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LMAPR2231 : Metallurgical and electrochemical processes Lab report : water electrolyzer and fuel cell

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1 Results

The results presented below are from two different laboratory days. The results associated with the first laboratory performed are indicated by an I in the experiment number, while those from the second laboratory are noted by an II.

1.1 Experiment I-1: Current-voltage characteristic of a water electrolyzer

Resistance $[\Omega]$	Voltage [V]	Current [A]	Observations
0.1	0.09	0	
0.33	0.18	0	
1	1.28	0.03	
3,3	2.93	0.09	Begin of O_2 gas release
10	3.6	0.8	Begin of H_2 gas release
33	3.8	1.06	
100	3.89	1.14	
330	3.93	1.17	
∞	3.95	1.18	

Table 1: Lab I - First experiment

1.2 Experiment I-2: Energy efficiency and Faraday efficiency of a water electrolyzer

Volume of H_2 gas $[cm^3]$	Time [s]	Voltage [V]	Current [A]
0	0	3.82	0.82
10	52	3.54	0.81
20	100	3.54	0.81
30	152	3.54	0.81
40	199	3.55	0.81
50	243	3.55	0.81
60	297	3.54	0.81
70	349	3.54	0.81
80	366	3.54	0.81

Table 2: Lab I - Second experiment.

1.3 Experiment I-3: Voltage-current characteristic and power curve of a PEM fuel cell

Resistance $[\Omega]$	Voltage [V]	Current [A]	Power [W]
∞	0.01	0	0
330	0.03	0	0
100	0.15	0.01	0.0015
33	0.21	0.01	0.0021
10	0.15	0.03	0.0045
3,3	0.08	0.03	0.0024
1	0.03	0.02	0.0006
0.33	0.02	0.02	0.0004
0.1	0.01	0.02	0.0002

Table 3: Lab I - Experiment 3

1.4 Experiment I-4: Energy efficiency and Faraday efficiency of a PEM fuel cell

Volume $[cm^3]$	Time [s]	Voltage [V]	Current [A]
0	0	0.21	0.02
5	810	0.16	0.015
10	1790	0.26	0.02
15	2430	0.35	0.03

Table 4: Lab I - Experiment 4

1.5 Experiment II-1: Voltage characterisation for 9 fuel cells in series

Voltage [V]
0.78
1.56
2.36
3.17
3.88
4.67
5.2
5.91
6.71

Table 5: Lab II - Verification of voltage addition for cells in series. The voltage is measured between the first cell and the n cell. This was done for a circuit with a resistance of 10Ω .

1.6 Experiment II-2: 3 PEM fuel cells in series

Volume of H_2 gas $[cm^3]$	Time [s]	Voltage [V]	Current [A]
0	0	0.8	0.07
5	185	1.15	0.11
10	300	1.23	0.12
15	400	1.24	0.12
20	490	1.25	0.12
25	590	1.26	0.12
30	690	1.26	0.12
35	785	1.25	0.12
40	893	1.25	0.12

Table 6: Lab II - Experiment 2: 3 PEM fuel cells in series

1.7 Experiment II-3: 6 PEM fuel cells in series

Volume of H_2 gas $[cm^3]$	Time [s]	Voltage [V]	Current [A]
0	0	0.8	0.07
5	101	1.45	0.14
12	152	1.75	0.17
15	181	1.77	0.17
20	212	1.87	0.18
25	248	1.88	0.18
30	285	1.92	0.19
35	312	1.95	0.19
40	342	1.95	0.19
47	390	1.99	0.19
50	406	1.98	0.19
55	436	1.93	0.19
60	464	1.94	0.19
65	500	1.96	0.19
70	526	1.95	0.19
75	562	1.94	0.19
80	593	1.97	0.19

Table 7: Lab II - Experiment 3: 6 PEM fuel cells in series

1.8 Experiment II-4: 15 PEM fuel cells in series

First trial						
Volume of H_2 gas $[cm^3]$	Time [s]	Voltage [V]	Current [A]			
0	0	1.41	0.14			
10	36	2.05	0.2			
20	61	2.14	0.2			
30	87	2.3	0.22			
40	110	2.32	0.23			
50	134	2.33	0.23			
60	161	1.96	0.19			
70	190	2	0.19			
80	219	1.99	0.19			

