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Renewable Hydrogen Production: Performance of an Alkaline Water Electrolyzer Working under Emulated Wind Conditions

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This work has been performed within a Research and Development contract on Hydrogen Energy granted by Acciona Biocombustibles S. A., a branch of Acciona Energía, to the Public University of Navarra and deals with the production of sustainable hydrogen from renewable primary energy sources. In this work, the results obtained in several experiments carried out with a commercial alkaline water electrolyzer of 5 kW working under the dynamic conditions typical of wind energy systems are presented. Actual wind speed data from a wind farm were considered and allowed us to establish the power profile that would give a wind turbine of a rated power equivalent to that of the electrolyzer under the considered wind conditions. This power profile was supplied to the electrolyzer by means of a power supply (wind emulator) designed and built by our group. The evolution of the stack voltage, efficiency, and temperature, as well as the purity of the produced hydrogen and oxygen, was monitored. The results showed that the electrolyzer behavior was reliable with high efficiencies, satisfactory gas purities, and fast dynamic response to the varying conditions imposed.

1. Introduction

Hydrogen exhibits unique characteristics that may allow it to lead in conjunction with electricity the future energetic model of our society by the way of the so-called *hydrogen economy*.¹ In fact, when obtained from water or biomass, it can be a fully renewable fuel; moreover, it can be stored in a variety of forms: gaseous, liquid, as metal hydrides, or adsorbed at high pressure on suitable porous solids. It can be easily transported and efficiently produced from and transformed into electricity, and its use as a fuel does not produce significant negative effects on the environment.^{2–4}

Nevertheless, some viewpoints are not so optimistic.^{5–7} One of the outstanding problems is the fact that the current world hydrogen production, which amounts to about 45 millions of metric tons per year corresponding to around 2% of primary energy demand, is not intended for energetic purposes.⁸ Its main end uses are methanol and ammonia synthesis as well as in oil refining processes. This means that if the hydrogen economy

were to take off, the resulting massive hydrogen demand would require an increase by orders of magnitude in the present world production capacity which is an impressive challenge, even if the hydrogen were to be set aside just for the transport sector.⁹ In addition, 96% of the current hydrogen production is based on fossil fuels: 48% is obtained from natural gas steam reforming, 30% from naphtha reforming, and 18% from coal gasification.⁸ This is therefore nonrenewable hydrogen whose production gives rise to greenhouse gas (CO₂) emissions. For example, the total CO₂ released when using natural gas amounts to about 10 kg/kg of produced hydrogen, and although separation and capture of the coproduced CO₂ with future technologies could reduce this figure to only 1 kg CO₂, there are serious doubts as to the feasibility of the long-term storage of the enormous CO₂ quantities that would be produced.⁹ The cost of avoiding CO₂ emissions with the current technology including compression transport and storage is estimated at around US \$57/ton of CO₂,⁸ that is, US \$570/ton of hydrogen produced from natural gas. Nevertheless, it is expected that fossil fuels still play a very important role in the short- and medium-term; however, a sustainable hydrogen economy cannot depend on those energy sources for hydrogen production.

There are several routes to renewable hydrogen production: ¹⁰ biomass processing, biological and solar thermal water splitting, and water electrolysis conducted with renewable primary energy sources. Promising examples of the first case are bioethanol steam reforming and biomass gasification.¹¹ As far as water electrolysis is concerned, it has the advantage that, since electricity is required, it can be implemented with well-

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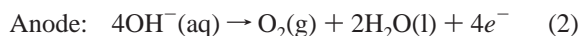
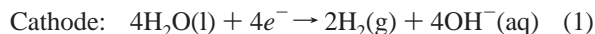
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established renewables such as hydro, wind, and solar photovoltaic power.^{12,13}

Water electrolysis using alkaline electrolytes, most frequently 25–35 wt % KOH in water, is a mature technology.^{14–16} When a suitable electric potential is applied to the electrodes (steel, nickel, nickel-coated steel, NiOOH, or mixed oxides containing cobalt) of an alkaline water electrolyzer, the following reactions take place:



where l, g, and aq stand for liquid, gas, and in aqueous solution, respectively. Electrons flow through an external circuit from the anode to the cathode where they generate hydrogen and hydroxide ions from water. As the operating temperature increases, the overvoltages decrease due to faster electrode kinetics and reduced ohmic resistances, but the increased risk of corrosion restricts the electrolysis temperature to values below 80–90 °C. The most important modern alkaline electrolyzers incorporate a stack of bipolar electrodes connected in series between a feeder anode on one end and a feeder cathode on the other. This is the so-called filter-press design which allows the construction of very compact electrolyzers suitable for working at relatively high pressures (up to about 3 MPa). The electrodes (frequently of circular shape) are placed on the surface of a diaphragm or membrane which becomes impregnated with the electrolyte. This configuration allows reducing greatly the distance between the electrodes and then the ohmic losses in the electrolyte. The membrane itself is very thin (less than 0.5 mm) leading to a low electrical resistance, on the order of $2 \times 10^{-5} \Omega/\text{m}^2$. The early asbestos diaphragms have been replaced by new composite materials based, for example, on polysulfones or oxide-ceramics containing NiO or alkaline-earth metals titanates.¹⁴

