

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.

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

Here n_j represents molar amount of produced/consumed compound j , v_j is its stoichiometric coefficient, F (96485 C mol⁻¹) is Faraday constant.

Electric charge Q can be calculated from **Eq. 2**.

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

PEM fuel cell

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.)

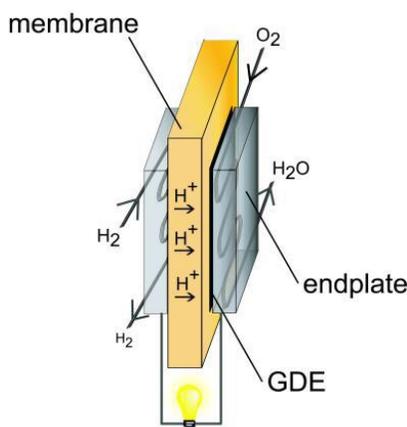


Figure 1 Scheme of PEM fuel cell

PEM fuel cell is particular type of fuel cell in which ionically conductive separator is represented by Proton Exchange Membrane, therefrom PEM. Scheme of PEM fuel cell is shown in **Fig. 1**. Anode space is supplied with hydrogen gas. Hydrogen is oxidized 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**.



Values $E_{2H^+/H_2}^0 = 0.00 \text{ V}$ and $E_{O_2/H_2O}^0 = 1.23 \text{ V}$ represent standard electrode potentials of individual electrode reactions described by **Eq. 3** and **4**.

Term “standard electrode potential” relates to the electrode potential of the given electrode reaction in equilibrium and under standard conditions, i.e. in our case: ($p(H_2) = p(O_2) = 101\,325 \text{ Pa}$, $a(H^+) = 1$, $T = 298 \text{ K}$). $p(H_2)$ and $p(O_2)$ 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**.

$$E_{eq} = E_{O/R}^0 - \frac{RT}{zF} \ln(\prod(a_j^{surf})^{\nu_j}) \quad \text{Eq. 6}$$

Here a_j^{surf} represents surface activity of specie j , ν_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**.

$$U = E_{cathode} - E_{anode} \quad \text{Eq. 7}$$

Thus, the theoretical voltage on H_2 - O_2 fuel cell at 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. The typical dependence of the fuel cell voltage on the current density is shown in **Fig. 2**.

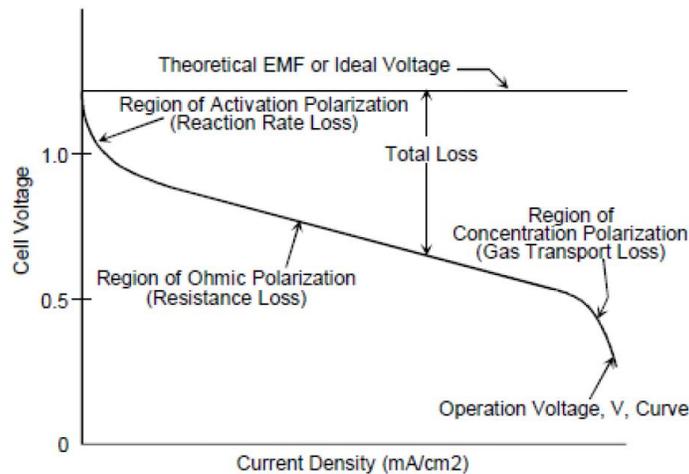


Figure 2 Schematic representation of fuel cell voltage-current density curve. From *Fuel Cell Handbook, 4th Ed., J.H. Hirschenhofer, D.B. Stauffer, R.R. Engleman, and M.G. Klett, 1998;* http://physics.oregonstate.edu/~hetheriw/energy/topics/doc/electrochemistry/fc/basic/fuel_cell_handbook_fourth_ed_fed_energy_tech_center_99.pdf, accessed 15.2.2013.

Current density j is ratio of total measured net current i and electrode geometric area A .

$$j = \frac{i}{A} [\text{A m}^{-2}] \quad \text{Eq. 8}$$

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.

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

- Region of **concentration polarization** is observed at high current densities. The transport of the fuel/oxidizing 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/oxidizing gas on the electrodes. Eventually the surface concentration of fuel/oxidizing gas become zero, this corresponds to zero cell voltage.

The question crucial for fuel cell practical application is what the optimal conditions for its operation are. 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**.

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

and then plotted as function of current density (together with voltage-current density curve with P being secondary y-axis.) Example is shown in **Fig. 4**.

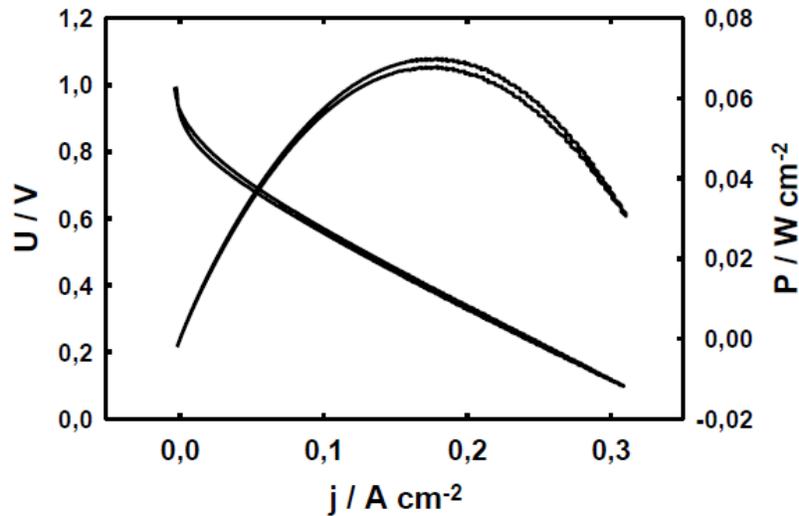


Figure 3 Example of voltage-current density curve and performance curve of

Experimental work

Aim of work:

Understanding advantages, disadvantages and the working principle of PEM fuel cell. Compare PEM fuel cell with another well-established current source.

