Experimental and modelling study of an electrochemical hydrogen compressor

Citation for published version (APA):

Document license:
CC BY

DOI:
10.1016/j.cej.2019.03.106

Document status and date:
Published: 01/08/2019

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.

Download date: 20. Sep. 2020
Experimental and modelling study of an electrochemical hydrogen compressor

Maria Nordioa, Filippo Rizzia,b, Giampaolo Manzolinib, Martijn Mulderc, Leonard Raymakersc, Martin Van Sint Annaland, Fausto Galluccia,⁎

⁎ Corresponding author.
E-mail address: f.gallucci@tue.nl (F. Gallucci).

HIGHLIGHTS
• The performance of the Electrochemical Hydrogen Compressor are analyzed.
• The EHC performance have been modelled in a 1D + 1D model implemented in Matlab®.
• High purities can be obtained for the H2 separation from N2 and CH4 and over 98% from He.
• An increase in the cathode pressure has shown a slight improvement in the obtained purity.

ARTICLE INFO
Keywords:
Electrochemical hydrogen compressor
Anode
Cathode
Purity
Hydrogen recovery factor
Energy consumption

ABSTRACT
The energy world is changing rapidly pushed also by the need for new green energy sources to reduce greenhouse gas emissions. The fast development of renewable energies has created many problems associated with grid management and stability, which could be solved with storage systems. The hydrogen economy could be an answer to the need of storage systems and clean fuel for transportation. The Electrochemical Hydrogen Compressor (EHC) is an electrochemical device, which could find a place in this scenario giving a solution for the hydrogen purification and compression for storage. This work analyzes, through experimental and modeling studies, the performance of the EHC in terms of polarization curve, Hydrogen Recovery Factor (HRF) and outlet hydrogen purity. The influence of many input parameters, such as the total inlet flow rate, the hydrogen inlet concentration, the contaminant in the feed, and the cathode pressure have been investigated. Furthermore, the EHC performance have been modelled in a 1D + 1D model implemented in Matlab® solving the Butler-Volmer system of equations numerically. The experimental campaign has shown that high purities can be obtained for the hydrogen separation from N2 and CH4 and purities over 98% feeding He. An increase in the cathode pressure has shown a slight improvement in the obtained purity. A comparison between PSA unit and EHC for a mixture 75% H2 – 25% CH4 at different outlet hydrogen pressure and purity was performed to analyze the energy consumption required. Results show PSA unit is convenient at large scale and high H2 concentration, while for low concentration is extremely energy intense. The EHC proved to be worthwhile at small scale and higher outlet hydrogen pressure.

1. Introduction
The energy world is changing rapidly pushed also by reduction of the greenhouse gas emissions. The great and fast development of renewable energies has created many problems in the grid management and stability, which could be solved with the joint force of a smart grid and storage systems. Even with the diffusion of renewable energy production, the pollution in the city related to transport has not decreased sufficiently. For these reasons, several groups and companies are investing an attempt to solve the problem of energy storage and city pollution through a future hydrogen economy [1,2]. The main challenge for a future hydrogen economy is the decrease in the costs related
Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Membrane area (m²)</td>
</tr>
<tr>
<td>c</td>
<td>Concentration (mol/m³)</td>
</tr>
<tr>
<td>D_i</td>
<td>Diffusion coefficient of component i in component j (m²/s)</td>
</tr>
<tr>
<td>x_i</td>
<td>Molar fraction of component i (-)</td>
</tr>
<tr>
<td>h_m</td>
<td>Mass transfer coefficient (m/s)</td>
</tr>
<tr>
<td>Sh</td>
<td>Sherwood number (-)</td>
</tr>
<tr>
<td>M_i</td>
<td>Molar mass of component i (kg/mol)</td>
</tr>
<tr>
<td>P</td>
<td>Total pressure (Pa)</td>
</tr>
<tr>
<td>P_l</td>
<td>Partial pressure (Pa)</td>
</tr>
<tr>
<td>R</td>
<td>Ideal gas constant (J/mol/K)</td>
</tr>
<tr>
<td>E</td>
<td>Potential (V)</td>
</tr>
<tr>
<td>F</td>
<td>Faraday's constant (A/mol)</td>
</tr>
<tr>
<td>i</td>
<td>Current density (A/cm²)</td>
</tr>
<tr>
<td>a</td>
<td>Charge transfer coefficient (-)</td>
</tr>
<tr>
<td>δ</td>
<td>Membrane thickness (µm)</td>
</tr>
<tr>
<td>K</td>
<td>Kinetic constant (mol₁/₂/s/m²)</td>
</tr>
</tbody>
</table>

The Electrochemical Hydrogen Compressor (EHC) can simultaneously compress and purify the hydrogen through the electrochemical reactions reported in Eqs. (1)-(3).

\[
\text{Anode: } \text{H}_2 \rightarrow 2\text{H}^+ + 2e^- \tag{1}
\]

\[
\text{Cathode: } 2\text{H}^+ + 2e^- \rightarrow \text{H}_2^{\text{HP}} \tag{2}
\]

\[
\text{Overall: } \text{H}_2^p \rightarrow \text{H}_2^{\text{HP}} \tag{3}
\]

Some other works, instead, focused more on the performance at low concentration [10]. The influence of CO₂ was barely analysed and mostly studied together with the presence of CO [11], and a possible recovery method such as pulsing as done by Gardner et al. [12].

The Electrochemical Hydrogen Compressor has many advantages with respect to the traditional technologies.

