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Multiscale Study of PEMFC in Marine Environment: Impact of a NaCl Spray on Durability

M. Lamard[a,b], B. Auvity[b], P. Buttin[a], S. Rosini[c], and C. Retière[a]

[a] CEA, CEA Tech Pays de la Loire, F-44340 Bouguenais, France
[b] Nantes Université, LTeN (CNRS UMR 6607), Polytech Nantes, 44300 Nantes, France
[c] Univ Grenoble Alpes, CEA, LITEN, F-38000 Grenoble, France

The present work investigates the effects of a salt spray injected into the airflow of Proton Exchange Membrane Fuel Cells (PEMFCs) at various time scales and contamination levels, with the final aim of identifying the appropriate protection for maritime applications. A dedicated experimental setup generates a sodium chloride (NaCl) mist in the cathode airflow to contaminate single cells and stacks. Constant current density tests led to lifetime shortening with partial recovery after cathode rinsing. Then, Membrane Electrode Assemblies (MEAs) post-mortem characterizations revealed that NaCl was present in the cathode gas diffusion layer, and chlorine reached the catalyst layer for high concentrations. Furthermore, chlorides enhanced current collectors and bipolar plates degradation as corrosion products were identified in MEAs and stack effluents. Overall, this study reports that NaCl effects on PEMFCs not only depend on the concentration but also on the MEA type, plate material, and startup/shutdown procedure.

Introduction

In the context of global warming, there is an urgent need to find solutions to reduce air contamination by replacing combustion engines. For that, technologies as Proton Exchange Membrane Fuel Cells (PEMFCs) can be used, as they produce electricity thanks to air and hydrogen by only rejecting pure water and heat. Thus, obtaining hydrogen from a renewable source reduces greenhouse gas emissions. This technology was first introduced almost two centuries ago, but there are still some issues concerning its durability. More precisely, the impact of an aggressive environment such as marine atmosphere can reduce the fuel cell (FC) performance. Indeed, even if industrial companies are interested in PEMFCs for maritime transportation, various air pollutants are found in harbors like nitrogen oxides or sulfur dioxide, but also specific contaminants such as sea salt. This last one is mostly composed of sodium chloride (NaCl) and can reach the membrane electrode assembly (MEA) when the cells are fed with marine air. However, few studies have addressed the problem of NaCl contamination. As reported by Mikkola et al. (1), chlorides did not affect as much as expected the MEA of a single cell whereas an increase in the high-frequency resistance was detected and explained by the presence of sodium ions in the membrane. Nine years later, Sasank et al. (2) revealed that seawater droplets reduced significantly the performance of an open-cathode PEMFC stack after 48 hours of contamination with partial recovery after clean water rinsing. In

line with these results, Uemura et al. (3) observed a degradation after NaCl particles injection at the cathode side of a single cell, which decreased the cathode active area. It should be noted that the degradation mechanisms require clarification, and the NaCl amount reaching the FC was very high compared to marine environments (1) or not even specified. Therefore, the objective of this experimental work is to verify and explain the trend of performance degradation for both single cells and stacks when exposed to a NaCl mist, with the final aim to predict the adaptations needed for PEMFC deployment in marine environment. Close attention is paid to the NaCl quantity injected into the airflow thanks to a dedicated experimental setup. Then, single cells and stacks contamination tests were carried out for various NaCl concentrations and duration times, at constant current density. In our approach, two types of MEAs and current collectors were used and compared for single cells. Finally, electrochemical tests and post-mortem analyses helped to evaluate the mechanisms that might be implied in the degradation. MEAs from a ship propulsion stack exposed to a real marine environment were additionally observed, which deterioration reinforced the pertinence of this study.

Materials and Methods

Contamination Setup

This subsection describes the setup used for polluting PEMFC single cells and stacks, in order to study the impact of a NaCl mist injected into the feeding airflow. Although in many ways similar to Uemura et al. setup (3), adjustments were made to inject a mist instead of solid particles, but also to be easily connected to the test benches when needed. Moreover, most of the couplings and tubes were chosen with chemically stable materials, to prevent the injection of corroded metallic impurities. An ultrasonic vibrator creates a NaCl mist in a buffer tank flushed by the airflow, which carries the salt spray. The droplets diameter is about 5 µm, as specified by the manufacturer. NaCl solutions to be sprayed were prepared with deionized water at several concentrations, which were linked to the final content of NaCl in the airflow thanks to qualification tests carried out.

Experimental Setup and Fuel Cells Specifications

Single Cells Setup. Single cells selected for the tests have an active area of 11.76 cm² (19.6 x 0.6 cm) and were mounted on the setup presented in Chevalier et al. (4), without the segmented channels. Two types of MEA were studied, from different suppliers, to compare their durability when exposed to NaCl. Type 1 has a platinum (Pt) loading of 0.5 mg/cm² for both electrodes whereas for type 2, the Pt amount is 0.4 mg/cm² for the cathode and 0.1 mg/cm² for the anode. It should be noted that MEAs type 1 were stored for four years without specific measures, which could have caused some damage and a limited reproducibility of performance. Oppositely, MEAs type 2 were fresh and specially ordered for this study. Copper current collectors coated with a gold thin film were used, with two straight channels for the gases. Then, all of the experiments were performed with a Biologic/Paxitech instrument driving the FC (FCT-50S). In order to preserve the equipment from corrosion during contamination tests, the air outlet containing NaCl traces was not connected back to the test station. It offered a means of collecting cell effluents, even though it did not allow tests under pressure.

