
Electrochemical characterisation of water electrolyzer and fuel cell

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May 5, 2025

I Introduction

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II Materials and Methods

The experiments were conducted following the procedures outlined in the reference document *LaboPAC 2025*, available on the Moodle website of the course [1], which provides a detailed description of the materials, equipment, and methodologies used. The laboratory session was divided into two lab sessions. The first lab session focused on the basic characterization of the water electrolyzer and the PEM fuel cell, while the second lab session involved a more in-depth analysis of the electrochemical processes occurring in fuel cells. Table. 1 is a brief summary of the experimental setup and Objective for the first lab session, which was divided into two main parts: the water

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electrolyzer experiments and the PEM fuel cell experiments. Four experiments were conducted during the first lab session. In these document, the experiments are referred to as *Exp1*, *Exp2*, *Exp3*, and *Exp4*. **Preciser quel electerolyseur on a eu et quel fuel cell. + Discuter des resisatnce utilisées**

Table. 1. Summary of the four main experimental quantities for Lab Session I, grouped by device type. The analysis done in each experiment is also indicated.

Experiment	Objective	Measured Quantities	Analysis
A – Water Electrolyzer Experiments			
<i>Exp1</i>	Determine the water decomposition voltage	Voltage (U), Current (I) for various resistances	Plot current vs. voltage, identify gas onset voltage, compare with theoretical value
<i>Exp2</i>	Evaluate efficiency of hydrogen production	Time t , Applied voltage (U), Current I , Volume of H_2 v_{H_2} produced	Plot H_2 volume vs. time, calculate energy and Faraday efficiencies
B – PEM Fuel Cell Experiments			
<i>Exp3</i>	Identify maximum power output of the cell	Voltage (V), Current (A) for various resistances	Plot voltage vs. current and power vs. current, determine Maximum Power Point (MPP)
<i>Exp4</i>	Evaluate efficiency during hydrogen consumption	Time t , Voltage U , Current I , Volume of H_2 v_{H_2} consumed	Plot H_2 consumption vs. time, calculate energy and Faraday efficiencies

Table. 2. *Exp1: Measured resistance, voltage, and current for the water electrolyzer.*

R (Ω)	U (V)	I (A)
0	0	0
0.1	0.105	0
0.33	0.67	0
1	1.43	0
3.3	3.19	0.24
10	3.52	0.8
33	3.64	1.04
100	3.68	1.1
330	3.69	1.14

Table. 4. *Exp2: Measured volume, current, and time for the water electrolyzer.*

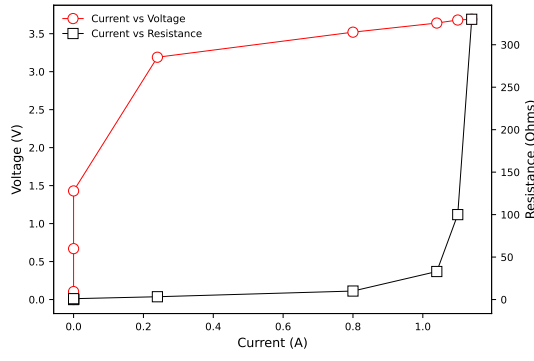
v_{exp} (cm³)	I (A)	t (s)
0	0	0
10	1	18
20	0.98	60
30	0.98	98.5
40	0.97	139.8
50	0.97	174.6
60	0.97	227.2
70	0.97	273.5
80	0.97	314.5

Table. 3. *Exp3: Measured resistance, voltage, current, and power for the PEM fuel cell.*

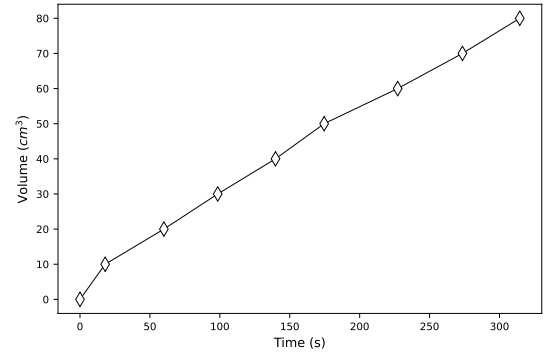
R (Ω)	U (V)	I (A)	P (mW)
∞	0.898	0	0.0
330	0.8	0.0025	2.0
100	0.76	0.0074	5.624
33	0.71	0.0203	14.413
10	0.65	0.0512	33.28
3.3	0.61	0.0975	59.475
1	0.48	0.124	59.52
0.33	0.354	0.1092	38.6568
0.1	0.33	0.1045	34.485
0	0.325	0.1018	33.085