Table 8: Lab II - Experiment 4.1: 15 PEM fuel cells in series

Second trial					
Volume of H_2 gas $[cm^3]$	Time [s]	Voltage [V]	Current [A]		
0	0	2.9	0.29		
10	16	3.07	0.31		
20	32	3.18	0.31		
30	48	3.26	0.32		
40	63	3.33	0.33		

Table 9: Lab II - Experiment 4.2: 15 PEM fuel cells in series

1.9 Experiment II-5: Methanol fuel cell

Resistance $[\Omega]$	Voltage [V]	Current [A]
∞	0.6	0
330	0.57	0
100	0.52	0
33	0.36	0.01
10	0.24	0.02
3.3	0.13	0.03
1	0.06	0.05
0.33	0.04	0.05
0.1	0.02	0.06
0	0.01	0.06

Table 10: Lab II - Experiment 5: Methanol fuel cell

2 Theoretical background

There are two main types of electrochemical systems: a fuel cell and an electrolyzer. The first one has the particularity to generate a current while the second one will consume some. The two systems studied here involve a proton exchange membrane (PEM).

2.1 PEM fuel cell

The overall reaction for a PEM fuel cell is:

$$O_{2(g)} + 2H_{2(g)} \to 2H_2O_{(l)}$$
 (1)

From this equation and under standard conditions, we can calculate the Gibbs free energy using the Gibbs free energy of formation of each molecule.

$$\Delta G_{react}^{\circ} = 2 \cdot \Delta G_{f,H_2O}^{\circ} - \Delta G_{f,O_2}^{\circ} - 2 \cdot \Delta G_{f,H_2}^{\circ} = 4 \cdot (-237.13) - 0 = -474.26 \ kJ/mol_{O_2}$$
 (2)

Using Nernst equations, we can than compute the equilibrium potential for this fuel cell:

$$E_{eq} = E_{eq}^{\circ} + \frac{RT}{zF} \ln \left(\frac{a_{O_2}}{a_{H_2}^2} \right)$$
 (3)

where $E_{eq}^{\circ} = \frac{-\Delta G_{react}^{\circ}}{zF}$ is the equilibrium potential in standard conditions, R the ideal gas constant, T the temperature (in Kelvin), z = 4 the number of electrons exchanged, F the Faraday's constant, a_{O_2} and a_{H_2} the activity of oxygen and hydrogen. Since these last two are gases, the activity is defined as the ratio between the partial pressure and the standard pressure ($p^{\circ} = 1$ bar). The activity of water is considered equal to 1 since it is a liquid, so it does not appear in our equation. We do not need the exact activities of oxygen and hydrogen but only the ratio between the two. Using the assumption of perfect gases, this ratio corresponds to the quotient of the number of moles of each species. Since we have twice as much hydrogen as oxygen according to stoichiometry, we get $E_{eq} \approx 1.225$ V at room temperature. This value corresponds to the maximum voltage a PEM fuel cell can deliver.

2.2 PEM electrolyzer

PEM electrolysis is a way of producing hydrogen through the electrolysis of water. We find the same elements as in the fuel cell (an anode, a cathode, a gas-tight membrane that lets H+ ions pass) but the reactions are different. A schematic illustration is shown in Fig. 1. At the anode, we find the oxidation reaction of water which will involve a release of gaseous oxygen:

$$2H_2O_{(l)} \to O_{2(g)} + 4H^+_{(aq)} + 4e^-$$
 (4)

On the other side, at the cathode, the reduction of H⁺ ions occurs with a production of hydrogen gas:

$$2H_{(aq)}^+ + 2e^- \to H_{2(g)}$$
 (5)

The overall reaction is thus:

$$2H_2O_{(l)} \to O_{2(g)} + H_{2(g)}$$
 (6)

By computing the Gibbs free energy of this reaction as done in Eq. 2, we obtain $\Delta G_{react}^{\circ} = +474.26 \, k J/mol_{O_2}$. The theoretical minimum voltage that should be applied in order to activate the electrolyzer can be computed using Nernst equations:

$$E_{cell}^{\circ} = E_{cathode}^{\circ} - E_{anode}^{\circ} \tag{7}$$

where the potential of the cathode and the anode are given by Nernst redox scale. We obtain $E_{cell}^{\circ} = -1.229V$. This negative sign means that this potential has to be applied in order to have a possible reaction.

