TALLINN UNIVERSITY OF TECHNOLOGY
SCHOOL OF ENGINEERING
Department of Mechanical and Industrial Engineering

INVESTIGATION OF X-RAY AND THERMAL ACTIVATION METHODS FOR FUEL CELLS AND ELECTROLYSERS

KÜTUSEELEMENTIDE JA ELEKTROLÜSAATORITE RÖNTGEN- JA TERMILISE AKTIVEERIMISE MEETODITE UURIMINE

MASTER THESIS

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Tallinn 2024

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Department of Mechanical and Industrial Engineering

THESIS TASK

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Study programme: Industrial Engineering and Management (MARM)

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Thesis topic:

(in English) *Investigation of x-ray and thermal activation methods for fuel cell and electrolysers*

(in Estonian) *Kütuseelementide ja elektrolüsaatorite röntgen- ja termilise aktiveerimise meetodite uurimine*

Thesis main objectives:

1. To review and study activation methods for electrolysers and fuel cells.
2. To compare thermodynamic behaviour of fuel cells and electrolysers under different heat treatment regimes.

Thesis tasks and time schedule:

No	Task description	Deadline
1.	Experiments with x-ray generators and analysis of its thermal effect on water.	01.02.2023
2.	Experiments with PEM fuel cells under different heat treatment regimes to study fuel cell thermodynamics.	21.06.2023
3.	Summarization and systemization of experimental data results. Writing thesis and publication.	28.02.2024

Language: English **Deadline for submission of thesis:** 20 May 2024

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Thermodynamic behaviour of proton exchange membrane fuel cell under different thermal treatment regimes

Konon Kesküll, Vitali Podgursky

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INTRODUCTION

In the face of environmental concerns and climate change, the community is increasingly turning its gaze towards sustainable energy solutions. As a result, there is a growing trend to move away from fossil fuels towards sustainable low-carbon sources of energy. Green energetics encompasses the utilization of renewable resources and the implementation of sustainable practices to meet energy needs while minimizing environmental impact [1]. The fundamental principle underlying green energetics is the recognition of finite fossil fuel reserves and the detrimental effects of their combustion on the environment, including air and water pollution, as well as greenhouse gas emissions. In contrast, sustainable energy sources offer a cleaner and more sustainable alternative, thereby mitigating climate change and promoting long-term environmental stability.

It is expected that greenhouse gas emissions will see an increase of 50% by 2040. Not even advanced emission control or combustion technologies would be able to keep this rise in check permanently. Thus, most European industries face major challenges regardless of future mitigation commitments, including increased competition with other regions that have competitive advantages through lower cost fuels or carbon taxes. Reducing greenhouse gases emissions comes down to combustion efficiency. While combustion efficiency can help lower emissions, existing industrial boiler systems struggle to achieve combustion efficiencies above 90 % [2].

There are opinions that the hydrogen energy might be one of the key points in achieving the sustainable energy production. One of the most abundant elements, hydrogen can be converted into the electricity with close to none of the by-products using fuel cells (FC). As well as hydrogen can be produced by water splitting using electrolysers (EL). However, despite the promise of hydrogen energy, numerous challenges and barriers persist on the road to widespread usage. Traditional methods of hydrogen production, such as steam methane reforming and electrolysis, are often characterized by high energy consumption, carbon emissions, and resource-intensive processes. Addressing these limitations and enhancing the efficiency of hydrogen generators and fuel cells represent critical avenues for advancing the transition towards a hydrogen-based economy.

In this thesis, the aim to explore the technologies which can improve the efficiency of the FC and water EL. The concept of FC and EL activation and understanding its benefits

and nature are the primary goals of this research. Thermal activation of FC and activation by so-called High Energy X-Ray Ceramic (HERC) effect are under investigation [3]. Through theoretical analysis of FC thermodynamics and empirical research with FC and HERC chips established in this thesis seeks to contribute to the burgeoning discourse on green energetics based on FC and EL and pave the way towards a more sustainable future.

Keywords: hydrogen, fuel cell, activation, master thesis.

1 REVIEW OF LITERATURE

1.1 Overview of renewable energy technologies

In recent years, the global focus on sustainability and environmental conservation has intensified, leading to a growing interest in green energy and sustainable power generation. This chapter provides a comprehensive overview of green energetics, sustainable energy, and various types of power generators that contribute to a more sustainable future [4].

Green energy encompasses a diverse range of renewable resources, each with its unique characteristics and applications. Among the most prominent types of green energy generators are:

- Solar Energy: Derived from the sun's radiation, solar energy can be harnessed through photovoltaic (PV) panels or concentrated solar power (CSP) systems to generate electricity and heat water for residential, commercial, and industrial use.
- Wind Energy: Wind turbines convert kinetic energy from the wind into electricity, making wind energy a reliable and scalable source of renewable power, particularly in regions with consistent wind patterns.
- Hydrogen Energy: Hydrogen fuel cells utilize hydrogen gas to produce electricity through an electrochemical process, offering a clean and efficient alternative to traditional combustion engines.
- Biomass Energy: Biomass refers to organic materials such as wood, agricultural residues, and organic waste, which can be converted into biofuels or burned directly to generate heat and electricity.
- Geothermal Energy: Geothermal power plants harness heat from the Earth's interior to generate electricity or provide direct heating and cooling for buildings, offering a reliable and continuous source of renewable energy.
- Tidal Energy: Tidal turbines capture energy from ocean tides and currents to generate electricity, providing a predictable and consistent source of renewable power in coastal regions.

While there are many options, the focus of this thesis is on hydrogen energy generators. Its main advantages would be versatility, scalability, high energy density and being clean and emission-free type of generator. Disadvantages would be challenges in transportation, storage, infrastructure development and production, since all of those steps are still costly, compared to others. The present study mainly focuses on the fuel cells (FC) properties, however generation of hydrogen by water electrolysis (EL) is also under investigation.

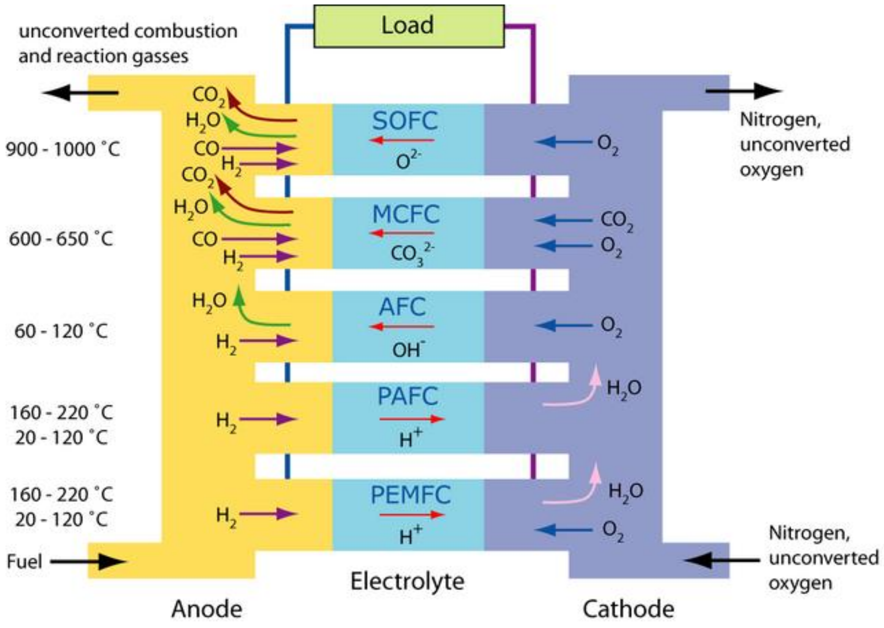

Figure 1.1. Working principal scheme of different types of FC [5]

There exist a variety of fuel cells, each type with its own operating temperatures, types of fuels and by-products (Figure 1.1). While some fuel cells can be compact and have a simple design, like acidic fuel cell (AFC), others might be more suited for industrial purposes, with more power output and complex design, e.g., molten carbonate fuel cell (MCFC) or solid oxide fuel cell (SOFC). Figure 1.1. shows the differences in working principles of fuel cells.

