Improving stability of chloralkaline high-temperature PBI-PEMFCs

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Abstract

This work focuses on the production of electricity using chloralkaline high temperature PEM fuel cells (HT-PEMFC) comparing, within the range 120-180 ºC, the performance of a cell equipped with a cathode containing a novel Ru/Pt catalyst manufactured at mild temperature conditions with another cell which contains a conventional Ru based catalyst (Ru$_{0.75}$Pt$_{0.25}$O$_2$). Performance of the cell equipped with the conventional electrode at 120 ºC is much better, but this situation reverses at higher operation temperatures, where the novel catalyst outperforms the conventional Ru$_{0.75}$Pt$_{0.25}$O$_2$ in terms of production of electricity. In addition, the new catalyst allows to operate even at 180 ºC, temperature at which the cell equipped with the conventional electrode is completely deteriorated. Results pointed out that materials are the bottleneck for the chloralkaline HT-PEMFC technology but opens the window for the search of new materials that help to improve their future development.

Keywords

PBI; high temperature PEM fuel cells; ruthenium catalyst; chloralkaline fuel cells
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Introduction

Energy storage is becoming a topic of the major interest. Because of the fast development and reinforced implementation of renewable energies[1], many technologies are being exhaustively studied, trying to find a suitable and sustainable solution to this challenge. Hydrogen storage has always been seen as the most environmentally-friendly alternative, but there are still many shortcomings that prevent its widespread application[2]. Nonetheless, currently technology is at TRL 9, with all the value chain fully developed and there is a plethora of key-on-hand commercial solutions.

However, research effort is increasing, because there is still room for improvements in electrolyzers and fuel cells that integrate the complete energy storage device. In this context, one of the most interesting developing alternatives for the hydrogen storage technologies consists of the use of the pair oxidant-fuel chlorine-hydrogen instead of the more conventional oxygen-hydrogen, both in the electrolyzer and in the fuel cell stages of the storage system[3]. Comparing this novel technology (hydrogen-chlorine) with the conventional process (hydrogen-oxygen), using chlorine as oxidant in a fuel cell presents advantages, which affect positively the performance of the fuel cell, such as fast kinetics and high standard potential. The equation 1 shows the global reaction is carried out in this system of the energy storage (see in Figure SM1):

\[
\text{charge} \quad \text{HCl}_{(aq)} \Leftrightarrow \text{H}_2(g) + \frac{1}{2} \text{Cl}_2(g) \quad E^0 = 1.36 \text{ V} \quad (1)
\]

It is important to highlight that the electrolytic conversion of hydrochloric acid or sodium chloride is a thoroughly evaluated process, because it is the base of the chloralkaline industry[4]. This process is based on the electrolysis of sodium chloride to produce hydrogen and chlorine, which are gases that can be used to generate electricity when it is
required [4]. Furthermore, this system can be coupled to renewable energies (such as solar panel), lowering production costs, and achieving a fuel that is sustainable with the environment (green hydrogen) [5]. However, the reverse process has been more superficially tackled and, unfortunately, few works can be found in the recent literature [6]. Thus, the higher redox potential of this pair is expected to lead to a better electrochemical performance during the operation in fuel cell mode, although materials deterioration has been highlighted as a major obstacle [7-10]. Anyhow, recent works have demonstrated that it is still a very interesting alternative, achieving up to 12 mA cm$^{-2}$ of current density and 7 mW cm$^{-2}$ of power density at 20ºC, similar values to those obtained at 40ºC [11]. However, working in this type of fuel cell deserves further studies. Thus, results obtained using electrochemically assisted absorbers have been recently found as very promising [12, 13], allowing to reach high efficiencies in the operation of chloralkaline fuel cells fed with liquids, without significantly damaging the materials of the cell over the duration of the tests made.

In this context, the use of higher temperatures is also seen as a promising option [14], although, again, materials robustness is seen as a major technological bottleneck. Ruthenium oxides are important catalysts for the modification in the oxidation state of chlorine, but these catalysts may have a negative influence on the service lifetime of the cell because they are known to promote the production of species that damages the PBI (polybenzimidazole) membrane [14]. Considering the very high oxidation potential of chlorine, in this work the use of a new type of cathode is proposed in which, instead of using a conventional ruthenium/platinum oxide catalyst, both metals are distributed in the electrode in softer conditions (a mixture of ruthenium chloride ($\text{RuCl}_3$) and chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot (\text{H}_2\text{O})_6$) is spread on the carbonaceous support of the cathode followed by a mild thermal treatment at temperatures below 200 ºC). Trying to see if it
can successfully activate the chemical chlorine reduction, while leading to a more robust fuel cell performance. The promising obtained results have pushed us to show these preliminary results, in which the evaluation of the operation of the fuel cell with the two cathodes at increasing temperatures ranging from 120 to 180 ºC is compared.

