Work 1. Characterization of PEM fuel cell

Introduction

Electrochemistry and electrochemical systems

Electrochemistry can be defined as the science of structures and processes at and through the interface between an electronic (electrode) and an ionic conductor (electrolyte). It follows from the definition that electrochemical reactions are heterogeneous processes taking place on the interface between two different conducting phases. In most cases one phase is represented by solid electronically conducting materials, e.g. metals, carbon, semiconductors.

Based on whether the process is spontaneous or not, electrochemical processes can be divided into two groups, i.e. galvanic and electrolytic. Spontaneous processes taking place in galvanic systems, e.g. batteries, accumulators, fuel cells, are characteristic by transformation of energy bonded in chemical compounds into electrical energy. In electrolytic systems the chemical reactions are taking place in consequence of electrical current passing the system due to external power supply. Based on the reaction Gibbs energy $\Delta_r G$ of the overall reaction (sum of half-reactions) it is possible to decide whether given system will behave as galvanic or electrolytic. If $\Delta_r G < 0$, process is spontaneous (galvanic system), when $\Delta_r G > 0$ process is not spontaneous (electrolytic system) and it would not take place unless electrodes are connected to an external power supply.

Faraday's law

Michael Faraday has formulated his electrochemical laws as early as in 1830's. He realized that the amount of substance produced/consumed by electrolysis is directly proportional to the amount of electrical charge Q that passed the system and inversely proportional to the number electrons required to produce/consume one molecule/atom. These 2 laws can be expressed by Eq. 1 known as Faraday's law

$$n_j = \frac{Q\, v_j}{zF} \quad [mol]$$
Eq. 1

Here n_j represents molar amount of produced/consumed compound *j*, v_j is its stoichoimetric coefficient, *F (=96485 C mol^{-1})* is Faraday constant.
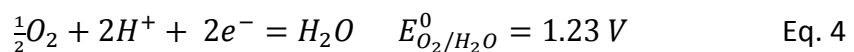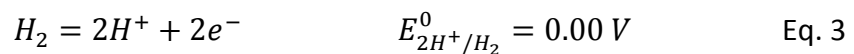
Electric charge Q can be calculated from Eq. 2.

$$Q = \int_0^t i\,dt \quad [C]$$
Eq. 2

PEM fuel cells

Fuel cells as a representative of galvanic system are intensively developed as one of the future alternative energy converters. They allow highly efficient conversion of chemical to electrical energy. This is because fuel cell operation is not limited by Carnot cycle as is the operation of classical heat engines such as turbines, combustion engines etc. There are many types of fuel cells. However the principle of operation stays the same. Simply said a fuel cell is a battery into which fuel and oxidant are continuously supplied. The "heart" of fuel cell consists of two electrodes separated by ionically conducting media. At the same time the ionically conducting separator divides fuel cell volume into two chambers to avoid mixing of fuel and oxidant. On one electrode the fuel is oxidized (electron removal), on the other one the oxidant is reduced (electron addition). However, because direct electric contact between the electrodes is not available, the electrons are forced to travel through external electric circuit and perform work. The ions generated either from fuel on the anode or from oxidant on the cathode are transported through the ionically conductive media towards the opposite electrode, where they react with the other product of the electrode reaction. (Please notice: By definition an electrode on which oxidation and reduction are taking place are called anode and cathode, respectively.)

PEM fuel cell is particular type of fuel cell in which ionically conductive separator is represented by <u>P</u>roton <u>E</u>xchange <u>M</u>embrane, therefrom PEM. Scheme of PEM fuel cell is shown in Fig. 1. Anode space is supplied with hydrogen gas. Hydrogen is oxidised on the anode according to Eq. 3. Produced H^+ are transported through the PEM membrane towards the cathode where they take part in cathodic reaction. In this reaction supplied oxygen is reduced under formation of water, see Eq. 4. The overall reaction taking place in fuel cell can be therefore expressed by Eq. 5.

$$H_2 = 2H^+ + 2e^- \qquad E^0_{2H^+/H_2} = 0.00 \, V \qquad\qquad \text{Eq. 3}$$

$$\tfrac{1}{2}O_2 + 2H^+ + 2e^- = H_2O \quad E^0_{O_2/H_2O} = 1.23 \, V \qquad \text{Eq. 4}$$

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$$\tfrac{1}{2}O_2 + H_2 = H_2O \qquad\qquad\qquad\qquad\qquad \text{Eq. 5}$$

Values $E^0_{2H^+/H_2} = 0.00 \, V$ and $E^0_{O_2/H_2O} = 1.23 \, V$ represent standard electrode potentials of individual electrode reactions described by Eq. 3 and 4. Term "standard electrode potential" relates to the electrode potential of electrode reaction in equilibrium and under standard conditions, i.e. in our case: ($p_{(H2)}$ = $p_{(O2)}$ = 101 325 Pa, $a_{(H+)}$ = 1, T = 298 K).

