

A wind-power fuel cell hybrid system study

Model of energy conversion for wind energy system with
hydrogen storage

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University
of Akureyri

A WIND POWER FUEL CELL HYBRID SYSTEM STUDY

Model of energy conversion for wind energy system with hydrogen
storage

Katarzyna Sobotka

A 30 credit units Master's thesis

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ABSTRACT

Hydrogen, as a form of long term storage for the excess energy from renewable sources, is a technically and economically viable option. However, the technology is not mature enough to compete with the other renewable energy possibilities. In this thesis, a study based on coupling a wind-turbine with a fuel cell to improve the utilization of wind power is presented.

A part of the energy produced by the wind-turbine is stored in the form of hydrogen and is then delivered for consumption at variable power through a fuel cell. A model was developed to determine the key technical parameters influencing the operation of a wind energy system with hydrogen storage. The model incorporates the simulation results of a 600 kW wind energy system with a 100 kW Proton Exchange Membrane Fuel Cell (PEMFC) and an electrolyzer. Dynamic modeling of various components of this small isolated system is presented for the period from 1.1.2006 to 31.1.2006. In this way, the energy availability can be estimated and is presented for hybrid installations. The study presents the technology of the system for each particular element.

This study is a general introduction for the wind energy system with hydrogen storage. Future studies should be more complex and detailed in order to understand and model the system with greater accuracy and to increase the possibility for the utilization of wind energy to generate hydrogen. This would enhance wind power competitiveness and sustain the continuously changing world energy demand.

PREFACE

In my work I wanted to investigate the background of the technological aspects of energy conversion in a wind energy system with hydrogen storage, with an intermittent energy supply in order to enhance the competitive potential of wind power and to sustain the ability of wind energy to meet changing world energy demands.

As the topic is very broad I focused my attention on the simple example of the system and basic simulations, but I wish to continue my work on this topic in future studies.

The majority of my work was based on the analysis of particular elements of the system and also a simple computation and simulation of the system.

I would like to thank RES | The School for Renewable Energy Science in Akureyri, Iceland and Connecticut Global Fuel Cell Center at the University of Connecticut, Storrs, USA for giving me the opportunity to complete my master program and thesis.

I wish to express my thanks to the staff of CGFCC and especially Dr. Trent Molter for valuable remarks, advices and time.

I would also like to thank the coordinators of the Fuel Cell and Hydrogen concentration: Þorsteinn Ingi Sigfússon and David Dvorak for professional inspiration and their constant support.

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1 INTRODUCTION

1.1 Background

The full benefits from hydrogen as a sustainable fuel can be achieved only when it is produced from renewable energy sources. Wind and solar energy, as the most abundant renewable energy sources, have experienced the greatest development during the last few years. Today, their technology is becoming economically feasible. Often these resources are widely available, or perhaps even the only available energy sources in some remote areas, and are often not integrated with a grid. The operation of a wind or solar based system highly depends on weather conditions and thus electricity generation is variable in time, and often the pattern does not actually follow the load demand. In order to fulfill the energy requirements during a period of low available resources, energy needs to be stored. The most popular way to store energy is batteries, but they lose their energy content rapidly and therefore they can be only used over a short time period. Batteries also have a limited life cycle and problems with depth of discharge, often requiring replacement of service. A better option might be storage in the form of hydrogen (which may offer the lowest marginal cost of energy storage of any available technology).

Molecular hydrogen does not exist in nature, thus it needs to be obtained in other ways. The only mature and available technology for producing hydrogen from renewable sources is water electrolysis, in which a molecule of water is split into oxygen and hydrogen by applying electricity. Electrolysers are based either on an alkaline electrolyte, mostly KOH, or a proton exchange membrane (PEM), where Nafion™ has been used as an electrolyte. This material has also been used as an electrolyte in PEM fuel cells. A water electrolysis system is comprised of a water electrolysis cell or module, a fluids subsystem which feeds water to and removes gases from the cell, and an electrical subsystem which provides control and power conditioning functions. The main components of the water electrolysis cell are the cathode, anode and separator. The cathode and anode must be corrosion resistant and be good electronic conductors. The hydrogen production capacities achievable through electrolysis range from a few cm³/min to thousands of m³/h and the efficiency of the process is above 70%. However, this process requires high energy densities, so this path can be expensive. Inexpensive hydrogen production can be achieved during off-peak consumption hours, when the excess of the electricity from either wind turbines or solar panels can be used for electrolysis to produce hydrogen. This hydrogen is often stored in the form of compressed gas in pressurized storage cylinders, but other storage alternatives also exist (cryogenic liquid, solid metal hydrates or in liquid hydrogen carriers like e.g. methanol). In periods of high electricity demand, but unfavorable weather conditions, hydrogen can be utilized for power generation by a highly efficient fuel cell in order to sustain the electricity demand.

Unlike batteries, fuel cells are devices that produce electricity as long as they are supplied with a fuel. They rely on direct electrochemical conversion of a fuel and therefore they are much more efficient than internal combustion devices, reaching operational efficiencies of 40%.

For small applications, below 100 kW, a proton exchange membrane (PEMFC) would be the most suitable choice. The advantages of PEMFCs are: good start-stop capabilities, operation in low temperature regime and high power density. A typical fuel cell consists of

the electrolyte, in contact with porous electrodes, on both sides. Low temperature fuel cells like PEM FCs require noble electrocatalysts to achieve practical reaction rates at the cathode and anode. In order to get usable voltages, the cells are combined in a stack, where they are electrically connected in a series by a bipolar separator plate.

Hydrogen based systems offer flexibility in sizing because of modularity of electrolyzers, fuel cells and storage tanks and thus can be adjusted to fulfill various needs and demands. The complexity of the hydrogen based system, to assure a continuous supply to meet the load demand, is very high, therefore the proper management of energy and fluxes between particular elements is essential. The schematic of the renewable energy source – fuel cell system (RES-FC) is shown in Figure 1.1.

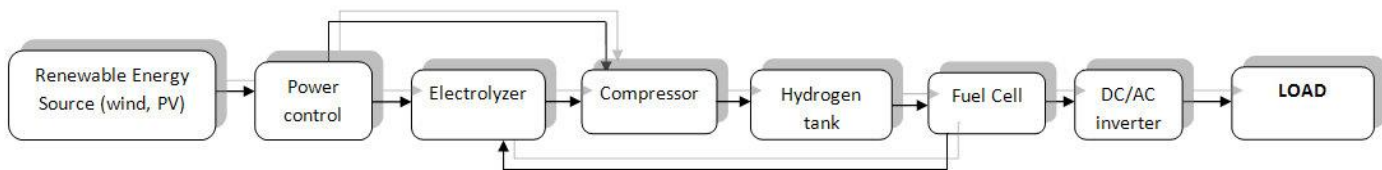


Figure 1.1 Renewable energy source – fuel cell system.

Operation of an electrolyzer and a fuel cell in combination with renewable energy source, especially wind and solar power, has several issues which need to be addressed. They are as follows:

a) Relative sizing of an electrolyzer and PV array or wind turbine

The electrolyzer may be sized to receive all the power generated by wind or PV, or a lower power than the maximum power output of a turbine or PV. With the first possibility, the electrolyzer would work with the same capacity factor as the primary energy source, but this option is likely less cost competitive. The second setup is more economically feasible, because the electrolyzer works at a higher capacity, but some of the electricity would be unutilized for directly creating hydrogen. It could be used as an additional energy input to the grid, but only at very intermittent intervals.

b) Intermittent operation

Renewable resources can fluctuate significantly from hour to hour and from season to season, causing variability in power output and thus variation in the power supply of the electrolyzer, therefore influencing the operation of the fuel cell. An example of the power fluctuations from a wind turbine has been presented in Figure 1.2. These devices need to tackle the problem of slow transients.



Figure 1.2 Fluctuations of instantaneous power on March 16, 2004 at the Cap-Chat (Quebec, Canada) wind farm 76 turbines.[Regie de l'énergie, Quebec, Canada, Dossier R-3526, Avril 2004].

Additionally, variability in power input to the electrolyzer can cause problems with thermal management. A proper operation of the electrolyzer depends on establishing a predictable working temperature. The electrolyzer needs time to warm up, and operation below a nominal input power can cause lower operational temperatures, resulting in lower efficiency. That is why robust strategies for operating the fuel cell and electrolyzer must be applied in order to prevent too frequent start-ups and shut-downs.

c) Output pressure

Compression of hydrogen is obtained by the use of piston or centrifugal compressors. The electricity consumption of the compressor is dependent on the pressure ratio and not the absolute pressure difference. Thus the use of pressurized electrolyzers should be taken into account, because it could reduce electricity consumption related to mechanical compression. During the operation of a PEM electrolyzer, hydrogen can be produced at various pressure levels, reaching the level of ~30 bar, but this results in higher cell voltages and also requires special design of the devices.

d) Oxygen generation

During the electrolysis production, oxygen is mostly ignored and vented, but this gas can be used later in the operation of the fuel cell in order to increase its performance. But the cost of oxygen production is approximately 4 times cheaper than hydrogen, thus further storing and usage would be at additional cost, without bringing overall benefits for system operation.

e) Water consumption

Hydrogen production from water requires a sufficient amount of purified water. Impurities in water can significantly reduce the lifetime of the electrolysis cell. Water is usually purified on-site, but water cleanup could add additional cost to hydrogen production. In a stationary system where hydrogen is used for energy storage, the water from the fuel cell could be cycled back to the electrolyzer with minimal purification. In this

case, water needs to be refilled due to the evaporation loss, requiring 25% higher water supply.

f) Efficiency

The overall efficiency of the RES-FC system is the ratio of energy delivered to the grid vs. energy produced by renewable sources. Production of hydrogen is correlated to electrolyzer efficiency. Higher voltage results in more hydrogen production, but lower efficiency. Designing the system can distinguish between size and cost of the device or efficiency. Also power is lost due to the parasitic losses of auxiliary devices. The efficiency of the electrolyzer ranges between 65-80%,

The efficiency of utilization of hydrogen in the fuel cell to create electricity is a function of cell voltage. With the increase of voltage, efficiency increases, but when more power (current) is drawn, the efficiency decreases. That is the reason fuel cells are typically operated in a range between 0.6 and 0.8V, with the efficiency level reaching 50%. Renewable energy source efficiencies are as follows: wind turbine 33-38%, PV array 13-16 %. Additional power drop is caused by voltage regulation devices (DC/DC and AC/DC converters), with which, for the typical commercial inverter, efficiency ranges between 80-95%.

g) Performance degradation in time and reliability

During electrolyzer operation, the voltage increase occurs in time due to equilibration of water content in the membrane and oxidation of the catalyst and other metallic components.

Also, currently available fuel cells have a short life time because of the degradation of the membrane. The life time of electrolyzer and fuel cell need to be taken into account when designing the system. But with the adequate design of the particular elements, their life time can be extended.

The other very important issue regarding hydrogen is safety. Improper handling and storage can pose some risk, because hydrogen has a low ignition temperature and a wide flammability range. Also, hydrogen flame is almost invisible. This could potentially cause harmful injuries because it is hard to notice. But, on the other hand, the safety of hydrogen lies in its high volatility and non-toxicity. Appropriate protection and proper use of systems based on hydrogen should guarantee safety and correct operation.

1.2 Objectives

Efficient operation of the RES-FC system in irregular conditions brings a lot of problems. The objective of this work is to create a system-level model that defines the relationship between elements of a Renewable Energy Source-Fuel Cell (RES-FC) system given at intermittent supply conditions and changing energy demand. The scope of this work is to create a conceptual energy storage architecture incorporating renewables, hydrogen generation, hydrogen storage and fuel cell power generation.

The objectives will be achieved by analysis and construction of a model for each element of the system. Then the input and output data will be defined and energy fluxes between elements will be calculated. Additionally, the efficiencies of each element and a

system will be defined. The conceptual model will be created in MS Excel. Finally, the simulation of an operation of the system model for variable input data and calculation of performance of the system and individual devices will be executed and the final results discussed.

2 REVIEW OF TECHNOLOGY

2.1 Wind energy

Wind energy is the fastest growing renewable energy sector. It increased more than fivefold globally between 2000 and 2007, but only selected locations have wind resources that are sufficiently strong and steady to be attractive for exploitation. Figure X. shows a wind resources map of the World.

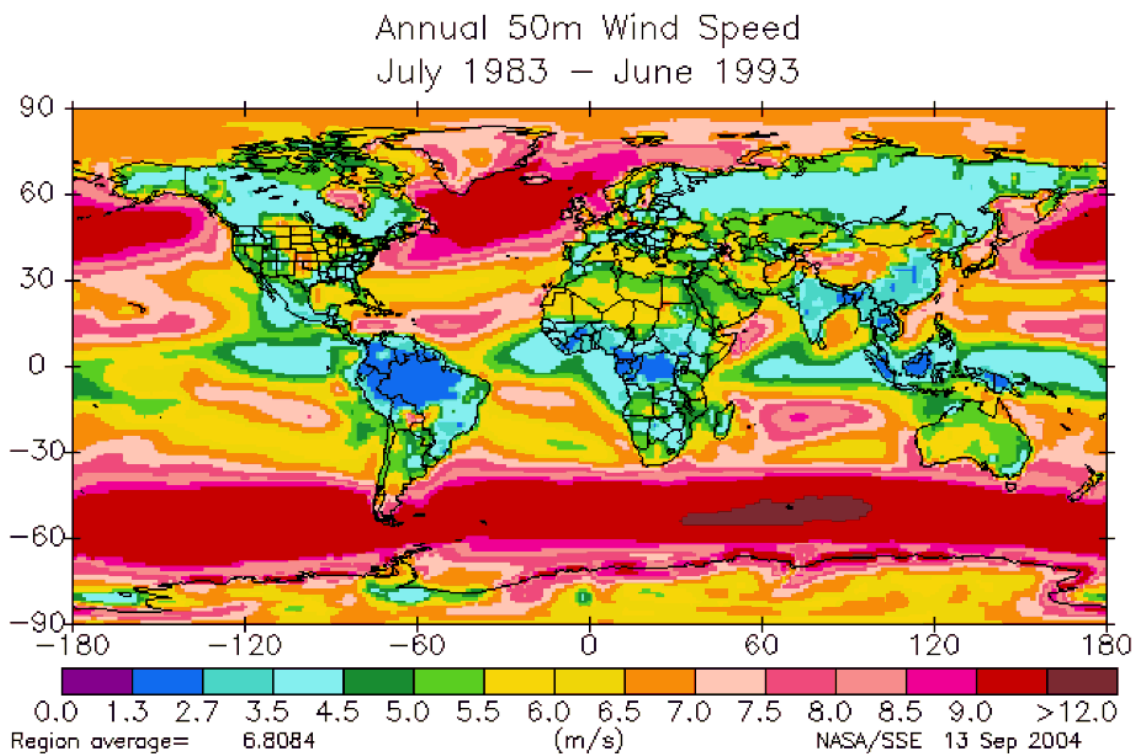


Figure 2.1 Wind resources map for the world. Source: NASA, GEOS-1 satellite.

Satellite data are the only wind data with global extent, but are less accurate because the data are indirect. Roughly 7 m/s and faster are economically worth exploiting today even in higher-cost offshore locations. In many areas, especially on land, the 6 m/s areas are already economically viable. The largest wind resources are above the oceans and decline in average quality in the central regions of large continental masses. However, the great continental plains are rich in wind resources. The coastal regions are of special interest because they have strong winds and they are close to most of the world's population and electricity use.

Wind energy has large seasonal variations for generation. It is very difficult to predict accurately the energy output from wind sources. The grid can absorb these seasonal variations, but only if the total wind power is less than 20% of total grid capacity. Because of the intermittent behavior of this energy source, wind turbines operate with a low capacity factor. In some regions, the grid owners impose penalties on wind farm operators for each undelivered kWh.

The penetration of wind power can be significantly increased by introducing advanced storage technologies like the establishment of hydrogen as an energy carrier. Utilization of hydrogen to produce electricity is controllable and can fulfill the grid demands when electricity from wind cannot be produced. To secure the reliability of the energy supply and optimize the total installation cost, the relation between the rated power of the wind power plant and the hydrogen system are important. It is economically favorable to oversize the wind turbine in order to reduce the need for long-term storage, but it would lead to more non-utilized wind energy, which will reduce the total efficiency of the system, but on the other hand it would reduce the energy cost.

Wind resources not only vary over a short time, but they also significantly fluctuate within seasons and years. These variations will strongly influence the performance of the system. Wind power also fluctuates from hour to hour, so robust strategies for on-line operations of electrolyzers and fuel cell must be applied in order to prevent too frequent start-ups and shut-downs. The way to improve the system operation is to incorporate the short term wind forecasts with planning and operational tools.

Wind energy can be converted to hydrogen via water electrolysis. The details of the process will be described in the following chapter "Electrolysis".

Direct combination of an electrolyzer with a wind turbine implies intermittent operation with a highly variable power output. A commercial electrolyzer is designed to operate within a narrow supply voltage range, and when the power input varies out of the design operation range, the internal voltage monitor controls will stop the operation. This protects the ancillary components, including the cell stack power conditioners, from electrical failure from over-current at low voltage and arcing at high voltage. However, an electrolyzer may be designed to separately supply the cell stacks with variable DC power with a wider range while providing ancillary power from a steady regulated supply. In this case there is a minimum voltage level at which to initiate electrolysis at a rate compatible with the balance of the plant, with the minimum requirements for electrolysis reaction, and at which the turbine can still function correctly through startup and normal operation.

The combination of a source, such as a wind turbine, with an electrolyzer may result in a lower efficiency due to the losses related to power/voltage matching. Voltage regulation, either AC/DC or DC/DC, would consume some power. These devices may be designed to operate with efficiency as high as 93–95%, but this high efficiency may be achieved only in a narrow power range. In a highly variable mode of operation, as with the input from the wind turbine, this efficiency may be considerably lower.

The economics of wind hydrogen systems significantly depend on the configuration of the system and its application, in addition to the available wind resources. An electrolyzer may be sized to receive all the power generated from a wind turbine, but it would operate with the same capacity factor as the wind turbine, which would be less economical feasible. A more cost-effective option may be to size the electrolyzer at a power lower than the wind turbine's maximum power output. In that case some of the power from the wind would not be utilized, but the electrolyzer would operate with a higher capacity factor. For any wind turbine availability and load profile there is an optimum electrolyzer capacity.

2.2 Wind turbines

2.2.1 Technology

The most popular configuration uses a horizontal axis, three-bladed rotor, an upwind orientation, and an active yaw system to keep the rotor oriented into the wind. The drive train consists of a low-speed shaft connecting the rotor to the gearbox, a 2- or 3-stage speed-increasing gearbox, and a high-speed shaft connecting the gearbox to the generator. Generators are typically asynchronous, induction, and operate at 550-690 V (AC). Some turbines are equipped with an additional small generator to improve production in low wind speeds. The second generator can be separate or integrated into the main generator. Each turbine for utility-scale applications is equipped with a transformer to step up the voltage to the on-site collection system voltage. The on-site collection system typically is operated at medium voltages of 25 to 35 kV. Figure 2.2 shows the major turbine components for a wind turbine.