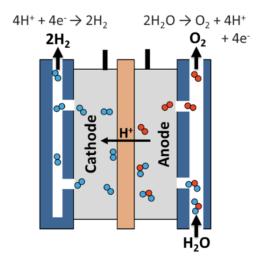


Figure 1: PEM electrolyzer

3 Lab session I: basic study of water electrolyzers and fuel cells

3.1 Experiment 1: Current-voltage characteristic of a water electrolyzer

During this first experiment, we noted the evolution of the current and the voltage according to the put resistance. These data are shown in Table 1. From these, we can plot the evolution of the current vs voltage evolution (see Fig. 2).

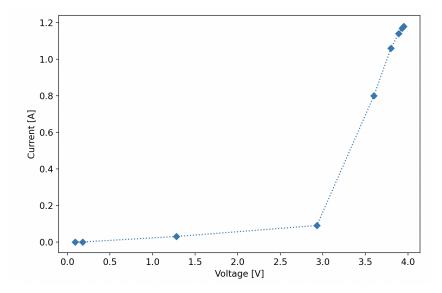


Figure 2: Current vs voltage evolution during experiment 1.

We observe a beginning of oxygen gas release (first bubbles) when the voltage reaches 2.93V and a beginning of hydrogen gas release from 3.6V. From the moment when oxygen is produced, hydrogen is also produced. This latency is perhaps due to the difference in volume of the two gases produced in stoichiometric quantity. Graphically, we observe a significant change in slope from the moment when oxygen is produced, indicating that the reaction is taking place. Theoretically, the reaction already starts at 1.28V (value exceeding the necessary potential). This is verified by the appearance of a current. However, this current is very low and the reaction is therefore very slow. The appearance of bubbles (larger gas volume) appears only well afterwards.

3.2 Experiment 2: Energy efficiency and Faraday efficiency of a water electrolyzer

For this second experiment, we were interested in the volume of gas produced as a function of time. In the first experiment, we noticed a release of hydrogen gas when a resistance of 10 Ω was applied. This resistance was chosen for the measurements of this second test. The results are reported in Table 2.

Both current and voltage are stable at 0.81A and 3.54V respectively. This is consistent since we do not change the resistance of our system. The evolution of the hydrogen gas volume is shown in Fig. 3. A linear evolution is observed whose speed can be approximated by the slope of the line. Using a linear regression, we then obtain a rate of $r_{\rm H_2} = 0.21 \ cm^3/s = 0.76 \ l/h$.

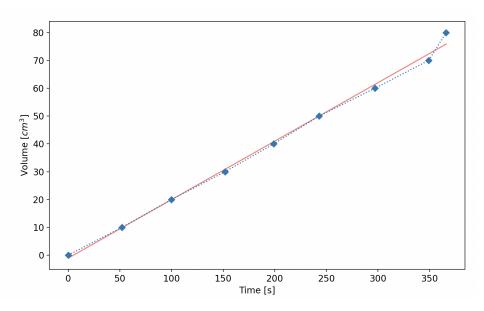


Figure 3: Evolution of Hydrogen gas release in time. The experimental results are indicated by the blue diamonds. The red curve is the linear regression of our data.

With this data, we can calculate the energy and Faraday efficiency. The energy efficiency is first defined as the ratio of the usable energy and the input energy. The input energy corresponds to the amount of energy dissipated by the electrolyzer during the production of Hydrogen. This input energy can be expressed as:

$$E_{input} = P \cdot t = V \cdot I \cdot t = 3.54 \cdot 0.81 \cdot 366 = 1049.47 \text{ J}$$
(8)

On the other hand, the usable energy is the chemical energy stored in H_2 . We have $80cm^3$ of H_2 produced at standard conditions (T = 25°C and p = 1 atm). Assuming this gas is ideal, we obtain an associated mass of

$$m = \text{MM} \cdot n = \text{MM} \cdot \frac{pV}{RT} = 2.016 \cdot \frac{101325 \cdot 80 \cdot 10^{-6}}{8.314 \cdot 298.15} = 6.59 \cdot 10^{-3} g$$
 (9)