$p_{(H2)}$ and $p_{(O2)}$ stands for partial pressure of H_2 and O_2 respectively, $a_{(H+)}$ represents activity of protons in the electrolyte, T is thermodynamic temperature.

Equilibrium electrode potential E_{eq} under non-standard conditions in can be calculated from Nernst equation, see Eq. 6.

$$E_{eq} = E^0_{O/R} - \frac{RT}{zF} \ln(\prod (a_j^{surf})^{v_j})$$

Eq. 6

Here a_j^{surf} represents surface activity of specie *j*, v_j is stoichiometric coefficient of j, R is universal gas constant. In the case of gases a_j^{surf} can be expressed as ratio of partial pressure of *i* and standard pressure. Reaction must be written as reduction.

By definition the cell voltage is given by difference between cathode and anode potential Eq. 7.

$$U = E_{Cathode} - E_{Anode} \quad [V]$$

Eq. 7

Thus the theoretical voltage on H_2-O_2 fuel cell in equilibrium (zero net current) at standard conditions is 1.23 V. However in practical applications a fuel cell is supposed to generate electric current. In consequence of this the cell voltage decreases below this theoretical value.
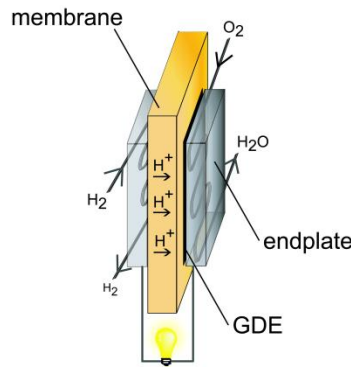
Fig. 1: *Scheme of PEM fuel cell.*

The typical dependence of the fuel cell voltage on the current density is shown in Fig. 2. Current density *j* is ratio of total measured net current *i* and electrode geometric area *A*.

$$j = \frac{i}{A} \quad [A \, m^{-2}]$$

Eq. 8

Three distinct regions can be distinguished on the voltage-current density curve. Each of them corresponds to the region where one of three following mechanisms of energy loss is dominant.

- Region of **activation polarization** can be found near equilibrium (zero current density) conditions. Activation polarization means that part of the generated energy is lost in order to raise the reaction rate of electrode reactions due to necessity to overcome activation energies of the reactions. Nearly exponential cell voltage decrease with

increasing current density is typical for this region as follows from theory of the reaction rates of electrode reactions.

- Region of **ohmic polarization** can be found in the middle-section of the voltage-current density curve. Energy is lost
    - due to transport of electric current in the electron conducting parts of the fuel cell and
    - mainly **due to transport of the protons in the PEM membrane**.

    Both of these are described by Ohmic law, Eq. 9. As overall cell resistance stays essentially constant over whole range of current densities the observed dependence is strongly linear.

$$\Delta U = i \cdot R_{cell} \quad [V] \qquad\qquad \text{Eq. 9}$$

- Region of **concentration polarization** is observed at high current densities. The transport of the fuel/oxidising gas to the surface of electrodes becomes the major limiting factor and concentration gradients are formed in the system. As consequence the cell voltage rapidly drops in accordance with the surface concentration of fuel/oxidising gas on the electrodes. Eventually the surface concentration of fuel/oxidising gas become zero, this corresponds to zero cell voltage.

