

Related topics

Electrolysis, electrode polarisation, decomposition voltage, galvanic elements, Faraday's law.

Principle and task

In a PEM electrolyser, the electrolyte consists of a proton-conducting membrane and water (PEM = Proton-Exchange-Membrane). When an electric voltage is applied, hydrogen and oxygen are formed. The PEM fuel cell generates electrical energy from hydrogen and oxygen.

The electrical properties of the electrolyser and the fuel cell are investigated by recording a current-voltage characteristic line. To determine the efficiency, the gases are stored in small gasometers in order to be able to measure the quantities of the gases generated or consumed.

Equipment

PEM fuel cell	06747.00	1
PEM electrolyser	06748.00	1
Connection box	06030.23	1
Resistor in plug-in box 10 Ohms	06056.10	2
Resistor in plug-in box 5 Ohms	06055.50	1
Resistor in plug-in box 2 Ohms	06055.20	1
Resistor in plug-in box 1 Ohm	06055.10	2
Short-circuit plug, black	06027.05	2
Gas bar	40466.00	1
Graduated cylinder, 100 ml. plastic	36629.01	1
Rubber tubing, i.d. 4 mm	39280.00	1
Rubber tubing, i.d. 6 mm	39282.00	1
Pinchcock, width 10 mm	43631.10	4
Tubing adaptor, ID 3-6/7-11 mm	47517.01	2
Wash bottle, plastic, 500 ml	33931.00	1

Beaker, 250 ml, bw form, plastic	36013.01	1
Stopwatch, digital, 1/100 sec.	03071.01	1
Barometer/Manometer, hand-held	07136.00	1
Lab thermometer, -10. .+100 °C	38056.00	1
Digital multimeter	07134.00	2
Power supply, universal	13500.93	1
Connecting cord, 500 mm, red	07361.01	3
Connecting cord, 500 mm, blue	07361.04	2
Connecting cord, 750 mm, red	07362.01	1
Connecting cord, 750 mm, blue	07362.04	1
Water, distilled, 5 l	31246.81	1

Problems

1. Recording the characteristic line of the PEM electrolyser.
2. Recording the characteristic line of the PEM fuel cell.
3. Determination of the efficiency of the PEM electrolysis unit.
4. Determination of the efficiency of the PEM fuel cell.

Set-up and procedure

1. Characteristic line of the PEM electrolyser
 - Fill both water reservoirs with water up to a level between the max. and min. marking lines.
 - Connect the electrolyser to the direct current (DC) port of the power supply in accordance with the experimental set-up in Fig. 1 and the circuit diagram in Fig. 2
 - It is advisable to begin with the highest voltage $U = 2$ V. In the process, the current may exceed the value of the maximum continuous current of $I = 2$ A for a short time. After approximately 1 min, the values for voltage and current become stable.

Fig. 1. Experimental set-up: Characteristic line of the electrolysis unit.

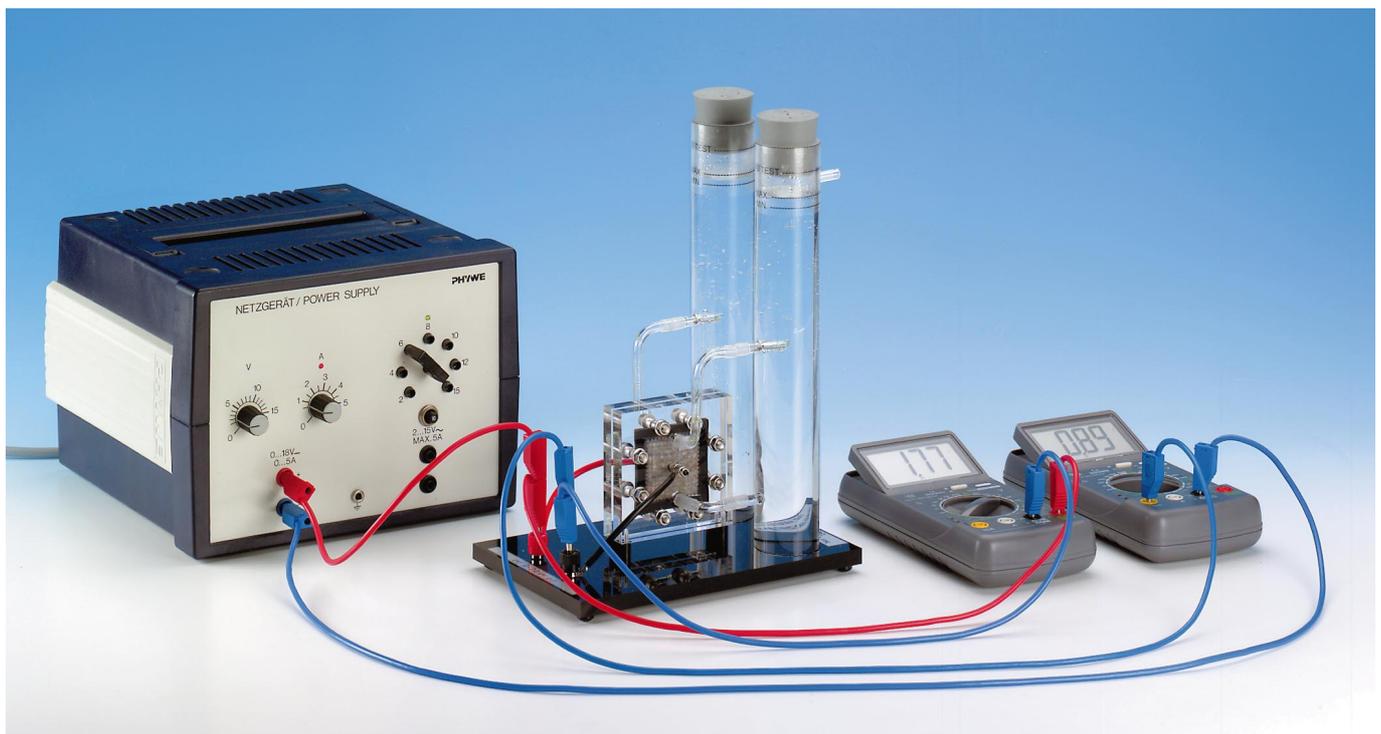


Fig. 2. Circuit diagram: Characteristic and efficiency of the electrolyser.