Stacks Setup. Stacks were constituted of five cells (MEAs type 2) with an active area of 220 cm². The geometry was different from the single cell setup, but the MEA composition was the same. Bipolar plates (BPs) were made of 316L stainless steel partially covered with graphite to improve the conductivity. The experiments were conducted with a homemade test bench at CEA Liten, commonly chosen for single cells and low-power stacks. Inlets and outlets were localized on the anode end plates side, closest to the MEA called cell 1. As for the single cells, effluents were collected at the air outlet to prevent the test bench from deteriorating.

Testing Procedures

Constant Current Testing. Constant current density tests were made at 0.5 A/cm² when polluting the airflow. After a conditioning step provided by the supplier, the FC was operated for approximately 20h at 0.5 A/cm². The operating conditions were a temperature of 60°C (for both gas lines and cell), relative humidity (RH) of 75% (single cells) and 50% (stacks), stoichiometry H_2/O_2 of 1.5/5 (single cells) and 1.5/2 (stacks), and minimum flow rates of 100 and 500 mL/min respectively for single cells. Then, the contamination setup filled with deionized water was connected to the cathode for acquiring a baseline. Finally, NaCl solutions were prepared at concentrations between 0.1 and 50 g/L for contamination tests at 0.5 A/cm², carried out under the same experimental conditions. More precisely, this corresponds respectively to 0.01 and 5 g/m^3 NaCl in the airflow, meaning 200 to 10^6 times higher than a natural marine environment (1). Post-processing included smoothing of the data collected to remove voltage drops due to the recording procedure and the occasional tube clogging. Furthermore, this treatment improved graph reading without cutting essential data.

Electrochemical Characterizations. To highlight the NaCl impact, several electrochemical tests were combined for various contamination stages. Polarization curves were plotted to track the overall variation in performance. Additionally, electrochemical impedance spectroscopy (EIS) spectra were obtained at 0.05 A/cm² and 0.4 A/cm² to study kinetics and mass transport phenomena. The frequency range was 2000 to 0.350 Hz with a signal amplitude of 10%. Cyclic voltammetry (CV) was completed at the cathode for the stack scale study only, because of the setup configuration. The voltage sweep range was 60 mV to 0.7 V at scan rates of 50 mV/s, 100 mV/s, and 200 mV/s. Three scans were saved for each cell at the scanning speeds studied. Concerning the equipment, the FCT-50S was directly driving the characterization procedures and recordings for single cells, with clean water humidification to avoid FC degradation during the tests. It was recognized that inevitable condensation droplets can momentarily clog the tube at the cathode entrance because of the low flow rate, resulting in a slightly noisy signal for EIS at 0.05 A/cm². Fortunately, this phenomenon is acceptable when studying the NaCl contamination itself or the FC global performance. On another note, procedures were controlled via an Autolab potentiostat to achieve EIS and CV on stacks. As flow rates were higher than for single cells, clogging did not occur at this scale.

Post-Mortem Analysis. Scanning Electron Microscopy (SEM) analyses coupled with Energy Dispersive X-Ray Spectroscopy (EDS) were carried out on MEAs and effluents. MEAs samples were coated and polished, thus obtaining a precise cross-sectional view to look for potential delaminations. Then, samples were peeled to observe rigorously each

layer. For single cells, both extremities were observed, whereas entrance, middle, and air outlet were studied for stacks. Concerning the stack effluents collected, they were put into a drying oven to obtain a powder for SEM-EDS characterization.

Results and Discussion

This section describes the single cells and stacks contaminations realized thanks to the dedicated setup mentioned earlier. Then, both scales results are compared to provide a solution for discriminating the direct and indirect effects of NaCl on PEMFCs, which will be explored in this paper and developed in future work.

Single Cells

As described above, two types of MEAs were studied for various time scales and contamination rates thanks to a specific setup injecting NaCl mist in the cathode airflow. The most relevant results are detailed in this paragraph.

Short duration contaminations. 30 minutes exploratory tests were carried out on MEA type 1, with an approximate NaCl amount in the airflow of 0.01 and 5 g/m^3. When the cell performance loss was about 0.1 V from the baseline, the contamination test was stopped and the cathode was humidified with deionized water again. As shown in Figure 1, 10 mg/m^3 NaCl during 30 minutes did not trigger perceptible loss of performance. It should be noted that the baseline signal fluctuates. As explained before, this is due to a condensation issue in the tubes and does not affect the global performance. Furthermore, the performance obtained during the baseline recording was not as high as expected for PEMFCs at 0.5 A/cm^2. This was probably caused by the use of an old MEA, as described earlier.