The Electrochemical Hydrogen Compressor can simultaneously compress and purify the Hydrogen while purifying it from other contaminants thanks to the Nafion® membrane that permits almost only the permeation of protons through it; a very small amount of other contaminants can permeate, as will be discussed later. Since it does not have movable parts, the compressed hydrogen is not contaminated by the oil necessary as a lubricant for movable parts and the maintenance needed for the system is low, decreasing the overall cost of this unit. Furthermore, the lack of movable parts avoids the production of noise, making the EHC more suitable for many applications where acoustical emission is a constraint. The EHC also has the advantage to be a compact device which promotes its scalability. Usually, for a large-scale system, the single units are placed in parallel with respect to the gas flow in order to process the required volume flow rate having the cells working at the same condition due to the same current to each unit. Another relevant advantage is the high efficiency at high compression ratio (β) and the fact that there is not a limit on the output pressure from an electrochemical point of view and the only limits are given by energy consumption limitations because of back diffusion or mechanical strength [7]. It could be possible to couple the EHC with fuel cells in order to recover the Hydrogen that is not used for the generation of electricity; indeed a small percentage of hydrogen is always wasted at the outlet of the PEMFC because it does not react on the active sites of the membrane. This outlet flow with a small percentage of hydrogen could be purified and recirculated by the EHC for further use, thus decreasing the losses and increasing the efficiency of the overall system [13].

Unfortunately, the EHC has some drawbacks that are similar to the disadvantages of fuel cells hindering the exploitation of this technology, which therefore still needs some further improvement to corner the market.

It is important to underline the high cost due to the materials used, especially the Platinum as catalyst for the reaction on the membrane and the polymeric membrane itself. The Platinum is necessary to resist the corrosive environments present in the Electrochemical Hydrogen Compressor also stabilizing its functioning. There have been trials to decrease the catalyst loading used – measured in milligram of Platinum per square centimeter – but this leads to the second disadvantage of these technologies: the degradation during the lifetime of the compressor which is mainly related to losses of catalyst due to different mechanisms, such as Platinum dissolution and CO poisoning in the case of presence of this contaminant in the inlet flow [14]. The CO poisoning is one of the main disadvantages, since it is detrimental also at low concentrations, it is adsorbed on the Platinum catalyst competing with the Hydrogen adsorption decreasing the active catalyst area. Other degradation problems are related to the decay of the characteristics of the Gas Diffusion Layer (GDL), that decreases the mass transport, and of the membrane that decreases the conductivity and increase the passage of contaminant and the back diffusion of Hydrogen.

The performance of the EHC are decreased because of mass transport limitations that hinder the hydrogen to reach the active sites of the membrane and so to be separated from the contaminants and to be transported and compressed to the cathode.

The present work contributes to characterize the EHC both from an experimental and modelling point of view to better understand the physical phenomena underlying the EHC operating principle. This work belongs to an European project named HyGrid which stands for a flexible hybrid separation system for hydrogen recovery from natural gas grids. The idea behind the project is the possibility to exploit the renewable electricity production excess which may occur during the day to produce hydrogen by electrolyzers. Otherwise, the electricity excess would be curtailed, hence, wasted. It is calculated that the electricity curtailed from renewable sources can be as high as 20% depending on installed capacity [15]. The produced hydrogen could be pumped to the natural gas grid in order to avoid building an infrastructure for storing the hydrogen. Moreover, the wide extension of the natural gas grid, especially through Europe could be exploited to distribute hydrogen. The aim of the project is the separation of the H₂ from the natural gas grid with a very low hydrogen concentration.

In order to separate hydrogen from a highly concentrated natural gas mixture, a novel configuration which contains three different units, enhancing the strengths of each, has been considered. The first unit contains Pd-Ag membranes, the second is the electrochemical hydrogen compressor and the last one is the temperature swing adsorption. The membrane has the purpose of separating the very low hydrogen content, the electrochemical compressor is optimal for a hydrogen content lower than 2%, while the temperature swing adsorption is used for purifying from the humidity and it is a good technology for small-scale.
systems. The Pd-Ag membrane reactor/module adopts steam as sweep gas in the permeate side to increase the permeation driving force.

The steam has to be condensed but to guarantee a high purity of the hydrogen stream, the hydrogen rich stream is sent to the temperature swing adsorption unit in order to remove the remaining humidity remained.

This work aims at giving more insight the electrochemical hydrogen compressor behavior in presence of different mixtures from a recovery, purity and electric consumption point of view.

This study has been carried out for different experimental conditions: different voltages, mixtures, hydrogen concentrations, total flow rate, cathode pressures and temperature. The developed model is based on the Butler-Volmer equation taking into account the losses and the mass transfer limitation in the gas diffusion layer.

The results obtained for this technology in terms of HRF, purity and energy consumption seem to be promising for the future development.

2. Experimental

2.1. Electrochemical hydrogen compressor description

An EHC was supplied by HyET Hydrogen, containing a single cell with an active area of 50 cm². The membrane used is Nafton 212. The graphite cell plates have a serpentine flow field design with three channels in parallel. On both ends of the EHC, cooling plates have been installed to ensure a constant temperature in the cell.

First of all, it was necessary to understand the behavior of the EHC related to different variables that can be changed during its operation. In literature, the behavior of the Fuel Cell is explained in detail [4,17,18] but only few papers are available about the EHC, which functioning is similar to the one of the Fuel Cell. For this reason, in the first experiments the dependence of the performance of the EHC on different parameters was analyzed, such as the concentration, flow rate, type of contaminants, cathode pressure and EHC temperature, in order to characterize and describe its functioning in different operating conditions. Initially, the analysis was focused on the amount of hydrogen passing through the membrane that reaches the cathode. The polarization curve played a remarkable role in the description of the performance of the EHC. The polarization curve gives information on the electrochemical resistance of the EHC. The voltage losses, usually called overpotential, can be divided into three regions: the active, ohmic and mass-transfer limiting regions [19]. It was accepted that in the low current density region, the active overpotential predominates. In the intermediate region, the cell internal resistance, mainly attributed to the membrane resistance, becomes the major factor resulting in a linear trend of the discharge curve in this region. In the high current density region, the overall cell reaction rate is limited by depletion of the reactants. Consequently, the mass-transfer overpotential becomes the dominant factor and causes a sharp decay in the current density at a constant applied voltage.

