

Fuel Cells

(experiment #57, 6.6.03)

Gruppe 176:
Sebastian Rammensee
Michael Reimer
Claudius Knaak

Part 1: Thermodynamics of the fuel cell

The following equation is called the Nernst Equation:

$$U_0(T, p) = U_{00}(T^0, p^0) - \frac{R \cdot T}{z \cdot F} \cdot \ln \left[\frac{p_{H_2O}}{p_{H_2} \cdot \sqrt{p_{O_2}}} \right]$$

where is

$U_{00}(T^0, p^0) = U_{rev} = 1.229V$ the reversible cell voltage under standard conditions

$R = 8.314 \frac{J}{K \cdot mol}$ the universal gas constant

T the temperature of the cell [K]

z = 2 the number of transferred electrons in each reaction

$F = 96487 \frac{C}{mol}$ the Faraday's constant

p_{H_2O} the pressure of water

p_{H_2} the pressure of hydrogen

p_{O_2} the pressure of oxygen

$$\Rightarrow U_0(T, p) = 1.229V - \frac{8.314 \cdot T}{192974} \cdot \ln \left[\frac{p_{H_2O}}{p_{H_2} \cdot \sqrt{p_{O_2}}} \right] V$$

We set the pressure of water to 1 bar = 10^5 Pa, because it is said in the script that the activity of water is 1.

The pressure of oxygen in synthetic air is $0.2 \cdot p_{Air}$ (p_{Air} = pressure of air).

When we use air the theoretical reversible cell voltage can be calculated in the following way:

$$\Rightarrow U_{0,Air}(T, p) = 1.229V - \frac{8.314 \cdot T}{192974} \cdot \ln \left[\frac{1}{p_{H_2} \cdot \sqrt{0.2 \cdot p_{Air}}} \right] V$$

and with oxygen instead of air:

$$\Rightarrow U_{0,Ox}(T, p) = 1.229V - \frac{8.314 \cdot T}{192974} \cdot \ln \left[\frac{1}{p_{H_2} \cdot \sqrt{p_{O_2}}} \right] V$$

where is

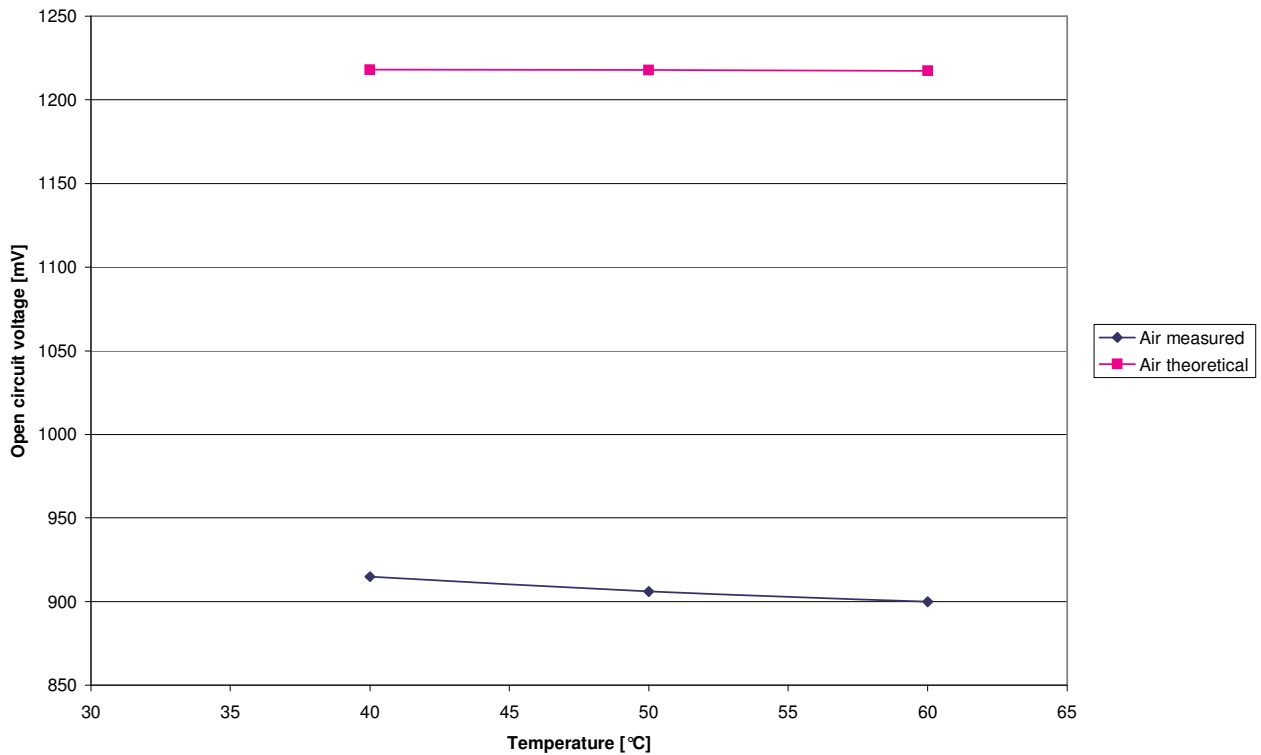
T: the temperature of the cell

p_{Air} the pressure of air as dimensionless multiples of 1 bar
 p_{H_2} the pressure of hydrogen as dimensionless multiples of 1 bar
 p_{O_2} the pressure of oxygen as dimensionless multiples of 1 bar

Part 1 – 1. Temperature dependency of the Nernst Equation

We measured the open circuit voltage at different temperatures (pressure = 1 bar) and calculated the theoretical values (with air):

Temperature	40 °C	50 °C	60 °C
Measured values [mV]	915	906	900
Theoretical values [mV]	1218.1	1217.8	1217.4

