Effects of Ammonia Impurities on the Hydrogen Flow in High and Low Temperature Polymer Electrolyte Fuel Cells

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Abstract

Fuel cells are a promising technology to use as a source of electricity and heat for buildings, and as an electrical power source for electric motors propelling vehicles. They consume hydrogen as fuel and oxygen to produce electricity, heat and water. Conventional fuels, such as natural gas, methanol, or even gasoline are reformed to produce the hydrogen required by the fuel cells. During the reforming process, impurities are inevitably obtained in the hydrogen flow. One of them is ammonia (NH₃) that can result in serious damage to the fuel cell operation. In this paper, the effects produced by different concentrations of NH₃ present in the hydrogen flow on the membrane electrode assembly (MEA) performance are studied, differentiating between irreversible and recoverable damages. Strictly experimental, the study includes both low and high temperature polymer electrolyte fuel cells (PEFC).

The NH₃ poisoning effect is analyzed and quantified by comparing the polarization curves. After the poisoning stage, the cells are subjected to a regeneration process (feeding the cell with neat H₂) with the aim of knowing the membrane’s recovery capacity. The experimental results demonstrate that in low temperature (LT)-PEFCs, the cell recovers its performance almost completely with a new exposure to neat H₂, in spite of the damage previously caused by the presence of traces of NH₃ in the anode feed stream. In contrast, in high temperature (HT)-PEFCs, the cell suffers irreversible damage, even with short time exposure to NH₃. The paper concludes with discussing the possible chemical interactions by which NH₃ affects the cell performance.

Keywords: Ammonia Poisoning, Diagnostic, Experimental Test, HT-PEFC, LT-PEFC

1 Introduction

Polymer electrolyte fuel cells (PEFC) are a promising technology of producing electricity from hydrogen, for both portable and stationary applications [1, 2]. The integration of a PEFC in a power generation system requires an thorough design in the balance of plant [3, 4] and a detailed power conditioning stage [5] to guarantee the best performance of the fuel cell. However, even if the balance of plant is optimized, the quality of the fuel supply (hydrogen purity) affects severely the fuel cell’s performance due to the presence of contaminants [6]. Through there is some example where ammonia is used as fuel in fuel cells (fuel cells type SOFC) [7], hydrogen continues to be the most wide-spread fuel and impurities in the flow feed are a barrier to the hydrogen oxidation reaction (ORR)[8–10].

Recently, high temperature polymer electrolyte fuel cells (HT-PEFC) are drawing attention owing to [11–13]: the rates of electrochemical kinetics are enhanced; the water management and cooling subsystem are simplified; the useful waste heat...
can be recovered; and, particularly, lower quality reformed hydrogen may be used as fuel. It is broadly known that HT-PEFC membranes tolerate higher CO concentrations than low temperature polymer electrolyte fuel cells (LT-PEFC). Therefore, they are more suitable for using with reforming gas; however, there is hardly any information about the influence of other pollutants, such as NH₃, with which the response may not be as suitable as previously assumed [14, 15].

On the other hand, ammonia can be considered not as a contaminant but as a fuel carrier [16], and even there are studies focused on the clean ammonia production [17] in the last stage of the hydrogen supply chain there is needed both ammonia separation and hydrogen purification process [18].

At present, several alternatives can be selected to produce the hydrogen according the raw material used in the conversion [19], see Figure 1. Globally, 48% of the hydrogen produced is derived from the reforming of natural gas. Other reforming processes followed by conventional fossil fuels such as oil (contributing 30% to global hydrogen production), coal (with 16%), and the last place are the hydrogen production from water splitting, mainly by electrolysis (with 6%). Additionally, the hydrogen used to feed fuel cells comes from commercial containers, the main option, or it is produced in situ. In the latter, production in situ, electrolysis [20], natural gas reformed (methane) and methanol obtained from biomass are the most common methods for producing hydrogen.