2.2. Description of the setup

A description of the setup is depicted in Fig. 1. The supplied inlet gas are methane, nitrogen, hydrogen, helium and carbon dioxide. The flow is governed by an electronic valve which receives as input the flow rate measured by mass flow controllers from Bronkhorst which have a maximum volume flow rate of 10 l/min for all the gases with exception of hydrogen which has a maximum volumetric flow rate of 2 l/min. The feeding pressure is regulated by a back pressure regulator with an integrated pressure gauge. At the inlet of the anode, the pressure is measured by a pressure gauge from Druck.

The pressure of the gases is measured at the inlet of the anode using another pressure gauge. Before the anode inlet, the gases are heated using two different tracing lines to allow the gases to reach the EHC at the same temperature of the unit. The maximum operating temperature of the feeding gas reached in the experiments is 28 °C. The set temperature imposed is slightly higher than the operating temperature of the EHC. In order to maintain the membrane perfectly humidified the gases fed to the anode have to be fully saturated with water at all times. A humidifier consisting of a bottle filled with distilled water through which the gases are bubbled is adopted. The bottle is heated with a magnetic hot plate stirrer.

The temperature set on the heating plate is the one that permits the gases in the upper part of the bottle to have the same temperature as the tracing line. It allows an easier water uptake by the gases avoiding an excessive cooling of the flow passing through the water. At the cathode side, the outlet pressure is regulated by a manual back-pressure regulator. The measurement of the pressure is done using a digital pressure gauge which has a ceramic sensor that can measure from 0 to 16 bar. The cathode outlet is sent to a condenser where it is cooled using ice in order to condense the water present in the steam avoiding water condensation in the flow meter and above all in the GC which could be damaged by liquid water during the measurement.

The temperature is monitored at different points in the setup, using K-type thermocouples.

The power supply used is from Elektronika which can range from 0 to 30 Volt and from 0 to 100 Amperes in potentiostatic mode.

All the values of the flow meters, pressure at anode, temperatures, voltage and current of the power supply are monitored and recorded via Intouch software of Wonderware. In addition another back pressure regulator and pressure gauge are included to be able to regulate the

Fig. 1. Schematic representation of the setup used for the experimental tests.
pressure of the line to 1.3 bar which is the pressure needed by the micro GC for the sample suction to be analyzed. The micro GC is the 490 Micro-GC from Agilent Technologies with detection limits equal to 10 ppm for Micropacked columns (carboxene) and 2 ppm for PLOT columns (Molsieve 5A) which are the first and second column used in this GC, respectively.

2.3. Experimental tests

Initially, the experiments were performed with pure gases to determine the crossover of the different gases through the membrane when driven by an imposed pressure difference between anode and cathode side. These experiments were performed at ambient temperature, without supplying any power to the EHC. The flow fed is 1 L/min, at atmospheric pressure at the cathode side while imposing an increasing pressure at the anode side up to 5 bar. The pressure at the anode side is increased in order to study the influence of the pressure difference across the membrane on the gas crossover when no voltage is supplied. Later on, experiments with pure hydrogen were performed at room pressure and temperature of 20 °C. The anode and cathode pressures were equal again to the ambient pressure. The supplied voltage has been varied to determine the current and the hydrogen separated. Very good humidification of the membrane is an important condition for proper conduction of the experimental tests [20]. The main purpose is to describe the polarization curve at different flow rates in order to analyze the different losses which are: the activation polarization, the ohmic and the concentration polarization. Registering the polarization curves the voltage variation can be ascending or descending or randomly scattered. All these different variations were performed to see if there was a relationship between the results and the steps order in the voltage, but it was not found any bounding relationship. The operating conditions applied in the tests with mixtures are summarized in Table 1.

The purity of the hydrogen has been measured for all of the experiments performed for a better understanding of the crossover mechanism. There are no limits imposed by the EHC concerning the concentration, composition, and total flow rate of the inlet gases.

Table 2 reports the limits present on some parameters and operating conditions because of technical limitations or EHC safety.

3. Modeling of the electrochemical hydrogen compressor

The simulation of the electrochemical hydrogen compressor was performed in Matlab®, using a 1-D domain. It is considered a simplified advancement along the x axis from anode to cathode side, assuming that the duct at both anode and cathode do not change their section area and shape. A variation of other parameters at both anode and cathode such as the total pressure, the total flow rate and concentration of hydrogen is considered, thus obtaining a 1D + 1D model. In this model many assumptions are necessary to simplify the computational burden. The implemented assumptions are listed below and shortly commented. Since the temperature and pressure are not near the critical ones, the ideality of the gases and of the mixture is a very good approximation.

Given the large cross-section of the current collectors and the high conductivity of the material (copper) it can be acceptable to neglect the electric resistance and therefore it is set to zero. The following assumptions have been used in the model:

- Ideal gas and mixture
- Zero resistance in solid conductors
- Steady state
- Constant temperature
- Constant contaminant across the anode channel
- Constant pressure drops over each element
- Perfectly humidified membrane
- No water clogging

To model the membrane, a diffusive membrane model approach was chosen treating the membrane system as a single phase. The system has no true pores but homogeneous phase where water and protons dissolve and move by diffusion. The Ohm’s law is used to describe proton movement. The assumption of a fully hydrated membrane has been made. Different models determine the membrane water content correlating the water activity or using Flory-Huggins theory. In this work this approach was neglected for simplicity.