Conversely, 5 g/m^3 NaCl provoked a sudden and severe drop in voltage from 0.36 to 0.1 V. Then, signal stabilization was observed a few minutes after the end of nebulization. Finally, deionized water humidification allowed a voltage recovery of 84%. Unexpectedly, after a week of washing procedures (conditioning cycles with changes in gas flow rate, pressure, and RH), the single cell recovered fully its initial performance, reaching 0.45 V at 0.5 A/cm^2. This value is higher than the baseline one, presumably because the conditioning time was too short.

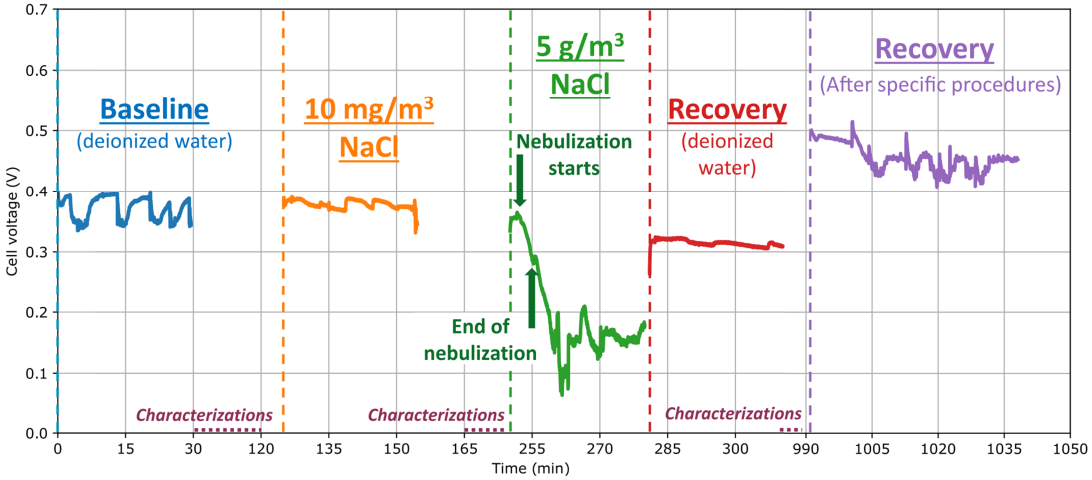


Figure 1. Single cell voltage time evolution depending on NaCl concentration (0.5 A/cm², 60°C, 75% RH, stoichio. 1.5/5 H_2/O_2 with minimum flow rates of 100 and 500 mL/min).

As expected, the voltage drop recorded when PEMFCs were exposed to NaCl is consistent with the literature (2, 3). Additionally, partial regeneration was also reported in Li et al. work (5), even if the pollutant introduced was hydrochloric acid. Nevertheless, initial performance recovery had never been obtained after NaCl contamination to our knowledge. In future, these short contamination tests will be replicated with MEA type 2, which baseline is about 0.65 V at 0.5 A/cm². Indeed, Baturina et al. (6) noticed that a higher cell voltage might increase chloride coverage of the catalyst.

Long contaminations. After the exploratory study, longer contamination tests were undertaken at 10 mg/m^3 NaCl air content on both MEA types, as illustrated in Figure 2. MEA type 1 was polluted for 24h, with night breaks. The decrease in voltage was about 24 mV/h, followed by a 30 min nitrogen (N_2) cathode rinsing step triggering 68% of performance recovery. Unpredictable increases or decreases in performance were observed when restarting the FC, which will be explored in further investigations.

Concerning MEA type 2, breaks were done only every weekend after the first 90h of contamination, to save time. As for type 1, partial recovery was visible after restarts, except for the first weekend (29h) where membrane dehydration occurred, presumably not linked to the NaCl presence. After 265h of contamination with an average voltage decrease of 3.3 mV/h, the FC was run with deionized water for 30h. The voltage drop was lower but present, which means that, contrary to high concentrated and short duration experiments, this recovery method is unlikely to be efficient. Perhaps NaCl remained in the MEA because of stronger interaction due to a longer contamination time, or a degradation process was triggered and continued even under clean water operation. However, as for the type 1 MEA, 30 min of N_2 rinsing helped to recover about 80% of initial performance.

