness reduction, indeed, involves the abatement of the ohmic losses due to the ions' conduction (thanks to the reduced length of their pathway), but, at the same time, the membrane permeability (and so the cross-over risk) suffers an increase. Additionally, a too thin membrane, leads to a too low mechanical resistance. Typically, a good compromise to mitigate all these issues is Nafion 115: the last digit indicates the membrane thickness, in this case equal to 5 thousandths of an inch (127 μm), while the first two are related to the Nafion equivalent weight, namely the grams of dry polymer corresponding to one mole of functional group. Such weight is, typically, equal to 1100 grams. Anyway, it is important that its value remains above 1000 g, otherwise Nafion becomes soluble in water.

Moreover, the addition of an inert polymer as a reinforcement of the membrane can help in the mechanical resistance enhancement, even if this has a negative consequence on the ionic conductivity.

To date, however, the research is going towards Nafion replacement materials which better satisfy the requirement of good ionic conductivity at higher temperature in order to use less precious catalysts. A commercialized alternative material is polybenzimidazole (PBI), a synthetic polymer able to tolerate high temperatures (it is used in the production of fabrics for firefighters). High boiling liquids, which can donate/accept protons, are added to the membranes obtained with PBI polymers: in this way PEM electrolysers are able to operate at temperatures higher than water boiling point (until 200 °C) because no humidification is needed in the electrolyte. Moreover, PBI materials, being enough chemically stable, can be used in AEM electrolysers in order to overcome the problem of the nucleophilic attack. Anyway, it has to be considered that, despite these advantages, they present a higher cross-over risk, compared to the one of Nafion.

Finally, like the other electrolysers, also PEM technologies represent the core of a whole electrolysis plant. Its scheme is reported in Figure 30, which shows that all the main components of AEM and PEM electrolysers are the same.

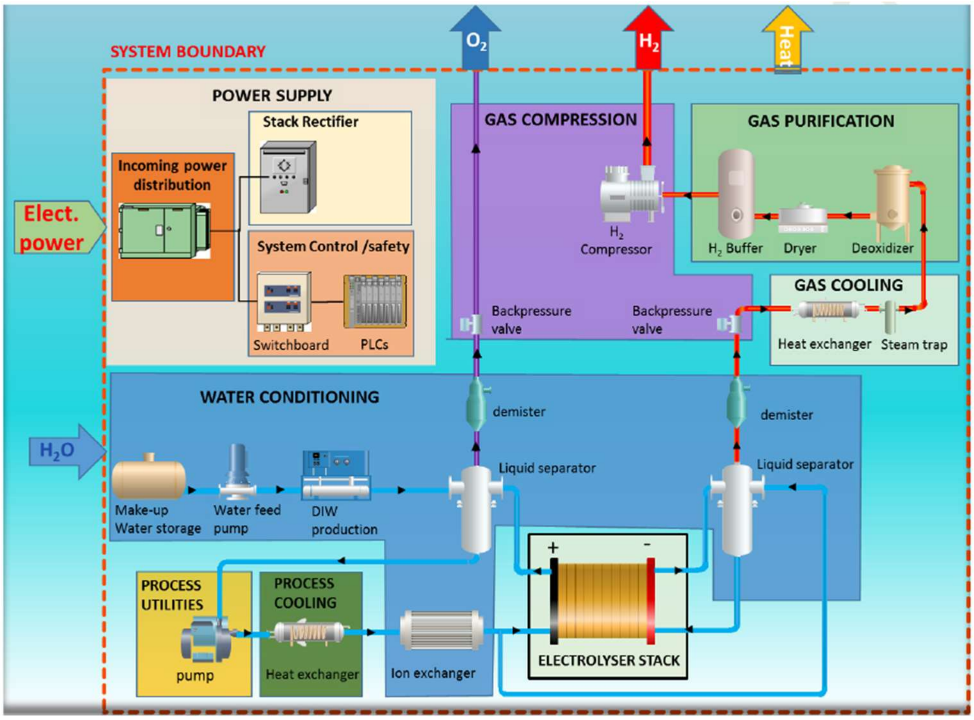

Figure 30 - Main components of an PEM water electrolysis system

Technical analysis of PEM electrolysers

As for the alkaline electrolysers, a technical analysis of PEM technologies was performed, comparing the various specifications contained in the datasheets of different suppliers, whose number is larger than the one of alkaline devices suppliers. Again, they are present especially in Europe, but also in America and Asia. In particular, the suppliers, grouped according to their countries, are the following:

- Europe
    - Areva H2Gen GmbH (France)
    - Diamond Lite S.A. (Switzerland)
    - Frames (The Netherlands)
    - GreenHydrogen.dk Aps (Denmark)
    - H-Tec Systems GmbH (Germany)
    - H2B2 (Spain)
    - iGas energy GmbH (Germany)
    - ITM Power (United Kingdom)
    - McPhy (France)
    - Nel (Norway)
    - Pure Energy Centre PEC (United Kingdom)
    - Siemens (Germany)
- America
    - Giner ELX (Massachusetts)
    - Cummins (Ohio)
    - Proton On-Site (Connecticut)
    - Teledyne Energy Systems (Maryland)
- Asia
    - Elchemtech (South Korea)
    - Toshiba Energy Systems & Solutions Corporation (Japan)

Moreover, some of the mentioned suppliers, such as GreenHydrogen.dk Aps, McPhy, Nel, Pure Energy Centre PEC, Cummins and Toshiba Energy Systems & Solutions Corporation are specialized in both alkaline and PEM electrolysers.

Like for the alkaline field, there are various PEM technologies, which can produce very different amounts of hydrogen. In this case, moreover, the range of possible hydrogen demands which can be satisfied is much wider. Indeed, it goes from 0.011 Nm^3/h to 22413 Nm^3/h, while the alkaline electrolysers start from 0.4 Nm^3/h and arrive to 4000 Nm^3/h.

The comparison of the available PEM electrolysers was done utilizing the same method as before, so the same Key Performance Indicators were used and the electrolysers were subdivided according to the hydrogen flow rate into the following four groups:

1. 0.011 – 6 Nm^3/h;
2. 10 – 78 Nm^3/h;
3. 100 – 580 Nm^3/h;
4. 1000 – 22413 Nm^3/h.

While the first three ranges are quite similar to those utilized for the alkaline devices, the last one appears much wider. In reality, it mainly includes electrolysers ranging from 1000 Nm^3/h to 4000 Nm^3/h, except for that produced by Siemens, able to deliver up to 22413 Nm^3/h.

Range 0.011 – 6 Nm^3/h

The following graphs (Figures 31 and 32), representing the increase of electrical power as a function of the increment of the hydrogen demand, for the first set of technologies.

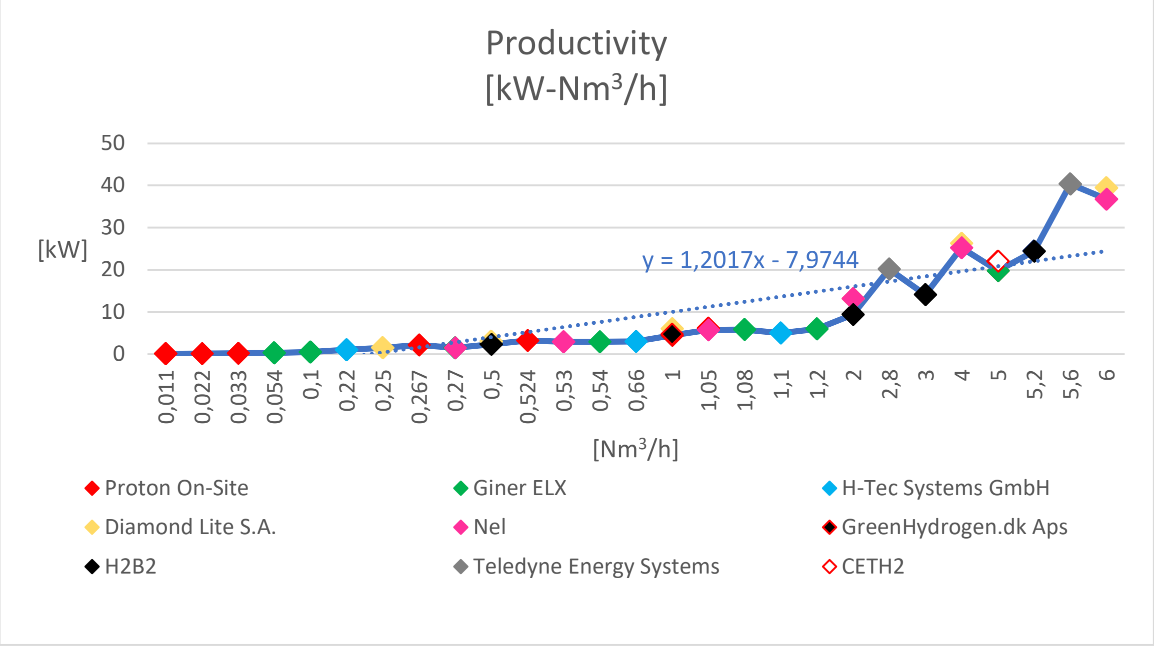

Figure 31 – Electrical input of PEM electrolysers as a function of the volumetric hydrogen production rate

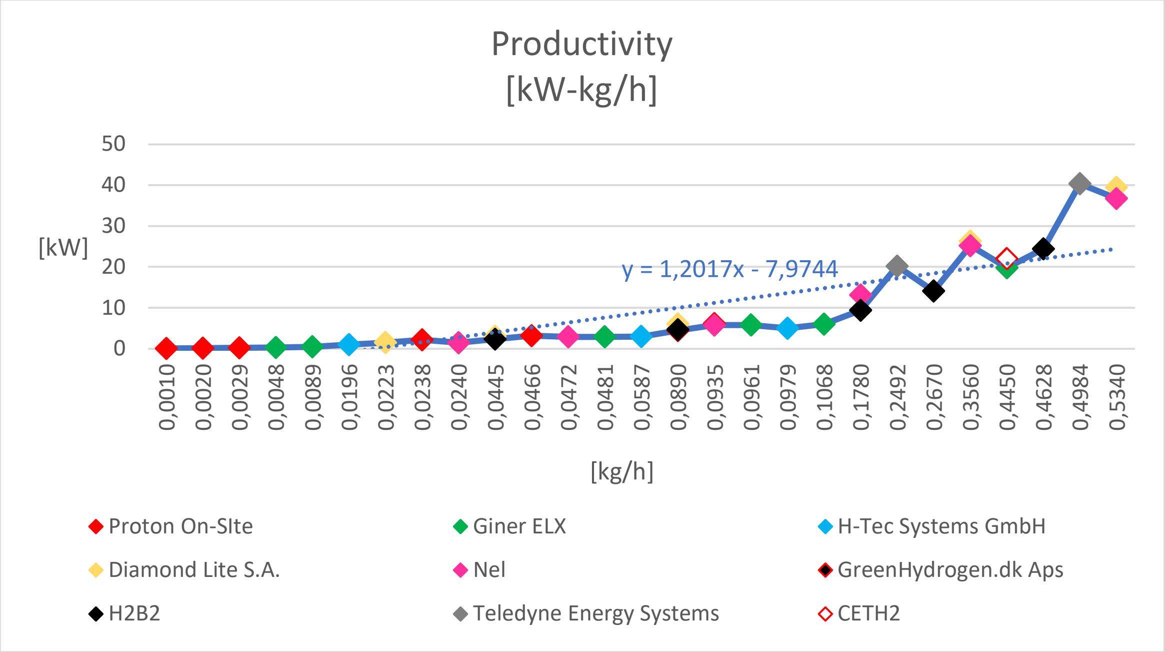

Figure 32 – Electrical input of PEM electrolysers as a function of the mass hydrogen production rate

They do not show a really linear trend, however, subdividing the entire range into two parts with values having roughly the same order of magnitude, like in the two following graphs (Figures 33 and 34), it emerges that the two trends follow a little more the interpolating line, even if with more evident deviations with respect to those seen for alkaline electrolysers.

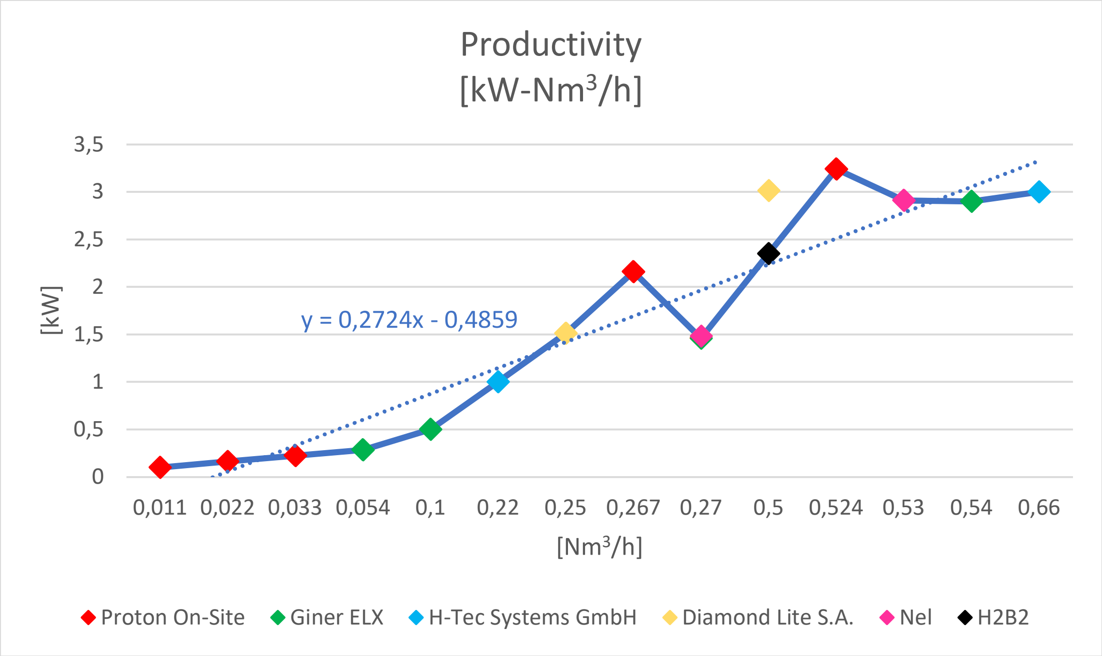

Figure 33 – Electrical input of PEM electrolysers as a function of the volumetric hydrogen production rate

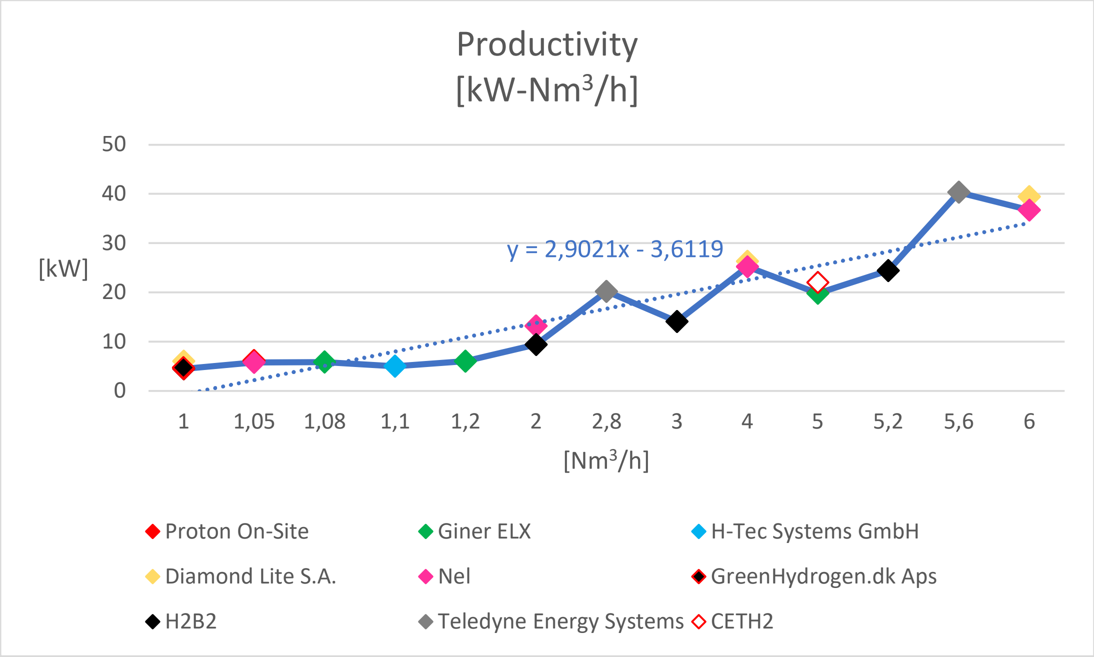

Figure 34 – Electrical input of PEM electrolysers as a function of the volumetric hydrogen production rate

Considering the range going from 0.011 Nm^3/h to 0.66 Nm^3/h, it can be seen from the graph that the major oscillations are due to the excessive electrical power requirements of Proton On-Site technologies for 0.267 Nm^3/h (G4800) and 0.524 Nm^3/h (S20) and to a large size decrease corresponding to a hydrogen flow of 0.27 Nm^3/h. This last point is associated to both Giner ELX PEMI electrolyser (1.46 kW) and Nel S10 electrolyser (1.48 kW). The second graph, from 1 Nm^3/h to 6 Nm^3/h, presents three main peaks due to Teledyne Energy Systems (HMXT-50 and HMXT-100), Nel (H4) and Diamond Lite S.A. (HOGEN H 4 m) technologies. In particular, these major increases of size correspond to hydrogen flow rates of 2.8 Nm^3/h and 5.6 Nm^3/h for Teledyne Energy Systems and 4 Nm^3/h for both Nel (25.2 kW) and Diamond Lite S.A. (26.3 kW).

Like in the case of 0.27 Nm^3/h and 4 Nm^3/h, there are other values of hydrogen demands which can be satisfied by more than one device, in particular:

- 0.5 Nm^3/h, with H2B2 EL0.5N (2.35 kW) and Diamond Lite S.A. HOGEN S 20 (3.02 kW) electrolysers
- 1 Nm^3/h, with GreenHydrogen.dk Aps P1 (4.46 kW), H2B2 EL1N (4.7 kW) and Diamond Lite S.A. HOGEN S 40 (6.03 kW) electrolysers
- 1.05 Nm^3/h, with Nel S40 (5.76 kW) and Proton On-Site S40 (6.12 kW) electrolysers
- 2 Nm^3/h, with H2B2 EL2N (9.4 kW), Diamond Lite S.A. HOGEN H 2 m (13.1 kW) and Nel H2 (13.1 kW) electrolysers
- 5 Nm^3/h, with Giner ELX Merrimack (19.8 kW) and CETH2 E5 (22 kW) electrolysers

- 6 Nm^3/h, with Nel H6 (36.7 kW) and Diamond Lite S.A. HOGEN H 6 m (39.4 kW) electrolysers.

Considering then all the technologies, those belonging to Giner ELX, H-Tec Systems GmbH, H2B2 and CETH2 are in most cases below the trend line, while the remaining devices are located above. Moreover CETH2, besides having a lower size compared to other similar technologies, presents also a really good flexibility, since it can vary its production between almost 0% to 100% of the nominal hydrogen flow. This operational window is characteristic also of Diamond Lite S.A. and Nel electrolysers, while those of H2B2 can arrive at a minimum of 10%. Considering the flexibility in terms of electrical power input, the most adaptable devices are those of Teledyne Energy Systems, which tolerate a load decrease down to 1% of the nominal value. Thus, although these devices are characterised by some of the largest sizes, they are advantageous, under the flexibility aspect, compared to H-Tec Systems GmbH and GreenHydrogen.dk technologies, which only arrive to 20% and 25%, respectively. Teledyne Energy Systems is then the most competitive provider also in terms of reactivity, since its technologies are able to immediately start operating after a 5 minutes nitrogen purge cycle. This quickness is equalized by H2B2, with a start-up time from an off situation (cold start-up time) shorter than 5 minutes and from a stand-by situation (cold start-up time) below 1 second. The remaining available data are those of H-Tec Systems GmbH: if on the side of the size and the specific energy consumption, discussed below, it is among the most competitive providers, on the side of the start-up times things are different, since its technologies need around one hour for a cold start-up and 30 seconds for a warm one. The data belonging to H-Tec Systems GmbH are the worst also for the durability: its stacks have a typical operational lifetime of 35000 hours, like those of CETH2, while the stacks of Teledyne Energy Systems arrive up to 61000 hours and those of Diamond Lite S.A. up to 80000 hours. For the overall system lifetime, instead, the only available information is that of Teledyne Energy Systems, which provides an operational lifetime of more than 25 years.

Focusing on the energy consumption normalized to the normal cubic meter of produced hydrogen (kWh/Nm^3), it can be seen in the Figures 35 and 36 that it is present an overall scale effect.

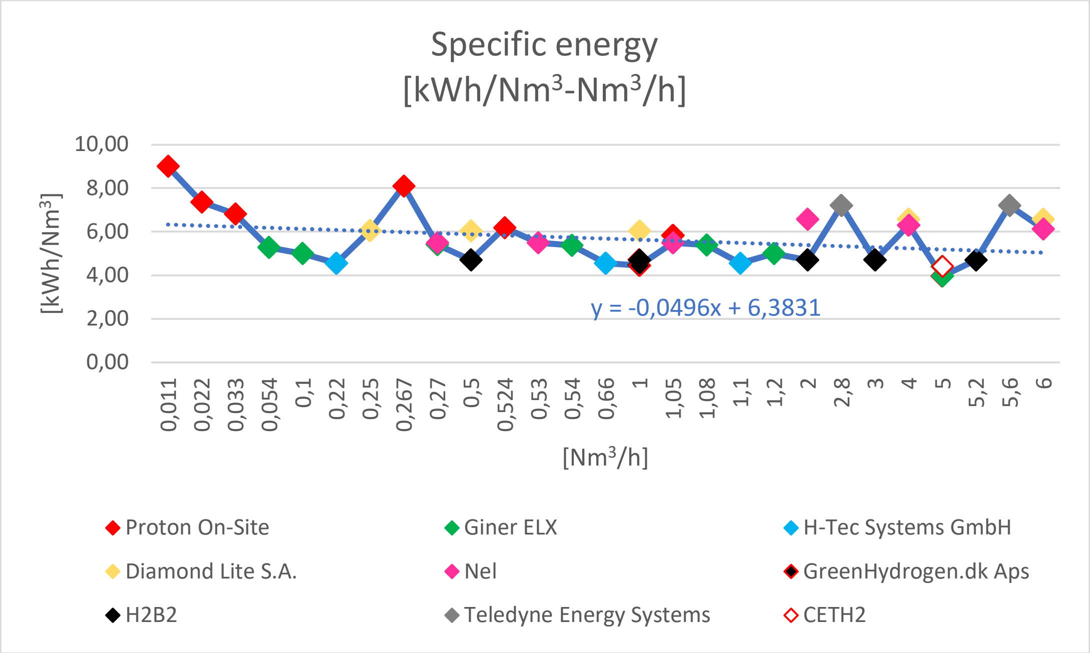

Figure 35 – Specific energy of PEM electrolysers as a function of the volumetric hydrogen production rate

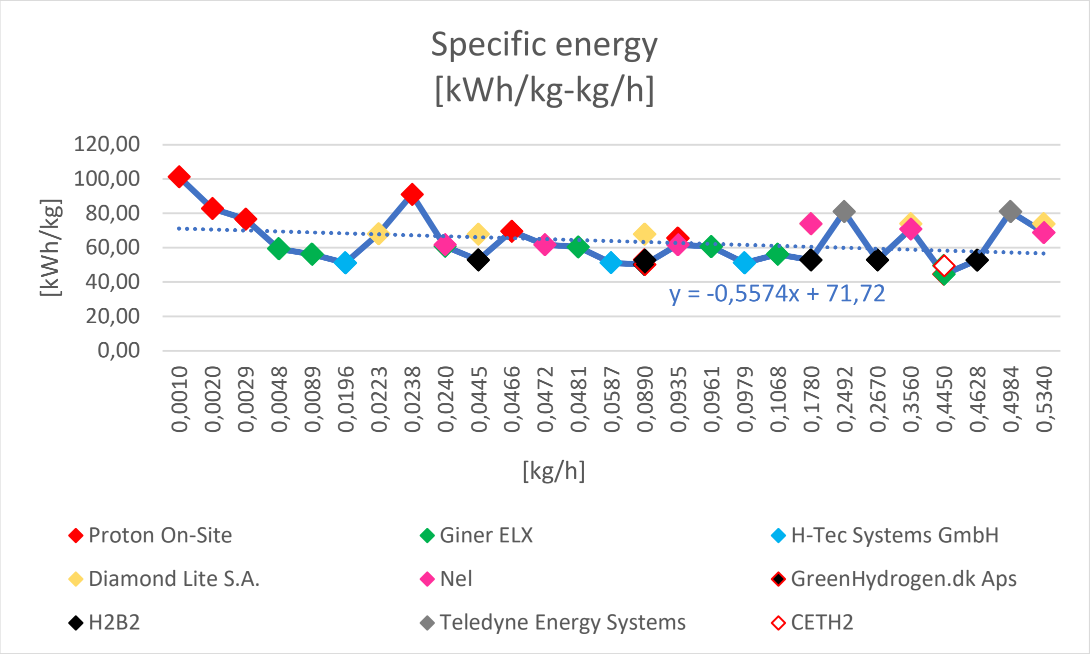

Figure 36 – Specific energy of PEM electrolysers as a function of the mass hydrogen production rate

Then, grouping the technologies on the basis of a similar hydrogen production, the following suppliers can be identified as optimal choice:

- H-Tec Systems GmbH (Stack Series-S: S 30/10 and Stack Series-S: S 30/30) and H2B2 (EL0.5N) for hydrogen flow rates up to 0.66 Nm^3/h;

- GreenHydrogen.dk Aps (P1), H-Tec Systems GmbH (Stack Series-S: S 30/50) and H2B2 (EL1N, EL2N and EL3N) for values between 1 Nm^3/h and 3 Nm^3/h;
- Giner ELX (Merrimack), CETH2 (E5) and H2B2 (EL5N) for hydrogen demands between 4 Nm^3/h and 6 Nm^3/h.

In particular, for hydrogen demands up to 0.66 Nm^3/h, the two mentioned suppliers offer technologies remaining below 5 kWh/Nm^3. Indeed, H-Tec Systems GmbH stacks require 4.55 kWh/Nm^3, while H2B2 electrolyser, with 4.70 kWh/Nm^3 consumes a little more, but the difference is practically negligible. In order to not excessively restrict the choice, also technologies arriving to 5.5 kWh/Nm^3 can be mentioned. These correspond to four electrolysers belonging to Giner ELX and two produced by Nel. Specifically, for Giner ELX they are PEMI electrolysers producing respectively 0.054 Nm^3/h (5.28 kWh/Nm^3), 0.27 Nm^3/h (5.41 kWh/Nm^3), and 0.54 Nm^3/h (5.37 kWh/Nm^3) and G5 (0.1 Nm^3/h with 5.0 kWh/Nm^3), while Nel technologies are S10 (0.27 Nm^3/h) and S20 (0.53 Nm^3/h), both requiring 5.49 kWh/Nm^3.

For hydrogen demands of 1 – 3 Nm^3/h, the most convenient suppliers, providing technologies with a specific energy consumption lower than 5 kWh/Nm^3 are: GreenHydrogen.dk Aps, H2B2 and H-Tec Systems GmbH. The first one produces a technology consuming 4.46 kWh/Nm^3 for 1 Nm^3/h of hydrogen, which is thus very similar to the stacks produced by H-Tec Systems GmbH, requiring 4.55 kWh/Nm^3 for 1.1 Nm^3/h. To the third supplier mentioned, H2B2, three technologies are related, consuming 4.70 kWh/Nm^3 for all the three hydrogen flows of 1 Nm^3/h, 2 Nm^3/h and 3 Nm^3/h. As before, also the electrolysers needing up to 5.5 kWh/Nm^3 are considered competitive. In this case, the suppliers involved are again Giner ELX and Nel. Giner ELX PEMI electrolyser for 1.08 Nm^3/h requires 5.39 kWh/Nm^3, while HP PEMI consumes 5.0 kWh for each normal cubic meter of hydrogen, producing 1.2 Nm^3/h. Then, Nel S40 electrolyser needs 5.49 kWh/Nm^3 for a production of 1.05 Nm^3/h of hydrogen.