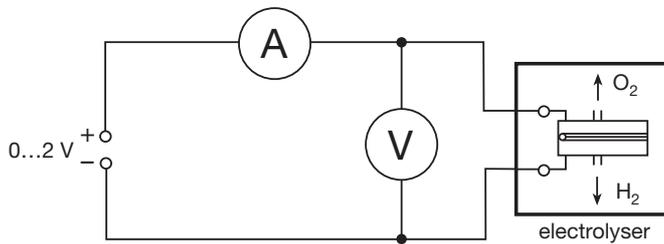
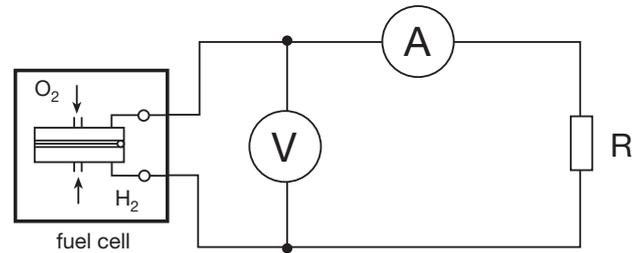
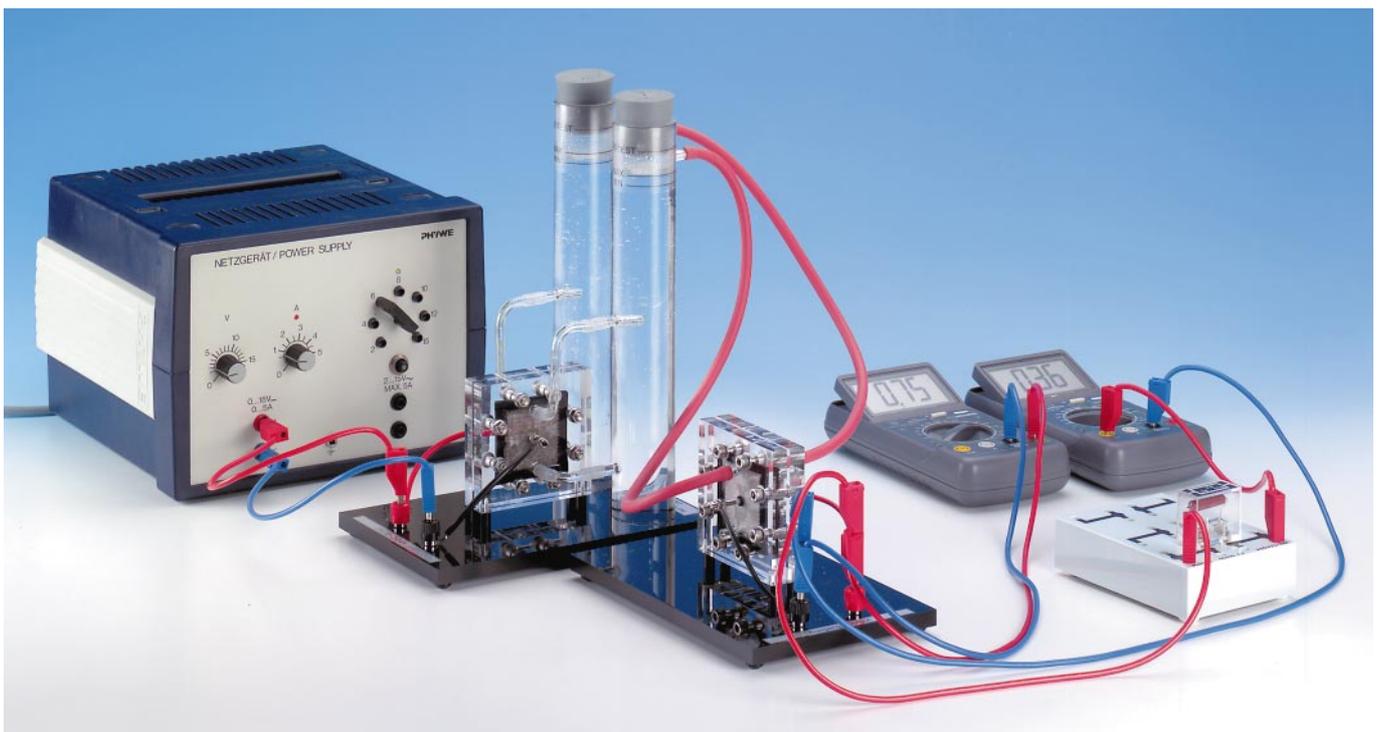


Fig. 4. Circuit diagram: Characteristic and efficiency of the fuel cell.



- Progressively decrease the current from the power supply using the current adjustment knob. In the process, the power supply adjusts the voltage electronically so that the current has the value set. This procedure has the advantage that stable values for voltage and current are achieved more rapidly in the electrolyser.
When the current adjustment knob has reached its minimum, even smaller values can be selected with the aid of the voltage adjustment knob. Before recording a measured value, wait approximately 1 min. until the current and voltage values have again become stable.
- 2. Characteristic line of the PEM fuel cell
 - For recording the characteristic line, the most simple method of providing the fuel cell with gas is to connect it directly with the electrolyser. However, it is also possible to take the gas from the gas bar, as described in the measurement of efficiency section.
 - The experimental set-up is performed according to Fig. 3 and the circuit diagram Fig. 4.
- Preparation of the electrolyser:
Connect pieces of thin rubber tubing, which are approximately 40 cm long, ($d_i = 4$ mm) to the upper outlet connections of the storage container on the electrolyser. Fill both water reservoirs up the "Gas test" line with distilled water. While doing so, hold up the tubing so that it also fills with water.
Put the rubber stoppers onto the storage containers in a manner such that no air bubbles form under them and then press them in tightly.
Hold the water-filled pieces of rubber tubing into a beaker filled with distilled water.
Connect the electrolyser to the power supply as shown in Fig. 2 and set a current of max. 2 A or an operating voltage of max 2 V.
- When hydrogen and oxygen escape from the pieces of rubber tubing into the beaker, press the ends of the tubing briefly together; remove them from the water, and connect them to the upper inlet connections of the fuel cell.
Drops of water which could perhaps still be present in the

Fig. 3. Experimental set-up: Characteristic line of the fuel cell.



tubes can interrupt the gas supply to the fuel cell. If this happens, the output voltage will drop. Lift the pieces of tubing briefly to allow the water to run out.