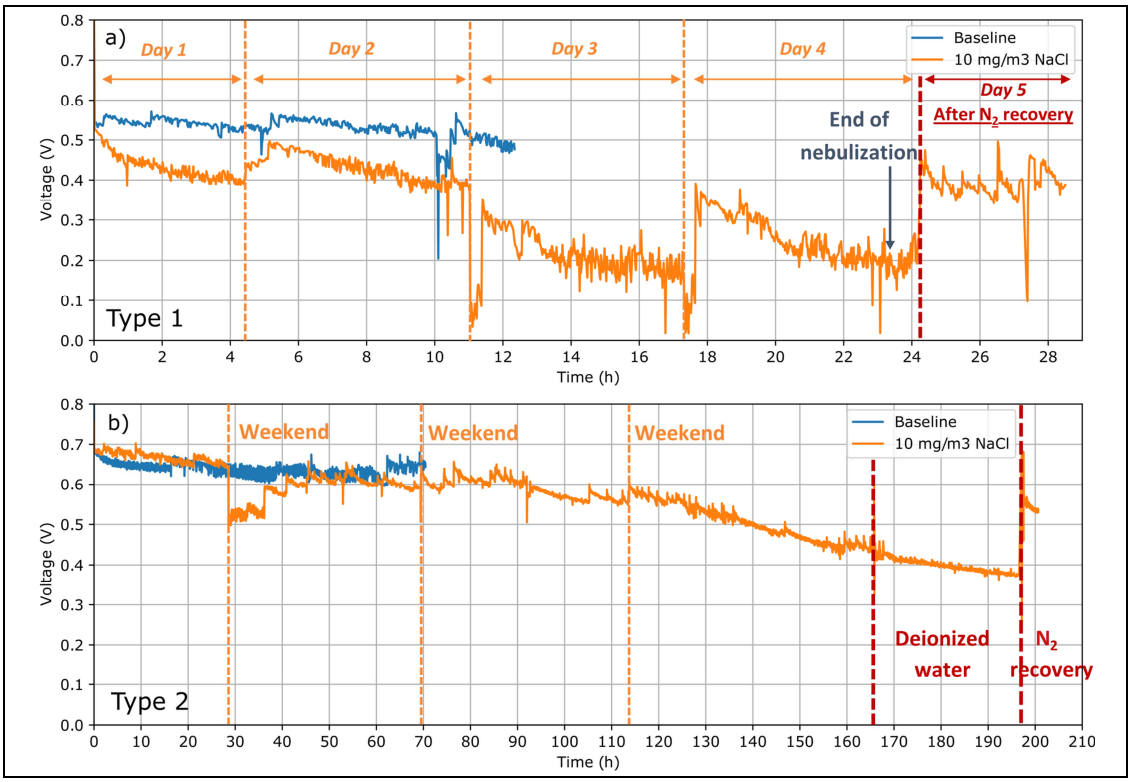


Figure 2. (a) Single cell voltage time evolution with a 10 mg/m^3 NaCl contamination for MEA type 1 and (b) for MEA type 2. Operating conditions: 0.5 A/cm², 60°C, 75% RH, stoichio. 1.5/5 H_2/O_2 with minimum flow rates of 100 and 500 mL/min.

Characterization tests were carried out for both MEAs although they did not yield additional information. Even if it was difficult to compare the results as the initial performance and contamination time were different, the degradation rate of MEA type 1 was about 8 times higher, supporting the idea that type 2 was likely to be more robust. Future tests with CV measurements might help to figure out if the catalyst poisoning rate increases with contamination time.

Post-mortem analyses. The single cell contaminated during the exploratory study was characterized by SEM-EDS. As illustrated in Figure 3.a), MEA sectional view shows delamination between the gas diffusion layer (GDL) and the cathode catalyst layer (CCL). NaCl was identified on GDL and chlorine significantly reached the CCL. Surprisingly, various metallic species including gold were detected on the GDL surface, as well as deposits containing Ni, Fe, Cr, and Mn, which are visible in Figure 3.b). These last impurities could come from corroded stainless steel connectors or test station parts. Furthermore, copper was strikingly found in the CCL. Most probably, copper current collectors were corroded by chlorides. Indeed, they were coated with a thin gold film deposited on a nickel diffusion barrier, which explains the presence of these elements.

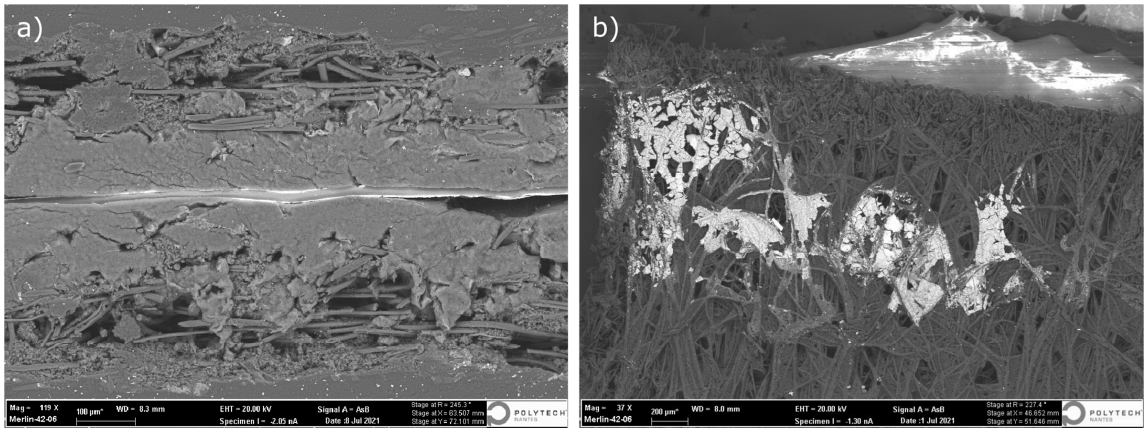


Figure 3. SEM images of the MEA contaminated with NaCl during the exploratory study, from (a) a cross-sectional view and (b) a view of the cathode GDL surface.