The third group (4-6 Nm^3/h), as most convenient suppliers includes: Giner ELX, CETH2 and H2B2. In particular, Giner ELX electrolyser, with a specific energy of 3.96 kWh/Nm^3 for 5 Nm^3/h, corresponds to one of the least energy-intensive PEM electrolysers. It is followed by CETH2 device, which for the same hydrogen flow rate consumes 4.40 kWh/Nm^3, and H2B2 electrolyser (4.69 kWh/Nm^3 for 5.2 Nm^3/h). In this third case, there are no electrolysers, apart from those mentioned, remaining below 5.5 kWh/Nm^3, since the rest of the technologies require more than 6 kWh/Nm^3.

Since H-Tec Systems GmbH, H2B2, GreenHydrogen.dk Aps, Giner ELX and CETH2 correspond to the most convenient suppliers, under the specific energy point of view, their corresponding indicators are mainly located below the trend line or, in some cases, overlap it, while most of the electrolysers provided by the remaining producers present a specific consumption higher than the interpolating value.

As in the previous cases, those technologies which present the lowest specific energies are characterised by the lowest cell voltages and highest conversion efficiencies. Considering the whole set of electrolysers (0.011 – 6 Nm^3/h), it emerges that the technologies considered as the most competitive, so those remaining below the 5 kWh/Nm^3 threshold, are characterised by a cell voltage lower than 2.0 V (1.62 – 1.93 V) and an efficiency never lower than 74.6% (74.6 – 88.6%). Whereas, the electrolysers mentioned as "second best option", arriving to 5.5 kWh/Nm^3, present a cell voltage ranging between 2.05 V and 2.25 V and an efficiency of 63.9 – 70.1%. For hydrogen flow rates up to 0.66 Nm^3/h, both H-Tec Systems GmbH electrolysers present values of cell voltage (1.86 V) and efficiency (77.2%) which differ minimally from those of H2B2 (1.93 V and 74.6%). These values are followed by those of Giner ELX G5 (2.05 V and 70.2%) and PEMI (2.16 – 2.22 V and 64.9 – 66.5%) electrolysers and, finally, by those of Nel S10 and S20 technologies (2.25 V and 63.9%). These considerations are almost unchanged for electrolysers producing 1 – 3 Nm^3/h of hydrogen. Indeed, GreenHydrogen.dk Aps P1 device is characterised by 1.83 V and 78.7% of efficiency, H-Tec Systems GmbH stacks typically operate with 1.86 V and an efficiency of 77.2% and all the three H2B2 electrolysers with 1.93V and 74.6%. Giner ELX HP PEMI and PEMI cell voltage and efficiency are, respectively, 2.05 – 2.21 V and 70.1 – 65.1%, while Nel S40 device arrives up to 2.25 V and down 63.9%.

Remaining in the context of 1 - 3 Nm^3/h of hydrogen, a note can be made on Giner ELX, since it produces two similar technologies: PEMI and HP PEMI, that differ mainly in the maximum hydrogen output pressure, around 20 bar for PEMI and 40 bar for HP PEMI. The point is that, under a solely technical point of view (not economical) HP PEMI is more convenient than PEMI, since the first can produce up to 1.2 Nm^3/h of hydrogen with a 70.1% efficiency (5 kWh/Nm^3), while the second provides 1.08 Nm^3/h with an efficiency of 65.1% (5.39 kWh/Nm^3).

Thirdly, for hydrogen demands of 4 – 6 Nm^3/h, Giner ELX Merrimack electrolyser, having a really low specific consumption, lowers the cell voltage to 1.62 V and raises the efficiency up to 88.6%. The other two competitive electrolysers, CETH2 E5 and H2B2 EL5N, instead, operate with respectively 1.80 – 1.92 V and 79.7 – 74.7%.

Finally, considering the dimensional aspect, almost all the values except for those related to H2B2, which provides the entire system footprint. Anyway, in most of cases the electrolyser covers around one half of the total area, thus, in order to compare the technologies, the value of 1.44 m^2 for the system can be translated into 0.72 m^2 for the electrolyser. Globally, the least requiring technologies, in terms of space, are those of Giner ELX, with an electrolyser footprint of 0.03 m^2 for technologies up to 1.2 Nm^3/h and 0.149 m^2 for those of 5 Nm^3/h. However, H-

Tec Systems GmbH for its stacks for 0.66 Nm^3/h even requires less space (0.024 m^2), but the difference with respect to Giner ELX is really negligible. For the hydrogen flow rates up to 3 Nm^3/h, all the footprints arrive at a maximum of 0.77 m^2, while for 4 – 6 Nm^3/h all the values are greater than 1 m^2, except for those of Giner ELX and H2B2.

Concluding, the most competitive suppliers for this first group of electrolysers going from 0.011 Nm^3/h to 6 Nm^3/h are **H-Tec Systems GmbH** (0.011 – 0.66 Nm^3/h), **GreenHydrogen.dk Aps** (1 – 3 Nm^3/h) and **Giner ELX** (4 – 6 Nm^3/h). However, this in only under the specific energy point of view, since for the smallest technologies, the really best choice is represented by **H2B2** electrolysers, which present only a slightly higher consumption than those of H-Tec Systems GmbH, but really shorter start-up times.

Range 10 – 78 Nm^3/h

The following description aims to compare the electrolysers of the second set, from 10 Nm^3/h to 78 Nm^3/.

The trend of the variation of the electrical consumption according to the hydrogen flow rate (Figures 37 and 38) is quite linear for hydrogen flow rates up to 47 Nm^3/h (4.18 kWh/kg), while it presents more fluctuations for greater values, mainly due to the higher electrical consumptions of Teledyne Energy Systems electrolysers (especially for 56 Nm^3/h) compared to those of similar technologies.

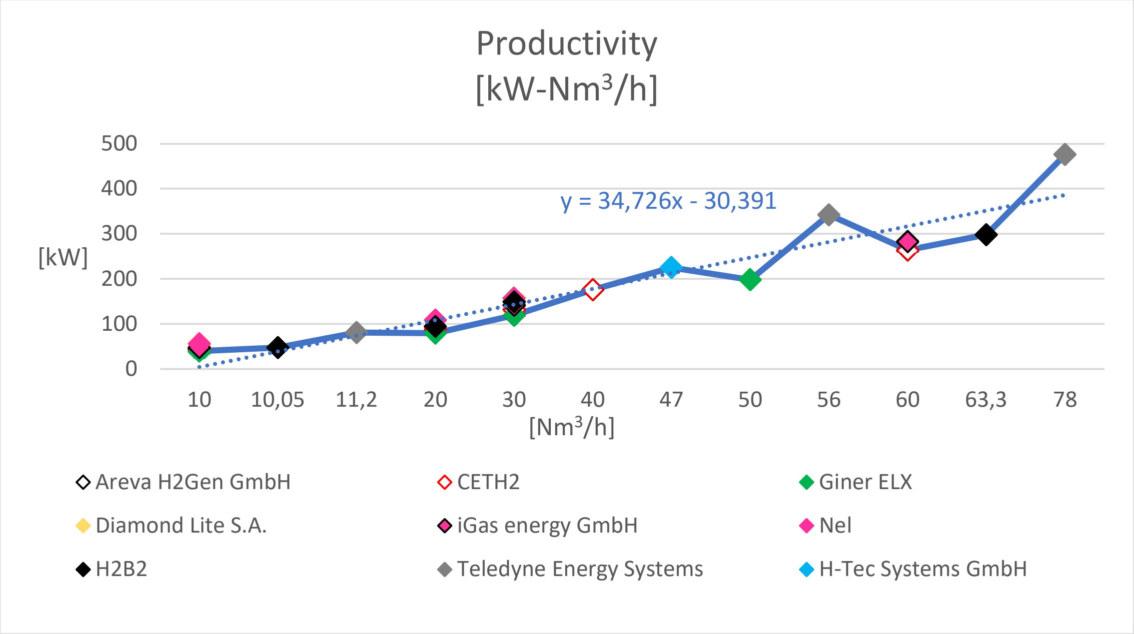

Figure 37 – Electrical input of PEM electrolysers as a function of the volumetric hydrogen production rate

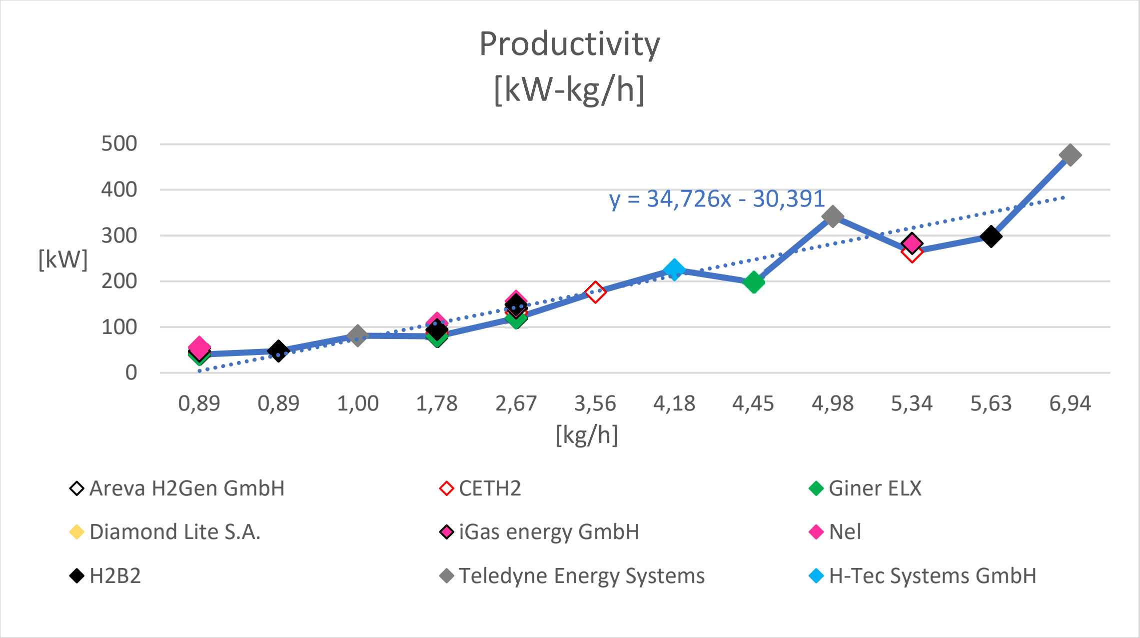

Figure 38 – Electrical input of PEM electrolysers as a function of the mass hydrogen production rate

Indeed, Teledyne Energy Systems TITAN EL-1000 electrolyser (56 Nm^3/h) requires 342 kW, while Giner ELX Allagash device (50 Nm^3/h) operates with 198 kW, as well as Areva H2Gen GmbH E60, CETH2 E60 and iGas energy GmbH (all for 60 Nm^3/h) require 264 kW and 283 kW the first two and the last respectively. H2B2 EL60N, too, with a higher production (63.3 Nm^3/h) than TITAN EL-1000, presents a smaller size (298 kW). Moreover, Giner ELX Allagash for 50 Nm^3/h presents a size reduction compared to the previous H-Tec Systems GmbH Series-Me ME 100/350 electrolyser (47 Nm^3/h and 225 kW).

Then, like for the previous group of PEM electrolysers, there are some technologies having different size for the same hydrogen flow rates. Three of these have already been mentioned (those of Areva H2Gen GmbH, CETH2 and iGas energy GmbH for 60 Nm^3/h), while the remaining ones (listed with increasing sizes) are those of:

- Giner ELX (39.7 kW), Areva H2Gen GmbH and CETH2 (both with 44 kW), iGas energy GmbH (47.1 kW), Diamond Lite S.A. and Nel (both with 55.8 kW) for 10 Nm^3/h;
- Giner ELX (79.4 kW), Areva H2Gen GmbH and CETH2 (both with 88 kW), H2B2 (94 kW), Diamond Lite S.A. and Nel (both with 108 kW) for 20 Nm^3/h;
- Giner ELX (119 kW), CETH2 (132 kW), iGas energy GmbH (141 kW), H2B2 (149 kW) and Diamond Lite S.A. and Nel (both with 157 kW) for 30 Nm^3/h.

For what concerning the specific energy consumption (Figures 39 and 40), first of all they can be noticed both the absence of scale effect and the difference between the minimum and maximum values.

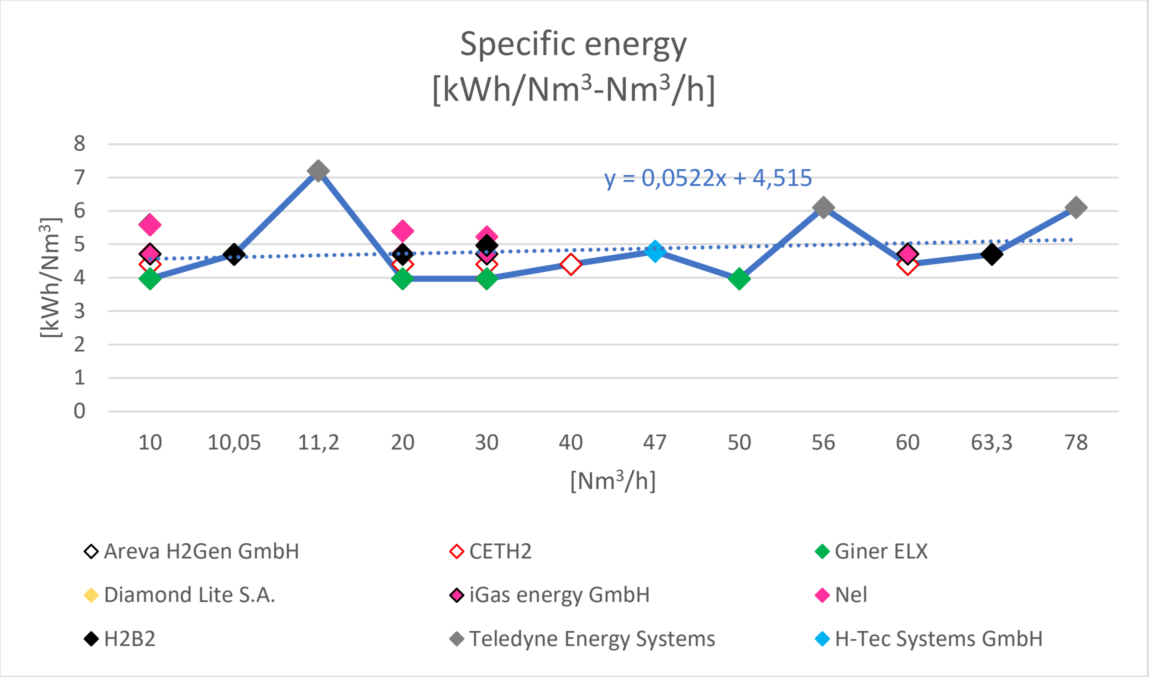

Figure 39 – Specific energy of PEM electrolysers as a function of the volumetric hydrogen production rate

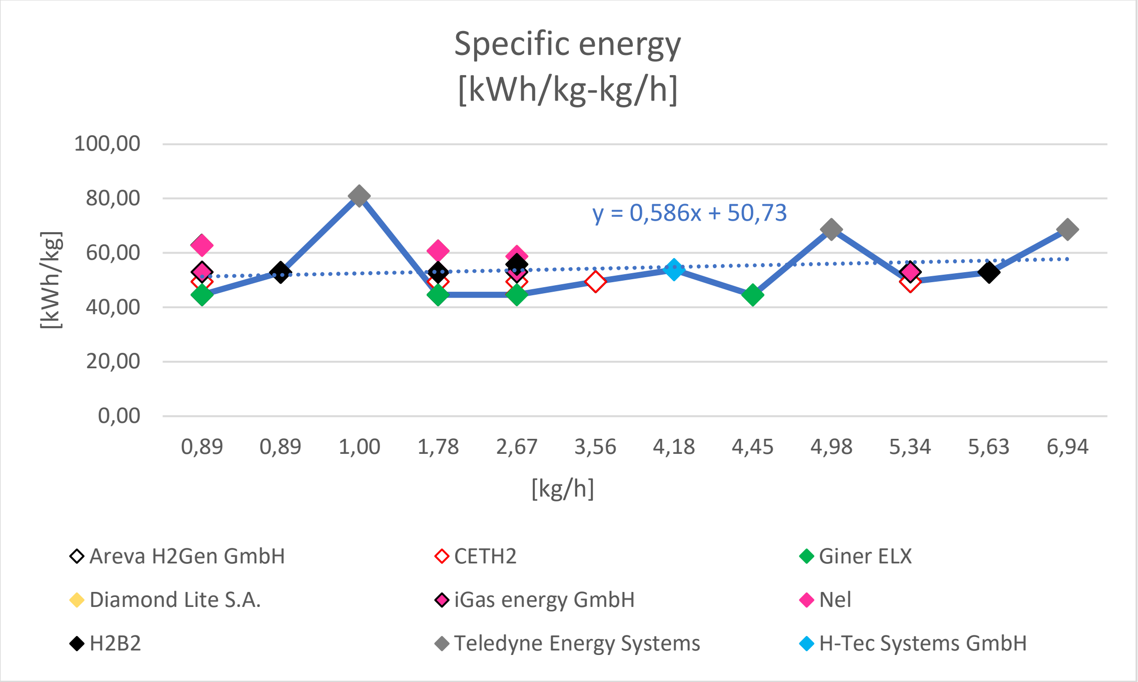

Figure 40 – Specific energy of PEM electrolysers as a function of the mass hydrogen production rate

Indeed, the lowest specific energies, all characteristic of Giner ELX technologies, are equal to 3.96 – 3.97 kWh/Nm^3 (44.5 – 44.6 kWh/kg), while the highest ones, all associated to Teledyne Energy Systems, are 6.1 kWh/Nm^3 (68.5 kWh/kg) and 7.2 kWh/Nm^3 (80.9 kWh/kg). However, most of the data are confined between 3.96 kWh/Nm^3 and around 5 kWh/Nm^3 and are located below the interpolating line (CETH2, and Giner ELX) or in correspondence of it (iGas energy

GmbH and H2B2). It is evident from the graphs that, for hydrogen flow rates comprised between 10 Nm^3/h (0.89 kg/h) and 50 Nm^3/h (4.45 kg/h), the most convenient supplier is Giner ELX, while for hydrogen demands between 50 Nm^3/h and 60 Nm^3/h the least consuming electrolysers are those of Areva H2Gen and CETH2. However, extending the comparison to the durability point of view, CETH2 cannot be considered among the most competitive suppliers since it offers stacks with an operational lifetime of 35000 hours, while iGas energy GmbH, with a specific consumption slightly higher (4.71 kwh/Nm^3), produces stacks with a durability of 80000 hours. Finally, for values around 80 Nm^3/h, the only available technology belongs to Teledyne Energy Systems.

Since some values of hydrogen flow rates can be covered by more electrolysers with different sizes, different specific energies correspond to those values. Such consumptions are characteristic of the following suppliers:

- Giner ELX (3.97 kWh/Nm^3), Areva H2Gen GmbH and CETH2 (both with 4.4 kWh/Nm^3), iGas energy GmbH (4.71 kWh/Nm^3), Diamond Lite S.A. and Nel (both with 5.58 kWh/Nm^3) for 10 Nm^3/h;
- Giner ELX (3.97 kWh/Nm^3), Areva H2Gen GmbH and CETH2 (both with 4.4 kWh/Nm^3), H2B2 (4.7 kWh/Nm^3), Diamond Lite S.A. and Nel (both with 5.4 kWh/Nm^3) for 20 Nm^3/h;
- Giner ELX (3.97 kWh/Nm^3), CETH2 (4.4 kWh/Nm^3), iGas energy GmbH (4.71 kWh/Nm^3), H2B2 (4.97 kWh/Nm^3), Diamond Lite S.A. and Nel (both with 5.22 kWh/Nm^3) for 30 Nm^3/h;
- Areva H2Gen GmbH and CETH2 (both with 4.4 kWh/Nm^3) and iGas energy GmbH (4.71 kWh/Nm^3) for 60 Nm^3/h.

Regarding the cell voltage, for most technologies (those characterised by 3.96 – 5 kWh/Nm^3), it remains below 2 V, except for the electrolyser of H2B2 for 30 Nm^3/h, which arrives to 2.04 V. In particular, the other lower values range between a minimum of 1.62 – 1.63 V for Giner ELX devices and a maximum of 1.96 V for H-Tec Systems GmbH. Then, considering again the range 3.96 – 5 kWh/Nm^3, the conversion efficiency characteristic of Giner ELX (88.4 – 88.6%) is the maximum one, while that of H2B2 for 30 Nm^3/h (70.6%) is the lowest one. The electrolysers characterised by specific energy consumptions higher than 5 kWh/Nm^3 have, instead, efficiencies typically comprised between 62.9% (Diamond Lite S.A. and Nel for 10 Nm^3/h) and 67.2% (Diamond Lite S.A. and Nel for 30 Nm^3/h). Teledyne Energy Systems electrolysers, operating with 6.1 – 7.2 kWh/Nm^3 present, finally, an efficiency even lower than

50%. Indeed, the last two devices (56 Nm^3/h and 78 Nm^3/h) operate with an efficiency of 57.5%, the first one (11.2 Nm^3/h) goes down to 48.7%.

Finally, considering the whole second group of electrolysers, it can be said that **Giner ELX** results surely the most competitive, with really low specific energy consumptions, although it does not provide any data regarding the flexibility, reactivity and durability. Then, for the highest values of hydrogen flow rates, **Areva H2Gen GmbH** provides only the system operational lifetime, equal to more than 20 years, and not that of the stacks: if this last one was comparable to that of iGas energy GmbH (more than 80000 hours), Areva H2Gen GmbH would be more competitive than iGas energy GmbH, since the first presents a lower specific energy consumption, otherwise **iGas energy GmbH** would represent a good compromise. Moreover, the electrolysers produced by Areva H2Gen GmbH have a good load flexibility, ranging from 0% to 100%, as well as those of CETH2, Diamond Lite S.A. and Nel. H2B2, instead, which provides technologies with the same specific consumption as that of iGas energy GmbH devices, does not provide any data regarding the durability, but it can be considered valid under the reactivity point of view, since its electrolysers require less than 5 minutes for the cold start-up and less than 1 second for the warm one. Another positive characteristic of H2B2 devices is their operational window in terms of flow range, since the production of hydrogen can vary from 10% to 100% of the nominal flow. Analysing the remaining data of reactivity and durability, it emerges that the technologies of iGas energy GmbH and Teledyne Energy Systems, apart those of H2B2, are the most reactive, since the first ones require 10 s for the warm start-up and the second ones are ready to operate after a 5 minutes nitrogen purge cycle. H-Tec Systems GmbH, instead, provides much less reactive electrolysers, needing almost one hour for the cold start-up and 30 s for the warm one. Under the stack durability point of view, iGas energy GmbH offers the most performant technologies (80000 hours), followed by those of Teledyne Energy Systems (43000 – 61000 hours), CETH2 and H-Tec Systems GmbH (both with 35000 hours). Regarding the system operational lifetime, the only data available are those of Areva H2Gen GmbH (20 years), iGas energy GmnH (more than 20 years) and Teledyne Energy Systems (more than 25 years).

This last supplier, offers technologies that, despite the high consumptions, are characterised not only by good reactivity and durability, but also by a wide operational window, since they can tolerate a decrease of the input electrical load until 1% of the nominal value. Moreover, Teledyne Energy Systems present the smallest footprint for electrolysers of around 10 Nm^3/h (1.79 m^2) and over 50 Nm^3/h (7.42 m^2). Anyway, the values of specific energy of its technologies are too high to make them competitive. For hydrogen flow rates in the middle, the supplier requiring the smallest surface is Diamond Lite S.A. (3.9 m^2). In this case, the value reported refer to the whole system and not only to the electrolyser itself, except for Giner ELX.

Range 100 – 580 Nm^3/h

The range of hydrogen production rates now taken into account goes from 100 Nm^3/h to 580 Nm^3/h. The size of the electrolysers (Figures 41 and 42) follows again a trend that is quite linear, even if some deviations are present, especially for 210 Nm^3/h, 403 Nm^3/h and 420 Nm^3/h.

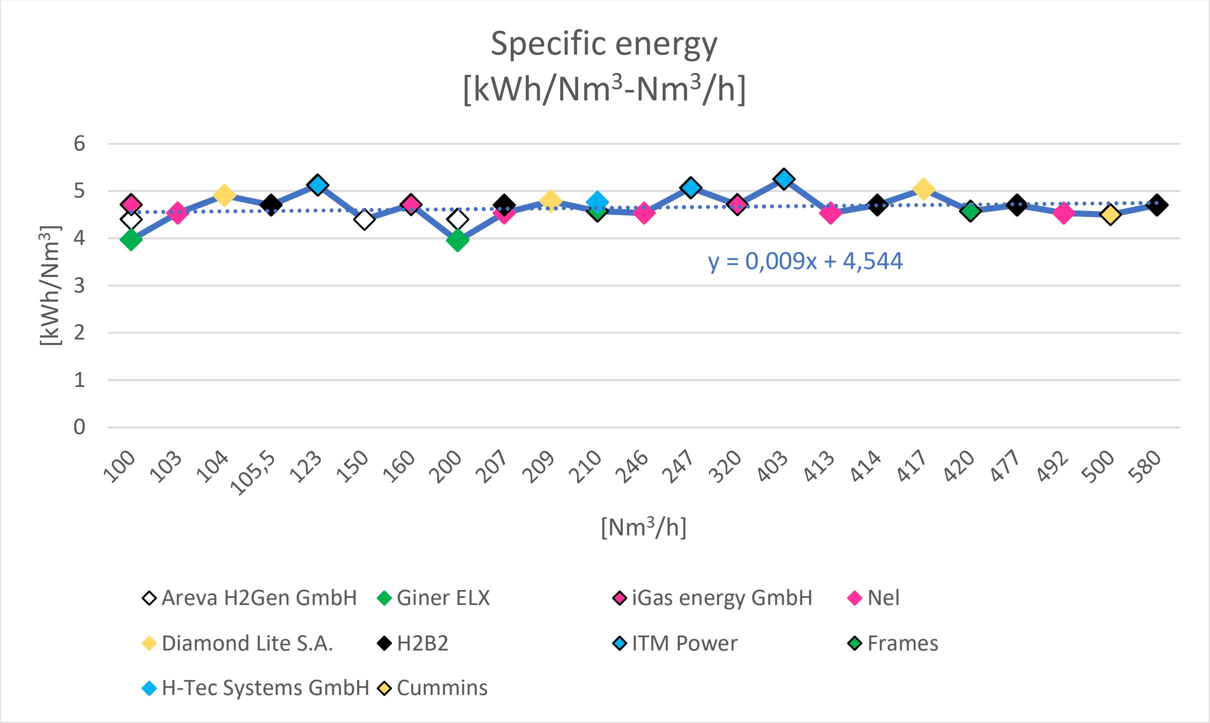

Figure 41 – Electrical input of PEM electrolysers as a function of the volumetric hydrogen production rate

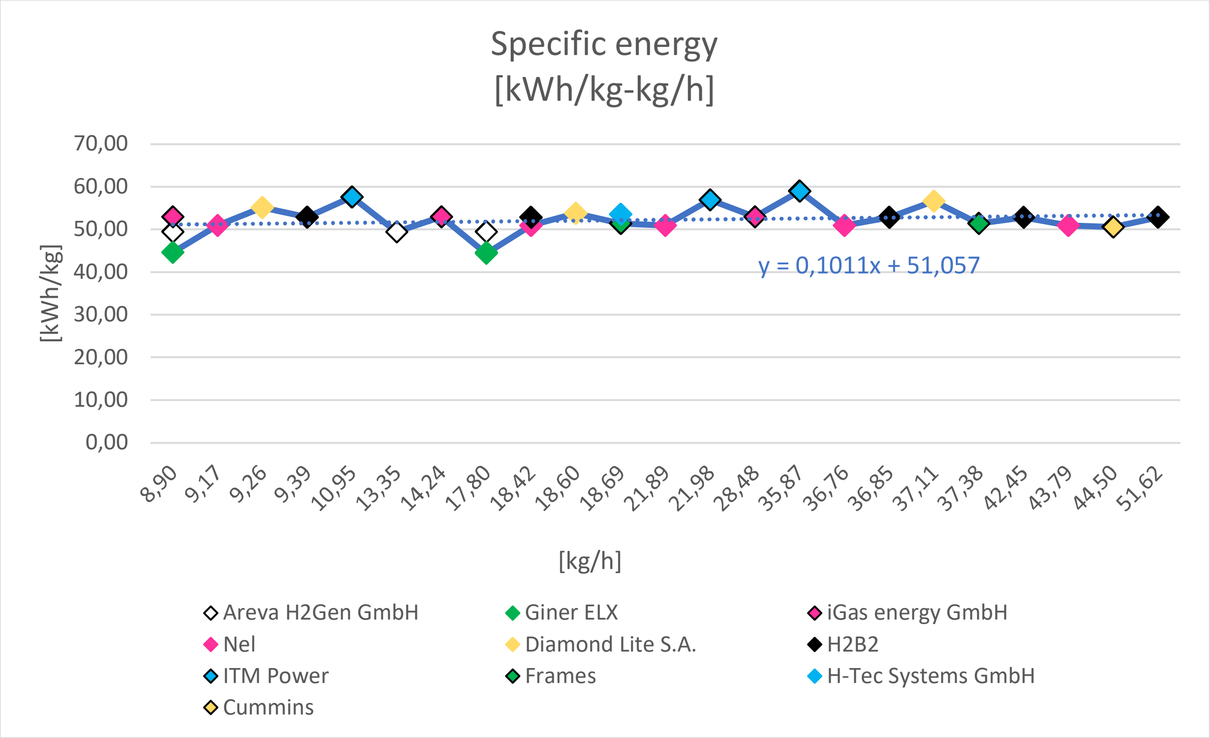

Figure 42 – Electrical input of PEM electrolysers as a function of the mass hydrogen production rate

The first deviation is due to the fact that Frames and H-Tec Systems GmbH present sizes that are, respectively, lower (960 kW) and equal (1000 kW) compared to that of the previous technology of Diamond Lite S.A., which produces 209 Nm^3/h of hydrogen with a size of 1000 kW. However, even if this difference appears in the graph, in the reality it is negligible. Then, the flow rate of 403 Nm^3/h is characteristic of the device of ITM Power, which presents an excessive size (2115 kW) compared to those of both the previous iGas energy GmbH electrolyser (1507 kW) and the subsequent Nel device (1871 kW). Finally, for 420 Nm^3/h, it can be noted a size decrease with Frames device, which operate with 1920 kW while the previous electrolysers of H2B2 (414 Nm^3/h) and Diamond Lite S.A. (413 Nm^3/h) require, respectively, 1946 kW and 2100 kW.