In the reforming process to produce hydrogen, it is unavoidable that impurities appear [9, 18]. The result is a hydrogen-rich gas called "reformate gas", which typically consists of 40–70% H₂, 15–25% CO₂, 1–2% CO, small amounts of inert gases (water vapour and nitrogen) and sulfur impurities [22]. However, ammonia can be also formed during the reforming process at levels up to 375 ppm in “neat” H₂, or even more if there are transients in the reformers [14]. Traces of NH₃ in the anode feed stream cause a decrease in cell performance. The severity of the effects depends on NH₃ concentration and time of exposure of the anode to the contaminant. High concentrations and a long exposure time can result in irreversible damage [13, 18]. Indeed, impurity substances can affect the water and/or gas transport behavior of the gas diffusion layer, resulting in mass transport decrease and fuel cell performance loss [24]. In this sense, impurities such as ammonia can react with hydrogen protons to form ammonium protons according to reaction Eq. (1):

\[
\text{NH}_3 + H^+ \rightarrow \text{NH}_4^+ 
\]  

(1)

The result is a decrease in gas transport and, therefore, a decrease in fuel cell performance.

In scientific papers, the effects of potential contaminants such as CO, CO₂ and H₂S have been well-studied [12, 15, 19–23]; however, only a few have been found that focus on the effect of NH₃ particles on LT-PEFC performance [14, 24–26]. The lack of research is even greater regarding the NH₃ effects on HT-PEFC [18, 27]. In terms of LT-PEFC, Soto et al. analyze in [14] the effects of high NH₃ concentrations on the MEA (membrane electrode assembly) performance (from 200 ppm to 1,000 ppm). In contrast, Zhang et al. [30] studied the effects of ammonia at fixed concentration (25 ppm) with long term exposure (> 6h), varying the relative humidity, but without the cell functioning, or operating. Additionally, very low concentrations (1–2 ppm) effects are studied in [31]; however, in this case, the NH₃ input is in the cathode side. A detailed study on the conductivity of Nafion® membranes in situ electrochemical impedance spectroscopy was explored by Hongsiirkarn et al. in [32]; though, the authors did not analyze the performance of the entire cell. Regarding HT-PEFC, Sun et al. presented in [33] the polarization curves and AC impedances of the cell after NH₃ poisoning. Moreover, the catalyst layer was scanned with the electron microscope.

In this paper, the effects of NH₃ particles in the hydrogen flow inlet (anode side) of both LT-PEFC and HT-PEFC are analyzed to determine the severity of potential damages, reversible or not, in the fuel cell’s performance. To highlight the novelty of the work, the study includes the NH₃ concentration ranges that previous research do not cover: from 25 ppm (for LT-PEFC) and 50 ppm (for HT-PEFC) to 250 ppm (for LT-PEFC) and 500 ppm (for HT-PEFC). These concentrations were selected according to the typical levels of impurities in reformed hydrogen, which can be up to 375 ppm [16, 28]. The reason why NH₃ concentrations values over LT-PEFC are half of those of HT-PEFC is explained in Section 2.3.

The need to research the effect of hydrogen pollutants in the performance of fuel cells is one of the requirements set by the European companies of the sector (grouped in the FCH JU, Fuel Cells and Hydrogen Joint Undertaking). The reason for this is to develop products that are reliable and competitive in economic terms to facilitate their introduction into the market and widespread implementation. Besides, the need for purification entails a high additional cost to the use of fuel cells (see Topic SP-JTI-FCH.2013.3.1) [35].

The applicability of the research work developed in this paper goes in line with two key aspects above commented: (i) the main hydrogen source is ammonia and (ii) HT-PEFC face to LT-PEFC are catching especial attention because they are more suitable for using with reforming gas. Then, regarding the first issue, almost the half of the global hydrogen production today comes from natural gas, NH₃ (Figure 1) and according to the second issue, one of the emerging technologies (high temperature) related with the most extended fuel cells (PEFC) allow to be fed with hydrogen produced in situ.
from natural gas reforming. Then, there will be useful to have proven results that show the importance of the presence of NH₃ pollutant particles in the hydrogen supply and its influence on the fuel cell performance.

The study carried out is presented as follows: Section 2 explains materials and methods; results and discussion are presented in Section 3. Finally, Section 4 gathers the conclusions and future studies are pointed out.

2 Experimental

Attending to poisoning mechanisms and mitigation strategies studied in scientific literature [36] in relation to the impurities effects on PEFC performance, in this section there will be explained the procedure and used material to carry out the experimental test. Then, firstly there will be explained the test bench used, next a detail of the high and low temperature membrane used during experimentation and the last parts of the section describe the gas supply facility and the procedure to make the experiments.