- The electrical data of the fuel cell are dependent on the gas throughput and the moistness of the membrane. To create a stable condition in the fuel cell, it should be allowed to run for approximately 5 min under no-load conditions and then operated for approximately 5 min with a fixed load resistor of, e.g., 2Ω .
- Connect load resistors of different sizes to the fuel cell according to the circuit diagram in Fig. 4. In each case measure the voltage U and the current I . First, measure the no-load voltage and then begin the measuring series with the largest resistance values.

Since the internal resistance of the ammeter can not be neglected with respect to the load resistor, always use the 10-A measuring range.

For resistance values smaller than 1Ω the values for current and voltage may not always be stable when an insufficient quantity of gas is supplied. Before making a measurement, the electric circuit should be opened for approximately 30 s, to ensure a good gas supply. Avoid short circuiting the fuel cell (max 10 s)!

3. Efficiency of the PEM electrolyser

- Preparation of the gas bar with 2 gasometers:
A gasometer consists of an Erlenmeyer flask with a cylindrical funnel and a bent glass tube mounted on it. Connect the reducing adapters with a short piece of rubber

tubing ($d_i = 6 \text{ mm}$) to each of the glass tubes on the gasometer.

Fill each of the gasometers via its cylindrical funnel with distilled water until the Erlenmeyer flask and the right-angled glass tube are filled and contain nearly no bubbles. Excess water then flows out via the glass tube and is collected in a beaker.

The filling heights of the cylindrical funnels are calibrated. It is advisable to check the exactness of these markings by filling the entire funnel with distilled water and then allowing it to flow into a volumetric measuring device.

- The experimental set-up for the determination of the electrolyser's efficiency is performed according to Fig. 5.
- Connect an approximately 40-cm-long piece of thin rubber tubing ($d_i = 4 \text{ mm}$) to the upper outlet connection of the storage container of the electrolyser.
- Fill both water reservoirs up the "Gas test" line with distilled water. While doing so hold up the tubing so that it also fills with water.
- Seal the water-filled pieces of rubber tubing with a hose clamp approximately 2 cm from their ends and attach them to the gasometers.
- Put the rubber stoppers onto the storage containers in a manner such that no air bubbles form under them and then press them in tightly so that no gas can escape.
- Open the hose clamps.
- Connect the electrolyser to the power supply according to Fig. 2, and set a current of approximately 1 A with the current adjustment knob.

Fig. 5. Experimental set-up: Efficiency of the electrolyser.



- The electrolyser generates hydrogen and oxygen in a ratio of 2:1.
The volume V_{H_2} of the hydrogen generated is measured as a function of the time t . Start the time measurement when the water in the cylindrical funnel (H_2) passes the lower mark.
 - Measure the voltage U and the current I during electrolysis.
 - Measure the room temperature ϑ and the ambient pressure p_{amb} .
 - To conclude the experiment, switch off the electrolyser and close the tubes to the gasometers with the clamps.
 - A repetition of this experiment with another current (e.g. 2 A) is facilitated, when, e.g., the gasometers must again be refilled for experiments with the fuel cell.
4. Efficiency of the PEM fuel cell
- To determine the efficiency of the fuel cell, both gasometers of the gas bar should be as full as possible.
To achieve this connect the two gasometers with the electrolyser (hose clamps open). Operate the electrolyser with maximum voltage (2 V) or maximum current (2 A). If the gas production exceeds the maximum volume capacity of the gasometer (approximately 250 ml), the excess gas escapes through the funnel into the atmosphere. As a consequence, not only the H_2 but also the O_2 gasometer can readily be completely filled using the electrolyser.
After filling the gasometer, switch off the electrolyser and tightly clamp the tubing behind the electrolyser.
 - Both gasometers should contain approximately 250 ml of gas.
- Perform the experimental set-up according to Fig. 6 and the circuit diagram in Fig. 4.
 - Tightly seal the lower outlet connections with short pieces of rubber tubing ($d_i = 4 \text{ mm}$) and hose clamps.
 - Connect each of the two upper inlet connections of the fuel cell to a gasometer.
 - Loosen the clamps on the connecting hoses between the gasometer and the fuel cell.
 - Connect a load resistor of 1Ω to the fuel cell in accordance with the circuit diagram in Fig. 4.
 - The fuel cell consumes hydrogen and oxygen in a ratio of 2:1. Measure the volume V_{H_2} of the consumed hydrogen as a function of the time t .
- Note:
- The values for voltage and current are not constant for longer periods of time, since the gas supply to the electrodes becomes poorer. Therefore, it is advisable to measure the time for the consumption of 25 ml of hydrogen in each case, and to flush the fuel cell with hydrogen and oxygen between measurements.
- Loosen the hose clamp on the lower outlet connection on the oxygen side of the fuel cell cautiously and allow approximately 25 ml of oxygen to flow through the cell. Tighten the clamp.
 - Then allow hydrogen to flow through in the same manner until the water level in the cylindrical funnel is approximately 1 mm above a calibration mark and retighten the clamp. Start measuring the time when the water level passes the calibration mark and stop measuring it when 25 ml of hydrogen have been used.

Fig. 6. Experimental set-up: Efficiency of the fuel cell.

