

A REVIEW ON WATER ELECTROLYSIS

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Abstract. Electrolysis is an electrochemical process in which electrical energy is the driving force of chemical reactions. Substances are decomposed, by passing a current through them. The first observation of this phenomenon was recorded in 1789. Nicholson and Carlisle were the first who developed this technique back in 1800 and by the beginning of the 20th century there were already 400 industrial water electrolysis units in use.

As mentioned before, water is decomposed to hydrogen and oxygen, by passing a current through it in the presence of suitable substances, called electrolytes. Electric current causes positively charged hydrogen ions to migrate to the negatively charged cathode, where a reduction takes place in order to form hydrogen atoms. The atoms formed then combine to form gaseous hydrogen molecules (H₂). On the other hand, oxygen is formed at the other electrode (the positively charged anode). The stoichiometry of the reaction is two volumes of hydrogen to one volume of oxygen. The most important part of the construction of electrolysis units is to use adequate electrodes to avoid unwanted reactions, which produce impurities in the hydrogen gas. Another necessary component of such a unit is a separating membrane that allows the passage of ions, or electrons and not oxygen, or hydrogen atoms. This membrane allows the gases to be kept separate in order to avoid the risk of an explosive mixture being formed in the electrolysis unit.

In the initial discovery of electrolysis, an acidic water solution was used, but nowadays there is a trend towards alkaline electrolytes such as potassium hydroxide (KOH). This technology offers the advantages of materials which are cheaper and less susceptible to corrosion compared to those required to handle acids. Electrolysis plants with normal or slightly elevated pressure usually operate at electrolyte temperature of 70-90°C, cell voltage of 1.85-2.05 V and consume 4-5 kWh / m³ of hydrogen, which is obtained at a purity of 99.8% and more. Pressure electrolysis units run at 6-200 bar and there is no significant influence on the power consumption. Because of its high energy consumption and also of the quite substantial investment, water electrolysis is currently used for only 4% of world hydrogen production.

Nowadays research and development into high efficiency electrolyzers is flourishing in many areas. A way of improving electrolysis units efficiency is by increasing the process temperature which lowers the voltage required to electrolyse the water, but also requires more expensive materials. Despite the fact that the total energy needed for the electrochemical decomposition of water decreases only slightly with increasing temperature, the reversible part of the energy requirement (ΔF), which is supplied as electrical energy, decreases considerably. Therefore an increasing amount of the total energy could be supplied as heat. At elevated temperatures (800-900°C) the electric power consumption is approximately only 3 kWh / m³ of hydrogen. It must be noted that this technology is still in the development stage.

Electrolysis is considered as the “cleanest” way to produce hydrogen, when the required electricity is derived from renewable energy sources. In countries with a lot of waterfalls, hydroelectricity can be used as the energy source for water electrolysis. Other renewable sources that could be used for supplying electrolysis units are solar, aeolic and geothermal energy. Photoelectrolysis, in which the photovoltaic cells are also electrodes that decompose water to hydrogen and oxygen gas could be used for the production of hydrogen. These technologies could be used in order to store energy as hydrogen, which can be transformed to electricity in fuel cells, when the natural source of energy is not available. The production of hydrogen through electrolysis using renewable energy sources has the smallest impact on the environment.

1. Historical background

The history of water electrolysis started as early as the first industrial revolution, in the year 1800, when Nicholson and Carlisle were the first to discover the ability of electrolytical water decomposing. By 1902 more than 400 industrial water electrolysis units were in operation and in 1939 the first large water electrolysis plant with a capacity of 10,000 Nm³ H₂/h went into operation. In 1948, the first pressurized industrial electrolyser was manufactured by Zdansky/Lonza. In 1966, the first solid polymer electrolyte system (SPE) was built by General Electric, and in 1972 the first solid oxide water electrolysis unit was developed. The first advanced alkaline systems started in 1978. The history ends up in our days with the development of proton exchange membranes, usable for water electrolysis units and fuel cells, by DuPont and other manufacturers, due to the developments in the field of high temperature solid oxide technology and by the optimization and reconstruction of alkaline water electrolyzers [1].

2. Theory of water electrolysis

The electrolysis of water is considered a well-known principle to produce oxygen and hydrogen gas. In Fig.1 a schematic of an electrochemical cell is presented. The core of an electrolysis unit is an electrochemical cell, which is filled with pure water and has two electrodes connected with an external power supply. At a certain voltage, which is called critical voltage, between both electrodes, the electrodes start to produce hydrogen gas at

the negatively biased electrode and oxygen gas at the positively biased electrode. The amount of gases produced per unit time is directly related to the current that passes through the electrochemical cell. In water, there is always a certain percentage found as ionic species; H^+ and OH^- represented by the equilibrium equation:

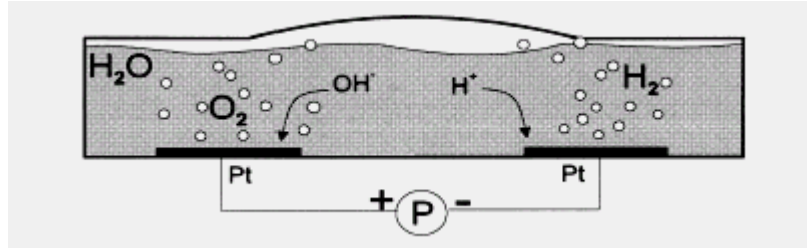


Fig.1: Sketch of an electrochemical cell [2].



Oxygen and hydrogen gas can be generated at noble metal electrodes by the electrolysis of water:

+ electrode (anode):



- electrode (cathode):



In case of acidic or basic water, the reactions which occur at the electrode interface are slightly different.

In water electrolysis there are no side reactions that could yield undesired byproducts, therefore the net balance is:



The minimum necessary cell voltage for the start-up of electrolysis, E_{cell}^o , is given under standard conditions (P, T constant) by the following equation:

$$E_{cell}^o = \frac{-\Delta G^o}{nF} \quad (4)$$

where ΔG^o is the change in the Gibbs free energy under standard conditions and n is the number of electrons transferred. In the case of a closed electrochemical cell, the conditions slightly change from standard conditions, open cell (P, T) = constant to closed cell (V, T) = constant because the change in the cell volume is smaller compared to that of pressure. Therefore, instead of ΔG^o , ΔA^o – free energy (Helmholtz) is used.

The necessary voltage for an electron to overcome the Helmholtz energy barrier is given below:

$$E_{cell}^o = \frac{-\Delta A^o}{nF} \quad (5)$$

$$\Delta A^o = \Delta H^o - TR\Delta n - T\Delta S^o \quad (6)$$

For the electrolysis of water, the standard reaction enthalpy is, $\Delta H^o = 285.8$ (kJ/mol), $\Delta n = 1.5$, $\Delta S^o(H_2) = 130.6$, $\Delta S^o(O_2) = 205.1$, $\Delta S^o(H_2O)(l) = 70$ J/mol K, $\Delta S^o_{tot} = 130.6 + \frac{1}{2} 205.1 - 70 = 163.14$ J/mol K, and $\Delta A^o = 233.1$ (kJ/mol). So, the minimum necessary cell voltage is $E_{cell} = 1.21$ V. In the case of an open cell, $E_{cell}^o = -\Delta G^o/nF = 1.23$ V, with $\Delta G^o = \Delta H^o - T\Delta S^o = 237.2$ kJ/mol (standard conditions, 1 bar, 25 °C).

In order for a reaction to get started, it is necessary to overcome an (extra) energy barrier, the activation energy E_{act} . The number of molecules able to overcome this barrier is the controlling agent of the reaction rate, r , and it is given by the statistical Maxwell – Boltzman relation which has an exponential behaviour: $r \sim r_o \exp(-E_{act}/RT)$. So, the activation energy expresses the speed with which a reaction takes place.

The maximum possible efficiency of an ideal closed electrochemical cell is defined by the following equation:

$$\epsilon_{max} = \frac{\Delta H}{\Delta A} = -\frac{\Delta H}{nFE_{cell}} \quad (7)$$

In reality, the efficiency of an electrochemical cell is given by:

$$\epsilon_{real} = -\frac{\Delta H}{nE_{elec}} \quad (8)$$

where ΔE_{elec} is the voltage to drive the electrochemical cell at I :

$$\Delta E_{elec} = \Delta A + IR + \Sigma \eta \quad (9)$$

Where R is the total ohmic series resistance in the cell including external circuit resistance, electrolyte, electrodes, membrane material; $\Sigma\eta$ is the sum of the overpotentials (activation overpotential at the two electrodes, and the concentration overpotential due to the mass transport of the gaseous products away from the anode and cathode surfaces). The balance energy, per mole, during water electrolysis is shown in Fig.2. The activation overpotential increases by increasing the current density and can be lowered by using electrodes which have a catalytic action, such as platinum.

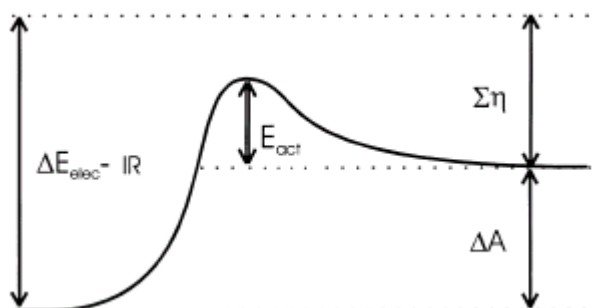


Fig.2: Energies involved in a reaction [2].