2.1 Test Bench and Fuel Cell

The experiments were carried out with a CT-1000 test station from FuelCon™ located in the fuel cell laboratory belonging to the Spanish National Institute for Aerospace Technology (INTA, Instituto Nacional de Técnica Aerospacal). The test station was able to operate cells up to 600 W and a maximum current of 100 A.

The tests were conducted with both galvanostatic and potentiostatic modes, and with flow-through operation mode; although, it was also possible to carry them out with dead-end operation mode. The operating parameters which were controlled were: (i) fuel flow (0.2–10 NL min⁻¹ in the anode); (ii) oxidant flow (0.4–20 NL min⁻¹ in the cathode); (iii) temperature of reactants; (iv) relative moisture of the reactants; (v) anode pressure; (vi) cathode pressure; and (vii) cell temperature. All bench piping and cell may be purged with N₂.

To characterize the influence of ammonia in the PEFC from high and low temperature, two experiments for PEFC whose stacks were made up by a single cell were designed. This was done so, knowing that the expected results from multi-cell stacks were to be similar.

The PEFC used for the experiments (Figure 3) has been a 50 cm² active area cell from Teledyne™ with three-channel parallel serpentine flow fields (channels of 0.76 mm wide and deep). The graphite bipolar plate’s layout is cross-flow with horizontal channels in both anode and cathode (Figure 4).

For the high temperature tests, two integrated heaters were used for temperature control. These consisted of cartridge heat-
ters located inside the final plates. Apart from this, the cell was insulated to reduce temperature gradients and a fan was necessary to remove the excess heat produced by the cell.

For the low temperature experiments, the test-bench FuelCon is equipped with a heating/cooling system controlled by a proportional-integral-derivative (PID) controller that is embedded into the test-bench and used for temperature control. This external heater consisted of a flexible resistance surrounding the cell. Apart from this, the cell was insulated in the same way as in the high temperature tests.

For both experimental tests (high and low temperature), a thermocouple (Rössel Messtechnik) located inside of one of the bipolar plates was used to measure the cell temperature.

2.2 Membranes

Membrane electrode assembly (MEA) from Danish Power Systems™ (Figure 5a), made from polybenzimidazole (PBI), were used for high temperature tests. The MEA had five layers and catalyst loading of 1.5 mg cm–2 in both anode and cathode side. Membrane thickness was 40 μm with Kapton edge reinforcement. The electrode area was 72 × 72 mm² and the active cell area 68 × 68 mm².

In contrast, a MEA from Paxitech™ (Figure 5b), made with Nafion™, were used in the low temperature experiments. The MEA had seven layers and catalyst loading of 0.5 mg cm–2 in both anode and cathode side. Membrane thickness was 50 μm. The active cell area was 68 × 68 mm². The MEA consist of a polymer electrolyte membrane (perfluorinated cation exchange membrane). Both sides were coated with a catalyst ink and combined with a GDL (gas diffusion layer). Apart from this, a 15 μm sub-gasket material and silicon gaskets around the active layers from GDL edge to outer edge of the polymer electrolyte were included. GDLs were pressed onto the catalyst active area and they were made of a carbonized non-woven material with a polytetrafluoroethylene (Teflon, PTFE) surface treatment. The sub-gasket material protected the active layer/GDL contact area and the polymer electrolyte membrane border.

2.3 Gases

To carry out the tests, ultra-high pure (99.999%) hydrogen and nitrogen pre-mixed at different concentrations mixtures, were provided by Praxair™. Bellows et al. [26] show that reformate mixtures contain around 40% of H₂. This means that ammonia can be formed during the processes at levels up to 150 ppm. Therefore, this may correlate up to 375 ppm in neat H₂ or even higher concentrations because of the transients in the reformers.

For high temperature experiments, the impurity (NH₃) concentrations for the anode were obtained from pre-mixed 50, 150, 300, and 500 ppm NH₃/H₂ concentration cylinders. These concentrations have been selected according to typical levels of impurities in reformed hydrogen up to 375 ppm [13].