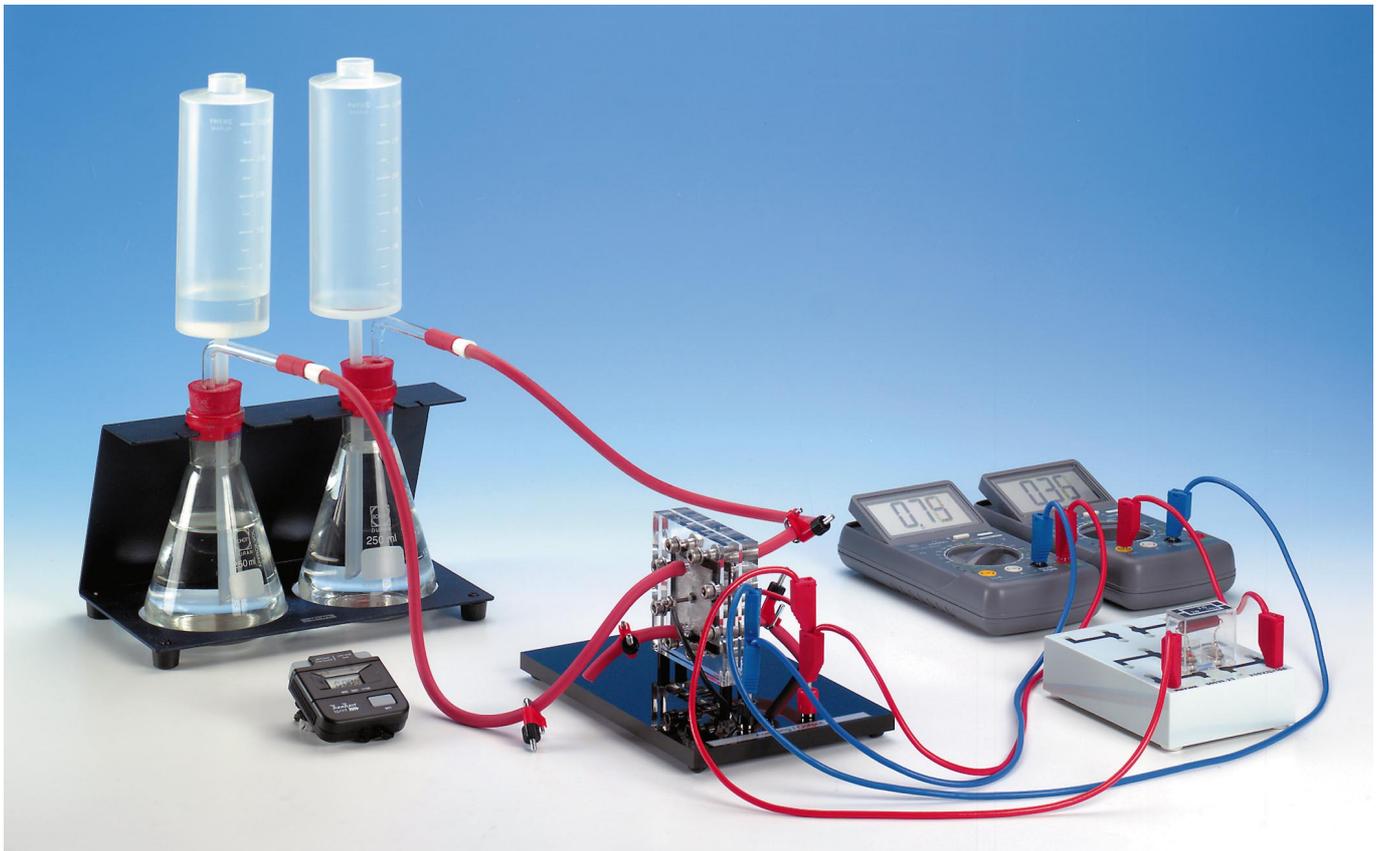


Fig. 7. Functional principle of a PEM electrolyser.

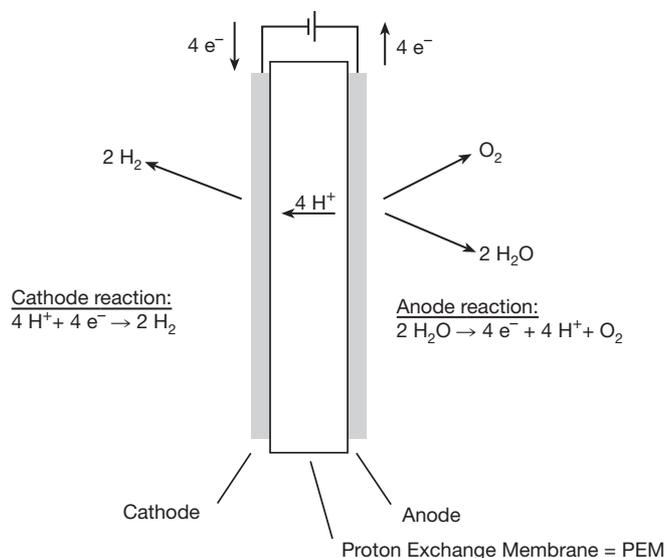
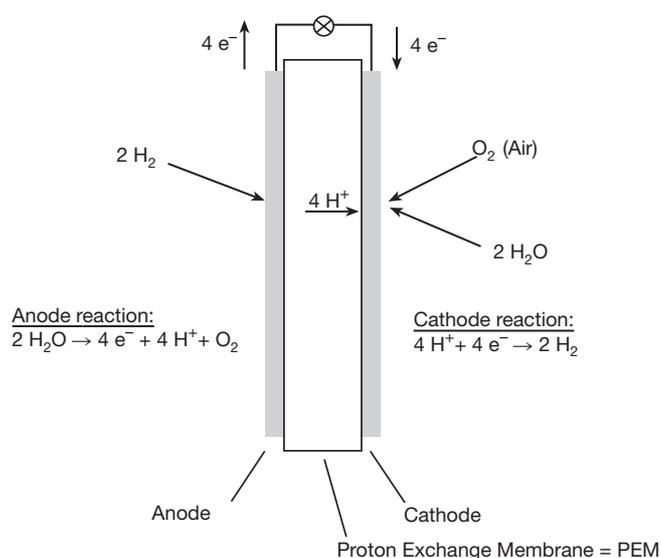


Fig. 8. Functional principle of a PEM fuel cell.