In the last years, the proton exchange membrane (PEM) water electrolyzers have been developed, and now, they are commercially available. In this case, the alkaline and corrosive electrolyte is replaced by a proton-conducting polymeric membrane, such as Nafion, sandwiched between the bipolar electrodes. Pure water breaks down in the anode into oxygen and protons which are conducted in hydrated form across the membrane to the cathode where they are reduced yielding hydrogen. The main advantages of this technology are that very high current densities (up to about 10 000 A/m²) and high-pressure operation (20 MPa) without mechanical compression can be achieved.^{16–18} However, investment costs are still high

and today's largest units reach a maximum production of 7 900 kg H₂/y with a power requirement of 63 kW.¹⁹

Recent advances in the field of water electrolysis also include the high-temperature electrolysis of water vapor. This is a very interesting concept since as temperature increases a higher proportion of the total energy required to electrolyze water can be supplied by thermal energy instead of electricity due to the concomitant decrease of ΔG° ; moreover, electrode overvoltages also decrease with increasing temperatures. In this case, solid oxide electrolytes are used, as ZrO₂ doped with Y₂O₃, which is an excellent oxygen ion (O²⁻) conductor at temperatures above 800 °C.^{14–16} Water vapor is decomposed at the cathode (nickel cermet) yielding hydrogen and O²⁻ anions that are conducted through the solid oxide membrane to the anode (nickel- or manganese-based perovskites) where they combine forming oxygen. Although this technology offers significant potential to improve water electrolysis efficiency, it is currently at a very early stage of development. A key issue is to overcome the difficulties of achieving high current densities due to insufficient electrode–electrolyte interfacial area, high electrical contact resistances, and internal resistances due to high solid-electrolyte thickness.

A recent analysis of electrolytic hydrogen production has showed that major current-day commercial electrolyzers use alkaline electrolysis with the bipolar electrodes filter-press technology.¹⁹ Energy efficiencies referred to the higher heating value of hydrogen (39.3 (kW h)/kg H₂) including energy consumed by the electrolysis process, and all auxiliary components vary from 56% for Proton's PEM electrolyzers to 73% for Stuart's (now Hydrogenics) and Norsk Hydro's alkaline units. Hydrogen purities are in the 99.8–99.9998% range, and design powers for maximum hydrogen production rates (320 000–380 000 kg/y) vary from only 2 up to 2300 kW.¹⁹ It has been estimated that in a future hydrogen economy, electrolyzers 10–100 times the size of today's largest units will be necessary to effectively utilize the low-cost electricity generated from wind and nuclear power.

The fact that hydrogen can be stored makes it a good complement of renewable energy sources as hydropower, photovoltaic, and wind energy since a storage system is required to smooth out the intermittent power input from them and overcome daily and seasonal discrepancies between energy availability and demand. Surplus energy can be stored in the form of hydrogen produced by water electrolysis. When the renewable energy production is not enough to meet the load demand, the stored hydrogen can be used (e.g., in a fuel cell) to produce electricity; of course, as hydrogen can be transported (e.g., through pipelines), other uses are also possible such as transportation with hydrogen-fueled vehicles.^{20,21} In the last years, great research efforts have been devoted to solar-hydrogen, that is, using solar photovoltaics (PV) to produce hydrogen via water electrolysis. Various solar-hydrogen systems at the level of demonstration plants have been described in the literature including water electrolyzers of several sizes ranging from only 1 kW (PEM)²² to 5, 10, and up to 26 kW (alkaline).^{23–25} A number of simulation studies have been also

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performed in order to assess the technical and economical feasibility of solar-hydrogen production mainly regarding stand-alone applications, that is, power systems that supply electricity without being connected to a main electric grid.^{20,26–28} One of the main advantages of solar-hydrogen systems is that solar panels generate DC power that can be easily matched with the power requirements of the electrolyzers at efficiencies higher than 93%.²¹ Moreover, PV technology is mature and well-developed and does not need frequent maintenance. However, the PV panels are expensive and require very large surfaces. Moreover, the efficiency is very low; therefore, the cost of the PV electricity is quite high. In spite of the very important development experienced by PV systems from the 1980s, the price of the installed modules can be still as high as US \$9–15/W, which seriously limits the possibility of large scale hydrogen production from PV in the future.^{21,29}