Conversely, for low temperature tests, the NH₃/H₂ stream had to be humidified because it was necessary to avoid membrane dehydration. However, it was not suitable to humidify directly the NH₃/H₂ stream because of the ammonia absorption in the de-ionized (DI) water, and there was a risk that the ammonia would stay in the humidifier instead of the NH₃/H₂ stream. To resolve this, the neat hydrogen stream was humidified to keep the membrane hydration and the NH₃/H₂ stream was not humidified to keep the ammonia in the NH₃/H₂ stream; and, after that, these two streams were mixed.
Therefore, the impurities of NH₃ concentrations for the anode were obtained by diluting the NH₃/H₂ stream with the humidified hydrogen stream. The flow rate of NH₃/H₂ concentration was controlled by a mass flow controller (MFC, Bronkhorst) for the inlet impurity (25, 75, 150, and 250 ppm). With this method (Figure 6), authors ensured that only neat hydrogen flows through the humidifiers. Hence, potential contamination of the humidifier by absorption of ammonia into the DI water was suppressed. This is why level of impurities were just 50% of those used in high temperature experimental tests. The humidifier temperature was controlled for the desired final (NH₃/H₂) concentration moisture.

2.4 Experimental Test Description

For each test, the amount of ammonia in the fuel and operating parameters values are shown in Table 1 (high temperature PEFC) and Table 2 (low temperature PEFC).

Polarization curves for different conditions were obtained following the FCTESTnet procedure for single cells and the technical specification IEC/TS 62282-7-1 of the IEC (International Electrochemical Commission) [30, 31].

All of the experiments included an activation stage which was used to reach the operating conditions and stabilization for the measurement phase where the change in the single cell voltage, generated by variation of the current density, was quantified.

For high temperature experiments, the manufacturer recommends to carry out a conditioning stage by fixing the current density at 200 mA cm⁻² for at least 50 h. The system keeps working to ensure stability in the measured voltage.

Following Table 1, a stoichiometric factor of 1.5 was fixed for the anode (λₐ) and 2.5 for the cathode (λₐ). The pressure and temperature were fixed in 1 bar and 160°C, respectively. The only parameter which varied was the fuel composition.

For low temperature experiments, the conditioning stage consists of increasing the current density up to 200 mA cm⁻². The system kept working up to 40°C. Following, the cell current was decreased up to OCV (open circuit voltage) and the humidification was then activated. Afterwards, the current density was increased up to 200 mA cm⁻² again and the system kept working up to a temperature of 60°C for 5 h [39]; the humidification was 100% in both anode and cathode. The system kept working to ensure stability in the measured voltage.

Figure 6 shows the stage sequences carried out for high and low temperature tests. In both cases, the first stage was to characterize the PEFC using neat H₂ as fuel. This experiment consisted of an activation stage which was used to reach the operating conditions. This activation stage was carried out with neat H₂ as fuel. After the activation stage, the following phase consisted of obtaining the polarization curves for a period of 2.5 h to know the initial behavior of the membrane without poisoning. When the activation and characterization were finished, a poisoning phase for 2 h using a H₂/NH₃ concentration was staged. After that, the polarization curves were obtained to compare the results with the initial ones. The final step was an attempt to regenerate the membrane. For this purpose, the presence of NH₃ was eliminated by using neat H₂ for 2 h, and carrying out a new characterization stage with neat H₂ (following the same testing procedure as used to develop the characterization of the PEFC [40]).

The described procedure was carried out to compare the results of the different characterization

![Fig. 6 Scheme of the ammonia mixing system for tests in LT-PEFC.](image-url)
3 Results and Discussion

In the following subsections, the cell performance working under different H₂/NH₃ concentrations are shown. The influence of the different H₂/NH₃ concentrations were studied for polymer electrolyte membranes under 2 h of high and low temperature exposure. Once the contamination process was finished, neat H₂ was fed as fuel to investigate the recovery of the cell performance in an attempt to achieve the same performance that was obtained before introducing NH₃. Thus, the attempt to regenerate the polymer electrolyte membrane was carried out with neat H₂ for 2 h.

3.1 HT-PEFC Experimental Tests

Firstly, the poisoning produced due to the presence of NH₃ in the anode fuel has been analyzed. To do this, the measured polarization curves at 160 °C (baselines, neat H₂ curves) have been used. The poisoning was acquired using different H₂/NH₃ concentrations (50, 150, 300 and 500 ppm) to compare them with the polarization curves obtained with neat H₂ as fuel.