Materials and Methods

The experimental set-up used in this work has an area of electrodes of 25 cm². Further details about the experimental set-up can be found elsewhere [15, 16]. Three Membrane Electrode Assemblies (MEAs) were made in this work for comparison purposes, named as MEA₁, MEA₂ and MEA₃. The electrodes were made by depositing different catalytic inks onto carbon paper and the MEAs were manufactured by hot pressing the electrodes with a commercial PBI membrane, which is doped with phosphoric acid (85% v/v) used as electrolyte, according to a procedure described elsewhere[12, 13]. The same catalyst was used for the anode, it consisted in a commercial Pt/C (40 % wt, Fuel cell store). The three assemblies were equipped with a Pt loading of 0.5 mgPt cm⁻² anode manufactured by dissolving commercial Pt/C catalyst into 30 mL of N, N-Dimethylacetamide (DMA) and spreading it by airbrushing onto a 5x5 cm² carbon paper electrode (H23C2 GDL, Freudenberg, Germany) in two sequential batches. After each of the two spreading steps, the paper was placed on a heating plate at 130ºC for 30 minutes for evaporation of the solvent. Same procedure was followed to manufacture the electrode used as cathode in MEA₃. Regarding the other cathodes, MEA₁ was prepared with 0.65 mg cm⁻² Ru₀.₇₅Pt₀.₂₅O₂ /C and MEA₂ with 0.5 mg cm⁻² RuCl₃ - H₂PtCl₆· (H₂O)₆/C. For the first electrode, Ru₀.₇₅Pt₀.₂₅O₂ catalyst was synthesized by the Pechini method and then, it was dissolved into DMA with PBI (2.5% w/w). 30 mL of this ink were spread by air brushing onto a 5x5 cm² carbon paper in two batches with intermediated evaporation of the solvent.
by placing the paper on a heating plate at 130°C for 30 minutes. For the second electrode, the catalytic ink consists of a mixture of RuCl₃ and H₂PtCl₆·(H₂O)₆ (molar ratio 3:1) and PBI (2.5 w/w) on DMA. As in the previous case, 30 mL of this ink were spread by air brushing onto a carbon paper (5x5 cm²) in two sequential batches. After each of the two spreading steps, the paper was placed on a heating plate at 130°C for 30 minutes for evaporation of the solvent. After that, the paper underwent thermal treatment for 2 hours at 180°C in an oven (Figure SM2 in Supplementary Materials).

For the operation as fuel cell, the electrochemical cell was connected to a potentiostat/galvanostat AUTOLAB PGSTAT 302N. The two first MEAs were conducted feeding with hydrogen gas (99.99%, PRAXAIR) and chlorine gas (99.9999%, CARBUROS METÁLICOS) at atmospheric pressure for 20 min and, while the third was operated feeding oxygen gas (99.995%, AIR LIQUID), instead of chlorine, just for comparison of the hydrogen-oxygen with the hydrogen-chlorine technology, and at atmospheric pressure for 10 min. When the fuel cell operated with MEA₁, experiments were carried out at a constant voltage of 0.5V (potentiostatic mode) and at a temperature range between 120-160 °C. The MEA₂ was conducted under galvanostatic conditions (constant current density of 20 mA cm⁻²) and at different temperatures: 120, 140, 160 and 180 °C. For experiments were carried out with MEA₃, the cell operated at a constant current density of 60 mA cm⁻² (galvanostatic mode) and an operating temperature of 120 °C. For further characterization, before and after each membrane-electrode assembly used and temperature a protocol test was carried out. In the first place, cyclic voltammetry (CV) measurements were performed at the potential limits of -1.7 V to 1.7 V with a scan rate of 50 mV s⁻¹. Then, linear sweep voltammetry (LSV) tests were carried out from the OCV to 0.002 V at 100 mV s⁻¹. Finally, experiments were carried out for 20 min for
MEAs and MEA3 were analyzed for 10 min to evaluate both the influence of the type of assembly used and the temperature.