For water electrolysis, under ideal reversible conditions, the maximum theoretical efficiency with respect to the electrical energy source would be $\epsilon_{\max} = 120\%$. Therefore, heat would have to flow into the cell from the surroundings. When the value of the denominator in Eq.7 becomes $1.48 nF$ (overpotential of $0.25V$), the electrochemical cell would perform at 100% efficiency. Under these conditions ($\Delta S = 0$, $\Sigma\eta = 0$, so $\Delta G = \Delta H$), the cell does not heat or cool and the value of $E_m = \Delta H / nF = 1.48 V$ is denoted as the thermoneutral potential. The electrochemical cell produces heat at potentials above $1.48 V$ and takes heat in at potentials below this value, under the condition that cell temperature is to be maintained constant. In practice, the IR drop may be ca $0.25V$. The overpotential η should be kept low so as to maximize the efficiency and to minimize the production of heat. On the other hand, the lower the overpotential the slower the reaction will occur, so we have to make a compromise. One of the best ways to increase the current without increasing the overpotential is to increase the contact areas between the electrodes and the liquid [2].

3. Methods of hydrogen production through water electrolysis

Despite the fact that the discovery of electrolytical water decomposing was first observed in acidic water, in industrial plants the alkaline medium is preferred, because corrosion is more easily controlled and cheaper construction materials can be used compared to acidic electrolysis technology. Other methods of hydrogen production, such as proton exchange membrane electrolysis, steam electrolysis have been developed in recent years. Hydrogen could also be generated as a byproduct during the chloralkali production. These technologies are briefly discussed in the next paragraphs.

3.1. Alkaline electrolysis

The principle of alkaline water electrolysis is schematically shown in Fig.3 in the example of the monopolar arrangement electrolyser. Two molecules of water are reduced to one molecule of hydrogen and two hydroxyl ions at the cathode. The hydrogen escapes from the surface of the cathode recombined in a gaseous form and the hydroxyl ions migrate under the influence of the electrical field between cathode and anode through the porous diaphragm to the anode, where they are discharged to $\frac{1}{2}$ molecule of oxygen and one molecule of water.

The oxygen recombines at the electrode surface and escapes as hydrogen does, as a gas. Whereas pressureless electrolyzers are mainly built in the monopolar arrangement, which is the simplest construction principle, pressurized species are manufactured in the so-called bipolar filter press arrangement. The main reasons for the bipolar arrangement are the savings in space and in electrical bus bars and housing material, which are essential if large pressurized plants need to be built. A small disadvantage of the bipolar type when compared to the monopolar, is the occurrence of shunt currents inside the electrolyte ducts of the bipolar electrolyser. In order to face this disadvantage, a more sophisticated design of the electrolyte and gas ducts and the application of a small protection current during operational shut-down times are necessary in bipolar water electrolyzers. To meet the demands of the future energy market, in which electrolyzers will have to serve as filling stations for vehicles in the environment of a town, rigorous reconstruction, optimization and safety implementation, is necessary.

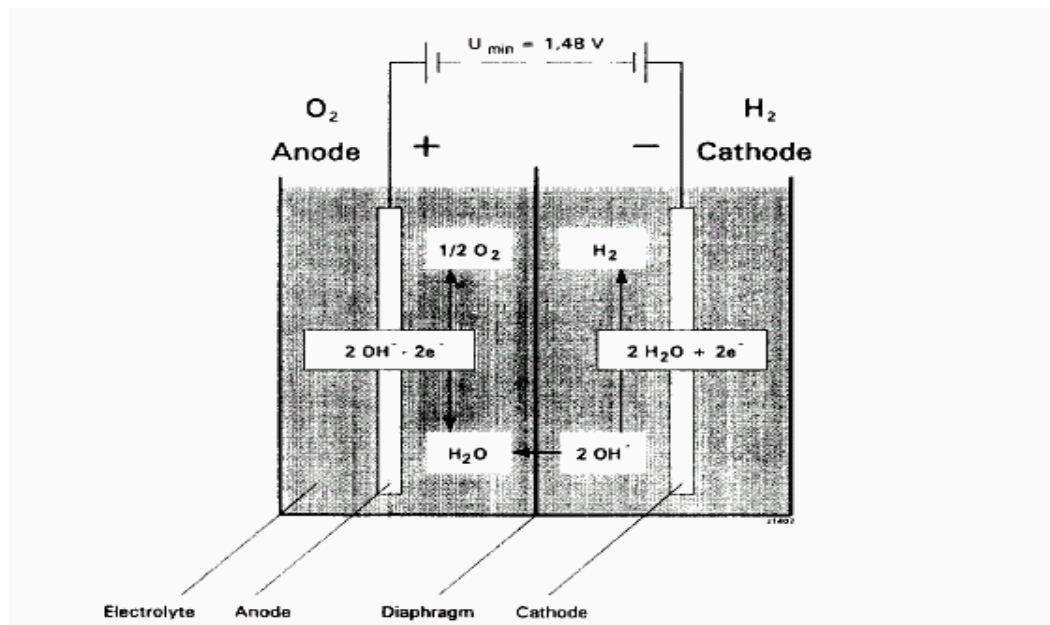


Fig.3: Principle of alkaline electrolysis [1].

One example of an advanced pressurized alkaline electrolyser is the prototype of the GHW (Gesellschaft für Hochleistungselektrolyse zur Wasserstoffherzeugung mbH), a company which is a foundation of Linde AG, MTU-Friedrichshafen and HEW. This electrolyser delivers hydrogen under 30 bar pressure, the bipolar cell stack is encapsulated in a pressure vessel and the cell stack itself consists of newly developed electrode-diaphragm units installed in rectangular polymer-framed cells. The cell stack inside the pressure vessel is surrounded by the feed water for the electrolysis process, i.e. the feed water, first, passes the interspace between the cell stack and pressure vessel, before it flows into the caustic electrolyte loop. Therefore, there is no pressure difference between the inside and the outside of the stack and the great number of cell gaskets separate only the lye from inside against the water from outside at a difference pressure of some mbar. Furthermore, only one large gasket has to bear the pressure at the door of the pressure vessel and it separates not only the lye from air, but also from water. This concept has the additional advantage that all the traces of caustic potash, which may come out of the cell stack during its lifetime are automatically recycled into the electrolyte loop. Furthermore, all cells are voltage controlled by the process computer for too high or too low values and the purity of the product gases is also controlled.

The newly developed cells and plant allow operation temperatures up to 150 °C and variable pressures ranging from 5 to 30 bar. The new EDE-units in the cells consist of the porous cathode, the diaphragm and the anode and allow current densities up to 10 kA/m², which is more than three times higher than the usual values of conventional low-pressure alkaline electrolysis plants. At these high values of current densities cell efficiencies of more than 80% were achieved. The pressure of 30 bar without further compression meets the demands of many consumers such as liquefaction of hydrogen, filling of hydride storage tanks, pipeline transport, fat hardening and so on. For high compression to 200 or 400 bar the expensive first piston compression stage can be saved [1].

3.2. Proton exchange membrane water electrolysis

The proton exchange membrane water electrolysis is based on the use of a polymeric proton exchange membrane as the solid electrolyte ('polymer electrolyte membrane') and was first proposed by General Electric for fuel cell, and later, electrolyser applications. The proton exchange membrane electrolyser technology was developed by ABB (formerly Brown, Boveri Ltd), Switzerland, over the years from 1976 to 1989. The following advantages of polymer electrolyte technology over the alkaline one have been proposed: (i) greater safety and reliability are expected since no caustic electrolyte is circulated in the cell stack; (ii) previous tests made on bare membranes demonstrated that some materials could sustain high differential pressure without damage and were efficient in preventing gas mixing; and (iii) the possibility of operating cells up to several amps per square centimeter with typical thickness of a few millimeters is theoretically afforded [3].

Ultrapure water is fed to the anode structure of the electrolysis cell which is made of porous titanium and activated by a mixed noble metal oxide catalyst. The membrane conducts hydrated protons from the anode to the cathode side. Appropriate swelling procedures have led to low ohmic resistances enabling high current density of the cells. The standard membrane material used in PEM water electrolysis units is Nafion™ 117 and is manufactured by DuPont. The cathode of such an electrolyser consists of a porous graphite current collector with either Pt or, in more recent designs, a mixed oxide as electrocatalyst. Individual cells are stacked into bipolar modules with graphite based separator plates providing the manifolds for water feed and gas evacuation. The

operation of the cells leads to electroosmotic water transport through the membrane from the anode to the cathode side.

The technology has been demonstrated on a 100 kW commercial scale in two units: Stellram/ATEL (1987-1990 and 1991-present) unit and SWB, Solar-Wasserstoff-Bayern GmbH (1990-1996) unit. The operation of these two electrolyzers has successfully demonstrated the feasibility of this technology for industrial hydrogen production. A major problem of electrolyzers of this type is the limited lifetime of the electrolysis cells. Perfluorinated sulfonic acid membranes such as Nafion have been shown to be extremely resistant to the oxidative power of oxygen and even ozone evolving anodes. Nafion is a copolymer of tetrafluorethylene and a perfluorinated vinyl-ethersulfonyl fluoride. This latter monomer gives rise to side chains with pendant sulfonic acid sites. The polymer morphology and the related properties of these membranes have been investigated in various applications, concluding that phase separation occurs in these polymers.

The first commercial scale PEM electrolyser was installed in 1987 at Stellram SA, a metallurgical specialty company, in Nyon, Switzerland. The unit was designed to produce up to 20 Nm³/h of hydrogen at a pressure of 1-2 bar. The plant consisted of 120 cells of 20 x 20 cm² active area each, grouped into four modules of 30 cells, and electrically connected in series. The modules were arranged into two vertical stacks which were compressed individually by a hydraulic system with a force of 350 N/cm². The individual cells were composed of a sheet of NafionTM 117, which was coated by a thin layer of Pt on one side. The Pt layer was applied using a proprietary electroforming technique and was used as the cathodic catalyst. Prior to applying the catalyst, the membranes were hydrated in an autoclave at a temperature of 130 °C for two hours in ultrapure water. After cooling down, the membranes were treated in 1 M HCl for 30min and subsequently rinsed in demineralized water.