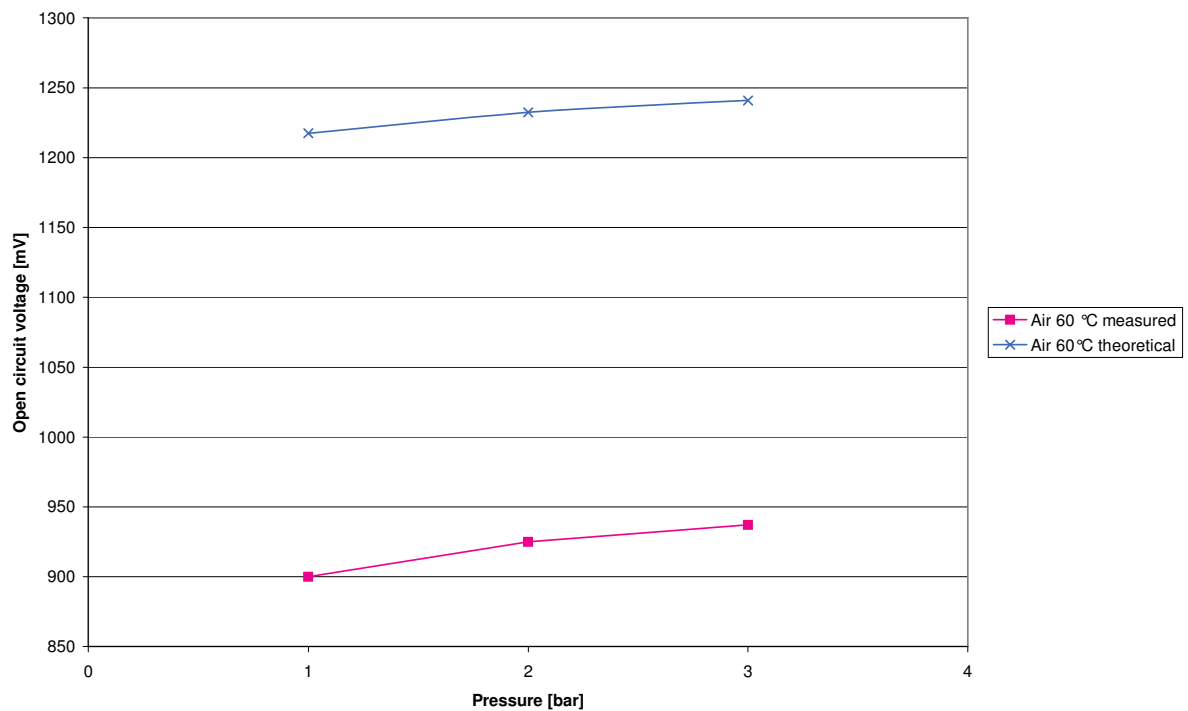
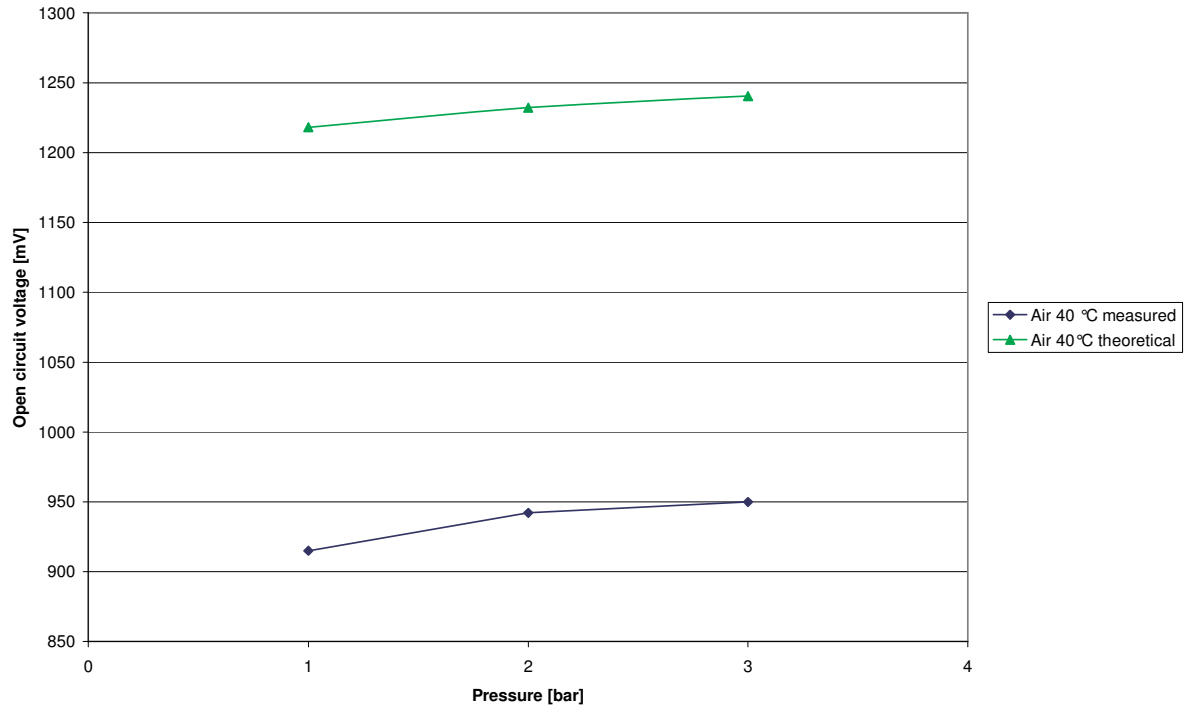


The Nernst Equation tells us that the open circuit voltage should decrease when we increase the temperature and this is exactly what we measured. The fact that our measured values are much lower than the theoretical values is an indication for the process not being reversible.