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:

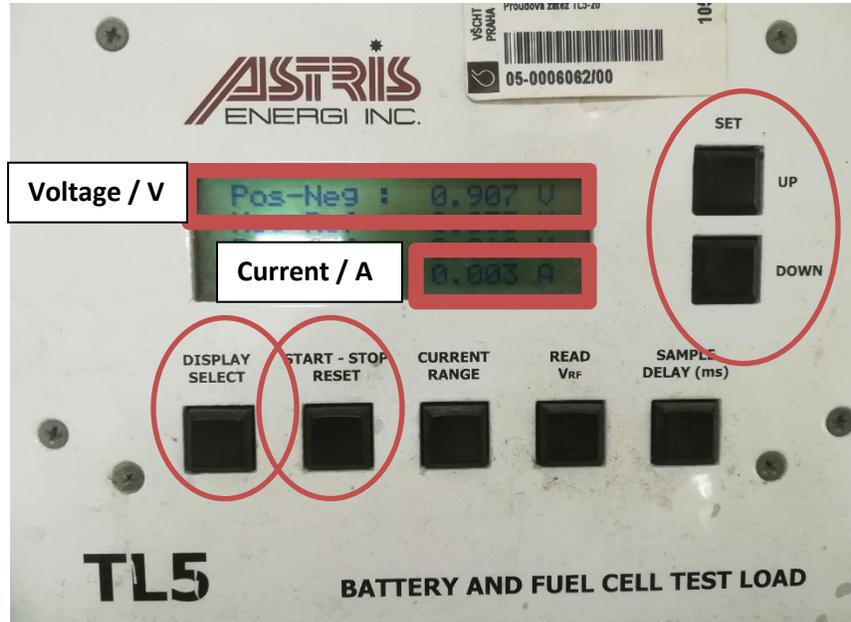


Figure 4 Front panel of electronic load Astris TL4A.

- turn on the load.
 - with button **DISPLAY SELECT** set display with Pos-Neg: choice
 - with button **START-STOP RESET** start current load
 - with buttons **SET UP/DOWN** set current to 0.35 A
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 10 seconds for voltage to stabilize
 - with buttons **SET UP/DOWN** set current to 0 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

Lab report: 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. Plot current density and performance density against voltage in one figure.

4. **HOME PREPARATION:** Try to calculate (before lab) theoretical voltage in the cell by means of Nernst equation (if you won't be able to calculate it at home, we will do it together at lab session; however, at least try it). Assume:
- water vapor pressure to be 2.5 kPa at 25 °C
 - fuel cell is operating at atmospheric pressure 101.325 kPa
 - both O₂ and H₂ entering the fuel cell are saturated with water vapor
 - how to calculate activity of each specie is stated in introduction part

5. 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 cm³ of H₂ (and determine the corresponding O₂ consumption)
 - with the stopwatch on your mobile phone or laboratory stopwatch measure time required for consume 5 cm³ of O₂ (and determine the corresponding H₂ consumption)
 - From Faraday's law and ideal gas law calculate time necessary to consume 5 cm³ of O₂ and 10 cm³ of H₂ at current of 1 A. Compare theoretical and measured time in your lab report.

6. Measure the voltage-current curve of another well-established current source (Ni-MH accumulator)
 - with buttons **SET UP/DOWN** set current to 0 A!!!
 - disconnect PEM fuel cell from load station
 - connect Ni-MH accumulator to load station
 - wait for about 10 seconds for voltage to stabilize
 - 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

Lab report: Because we don't know the area of electrodes in accumulator don't try to calculate current density. Plot only current curve against voltage.

7. Summarize your results and discuss them in laboratory protocol.
 - Write some short introduction about fuel cells (approx. half a page) with all used equations etc.
 - Plot current density and performance density against voltage for fuel cell in one figure. Clearly point out in the figure where are three distinct regions (activation polarization, ohmic polarization, concentration polarization) with either line or arrows.
 - Compare theoretical and measured time regarding validation of Faraday's law (write used equations)
 - Calculate theoretical equilibrium voltage by means of Nernst equation (write used equations with variables as well with values)
 - Discuss your results

Lab report is expected to be submitted in a week unless you have major issues. If you are working in a group one report per group is enough.

Contact for questions and submitting lab report: **Michal Carda, M.Sc.; cardam@vscht.cz; (room A23)**

Attachment

Table for your measurement (you can print it out for easier data collection):

U / V	I_{FC} / A	I_{accu} / A
~ 0		
0.03		
0.04		
0.05		
0.08		
0.1		
0.15		
0.2		
0.25		
0.3		
0.35		
0.4		
0.45		
0.5		
0.55		
0.6		
0.65		
0.7		
0.75		
0.8		
0.9		
1.0		