For the gas diffusion layer, steady-state operation and gas phase was chosen. The diffusion media are often composed of either a single gas diffusion layer or a composite structure of a gas diffusion layer and a microporous layer. Only the gas diffusion layer was considered in the proposed model. Moreover approximation of GDL pore shape with a regular geometry of a sphere was considered. Four different types of transport could be analysed for the description of the GDL: Knudsen flow, viscous flow, ordinary diffusion and surface flow. Ordinary continuum diffusion was adopted to take into account the different species of a mixture moving relative to each other under the influence of concentration, temperature and/or other external force gradients. The modelling focused on the pores in the substrate while the interaction of the gas and solid, which should be described through kinetic theory was neglected. The model neglects conductivity calculations since the GDL is made of carbon.

The catalyst layer is considered as an interface layer without single pores. This assumption, means that the catalyst layers are infinitely thin. Faraday’s law is used for mass balance between the membrane and the diffusion medium.

The Butler-Volmer equation is the core of the model and it has been used as described in Eq. (1) for the anode and (2) for the cathode, assuming simple charge transfer kinetics [21–23].

\[ i_{\text{anap}} = F K_a \left[ a_0 H_{\text{a}}^{0.5} e^{\frac{\alpha_F \left( E_{\text{Nernst,a}} + E_{\text{act,a}} \right)}{RT}} - e^{-\frac{\alpha_F \left( E_{\text{Nernst,a}} + E_{\text{act,a}} \right)}{RT}} \right] \]  

\[ i_{\text{cathap}} = F K_c \left[ a_0 H_{\text{c}}^{0.5} e^{\frac{\alpha_F \left( E_{\text{Nernst,c}} + E_{\text{act,c}} \right)}{RT}} - e^{-\frac{\alpha_F \left( E_{\text{Nernst,c}} + E_{\text{act,c}} \right)}{RT}} \right] \]  

The subscript “a” refers to anode, and the subscript “c” refers to cathode. The \( a_{H_2} \) represents the activity of the hydrogen which is computed using the partial pressure of hydrogen on the catalyst surface assuming negligible pressure drop across the gas diffusion layer (GDL). The parameters \( K_a \) and \( K_c \) are the kinetic constant for oxidation and reduction of hydrogens, respectively. These values are obtained from fuel cell literature. While \( \alpha \) is the transfer coefficient which has been considered equal for the anode and cathode side.

The current \( i_{\text{anap}} \) must be equal for both the equations and is the current density computed for each element of the model. \( E_{\text{Nernst}} \) and \( E_{\text{act}} \) are the Nernst potential and the activation polarization losses.

The imposed voltage to the EHC is equal to the sum of the Nernst potential plus the ohmic and activation losses are reported in Eq. (3).

\[ E_{\text{Total}} = (E_{\text{Nernst,a}} + E_{\text{act,a}}) - (E_{\text{Nernst,c}} + E_{\text{act,c}}) + E_{\text{Ohm}} \]  

In order to separate the activation losses from the Nernst potential, the latter is written as in Eqs. (4) and (5), where \( x_H \) is the surface concentration of the hydrogen on the anode catalyst.

\[ E_{\text{Nernst,a}} = \frac{RT}{n_F} \ln \left( \frac{1}{x_H} \right) \]  

Table 1

<table>
<thead>
<tr>
<th>List of experiments performed with mixtures.</th>
<th>Range of values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen concentration [%]</td>
<td>20% 50% 80%</td>
</tr>
<tr>
<td>Contaminant ( N_2 )</td>
<td>CH₄ He</td>
</tr>
<tr>
<td>Cathode pressure [bar]</td>
<td>1.3 2.3 3.3</td>
</tr>
<tr>
<td>Anode volume flow rate [l/min]</td>
<td>1 1.5 2</td>
</tr>
</tbody>
</table>
Table 2
List of operating limits of the electrochemical hydrogen compressor.

<table>
<thead>
<tr>
<th>Limit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum flow</td>
<td>50 ml/min</td>
</tr>
<tr>
<td>Max Pressure difference</td>
<td>3 bar</td>
</tr>
<tr>
<td>Max EHC temperature</td>
<td>60 °C</td>
</tr>
<tr>
<td>Max Voltage</td>
<td>0.8 V</td>
</tr>
<tr>
<td>Max Current density</td>
<td>1.2 A/cm²</td>
</tr>
</tbody>
</table>

\[
E_{\text{I,act,c}} = -\frac{RT}{n_F} \ln \left( \frac{p_i}{p_{\text{amb}}} \right)
\]  

(5)

These two equations already account for the mass transfer loss which is consequence of the lower hydrogen concentration at the membrane surface with respect to the bulk concentration fed.

To compute the hydrogen surface concentration, the formula reported in Eq. (7) is used which is derived from Eq. (6).

\[
i_{\text{app}} = \frac{n_e F \Delta C}{\Delta x}
\]  

(6)

\[
x_i = x_{\text{H}_2,\text{bulk}} - \frac{i_{\text{app}} RT}{n_0 n_F \overline{F}}
\]  

(7)

The coefficient \(\Delta x\) is the mass transfer coefficient which describes the mass transfer resistance in the GDL. It was calculated from molecular diffusivity computed with the Fuller equation corrected by the ratio of porosity and tortuosity, and the mass transfer resistance in the catalyst layer (CL) which is fitted from the experimental data.