Table. 5. *Exp4: Measured time, voltage, current, and hydrogen volume for the PEM fuel cell.*

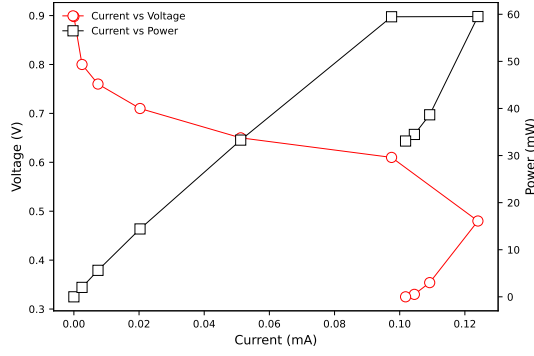
t (s)	U (V)	I (A)	v_{exp} (cm³)
0	0.35	0.055	0
490	0.413	0.0762	2.5
639	0.484	0.078	5
918	0.492	0.0791	7.5
1122	0.493	0.0786	10
1380	0.49	0.0786	12.5
1620	0.484	0.0786	15



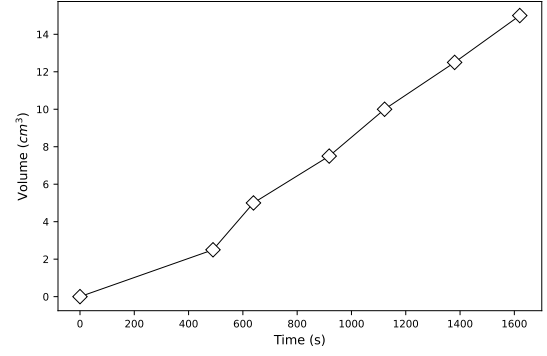
(a) Voltage vs. Current for Experiment 1.



(b) Time vs. Volume for Experiment 2.



(c) Power vs. Current for Experiment 3.



(d) Time vs. Volume for Experiment 4.

Fig. 1. Summary of experimental results for the water electrolyzer and PEM fuel cell.

III Discussion

III.A Theoretical Background

The reaction in a PEM fuel cell is given in Table 6.

Table 6. Reactions at the electrodes and overall reaction for a PEM fuel cell.

Electrode	Reaction	Location
Anode	$H_{2(g)} \rightarrow 2H_{(aq)}^+ + 2e^-$	Oxidation
Cathode	$O_{2(g)} + 4e^- + 4H_{(aq)}^+ \rightarrow 2H_2O_{(l)}$	Reduction
Overall Reaction	$O_{2(g)} + 2H_{2(g)} \rightarrow 2H_2O_{(l)}$	-

The Nernst equation gives the cell potential:

$$V_{eq} = V_{eq}^{\circ} - \frac{RT}{zF} \ln \left(\frac{a_{red}}{a_{ox}} \right) = V_{eq}^{\circ} - \frac{RT}{zF} \ln \left(\frac{a_{H_2O}}{a_{H_2}^2 a_{O_2}} \right) \quad (1)$$

where V_{eq}° is the standard cell potential, R is the gas constant, T is the temperature in Kelvin, n is the number of electrons involved in the reaction, F is the Faraday constant, and a_{H_2O} , a_{H_2} , and a_{O_2} are the activities of the species involved in the reaction. Since water is liquid, the activity of water is assumed to be 1. The activities of the gases are assumed to be equal to their partial pressures divided by the standard pressure (1 bar). Moreover, the pressure of the oxygen is assumed to be equal to the pressure of the hydrogen and is equal to P , the service pressure of the electrolyzer (1 bar) [2]. Notice that the oxydation and reduction reaction at the electrode is function of the concentration of hydrogen ions in the electrolytes, i.e. the pH. The equilibrium potential can be computed thanks to the Nernst equation, this computation is made in the *LMAPR2231 Metallurgical and Electrochemical Course* [3]. The E-pH diagram is shown at the Figure 2. It is important to note that the reaction at the electrode and at the cathode have the same slope. In induce that, since the cell potential is the difference of the equilibrium potential at the anode and at the cathode, the cell potential is indepedent of the pH.

