



Innovative water management in micro air-breathing polymer electrolyte membrane fuel cells

Nicolas Karst^{a,*}, Vincent Faucheux^b, Audrey Martinent^b, Pierre Bouillon^a, Jean-Yves Laurent^b, Florence Druart^c, Jean-Pierre Simonato^b

^a STMicroelectronics, 16 rue Pierre et Marie Curie, BP 7155, 37071 Tours Cedex 2, France

^b Commissariat à l'Energie Atomique (CEA) LITEN-DTNM-LCI, 17 av. des martyrs, 38054 Grenoble Cedex 9, France

^c Laboratoire d'Électrochimie et de Physicochimie des Matériaux et des Interfaces (LEPMI), UMR 5631 CNRS-INPG -UJF, ENSEEG, BP 75, 38402 Saint Martin d'Hères, France

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ABSTRACT

The role of cathodic cover opening ratio on water management was investigated for micro air-breathing polymer electrolyte membrane fuel cells (PEMFCs). The results demonstrate the possibility to manage water content in micro-PEMFC using cover opening ratio variation. By measuring the internal resistance of a cell in various cover configurations ($0.33 \Omega \text{ cm}^2$ to $4.0 \Omega \text{ cm}^2$), the influence of cover opening ratio on water management was shown. Indeed, for a cell situated in a 10% relative humidity atmosphere and operated at 0.5 V, the addition of a 5% opening ratio cover allowed to reach similar current densities (270 mA cm^{-2}) to those recorded for the same potential at 70% relative humidity without cover. Although the starting current density for a cell operated at 60°C without gas humidification was extremely low (15 mA cm^{-2}), the total closure of the cover allowed to maintain the water produced and accumulated by the cell at the cathode, and current density of 800 mA cm^{-2} were reached after height minutes of operation. The influence of the opening ratio on back-diffused water was also evaluated and the maximum of back-diffused water was observed for a cell operated with a 5% cover opening ratio and represented 33% of the total water product at 150 mA cm^{-2} .

A new method of anodic water evacuation, which does not increase the cell volume and which does not require any control tool was carried out and experimentally evaluated.

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1. Introduction

Due to the arrival of portable electronic devices on the market which require much higher energy densities for long term operation, the polymer electrolyte membrane fuel cell (PEMFC) has attracted a strong renewed interest in the past few years [1]. However, in order to be compatible with wandering applications it is necessary to miniaturize them [2–4]. Moreover, for the sake of simplicity, cost reductions and energy saving, it is essential to limit the number of auxiliaries necessary to the performance of the PEMFC, such as compressors, humidifiers and heat exchangers [5]. This is why air-breathing fuel cells which use oxygen directly from the air appear particularly attractive for such applications.

In this case, it is essential for the cathode of the PEMFC to be in direct contact with the air in order to allow diffusion of oxygen to the cathodic active layer in a passive manner. However,

because of its portable application it is impossible to leave the cell completely exposed to the outside and thus it is necessary to protect it by confining as much as possible, which will nevertheless cause gas diffusion and water management problems at the same time. Indeed, in an air-breathing fuel cell, the removal of the water present at the cathode is performed only by evaporation and the opening ratio of the cell on the cathodic side will be critical.

Several studies on classical membrane electrode assembly (MEA) fuel cell [6,7] were focused on the effect of cathode opening ratio on cell performance and water management. Jeong et al. [7], observed an increase in ohmic resistance and activation loss with the increase of the cathode opening ratio. This was due to a lower ionic conductivity resulting from an increase in evaporation of product water and to higher in-plane electrical resistance resulting from a lengthening of the electron pathways to reach the cathodic current collector through a gas diffusion layer. Thus, because the openings are directly realized in the cathodic current collector it is difficult to distinguish the losses due to either electrons collecting or cell flooding or drying. In the structure presented herein (Fig. 1), the cover being independent of the active part of the cell, the variation of its opening ratio does not directly influence the

* Corresponding author. Tel.: +33 4 38 78 01 77; fax: +33 4 38 78 51 17.
E-mail addresses: nicolas.karst@cea.fr, nicolas.karst@st.com (N. Karst).

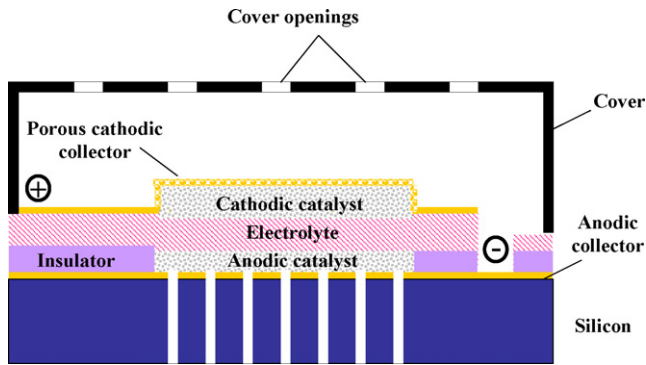


Fig. 1. Schematic cross-sectional view of our micro-PEMFC.

ohmic losses. This enabled us to study the effect of opening ratio only on the water and gas management.

