Energetic assessment of high-pressure PEM electrolyzers for the production of hydrogen at 900 bar for Hydrogen Refueling Stations

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RESUMEN: *Los electrolizadores cuando trabajan a presión presentan un aumento de la energía específica necesaria para disociar el agua en hidrógeno y oxígeno. Sin embargo, se espera que se produzca un ahorro en términos globales de planta en la producción de hidrógeno a altas presiones debido al ahorro energético obtenido en las subsiguientes etapas de compresión del hidrógeno gaseoso. En un contexto en el que se prevé que el estándar de las estaciones de servicio de hidrógeno para aplicaciones móviles sea gas comprimido a 700 bar, tiene especial interés el empleo de electrólisis presurizada. En este trabajo se lleva a cabo un análisis energético de la producción de hidrógeno a 900 bar mediante un electrolizador PEM de alta presión funcionando a presiones entre 1 bar y 130 bar, seguido de cuatro etapas de compresión con refrigeración intermedia. Los resultados de este estudio demuestran que se obtiene un ahorro energético en determinadas condiciones.*

ABSTRACT: *Electrolyzers working under pressure present an increase in specific energy demand for the dissociation of water into hydrogen and oxygen. However, energy savings are expected in global terms of plant when hydrogen is produced at high pressures, as a result of energy savings obtained in the subsequent compressions of gaseous hydrogen. In a context, wherein the standard of hydrogen refuelling stations for mobile applications will be compressed at 700 bar, the use of pressurized electrolyzers presents especial interest. This work assesses the energy needed to produce hydrogen at 900 bar by using a high pressure PEM electrolyzer working at operating pressures ranging from 1 bar to 130 bar, followed by four stages of compression with intercooling. The results of this work show that there are energy savings under specific conditions.*

Palabras clave*: Electrolizador de alta presión, análisis energético, Hidrogenera, Hidrolinera, PEM, PEMEC*
Keywords: *High-pressure Electrolyzer, energetic analysis, Hydrogen Refueling Station, PEM, PEMEC*

1. INTRODUCTION

European Governments are starting to consider hydrogen energy not only due to their environmental advantages but also due to the strategic capability of enabling fuel independence from third countries. Such sentiment has risen since the Ukrainian gas crisis [1]. Hydrogen, a fuel able to favor independency from fossil fuel providers, can be produced using electrolysis of water, powered by renewable energies.

In a purely renewable context, the best suited electrolyzers are those of low temperature as they do not require for high temperature heat sources, which are not usually found in the whereabouts of the renewable farms [2]. In addition, an advantage of low temperature electrolyzers is that their respective plants take less time to achieve steady state than those of high temperature. This is especially important as intermittency in electric power generation is inherent to renewables, and steady state is where electrolytic plants operate at peak efficiency.

The rise in operating pressure affects the overall efficiency of the electrolysis stacks in two ways, voltage efficiency and faradaic efficiency [3]. Both efficiencies have dependence on the operating pressure, however, voltage efficiency can be misleading when working at different conditions than the standard ones. This is because such efficiency is the ratio of two pressure dependent variables, namely, reversible voltage E (T, p) and the measured voltage of the cell V_{cell} (T,p,j), which in addition of the two previous variables it also depends on the current density j, see Fig. 1.

That is the reason why energetic assessment of electrolytic plants should be based in specific energy consumption per mass of hydrogen produced at the desired thermodynamic state instead of efficiencies.

Since the release of Toyota Mirai, it seems that compressed hydrogen at 700 bar is going to be the standard at Hydrogen Refueling Stations (HRS). In this regard, low temperature electrolysis plants have the potential of power saving since they can operate with pressurized water, reducing spent energy in subsequent compressions. In addition, HRSs will probably have a cascade layout regarding storage tanks, with the aim of energy saving [4]. In such layout, the first tank of the cascade supply system would have a pressure between 100 bar and 200 bar, followed by other tanks at greater pressure until an ultimate pressure of 900 bar is reached [4].

