



# Chloralkali low temperature PEM reversible electrochemical cells

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## ABSTRACT

This work demonstrates the viability of MEAs based on Nafion membranes for being used in reversible electrochemical cells for the chloralkali process. It also shows the effect of the operation temperature, from room temperature up to 80 °C, and humidification of the chlorine stream on the performance of these cells as fuel cell. Results demonstrate that these cells can be operated in reversible mode, yielding a current density of approximately 12 mA cm<sup>-2</sup> at a cell potential of 0.5 V, when operating as fuel cells fed with gaseous chlorine and hydrogen. The maximum power density achieved is 7.0 mW cm<sup>-2</sup>, which is much higher than that obtained with the same system fed with hydrogen and chlorine dissolved into liquid electrolytes. It is important to operate at room temperatures because efficiency decreases dramatically with temperature in an irreversible way, affecting the electrode. Humidification is necessary for the hydrogen stream and convenient for the chlorine stream, although it does not solve the irreversible cell damage caused by operation at high temperatures. Current efficiency of chlorine production is above 95 %, when operating as electrolyzer feeding a solution containing 2.0 M of NaCl. The rate of production of chlorine was 45.4 mmol h<sup>-1</sup> at 100 mA cm<sup>-2</sup> and the Cl<sub>2</sub>/O<sub>2</sub> molar ratio is 9.54, which is much higher than the values obtained in previous works which are between 3 and 5.

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## 1. Introduction

Energy storage is a widespread subject of interest to humankind. Renewable energies have been put in the limelight and numerous researchers have increased their efforts in developing alternative power sources. However, it is not enough, and humankind needs for the development of robust energy storage systems at various scales, from small devices to large facilities. These devices may help to balance energy production and its demand. In this context, there are many electrochemical solutions to solve this major supply problem, from the combination of electrolyzers and fuel cells to different types of batteries, including redox flow batteries (RFBs). All of them are based on the reversible conversion of electricity into chemicals [1] and many of them have been studied for decades or, even, centuries. RFBs are a special type of electrochemical storage devices. These systems have emerged as relevant candidates to address the sustainable energy generation. The most common and mature RFB is the vanadium redox flow battery (VRFB), a type of battery extremely scalable, long-lasting operation time and long lifecycle [2]. However, this technology is not fully

mature and there is still gap for further research, because not a clearly advantageous solution has been found till now, and the necessity of these storage systems is more and more acute from day to day [3, 4]. In 2021, Sánchez-Díez et al. [5] have analysed VRFBs technologies and their maturity level, concluding that the development of new cell configurations does not improve the power density values, achieving between 10 and 40 mW cm<sup>-2</sup> at most.

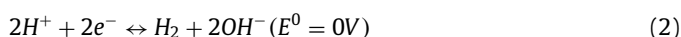
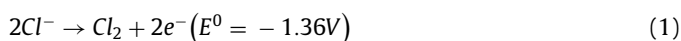
Because of its simplicity, and wide availability of its raw matter, hydrogen technology has been highlighted as one of the most promising alternatives. Both, electrolyzers to produce hydrogen and fuel cells to regenerate electricity from stored hydrogen are at very high technology readiness levels (TRLs), with all the elements of the value chain interacting well and being already developed, up to a degree suitable as to provide real solutions from the private sector to this very important problem. The weakest point remains to be the hydrogen storage, because this species has a very low energetic density and there is not a good and clear option nowadays to fulfill this goal. Also, there is another chance for improvement in hydrogen technologies: the development of processes which allow to improve the efficiency of the electrolysis or fuel cell stages, such as the Westinghouse cycle, in which a thermo-electrochemical approach is proposed to optimize the electrolytic efficiency, by reduc-

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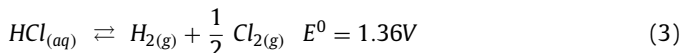
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ing the cell voltage required for the production of hydrogen and oxygen [6].

In this context, in the search for more efficient systems, the chloralkali process appears as a very promising alternative. Basically, this process is based on the electrolysis of brackish solutions of sodium chloride to produce hydrogen and chlorine when surplus energy is produced, and in the regeneration of electricity when it is required, using the same chlorine and hydrogen previously produced [7]. As chlorine is a more powerful oxidant than oxygen, operation advantages can be expected in fuel cell mode, when comparing this novel technology with the conventional process. The first stage, that is the formation of chlorine and hydrogen, is at a very high TRL because it is the base of the chloralkali industry, which is one of the most powerful chemical industries nowadays. The anode and cathode reactions are shown in Eqs. (1) and (2).



Use of well-known formulations of mixed metal oxides (MMO) electrodes and special design of cells are behind the very high efficiencies of this process, which seems to be limited only by the performance of the membranes. The second stage, production of electricity from chlorine and hydrogen, is not well-developed as the first stage, and a lot of work must be carried out to optimize the performance of fuel cells fed with chlorine and hydrogen. Chlorine has appealing properties such as fast kinetics and high standard potential [12]. As an alternative to the conventional hydrogen-oxygen ( $H_2$ - $O_2$ ) fuel cell energy storage system, reversible hydrogen-chlorine ( $H_2$ - $Cl_2$ ) fuel cells are increasingly being used, because of their high potential for energy storage, which work according to the reaction 3.