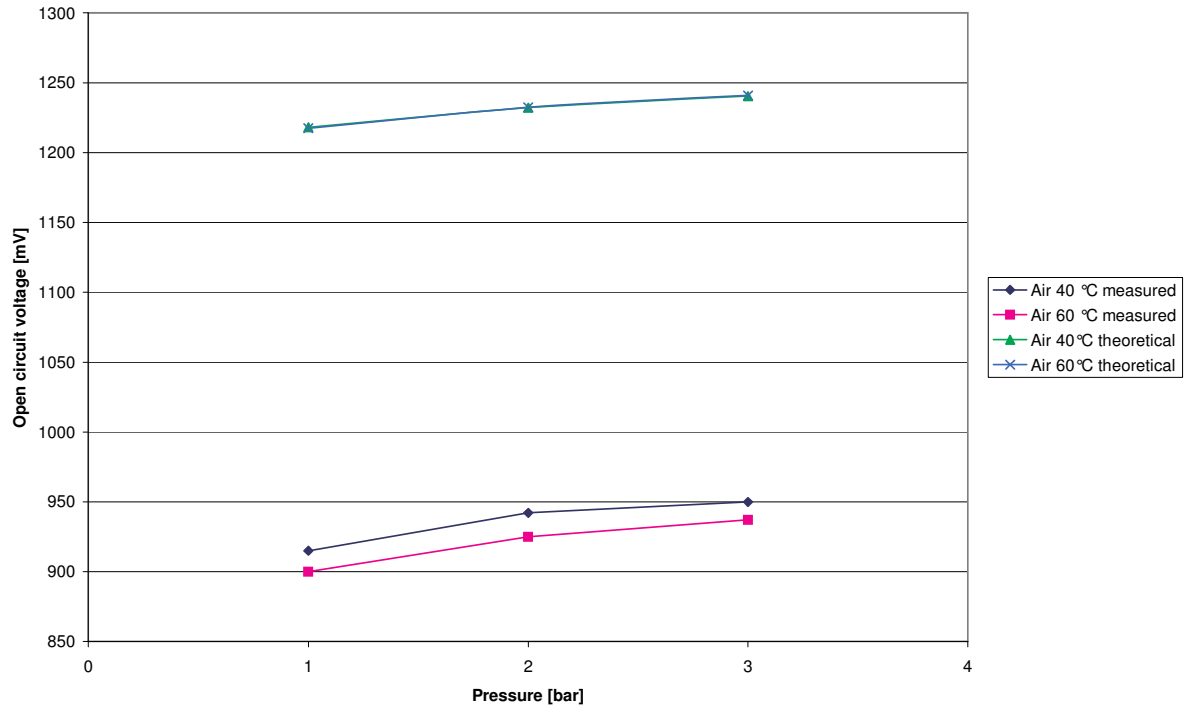
Part 1 – 2. Pressure dependency of the Nernst Equation

This time we measured the open circuit voltage at different pressures, once at 40°C and once at 60°C. Again, we also calculated the theoretical values (with air):

Pressure	1 bar	2 bar	3 bar
40°C, measured [mV]	915	942	950
40°C, theoretical [mV]	1218.1	1232.2	1240.4
60°C, measured [mV]	900	925	937
60°C, theoretical [mV]	1217.4	1232.4	1241.1



