Anfängerpraktikum

Experiment A52

PEM- Fuel cell

1. Concept of PEM-Fuel cell

Introduction: The fuel cell is a device that converts the enthalpy of a chemical reaction into electrical energy and heat with high efficiency. Sir William Robert Grove (1811-1896) is considered the father of the fuel cell. Based on the principles of physical chemistry, Wilhelm Ostwald (1853-1932) predicted a surprisingly high efficiency of a fuel cell of 83%. In our fuel cell, the reaction of the O_2 and H_2 molecules leads to water, which is associated with electricity generation and heat emission.

PEM (Proton Exchange Membrane) is the most commonly used type of fuel cell. The PEM fuel cell consists of an anode (left), a membrane (middle), a cathode (right) and an electrical load. Anode serves as a catalyst for the dissociation of the H_2 molecules and cathode serves as the electron donor for adsorbing O_2 molecules. The membrane (plastic foil or gelatinous material) acts as a filter, allowing only protons to pass through. The membrane is electrically separated from the anode and cathode by an electrolyte and is also tight for the gas molecules.

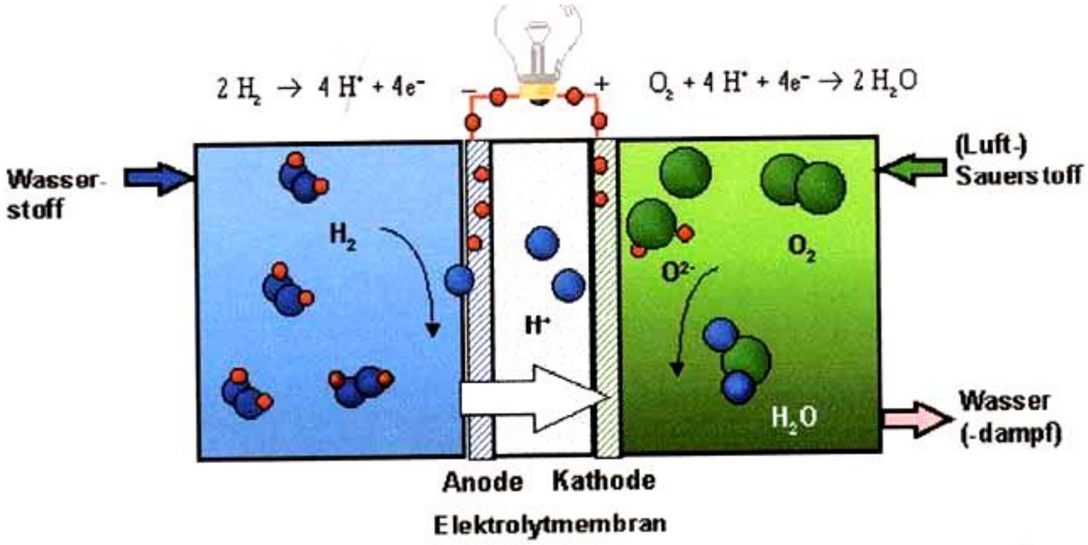

Fig. 1 Scheme of the PEM - Fuel cell

Hydrogen is passed to the anode, where after dissociation at catalytic reaction sites (mostly Pt nanoparticles), separation into electrons (e-) and protons (H+) also takes place:
$2\ H_2 \rightarrow 4\ H^+ + 4\ e^-$. The H^+-particles migrate through the membrane towards the cathode, where the formation of H_2O occurs as a result of the recombination of H^+, O_2^- and e^-, $O_2 + 4\ H^+ + 4\ e^- \rightarrow 2\ H_2O$. So there is a shortage of electrons (O_2) at the cathode and an excess of electrons (4 e^-) at the anode (H_2). The anode electrons can only reach the cathode through a load resistance **R** and thus contribute to usable current. [see also literature 1-8]

2. Goal of the Experiment

a) Optimizing of the electric Power of the Fuel cell (recording of the chracteristic U-I curve)
b) Determining of the energetic efficiency of the Fuel cell
c) Determining of the Faraday efficiency