Again, like in for 210 Nm^3/h, there are some values of hydrogen flow rates satisfied by more electrolysers, in particular:

- Giner ELX (397 kW), Areva H2Gen GmbH (440 kW) and iGas energy GmbH (471 kW) for 100 Nm^3/h
- Giner ELX (790 kW and 794 kW) and Areva H2Gen GmbH (880 kW) for 200 Nm^3/h
- Nel (938 kW) and H2B2 (973 kW) for 207 Nm^3/h.

The specific energy (Figures 43 and 44) does not present a scale effect and does not follow a linear trend since, even if many values are placed on the interpolating line, the oscillations due to the other technologies are not negligible.

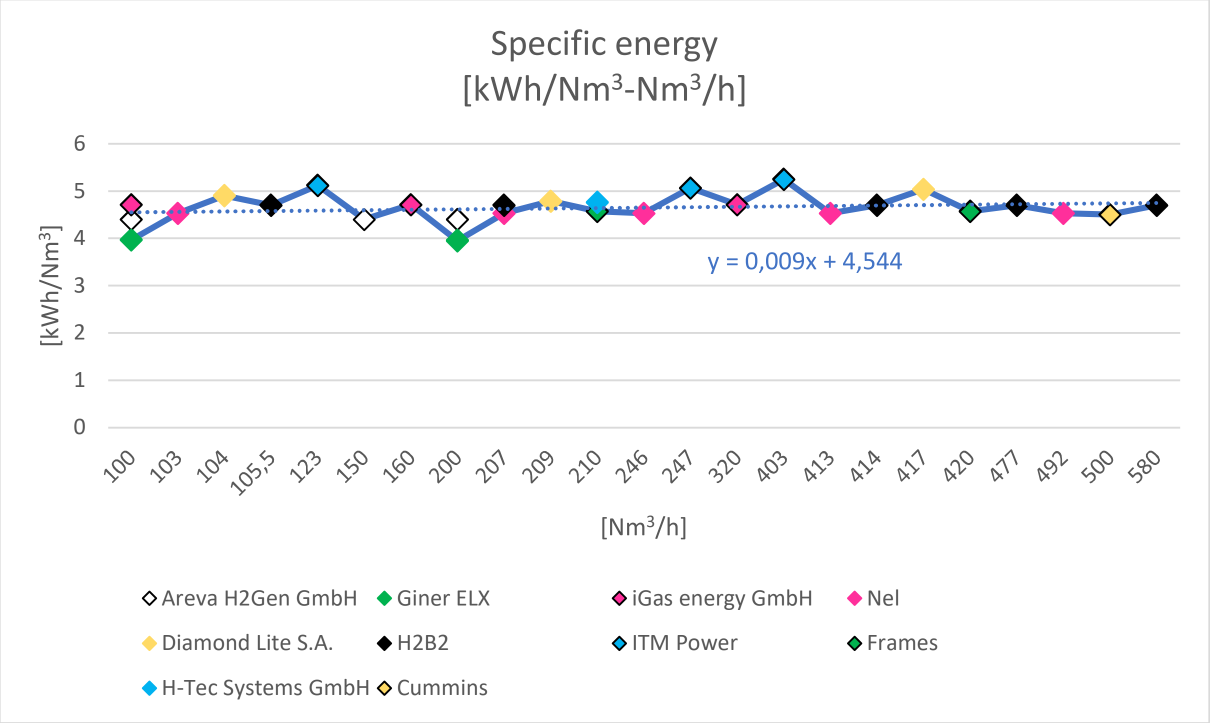

Figure 43 – Specific energy of PEM electrolysers as a function of the volumetric hydrogen production rate

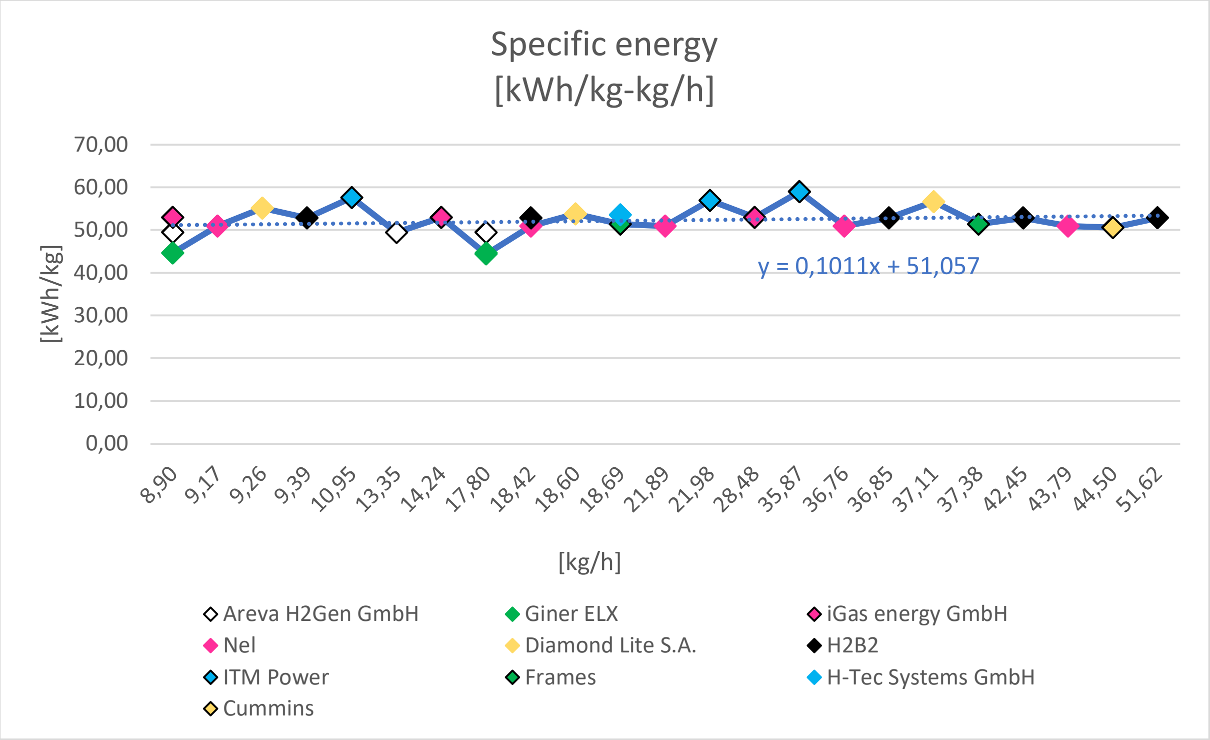

Figure 44 – Specific energy of PEM electrolysers as a function of the mass hydrogen production rate

In particular, it can be noticed that the specific energies corresponding to Giner ELX are placed below the trend line and present the lowest values (3,95 – 3,97 kWh/Nm^3), while those of ITM power produce the major deviations above. ITM Power device for 403 Nm^3/h is then the one that presents the highest specific energy (5,25 kWh/Nm^3). A positive aspect is given by the fact that almost all the electrolysers present a specific energy that is lower than 5,0 kWh/Nm^3.

In order to analyse more in detail the specific energy, the cell voltage and the conversion efficiency, the range of flow rates considered can be further subdivided according to the following levels of production: 100 - 160 Nm^3/h, 200 - 320 Nm^3/h, 403 - 492 Nm^3/h and 500 - 580 Nm^3/h. For values up to 160 Nm^3/h, **Giner ELX** is the supplier providing the most performant technology, with 3,97 kWh/Nm^3, 1,63 V and an efficiency of 88,3%. Giner ELX is then the most convenient supplier also for the second range, with a specific energy equal to 3,95 – 3,97 kWh/Nm^3, a cell voltage of 1,62 – 1,63 V and 88,3 - 88,8% of efficiency. For the third range, the most competitive technologies are those of **Nel** for 413 Nm^3/h and 492 Nm^3/h, since they are both characterised by a specific energy of 4,53 kWh/Nm^3, which is anyway almost the same of Frames electrolyser for 420 Nm^3/h (4,57 kWh/Nm^3). These value translate into a cell voltage of 1,86 – 1,87 V and an efficiency equal to 76,7 – 77,4%. Finally, greater values of hydrogen flow rate, only two technologies can be considered: that of **Cummins** for 500 Nm^3/h and that of H2B2 for 580 Nm^3/h. Between them, the first one, with a specific energy of 4,5 kWh/Nm^3, a cell voltage of 1,84 V and an efficiency equal to 77,9%, is the is a little more performant.

Then, focusing on a view comprehensive of the flexibility, reactivity and durability data the only supplier providing almost all the data is **iGas energy GmbH**: its technologies are characterised by the possibility of reducing the load until 10% of the nominal value, by a warm start-up time of 10 seconds and by system and stack operational lifetimes of respectively 20 years and 80000 hours. Moreover, the technologies of iGas energy GmbH have a specific energy that is not too much high (4,7 kWh/Nm^3): this, together with the fact that the values of flexibility, reactivity and durability roughly correspond to the optimal ones for water electrolysers, makes these devices good compromise.

From a geometrical point of view, Diamond Lite S.A., together with H-Tec Systems GmbH and Cummins present the lowest values referring to the system footprint (again, those of Giner ELX are comprehensive only of the electrolyser, so they cannot be included in the comparison). In particular, for a production of 100 - 160 Nm^3/h, the smallest footprint is that of Diamond Lite S.A., requiring only 7,81 m^2 against the 71,5 – 100 m^2 of Nel. In the middle, with around 29 m^2, we can find Areva H2Gen GmbH, H2B2 and ITM Power. Instead, for hydrogen flows of 200 - 320 Nm^3/h, the most convenient option is no more Diamond Lite S.A., but it is H-Tec Systems

GmbH, requiring only 3,6 m^2. In this case, the only comparable systems are those of Diamond Lite S.A. (7,81 m^2) and Frames (14,9 m^2), while Areva H2Gen GmbH (29,7 m^2), H2B2 (28,8 m^2) and ITM Power (37 m^2) are again in the middle, since Nel reports 71,5 – 100 m^2 for its systems. For 403 – 492 Nm^3/h, the lowest surface is again that required by Diamond Lite S.A. (10 m^2), followed by Frames and H2B2 (29 m^2), ITM Power (44,5 m^2) and Nel (160 m^2). Finally, for flow rates of 500 – 580 Nm^3/h, Cummins represents the first choice (7.43 m^2), since H2B2 systems are characterised by a footprint of 57,6 m^2.

Range 1000 – 22413 Nm^3/h

The last set of electrolysers contains those technologies producing hydrogen flow rates greater than or equal to 1000 Nm^3/h. The most typical maximum hydrogen flow rates correspond to the values of 1000, 2000 and 4000 Nm^3/h, anyway, the SILYZER 300 electrolyser belonging to Siemens is able to produce up to 22413 Nm^3/h. For this reason, the graphs (Figures 45 and 46) showing the electrolysers size as a function of the productivity were replicated without considering the Siemens device for 22413 Nm^3/h (Figures 47 and 48), in order to appreciate a more real trend.

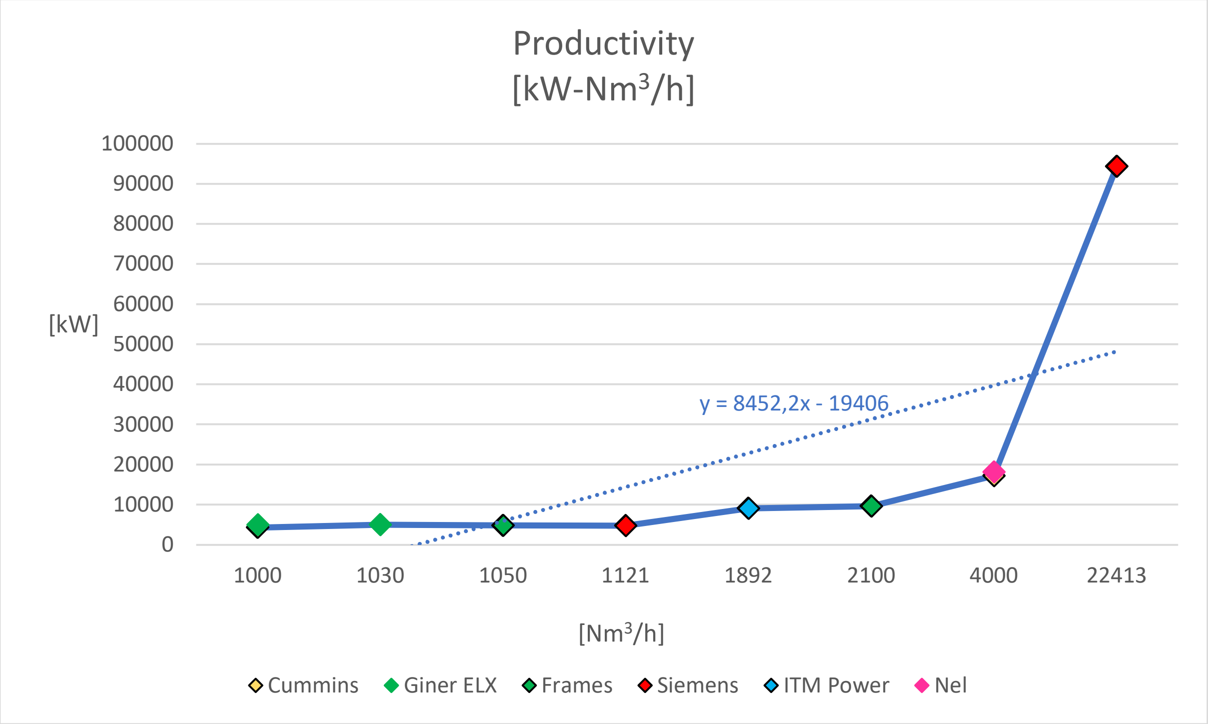

Figure 45 – Electrical input of PEM electrolysers as a function of the volumetric hydrogen production rate

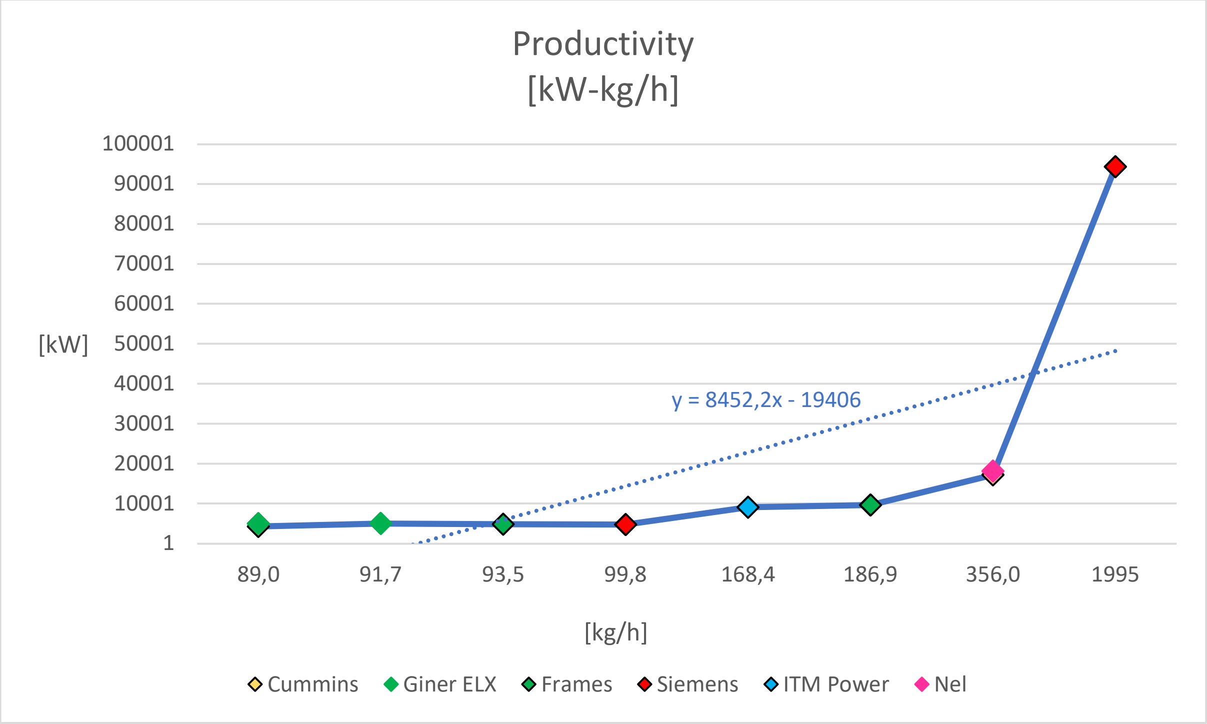

Figure 46 – Electrical input of PEM electrolysers as a function of the mass hydrogen production rate

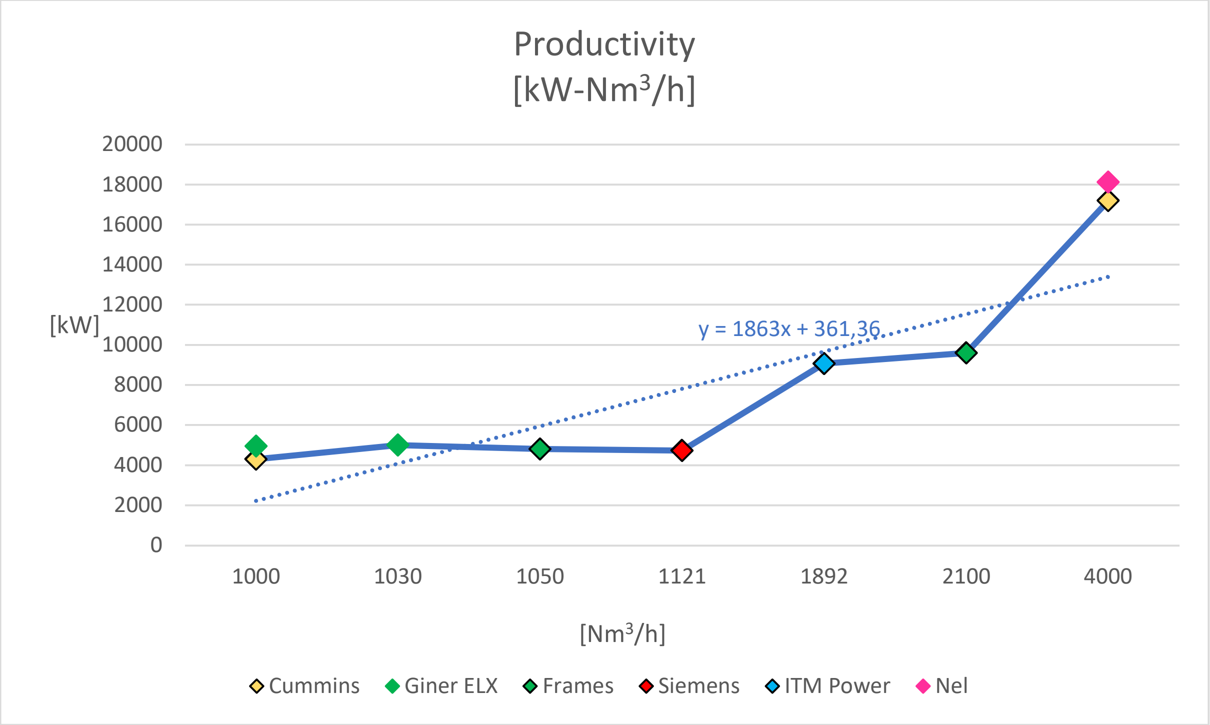

Figure 47 – Electrical input of PEM electrolysers as a function of the volumetric hydrogen production rate

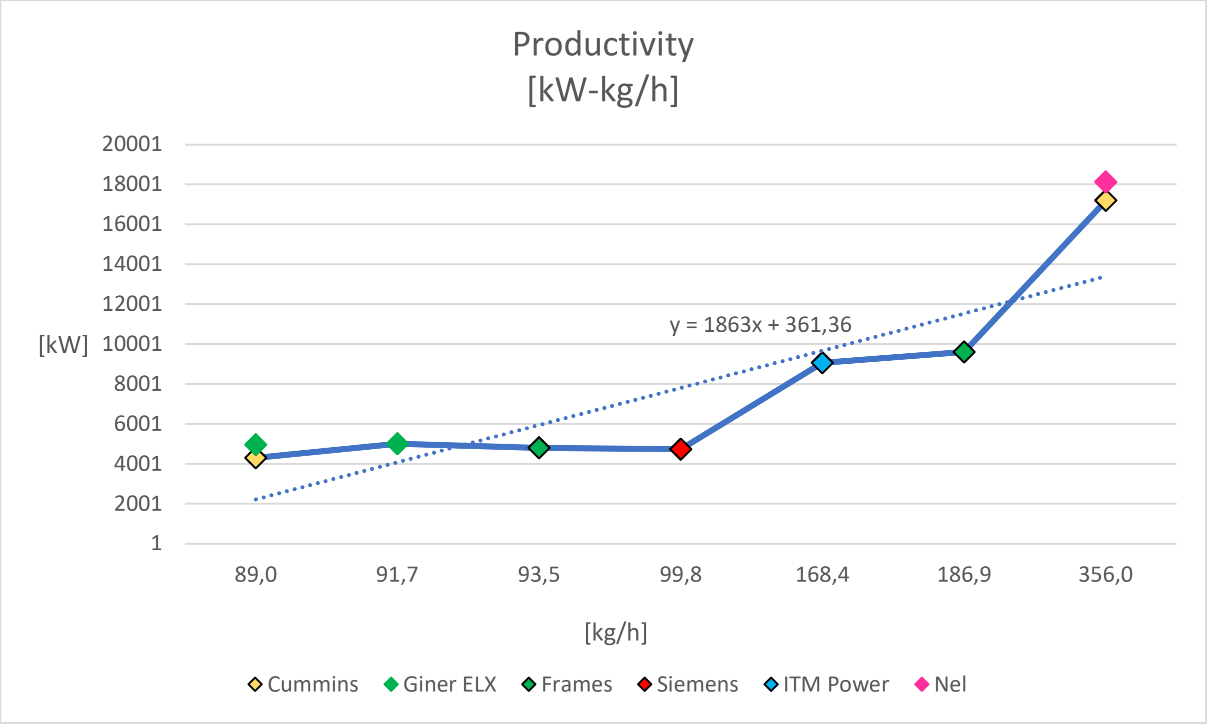

Figure 48 – Electrical input of PEM electrolysers as a function of the mass hydrogen production rate

Indeed, the last two graphs show a trend that is not perfectly linear, but it better approximates the trend line with respect to the first two graphs. The electrolysers of Cummins, like those of Giner ELX and Nel, are placed above the trend line, while the remaining ones are located below, except for that of ITM Power which is almost on the interpolating line. Moreover, for both 1000 Nm^3/h and 4000 Nm^3/h two technologies can be identified, respectively provided by Cummins (4300 kW) and Giner ELX (4950 kW) and by Cummins (17200 kW) and Nel (18120 kW).

Then, even if from the graphs showing the trend of the specific energy (Figures 49 and 50) it seems that it is characterised by significant oscillations, in reality it varies between 4,21 kWh/Nm^3 (Siemens for 22413 Nm^3/h) and 4,95 kWh/Nm^3 (Giner ELX for 1000 Nm^3/h). Then, even if from the graphs showing the trend of the specific energy (Figures 49 and 50) it seems that it is characterised by significant oscillations, in reality it varies between 4,21 kWh/Nm^3 (Siemens for 22413 Nm^3/h) and 4,95 kWh/Nm^3 (Giner ELX for 1000 Nm^3/h). Moreover, the technologies of Cummins that, in terms of size are placed above the trend line, in this case are located below, presenting specific consumptions of 4,30 kWh/Nm^3 and thus close to the minimal ones. Finally, the overall trend shows the presence of the scale effect. Comparing the electrolysers with common hydrogen flow rates, it emerges that for 1000 Nm^3/h Siemens (4,22 kWh/Nm^3) is in competition with Cummins (4,30 kWh/Nm^3).

Regarding the cell voltage and the conversion efficiency, their ranges are, respectively, 1,72 – 2,03 V and 70,9 – 89,3% and correspond to the typical optimal values.