**Physical characterization.** The morphological characteristics of the electrodes were visualized with the aid of a Scanning Electron Microscope (SEM). The elemental chemical composition of the layers of the electrodes was studied through energy-dispersive X-ray (EDX) spectroscopy coupled to SEM equipment. Analyses were performed using a JEOL JCM 5700 at a 10 kV voltage with 80000x magnification.

**Electrochemical characterization.** The electrochemical measurements were performed in a conventional three-electrode cell connected to a potentiostat/galvanostat AUTOLAB PGSTAT 302N. The counter electrode was a platinum (Pt) wire, an Ag/AgCl as reference electrode and a working electrode of 2 cm² of geometrical area which consisted of RuCl₃-H₂PtCl₆·(H₂O)₆/C anode. Consecutive scans (CV measurements) to determine the morphology of the electrode were carried out with potential limits of -0.5–1.30 V with a scan rate of 50 mV s⁻¹ in a 1 M hydrochloric acid solution at room temperature. The electrocatalytic activity of the anode towards Chlorine Evolution Reaction (CER) was studied by means of (LSV) performed from 0.01 to 1.50 V (vs Ag/AgCl) reference electrode at 1 mV s⁻¹. The Electrochemical Impedance Spectroscopy (EIS) experiments were obtained applying potential 1.12 V (determined from LSV analysis corresponding to the CER onset potential), covering a frequency range between 0.01 Hz–10000 kHz and using an amplitude signal of 10 mV.

**Results and Discussion**

Figure 1 shows the electrochemical characterization of the novel electrode used as cathode in MEA₂. This characterization consisted of a half-cell study in hydrochloric acid 1.0 M electrolyte using a platinum counter electrode and Ag/AgCl as reference electrode. The linear sweep voltammetry (Figure 1a) shows three oxidation peaks at approximately
0.15 (Peak 1), 0.55 (Peak 2) and 1.05 V (Peak 3) vs Ag/AgCl, which may be related with the oxidation of Ru (II) to Ru (III), from Ru (III) to Ru (IV) and from Ru (IV) to Ru(VI) [17, 18]. At high potential (> 1.25 V), Oxygen Evolution Reaction (OER) is shown on the surface, while the CER potential is observed around 1.1-1.2V. In the cyclic voltammograms shown in Figure 1c, it is seeming how the first peak increases after the first cathodic scan confirming the formation of Ru (II) species which should be almost negligible in the pristine electrode. Also, it is important to note the decrease in the height of the cathodic peak associated to Ru (IV) which can be explained in terms of the non-reversibility of the reduction of the RuO$_2$ formed. Moreover, the activation of the first peak which may correspond to the transition between Ru (II) and Ru (III), as Doblhofer et al.[19] suggested. In addition, it is worth noting the fast stabilization in the dynamic response, after the first oxidation scan, which indicates that no electrochemical-chemical processes are occurring in the system during the linear sweep and cyclic voltammetries. The decrease in the height of peaks after the use of the electrode indicates the stabilization in the catalytic layer after its use. Important to state that in this case, no significant differences are observed among the different cycles. Regarding the EIS measurements (Nyquist plot) (Figure 1b), which was carried out at the potential of 1.12V vs Ag/AgCl corresponding to the CER onset potential (the choice of the potential was based on the CV data), the two semicircles may indicate the existence of a double catalytic layer which can be related with the ruthenium and the platinum sprayed onto the carbon paper, which is used as electrode material. The semicircle at the high-frequency range (inset on Figure 1b) suggests a contribution of the inner surface of the coating. Hence, the methodology used to prepare the electrode is able to generate a surface in which the spread metals are active. Furthermore, this plot obtained was fitted with a characteristic equivalent circuit, being $R_\Omega$ to solution resistance, $R_{p1}$ and $R_{p2}$ to charge-transfer resistances, and $Q_{f1}$ and
Qf2 to the pseudo-capacitances (represented by a constant phase element (CPE) due to the heterogeneous nature of the surface of the electrode). The RΩ is 0.93 Ω, whose value is 100 times less than a conventional electrode [20]. Rp1 and Rp2 are related to the oxide film, attributing each of the resistances to the metals dispersed individually (Ru and Pt), obtaining resistance values of 2.35 and 21.6 Ω, respectively. These values are lower than for pure compositions of Ti/RuO2 (74.1 Ω) [21]. The pseudo-capacitances show us that the surface of the electrode is very rough and heterogeneous (Qf1= 0.33 mF and Qf2=0.11 F). It is important to analyse the electrode after its use in the fuel cell, which worked up to 180ºC (Figure 1d). The response to cyclic voltammetry measurements is very different than expected. In this case, the size of the metallic Ru peaks decreased, suggesting a slight decrease in the coating, as can be seen in the SEM images (Figure 5c-d), which are later displayed and analysed.
Figure 1. Electrochemical characterization of the novel Ru/Pt electrode used in MEA$_2$ in half cell in HCl 1.0M. Reference electrode Ag/AgCl; Counter electrode: Pt. a) linear sweep voltammetry of the pristine electrode at a scan rate of 1 mV/s; b) EIS recorded at 1.12 V 10-10000 Hz; c) cyclic voltammetry of the pristine electrode at scan rate of 50 mV/s for 10 cycles; d) cyclic voltammetry of the electrode after operation in the fuel cell at scan rate of 50 mV/s for 10 cycles. Inset: expanded view of high frequency region.