3. Conduction of the Experiment

First of all, all modules of the apparatus are to be identified and the structure found is to be compared with the scheme (Fig. 2).
To initiate the function of the Fuel Cell, the electrodes must be moistened. This is achieved by injecting de-ionized water into the two inputs I_1 and I_2 at the electrostatic precipitation unit until the membrane is visibly soaked (dark grey). Then, after approx. 2 minutes, the O_2 and H_2 channels of the electrochemical unit are rinsed. For this purpose, a pressure of approx. 0.3 bar is set at the reducing valves P_1 and P_2 in both gas cylinders and then the two terminals U_1 and U_2 at the outlet hoses are opened, so that an uninterrupted flow of the gases is possible. Then the shut-off valves V_1 and V_2 can be opened easily. After approx. 5 seconds the terminals U_1 and U_2 should be closed again.

A. The power curve of the fuel cell

The power of the fuel cell depends on the load resistance **R**. In the following experiment it is to be investigated at which resistance and at which current intensity the power output of the fuel cell is optimal. At the input pressures $p(O_2)/p(H_2)=0.3/0.3$ (bar) the dependence of the voltage **U** and the current **I** on the load resistance **R** is to be recorded. The data are to be represented in the form of the characteristic **U-I** curve.
For the first part of the experiment, the resistance decade **R** and the ammeter **A** are connected as shown in Fig. 2. The voltage **U** at the Fuel cell electrodes and the current **I** through the resistor **R** are recorded using the *Brennstoffzelle.vi* program for 10 selected **R** values from the range 0 to 10. The pairs of values should each be recorded in a period of 60 seconds to obtain a representative average value. For each **R** value the power output can now be calculated using the equation **P=UI**. From the diagram **P** as a function of **I**, the current **I*** and the ohmic resistance **R*** at which the maximum electrical power P_{max} was delivered are determined.

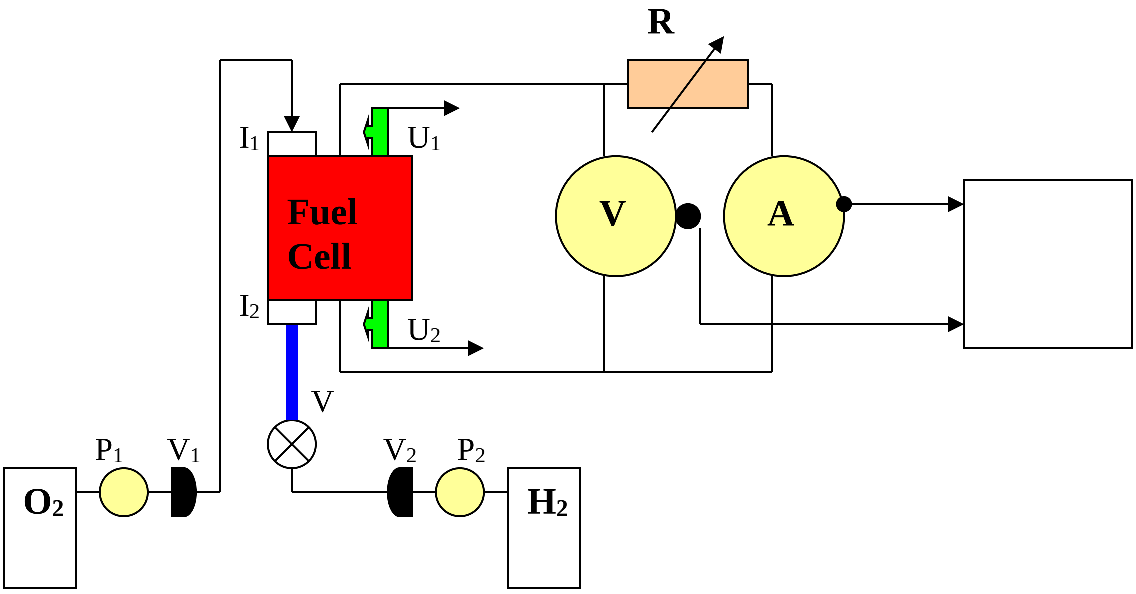

Fig. 2 Scheme for recording of the characteristic U-I curve of the fuel cell

Two further **U-I** experiments will be performed at different $\eta=p(O_2)/p(H_2)$ pressure ratios: 0.2/0.4 bar, 0.4/0.2 in bar. In both cases the **U-I** data obtained by **R** variations shall be presented in the form of the **U-I** curves.