The first step to determine the solution of the model consists of solving the system of Eqs. (1)–(3), using the Matlab® function “fsolve” which is based on the Trust-Region algorithm. In some conditions, such as a low hydrogen concentration in the feed, or a high voltage imposed, this method was not able to find a solution for the current density \(i_{\text{app}}\). After a detailed analysis, it was found that the problem approaches the precision limit of Matlab® which was forced to find an imaginary solution. To solve this problem, the Bisection method was adopted which has the disadvantage of being slower in finding the solution, but it is capable to always find it if bracketed by the initial interval, avoiding imaginary solutions. The results are obtained through an iterative procedure starting from a literature value and fitting the results with a graphical method. The corresponding obtained ratio between membrane thickness and conductivity is equal to 0.3 Ω·cm². Furthermore, it is assumed \(K_\text{n} = K_\text{f} = 0.1 \frac{\text{mol} \cdot \text{cm}^2}{\text{V} \cdot \text{cm}^3} \), which is consistent with available information from literature [7].

The model also implements the contaminant crossover driven by the partial pressures between anode and cathode in order to calculate the hydrogen purity.

4. Results and discussion

4.1. Pure gases permeation mechanisms

Fig. 2 shows the volumetric flow rate of the contaminant measured at the cathode as a function of the pressure difference between the anode and cathode. It is a linear trend with the pressure. The main parameters affecting the crossover through the membrane are the solubility of the gas in water, the permeance of the gas in the membrane and the kinetic diameter which could give an indication on the molecular size of the gas. The high crossover of carbon dioxide can be explained by water solubility and permeance through the Na2CO3 30% solution and in a carbonate-bicarbonate alkali metal solution supported on CelGard 2400 uncharged films [26].

These considerations about the crossover driven by a pressure gradient should be kept in mind when the purity of the outlet gases from the cathode is analyzed during the operation of the compressor, since they are directly related to the properties of the gases, even if also other mechanisms will participate during the EHC operation, as will be later explained. To confirm of the considerations carried out on the main mechanism allowing the gases crossover, the CO2 and the He flow rate at different temperatures has been measured at the cathode side for a 50% H2 mixture, cathode and anode pressure of 1.3 bar. As it has been depicted in Fig. 3, the CO2 flow rate permeating through the Nafion® membrane, decreases with temperature while the helium flow rate increases with temperature. These results are consistent with literature data of CO2 water solubility and He permeance in Nafion® at different temperature [24,27].

Afterwards, the performance of the electrochemical hydrogen compressor has been analyzed in case of pure gas tests to determine the IV curve [28].

Fig. 4, shows the polarization curve in case of pure hydrogen. It is possible to recognize a linear trend which describes the ohmic losses, while the initial part which characterizes the activation polarization losses is negligible. The activation polarization losses are not visible in the electrochemical hydrogen compressor, contrary to fuels cells, because the hydrogen oxidation reaction takes place very fast. At around 0.4 V the saturation occurs and the trend is no longer linear due to the concentration polarization losses. At low voltages, the impact of the hydrogen flow rates is negligible, while the aspect is more relevant at high voltages where differences in the current appear. The concentration losses are also known as gas transport losses. During an electrochemical process, the hydrogen is consumed at the electrode. This leads to the concentration gradient and loss of potential due to the inability of the surrounding material to maintain the initial bulk concentration. The losses due to the concentration gradient and depletion of reactants at the electrode are known as concentration losses. Indeed, current discrepancy at high current density, when different total flow rate are fed, are due to changes in mass transport mainly caused by depletion.

4.2. Hydrogen concentration influence

Then, experiments with three different mixtures H2–CH4, H2–He and H2–N2 and have been performed (see Fig. 5).

The presence of other gases slightly increases the concentration losses at the highest currents. Indeed, for the case of 20% H2 around 0.4–0.5 A/cm², it is possible to observe that the polarization curve...
must always be positive, so the flux through the porous electrode cannot exceed the value it achieves when the hydrogen concentration at the electrode surface reaches zero.

The polarization curves with methane and nitrogen seem to have a more pronounced mass transfer limitation compared to helium. Indeed, at the same voltage, in the case of the He-H₂ mixture, the current is higher likened to the other gases. The current difference between He-H₂ and N₂, or CH₄ – H₂ mixture is more crucial at higher current density. The reason has to be found in the concentration polarization losses which are responsible of a discrepancy between bulk and surface hydrogen concentration. The real driving force due to the concentration of hydrogen near the surface of the membrane is different and lower compared to the concentration at the bulk of the anode. We can distinguish two different mass transport phenomena: from the bulk of the channels to the surface of the GDL and from the surface of the GDL to the surface of the active catalyst layer.

The mass transfer coefficient of Eq. (6) gives an information on the diffusion speed of the gas. Since CH₄ and N₂ have similar binary diffusivity and lower than He, the mass transfer coefficient is lower resulting in slower diffusion and higher mass transfer limitation. As additional information, the values of the binary diffusivity has been reported in Table 4 for different contaminants. This gives an explanation of the current discrepancy in presence of He-H₂ compared to the other mixtures.

After this first analysis of the polarization curves, the hydrogen recovery factor is determined for different hydrogen concentrations and for different contaminants starting with He.

In Fig. 6, the HRF is shown for a H₂-He mixture with different hydrogen concentrations keeping the same total feed flow rate. This chart is representative of all the different contaminants which lead to the same considerations. The lower the hydrogen concentration at the inlet, the higher the HRF. It is important to underline in this comparison, that the permeated hydrogen is not the same for the different hydrogen concentrations in the feed.

The case of 20% of hydrogen in the feed shows a horizontal asymptote, which is related to the limiting current reached because of concentration polarization. The purity of the hydrogen has been analyzed and Fig. 7 shows the results for the mixture H₂-He.

The highest value of the purity is reached for the case of 20% in helium at the feed, which corresponds to a maximum value of 99.97%. In the case of 50% and 80% molar fraction of helium in the feed the maximum value reached is 99.87% and 99.73% respectively. All these values are competitive with respect to other technologies for the hydrogen purification [29]. On the other hand, the lowest value, neglecting the first one at 0.021 V, is reached for the case of 80% of helium fed and corresponds to a purity of 99.52%.