The problem of water management in PEMFC is not only limited to the cathode side. Indeed, because of a concentration gradient, some of the water produced at the cathode, diffuses back to the anode [8–11]. In laboratory conditions, the water removed at the anode side is extracted by the hydrogen gas flow. However, for safety reasons and in order to avoid important matter losses, it is impossible within the framework of the final application to reject hydrogen in the atmosphere. Thus, it is necessary to function in dead-end mode and the water removed to the anode must then be evacuated by other means. On the one hand, in order to avoid cell flooding, it is essential to remove water excess from the anode as well as the cathode, but on the other hand it is necessary to keep an optimal hydration of the membrane in order to ensure high protonic conductivity [12,13].

In this paper, we present results on the influence of the opening ratio of a cathode cover on the electrical performance and on the back-diffusion of water. Moreover, a solution allowing the startup of a cell in a dry state and a solution to remove the back-diffused water are proposed.

2. Experimental

2.1. Cell design

The micro-PEMFC prepared in our laboratory was designed and manufactured within the scope of a will of innovation and technological breakthrough compared to the traditional PEMFC, where each component is separately manufactured before being assembled. It presents an innovative architecture using the techniques coming from micro-electronics, for the realization of the support as well as the deposition of the various layers composing the active parts of the cell. In view of a future industrialization, our micro-PEMFCs were directly manufactured on a silicon pre-etched substrate. The various layers composing these micro-PEMFCs are presented schematically in Fig. 1. The support of micro-PEMFC was manufactured from a 500 μm thick and 150 mm diameter silicon

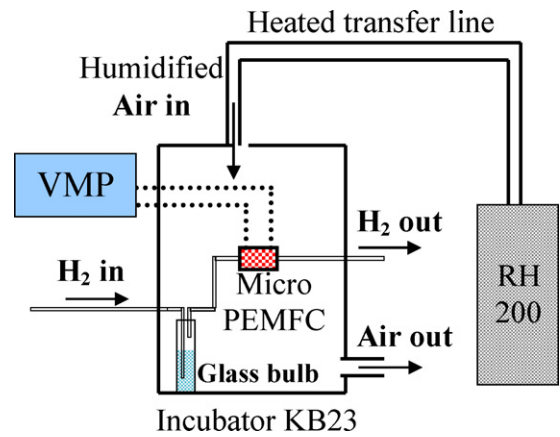


Fig. 3. Schematic view of measurement system to monitor micro-PEMFCs in controlled environmental conditions.

substrate. We achieve to realize 47 micro fuel cells of 1 cm^2 active area. The hydrogen was supplied to the active surface by channels etched in the substrate. A 1 μm thick gold layer used as anodic collector was deposited by physical vapour deposition (PVD) over the whole substrate. In order to achieve the electrical insulation and the localization of each of the 47 micro fuel cells, a dry film was laminated onto the substrate surface. The cathodic and anodic active layers were deposited by ink jet printing techniques using an ink formulated with C/Pt (40 wt.% Pt on XC72 from Etek Inc.), electrolyte (DE521 Nafion solution from Ion Power Inc.) and various solvents such as isopropanol, ethylene glycol and water. The proportions of these solvents were adjusted in order to ensure a satisfactory dispersion of the particles and to obtain a given viscosity of about 3 mPa s imposed by the ink jet method. As the quantity of dry matter contained in the ink is lower than 5%, it was necessary to print several layers in order to obtain a sufficient thickness. The anode and the cathode were respectively 10 μm and 20 μm thick. A 30 μm thick membrane was obtained by coating of a dispersion of D-2021 Nafion solution (from Dupont) on the anode. To complete the cell, a gold layer (0.5 μm) was deposited on the cathode. This layer was relatively thin in order to allow the diffusion of oxygen to the active layer. Once these various stages were completed, the micro fuel cells were cut out and assembled on an aluminium case in order to be electrically tested. In Fig. 2, images of the complete wafer comprising 47 cells, and an assembled cell on an aluminium case are presented.