Thus, although the redox pair  $Cl_2/Cl^-$  compares favorably with respect to the  $O_2/H_2O$ , from the thermodynamic and kinetic points of view, water management into the cell has become a very serious problem, which seems to be particularly difficult to be overcome with typical proton exchange membranes (PEMs) [7-10]. Because of that, different approaches have been evaluated, from increasing operation temperatures using other types membranes such as polybenzimidazole (PBI) [11] to the design of new cells in which liquid electrolytes are used instead of gases [12, 13] for the operation in fuel cell mode. Thus, it has been demonstrated that the process can be operated in divided cells with electrodes assembled with the membrane (forming a MEA, that is, a membrane electrode assembly) or separated from this element and facing each other in different compartments of the cell. In these cells, hydrogen can be added as gas or absorbed/mixed into a liquid electrolyte, being particularly efficient dispersions gas-liquids containing microbubbles of hydrogen [13]. Trying to overcome problems associated to the dehydration of the membranes, in all these works, chlorine was not added directly as a gas, but absorbed into a solution of a liquid electrolyte. Regarding the electrodes, many improvements have been proposed in recent years, focusing mainly on the catalyst loading used. The aim is to use the catalyst as efficiently as possible and, thus, to find a robust catalyst layer, capable of being used over a long period of time. Platinum (Pt) is commonly employed to increase the kinetics of the hydrogen redox reaction in reversible fuel cells. This electrocatalyst showed a good performance in the reduction of water to hydrogen when the cells were operated as electrolyzer, using a Pt loading of  $0.65 \text{ mg cm}^{-2}$ , value similar to that reported by Thomassen et al. [14]. Regarding the electrode in charge of the electrochemistry of chlorine, it was pointed out that ruthenium played a very important role in

the oxidation of chlorides and reduction of chlorine [15]. In previous work, the influence of the chlorine-side electrode composition on the performance of reversible chlor-alkali cells has been studied, by modifying the molar ratio Ru:Pt in the range 1-9, and a maximum power density of  $3.6 \text{ mW cm}^{-2}$  was achieved when the Ru:Pt ratio was 3:1 [16]. The Ru loading reported in this work was  $0.65 \text{ mg cm}^{-2}$ , an amount comparable to that of Pt used on the hydrogen-side electrode. Huskinson et al. [17] showed that Ru loadings as low as  $0.15 \text{ mg cm}^{-2}$  exhibited much higher activities towards the chlorine electrochemical reactions.

In supporting the lifetime of the electrode, the catalytic activity of the electrode hardly changes between before and after operation in both electrolyser and fuel cell modes, as reported in previous works by Carvela et al. [16, 18]. These findings confirm that the electrodes used are robust and can be used for a long period of time.

Taking into account this background, this work aims to evaluate the performance of the technology when hydrogen and chlorine gas are fed to the fuel cell mode working at low temperatures (below water boiling point at atmospheric pressure), paying special attention to the necessity of hydration of the membrane and the viability of using this electrochemical cell also as a reversible PEM fuel cell. Fig. 1 shows a scheme of the reversible hydrogen-chlorine PEM fuel cell used in this work and the processes which are expected to occur during as fuel cell (part a) or as electrolyzer (part b) operation mode. To face this objective, an electrochemical cell with an electrode surface of  $25 \text{ cm}^2$ , and fed with gaseous hydrogen and chlorine, was tested to produce electricity at temperatures ranging from 20 to  $80 \text{ }^\circ\text{C}$ . It was also checked the behavior of the system when it is used as reversible cell, by evaluating the performance of operation of sequences fuel cell-electrolyzer-fuel cell.

## 2. Materials & methods

### 2.1. Electrochemical set-up

Fig. 2 shows schematically the set-up used during this work, operating in fuel cell mode.  $H_2$  gas (99.99 %, PRAXAIR) and  $Cl_2$  gas (99.9999 %, CARBUROS METÁLICOS) were fed to the anodic and cathodic compartments, respectively. The hydrogen and chlorine streams were humidified by bubbling the gaseous streams throughout a tank with water. For non-humidified chlorine gas experiments, the dry gas stream was added directly to the cell. Both  $H_2$  and  $Cl_2$  flow rates are maintained at  $0.1 \text{ L min}^{-1}$ .

When the system was operated as electrolyzer, it worked in recirculation mode, with two peristaltic pumps continuously recycling the concentrated solutions of NaCl (2.0 M). Additional details of this system can be found elsewhere [16, 18].

The electrochemical PEM cell consisted of two bipolar plates fabricated in non-porous graphite (SGL Carbon), with a quadrangular geometry whose dimensions are 150 mm length and 20 mm thickness. The geometrical area of each electrode was  $25 \text{ cm}^2$  and dimensions of the multiple-serpentine flow channels were: channel width and depth 2 mm and 1 mm, respectively, landing between channels 2 mm. A Nafion 117 membrane, used as a Proton Exchange Membrane, was pre-treated by immersion in Milli-Q water for 15 min at  $85 \text{ }^\circ\text{C}$ , followed by immersion into 5% hydrogen peroxide for 30 min, rinsing with Milli-Q water, ion-exchanged twice in 0.05 M  $H_2SO_4$  for 30 min and, finally, washed with Milli-Q water four times, for 15 min each time. This treated membrane was sandwiched between a couple of electrodes, which were manufactured by spraying catalyst inks on a carbon paper support. For the electrode in charge of the electrochemistry of chlorine, the catalyst inks consisted of a commercial  $RuO_2$  catalyst (ALDRICH), Nafion® perfluorinated resin solution (5% wt., ALDRICH) and 2-