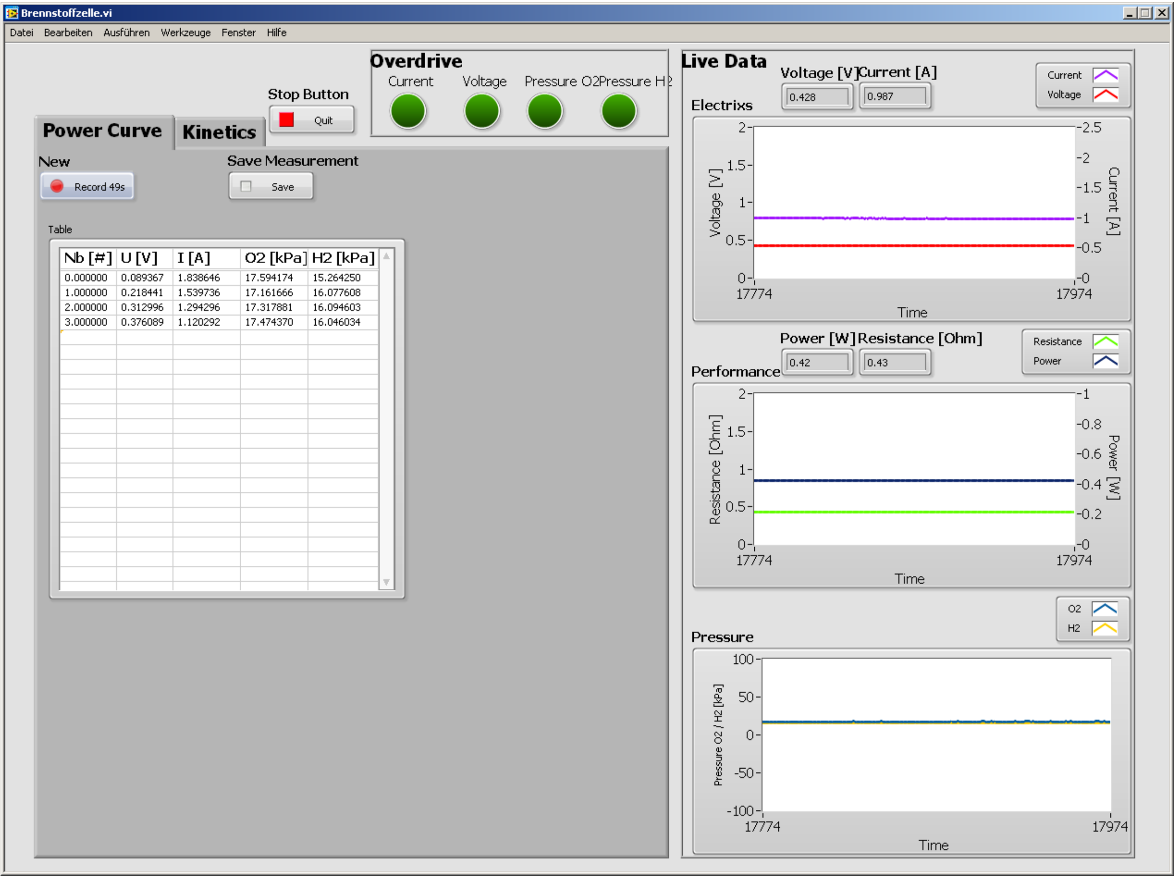

Fig. 3: the program *Brenstoffzelle.vi* for recording the power curve.