Proton Exchange Membrane (PEM) FC offer several advantages over other types of fuel cells, making them particularly attractive for various applications. The thermodynamics of PEM FC will be discussed in next chapter. Some key advantages of PEM FC include:

- High efficiency: PEM FC operate at high efficiency levels, typically ranging from 40% to 60%, making them one of the most efficient types of fuel cells available.
- Quick start-up and response times: PEM FC have rapid start-up and response times, allowing for on-demand power generation and responsiveness to fluctuations in electrical demand.
- Compact and lightweight design: PEM FC feature a compact and lightweight design, thanks to their use of a solid polymer electrolyte membrane as the electrolyte material.

- Low operating temperature: PEM FC operate at relatively low temperatures compared to other fuel cell types, typically between 60 °C and 80 °C.
- Enhanced durability and longevity: PEM FC exhibit improved durability and longevity compared to some other fuel cell types, attributed to their solid polymer electrolyte membrane, which offers greater resistance to degradation and chemical contamination.
- Low emission profile: PEM FC produce minimal emissions during operation, with water vapor and heat being the primary by-products.

Disadvantages of PEM FC:

- The high cost of membrane catalyst: The catalyst of PEM can be made from heavy or noble metals that improve reaction speed. The most usual metal is platinum (Pt). The cost of platinum catalyst, up to 40% of total fuel cell cost, is one of reasons why PEM fuel cells are not as widespread;
- Water management sensitivity: The membrane and the catalyst can be easily polluted with excess water or unwanted chemical compounds that reside on the surfaces if not cleaned in time properly;

Interdisciplinary approach may provide an opportunity to address or analyse the benefits of sustainable energy from different point of view. For example, pyroelectric technology can be connected to green energetics, albeit indirectly, through its potential applications in energy harvesting and efficient utilization of energy resources. While pyroelectric technology itself does not directly produce renewable energy like solar panels or wind turbines, it can play a significant role in enhancing the efficiency and sustainability of energy systems in several ways:

- Waste heat harvesting: Pyroelectric materials have the unique ability to generate electric charge in response to temperature changes.
- Energy-efficient sensors and actuators: Pyroelectric materials are commonly used in sensors and actuators for detecting and responding to thermal changes.
- Thermal energy harvesting for IoT devices: With the proliferation of Internet of Things (IoT) devices, there is a growing demand for self-powered sensors and electronics that can operate autonomously without the need for external power sources or frequent battery replacements.
- Thermal energy conversion for portable electronics: Pyroelectric materials can also be integrated into portable electronic devices, such as smartphones, wearable gadgets, and medical implants.
- Research and Development of advanced energy technologies: Beyond direct applications, pyroelectric research contributes to the broader field of materials

science and renewable energy technologies. Pyroelectrics can be used as activation elements in the fields of production or consumption of energy.

1.2 Thermodynamics of fuel cells and water electrolysers

The second part of this work involves study and understanding working principles of fuel cells and electrolysers. As the experimental part of the present study deals with mainly FC, the theory of electrolysers will be considered only briefly.

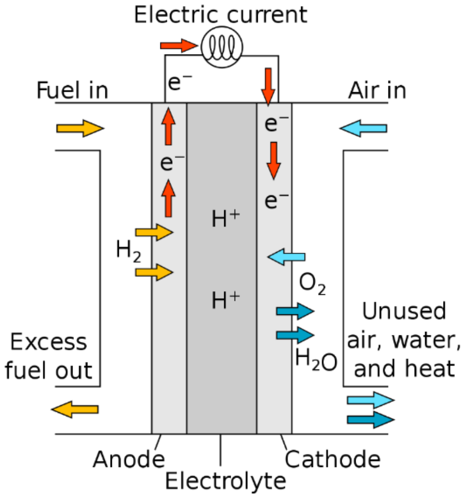

Figure 1.2. The schematic view of PEM fuel cell [6]

The proton exchange membrane fuel cell (PEMFC) consists of pair of electrodes and a membrane with a catalyst designed for the specific reactions in-between. The working principle of fuel cell is that it requires the fuel (usually hydrogen gas H_2) and an oxidizer (an oxygen gas O_2). The catalyst separates the hydrogen molecules in such way that it forces negative ions (electrons) to go through a closed contour, creating a direct current. Other ions (i.e., positive protons) are allowed to pass through the membrane on the other side of the cell. Hence, the exchange of protons is happening on the working surface of the membrane. Then, they recombine with oxidizer molecules to form water molecules H_2O. The overall reaction is:

$$2H_2 + O_2 \rightarrow 2H_2O + Q \qquad (1.2.1)$$

, where Q – heat.

Reactions on anode and cathode are:

Anode: $2H_2 \rightarrow 4H^+ + 4e^-$

Cathode: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

One of main advantage of PEM fuel cells (that it also shares with alkaline fuel cell) is ability to form stacks to increase energy density and power output. The single fuel cell is a multi-layered Membrane Electrode Assembly (MEA). A typical MEA is composed of a polymer electrolyte membrane (PEM), two catalyst layers, and two gas diffusion layers (GDL).

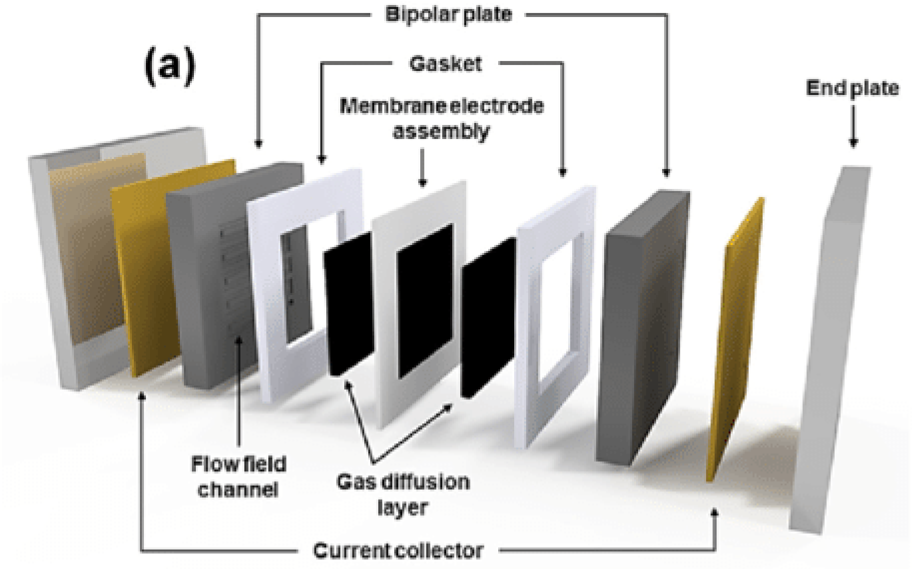

Figure 1.3. Example of membrane electrode assembly of PEM fuel cell [7]

Gas diffusion layer is a thin and porous sheet that must provide high electrical and thermal conductivity and chemical and corrosion resistance, in addition to controlling the proper flow of reactant gases (hydrogen and air) and managing the water transport out of the MEA. This layer must also have controlled compressibility to support the external forces from the assembly, and not deform into the bi-component plate channels to restrict flow.

Different classes of fuel cells are made for different purposes, operate at different temperature ranges and have slightly separate half-reactions on both anode and cathode of the membrane.

Thermodynamics of gases in retrospect to fuel cells suggest that maximum theoretical output voltage (also known as ideal equilibrium potential) of fully reversible fuel cell is related to free-energy change in electrochemical reaction between hydrogen and oxygen gases. It must be noted that all relations in thermodynamics and calculations were made with respect to standard temperature and pressure. To represent a relationship between ideal equilibrium potential and standard electrode potential, the Nernst equation general form can be used for the overall cell reaction it to determine equilibrium potential at any temperature for any fuel cell. The maximum fuel cell performance or reversible (equilibrium) fuel cell voltage (standard potential) can be estimated based on equilibrium thermodynamics and electrochemistry analysis [6-9].