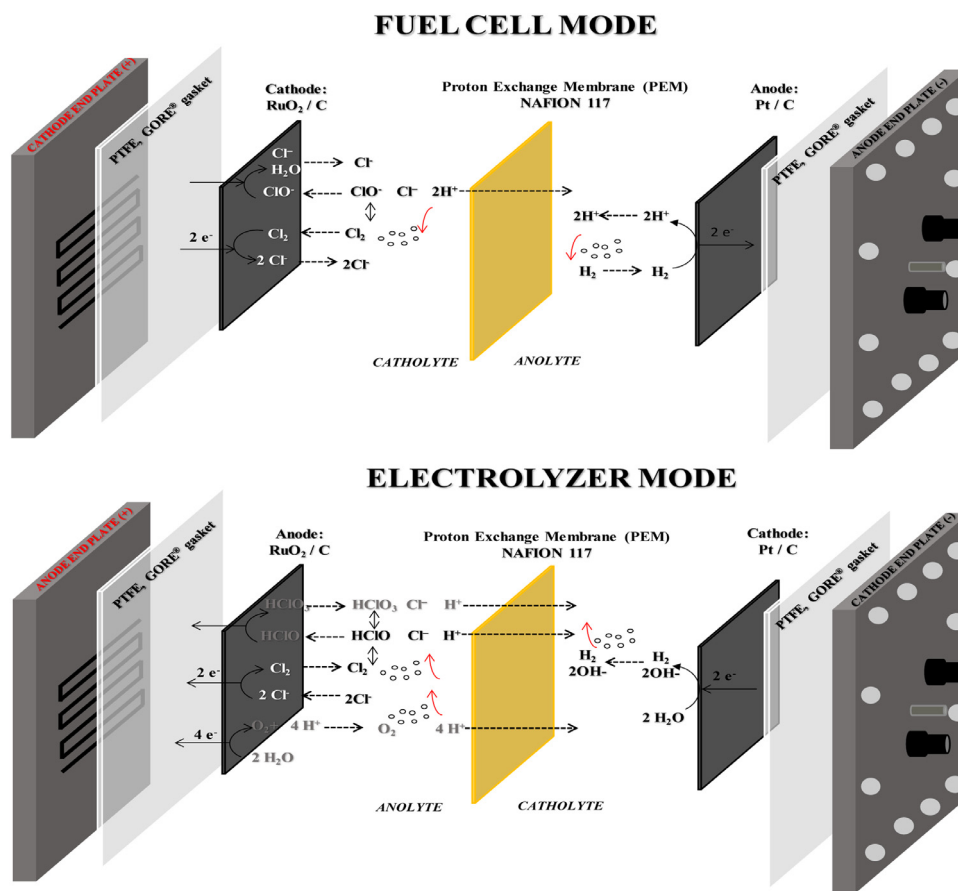


Fig. 1. Scheme of the expected reactions in the reversible hydrogen/chlorine electrochemical PEM fuel cell

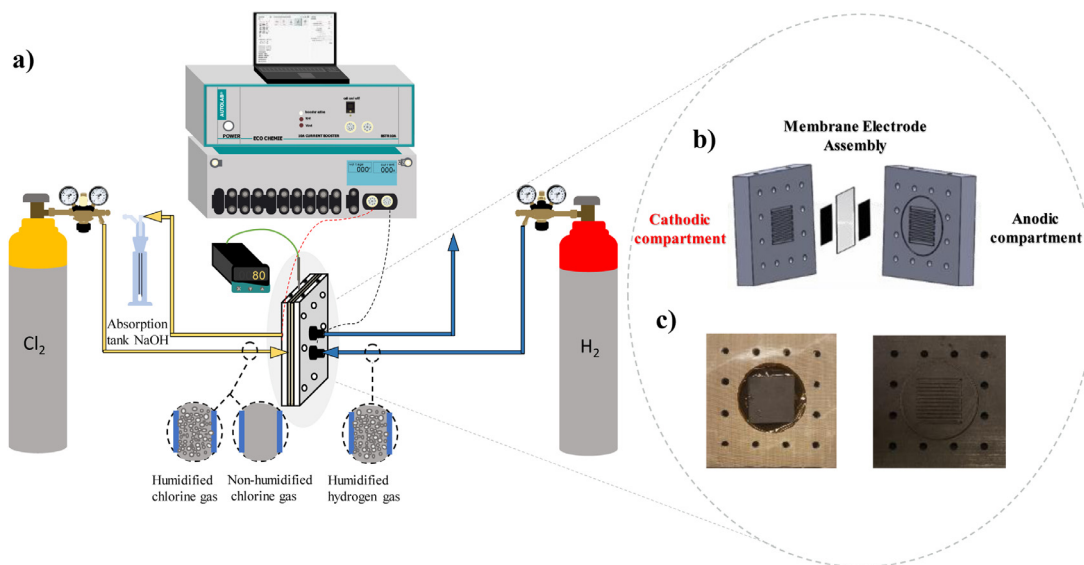


Fig. 2. Scheme of the experimental set-up used in this work a) Flow diagram b) Electrochemical cell c) Image of the actual cell, showing the MEA and a quadrangular graphite endplate.

propanol (99.9% wt., PANREAC). For the electrode in charge of the electrochemistry of hydrogen, a commercial Pt/C catalyst (40 % wt. Pt, Fuel Cell Store) was used. The Pt and Ru loadings on the electrodes were 0.65 mg/cm<sup>2</sup>, same metal precious loading as that used in previous work [16, 18]. The MEA was inserted into the cell between two poly-tetrafluoroethylene (PTFE, GORE®) gasketing to seal the cell assembly.