The question crucial for fuel cell practical application is what are the optimal conditions for its operation. From the point of view of power density (at given temperature, gas flow rates and gas composition) the answer is given by so called performance curve. Power density *P* of the fuel cell can be calculated according to Eq. 10.

$$P = j \cdot U \quad [W\ m^{-2}] \qquad\qquad \text{Eq. 10}$$

and then plotted as function of current density (together with voltage-current density curve with *P* being secondary y-axis.)
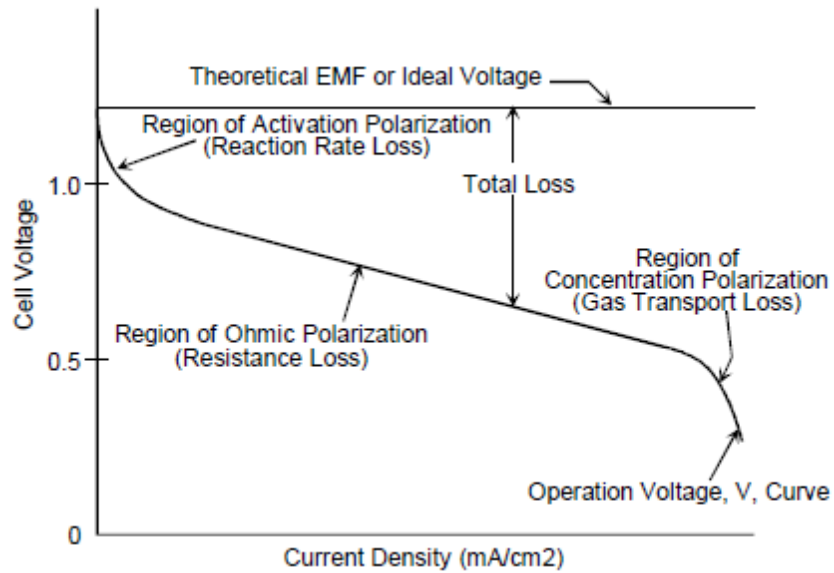
Fig. 2: Schematic representation of fuel cell voltage-current density curve. *From Fuel Cell Handbook, 4th Ed., J.H. Hirschenhofer, D.B. Stauffer, R.R. Engleman, and M.G. Klett, 1998; http://physics.oregonstate.edu/~hetheriw/energy/topics/doc/electrochemistry/fc/basic/fuel_cell_handbook_fourth_ed_fed_energy_tech_center_99.pdf, accessed 15.2.2013.*

Experimental work

*Aim of work:* Understanding the working principle of PEM fuel cell.

Safety precautions: Wear safety glasses and laboratory coat at all times in the laboratory. Hydrogen is extremely flammable gas.

Apparatus:
1) Fuel Cell
2) Hydrogen reservoir - glass burette
3) Oxygen reservoir - glass burette
4) Electric load

Tasks:

1) assemble apparatus:
   - connect fuel cell with electric load by supplied cables.
   - check volume of water in reservoirs.
   - close metal clips on the hoses between glass burette and fuel cell.
   - connect electric load to electric network.
   - fill the glass burettes with water from reservoirs.
   - fill the glass burettes with H_2 and O_2.

2) electric load setting:
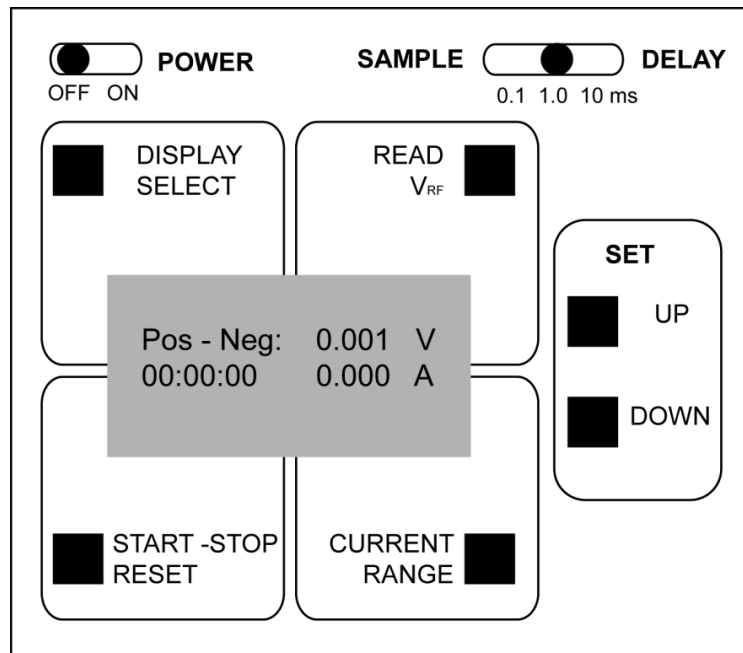
Fig. 3: Front panel of electronic load Astris TL4.