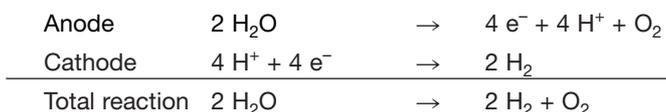


- Measure the voltage U and the current I at the beginning and at the end of the time interval.
- Again flush the fuel cell with oxygen and hydrogen, and perform a new time measurement for the consumption of 25 ml of hydrogen.
- Measure the room temperature ϑ and the ambient pressure p_{amb} .
- A repetition of this experiment with another load resistor (e.g. 2Ω) is facilitated, when, e.g., the gasometers have been refilled for another experiment with the electrolyser.

Theory and evaluation

The principal part of the PEM electrolysis unit and the PEM fuel cell is a membrane-electrode unit. A layer of catalyst material has been applied to both sides of the thin proton-conducting membrane (PEM = proton exchange membrane). These two layers form the anode and cathode of the electrochemical cell.

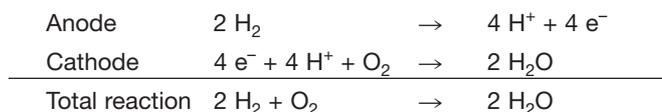
In the electrolyser the following reaction occurs (Fig. 7):



On the anode side gaseous oxygen, electrons and H⁺ ions are formed when an external voltage is applied. The H⁺ ions pass through the proton-conduction membrane to the cathode and form gaseous hydrogen there with the electrons flowing through the external conducting circuit.

The fuel cell functions by the inverse principle. In electrolysis electrical energy is transformed into chemical energy and stored in the form of hydrogen and oxygen; in the fuel cell chemical energy in the form of hydrogen and oxygen is directly converted, i.e. without a combustion process, into electrical energy. Hydrogen and oxygen react to form water, giving up electricity and heat.

In the fuel cell the following reaction occurs (Fig. 8):



Since the gaseous hydrogen which is supplied to the anode is oxidised, it decomposes due to the catalytic action of the electrode (e.g. platinum) into protons and electrons. The H⁺ ions pass through the proton-conducting membrane to the cathode side. The electrons pass through the closed outer electrical circuit to the cathode and do electrical work in this manner. The gaseous oxygen which is supplied to the cathode is reduced. In the process water is formed in addition to the protons and electrons.

If a hydrogen and an oxygen electrode are located in an electrolyser or a fuel cell, there is a potential difference ΔE between the two electrodes. It is temperature dependent; its theoretical value can be calculated from the free enthalpy of reaction ΔG and is equal to

$$\Delta E = 1.23 \text{ V at } 25^\circ\text{C.}$$

In electrolysis, the applied voltage must be at least as large as this theoretical cell voltage in order for a current to be able to flow. In the fuel cell the maximum terminal voltage can be as large as this theoretical value. In both the electrolyser and the fuel cell, additional potentials occur at the electrodes:

In the electrochemical equilibrium, phase boundary potentials between the electrode and the membrane also occur at the electrodes. In the process, there is a continuous exchange of charges between the two, but the gross reaction is equal to zero.

If, in addition, a current flows through the electrolyser or the fuel cell, the electrochemical equilibrium at the electrodes is disturbed. The electrode potential takes on another value, which is dependent on the current density, due to various reactions at the electrode. This deviation from the equilibrium

value is termed “electric polarisation”, i.e. the electrode becomes polarised.

The characteristic lines of the electrolyser and the fuel cell thus exhibit a nearly linear course only at larger values of current; in this region the movement of the ions through the membrane is decisive.

The quantity of substance n liberated at an electrode can be calculated using Faraday’s law.

$$n = \frac{I \cdot t}{z \cdot F} \quad (1)$$

where I = current, t = time, z = number of electrons required to liberate a molecule, F = Faraday’s constant,

$F = 96,487 \text{ As/mol}$

In this experiment gases are evolved. The volume of a substance quantity n can be determined using the general gas equation.

$$V = \frac{n \cdot R \cdot T}{p} \quad (2)$$

where T = absolute temperature, p = pressure, R = general gas constant $R = 8.31 \text{ J/(mol K)}$

If a current I flows in an electrolyser, the following gas volume per unit time is generated according to Equations (1) and (2):

$$\frac{V}{t} = \frac{I \cdot R \cdot T}{z \cdot F \cdot p} \quad (3)$$

In the fuel cell, this gas volume per unit time is required in order that the current I can flow.

To determine the efficiency of the electrolyser and the fuel cell, the electrical W_{el} and the chemical W_{H_2} energies of the generated or required hydrogen are calculated.

$$W_{el} = U \cdot I \cdot t \quad (4)$$

$$W_{H_2} = n \cdot H \quad (5)$$

where U = voltage, I = current, t = time, n = quantity of hydrogen, H = molar caloric content (molar reaction enthalpy) of hydrogen

One differentiates between the lower caloric content H_u and the upper caloric content H_o .

Molar caloric content of hydrogen:

$H_u = 242.0 \text{ kJ/mol}$

$H_o = 266.1 \text{ kJ/mol}$

The difference between the two is the molar enthalpy of vapourisation (condensation enthalpy) q of water.

$$H_o = H_u + q \quad (6)$$

The efficiency of the electrolyser is greatly dependent on the respective operating condition. If it has not been used for a long time, the current intensity at 2 V can be smaller than shown in the table; after a long period of operation, sometimes much larger (e.g. greater than 4 A).