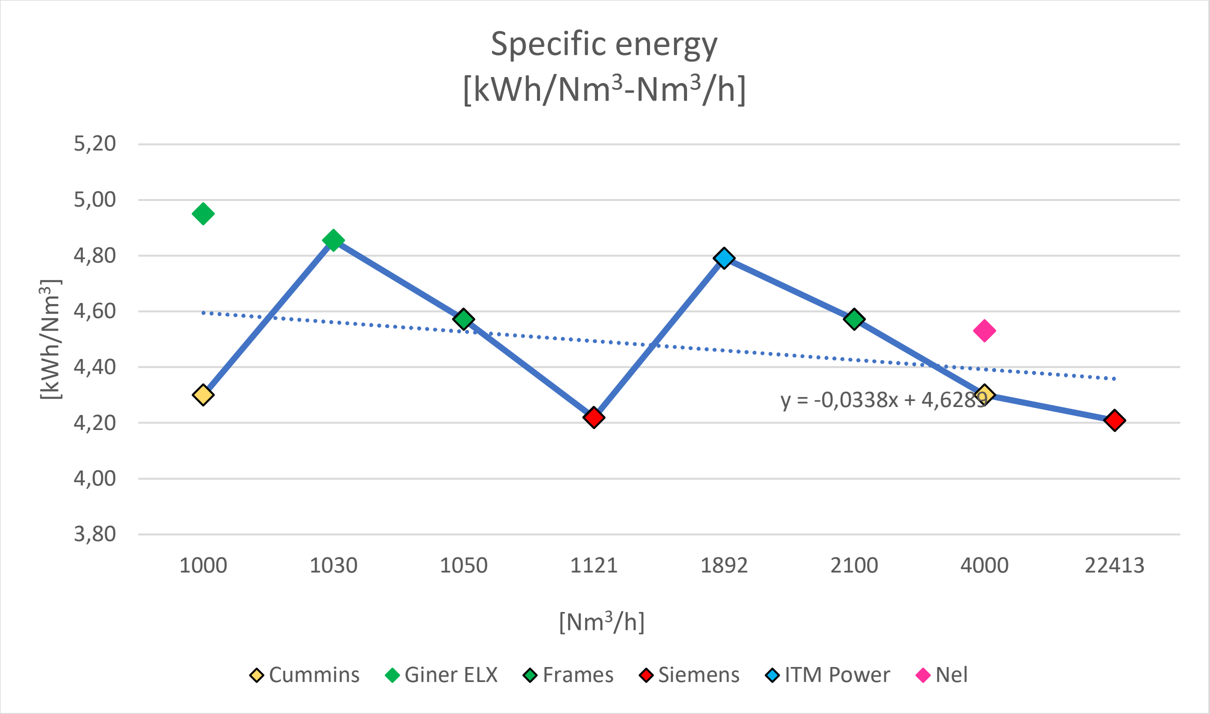

Figure 49 – Specific energy of PEM electrolysers as a function of the volumetric hydrogen production rate

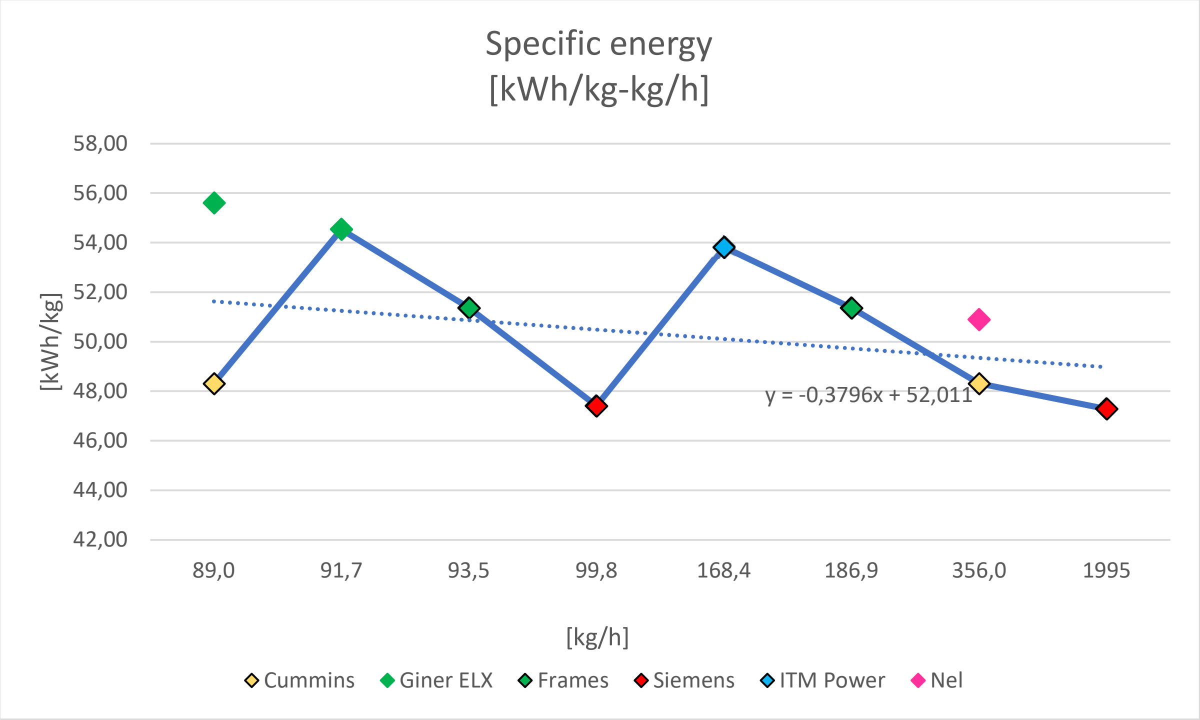

Figure 50 – Specific energy of PEM electrolysers as a function of the mass hydrogen production rate

Concerning the reactivity and durability of the technologies, already in the first groups there were few values for a right comparison: in this last case, instead, the only available data are the cold start-up time of Siemens SILYZER 300 electrolyser (less than 1 minute) and the stack/system operational lifetimes of Cummins electrolysers (80000 hours and 20 years respectively). While the second specification corresponds to the typical maximum durability for PEM electrolysers and systems, the first one does not correspond to the optimum but represents anyway a good reactivity, especially because these electrolysers have to cover a larger power range compared to the smallest ones in order to arrive to the maximum power. From the point of view of the flexibility, instead the reported values are similar to those of electrolysers for smaller production rates: Nel device can operate with a minimum hydrogen flow corresponding to 10% of the nominal one, while both Siemens and Cummins electrolysers are able to work with only 5% of the nominal input power. In particular, Cummins is noteworthy, since its technologies can reach peaks of 125% of the nominal input power. Finally, Cummins, is the supplier requiring the smallest system area for both the outputs of 1000 Nm^3/h (19.32 m^2) and 4000 Nm^3/h (500 m^2).

Final comparison of PEM water electrolysers

Now, referring to the previous considerations about PEM electrolysers suppliers, it can be said which are globally the most competitive for this water electrolysis field.

Nel and Giner ELX, are those covering the widest range of flow rates: the first produces technologies going from 0.27 Nm^3/h of hydrogen to 4000 Nm^3/h, while the second is suitable in a range of 0.02 – 1028 Nm^3/h. After them, those which range the most in terms of hydrogen produced are Diamond Lite S.A., H-Tec Systems GmbH and H2B2, all present in the first three groups considered. Those belonging to only two out of the four groups considered are: CETH2, Teledyne Energy Systems, Areva H2Gen GmbH, iGas energy GmbH, Frames, ITM Power and Cummins. In particular:

- CETH2 and Teledyne Energy Systems can be found in the first two sets, since their technologies ranges are, respectively, 5 – 60 Nm^3/h and 2.8 – 78 Nm^3/h;
- Areva H2Gen GmbH (10 – 200 Nm^3/h) and iGas energy GmbH (10 – 320 Nm^3/h) produce technologies of medium size;
- Frames (210 – 2100 Nm^3/h), ITM Power (123 – 1892 Nm^3/h) and Cummins (500 – 4000 Nm^3/h) are suitable for technologies of medium/large size.

The remaining suppliers, Proton On-Site, GreenHydroge.dk Aps and Siemens, focus instead on the smallest technologies in the first two cases and on the biggest technologies in the last case.

Considering the for groups divided, it is now reported a summary of the most competitive suppliers in terms of technologies performance.

First group (0,011 –6 Nm^3/h)

The first set of electrolysers was further subdivided into three ranges:

1. 0,011 – 0,66 Nm^3/h

   H-Tec Systems GmbH presents the lowest specific energy (4,55 kWh/Nm^3),closely followed by **H2B2** (4,70 kWh/Nm^3). Moreover, even if H-Tec Systems GmbH is the most competitive supplier under the consumptions perspective, it is not the most convenient on the side of flexibility and reactivity.
2. 1 – 3 Nm^3/h

   GreenHydrogen.dk Aps presents a specific energy (4,46 kWh/Nm^3 for 1 Nm^3/h) really similar to that presented by **H-Tec Systems GmbH** (4,55 kWh/Nm^3 for 1,1 Nm^3/h). Moreover, also **H2B2**, with 4,7 kWh/Nm^3 for 1 – 3 Nm^3/h, presents specific consumption only slightly higher.
3. 4 – 6 Nm^3/h

   Giner ELX (3,96 kWh/Nm^3 for 5 Nm^3/h) constitutes the most competitive supplier, followed by **CETH2** (4,4 kWh/Nm^3 for 5 Nm^3/h) and **H2B2** (4,69 kWh/Nm^3 for 5,2 Nm^3/h).

Second group (10 – 78 Nm^3/h)

Giner ELX is the supplier presenting the lowest specific energy (3,97 kWh/Nm^3) for hydrogen flow rates lower of maximum 50 Nm^3/h, while, for greater values, the most competitive supplier is **Areva H2Gen GmbH** (4,4 kWh/Nm^3) if its stack operational lifetime is comparable to that of **iGas energy GmbH** (4,71 kWh/Nm^3), otherwise this last supplier represents a good compromise.

Third group (100 – 580 Nm^3/h)

Giner ELX (3,95 kWh/Nm^3) is globally the most competitive supplier, but, further subdividing the range, other considerable suppliers can be identified, in particular:

- **Giner ELX** (3,95 kWh/Nm^3) for hydrogen flows of 100 – 320 Nm^3/h, with **iGas energy GmbH** (4,71 kWh/Nm^3) which represents a good compromise
- **Nel** (4,5 kWh/Nm^3), followed by **Frames** (4,57 kWh/Nm^3) for 403 – 492 Nm^3/h
- **Cummins** (4,5 kWh/Nm^3) for 500 – 580 Nm^3/h.

Fourth group (1000 – 22413 Nm^3/h)

Siemens is the provider presenting the lowest specific consumption (4,2 kWh/Nm^3), but considering the technologies with similar productions, it emerges that it is closely followed by Cummins (4,3 kWh/Nm^3) in the case of 1000 Nm^3/h of hydrogen.

The following table (Table 4) reports the average value for the main key performance indicators utilized as a means of comparison.

Hydrogen flow rate [Nm^3/h]	**0,011 – 6**	**10 – 78**	**100 – 580**	**1000 – 22413**
Electrical power consumption [kW]	10,1	152	1222	17210
Flow range	0 – 100% 10 – 100%	0 - 100% 10 – 100%	0 - 100% 10 – 100%	10 – 100%
Load range	-	1 – 100% 10 - 100% 20 - 100%	5 – 100% 10 - 100% 20 – 100%	5 - 100% 5 – 125%
Electrolyser specific energy consumption [kWh/Nm$^{3]}$	5,72	4,90	4,62	4,53
Electrolyser specific energy consumption [kWh/kg]	64,5	55,2	52,0	50,9
Cell voltage [V]	2,34	2,01	1,89	1.86
Electrolyser conversion efficiency (HHV)	63,3%	72,9%	76,3%	77,7%
Cold start-up time* [min]	≤ 5 min < 60 min	≤ 5 min < 60 min	≤ 5 min < 60 min	< 1 min
Warm start-up time* [s]	< 1 s 30 s	< 1 s 10 s 30 s	< 1 s 10 s 30 s	-
System operational lifetime [years]	> 25	> 25 > 20	≥ 20	20
Stack operational lifetime [hours]	80.000 43.000 – 61.000 35.000	> 80.000 43.000 – 61.000 35.000	≥ 80.000 35.000	80.000
Footprint [m^2]	0,88	8,90	50,3	194

Table 4 – Average values of the main Key Performance Indicators

* The available data are too few to be averaged, so these values have been inserted in this table for completeness, but they will not be considered in the following description.

As for the alkaline electrolysers, the size increases of one order of magnitude with the productivity and follows a globally linear trend (Figure 51 and 52) with some more evident deviations upward between 20 Nm^3/h and around 100 Nm^3/h and downward from 400 Nm^3/h. The first deviation means that the corresponding technologies present bigger sizes than the expected ones, while the second deviation means the contrary.

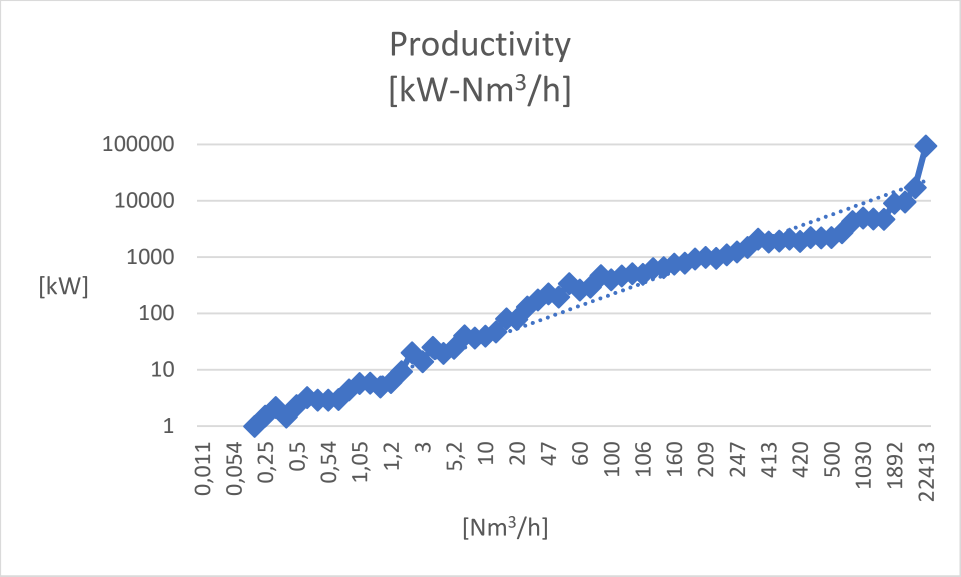

Figure 51 – Electrical input of PEM electrolysers as a function of the volumetric hydrogen production rate

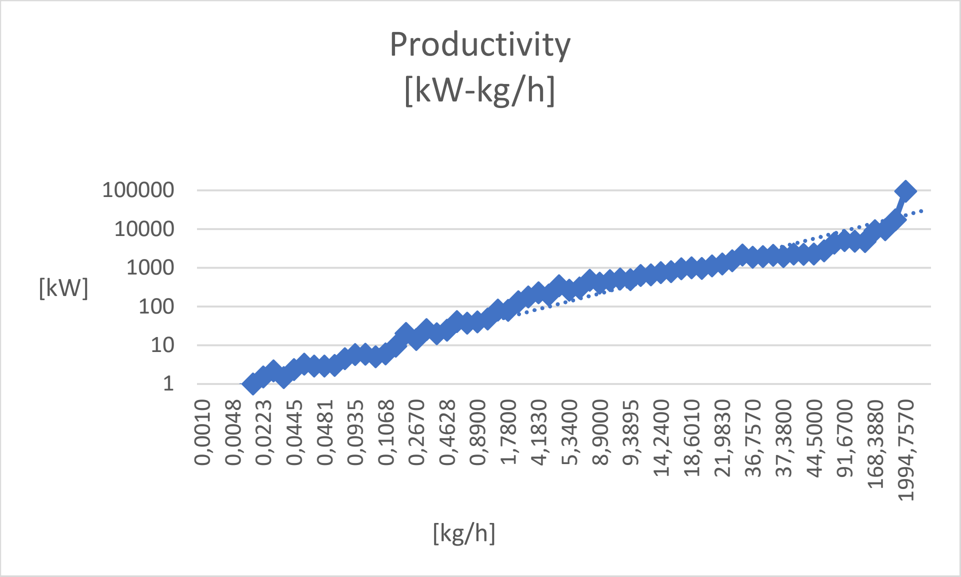

Figure 52 – Electrical input of PEM electrolysers as a function of the mass hydrogen production rate

The input power can be varied down to a minimum corresponding to 1 – 20% of the nominal value and in some cases can be incremented up to 125%, meaning that PEM electrolysers are characterised by a really good flexibility. This is confirmed also by the operational range in terms of hydrogen flow, which can vary from around 0% up to 100% of the nominal value.

The specific energy, whose overall trend is showed in Figures 53 and 54, for values up to 100 Nm^3/h is characterised by evident fluctuations which go from the minimal values to the maximum ones, while it takes a linear trend for higher values. However, considering both the average values and the total ones, an overall scale effect emerges.

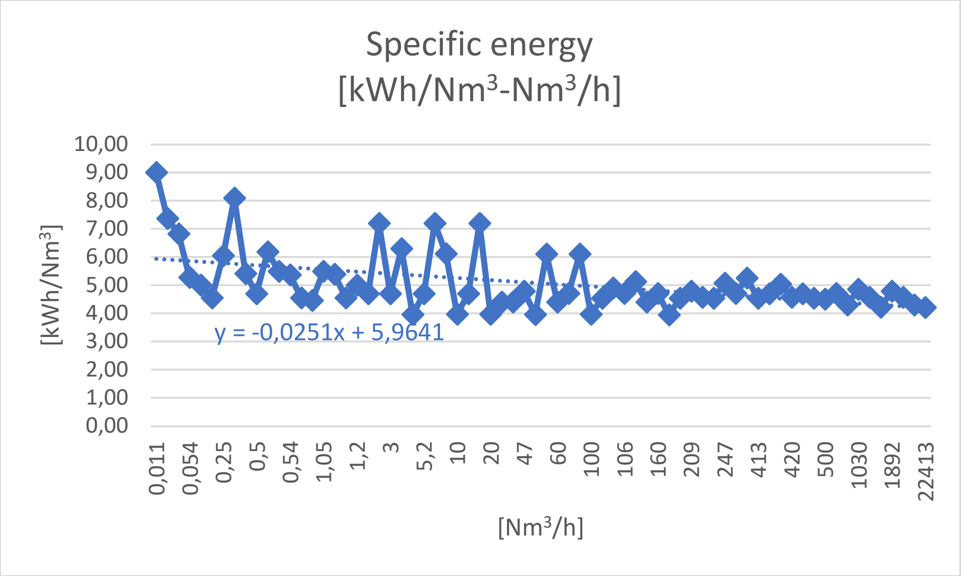

Figure 53 – Specific energy of PEM electrolysers as a function of the volumetric hydrogen production rate

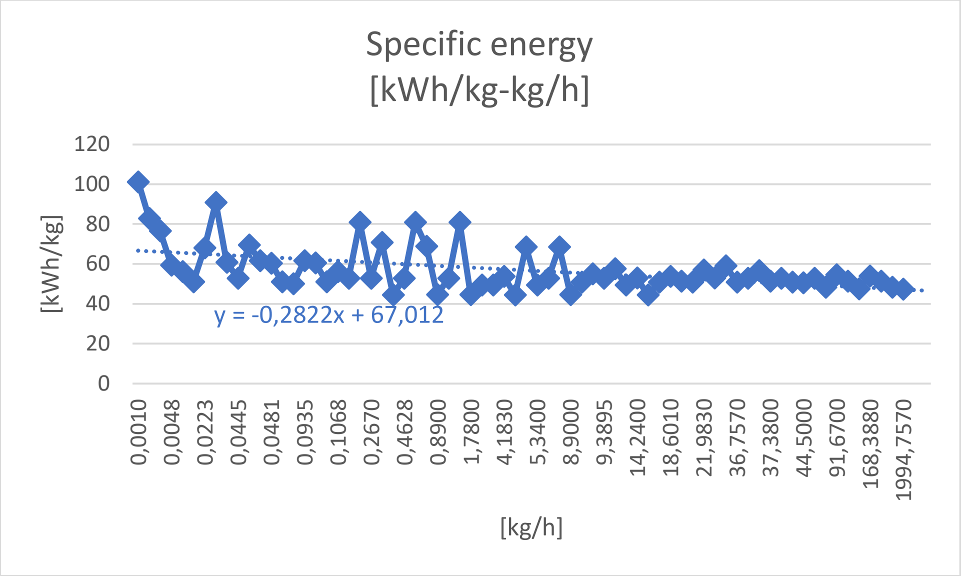

Figure 54 – Specific energy of PEM electrolysers as a function of the mass hydrogen production rate

In particular, the smallest electrolysers (0,011 – 6 Nm^3/h) present an average specific consumption of 5,72 kWh/Nm^3 (64,5 kWh/kg), while for the remaining devices it goes below 5,0 kWh/Nm^3, arriving to 4,53 kWh/Nm^3 (50,9 kWh/kg) for the biggest electrolysers.

The same observations done for the specific energy can be reported for the cell voltage and the conversion efficiency. The smallest devices are those with the highest voltage (2,34 V) and the lowest efficiency (63,3%), while the biggest ones present the lowest cell voltage (1,86 V) and the highest efficiency (77,7%). While an efficiency of 63,3% corresponds to the typical minimum value, it reaches almost the maximum with 77,7%.

In terms of durability, all the four classes of technologies are almost similar, presenting a system lifetime of 20 – 25 years and a stack lifetime which goes from 35.000 hours up to more than 80.000 hours.

Finally, it can be noted that in average the footprint increases of one order of magnitude with the hydrogen productivity.

Concluding, as for the alkaline electrolysers, the average values are useful to give a global idea of the operational parameters of PEM electrolysers, but it is important to know also the overall ranges (Table 5).

	Minimum	**Maximum**
Current density [mA/cm^2]	0	3000 (up to 20 A/cm^2)
Electrolyser specific energy consumption [kWh/Nm^3]	3,95	9,0
Cell voltage [V]	1,62	3,69
Electrolyser conversion efficiency (HHV)	39,0%	88,8%

Table 5 – Typical operating parameters of PEM water electrolysers

The typical operating current density goes from 0 mA/cm^2 up to 3000 mA/cm^2, but it can also reach values of 20 A/cm^2 [2]. Then, the minimum value of the specific energy is 3,95 kWh/Nm^3 while the maximum one is 9,0 kWh/Nm^3; however, the typical maximum is lower, around 5,5 – 6,0 kWh/Nm^3. Indeed, a value so high as 9,0 kWh/Nm^3 appears only once and is characteristic of a technology of Proton On-Site. From this value derive the upper and lower extremes of, respectively, the cell voltage and electrolyser conversion efficiency ranges (3,69 V and 39,0%), too. Moreover, also other values of specific energies belonging to this supplier are higher than the usual maximum one, but since it is the only one providing technology with really small productions, such as 0,011 Nm^3/h, it cannot be considered as representative as other suppliers. In addition, the lower performances can be related to the difficulty of producing devices for such small hydrogen flow rates; in fact, for hydrogen demands like 0,524 Nm^3/h and 1,05 Nm^3/h, the specific energy goes down to 6,18 kWh/Nm^3 and 5,83 kWh/Nm^3, respectively.

Even if the ranges of cell voltage an electrolyser efficiency are, respectively, 1,62 – 3,69 V and 39,0 – 88,8%, it can be said that typical maximum cell voltages are 2,2 V, while the efficiency is usually comprised between 60% and 82%.

2.2.4.3. Solid oxide electrolysis cells

2.2.4.3.1. Oxygen anion conducting solid oxide electrolysis cells

Solid oxide electrolysis cells (SOECs) are electrochemical devices requiring 1-200 kW of electric power and operating at high temperature (800-1000 °C). According to the following equation

$$\Delta G = \Delta H - T\Delta S$$

an increase of the cell operating temperature T produces a decrease of the Gibbs free energy change ΔG of the water splitting reaction and, thus, of the open circuit voltage. Moreover, a higher temperature leads to a decrement of the overvoltages related to the three transport phenomena. The first resulting benefit is the reduction of the cell voltage and, so, of the electric power required by the cell, leading to an improvement of water electrolysis efficiency. A second advantage is the possibility of using enough cheap non-platinum group materials as catalysts.

Solid oxide electrolyzers are, thus, the best devices, among the main three types described, with efficiencies arriving nearly to 100% with current densities of practical interest (around 1 A/cm^2). Such characteristics make them very promising in the fields of hydrogen production and electricity storage.

Given the high operating temperatures, water entering these electrolyzers, in the cathodic compartment, is in steam phase, in order to avoid liquid evaporation that would drop down the temperature of the device. The latent heat necessary to obtain steam from liquid water is supplied inside an evaporator, placed at the water entrance of the electrolyzer. Part of such thermal energy can be directly provided by the exiting oxygen and hydrogen flows, while the remaining quantity has to be supplied from the outside.

After its entrance in the cathode, water vapor undergoes a reduction reaction, giving hydrogen and O^{2-} ions as products:

$$H_2O + 2e^- \rightarrow H_2 + O^{2-}$$

Such ions, conducted by the electrolyte, go to oxidize in the anode, releasing oxygen and the electrons required by the cathodic half-reaction:

$$O^{2-} \rightarrow 2e^- + \frac{1}{2}O_2$$

As in the previous cases, the half-reactions result in the water splitting:

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

For what concerning the materials utilized, the ceramic electrolyte is the one that enables the use of such high operational temperatures and of a pressurized configuration.

Typically, it is made of Yttria-stabilized Zirconia (YSZ), a ceramic material in which an yttrium oxide, such as 8% moles of Y_2O_3, is added to the cubic crystal structure of the zirconium dioxide ZrO_2. This means that some Y^{3+} ions go to substitute an equal number of Zr^{4+} ions, creating vacant sites for O^{2-} ions This kind of electrolyte is not permeable to gases, so hydrogen and oxygen with a purity greater than 99.99% (in the dry form) can be obtained.

Regarding the electrodes, they are both ceramic and porous in order to allow an easy gas transport and at each pore there are both an electronic and an ionic phase, in order to generate a three phase boundary site.

The anodic compartment is a Mixed Ionic Electronic Conductor (MIEC) characterized by good electronic and ionic conductivities. The most used is the lanthanum-strontium-manganite oxide (LSM), which is chosen for its similarity with YSZ in terms of coefficient of volumetric modification with temperature. This avoids serious damages to the cell during great variations of temperature. The LSM structure is a perovskite one (ABO_3) with the general formula $La_{1-x}Sr_xMnO_3$, where *x* represents the doping level (lanthanum is doped with strontium). It has a cubic structure in which the vertices sites (A) are occupied by lanthanum and strontium atoms, while in the centre of the cube (B) there is the manganite atom. The result of the doping is an enhancement of the electronic conductivity, resulting from the extra holes in the valence band created by the replacement of some lanthanum atoms (valence 3+) with strontium ones (valence 2+).

The cathode is a cermet (ceramic and metallic) material, composed of a metallic nickel phase for the electrons' conduction and a support ceramic phase, for ions' transport, equal to the one of the electrolyte (YSZ), in order to overcome problems related to thermal expansion.

The structure of solid oxide electrolyzers can be planar or tubular, with steam feeding and hydrogen releasing in the inner part of the tube and oxygen production in the outer one. Planar SOECs, compared to the tubular ones, have some disadvantages consisting in a lower mechanical and thermal strength and in a higher need of a sealing material between anodic and cathodic compartments, aimed at avoiding mass transport between the two sides. However, planar cells are more attractive compared to the others, thanks to a better manufacturability, a higher electrochemical performance, deriving from the more uniform distribution of gas species and a clearer distribution of operational parameters such as temperature and current. Under this last aspect, instead, tubular cells necessitate of further investigations.

Finally, as in the previous configurations described, all the cells composing the stack are separated by an interconnector for the circulation of water vapor and the collection of produced gases. It is made of Crofer 22 APU, which has a similar volumetric modification with respect to YSZ. Such interconnector material contains chromium, an element that, with high temperatures, can evaporate and react with the oxygen present in the anode, creating a resistive layer of chromium oxides on its surface, causing an increment of the ohmic losses. Getters that take chromium away and a coating on the interconnector surface in contact with the anode can help in mitigating this problem.

Regarding the operating conditions, solid oxide electrolyzers typically operate with a voltage around 1.3 V, which is lower than the one of the alkaline and PEM devices (1.6-1.8 V), requiring, thus a lower amount of specific energy. In fact, the typical value is 3.2 kWh/ $Nm^3_{H_2}$, while the limit one (considering 1 V of open circuit voltage) is 2.5 kWh/ $Nm^3_{H_2}$. The operating pressure, instead, is a trade-off between the Nernstian effect, caused by the increased partial pressure of products and the economic saving deriving from a reduced need of subsequent hydrogen compression. The result of this balance is a value of around 50 bar.

Two important issues concerning solid oxide electrolyzers are related to the production of pure oxygen. They correspond to the Nernstian effect and the delamination of the cell at the interface between the anode and the electrolyte. The Nernstian effect derives from the high partial pressure of oxygen due to its purity. The delamination regards the anodic LSM layer in contact with the YSZ layer of the electrolyte and is present with high values of current density because this means high oxygen production rates. After this damage, no more contact between the two parts is present and the degradation of the cell is irreversible. In order to decrease the partial pressure of the oxygen and reduce both the Nernstian effect and the cell delamination, sweep gases such as helium and nitrogen are sent to the anode.

Another problem, instead, related to the high temperatures, is the enhancement of the mutual diffusion of electrolyte and electrodes materials across their interfaces. This can result in the formation of insulating layers that drop down the efficiency of the cell and in a rapid degradation of the technology.