2.2. Measurement apparatus

A schematic of the experimental setup used to study the effect of relative humidity and cover opening ratio on the electrical performance of a micro fuel cell is presented in Fig. 3. In order to characterise the cell at various humidity values, a relative humidity generator (RH200, VTI Corporation) was connected through a heated line transfer to a 20L incubator with

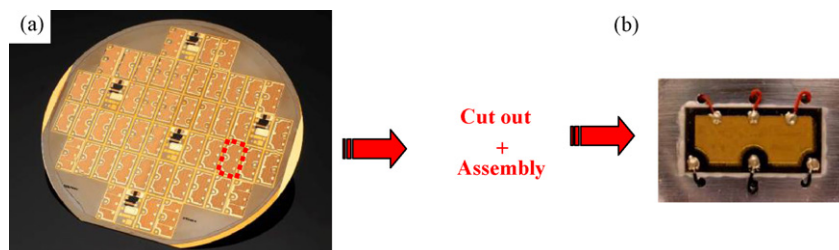


Fig. 2. (a) Si wafer entirely processed comprising 47 micro-PEMFCs. (b) Assembled cell on an aluminium substrate.

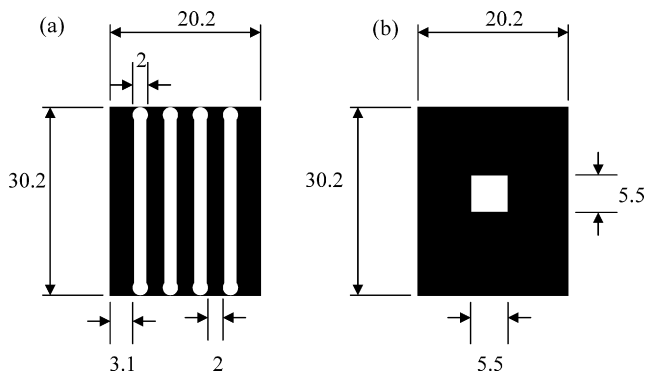


Fig. 4. Depiction of the cover opening rates: (a) 40%, (b) 5% (unit: mm).

adjustable temperature. To rapidly reach desired relative humidity, the flow of humidified air entering in the incubator was fixed at $5000 \text{ cm}^3 \text{ min}^{-1}$. Brooks Instrument flow meters were used to control the hydrogen flow rates between $0.5 \text{ cm}^3 \text{ min}^{-1}$ and $10 \text{ cm}^3 \text{ min}^{-1}$.

The water balance measurements were not carried out in the environmental chamber but at ambient temperature. Ambient temperature and relative humidity were recorded using a Rotronic HygroPalm HP21. During the water balance experiments, the cell temperature was controlled using a hot plate and the water removed to the anode was collected by condensation of the water carried by hydrogen flow.

The I - V curves and the AC impedance spectra were obtained using a VMP3 (Biologic Co.) in potentiostatic mode. A 10 mV amplitude sinusoidal signal was used and the frequencies were ranged from 100 kHz to 0.1 Hz.

3. Results and discussion

3.1. Influence of cover opening ratio on cathode water management

A micro-PEMFC was placed in the environmental chamber at a temperature of 30°C and as depicted in Fig. 4, three different opening ratios of cover were studied: 5%, 40% and 100% (*i.e.* without cover).

For each opening ratio, two relative humidities were examined: 10% and 70%. The cell was maintained at a temperature close to that of the chamber by fixing it on a heat sink of 1.5 KW^{-1} thermal resistance in order to evacuate the heat produced during the electrochemical reaction [14]. The maximum cell temperature recorded by using such a system was 31.3°C . The hydrogen used for these experiments was humidified by passing through a glass bulb partly filled with water (see Fig. 3). A hydrogen flow of $8.5 \text{ cm}^3 \text{ min}^{-1}$ was supplied to the cell.

Once the desired relative humidity was reached in the chamber, the cell was left at open circuit voltage (OCV) for 3 h in order to stabilize membrane hydration [12,15]. The OCV value was read after 3 h and then a range of voltages (0.8–0.15 V) was imposed to the cell. The resulting current density was read after 30 min of operation and an impedance spectrum was then recorded. It should be noted that after every 30 min cycle the cell was stabilized at OCV for 15 min in order to remove water excess at the cathode. Fig. 5(a) and (b) shows polarisation curves and ohmic resistances respectively obtained with the same cell for three cover opening ratios of 5%, 40% and 100% when the cell was operated in a 10% relative humidity atmosphere at 30°C .