At the standard conditions, we can determine the Gibbs free energy change of the overall electrochemical reaction from the cell potential at those conditions thanks to this formula:

$$-\Delta G^\circ = n \cdot F \cdot V_{eq}^\circ \quad (2)$$

where $V_{cell,eq}^\circ = V_{cathode}^\circ - V_{anode}^\circ$, n is the number of electrons involved in the reaction, 4 in this case, and F is the Faraday constant. From the Table 7, The standard electrode potentials are $V_{anode}^\circ = 0$ and $V_{cathode}^\circ = 1.229$. The cell potential is $V_{cell,eq}^\circ = 1.229$. This is the maximun value of potential that can be deliver by the fuel cell, when no current is taken. The standard Gibss free energy is $G^\circ = -474.32 \frac{kJ}{2mol(H_2O)} = -237.16 \frac{kJ}{mol} = -56.64 \frac{kcal}{mol}$. This is consistent with the Gibbs free energy change of the overall electrochemical reaction of Hydrogen shonw in the Table. 7.

Table. 7. Theoretical Cell Potentials of Various Oxidation Reactions at 25°C.

Fuel	Reaction	ΔG^0 (kcal mol ⁻¹)	V_a^0 (V)
Hydrogen	$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$	-56.69	1.229
	$H_2 + Cl_2 \rightarrow 2HCl$	-62.70	1.370
Propane	$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$	-503.90	1.093
Methane	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	-195.50	1.060
Carbon monoxide	$CO + \frac{1}{2}O_2 \rightarrow CO_2$	-61.45	1.333
Ammonia	$NH_3 + \frac{3}{2}O_2 \rightarrow \frac{3}{2}H_2O + \frac{1}{2}N_2$	-80.8	1.170
Methanol	$CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O$	-168.95	1.222
Formaldehyde	$CH_2O + O_2 \rightarrow CO_2 + H_2O$	-124.7	1.350
Formic acid	$HCOOH + \frac{1}{2}O_2 \rightarrow CO_2 + H_2O$	-68.2	1.480
Hydrazine	$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$	-143.9	1.560
Zinc	$Zn + \frac{1}{2}O_2 \rightarrow ZnO$	-76.05	1.650
Sodium	$Na + \frac{1}{2}H_2O + \frac{1}{2}O_2 \rightarrow NaOH$	-71.84	3.120
Carbon	$C + O_2 \rightarrow CO_2$	-94.26	1.020

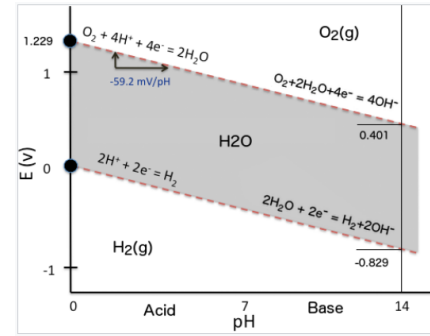


Fig. 2. E-pH diagram of water. The diagram shows the thermodynamic stability of water in terms of its potential (E) and pH. The shaded area indicates the region where water is stable, while the lines represent the boundaries between different species [4].

The same reasoning can be done for a PEM electrolyzer producing oxygen and hydrogen. The reactions at the

electrodes in this case would be:

Table. 8. Reactions at the electrodes and overall reaction for a PEM electrolyzer.

Electrode	Reaction	Location
Anode	$2H_2O_{(l)} \rightarrow O_{2(g)} + 4e^- + 4H_{(aq)}^+$	Oxidation
Cathode	$4H_{(aq)}^+ + 4e^- \rightarrow 2H_{2(g)}$	Reduction
Overall Reaction	$O_{2(g)} + 2H_{2(g)} \rightarrow 2H_2O_{(l)}$	-

A PEM electrolyzer works like a PEM fuel cell but in reverse. However, the key difference is that in an electrolyzer, this voltage represents the minimum required to start the reaction, rather than the maximum produced. The standard electrode potential at the anode and the cathode are respectively $V_{anode}^\circ = 1.229$ and $V_{cathode}^\circ = 0$ which gives a negative standard cell potential $V_{cell,eq}^\circ = -1.229$ and thus a positive Gibbs free energy at the standard condition $G^\circ = 474.32 \frac{kJ}{2mol(H_2O)} = 237.16 \frac{kJ}{mol} = 56.64 \frac{kcal}{mol}$. This global reaction is thus not thermodynamically favored at the standard conditions [5].