To go further, we need a parameter expressing the maximum energy that can be retrieved from H_2 combustion. We will take the Higher Heating Value (HHV), which represents the energy retrieved at complete combustion of H_2 and condensation of the vapour formed. Knowing that this value for Hydrogen is 39.39 kWh/kg [1], we obtain a value of $E_{usable} = 934.49$ J. The energy efficiency is thus:

$$\eta_{energy} = \frac{E_{usable}}{E_{input}} = \frac{934.85}{1049.47} = 0.89 \tag{10}$$

The Faraday efficiency is now defined as the ratio between the experimental volume of H_2 produced and the theoretical volume. The experimental one is $80cm^3$ as mentioned before. Using Faraday's law of electrolysis (where ν is the valence of the ion) and the equation of state for ideal gas, we obtain:

$$V_{theoretical} = \frac{i \cdot t \cdot RT}{v \cdot F \cdot p} = \frac{0.81 \cdot 366 \cdot 8.314 \cdot 298.15}{1 \cdot 96485.33 \cdot 101325} = 75.17 \ cm^3$$
 (11)

The Faraday efficiency can then be expressed as

$$\eta_{\text{Faraday}} = \frac{V_{exp}}{V_{theoretical}} = 1.06 \tag{12}$$

As we can see, the Faraday efficiency is out of range. This can be explained by experimental error. Standard temperature and pressure were used without real measures. Time may also be an issue. Each

time taken may be with an error of 10 to 15 seconds due to tube precision. This precision may also cause slight volume differences for V_{exp} .

The energy efficiency is, however, lower than that of Faraday. This is due to the various possible losses in our system (overpotential losses, heat losses, system inefficiencies in the power supply for example). These factors can all contribute to reducing the energy efficiency of the system compared to the ideal Faraday efficiency.

3.3 Experiment 3: Voltage-current characteristic and power curve of a PEM fuel cell

As a third experiment, we wanted to find the maximum power with associated current and voltage. We repeated Experience I on our fuel cell. Arrows have been added between the different points of our experiment to facilitate the reading of the evolution of current and voltage.

At the beginning of this test, the resistance is infinite and we are facing an open circuit. It is therefore consistent to have no current flowing but we should observe an electrical voltage, called open-circuit-voltage. The initial values of our graphs are far too low. At the end, the resistance is now zero and we are facing a short circuit. In this one, we observe a zero voltage with a relatively high current.

To better understand our results, we turned to the literature. In Fig 6, the theoretical results presented by [2] are illustrated. They found an open-circuit-voltage around 1.2V which is decreasing as the current increases. Therefore, our results do not seem consistent. Since we have a zero potential initially, we can assume that the applied resistance was not really infinite but well and truly finite and of very small value. Perhaps one of the connections was maybe not correct or, as indicated in the statement of this laboratory, the separator may not be moistened enough. A new experiment should be done to get a correct characterization.

Since the results of our power curve are based on our potential and current results and we have just seen that these are not correct, it is important to have a critical look on the results obtained. In general, our curve seems to have the right shape, presenting a maximum. We can denote that 10 Ω is the best resistance that maximises power at 4.5 mW. It is the Maximum Power Point associated with a current of 0.03 A and a voltage of 0.15 V.

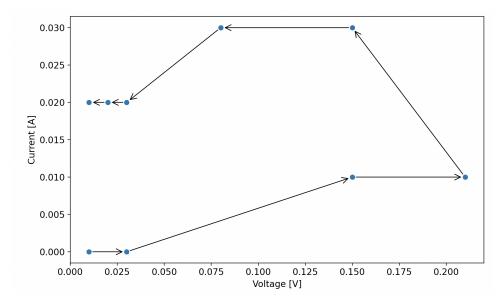


Figure 4: Current vs Voltage evolution. The arrows indicate the evolution of the experimental results indicated by the blue dots.