   - turn on the load.

- set the sample delay to 1.0 ms.
- with button **DISPLAY SELECT** set display with Pos-Neg: choice.

3) measure voltage-current density curve and performance curve of the PEM fuel cell
    - set bubble flow rate by loosening metal clips on the hoses between glass burette and fuel cell to two bubbles per second.
    - wait for about 30 seconds for voltage to stabilize.
    - write down values of voltage and current.
    - press button **START-STOP RESET.**
    - with buttons **SET UP/DOWN** set current to 0.02 A.
    - write down value of voltage and current.
    - repeat this procedure for the following current values: 0.03, 0.04, 0.05, 0.06, 0.08, 0.1, 0.15, 0.2, …. 0.8, 0.9 and 1.0 A. For each current write down corresponding value of cell voltage.

From known area of the electrodes (2.5 cm x 2.5 cm) calculate current density. Calculate actual performance (power density) of the cell for each current density. Calculate theoretical voltage in the cell by means of Nernst equation. Assume:
- water vapour pressure to be 2.5 kPa at 25 °C.
- fuel cell is operating at atmospheric pressure 101.325 kPa.
- both O_2 and H_2 entering the fuel cell are saturated with water vapour.

4) Validate Faraday's law:
    - set current to 1.0 A.
    - set bubble flow rate by loosening metal clips on the hoses between glass burette and fuel cell to one bubble per ten seconds.
    - with the stopwatch on your mobile phone or laboratory stopwatch measure time required to consume 10 cm^3 of H_2 (and determine the corresponding O_2 consumption).
    - with the stopwatch on your mobile phone or laboratory stopwatch measure time required for consume 5 cm^3 of O_2 (and determine the corresponding H_2 consumption).

From Faraday's law and ideal gas law calculate time necessary to consume 5 cm^3 of O_2 and 10 cm^3 of H_2 at current of 1 A. Compare theoretical and measured time.

5) Summarize your results and discuss them in laboratory protocol.
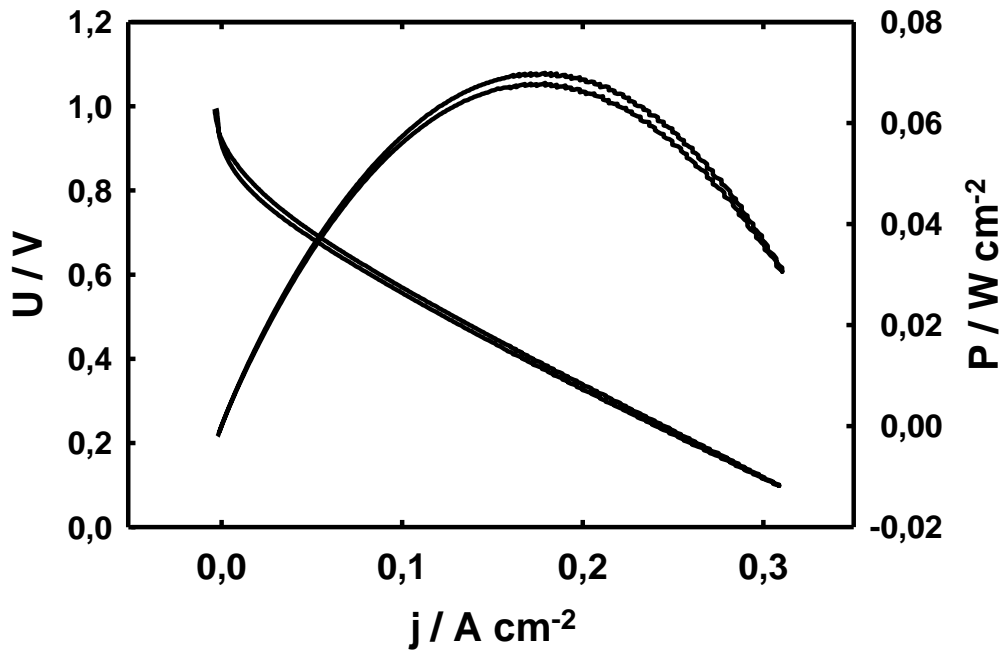
Fig. 4: Example of voltage-current density curve and performance curve of PEM fuel cell.