III.B Faradic Efficiency

The theoretical volume of hydrogen produced, v_{theo} , is given by:

$$v_{theo} = \frac{i \cdot t \cdot R \cdot T}{z \cdot F \cdot p} \quad (3)$$

where i is the current, t is the time, R is the gas constant, T is the temperature, z is the number of electrons involved in the reaction ($z = 2$ for hydrogen), F is the Faraday constant, and p is the pressure.

The Faradic efficiency, η_{Farad} , is calculated as:

$$\eta_{Farad} = \frac{v_{exp}}{v_{theo}} \times 100 \quad (4)$$

Table. 9. Faradic efficiencies of each measurement for Experiment 4.

v_{exp} (cm ³)	i (A)	t (s)	v_{theo} (cm ³)	η_{Farad} (%)
0	-	-	-	-
2.5	0.0762	490	2.8	89.3
5	0.078	639	5.2	96.2
7.5	0.0791	918	7.8	96.1
10	0.0786	1122	10.1	99.0
12.5	0.0786	1380	12.4	100.8
15	0.0786	1620	14.8	101.4

III.C Experimental Results

III.C.1 Exp1: Water Decomposition Voltage

Figure. 3 shows the voltage as a function of the current and the current as a function of the resistance. The voltage increase rapidly with the current before reaching a plateau. There is no current until the voltage reach 3.19 V. This value is a lot above the theoretical value of 1.23 V. The change of slope means that the reaction is starting. Gas bubbles are formed on the electrodes. The different between the theoretical and experimental value may be due to the fact to lost in the electrical circuit and by the fact that only discrete values of resistance was tested. **note du degagement gazeux**

III.C.2 Exp2: Efficiency of Hydrogen Production

From the experiment 1, the power consumed by the electrolyzer is given by the product of the current and the voltage. Taking the data from The Table 2, the power can be computed and plotted as a function of the resistance.

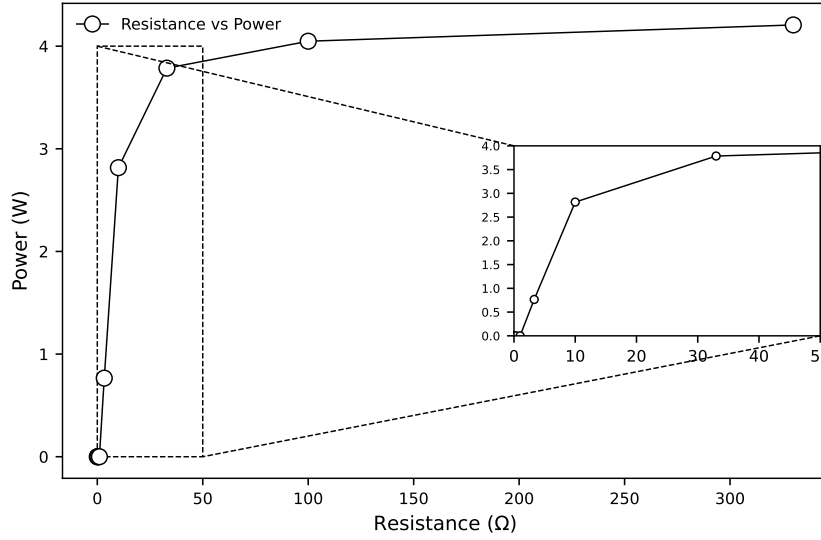


Fig. 3. Power as a function of the resistance for Exp1. The zoom on the right shows the power for resistances between 0 and 50 Ω .

For this experiment, a resistance of 33 Ω was chosen. From experiment 1, it was observed that higher resistance leads to higher power. However, since the volume of gas is proportional to the current (see Eq. 5), a trade-off was made between efficiency and data accuracy. A resistance of 33 Ω was deemed a good compromise.

The average production rate was calculated by taking the mean of $\frac{\Delta v}{\Delta t}$ between each successive data point. This resulted in an average production rate of 0.276 cm³/s.