In addition, the high temperatures are unable to make enough high the ionic conductivity of YSZ, which remains lower than the one of polymer and liquid electrolytes. Hence, the ohmic losses constitute a limiting factor for this kind of devices. In order to overcome the problem, the main approach is the thinning of the membrane: to date systems use membranes of around 100 µm of thickness, while a reduction until 20 µm is necessary, but done at the expense of the mechanical stability of the electrolyte. In order to not excessively weaken the cell from a mechanical point of view, anode-supported and cathode-supported cells have been developed. In the first case, the anode is thicker than the cathode and compensates for the loss in mechanical strength of the electrolyte, giving the necessary mechanical stability to the entire device. In the second situation the same thing is done by the cathode.

A last notable concern is given by the fact that, despite the choice of materials with similar thermal expansion coefficients, long turn-on and turn-off procedures are anyway necessary in order to not damage the device during the temperature changes.

Concluding, even if solid oxide electrolyzers represent a promising technology for clean hydrogen production purposes, the described problems make them a technology not yet so marketable, but which needs further studies and developments.

2.2.4.3.2. Proton conducting solid oxide electrolysis cells

During the last years, the research focused also on an alternative device with respect to traditional solid oxide electrolyzer. It is the proton-conducting solid oxide electrolysis cell, called "Proton-conducting electrolysis cell" (PCEC) or H-SOEC. The half-reactions in the electrodes are the same as in PEM devices, with steam feeding and oxygen release at the anodic side and hydrogen production in the cathode. In this case, differently from the oxide ion-conducting SOECs, the produced hydrogen is dry, giving the advantage of no need of subsequent separation from water.

This is a promising electrolysis technology (even more advantageous than traditional SOECs), thanks to its high efficiency and flexibility towards different operating conditions. Moreover, an interesting aspect is the possibility of working with relatively low temperatures (400-800

°C) with respect to the levels of traditional solid oxide electrolysis cells, ensuring, anyway similar values of open circuit voltage (around 1.15 V) and current density (0.75-1.5 A cm^{-2}). This is possible thanks to the fact that the proton is less massive than the oxygen anion, thus its mobility is facilitated, reducing the ohmic losses. In order to further reduce the electrolyte ohmic resistance, the most common approach is its thinning: with a reduction of its thickness to a few micrometres, a high electrochemical performance can be achieved, assuring a working temperature lower than 600 °C. The most widely-used method is the pulsed laser deposition (PLD): a laser beam strikes a target composed of the material of interest, vaporizing and depositing it on a substrate. Electrolyzers produced with a PLD-formed electrolyte provide a high performance, thanks to the reduced thickness of the electrolyte layer (reduced ohmic losses) and the low risk of crossover of produced gases.

Some experiments showed that the best materials for the electrolyte are yttrium-doped $BaZrO_3$ and $BaCeO_3$: they have both alone a high proton conductivity, but, if combined together, the result is an advantageous improvement of both mechanical and chemical stability.

Anyway, beside a high proton conductivity, this kind of materials presents a quite good electronic conductivity, too. This is a negative point because it involves current leakages through the electrolyte, leading to a decrease of both energy efficiency of the global system and faradaic efficiency of electrolysis, that describes the capacity of charge transfer of the system.

Concluding, even if proton-conducting electrolysis cells represent one of the most attractive technology in the hydrogen production field, before their commercialization additional studies are necessary about their operating conditions and long-term stability.

2.2.4.4. Molten carbonate electrolysers

Molten carbonate electrolyzers, with an operating temperature of 620-680 °C, are the second typology (still in a research phase) of high temperature electrolysis cells. Their cathode is typically made of Ni-based alloys, while in the anode nickel oxide operates as catalyst. The electrolyte is composed of molten carbonate suspended in a porous ceramic matrix: the necessity of maintaining the electrolyte liquid is the reason for the high temperatures. A peculiarity of these devices is the fact that, in order to carry on the reaction producing hydrogen, not only H_2O (in steam phase) is needed, but also CO_2.

Indeed, the main reaction in the hydrogen electrode (cathode) is the following steam electrolysis:

$$H_2O + CO_2 + 2e^- \rightarrow CO_3^{2-} + H_2$$

which produces hydrogen and CO_3^{2-} ions starting from H_2O, CO_2 and the electrons coming from the anode. Anyway, this is not the only one reaction happening in the cathodic side because two side reactions, both leading to the formation of carbon monoxide CO, can take place. The first one is the electrochemical reaction of carbon dioxide CO_2:

$$2CO_2 + 2e^- \rightarrow CO_3^{2-} + CO$$

Anyway, such a transformation is slower compared to steam electrolysis and so not expected to occur. The other possibility for the formation of CO is the reverse water gas shift:

$$CO_2 + H_2 \rightarrow H_2O + CO$$

The equilibrium of this last reaction is reached due to the operating temperature and the presence of nickel catalyst and leads to a real formation of CO.

Thus, at the exit of the cathode it is found a mixture of hydrogen, carbon monoxide and unreacted species (steam and carbon dioxide, which are supplied in excess to avoid cell starvation) that has to be treated in order to obtain the required hydrogen purity. Part of the final amount of hydrogen is then recirculated towards the cathodic inlet in order to maintain a reducing atmosphere inside the electrode, protecting the materials from the oxidation.

In the anode the following reaction occurs, forming CO_2, O_2 and the electrons necessary for the cathode:

$$CO_3^{2-} \rightarrow CO_2 + \frac{1}{2}O_2 + 2e^-$$

Moreover, the exiting CO_2 can be recirculated towards the cathode inlet, in order to avoid the necessity of an external source. Anyway, this option implies the presence of a system which separates carbon dioxide from oxygen.

The anodic half-reaction, together with the steam electrolysis, give the water decomposition reaction into hydrogen and oxygen:

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

Finally, for what concerns the state of the art of these devices, even if they are not on the market yet, they are seen as a promising technology for hydrogen production, given the stable and satisfying performances obtained in long term tests. In particular, it has been noticed that performances are higher if the concentration of hydrogen, carbon dioxide and steam is increased in the hydrogen electrode.

2.2.4.5. Photoelectrolysis

2.2.4.5.1. General features

The photoelectrolysis is a process occurring by means of the combination between the photovoltaic effect[7] and the electrolysis process with the aim of directly use the solar irradiance to split water molecules into hydrogen and oxygen. The related device is the *photoelectrochemical cell (PEC)*: it is composed by two electrodes in a watery solution containing the electrolyte, driving an electrochemical process. The difference with respect to classical electrolyzers is that at least one of the two electrodes is a semiconductor (photoanode and photocathode), used as a catalyst itself. When a n-type semiconductor is used, since it has an excess of electrons, it is a photoanode, while for the photocathode a p-type semiconductor, having a surplus of electron-holes, is required. If only one electrode is made up of a semiconductor material, the other one (counter-electrode) is made of metal.

The photoelectrolysis takes place only when the energy content of the incident photon is greater than or equal to the energy necessary to split a water molecule, that is (at NTP):

$$\Delta\bar{g} = 237.2\ \frac{kJ}{mol}$$

The previous value can be rewritten including the Avogadro constant, according to which the number of molecules contained in a mole of a certain substance is around $6.022\cdot10^{23}$, and the fact that 1 eV corresponds to $1.602\cdot10^{-19}$ J:

$$\Delta\bar{g} = \frac{237.2\ \left[\frac{kJ}{mol}\right]}{6.022\cdot10^{23}\left[\frac{molecules}{mol}\right]} = 3.94\cdot10^{-22}\frac{kJ}{molecule} = 2.46\ \frac{eV}{molecule}$$

This last value corresponds to the energy necessary to separate two electrons from the water molecule, so, considering a single electron, the minimum photon energy is

$$\Delta\bar{g} = 1.23\ \frac{eV}{e^-}$$

that corresponds to the minimum value of semiconductor bandgap.

Anyway, there are other aspects such as the ions' conduction through the electrolyte which require additional energy. Hence, the real necessary bandgap is comprised between 1.6 and

---

[7] The photovoltaic effect occurs when a material, typically a semiconductor one, absorbs sufficiently energetic photons, causing the excitement of some electrons, which move from the valence band to the conduction band leaving corresponding electron-holes in the valence band.

1.8 eV. This limits the fraction of solar irradiance able to drive the photoelectrolysis process to the lowest wavelengths, calculated according to the following equation:

$$\lambda = \frac{h \cdot C}{\Delta\bar{g}}$$

where

- h is the Planck constant;
- C is the speed of light;
- $\Delta\bar{g}$ is the energy bandgap.

Finally, it has also to be considered that the real amount of available solar irradiance depends on the atmospheric conditions and the relative position between the sun and the photovoltaic panels.

2.2.4.5.2. System configurations

The PEC cells have two main different configurations which include the presence of a semiconductor material in only one electrode (with the other one that is a classic electrode) or both. In addition, they can operate alone or coupled with a photovoltaic system.

For what concerns the photoelectrodes, one of the most considered materials is the titanium dioxide (TiO_2), with which the PEC water-splitting concept was proposed by Fujishima and Honda in 1972. This semiconductor is good for what concerns the stability in an aqueous environment and the cost, but it has a high rate of charge (electrons and electron-holes) recombination and a too high value of bandgap compared to what it is necessary. In fact, its band gap is around 3.2 eV: this means that the surplus is lost in form of heat, causing a decrease of the process efficiency. In addition, another disadvantage of metal oxides like TiO_2 is their limited light absorption, that, anyway, can be enhanced by means of a dye (dye-sensitized cells) or a hydrogenation process which turns the semiconductor colour from white to black.

However, the reaction with hydrogen is not able to enhance the charge separation. For this purpose, a junction between semiconductors is useful, since the difference between their Fermi levels[8] creates an inner electric field which helps in separating the charges. Anyway, since this electric field is too weak for promoting an effective migration of the photoexcited charges, noble metals (e.g. Ag, Pt, Pd, and Au) are additioned to the semiconductor, improving

---

[8] The Fermi level, in solid state physics, corresponds to the maximum energy level that an electron can occupy at a temperature corresponding to the absolute zero.

its catalytic activity. What is important in noble metals is their work function, which is the minimum energy necessary to extract an electron from a metal. It can be supplied by a photon, which transfers its own energy directly to the electron. If this energy is sufficient, the electron can go out from the material. Again, the difference between the work functions of noble metals gives rise to built-in electric fields useful for charge separation. So, in order to both improve the light absorption and the charge separation, the integration of multiple junctions of hydrogenated semiconductors in one heterostructure with different noble metals is an optimal solution. As an example, in the latest experiments, platinum (Pt) and silver (Ag) were used as noble metals.

In addition, a nano-structuring of the photoelectrodes is useful for lowering the possibility of electron-hole pairs recombination because it reduces the transfer times of such charge carriers. Anyway, it causes also significant disadvantages such as the reduction of both power conversion efficiency and durability of the devices.

Single photoelectrode

The configuration with a single photoelectrode can involve a photoanode coupled with a metal cathode or a photocathode coupled with a metal anode.

When using a photoanode, photons $h\nu$ incident on it with an energy greater than the semiconductor energy bandgap are absorbed. As a consequence, a flow of electrons e^- (going to the metal cathode) is created by their excitement from the valence band to the conduction band, leaving an electron-hole h^+ in the valence band for each electron excited:

$$2h\nu + semiconductor \rightarrow 2h^+ + 2e^-$$

The holes move to the photoanode-electrolyte interface to react with water, releasing oxygen O_2 and protons H^+:

$$2h^+ + H_2O \rightarrow \frac{1}{2}O_2 + 2H^+$$

These two reactions, globally, give the following one

$$H_2O + 2h\nu \rightarrow 2e^- + 2H^+ + \frac{1}{2}O_2$$

in which the separation of charge $2e^- + 2H^+$ is evident. It generates a voltage gradient that is the driving force for protons migration from the photoelectrode to the counter electrode. Here, the reduction of protons by means of the electrons coming from the photoanode produces hydrogen:

$$2H^+ + 2e^- \rightarrow H_2$$

Hence, the global reaction of the photoelectrolysis process is:

$$H_2O + 2h\nu \rightarrow H_2 + \frac{1}{2}O_2$$

If, instead, the cell design involves a photocathode coupled with a metal anode, the electrons excited by the photons go to reduce water at the interface between the photocathode and the electrolyte, according to the following reaction:

$$h\nu + 2e^- + 2H_2O \rightarrow H_2 + 2OH^-$$

So, the cathode, besides hydrogen, produces also OH^- ions which go through the electrolyte towards the anode. Here, their oxidation occurs, producing water and oxygen:

$$2OH^- \rightarrow 2e^- + \frac{1}{2}O_2 + H_2O$$

Anyway, photoelectrolysis with a single photoelectrode is disadvantageous because an additional voltage is needed to carry on the process when the semiconductor bandgap is not appropriated for water splitting reaction potential or when a delay in the electron-hole recombination is necessary. Since the additive voltage has to be supplied from the external, extra costs are required.

Dual photoelectrode

In order to solve the problems related to the limited fraction of absorbed solar spectrum and the potential needed for the water splitting, different semiconductor materials are used. Semiconductors with high and low bandgaps are combined in a tandem design, which involves a n-type semiconductor as photoanode and a p-type semiconductor as photocathode. The resulting device is the *n/p PEC cell*, whose solar to hydrogen (STH) efficiency is higher compared to the one of devices with a single photoelectrode, but still too low (below 1.0%) to meet expectations. The photovoltages of the electrodes are summed together, in order to obtain a value suitable for water splitting. This is advantageous because materials with lower bandgaps can be utilized to absorb a larger portion of sunlight corresponding to the visible and near-infrared regions of the solar spectrum.

The tandem configuration can have the photoelectrodes physically separated or combined into a monolithic cell. The first option is, in turn, divided into two possibilities: one with the photoelectrodes side by side and, so, illuminated by the whole solar spectrum (illumination mode P) and one, more efficient, with each photoelectrode facing the other (illumination mode T). Both the cases need a glass substrate with a conducting layer: with the illumination mode P, it is placed on each semiconductor, while in the illumination mode T only one layer is needed between the electrodes, but it has to be transparent.

The monolithic cell needs a metal transparent conducting oxide (TCO) substrate between the two photoelectrodes. It can be single, with the photoanode deposited on one side and the photocathode on the other side, or it can happen that both the photoelectrodes are deposited on their own substrates, then electrically connected. Moreover, for both the technologies involving separated photoelectrodes with illumination mode T and monolithic cell, the semiconductor with the highest bandgap has to be placed first (in front of the sunlight), in order to enable less energetic photons to reach the other semiconductor.

Finally, by the use of mirrors, these devices can be illuminated by sunlight on both sides, but with higher costs and design complexity.

Photoelectrochemical and photovoltaic systems

An alternative configuration is a tandem design composed by the photoelectrochemical cell coupled with photovoltaic cells (PEC/PV tandem design), which are able to offer to the photoelectrodes the photovoltage necessary to have the electrolysis process driven only by the sunlight. This kind of configuration relaxes the restrictions on the semiconductors' material, but it is important to pay attention to the harmonization of the solar light absorption between PV and PEC cells. The most diffused device is a monolithic one, composed by a p-type gallium indium phosphide (p-$GaInP_2$) photocathode, absorbing the visible part of the solar spectrum, coupled with a GaAs p/n-junction, absorbing the near-infrared part of the spectrum transmitted by the photocathode. Anyway, even if this kind of system seems to be promising, it is still too expensive and not ready for the market level.

In alternative, instead of classical photovoltaic panels, solar concentrators and photovoltaic thermal systems (PV/T) can be used. The first ones have a great potential of large-scale applications, leading to a reduction of the necessary amount of materials and related costs. The second ones are hybrid devices which combine photovoltaic cells and solar thermal collectors. In this way, they are able to convert solar radiation into both electrical and thermal energy. A PV/T system operates together with a hybrid reactor (driving the photoelectrolysis) and a solar spectral splitter in the following way: the solar splitter separates the incident sunlight according to the solar energy absorbing characteristics of the hybrid reactor's photocathode, directing towards it the fraction of solar spectrum that it is able to utilize and sending the rest to the PV/T system. This latter one produces electricity aimed to feed the hybrid reactor and the heat recovered by its cooling down can be a valuable product of the whole system or it can be sent to the reactor when its operating temperature is higher than the environmental one.

According to the quantity of available sunlight, the reactor can operate in two different modes: when the light is not sufficient (during the night or cloudy days) it uses electricity to produce gaseous H_2, while, when it is allowed by the sunlight, H_2 is produced by means of photoelectrolysis.

Concluding, even if hydrogen production via photoelectrolysis is considered as a promising process, it still needs further improvements of the overall efficiency, which is very low (under 10%). Indeed, the main objectives are represented by a STH efficiency of at least 10%, with a 10-year lifetime and a hydrogen production cost of \$2-\$4 per kg.

2.2.5. Microbial electrolysis cells

Microbial electrolysis cells (MECs) are devices which exploit a low electric power input in order to generate hydrogen from the microbial decomposition of organic compounds. These last ones can be those contained in wastewater, for the treatment of which MECs are particularly attractive. Like the common electrolytic cells, microbial electrolysis ones are composed by an anode and a cathode separated by an ion exchange membrane (IEM). The electrodes are preferably contained in two different chambers rather than in a single one, in order to obtain high-purity hydrogen. One electrode (typically the anode) or both contain an electroactive biofilm which catalyzes the oxidation of organic pollutants that are inside the wastewater, extracting H^+ ions and electrons and producing CO_2 as a by-product. Both ions and electrons are conducted towards the cathode, where, using the external electric input, H^+ ions are reduced to H_2 gas. Many tests on this kind of devices have been done at a laboratory scale, giving satisfying results. In fact, compared to other wastewater treatment systems such as the activated sludge pool (ASP)[9], microbial electrolysis cells necessitate a lower energy consumption. Anyway, despite the good performance obtained in laboratory, the usage of these devices at an industrial scale is still not so convenient because of the high capital cost. It derives from the materials used in the cathode: usually they are based on carbon, such as graphite and carbon felts which are functional but very expensive. In addition, the production

---

[9] The activated sludge pool biologically treats non-settleable substances present within the wastewater converting them, by means of blowed oxygen, into a settleable sludge that can be removed.

of graphite and virgin carbon felts implies a large energy consumption, fact that raises doubts on the effective positive environmental impact of MECs.

Finally, microbial communities used as biocatalyst in these devices significantly affect the overall performance of hydrogen production, so their behaviour has to be kept under control in order to improve the MECs efficiency.

3. Economic analysis of alkaline and PEM electrolysers

The aim of the economic analysis is to give an overview of the variation of the hydrogen production cost depending on the level of productivity, and thus the size, of the electrolytic systems. It was performed hypothesizing a continuous operation of the systems throughout the year and the following cost assumptions.

The Capital Expenditure (CAPEX) and Operating Expenditure (OPEX) were composed as follows:

1. Capital Expenditure (CAPEX)
    a. Plant construction
        i. Civil works
        ii. Electrolyser
        iii. Auxiliary components
    b. Stack replacement
2. Operating Expenditure (OPEX)
    a. Electricity
    b. Feed water
    c. Maintenance
    d. Workers

<u>CAPEX</u>

The Capital Expenditure was composed by the costs related to the plant construction, before it gets into operation, and those due to the stack replacement. This last cost item derives from the fact that the typical system operational lifetime, as already seen in the technical analysis, is between 20 and 25 years, while the stacks durability is much shorter, so they need to be replaced at least once during the whole system lifetime. The plant construction costs divide into three voices: civil works, for which a representative value of 150 € per square meter of plant has been utilised, electrolyser and auxiliary components. In most cases, the costs of the electrolyser and auxiliary components were calculated basing on average specific values coming from literature articles, since many suppliers do not provide any economic information regarding their products. In particular, a specific cost of 340 €/kW was considered for the alkaline electrolysers, while the analysis of PEM devices was based on a value equal to 420 €/kW. The only exception was constituted by the PEM electrolysers produced by Teledyne Energy Systems, since in this case the real prices were available: the three electrolysers belonging to the TITAN HMXT SERIES were analysed with specific costs of 1120 €/kW (HXMT-50), and 686 €/kW (HXMT-100 and HXMT-200), while the two TITAN EL electrolysers with 539 €/kW (EL-1000) and 475 €/kW (EL-1400).

For what concerning the auxiliary components, their cost was derived from specific prices ranging between 700 €/kW and 1700 €/kW for the alkaline field and between 1000 €/kW and 1500 €/kW for the PEM field. In particular, the two ranges were subdivided as follows (Table 6):

Hydrogen flow rate range	**Alkaline**	**PEM**
< 10 Nm^3/h	700 €/kW	1000 €/kW
10 – 100 Nm^3/h	1000 €/kW	1200 €/kW
100 – 1000 Nm^3/h	1300 €/kW	1300 €/kW
> 1000 Nm^3/h	1700 €/kW	1500 €/kW

Table 6

Again, for Teledyne Energy Systems were considered different values: 2879 €/kW and 1764 €/kW for the TITAN HMXT SERIES and 1386 €/kW and 1222 €/kW for the TITAN EL SERIES. Moreover, the specific cost of the overall systems was made available also by other suppliers, in particular: Cummins (2000 €/kW for the alkaline systems and 800 – 1200 €/kW for the PEM ones), H-Tec Systems GmbH (1500 €/kW for its PEM systems) and H2B2 (1000 €/kW for its PEM systems).

Finally, the cost for the stack replacement was considered equal to the cost for the first electrolyser purchase.

The economic calculations were performed also under the hypothesis of a non-repayable share equal to 20%, thus lowering the CAPEX value. However, the resulting benefit was not so considerable, since the hydrogen cost generally decreased only by 0,1 – 0,2 €/kg.

<u>OPEX</u>

The Operating Expenditure has four contributions: the cost of electricity needed to feed the electrolytic system, the cost of the feed water that must be split into hydrogen and oxygen, the plant maintenance cost and the cost of workers. Concerning the electricity cost, two situations were evaluated: in the first case the it was produced by a non-renewable plant, while in the second one the electricity came from renewable sources. For the non-renewable scenario, the electricity cost resulted from an average of the Single National Price of the last years reported by *Gestore Mercati Energetici* (52 €/MWh), increased by 200% to take into account possible risks. The same average value was then used as a reference for the renewable scenario, but in this case it was increased by 300 €/MWh in order to account for the loss of incentives resulting from the fact that the renewable electricity produced is not injected into the grid but it is fed into the electrolyser. The feed water cost was taken equal to 3,58 €/m^3 as reported by the *Autorità d'ambito Torinese 3* for water of industrial use with full rate. The expenditure for the maintenance of the plant was considered as 3% of the plant construction costs. Finally, the cost of workers was calculated considering an administration employee (65.000 €/year) and two ordinary maintenance workers (50.000 €/year each).

Taxes

The EBIT (Earnings Before Interests and Taxes) was taxed with a tax rate equal to 27,9%, which is comprehensive of the corporate income tax and the regional tax on productive activities.

Returns

A water electrolysis system presents two mainly economic returns, associated with the sale of the hydrogen and oxygen produced. The oxygen selling price was maintained fixed at 0,07 €/kg, while the hydrogen cost was varied: it was chosen as the final hydrogen cost the minimal one allowing to obtain a positive Net Present Value (NPV) at the end of the system operational lifetime. The Net Present Value is an economic indicator which enables to establish the value of future payments at present: a positive NPV means that the projected earnings from an investment exceed the anticipated costs. For this economic analysis, the NPV was calculated assuming a Weighted Average Cost of Capital (WACC) equal to 6%.

All the obtained hydrogen costs were associated to an Internal Rate of Return (IRR), a measure of an investment profitability, equal to 6% or 7%. Fixing then a target value equal to 8% for the rate of return of capital, it emerged that this was obtained incrementing the hydrogen cost typically of 0,1 – 0,2 €/kg.

According to the hydrogen cost, two different types of pay back time were calculated: one is based on the Net Cash Flow (NCF), while the other one accounts for the Discounted Net Cash Flow (DCF). The Net Cash Flow is given by the difference between the total cash in and the total cash out, while the Discounted Net Cash Flow takes into account the loss of value that the NCF will have in the future. Both NCF and DCF are negative during the period of construction, given the absence of returns, while with a profitable investment they become mostly positive (except in correspondence of the stacks replacement), since earnings are produced. For what was said, the DCF is always lower than the corresponding NCF meaning that the earnings calculated on the basis of the value that money is thought to have in the future are lower than those calculated on the basis of the present value. As a consequence, the pay back time associated to the DCF, which is a more realistic indicator, is longer than that corresponding to the NCF.

Electrolysers comparison

The economic comparison of the electrolysers was conducted in order to assess which are the most competitive technologies for the hydrogen selling. The economic analysis follows the same line as the technical one, comparing alkaline and PEM electrolysers by means of the subdivision into the same four groups basing on similar hydrogen flow rates. However, a detailed evaluation of the first group (up to 10 Nm^3/h) is not reported because while the most common costs (for hydrogen demands higher than 10 Nm^3/h), expressed as expenditure per kilogram of hydrogen, came out comprised between 9 €/kg and 15 €/kg, already in the set of electrolysers ranging between 10 Nm^3/h and 100 Nm^3/h, in some cases they increased up to 35 €/kg. Hydrogen demands lower than 10 Nm^3/h presented costs much higher than 35 €/kg, so not competitive.

For the electrolysers for which it is reported not only the nominal value of hydrogen flow rate, but the entire production range, the economic analysis was performed basing on the upper extreme. Thus, in the following description these technologies will be taken into consideration only in relation to their maximum production capacity.

Range 10 – 100 Nm^3/h

The Table 1 of Appendix reports the main economic results for both alkaline and PEM electrolytic systems producing between 10 Nm^3/h and 100 Nm^3/h of hydrogen. For each system the following values are reported:

- the total CAPEX (comprehensive of civil works, first purchase of the electrolyser and subsequent replacement(s), purchase of auxiliary components)
- the minimum hydrogen cost necessary to obtain a positive Net Present Value considering both non-renewable and renewable electricity sources
- the Internal Rate of Return

- the Net Present Value
- the Pay Back Time referred to the Net Cash Flow
- the Pay Back Time referred to the Discounted Net Cash Flow
- the hydrogen price corresponding to a target value of Internal Rate of Return equal to 8%.

Under the assumptions done for the electricity price, the hydrogen cost in the case of renewable electricity is roughly double than the value associated to non-renewable energy. In order to avoid repetitions, the analysis will be thus conducted basing only on the hydrogen cost deriving from non-renewable energy sources. Moreover, not only for this set of electrolysers, but also for the next ones, the costs deriving from renewable electricity are really excessive to be considered competitive with those related to non-renewable electricity production.

For hydrogen flow rates around **10 - 15 Nm^3/h**, there are various alkaline and PEM electrolysers available as possible options. The alkaline technologies are: HySTAT – 15-10 of Cummins, McLyzer 10 – 30 and Piel H of McPhy and the technologies for 10 Nm^3/h and 16 Nm^3/h of Pure Energy Centre PEC. Whereas, the PEM electrolysers considered are: E10 of Areva H2Gen GmbH, E10 of CETH2, C10 of Diamond Lite S.A., Merrimack of Giner ELX, EL10N of H2B2, gEl 10-300 PEM MD of iGas energy GmbH, C10 f Nel and HMXT-200 of Teledyne Energy Systems. The cost of the hydrogen produced by these electrolysers is higher compared to that characteristic of electrolysers with a bigger size. Indeed, there are no values which go under 20 €/kg: the most economic options are the two **PEM** electrolysers E20 of **Areva H2Gen GmbH** and **CETH2**, with **20,4 €/kg**, followed by EL20N of H2B2 with 20,6 €/kg. Moreover, many of the remaining technologies present hydrogen selling costs which are higher than 30 €/kg.

For hydrogen demands of **20 Nm^3/h**, the hydrogen cost is comprised between **19,2 €/kg** and 23,4 €/kg. In particular, the lowest price is associated to two electrolysers: the **alkaline McPhy** McLyzer 20-30 and the **PEM Giner ELX** Merrimack. All the remaining technologies producing 20 Nm^3/h of hydrogen operate with a production cost higher than 20 €/kg, except for the alkaline device of Pure Energy Centre PEC (19,6 €/kg).