B. Ideal Efficiency

The ideal efficiency of a reactor is defined as follows:

$$\eta_{Ideal} = \Delta G / \Delta H \qquad (1)$$

The ratio of the free reaction enthalpy ΔG (the work released during the reaction, e.g. in the form of electrical energy, I^2Rt) and the reaction enthalpy ΔH (the energy released during the reaction) reaches the theoretical value of 0.83 % (according to Ostwad). In the real fuel cell system, this value is not reached due to voltage losses that act as heat.

C. Determining of the energetic Efficiency

Further experiments are carried out at the resistor R^*, where the power maximum was found.

The experiment to determine the energy efficiency E is based on a series of measurements of the time t required to consume certain amounts of H_2 V_k. The same measuring procedure is repeated for 5 different V_k volumes of the H_2 reservoir. Hoses of different lengths Lk ($V_k = \pi d^2 L_k/4$) are each filled with the same H_2 pressure of 1.5 bar and emptied under the same pressure conditions on the O_2 side (1.5 bar) by cold H_2 combustion.

Important: The connected pressure gauges indicate the overpressure against atmosphere, a Display of "50.0" corresponds to a pressure of 1.5 bar, for example!

The reservoir is refilled by first flushing the H_2 channel with H_2 when terminal U_2 is open and closing it again after 5 seconds (first the terminal, then valve V). The course of the reaction can be monitored by recording the voltage, current or pressure values using the *Brenstoffzelle.vi*- program.

The energy efficiency E of a fuel cell is defined as a ratio of the usable energy $E_{useable}$ to the total energy supplied E_{added}: $\eta = {E_{useable}}/{E_{added}}$.

For an H_2/O_2-PEM - Fuel cell the following applies: $E_{useable} = E_{electric}$ und $E_{added} = E_{hydrogen}$, where $E_{hydrogen}$ is the energy produced by the combustion of a quantity of hydrogen:
$\eta_E = {E_{electric}}/{E_{hydrogen}}$,that is:

$$\eta_E = \frac{U \cdot I \cdot t}{n \cdot \Delta H_R} \qquad (2)$$

ΔH_R – Molar reaction enthalpy, ~ 286 kJ/mol (exakt Value to be looked up!)
U – Voltage in V
I – Current in A

The consumed quantity of hydrogen is to be calculated using the ideal gas law, which is valid in the pressure range prevailing during the experiment with a very good approximation.
For voltage and current, the initial values I0 and U0, which can be read off the measuring instruments, are used for simple, approximate calculations (note values separately!).

This results in:

$$\eta_E = \frac{U_0 \cdot I_0 \cdot t \cdot R \cdot T}{p \cdot V_{tot} \cdot \Delta H_R} \qquad (3)$$

Please note that the total volume is made up of the volume of the hose to be replaced and an additional "dead volume" (supply lines to the Fuel cell / pressure gauge) (see Fig. 4), i.e. $V_{tot} = V_k + V_{dead}$.

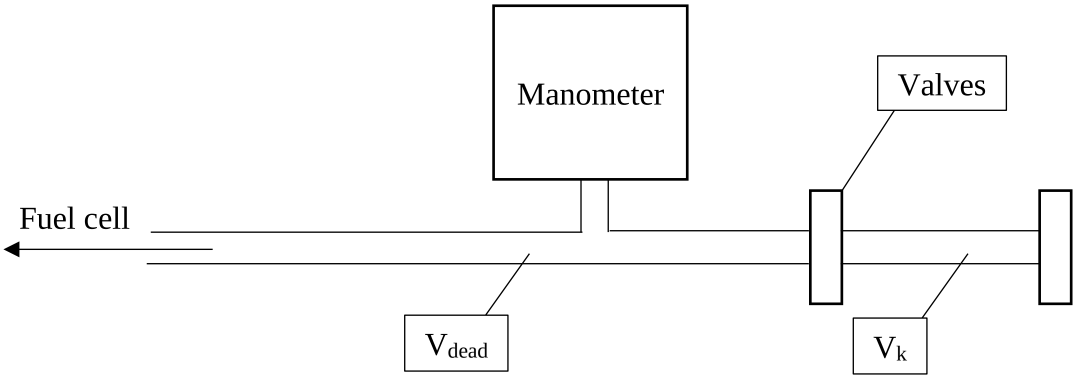

Fig. 4: Darstellung des Totvolumens

Overall, the effective efficiency can therefore be calculated using the following equation:

$$\eta_E = \frac{U_0 \cdot I_0 \cdot t \cdot R \cdot T}{p \cdot \left(V_{dead} + \frac{\pi \cdot d^2 \cdot L_k}{4}\right) \cdot \Delta H_R} \qquad (4)$$

Since the "dead volume" cannot be measured directly, it is determined indirectly from plotting the tube volumes against the reaction time, as shown in Fig. 4. (The diagram $V_k(t)$ represents a straight line).

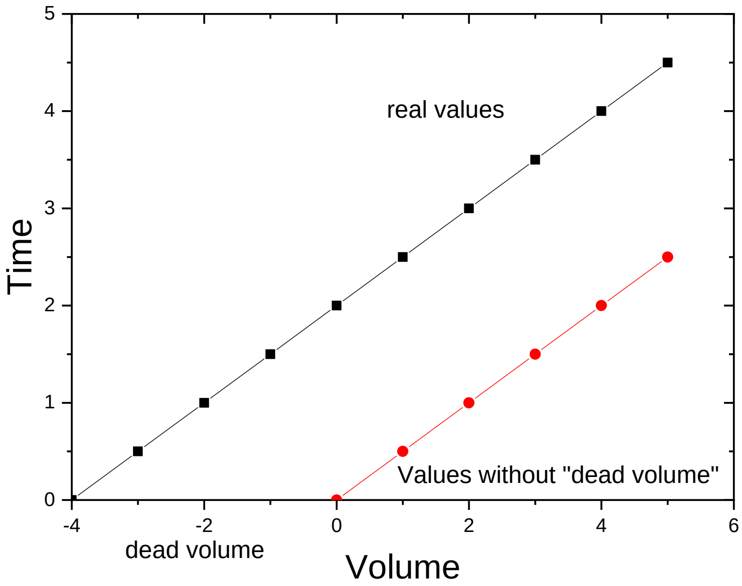

Fig. 5: The Volume against the reaction time. The “dead volume” can be determined by a linear regression

Finally, the reaction time t shall be defined after which the hydrogen quantity in the total volume can be considered as consumed.
This is determined by the measurement curve recorded by the computer (Fig. 6):
If the largest part of the hydrogen is consumed, the curve shows a more or less sharp jump, depending on the total volume, through which the perpendicular to the time axis is dropped in such a way that the same area is included with the tangents to the curve to the left and right (corresponds to the search for the inflection point of the curve if the curve is symmetrical).
The point of intersection is a good approximation of the reaction time.