Assuming the produced hydrogen is dry and behaves as an ideal gas, the theoretical volume can be calculated using the equation:

$$v_{theo} = \frac{i \cdot t \cdot R \cdot T}{z \cdot F \cdot p} \quad (5)$$

where T is the ambient temperature, p is the atmospheric pressure, and n is the number of moles. The number of moles n is related to the time t and current i by Faraday's law of electrolysis: $i \cdot t = n \cdot z \cdot F$, where z is the number of electrons involved in the reaction, which is 4 in this case. The relation between the volume and the number of moles is given by the ideal gas law: $pv = nRT$. The table below gives the v_{exp} , v_{theo} and η_{Farad} associated to the time and current points taken during the experiment as

$$\eta_{Farad} = \frac{v_{exp}}{v_{theo}} \quad (6)$$

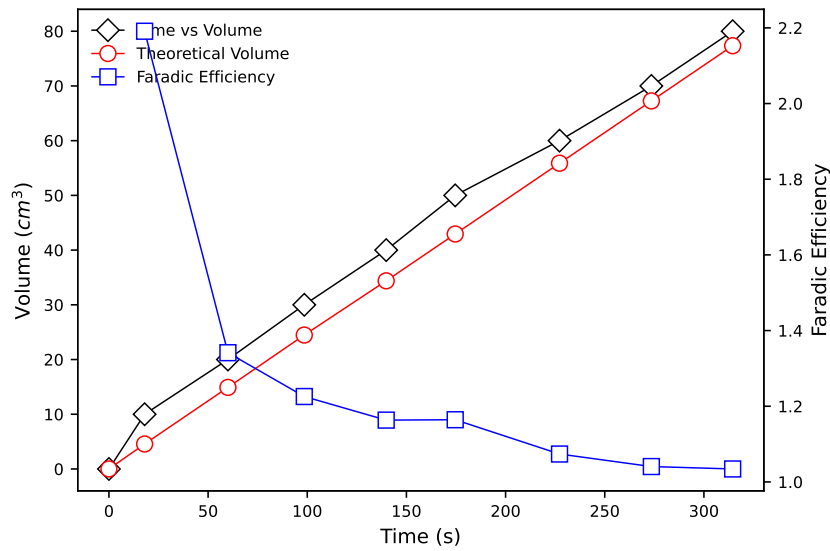


Fig. 4. Volume of hydrogen produced as a function of time for Exp2 with the theoretical volume. The red line is the theoretical volume of hydrogen produced. The blue line is the Faradic efficiency.

Table. 10. Faradic efficiencies of each measurement for Experiment 2.

v_{exp} (cm ³)	η_{Farad} (%)
0	-
10	89.1
20	54.6
30	49.9
40	47.3
50	47.4
60	43.7
70	42.3
80	42.1

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III.C.3 Exp3: Maximum Power Output of the Cell

The Maximun power point (MPP) is the value of current density and voltage that maxime the power. The resistance that gives the MPP is $1\ \Omega$ with a power of 59.5 mW.

III.C.4 Exp4: Efficiency during Hydrogen Consumption

For this experiment, we chose a resistance of $1\ \Omega$. This seemed to be the best choice since, from experiment 3, we calculated that it was the resistance that gives the most power.

Following the same reasoning as for experiment 2, we found the Faradic efficiency for each measurements in Table 9.

IV Conclusion

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References

- (1) Institute of Mechanics, Materials and Civil Engineering LaboPAC 2025: Electrochemistry of Fuel Cells, Available on Moodle for the LMAPR2231 Electrochemistry of Fuel Cells course; Louvain School of Engineering, 2025.
- (2) Société Chimique de France *L'Actualité Chimique* **1995**, Numéro 196, 39.
- (3) Proost, J. Metallurgical and Electrochemical Processes (LMAPR2231), 5 ECTS credits; 30h lectures + 22.5h practicals; taught in English (French-friendly); offered in Q2, Louvain-la-Neuve, Belgium, 2025.
- (4) LibreTexts 4.3: Electrochemical Potentials LibreTexts, [https://chem.libretexts.org/Bookshelves/Inorganic_Chemistry/Introduction_to_Inorganic_Chemistry_\(Wikibook\)/04%3A_Redox_Stability_and_Redox_Reactions/4.03%3A_Electrochemical_Potentials](https://chem.libretexts.org/Bookshelves/Inorganic_Chemistry/Introduction_to_Inorganic_Chemistry_(Wikibook)/04%3A_Redox_Stability_and_Redox_Reactions/4.03%3A_Electrochemical_Potentials) (accessed 03/10/2024).
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