Considering hydrogen requests of **30 Nm^3/h**, the suppliers involved are: GreenHydrogen.dk Aps (A30) and Pure Energy Centre PEC (32 Nm^3/h device) for the alkaline options and CETH2 (E30), Diamond Lite S.A. (C30), Giner ELX (Merrimack), H2B2 (EL30N), iGas energy GmbH (gEl 30-300 PEM MD) and Nel (C30) for the PEM options. The most convenient system is a **PEM** one, provided by **Giner ELX**, with **15,6 €/kg**. This price is similar to that characteristic of the hydrogen produced by the alkaline GreenHydrogen.dk A,ps A30 electrolyser (15,9 €/kg), while all the other values are a little higher even if they never exceed 18,3 €/kg.

Considering a production level of **40 Nm^3/h**, only an alkaline electrolyser and two PEM ones can be compared. The first is that of **Pure Energy Centre PEC** producing 42,62 Nm^3/h, while the other two are E40 electrolysers of Areva H2Gen GmbH and CETH2. The most competitive is the **alkaline** system, producing hydrogen at **14,5 €/kg**, however, both the PEM options do not differ much, with 15,1 €/kg.

In the case of **50 Nm^3/h**, the only two possibilities are both **PEM** electrolysers. Between the two, the most economic choice is **Giner ELX** Allagash electrolyser (**12,8 €/kg**), since the other one, H-Tec Systems GmbH ME 100/350 device, produces hydrogen with a cost of 15,4 €/kg.

For hydrogen demands of **60 Nm^3/h**, the range of choice is wider, especially in the PEM field. The alkaline possibilities are HySTAT-60-10 of Cummins and A60 of GreenHydrogen.dk Aps, while the suitable PEM systems correspond to E60 of Areva H2Gen GmbH and CETH2, EL60N of H2B2, Gel 60-300 PEM MD of iGas energy GmbH andEL-1000 of Teledyne Energy Systems. In order to obtain hydrogen at the lowest price, the optimal choice is the **alkaline** system of **GreenHydrogen.dk Aps** (**12,35 €/kg**), although most of the remaining technologies are not so expensive, too, since the hydrogen is produced at a cost of maximum 13,7 €/kg, except for that of Teledyne Energy Systems (17,2 €/kg).

Finally, for hydrogen demands higher than 60 Nm^3/h, the available options are less numerous. Indeed, the only two solutions are the **PEM** EL-1400 electrolyser of **Teledyne Energy Systems**, which produces **78 Nm^3/h** of hydrogen at a cost of **15,9 €/kg** and the **alkaline** A90 device of **GreenHydrogen.dk Aps**, delivering **90 Nm^3/h** of hydrogen at the significant lower price of **11,5 €/kg**.

The following three graphs (Figures 55, 56 and 57) summarize the variation of the hydrogen costs identified as lowest ones as a function of the productivity and the respective system size.

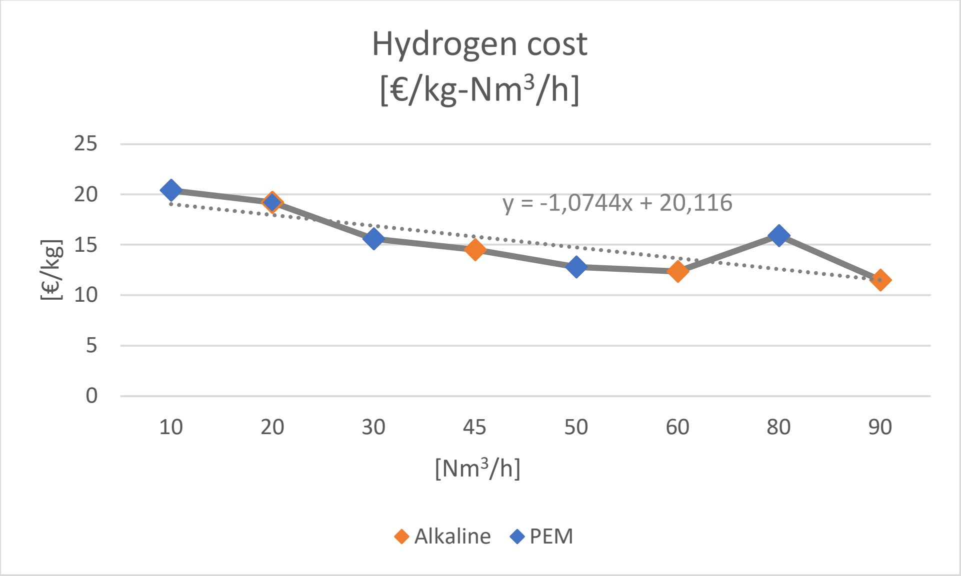

Figure 55

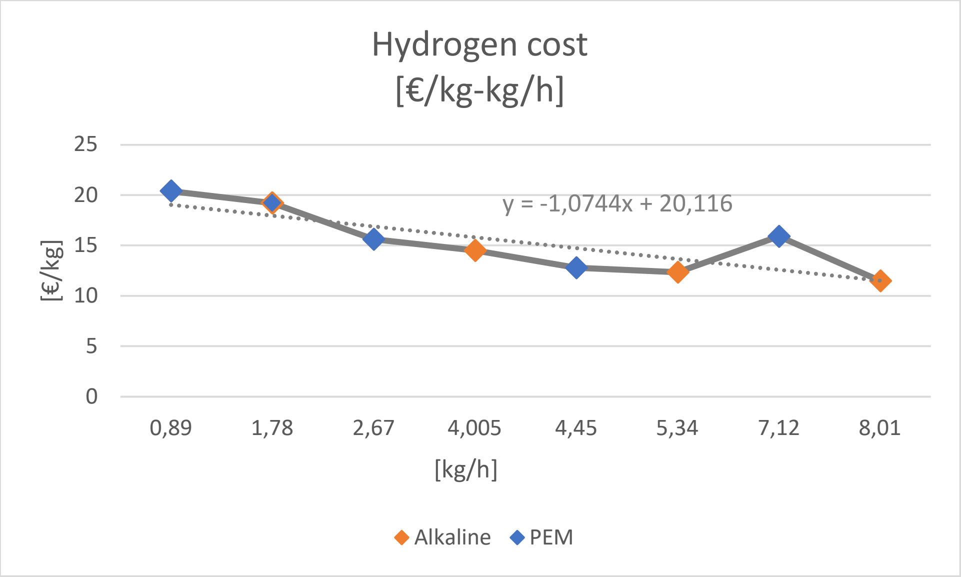

Figure 56

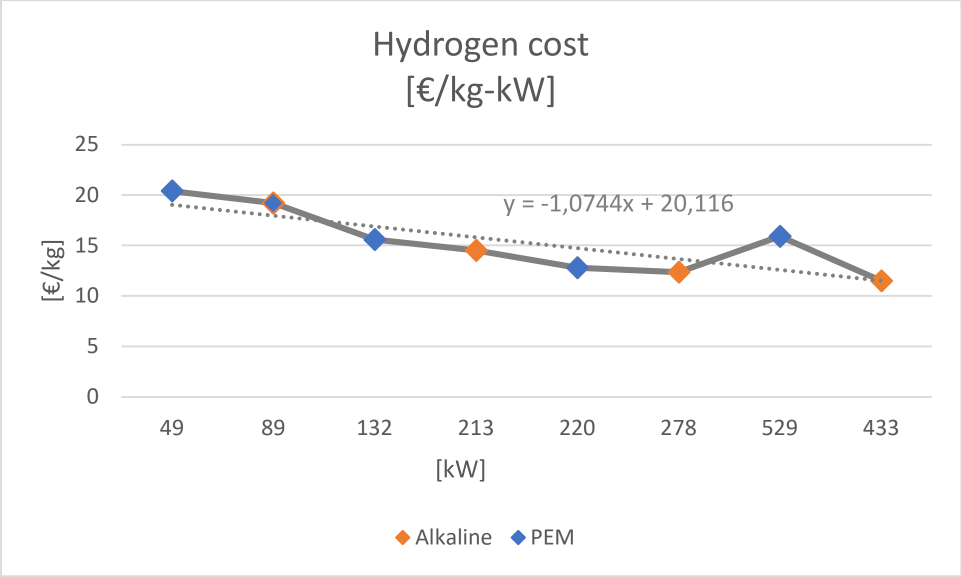

Figure 57

In general, the hydrogen cost decreases with the increasing of the productivity (size), except in the case of 80 Nm^3/h, characterised by a cost increment due to the system belonging to Teledyne Energy Systems. All the hydrogen costs are associated to an internal rate of return equal to 6 – 7%, while, imposing a target value equal to 8%, all the prices rise up by 0,05 – 0,3 /kg.

The following table (Table 7) shows the variation of the total CAPEX depending on the system productivity and the type of technology.

	Alkaline CAPEX	**PEM CAPEX**
10 – 15 Nm^3/h	Min.: 106.000 € (Pure Energy Centre PEC) Max.: 154.000 € (McPhy)	Min.: 71.000 € (Giner ELX) Max.: 323.000 € (Teledyne Energy Systems)
20 Nm^3/h	Mn.: 118.000 € (McPhy) Max.: 141.000 € (Pure Energy Centre PEC)	Min.: 140.000 € (Giner ELX, H2B2) Max.: 266.000 € (Areva H2Gen GmbH, CETH2)
30 Nm^3/h	Min.: 181.000 € (GreenHydrogen.dk Aps) Max.: 229.000 € (Pure Energy Centre PEC)	Min.: 210.000 € (Giner ELX) Max.: 398.000 € (CETH2)
40 Nm^3/h	Unique: 279.000 € (Pure Energy Centre PEC)	Unique: 532.000 € (Areva H2Gen GmbH, CETH2)
50 Nm^3/h	-	Min.: 348.000 € (Giner ELX) Max.: 755.000 € (H-Tec Systems GmbH)
60 Nm^3/h	Min.: 307.000 € (GreenHydrogen.dk Aps) Max.: 696.000 € (Cummins)	Min.: 457.000 € (H2B2) Max.: 1.000.000 € (Teledyne Energy Systems)
80 – 90 Nm^3/h	479.000 € (GreenHydrogen.dk Aps)	1.300.000 € (Teledyne Energy Systems)

Table 7

Looking at the table above, it is clear that investment costs of alkaline systems are generally lower than those of PEM technologies. Moreover, for hydrogen flow rates going from 20 Nm^3/h up to 60 Nm^3/h, those systems producing hydrogen at the lowest price are the same that present the lowest investment cost.

All these investment costs are recovered, on average, within 11 – 12 years considering the pay back time referred to the net cash flow and within 18 – 19 years basing on the pay back time referred to the discounted net cash flow. Incrementing the hydrogen cost of around 3 €/kg, both the pay back times reduce up to 2 – 4 years (this is valid also for the bigger electrolysers described below). However, when the starting value is already higher than 18 – 20 €/kg, a further increment is excessive.

Range 100 – 1000 Nm^3/h

The Table 2 of Appendix reports the main economic results for both alkaline and PEM electrolytic systems producing between 100 Nm^3/h and 1000 Nm^3/h of hydrogen.

Considering a hydrogen flow rate of **100 - 160 Nm^3/h**, various alkaline and PEM systems can be considered. In particular, the alkaline options are: Cummins HySTAT – 100-10, McPhy McLyzer 100-30, Nel A150 and AC150. Whereas, PEM systems are: H2B2 EL100N, iGas energy GmbH gEl 100-1250 PEM MD and gEl 160-1250 PEM MD, ITM Power HGas1SP, Nel M100 and MC100 and Giner ELX Allagash. The lowest hydrogen cost, **9,7 €/kg**, is characteristic of the **alkaline Nel** A150 electrolyser, while the other prices range between 10,9 €/kg (Nel AC150) and 12.3 €/kg (Cummins HySTAT 100 – 10) for the alkaline systems and between 10.7 €/kg (Giner ELX Allagash) and 12,8 €/kg (ITM Power HGas1SP) for the PEM ones.

For hydrogen flow rates of **200 Nm^3/h**, the involved suppliers are: McPhy (McLyzer 200-30) for the alkaline field and Areva H2Gen GmbH (E200), Diamond Lite S.A. (M200), Frames (1 MW system), H-Tec Systems GmbH (ME 450/1400), H2B2 (EL200N), ITM Power (HGas2SP), Nel (M200, MC200 and MC250) and Giner ELX (Allagash and GenFuel 1 MW system). This time the lowest hydrogen costs come from two **PEM** electrolysers, both of **Giner ELX**: Allagash (**9,6 €/kg**) and GenFuel 1 MW system (9,7 €/kg).

Hydrogen demands around **300 Nm^3/h** can be covered by the following suppliers: **Nel** (A300 and AC300) for the alkaline part and iGas energy GmbH (gEl 320-1250 PEM MD) for the PEM part. As most of the times, the most convenient hydrogen price belongs to the **alkaline** technology, with **8,9 €/kg**. The costs associated to the other technologies are, instead, higher than 10 €/kg.

The penultimate values of hydrogen flow considered for this group of electrolysers is that equal to **400 – 500 Nm³/h**. The alkaline electrolysers available for this values are only two: McLyzer 400-30 of McPhy and A485 of **Nel**. Among the PEM electrolyser there are instead much many options: M400 of Diamond Lite S.A., the 2 MW system of Frames, EL460N and EL580N of H2B2, HGas3SP of ITM Power, M400, MC400 and MC500 of Nel and HyLYZER – 500 – 30 of Cummins. Like in the previous range, for the hydrogen lowest price the choice falls on the **alkaline** system, which produces hydrogen at **8,6 €/kg**. For the other alkaline electrolyser, this value is a bit higher (9.3 €/kg), but however lower than all those characteristic of PEM electrolysers, higher than 10 €/kg.

Finally, the remaining technologies are those suitable for hydrogen demands of **580 – 970 Nm³/h**. They are mainly alkaline systems, while only one is a PEM electrolyser. The alkaline options are: IHT Industrie Haute Technologie S.A. Type S-556 electrolyser, McPhy Augmented McLyzer 800-30 and Nel A1000, while H2B2 EL580N is the PEM electrolyser. Once again, all the hydrogen costs are around 10 €/kg, except for that of the **alkaline Nel** A1000 electrolyser (**8,4 €/kg**).

All the hydrogen costs representative of the different hydrogen flow rates are reported in the following three graphs (Figures 58, 59, 60) as a function of the hydrogen flow rate and of the system size. From them, it can be noticed that increasing the level of the productivity, the hydrogen cost decreases.

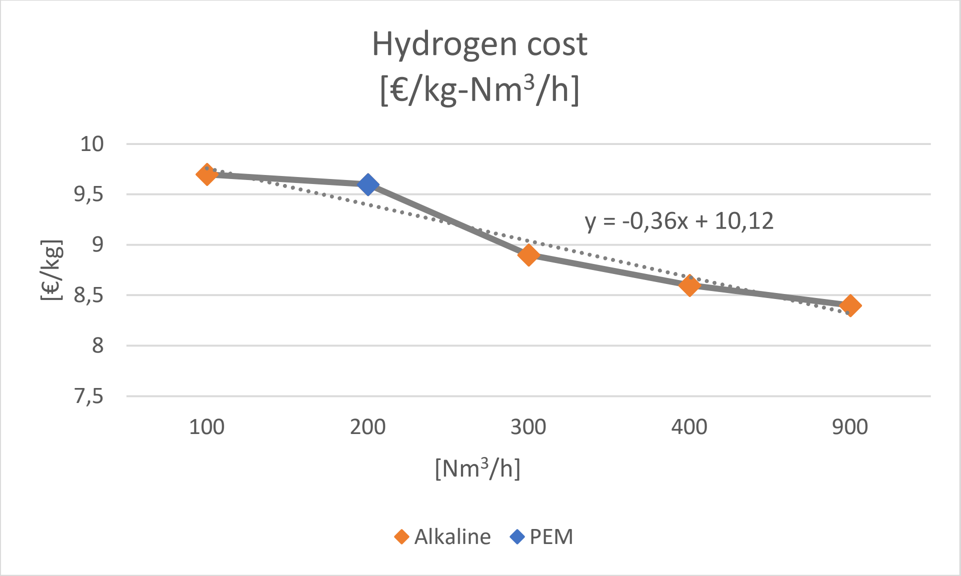

Figure 58

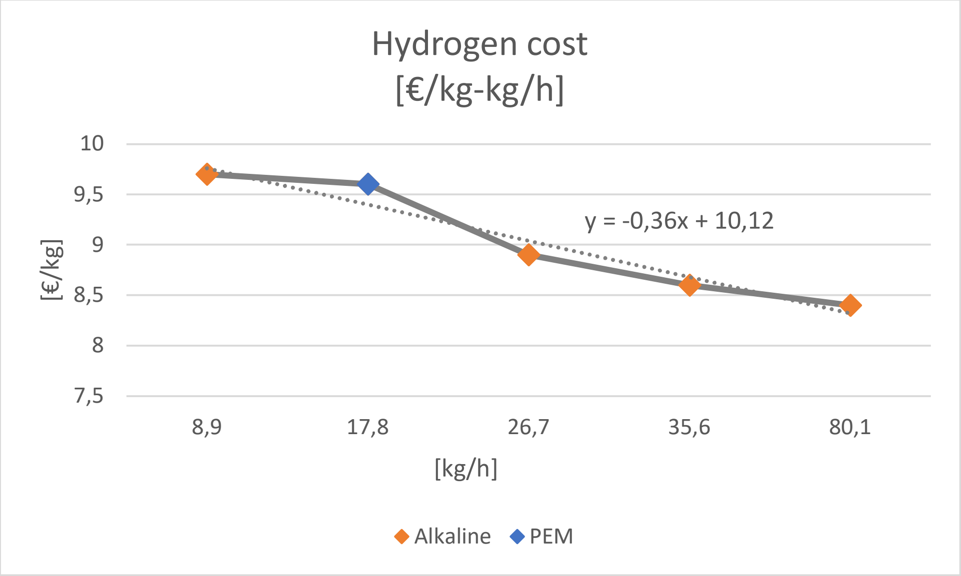

Figure 59

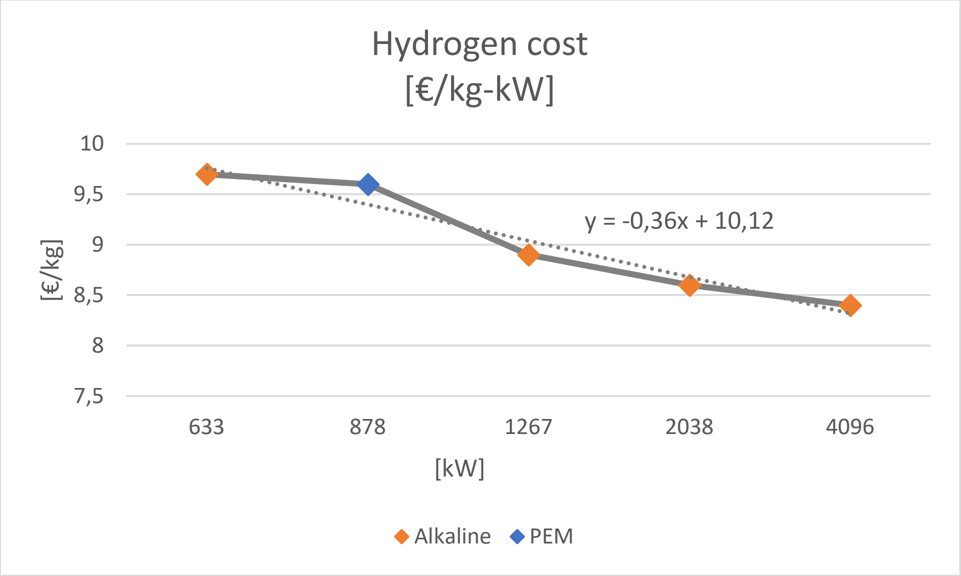

Figure 60

The typical investment costs of this set of electrolysers can be subdivided as follows (Table 8):

	Alkaline CAPEX	**PEM CAPEX**
100 – 160	Min.: 800.000 € (McPhy) Max.: 1.200.000 € (Nel)	Min.: 700.000 € (H2B2, Giner ELX) Max.: 1.400.000 € (iGas energy GmbH)
200	Unique: 1.500.000 € (McPhy)	Min.: 1.500.000 € (H2B2, Giner ELX) Max.: 3.300.000 € (H-Tec Systems GmbH)
300	Min.: 2.000.000 € (Nel) Max.: 2.300.000 € (Nel)	Unique: 2.800.000 € (iGas energy GmbH)
400 - 500	Min.: 2.900.000 € (McPhy) Max.: 3.300.000 € (Nel)	Min.: 2.300.000 € (H2B2)

		Max.: 4.100.000 € (Nel, Cummins)
580 - 970	Min.: 6.300.000 € (IHT Industrie Haute Technologie S.A.) Max.: 6.600.000 € (Nel)	Unique: 4.100.000 € (H2B2)

Table 8

For hydrogen flow rates between 100 Nm^3/h and 500 Nm^3/h, the minimum values of PEM investment costs are equal or lower than those of alkaline systems, but the maximum ones are generally much higher. For the range 580 – 970 Nm^3/h, the difference between alkaline and PEM systems CAPEX is due to the fact that the alkaline technologies involved produce between 760 Nm^3/h and 970 Nm^3/h of hydrogen, while the unique PEM system is characterised by a production of 580 Nm^3/h and thus present a lower investment cost.

Moreover, for hydrogen flow rates of 200 Nm^3/h and 300 Nm^3/h, the same electrolysers presenting the lowest hydrogen cost are those which require the lowest investment cost.

Range 1000 – 22413 Nm^3/h

Finally, the last set of electrolysers (Appendix, Table 3) is that for hydrogen demands higher than 1000 Nm^3/h.

Starting from hydrogen demands of **1000 Nm^3/h**, they can be satisfied by three **PEM** electrolysers: **Cummins** HyLYZER – 1000 – 30, Frames 5MW module and Giner ELX GenFuel 5MW. Among the three possibilities, that provided by Cummins produces hydrogen at the lowest price (**9,65 €/kg**), while the other two prices correspond to 10,2 €/kg (Frames) and 11,2 €/kg (Giner ELX).

For hydrogen requirements around **2000 Nm^3/h**, **Thyssenkrupp Uhde Chlorine Engineers GmbH** 10 MW module (alkaline) and Frames 10 MW and ITM Power HGasXMW (both PEM) electrolysers are taken into account. The resulting hydrogen cost is lower from the **alkaline** technology. Indeed, it can produce hydrogen at **9,7 €/**, while Frames and ITM Power systems arrive to a minimum of 10,1 €/kW and 10,6 €/kW, respectively. Again, all the pay back times are similar (11,5 – 12,5 years for PBY (NCF) and 18 – 19.5 years for PBT (DCF)), but, considering as before a hydrogen cost of 12 €/kg, they arrive to minimal values of around 2,5 years (PBT (NCF)) and 3 years (PBT (DCF)) for Nel, while the remaining ones are equal to maximum 6 years (PBT (DCF) of ITM Power). With 15 €/kg, the major improvements of pay back times are for the PEM systems, characterised by decrements up to 3 years.

Finally, for hydrogen flow rates of **4000 Nm^3/h**, the possible options are again two alkaline electrolysers and two PEM ones. The first alkaline system is Nel A3880, already described for

2000 Nm^3/h of hydrogen, while the other one is Thyssenkrupp Uhde Chlorine Engineers GmbH 20 MW module. The two PEM technologies are Cummins HyLYZER – 4000- 30 and Nel M4000. Again, the lowest hydrogen price is associated to an **alkaline** system, that produced by **Nel** (**8,5 €/kg**). The other costs are: 9,6 €/kg (Thyssenkrupp Uhde Chlorine Engineers GmbH), 9,5 €/kg (Cummins), 10 €/kg (Nel M4000). One more time, the pay back times are high, especially that of Nel M4000 referred to the net cash flow (18 years compared to 12 years of the others), but are significantly shorter with a hydrogen cost of 12 - 15 €/kg.
Hydrogen demands higher than 4000 Nm^3/h can be covered only by the **PEM** electrolyser SILYZER 300 supplied by **Siemens**, which arrives up to **22413 Nm^3/h** with a hydrogen cost of **9,2 €/kg**.

The lowest hydrogen costs related to the indicated flow rates (and respective sizes) are summarized in the following graphs (Figures 61, 62, 63).

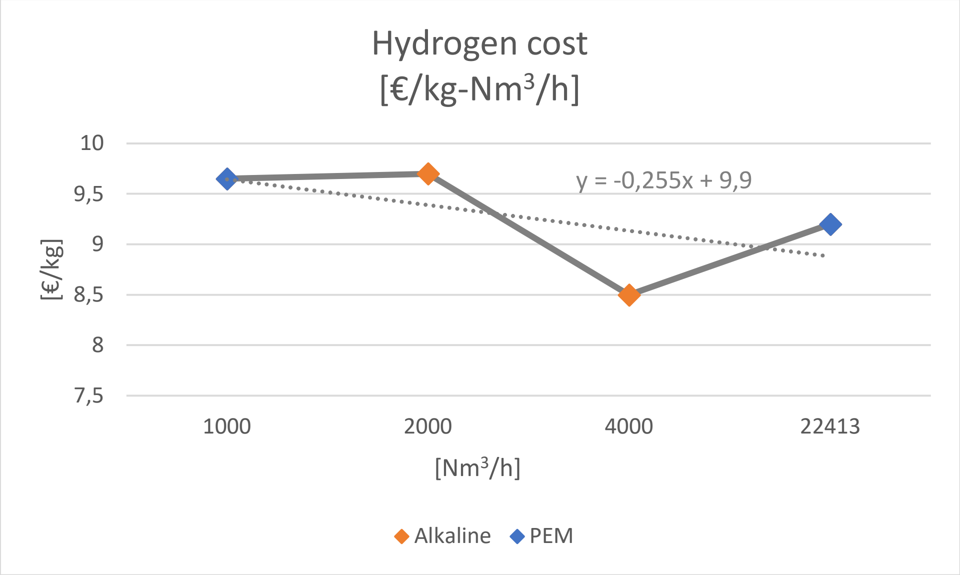

Figure 61

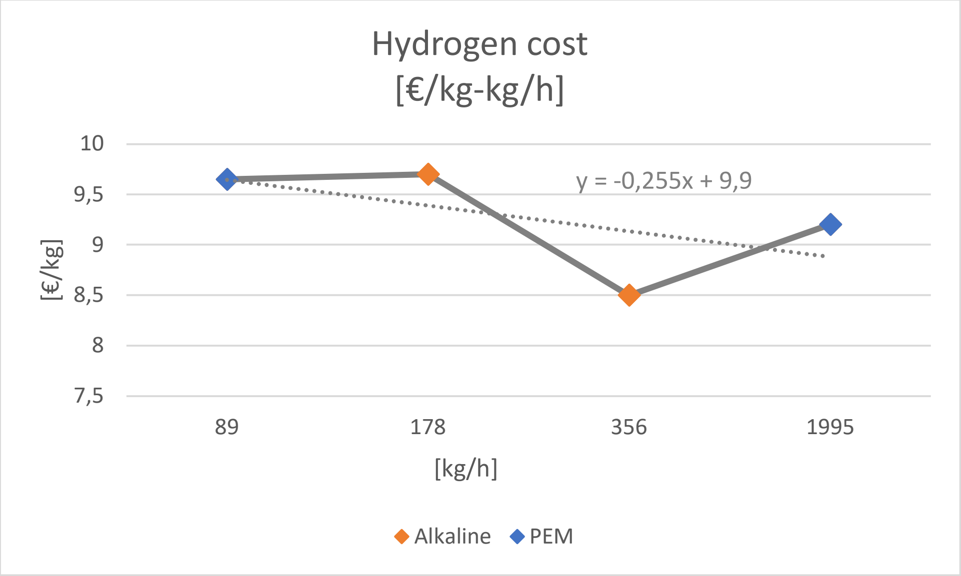

Figure 62

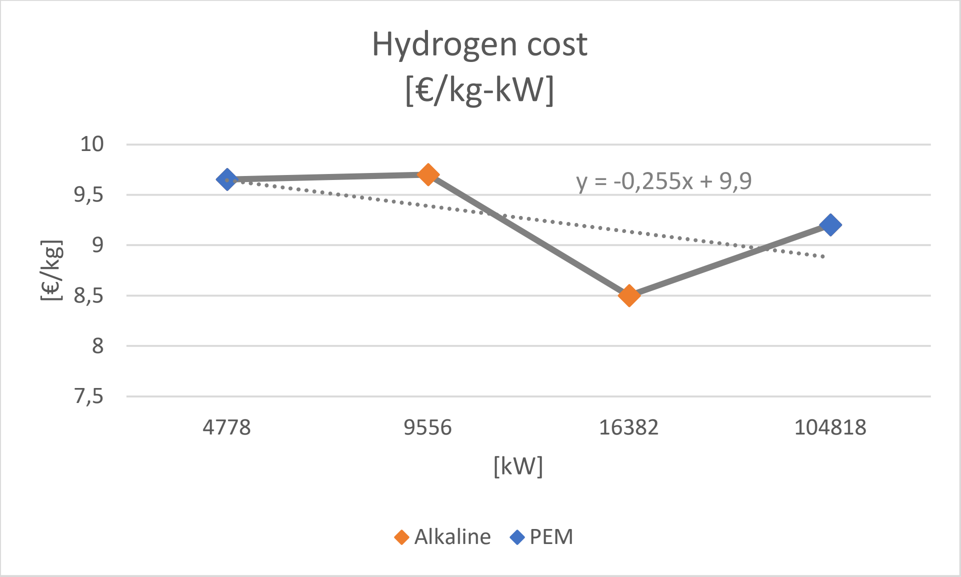

Figure 63

Differently from the previous cases, the increase of hydrogen production (and size) is not followed by a general decrease of the hydrogen cost. However, only four data are not suitable to produce a significant trend.