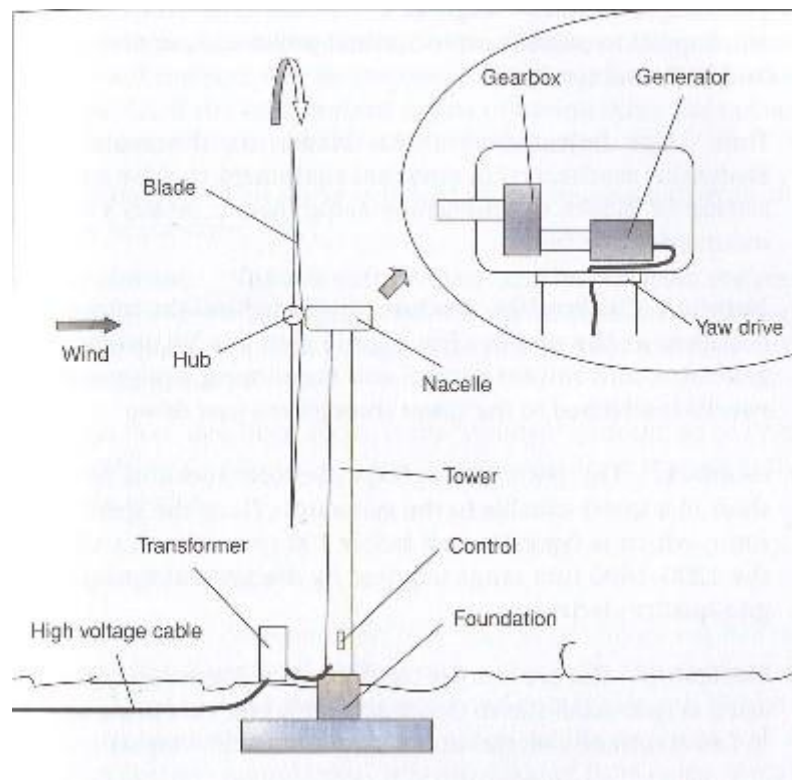


Figure 2.2 Major Turbine Components

As shown in Figure X, power production from a wind turbine is a function of wind speed. The relationship between wind speed and power is defined by a power curve, which is unique to each turbine model and, in some cases, unique to site-specific settings. In general, most wind turbines begin to produce power at wind speeds of about 4 m/s, achieve rated power at approximately 13 m/s, and stop power production at 25 m/s. Variability in the wind resource results in the turbine operating at continually changing power levels. At good wind energy sites, this variability results in the turbine operating at approximately 35% of its total possible capacity when averaged over a year.

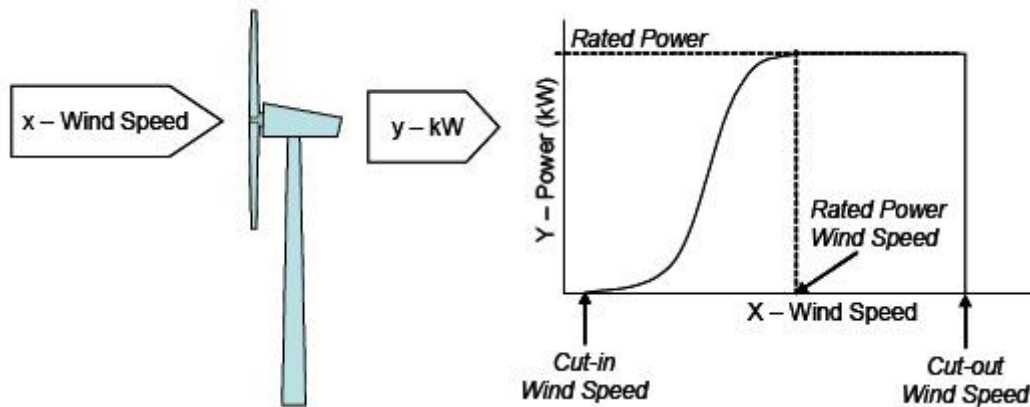


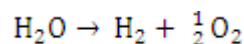
Figure 2.3 Relationship of Wind Speed to Power Production

The ratio of a turbine's rotor swept area to the rating of the turbine is known as the specific rating. No 'best' relationship between rotor diameter and generator rating exists. Designers of modern turbines appear to have settled on a range of specific ratings from 0.32 to 0.47 kW/m², as this range presents the best compromise between energy capture, component loading, and costs. Turbines at sites with lower wind speeds (such as 7.0 to 7.5 m/s annual average at hub height) tend to have larger rotors and lower specific ratings to improve energy capture. Turbines at high-wind-speed sites (exceeding 9 m/s) tend to have smaller rotors and higher specific ratings. The smaller rotor helps to reduce loads on components and thus improves reliability in these aggressive wind sites.

2.3 Electrolysis

2.3.1 Principles

When an electric DC current is passed by two electrodes in water, hydrogen, oxygen and heat are created by electrolytic water decomposition according to the following reaction:



Pure water is a very poor ionic conductor and for this reason a conductive electrolyte must be added so that the reaction can proceed at a technically acceptable voltage. The electric voltage applied to the two electrodes must exceed a minimum value, termed the decomposition voltage. This is determined by the Gibbs' enthalpy of water splitting and is a function of the pressure and temperature, at the temperature of 25°C and a pressure of 1 bar, it is 1,23V.

The theoretical energy required for the electrolysis reaction to occur is express by the following equation:

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

Where: ΔH is the enthalpy change of the reaction, ΔG is the change of the Gibbs free energy, T is the temperature and ΔS is the entropy change.

The enthalpy change under the standard conditions (STP: T=298,15 K and P=1 bar) equals 285,8 kJ/mol. This value corresponds to the higher heating value HHV, which is defined as the amount of heat released by a sample fuel at a temperature of 25 C when it is combusted and the products have returned to a liquid state at an initial temperature.

The change in the Gibbs free energy at the standard conditions equals 237,2 kJ/mol.

It means that 237,2 kJ/mol out of 285,8 kJ/mol needs to be supplied by electricity and the remaining part could be theoretically supplied either by electricity or by heat. However, in the real conditions for low temperature electrolysis all of this energy, and some more to overcome losses, is provided by electricity.

Another thermodynamic characteristic of electrolysis is the reversible voltage. It expresses the minimum electrical potential needed to drive the electrolysis reaction. It is expressed by the formula:

$$E_{\text{rev}} = \frac{\Delta G}{2F}$$

where: 2 is the number of electrons which need to pass to split each water molecule and F is the Faraday constant. For standard conditions the reversible voltage is equal 1,23 V.

Thermoneutral cell voltage is a voltage at which a perfectly efficient cell would operate if electricity provided the entire energy requirement. It is expressed by the formula:

$$E_{\text{tn}} = \frac{\Delta H}{2F}$$

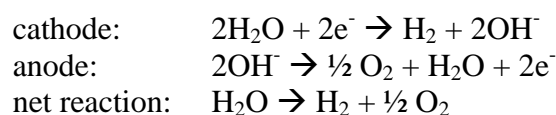
For standard conditions it equals 1,48 V.

When the cell operates below the reversible voltage, no water splitting occurs. When it operates between the reversible and thermoneutral voltage the electrolysis process is endothermic and additional heat needs to be supplied in order to split water. For voltages above the thermoneutral voltage, the process is exothermic and all energy comes from electricity. Additional heat needs to be removed.

Both E_{rev} and E_{tn} are a function of the temperature, pressure and electrolyte composition.

The main components of the water electrolysis cell are the cathode, anode and separator. The cathode must be corrosion resistant in the electrolyte at reducing potentials, be a good electronic conductor and have structural integrity. It should catalyze the oxygen evolution as effectively as possible. Both electrodes are separated from each other by a diaphragm or a membrane impermeable to the gases.

For alkaline electrolysis, potassium hydroxide (KOH) typically in a concentration of 25-30% (by weight) is the most used component to increase water conductivity. The alkaline electrolyte reaction goes as follow:



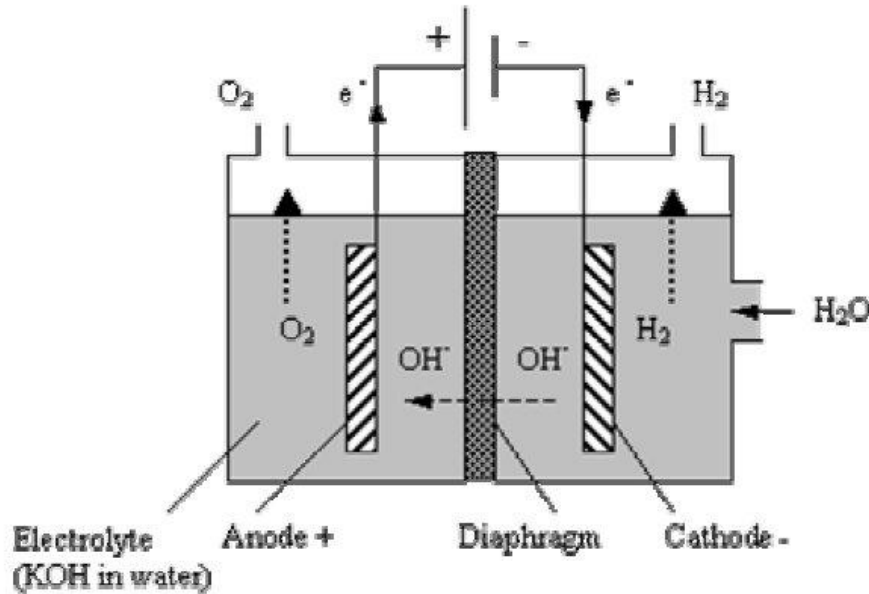


Figure 2.4 Principle of alkaline water electrolysis (AWE)

The alkaline electrolysis takes place at a temperature around 80°C and a pressure in the range of 1 to 30 bar. Alkaline electrolytes have been preferred in actual applications, mainly because of fewer corrosion problems. To precede alkaline electrolysis steadily, hydroxyl ions (OH^-) must continuously migrate from the cathode to the anode, in a way that prevents the intermixing of hydrogen and oxygen. To this end, a separator (diaphragm or membrane) is placed between the electrodes. This separator must allow the free passage of ions, while acting as a barrier to keep the gases apart.

To increase the recombination rates of atomic hydrogen and oxygen, catalysts are applied to the surface of the electrodes. Without a catalytic coating, atomic hydrogen would build up on the cathode surface, hence reducing the current flow and slowing the production of hydrogen gas.

In alkaline electrolysis water is generally fed to the circulating electrolyte, which is also a way to remove the waste heat produced by the electrolysis reaction and control the process temperature.

All traditional alkaline electrolyzers use the so called zero gap design. In this design the anode and the cathode are placed at zero gap on each site of a diaphragm, which acts as a filter that prevents mixing of the oxygen and the hydrogen. Placing the two electrodes as close as possible to each other, the ohm loss in the electrolyte is reduced. Additionally when the gas bubbles are produced, they will be transported to the rear site of the electrodes through holes in the perforated electrodes and thus not block the current of ions between the two electrodes.

Acid solutions are not used today in practical water electrolysis, but instead acid membranes offer an alternative to liquid alkaline electrolytes. Their main feature of membrane is high proton conductivity and a very low electronic conductivity. It means that they allow the migration of protons between the electrodes, while preventing electrons from going through the same way. Electrons have to pass by an external circuit to go from one electrode to the other.

For acidic electrolyte the reactions proceed as follow:

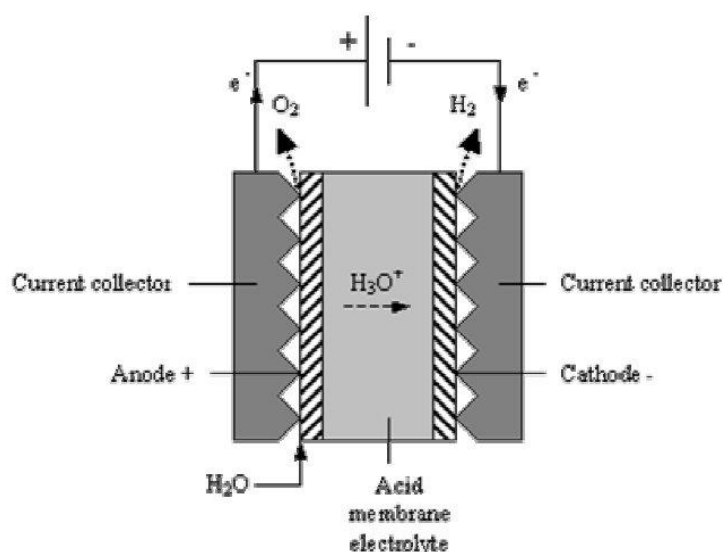
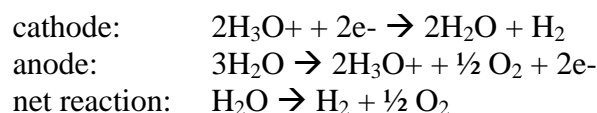


Figure 2.5 Principle of solid polymer electrolysis (SPE).

The polymer membranes serve both the roles of electrolyte and separator. Most membrane materials are based on sulphonated fluoropolymers to conduct protons. The most well known membrane material is Nafion®, which has been developed by DuPont and used in both electrolyzers and PEM fuel cells. A key property of sulphonic acid is that it is highly hydrophilic – it attracts large amounts of water, and on the other hand the fluoropolymer is hydrophobic – it repels water. Within hydrated regions, the H^+ ions (protons) are relatively free to move, thus creating a diluted acid. Between the hydrated regions, it is still possible for H^+ ions to migrate short distances through the supporting long molecule structure, but with more difficulty. Therefore a well-hydrated membrane is a key facilitator for allowing protons to flow and the overall electrolysis reaction rate.

The upper temperature limit of the proton exchange membrane is around 125-150°C, but most electrolyzers operate in liquid water regime, at a temperature of 80°C. Higher operating temperatures, in order to get better kinetic reactions, could be achieved with new polymer membrane materials or even ceramic proton-conducting materials. But higher temperatures generate more heat. To remove the waste heat, water needs to be supplied and circulated at a sufficient rate over the anode side.

Each electrode is usually made of a thin layer of carbon-supported platinum catalyst, bonded to the membrane electrolyte. Platinum is considered to be the best catalyst for both the anode and cathode, because of good thermodynamic and kinetic properties. The use of platinum is the greatest cost of the electrolyzer, but the required amount has been considerably reduced recently.

The advantage of solid polymer electrolysis is that it operates at higher current density than alkaline electrolysis. Therefore in spite of higher material costs, a PEM electrolyzer requires lesser cell area than an alkaline electrolyzer to produce hydrogen at the same rate and high efficiency while in a more compact design.

2.3.2 Design of electrolyzers

In order to obtain the actual amount of hydrogen, electrolyzers are composed of multiple amounts of electrolysis cells or pairs of electrodes. There are two types of electrolyzer design: monopolar (the tank type) and bipolar (the filter-press type).

In a monopolar configuration, each of the electrodes is connected and fed by a separate current and has a single polarity, so it is either a cathode or an anode. The cells are connected parallel and the voltage across the whole tank is the same as the voltage across any individual cell, regardless of the number of electrodes. The voltage is typically 1,2 -2 Volts. This configuration is simple, robust and easy to maintain. It also contains inexpensive parts; however it has higher power consumption due to the drop in electric potential

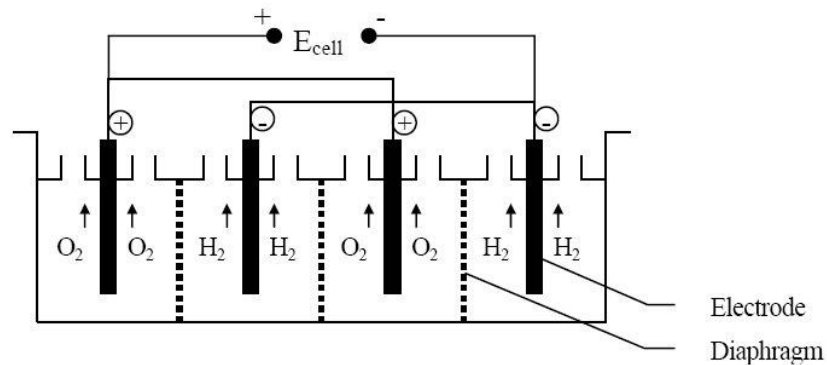


Figure 2.6 Principles of a monopolar design

For bipolar configuration, each electrode has a cathode and an anode side. Each cell is connected in a series and its current is fed to the end plate electrodes. The voltage across the whole stack is equal to the number of cells multiplied by the voltage of an individual cell. This design is more compact, more efficient, works in higher current densities and can operate at higher pressures and temperatures, but the design is more complex.

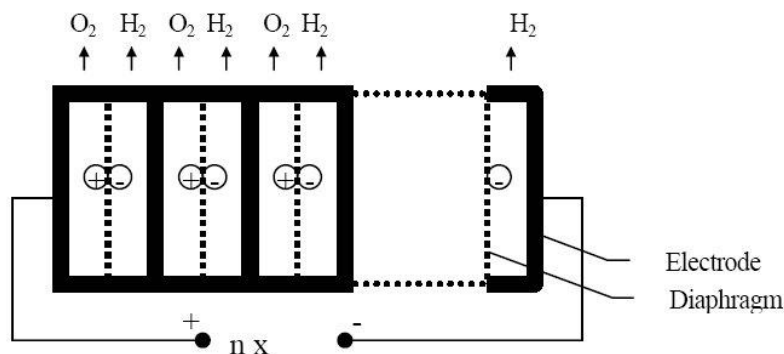


Figure 2.7 Principles of a bipolar design

Additionally each type of electrolyzer needs either rectifiers or AC/DC converters in order to use the alternative current. To minimize the inefficiencies the tank electrolyzers are connected in a series to increase the overall voltage and the filter-press electrolyzers are connected in parallel and in a series to combine the production rate and the optimal voltage of the plant.

2.3.3 Efficiency of electrolysis

Different sources give different definitions of the efficiency of electrolysis. The most general definition of efficiency is:

$$\text{Energy efficiency} = \frac{\text{Energy output}}{\text{Total energy input}}$$

The energy efficiency of an electrolyzer has been defined as “the energy that ideally could be recovered by reoxidation of the hydrogen and oxygen coproducts to water (the heating value of hydrogen), divided by the energy supplied to the electrolysis system in electrical form”. In the case of water electrolysis, the energy input is electrical energy.

$$\text{Energy efficiency of water electrolysis} = \frac{\text{Heating value of hydrogen output}}{\text{Total electrical energy input}}$$

Some references use the lower heating value (LHV) of hydrogen while others use its higher heating value (HHV) to calculate the energy efficiency of electrolysis. In this research, the HHV value is always the one used, as it better reflects the full energy content of hydrogen.

According to this definition, the efficiency can exceed the value by 100%, because it does not take thermal energy inputs into consideration. This is in the case where an electrolyzer operates below the thermoneutral voltage, when heat from the surroundings is used as an energy input and this is not considered in that definition.

At the cell level, the energy efficiency of the electrolysis process could be defined as the ratio of the thermoneutral voltage (for liquid water at 25°C (298K) and pressure 1 bar – U_{HHV} = 1.48 Volts) to the actual cell voltage (E).

The energetic efficiency of the water electrolysis is defined by:

$$\eta = \frac{U_{\text{HHV}}}{E}$$

Depending on the particular electrolysis technology and operating conditions, the efficiency varies in the 75-95% range, based on the HHV value of the hydrogen produced. The corresponding range for the LHV value of hydrogen is 63-80%.

But if we consider electricity as an energy derived from another energy source (e.g. coal, natural gas, etc.) the overall efficiency of hydrogen production by electrolysis can drop dramatically, down to the 30% range.

2.3.4 Cell voltage

The power consumption of an electrolysis cell is directly proportional to the cell voltage and inversely proportional to its current efficiency.

The current efficiency is the ratio of the number of electrons theoretically required to produce a given amount of hydrogen (two electrons for each molecule of hydrogen produced) over the actual number of electrons supplied by the electrical current in producing this amount of hydrogen.

$$\text{current efficiency} = \frac{\text{Volume of generated H}_2 \left(\frac{\text{Nm}^3}{\text{h}} \right) \times 96487 \left(\frac{\text{C}}{\text{mol e}^-} \right) \times 2 \left(\frac{\text{mol e}^-}{\text{mol H}_2} \right)}{\text{Current (A)} \times 3600 \left(\frac{\text{s}}{\text{h}} \right) \times 0,0224 \left(\frac{\text{Nm}^3}{\text{mol H}_2} \right)}$$

Current efficiency is usually very close to 100%, the parameter of importance in evaluating water electrolysis cells design depends on the cell voltage.

Water electrolysis under actual conditions demands a cell voltage E that is substantially higher than the reversible value E_{rev} . It has to overcome the electrical resistance in the electrodes, in the electrolyte between the electrodes, and in the separator. Additionally, it has to cover the overpotentials at the electrodes, which are kinetically determined. The cell voltage can then be expressed as:

$$E = E_{\text{rev}} + \eta_c + \eta_a + jR^*$$

where: η_c is the cathodic overpotential (hydrogen overvoltage), η_a is the anodic overpotential (oxygen overpotential), j is the current density and R^* is the sum of the electrical resistance.

The electrical resistance in the electrodes is determined by the material and design of the electrodes and the temperature.

The overpotentials are determined by the activity of the electrode surfaces, the electrolyte composition and temperature

The ohmic resistance related to the flow of electrons through current-collecting is relatively unimportant in the bipolar design, though it is not negligible in monopolar electrolyzers.