Continuing the analysis, the most important feature of these curves is the trend of the purity as function of the voltage. Ignoring the first point at low voltage, it is possible to see that as the voltage is reduced there is a slight decrease in the purity. In fact, with a decreasing voltage the current decreases faster with respect to the crossover of the contaminant. This is because the contaminant crossover is mostly driven by a difference in the partial pressures between the anode and cathode, which does not change significantly with the voltage.

This aspect is very relevant for very low hydrogen flow rates (see the first point of these charts which has a strongly reduced purity with

<table>
<thead>
<tr>
<th>Gas</th>
<th>Water Solubility [g/kg water] at 20 °C</th>
<th>Permeability in dry Nafion® [barrer]</th>
<th>Kinetic diameter [pm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbon dioxide</td>
<td>1.65</td>
<td>2.4</td>
<td>330</td>
</tr>
<tr>
<td>hydrogen</td>
<td>0.0016</td>
<td>41</td>
<td>289</td>
</tr>
<tr>
<td>helium</td>
<td>0.0015</td>
<td>9.3</td>
<td>260</td>
</tr>
<tr>
<td>nitrogen</td>
<td>0.019</td>
<td>0.26</td>
<td>364</td>
</tr>
<tr>
<td>methane</td>
<td>0.024</td>
<td>0.102</td>
<td>380</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Gas</th>
<th>Fuller Diffusivity [cm$^2$ s$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Helium</td>
<td>1.75</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.7651</td>
</tr>
<tr>
<td>Methane</td>
<td>0.7013</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>0.6496</td>
</tr>
</tbody>
</table>
performed at the same power consumption because the voltage and the dissipation, in this case, the total feed consumption as depicted in Fig. 9.

It may be seen that a higher specific energy consumption is needed to achieve the same HRF at higher hydrogen concentrations in the feed. Furthermore, from this chart, it is clear that when the limiting current is reached it is meaningless to further increase the voltage as the HRF will not increase. It is important to outline that the total hydrogen permeating at the cathode side is not the same for different hydrogen concentrations in the feed. Since the hydrogen permeated decreases at lower hydrogen concentration, the energy consumption required is reduced at 20% H2 – 80% He.

Then, experimental tests have been performed changing the total feed flow rate with different hydrogen concentrations to be able to obtain the same current density so to compare HRF at the same energy consumption as depicted in Fig. 9.

The first consideration is related to the opposite trend of the HRF with the hydrogen concentration compared to Fig. 6. As already mentioned, in this case, the total flow rate has been changed in order to get the same hydrogen flow rate at the cathode side. This comparison was performed at the same power consumption because the voltage and the current obtained were equal. Keeping the same power consumption, it is more difficult to recover hydrogen when the hydrogen concentration at the feed is lower.

Plotting the volumetric flow rate of the contaminant, in this case helium, to the cathode side, it can be noted that this quantity is related not to the voltage but to the hydrogen permeation through the cathode as reported in Fig. 10.

A linear trend of the flow rate of the contaminant is found as a function of the hydrogen flow rate permeating at the cathode side. In the case of 80% of hydrogen in the feed, this trend is less clear because of the experimental error and unstable conditions. This linear trend can be explained by two physical phenomena: (i) the higher the volumetric flow rate of hydrogen the higher becomes the partial pressure of the contaminant at the anode and (ii) the influence of the water drag which carries along a quantity of contaminants which increase with the current [7].

It is important to present and discuss the encountered problems related to the stability of the EHC regarding in general the external conditions and focusing on the two problems related to the water management: the dehydration of the membrane and the water clogging.

The repeatability of the experiments greatly suffered because of the variation of the external conditions and because of different degrees of hydration of the membrane during the different experiments performed. This problem is well known from the literature when talking about Fuel cells and EHC [30].

External conditions are playing an important role on the performance of the EHC. As it is easy to imagine the external conditions such as temperature, pressure, and humidity of air, are not always constant and this has an influence on the performance of the EHC.

Then, it is possible to notice the agglomerate of blue triangles in the measurement of 80% of helium which are in correspondence of the limiting current. These points should be perfectly overlapping, but the scattering highlights the magnitude of the uncertainty in the measurements performed because of the somewhat unstable conditions and differentiated caused by voltages between the different measurements and the corresponding slight differences in the current. Although this difference in the measurement with 20% hydrogen is also present, it is possible to underline the linear trend of the contaminant crossover as a function of the hydrogen flow rate at the cathode. Another feature that can be highlighted is the higher crossover of contaminants in case of higher initial concentration at the inlet feed, as it could have been expected. Finally, it is also interesting to notice how the first points of the three series, which were taken at the same voltage, are shifted to the right as the hydrogen concentration in the feed increases, highlighting a stronger influence of the concentrations polarization for lower concentration of hydrogen fed at the anode.

When replacing He with CH4, the GC didn’t measure any methane, meaning that the concentration of this contaminant at the outlet is below the accuracy limit of the micro GC which is equal to 10 PPM and leads to a purity higher than 99.99%. Many tests were performed at different conditions, but the CH4 concentration was never detected at the outlet of the cathode. For this reason, there are no charts related to the purity of methane and the purity is always assumed to be equal to 100%.

Afterward the case of nitrogen was tested, expecting to have the same result as for methane. This expectation was indeed confirmed and

![Fig. 6. HRF for a mixture of hydrogen and helium at different hydrogen molar fraction at the same total feeding flow rate.](image)

![Fig. 7. Hydrogen purity for a mixture of hydrogen and helium at different hydrogen molar fraction.](image)

![Fig. 8. Energy consumption plot with respect to HRF for H2-He mixture at different hydrogen concentration.](image)
also in this case it was not possible to measure any presence of contaminant at the cathode.