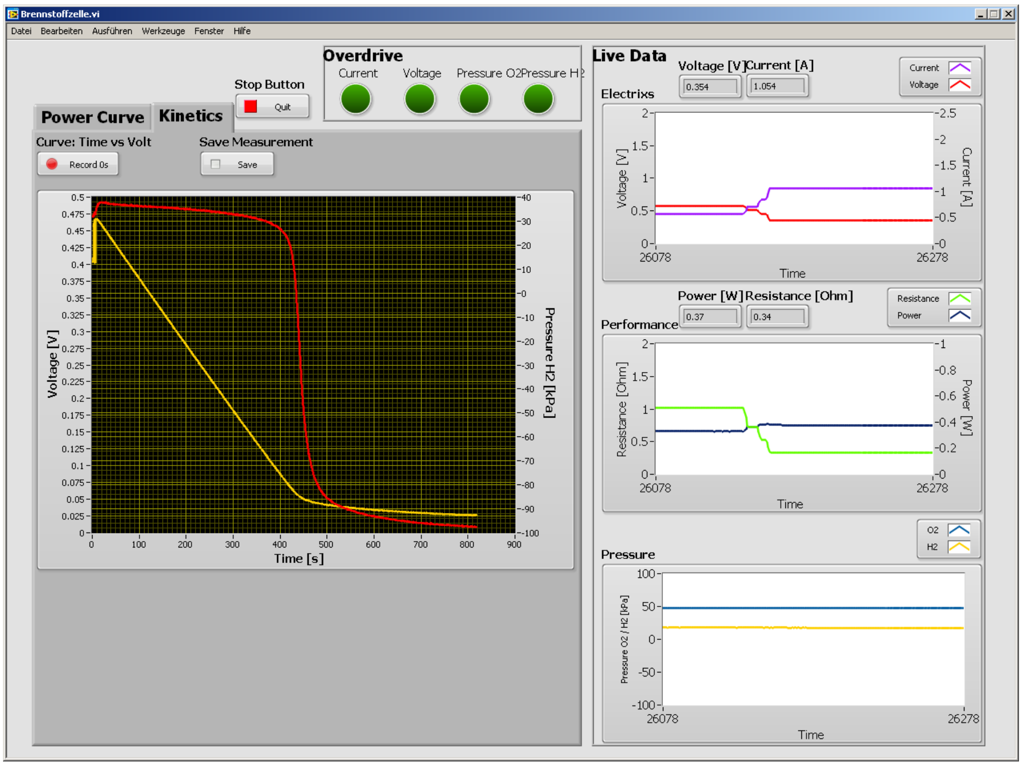

Fig. 6 Overlook of the program *Brenstoffzelle.vi* to determine the reaction time t.

For each Volume the Value η_E can be calculated by equation (4), the mean value in this series is representative for the energetic efficiency.

D. Determining the Faraday Efficiency

Faraday's first law establishes a relation between the amount of hydrogen consumed and the electricity generated. It is based on the fact that an H atom is the carrier of an electron that contributes to the usable current during the anode reaction. The Faraday efficiency of a Fuel cell represents a ratio between the amount of H_2 that was actually consumed during the reaction and the amount of H_2 that was calculated at the same reaction time using Faraday's law:

$$\eta_E = \frac{V_{H_2}(calculated)}{V_{H_2}(used)} \eta_{Faraday} = \frac{V_{H_2}(berechnet)}{V_{H_2}(verbraucht)}$$

Nach Faraday lässt sich V_{H2} wie folgt berechnen:

$$V_{H_2}(calculated) = \frac{I \cdot t \cdot R \cdot T}{F \cdot p \cdot z} \qquad (5)$$

R – Gaskonstante, 8,314 J/mol K
p, T – Druck (Pa = N/m^2) und Umgebungstemperatur (K)
F – Faradaykonstante 96485 C/mol
Z – die Anzahl der Elektronen, um ein H_2O Molekül zu bilden, z(H_2)=2

In this part of the experiment, the value pairs V and t obtained in the last measurement are used to calculate the theoretical H2 quantities and thus determine the Faraday efficiency. Based on the 5 values, the mean value of the efficiency is determined. The data are to be processed and displayed using the Excel or Origin program.

Topics and questions:

1. EMF and electrode potentials in an electrochemical cell
2. nernst equation for the EMF of a fuel cell.
3. discuss the progression of the U-I curves measured here under different working conditions at the fuel cell.
4. calculate the value of the ideal energy efficiency.
5. Why is $\eta_{Faraday} < \eta_{ideal}$?
6. what physical mechanisms can explain the $\eta_{Faraday} < 1$ relation?
7. calculate the maximum value of the electromotive force, EMF, that should be achievable with a PEM fuel cell, 1.23 V (open-circuit voltage vs standard electrode potential)
8. describe the microscopic structure of the electrode and membrane material
9. describe the dependence of the electromotive force U on p(O2) and p(H2) using the Nernst equation
10. compare the efficiency of a PEM fuel cell with the efficiency of the Carnot process.

Literatur (german)

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