2.3.5 Current density

The voltage and specific energy use are directly affected by the operating current density. The resistance inside an electrolytic cell goes up with an increase in current density, and thus the operating voltage also increases proportionally and depends on the electrolysis technology and cell design. For alkaline electrolysis the operational voltage increases more vehemently with the current density than for solid electrolyte electrolysis and this explains why solid polymer electrolyzers require less electrode surface area than alkaline electrolyzers. For each design there is an optimum current density that minimizes the overall cost of hydrogen.

2.3.6 Effect of Operating Conditions

a) Temperature

Increasing the electrolysis temperature reduces the reversible voltage E_{rev} , and therefore the electrical energy input. When temperature is increased from 250°C to 1000°C, the electrical input can be reduced by about 25%. However, the overall theoretical amount of energy required to perform electrolysis at a high temperature is not lower, but rather slightly higher. The advantage of higher temperature electrolysis is to use heat as an energy input, and increased efficiency due to improved kinetics.

b) Pressure

The pressure of electrolysis influences the energy requirements for electrolysis. The relationship between temperature and pressure T on the reversible voltage is expressed by the Nernst equation:

$$E_{rev,T,P} = E_{rev,T,P=1} + \frac{RT}{nF} \ln \frac{a_{H_2}(a_{O_2})^{1/2}}{a_{H_2O}}$$

where R- the universal gas constant, n – number of electrons to split each molecule of water (n = 2), F- the Faraday constant, a –activity of species, $E_{rev,T,P=1}$ – reversible voltage at temperature T [K] and standard pressure P = 1 bar.

The activity coefficients of hydrogen (a_{H_2}) and oxygen (a_{O_2}) can be obtained from the pressure ratio to atmospheric pressure: $a_{H_2} = P_{H_2}/P_O$ and $a_{O_2} = P_{O_2}/P_O$. It can be assumed that $P_{H_2} = P_{O_2} = P$, because the pressure on the hydrogen side and the oxygen side is the same. Additionally the activity of water can be approximated as 1 and $P_O = 1$ bar, the Nernst equation is simplified to:

$$E_{rev,T,P} = E_{rev,T,P=1} + \frac{3RT}{4F} \ln P$$

For the temperature T= 298k, the voltage increase with the increase of pressure goes as follows:

Pressure P [bar]	10	30	50	100	200
$\Delta E_{rev,T,P}$ [V]	0,044	0,065	0,075	0,089	0,102

So an electrolyzer operating with 10 bar output at 1.55 V might need only 1.608 V to operate at 200 bar, based on theoretical considerations. (1.55 V + (102 mV – 44 mV) = 1.62 V).

The high-pressure electrolysis is the most efficient way of compressing produced hydrogen, because it requires less energy than pressurizing it by a compressor itself, although pressure in the range of 400 bar would cause mechanical constraints on the electrolyzer and increase the capital cost of the device. Depending on the required hydrogen output pressure, specific strategies need to be applied: either the compressor can be eliminated from the system if low pressure is required, a single-stage compressor can be applied when the produced hydrogen is already pressurized or multi-stage compressors are required when the final hydrogen has to have high pressure, but it was produced from low-pressure electrolysis.

2.3.7 Overall Energy Use of an Electrolyzer Cell

The specific energy use of an electrolyzer can be estimated from the single cell operating voltage (E) and current efficiency (η_i) and can be calculated from the following formula:

$$K = 26589 \times \frac{E}{\eta_i}$$

26589 kAh is the numbers of electrons (e-) required to obtain one kilogram of hydrogen from water electrolysis.

$$\frac{2e^-}{H_2} \times \frac{1000 \text{ g } H_2}{2,016 \text{ g } H_2 / \text{mol } H_2} \times \frac{96487 \text{ C}}{\text{mol } e^-} \times \frac{1 \text{ kA}}{1000 \text{ C/s}} \times \frac{1 \text{ h}}{3600 \text{ s}} = 26589 \text{ kAh}$$

This equation does not include the energy needed to deionize water or to convert AC to DC current for the electrolyzer, but it gives a good estimation of the electrolyzer itself.

	AWE			SPE	HTE
<i>Technology</i>	Conventional alkaline electrolyzer	Advanced alkaline electrolyzer	Inorganic membrane alkaline electrolyzer	Solid polymer electrolyzer	High temperature electrolyzer
<i>Cell voltage, V</i>	1,8-2,2	1,5-2,5	1,6-1,9	1,4-2,0	0,95-1,3
<i>Current density, A/cm²</i>	0,13-0,25	0,20-2.0	0,2-1,0	1,0-4,0	0,3-1,0
<i>Temperature, °C</i>	70-90	80-145	90-120	80-150	900-1000
<i>Pressure, bar</i>	1-2	Up to 120	Up to 40	Up to 400	900-1000
<i>Electrolyte</i>	25-35% KOH	25-40% KOH	14-15% KOH	Perfluorosulfonic acid membrane	Solid Y ₂ O ₃ -stabilized ZrO ₃ 80
<i>Cell efficiency</i>	77-80%	80-90%	85-95%	85-98%	90-100%
<i>Power consumption kWh/Nm³H₂</i>	4,3-4,9	3,8-4,3	3,6-4,0	3,6-4,0	2,5-3,5

2.4 Storage methods

In order to overcome daily and seasonal difference between energy availability and demand, hydrogen needs to be stored. Hydrogen can be stored in a form of gas, liquid, and also as a hydride.

Hydrogen is very light, with very small density compound. This means that a small amount occupies a large volume. Therefore the volumetric density of hydrogen has to be increased. Classical high-pressure tanks made out of steel are filled up to 200 bar and

tested up to 300 bar, whereas tanks made out of reinforced carbon fiber materials, presented on a Fig 1, can store hydrogen up to the pressure of 600 bar, but recently are filled up to 450 bar. Now, the goal of automotive industry is the storage of gaseous hydrogen at a pressure of 700 bar for common use. This requires novel material composites, which can resist high pressure and not allow materials to become brittle. With the higher pressure, the gravimetric density increases, however during a drop of pressure, additional pressure control would be essential and the compression itself is a very complicated, dangerous and expensive process.

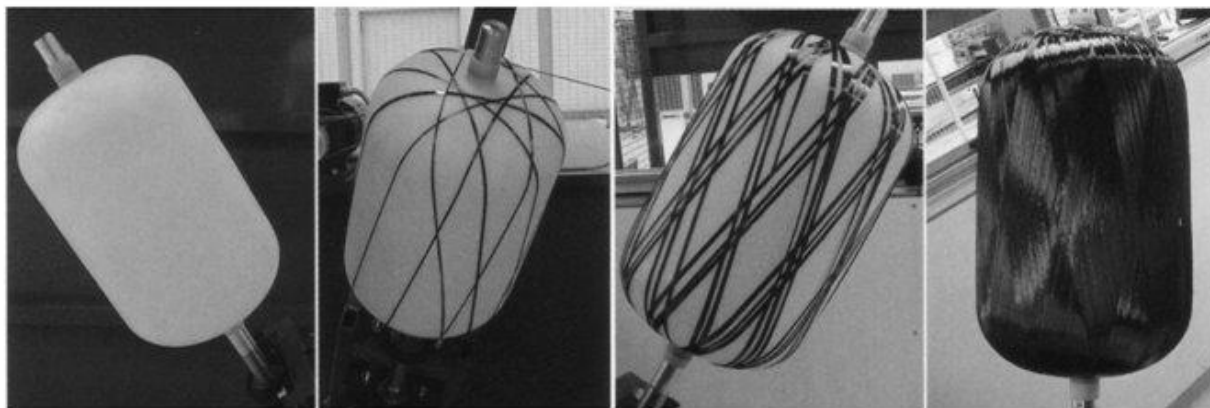


Fig 1. Carbon-fibre-reinforced hydrogen tanks (Ref: Dynetek Europe GmbH, Breitscheider Weg 117a, D-40885 Ratingen, URL: <http://www.dynetek.de>)

To increase the gravimetric density, hydrogen can be converted into a liquid or even solid form. The density of liquid hydrogen is 70.8 kg m^{-3} in comparison with 70.6 kg m^{-3} for solid hydrogen. But the condensation temperature of hydrogen at 1 bar is -252°C , it means that this process is very energy intensive. Liquid hydrogen is mainly used when high storage density is indispensable, for example in aerospace applications.

Hydrogen can form metal hydrides with some metals and alloys. Hydrogen in a molecular form is absorbed in the lattice of specific metals or alloys. In this way, the volumetric density is comparable to the liquid form, but taking into consideration the mass of the metal, the gravimetric density is rather low. At present the highest achievable density is in the range of $0,07 \text{ kg H}_2/\text{kg metal}$ in a high temperature. Hydrogen in a solid form is the safest way to store energy, especially for stationary and mobile applications. The main problematic issues for solid storage are the weight of the tank, high desorption temperature, low desorption kinetics, long recharge time, high pressure and heat transfer.

There are several novel methods of hydrogen storage like on the activated surface of carbon, in glass microparticles or polihydride complexes. Those technologies could improve gravimetric and volumetric density of the hydrogen storage, but they are still under development and have not been implemented in industry. Comparison of different materials for hydrogen storage is presented on the Figure 2.8.

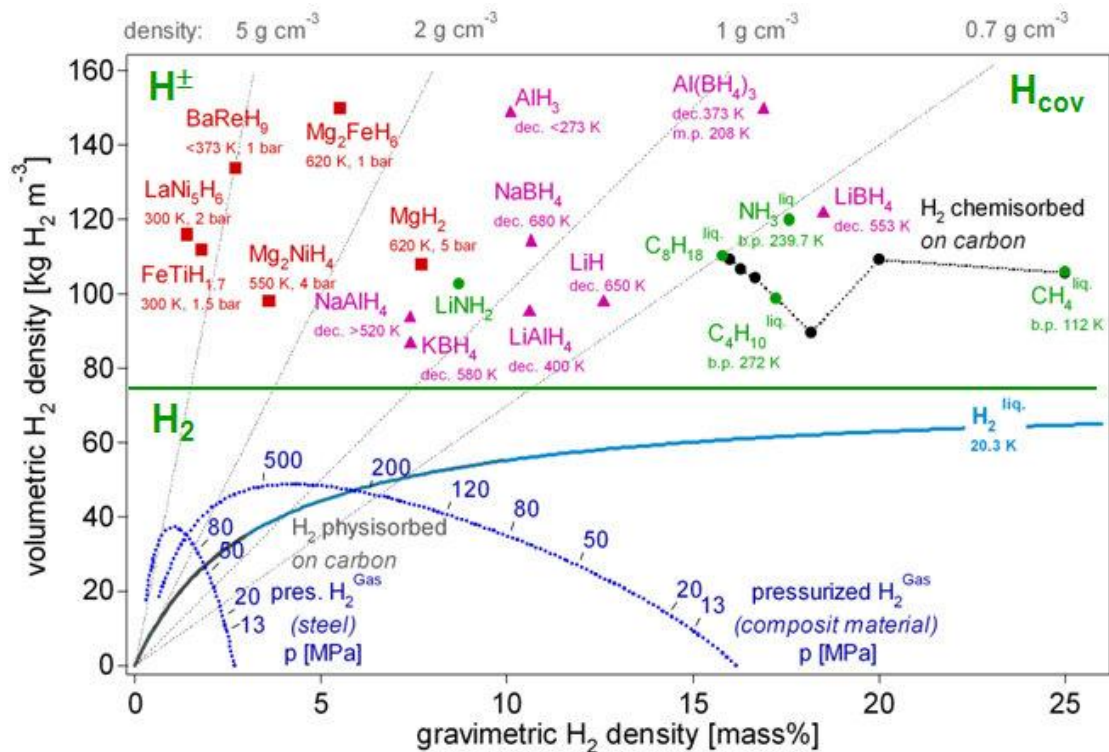
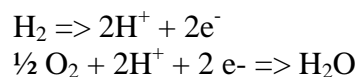


Figure 2.8 Comparison of metal hydrides, carbon nanotubes, petrol and other hydrocarbons in terms of stored hydrogen per mass and per volume.

2.5 Fuel Cells

2.5.1 Principles

A fuel cell is a device which produces electricity as long as it is supplied with fuel. In a fuel cell the stored chemical energy from the fuel is transformed into electrical energy. The difference between the fuel cell and a combustion engine depends on the manner by which energy is converted. In internal combustion engines, heat generated from combustion needs to be converted into mechanical energy and then into electrical energy, causing losses at each level of transformation. In contrast, fuel cells produce electricity from a chemical reaction. In a simple fuel cell, two half reactions process as follow:



The protons migrate through the electrolyte and combine with the oxygen, usually from air, at the cathode to form water. The electrons are routed through an external circuit where they produce direct current (DC). Those devices can reach an efficiency of 40%. Fuel cells can operate on pure hydrogen, but also on reformed fuel, like methane, because they are not poisoned by CO₂.

The performance of the fuel cell system can be described by the interdependence of current and voltage. It is presented in the form of a graph, called a current-voltage (i-V) curve. The voltage output is a function of current, normalized by the area of the fuel cell, giving current density. An ideal fuel cell would supply any amount of current, while maintaining

constant voltage, determined by thermodynamics. However, in real life, the actual voltage output of a fuel cell is less than the ideal thermodynamically predicted voltage and the more current is drawn from a fuel cell, the lower the voltage output of the cell due to unavoidable losses, limiting the power.

The more current is drawn from the cell, the greater the irreversible losses, causing a decrease in voltage output. There are three major types of fuel cell losses:

1. Activation losses - due to electrochemical reaction
2. Ohmic losses - due to ionic and electronic conduction
3. Concentration losses - due to mass transport.

The real voltage output for a fuel is a function of thermodynamically predicted voltage and losses and can be presented in the following way:

$$V = E_{\text{thermo}} - \eta_{\text{act}} - \eta_{\text{ohmic}} - \eta_{\text{conc}}$$

where: V – real output voltage, E_{thermo} – thermodynamically predicted voltage output, η_{act} – activation losses, η_{ohmic} – ohmic losses, η_{conc} - concentration losses.

The power of the fuel cell is determined by the equation:

$$P = i V$$

P -power (W), i - current density (A/cm²), V - voltage (V)

The other characteristic of a fuel cell is a power density curve, which shows the power density delivered by a fuel cell as a function of the current density.

Schematic i - V and power density curve is presented in Figure 2.9.

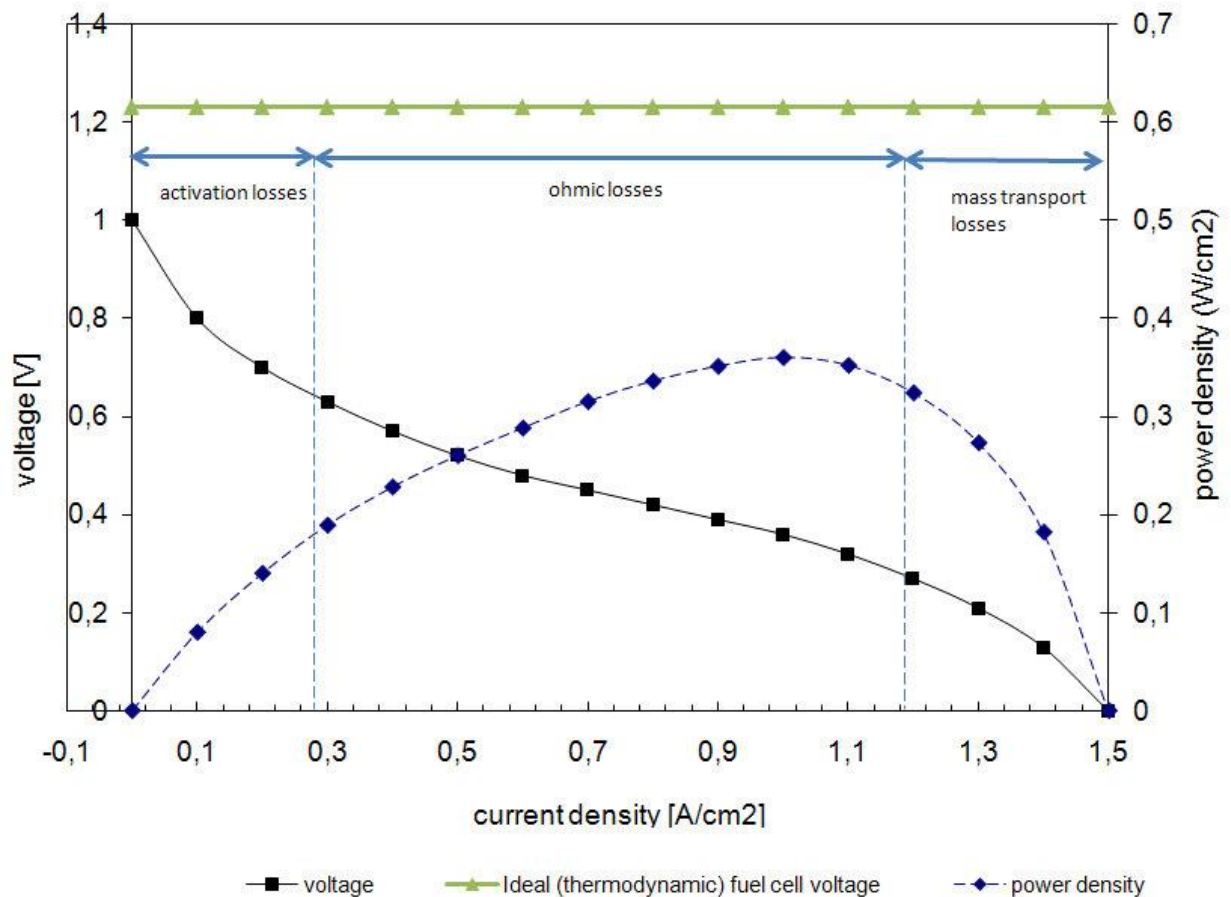


Figure 2.9 I-V and power curve for a fuel cell

Fuel cell power density increases with increasing current density, reaches a maximum, and then falls at still high current densities. Fuel cells are designed to operate at or below the power density maximum. At current densities below the power density maximum voltage efficiency improves, but power density falls. At current densities above the power density maximum, both voltage efficiency and power density fall.

The potential of the system to perform electrical work is measured by voltage. The theoretical, standard state reversible voltage is:

$$E^0 = - \frac{\Delta g_{rxn}^0}{nF}$$

where: Δg_{rxn}^0 is the standard-state free-energy change for the reaction ($\Delta g_{rxn}^0(T) = \Delta h_{rxn}^0 - T\Delta s_{rxn}^0$), n – number of moles of electrons transferred, F – Faraday's constant.

At standard conditions, the highest possible voltage to yield for hydrogen-oxygen fuel equals 1.23 V.

In order to get the usable voltage, fuel cells are assembled in stacks.

The reversible fuel cell voltage is highly dependent on operating conditions like temperature, pressure and activities of the species.

The correlation of a voltage and temperature is represented in the following equation:

$$\frac{dE}{dT} = \frac{\Delta s}{nF}$$

Where: Δs is entropy change

For fuel cells Δs is negative, therefore reversible fuel cell voltage tends to decrease with increasing temperature.

Voltage varies with pressure as follow:

$$\frac{dE}{dp} = -\frac{\Delta v}{nF}$$

Where: Δv is volume change.

The variation of the reversible cell voltage with pressure is related to the volume change of the reaction. If the volume change of the reaction is negative, then the cell voltage will increase with increasing pressure.

Pressure and temperature have a minimal effect on reversible voltage. Chemical activity has a more significant influence, which is given by the Nernst equation:

$$E = E^0 - \frac{RT}{nF} \ln \frac{\prod a_{products}^{v_i}}{\prod a_{reactants}^{v_i}}$$

The Nernst equation provides a relationship between the ideal standard potential (E^0) for the cell reaction and the ideal equilibrium potential (E) at other temperatures and partial pressures of reactants and products. Once the ideal potential at standard conditions is known, the ideal voltage can be determined at other temperatures and pressures through the use of these Nernst equations. According to the Nernst equation for the hydrogen reaction, the ideal cell potential at a given temperature can be increased by operating at higher reactant pressures, and improvements in fuel cell performance have, in fact, been observed at higher pressures. The Nernst equation does not fully account for the temperature effects.