Thus, the sudden loss of performance can be due to sodium ions blocking the ionomer sulfonate sites (7) or/and chlorides directly contaminating, more or less reversibly, the platinum catalyst (6). However, current collectors and stainless steel corrosion enhanced by the presence of chlorides should be considered too, as the cations that can deteriorate the electrolyte membrane (8, 9).

Stacks

For studying NaCl impact on more powerful systems, comparable experiments were carried out on stacks, as detailed in this section. Investigations with high NaCl concentrations were conducted, although deeper experiments are planned for the future.

Contaminations. A reference stack was operated for 360h under pure water humidification at 0.5 A/cm², showing stable performance with a negligible voltage drop of 0.012 mV/h. Then, a stack with fresh MEAs was contaminated by a 5 g/m^3 NaCl mist. Contrary to the baseline stack behavior, inspection of Figure 4.a) indicates that cell voltages oscillated after no later than 3h of contamination meanwhile outgoing effluents started getting orange. The stack became unusable after 8h, because of cell 4 sudden voltage drop. A characterization cycle, meaning CV, EIS, and polarization curves measurements under pure water helped recover 95% of performance.

Another new stack was polluted with 0.5 g/m^3 NaCl. As pointed out in Figure 4.b), the first contamination step resulted in unstable voltage after 10h, followed by a sharp voltage drop for cell 5. As for the previous experiments, this degradation was accelerated during polarization curves. Then, an excellent performance recovery of 96% was obtained after characterization cycles and 13h of operation under pure water mist. When the effluents became again colorless, a second contamination was investigated. In this case, the voltage dropped faster because of cells 1 and 5 failures, with once more an overwhelming regeneration of 95%.

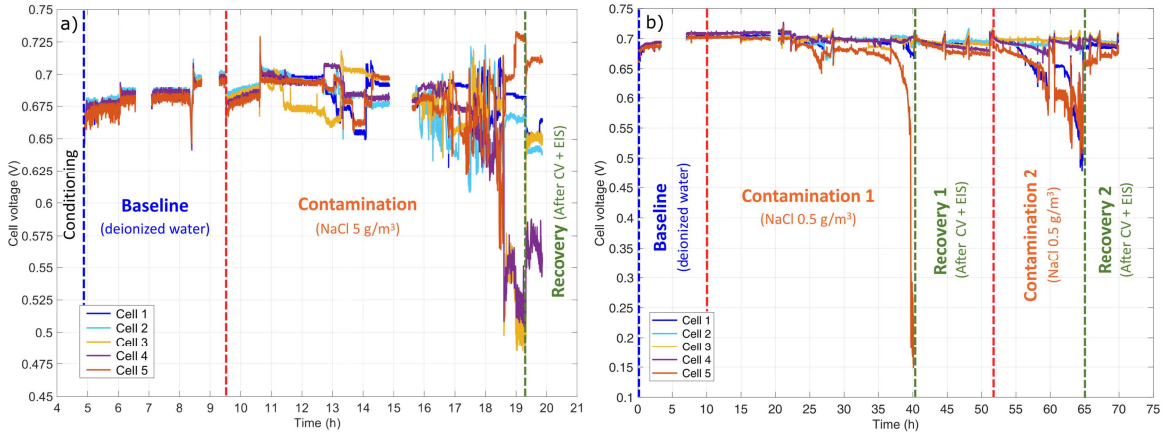


Figure 4. (a) Cell voltage time dependences for a 5 mg/m^3 NaCl contamination and (b) for a 0.5 mg/m^3 NaCl contamination (0.5 A/cm², 60°C, 50% RH, stoichio. 1.5/2 H_2/O_2).

Most relevant polarization curves and EIS spectra of the stack contaminated with 0.5 g/m^3 NaCl can be found in Figure 5. Polarization curves highlight the excellent recovery obtained after both contamination steps, which plots are overlapped. As evident when comparing EIS spectra, the mass transfer semi-circle was extremely large after the first contamination and decreased after the recovery step. This trend seems to suggest that mass transfer limitation was dominant, meaning the contact between air and triple points was reduced because of NaCl presence, but fortunately recovered after rinsing.