The anode catalyst for oxygen evolution was a Ru/Ir mixed oxide, applied as a PTFE-bonded powder to the surface of a porous Ti current collector, which consisted of a graphite-PTFE composite bonded to a brass wire mesh. Water is circulated through the anode manifolds in order to maintain equal temperature distribution over the entire membrane/electrode area. The temperature of the system is measured at the outlet of the anode loop. The purity of the gases is measured using online instrumentation.

The nominal operating conditions for the plant at start-up were: 400 A (i.e. 10 kA/m²), at 80 °C. Cell voltages at these operating conditions were typically of the order of 1.75 V. The plant was operated at variable load, according to the hydrogen needs of the metallurgical process, for approximately 15000 hours before it had to be shut down completely in 1990, because the hydrogen concentration in the oxygen had exceeded the safety limit (3%). By this time the voltage across a number of cells had drastically dropped, indicating short circuits within these cells as the reason for gas leakages and gas purity problems. The 120 cells were disassembled and after replacing all the membranes and electrocatalytic layers and part of the current collectors and bipolar plates, the plant was reassembled and transferred to an experimental site of the Swiss electric utility company, ATEL in 1991. Except for the cathode catalyst, the cells in the revamped ATEL version were made up using the same materials. The ATEL plant was equipped with cathode electrocatalysts prepared from mixed oxides of Ir and Ru and applied to the cathode current collector surface.

The design of the second PEM water electrolysis demonstration plant, Solar Wasserstoff Bayern (SWB), was slightly different from the Stellram plant. The most important differences were: the thickness of the bipolar plates of the cell stacks was reduced. All 120 cells were assembled into one stack consisting of three modules of 40 cells each. The hydraulic compression of the cell stack was replaced by a mechanical system with springs in order to allow for thermal expansion. The nominal clamping pressure was the same as in the Stellram/ATEL plant. As in the revamped ATEL plant, the cathode catalyst consisted of the same material as the anode catalyst (Ir/Ru oxide) [4].

3.3. Steam electrolysis

One of the major problems of conventional electrolyzers is their high electricity consumption. Steam electrolysis is a technology that reaches higher total energy efficiency compared to alkaline and proton exchange membrane electrolysis.

From the thermodynamic viewpoint of water decomposition, it is more advantageous to electrolyze water at high temperature (800-1000 °C) because the energy is supplied in mixed form of electricity and heat. The main advantage is that a substantial part of the energy needed for the electrolysis process is added as heat, which is much cheaper than electric energy. In addition, the high temperature accelerates the reaction kinetics, reducing the energy loss due to electrode polarization, thus increasing the overall system efficiency. Typical high temperature electrolyser such as the German HOT ELLY system achieves 92% electrical efficiency while low temperature electrolyzers can reach at most 85% efficiency. The high temperature system employs oxygen ion conducting ceramics as the electrolyte (ZrO₂ stabilised by Y₂O₃, MgO or CaO). The fluid to be dissociated is 200 °C steam which after being further heated to 800-1000 °C enters on the cathode side. After the steam is split to hydrogen gas and O⁻ ions, the oxygen ions are transported through the ceramic material to the anode, where they discharge and form oxygen gas. Despite this high efficiency with respect to electricity, the high temperature system still produces hydrogen at about four times the cost of the steam reformed hydrogen.

In conventional steam electrolyzers, the gas supplied to the cathode side (where water is decomposed) is usually a mixture of steam and hydrogen, while the gas supplied to the anode is usually air. At zero current, the system has an open-circuit voltage of 0.8 to 0.9 V, depending on the hydrogen/steam ratio and on operating temperatures. This open-circuit voltage is even higher for water electrolysis. In order to electrolyze water, a voltage that opposes and is higher than the open circuit voltage must be applied in order to pump oxygen from the steam side to the air side. Clearly, much of the electricity used, 60 to 70% of the total electrical power, is wasted forcing the electrolyser to operate against the high chemical potential gradient for oxygen. In addition, the liberation of oxygen coming from the decomposition of water into the air stream at the anode side is clearly a waste.

A new approach to reduce the electricity consumption in electrolyzers was achieved by using natural gas in order to reduce the chemical potential difference across the electrolyser cell. The concept is called Natural-Gas-Assisted-Steam Electrolysis (NGASE). In this new technology, the air in the anode side is replaced with natural gas in order to lower the open circuit voltage and thereby the electricity consumption. The reducing character of natural gas helps to lower the chemical potential difference between the two sides of the electrolyser. The scale-up to large water electrolysis units using this technology is currently under development [5].

3.4. Hydrogen as a byproduct from chlor-alkali production

The main product of the chlor-alkali electrolysis process, which uses NaCl as a raw material, is chlorine. The industrially used electrolysis cells are the mercury, the diaphragm and the membrane cell. Owing to environmental and economical reasons, a large amount of the required chlorine is currently produced by the relatively new membrane processes. In these processes the cathode and the anode compartment in the electrolysis cell are usually separated by a cation selective membrane of about 50-200 μm thickness. The anode compartment is fed with a brine solution (a typical concentration of about 180-200 g/L NaCl, and pH from 1 to 4.5). At the anode chloride ions are converted to gaseous chlorine. The cathode compartment is fed with water and at the cathode water is transferred into gaseous hydrogen and hydroxyl ions. The sodium ions diffuse and migrate through the cation selective membrane from the anode to the cathode compartment. Sodium combined with hydroxyl ions leaves the membrane cell as sodium hydroxide (concentration of 23-25 wt%) Schematically, this process is demonstrated in Fig.4.

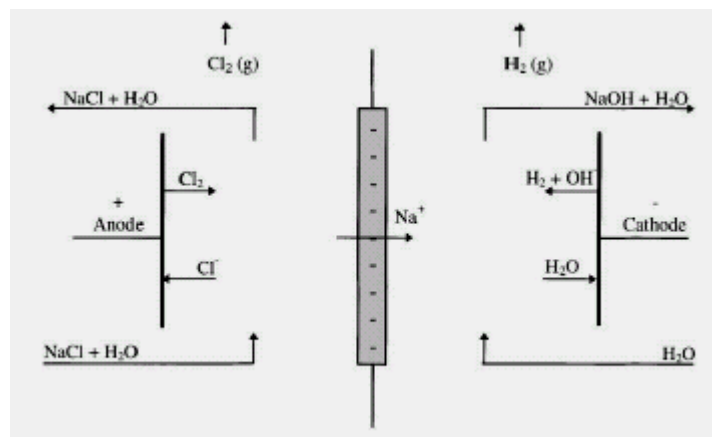


Fig.4: Representation of a cell unit in the chlor-alkali process (Van der Stegen et al, 1999).

A potential difference between the anode and the cathode is sustained (2-4 V) in such a way that the desired current density is obtained (typically 2000-5000 A/m^2). The membrane surface is about 1-3 m^2 . The membrane cells as presented in Fig.4 are serially coupled in a stack where about 20 to more than 100 of these cells are present. The membranes used in the chlor-alkali electrolysis are cation selective membranes, made of a cross-linked polymeric network on which functional groups are fixed. In the membranes incorporated to chlor-alkali electrolysis units, two types of active groups are attached to the matrix: carboxylic groups and sulfonic groups. The transport and sorption properties of a specific layer can be adjusted by the number of moles of active groups per kilogram dry polymer (equivalent weight). The sulfonic groups of the membranes are reinforced with Teflon wires to increase the mechanical stability of the membrane. The sulfonic layer is mostly placed at the anode side of the cell in order to prevent the protonation of the carboxylic groups in the carboxylic layer which could occur in the relatively acidic environment as present in the anode compartment. In the presence of a small pressure difference (0.1 bar) between the anode and the cathode, the membrane is pressed against the anode to decrease the mass transfer from the anode to the membrane, where due to the lower electrolyte concentration, the electrical resistance is greater than in the cathode. The distance between the cathode and the membrane is about 1mm. These electrolysis units operate at atmospheric pressures and at a temperature of 80-95 $^{\circ}\text{C}$ [6].

4. Electrode development for water electrolysis

Industrial water electrolysis cells typically employ stainless steel or nickel-based electrodes which operate in a potassium hydroxide solution at a concentration range of 6-9 mol/l and a temperature range of 60-80 °C. The overall energy efficiency of electrolysis is partly related to the hydrogen evolution reaction (HER). Nickel shows a high initial electrocatalytic activity towards the HER, however, it experiences extensive deactivation as a cathode during alkaline water electrolysis. Deactivation of the cathode is manifested by either a current loss at a fixed electrode potential or an increase in hydrogen overpotential at a constant current. To avoid such problems and enhance the overall energy efficiency of water electrolysis units, state-of-the-art electrodes have been developed by many researchers. A brief summary of the most important electrode development for water electrolysis is presented in this paragraph.

According to Abouatallah et al [7], the problem of nickel undergoing significant deactivation as a cathode during alkaline water electrolysis under certain conditions can be confronted by the addition of dissolved V_2O_5 . It was found that the dissolved vanadium oxide reactivates the nickel cathode and forms a vanadium-bearing deposit. Furthermore, vanadium addition did not appear to enhance the electrocatalytic activity beyond that for fresh nickel.

In another study, Bocutti et al [8] investigated the hydrogen evolution reaction (HER) on Ni-LaNi₅ and Ni-MmNi_{3.4}Co_{0.8}Al_{0.8} electrode materials in 1 mol dm⁻³ NaOH solution. The steady-state polarization curves and electrochemical impedance spectroscopy experimental data showed a pronounced improvement in HER kinetics when these electrode materials were used. The electrochemical results were in accordance with the Volmer-Heyrovsky mechanism. The kinetic results indicated a more effective improvement in the Heyrovsky step, suggesting an electrocatalytic synergistic effect of the hyper-electronic character of the rare-earth element on the electrode surface.