2.5.2 Fuel Cell efficiency

The fuel cell efficiency is a function of cell voltage. The theoretical fuel cell efficiency is:

$$\varepsilon_{thermo} = \frac{\Delta G}{\Delta H}$$

Where ΔG is the Gibbs free energy, ΔH is enthalpy.

The theoretical fuel cell efficiency, obtained from the above definition equals 83%. Since the actual voltage of an operational fuel cell is lower than the reversible potential, the fuel cell efficiency is always lower than the theoretical one. The two major reasons are: voltage losses and fuel utilization losses. The real efficiency of a fuel cell may be calculated as:

$$\varepsilon_{real} = (\varepsilon_{thermo}) \times (\varepsilon_{voltage}) \times (\varepsilon_{fuel})$$

Where: ε_{thermo} - reversible thermodynamic efficiency cell, $\varepsilon_{voltage}$ - voltage efficiency of the fuel cell, ε_{fuel} – the fuel utilization efficiency.

The voltage efficiency includes the losses due to irreversible kinetic effects in the fuel cell. It is the ratio of the real operating voltage of the fuel cell (V) to the thermodynamically reversible voltage of the fuel cell (E).

$$\varepsilon_{voltage} = \frac{V}{E}$$

The fuel utilization efficiency accounts for the fact that that not all of the fuel provided to a fuel cell will contribute to the electrochemical reaction. It is the ratio of the fuel used by the cell to generate the electric current versus the total fuel provided to the fuel cell.

$$\varepsilon_{fuel} = \frac{i/nF}{v_{fuel}}$$

Where i is the current generated by the fuel cell and v_{fuel} is the rate at which fuel is supplied to the fuel cell (mol/sec).

Combining thermodynamics, irreversible kinetic losses and fuel utilization, the real efficiency of the fuel cell can be expressed as:

$$\varepsilon_{real} = \left(\frac{\Delta g}{\Delta h_{HHV}} \right) \times \left(\frac{V}{E} \right) \times \left(\frac{i/nF}{v_{fuel}} \right)$$

2.5.3 Fuel Cell types

Fuel Cells can be differentiated among five major types, depending on the electrolyte, but all of them have the same principles of performance. They work in different temperature regimes and differ by the type of fuel used.

a) Proton Exchange Membrane Fuel Cell (also known as: Polymer electrolyte membrane fuel cell) PEMFC.

PEMFC employ as a membrane the thin solid polymer layer (~30 μm) such as perfluorosulfonated acid known as Nafion®. This polymer is permeable to protons when it is saturated with water, but it does not conduct electrons.

This type of fuel cell operates on hydrogen, oxygen from the air, and water and does not require corrosive fluids like some fuel cells. They are typically fueled with pure hydrogen supplied from storage tanks or on-board reformers.

At the anode, the hydrogen molecule is split into hydrogen ions and electrons. The protons (H^+) permeate across the membrane to the cathode while the electrons flow through an external circuit and produce electric power. Oxygen, in the form of air, is supplied to the cathode and combines with the electrons and the hydrogen ions to produce water. The reactions at the electrodes are as follows:

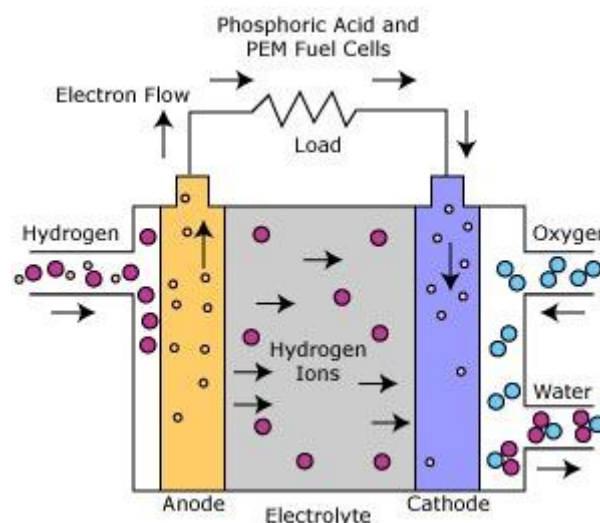
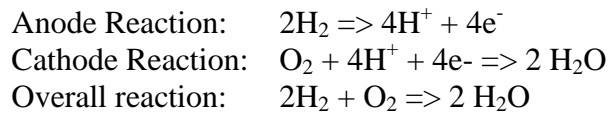


Figure 2.10 Cross section of Proton Exchange Membrane Fuel Cell (PEMFC)

PEMFC operate at low temperature, typically around 60 and 80°C, which allows for a rapid start-up (less warm-up time) and results in less wear on system components, resulting in enhanced durability. However, it is required that a noble-metal catalyst be used to separate the hydrogen's electrons and protons. The typical catalyst is platinum, with loadings of about 0,3 mg/cm², which make these fuel cells expensive. The platinum catalyst is also extremely sensitive to CO poisoning, making it necessary to employ an additional reactor to reduce CO in the fuel gas if the hydrogen is derived from an alcohol or hydrocarbon fuel. When the hydrogen fuel contains small amounts of CO, then platinum alloys like Pt-Ru can be used to decrease the sensibilities of the catalyst.

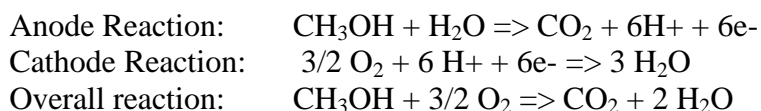
Temperatures near 100°C are not high enough to perform useful cogeneration. Also, since the electrolyte is required to be saturated with water to operate optimally, careful control of the moisture of the anode and cathode streams is important, especially for operation below the freezing point.

PEM fuel cells have the highest power density among all the other types, so it makes them compact and lightweight. Other advantages result from the electrolyte being a solid material, compared to a liquid. The sealing of the anode and cathode gases is simpler with a solid electrolyte, and therefore, less expensive to manufacture. The solid electrolyte has fewer problems with corrosion, compared to many of the other electrolytes, thus leading to a longer cell and stack life.

PEM fuel cells are used primarily for transportation applications and some stationary applications. Due to their fast startup time, low sensitivity to orientation, and favorable power-to-weight ratio, PEM fuel cells are particularly suitable for use in passenger vehicles, such as cars and buses. A significant barrier to using these fuel cells in vehicles is hydrogen storage. Most fuel cell vehicles powered by pure hydrogen must store the hydrogen on-board as a compressed gas in pressurized tanks. Due to the low-energy density of hydrogen, it is difficult to store enough hydrogen on-board to allow vehicles to travel the same distance as gasoline-powered vehicles before refueling.

b) Direct Methanol Fuel Cells (DMFC)

DMFC is similar to the PEMFC in that the electrolyte is a polymer and the charge carrier is the hydrogen ion (proton). However, the liquid methanol (CH_3OH) is oxidized in the presence of water at the anode generating CO_2 , hydrogen ions and the electrons that travel through the external circuit as the electric output of the fuel cell. The hydrogen ions travel through the electrolyte and react with oxygen from the air and the electrons from the external circuit to form water at the anode completing the circuit.



The efficiency of current direct-methanol fuel cells is low (around 25%) due to high penetration of methanol through the membrane material used, which is known as methanol crossover.

These cells have been tested in a temperature range from about 50°C-120°C. This low operating temperature has no requirement for a fuel reformer. One of the drawbacks of the DMFC is that the low-temperature oxidation of methanol to hydrogen ions and carbon dioxide requires a more active catalyst, which typically means a larger quantity of expensive platinum catalyst is required than in conventional PEMFCs. This increased cost is, however, expected to be more than outweighed by the convenience of using a liquid fuel and the ability to function without a reforming unit.

Direct methanol fuel cells do not have many of the fuel storage problems typical of some fuel cells because methanol has a higher energy density than hydrogen—though less than gasoline or diesel fuel. Methanol is also easier to transport and supply to the public using our current infrastructure because it is a liquid, like gasoline, but on the other hand, one big concern driving the development of alcohol-based fuel cells is the fact that methanol is toxic.

Direct methanol fuel cell technology is relatively new compared with that of fuel cells powered by pure hydrogen, and the main application is in powering mobile phones and laptop computers.

c) Phosphoric acid fuel cell (PAFC)

PAFC uses an electrolyte that is phosphoric acid (H_3PO_4) with a concentration ranging up to 100%. The ionic conductivity of phosphoric acid is low at low temperatures, so PAFCs are operated at the upper end of the range 150°C–220°C. The matrix used to retain

the acid is usually SiC and the electrocatalysts (platinum) are employed in both: the anode and cathode.

The charge carrier is the hydrogen ion. The hydrogen introduced at the anode is split into its protons and electrons. The protons migrate through the electrolyte and combine with the oxygen, usually from air, at the cathode to form water. The electrons are routed through an external circuit where they can perform useful work and generate heat.

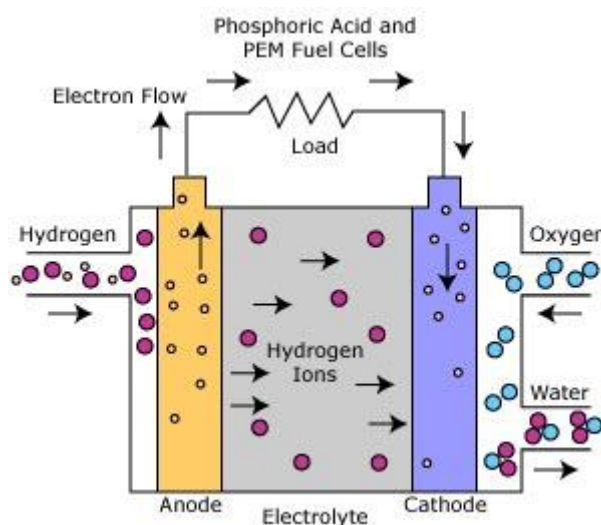
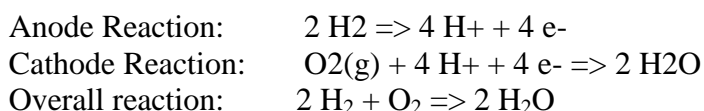


Figure 2.11 Cross section of Phosphoric acid fuel cell (PAFC)

The PAFC functions at efficiency greater than 40% in generating electricity. When operating in cogeneration applications, the overall efficiency is approximately 85%. The waste heat is capable of heating hot water or generating steam at atmospheric pressure. In addition, CO₂ does not affect the electrolyte or cell performance and can therefore be easily operated with reformed fuels. Simple construction, low electrolyte volatility and long-term stability are additional advantages. However, the power density is rather small making PAFCs typically large and heavy.

This type of fuel cell is usually used for stationary power generation, but some PAFCs have been used to power large vehicles such as city buses.

d) Alkaline Fuel Cell (AFC)

AFC uses as an electrolyte a solution of potassium hydroxide (KOH). The concentration of KOH can vary with the fuel cell's operating temperature. High-temperature AFCs operate at temperatures between 100°C and 250°C and newer AFCs operates at lower temperatures of roughly 23°C to 70°C. The charge carrier for an AFC is the hydroxyl ion (OH⁻) that migrates from the cathode to the anode where they react with hydrogen to produce water and electrons. Water formed at the anode migrates back to the cathode to

regenerate hydroxyl ions. Therefore, the chemical reactions at the anode and cathode in an AFC are shown below.

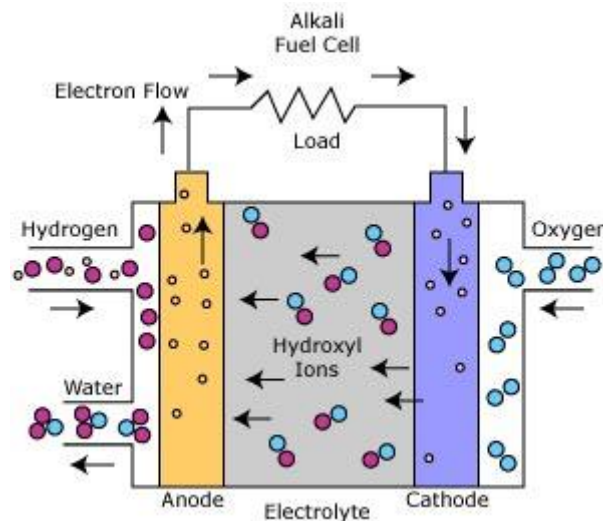
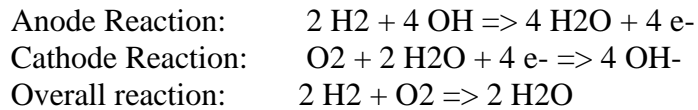


Figure 2.12 Cross section of Alkaline Fuel Cell (AFC)

The technology of AFC is well developed and their efficiency reaches 70%. Its high performance is due to the rate at which chemical reactions take place in the cell. However, they are very sensitive to CO_2 , which can be present in fuel or in air, poisoning it rapidly, and severely degrading the fuel cell performance and shortening the cell's lifetime. Therefore, those kinds of fuel cells are limited to closed environments, such as outer space and submarines. The only fuels for them are pure hydrogen and oxygen. Furthermore, molecules such as CO , H_2O and CH_4 , which are harmless or even work as fuels to other fuel cells, are poisons to an AFC.

Besides, they are cheap to manufacture because they do not need expensive catalysts. AFC have been used in space technology. The fuel cells on board these spacecraft provide electrical power for on-board systems, as well as drinking water. AFC stacks have been shown to maintain sufficiently stable operation for more than 8,000 operating hours. To be economically viable in large-scale utility applications, these fuel cells need to reach operating times exceeding 40,000 hours, something that has not yet been achieved due to material durability issues.

e) Molten Carbonate Fuel Cell (MCFC)

Molten Carbonate Fuel Cells (MCFC) are high-temperature fuel cells that use an electrolyte composed of a molten mixture of carbonate salts. Two mixtures are currently used: lithium carbonate and potassium carbonate, or lithium carbonate and sodium carbonate. To melt the carbonate salts and achieve high ion mobility through the electrolyte, MCFCs operate at high temperatures (650°C and above). Molten carbonate fuel cells are not sensitive to carbon monoxide or carbon dioxide poisoning—they can

even use carbon oxides as fuel—making them more attractive for fueling with gases made from coal.

When heated to a temperature of around 650°C, these salts melt and become conductive to carbonate ions (CO_3^{2-}). These ions flow from the cathode to the anode where they combine with hydrogen to give water, carbon dioxide and electrons.

Anode Reaction: $\text{CO}_3^{2-} + \text{H}_2 \Rightarrow \text{H}_2\text{O} + \text{CO}_2 + 2\text{e}^-$

Cathode Reaction: $\text{CO}_2 + \frac{1}{2}\text{O}_2 + 2\text{e}^- \Rightarrow \text{CO}_3^{2-}$

Overall reaction: $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) + \text{CO}_2(\text{cathode}) \Rightarrow \text{H}_2\text{O}(\text{g}) + \text{CO}_2(\text{anode})$

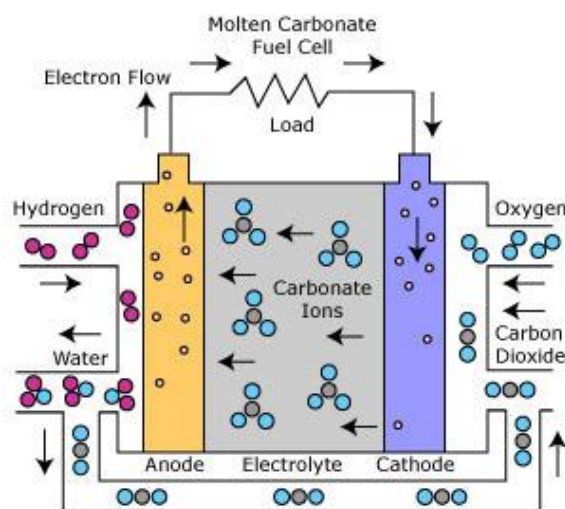


Figure 2.13 Cross section of Molten Carbonate Fuel Cell (MCFC)

Molten carbonate fuel cells can reach efficiencies approaching 60%. When the waste heat is captured and used, overall fuel efficiencies can be as high as 85%. Because they operate at that temperature regime, expensive catalysts are not used, reducing costs.

The higher operating temperature of MCFCs has both advantages and disadvantages compared to the lower temperature fuel cells. At the higher operating temperature, fuel reforming of natural gas can occur internally, eliminating the need for an external fuel processor. Additional advantages include the ability to use standard materials for construction, such as stainless steel sheets, and allow the use of nickel-based catalysts on the electrodes, reducing total costs. The by-product heat from an MCFC can be used to generate high-pressure steam that can be used in many industrial and commercial applications. The high temperatures and the electrolyte chemistry also have disadvantages. It requires significant time to reach operating conditions and responds slowly to changing power demands. These characteristics make MCFCs more suitable for steady power purposes. The carbonate electrolyte can also cause electrode corrosion and decreasing cell life. Furthermore, since CO_2 is consumed at the anode and transferred to the cathode, the introduction of CO_2 and its control in the air stream becomes an issue for achieving optimum performance that is not present in any other fuel cell.

f) Solid-Oxide Fuel Cell (SOFC)

SOFC employs a ceramic, nonporous metal oxide, usually Y_2O_3 -stabilized ZrO_2 as an electrolyte. The ionic charge carriers in SOFC are O_2^- ions. At the cathode, the oxygen molecules from the air are split into oxygen ions with the addition of four electrons. The oxygen ions are conducted through the electrolyte and combine with hydrogen at the anode, releasing four electrons. The electrons travel an external circuit providing electric power and producing by-product heat. The half reactions proceed as follow:

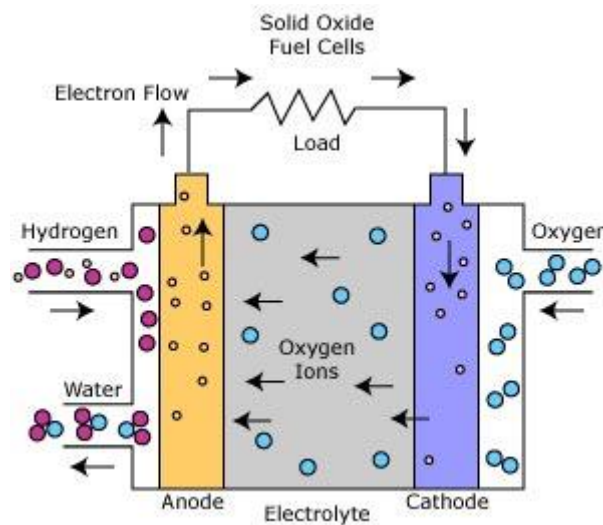
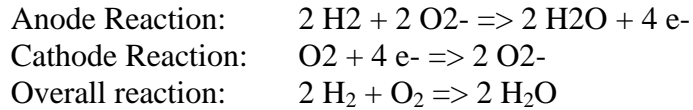


Figure 2.14 Cross section of Solid-Oxide Fuel Cell (SOFC)

SOFC has two configurations that are being investigated: planar (flat panel) and tubular. SOFCs operate at temperatures higher than 600°C , up to 1000°C , resulting in a long start-up time due to the time needed to reach operating temperature and, additionally, they respond slowly to changes in electricity demand. For those reasons, they are considered for high-power applications including industrial and large-scale central-electricity generating-stations. They are highly efficient (60%), and furthermore the high operating temperature allows cogeneration applications to create high-pressure steam that can be used in many other applications. Combining a high-temperature fuel cell with a turbine into a hybrid fuel cell further increases the overall efficiency of generating electricity with the potential for an efficiency of more than 70%. The very high operating temperature of the SOFC has both advantages and disadvantages. The high temperature enables them to tolerate relatively impure fuels, such as those obtained from the gasification of coal or gasses from industrial process and other sources. However, the high temperatures require more expensive materials.

g) Regenerative Fuel Cells (RFC)

The Regenerative Fuel Cell (RFC) is a system that can operate in a closed loop and could serve as the basis of a hydrogen economy operating on renewable energy. Fuel cells

generating electricity, heat, and water from hydrogen and oxygen would be used throughout the economy, powering industry, vehicles, and houses. The hydrogen would be generated from the electrolysis of water, splitting it into its constituent components of hydrogen and oxygen, using renewable energy sources such as wind, solar, or geothermal. Such a system would not require any specific type of fuel cell, but would need an infrastructure to deliver hydrogen to the many fuel cells in use. However, the infrastructure currently does not exist for hydrogen delivery. Also, the initial cost of electricity would be high, but would decrease as costs decrease for each of the components: fuel cells, hydrogen storage, and delivery, renewable energy collection, etc. This is a comparatively young fuel cell technology being developed by NASA and others.