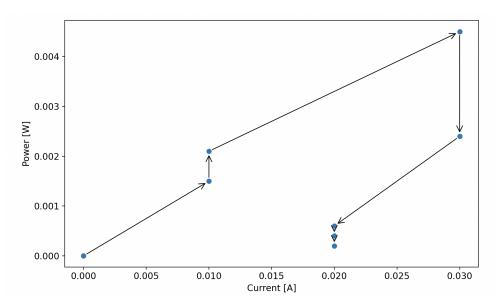


Figure 5: Power evolution in function of current. The arrows indicate the evolution of the experimental results indicated by the blue dots.

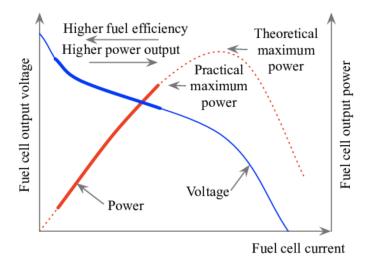


Figure 6: Theoretical polarization curves for a PEM fuel cell [2].

3.4 Experiment 4: Energy efficiency and Faraday efficiency of a fuel cell

Previously, we have characterised the consumption and related efficiency for the PEM electrolyzer. In this section, we will reproduce the same calculations but for the fuel cell. As the maximum power is observed with a resistance of 10 Ω , this is the one we will also apply in this experiment. The obtained results are reported in Table 4.

We could notice slight variations in our current and voltage during this experiment as shown in the corresponding table. In order to be able to calculate our yields, we will take the average of the experimentally obtained values as the current and voltage. This gives us a current of 0.021 A and a voltage of 0.245 V. Hydrogen gas was consumed over time as shown Fig. 7. Again we can observe a linear evolution. The consumption rate is then described by the slope of the line (a linear regression having been done to obtain it). According to our data, we obtain a rate of $r_{\rm H_2} = 0.00601 \ cm^3/s = 0.022 \ l/h$.

As defined for the experiment 2 in subsection 3.2, we can now calculate the energy and Faraday efficiency. The usable energy is here given by the fuel cell:

$$E_{output} = P \cdot t = V \cdot I \cdot t = 0.245 \cdot 0.021 \cdot 2430 = 12.5 J$$
 (13)

In view of the very slow speed of our reaction, the volume of gas consumed is only $V_{exp} = 15 \text{ cm}^3$ in total. This corresponds to a mass of $m_{\text{H}_2} = 1.24 \cdot 10^{-3} \text{ g}$ and an input energy of $E_{input} = 175.28 \text{ J}$, still using the Higher Heating Value for the same reasons as before. The energy efficiency can thus be expressed as:

$$\eta_{energy} = \frac{E_{output}}{E_{input}} = \frac{12.5}{175.28} = 0.0713 \tag{14}$$

For the Faraday efficiency, we need the theoretical volume:

$$V_{theoretical} = \frac{i \cdot t \cdot RT}{v \cdot F \cdot p} = \frac{0.021 \cdot 2430 \cdot 8.314 \cdot 298.15}{1 \cdot 96485.33 \cdot 101325} = 12.94 \ cm^3$$
 (15)

And we thus obtain:

$$\eta_{\text{Faraday}} = \frac{V_{exp}}{V_{theoretical}} = 1.16 \tag{16}$$

As for the characterization of the electrolyzer, we can invoke here experimental errors in time, current and voltage as well as pressure and temperature which were not measured at the time of the laboratory. Moreover, Faraday's law for electrolysis is only valid at constant current. In our case, we should have obtained the total electric charge Q by integrating the current over time. If we account for all these errors, we should have a Faraday efficiency of nearly 100% as explain in [3].

The energy efficiency is still lower than the Faraday efficiency. However, this energy efficiency is expected to be in the range of 50% [4], which we are very far from achieving here. We can assume a problem of humidity or heat evacuation maybe (at very small scale).

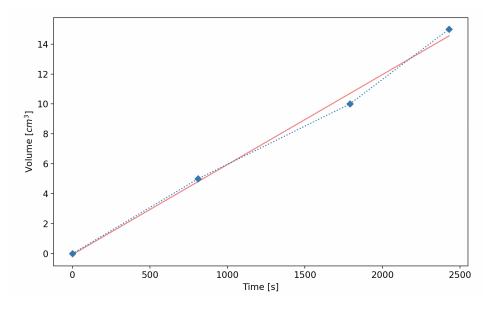


Figure 7: Evolution of H_2 gas consumed in function of time. The experimental results are indicated by the blue diamonds. The red curve is the linear regression of our data.