To start, chemical reaction in fuel cell can be written in its simplest basic form with oxidizer and reducer:

$$Ox + ne^- \leftrightarrow Red \tag{1.2.2}$$

Chemical potential μ of this reaction is difference between energy required to take electrons and energy required to give electrons. This solution extends to an electrochemical potential as well. The ratio of oxidized to reduced molecules is equivalent of ratio of probability of being oxidized to a probability of being reduced. It can be written in terms of Boltzmann constant factor k:

$$\frac{[Red]}{[Ox]} = \exp\left(\frac{n\mu}{kT}\right) \tag{1.2.3}$$

By taking the natural logarithm, a following equation is derived:

$$\mu = \mu^{\circ} + \frac{kT}{n}\ln\frac{[Red]}{[Ox]} \tag{1.2.4}$$

To convert chemical potential μ to electrical potential E, the equation must be divided by elementary charge e. Next, by definition of Faraday constant and gas constant:

$$\frac{k}{e} = \frac{RN_A}{N_AF} = \frac{R}{F} \tag{1.2.5}$$

The formula can be derived for electric potential:

$$E = E^{\circ} + \frac{RT}{nF}\ln\frac{[Red]}{[Ox]} \tag{1.2.6}$$

In this case no current flows throw the cell. For the fuel cell reducers and oxidizers can be changed to reaction’s products and reactants. In general, partial pressures can be used for concentration and moles in most chemical problems. Derived relation between the standard potential and open-circuit voltage, i.e., measurable quantity is provided by Nernst equation [8].

$$E = E^{\circ} + \frac{RT}{2F}\ln\frac{p_{H_2}}{p_{H_2O}} + \frac{RT}{2F}\ln p_{O_2}^{1/2} \tag{1.2.7}$$

It was previously stated that in some cases increase in temperature and pressure might increase the efficiency of a fuel cell. In addition, manipulations on modifying fuel cell parameters might yield positive results as well. Using different techniques, such as hydrogen activation or photo-enhanced electrolysis is also worth researching. Such methods are not limited to fuel cells. Some industrial generators and engine installations would have pre-processing routines or catalysts for the fuel to increase its combustion efficiency and reduce waste products' ratio. The same can be theoretically be done with hydrogen fuel in a fuel cell, which is also one of the main topics of this study. However, that is not the case for an ideal reversible fuel cell.

From the second law of thermodynamics, the change in free energy, or maximum useful work, can be obtained when a fuel cell operating irreversibly and is dependent upon temperature [7]. This free energy is called Gibb's free energy and denoted as *ΔG*. Through Nernst equation it can be shown, that for ideal H_2/O_2 cell electric potential is dependent on free energy change, which in turn is dependent on temperature and pressure:

$$\varDelta G_f = \Delta G_f^{\circ} + RT \ln \frac{p_{H_2}}{p_{H_2O}} + RT \ln p_{O_2}^{1/2} \qquad (1.2.8)$$

Additionally, based on equilibrium thermodynamic analysis, namely using Gibbs-Helmholtz equation, the relation between thermodynamic potentials at constant pressure can be shown:

$$\varDelta H = \varDelta G - T\left(\frac{\delta \Delta G}{\delta T}\right)_P \qquad (1.2.9)$$

, where

H – total energy of the system or enthalpy change, J,

T – temperature, K,

G – Gibbs free energy, or the energy available to do useful work, J.

From this formula, entropy change *ΔS* can be expressed as a rate of free energy change as function of temperature change rate. Since entropy change is negative for the FC reaction with liquid water as product, Gibbs free energy change *ΔG* can be expressed in general form, as:

$$\varDelta G = \varDelta H - T\varDelta S \qquad (1.2.10)$$

Now we can substitute both formulae:

$$\varDelta G + T\varDelta S = \varDelta G - T\left(\frac{\delta \Delta G}{\delta T}\right)_P \qquad (1.2.11)$$

By cancelling ΔG out we get:

$$\Delta S = -\left(\frac{\delta \Delta G}{\delta T}\right)_P \tag{1.2.12}$$

The fact that Gibbs's free energy change is maximum work done on system, by equation:

$$\Delta G = -nFE_{cell} \tag{1.2.13}$$

the next equity can be found by substitution and dividing by *nF*:

$$\left(\frac{\delta E_{cell}}{\delta T}\right)_P = \frac{\Delta S}{nF} \tag{1.2.14}$$

Finally, the change of reversible cell potential E_{cell} can be expressed as:

$$E_{cell} = E_{cell}^0 + \frac{\Delta S}{nF}(T - T^0) \tag{1.2.15}$$

This equation at constant pressure shows the variation of the reversible voltage with the temperature. The term $\Delta S/nF$ graphically represents the slope of the line of E_{cell} vs. T.

Enthalpy change ΔH value can be taken directly from the table as its calculation is out of scope of this work [6-10]. It should be noted, that since heat capacity effects are generally minor, for general calculations, ΔH and ΔS values are usually assumed independent of temperature.

The basic thermodynamic data of enthalpy of formation and absolute entropies of formation for fuel cell reaction can be compiled into table.

Table 1.2.1 Values of enthalpy and entropy for fuel cell reaction

	h^o_f, kJ/mol	s^o_f, kJ/(mol·K)	ΔG^o_f, (kJ/mol)
Hydrogen, H_2	0	0,131	0
Oxygen, O_2	0	0,205	0
Water liquid, H_2O (l)	-285,8	0,07	-237,2
Water vapour, H_2O (g)	-241,8	0,189	-228,6

Additionally, entropy change ΔS can be expressed as difference between amount of heat rejected per mole of products and reactants. Following equation can be used for both liquid (High Heating Value) and vapour (Low Heating Value) water:

$$\Delta S_{H_2O(l)\,HHV} = (s^{\circ})_{H_2O} - \left[(s^{\circ})_{H_2} + \frac{1}{2}(s^{\circ})_{O_2}\right] = 0{,}07 - [0{,}131 + 0{,}1025] = -0{,}163\ \frac{kJ}{mol \cdot K}$$

(1.4.16)

$$\Delta S_{H_2O(l)\,LHV} = (s^{\circ})_{H_2O} - \left[(s^{\circ})_{H_2} + \frac{1}{2}(s^{\circ})_{O_2}\right] = 0{,}189 - [0{,}131 + 0{,}1025] = -0{,}0445\ \frac{kJ}{mol \cdot K}$$

Theoretical slope coefficients can be calculated for water in liquid and gaseous phases:

$$\frac{\Delta S}{nF} = -\frac{0{,}163\frac{kJ}{mol}}{2 * 96493\ C} = -0{,}00085 \qquad (1.2.17)$$

$$\frac{\Delta S}{nF} = -\frac{0{,}0445\frac{kJ}{mol}}{2 * 96493\ C} = -0{,}00023 \qquad (1.2.18)$$

At constant pressure and temperature (T = 295,15 K), it is easier to calculate cell potential by using relation (1.2.10) and Faraday constant relation (1.2.13) and tabulated data from Table 1.1.

Hence, Gibbs' free energy change ΔG can be calculated for liquid water:

$$\Delta G_{H_2O(l)\,HHV} = -285{,}8\ \frac{kJ}{mol} - 298{,}15\ K \cdot \left(-0{,}163\ \frac{kJ}{mol \cdot K}\right) = -237{,}1\frac{kJ}{mol} \qquad (1.2.19)$$

Electric reversible potential can now be calculated, knowing Gibbs' free energy change, Faraday's constant and number of moles:

$$E_l^{\circ} = -\left(\frac{-237{,}1\frac{kJ}{mol}}{2 \cdot 96{,}48\frac{kC}{mol}}\right) \cong 1{,}23\ V \qquad (1.2.20)$$

This potential, also known as standard potential, equals 1,23 V for liquid water as a reaction product, correspondingly, for the water vapour phase this potential equal to 1,18 V. It cannot, however, ever be achieved in practice due to irreversible losses inside the real fuel cell. The dependence E(T) for ideal reversible fuel cell (RFC) is shown in Figure 1.4.