Later on, experimental tests are carried out changing the total flow rate between 1, 1.5 and 2 l/min maintaining a constant concentration of hydrogen equal to 20% and a concentration of 80% for the nitrogen. The results are depicted in Fig. 11.

The polarization curves are influenced by the total hydrogen flow at the inlet of the anode. The higher the total flow rate the higher the inlet hydrogen flow rate and so the corresponding limiting current. Accordingly, the concentration losses are visible for higher currents in the case of higher inlet flow rates.

To study the influence of the cathode pressure on the performance of the electrochemical hydrogen compressor, a sequence of three values was registered changing only the pressure with a fixed voltage. The experiments were performed at room temperature and the value of the anode pressure was set to 1.3 bar, whereas, the cathode pressure was varied with the following values: 1.3, 2.3, 3.3 bar.

The results for the case with helium as contaminant were recorded with a concentration of hydrogen of 50% and 1 l/min as the total volume flow rate fed at the anode inlet. In Fig. 12, the hydrogen volumetric flow rate at the cathode in standard l/min and the purity as a function of the cathode pressure are depicted.

From this first chart, it is immediately evident the decline of the flow rate of hydrogen with the growth of the cathode pressure as expected from the theory and the Nernst potential [31]. Furthermore, the purity seems constant with the pressure and it is not visible any evident trend. A decreasing trend is evident with an increasing pressure, even if the percentage variation is not so large. Matching the decreasing flow rate in the contaminant and the decreasing flow rate of hydrogen at the cathode, it is possible to explain the almost constant trend of the purity in the afore mentioned chart.

### 4.3. Temperature influence

The influence of the temperature was investigated in this work. A mixture of 50% H2-50% N2 has been fed at the anode side. The polarization curve has been registered while changing the temperature from 19 to 28 °C.

As it is possible to see in Fig. 13, the current and the hydrogen permeated increase the temperature due to the positive effect on the proton conductivity; indeed the membrane resistance decreases with temperature. This aspect overcomes the Nernst potential reduction. The activation polarization losses increases also with temperature while the concentration polarization losses decreases because of the higher diffusivity.

### 4.4. Modeling results

The experimental campaign was also used to validate of the Matlab® model. Simulations with different hydrogen concentrations for the H2-Ch4 mixtures at different voltages were performed. The resulting i-V curves and H2 purity are plotted in Fig. 14 and 15 together with the corresponding experimental results. It can be noted that the model seems to be quite accurate in the prediction of the EHC performance even if it is based on simple equations and neglects many different phenomena. The model fits also the dependence of the limiting current on the contaminant fed. However, there are some discrepancies because of the scattering of the limiting current present in the experimental results [9] and the gas contaminant influence is neglected in the mass transfer coefficient of the Catalyst Layer, which was assumed constant for all the cases.

The model could predict within a reasonable range of error (lower than 5% for the polarization curve and lower than 0.05% for purity) the different mixtures tested. The mass transfer limitations implemented were validated correctly. The values of the mass transfer coefficient obtained in the simulation, are comparable to the mass resistance of a Micro Porous layer [16].

Then the capacity of the model is tested to describe the polarization curve with different hydrogen concentrations, the contaminant cross-over and the purity as depicted in Figs. 14 and 15. Fig. 15 show a good fitting of the computed purity as a function of the voltage for the case of helium as contaminant feeding 1 l/min with different hydrogen concentrations.

### 5. Energy comparison between PSA unit and EHC

The developed model was later used for an energy comparison...
between the performance of the EHC and a conventional plant for hydrogen purification and compression. The conventional plant selected is composed by Pressure Swing Adsorber (PSA) with an intercooled compressor to reach the required pressure for the system operation. This comparison has the scope of giving a general evaluation for a hydrogen compressor to reach the required pressure for the system operation.

The gas mixture is coming from the grid at different pressures: 6, 8, 10, 12 and 14 bar. From literature is known the PSA is not able to reach such a high outlet pressure, but they can give a more general understanding of this new technology, its strength and weakness points and what could be its future fields of application.

The evaluating criteria of the following comparison are:

- Energy consumption at the same H₂ pressure outlet and at the same HRF
- H₂ purity
- Reliability of the system

The considered assumptions are:

- EHC purity is based on experimental data obtained from a lab unit system at lower pressure than the one evaluated in the analysis
- The ohmic resistance of the EHC considered for the comparison is the same of the lab scale unit
- HRF and purity of PSA are based on literature results [32,33]
- Product goal of the analysis is to separate 25 kg/day of H₂ starting from 30% CH₄ – 70% H₂ and 75% CH₄ – 25% H₂
- The gas mixture is coming from the grid at different pressures: 6, 8, 10, 12 and 14 bar

The case study for the energy comparison is taken from the HyGrid project in which this work takes part. As mentioned above, the idea of this project is to exploit the Natural Gas network to store and distribute hydrogen. Successively, it will be possible to extract the hydrogen when and where necessary. The hydrogen concentration considered in this project is 10%, but the performance of the EHC, obtained from the experiments of this work, are available for higher concentration. Furthermore, it is not possible to find in literature a PSA system that is able to work with such low hydrogen inlet concentration. For these reasons, the comparison was performed for a 30% CH₄ – 70% H₂ mixture case and for 75% CH₄ – 25% H₂ to show the potentiality of the electrochemical hydrogen compressor at different concentrations. For the considered H₂ concentrations, experimental and modeling results for the PSA system are available in literature [32,33].