The kinetics of the hydrogen evolution reaction (HER) of a similar alloy electrode (MmNi_{3.6}Co_{0.7}Mn_{0.4}Al_{0.3}) were studied by Wei-Xiang Chen [9]. The electrocatalytic activity of the metal hydride (MH) for the HER was greatly improved by immersing the hydrogen storage alloy electrode in a hot alkaline solution containing KBH₄. After surface modification, the exchange current density for HER of metal hydride electrode was increased, and the apparent activation energy of HER was decreased from 35.6 kJ/mol for untreated MH electrode to 29.4 kJ/mol for MH electrode treated in a hot 6M KOH solution, and to 22.7 kJ/mol for MH electrode containing 0.05M KBH₄. The Ni-rich layer on the surface area of the alloy was augmented after the surface modification, leading to the enhancement of the adsorption of the hydrogen atom on the alloy surface, which being an intermediate for HER. These were the most important reasons for the improvement in the electrocatalytic activity for HER on the MH electrode.

Hu and Lee [10] developed and tested composite electrodes for hydrogen evolution reaction. The electrode used as cathode composed of Ti₂Ni hydrogen absorbing alloys. A Ni-Mo electrocatalyst was also prepared for alkaline water electrolysis. The electrocatalytic properties of the hydrogen evolution reaction were carried out in a 30 wt % KOH solution at 70 °C. The surface morphology and chemical composition of the cathode were also studied. The results of this study demonstrated that the composite cathode had a low hydrogen overpotential (ca. 60mV at 70 °C in 30 wt% KOH) and very good stability under conditions of continuous electrolysis and intermittent electrolysis with power interruption shutdown.

Hu (2000) also studied other new electrocatalysts consisting of hydrogen storage alloys, such as MmNi_{3.6}Co_{0.75}Mn_{0.4}Al_{0.27} alloy, LaNi_{4.9}Si_{0.1} alloy and Ti₂Ni alloy. Nickel-molybdenum coatings were also prepared. Their electrocatalytic activity for hydrogen evolution and their time stability were studied in 30 wt% KOH at 70 °C. The experimental results showed that the activity for hydrogen evolution increases when a molybdenum content increase occurs and is dominated by electrode surface composition. The hydrogen storage alloys inside the electrodes mainly serve the functions of enhancing corrosion resistance against power interruptions through electrochemically releasing absorbed hydrogen. These new electrocatalysts proved to not only having a low hydrogen overpotential, but also excellent time stability under both continuous and intermittent electrolysis.

Suffredini et al [12] reported improvements and alternatives for the preparation of high area Ni and Ni-Co coatings as well as the deposition of a highly active Ni-Fe layer on mild steel substrates. They also described the formation of spinel NiCo₂O₄ layers on substrates according to the Sol-Gel method. To obtain high area Ni and multilayer Ni-Co alloy coatings, a new electrodeposition methodology that allows the complete removal of Zn was used. This generated highly porous surfaces with roughness factors of 2200 for Ni and 4400 for Ni-Co. The hydrogen overpotential measured for these coatings at 135 mA/cm² and 70 °C were 0.1 and 0.09 V respectively. Analyses by SEM and dissolution voltametry suggested that the activation removed a passivating layer on the surface, revealing an active Ni-Fe phase. Long term operation in 4M NaOH at 135 ma/cm² showed a hydrogen overpotential of 0.16 V at 70 °C, a value significantly lower than 0.35 V found for smooth Ni or 0.49 V for an equivalent metallurgical alloy. Active anodes were prepared by the synthesis of NiCo₂O₄ spinel oxides on Ni and Ti substrates. These coatings showed an oxygen overpotential of approximately 0.3 V, which is 0.6 V less than that obtained for pure Ni oxide anodes, under the same conditions.

Sheela et al [13] have investigated the behavior of zinc-nickel alloy electrodeposits for water electrolysis. In this study Zn-Ni alloys of various compositions were prepared. A suitable electrolyte and conditions to produce alloys of various compositions were identified. The alloys were produced on electroformed nickel foils and were etched in caustic to leach out zinc and produce the Raney type, porous electrocatalytic surface for hydrogen evolution. The electrodes were tested by polarisation measurements, to evaluate their Tafel parameters, cyclic voltammetry, to test the change in surface properties on repeated cycling, scanning electron microscopy to identify their microstructure and X-ray diffraction. The experimental results showed that the catalytic activity as well as the lifetime of the electrodes produced from 50% zinc alloy was found to be better than others. Alloys having higher nickel contents were not so useful.

Tavares and Trasatti [14] developed state-of-the-art electrodes for hydrogen evolution. In these electrodes RuO₂ particles were co-deposited with Ni onto smooth or rough Ni supports from Ni baths of different compositions, expediently named Watts, Chloride and Thiosulfate baths. Cyclic voltammetry, X-ray, diffraction, EDX and SEM were used for the characterization of these electrodeposits. The electrocatalytic activity of these layers for hydrogen evolution from alkaline solutions was determined by quasi-stationary polarization curves. The experimental results showed that activity increased with RuO₂ in the Ni deposit up to a limiting value. Sulphur was co-deposited from thiosulfate baths, and its presence clashed with the effect of RuO₂. Co-deposition from Watts baths proved to be the most effective. Stability tests demonstrated that Ni + RuO₂, co-deposits were stable under condition of constant as well as intermittent electrolysis. It must be noted that, in the latter case stability turned out to depend on the content of RuO₂ in the layer.

Iwakura et al [15] studied the electrochemical properties of the same Ni/(Ni + RuO₂) active cathodes for hydrogen evolution in the process of chlor-alkali electrolysis. The active cathodes were prepared by simultaneous electrodeposition of Ni and RuO₂ on a Ni substrate from an electrolyser solution (Watts bath) in which RuO₂ particles were suspended by vigorous stirring. The cathodes were electrochemically characterized and the results showed that the enhanced electrocatalytic activity of the cathodes was mainly ascribable to the increase of active sites or the content of RuO₂ particles. The performance of these new developed electrodes was evaluated for the use in a chlor-alkali electrolysis in a laboratory scale. The hydrogen overvoltage of the cathodes was confirmed to be very low and the high durability was observed under the industrial chlor-alkali electrolysis conditions. In addition, these cathodes were found to have excellent tolerance to repeated short-circuiting.

5. Hydrogen production from RES

Water electrolysis is the best way to produce hydrogen without polluting. Nevertheless when fossil fuels are used as the primary source of electricity, the problem of environmental pollution remains unsolved. Therefore, electricity provided from renewable energy sources is essential for the production of emission-free hydrogen, since:

- (i) water on earth is abundant
- (ii) hydrogen is provided from abundant renewable energy sources
- (iii) hydrogen oxidation for the production of electrical energy (in fuel cells) only produces water, which can be recycled

Hydrogen production from solar energy cost is rather high, approximately 100\$/GJ. Except the photovoltaic panels required for this process, water electrolysis units are also expensive. Aeolic energy usage cost for the production of hydrogen is nowadays 15-20\$/GJ, but a reduction is expected in the near future.

5.1. PV-electrolysis

A significant number of solar-hydrogen power systems have been installed all around the world. These systems usually consist of PV panels, water electrolysis units and hydrogen storage systems. A typical PV-electrolysis system was installed during Solar-Wasserstoff-Bayern Hydrogen demonstration project at Neunburg Vorm Wald, Germany, where basic technologies of the hydrogen cycle utilizing electric power generated from solar energy were tested.

Basic system components (PV solar generators, water electrolyzers, catalytic and advanced conventional heating boilers, a catalytic heated absorption type refrigerator, fuel cells for stationary and mobile application, an automated liquid hydrogen filling station and a gaseous hydrogen filling station) were installed at a demonstration facility for a potential energy supply based on hydrogen. In more detail, nine fields of solar generators employing monocrystalline, polycrystalline and amorphous silicon technology with a total rated power of 370 kW_p and efficiencies of 9-13% (crystalline) and 5% (amorphous) accompanied with electric power conditioning were installed. There were also two low-pressure water electrolyzers with nominal power of 111kW_{el} and 100 kW_{el} and a total maximum hydrogen output of 47 Nm³/h and an alkaline pressure-type electrolyser, 100 kW_{el} running at 32 bar. In addition there were two fuel cell plants employing different technologies, alkaline type of 6.5 kW_{el}, phosphoric acid type of 79.3 kW_{el} and 42.2 kW_{th} (hydrogen fuel) or 13.3 kW_{th} (natural gas fuel) output. A fuel cell

plant with proton-exchange membrane operating with air as the oxidizer and rated power output of 10 kW_{el} for mobile application was also tested.

The study of this system showed that the operation of most of DC-DC and DC-AC converters was not immediately satisfactory due to the prototype nature of these units. On the other hand, the two low-pressure advanced-technology electrolyzers (zero gap geometry, absence of asbestos diaphragms activated electrodes, increased current density) exhibited significantly lower specific energy consumption than conventional designs (4.5 kWh/m³ H₂ at rated current). Some problems occurring with the alkaline electrolyser, notably inadequate purity of the gases were successfully confronted. The alkaline pressure-type electrolyser characteristics were: 30 bar pressure, operation with intermittent power sources and quick responses on load changes. The specific electrolyser operated at 105°C, with specific energy consumption of 4.7 kWh/m³ H₂ at rated current, and a current density of 8.4 kA/m², at rated load.

Hydrogen and oxygen generated by the two low-pressure electrolyzers required subsequent compression in order to be stored as pressurized gases. Both product gases were cleaned of impurities by catalytic combustion. In general the storage system performed well. Regarding fuel cell plants, the alkaline fuel cell plant proved to be too sensitive, due to its complexity. Furthermore its usability was compromised by the risk of irreversible damage to the nickel anode. The phosphoric acid fuel cell was considered as an alternative to conventional heat-and-power cogeneration plants, as it incorporated the possibility of heat decoupling. Apart from small periods the phosphoric acid fuel cell plant operated at rated capacity, while output and load change response conformed to expectations. The mobile fuel cell plant (proton exchange membrane) proved to be suitable for providing power to a forklift truck [16].