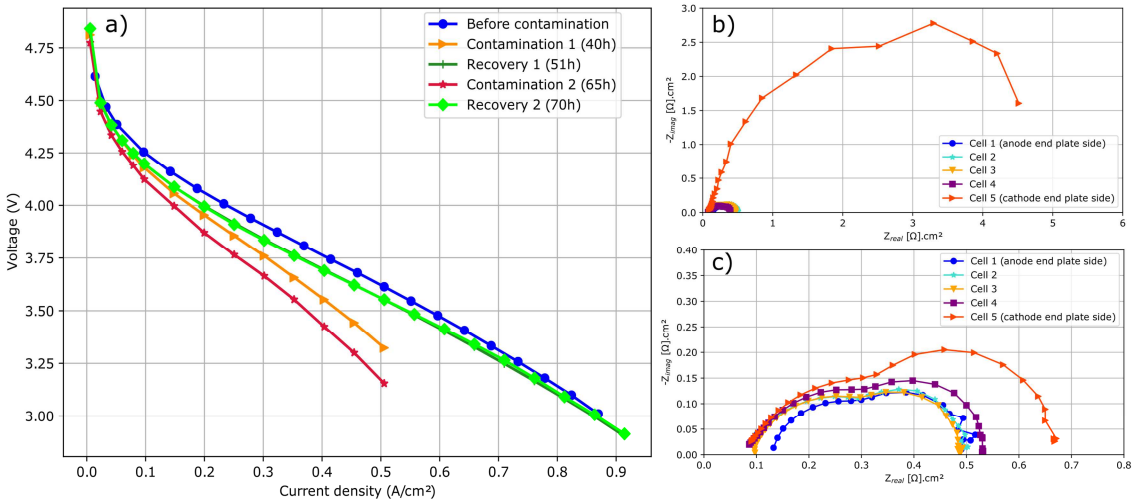


Figure 5. (a) Polarization curves of the stack contaminated by 0.5 mg/m^3 NaCl. (b) EIS spectra recorded at 0.4 A/cm², at the beginning of recovery 1 (40h) and (c) at the end of recovery 1 (51h) (60°C, 50% RH, stoichio. 1.5/2 H_2/O_2).

Concerning the CV tests, the results were somewhat unexpected. Indeed, the electrochemical surface area (ECSA), which is proportional to the charge values given in Figure 6, was not reduced with NaCl contaminations. Surprisingly, for the most degraded cells, meaning 1 and 5, the charge slightly increased after NaCl exposure and decreased under clean mist operation, from 12.0 to 10.6 C for cell 5 first contamination/recovery step.

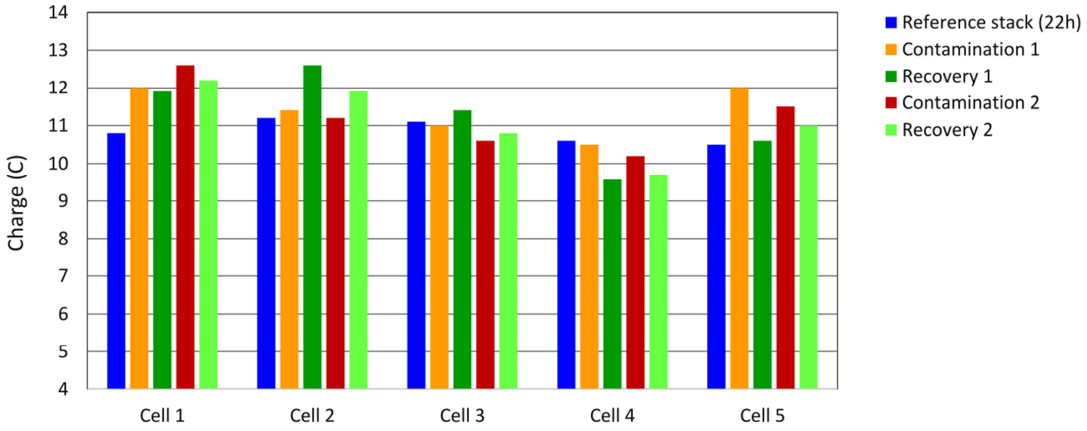


Figure 6. Charge obtained with cathode CV measurements during NaCl contamination (third scan, 50 mV/s, 0.5 g/m^3 NaCl, 60°C, 50% RH, stoich. 1.5/2 H_2/N_2).

This trend is inconsistent with literature (3, 10), where authors usually reported a decrease in ECSA when MEAs were exposed to chlorides, because of their adsorption on the platinum catalyst. To explain this somewhat problematic mismatch, deeper investigations are needed, including longer contamination tests.

Post-mortem analyses. Observations were undergone on collected effluents and cell 4, which was the most degraded of the 5 g/m^3 NaCl polluted stack. As illustrated in Figure 7, the BPs were corroded, especially close to the air inlet. SEM coupled with EDS confirmed the predicted link between these corrosion marks and the effluents impurities, which were both identified as NaCl and stainless steel corrosion products (Fe, Cr, and Ni). As evident from the MEA cross-sectional view, GDL and CCL were strongly delaminated. Moreover, particles composed of Na, Cl, Fe, and Cr were found on the cathode GDL and micro-porous layer surfaces at the air inlet. As for single cells, chlorides reached the CCL. However, impurities were only present on the cathode GDL surface in the middle of the cell, and neither element was encountered at the air outlet. Likewise, all the MEA portions studied were clean on the anode side.