At present, none of the fuel cell types are ready for commercial application. The main drawbacks of this technology are: significant cost, low power density, unreliability and durability. PEMFCs and SOFCs present the best prospects for continued development and further application. Due to their high power density and low operating temperatures, the PEMFC and the DMFC can be applied in portable power applications like mobile phones and computer. At present, PEMFCs are applied in transportation. The PEMFC and the SOFC can be used in small scale stationary generation like residential power supply. High-power applications (above 250 kW) are best supplied by SOFC. High-temperature fuel cells offer attractive efficiency and fuel flexibility. They also generate higher quality waste heat, which can be used in combined applications. While all fuel cells operate best on hydrogen, those operating at higher temperatures offer improved impurity tolerance and the possibility of internal reforming of hydrocarbon fuels to yield hydrogen.

Table 1 Comparison of Fuel Cell Technologies Sources: “Fuel Cells Fundamentals“,DOE Department of Energy Hydrogen Program

	PEMFC	PAFC	AFC	MCFC	SOFC
Electrolyte	Polymer membrane	Liquid H ₃ PO ₄ (immob.)	Liquid KOH (immob.)	Molten carbonate	Ceramic (Yttria stabilized zirconia)
Charge carrier	H ⁺	H ⁺	OH ⁻	CO ₃ ²⁻	O ²⁻
Operating temperature	50 - 100°C	150 - 200°C	90 - 100°C	600 - 700°C	600 - 1000°C
Catalyst	Platinum	Platinum	Platinum	Nickel	Perovskites (ceramic)
Cell components	Carbon based	Carbon based	Carbon based	Stainless based	Ceramic based
Fuel compatibility	H ₂ , methanol	H ₂	H ₂	H ₂ , CH ₄	H ₂ , CH ₄ , CO
Electrical efficiency (%)	53-58% (transportation) 25-35% (stationary)	>40%	60%	45-47%	35-43%
Combined Heat and Power (CHP) Efficiency (%)	70-90% (low-grade waste heat)	>85%	>80% (low-grade waste heat)	>80%	<90%
Power density (mW/cm²)	300-1000	150-300	150-400	100-300	250-350
Power range (kW)	0,001-1000	50-1000	1-100	100-100000	10-100000
Internal Reforming	No	No	No	Yes	Yes
CO tolerance	Poison (<50ppm)	Poison (1%)	Poison (<50ppm)	Fuel	Fuel
Balance of plant	Low-moderate	Moderate	Moderate	Complex	Moderate

Applications	<ul style="list-style-type: none"> -Backup power -Portable power -Small distributed generation -Transportation -Specialty vehicles 	<ul style="list-style-type: none"> - Distributed generation 	<ul style="list-style-type: none"> - Military - Space 	<ul style="list-style-type: none"> -Electric utility -Large distributed generation 	<ul style="list-style-type: none"> -Auxiliary power -Electric utility -Large distributed generation
Advantages	<ul style="list-style-type: none"> -Solid electrolyte reduces corrosion & electrolyte management problems -Low temperature -Quick start-up 	<ul style="list-style-type: none"> -Higher overall efficiency with CHP -Increased tolerance to impurities in hydrogen 	<ul style="list-style-type: none"> -Cathode reaction faster in alkaline electrolyte, leads to higher performance -Can use a variety of catalysts 	<ul style="list-style-type: none"> -High efficiency -Fuel flexibility - Can use a variety of catalysts - Suitable for CHP 	<ul style="list-style-type: none"> -High efficiency -Fuel flexibility - Can use a variety of catalysts -Solid electrolyte reduces electrolyte management problems -Suitable for CHP - Hybrid/GT cycle

**Direct Methanol Fuel Cells (DMFC) are a subset of PEM typically used for small portable power applications with a size range of about a subwatt to 100W and operating at 60 - 90°C.*

2.6 Safety

Hydrogen poses specific challenges regarding its safe use, due to the ease with which it leaks, its low-energy ignition, wide range of combustible fuel-air mixtures, buoyancy, and its ability to weaken metals. Liquid hydrogen poses additional challenges due to its increased density and extremely low temperatures. The safest method of storage of hydrogen is in the form of hydrides, but this technique has other drawbacks which were described in the section “Hydrogen Storage”.

To guarantee safe operation of hydrogen installations, special safety measures need to be taken. The modern approach to hydrogen safety is proactive, where risks are measured and managed, not taken. Hydrogen has some specific properties that, in comparison with other fuels, make it less hazardous. However, other characteristics of the compound make it more dangerous. Hydrogen is the lightest and the smallest element. It is colorless,

odorless, tasteless, non-toxic and non-poisonous all at the same time. Because of the size of the molecule, hydrogen has a greater propensity to escape through small openings in comparison with other fuels. In the event of a leak, hydrogen will disperse much faster than any other fuel and because of its smaller energy density compared to natural gas, the amount of energy released would be smaller.

The range of hydrogen's flammability is wide: between 4% and 75% of the volume ratio of hydrogen in air. The other fuels have much lower flammability ranges in air: natural gas at 5,3-15% and gasoline at 1,4-7,6%. Nevertheless, the range itself has a small practical meaning, because in case of a leak, the key parameter which determines the ignition is the lower flammability limit, which in case of hydrogen is higher than gasoline and slightly lower than natural gas. In open air situations hydrogen disperses quickly and may not even reach the lower flammability limit of 4%. The ignition energy is a function of fuel/air ratio and for hydrogen reaches the minimum value at 25%-30%. The value of the ignition energy in the aforementioned flammability level amounts to 0,02 mJ, which is around one level of magnitude lower than other fuels. At lower flammability levels, the ignition energy is comparable to natural gas.

Hydrogen has the lowest explosive energy per unit of stored energy in the fuel. Therefore, a given volume of hydrogen would have 22 times less the explosive energy than the same volume filled with gasoline vapor.

Hydrogen burns with a pale blue, almost invisible flame, which can be dangerous for people who are in the vicinity of hydrogen fire, because the flame may not be observable. In comparison with other fuels, the hydrogen flame temperature is higher. In order to increase flame detection, special chemicals can be added to make hydrogen flame visible.

From an environmental perspective, hydrogen is the cleanest fuel because the only emission released to the atmosphere is water vapor. In the event of a leak, hydrogen does not have any negative effects on the environment.

Table 2 Properties comparison of hydrogen, natural gas and gasoline

Property	Hydrogen	Natural Gas	Gasoline
Colour/Toxity	None/no	None/no	Yes/yes
Odor	Odorless	Mercaptan	Yes
Specific Gravity (air = 1)	0,07	0,424	Liquid
Environmental impact - Leak - Fuel	None None	None CO2/NOx	CnHn CO2/NOx
Diffusion Coefficient cm ³ /sek	0,61	0,15	Liquid
Flame temperature °C	2318	2148	>500
Flammability range- in air	4-75%	5,3-15%	1,4-7,6%
Ignition energy mJ	0,02	0,29	0,20
Auto Ignition Temp °C	520	<500* *Depends on composition	440
Heat Value – kJ/kg	119 972	50 020	41 847
Energy Density – MJ/Nm ³	10 783	35 882	104,4

Additionally, hydrogen at high pressures and ambient temperatures weakens component materials and metals. It occurs when hydrogen permeates into lattice structure of the

material, causing a significant loss of strength and endurance, finally leading to failure. The phenomenon is avoided by proper design and selection of materials.

Liquid hydrogen, however, poses a different set of safety questions. The main issues concern a risk of cold burns, longer duration of leaks etc. The temperature of hydrogen in its liquid form is around -253°C . It is cold enough to liquefy atmospheric oxygen, which can be an explosion hazard. A large spill of liquid hydrogen has some characteristics similar to gasoline spills. However, it dissipates much faster. Liquid hydrogen can explode, for example in the event of the vehement vapor expansion of a boiling liquid due to a pressure relief valve failure.

Liquid hydrogen requires complex storage technology, such as special thermally insulated containers and requires special handling common to all cryogenic substances. Even with thermally insulated containers it is difficult to keep at such a low temperature, and the hydrogen will gradually leak away, typically at the rate of 1% per day.

In conclusion, proper design of hydrogen systems and correct usage should guarantee safe operation. In comparison with other fuels, hydrogen cannot be unambiguously characterized as more dangerous than other fuels.

2.7 Already existing projects

Water electrolysis is suitable to be used in conjunction with photovoltaics (PVs) and wind energy. There is a good match between the polarization curves of renewable energy sources and electrolyzers, and thus they can be matched directly with no power tracking electronics and yield a relatively high efficiency ($>93\%$ coupling efficiency).

There are already existing hybrid wind-hydrogen systems. One of the pilot projects is located on the Island of Unst, in the northernmost part of the United Kingdom. The aim of Promoting Unst Renewable Energy (PURE) project has been to demonstrate how wind power and hydrogen technology can be combined to provide the energy needs for five business units in a remote, rural industrial estate.

The wind resources in Shetland are among the best in Europe if not the world (studies have shown, that the net load factor output is over 50% on the basis of the five existing commercial wind turbines in Shetland), but its intermittent and unpredictable nature means that it requires a significant amount of load management and energy storage in order to provide a dependable energy supply. Additionally, the electricity network on the island is limited. It cannot accommodate any more firm connections from renewable sources, and thus any system has to be developed as an off-grid system, or must incorporate a substantial amount of storage to provide a guaranteed supply.

Two 15-kW wind turbines provide electricity. During low periods of demand or higher wind speeds, the excess electricity is sent to an electrolyser, which requires around 2-7 kW, daily producing an average 2 kg of hydrogen. Next, hydrogen is stored in a high pressure container and then dispensed to fill hydride cylinders. The cylinders are used in a fuel cell/battery hybrid vehicle and other hydrogen applications as an alternative to fossil fuels (Figure 2.15).

A back-up power supply was also installed. The system contains a 5kW fuel cell and an inverter, which converts the output power of the fuel cell from Direct Current (DC) into Alternating Current (AC). A battery based electric vehicle was converted to run with a hydrogen fuel cell, which is now fuelled exclusively by the PURE system, using hydrogen produced from the renewable source.

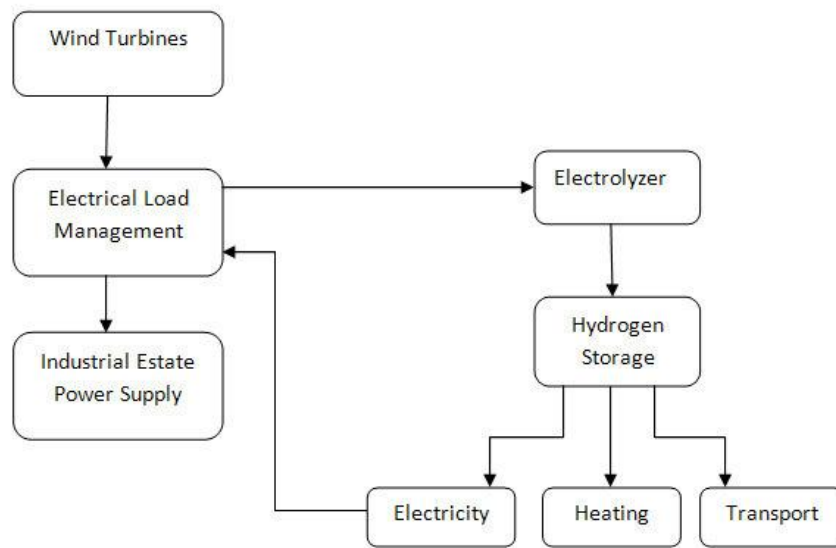


Figure 2.15 Components of the PURE project (Ref: PURE)

The other pilot project is located on the island Utsira, Norway. It is a small island with 240 inhabitants. The island characterizes very good wind conditions, but also small (reaching a peak load of 900 kW) and variable electricity demands. The wind-hydrogen project was coordinated by Norsk Hydro. The aim of the project has been to demonstrate an autonomous energy system and to integrate established and new technology with renewable energy sources to create a viable renewable energy system. The main components of the system are: a) two 600 kW wind turbines from Enercon operating during good wind conditions. The wind turbines operate at wind speeds in the range of 2.5-25 metres/second. From 25 m/s, the output power declines to 34 m/s, at which point the windmills shut down automatically; b) a 48 kW (10 Nm³ H₂/hr) alkaline electrolyzer converting excess wind energy to hydrogen; c) a 5 kW compressor increasing the pressure of the hydrogen up to 200 bar; d) a 12 m³ H₂-storage tank (equivalent to 2400 Nm³ of hydrogen gas), having enough capacity to sustain two full days without wind power; e) a 10 kW fuel cell and a 55 kW hydrogen combustion engine/generator providing the power when power from the wind turbine is not sufficient to cover the demand; f) a 5 kWh flywheel and a 100 kVA synchronous machine, helping to maintain a stable power supply from the plant to the grid; g) and a 35 kWh battery providing emergency back-up power. This system provides electricity to 10 household (Figure 2.16).

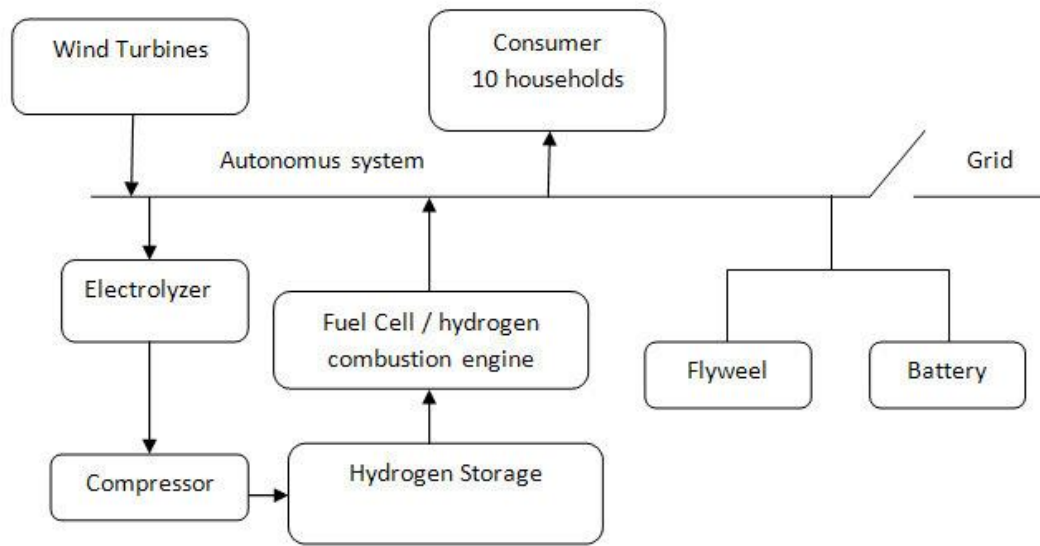


Figure 2.16 The Utsira Wind-Hydrogen Project (Ref: Norsk Hydro)

The main achievements of Utsira project are:

- More than 6 months in Stand-Alone mode
- Availability – 90%
- Power quality – very good
- Customers satisfied – no complaints
- Good media coverage, several publications, several presentations in conferences and at fairs
- Contribution to local economy

Some final results of the project go as follow:

- During the period one can see that the wind power decreases and cannot supply the demand. In this period the H2-engine is started and is balancing the load (Figure 2.17).

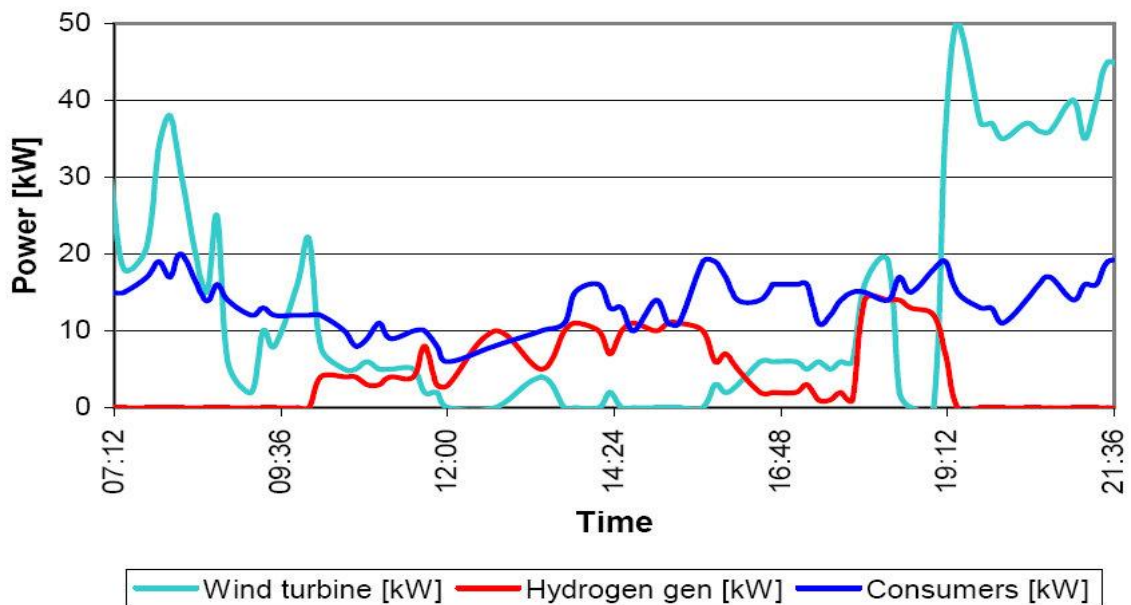


Figure 2.17 Example of operation Utsira system in a case of power shortage

The Utsira project shows that it is possible to supply remote areas with wind power alone using hydrogen as a storage medium. Still there are several things to improve in order to make the system competitive, both technically and economically, against alternative systems like wind-diesel. However, several elements have been identified that, together with the ongoing day-to-day improvement of the plant, will improve the system quality. These include:

- Utilisation of surplus energy (today 80% not used),
- Utilisation of H₂ (possibly also O₂) for other purposes,
- More effective re-electrification (smaller H₂-storage),
- Hybrid solutions (diesel, PV, biofuel,...),
- Load control and production forecasting,
- Heat utilization.

Hybrid technology is being developed in many countries, but wind-energy systems are still in the beginning stages of development. Further research and development initiatives on the international level are necessary to obtain state-of-the-art systems. At present the international community shows interest in testing and evolving those kinds of projects.

3 CASE STUDY

3.1 Introduction

Hydrogen has been regarded as a promising energy in a fuel cell carrier for renewable energy sources. In isolated power systems based on wind energy, hydrogen can be produced from water electrolysis when the power output exceeds the load. When the power output from the wind turbine is not sufficient to feed the isolated load, stored hydrogen is utilized for power generation. Hydrogen methods offer great flexibility in sizing because of the modularity of electrolyzers, storage tanks and fuel cells. The limiting factor for renewable energy is a small grid capacity for variable power production which does not follow the demand.

A general illustration of a hydrogen storage system coupled with a wind power plant is shown in a Figure 3.1.