In Table 5 are reported the different operating conditions considered for the energy comparison performed in terms of HRF depending on the outlet hydrogen pressure. The hydrogen separated by the EHC is assumed with a purity of 100% because of the experimental results described in Section 4.2. From literature is known the PSA is not able to reach such a high outlet purity but higher the adsorption purity, higher the hydrogen purity.

As described in Table 6 at different inlet pressure corresponds a different HRF. Regarding the energy consumption and purity criteria, Fig. 17 shows the results for the 30% H₂ – 70% CH₄ mixtures at a pressure for 50% He – 50% H₂ gas mixture at 0.304 V.

**Fig. 12.** Hydrogen volumetric flow and purity as a function of the cathode pressure for 50% He – 50% H₂ gas mixture.

**Fig. 13.** Polarization curves changing the temperature for a mixture of 50% H₂ – 50% N₂ and a total flow rate of 1 l/min.

**Fig. 14.** Comparison between the experimental and modeling results of the polarization curve for different hydrogen concentrations in a methane-hydrogen mixture.

**Fig. 15.** Comparison between the experimental and modeling results for the hydrogen purity as a function of the voltage for a helium-hydrogen mixture.
different inlet pressure. For the comparison performed, the same HRF has been considered for PSA unit and EHC, indeed the voltage was changed in accordance with that.

The main consideration is related to the 100% purity obtainable from the EHC at any HRF and cathode pressure considered, which is not possible to achieve with the PSA system, in which depending on the adsorption pressure it is possible to increase the purity, decreasing the HRF.

The second advantage of the EHC is related to the decreasing energy consumption trend with the hydrogen concentration, the mixture type, the total oxygen flow rate and temperature.

It is important to underline the lower energy consumption required for the PSA unit compared to the EHC in case of lower hydrogen outlet pressure until 10 bar. The purity obtained is lower in those cases for the PSA compared to the EHC.

Anyway, these results show the benefit of using the EHC compared to PSA unit because it decreases the energy consumption, pressurizing more the hydrogen at the cathode side when the HRF is lowered. In case of PSA unit, the non-hydrogen component is adsorbed at elevated pressure and discharged at lower pressure. If the incoming gas mixture is from high pressure stream (natural gas grid), the non-hydrogen stream needs to be compressed to be sent back to the natural gas grid. Precisely for this reason, lower the hydrogen concentration in the inlet stream, higher the energy consumption required for the separation.

The energy consumption trend for PSA unit is linear with the hydrogen outlet pressure while for the EHC the difference between the analyzed cases is less relevant because it is related to the HRF considered in the simulation. It is important to underline the studied comparison is for a mixture of 70% H₂ – 30% CH₄ while for lower hydrogen concentration, the energy consumption of the mechanical compressor necessary to compress back to the feed the non-hydrogen component increases drastically as showed in Table 4. Indeed, for a low hydrogen concentration the difference between the energy consumption required in a PSA unit and an electrochemical hydrogen compressor is severe.

Moreover, the outlet hydrogen pressure chosen in this configuration is 6 bar which guarantee a hydrogen purity of 99.85%, while for a richer purification, it is necessary to increase the adsorption pressure which results in an even higher energy consumption required for the PSA unit. As mentioned previously, lower the hydrogen concentration in the feed, higher the energy consumption required for a PSA unit and smaller the scale, less energy and economic convenient is the PSA system for hydrogen separation.

Regarding the reliability of the analyzed systems, PSA units are commercially available and developed in the market. The key reasons for such growth in this technology are:

- An extra degree of thermodynamic freedom for describing the adsorption process, which introduces flexibility in PSA unit designing
- Numerous microporous-mesoporous families of adsorbents which show different adsorptive properties for gas separation

Although simple in concept, a practical PSA process can be fairly complex because it involves a multicoloum design where the adsorbents operate under a cyclic steady state using a series of sequential non-isothermal, non-isobaric, and non-steady-state steps.

Regarding the reliability of the EHC, even if the obtained results, provide evidence of promising unit for hydrogen separation and compression, at large scale system, it is still far from being competitive. Further studies and research are needed to make the unit competitive with the traditional plants. Indeed, membrane humidification and water management require advancement, especially at higher temperatures, to guarantee stable conditions. The commercial polymeric membranes have a maximum expected lifetime of 5 years [34].

6. Conclusion

Experimental and modeling tests have been performed on an electrochemical hydrogen compressor, in order to understand the performance on the hydrogen recovery factor and hydrogen purity changing the hydrogen concentration, the mixture type, the total flow rate and the temperature.

The results obtained for this technology in terms of HRF and purity seem to be promising for a good future development. One of the main differences compared to fuel cells is related to the negligible activation polarization losses because of the fast hydrogen oxidation reaction. The purity resulted to be 100% in the case of nitrogen and methane as
contaminant and almost always above 98% for the case of helium. Moreover, the temperature has a positive effect on the hydrogen separation because it increases the membrane conductivity, decreasing the ohmic resistance.

The developed Matlab® model is capable of predicting the polarisation curves and the purity of the outlet hydrogen. Future works could also implement the influence of water and improved the description of the influence of pressure and back diffusion and testing the model at higher pressures and temperatures.

The Electrochemical Hydrogen Compressor is still a quite new technology which needs much research work on many different fields to be better perfected and become more competitive with what are the today traditional plants. Further studies are necessary also to understand purification properties in a wider range of conditions such as higher temperatures, higher anode and cathode pressures, and lower inlet concentrations of hydrogen.

Finally, a studied case with 75%H₂ – 25%CH₄ and 30% H₂ – 70%CH₄ shows the convenience to work with EHC at high hydrogen outlet cathode compared to PSA unit which is not interesting at lower H₂ concentration and small scale system.

Acknowledgements

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking under grant agreement No. 700355. This Joint Undertaking receives support from the European Union’s Horizon 2020 research and innovation.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ccej.2019.03.106.

References