Ohmic resistance values were extracted from impedance spectra at the intersection point at high frequencies between the x-axis

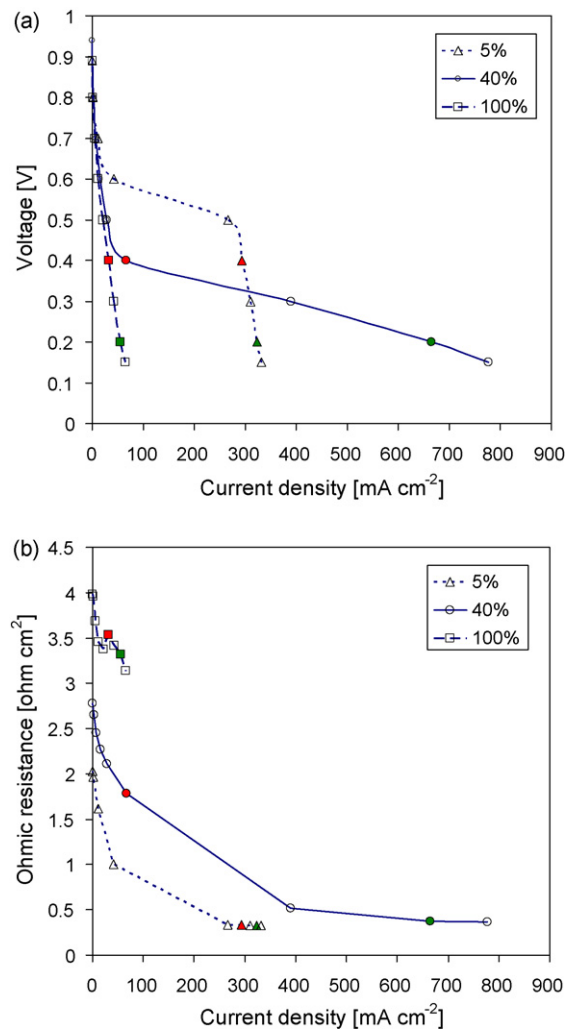


Fig. 5. (a) Polarisation curves for a cell operated at 30°C and 10% of relative humidity with opening rates 5% (triangles), 40% (circles) and 100% (squares). (b) Ohmic resistances extracted from impedance spectra for a cell operated at 30°C and 10% of relative humidity with opening rates of 5% (triangles), 40% (circles) and 100% (squares). Red point 0.4 V, green point 0.2 V. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

and the Nyquist plot [16,17]. Depending on the cover opening ratios and operating points (voltage and current density) the electric performances of the cell were found to vary considerably. At 0.4 V (red point in Fig. 5), current density increased and ohmic resistance was lowered with reduction of cover opening ratios, due to a decrease of water evaporation and optimal humidification of the membrane [18]. At 0.2 V (green point in Fig. 5), the maximum current density was obtained with a cover opening ratio of 40%. Indeed, at a cover opening ratio of 100% the current densities recorded were very low and corresponded to high ohmic resistance characteristic of the cell drying. At 5% and 40% cover opening ratios, the ohmic resistance values were similar but in the first configuration, oxygen diffusion was very limited even for medium current densities ($<350 \text{ mA cm}^{-2}$). In this case the diffusion of oxygen could either be limited by the low ratio of opening or by the presence of a large quantity of water both in the volume and on the cathode surface. In order to discriminate between the previous assumptions, we performed the same experiment with a 5% cover opening ratio but at higher ambient and cell temperature (45°C). The maximum current density obtained for a temperature of 45°C was almost three times higher (900 mA cm^{-2}) compared to the one obtained for a temper-