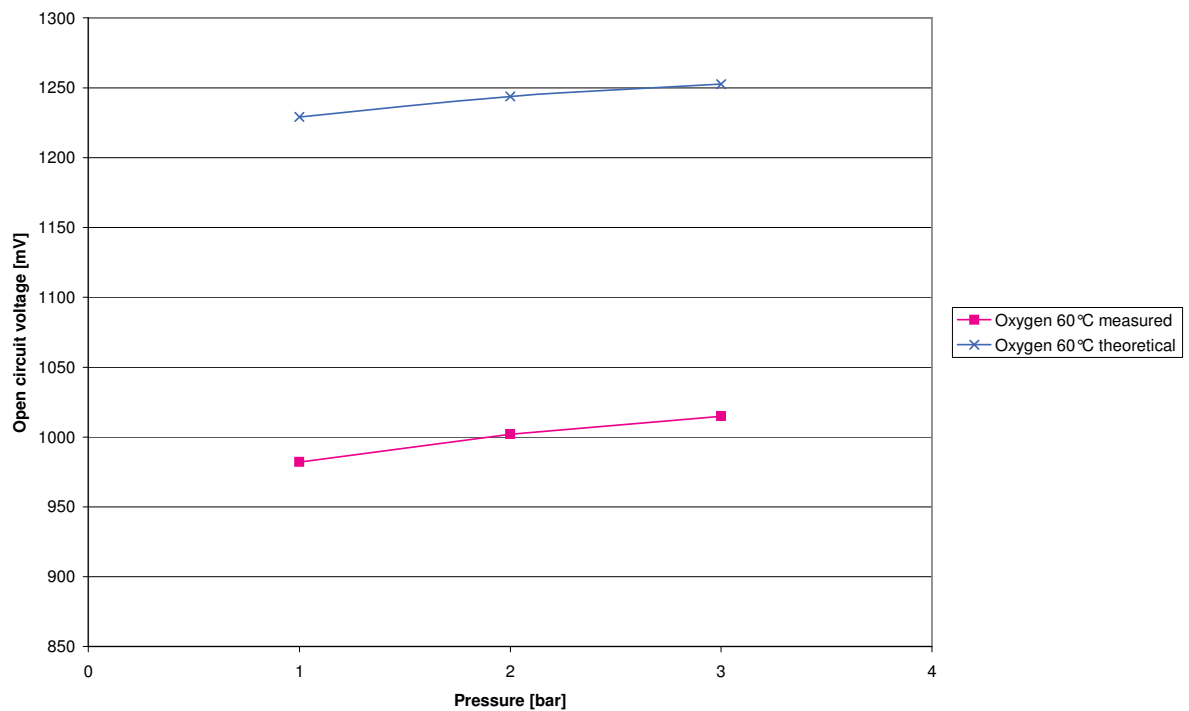
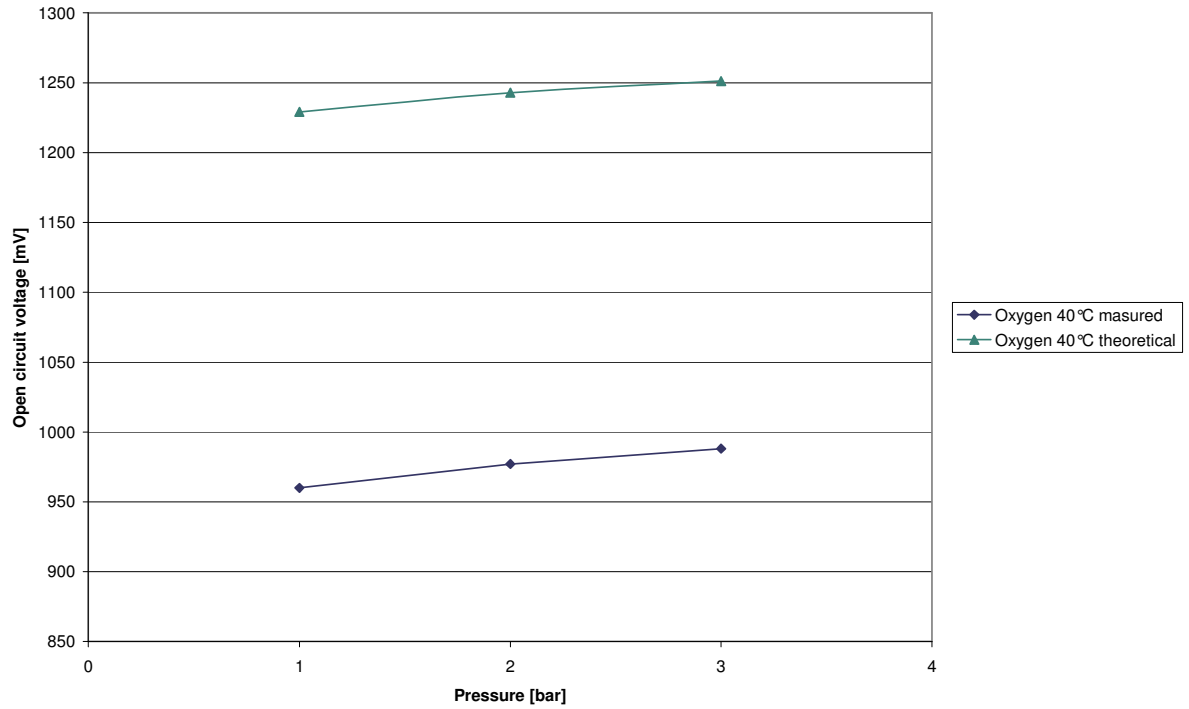
Again we measured what the Nernst Equation tells us: while temperature is constant and pressure increases the open circuit voltage also increases. In the following diagram we put the two diagrams above together, so one can compare the differences between the two temperatures. As we said in the last topic you can see that when temperature increases the open circuit voltage decreases.



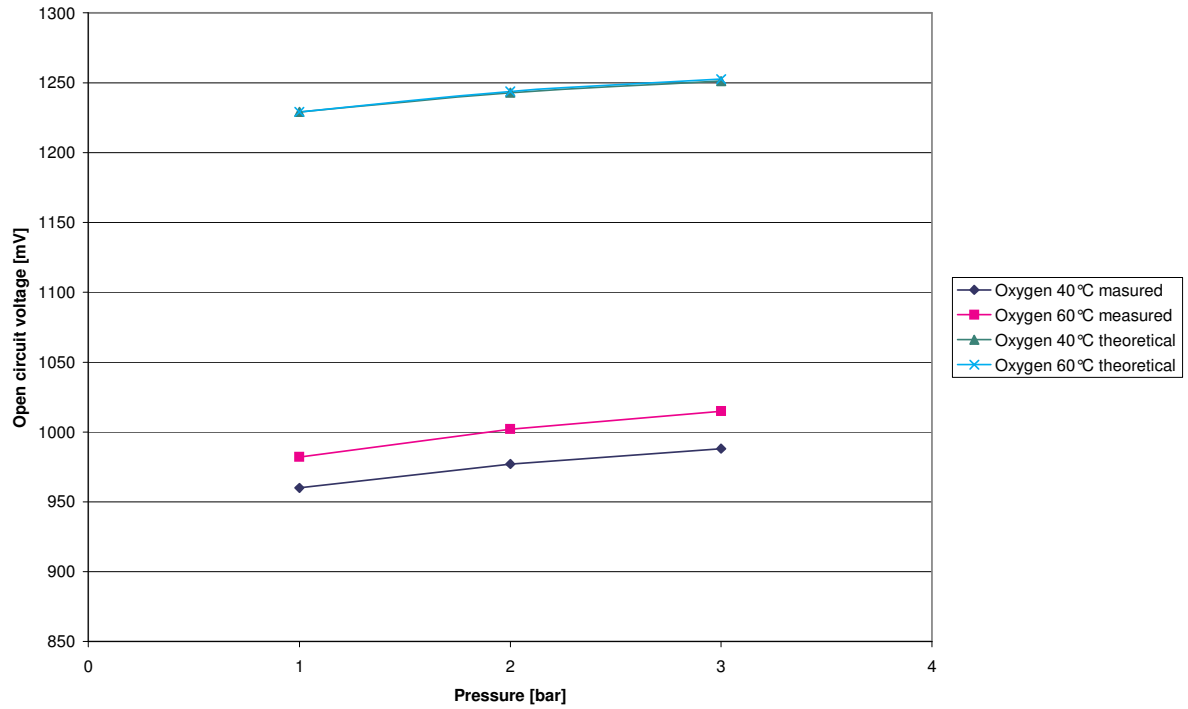
Part 1 – 3. Dependency of the Nernst Equation on partial pressure