On the other hand, wind power is the fastest growing renewable energy sector with more than 55 000 MW installed worldwide. Wind electricity may be produced at very low costs (e.g., US \$0.04/(kW h)) in regions with good wind resources, and the capacity of the commercial wind turbines has grown to about 2500 kW with capital costs less than US \$1,000/kW.²¹ Therefore, due to the comparatively low cost of wind technology, wind-powered water electrolysis has a great potential to become the first economically viable technology to produce large amounts of renewable hydrogen in the near future. Nevertheless, contrary to the case of PV, there are very few examples in the literature describing the operation of wind–hydrogen systems.³⁰ At present, most work in this field has been dedicated to the modeling and simulation of these systems,^{31–33} as well as to the development of suitable controllers and electronic converters in order to match the wind power output to the electrolyzer power requirements,^{34,35} which is a crucial

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Figure 1. Photograph of the installed HySTAT alkaline water electrolyzer (courtesy of Hydrogenics) showing the cell stack (bottom) and gas separators (center).

issue in this case due to the characteristics of the varying power generated by wind turbines.

One of the inherent drawbacks of wind power is its highly intermittent nature, which is the main obstacle to achieving a greater penetration of this renewable resource into the electricity market. This is also the cause of the low capacity factor of wind-powered systems, usually below 40%. Moreover, any scenario contemplating direct coupling of a water electrolyzer to a wind turbine implies also intermittent operation of the electrolyzer.²¹ However, although water electrolysis is a mature technology, it should be noted that the electrolyzers currently available in the market are designed for stationary grid-connected operation whereas there is a lack of technical data and operational experience regarding the use of these units for long-term intermittent operation. This fact, in conjunction with the very high investment, costs associated with electrolysis plants are the main problems that are delaying the development of wind–hydrogen systems.^{21,30}

In this context, this work aims at contributing to providing information about the operation of an alkaline 5 kW commercial water electrolyzer under emulated intermittent conditions generated from actual wind speed data. Emphasis has been put on the electrolyzer efficiency, evolution of the cells stack temperature, and the purity of the produced hydrogen and oxygen.

2. System Description

The commercial alkaline water electrolyzer is of bipolar filter-press type (model H2 IGen 300/1/25 formerly from Vandenborre and Stuart Energy, now HySTAT from Hydrogenics).³⁶ The electrolyzer is shown in Figure 1. This unit has a cell stack

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Figure 2. Photograph of the commercial electric power supply (left) and the wind emulator (center).

consisting of 22 circular electrolysis cells (300 cm² of surface area) connected in series. Each cell contains two bipolar electrodes separated by a proprietary advanced alkaline inorganic ion-exchange type membrane (Vandenborre IMET) which prevents the mixing of the hydrogen produced in the cathode and the oxygen produced in the anode. Deionized water (1–2 μ S/cm) required for the electrolysis process is obtained from the feedwater supply by means of an integrated ion-exchange purifying system. The electrolyte is 30 wt % KOH in water, and no pump is required for its circulation from the gas separators to the cell stack. The electrolyzer was designed to yield a rated hydrogen production of 1 Nm³/h at an operating pressure of up to 2.5 MPa, temperature of 65 °C, and stack voltage and current of 43 VDC and 120 A, respectively. The overall power consumption is 4.90 (kW h)/(Nm³ H₂) of which 4.20 (kW h)/(Nm³ H₂) are required by the electrolysis.

An electric power supply (EPS) is also provided together with the electrolyzer. This power unit operates connected to the main electric grid and essentially consists of a transformer and a three-phase half controlled rectifier bridge with thyristors and diodes which converts the AC current from the grid into a DC current. This current is supplied to the electrolyzer in the form of a steady state average current ranging from 35 to 100% of the rated current (120 A). It also incorporates the safety system that prevents the electrolyzer from operating under hazardous conditions. It should be noted that once the electrolyzer is switched on, a minimum current (in our case 40 A) should be fed to the cell stack in order to protect the electrodes against corrosion as well as avoiding dangerous mixing of the generated hydrogen and oxygen by diffusion through the membranes. However, the commercial power supply is not intended to run at variable operating conditions such as those that appear in wind energy systems. In order to emulate these conditions, a new power supply based on IGBTs (Insulated Gate Bipolar Transistors) which is driven by means of a microcontroller, has been designed and built by our group.^{37,38} This unit is an electronic converter capable of supplying the electrolyzer with

any power shape previously programmed in the microcontroller. Therefore, it is in fact a wind energy system emulator that can emulate the variable operating conditions of these systems such as transient power steps, wind gusts, etc. The commercial EPS and the wind emulator are shown in Figure 2.