3.5 To go further: is liquid water needed?

In this last section, we would like to add the results obtained by Fernando Rocha after a very interesting discussion. The research question was: is water needed in both cylinders of our PEM electrolyzer? If not, could we do without liquid water altogether?

Initially, we had water in both cylinders of our system: one for the anode and one for the cathode. First of all, it is interesting to note that water could react at the cathode as well as at the anode. The half-reactions of reduction or oxidation would then be as follows:

Cathode:
$$H_2O + 1e^- \rightarrow \frac{1}{2}H_2 + OH^-$$
 (17)

Anode:
$$H_2O \to 2H^+ + 2e^- + \frac{1}{2}O_{2(g)}$$
 (18)

However, since our membrane only allows protons to pass, only Reaction 18 will be possible in our electrolyzer and we find back the equations developed in subsection 2.2. We can therefore already conclude that only the anode needs water to make our electrolyzer work. In a fuel cell, the opposite result would be obtained: water is needed at the cathode. It is necessary to facilitate the oxygen reduction reaction. During operation, water is produced at the cathode as a byproduct of the electrochemical reaction that occurs there. This water helps to maintain a humid environment at the cathode, which is necessary for efficient operation of the fuel cell.

It remains to be seen whether the water requirement can also be met by the water vapour in the air or whether liquid water is really needed. Three tests were carried out. First, the circuit current with the electrolyzer was observed when both electrodes were dry; a value of 0.04 A is observed. On the day of the laboratory, it had rained well during the night and the air was therefore relatively well humid. This first experiment allows us to see that the cell can theoretically work with water vapor but the efficiency is greatly reduced.

For the second test, liquid water was added at the cathode only and a current of 0.5 A is observed. This is still far from the current observed in the first experiment in this laboratory, described in Section 3.1. This presence of liquid water undoubtedly helps to humidify the membrane and thus facilitates the oxidation reaction that takes place at the anode.

Finally, liquid water was added to both electrodes. The current associated with this experiment is 1A. We can conclude that the presence of water at the anode is really necessary for a good efficiency of our cell. However, this efficiency will also depend on the possible contact surface with water. It is interesting to maximize it.

4 Lab session II: Advanced electrochemical characterisation of a fuel cell

In order to further explore the greatness of fuel cells, we made a setup with cells in series. Hydrogen consumption was studied with 3, 6 and 15 cells in series. Afterwards, we tried a replacement for hydrogen with methanol.

4.1 Study of the consumption of PEM fuel cells in series

The first experiment we performed allowed us to verify one of the basic laws of electricity: the addition of the voltage when putting our cells in series. The associated data are presented in Table 5. It can be seen that the voltage between the start terminal and a number of cells increases linearly. This observation was observed for each of the subsequent experiments except for the first test with 15 fuel cells in series. An unexplained drop in potential appeared around cell 12, implying a much lower measured potential. A second experiment with 15 cells in series was therefore performed but with a lower volume of hydrogen. During this last experiment, no abnormal drop was verified. We will therefore give preference to the data associated with Table 9 for the experiment with 15 fuel cells in series.

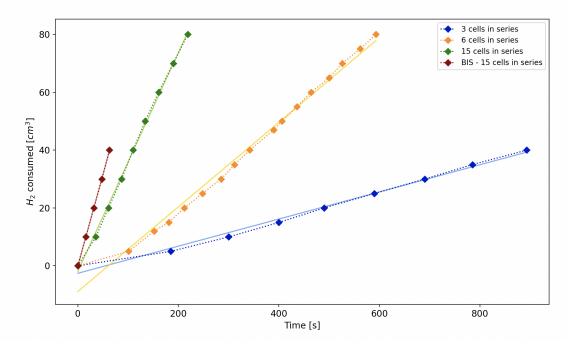


Figure 8: Gas consumption of PEM fuel cells in series. The experimental results are indicated by the diamonds. The light curve behind corresponds to the linear regression of our data.