### 2.2. Electrochemical cell characterization procedure

The electrochemical cell was connected to a potentiostat/galvanostat AUTOLAB PGSTAT 302N. For the operation as fuel cell, all experiments were conducted at potentiostatic mode (constant voltage of 0.5V) and at atmospheric pressure for 20 min. In fuel cell mode, experiments were conducted at different tempera-

tures: 20, 40, 60 and 80 °C. For the operation as electrolyzer, the cell was operated under galvanostatic conditions (constant current density of 100 mA cm<sup>-2</sup>), at atmospheric pressure and room temperature for 100 min. For further characterization, a protocol test was carried out for each temperature and operation mode. This protocol test consists of the following routine: 1) Cyclic voltammeteries (CV): these electrochemical analyses were carried out from -1.7 V to 1.7 V using a sweep rate of 50 mV s<sup>-1</sup>; 2) Potentiostatic polarization curves: they were performed from the OCV to 0.002 V with a scan rate of 100 mV s<sup>-1</sup>; 3) Potentiometric (0.5 V in fuel cell mode) and chronoamperometric (100 mA cm<sup>-2</sup> in electrolyzer mode) tests: carried out for 20 min to evaluate the influence of the temperature in the performance of the fuel cell.

### 2.3. Chemical analysis

To determine the chlorine that reacted, the chlorine was measured at the inlet and outlet (non-reacted) of the cell. The non-reacted chlorine was collected in an absorber with 2M NaOH at the outlet of the cell, and it was measured as hypochlorite by spectrophotometry using an Agilent 300 Cary series UV-Vis spectrophotometer (wavelength of 293 nm). In the case of the experiments with humidified chlorine gas, the chlorine dissolved in the tank with water used as humidifier was determined by an iodometric titration as described elsewhere [19] to determine what was the exact amount of humidified chlorine gas fed to the cell. The pH was measured with a GLP22 Crison pH meter. Further details about chemical characterization can be found elsewhere [16, 18].

## 3. Results & discussion

### 3.1. Operation as reversible cell

Fig. 3 shows the performance of the reversible electrochemical cell when it was used into a sequence fuel cell-electrolysis-fuel cell mode. This comparison is carried out in terms of 1) the current density produced for a cell voltage of 0.5 V, when chlorine and hydrogen gases are both humidified and fed to the electrochemical cell and it operates as a fuel cell, and 2) voltage required to provide 100 mA cm<sup>-2</sup>, when after operating as fuel cell, the feeding of the electrochemical reversible cell is changed to a 2M sodium chloride aqueous solution in both compartments and it operates as electrolyzer.

As seen, the same cell can operate at 20 °C in both modes, giving a stable response which fuel cell operating mode. As it can also be observed, the current density exerted in fuel cell mode is maintained in the range 8.0-14.9 mA cm<sup>-2</sup>, with an average value of 12.4 mA cm<sup>-2</sup> in the first period and 10.8 mA cm<sup>-2</sup> in the second period (range from 8.4 to 17.5), which means that the average operation power as fuel cell is 5.8 mW cm<sup>-2</sup>. This value is higher than those obtained in previous works [18], in which different types of cells were used for the same processes trying to feed the fuel cell with liquids instead of gases. Thus, feeding chlorine dissolved in water into the cathodic compartment and hydrogen dissolved in 2M NaCl the cell yielded powers ranging from 0.61 to 3.65 mW cm<sup>-2</sup> (depending on the size of bubble of hydrogen and use of membrane electrode assembly or separate electrodes and membrane) and 2.43 mW cm<sup>-2</sup> when hydrogen gas was fed into the anodic compartment. In all cases, a solution containing the chlorine was fed to the cathode. All this, points out that strategy proposed in this work for the operation of the reversible electrochemical cell can suit well to the target required. Regarding the electrolyzer mode, operation voltages required to keep 100 mA cm<sup>-2</sup> oscillate between 2.1 and 5.8 V with an average value of 4.5V. These values are a little bit higher than the approx. 3.5 V obtained for a separate compartment cell fed with 2M NaCl, in

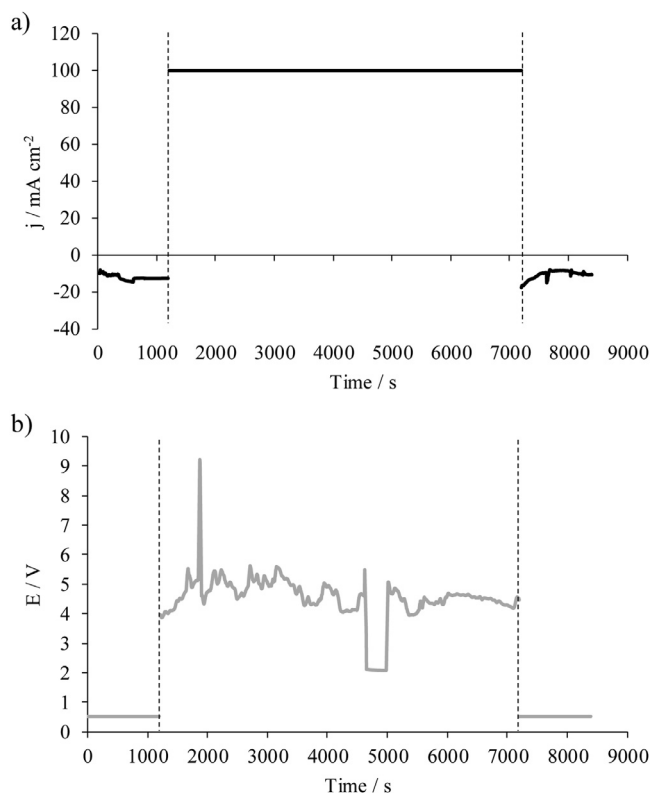


Fig. 3. Performance of the reversible electrochemical cell during the operation of the cell with the sequence fuel cell-electrolyzer-fuel cell at 20°C. a) Current densities and b) cell voltages recorded. Chlorine and hydrogen were both humidified and fed in the operation as fuel cell (0.5V). Aqueous solution with NaCl 2M were added to both compartments of the cell in the operation as electrolyzer (100 mA cm<sup>-2</sup>).