Figures 9–12 show the differences between the polarization curves obtained using neat H₂, the different H₂/NH₃ concentrations were studied for polymer electrolyte membranes under 2 h of high and low temperature exposure.
Llerena et al.: Effects of Ammonia Impurities on the Hydrogen Flow

After poisoning, the MEA is completely damaged. Each MEA shows a slightly different behavior because it is handmade, and is not industrial. Therefore, each MEA has its own baseline so each poisoning can only be compared to its own MEA baseline.

Additionally, Figure 13 shows the nominal cell current (at 0.5 V) provided by the cell after poisoning stage with the different H₂/NH₃ concentrations, and Figure 14 shows the nominal cell current (at 0.5 V) after the regeneration stage with neat H₂.

Table 3, based on Figures 13 and 14, shows how for the different H₂/NH₃ concentrations (50, 150, 300, and 500 ppm), after the 2 h of poisoning stage, the performance of the polymer electrolyte membrane decreases 1.29%, 7.91%, 17.18%, and 19.34%, respectively. These values are acquired with respect to the first and the last value obtained from the cell nominal current in the poisoning stage (Figure 13). In contrast, after the regeneration stage, the cell performance continues to decrease even more, 2.06%, 3.38%, 6.06%, and 6.02%, respectively, according to the first value and the last value obtained from the cell nominal current in the 2 hours regeneration stage (Figure 14). That is, in high temperature experiments, the cell does not regenerate; but rather H₂ regeneration after contamination produces an even worse performance as if the contamination further continued.
3.2 LT-PEFC Experimental Tests

Like the HT-PEFC experiments, the authors analyzed the poisoning produced due to the presence of NH\textsubscript{3} in the anode fuel in a LT-PEFC. In order to do this, the measurement of the polarization curves at 60°C (baselines, neat H\textsubscript{2} curves) were used. After that, the poisoning was determined using different H\textsubscript{2}/NH\textsubscript{3} concentrations (25 ppm, 75 ppm, 150 ppm, and 250 ppm) and analysing the difference obtained with the experiment using neat H\textsubscript{2} as fuel.

Figures 15–18 show the differences between the polarization curves obtained using neat H\textsubscript{2}, different H\textsubscript{2}/NH\textsubscript{3} concentrations as fuel and after the regeneration stage with each H\textsubscript{2}/NH\textsubscript{3} concentration. Figure 19 shows the nominal cell current (at 0.5 V) available by the cell after exposure to NH\textsubscript{3} contaminants, and Figure 20 shows the nominal cell current (at 0.5 V) after the regeneration stage with neat H\textsubscript{2}.

Table 4 shows how for the different H\textsubscript{2}/NH\textsubscript{3} concentrations (25, 75, 150, and 250 ppm), after 2 h of poisoning stage, the performance of the PE cell decreases 27.01%, 34.40%, 46.13%, and 71.18%, respectively. As it has been commented before, these values are obtained with respect to the first and the last value acquired from the cell nominal current in the poisoning stage (Figure 19). Conversely, after the regeneration stage, the performance of the polymer electrolyte membrane improves 2.84%, 10.22%, 21.30%, and 64.09%, respectively, according to the first value and the last value obtained from the cell nominal current in the 2 hours-regeneration stage (Figure 20).
However, the baseline is not achieved in none of the experiments after the regeneration stage.

Once the experimental results have been presented, we are going to comment some issues related with them. Regarding HT-PEFC, it is necessary to point out that even for low concentrations of NH₃ in the fuel, noticeable losses are observed on the polarization curves. The results obtained (Figures 9–12) show that an increase of NH₃ concentrations results in higher losses. When the poisoning stage is completed, neat H₂ is fed as fuel so as to analyze the cell performance recovery, trying to achieve the baseline acquired before the poisoning stage. If only a dilution effect exists, once the H₂/NH₃ concentration is changed by neat H₂, the cell performance would be completely recovered. Nevertheless, this is not the case, and the polarization curve obtained after the regeneration stage shows worse cell performance than after the exposure to NH₃ contaminants. Indeed, even after operating the cell for hours using neat H₂ for the regeneration stage, the baseline is not achieved in none of the experiments. Because of this, such behavior suggests the presence of a compound adsorbed on the platinum surface which cannot be completely eliminated by just using neat H₂.