A small-scale solar hydrogen plant was installed on the Markus Friedli residential house in Switzerland. This power system consisted of a photovoltaic field with total nominal peak power of 7.4 kW_p, a control unit and a DC-DC converter, used to maximize the hydrogen production, and to increase the charging efficiency of the lead acid batteries, a commercial alkaline (KOH) type membrane electrolyser with maximum power of 10 kW, originally designed for continuous hydrogen production from the AC grid and a metal hydride storage tank of 91 L and 235 kg filled with a hydrogen absorbing alloy (multi-substituted derivative of TiMn₂). The metal hydride storage tank was connected to house appliances such as a stove and a laundry machine, and a second metal hydride tank was located in a minibus running on hydrogen. A purification unit, an intermediate storage cylindrically shaped steel vessel of about 450 L capacity, in the pressure range 0.6 – 1.9 bar, and a compressor that compresses hydrogen to 29 bar were also installed. It must be noted that for the specific intermittent operation from PV power of the water electrolysis unit the AC-DC original rectifier was replaced by a DC-DC converter, and the operating power was limited to a lower threshold of 1.4 kW for reasons of safety, and to an upper threshold of 4.6 kW to minimize wear. The solar hydrogen plant although operating with an intermittent power source, it is producing hydrogen without major problems for a period of seven years [16].

A simple solar hydrogen production unit was installed in Stuart Energy renewable test site at Toronto, Canada. The system consisted of a PV flat panel array, which has a nominal peak power of 2.45 kW_p, and provided 12 V_{DC} (nominal) to an electrolyser consisting of a cell bank of six “meteorological” type electrolysis cells. The oxygen produced by the electrolysis unit is vented to the air, while the hydrogen gas filled a gas holder, which supplied a small single stage compressor. The hydrogen was then compressed to 7 bar and stored in a small conventional tank having a capacity of 17 Nm³ at this pressure. A separate PV array was also installed in order to charge batteries that provide power to the control system and the compressor motor. The electrolyser was supplied by The Electrolyser Corporation Ltd. and consisted of 6 SM-4 meteorological cells connected in series. The peak current rating of the cells was 250 A. The cells were two-plate unipolar design with a capacity of 19 L of electrolyte per cell. A water seal was used in order to maintain equal pressures in the two cells. There were no electrical controls on the electrolyser. The project of this goal was to match best the two systems (PV and electrolyser). The experimental results showed that the highest production occurred when the electrolyser was “voltage limited”, the voltage – current curve was to the right of the maximum power point operating curve, due to the improved cell efficiency of the system. Such a system would increase the number of cells and reduce the current density, thereby raising cell efficiency [16].

The Phoebus Juelich demonstration plant could be considered as a typical example of energy storage in the form of hydrogen produced from electrolysis supplied with solar energy. This demonstration plant has been designed to provide autonomous electricity supply to the central library building of the Research Centre Juelich with an installed capacity of 38 kW_{el}. The major components of the plant were: 1) a photovoltaic field of monocrystalline modules with a nominal peak power output of 43 kW_p, 2) a pair of DC-DC converters (5 kW each) for each photovoltaic field, 3) a system of 110 lead batteries with a capacity of 304 kWh, 1380 Ah over 10 hours, 4) a bipolar 21 cell electrolyser with an active cell area of 2500 cm², a current of 750 A, a current density of 3 kA/m², with 30% KOH solution, 80°C operation temperature, an operating pressure of 7 bar and 90% efficiency in design load operation at a power rating of 26 kW and maximum hydrogen production of 6.5 Nm³/h, 5) a storage system for hydrogen and oxygen leaving the electrolyser, consisting of 18 pressure bottles of 1.4 m³ each and a total geometrical volume of 25 m³ for H₂ (3000 Nm³ H₂), containing compressed hydrogen at 120 bar, and 6) an alkaline fuel cell system consisting of KOH gas diffusion electrode fuel cell manufactured by Siemens (BZA 4-2

type) with a power output of 6.5 kW at 48 V and 135 A, with a system efficiency at design load of 63% (LHV of H₂) and 70% at 30% partial load. The main goal of this project was to test the required storage system using hydrogen as the energy carrier. During the project there was an effort of replacing the alkaline fuel cell with two proton exchange membrane fuel cells with nominal power of 2.5 kW. The operation of these two fuel cells was not satisfactory. A high-pressure electrolyser (5 kW at 120 bar) and a two-stage solar thermal metal-hydride compressor (120 bar) were developed as an alternative to mechanical compression. In summary, the goal of an autonomous supply with purely renewable energy in automated operation was achieved, but the weak point of such a system was the fuel cell plant [16].

Hydrogen generated by water electrolysis supplied with solar energy proved to be a practical storage medium during the Schatz Solar Hydrogen Project, which took place at the Humboldt State University Telonicher Marine Laboratory. From the experimental results, it was derived that solar hydrogen could be a reliable and abundant energy source for our society. The system consisted of a PV array, a set of batteries, an electrolyser, three steel conventional storage tanks, a PEM fuel cell and an inverter. In more detail, the PV array consisted of 192 Arco M75 modules, configured into 12 sub-arrays operating at 24 V_{DC}. The nominal power rating for the array was 9.2 kW_p. The battery was included in the system in order to function as a buffer between the PV array and the inverter, since solar power is intermittent. Initially, the system contained a 37 Ah NiCd battery, which was replaced by four Exide GC-4, 6V, 220 Ah batteries. The electrolyser incorporated into the system was a medium pressure, bipolar, alkaline unit of Teledyne Brown Engineering, consisting of a 12 cell electrolysis module, which was able to deliver 20 standard liters per minute of hydrogen gas at a current of 240 A at 240 V_{DC}. This module contained an electrolyte of 25% (wt/wt) potassium hydroxide. The specific electrolysis unit had a nominal power of 6.0 kW and supplied pressurized hydrogen, thus there was no need for supplementary compression. The product hydrogen gas (at a pressure of 7.9 bar) was stored in three conventional tanks with a total capacity of 5.7 m³ and provided approximately 133 kWh at the higher heating value of hydrogen, which operated the load (600 W) for 110 hours assuming a fuel cell efficiency of 50%. The proton exchange membrane fuel cell used low-pressure air (0.2-3.5 bar) as the oxidant and consisted of 48 cells in series, each of which had an active area of 150 cm² for a peak output of 1.5 kW. The membrane and electrode assemblies consisted of DuPont Nafion™ 115 as the membrane and E-TEK solid polymer electrolyte electrodes with 1 mg/cm² platinum loading. Over eight years of operation each system component had the following efficiencies:

- Faraday	96.4%
- Electrolyser	79.2%
- Voltage	84.0%
- Fuel Cell	43.1%
- Overall electrical storage	34.0%

INTA (Instituto Nacional de Tecnica Aeroespacial, Spain) started in 1990 a program in which energy from PV panels supplied an electrolysis unit and the hydrogen gas was stored in metal hydride and pressurized tanks for usage in fuel cells in periods when the natural source is not available. The main components of the pilot plant were:

- A photovoltaic field composed of 144 modules (36 cells each) with total nominal power of 8.5 kW_p
- A 5.2 kW alkaline electrolyser, equipped with an adjustable control unit that allows both automatic and safe operation and different operation modes. To provide optimum direct coupling with the PV array, the control unit was able to select the number of operating cells as a function of the solar radiation
- A storage system consisted of both a metal hydride storage tank and a pressurized tank at 200 bar. The hydrogen produced by the electrolyser was directed initially to an intermediate buffer, from which it could be transferred to one of the two above storage systems. The metal hydride storage system consisted of an intermediate buffer, a hydrogen purification unit, a metal hydride container and a cooling water supply system. The pressurized gas system also used the same intermediate buffer and the purification unit as the metal hydride storage system
- A 10 kW phosphoric acid fuel cell system consisted also of a methanol reformer to permit operation with methanol. The fuel cell stack had 135 bipolar single cells connected in series that supplied a maximum current of 125 A and 85 V. The open circuit voltage used was 130 V. The electrolyte was 98% H₃PO₄ and the electrodes were fed countercurrently with H₂ and air. The unit was air-cooled. The methanol reformer operated at a temperature of approximately 370 °C and the methanol/hydrogen conversion rate amounted to greater than 90%

The study of the experimental results over a long period of time showed that INTA's solar hydrogen production, storage and utilization facility has been in operation successfully, and the main objectives of this project (study of the feasibility of solar hydrogen production, evaluation of different component technologies etc.) were reached [16].

Stand-alone small size photovoltaic hydrogen energy systems are proposed for remote and isolated applications, such as telecommunications, isolated houses on small islands, and remote environmental monitoring

stations. The assessment of the efficiency of hydrogen used as a storage medium of electrical energy generated by PV panels and the design and test of such a small system were the main goals of a project called SAPHYS (Stand-Alone Small Size Photovoltaic HYdrogen Energy System). This project was supported by the European Commission in the context of the Non-Nuclear Energy Programme Joule-II.

The small-size plant consisted of a photovoltaic array backed by battery storage, an electrolyser, a hydrogen storage system and a solid polymer fuel cell. The PV array consisted of 180 single crystalline modules produced by different manufacturers (Arcosolar, Helios and Italsolar), configured into 8 sub-arrays. All sub-arrays were wired for a nominal $36 V_{DC}$ operation and a $60 V_{DC}$ open circuit voltage with a rated power of 5.6 kW at nominal conditions ($1000 W/m^2$; $25^\circ C$). Each array was directly connected to the bus bar. The battery installed had a storage capacity of 51 kW, configured as $34 V_{DC}$, (1500 Ah). The hydrogen storage capacity was designed to be approximately $300 Nm^3$, but actually it was somewhat lower. The maximum pressure in the hydrogen tank was about 20 bar. An electronic load which simulated the demand of two isolated houses was generated.