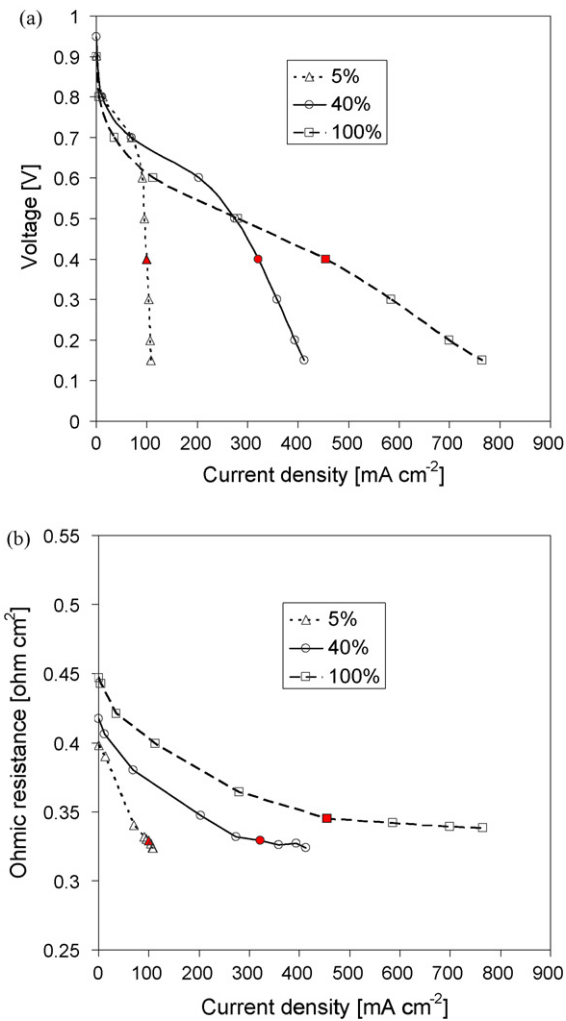


Fig. 6. (a) Polarisation curves for a cell operated at 30 °C and 70% of relative humidity with opening rates of 5% (triangles), 40% (circles) and 100% (squares). (b) Ohmic resistances extracted from impedance spectra for a cell operated at 30 °C and 70% of relative humidity with opening rates of 5% (triangles), 40% (circles) and 100% (squares). Red point 0.4 V. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

ature of 30 °C. Thus, the problem of oxygen diffusion observed for a cover opening ratio of 5% was only attributed to cell flooding.

As shown in Fig. 6, a different behaviour was observed at a relative humidity of 70%. For instance, at 0.4 V (red point in Fig. 6), current density decreased with reduction of cover opening ratios. Because of a higher water concentration in air, cell flooding appeared for lower current densities. Indeed, at a cover opening ratio of 5%, the cell flooding began at current densities below 100 mA cm⁻². However, the drying observed previously at a cover opening ratio of 100% for low current densities was clearly lower at 70% relative humidity. Effectively, as shown in Fig. 6(b), at low current densities the ohmic resistance values were lower at 70% than at 10% relative humidity, indicating an improved hydration of the cell.

According to the results presented above, it is clear that the cover opening ratios play an essential part in micro fuel cell water management. Indeed, low cover opening ratios allow a decrease in the cell drying for low relative humidities and current densities. On the opposite, high opening ratios lead to a decrease in the cell flooding for high relative humidities and current densities. This is why we propose a device enabling the regulation of water flows in a micro-PEMFC by modifying the cover opening ratio [19].

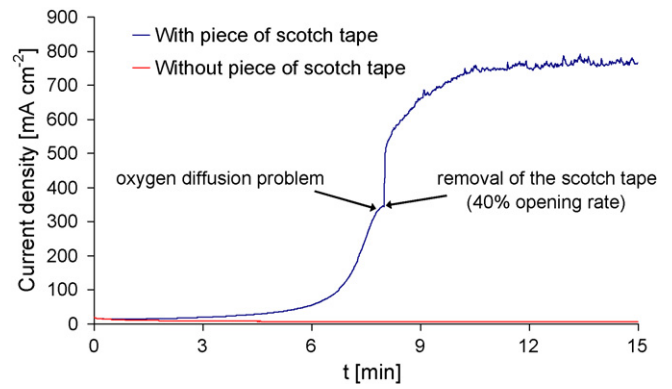


Fig. 7. Cell starting at a potential of 0.15 V and a cell temperature of 60 °C in a dry state in two different cover configurations.

In order to allow the starting of a fuel cell in a dry state, the gases are generally humidified [20,21] beforehand using a voluminous system incompatible with a portable application. In this section we present a solution allowing the starting of a dry cell without preliminary humidification of the gases.

In order to keep the cell in a thorough dry state, it was placed on a hotplate at a temperature set to 60 °C for 3 h and under a dry hydrogen flow of 8.5 cm³ min⁻¹. In order to confirm the dry state of the cell, measurements of resistances were carried out at OCV before each experiment. Two separate experiments were carried out on the same cell maintained at a temperature of 60 °C. In the first experiment (red curve in Fig. 7) the cell was operated with a cover having an open ratio of 40%. In the second experiment (blue curve in Fig. 7) the same cover was closed using a piece of scotch tape.

The cell was run in a potentiostatic mode at a cell potential of 0.15 V in order to reach high current densities. The curves showing the current density evolution as a function of time for each experiment are presented simultaneously in Fig. 7. We can see in both cases that because of an important drying (the ohmic resistance was measured to be approximately 8 Ω cm²) the starting current density was extremely low (15 mA cm⁻²). This value of current density was constant throughout the experiment for the cell with the open cover indicating that this one does not manage to hydrate itself with time.