Figure 2 compares the performance of the three fuel cells equipped with the PBI based MEAs prepared in this work to operate at high temperature (120 °C). Two of them were fed with chlorine and hydrogen (MEA$_1$ and MEA$_2$) and the other with oxygen and hydrogen (MEA$_3$). As seen, the type of oxidant fed is relevant for the OCV which, as expected, is higher when using chlorine. In turn, because of the similar ohmic loses (reflected on the slopes of the E vs j plot), this higher OCV makes that the maximum power density, and also the maximum current intensity which can be achieved, are higher when chlorine is fed, pointing out the most important advantage of chloralkaline fuel cells and, hence, why it is important their development. As shown in Part b of the Figure 2, this is reflected on the performance during operation, in which it can be noticed that, for similar conditions, the power obtained in the system fed with chlorine (MEA$_1$) is almost three times higher than the reached feeding oxygen as oxidant (MEA$_3$).
Figure 2. Comparison of hydrogen-chlorine and oxygen chlorine fuel cells operated at 120 °C. A) polarization curves; b) power exerted during operation. Black Continuous Line: H$_2$-Cl$_2$ fuel cell equipped with MEA$_1$. Grey Continuous Line: H$_2$-Cl$_2$ fuel cell equipped with MEA$_2$. Black dotted Line: H$_2$-O$_2$ fuel cell equipped with MEA$_3$.

Regarding the other cell for which results are shown in the Figure (MEA$_2$), performance is much worse. In this cell, instead of using a conventional electrode with a platinum ruthenium oxide coating, and considering the strongly oxidative conditions reached in the nearness of this electrode, a novel electrode was proposed, trying to see if this processing shows catalytic properties and if the action of the chlorine oxidants during operation may exhibit an advantage regarding stability, avoiding one of the key problems found for the chlorine-hydrogen technology at high temperatures: the damage of the membrane. As seen, resistance of the cell (related to the slope of the V vs j plot) is much higher in this case and this fact reflects on a worse performance at this temperature. Nevertheless, it is interesting to see that, despite this worse performance at 120 °C, there is an important production of electricity which indicates a suitable performance of the catalysts on the surface of the cathode during the operation of the cell.

Both fuel cells fed with chlorine followed sequential tests at higher temperatures within the ranges typically used for PBI based fuel cells (up to 180 °C). Figure 3 shows their performance at 140, 160 and 180 °C. As stated before, it is clear that at low temperatures the system with the conventional electrode (MEA$_1$) outperforms the system with the ruthenium chloride catalyst (MEA$_2$). However, as the temperature increases the situation reverses and the cell equipped with the MEA$_2$ starts showing better results.
Figure 3. Comparison of the performance of the two Cl\textsubscript{2}-H\textsubscript{2} fuel cells operated at higher temperatures (140-180 °C). Black continuous lines MEA\textsubscript{1} (at constant voltage); Grey continuous lines MEA\textsubscript{2} (at constant current density). a) Operation performance during short time operation at the four temperature ranges: Continuous line: current density; Discontinuous line: cell voltage. b) Comparison of polarization curves. Continuous line: 140°C; discontinuous line 160 °C

In addition, the conventional system breakups during the operation at 160°C, while MEA\textsubscript{2} did not suffer any relevant change in the production of electricity and even it shows a better performance associated to a lower resistance at this temperature. This better performance is also seen in the polarization curves, which are compared for both cells after the operation tests and which demonstrates that temperature does not have a positive influence on results and that the new electrode outperforms the conventional ruthenium oxide coating electrode, demonstrating its good characteristics for the operation at higher temperatures. Even, a decrease in the cell voltage was observed at 180 °C, being the system capable to keep the intensity in the required value.