The electrolyser unit consisted of a Metkon-Alyzer Model 0100 framework assembled with advanced cells designed and manufactured by KFA for solar application, capable of operating up to 20 bar. Apart from high energy efficiency and good dynamic performance in operation with intermittent power sources, a very important requirement for solar-operated water electrolysers is the possibility of operating over a wide range with high current yields and sufficient gas purities. In order to match the actual plant power, the specific electrolyser of 2.5 kW was revamped for 5 kW, the required power according to the results of simulations. This was done in co-operation with Casale Chemicals S.A. The electrolyser stack consisted of 17 cells, connected in a bipolar configuration, with a single-electrode surface of $600 cm^2$. The overall efficiency calculated at $80^\circ C$ and a rated power of 5 kW was approximately 87% (HHV). This high level of efficiency was achieved by using state-of-the-art electrodes and diaphragms.

The fuel cell unit installed, was a Ballard Power Generator System (PGS) 103A (SPFC) electrical generator. It was rated at $3 kW_{DC}$ power, and used air as an oxidant. The electrolyte used in this fuel cell was Nafion 117. It was designed mainly for demonstration and evaluation. The fuel cell main characteristics were: the capability to operate at low temperature (about $72^\circ C$); a short start-up period; no significant stand-by problems; simple installation and operation; quick response to load changes; and high efficiency. It was configured to operate as a stand-alone unit for pressures of hydrogen up to 3.1 bar and pressures of air system up to 4.4 bar.

From this project, it was concluded that there were some technical problems associated with hydrogen production by PV-powered electrolyser, but these problems were not insurmountable. Measurements on this field showed that PV-Hydrogen systems are feasible and reliable enough, and require limited maintenance. According to SAPHYS project results, the electrolyser technology appeared to be mature enough for solar application. The electrochemical effects of operation for periods with an intermittent power source and consequent deterioration of yields with time has to be tested in the future. Although the electrolyser proved to be reliable and operated successfully, there were some problems with the auxiliary equipment required for its operation (water demineralization unit, compressed air treatment unit, and inert gas). Faults in auxiliary operations were the main cause of power system stops. The complexity and high costs of solar hydrogen systems of this type limit their applicability to isolated locations where high costs for electricity and fuel could create conditions favorable for on-site energy production and storage [16].

During a solar hydrogen research project, which took place at Helsinki University of Technology, Vanhanen et al [17] studied the performance of a phosphoric acid fuel cell, which was connected to a small scale autonomous solar hydrogen energy system. In this solar hydrogen system, excess summer photovoltaic electricity was fed to an electrolyser to produce hydrogen, which was stored over the season to be converted back into electricity in a fuel cell in the winter. A battery was also used as a short-term storage. In summary, the main components of the specific system were a $1.3 kW_p$ photovoltaic array, a 14 kWh lead acid battery, a 0.8 kW alkaline pressurized (25 bar) electrolyser, a 0.5 kW phosphoric acid fuel cell, a $200 Nm^3$ steel vessel hydrogen storage and a 0-0.5 kW controllable resistive load. The system components were connected electrically in parallel without any DC-DC converters. All the electric components have been modeled and their interfacing was studied by numerical simulations. The entire system was controlled by switching on and off the components depending on the state of battery described by the voltage and the state of charge (SOC) estimated as a function of the currents charged and discharged. The experimental measurements showed that the system had a voltage efficiency of approximately 60%, but the hydrogen losses due to the open-end stack construction and the electric losses due to the pre-heating decrease the operational efficiency. According to this study an operational efficiency of 48% could be achieved by modifications in the gas supply system and the operation strategy. It must be noted that these modifications were quite difficult to implement.

5.2. Wind-electrolysis

Over the last years, wind power has established itself as an economic grid-connected electricity generating technology, but its use in stand-alone power systems has been limited, because of the lack of suitable and economically viable technologies for energy storage. Hydrogen produced via water electrolysis could be such a storage medium in the near future, especially in isolated remote areas, where the cost of electricity is high. While

a lot of research effort has concentrated on utilizing photovoltaic systems to generate hydrogen through water electrolysis, the possibility of connecting electrolysers to wind turbines has received less attention, since wind turbines deliver more irregular power compared to a solar photovoltaic power module. Nevertheless, a number of demonstration wind electrolysis units have already been installed.

The most typical example of such a unit is the demonstration wind powered hydrogen production plant at ENEA's Casaccia Research Centre in Italy. The wind hydrogen plant consisted of a wind turbine, an electrolyser, a DC-DC converter and a battery storage system. This project was concentrated on the production of hydrogen and not on the large scale storage or utilization, thus the product gases were being released to the atmosphere. The plant is schematically presented in Fig. 5.

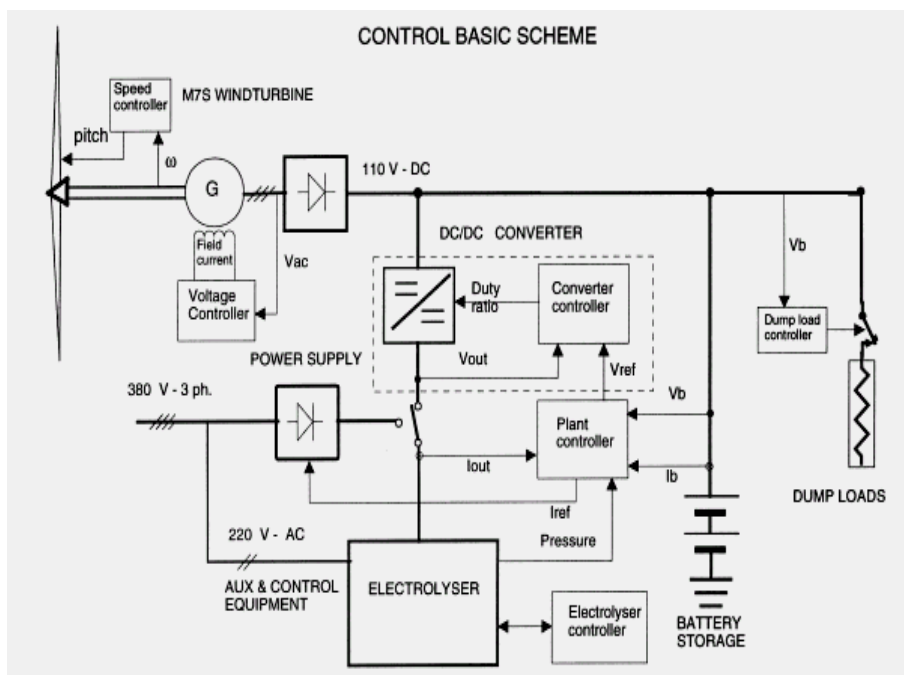


Fig. 5: Basic scheme for demonstration wind-powered hydrogen generation plant, ENEA Casaccia Research Centre (Dutton et al, 2000).

More specifically, two wind turbines were used during the course of this project. The North Wind L-916 by Northern Power Systems of Vermont, USA, which was installed at Rutherford Appleton Laboratory's (RAL) Wind Test Site and the Riva Calzoni M7S wind turbine installed at the ENEA Casaccia Research Centre near Rome. In the end, the wind-hydrogen demonstration plant was designed around the 5.2 kW Riva Calzoni M7S wind turbine at ENEA. This turbine was driving its synchronous generator at variable speed. The resulting variable frequency AC power output was then rectified and supplied a DC bus that fed the electrolyser and the battery storage. The wind regime on the specific site is not particularly favorable (annual mean wind speed of 2.7 m/s), which led to a specification of power rating for the electrolyser lower than the optimal for a more windy site. The results of modeling suggested that for a stand-alone application, the economic optimum depends on the wind regime of each site, the rating of additional energy storage components, and the utilization potential for excess electricity. For the specific hydrogen plant, a preliminary estimate of the most suitable electrolyser rating resulted in the conclusion that a 1kW_e electrolyser would be the best solution for this application.

An electrolyser from von Hoerner System GmbH was selected due to economical reasons. The system had the following main features: a nominal power of 2.25 kW, a nominal voltage of 50 V, and pressurized operation at 20 bar. It also featured fully automatic operation (with the exception of an electric current limitation of less than 20 amps during start-up, to be implemented separately). There was no need for system inertization and cell polarization after shutdown. The electrolysis unit was supposed to hold the internal pressure for some days (weeks) in "stand-by" condition, and immediately re-start the process whenever the current was supplied again, but it failed to do so. The measurement of hydrogen flow rate was derived from pressure and temperature measurements performed on a 50 liter/20 bar bottle placed at the hydrogen gas outlet. A 10 kW alkaline electrolyser HYSOLAR (HE2) by Casale Chemicals was used in laboratory tests carried out by DLR in Stuttgart to explore the effects of intermittent operation.

The von Hoerner System electrolyser was designed to operate in three possible "normal" states: start-up, normal operation and shut-down. The start-up phase corresponded to starting the process with an initial pressure less than the nominal (20 bar). During start-up, the device operated at variable current, with the limitation of the current being lower than 20 amps unless the internal pressure is greater than 3 bar. At higher values of pressure,

low current levels were not recommended, in order to reach the nominal pressure as soon as possible. During start-up phase, no gas was sent to the storage bottle, while some gas was vented to the atmosphere in order to maintain its quality within safety limits. When the nominal pressure was reached, the device was starting supplying hydrogen to the storage bottle. The current was able to vary in a range from (nominally) zero to maximum current (47 A). However, current values lower than 20 amps were not recommended so as to keep a good gas quality. The stand-by phase corresponded to operation with zero input current. In these conditions, the device did not produce any gas flow to the bottle, but should have been able to hold the internal pressure (for some days, or even weeks, according to the manufacturer), while waiting for restoration of the current supply (i.e. as soon as wind power was available).