In order to fulfill the safety standards and obtain the license from the local authorities, the electrolyzer was installed in a dedicated separate gas-proof room. Electrical components placed in this room such as illumination, hydrogen gas sensors, and fans for forced ventilation were explosion proof. At the current state of our study, we are only concerned with the intermittent operation of the electrolyzer, so no gas storage is carried out and the produced hydrogen and oxygen are safely vented to the atmosphere through separate pipes at a suitable height and separation according to the safety requirements and manufacturer recommendations.

3. Wind Emulator Programming and Experimental Procedures

In this work, actual wind speed data from a wind farm (Sierra del Perdón, Navarra, in northern Spain) located at an altitude of about 1000 m have been considered. Speed data consisted of values measured at 10 min intervals and 20 m above the ground level. A statistical analysis of the available data has evidenced that the Rayleigh's distribution satisfactorily describes the probability density function of the wind speed for the wind farm under consideration:³⁹

$$f(v) = \frac{2v}{c^2} \exp\left[-\left(\frac{v}{c}\right)^2\right] \quad (3)$$

where $f(v)$ is the probability of observing wind speed v (m/s) and c is the so-called scale parameter, in our case 9.85 m/s.

(36) <http://www.hydrogenics.com> (accessed Sept 2006).

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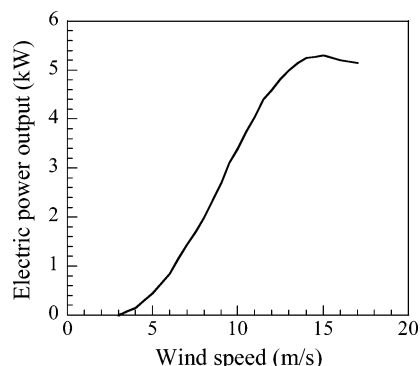


Figure 3. Power curve of the Westwind MUERI wind turbine.

As our main objective is to study the performance of the electrolyzer under dynamic conditions such as those appearing in wind systems, we have powered the electrolyzer with the wind emulator previously programmed according to the wind conditions of interest. The procedure employed has been as follows:

(1) Once the daily and monthly variability of the wind speed has been analyzed, the period of time to be emulated is selected according to criteria such as the frequency of the speed changes, intensity of these changes, inclusion of prolonged periods with high or low wind speed, number of electrolyzer shutdowns due to excessively high or low wind speeds, etc.

(2) The electric power to be supplied to the electrolyzer is established as a function of the wind speed data taking into account the power curve of the emulated wind turbine.

(3) The electrolysis current is calculated from the electric power using the voltage–current (or polarization) curves of the electrolyzer.

(4) As a result of the preceding steps, a relationship between the electric current and time, corresponding to the period of time and wind turbine previously selected, is available and used to program the microcontroller of the wind emulator, which is then ready to supply the water electrolyzer with the dynamic current–time profile.

As far as the size of the wind turbine is concerned, a small unit (Westwind MUERI) with the same rated power than the one of the electrolyzer (5 kW) was selected.⁴⁰ This implies that the electrolyzer will operate with the same capacity factor as the wind turbine.²¹ The wind turbine has a permanent magnet synchronous machine, a rotor diameter of 5.1 m, and a rotor rotational speed in the 120–750 rpm range. According to the manufacturer specifications, the cut-in speed is 3 m/s, the nominal speed is 14 m/s, and the cut-out speed is 16 m/s. The power curve of the wind turbine is shown in Figure 3.

The electrochemical behavior of the electrolyzer has been characterized from a series of experimental voltage–current curves obtained at 0.5 MPa and temperatures ranging from 35 to 65 °C in the mode of decreasing current at 5 A intervals;³⁷ these are known also as polarization curves. The decreasing current mode was chosen simply for experimental convenience. Very similar results were obtained in several runs performed in the increasing current mode. The average cells stack voltage and current were recorded automatically during the several runs whereas the stack temperature remained constant within ± 0.3 °C at the pre-established value. Taking into account that for a stack of electrolysis cells connected in series the electrical power is given by the product of the current and the total cells stack voltage, the polarization curves can be also depicted relating the electric current and the electric power of the stack. This is shown in Figure 4 for the electrolyzer considered in this work. It can be seen that as the electrolysis current increases the required electric power increases almost proportionally to the current. In the range of the operating temperatures, the effect of the temperature on the polarization curves is not significant. Nevertheless, it can be appreciated that the electric power required

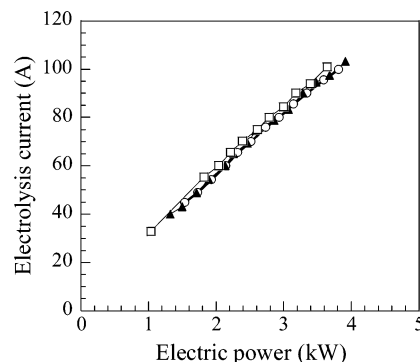


Figure 4. Polarization curves of the HySTAT water electrolyzer from Hydrogenics in terms of the electric power input at 0.5 MPa and 35 (○), 45 (▲), and 55 °C (□).