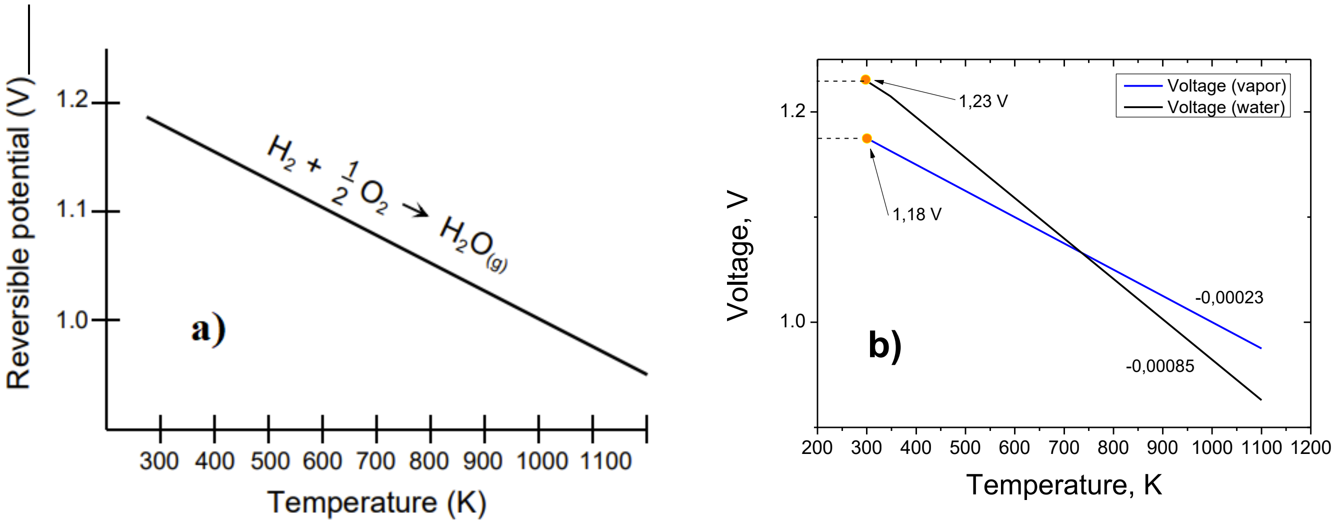

Figure 1.4. a) RFC potential for water in vapour phase [8] and b) RFC potentials for liquid and vapour phases (this study)

The results of calculations in the present study can be compared with previously published results [8], see Figure 1.4. It can be seen that they are quite similar.

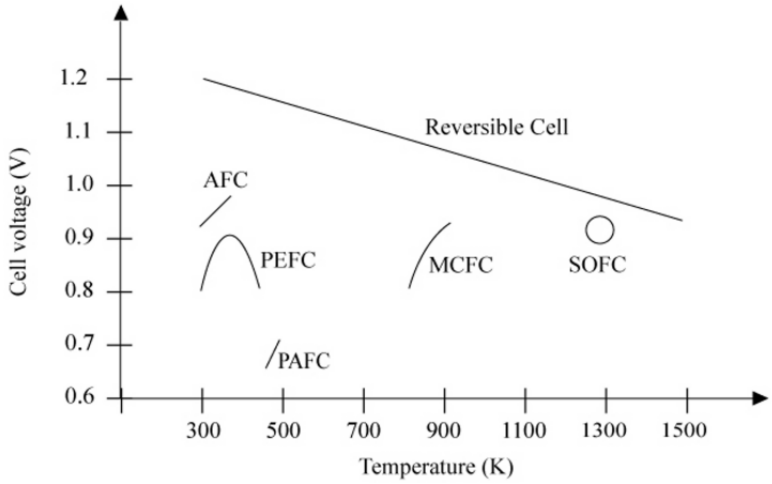

Figure 1.5. The behaviour of different types of FC under real environmental conditions [7]

It should be stressed that reversible (ideal) FC voltage dependence on temperature shown in Figure 1.5 is a calculation using equilibrium thermodynamics approach for gases. The behaviour of the real FC, for instance, PEM, alkaline FC, solid oxide FC, *etc.* under different conditions can strongly differ from the theoretical prediction and depends on the type of FC, current density, gas pressure, FC materials, *etc.* [11], see Figure 1.5.

It was shown, that majority of main fuel cell classes experience an increase in productivity with the increase of operating temperature, up to a certain point, where fuel cell cannot operate at all. There is, however, a special case of fuel cell with PEMFC. While it was proven that actual voltage of fuel cell will be always lower than theoretical equilibrium voltage defined by Gibbs and Nernst equations, this actual voltage will be further lowered due to irreversible losses inside the fuel cell itself. Different types of losses occur at different levels of productivity, ultimately depending on the load in electrical circuit and electric current flow [6,8,10].

Those losses are also part of the polarization curve of fuel cell (as it can be seen on Figure 1.11).

Mainly those losses divided into three major types:

1. Activation losses – as was already mentioned in previous chapter, activation losses occur at low currents and happen due to losses at the stage of gas crossover through the gas diffusion layers of the fuel cell membrane. Usually, it is connected to the resistance of the membrane itself;
2. Ohmic losses – electrical losses due to the nature of conductors, grows proportionally with current and voltage;
3. Mass transfer/transport losses – occur at high current densities. These losses happen since performance of fuel cell is highly determined by reactant and product concentrations on the interface, the catalyst layer. Due to limited chemical reaction speed, losses occur when the consumption is too fast for reaction to maintain concentrations;

It must be noted that polarization curves do not show the correspondence of voltage due to thermodynamic effect of temperature and only shows dependence on electric and internal parameters. While it was not mostly applicable during experimental part, polarization curves are crucial for understanding the nature of fuel cell.

Finally, it was also worth to compare dependence *E(T)* in the case of water electrolysis. The chemistry on the electrodes for particular type of FC and EL is similar, the main difference that electrolysis is endothermic process, however conversion of chemical energy of gases into electrical energy in FC is exothermic one.

LeRoy et all. [11] estimated *E(T)* in case of water electrolysis, i.e., dependence of applied voltage to water splitting on temperature. The empirical expressions were made to predict behaviour of electrolysis voltage.

$$E^{\circ}_{rev,t} = 1{,}5184 - 1{,}5421 \cdot 10^{-3} T + 9{,}523 \cdot 10^{-5} T ln T + 9{,}84 \cdot 10^{-8} T^2 \qquad (1.2.18)$$

The first linear coefficient of this equation, which equals to -0.0015421 and above calculated -0.00085 for fuel cells in equation (1.4.17) are very similar. The dependence E(T) for electrolysers is shown in Figure 1.6, which looks similar to graphs shown in Figure 1.4 for E(T) for FC.

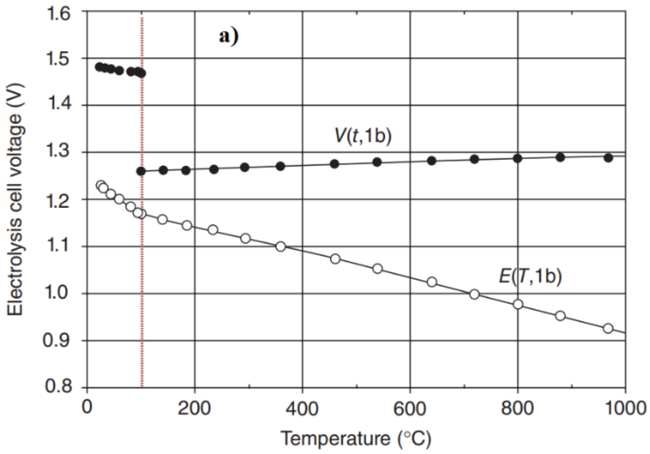

Figure 1.6. E(T) graph for water electrolyser [13]

1.3 Principles of X-ray pyroelectric technology

Pyroelectric effect can be one of possible opportunities in improving the usage, power output, sustainability of hydrogen generators and fuel cells (see following Section).

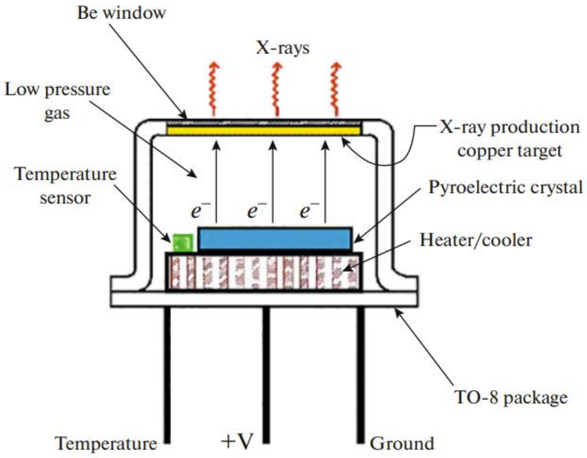

Figure 1.7. The circuit diagram of the Amptek COOL-X pyroelectric X-ray source [14]

As it was shown heat losses can be converted into emission by pyroelectrics. Different pyroelectric technologies use this principle in many ways. Figure 1.7 shows the principal scheme of a device, capable to generate x-rays due to a pyroelectric effect in vacuum.