The step-down DC-DC converter comprised of three 0.8 kW units (each a standard industrial production isolated converter manufactured by Power Control Systems) working in parallel and could supply a voltage linearly variable from 7 to 50 V, which was controlled by a 0-10 V_{DC} signal. The battery storage unit comprised 54 series-connected lead-acid cells with a nominal voltage of 2 V each and a nominal capacity of 330 Ah, for a total nominal capacity of 35.6 kWh. It must be noted that the full extent on this large capacity was probably not completely available, due to battery aging.

During the wind hydrogen plant operation, specific problems were observed. Regarding the electrolysis unit, most of the problems were due to high impurity levels of hydrogen in oxygen during operation at low current levels and high impurity levels of oxygen in hydrogen after some hours of stand-by operation, both conditions lead to alarms and automatic plant shutdown. In addition, the rate of pressure loss during stand-by was very high. To confront these malfunctions, all flanges and pipe connections were checked and tightened, Teflon pipes were substituted with PVC pipes in gas quality measurement lines. In order to prevent pressure drop during stand-by and to prevent pollution of sensor atmosphere, voltage-controlled valves were installed in the gas quality sensors, since original plastic non-return valves were proved to be inadequate. These actions solved most of the problems, with only exception the bad oxygen quality at low currents. The overall cell stack efficiency (relative to LHV of hydrogen) was found to be typically around 40%, with a maximum of 45% around nominal current. These values were very low compared to the values in excess of 60% found for the HYSOLAR Electrolyser 2 at DLR, Stuttgart. On the wind turbine side, it has been proved that a variable wind speed turbine, equipped with a synchronous generator, the decoupling provided by the AC-DC(/AC) interface removed the resonant mode of the direct grid coupling and the power fluctuations due to tower shadow and rotational sampling of wind shear over the turbine rotor. The power smoothing was typically effective on time scales of up to 20 seconds [16, 18].

Another wind-hydrogen system has been installed at the University of Quebec at Trois-Rivieres, in Canada. This system really operated in stand-alone mode [19]. The main results concerning the operation of the PEMFC were described by Agbossou et al [20]. The system consisted of the following components:

- A hybrid energy system provided from Bergey Windpower Co, model Excel. This was composed of a wind turbine that was able to deliver a maximum output power of 10 kW. The wind turbine was installed on a 30 m tower. The production of electricity starts at a minimum wind speed of about 3.4 m/s and reaches the maximum rated power of 10 kW at wind speeds of 13.0 m/s. The wind turbine was coupled to a Golden Genesis GP 64 PV array with a maximum output power of 1 kW. The voltage produced by these sources was regulated and converted to a 48 V on a DC bus. A set of batteries connected in a series/parallel configuration acted as a buffer between the load and the power sources.
- A 5 kW electrolyser manufactured by Stuart Energy Systems, which was able to deliver up to 1 m³/h of hydrogen, subsequently purified, dried and compressed at 7 bar (a).
- The hydrogen was further compressed to 10 bar, and directed to a storage tank with a capacity of 3.8 m³ (water capacity). This represents approximately 125 kWh of stored energy based on HHV of hydrogen (if all the hydrogen could be retrieved from the storage tank down to 0 bar).
- A 5 kW-24 V_{DC} proton exchange membrane fuel cell stack, model MK5-E, manufactured by Ballard Power Systems, with an effective voltage output of 19-35V.
- 48 V deep-discharge batteries for voltage stabilization, of 42.24 kWh storage capacity
- A 12 kW water cooled Dynaload.
- A DC bus controller including the batteries for energy transfer.
- A DC-AC inverter, which was able to deliver a constant 60 Hz 115 V output to the load.

The energy management of this system is autonomously controlled through the state of charge (SOC) of the batteries [19]. Initially, the batteries SOC had been set to start the electrolyser at 99% or above and to stop it at 90% SOC. However, due to insufficient current from the primary sources, the electrolyser was mainly supplied from the batteries, so the SOC levels were later set to 90% and 84% respectively. The performance of the system is presented for a typical day and for long-term operation. During the 'typical day', the maximum available power was 1.5 kW from the wind turbine and 250 W from the PV array. During the long-term operation, the maximum available power was 2.7 kW from the wind turbine and 281 W from the PV. The available power is very low compared to the nominal 11 kW. There was an interval of circa 6 min. between compressor operations of 2 min. duration. This high frequency of startups (8/hour) is generally not recommended by the manufacturers of

compressors. Unfortunately, there is no information regarding the availability and eventual problems related to the compressor.

The current efficiency, i.e. utilization factor of the electrolyser was 85%, the overall efficiency of the electrolyser with the compressor running was 60%, and the overall efficiency of the electrolyser when the compressor was not running was 65% [19]. According to the definition of the relative efficiencies, the only difference between the two would concern the power consumption of the compressor, the control unit and the leakage of hydrogen. It has not been stated, but it may also include the power consumption for the purification and drying of the hydrogen.

According to Agbossou et al [20], for the same system, the electrolyser efficiencies without compressor are 65% at ambient temperature around 23 °C and 71% at 55 °C. There is a decrease of 5% in these efficiencies when hydrogen is compressed. Assessing the experimental results, it was estimated that for an average wind speed at the test site of 6 m/s which translates in an average wind turbine power of approximately 2 kW, the hydrogen production rate was about 0.4 Nm³/h. The hydrogen was then directed from the buffer tank through a compressor to the hydrogen storage system. In addition to the low-pressure storage, Agbossou et al are also testing a high-pressure option at 207 bar using a high-pressure compression manufactured by FuelMaker Corporation. This compressor has a 4.5 Nm³/h flow and uses 1.6 kW input power. The compressed hydrogen will be stored in high pressure tanks of a volume of 110 L each.

The load-leveling electrical system is composed of the 5 kW fuel cell system connected to the DC bus, through a regulated DC-DC converter (24/48 V). The specific fuel cell consists of a total of 35 cells connected in series. Each cell has a surface area of 225 cm². The membrane electrode assembly (MEA) consists mainly of graphite electrodes and a DowTM membrane. The reactant gases (hydrogen and air) are humidified within the stack. The hydrogen is recirculated at the anode and the air is directed to the cathode. The hydrogen pressure at the stack anode inlet and the air pressure at the cathode inlet and outlet are kept at 3 bar. The DC-DC converter has an efficiency that exceeds 95%. The efficiency of the fuel cell system in converting hydrogen into electricity is approximately 45% when delivering a power of 4 kW. Therefore, the overall efficiency of the load-leveling electrical system is about 42%. This system is proposed for providing stabilized electrical power for communication stations.

Another interesting wind-electrolysis system has been studied in the Complex Laboratory of Alternative Energy at the Technical University of Applied Sciences Stralsund, in Germany [21]. The wind turbine is of the Ventis 20-100 type, with a nominal power output of 100 kW. The two-speed asynchronous generator with 20 kW and 100 kW runs at 1000 rpm or 1500 rpm respectively. The alkaline electrolyser by Elwatec GmbH Grimma delivers hydrogen at up to 25 bar and a hydrogen compressor can be used to increase the pressure up to 300 bar. Upon exiting the electrolyser, the hydrogen is purified and dried. The hydrogen storage tank has a geometrical volume of 8 m³ and contains 200 Nm³ H₂ at 25 bar. It is filled in 50 hours at nominal electrolyser capacity (4 Nm³/h H₂). Independently of the operating point, approximately 0.3 m³/h of hydrogen flow through a bypass to the gas quality sensor.

For steady state operation, the nominal current is set to 120 A. Initially, when the system is at ambient temperature and pressure, the control system applies a current limitation until the pressure in the system attains 13 bar. At this point, the hydrogen delivery can start. Upon reaching the 13 bar, the initial current limitation is switched off and the actual current is only limited by the temperature. It takes circa 45 minutes for the electrolyser to achieve the operating temperature of 75°C and therefore the nominal current of 120 A. The reported efficiency of the electrolyser, approximately 56% with respect to LHV is very low [21].

The electrolyser has also been tested under a controlled operating regime, probably through a simulator of variable power input. By looking attentively at the results presented in the papers by the Fachhochschule Stralsund [21, 22], there has been no direct connection between the wind turbine and the electrolyser, although this seems to be the aim of the study. Unfortunately, the results are incomplete and not well presented.

5.3. Geothermal energy-electrolysis

Geothermal energy can be used as a thermal energy source to supply heat for high temperature electrolysis and thereby substitute a part of the electricity needed. Jonsson et al [23] conducted a feasibility study exploring the use of geothermal energy in hydrogen production. Geothermal energy could supply energy to the German high temperature model HOT ELLY, which operates at 800-1000°C. Geothermal fluid was used to heat fresh water up to 200 °C, generating steam. The steam is further heated to 900 °C by utilizing heat produced within the electrolysis unit. The electrical power of this process was reduced from 4.6 kWh per normalized cubic meter of hydrogen (kWh/Nm³ H₂) for conventional process to 3.2 kWh/Nm³ H₂ for the HOT ELLY process implying electrical energy production of 29.5%. The geothermal energy needed in the process of hydrogen production through high temperature electrolysis was estimated to be approximately 0.5kWh/Nm³ H₂. The price of geothermal energy was approximately 8-10% of electrical energy. This way a substantial reduction of production cost of hydrogen could be achieved. According to this study, using high temperature electrolysis supplied with geothermal steam at 200°C, would result in a reduction of the production cost by approximately 19%.

5.4. Photoelectrolysis

Hydrogen can also be produced by photoelectrolysis of water, which is another concept of water decomposition using solar energy as the driving force. Fujishima and Honda [24] were the first to report the generation of hydrogen and oxygen in a photoelectrochemical cell using a TiO₂ electrode illuminated with near ultraviolet light. Many other researchers have also studied this phenomenon since then.