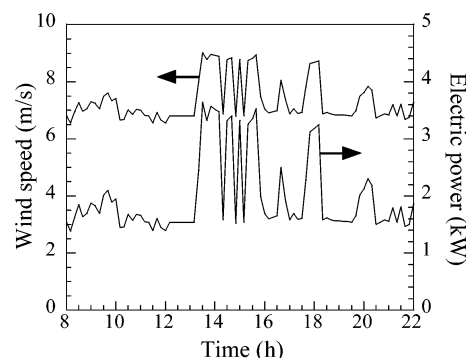


Figure 5. Evolution with time of the wind speed and electric power output expected for a Westwind MUERI wind turbine (5 kW nominal) during the period selected to emulate the wind–hydrogen system.

to sustain a given electrolysis current increases as the cell stack temperature decreases due to the higher internal (electrolyte and membranes) electric resistances.⁴¹ Due to the small variation of the current with the stack temperature, the polarization curve at 45 °C was chosen as being representative of the electrolyzer behavior.

4. Results

In order to show an example of the electrolyzer performance under transient conditions, a period of 14 h of a typical day with good wind conditions in the Sierra del Perdón's wind farm has been selected. The evolution with time of the wind speed during this period and the electric power output expected from a Westwind MUERI wind turbine according to its power curve (see Figure 3) are shown in Figure 5. As it can be seen, the wind speed did not decrease from about 6.5 m/s whereas several speed peaks up to 8 and 9 m/s were suddenly achieved after a stable initial period of 5 h at about 7 m/s. This wind speed profile would allow the wind turbine to give an electric output power to the electrolyzer, which matches the speed profile, ranging between 1.5 and 3.5 kW. Taking into account the polarization curve of the electrolyzer, the electric power generated by the wind turbine directly coupled to the electrolyzer gives rise to the current–time profile depicted in Figure 6 in the cells stack. It can be seen that the shape of this profile coincides with that of the electric power input. The current starts at around 45 A; then, several current peaks of up to 100 A will be experienced by the electrolyzer. The microcontroller of our wind emulator was programmed with this current–time profile in order to power the electrolyzer under conditions emulating the selected

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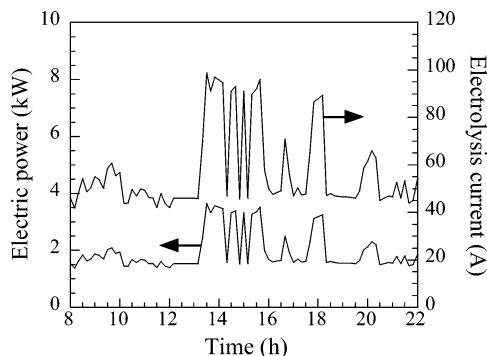


Figure 6. Evolution with time of the electrolysis current in a HySTAT water electrolyzer (Hydrogenics) according to the emulated electric power input from a Westwind MUERI wind turbine.

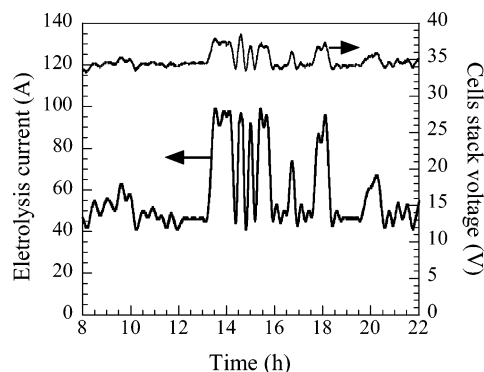


Figure 7. Evolution of the total voltage established in the electrolyzer cell stack as a result of the passage of the electrolysis current.

wind-energy system. The following describes the response of the electrolyzer to the imposed intermittent working conditions.

The total voltage established between the feeder electrodes of the cell stack as a result of the flowing of the electric current supplied by the wind emulator is shown in Figure 7. The stack voltage remains relatively stable at about 34 V, that is, 1.54 V per electrolysis cell; however, when the electric current changes, the response of the stack voltage is very fast matching of the current–time profile. Interestingly, the amplitude of the voltage variations is remarkably attenuated compared to that of the current. For example, between 14 and 15 h, the wind speed rapidly increases giving rise to a change of the electrolysis current from 45 to about 100 A; however, the stack voltage only passes from 34 to around 39 V.