The pyroelectric crystal is located in a miniature vacuum chamber on an isolated substrate that can be heated or cooled. A copper foil target is installed on the side opposite to the crystal surface. During heating of the substrate, a high negative potential appears on the free crystal surface, which leads to electron emission. Free electrons are accelerated from the working surface of the pyroelectric crystal to the copper target. Upon such interaction of accelerated electrons with target atoms, X-ray radiation is generated. During cooling, the pyroelectric crystal is repolarizing, which leads to appearance of free electrons in a cloud of ionized gas in vicinity of its working surface. In this case, the crystal itself becomes the target.

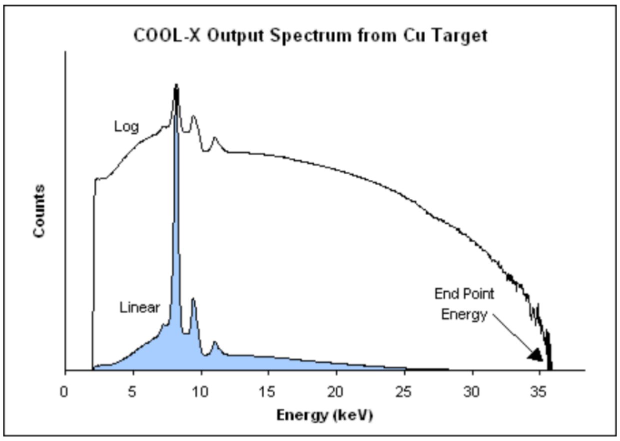

Figure 1.8. COOL-X output spectrum from copper target without tantalum [14]

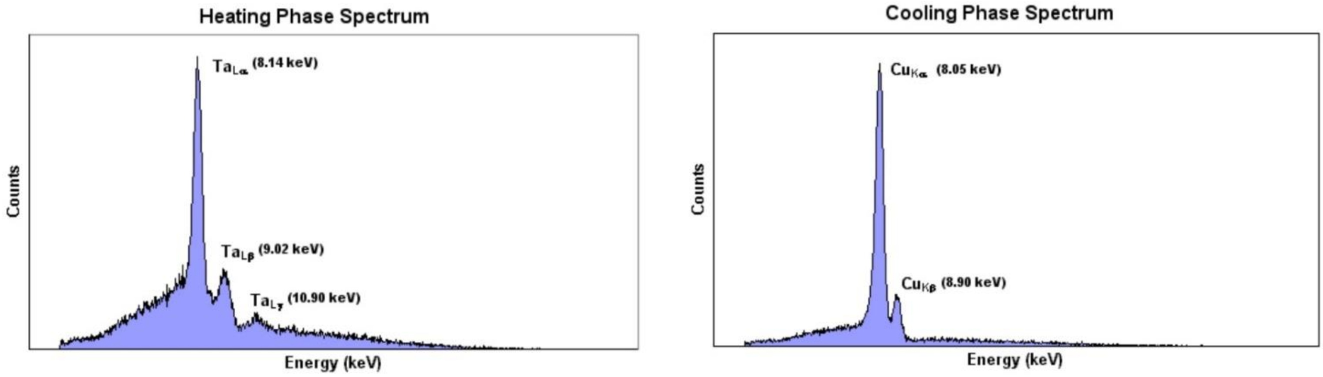

Figure 1.9. COOL-X pyroelectric crystal heating and cooling phase spectrums [14]

Figures 1.8. and 1.9. show the differences in spectrums for tantalum (Ta) and copper (Cu) targets under heating or cooling. When crystal temperature is changing, it exhibits a spontaneous change of polarization. The dependence is reciprocal, i.e., polarization decreases with temperature increase. Depending on the polarization change, electrons are attracted in different directions, either to the crystal surface (Ta), or to the ground target (Cu). Depending on the surface electrons impinge on, they produce x-rays with different energies. The cycle can vary from 2 to 5 minutes.

Novel and miniature x-ray generators do not use radioisotopes or high-power energy tubes. Most of the x-ray generators are unique in their design and should not be compared to other generators as they have different applications and properties. In general, it is a self-sustained solid-state system which generates emission when crystal is thermally cycled. This leads to one of the main properties of this x-ray generator; that its working regime happens only during heating and cooling. It is quite difficult or not possible to control or change the spectral characteristics inside this source. However, external control of parameters, mainly amount heat applied, is quite possible.

Estonian startup company EFENCO OÜ has patented a technology, similar to those vacuum-based emission generators. The technology and a project associated with it are called HERC (High Energy Ray Ceramic) [3]. HERC is a patented technology that harnesses waste heat from chemical reactions and other heat sources to generate low-temperature plasma, using a range of self-powered vacuum nano-electronic chips.

HERC chip generates low-temperature plasma by converting waste heat from redox reactions and other heat sources into a flux of ionizing radiation during the burning of gases (Hydrogen, natural gas, *etc.*). The technology results in lower fuel usage and reduced emissions as less fuel is burned to achieve the same energy output. HERC is embodied as a family of self-powered vacuum nanoelectronical units in a form factor from a chip to nanoceramic tiles. Cost-effective technology is mainly meant for retrofitting existing combustion boilers in industrial heating systems. Primary target group include industrial operators with natural gas-based heating systems that have a heat power capacity greater than 1 megawatt (MW).

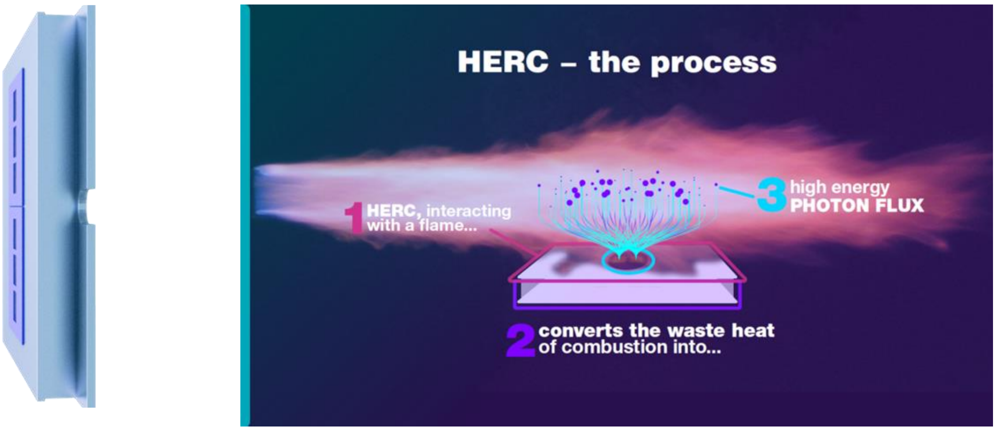

Figure 1.10. HERC chip and working principle in combustion technology [15]

The HERC prototype has demonstrated an 18% combustion efficiency gain in industrial validation in 2022 with durability pilots started in the summer of 2023. Potentially, it can have up to 40% efficiency with natural gas and up to 70% with hydrogen gas in combustion process.

While it is important solution for energy conversion in fuel combustion field, the present study also focuses on possible applications of HERC technology in electrochemistry, including fuel cells and electrolysers.

1.4 Review of activation methods

1.4.1 Activation of fuel cells

Unlike the electrolyser, fuel cell reactions occur spontaneously. However even in this case, the rate of reaction is not high due to presence of potential barrier or activation barrier, hence the use of the catalyst is necessary. In addition, there are other irreversible losses occurring during working of the fuel cell.

The activation losses are non-linear with current output, typically, the activation losses introduce a sharp initial drop in the cell open circuit with increasing current. The losses are different at each electrode (the anode and cathode) because the electric double layer configuration is different. These losses are directly related to the energy barrier (resistances) for oxidation and reduction at the electrodes. The slow reaction rates can be affected by using catalysts (Pt, Ni, Pd), increasing the temperature and increasing the electrode area (porous with microstructure). The effect of temperature increase through various means is the most promising way of increasing the efficiency of fuel cell in experimental part. Activation losses, along with other types of losses, can be graphically represented through polarization curves, see Figure 1.11.