Here we did all measurements of *Part 1 – 2*. again with oxygen instead of air and we calculated the theoretical values (with oxygen):

Pressure	1 bar	2 bar	3 bar
40°C, measured [mV]	960	977	988
40°C, theoretical [mV]	1229	1243	1251.2
60°C, measured [mV]	982	1002	1015
60°C, theoretical [mV]	1229	1243.9	1252.7



These diagrams look similar to the last ones, but especially when you compare the following diagram with the last one from *Part 1 – 2*, you can see that this time the open circuit voltages are higher. The reason for this lies in the fact that partial pressure of oxygen is higher than in the diagrams of *Part 1 – 2*.

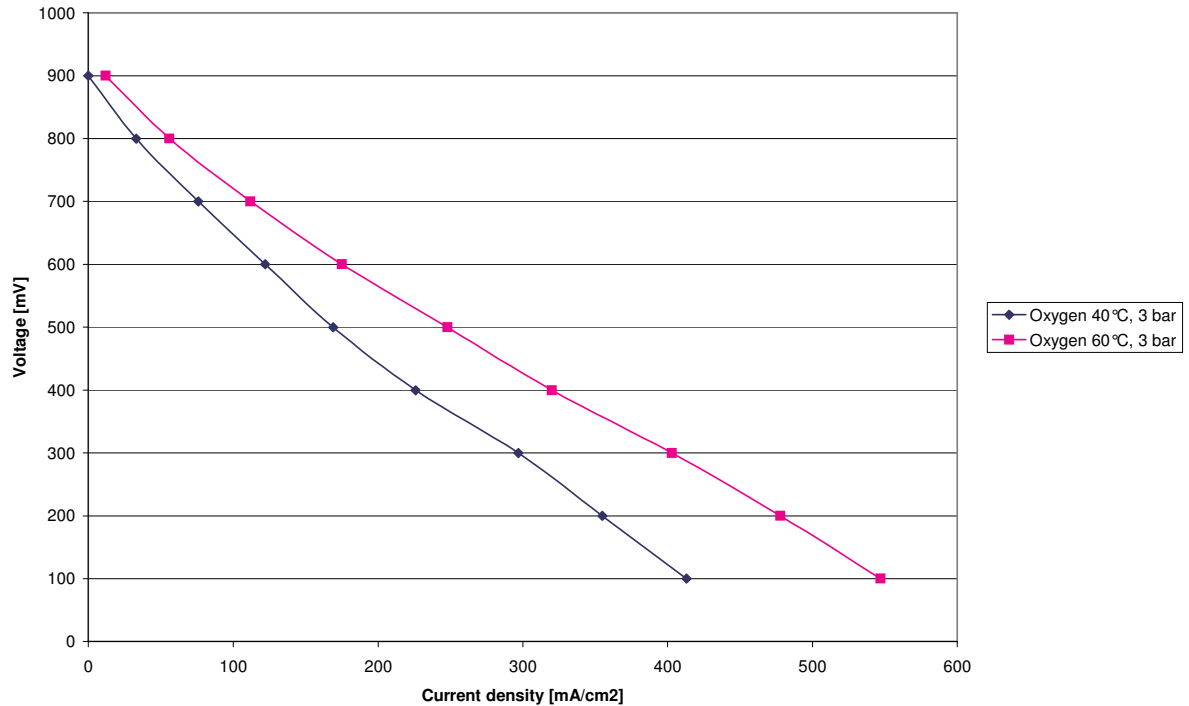


Part 2: Kinematics of the fuel cell

Part 2 – 1. Temperature dependency of the current-voltage-curve

At temperatures of 40°C and 60°C (pressure = 3 bar) we measured current-voltage-curves with oxygen:

Voltage [mV]	Current density [mA/cm ²] (40°C)	Current density [mA/cm ²] (60°C)
900	0	12
800	33	56
700	76	112
600	122	175
500	169	248
400	226	320
300	297	403
200	355	478
100	413	547