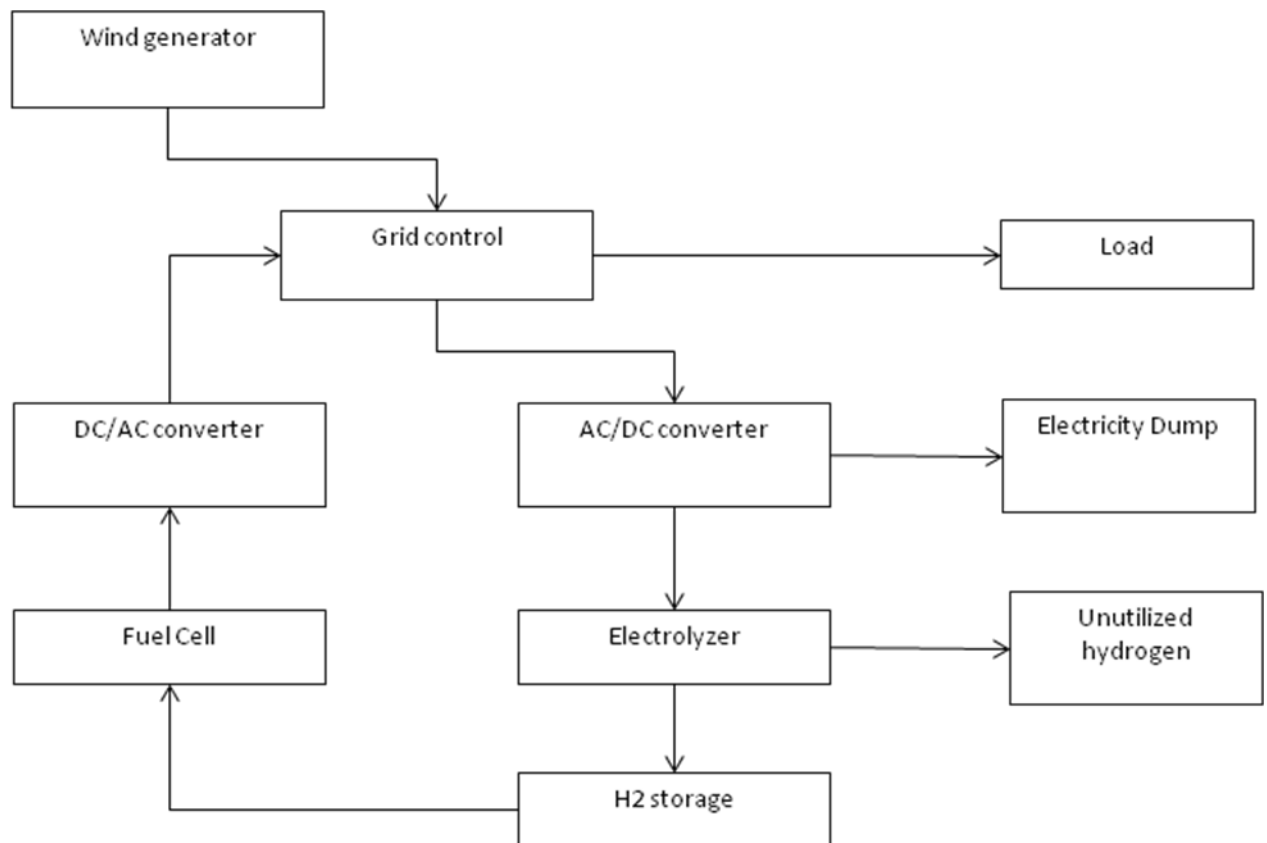


Figure 3.1 Wind-fuel cell system

This logistic model represents the system, where the power produced by the wind turbine is split into two branches, one delivering the energy to sustain the load and the second one powering the hydrogen production path, which contains a high pressure electrolyzer, a storage tank for compressed hydrogen and a fuel cell. When the wind power output exceeds the capacity of load, then the electrolyzer produces hydrogen, which then is stored in a compressed form in a tank. When the load demand cannot be carried out by the

wind generator, hydrogen is fed to a fuel cell to produce electricity, which is then lead to the final receiver. A controllable dump load is operated if the electrolyzing system is not capable of absorbing all the excess wind power and also the unutilized hydrogen can be used to fill the tanks and exported, thus increasing the whole efficiency of the system, bringing in additional income. The next points discuss the major components of the system in detail for a specific case.

a) Wind turbine

Given the relatively small electricity demand for the particular example, a horizontal axis pitch-controlled wind turbine 600 kW is taken as a main source of power.

The production of electricity starts from a minimum wind speed 3 m/s and reaches the nominal rated output power at a speed of 15 m/s and the turbine's cut off speed is 25 m/s. The power curve for the following wind generator is shown in Figure 3.2.

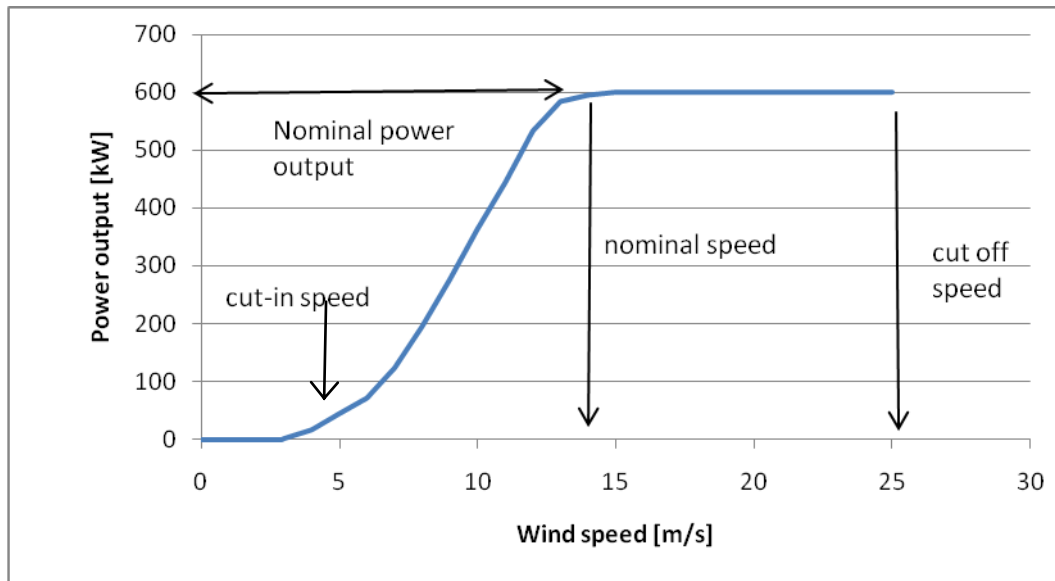


Figure 3.2 600 kW wind turbine power curve as a function of wind speed.

The wind velocity is highly intermittent on an hourly, daily, seasonally and yearly basis. Figure 3.3 shows typical fluctuations in wind power energy production over a period of 11 months, from 1.01 to 30.11, for hourly data from the station Ijmuiden in the Netherlands (data obtained from "Royal Netherlands Meteorological Institute"). The maximum observed wind speed was 21.5 m/s. The average wind speed was 6.5 m/s. The calm was observed only for 3 hours, however the time when the wind did not reach the cut in speed was 2088 hours, meaning that in total there were 87 days without a wind energy supply. The total energy production for this period was 1237646 kWh. One of the important coefficients measuring the wind turbine performance is the capacity factor. It refers to actual annual energy output divided by the theoretical maximum output, if the machine was running at its rated (maximum) power during all of the hours of observation. Capacity factors may theoretically vary from 0 to 100 per cent, but in practice they will usually range from 20 to 70 per cent, and mostly be around 25-30 per cent. In this example the capacity factor equals 26 per cent.

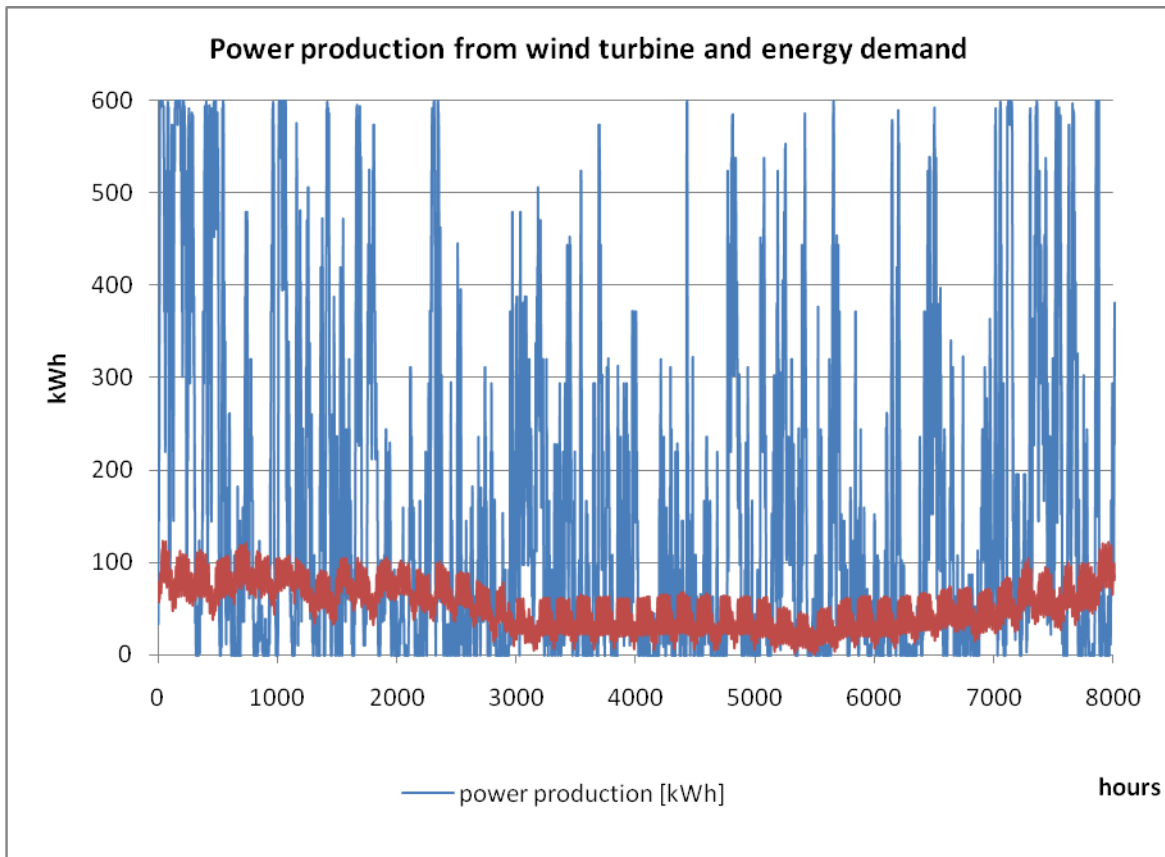


Figure 3.3 Power production from wind turbine and energy demand

The figure also shows the corresponding energy demand during the same period. The electricity demands are irregular in time. Higher energy demands are visible during cold and darker months, when more electricity is used for heating and lighting. Also, the energy demand follows a specific daily pattern: the peak demands are in the morning and evening. The total energy demand for the following period was 447688 kWh, with the peak power demand of 123 kW and an average of 56kW.

However, the wind resources are not always available in real time to fully sustain the electricity demands, whereas an energy blackout is not permitted. Thus converting the excess energy and storing it in a form of hydrogen is a reliable solution. In comparison with commonly used battery storage, hydrogen has special long-term storage advantages due to its inherent high mass energy density. The other advantage in using hydrogen as compared to batteries is its storage convenience, and it has relatively low tank costs.

b) Electrolyzer

The electrolyzer used in this example is a high pressure proton exchange membrane electrolyzer, which produces hydrogen in an already compressed form under the 200 bar pressure and includes all ancillary equipment for hydrogen handling and control. Hydrogen pressurization during production is quasi-reversible and is therefore achieved at lower cost than using compressors. The efficiency of the electrolyzer is defined as the ratio of energy carried by the produced hydrogen stream divided by the electrical energy necessary for its production, and is a function of the operational pressure and the power density required. Rectifiers powering the electrolyzers appear with ramp time in the order of 200 ms. This is more than adequate for handling the wind turbine power drifts.

In this case two examples of electrolyzers were considered: the first one with a total power input of 160 kW, hydrogen output of 35 Nm³/h and power consumption of 4,57 kWh/Nm³ and the second one with a power input of 300 kW, 5kWh/Nm³ and hydrogen production of 60 Nm³/h. For simplicity's sake, the generator efficiency is set at the level of 53% for net production based on the higher heating value (HHV) for both of the electrolyzers.

c) Hydrogen storage

A tank of capacity of 3000 Nm³ of hydrogen is used. The compressibility factor of hydrogen with 200 bar is equal to 1.132, thus allowing the storage of 16.98 m³ of compressed hydrogen. A limiting factor for a storage pressure is the permeability and stress rupture limit of the material from which the tank is made. Gravimetric energy density of hydrogen equals 33.3 kWh/kg and volumetric energy density is 3kWh/Nm³.

In this case, hydrogen was stored up to the highest volume and the excess of hydrogen was dumped and thus could be supplied to additional tanks and exported. In this case the efficiency of the system increased significantly.

d) Fuel cell

In this study the proton exchange membrane fuel cell (PEMFC) of the nominal power output of 100 kW has been applied. The efficiency of a fuel cell is dependent on the amount of power drawn from it. Drawing more power means drawing more current, this increases the losses in the fuel cell. For the simplicity of calculations, the efficiency of the stack has been established at the level of 49%.

e) Auxiliary equipment

The system components have substantially different voltage–current characteristics, and they are integrated on a bus power conditioning device for effective power management. Coupling of a source, such as a wind turbine, with an electrolyzer may result in a somewhat lower efficiency because voltage regulation, either AC/DC or DC/AC, would consume some power. These devices may be designed to operate with efficiency as high as 93–95%, but this high efficiency may be achieved only in a very narrow power range. In a highly variable mode of operation, such as with input from the wind turbine, this efficiency may be considerably lower.

In the following example both efficiencies for the converters are equal, at 90%.

3.2 Hybrid system operation

In order to analyze the operation of the system a model has been developed which takes into account the characteristics and efficiencies of the devices and performs all necessary internal power loops. The input data are hourly wind speed data over a time of 11 months and the model calculates the energy flux between the different devices, the hydrogen production rate and storage level, and the power availability in the FC and the direct power branch. Depending on the size and efficiency of the devices selected (WT, FC, EL, H₂ tanks), it is possible to calculate the off-duty period over a year, i.e. the period when no H₂ is available for electricity production by the FC, and there is no electricity supply from the wind generator.

The goal of this study is to examine the possibility of maximizing the utilization of available wind energy in periods with the significant surplus of energy production, thanks to converting the excess of produced electricity in the form of hydrogen. The other objective is to minimize the amount of hydrogen that is not supplied.

The first target is handled by supplying the excess of power to the electrolyzer in a period with high wind power output. The second goal is secured by the size and control strategy of the particular elements of the storage system. The aim is to ensure the electricity supply, either by the direct branch or that hydrogen will be always available during long periods with low wind speed.

An important decision is at which point during the year the system should start up. The optimum performance is achieved when high wind potential coincides with low hydrogen storage levels in order to fill the tanks. This can be achieved by placing the start of the operation on the seventh hour of the operation system, where the energy demands are considerably lower than the energy supply.

The overall system efficiency, that is the ratio of energy delivered ($E_{supplied}$) vs. the energy produced by the wind turbine (EWT) over a study period:

$$\eta = \frac{E_{supplied}}{W_{wt}}$$

The split of energy between the direct and the FC branch determines the level of hybridization of the system. The level of hybridization, using the ratio:

$$\sigma = \frac{WT_{direct}}{FC}$$

Where WT_{direct} is the nominal power of a wind power delivering the same energy per the study period as the direct branch of the hybrid system and FC is the power delivered by the FC throughout the study period.

The power supply is guaranteed by the direct supply from the wind generator and a fuel cell. The electrolyzer operates when the wind power output exceeds the capacity of the load and a controllable load is operated if the electrolyzer is not capable of absorbing all the excess wind power.

The power shortage at a time step is:

$$P_{shortage}(t) = P_{generator}^{wind}(t) - P_{load}(t)$$

$P_{shortage}(t)$ - shortage of electricity supply,

$P_{generator}^{wind}(t)$ - electricity supplied by wind turbine,

$P_{load}(t)$ - power needed to meet the load demand.

The power excess at a time step is:

$$P_{excess}(t) = P_{load}(t) - P_{generator}^{wind}(t)$$

$P_{excess}(t)$ - shortage of electricity supply,

$P_{load}(t)$ - power needed to meet the load demand,

$P_{generator}^{wind}(t)$ - electricity supplied by wind turbine.

The power balance for the hybrid system at a time step is:

$$P_{generator}^{wind}(t) + P_{FC}(t) = P_{electrolyzer}(t) + P_{load}(t) + P_{dump}(t)$$

$P_{generator}^{wind}(t)$ - electricity supplied by wind turbine,

$P_{FC}(t)$ – electricity supplied by the fuel cell,

$P_{electrolyzer}(t)$ power needed to supply the electrolyzer,

$P_{load}(t)$ - power needed to meet the load demand,

$P_{dump}(t)$ - dump power.

Total power deficit

$$P_{deficit}(t) = P_{generator}^{wind}(t) + P_{FC}(t) < P_{load}(t)$$

$P_{deficit}(t)$ - total power deficit,

$P_{FC}(t)$ – electricity supplied by the fuel cell,

$P_{load}(t)$ - power needed to meet the load demand.

Electrolyzer operation at the time step is:

$$P_{electrolyzer}^{min}(t) \leq P_{electrolyzer}(t) \leq P_{electrolyzer}^{max}(t) \text{ or } P_{electrolyzer}(t) = 0$$

$P_{electrolyzer}^{min}$ - power consumption at minimum hydrogen production rate = 5-20% of nominal power,

$P_{electrolyzer}^{max}$ - capacity of electrolyzer

For the proper operation of the electrolyzer, in order to avoid the variable operation, it is either working at minimum hydrogen production rate or is switched off. It could be better to maintain hydrogen production, even when the wind generation drops to zero, because of mechanical wear and possibility of electrochemical degradation related to frequent on/off switching. In the following example the minimum hydrogen production rate equals 20%

Hydrogen volume storage balance in a time step is:

$$V_{hydrogen}^{produced}(t) = V_{hydrogen}^{stored}(t) + V_{hydrogen}^{load}(t) + V_{hydrogen}^{unutilized}(t)$$

$V_{hydrogen}^{stored}(t)$ – volume of hydrogen stored,

$V_{hydrogen}^{produced}(t)$ – volume of hydrogen produced,

$V_{hydrogen}^{load}(t)$ – volume of hydrogen required for a fuel cell to sustain the load,

$V_{hydrogen}^{unutilized}(t)$ - volume of unutilized hydrogen.

The amount of hydrogen that can be stored and extracted is limited by the maximum allowable storage levels, determined by the capacity of the tank.

$$V_h^{min} \leq V_h(t) \leq V_h^{max}$$

If there is not enough stored hydrogen to cover the hydrogen demands at the time step, there will be a shortage of hydrogen represented by

$$V_{shortage}^{hydrogen}(t) = V_{stored}^{hydrogen}(t) - V_{hydrogen}^{load}(t)$$

$V_{shortage}^{hydrogen}(t)$ – shortage of hydrogen mass in a time step t.

Fuel cell energy supply

Fuel cell energy supply equals the energy deficit between the energy load and a wind supply, divided by the efficiency of a fuel cell.

$$P_{FC} = (P_{load} - P_{wind})/\eta_{FC}$$

$P_{FC} - P_{FC}(t)$ – electricity supplied by the fuel cell,

P_{load} - power needed to meet the load demand,

P_{wind} - electricity supplied by wind turbine,

η_{FC} - efficiency of the fuel cell.

Strategy of operation

For the system considered here, the objectives of the control strategy are to:

1. sustain the electricity demand by providing the maximum available wind power to the load,
2. supply electricity to the electrolyzer, when the excess wind energy is available,
3. dump the excess of unused energy.

When the wind energy supply is greater than the load, then the difference between them is an energy excess.

$$P_{wind} > P_{load} \text{ then } P_{wind} - P_{load} = P_{excess}$$

The energy excess can deliver the power to the electrolyzer and unused power, which cannot be utilized by the electrolyzer, is dumped.

$$P_{excess} = P_{electrolyzer} + P_{dump}$$

If all the excess energy supplies the electrolyzer's demands, the power dump is zero.

$$P_{excess} = P_{electrolyzer} \Rightarrow P_{dump} = 0$$

When the power excess is lower than the minimum power consumption of the electrolyzer, then the electrolyzer is switched off and all excess energy is dumped.

$$P_{excess} < P_{electrolyzer}^{min} \Rightarrow P_{electrolyzer} = 0 \text{ and } P_{excess} = P_{dump}$$

When the power excess is greater than the maximum power consumption of the electrolyzer, then the electrolyzer operates on the nominal power and the difference between excess energy and maximum electrolyzer power is dumped.

$$P_{excess} > P_{electrolyzer}^{max} \Rightarrow P_{excess} - P_{electrolyzer}^{max} = P_{dump}$$

Total energy dump is equal to the surplus of wind energy, which exceeds the electrolyzer demands and the energy, which is lower than electrolyzer demands.

$$P_{total}^{dump} = P_{surplus}^{dump} + P_{shortage}^{dump}$$

4 RESULTS

4.1 Typical operation

In order to demonstrate the behaviour of the system, a typical set of component sizes has been chosen and has simulated its operation over a time of 11 months. A medium-size installation is considered, powered by a 600 kW wind turbine. As an input, the model uses the hourly wind data. The hybrid system may deliver 100 kW constant power through the PEMFC when combined with a 160 kW or 300 kW electrolyzer and hydrogen tanks of 3000 Nm³ capacity.