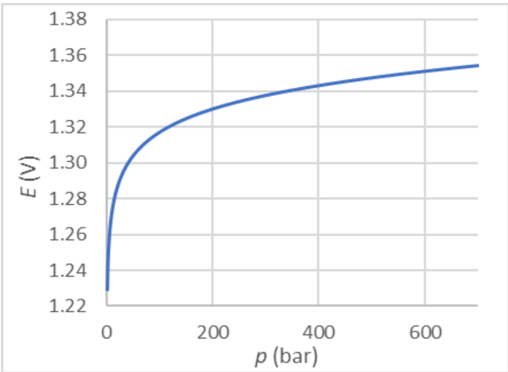

Fig. 1. Variation of the reversible voltage E with the pressure, at 298.15 K. Own development.

The aim of this work is to assess the specific energy needed to produce hydrogen at 900 bar by using different working pressures in the electrolyzers, and using compressors to conduct hydrogen to the desired ultimate pressure.

2. EXPERIMENTAL

The assessment is performed with data obtained from reference [5]. Such reference provides a dataset of a real high-pressure PEM electrolyzer at pressures ranging from 1 bar to 130 bar at a current density of 500 mA/cm^2 and a mean temperature of 88 ºC. In this work, the water source is considered at 25 ºC and a pressure of 1 bar. The water is first pumped by a high-pressure pump and then heated by ohmic heating. A diagram of the plant is shown in Fig. 2.

The assessment is done so that, the remaining compression needed to achieve 900 bar is performed by a set of 4 isoentropic compressors with intercooling.

The compression ratio of the four compressors is the same to keep the energy consumption at a minimum for such layout. Therefore, the compression ratio for such layout is calculated as the fourth root of the division of the target pressure p_f by the electrolyzer working pressure p_{ec}, $r_p = \sqrt[4]{(p_f/p_{ec})}$.

The increase in pressure at the electrolyzer increases the cross-permeation of oxygen. In order to regain purity in the produced hydrogen, an autocatalytic recombiner is used to transform undesired oxygen into water, penalizing the amount of hydrogen obtained at the cathode. After water separation, the hydrogen purity is greater than 99.99% in volume.

Calculation of thermodynamic properties is performed using NIST Refprop© [6]. For such calculations, as there are different substances present