1. Current-voltage characteristic of the PEM electrolyser

Table 1

U/V	I/A
2.00	2.69
1.91	2.20
1.81	1.50
1.75	1.00
1.68	0.51
1.61	0.21
1.55	0.11
1.51	0.06
1.40	0.03
0.99	0.02
0.40	0.00

The measured values in Table 1 are plotted in Fig. 9. From the linear segment of the characteristic line, the decomposition voltage U_z is determined as the intersection of the extended straight line with the U axis:

$$U_z = 1.60 \text{ V}$$

2. Characteristic line of the PEM fuel cell

Table 2

R/Ω	Combination	U/V	I/A
Infinite		0.93	0.00
28	= 10 + 10 + 5 + 2 + 1	0.83	0.02
25	= 10 + 10 + 5	0.82	0.03
20	= 10 + 10	0.81	0.04
15	= 10 + 5	0.80	0.05
10		0.79	0.97
7	= 5 + 2	0.78	0.11
5		0.76	0.14
4	= 2 + 2	0.75	0.18
3	= 2 + 1	0.74	0.24
2		0.72	0.35
1		0.68	0.71
0.83	= 1 // 5	0.67	0.71
0.67	= 1 // 1	0.63	1.10
0.40	= 1 // 1 // 2	0.62	1.30
0.37	= 1 // 1 // 2 // 5	0.61	1.41

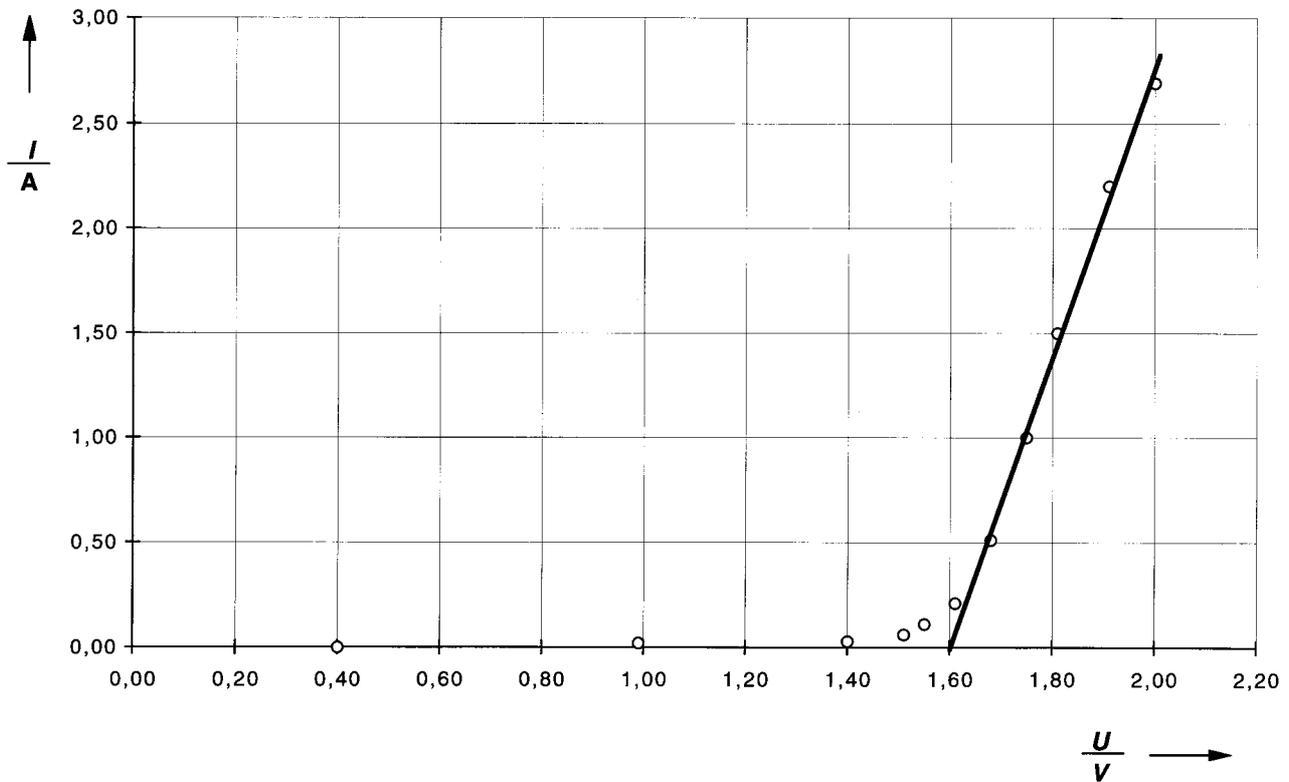
The efficiency of the fuel cell is a function of the gas pressures, the gas throughput, the moistness of the membrane and the temperature.

The measured values in Table 2 are plotted in Fig. 10. The no-load voltage is

$$U_0 = 0.93 \text{ V.}$$

For greater values of current, the characteristic line in Fig. 10 exhibits a nearly linear course. If the characteristic line deviates from a linear course in this region, it is possible that the supplies of hydrogen and oxygen to the fuel cell are inadequate.

Fig. 9. Current-voltage characteristic line of a PEM electrolyser.



3. Efficiency of the PEM electrolyser

Table 3.1

$I = 1.02 \text{ A}$ $U = 1.71 \text{ V}$
 $p_{\text{amb}} = 984 \text{ hPa}$ $\vartheta = 21^\circ\text{C}$

V_{H_2}/ml	$t/\text{min:s}$	t/s
0	0:00	0
25	3:27	207
50	6:50	410
75	10:18	618
100	13:42	822
125	17:08	1028
150	20:40	1240
175	24:16	1456

Table 3.2

$I = 2.01 \text{ A}$ $U = 1.83 \text{ V}$
 $p_{\text{amb}} = 984 \text{ hPa}$ $\vartheta = 21^\circ\text{C}$

V_{H_2}/ml	$t/\text{min:s}$	t/s
0	0:00	0
25	1:42	102
50	3:24	204
75	5:07	307
100	6:49	409
125	8:34	514
150	10:15	615
175	12:03	723

The measured values in Tables 3.1 and 3.2 are plotted in Fig. 11. From the slope of the straight lines, the generated volumes pro unit time V_{H_2}/t (measured) can be read off.

They are compared with the theoretical values according to equation (3) and from this the gas yield, i.e. the so-called current efficiency, is calculated.

The pressure generated by the column of water in the gasometer must be added to the measured ambient pressure p_{amb} . This has an average value of approximately 20 hPa.

On the other hand the produced hydrogen is saturated with steam, whose partial pressure is 23 hPa. As these two effects compensate each other, no correction of the pressure has to be performed.