By considering the slope of the linear evolution of our data, we can estimate the rate of gas consumption. We obtain the following results:

- 3 cells in series: $r_{\rm H_2}=0.047~cm^3/s=0.17~l/h$
- 6 cells in series: $r_{\text{H}_2} = 0.15 \ cm^3/s = 0.54 \ l/h$
- 15 cells in series: $r_{\rm H_2} = 0.38 \ cm^3/s = 1.37 \ l/h$
- BIS 15 cells in series: $r_{\rm H_2} = 0.63~cm^3/s = 2.27~l/h$

As we would expect, the consumption rate increases as the number of cells increases. It is however surprising to see that the speed almost doubles between our two experiments with 15 cells in series. In

view of the inexplicable drop in potential between two cells that we mentioned previously, it is clear that a disturbing element was present during this experiment. One hypothesis we can put forward for this is that the cells were not well purged before performing this experiment. There remained perhaps other gases than hydrogen at the end of our cells, preventing the good progress of our reactions.

With a single cell, we had obtained an energy yield that was far too low and a Faraday yield that was a little too high. We can also calculate these values for the different installations made. The results are summarized in Table 11. The current and voltage evolution are given in Fig. 9. Since these do not vary much, we will use an average value of our observations for the current and voltage used in the equations. The evolution of power is also shown in Fig. 10. As expected, it is increasing with the number of cells. We can also see that the first test made with 15 cells was really not conclusive since the evolution of the power is very close to the one obtained with only 6 cells.

To calculate the Faraday efficiency of our installations, we will use the same formula as in section 3.4 but now taking into account the number of cells as explained by [5]: the theoretical hydrogen quantity must be multiplied by the number of cells n_c . We then obtain:

$$\eta_{\text{Faraday}} = \frac{V_{exp}}{n_c \cdot V_{theoretical}} \tag{19}$$

Number of cells n_c	Current [A]	Voltage [V]	E_{output} [J]	$V_{theoretical} [cm^3]$	η _{energy} [%]	η _{Faraday} [%]
3	0.12	1.25	133.95	27.17	28.66	49.07
6	0.19	1.92	216.33	28.57	23.14	46.67
15	0.21	2.14	98.42	11.66	10.53	45.74
15 - Bis	0.31	3.15	61.52	4.95	13.16	53.87

Table 11: Evaluation of the efficiency of our installations with several PEM fuel cells in series.

As far as energy efficiency is concerned, it can be noticed that it decreases with the increase of the number of cells in series. The lowest efficiency is observed for the first test with 15 cells in series. This is consistent with the previous observations and the voltage drop observed between cells. In theory, we would have expected to see the energy yield decrease with the number of cells due to losses associated with the additional electrical connections between the cells. These losses may include resistance in the electrical contacts and wiring, as well as losses due to any imbalances in the performance of the individual cells. So we should have had the highest efficiency with a single cell. But this is not what is observed since the efficiencies that we have just calculated are better than the one for a single cell (we obtained an efficiency of 7% - see section 3.4).

In terms of Faraday efficiency, we observe values that correspond to about half of the one obtained with a single cell. A lower Faraday efficiency indicates that the amount of electron used is much lower than it would be if the reaction proceeded completely as expected. According to Ohm's law, if we suppose that each cell corresponds to the same resistance, the current flowing in each cell will decrease proportionally to the increase of the observed potential. This decrease in current implies that a smaller quantity of electron arrives at the cell. This could explain the decrease in Faraday efficiency due to the addition of cells in series.

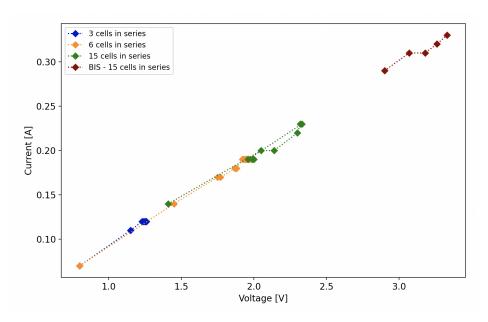


Figure 9: Current vs Voltage evolution. The experimental results are indicated by the diamonds.