The results shown in Figures 9 and 10 point out that after the regeneration stage for low NH₃ concentrations, the performance is similar to the polarization curve obtained after the poisoning stage. Additionally, for high NH₃ concentrations, the cell performance results to be even worse than the polarization curve obtained after the poisoning stage, Figures 11 and 12. Thus, we can conclude that for HT-PEFC as the poisoning increases, the cell’s performance after the regeneration stage worsens even more than the original.

In relation to the cell nominal current, from Figure 13 we can observe how the membrane resistance increases during the 2 hours-poisoning stage and this is due to the poisoning of the membrane because of the ammonia. Moreover, Figure 14 shows that the membrane resistance keeps stable during the 2 hours-regeneration stage. Additionally, we can foretell that even after 2 h of regeneration stage, there is no recovery of the membrane.

Concluding with HT-PEFC, Table 3 shows that during the poisoning stage, the cell performance decreases. The decrease depends on the H₂/NH₃ concentration of every experimental test, namely the greater the poisoning, the larger the decrease. Thus, we can assume that after 2 hours-poisoning stage, the polymer electrolyte membrane performance decreases 1.29%, 7.91%, 17.18%, and 19.37%, respectively. After 2 hours-regeneration stage, the performance continues to decrease 2.06%, 3.38%, 6.06%, and 6.02%, respectively (between 300 and 500 ppm it stabilizes). Therefore, the baseline is not achieved in none of the experimental tests after the regeneration stage.

The behavior for the low current densities can be justified by the activation losses and, because of that, the membrane conductivity does not have much influence. Otherwise, when the current density increases, the system is affected by ohmic losses and it is influenced by the state and the conductivity of the membrane. This can be explained due to the fact that the MEA used in the experiments was built from an acid doped polybenzimidazole (PBI) membrane containing phosphoric acid in HT-PEFC: the most likely mechanism by which performance drops is the formation of some type of ammonium phosphate which decreases the protonic activity (Figure 21a). The negative effect gradually starts at the anode catalyst layer, the first region exposed, and continues into the membrane as the ammonia diffuses up to reach the cathode [13]. Figure 21b shows the result obtained from microscopy, where effectively the formation of ammonium phosphate in the membrane-cathode surface can be observed.

Then again, from LT-PEFC tests, polarization losses are also observed, even for low concentrations of NH₃ in the fuel, which agrees with the previous work developed to study the NH₃ poisoning in LT-PEFC. Experimental results (Figures 15–18) show that, as in the case of HT-PEFC, higher performance losses are due to an increase in NH₃ concentrations. When the poisoning stage is finished, neat H₂ is fed as fuel in the regeneration stage to analyze the cell’s performance recovery. The purpose of doing this is the same for that of the HT-PEFC tests. However, for LT-PEFC, the polarization curve obtained after the regeneration stage should be nearly to that of the neat H₂ polarization curve. The baseline is almost achieved for the tests of 25 and 75 ppm of NH₃. However, the baseline is not achieved for higher NH₃ concentrations (150 and 250 ppm of NH₃) even after operating the cell for 2 h of regeneration stage using neat H₂.

**Table 4** LT-PEFC experimental test: Performance losses after poisoning and regeneration stage.

| Concentration / ppm NH₃ | Long Term Exposure / % | Regeneration / % |
|-------------------------|------------------------|-----------------|
| Test 5: 25              | −27.01                 | +2.84           |
| Test 6: 75              | −34.40                 | +10.22          |
| Test 7: 150             | −46.13                 | +21.30          |
| Test 8: 250             | −71.18                 | +64.09          |

**Fig. 21a** LT-PEFC experimental test: Polymer Electrolyte Membrane Long Term Exposure / % Regeneration / %

**Fig. 20** LT-PEFC experimental test: Nominal cell current comparative (at 0.5 V) after regeneration stage.
Additionally, Figure 19 shows that the membrane resistance increases during the 2 hours-poisoning stage and this is due to the poisoning of the membrane by the ammonia. In contrast, Figure 20 shows that the membrane resistance decreases during 2 hours-regeneration stage. This is due to the recovery of the membrane by way of the neat hydrogen.