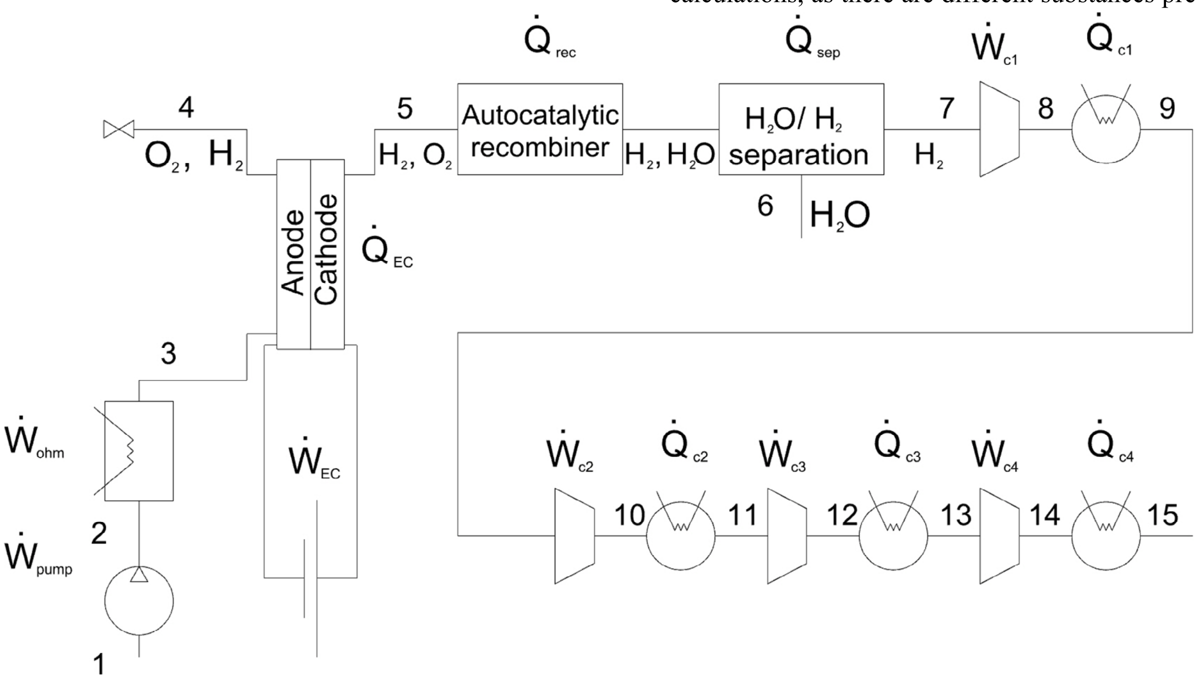

Fig. 2. Diagram of the electrolysis and compression plant. The plant is composed by a high pressure electrolyzer working at different pressures followed by an autocatalytic recombiner to remove the cross-permeated oxygen by reacting it with hydrogen to transform it into water. Then, there is the set of isoentropic compressors with intercooling.

in the plant, the properties of the different substances have been set to the formation enthalpies and entropies at 298.15 K and 1 bar as shown in the JANAF thermochemical tables [7].

3. RESULTS AND DISCUSSION

Fig. 3 shows the total specific work *(W)* to obtain 1 kg of hydrogen at 900 bar at different pressures in the electrolysis cell stack shown in Fig. 2. The total amount of work includes that of the high-pressure pump, the electric heating of water, the power consumed at the electrolysis cell, and the 4 subsequent stages of compression.

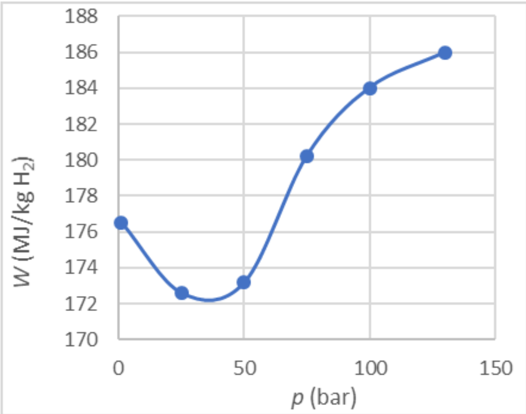

Fig. 3. Total specific work for the production of H_2 at 900 bar as a function of the working pressure of the electrolyzer.

As can be seen in Fig. 4 the specific work of the electrolyzer (*Wec*) per kg of hydrogen generated at 900 bar increases with the pressure of the electrolyzer.

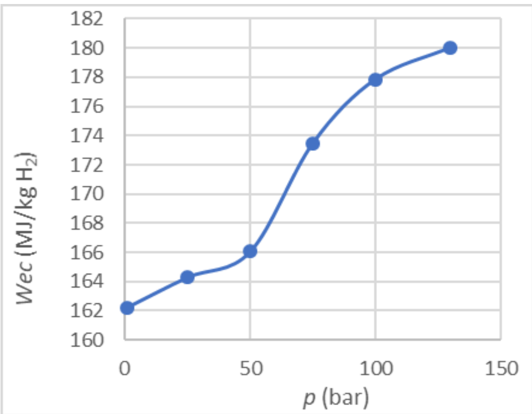

Fig. 4. Specific work of water dissociation in the electrolyzer per kg of H_2 at 900 bar, as a function of the working pressure of the electrolyzer.

In Fig. 5, the needed work for compression of gaseous hydrogen (*Wcomp*) per mass of hydrogen produced at 900 bar drops with the increase of the operating pressure of the electrolyzer.