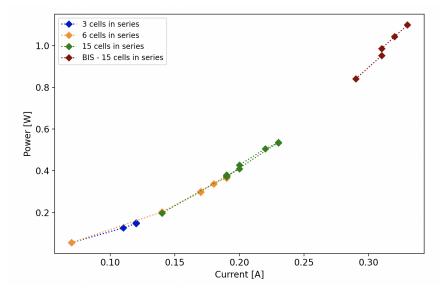


Figure 10: Power evolution in function of current. The experimental results are indicated by the diamonds.

4.2 To go further: Methanol fuel cell

For this last test, we had the opportunity to experiment with a methanol fuel cell. A diagram of this new cell is shown in Figure 11. At the anode, we find the oxidation reaction of Methanol CH_3OH which will release carbon dioxide $CO_{2(g)}$:

$$CH_3OH_{(l)} + H_2O_{(l)} \rightarrow CO_{2(g)} + 6H^+ + 6e^-$$
 (20)

At the cathode, we have the reduction of oxygen following:

$$O_{2(g)} + 4H^{+} + 4e^{-} \rightarrow 2H_{2}O_{(l)}$$
 (21)

This gives us an overall reaction:

$$CH_3OH + \frac{3}{2}O_2 \to CO_2 + 2H_2O$$
 (22)

In order to compare the values with those of the PEM fuel cell, we will calculate the Gibbs free energy for one mole of O₂. Therefore, the Gibbs free energy under standard conditions is:

$$\Delta G_{react}^{\circ} = \frac{2}{3} \Delta G_{f,CO_{2}}^{\circ} + \frac{4}{3} \Delta G_{f,H_{2}O}^{\circ} - \frac{2}{3} \Delta G_{f,CH_{3}OH}^{\circ} - \Delta G_{f,O_{2}}^{\circ} = -419.84 \ k \text{J/mol}_{O_{2}} \tag{23}$$

We can then express the equilibrium potential using Nernst equations:

$$E_{eq} = E_{eq}^{\circ} + \frac{RT}{zF} \ln \left(\frac{a_{O_2}}{a_{CO_2}^{2/3}} \right) \approx 0.73 \text{ V}$$
 (24)

where equilibrium potential is given by $E_{eq}^{\circ} = \frac{\Delta G_{react}^{\circ}}{zF}$. Theoretically, a methanol fuel cell can thus deliver less voltage than a PEM fuel cell as previously calculated. Moreover, it has the big disadvantage of producing carbon dioxide during its use. The whole point of greener energy is therefore lost.

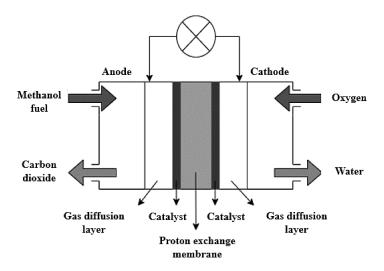


Figure 11: Schematic of a Methanol fuel cell

The voltage-current characteristic curve for a methanol fuel cell obtained experimentally is shown in Fig. 12. To verify our results, we will compare it with the curve obtained from the literature, shown in Fig. 13. We can see that the starting value as well as the general shape of the curve are similar on both graphs. The tendency of this polarization curve is to decrease, implying that the voltage output of the cell is decreasing as the current is increased. This could be due to methanol crossover for example. It is defined as the transport of methanol across the membrane from the anode side to the cathode side. It has been recognized as the most important technical obstacle causing major performance losses in methanol fuel cells [6].

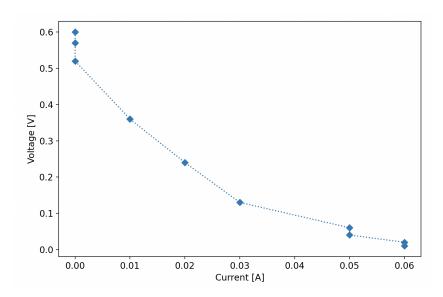


Figure 12: Voltage-current evolution for a Methanol fuel cell.

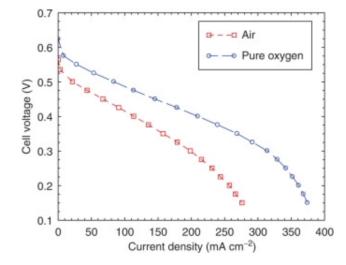


Figure 13: Performance comparison of the Direct Methanol Fuel Cell (DMFC) fed with pure oxygen or air [7].

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