As it was shown in the Figure, the energy demand does not follow the energy production from wind energy, which is highly intermittent in time. Total shortage of electricity over the study time was 132631 kWh, with the maximum power deficit at the level of 122 kW and the average value of 16.5 kW. In total, by 3213 of 8016 hours the electricity could not be ensured by the direct supply from the wind turbine. Total electricity excess was available by 4796 hours, with the total value of 924595 kWh. The peak value was 575 kW, and the average rate of 115 kW. The use of the energy excess has great potential.

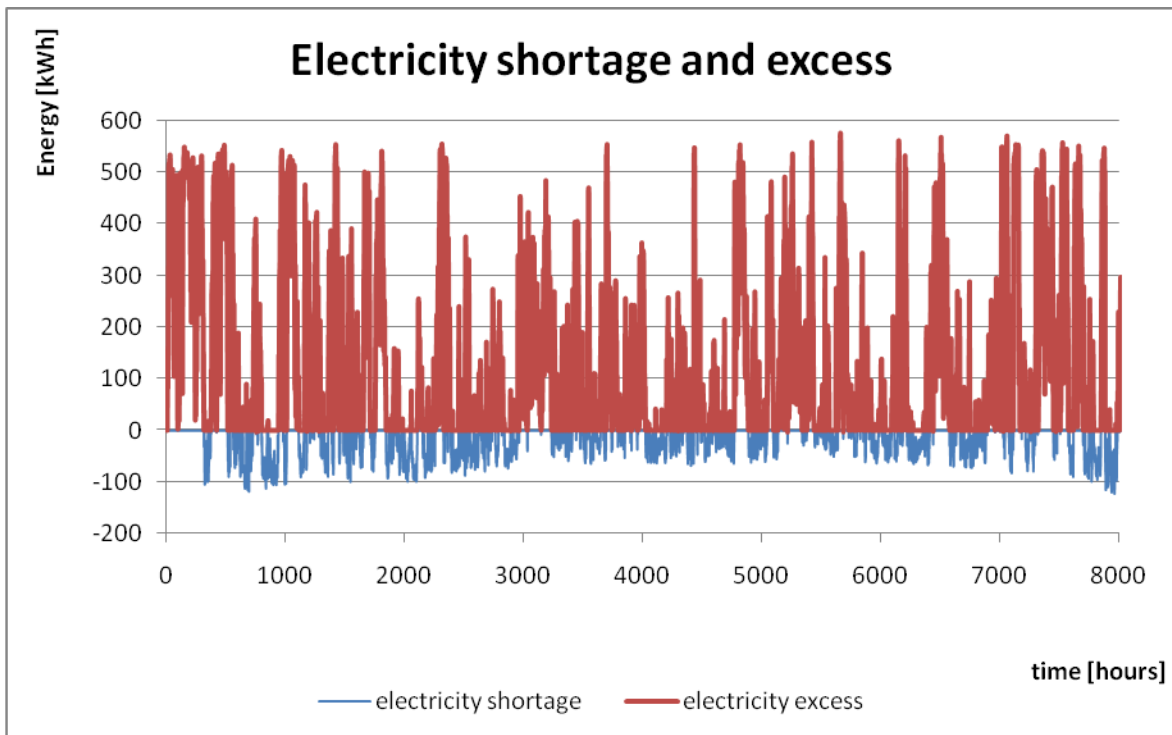


Figure 4.1 Shortage and excess of electricity

To ensure long term energy storage, a part of the excess energy can be converted using the electrolyzer to hydrogen. Two electrolyzer examples have been considered: 160 kW, producing 35 Nm³/h of hydrogen and 300 kW, producing 60 Nm³/h. The power consumption per Nm³ was 4.57 kWh and 5.00 kWh, respectively. The electrolyzer can be operated by 3859 hours, where the minimum power input is equal to 20% of nominal power.

For the first example, total energy input to the electrolyzer is 488512 kWh and the total dump is 349891kWh, with the peak value of 375 kWh by 3008 hours. The wind energy increased significantly. For the higher input electrolyzer, total hours of operations were 4797 kWh, with a total energy consumption of 715212 kWh, thus the total energy dump decreased to the value of 124202 kWh with the number of hours at 1061.

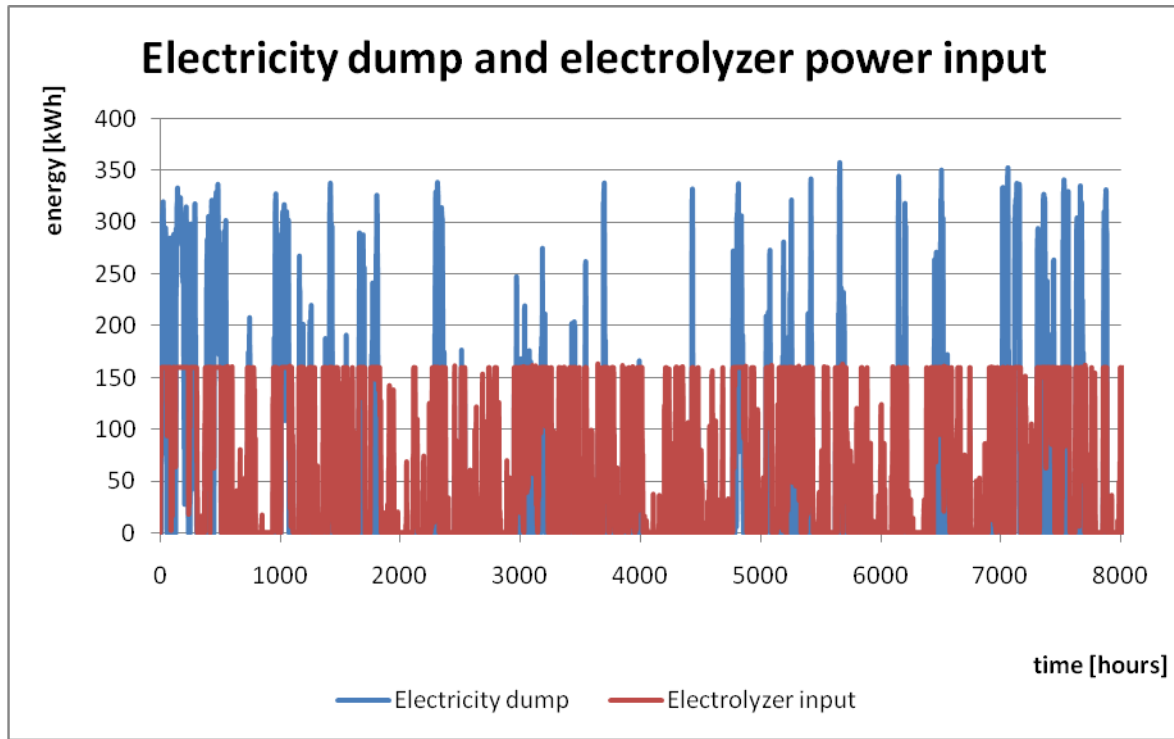


Figure 4.2 Electricity dump and electrolyzer power input for nominal power 160 kW

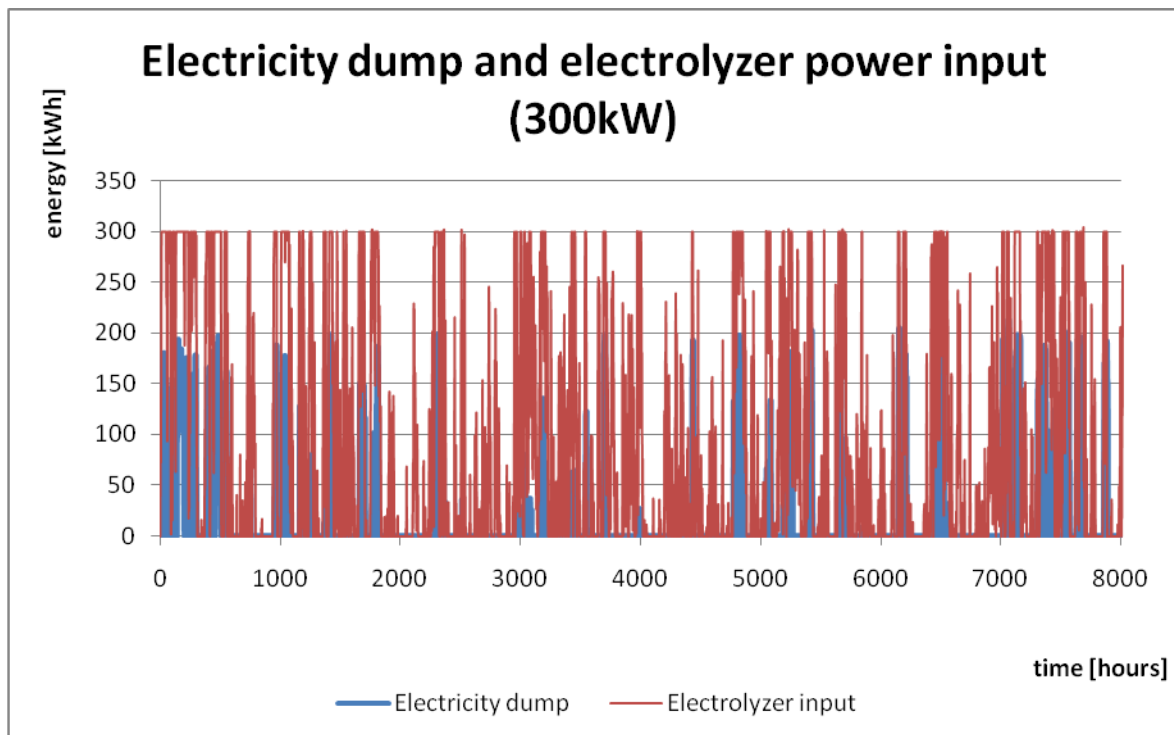


Figure 4.3 Electricity dump and electrolyzer power input for nominal power 300 kW

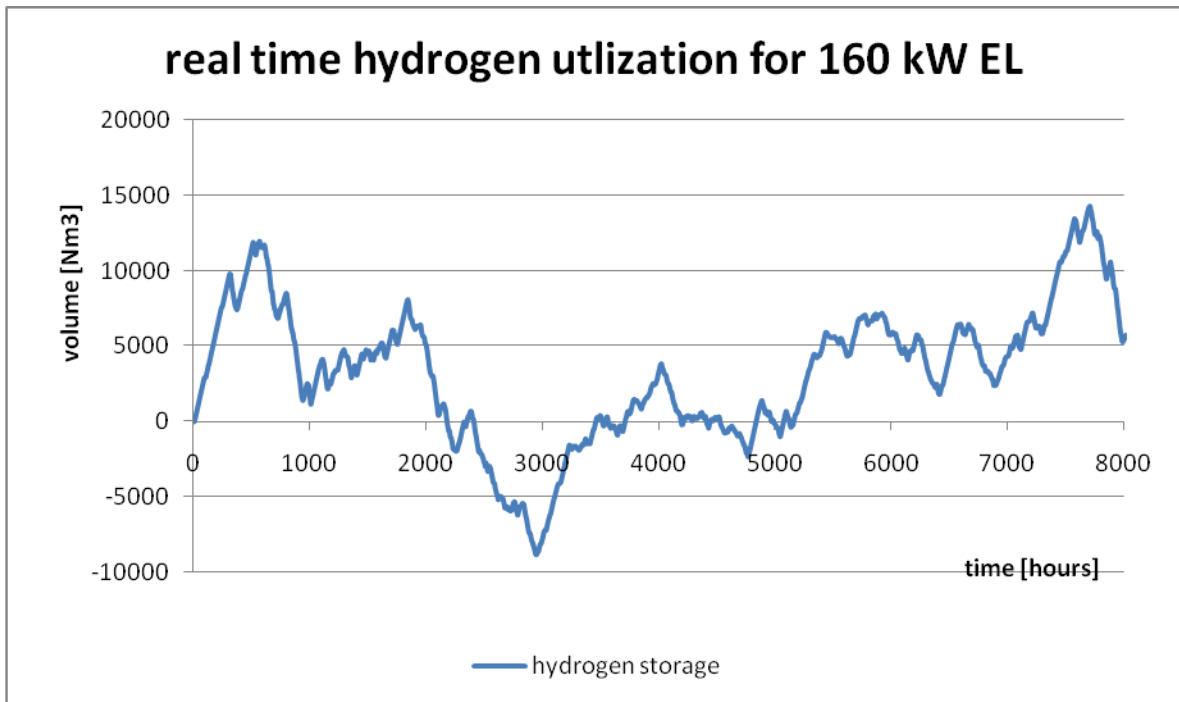


Figure 4.4 Real time hydrogen utilization in the system with 160 kW electrolyzer

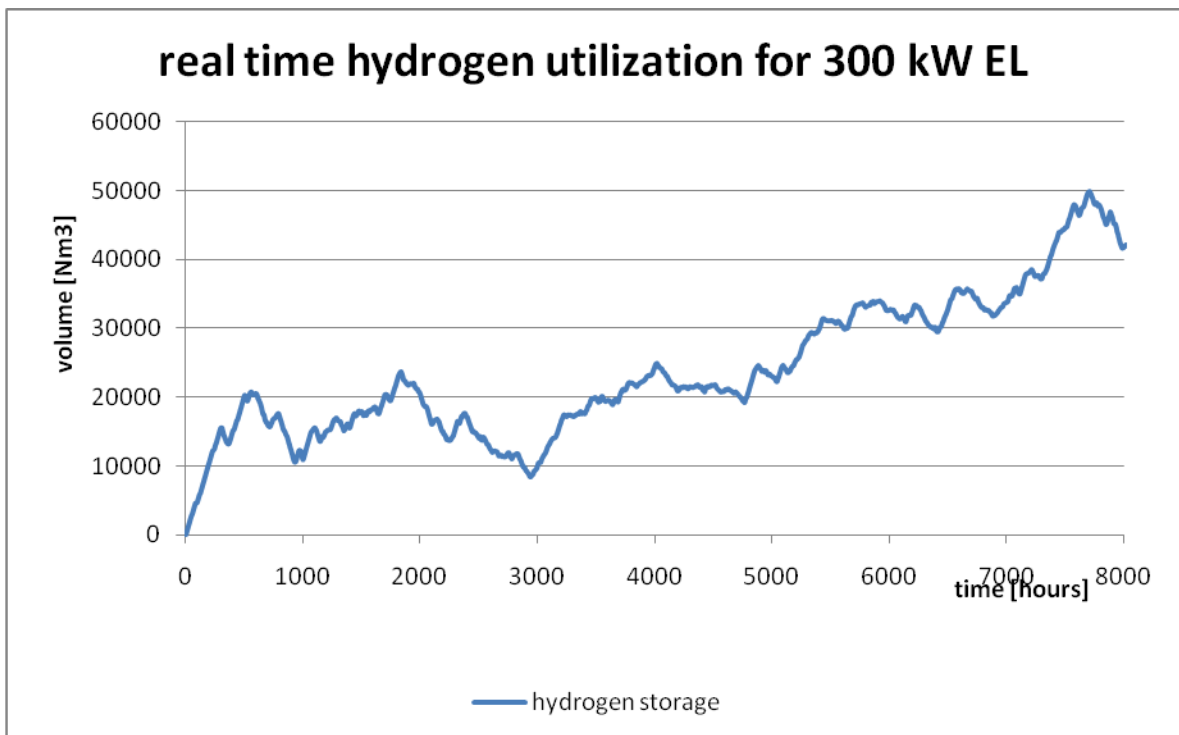


Figure 4.5 Real time hydrogen utilization in the system with 300 kW electrolyzer

When hydrogen is derived from a 160 kW electrolyzer with the following demand, at a certain point all hydrogen will be used and the tanks will be empty. This situation takes 1872 hours. For the system with the 300 kW electrolyzer, the hydrogen supplies are always guaranteed, however in both cases the hydrogen tanks are too small. The present capacity does not influence the deficit of hydrogen, but it causes greater hydrogen dump. In that

case, larger hydrogen input would be necessary and the surplus of the gas could be exported or be a fuel for transportation systems and constitute additional income. The total hydrogen peak does not exceed the value of 92 Nm^3 to sustain the load, and the total hydrogen demand is 105054 Nm^3 . Thus, it is highly recommended that in order to use the wind power the surplus of hydrogen should be utilized efficiently.

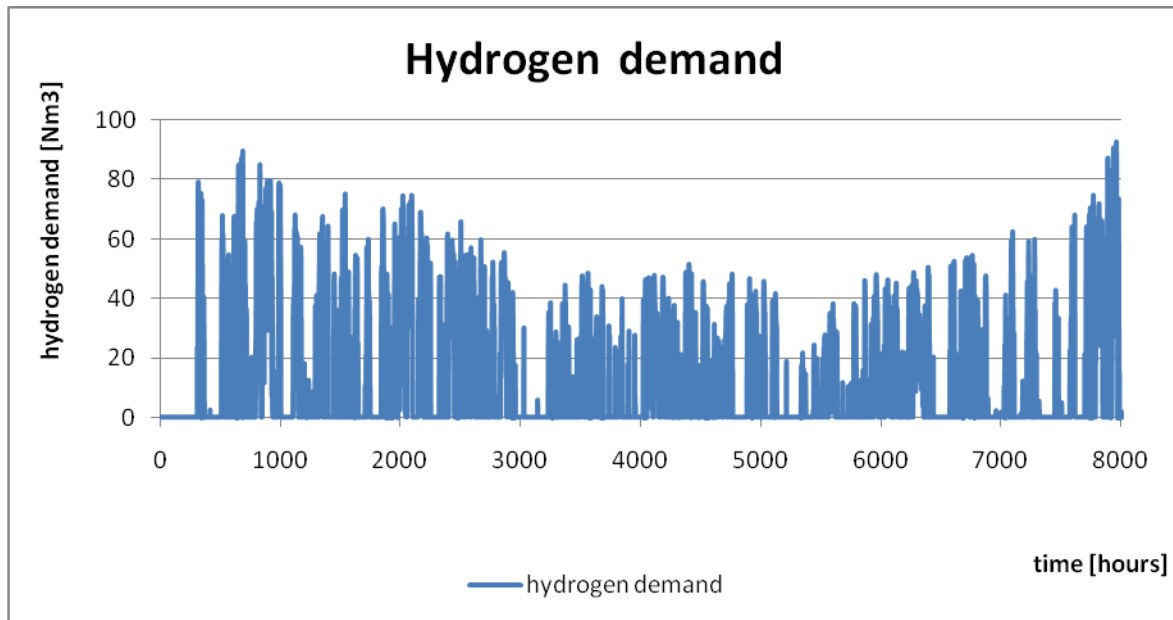


Figure 4.6 Hydrogen demand in time

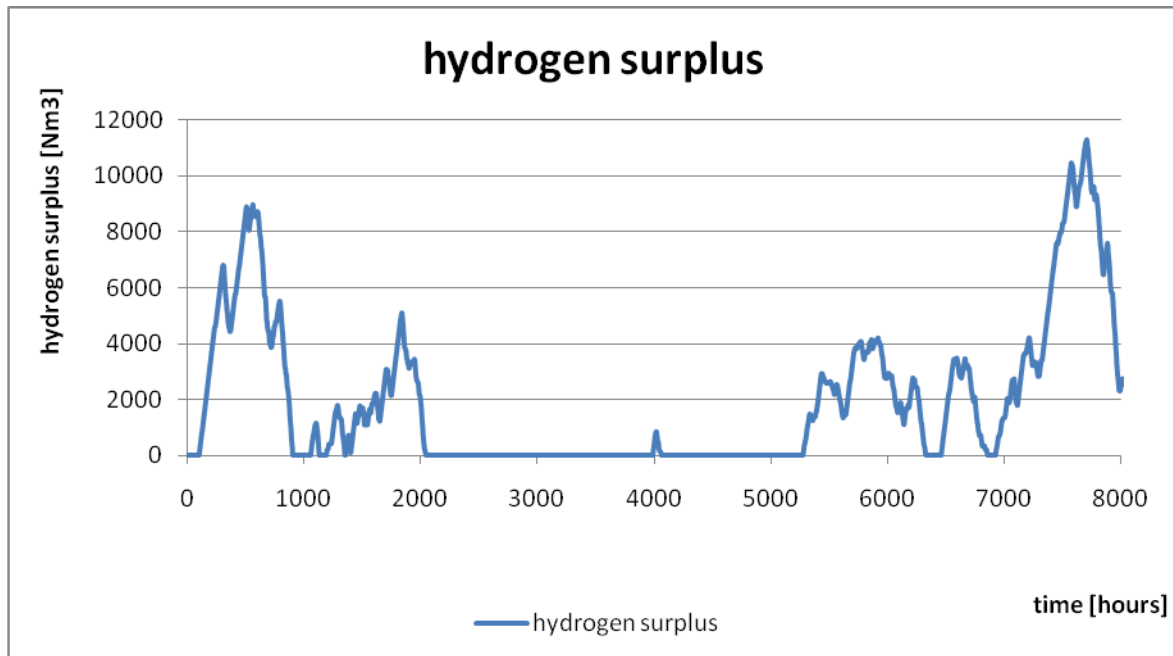


Figure 4.7 Hydrogen surplus

As a second source of energy, the PEM with a maximum power output of 104 kW has been used to utilize the stored hydrogen and supply electricity to the grid. The power curve is shown in Figure 4.8.