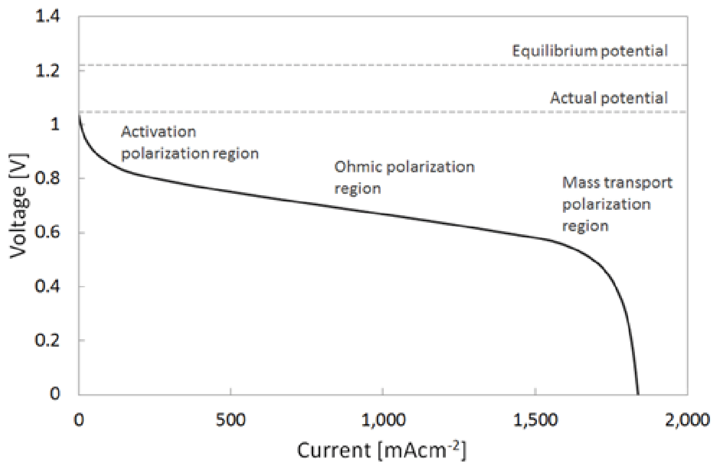

Figure 1.11. I-V curve of the fuel cell with polarization loss regions [7,16]

Different methods exist to minimize those activation losses.

- Thermal activation – usually that involves increasing the temperature of reactant gases. Usually that leads to starting new reactions and faster chemical reaction rates. Although, the reaction is spontaneous, unlike in the electrolyser, a fuel cell can still benefit from increasing the temperature, which will be discussed later.
- Catalyst activation – another type connected to chemical reactions. A careful and thorough approach is vital for selection of catalyst. Specific type, amount, mixture and composure of the chemical catalyst can both greatly improve or stall the rate of reaction or omit the reaction at all.
- Microwave activation – relatively known and studied type of activation for fuel cells. Some inventions and patents develop and test the model of exposing either reducing or oxidizing agents of fuel cell reaction with microwave emission.

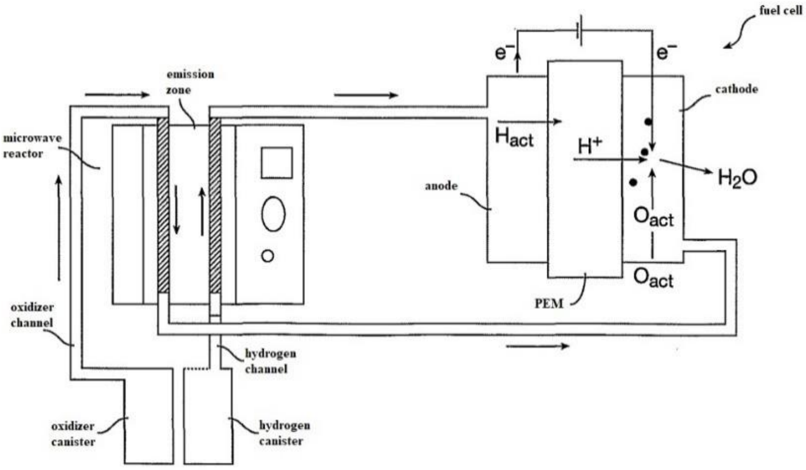

Figure 1.12. Installation scheme for gas activation of fuel cell by using microwaves [17]

With few exceptions, so called single mode generators working at a 2.45 GHz frequency are also used for heating catalysts. Multimode systems, in which a larger number of different modes are generated, were largely used for the preparation of catalysts. A microwave generator placed in the vicinity is usually enough to significantly increase efficiency of reaction. Moreover, the models and installations of these types or similar to those do not require significant power sources by default. Those microwave generators can yield significant improvements event at levels of up to 10 W. However, there also present effects of non-thermal nature connected to the microwaves, despite appearing rarely. Importantly, clear cut separation between thermal and nonthermal effects is necessary for revealing the real action of a microwave field on catalytic (and, on the whole, chemical) reactions. Some methods of activation are connected to the structure of the fuel cells or their characteristics. In case of some fuel cells, that includes control of operational parameters, such as voltage control, current control, combined current-voltage control, voltage-temperature control, pressure-temperature control or oxidative stripping. Activation can be implemented with less measurable parameters. In-case of PEM fuel cell, these pre-activation mechanisms can involve decontamination of Pt catalyst, steaming, boiling, cleaning of MEAs or membranes or extensive hydrogen pumping. It was proven by authors of this installation that fuel cells with microwave activation and without Pt catalysts performed better than fuel cells with sophisticated electrodes in state-of-art conditions.

- Light activation – involves using electromagnetic emission, usually in the form of sunlight and laser to activate reactant gases. Some reactions are susceptible and sensitive or may only occur in the presence of sunlight.
- Activation using ionizing radiation (alpha, beta, gamma, x-ray) - although, there is no record of studies about using x-rays directly to improve efficiency of fuel cell, however, fuel cells are actively used in x-ray absorption spectroscopic studies (XAS) of the membranes or in developing novel design for working in operando spectroscopic experiments. Outside fuel cell industry, various radiation types (gamma irradiation, electron and neutron beams, RF or sound range waves, and irradiation by UV and IR lights) are extensively used in material preparation and for the initiation and stimulation of chemical processes.

  Using HERC effect (x-ray): it is believed that using HERC chip can produce multiple effects, including thermal and catalytic activation.

To conclude, various types of emissions could be used for activation or stimulation of chemical reactions. PEMFC working principle is based on electrochemical reaction, which opens a possibility for research and development of method of using those emissions to improve the fuel cell. As it was mentioned, there are many types of emissions, such as visible light, x-rays or microwaves that could be used as a solution. However, the literature suggest that the microwave emission and x-ray radiation could bring the best results and be the most sustainable and viable to produce. Specifically, the pyroelectric effect and its capability to generate x-ray emission will be discussed and reviewed.

1.4.2 Activation of electrolysers

Generally, reactions of electrolysis are thermodynamically unfavourable, which means, the reactions in electrolyser are not spontaneous and requires external energy supply. Activation method of electrolysers focuses more on increasing the efficiency of the reaction through temperature control, reducing electrolyte and electrode resistances, *etc.*

- Thermal activation - the mass flow of hydrogen increases with increasing the temperature and concentration of electrolyte. Due to the high temperature, electrical potential required to rupture of the water molecule decreases. Hence, increasing temperature increases the reaction speed;
- Photo activation – the possibility was analysed to use different wavelengths of visible light spectrum to improve water electrolysis. For example, the sunlight usage result in strengthening the electric field in the water electrolysis thus enrich the water splitting. The surface tension and the electrical conductivity can be measured to validate the effect of hydrogen bond breaking.

  Lasers or other optical amplification technologies can also be used for electrolyser activation. Patent, involving the device with this purpose, is explained below [18]. The device contains at least one source of electromagnetic emission (emitter), for example, a laser diode with wavelengths (frequencies) corresponding to one of excitation potentials of a water molecule in range from 1 μm to 200 μm, mainly 1,39 μm, consuming very little power in a process. The installation is divided into two parts. The first part is a high-frequency pulse generator, that is capable of generating high voltage impulses up to 3 kV. The second part is vessel, which casing is made of electroconductive surfaces. The vessel has a conductive rod at the centre. The generator is connected to conductive surfaces and the rod that act as electrodes of a vessel in which electrolysis occurs. In this installation the water steam was used, instead of liquid water. At the end, the gas releasing from the reaction zone was ignited. Then, the luminous flux of burning gas was measured and power output was calculated. Experiments showed that there was an increase in intensity of glow of gas and an increase in power output from 2 mW to 2,5 mW. Therefore, with the inclusion of a source of electromagnetic emission into the installation, decomposition of water into hydrogen and oxygen increased by approximately 25%. Consequently, it was possible to create an installation with more than one laser diodes. It is advised by developers, that laser diodes would have different wavelengths. With the addition of more laser diodes into the installation, with different angular offsets and wavelengths of 1,39 μm, 2,27 μm and 3,41 μm, the results yielded an efficiency boost of 33%, 40% and 50% respectively. Additionally, an installation with three laser diodes of 1,39 μm was tested and gave 40% higher output efficiency. Hence,