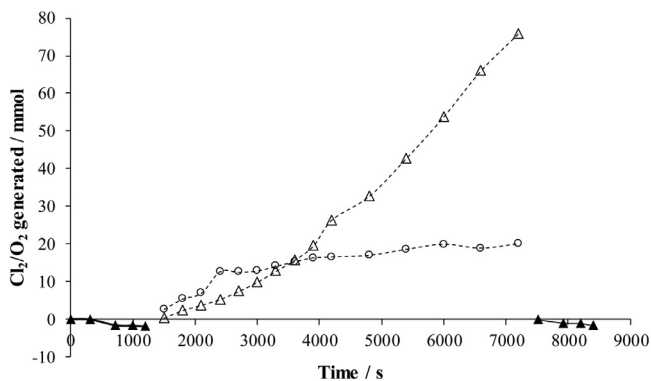


Fig. 4. Speciation during operation in fuel cell and electrolyzer mode. ○ the cumulative oxygen production in electrolyzer mode; △ the cumulative chlorine production in electrolyzer mode; ▲ the cumulative chlorine consumption in fuel cell mode.

which a previous study on the composition of the anode was made [16] but similar to the approximately 4.5 V reached in this system with gas feeding, pointing out the good design of the MEA. An interesting observation is that current density increases just after changing from electrolyzer to fuel cell mode, which indicates that hydration of the membranes is required for a proper operation and that using liquid electrolyte helps in the first moments to obtain a good performance, that later is stabilized.

Fig. 4 shows the speciation obtained in fuel cell and electrolytic modes. Thus, during electrolysis tests, the Cl<sub>2</sub> and O<sub>2</sub> produced were measured, whereas, in the fuel cell tests the chlorine consumed was measured. It is important to state that this chlorine is calculated by difference between the chlorine fed and the chlorine

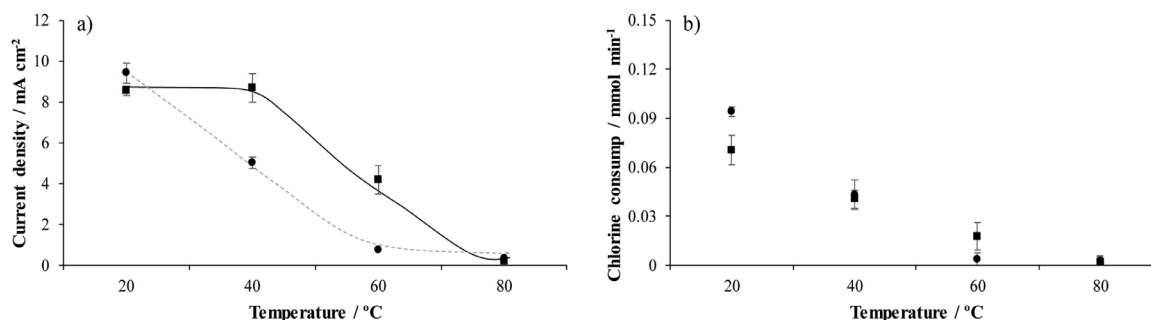


Fig. 5. Influence of temperature on current density (part a) and chlorine consumption (part b) during operation at different temperatures: ● No humidification ■ humidified

retained in an absorption tank containing 2 M NaOH, placed just at the outlet of the cell and as it is not possible to retain all the surplus chlorine from the electrochemical cell, the chlorine gas is measured at the outlet of the absorption tank by means of a gas flowmeter. The rate of consumption of chlorine was 5.37 mmol h<sup>-1</sup> in the first period of operation as fuel cell and 5.23 mmol h<sup>-1</sup> in the second (after the cell was operating in electrolysis mode). From these data, it was obtained a coulombic efficiency of 93.2 % for the first period and 90.9 % for the second period. On the other hand, the rate of production of chlorine was 45.4 mmol h<sup>-1</sup> (1.82 mmol h<sup>-1</sup>cm<sup>-2</sup>), value which is very close to the maximum faradic rate for the applied current density (46.6 mmol h<sup>-1</sup>), indicating a current efficiency of 97.3 %. This speciation demonstrates the feasibility of this technology, feeding the same cell sequentially with gases in the operation as fuel cell and with liquids as electrolyzer, which becomes an important point for its use in the storage of energy.

Combining the information obtained from energy and speciation measurements, the specific efficiency of this reversible fuel cell can be calculated. In the case of the fuel cell mode the average value considering the two times that the cell was operating as fuel cell is around 26.0 Wh/mol Cl<sub>2</sub>. In the operation as electrolyzer, the obtained value is 4.05 mmol Cl<sub>2</sub>/Wh. Regarding the formation of oxygen, which is a non-desired byproduct in the electrolyzer operation mode, the O<sub>2</sub> formation was also measured and is also shown in Fig. 4. During a first stage, the production of oxygen is more favored than that of the chlorine, obtaining a Cl<sub>2</sub>/O<sub>2</sub> ratio, in molar units, of 0.42. Then after 1200 s, the situation reverses and the ratio increases up to 9.54 which is much higher than the values obtained in a previous work [16], where it was obtained a maximum Cl<sub>2</sub>/O<sub>2</sub> ratio of approximately 3.5.

### 3.2. Influence of operation temperature and humidification in the operation as fuel cell

Fig. 5 compares the average current densities obtained at four different temperatures when 0.5 V are fixed as operation target of the fuel cell and with the chlorine stream humidified and non-humidified. All tests were made in duplicate (with two different MEAS made with the same procedure, each) and error bars inform about the differences between tests. As seen, increasing temperature has a negative effect on the current produced. This decrease is very noticeable when the chlorine streams is not humidified and makes the current obtained almost negligible at 80 °C. Same trend is observed when the chlorine stream is humidified but, in this case, the system can operate successfully at 40 °C, yielding currents that are like those recorded at 20 °C.