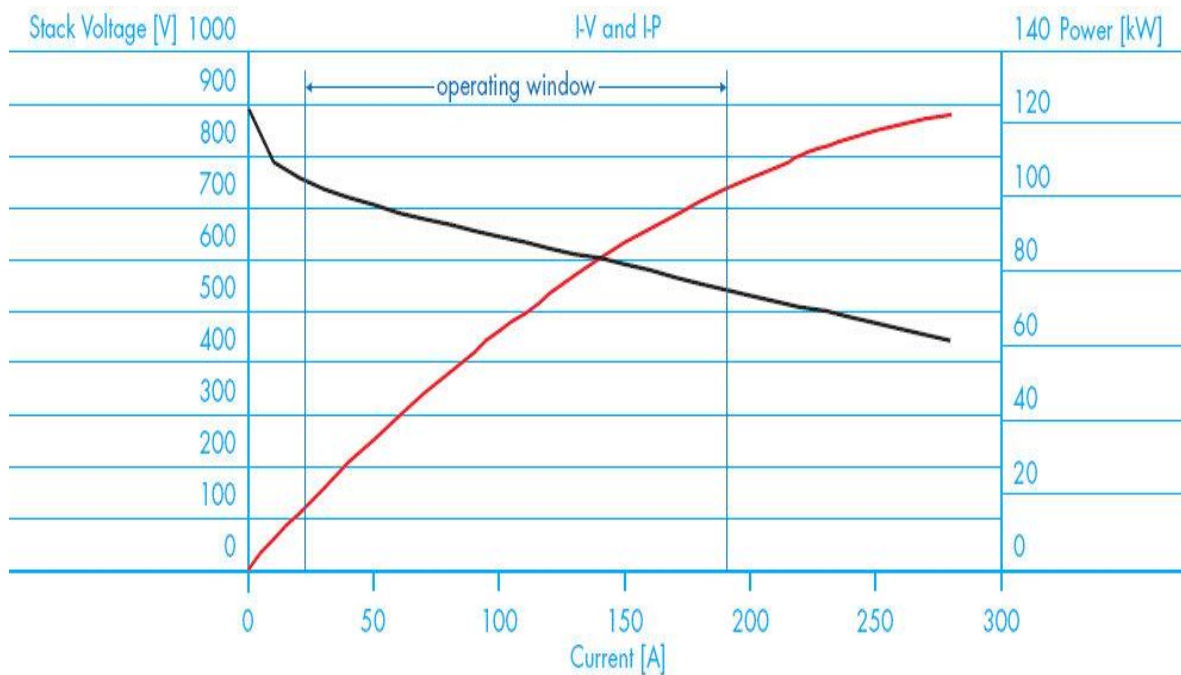


Figure 4.8 I-V and a power power curve for the selected fuel cell.

The total energy supplied by a fuel cell is 137207 kWh by 3213 hours. However, by 37 hours, the fuel cell is not able to ensure the total energy demand because the electricity shortage exceeds the rated power of the device. This assumption is made only when there is enough hydrogen in the tank to feed the fuel cell. The maximum fuel cell power shortage is 18 kWh. However, if the supply of hydrogen is not enough to feed the fuel cell, as it happened with the 160 kW electrolyzer, the fuel cell would deliver 108514 kWh in total and the operational time would drop to 2400 hours.

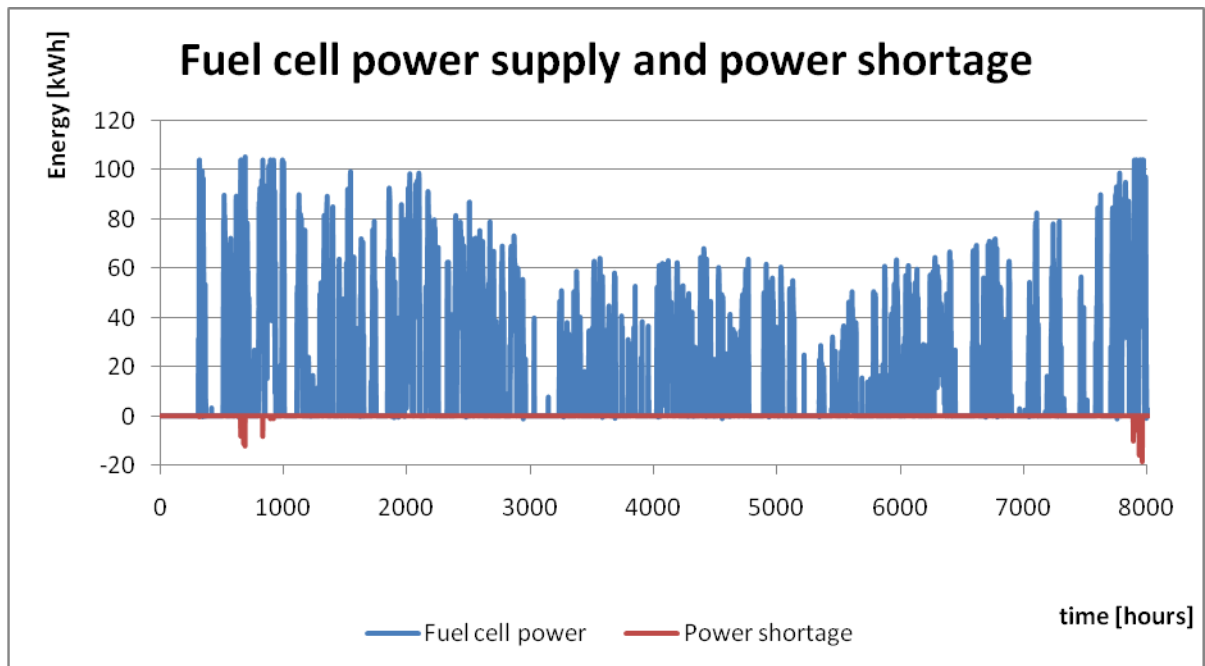


Figure 4.9 Fuel cell power supply and power shortage, when the hydrogen is always available

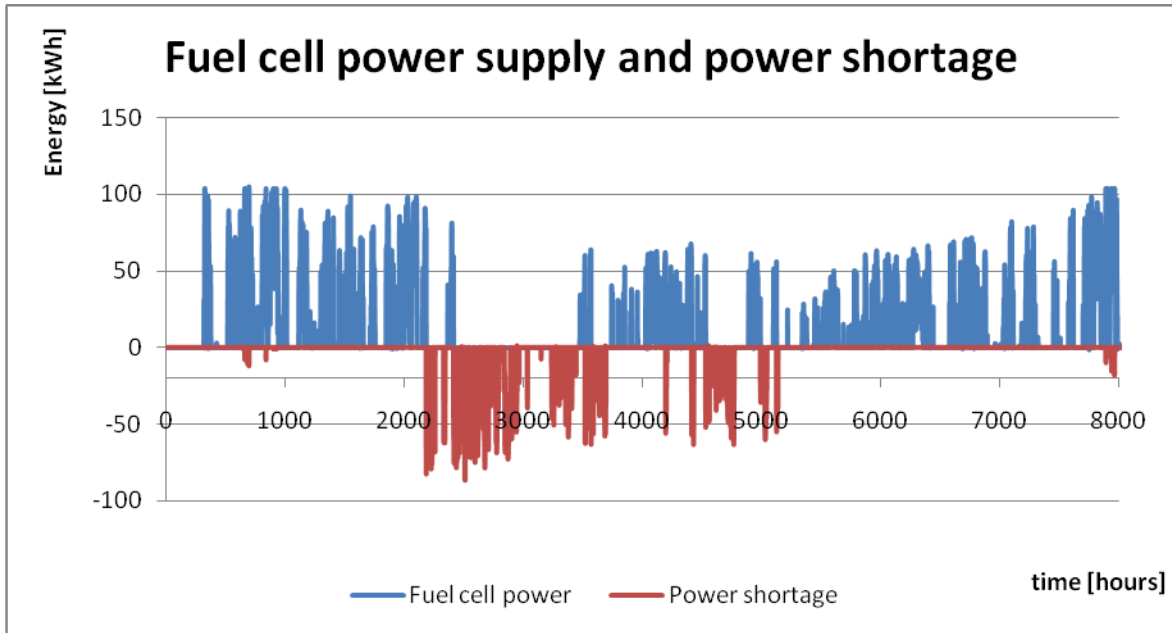


Figure 4.10 Fuel cell power supply and power shortage, when the hydrogen is limited by production rate

In this case, a backup system in the form of a battery would be necessary. Depending on the battery type, the total mass and cost of the battery varies. The comparison has been presented in the Table 3.

Table 3 Comparison of batteries storage

Battery type	Cost [\$ per Wh]	Gravimetric density [Wh/kg]	Total mass [kg]
Lead acid	\$0.17	41	440
Alkaline long-life	\$0.19	110	163
Carbon-zinc	\$0.31	36	500
NiMH	\$0.99	95	190
NiCad	\$1,50	39	462
Lithium-ion	\$4.27	128	141

The overall energy supply for the grid is presented in Figure 4.11

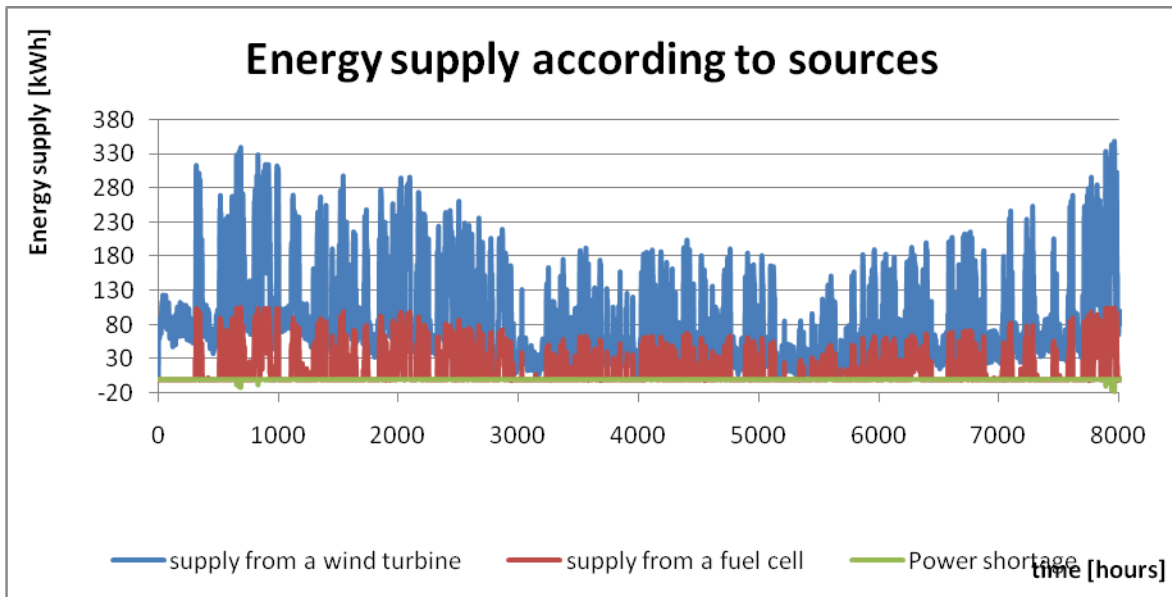


Figure 4.11 Energy supply according to sources

The overall efficiency of the hybrid system is 36.5% contrary to the 25.4% wind based system in which the hybridization level equals 2.29, meaning that wind energy supplies 2.29 more electricity than a fuel cell. The efficiency of the whole system could be increased if the dissipated heat from the fuel cell could be utilized for a heat supply.

Direct supply from WT, energy demand and hydrogen production rate

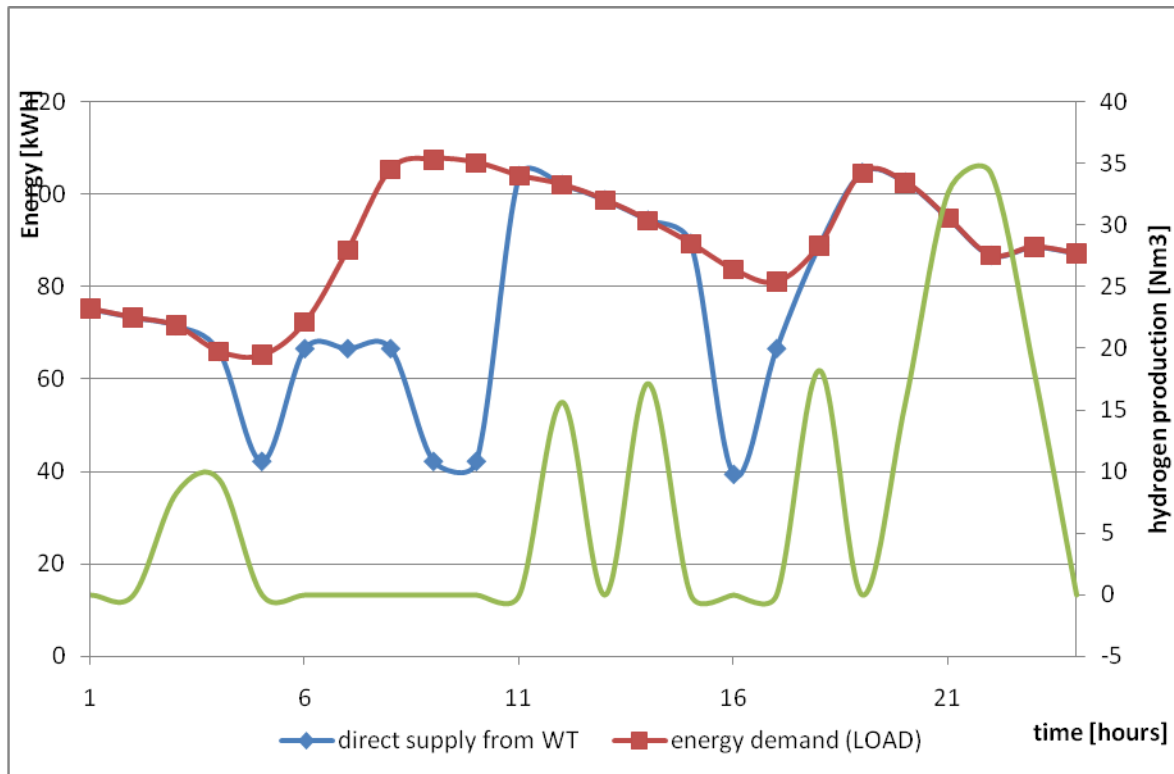


Figure 4.12 Direct supply from wind turbine and energy demand combined with hydrogen production rate for the period of 24 hrs

Figure 4.12 shows the difference between the direct supply of electricity from the wind generator and electricity demands required by the load and hydrogen production rate over a period of one day.. Hydrogen can be only produced in the time, where the energy demands are fulfilled by direct supply from the wind turbine.

Power production and electricity excess in a relation with hydrogen production rate

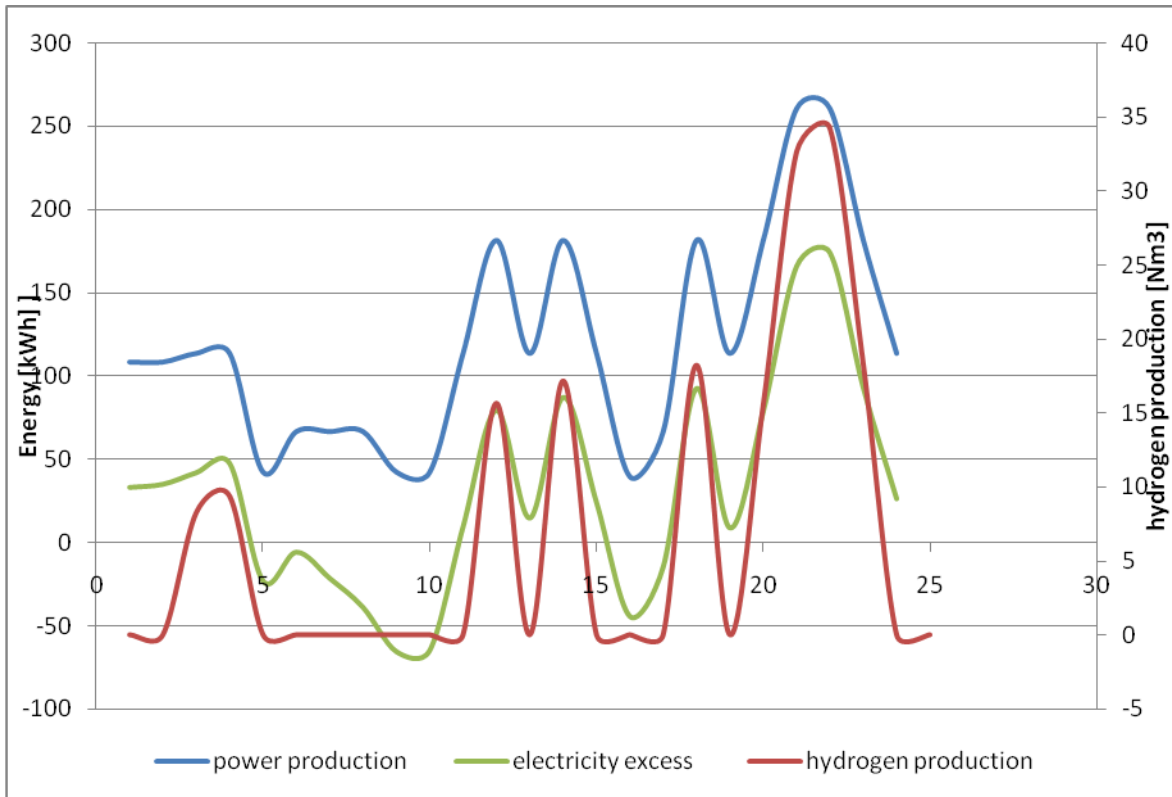


Figure 4.13 Power production and electricity excess in a relation with hydrogen production rate.

There is a relation between the rate of hydrogen production and electricity excess. Hydrogen is only produced when there is an excess of electricity.

5 CONCLUSIONS

The study presents the technology of the wind hydrogen system and simulates its operation over 11 months with an hourly time step. The variable nature of power production from wind is a limiting factor in ensuring a stable and reliable power supply. This study demonstrated the potential of hybrid wind-turbine and hydrogen system to increase the penetration of this type of hybrid system into energy markets.

The hybrid system delivers the required energy from wind power and the lacking energy is supplied by hydrogen, which is fed to the fuel cell. As a result, the electricity production from the system is more reliable than a lone wind generator, and is fully renewable. Additionally, applying the hydrogen as an energy storage system, the total energy efficiency increases from 25.4% to 36.5%. Additional efficiency increases could be achieved by employing a heat supply from a fuel cell.

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