Table 3.3

Experimental conditions	V_{H_2}/t measured	V_{H_2}/t theoretical	Gas yield
$I = 1.02 \text{ A}$ $U = 1.71 \text{ V}$	0.121 ml/s	0.131 ml/s	92 %
$I = 2.01 \text{ A}$ $U = 1.83 \text{ V}$	0.243 ml/s	0.258 ml/s	94 %

$$p = p_{\text{amp}} = 984 \text{ hPa}$$

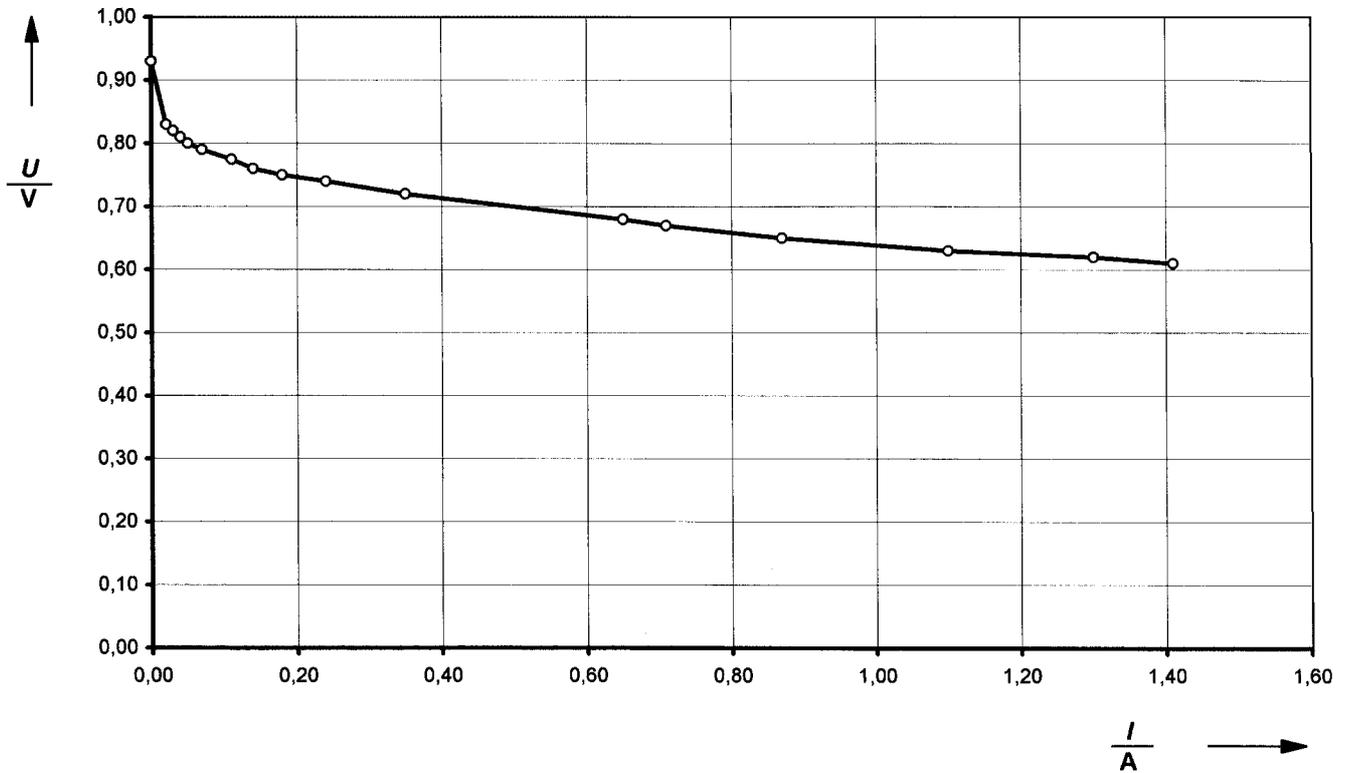
$$T = 294 \text{ K}$$

The missing gas is due to diffusion losses within the cell.

The efficiency of the electrolyser can be calculated using equations (4) and (5)

$$\eta = \frac{W_{\text{H}_2}}{W_{\text{el}}} = \frac{H_0 \cdot n}{U \cdot I \cdot t} \quad (7)$$

Fig. 10. Current-voltage characteristic line of a PEM fuel cell.



Using the general gas equation (2), the measured volumes V of hydrogen are converted to substance quantities n . Thus, one obtains the following for the efficiency:

$$\eta = \frac{H_0 \cdot p \cdot V}{R \cdot T \cdot U \cdot I \cdot t} \quad (8)$$

In addition, a correction factor should be taken into consideration at this time, if the volume marks on the gasometer funnels have been checked with a volume measuring device. In our case one measurement showed the following:

250 ml in gasometer = 255 ml in volume measuring device

$$V_{\text{corr}} = 1.02 \cdot V_{\text{H}_2}$$

Table 3.4

$p = p_{\text{amb}} = 984 \text{ hPa}$
 $T = 294 \text{ K}$

Operating conditions	Efficiency
$I = 1.02 \text{ A}$ $U = 1.71 \text{ V}$	82 %
$I = 2.01 \text{ A}$ $U = 1.83 \text{ V}$	78 %

The efficiency of the electrolyser is somewhat larger at 1.71 V / 1.02 A than for 1.83 V / 2.01 A. The gas yield is the same in both cases.

4. Efficiency of the PEM fuel cell

Table 4.1 (load resistance 1 Ω)
 $p_{\text{amb}} = 984 \text{ hPa}$ $\vartheta = 22^\circ\text{C}$

Mark	V_{H_2}/ml	$t/\text{min:s}$	U/V	I/A
225		0:00	0.68	0.67
200	25	4:42	0.66	0.65
175		0:00	0.67	0.66
150	25	4:47	0.66	0.64
125		0:00	0.67	0.65
100	25	4:57	0.65	0.64
75		0:00	0.67	0.65
50	25	4:42	0.65	0.63