Thermal management is a very important issue of the operation of water electrolyzers because the operating temperature should be maintained within suitable limits to ensure safe and efficient operation as well as to preserve the electrodes and membranes from corrosion and other problems that shorten their useful life. The evolution with time of the cell stack temperature under the emulated wind conditions coupled with the electric power supplied to the electrolyzer are depicted in Figure 8. It can be seen that the stack temperature does not remain stable and changes according to the electric power input. The maximum temperature variation during the experiment hardly surpassed 10 °C and was far from the higher allowable limit of 65 °C for the electrolyzer under consideration. The high inertia characteristic of the heat transport processes is apparent in Figure 8 where the temperature changes are slow compared to that of the supplied electric power.

Efficiency in the conversion of the electric power input into chemical energy in the form of hydrogen produced via water electrolysis is of primary importance to evaluate the economic

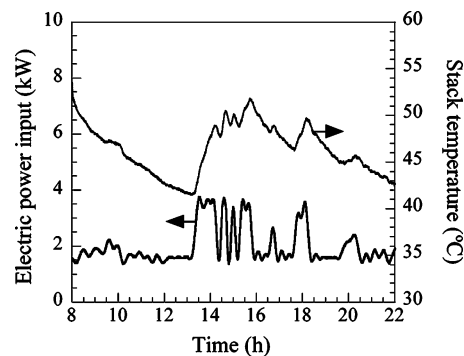


Figure 8. Evolution with time of the cell stack temperature and the electric power supplied to the electrolyzer.

feasibility of wind–hydrogen systems.^{21,30} It is customary to define the efficiency of the hydrogen-energy systems as referring to the lower heating value (LHV) of hydrogen (33.3 (kW h)/(N m³ H₂));¹⁶ thus

$$\text{efficiency} = \frac{\text{LHV of H}_2 \text{ (33.3 (kW h)/kg H}_2\text{)}}{\text{specific energy use ((kW h)/kg H}_2\text{)}} \quad (4)$$

The specific energy use in the electrolytic process has been calculated as follows:

$$\text{specific energy use ((kW h)/kg H}_2\text{)} = \frac{UI(\text{kW})}{\text{hydrogen production (kg H}_2\text{/h)}} \quad (5)$$

where U (kV) is the total voltage in the cells stack and I (A) is the electrolysis current. In this work, the efficiency in the conversion of the electrolysis current has been assumed to be 100% since it was not possible to independently measure the produced hydrogen. This is a reasonable approximation for bipolar filter-press type alkaline water electrolyzers;¹⁴ therefore, the total hydrogen production has been estimated according to⁴¹

$$\text{hydrogen production (kg H}_2\text{/h)} = \frac{n_c I}{zF} \frac{2}{1000} 3600 \quad (6)$$

where n_c is the number of cells connected in series, in our case 22; I (A) is the electrolysis current; z is the number of charges transferred per hydrogen molecule (2); and F is the Faraday's constant (96,485 (A s)/mol).

The evolution with time of the electrolyzer efficiency and the specific energy use for hydrogen production as defined by eqs 4 and 5, respectively, are shown in Figure 9. It can be seen that the energy required by the electrolysis process remains relatively stable at about 42 (kW h)/kg H₂, which results in an efficiency referring to the LHV of hydrogen on the order of 79%. The small peaks observed in the specific energy consumption up to about 45 (kW h)/kg H₂ are coincident with the changes in the wind speed; as a result, the electrolyzer efficiency based on the stack voltage slightly decreases to around 74% for the periods of highest wind speed.

Finally, both due to safety and product quality reasons, the purity of the produced hydrogen and oxygen was examined. The HySTAT electrolyzer includes sensors that continuously monitor the content (vol %) of H₂ in the produced O₂ as well as the O₂ content in the produced H₂. The evolution of the readings of these sensors is shown in Figure 10. It can be seen that the content of O₂ in the H₂ was very low and remained almost constant between 0.02 and 0.03%; the produced hydrogen was therefore very pure. Our electrolyzer does not include any

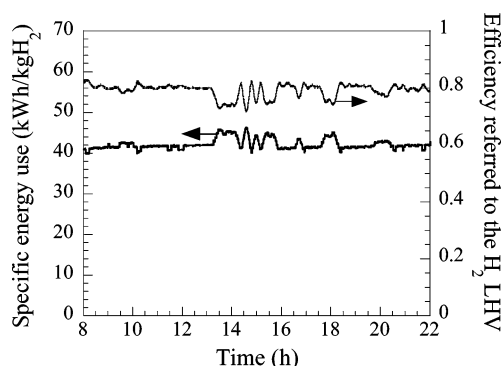


Figure 9. Evolution with time of the specific energy use for hydrogen production and the electrolyzer efficiency referred to the lower heating value (LHV) of H_2 .