Figure 4 compares the voltametric behavior of the two Cl\textsubscript{2}-H\textsubscript{2} fuel cells in the temperatures range from 120 to 160 °C. As seen, the electrochemical response is highly dependent on the temperature.
Figure 4. Cyclic voltammetries of MEA$_1$ (black line) and MEA$_2$ (grey line) after each of the tests carried out within the range 120-160 °C. Inset: zoom view of CV measurements in the range 0-1V.

For the case of the conventional Ru$_{0.75}$Pt$_{0.25}$O$_2$ electrode (MEA$_1$), there is a decrease in the activity with the increase in the temperature, while for MEA$_2$ there is an important increase up to 140 °C, and then a decrease in 160 °C. Although, the response in those conditions is even much higher than that obtained at 120 °C. As highlighted in the inset, the current provided in the operation as fuel cell does not differ at 140 and 160 °C and they are much higher than those obtained with MEA$_1$ pointing out the good performance of these electrodes in this high range of temperatures and their promising features for future work, trying to optimize the performance of the chlorine-hydrogen fuel cells for the improvement in the chloralkaline storage of energy.

Figure 5 shows the SEM images of pristine and postmortem (referring to the electrode used in the fuel cell that worked up to 180°C and lowered the operation temperature to
120°C, showing its irreversibility) electrodes of MEA_2. Besides, the EDX spectra and a map of the pristine electrode are also shown.

Figure 5. SEM images and EDX spectrum of MEA_2 electrodes before their use: a), b), and postmortem: c) and d).

It can be observed that the Ru based catalysts are on the outer surface of the electrodes and mask the platinum catalyst. Moreover, the surface of the electrode changed after it used as it can be determined from the comparison of pristine and postmortem electrode (Figure 5a and Figure 5c). Thus, the particles that appear clearly in the pristine electrode do not appear as clear in the used electrode. Moreover, the EDS data (Table SM1) shows the peak of Pt appears when an energy of 25 kV is applied in the microscope, which means that the Pt compounds are not in the outer surface of the electrode.

On the other hand, Figure 6 shows the SEM images of the pristine and postmortem Ru_{0.75}Pt_{0.25}/C based electrodes used in MEA_1. It is observed that the surface of the electrode changed after its use in the fuel cell and the particles of catalyst observed clearly in the pristine electrodes are not observed so clear after its use, suggesting that those
particles would have sintered or melted, because of the harsh conditions that occur in the electrode surface during the operation of the fuel cell, those are high temperatures (180 °C) and phosphoric acid as electrolyte.

![SEM images of electrodes](image)

Figure 6. a) SEM images of electrodes Ru$_{0.75}$Pt$_{0.25}$/C before their use and, b) SEM images of electrodes Ru$_{0.75}$Pt$_{0.25}$/C postmortem.

Furthermore, semiquantitative EDS data (Table SM2) shows the presence of C, O, Ru, Cl and Pt in the deposited oxide film. From the EDX spectra it can be observed that in this case, characteristic peaks of Pt were not observed in the postmortem electrodes even applying very high energies in the microscope. This could explain the low performance obtained at high temperatures. As it has been pointed out in previous works[3, 12, 13], Pt has a positive effect in the chloralkaline reversible electrochemical cells, and the better performance obtained with MEA$_2$ can be explained in terms of the higher retention of active platinum.

**Conclusions**

Chloralkaline fuel cells equipped with phosphoric acid doped PBI membranes can be successfully operated at temperatures above 100 °C feeding gaseous chlorine and hydrogen without humidification, overcoming the performance of H$_2$-O$_2$ PBI based PEM fuel cells. Use of Ru$_{0.75}$Pt$_{0.25}$O$_2$ is advantageous at 120 °C but the MEA is broken at 160 °C. Opposite, the use of a novel electrode made by mild thermal processing of directly
spread ruthenium chloride / chloroplatinic acid hexahydrate catalyst onto the cathode surface allows the operation up to 180 °C showing much better performance than the ruthenium-platinum oxide catalyst at temperatures within the range 140-160 °C. These results are promising and ask for further work trying to optimize the performance of high temperature chloralkaline storage of energy.

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References