Regarding to chlorine consumed (Fig. 5b), important differences are found within the complete range of temperatures tested. As it can be observed in Fig. 5b, the chlorine consumption decreases with temperature for both cases studied, humidified and non-humidified chlorine stream. However, this decrease is less stressed

when it was worked under humidification conditions. As the operating temperature was increased, considerable differences in consumption are observed, being 18 % higher for the system working with humidified chlorine at 60 °C as compared to the same operation conditions using non-humidified chlorine.

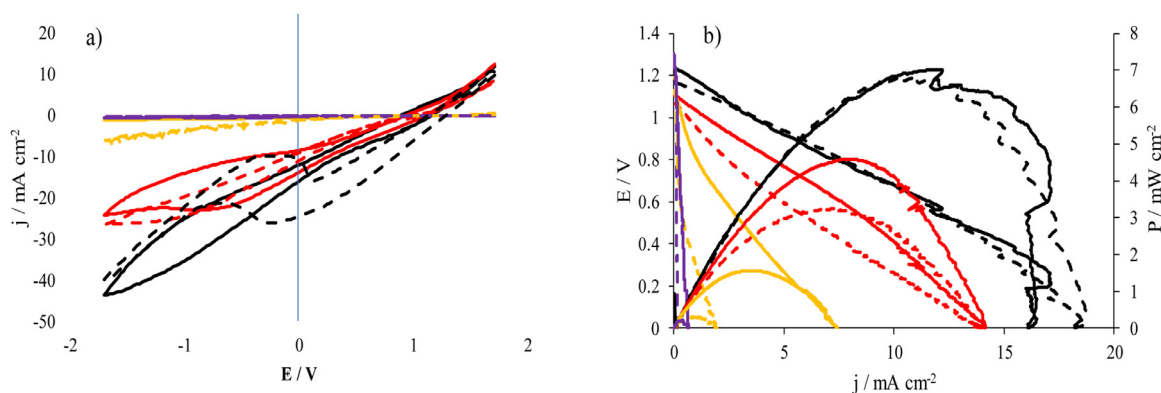
The efficiency of the system in terms of Wh mol<sup>-1</sup> of chlorine was calculated. Thus, obtained values ranged from lowest 16.7 Wh mol<sup>-1</sup> obtained at 20 °C in the cell fed with chlorine without humidification to the highest 39.6 Wh mol<sup>-1</sup> obtained at 60 °C in the cell fed with humidified chlorine. In the tests shown in Fig. 3, values as high as 26.3 Wh mol<sup>-1</sup> were reached, which means that reproducibility of results is high. These values are high as compared to other previously reported in the literature [16, 18]. Thus, values from 0.05–0.5 Wh mol<sup>-1</sup> have been recently reported for this type of cells. Moreover, these results point out that the humidification of the chlorine stream is recommended when the temperature is increased until a certain value.

Fig. 6 shows the voltametric behavior and the polarization curves drawn after the operation tests in fuel cell mode at different temperatures, when the chlorine stream is fed without or with previous humidification. As seen, the differences are not only found at high temperatures but also in the lower range of temperatures with peaks more clearly marked in the case of the humidified chlorine. Regarding polarization curves, a plot was made to clearly see the huge differences obtained and which support the necessity of operation at low temperatures when using this technology, because of the much worse results obtained at temperature over 40 °C. On the other hand, the domination of voltametric curves by linear regions (Fig. 6a) projects ohmic control, this tendency being greater as the temperature of the system increases, regardless of the chlorine stream fed to the cell. This increase in temperature causes a dehydration of the membrane, which is reflected in the ohmic resistance of the system, obtaining a minimum value of 535 mΩ when working at 20 °C and a maximum value of 15.7 Ω at 80 °C.

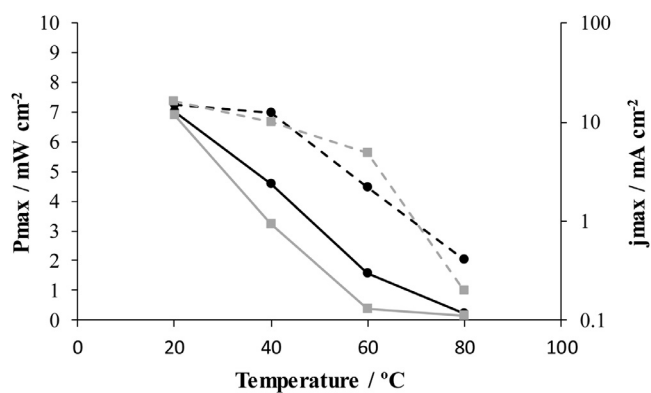
From the polarization curves, two important parameters (maximum power density and maximum current density) are obtained and compared in Fig. 7.

Thus, the maximum power which can be yielded by the fuel cell is around 7.0 mW cm<sup>-2</sup>, which is 3 times higher than the value obtained using a cell in which the anolyte consists of chlorine dissolved into 2M NaCl solution and the cathode is fed hydrogen gas stream, and 14.3 % higher than the value obtained using an electro-absorber fed with fine bubbles of H<sub>2</sub> in NaCl 2.0 M aqueous solution and chlorine dissolved into 2M NaCl solution. It is also important to see that the maximum current densities reachable are over 10 mA cm<sup>-2</sup>, which it is a really good value for practical purposes [16].