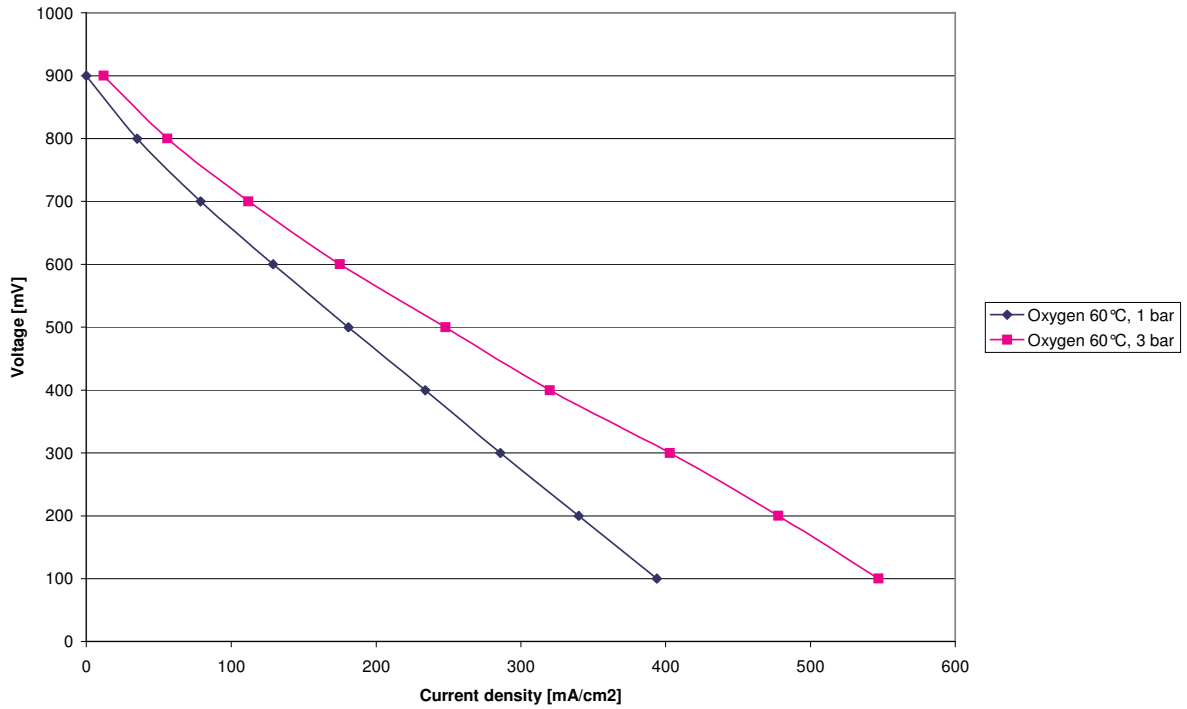


Both curves are nearly linear, so we can say that at this range of voltage the dominant factor is the Ohm Resistance. We see that at higher temperature the current density is also higher. This can be explained in the following way: at higher temperature the reaction goes faster and a faster reaction leads to higher current.

Part 2 – 2. Pressure dependency of the current-voltage-curve

In this part of the experiment we additionally measured at 60°C another current-voltage-curve, but with a pressure of 1 bar:

Voltage [mV]	Current density [mA/cm ²] (60°C)
900	0
800	35
700	79
600	129
500	181
400	234
300	286
200	340
100	394

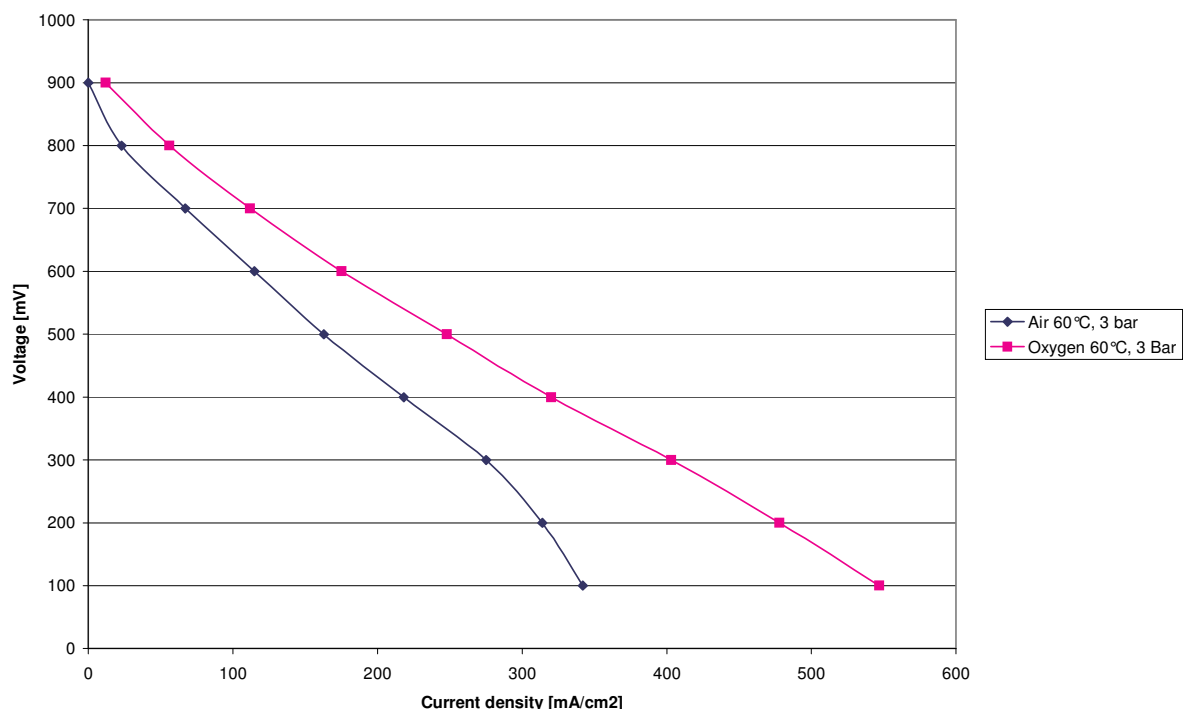


With our last measurements at 60°C and 3 bar, you can see in this diagram that at higher pressure the voltage is also higher. Again this result is just the same we got at *Part 1 – 2*. but now with current.