additional gas purification system; however, H_2 purities higher than 99.99% are relatively easy to achieve in complete commercial units incorporating drying systems. The H_2 content in the O_2 was significantly higher, although it did not surpass 0.2 vol %. It should be noted that this is a value ten times lower than the one set to automatically shut down the electrolyzer, which is customarily established at 2 vol %; this value is about 50% of the lower explosive limit of H_2 – O_2 mixtures (4.6 vol %).^{21,30} Comparing Figures 5 and 10, it is clear that the purity of the produced gases increases as the wind speed and, then, the electrolysis current increase. The electrolyzer operated satisfactorily within the safety limits during the experiment under transient conditions.

5. Discussion

The fast response of the stack voltage shown in Figure 7 matching the transient current–time profile suggests an essentially ohmic behavior of the electrolyzer in the range of operating conditions of the experiment. This is in accordance with the polarization curves of the electrolyzer.³⁷ In fact, for electrolysis currents above 40 A, the relationship between the stack voltage and the electrolysis current is almost linear, thus indicating that the electrolyzer behavior is governed by the electric resistances of the electrolyte, electrodes, and membranes. This also explains that the electric power required to sustain a given electrolysis current increases as the cell stack temperature decreases (see Figure 4) since the electrolyte and membranes conductivity increases with increasing temperatures.⁴¹ The fact that the stack voltage variations are significantly attenuated compared to that of the electric current can be explained taking into account that there is a lower limit for the voltage which is given by the thermoneutral cell voltage (U_m^0):^{14–16}

$$U_m^0 = \frac{\Delta H^\circ}{zF} = \frac{286\,000}{2 \times 96\,485} = 1.48 \text{ V} \quad (7)$$

where ΔH° (286 kJ/mol) is the standard enthalpy change for the water decomposition reaction. As the stack under consideration is composed of 22 electrolysis cells connected in series, this gives a total stack voltage under thermoneutral conditions of $22 \times 1.48 = 32.6$ V. This means that at 32.6 V water electrolysis is conducted without thermal effect. Stack voltages above this value give rise to heat liberation, whereas below 32.6 V additional heat has to be supplied to carry out water electrolysis. At present, commercial water electrolyzers do not incorporate heating systems since they are designed in such a way that the electrolysis process is used to sustain the stack temperature at an adequate level. To this end, the stack voltage

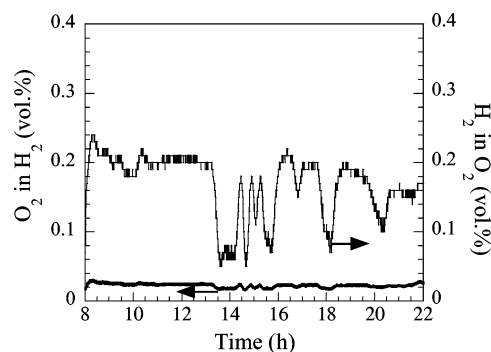


Figure 10. Evolution of the content of H_2 in the produced O_2 and the content of O_2 in the produced H_2 .

must be above the value corresponding to thermoneutral conditions in order to maintain stack temperatures well above room temperature. As a matter of fact, low electric currents leading to cell voltages below 1.48 V give rise to alarms and automatic plant shutdown if the situation persists for more than 10 min. As can be seen in Figure 7, during the experiment, the stack voltage was slightly above the lower limit of 32.6 V. It should be noted that, according to Figures 3 and 4, sustained wind speeds below 5–6 m/s would cause electrolyzer shutdown. As we will see later, the reasons for shutdown are not only due to operation below thermoneutral conditions.

Regarding the cell stack temperature, it is clear that it depends on the electric power input (see Figure 8), that is, on the electrolysis current and the stack voltage. As explained above, at stack voltages above the thermoneutral value (32.6 V), water electrolysis is carried out with liberation of heat since the energy supplied is higher than that required for water decomposition. Under these conditions, heat can be accumulated in the stack resulting in increased temperatures. Obviously, the thermal energy liberated depends on both the electric current and the difference between the actual and thermoneutral voltages. This explains that the stack temperature decreases when the electric power decreases too. On the other hand, it can be seen in Figure 8 an initial period in which the temperature decreases in spite of the almost constant electric power supplied to the electrolyzer. This was due to the experimental procedure followed to perform the experiment. Prior to starting the emulation of the selected wind conditions, the stack was allowed to reach a favorable working temperature of 55 °C. Thus, it was preheated by passing a constant current of 100 A for about 2 h through the cell stack. Once this temperature was reached, the emulation of the wind conditions was started, and as a result, the current decreased to 45–55 A, as shown in Figure 6. This is the reason for the initial decrease of the temperature from about 54 to 42 °C that can be appreciated in Figure 8 until the electric power input again increases.