Regarding the recovery stage, as shown in Table 4 (made from Figures 19 and 20), for the different H₂/NH₃ concentrations, after 2 hours-poisoning stage, the performance of the polymer electrolyte membrane decreases 27.01%, 34.40%, 46.13%, and 71.18%, respectively. After the 2 hours-regeneration stage, the recovery of the performance is 2.84%, 10.22%, 21.30%, and 64.09%, respectively. This is a huge difference from the HT-PEFC test; because in that case, after the regeneration stage, the cell performance is not recovered but worsens.

Then, accordingly, data point to the presence of a compound adsorbed on the platinum surface which can be partially eliminated by just using neat H₂.

There are several possible mechanisms by which NH₃ affects the PE fuel cell performance in LT-PEFC. The membrane conductivity decreases by the ammonia reacting with the protons of the protonic membrane forming NH₄⁺ (Figure 22).

The same effect could be possible within the catalyst layer, which contains recast ionomer in protonic form (Figure 23). NH₃ crosses over to the cathode inhibiting the O₂ reduction reaction (ORR) [13], [23]. Similarly, the anode catalyst could inhibit hydrogen oxidation because of NH₃ adsorption onto Pt.

Finally, it is worth noticing that Borup et al. [23] and Uribe et al. [13] showed how cyclic voltammetry (CV) of the anode, after exposure, does not indicate any noticeable NH₃ adsorption onto the catalyst layer; however, the degradation mechanism seems to be a protonic conductivity loss. After the study carried out in this work, it can be assumed that NH₃ reacts with ionomeric H⁺ producing NH₄⁺, which results in an increased of the protonic activity.

4 Conclusions

This paper contributes to the few studies that cover the effects of NH₃ on high and low temperature PE fuel cells showing the mechanisms by which the membrane performance decreases after a poisoning stage.

The need to have research works related with this subject can be justified because on the one side, the main hydrogen source today in the world is ammonia and on another side, there is arising a fuel cell technology, HT-PEFC, which can operate with lower quality hydrogen produced by reforming process. But, it is unavoidable the presence of impurities in the hydrogen gas produced and although the influence in the fuel cell performance of some pollutant particles, such as CO, CO₂ and H₂S have been widely studied, traces of NH₃ have been scarly addressed in scientific literature.
Additionally, the need to research the effect of hydrogen pollutants in the performance of fuel cells is one of the requirements set by the FCH JU. Based on above, the results presented in this paper contribute to meet with these global objectives.

Regarding the tests carried out (low and high temperature), the results clearly show that the presence of traces of NH₃ in the anode feed stream poisons the membrane electrode assembly resulting in downstream cell performance. The poisoning depends on the amount of NH₃ in the anode feed stream.

As for the experiments with LT-PEFC, the performance shows a recovering during the 2 hours-regeneration stage. The recovery mechanism possibly involves proton generation by anodic hydrogen oxidation current. Conversely, for tests with HT-PEFC, the performance decreases even during the 2 hours-regeneration stage.

On the basis of the results obtained, it was confirmed that longer exposure time in HT-PEFC, decreases the cell performance to unusable levels and the cell never recovers to original conditions. In contrast, with LT-PEFC, despite severe poisoning with ammonia, the performance degradation is in most cases reversible, but only after operating with neat hydrogen for long periods of time.

Finally, based on achieved results (analysis of the electrical behavior) authors are working on studying the effect of pollutants in high and low MEAs regarding physical properties like temperature, relative humidity and analysis of regeneration processes.

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**List of Symbols**

- \( \lambda_a \) Anode stoichiometric
- \( \lambda_c \) Cathode stoichiometric
- MEA Membrane electrode assembly
- MFC Mass flow controller
- NH₃ Ammonia
- NH₄⁺ Ammonium ion
- NL Normal litres
- N₂ Nitrogen
- OCV Open circuit voltage
- O₂ Oxygen
- PBI Polybenzimidazole
- PEFC Polymer electrolyte fuel cells
- PTFE Polytetrafluoroethylene
- PID Proportional-integral-derivative
- Pt Platinum
- ppm parts per million
- RHa Relative humidity of anode
- RHc Relative humidity of cathode
- V Volt
- X⁺ Cations contaminants

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