Part 2 – 3. Dependency of the current-voltage-curve on partial pressures

Now we measured a current-voltage-curve with air instead of oxygen. We set pressure to 3 bar and temperature to 60°C:

Voltage [mV]	Current density [mA/cm ²] (60°C)
900	0
800	23
700	67
600	115
500	163
400	218
300	275
200	314
100	342

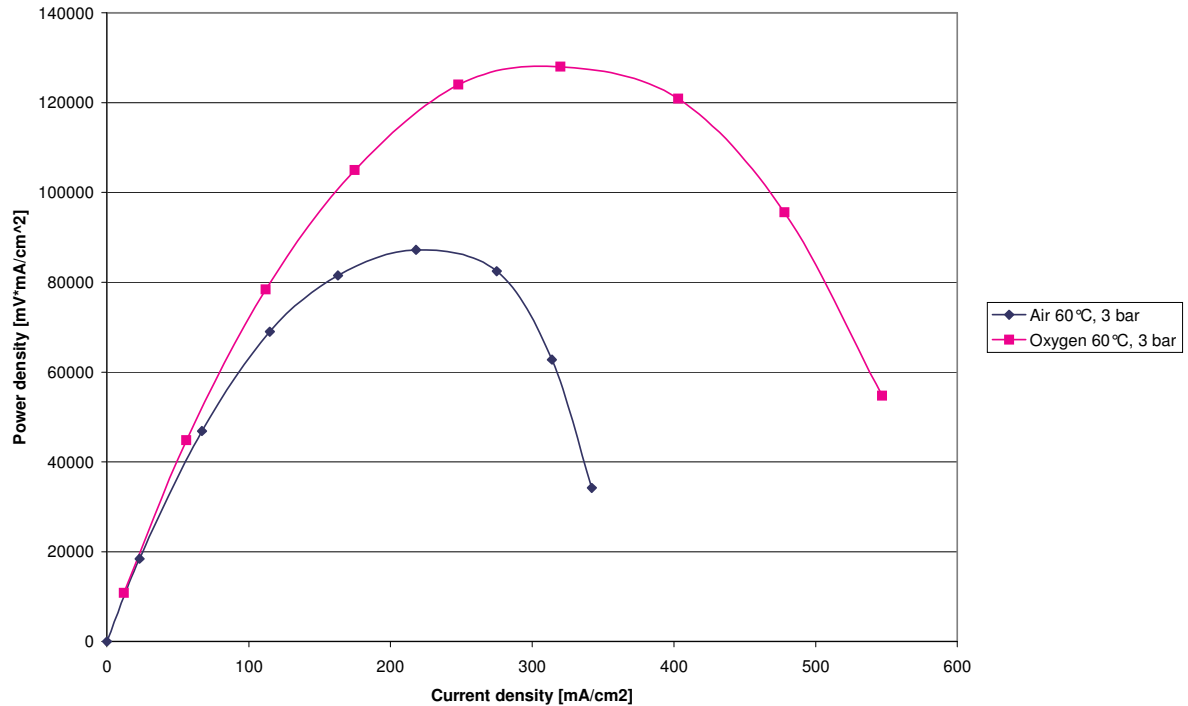


Here you can see that when the partial pressure of oxygen is lower, then the voltage is also lower. So this is just what you would expect and it's the same result like in *Part 1 – 3*. But that's not all. The curve of air is not only lower than the curve of oxygen, it also decreases much faster at low and at high current densities. The reason for this is that at higher current the reaction goes faster and as in air there isn't enough oxygen for reaction being at a constant level the current goes down. And when the current goes down also the voltage goes down and this is what you can see in the diagram.

We also did some more diagrams (same conditions as in *Part 2 - 3*.), in order to decide which cell-voltage is best for working with the fuel cell:

Current density – power - curve (at 60°C, 3 bar):

Air		Oxygen	
Current density [mA/cm ²]	Power density [mV*mA/cm ²]	Current density [mA/cm ²]	Power density [mV*mA/cm ²]
0	0	12	10800
23	18400	56	44800
67	46900	112	78400
115	69000	175	105000
163	81500	248	124000
218	87200	320	128000
275	82500	403	120900
314	62800	478	95600
342	34200	547	54700



Current density – degree of effectiveness – curve (at 60°C, 3 bar):

First we have to calculate the **degree of effectiveness**:

$$\epsilon_{FC} = \epsilon_{th} \cdot \epsilon_v \cdot \epsilon_F \cdot U \cdot \epsilon_H$$

where is

ϵ_{th} : thermic - effectiveness

ϵ_v : voltage - effectiveness

ϵ_F : Farraday - effectiveness

U : turnover of the fuel

ϵ_H : calorific value - effectiveness

According to the script we set ϵ_F , U and ϵ_H to 1 and ϵ_{th} to 0,83. ϵ_v is calculated in the following way:

$$\epsilon_v = \frac{U}{U_{rev}}$$

where is

U: voltage

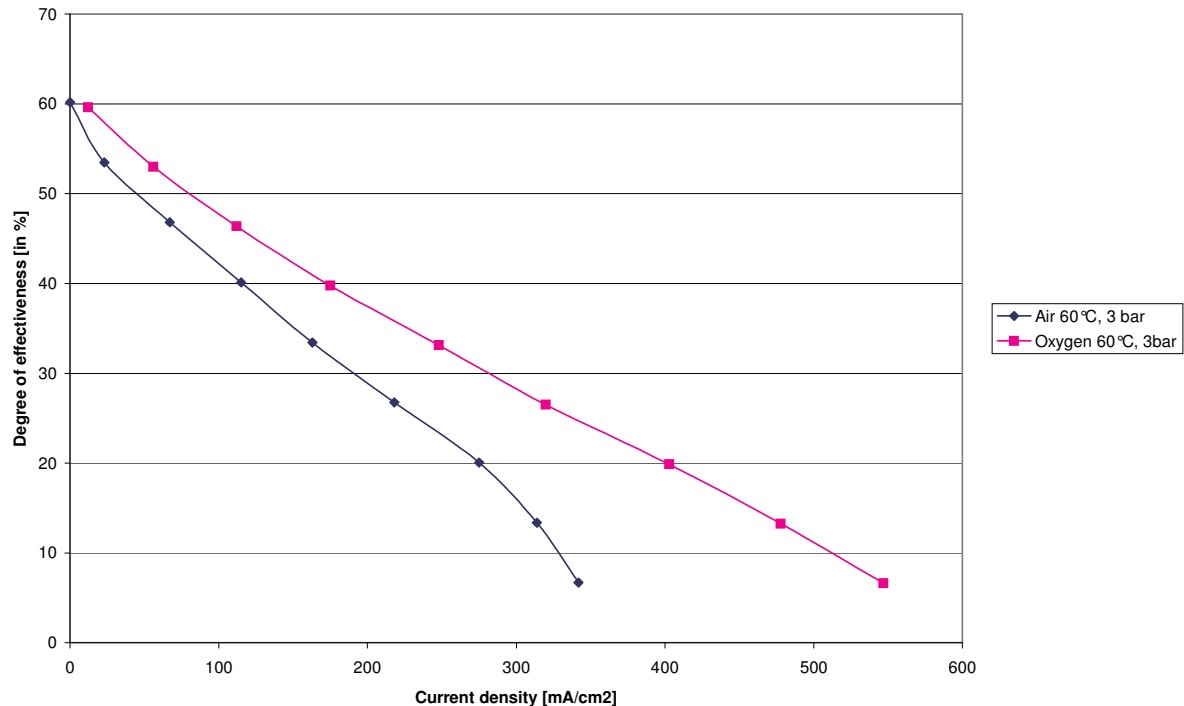
U_{rev} : theoretical voltage

The results are the following equations:

$$\varepsilon_{FC} = 0.83 \cdot \frac{U}{1241.1} \text{ (air)}$$

$$\varepsilon_{FC} = 0.83 \cdot \frac{U}{1252.7} \text{ (oxygen)}$$

This leads us to the following diagram:



If one is asked which voltage is best to run the fuel cell you choose the voltage at which you get most power. So if you run your fuel cell with air at a temperature of 60°C and with pressure of 3 bar then the best voltage is when the current density is about 220 mA/cm². Therefore the voltage is about 400 mV. When you run your fuel cell at same conditions but with oxygen instead of air, the best voltage is also about 400 (and current is about 320 mA/cm²).

Answering the questions

- 1. When you running the cell, you can only measure 0 V of the cell voltage, what might be the reason? What might happen when you can not get any current at any cell Voltage?**

The reason for only measuring 0 V of the cell voltage could be a shortcut. Because of the voltage the cell could dry out and then the reaction would stop.

- 2. What happens, there is a small hole in your membrane electrode assembly, but you still trying to run the PEMFC?**

The cell heats up and can even explode, because oxygen and hydrogen can interact directly in an not controllable way.

- 3. What is the priority of the electrochemical catalyst for PEMFC? How would you make the catalyst and MEA in order to make the H₂ oxidation or O₂ reduction as**

quick as possible? In order get good performance of fuel cell, what kind of operating conditions would you like to choose?

To divide H_2 into $2H^+ + 2e^-$.

The catalyst should have a big surface, because then more H^2 can be divided at the same time. We need the right amount of water in the cell, because when there is too much water the reaction would stop. On the other hand the membrane can't transport H^+ when there is no water and therefore there won't be any reaction. The next point is that Pt mustn't be in contact with CO, otherwise Pt would be deactivated by CO and the reaction would stop, too. And finally, we should run the fuel cell at the right voltage to get most possible power (according to the last point of *Part 2 – 3.*)

4. Could you give some examples of proton conducting materials, which can serve as an electrolyte? As a solid electrolyte, it means that they should be chemically, thermally (up to 200 0C) and mechanically stable, they should be gas tight, the permeability of H_2 O_2 as well as MeOH through the membrane should be very small. They should have high proton conductivity.

The Nafion® – 117 membrane is commercially used.

5. As we know, there should be a certain amount of water in the polymer electrolyte membrane, in order to provide enough proton conductivity, but the amount of water should not be too much, otherwise, it will block the way for reactants such as H_2 and O_2 reaching the catalyst. The way we are using now is using internal humidifying, do you have any other better solution to this to keep the MEA especially the anode side wet?

No, we don't.

6. The power for running a car at an average speed of 100 km/h is ca. 57 kW, and for a PEMFC, it provide ca. 200 mA/cm² current density at 700 mV with a platinum loading of 0.45 mg/cm². In order to supply enough power for car, how much platinum do we need? How much does those Pt cost? Provided that the fuel utilisation is ca. 95%, how much H_2 should we store on the car in order to run 500 km? What methods would you suggest to store H_2 in the car? When run PEMFC At 700 mV, how is the theoretical cell efficiency?

$$P_{v=100 \text{ km/h}} = 57 \text{ kW}, \frac{I}{A} = 200 \frac{\text{mA}}{\text{cm}^2}, U = 700 \text{ mV}, \rho_{Pt} = 0.45 \frac{\text{mg}}{\text{cm}^2}$$

$$\rho_{Pt} = \frac{m_{Pt}}{A}$$

$$P = U \cdot I$$

$$I = \frac{I}{A} \cdot A$$

$$\Rightarrow A = I \left(\frac{I}{A} \right)^{-1} \Rightarrow A = \frac{P}{U \cdot \frac{I}{A}}$$

$$\Rightarrow m_{Pt} = \rho_{Pt} \cdot \frac{P}{U \cdot \frac{I}{A}} = 0.45 \cdot 10^{-3} \frac{\text{g}}{\text{cm}^2} \cdot \frac{57000 \text{ W}}{0.7 \text{ V} \cdot 0.2 \frac{\text{A}}{\text{cm}^2}} = 183 \text{ g}$$

If we expect the car to drive 500 km with an efficiency of 95% and an average speed of 100 km/h we would need a energy of about $W = P \cdot t = 57\text{kW} \cdot 5\text{h} \cdot 95\% = 270\text{kWh} = 972\text{MJ}$

As said in the script: with 2 kg H₂ you get 20kW, so in 5 h you get an energy of 50 kWh by using 1 kg H₂. Therefore we need 5.4 kg H₂.

We suggest to store H₂ in a high pressure tank.