In electrolyzer mode, liquid is fed to both compartments of the electrochemical cell and, hence, it is not expected dehydration of the MEA with the operation at high temperature. Conversely, in



**Fig. 6.** Voltammeteries (Part a) and polarization curves (part b) drawn after operation at 20°C (continuous black), 40°C (red), 60°C (yellow) and 80 °C (purple). Discontinuous line: humidified chlorine. Continuous line: chlorine without humidification



**Fig. 7.** Maximum power density (continuous line) and maximum current intensity (discontinuous line) reached by the systems fed with non-humidified (circles) and humidified (squares) chlorine stream.

operating in fuel cell mode with both chlorine and hydrogen fed in gaseous streams, this problem may become important, especially when temperature approaches the boiling point of water. So, in order to make the system easier it was studied the effect of the humidification of the fed streams when the cell operated in fuel cell mode. When hydrogen stream is not humidified, the cell does not work after a very short period, even at 20 °C. So, it can be claimed that is mandatory humidify the hydrogen stream. On the other hand, Fig. 8 shows the effect of the humidification of the chlorine stream.

Thus, as shown in Fig. 8, the operation current densities of the fuel cell at 20 °C during its first use is quite similar, regardless of the humidification of the chlorine stream, and therefore the average current density was 9.41 mA cm<sup>-2</sup> for non-humidified and 8.55 mA cm<sup>-2</sup> for humidified chlorine stream. This means that with the humidity of the hydrogen stream is more than enough to warrant a suitable operation of the fuel cell. However, when the cell is operated at higher temperature and, then operation temperature comes back to 20 °C, there is an important loss of performance characteristics which, in addition, seems to be irreversible, because the operation current densities do not recover the initial values.

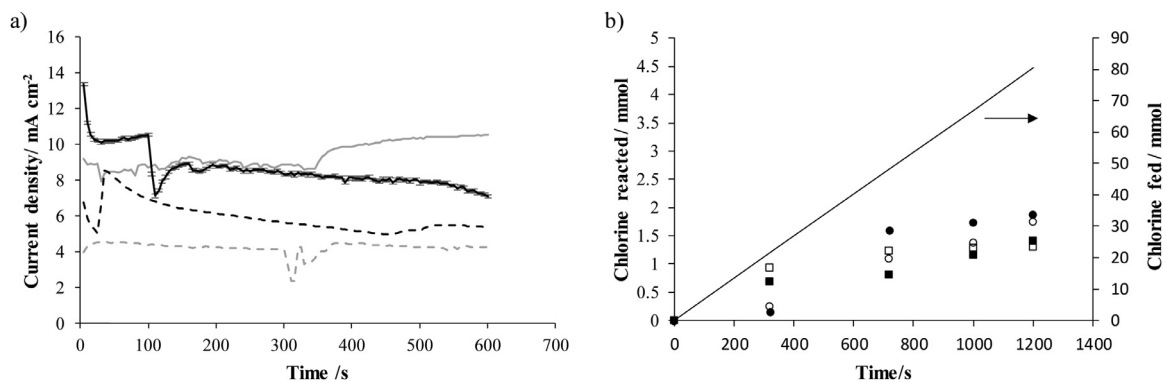
In fact, the current density decreases continuously in both systems, and there is an abrupt change for longer times in the system without chlorine humidification. Thus, the average current density decreases by an 74.3% without humidification (from 12.3 down to 3.2 mA cm<sup>-2</sup>), which means 2.3 times higher than when the systems are humidified (the decrease here was from 8.3 down to 5.6

mA cm<sup>-2</sup>). Hence, the recovery in the humidified system is better than in the system operated with the dry chlorine stream, although not enough and advises against the use of high temperatures with this system equipped with MEAs based on Nafion. Regarding chlorine consumed, there are no significant differences associated with the humidification when operating a 20 °C. However, the consumption decreases when the cell has undergone operation at high temperature without humidification. Also, worth to point out that current densities reached with humidification with the pristine system are substantially lower than in the dry system with a decrease of 33%, which can be explained in terms of the dilution of the chlorine reagent with water.

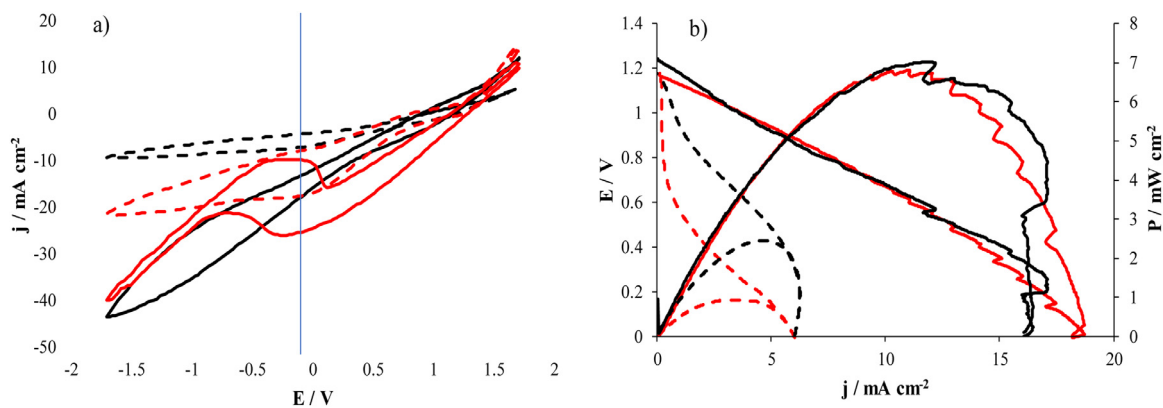
Fig. 9 shows the voltamperograms and the polarization curves obtained just after finishing the operation tests. As seen, there are no important differences between the behavior of the system, which does not undergo an increase in the temperature, although the peaks for the reduction of chlorine are less clearly observed and seems to shift to higher overpotentials when the chloride stream is not humidified. However, in the systems with MEAs which operated at high temperature, current values are much lower, in particular in the case in which no humidification of the chlorine stream is carried out, suggesting an increase in the resistance, which can be associated to the dehydration of the membrane and to the irreversible loss of properties. Anyway, despite the reduction in size, the reduction peak is observed at the same voltage.