Concerning the cell with the closed cover, we observed that during the first 2 min the current density did not vary significantly. In this configuration, the rather small amount of water produced and accumulated by the cell during the first 2 min led to a progres-

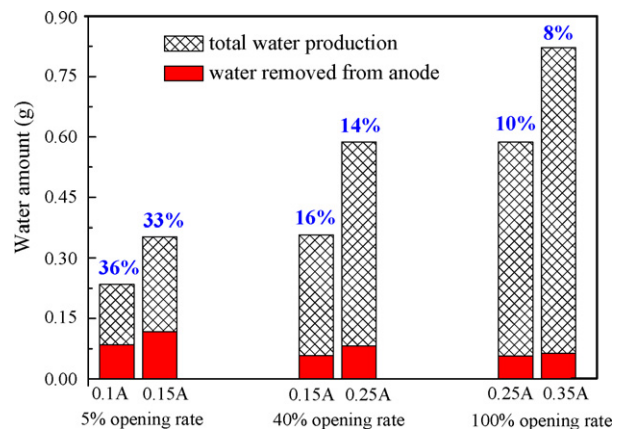


Fig. 8. Water amounts measured for a cell operated at ambient conditions and at a cell temperature of 30 °C with cover open rates of 5%, 40% and 100% for several currents.

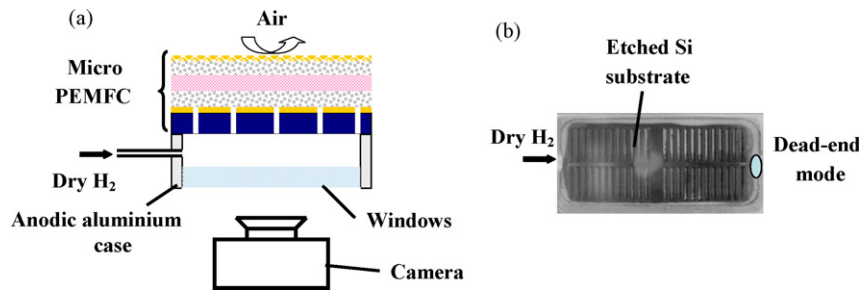


Fig. 9. (a) Schematic view of the transparent micro-PEMFC. (b) Image of the transparent micro-PEMFC.

sive increase in relative humidity inside the cover and allowed an increase of current density. However, after 8 min of operation we noted a decrease in current density due to a lack of oxygen diffusion. Afterwards, the piece of scotch tape was removed and a sudden increase in current density was observed, followed by a progressive stabilization until approximately 800 mA cm^{-2} . If no variation in the operational parameters (temperature, relative humidity, etc.) is observed, the cell can continue to function with such performance without need to supply humidified gases. The same experiment was carried out at a cell potential of 0.6 V and similar results were found. However the time needed to reach a good cell hydration in this configuration was longer. Hence, in order to decrease the starting time at high cell potential, the cell can first be operated in a degraded mode ($<0.15 \text{ V}$) before raising the potential at desired value.

To resume, with this innovative system, it is possible to start a cell even when it is in a marked dry state. However, the time to start the fuel cell is relatively long and not fully compatible with the final application. Nevertheless, the operating temperature studied here constitutes the high limit described by the specification of the micro fuel cell. If the cell operates at lower temperatures, membrane hydration will be higher and time necessary to start the cell will be also shorter.

3.2. Influence of cover opening ratios on water back-diffusion

The water was collected at the anode outlet by passing the hydrogen flow through a glass bulb, which was cooled in an ice bath. Thus, the steam carried by hydrogen flow was condensed on the glass bulb walls. At the end of the experiment the anodic chamber was swept for 1 min by a large dry nitrogen flow in order to remove any water residue. For each experiment the same cell was operated for 7 h at a given current density and the quantity of back-diffused water accumulated in the glass bulb was determined by weighing. The temperature of the room in which the experiments were carried out was controlled and only small fluctuations were recorded (23.9°C and 24.6°C). The relative humidity was recorded before each measurement and ranged from 30.2% to 35.8%. In order to keep cell temperature constant, it is fixed on a hotplate set at 30°C .

Water balance measurement results are presented in Fig. 8 for the same cell operated with various cover opening ratios at several current densities. The hatched columns represent the calculated total water produced by the cell in agreement with Faraday's law and the red columns represent the experimental amount of water collected at the anode outlet. Above each column a figure corresponding to the measured fraction of back-diffused water compared to the calculated total water production is indicated.

The lower the cover opening ratio, the larger the fraction of water was removed from the anode. For instance, the fraction of water removed from anode decreased from 33% to 16% when the opening ratio increased from 5% to 40% for a cell operating at a

current of 150 mA . This can be attributed to the fact that for the same current and when the opening ratio is decreased, the evaporation on the cathode side decreased, leading to a larger water concentration gradient between the anode and the cathode side, and thus to a more important fraction of back-diffused water. For the three opening ratios studied here, the amount of back-diffused water increased with current and the fraction of water removed from the anode decreased with current.