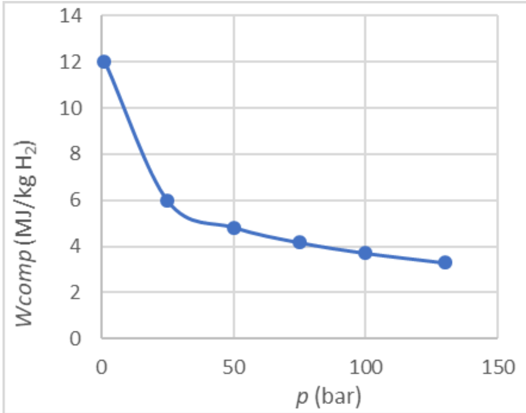

Fig. 5. Work consumed at the electrolyzer per kg of H_2 generated at 900 bar as a function of the working pressure of the electrolysis cell stack.

Fig. 6 shows the drop of the hydrogen purity at the cathode as a result of the increase of cross-permeated oxygen with the working pressure of the electrolyzer. This drop is translated as a loss in faradaic efficiency.

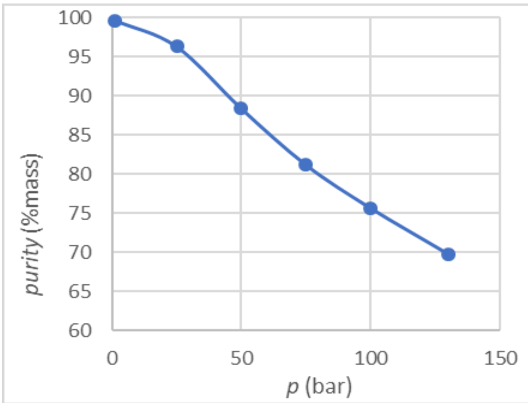

Fig. 6. Purity of cathode H_2 before autocatalytic recombiner as a function of the working pressure at the electrolysis cell stack.

The results of this work reveal that there is an optimum region regarding energy saving for the production of pressurized hydrogen at 900 bar. Under the studied conditions, such region is found at electrolysis cell pressures between 20 bar and 50 bar. The main reason of this is mainly due to the drop of faradaic efficiency caused by the increase in cross permeation of gases, which can be seen in Fig. 6 by means of the drop in hydrogen purity prior to the autocatalytic recombiner.

4. CONCLUSIONS

An assessment on the consumption of energy at a high-pressure PEM electrolyzer at pressures ranging from 1 bar to 130 bar has been made. The loss of faradaic efficiency with the pressure of the electrolyzer has shown that there is a minimum in power consumption when the target pressure of hydrogen is 900 bar.

Prior to attempt further compression in electrolyzers, better membranes regarding cross permeation of oxygen and hydrogen should be developed. This is very important as the loss in faradaic efficiency due to cross permeation has proved critical at high-pressures.

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Bibliography

[1] Z. D. Boren, "Putin threatens to cut off gas supplies to Europe," 2015-02-26 2015.

[2] R. d'Amore-Domenech and T. d. J. Leo Mena, "Assessment of seawater electrolytic processes using offshore renewable energies," in *International Congress of International Maritime Association of the Mediterranean*, Lisbon, 2017: CRC Press.

[3] A. Godula-Jopek, *Hydrogen production: by electrolysis*. John Wiley & Sons, 2015.

[4] L. Halonen *et al.*, "Design proposal for a Mobile Hydrogen Fueling Station," p. 41. Accessed on: 07 July 2017. Available: http://www.hydrogencontest.org/pdf/2014/Humboldt-HEF%20Contest%20Entry.pdf

[5] P. Millet, S. A. Grigoriev, and V. I. Porembskiy, "Development and characterisation of a pressurized PEM bi-stack electrolyzer," *International Journal of Energy Research,* vol. 37, no. 5, pp. 449-456, 2013.

[6] E. W. Lemmon, M. L. Huber, and M. O. McLinden, "NIST Standard ReferenceDatabase 23: Reference Fluid Thermodynamic and Transport Properties - REFPROP. 9.0," ed. Gaithersburg, 2010.

[7] M. W. Chase, "NIST—JANAF Thermochemical Tables (Journal of Physical and Chemical Reference Data Monograph No. 9)," *American Institute of Physics,* 1998.