Finally, Table 9 reports the ranges of investment costs for this last group of electrolysers.

	Alkaline CAPEX	PEM CAPEX
1000 Nm^3/h	-	Min.: 8.000.000 € (Cummins) Max.: 11.000.000 € (Giner ELX)

2000 Nm^3/h	Unique: 19.000.000 € (Thyssenkrupp Uhde Chlorine Engineers GmbH)	Min.: 19.000.000 € (ITM Power) Max.: 20.000.000 € (Frames)
4000 Nm^3/h	Min.: 32.000.000 € (Nel) Max.: 38.000.000 € (Thyssenkrupp Uhde Chlorine Engineers GmbH)	Min.: 35.000.000 € (Cummins) Max.: 37.000.000 € (Nel)
> 4000 Nm^3/h	-	Unique: 197.000.000 € (Siemens)

Table 9

While hydrogen flow rates equal to 1000 Nm^3/h and greater than 4000 Nm^3/h are associated only to PEM electrolysers, for the intermediate ones a comparison between the two types of technologies can be done. In particular, for values around 2000 Nm^3/h, alkaline and PEM systems present similar investment costs, while CAPEX of PEM devices are higher than alkaline ones in the case of 4000 Nm^3/h. Considering the three levels of hydrogen flow rate for which a comparison of devices can be done (1000, 2000, 4000 Nm^3/h), all the systems producing hydrogen at the lowest cost present also the lowest CAPEX.

Concluding, the following three graphs (Figures 64, 65 and 66) report the overall hydrogen cost trend comprehensive of all the three sets of electrolysers. It is evident that the hydrogen price presents a scale effect, since it decreases with the increase of the hydrogen production (system size) and that the distribution of the lowest hydrogen costs is equally divided between alkaline and PEM electrolysers.

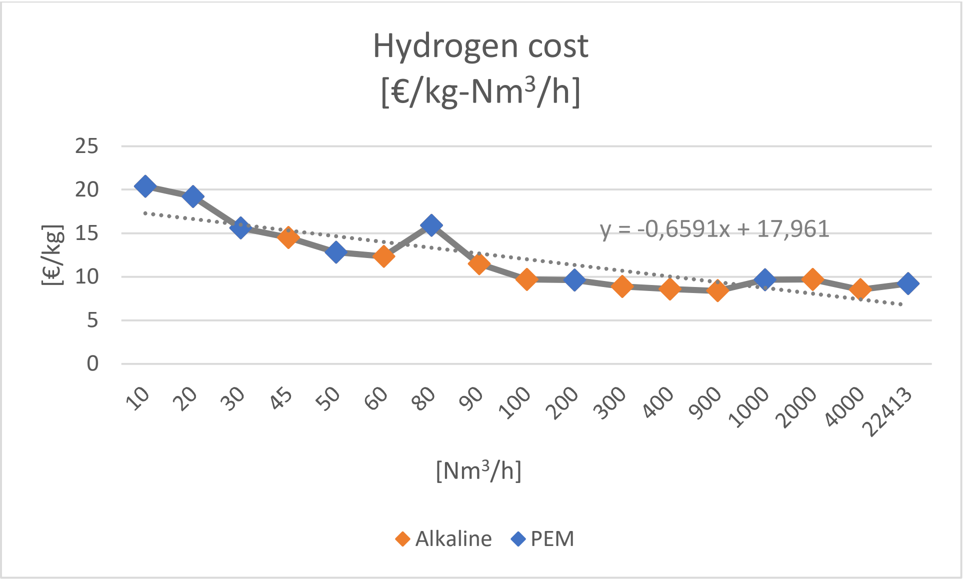

Figure 64

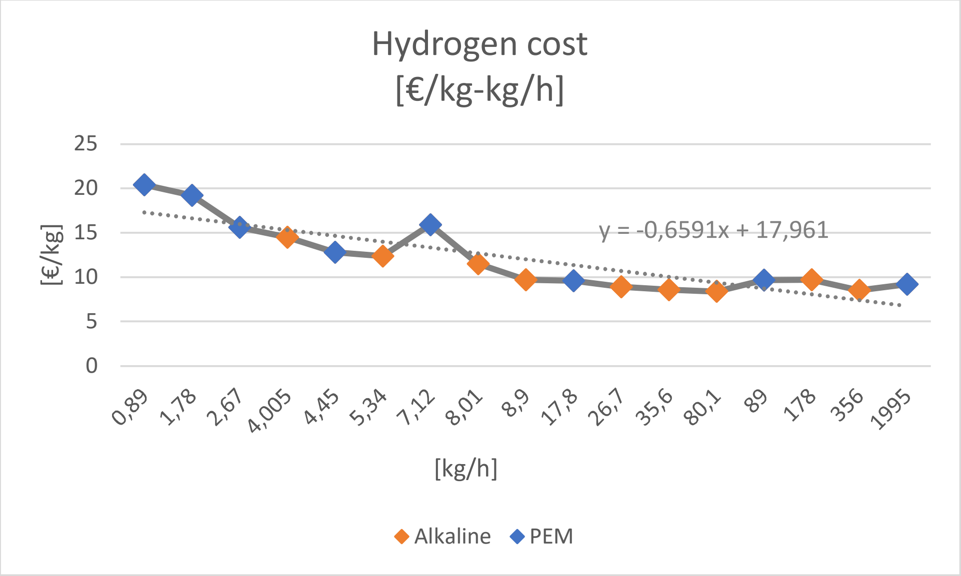

Figure 65

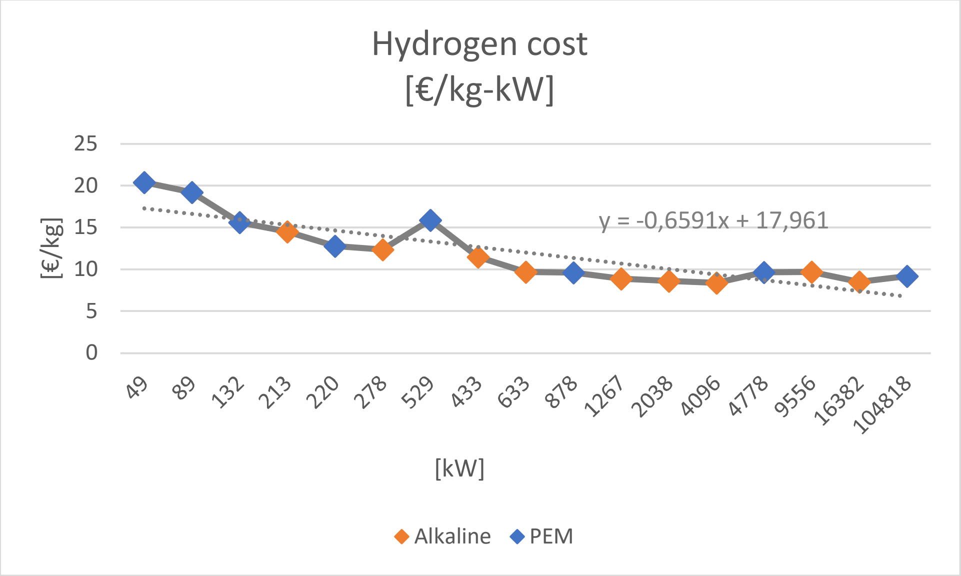

Figure 66

4. Conclusions

In order to have a global vision of alkaline and PEM electrolysers, a final comparison under a technical and economic point of view was done. The following table (Table 10) reports the average value of the Key Performance Indicators identified in the technical analysis.

	Alkaline	**PEM**	**Alkaline**	**PEM**	**Alkaline**	**PEM**	**Alkaline**	**PEM**
Hydrogen flow rate [Nm^3/h]	**0.4 – 8.66**	**0.011 – 5.6**	**10 – 90**	**10 – 78**	**100 – 970**	**100 – 580**	**2000 – 4000**	**1000 – 22413**
Electrical power consumption [kW]	18.9	10.1	149	152	1714	1222	12776	17210
Flow range	20 – 100%	0 - 100% 10 – 100%	15 – 100% 20 – 100%	0 - 100% 10 – 100%	15 – 100%	0 - 100% 10 – 100%	15 – 100%	10 – 100%
Load range	-	1 – 100% 20 – 100% 25 - 100%	10 – 100% 25 – 100% 40 – 100%	1 – 100% 10 - 100% 20 - 100%	5 – 100% 25 – 100%	5 – 100% 10 - 100% 20 – 100%	10 – 100%	5 - 100% 5 – 125%
Electrolyzer specific energy consumption [kWh/Nm^3]	5.34	5.72	4.63	4.90	4.20	4.62	4.20	4.53
Electrolyzer specific energy consumption [kWh/kg]	60	64.5	52.0	55.2	47.2	52.0	47.2	50.9
Cell voltage [V]	2.19	2.34	1.90	2.01	1.72	1.89	1.72	1.86
Electrolyzer conversion efficiency (HHV)	66.1%	63.3%	76.4%	72.9%	84.0%	76.3%	83.8%	77.7%
Cold start-up time [min]	-	≤ 5 min < 60 min	-	≤ 5 min < 60 min	-	≤ 5 min < 60 min	-	< 1 min
Warm start-up time [s]	-	< 1 s 30 s	-	< 1 s 10 s 30 s	-	< 1 s 10 s 30 s	-	-

System operational lifetime [years]	-	> 25 years	20 years	> 25 years > 20 years	20 years	≥ 20 years	-	20 years
Stack operational lifetime [hours]	-	80000 hours 43000 – 610000 hours 35000 hours	≥ 80000 hours	> 80000 hours 43000 – 610000 hours 35000 hours	80000 - 131400 hours	≥ 80000 hours 35000 hours	-	80000 hours
Footprint [m^2]	1.3	0.88	7.73	8.90	113	50.3	770	194

Table 10 – Average values of the Key Performance Indicators of alkaline and PEM electrolyzers

For both the technologies, the average size increases of one order of magnitude with the hydrogen productivity. Moreover, alkaline and PEM electrolysers present nearly the same consumptions for all the ranges of hydrogen flow rates, as showed also by Figures 67 and 68, which report the size as a function of the hydrogen productivity.

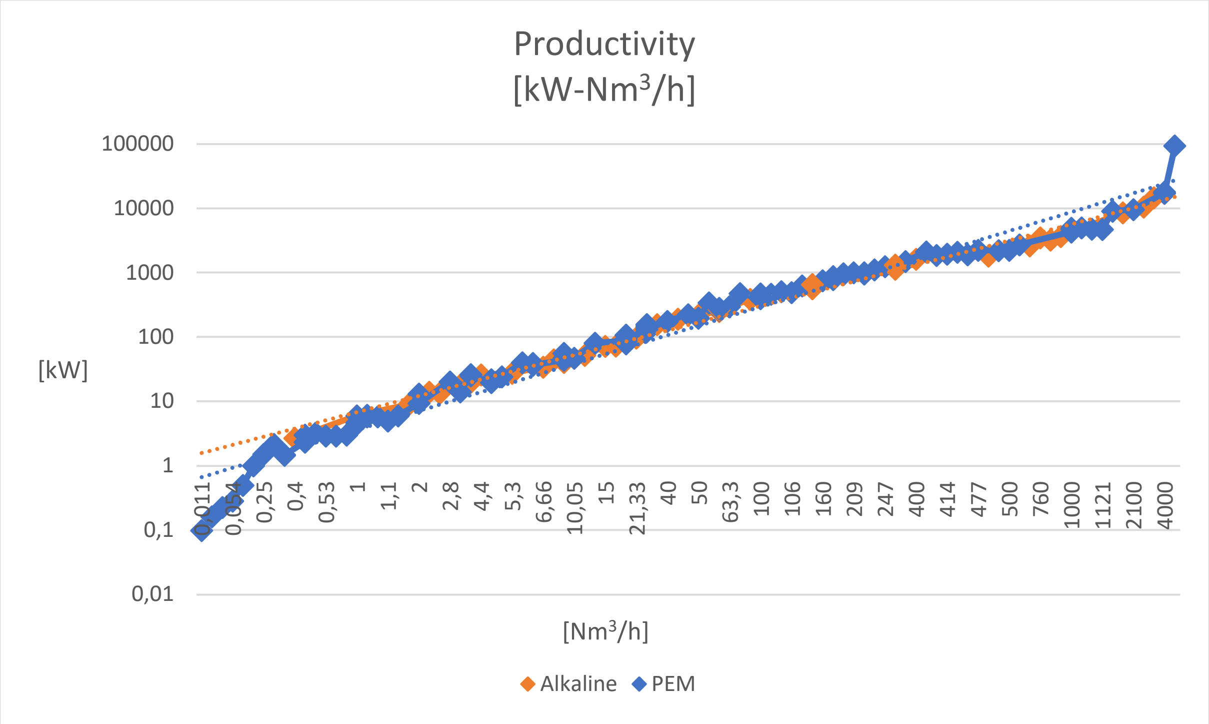

Figure 67

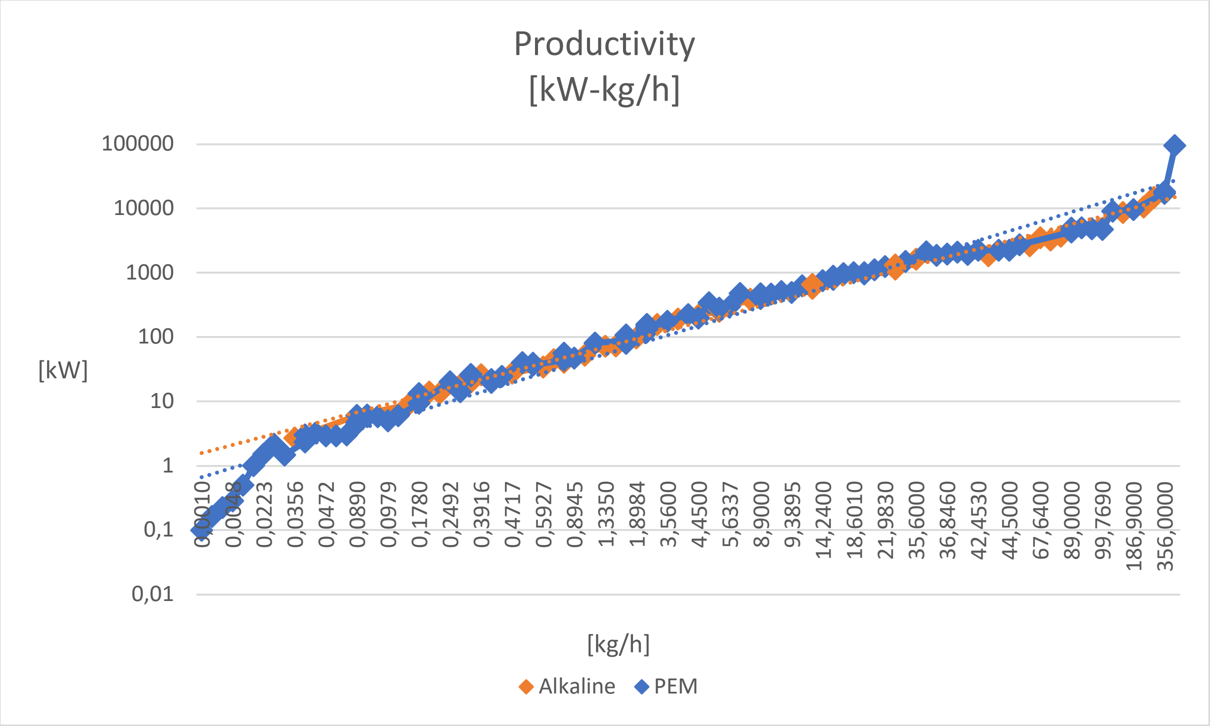

Figure 68

PEM electrolysers are more flexible in terms of input power, ranging from 1% to 100% (sometimes even 125%) of the nominal load. This greater flexibility is confirmed also by the operational window in terms of flow range: while alkaline electrolyzers do not go under 15% of the nominal hydrogen flow, PEM devices can reach almost 0%.

Then, the average values of the specific energy results higher for PEM electrolysers in all the four cases, however, looking at the following two graphs (Figures 69 and 70) it can be seen that this is true for hydrogen flow rates higher than 100 Nm^3/h, while for lower ones in many cases PEM electrolysers are less consuming than the alkaline ones.

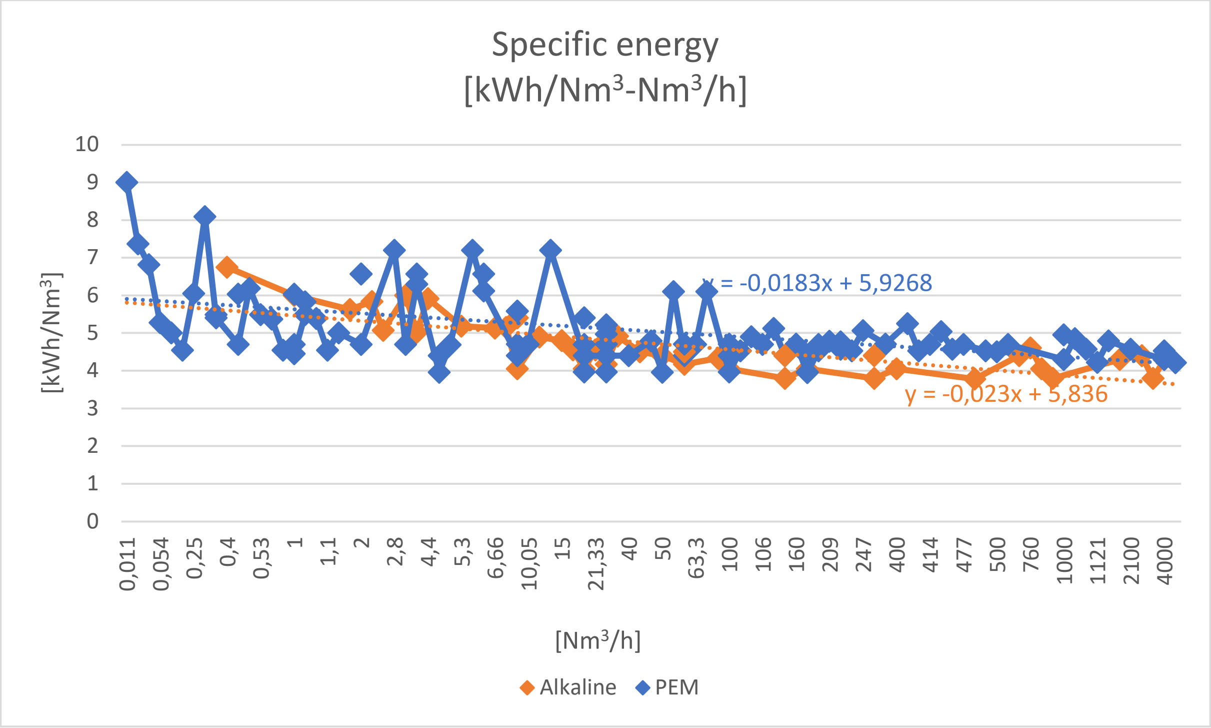

Figure 69

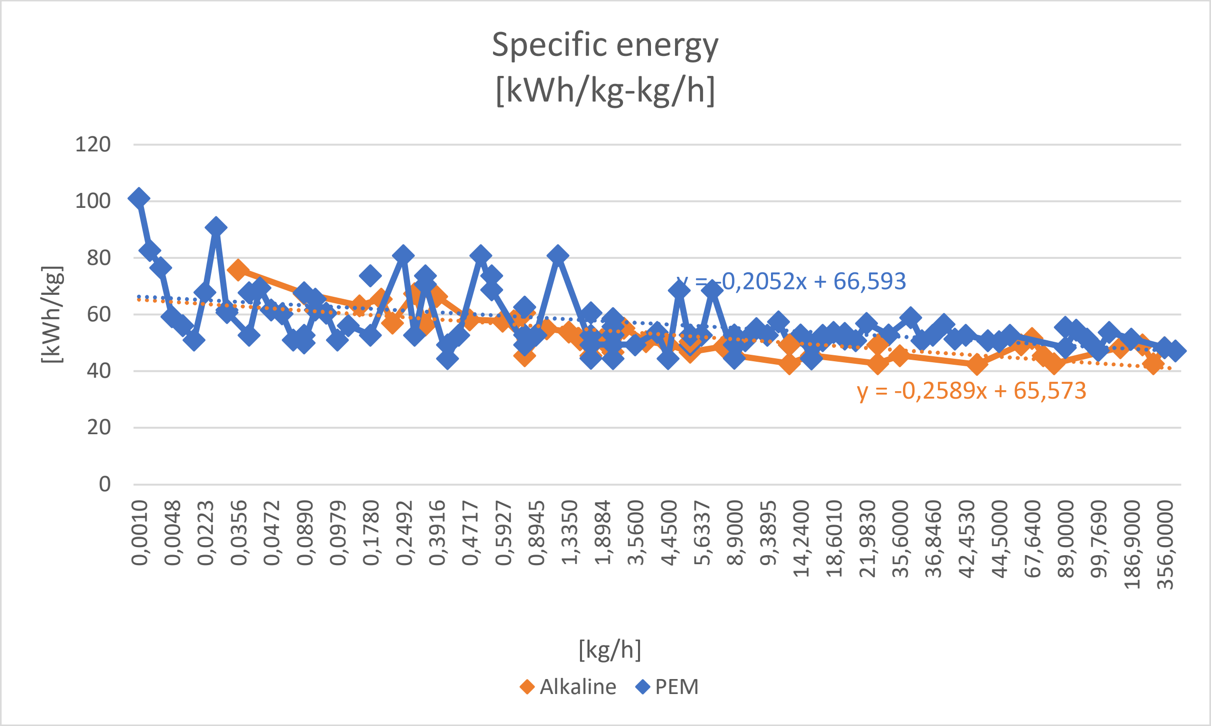

Figure 70

This reveals that, for hydrogen flow rates higher than 100 Nm^3/h, alkaline electrolyzers are more efficient in converting the electrical energy input in order to produce hydrogen. However, both the technologies present a scale effect, which is confirmed also by the average values of Table 10.

The higher average values of specific energy that characterise PEM electrolysers, translate into higher values of cell voltage and lowest values of conversion efficiency. Moreover, for both alkaline and PEM technologies, the scale effect of the specific energy reflects on a decrease of cell voltage and an increase of efficiency when increasing the hydrogen flow rate. In particular, the cell voltage decreases from 2,19 V to 1,72 V for alkaline electrolysers and from 2,34 V until 1,86 V for PEM devices. The increment of the efficiency is from 66,1% up to 83,8% for alkaline technologies and from 63,3% up to 77,7% for the others.

Then, both the stack and system operational lifetimes are similar for alkaline and PEM electrolyzers: 20 – 25 years for the system and around 80000 hours (sometimes more for PEM electrolyzers) for the stacks, even if sometimes alkaline stacks must be replaced after only 35000 hours.

Under the reactivity point of view, the only available data are those of PEM electrolysers, thus a comparison cannot be done.

Finally, considering the footprint, only the technologies of the second sets can be considered: the required surface is very similar in both alkaline (7.73 m^2) and PEM (8.90 m^2) cases.

Analysing then both the types of technologies also under the economic point of view it came out that those technologies presenting the lowest specific consumptions are typically the same that are able to produce hydrogen with the lowest cost. In particular, the alkaline identified electrolysers belong to McPhy, GreenHydrogen.dk Aps, Pure Energy Centre PEC (10 – 90 Nm^3/h), Nel (100 – 970 Nm^3/h), Thyssenkrupp Uhde Chlorine Engineers GmbH and Nel (2000 – 4000 Nm^3/h). The PEM devices, instead, are produced by: Giner ELX, Areva H2Gen GmbH (10 – 78 Nm^3/h), Giner ELX again (100 – 580 Nm^3/h) and Siemens (1000 – 22413 Nm^3/h).

All that has just been said basing on the average Key Performance Indicators subdivided by range of hydrogen flow rate is confirmed by the values reported in Table 11, which contains the most important operating parameters of alkaline and PEM electrolyzers.

	Current density [mA/cm^2]		**Electrolyzer specific energy consumption [kWh/Nm^3]**		**Cell voltage [V]**		**Electrolyzer conversion efficiency (HHV) [%]**	
	Alkaline	**PEM**	**Alkaline**	**PEM**	**Alkaline**	**PEM**	**Alkaline**	**PEM**
Minimum	200	0	3.78	3,95	1.55	1.62	52,0	39,0
Maximum	500	3000 (up to 20 A/cm^2)	6,75	9,0	2,77	3,69	92,8	88,8

Table 21 - Typical operating parameters of alkaline and PEM water electrolyzers

The first thing that stands out from the table is the relevant increase of current density passing from traditional alkaline water electrolyzers to PEM water electrolyzers: while the first usually reach a maximum of 500 mA cm^{-2}, the other ones are able to operate with current densities up to 3000 mA cm^{-2}, sometimes even 20 A cm^{-2} [2]. This is possible thanks to their zero-gap configuration, with the solid electrolyte in direct contact with the electrode's catalyst layers. This means that the cross-over risk is very low and the bubble effect is avoided, enabling the production of greater hydrogen flow rates, which correspond to higher values of current density. Furthermore, the presence of the solid electrolyte results in two more advantages: the possibility of producing hydrogen with higher purity than alkaline devices, typically up to 99.9999%, thanks to the reduction of gas cross-over, and the ability to tolerate considerable differential pressures (up to 350 bar [2]) between the electrodes, in particular if an inert support is added to increase the mechanical resistance. Such a pressure value can avoid a subsequent hydrogen compression for storage and transportation, offering a reduction of capital and operating costs. Anyway, a compression system can be necessary if hydrogen is produced for mobility purposes, which typically need hydrogen pressurized up to 700 bar. Anyway, even if the gas cross-over risk is low, it is not null, so a higher pressure difference between the electrodes results in a greater hydrogen diffusion from the cathodic to the anodic side of the electrolyzer, since the polymer membrane is not 100% gas proof. The gas diffusion occurs according to the following Fick's law, the same used in the calculation of the cell voltage:

$$\dot{n} = S \cdot D^{eff} \cdot \nabla c$$

According to this equation, the molar flow of hydrogen across the membrane $\dot{n}$ is directly proportional to its surface S, to the effective diffusion coefficient D^{eff} and to the concentration gradient ∇c of hydrogen between cathode and anode. This latter dependence implies the fact that the rate of hydrogen diffusion is directly proportional to the difference of partial pressure of hydrogen between the two electrodes. Since hydrogen is more concentrated in the cathodic compartment, its partial pressure here is higher and it tends to move towards the cathodic side. Hydrogen diffusion across the membrane leads to the formation of explosive gas mixtures with oxygen within the anodic compartment. A second issue consequent to an increase of the operating pressure is the higher solubility of hydrogen and oxygen in water. This helps the transport of the two species across the hydrated membrane and leads to their recombination on the electrode surface, presenting again the risk of explosive gas mixtures or, anyway, a decrease of gas purity. These problems constitute the reason of the limit of maximum operating pressure at 350 bar.