Based on these results, it appears that the amount of water removed from the anode is relatively considerable, particularly if several cells are placed in series as envisaged in the final application. Such a system has to be able to work in a continuous way for several days, it is thus essential to evacuate water removed in the anodic chamber.

3.3. Visualisation and evacuation of back-diffused water at the anode

Among the many studies in PEMFC water observation by using transparent cells [22–26], very few attempted to visualize back-diffused water at the anode side [25,26], and experiments were not carried out on air-breathing PEMFC.

In order to visualize back-diffused water, a transparent micro-PEMFC was built by drilling a 2 cm^2 hole in the anode aluminium case and by inserting a transparent window. A diagram of the transparent micro-PEMFC is presented in Fig. 9(a). Images were taken during the cell operation using a camera positioned below. An image of the transparent cell before operation is shown in Fig. 9(b).

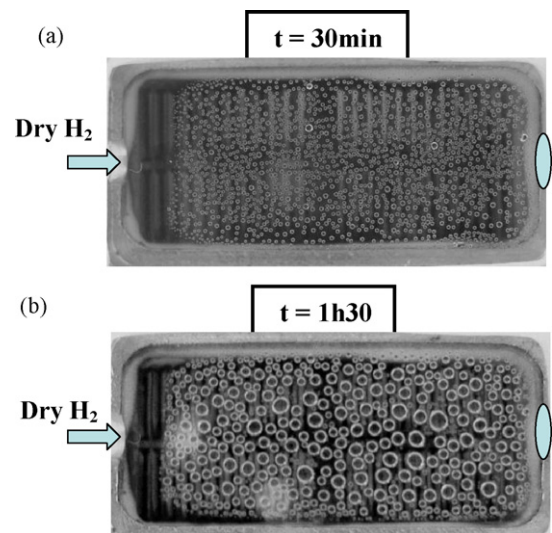


Fig. 10. (a) Image of water removed from anode after 30 min operation at 150 mA cm^{-2} . (b) Image of water removed from anode after 1.5 h operations at 150 mA cm^{-2} .

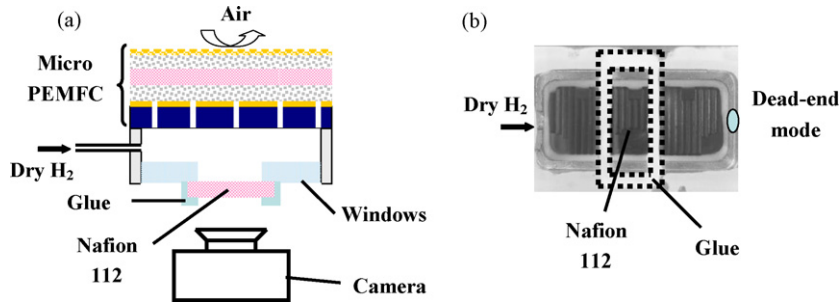


Fig. 11. (a) Schematic view of the anodic water evacuation system. (b) Image of the anodic water evacuation system (the adhesive seal surrounding the membrane is marked by the dotted line).

The cell was supplied with dry hydrogen in dead-end mode and operated with a 40% cover open ratio.

Fig. 10 shows the liquid water in the anode chamber when the cell was operated at a current density of 150 mA cm^{-2} under ambient conditions (25°C , 30% relative humidity) after 30 min (Fig. 10(a)) and 1.5 h (Fig. 10(b)). The water did not condense near the hydrogen input but slightly after indicating that liquid water appears only when the gas phase is saturated [25].

The solution proposed to evacuate back-diffused water, is the addition of a water exchange membrane on a part, or on the whole, of the back surface of the anodic room [27]. It is necessary that this membrane, in addition to its properties of water exchange, is hydrogen tight and airtight, in order to avoid a mixed potential of the anode. A valuable material well adapted for this purpose is a Nafion membrane, for instance a Nafion 112 membrane. Fig. 11 shows a diagram (Fig. 11(a)) and an image (Fig. 11(b)) of the back-diffused water evacuation system. An opening was first made in the transparent PEMFC windows, and then a piece of membrane (0.3 cm^2) was stuck on the hole using hydrogen tight glue. For clarity, the adhesive seal surrounding the membrane present on the image of Fig. 11(b) is marked by the dotted lines.

Fig. 12 shows images of the back-diffused water in a micro-PEMFC after 30 min of operation with this system at current densities higher than 150 mA cm^{-2} (current density for which we

observe an important water condensation on the window (Fig. 10)) and with a 40% cover open ratio. It should be noted that the membrane was not hydrated beforehand. As shown in Fig. 12(a), a part of the back-diffused water still condensed on the window which means that the Nafion 112 membrane (0.3 cm^2) does not allow total removing of the back-diffused water for current densities higher or equal to 250 mA cm^{-2} . On the contrary, as shown in Fig. 12(b), no trace of liquid water was observed on the window when the cell was operated at a current density of 190 mA cm^{-2} .