Regarding polarization curves, not relevant differences are found between the maximum power density and the maximum current density when the systems are operated only at 20 °C. After operation at higher temperature, the maximum power yielded by the cell decreases importantly, especially in the case of the cell fed with non-humidified chlorine, although the maximum current density is similar in both cases, regardless of the humidification, which means that: 1) the decrease in the resistivity is similar in both cases as the OPC is the same and 2) that differences are mainly produced in the first zone of the polarization curve.

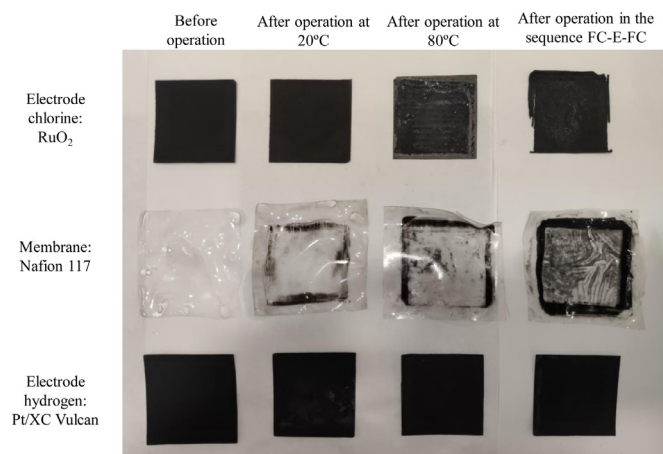
On the other hand, Fig. 10 shows a picture of the components of the cell before and after operation at different temperatures (20°C and 80°C), when they were used in FC-E-FC mode and where it can be seen how the operation at high temperatures damages the electrode in charge of the electrochemistry of chlorine in the surface that is facing the membrane but not the membrane or the other electrode, which apparently remains with the same initial properties. Strong oxidizing power of chlorine and its effect on the electrode components at high temperature advises in favor of the further study of the composition of this electrode to achieve a higher robustness and stability.



**Fig. 8.** Changes in the current density (part a) and chlorine consumption (part b) during operation at 20 °C at different conditions (constant cell voltage of 0.5V). ■ No humidification first use (black continuous line in part a) □ no humidification after operation at 80°C use (black discontinuous line in part a) • humidified first use (grey continuous line in part a) ○ humidified after operation at 80°C use (grey discontinuous line in part a). Continuous line in part b: chlorine fed. H<sub>2</sub> and Cl<sub>2</sub> flow rates: 0.1L min<sup>-1</sup>



**Fig. 9.** Voltammeteries (part a) and polarization curves (part b) obtained after performance tests. Discontinuous: after operation at 80°C; Continuous: operation only at 20 °C. Red: humidified; black: non humidified. Scan rate: 100 mV s<sup>-1</sup>.



**Fig. 10.** Pictures of the components of the cell before operation, after operation only at 20 °C and after use at high temperatures and after use in a sequence fuel cell-electrolyzer-fuel cell.

#### 4. Conclusions

From this work, the following conclusions can be drawn:

- It is possible to operate in reversible mode a PEM fuel cell with the chloralkali process feeding gaseous chlorine and hydrogen in the operation as fuel cell and an aqueous solution 2M in NaCl in the operation as electrolyzer.
- Operation of the reversible cell in electrolyzer mode feeding 2M NaCl aqueous solution allows to obtain 45.4 mmol/h of chlorine

with a current density of 100 mA cm<sup>-2</sup>. During a first stage, the production of oxygen is more favored than that of the chlorine with a Cl<sub>2</sub>/O<sub>2</sub> ratio in molar units of 0.42. Then, the situation reverses and the ratio increases up to 9.54.

- Operation of the reversible cell in fuel cell mode feeding gaseous chlorine and hydrogen allow to obtain 12 mA cm<sup>-2</sup> at 0.5 V. This average value is maintained after operation as electrolyzer. Regarding the maximum power reachable with this device is 7.0 mW cm<sup>-2</sup> which is much higher than that obtained with the same system fed with hydrogen and chlorine dissolved in liquid electrolyte. Regarding specific power, in the operation as fuel cell was near to 26 Wh/mol Cl<sub>2</sub> and in the operation as electrolyzer the value obtained is 4.05 mmol Cl<sub>2</sub>/ Wh.
- The humidification of hydrogen stream is mandatory, whereas in the case of the chlorine stream is recommended to enter the system, thus improving the performance of the fuel cell at high temperatures. Regarding the efficiency, the maximum value was 39.6 Wh mol<sup>-1</sup> with humidified chlorine, being twice times higher than the value obtained without chlorine.
- Temperature affects negatively to the performance of the reversible cell operating in fuel cell mode, decreasing importantly the efficiency and in an irreversible way, being not possible to recover the initial performance after reduction of temperature.

#### Declaration of Competing Interest

On behalf of all coauthors, I declare that this paper has no conflict of interest. It was only submitted to this journal and the financial supporting agencies have been included in the acknowledgements. The file submitted has been approved by all coauthors.

### Credit authorship contribution statement

**Mireya Carvela:** Investigation, Methodology, Writing – original draft, Formal analysis. **Justo Lobato:** Writing – review & editing, Supervision, Validation, Data curtion, Writing – review & editing. **Manuel Andrés Rodrigo:** Writing – original draft, Writing – review & editing, Supervision, Validation, Funding acquisition, Project administration.

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