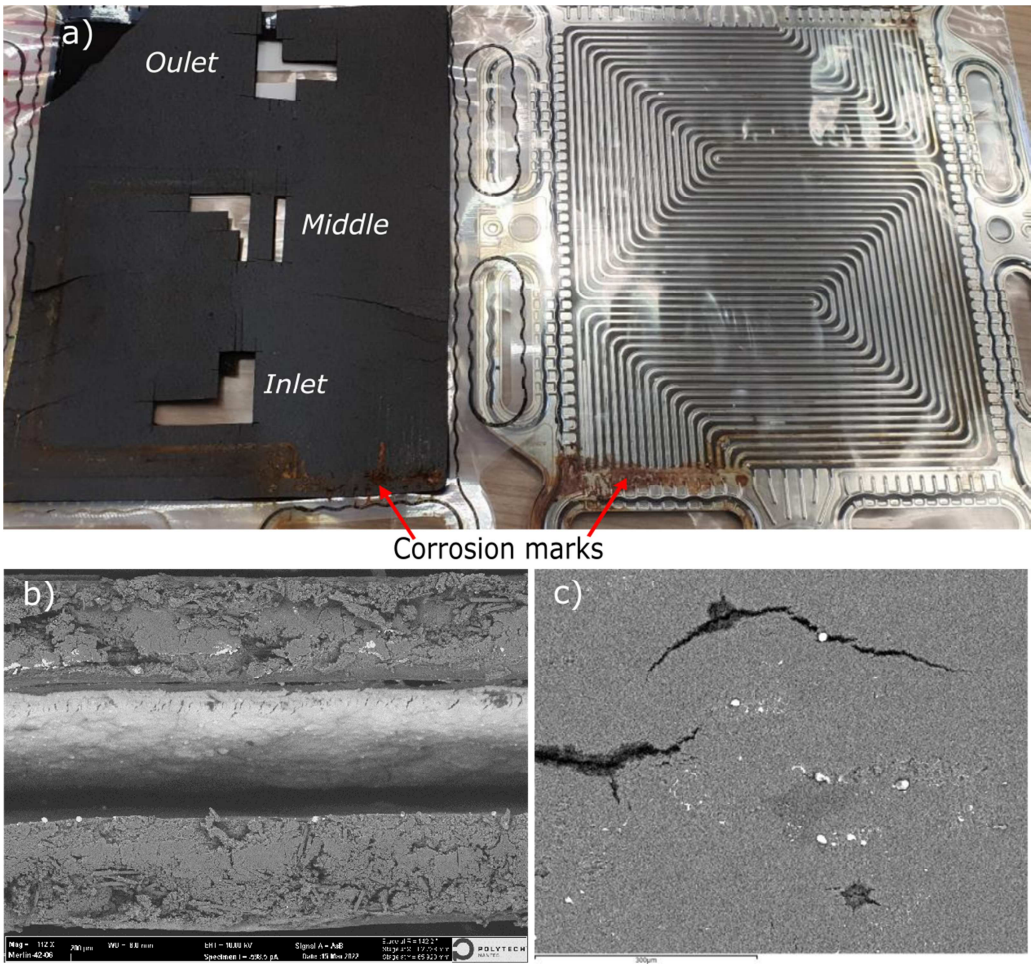


Figure 7. (a) Picture of cathode MEA and BP contaminated with 5 g/m^3 NaCl. (b) SEM observations of a cross-section and (c) cathode micro-porous layer close to the air inlet.

These results are consistent with single cells post-mortem analyses, consolidating the possibility of BPs corrosion enhancement when exposed to chlorides. Corroded particles were largely evacuated in effluents, but some of them could clog the GDL pores during the contamination, explaining the mass transport limitation observed. Then, a great part of impurities was probably released with rinsing, explaining the satisfactory regeneration also evidenced by ultimately colorless effluents. Furthermore, chlorides contaminated the CCL, even if the stack was polluted no later than 8h followed by a clean mist operation. Further work will help to know if delaminations are specific to NaCl exposure, and if corrosion particles and chlorine remain in the MEA after longer rinsing steps.

Beyond the scope of this study, a 35 kW PEMFC stack used for ship propulsion 10 years ago was analyzed. Even if performance did not decrease after 50h of operation in a marine environment, post-mortem characterizations revealed surprising observations. Indeed, as for laboratory tests, corrosion marks from BPs were visible on the MEAs (Figure 8) and identified as Fe, Cr, Ni, Mo, and Cl in the cathode GDL. This result provides the first evidence for PEMFC degradation when deployed for a maritime application. The next stage is to find out if longer sea operations result in chlorides reaching the CCL, with the final consequence to reduce the available power.