In order to evaluate the capacity of a Nafion 112 membrane to exchange water with the environment, the device presented in Fig. 13 was realized.

We prepared an opening in a blue sticking plastic, and 6 cm^2 of a Nafion 112 membrane was positioned on the sticky face closing the opening previously realized. We stuck the unit on a compartment that contained water. The device was then placed on a precision scales and the weight evolution was monitored. The quantity of water evacuated at room temperature and relative humidity through a Nafion 112 membrane evolved linearly as a function of time and a water flow of $0.1 \text{ mg min}^{-1} \text{ cm}^{-2}$ was measured. It should be noted that the same experiment was achieved by sticking a piece of Scotch tape on the Nafion 112 membrane, and in this case no weight evolution was recorded which allowed to validate the sealing of the device. It must be emphasized that the amount of water evacuated through a Nafion membrane should also depend on other parameters, such as active surface, thickness and chemical nature. Indeed, Peled et al. [28] developed membranes with water permeability approximately twenty times higher than that of a Nafion 117 membrane, allowing evacuation of larger quantities of water with smaller surfaces.

Contrary to the classical back-diffused water evacuation system, the solution presented here is extremely simple. It does not increase the global volume of the micro-PEMFC and it does not require any tool for control of the water evacuation since it takes place continuously.

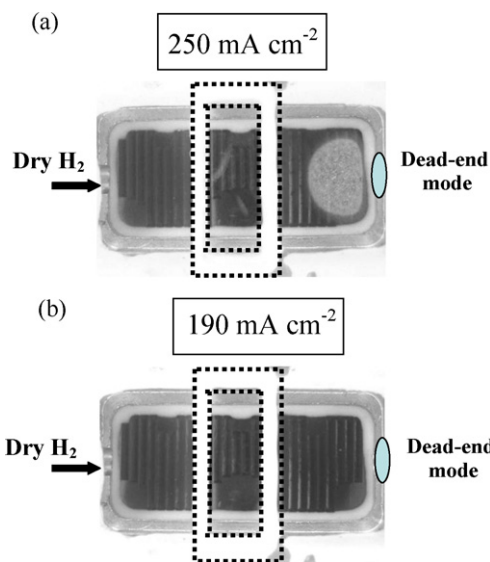


Fig. 12. (a) Image of water removed from anode after 30 min for a cell operated at 250 mA cm^{-2} equipped with an anodic water evacuation system. (b) Image of water removed from anode after 30 min for a cell operated at 190 mA cm^{-2} equipped with an anodic water evacuation system (the adhesive seal surrounding the membrane is marked by the dotted line).

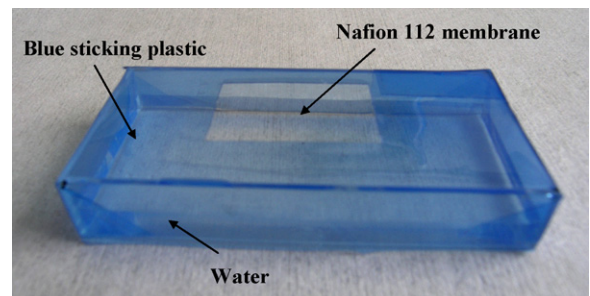


Fig. 13. Device used to evaluate the capacity of a Nafion 112 membrane to exchange water with the environment.

4. Conclusion

The effect of the opening ratio of a cover on water management in micro-PEMFC was experimentally investigated. We demonstrate that according to current density and environmental conditions under which the cell operates, it is possible to decrease cell flooding or drying by varying the cover opening ratio. We report a new method to start a micro air-breathing PEMFC in a dry state by closing the cover openings, allowing a progressive self-hydration of the cell. Water balance measurements allowed us to show the influence of cover opening ratio on water back-diffusion. For a defined current density, the amount of water removed from anode side increased with cover opening ratio reduction and fractions of back-diffused water higher than 30% were found when the cell was operated at 150 mA cm^{-2} with a cover open only at 5%. For long time cell operation, that implies that the anodic water has to be removed. Known systems generally used for the anodic water evacuation are too voluminous and too expensive to be easily suitable with portable applications. A new technique to remove anodic water was investigated by adding a Nafion 112 membrane on the back surface of the anodic room, and its effectiveness was experimentally proved. Those breakthroughs concerning the crucial water management issue open the way for fabricating micro air-breathing PEMFC with improved performances.

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