As far as the specific energy consumption required by the electrolysis process is concerned, it is remarkable that it remains relatively stable between 40 and 45 (kW h)/kg H_2 in spite of the very transient conditions imposed by the emulated wind regime. This can be explained taking into account that the specific energy consumption does not depend directly on the electric current, as can be seen by combining eqs 5 and 6:

$$\text{specific energy use ((kW h)/kg } H_2) = \frac{U(\text{kV})zF}{7.2n_c} \quad (8)$$

The specific energy use varies proportionally with the cell stack voltage, whose dependence on the electric current is significantly attenuated (see Figure 7), as explained above, and is apparent

from the polarization curves of the electrolyzer.³⁷ Consequently, the electrolyzer efficiency referring to the H_2 LHV remains also relatively stable between 74 and 83% at electric current varying between 35 and 80% of the nominal load (120 A). The efficiency of the electrolyzer is inversely proportional to the stack potential (see eqs 4 and 8).²¹ Therefore, as the stack voltage increases with the electrolysis current, it can be seen that the efficiency decreases, although slightly, at increasing H_2 productions, that is, at increasing wind speeds and electric power inputs. Nevertheless, the efficiency of the HySTAT alkaline water electrolyzer from Hydrogenics is very high, even at the highest electric loads. In this regard, Dutton et al.³⁰ obtained efficiencies relative to the LHV of H_2 of only 40–45% with a 2.25 kW Hoerner System electrolyzer and 60% with a 10 kW HE2 electrolyzer, both under intermittent wind-condition operation. In the case of hydrogen production under solar PV conditions, Hollmüller et al.²³ obtained 62% average efficiency with a 5 kW electrolyzer based on Vandenberg technology as in the case of the one considered in our study. Hug et al.²⁴ found 70% efficiency for a 10 kW advanced alkaline electrolyzer at nominal load, and Barthels et al.²⁵ measured up to 88% efficiency for a 26 kW electrolyzer in the PHOEBUS-JÜLICH demonstration plant in Germany. As can be appreciated from these data, the efficiency increases with the nominal size of the electrolyzers.

Finally, our results regarding the purity of the produced hydrogen and oxygen are in accordance with previous studies considering the intermittent operation of water electrolyzers. In fact, high purity (better than 99.8%) hydrogen is normally produced; however, it is a common feature of water electrolyzers that the purity of the produced gases decreases as the electric load decreases too.^{21,24,25,30} As a result, automatic shutdown of the electrolyzer can occur at low electric loads due to the fact that the stack voltage can become lower than that corresponding to thermoneutral conditions as well as to the increased risk of achieving hazardous concentrations of H_2 in the O_2 . The hydrogen flammability limits in O_2 are between 4.6 and 93.9%; therefore, it is easier to achieve the lower explosive limit. This is why commercial electrolyzers do incorporate sensors to monitor the content of H_2 in the O_2 , whereas the inclusion of sensors to measure the O_2 content in the H_2 is usually optional.

At very low electric loads, the rate at which H_2 and O_2 are produced may be lower than the rate at which these gases permeate through the cells membranes, which is especially true for H_2 due to its high diffusivity. This problem is more pronounced in alkaline than in PEM electrolyzers.²¹

6. Conclusion

The performance of a commercial water electrolyzer of 5 kW (HySTAT from Hydrogenics) has been studied under intermittent working conditions relevant to wind–hydrogen systems. The electric power input characteristic of a wind turbine of comparable nominal power has been emulated and supplied to the electrolyzer using actual wind speed data from a wind farm and an IGBT-based electronic converter driven by means of a microcontroller. The results have shown that the electrolysis cell stack voltage readily matches the electric current–time profile, suggesting an essentially ohmic behavior governed by the internal resistances associated to the electrolyte and cells components: bipolar electrodes and inorganic membranes, as expected from the range of current densities considered in this work. The stack temperature does not remain stable and changes according to the electric power input, although it remained within a suitable operating range. The electrolyzer behaved very efficiently, 74–83% (based on the stack voltage) relative to the lower heating value of hydrogen. The efficiency was only little affected by the transient regime of operation. The hydrogen produced was very pure, with oxygen contents always below 0.2 vol % and, consequently, far from hazardous conditions. In accordance with previous reports, the purity of the produced gases decreased at decreasing electric loads. In general, the electrolyzer behavior was reliable. Additional experiments of considerably higher duration are under consideration in order to complement these promising results.

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