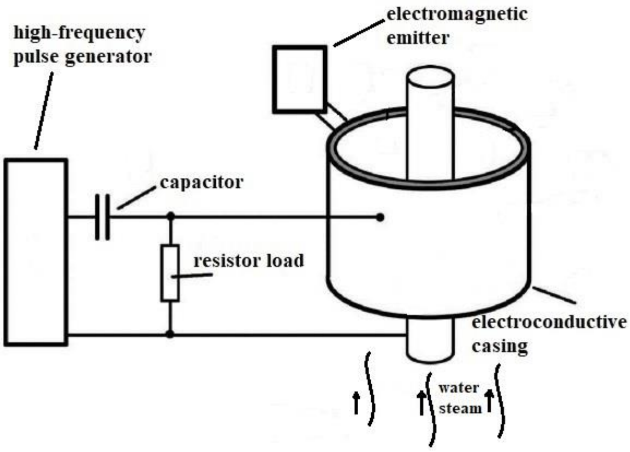

Figure 1.13. Water steam electrolysis installation with electromagnetic emitter [18]

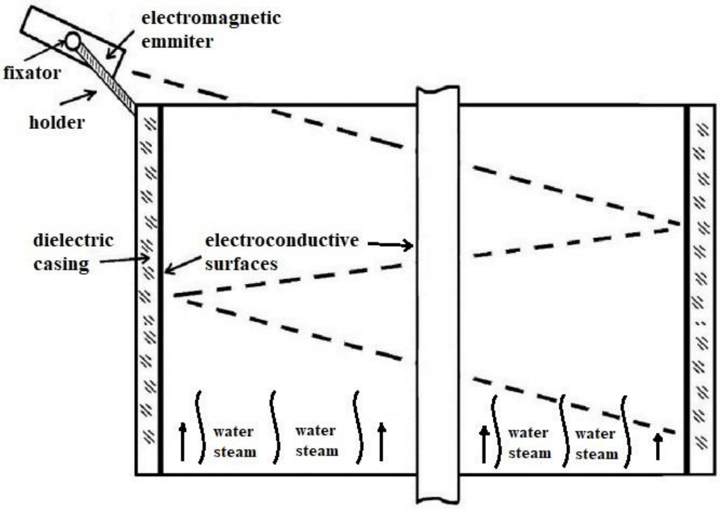

Figure 1.14. Cross-section of electroconductive casing with marked components and laser tracers [18]

using different wavelengths was practically more profitable. The proposed technical solution relates to the field of electrochemical technology and can be used to create devices for hydrogen production and oxygen as fuel, including at energy-intensive industrial facilities. The disadvantages of the device include insufficient complete decomposition of water steam into hydrogen and oxygen, and the complexity of the scheme;

- Microwave activation – it is possible to improve or develop a way of stable hydrogen production by using specific frequencies of microwave emission. An example of a research carries a patented technology that involves decomposition of water in resonant cavity that is fed with microwave energy. The cavity should contain one or more electrolytic cells comprising a synthetic plastic material, glass or other non-energy absorbing containers holding the water to be electrolyzed. Microwave energy at a frequency of 915 MHz (allocated for industrial use by governmental authority) is considered to be particularly effective in this method. The system is designed to be portable, which comes as an advantage for on-going hydrogen production for hydrogen combustion engines or vehicles. Drawback of this system would be the soft requirement of electrolyte. Suitable amounts of salts may be added to the water to produce the conductive negative ions.
- Activation using ionizing radiation (alpha, beta, gamma, x-ray). Water radiolysis is a method of efficient hydrogen production by using ionizing radiation (alpha, beta, gamma, x-ray). When water is irradiated it can split apart into different combinations of electrons, hydroxide, peroxide and proton (e^-, OH^-, H_2O_2 and H^+).

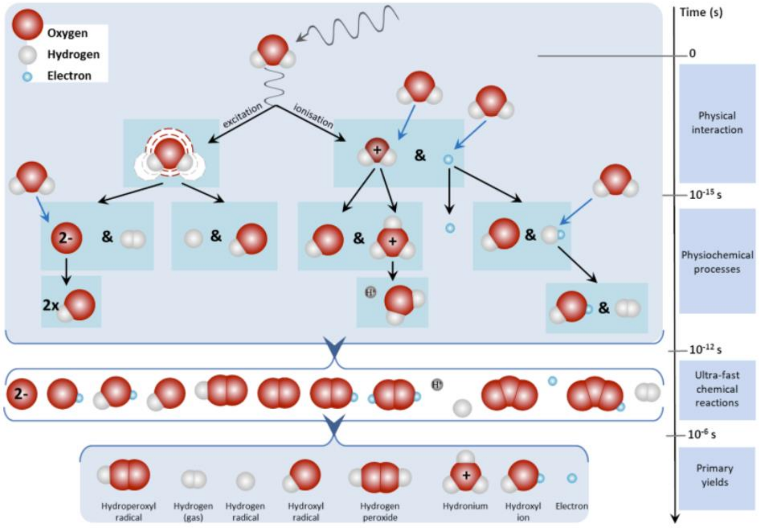

Figure 1.15. A diagram of water radiolysis primary reactions [19]

These different species undergo a series of ultra-fast reactions that depend on the ability of these chemical fragments to diffuse through the water. When an individual gamma ray passes through bulk water it creates a track of ionized water molecules that spread out as they begin to react. Gamma rays travel very far in water which leads to a lot of water being ionized. It was also shown that production of hydrogen from water using hydrogen peroxide H_2O_2 as transition state is energetically affordable and efficient method [20]. A patent suggests a method of hydrogen production by using UV-emission to produce hydrogen peroxide. In this method, solid ice is used an A simple installation consists of a chamber containing ice and mounted above the surface of a block of ultraviolet lamps (ultraviolet radiation sources) emitting the surface, the assembly of which is carried out by the government pumping source with a balloon storage tank, liquid hydrogen peroxide is collected in the storage tank. After this, the parts are sent for recycling or fuel batteries. Thus, obtaining hydrogen from the phase state of water in the form of ice becomes economically profitable with a positive energy yield.

Using HERC effect (x-ray), it is believed that using HERC chip can produce multiple effects, including thermal and catalytic activation and radiolysis.

1.5 Aims of the thesis

Aims of the study is the investigation of the possibility of applying HERC effect and other activation methods to increase the efficiency of the energy production by using of hydrogen (fuel cells) and production of hydrogen (electrolysers). Introduction of HERC is considered as a new method of activation. As well as, it is important to stress that application of activation methods must be based on the thorough understanding of the thermodynamics of fuel cells and electrolysers. Therefore, the attention was shifted to the investigation of detailed thermal behaviour of fuel cells, as well.

- The experiments with the effect of x-ray emission into the water were conducted with the help of the HERC chips produced by Efenco OÜ. The aim was an estimation of HERC chip influence on the water temperature, namely an increase in temperature of the water surrounding the chip.
- Investigation of thermodynamic behavior of fuel cells under different heat treatment regimes. The aim of this part was investigation of the thermodynamic behaviour of PEM FC and comparison with the theoretical behaviour of ideal reversible fuel cell.

2 MATERIALS AND METHODS

An approach to increase the efficiency of the FC and water EL is using HERC effect. It was mentioned in Section 1.4 about the expected influence of HERC effect on the FC and EL functionality. The experimental section is divided into two parts in regards to potential application of HERC effect to FC and EL, namely Sections 2.1 and 3.1 is for EL and Sections 2.2 and 3.2 are for FC.

2.1 HERC chip influence on the water temperature

Thermal and catalytic activations and radiolysis in the case of possible HERC effect influence on the water EL were mentioned in Section 1.4.2. Thus, one can expect the change in water temperature from one side and pH factor and conductivity (due to radiolysis) from another side, which are the measurable quantities. Indeed, in the case of possible application of HERC chip in electrolysis, due to relatively high power of the HERC chip, at least one can expect an increase in water temperature which can result in increase in hydrogen production (see Section 1.2.1).

As was stated, the main working principle of the HERC chip is emission of radiation, which can influence the water chemistry and temperature. In the case of radiolysis, generation of e^-, OH^-, H_2O_2 and H^+ could influence pH factor and conductivity. It should be stressed that for the measurement of pH factor and conductivity, the pH/Conductivity/Temperature bench meter (HI5521 Hanna instrument) was applied [21]. However, the experimental conditions for generation of the HERC effect needs permanent change in temperature, which result in instability during pH and conductivity measurements. However, measurement of pH and conductivity needs highly stable temperature during measurement. Therefore, after initial tests the measurements of pH and conductivity were declined and only measurements of temperature were continued. Finally, due to delay with production of the desirable type of the HERC chip, no experiments were done on the water EL.