Considering now the electrical consumption, as already emerged from the average values in Table 10, the electrical requirements of PEM electrolyzers per unit of hydrogen flow rate (kWh/Nm^3) are a bit greater than those of alkaline devices. Indeed, the values reported in the analyzed datasheets range from 3,78 kWh/Nm^3 to 6,75 kWh/Nm^3 for alkaline technologies and from 3,95 kWh/Nm^3 to 9,0 kWh/Nm^3 for PEM ones. Anyway, typical maximum specific energies of alkaline electrlysers remain below 5,5 kWh/Nm^3, while this maximum value is 5,5 – 6,0 kWh/Nm^3 for PEM ones.

Indeed, a value so high as 9,0 kWh/Nm^3 appears only once and is characteristic of a technology of Proton On-Site. From this value derive the upper and lower extremes of, respectively, the cell voltage and electrolyzer conversion efficiency ranges, too. Moreover, also other values of specific energies belonging to this supplier are higher than the usual maximum one, but since it is the only one providing technology with really small productions, such as 0,011 Nm^3/h, it cannot be considered as representative as other suppliers. Moreover, the lower performances can be related to the difficulty of producing devices for such small hydrogen flow rates; in fact, for hydrogen demands like 0,524 Nm^3/h and 1,05 Nm^3/h, the specific energy goes down to 6,18 kWh/Nm^3 and 5,83 kWh/Nm^3, respectively.

The same things can be said for the cell voltage and the electrolyzer conversion efficiency. The minimum cell voltage is similar for both alkaline and PEM electrolyzers (1.55 V and 1.62 V, respectively), while the maximum one is 2,77 V in the alkaline case and 3,69 V in the PEM case. Even so, as for alkaline electrolyzers the typical maximum cell voltage is around 2.0 V, also for PEM ones it is lower than 4.1 V and usually stops at 2.2 V. Finally, the electrolyzer conversion efficiency, globally lower for PEM electrolyzers, typically ranges from around 60% up to 82%, reaching in some cases the maximum values reported in Table 11.

Dynamic aspect

When the electrolysers are fed by electricity coming from renewable energy sources, presenting fluctuations in the electrical energy production, or from an electricity grid characterised by significant peaks, it is important to consider the combination of the following two indicators:

1. Load range, so the operational window in terms of percentage of nominal input power that an electrolyser can tolerate
2. Response time, so the amount of time needed to change the level of production according to the variation of input power.

PEM electrolysers present a greater flexibility compared to alkaline ones, having a wider operational window, and shorter response times which make them more dynamic. Indeed, typical load ranges for alkaline electrolysers are comprised between 5% and 110% of the nominal input power, while PEM electrolysers can range from almost 0% to 125 – 160% of nominal power. Since

PEM electrolysers present shorter response time compared to alkaline ones, they are able to change faster their level of production. This is confirmed by the values of the power ramp-up rate, an indicator representing the percentage of increase of power per second, provided by the following suppliers:

- Enapter (alkaline anion exchange membrane electrolyser): 0.06 %/s
- Diamond Lite S.A. (PEM): ≥ 15 %/s
- H-Tec Systems GmbH (PEM): 2.67 %/s
- Siemens (PEM): 10 %/s
- Giner ELX (PEM): 10 %/s

Unfortunately, for alkaline electrolysers only one example is available, but it can easily be noted the difference present between alkaline and PEM technologies. In fact, when PEM electrolysers present a size sufficiently large to be installed in an industrial plant, the can directly operate in the electricity market, exploiting peaks in the electricity grid to produce hydrogen, avoiding thus waste of electric power.

Efficiency degradation

PEM electrolysers are better than alkaline ones under the dynamic point of view, but looking at the efficiency and its annual degradation, things are different. As showed in the graph below (Figure 71), PEM electrolysers with small/medium productivity (up to 100 Nm^3/h) have higher efficiencies, except in some cases, with respect to alkaline ones with similar hydrogen flow rates. Anyway, it has to be said that the lowest values that alkaline electrolysers can reach are always higher than the worst of PEM electrolysers. Then, looking at bigger values of productivity, it is evident that alkaline devices are more efficient. In addition to this, PEM electrolysers typically present larger values of yearly efficiency degradation. In fact, many literature articles report a loss of efficiency equal to 0.25 – 1.5 %/year for alkaline electrolysers and 0.5 – 2.5 %/year for PEM ones. An example for PEM electrolysers is an average efficiency degradation of 1.11 %/year for H2B2 technologies.

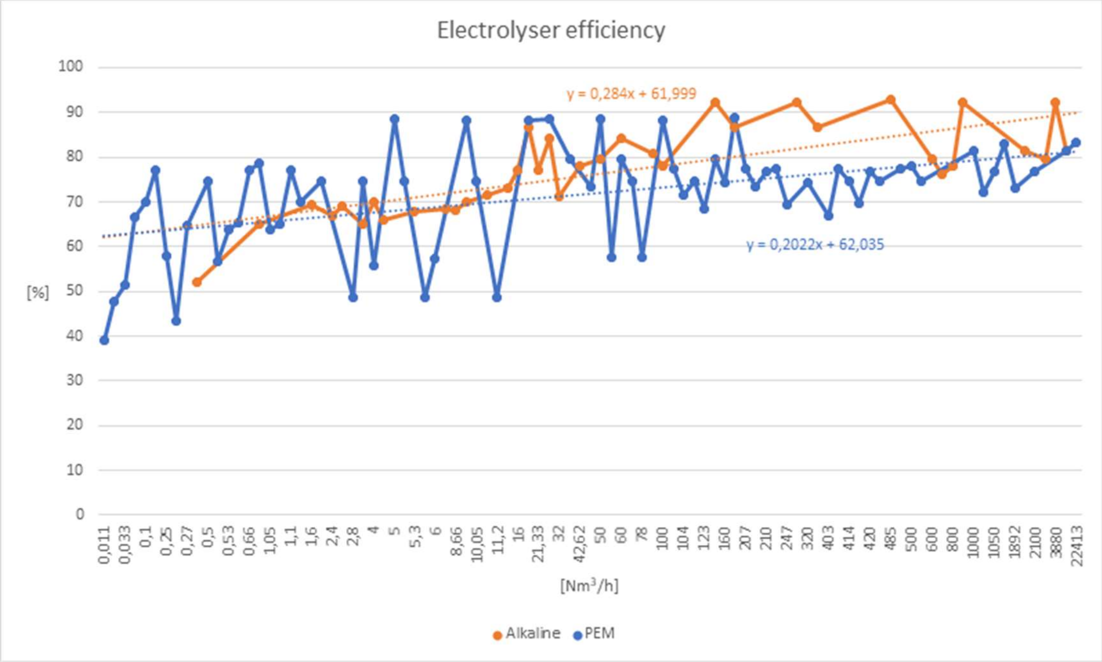
Electrolyser efficiency
y = 0,284x + 61,999
y = 0,2022x + 62,035
[%]
100
90
80
70
60
50
40
30
20
10
0
0,011
0,033
0,1
0,25
0,27
0,5
0,53
0,66
1,05
1,1
1,6
2,4
2,8
4
5
5,3
6
8,66
10,05
11,2
16
21,33
32
42,62
50
60
78
100
104
123
160
207
210
247
320
403
414
420
485
500
600
800
1000
1050
1892
2100
3880
22413
[Nm³/h]
● Alkaline
● PEM

Figure 71

Appendix

<table>
<tr><th colspan="11">Alkaline</th></tr>
<tr><th>Supplier</th><th>Electrolyser</th><th>Hydrogen flow rate [Nm^3/h]</th><th>CAPEX [€]</th><th>H_2, non-renewable [€/kg]</th><th>H_2, renewable [€/kg]</th><th>Internal Rate of Return [%]</th><th>Net Present Value (NPV) [€]</th><th>Pay Back Time (PBT) – NCF [years]</th><th>Pay Back Time (PBT) – DCF [years]</th><th>H_2 price with IRR target 8% [€/kg]</th></tr>
<tr><td>Cummins</td><td>HySTAT-15-10</td><td>15</td><td>186.695</td><td>25</td><td>36,8</td><td>6,0</td><td>4.164</td><td>12</td><td>19</td><td>25,2</td></tr>
<tr><td></td><td>HySTAT-60-10</td><td>60</td><td>696.259</td><td>13,7</td><td>24,8</td><td>6,0</td><td>3.648</td><td>12</td><td>20</td><td>13,9</td></tr>
<tr><td>GreenHydrogen.dk Aps</td><td>A30</td><td>30</td><td>181.686</td><td>15,9</td><td>26,1</td><td>7,0</td><td>12.244</td><td>9,5</td><td>17,5</td><td>15,95</td></tr>
<tr><td></td><td>A60</td><td>60</td><td>307.460</td><td>12,35</td><td>22,55</td><td>7,0</td><td>15.794</td><td>10</td><td>18,5</td><td>12,4</td></tr>
<tr><td></td><td>A90</td><td>90</td><td>479.504</td><td>11,5</td><td>22,1</td><td>6,0</td><td>8.774</td><td>13</td><td>19,5</td><td>11,6</td></tr>
<tr><td>McPhy</td><td>McLyzer 10-30</td><td>10</td><td>128.396</td><td>32,5</td><td>44,7</td><td>7,0</td><td>4.803</td><td>12</td><td>18,5</td><td>32,7</td></tr>
<tr><td></td><td>H</td><td>3 – 10</td><td>154.018</td><td>34,7</td><td>49,4</td><td>6,0</td><td>1.409</td><td>12</td><td>19,5</td><td>35</td></tr>
<tr><td></td><td>McLyzer 20-30</td><td>20</td><td>118.134</td><td>19,2</td><td>29,1</td><td>7,0</td><td>10.887</td><td>12</td><td>17</td><td>19,25</td></tr>
<tr><td>Pure Energy Centre PEC</td><td>10 Nm^3/h</td><td>10,66</td><td>134.033</td><td>30,9</td><td>42,9</td><td>6,0</td><td>1.278</td><td>12</td><td>19,5</td><td>31,1</td></tr>
<tr><td></td><td>16 Nm^3/h</td><td>16</td><td>106.380</td><td>22,9</td><td>34,0</td><td>7,0</td><td>7.634</td><td>12</td><td>17,5</td><td>22,95</td></tr>
<tr><td></td><td>21 Nm^3/h</td><td>21,33</td><td>141.642</td><td>19,6</td><td>30,7</td><td>7,0</td><td>10.856</td><td>12</td><td>17</td><td>19,65</td></tr>
<tr><td></td><td>32 Nm^3/h</td><td>32</td><td>229.239</td><td>17,0</td><td>29,1</td><td>6,0</td><td>6.983</td><td>12,5</td><td>19</td><td>17,1</td></tr>
<tr><td></td><td>42 Nm^3/h</td><td>42,62</td><td>279.276</td><td>14,5</td><td>25,5</td><td>7,0</td><td>12.702</td><td>12</td><td>18</td><td>14,6</td></tr>
<tr><td colspan="11">PEM</td></tr>
<tr><td>Areva H2Gen GmbH</td><td>E10</td><td>10</td><td>134.802</td><td>31</td><td>41,75</td><td>7,0</td><td>4.442</td><td>11</td><td>18,5</td><td>31,05</td></tr>
<tr><td></td><td>E20</td><td>20</td><td>266.199</td><td>20,4</td><td>31,15</td><td>7,0</td><td>9.199</td><td>10,5</td><td>18,5</td><td>20,45</td></tr>
<tr><td></td><td>E40</td><td>40</td><td>532.562</td><td>15,1</td><td>25,9</td><td>7,0</td><td>15.260</td><td>11</td><td>19</td><td>15,15</td></tr>
<tr><td></td><td>E60</td><td>60</td><td>797.031</td><td>13,3</td><td>24,1</td><td>6,0</td><td>6.776</td><td>11</td><td>19,5</td><td>13,4</td></tr>
<tr><td>CETH2</td><td>E10</td><td>10</td><td>134.802</td><td>31</td><td>41,75</td><td>7,0</td><td>4.442</td><td>11</td><td>18,5</td><td>31,05</td></tr>
<tr><td></td><td>E20</td><td>20</td><td>266.199</td><td>20,4</td><td>31,15</td><td>7,0</td><td>9.199</td><td>10,5</td><td>18,5</td><td>20,45</td></tr>
<tr><td></td><td>E30</td><td>30</td><td>398.789</td><td>16,85</td><td>27,6</td><td>7,0</td><td>8.710</td><td>11</td><td>19</td><td>16,9</td></tr>
<tr><td></td><td>E40</td><td>40</td><td>532.562</td><td>15,1</td><td>25,9</td><td>7,0</td><td>15.260</td><td>11</td><td>19</td><td>15,15</td></tr>
</table>

	E60	60	797.031	13,3	24,1	6,0	6.776	11	19,5	13,4
Diamond Lite S.A.	C10	10	98.541	33,2	46,8	7,0	6.189	12	18	33,3
	C20	20	209.352	23,4	35,4	7,0	11.781	12	18	23,5
	C30	30	275.277	18,3	31,1	7,0	15.642	12	18	18,4
Giner ELX	Merrimack	10	71.823	29,8	39,5	7,0	4.786	12	18	29,9
		20	140.241	19,2	28,9	7,0	5.924	12	18	19,3
		30	210.807	15,6	25,3	7,0	9.182	12	18,5	15,7
	Allagash	50	348.460	12,8	22,4	7,0	29.613	12	17	12,85
H-Tec Systems GmbH	ME 100/350	47	755.700	15,4	27,1	7,0	38.076	10,5	18	15,5
H2B2	EL10N	10,05	73.348	31,0	42,5	6,0	1.089	13	19,5	31,1
	EL20N	20	146.084	20,6	32,1	7,0	11.246	12	17	20,65
	EL30N	30	230.296	16,7	28,2	7,0	19.938	12	17	16,75
	EL60N	63,3	457.819	13,3	24,8	6,0	12.767	13	19	13,4
iGas energy GmbH	gEl 10-300 PEM MD	10	82.850	31,3	42,8	7,0	3.682	12	18	31,4
	gEl 30-300 PEM MD	30	248.451	17,2	28,7	7,0	13.777	12	18	17,3
	gEl 60-300 PEM MD	60	496.606	13,7	25,2	7,0	33.747	12	17,5	13,8
Nel	C10	10	98.541	33,2	46,8	7,0	6.189	12	18	33,3
	C20	20	209.352	23,4	35,4	7,0	11.781	12	18	23,5
	C30	30	275.277	18,3	31,1	7,0	15.642	12	18	18,4
Teledyne Energy Systems	HMXT-200	11,2	323.698	35,2	52,8	7,0	9.657	11,	20	35,4
	EL-1000	56	1.086.035	17,2	32,1	7,0	34.470	11,5	20	17,3
	EL-1400	78	1.333.173	15,9	30,9	6,0	3.880	12	25	16,1

Table 1

Alkaline										
Supplier	Electrolyser	Hydrogen flow rate [Nm^3/h]	CAPEX [€]	H_2, non-renewable [€/kg]	H_2, renewable [€/kg]	Internal Rate of Return [%]	Net Present Value (NPV) [€]	Pay Back Time (PBT) – NCF [years]	Pay Back Time (PBT) – DCF [years]	H_2 price with IRR target 8% [€/kg]
Cummins	HySTAT-100-10	100	1.157.459	12,3	23,3	6,0	15.752	12	19,5	12,5
IHT Industrie Haute Technologie S.A.	Type S-556 electrolyser	760	6.313.418	10,2	21,5	7,0	251.001	12	18,5	10,3
McPhy	McLyzer 100 - 30	100	807.459	11,9	22,9	7,0	54.142	12	17,5	12
	McLyzer 200-30	200	1.475.400	9,8	19,7	6,0	30.695	12	19	9,9
	McLyzer 400-30	400	2.924.550	9,3	19,2	7,0	160.414	12	18	9,4
	Augmented McLyzer 800-30	800	6.476.500	10	21,0	7,0	230.709	12	19	10,1
Nel	A150	50 - 150	1.039.633	9,7	18,9	7,0	97.583	11,5	17	9,75
	AC150	150	1.207.733	10,9	21,7	6,0	2.572	12,5	20	11,1
	A300	150 - 300	2.064.267	8,9	15,7	6,0	21.751	12,5	19,5	9,0
	AC300	300	2.389.217	10,2	18,2	6,0	38.478	12	19	10,35
	A485	300 - 485	3.306.421	8,6	17,9	6,0	76.477	12	19	8,7
	A1000	600 - 970	6.629.962	8,4	17,7	6,0	27.518	12,5	19	8,55
PEM										
Areva H2Gen GmbH	E100	100	824.814	11,7	22,5	7,0	39.268	12	18	11,8
	E150	150	1.234.992	11	21,7	7,0	66.194	12	18	11,1
	E200	200	1.645.170	10,6	21,4	6,0	27.431	12,5	19	10,75

Diamond Lite S.A.	M100	104	922.038	12,7	24,6	7,0	71.946	12	17,5	12,8
	M200	209	1.865.616	11,4	21,4	7,0	116.575	12	18	11,5
	M400	417	3.916.839	11,4	23,7	7,0	135.045	12	19	11,5
Frames	1 MW	0 - 210	1.992.096	10,9	22,1	7,0	63.287	12	19	11
	2 MW	0 - 420	3.584.195	10,4	21,6	7,0	137.318	12	18,5	10,5
H-Tec Systems GmbH	ME 450/1400	210	3.352.067	11,8	23,4	7,0	103.847	11	18,5	11,9
H2B2	EL100N	105.5	763.751	12	23,5	7,0	46.545	12	17,8	12,1
	EL200N	207	1.493.938	11	22,5	7,0	76.725	12,5	18	11,1
	EL400N	414	2.383.556	10,5	22,0	7,0	187.621	12	18	10,55
	EL460N	477	3.437.071	10,4	21,9	7,0	113.569	13	19	10,5
	EL580N	580	4.183.980	10,3	21,8	6,0	41.605	13	20	10,4
iGas energy GmbH	gEl 100-1250 PEM MD	100	882.612	12,35	23,9	6,0	27.848	12,5	19	12,45
	gEl 160-1250 PEM MD	160	1.409.504	11,1	23,1	7,0	98.005	12	17,5	11,7
	gEl 320-1250 PEM MD	320	2.815.643	10,8	22,4	6,0	7.520	13	20	10,95
ITM Power	HGas1SP	123	1.179.031	12,8	25,3	7,0	39.052	12,5	19	12,9
	HGas2SP	247	2.337.972	11,8	24,2	6,0	57.490	12,5	19	12
	HGas3SP	403	3.949.974	11,9	24,7	7,0	230.546	12	18	12
Nel	M100, MC100	103	884.950	11,9	23	7,0	48.953	12	18	12,0
	M200, MC200	207	1.763.290	10,8	21,9	6,0	19.814	12,5	19,5	10,95
	MC250	246	2.084.599	10,7	21,8	7,0	132.860	12	18	10,8
	M400, MC400	413	3.512.376	10,3	21,4	6,0	69.817	12,5	19	10,4
	MC500	492	4.164.997	10,2	21,3	6,0	41.093	13	19,5	10,35
Giner ELX	Allagash	100	741.484	10,7	20,5	6,0	9.051	13	19,5	10,8
		200	1.481.669	9,6	19,3	6,0	15.563	13	19,5	9,7
	GenFuel 1 MW system	200	1.474.211	9,7	19,4	7,0	63.950	12	18,5	9,8
Cummins	HyLYZER – 500 - 30	500	4.155.678	10,2	21,2	7,0	255.722	12	19	10,3

Table 2

	Alkaline									
Supplier	Electrolyser	Hydrogen flow rate [Nm^3/h]	CAPEX [€]	H_2 price, non-renewable [€/kg]	H_2 price, renewable [€/kg]	Internal Rate of Return [%]	Net Present Value (NPV) [€]	Pay Back Time (PBT) – NCF [years]	Pay Back Time (PBT) – DCF [years]	H_2 price with IRR target 8% [€/kg]
Nel	A3880	2400 - 3880	32.978.238	8,5	17,8	7,0	1.272.551	12	18,5	8,6
Thyssenkrupp Uhde Chlorine Engineers GmbH	10 MW module	2000	19.283.944	9,7	20,2	7,0	1.142.534	11,5	18	9,8
	20 MW module	4000	38.452.389	9,6	20,1	6,0	1.147.096	12	19	9,8
	PEM									
Cummins	HyLYZER – 1000 - 30	1000	8.975.565	9,65	20,0	6,0	224.807	12	19	9,8
	HyLYZER – 4000 - 30	4000	35.965.667	9,5	19,8	6,0	1.073.980	12	19	9,6
Frames	5 MW	1050	10.020.462	10,2	21,4	6,0	137.130	12,5	19,5	10,35
	10 MW	2100	20.036.462	10,1	21,3	6,0	288.847	12,5	19,5	10,3
Giner ELX	GenFuel 5MW system	100 - 1000	11.529.000	11,2	23,5	6,0	60.074	12.5	20	11,4
ITM Power	HGasXMW	1892	18.918.134	10,6	22,3	6,0	614.468	12	19	11
Nel	M4000	4000	37.891.400	10	21,1	7,0	1.548.627	18	18,5	10,1

Siemens	SILYZER 300	1121 - 22413	197. 297.787	9,2	19,5	6,0	467.620	12,5	20	9,4

Table 3

Bibliography and sitography

[1] Vincent I, Bessarabov D. Low cost hydrogen production by anion exchange membrane electrolysis: a review. Renew Sustain Energy Rev 2018.

[2] Grigoriev SA et al., Current status, research trends, and challenges in water electrolysis science and technology, International Journal of Hydrogen Energy, https://doi.org/10.1016/j.ijhydene.2020.03.109

[3] Aliyev AS, Guseynova RG, Gurbanova UM, Babanly DM, Fateev VN, Pushkareva IV, Tagiyev DB. Electrocatalysts for water electrolysis. Chem Prob (Kimya Problemləri) 2018;3(16):283-306

[4] Amores E., Rodriguez J., Carreras C. *Int. J. Hydrogen Energy.* 2014, vol. 1, pp. 844-849.

[5] Paidar M., Fateev V., Bouzek K. Electrochimica Acta, 2016, vol. 209, pp.737-756.

[7] G. Merle, M. Wessling, K. Nijmeijer, Journal of Membrane Science 377 (2011) 1-35.

[6] https://chem.libretexts.org/Bookshelves/Inorganic_Chemistry/Book%3A_Introduction_to_Inorganic_Chemistry/08%3A_Ionic_and_Covalent_Solids_-_Structures/8.07%3A_Spinel%2C_Perovskite%2C_and_Rutile_Structures

[8] F. Allebrod, C. Chatzichristodoulou, P.L. Mollerup, M.B. Mogensen, Journal of Power Sources 229 (2013) 22-31

[9] P. Fortin, T. Khoza, X. Cao, S.Y. Martinsen, A. O. Barnett, S. Holdcroft, Journal of power Sources (2020) 227814

[10] Prof. Massimo Santarelli. *Celle a combustibile a membrana polimerica. Descrizione generale della cella e dei suoi principi di funzionamento.*

[11] Libin Lei, Jihao Zhang, Rongfeng Guan, Jianping Liu, Fanglin Chen, Zetian Tao. *Energy storage and hydrogen production by proton conducting solid oxide electrolysis cells with a novel heterogeneous design.*

[12] Dmitry Medvedev. *Trends in research and development of protonic ceramic electrolysis cells*

[13] Tucker MC, *Progress in metal-supported solid oxide electrolysis cells: A review*, International Journal of Hydrogen Energy, https://doi.org/10.1016/j.ijhydene.2020.06.300

[14] Domenico Ferrero, Andrea Lanzini, Massimo Santarelli, Pierluigi Leone. *A comparative assessment on hydrogen production from low- and high-temperature electrolysis*

[15] Matthias Koj, Jingcan Qian, Thomas Turek. *Novel alkaline water electrolysis with nickel-iron gas diffusion electrode for oxygen evolution*

[16] Galin Borisov, Hristo Penchev, Katerina Maksimova-Dimitrova, Filip Ublekov, Elefteria Lefterova, Vesselin Sinigersky, Evelina Slavcheva. *Alkaline water electrolysis facilitated via non-precious monometallic catalysts combined with highly KOH doped polybenzimidazole membrane.*

[17] European Commission. *Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the regions. A hydrogen strategy for a climate-neutral Europe.* Brussels, 8.7.2020.

[18] https://www.ilpost.it/2020/02/02/green-deal-europeo/

[19] Yu S et al., *Rational design and fabrication of TiO_2 nano heterostructure with multi-junctions for efficient photocatalysis*, International Journal of Hydrogen Energy, https://doi.org/10.1016/j.ijhydene.2020.07.184

[20] Mahmoud Ahmed, Ibrahim Dincer. *A review on photoelectrochemical hydrogen production systems: Challenges and future directions.*

[21] Meng Ni, Michael K.H. Leung, Dennis Y.C. Leung. *Technological development of hydrogen production by solid oxide electrolyzer cell (SOEC).*

[22] Stefan Fogel, Holger Kryk, Uwe Hampel. *Simulation of the transient behaviour of tubular solid oxide electrolyzer cells under fast load variations.*

[23] Siriporn Yossan, Li Xiao, Poonsuk Prasertsan, Zhen He. *Hydrogen production in microbial electrolysis cells: Choice of catholyte.*

[24] Daniel Indiana Carlotta-Jones, Kevin Purdy, Kerry Kirwan, James Stratford, Stuart R. Coles. *Improved hydrogen gas production in microbial electrolysis cells using inexpensive recycled carbon fibre fabrics.*

[25] Masoud Hasany, Mohammad Mahdi Mardanpour, Soheila Yaghmaei. *Biocatalysts in microbial electrolysis cells: A review.*

[26] Barelli L et al., *High temperature electrolysis using Molten Carbonate Electrolyzer*, International Journal of Hydrogen Energy, https://doi.org/10.1016/j.ijhydene.2020.07.220

[27] IRENA (2018), *Hydrogen from renewable power: Technology outlook for the energy transition*, International Renewable Energy Agency, Abu Dhabi.

[28] N.A. Burton, R.V. Padilla, A.Rose, H. Habibullah. *Increasing the efficiency of hydrogen production from solar powered water electrolysis.*

[29] Georgios Tsotridis, Alberto Pilenga. *EU harmonised terminology for low temperature water electrolysis for energy storage applications*, EUR

[30] Liu W et al., *The production and application of hydrogen in steel industry*, International Journal of Hydrogen Energy, https://doi.org/10.1016/j.ijhydene.2020.12.123

[31] Duncan Kushnir, Teis Hansen, Valentin Vogl, Max Åhman. *Adopting hydrogen direct reduction for the Swedish steel industry: A technological innovation system (TIS) study*

[32] https://www.h2future-project.eu/technology

[33] Valentin Vogl, Max Åhman, Lars J. Nilsson. *Assessment of hydrogen direct reduction for fossil free-steelmaking*

[34] R. Yukesh Kannah, S. Kavitha, Preethi, O. Parthiba Karthikeyan, Gopalakrishnan Kumar, N. Vo. Dai-Viet, J. Rajesh Banu. *Techno-economic assessment of various hydrogen production methods – A review*

[35] Alexander Buttler, Hartmut Spliethoff. *Current status of water electrolysis for energy storage, grid balancing and sector coupling via power-to-gas and power-to-liquids: A review.*

Figures sitography

[Figure 1] Ernesto Amores, Jesús Rodrígues, José Oviedo, Antonio De Lucas-Consuegra. *Development of an operation strategy for hydrogen production using solar PV energy based on fluid dynamic aspects*

[Figure 2] Ali Keçebaş, Muhammet Kayfeci, Mutlucan Bayat. *Electrochemical hydrogen generation*

[Figure 23] L Georgios Tsotridis, Alberto Pilenga. *EU harmonised terminology for low temperature water electrolysis for energy storage applications*, EUR

[Figure 25] L Georgios Tsotridis, Alberto Pilenga. *EU harmonised terminology for low temperature water electrolysis for energy storage applications*, EUR

[Figure 30] L Georgios Tsotridis, Alberto Pilenga. *EU harmonised terminology for low temperature water electrolysis for energy storage applications*, EUR