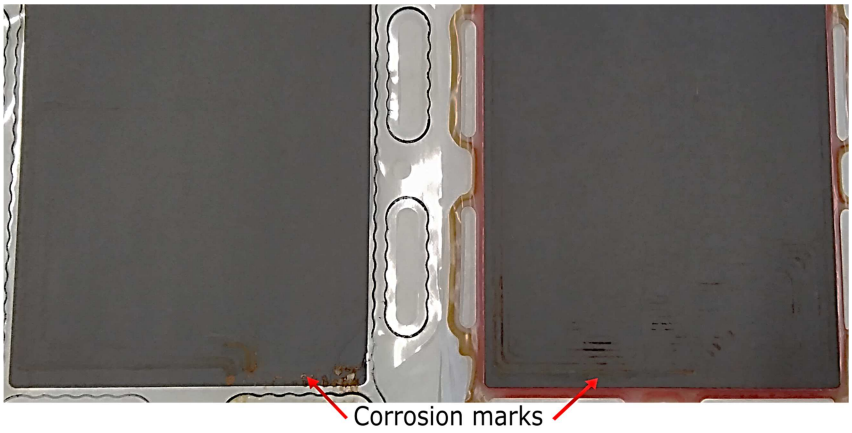


Figure 8. Picture of a cathode MEA contaminated with 5 g/m^3 NaCl (on the left) and another one from a stack operated 50h in a marine environment (on the right), both showing corrosion marks close to the air inlet.

Single cells with graphite current collectors

Both scales experiments highlighted a decrease in PEMFC performance with partial recovery after clean mist rinsing. Chlorides corroded the metallic plates, which products could limit air transportation through the GDL, and even contaminate the membrane. Therefore, a slightly different single cell setup was realized to discriminate the NaCl direct impact on the MEA and the indirect corrosion particle effects. Indeed, the cathode plate was replaced by a graphite one, which is more adapted to severe environments. The copper current collector was kept on the anode side, as it was not directly exposed to NaCl spray.

Contamination tests were carried out in this configuration with 10 mg/m^3 NaCl. The evolution of the cell voltage as a function of time is shown in Figure 9 for the entire contamination test. In accordance with the previous results, there was a significant decrease in performance when the single cell was exposed to NaCl mist. The polarization curves recorded at various contamination times confirmed that no more than 50h of continuous pollution provoked a drastic performance loss.

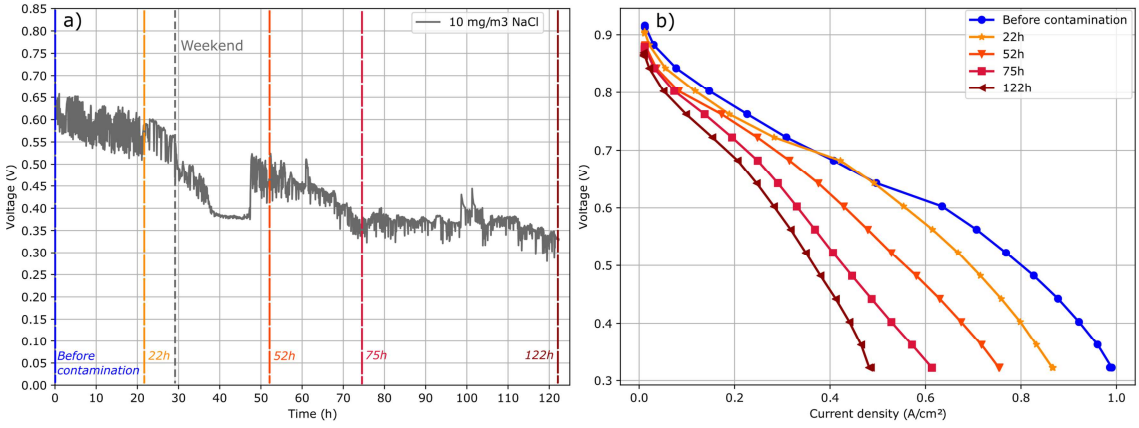


Figure 9. (a) Contamination time dependence on the voltage at 0.5 A/cm² and (b) polarization curves associated for a single cell assembled with a graphite current collector at the cathode (10 mg/m^3 NaCl, 60°C, 75% RH, stoichio. 1.5/5 H_2/O_2).

These results corroborate the direct impact of NaCl on PEMFC. In the future, post-mortem analyses will reveal if metallic elements are still found in the MEAs with the use of a graphite current collector at the cathode side. Moreover, SEM-EDS observations are needed as well on the membrane to determine if sodium or iron could be a source of damage.

Conclusion

To our knowledge, this study has contributed to the literature in many ways:

(1) First, it confirmed the significant performance degradation of PEMFC single cells and stacks when exposed to NaCl at various concentrations, for two MEA types.
(2) An excellent regeneration was obtained for short contaminations.
(3) Even if CCL irreversible degradation was not proven, they contained chlorides for high NaCl concentrations, which remained after a rinsing step.
(4) Chlorides corroded gas plates for both scales, which led to the formation of metallic impurities reaching the MEA and limiting the mass transportation of gases to the triple point boundaries.
(5) A real case study acknowledged the impact of NaCl on PEMFC exposed to a marine environment.

Further study will help to determine if sodium is present in the membrane or not, and lower concentrations will be studied to find out an impact threshold. Moreover, CV tests on single cells will help to understand the unclear stacks ECSA observations.

Acknowledgments

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