The conversion of solar energy into useful forms of energy can be divided into thermal and photonic processes. In solar photonic processes, the solar photons are absorbed directly into an absorber, without complete conversion to heat. The absorber can either convert part of the photon energy to electricity (as in a photovoltaic cell), or store part of it as chemical energy in an endergonic chemical reaction (as in photosynthesis or the decomposition of water to hydrogen and oxygen). The latter process is the solar photoproduction, or photoelectrolysis of water. Most systems can be classified under one of the following categories: i) Photochemical Systems (sunlight is absorbed by isolated molecules in a solution), ii) Semiconductor Systems (sunlight is absorbed by a semiconductor, either as a suspended particle in a liquid or as a macroscopic unit in a PV cell or an electrochemical cell), iii) Photobiological Systems (sunlight is absorbed by a chloroplast or algae in a configuration coupled to a hydrogen-generating enzyme) and iv) Hybrid Systems (combination of the previous three).

In photochemical systems, since pure water does not absorb solar radiation, except in the infrared, where photon energies are too low to simulate photochemical action, any photochemical process to drive the decomposition of water must involve a sensitizer, which is a molecule or semiconductor that is able to absorb sunlight and stimulate photochemical reactions which lead to the generation of hydrogen and oxygen gases. The only photochemical system in which a complete water-splitting reaction has been recorded is the work of Katakis et al [25, 26], where tris-[1-(4-methoxyphenyl)-2-phenyl-1,2-ethyleno-dithiolenic-S,S'] tungsten was used as a sensitizer and MV²⁺ as an electron relay.

In photoelectrochemical cells, a light-absorbing semiconductor is used as either the anode or the cathode (or both) in an electrochemical cell. In the cell of Fujishima and Honda [24], a single crystal of titanium dioxide was used as the photoanode and electrons released from the anode were directed through a wire to a Pt electrode, at which hydrogen evolved. The most efficient cells (~13%) are reported to be those involving a p-InP photocathode, onto which tiny pieces of Pt have been deposited.

In photobiological systems, photosynthetic organisms carry out an energy-storing fuel production reaction, which stores solar energy. Normally, photosynthetic systems do not evolve hydrogen, but rather reduce CO₂ to carbohydrates. Nevertheless, it is possible to modify the conditions if the reducing end of the photosynthetic process is coupled to a hydrogen-evolving enzyme, such as hydrogenase or nitrogenase. The most effective photobiological systems for hydrogen/oxygen generation are those based on microalgae, such as green algae and cyanobacteria. Efficiencies under ideal conditions approach approximately 10%, but a big difficulty arises from the fact that the algal systems saturate at solar irradiances above 0.03 suns [27].

6. Water electrolysis modeling and simulation

In recent years, an increasing number of mathematical models describing water electrolysis process have been developed. Some of these models have been incorporated into simulation programs, which can be used for the optimization, dimensioning etc of hydrogen energy systems.

6.1. Modeling of water electrolysis for hydrogen production

The work of Ulleberg [28] is the most typical example of water electrolysis modeling. The electrode kinetics of an electrolyser cell can be mathematically modeled using empirical current-voltage (I-U) relationships. Many researchers have proposed empirical I-U models for electrolyser, but the basic form of the I-U curve that will be presented next, is based on the work of Griesshaber and Sick [29] and is given by the following equation, provided the temperature is known:

$$U = U_{rev} + \frac{r}{A} I + s \log \left(\frac{t}{A} I + 1 \right) \quad (10)$$

where:

U	operation cell voltage, V
U_{rev}	reversible cell voltage, V
r	ohmic resistance of electrolyte, Ω
s, t	coefficients for overvoltage on electrodes
A	area of electrode, m ²
I	current through cell, A

To properly model the temperature dependence of the overvoltages, Eq. (10) is modified into a more detailed I-U model which takes into account the temperature dependence of the ohmic resistance r and the overvoltage coefficients s and t . The following equation, which describes the temperature dependent model was proposed by Ulleberg [28]:

$$U = U_{rev} + \frac{r_1 + r_2 T}{A} I + (s_1 + s_2 T + s_3 T^2) \log \left(\frac{t_1 + t_2 / T + t_3 / T^2}{A} I + 1 \right) \quad (11)$$

where:

- r_i parameters for ohmic resistance of electrolyte, ($i = 1 \dots 2$)
- s_i, t_i parameters for overvoltage on electrodes, ($i = 1 \dots 3$)
- A area of electrode, m^2
- T temperature of electrolyser, $^{\circ}C$

The empirical parameters mentioned above can be numerically calculated using non-linear regression techniques.

The temperature of the electrolyte of the electrolyser, which affects the I-U curve and the Faraday efficiency can be estimated using simple or more complex thermal models. Ulleberg [28] proposed a method in which T is calculated from a lumped thermal capacitance model. In general, the thermal energy generated in an electrolyser due to inefficiencies in the cells is partly stored in the surrounding mass and partly transferred to the ambient, either by natural processes or by auxiliary cooling.

The overall thermal energy balance on the electrolyser could be expressed by the linear, first-order, non-homogeneous differential equation (12):

$$\frac{dT}{dt} + aT - b = 0 \quad (12)$$

which has the following solution:

$$T(t) = \left(T_{ini} - \frac{b}{a} \right) \exp(-at) + \frac{b}{a} \quad (13)$$

where:

- T_{ini} temperature of cell at initial conditions, $^{\circ}C$

The temperature T of the electrolyte is proposed to be calculated using methods of successive substitution [28].

6.2. Simulation tools for hydrogen production from RES

The mathematical models of water electrolysis combined with models describing the behavior of other hydrogen energy systems components have been incorporated into software packages (TRNSYS, MATLAB Simulink, etc) which can simulate a system where hydrogen is produced from renewable energy sources. TRNSYS is a transient simulation program, which is able to perform parametric studies in order to find possible system configurations for different climates and loads. An extra TRNSYS library of hydrogen energy models called HYDROGEMS has also been developed at the Institute for Energy Technology (IFE, Norway). This library includes among others component subroutines for alkaline water electrolysis, high-pressure hydrogen gas storage, proton exchange membrane fuel cells (PEMFC), and alkaline fuel cells (AFC). The models were tested and verified against various existing hydrogen energy demonstration plants. According to its developers, this library with a few modifications can be integrated into other simulation programs such as MATLAB Simulink [30].

Ulleberg and Morner [31] have used these tools in order to simulate a solar – hydrogen system composed of a PV array, an electrolyser, a hydrogen storage, a fuel cell, a catalytic burner, a lead-acid battery, DC/DC converters, DC/AC inverters, a solar collector and a water storage tank. In this study simulations were performed for conventional low energy dwellings located in northern latitudes. Different system configurations and operation schemes were tested. The simulation results showed that the size of the solar-hydrogen system for a conventional low energy house sited in Trondheim, Norway ($63^{\circ}N$) should be quite large. This could be attributed to the high energy demands assumed and to the low insolation available. Simulation runs of the same dwelling located in lower latitudes, in climates with higher insolation, and/or with lower energy demands (e.g. future dwellings), showed that the size of the solar-hydrogen system could be significantly reduced. According to this study, minimizing the thermal and electrical loads before designing a solar-hydrogen system for energy self-sufficient buildings is very important.

Ulleberg and Pryor [32] tried to optimize the integration of hydrogen systems powered with renewable energy sources in diesel engine mini-grids. They used TRNSYS in order to simulate the integration of a wind energy conversion system and a hydrogen system consisting of an electrolyser, a hydrogen storage tank, and a fuel cell into an existing diesel engine system. The existing diesel engine mini-grid system with nominal power of 1.5 MWp and 4 GWh/year is located on an island approximately 40 km off the coast of Western Australia. The site has high wind speeds and relatively high fuel costs. At first, the integration of a wind turbine was simulated (Diesel-Wind system) and then the hydrogen energy system was studied (Diesel-Wind-Hydrogen). The simulation results showed that replacing a diesel generator with a hydrogen fuel cell system can lead to significant fuel savings combined with a very significant reduction in dumped energy compared to the diesel system only, or the alternative of the diesel-wind system. It was also indicated that there is a technical optimal diesel-wind-hydrogen system design that minimizes the diesel fuel consumption and on/off switching the gen sets.

A similar computer simulation study related to a planned wind-hydrogen demonstration project on an island off the west coast of Norway has been performed by Glockner et al [33]. The purpose of this study was to present solutions on design and control strategy of a wind-hydrogen system for the building application. An economical model was also developed and linked to the output of the simulation study. Two solutions were proposed: one where the wind energy conversion system was dimensioned to exploit the extremely good conditions on the island and export the surplus energy to the local grid, and another where the wind-hydrogen system was operated in a stand-alone mode. The hydrogen system simulated consisted of an advanced high-pressure electrolyser from GHW with a nominal power rating of 225 kW at normal operation conditions of 30 bar and 80°C, a pressurized air-H₂ proton exchange membrane fuel cell operating at a temperature of 80 °C and a feed-gas pressure of 3 bar, a two-stage compressor, a hydrogen storage and a hydrogen burner with an energy efficiency of 95%. According to the results of the simulations the size of the hydrogen storage is dependent on the size of the wind turbine and the operation mode of the system. For stand-alone operation the storage unit contributes significantly to the investment costs. A preliminary economic analysis conducted in this study showed that the wind-hydrogen system has an investment cost four-times higher than a respective wind-diesel system. Using a heat buffer and increasing the maximum power of the wind turbine could reduce the size of the hydrogen storage. In periods with excess wind power the wind energy conversion system could supply an electric boiler connected to a heat buffer. In this case the hydrogen power may not be needed at all or at least its size could be significantly reduced.

El-Shatter et al [34] used MATLAB SIMULINK software in order to simulate a hybrid PV-fuel cell system. The system was composed of a polycrystalline PV array Solarex module type MSX-56, a Unipolar Stuart cell electrolyser, a hydrogen storage tank, a proton exchange membrane fuel cell stack, and the 72 V_{DC}, 31A load. Fuzzy regression model (FRM) was applied for maximum power point tracking to extract maximum available solar power from PV arrays under variable insolation conditions.

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