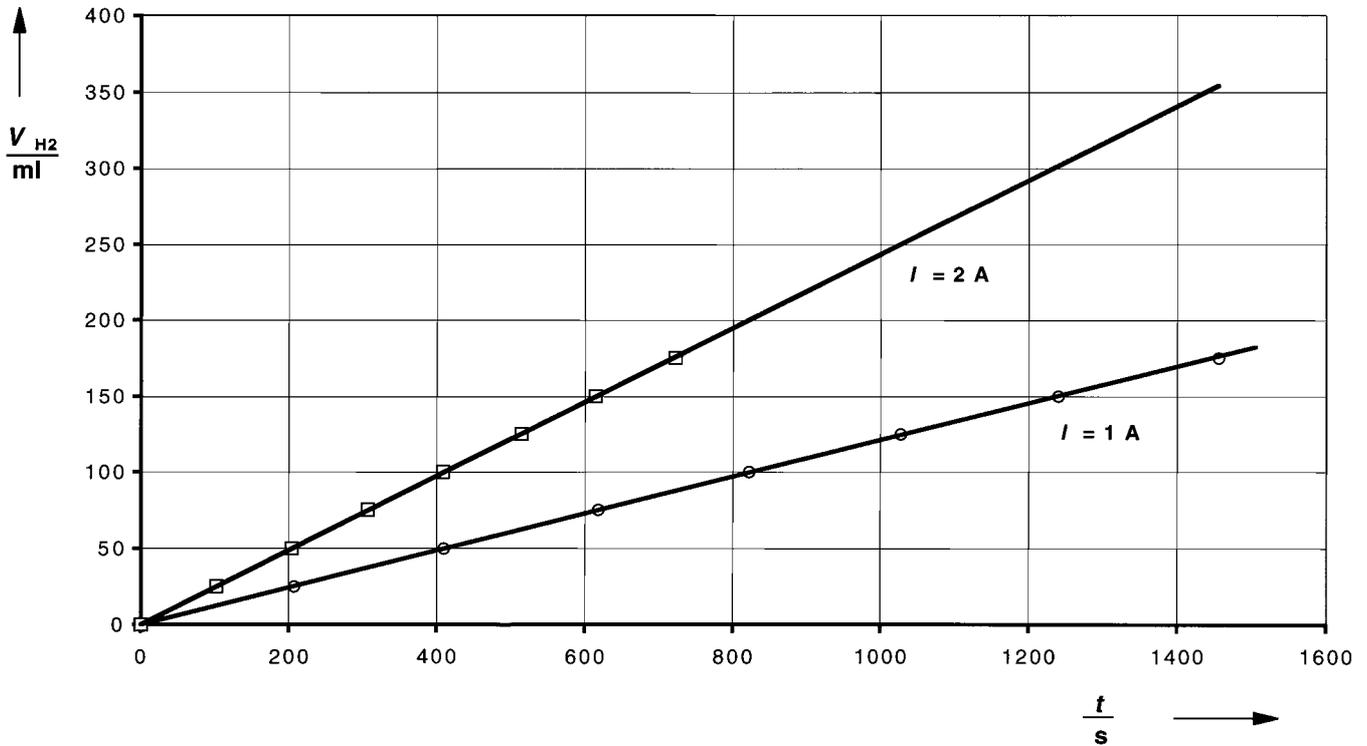
Mean values: $t = 287 \text{ s}$ $U = 0.66 \text{ V}$ $I = 0.65 \text{ A}$

Table 4.2 (load resistance 2 Ω)
 $p_{\text{amb}} = 984 \text{ hPa}$ $\vartheta = 23^\circ\text{C}$

Mark	V_{H_2}/ml	$t/\text{min:s}$	U/V	I/A
225		0:00	0.75	0.35
200	25	9:05	0.75	0.35
175		0:00	0.75	0.35
150	25	9:07	0.73	0.34
125		0:00	0.75	0.35
100	25	8:57	0.75	0.35
75		0:00	0.75	0.35
50	25	8:51	0.74	0.35

Mean values: $t = 540 \text{ s}$ $U = 0.75 \text{ V}$ $I = 0.35 \text{ A}$

Fig. 11. Volume of the hydrogen generated by the PEM electrolyser as a function of time at different current I .



The pressure generated by the column of water in the gasometer must be added to the measured ambient pressure p_{amb} . This has an average value of approximately 20 hPa. On the other hand the produced hydrogen is saturated with steam, whose partial pressure is 23 hPa. As these two effects compensate each other, no correction of the pressure has to be performed.

$$p = p_{amb}$$

The theoretically required gas volume, determined according to equation (3), is compared with the measured one, and from this the gas utilisation is calculated.

Table 4.3

Operating conditions	V_{H_2}/t measured	V_{H_2}/t theoretical	Gas utilisation
$I = 0.65$ A, $U = 0.66$ V $p = 992$ hPa, $T = 295$ K	0.0871 ml/s	0.0832 ml/s	96 %
$I = 0.35$ A, $U = 0.75$ V $p = 998$ hPa, $T = 296$ K	0.0463 ml/s	0.0447 ml/s	97 %

The missing gas is due to diffusion losses within the cell.

The efficiency of the fuel cell is calculated using equations (4) and (5).

$$\eta = \frac{W_{el}}{W_{H_2}} = \frac{U \cdot I \cdot t}{n \cdot H} \quad (9)$$

Due to the reaction occurring in the fuel cell, the upper calorific content H_o must be used to calculate the efficiency. In

industry, it is however normal to calculate with the lower calorific content H_u because the heat of condensation only generates heat and no electrical energy. The two results are compared in Table 4.4.

The measured volumes V of hydrogen are converted to substance quantities n using the general gas equation (2). In this way one obtains the following for the efficiency:

$$\eta = \frac{R \cdot T \cdot U \cdot I \cdot t}{H_o \cdot p \cdot V} \quad (10)$$

In addition, a correction factor should be taken into consideration at this time, if the volume marks on the gasometer funnels have been checked with a volume measuring device. In our case one measurement showed the following:
250 ml in gasometer = 255 ml in volume measuring device

$$V_{corr} = 1.02 \cdot V_{H_2}$$

Table 4.4

Operating conditions	Efficiency (using H_o)	Efficiency (using H_u)
$I = 0.65$ A, $U = 0.66$ V $p = 992$ hPa, $T = 295$ K	42%	49%
$I = 0.35$ A, $U = 0.75$ V $p = 998$ hPa, $T = 296$ K	48%	57%

The efficiency of the fuel cell is somewhat larger at 0.75 V / 0.35 A than at 0.66 V / 0.65 A. The gas yield is the same in both cases.