As it can be seen in Figures 2.1. and 2.2., the chips are to be submerged into clean water or water-based alkali solutions. The vessel should be preheated to cause the chip working. For a better flow of procedure, chips were placed onto the platform for easier submerging (see Appendices 1-3). Platform was designed and machined from Teflon with the purpose to use in aggressive environment, including alkaline solution used in electrolysis.

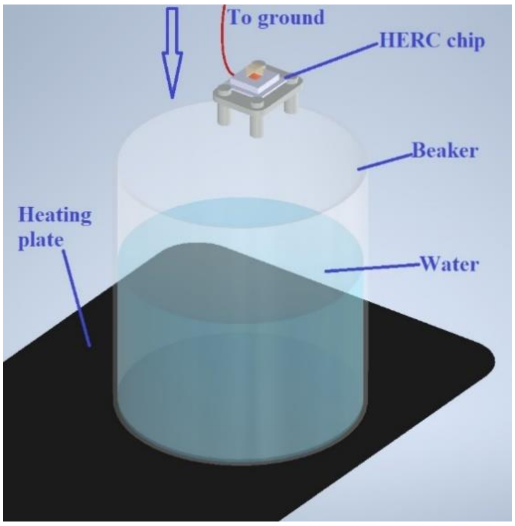

Figure 2.1. A chip outside the beaker is to be put into the water

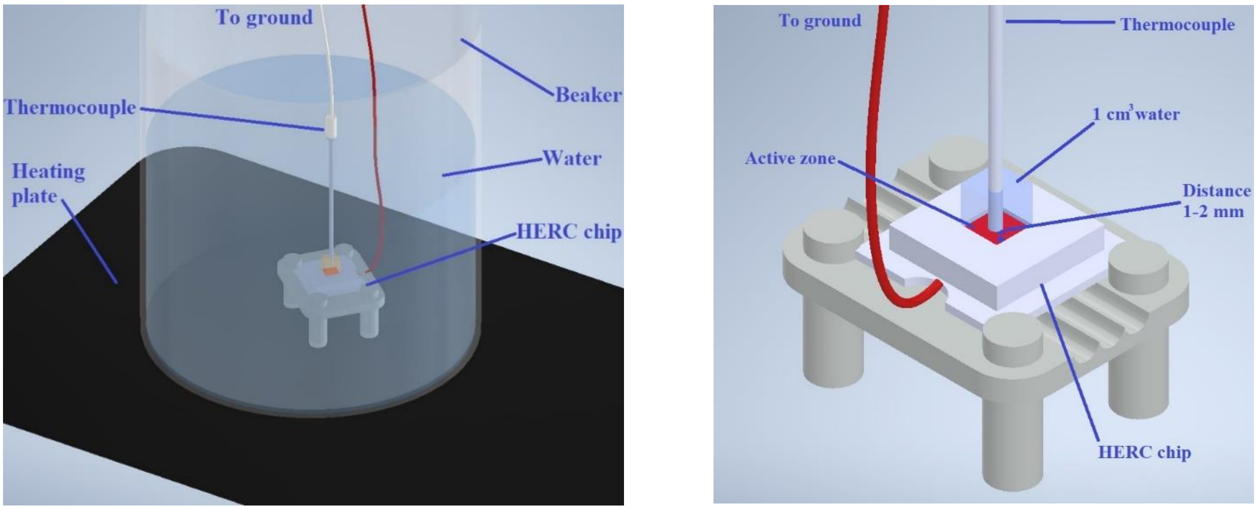

Figure 2.2. A HERC chip inside the beaker with thermocouple and close-up view

Measurements were made with apparatus with possibility of changing measurement test probes.

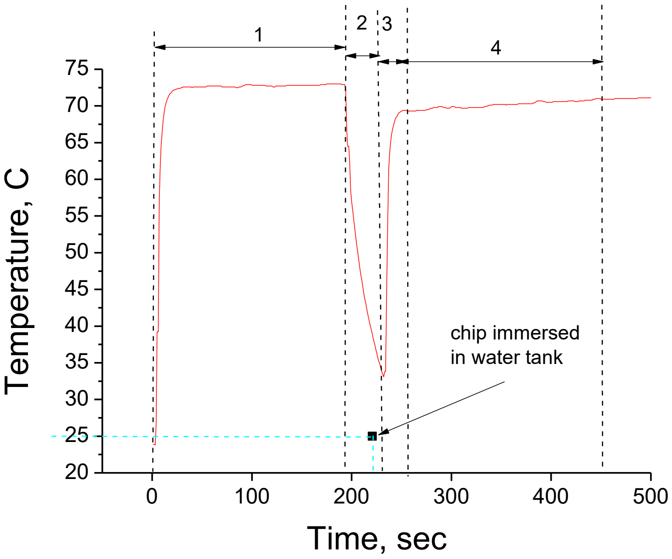

Figure 2.3. Temperature changes on the thermometer during thermal cycle in experiment

The procedure of the experiment (later, in the context of HERC chip, referred as a thermal cycle) and measurable data can be divided into 4 parts, as it is shown in the Figure 2.3.:

1 – Beginning of measurement. Thermometer is put inside the water to control and stabilize the water temperature. No HERC chip is used. Usually takes 180 seconds;

2 – Thermometer is taken out of the water. On cool air, measured temperature rapidly decreases. HERC chip is carefully lowered into the water vessel (2-3 seconds). Chip activation period begins at this stage.

3 –Thermometer is quickly put back into the water as close as possible to HERC chip (2-3 seconds). Thermometer registers changes in ambient water temperature.

4 –Long-term effect of HERC chip on water temperature is observed. Usually lasts till the end of the measurement.

Thermometer with K-type thermocouple was used to measure the temperature.

In order to roughly predict the results of experiment, a time and power consumed needed to be calculated to analyse the heating of water. A formula for calculation of required heat to raise the temperature Q can be used:

$$Q\mathrm{t} = cm(T_f - T_i) \tag{2.1.1}$$

, where

Q – amount of heat required, J,

c – specific heat capacity of water, c = 4186 J/(kg·K),

m – mass of water, kg,

T_f, T_i – final and initial temperature, K;

The thermal conductivity of water at 20 °C is 0,6 W/m K, far from the thermal conductivity of metals, such as copper (384 W/[m·K]), but slightly higher than air (0,026 W/[m·K]). In other words, the thermal conductivity of water is low [22].

Chip's size of the active zone window in the form of square with area of 1 cm^2 can be supposed. Due to the fact that water has relatively poor thermal conductivity, it is assumed that 1 cm^3 is the maximum volume that can be heated, it is assumed that volume of the water outside of 1 cm^3 will be unaffected during the heating for some fractions of second. The average power output of the HERC chip ranges between 0,1 - 1 W. It is also assumed that chip is always working at 100% efficiency.

Assuming the maximum power output of 1 W, and also knowing heater's efficiency and total amount of heat required, time and duration of heating can be calculated as well:

$$time = \frac{Q_{total}}{\mu \cdot P} = \frac{4{,}186 \frac{J}{g \cdot C^{\circ}}}{1\ W} \cong 4\ s \tag{2.1.2}$$

Correspondingly, if power output is the smallest possible of 0,1 W, the time required to heat a water volume increases proportionally:

$$time = \frac{4{,}186 \frac{J}{g \cdot C^{\circ}}}{0.1\ W} \cong 40\ s \tag{2.1.3}$$

Those two simple formulae were essential for providing some background knowledge to the results of experimental part.

Experiment usually involved a long-term measurement, due a floating result. In accordance with Figure 2.3, the same procedure was made several times during different experiments.

2.2 Thermal behaviour of PEM Fuel Cell

According to the initial plan, it was suggested to use HERC chip to increase an efficiency of the PEMFC (see Section 1.4.1). However, due to delay in the development and construction of the desirable type of the HERC chip, the work with the activation of FC by HERC chip was not carried out. Instead, the investigation of the influence of the temperature on the properties of the FC was established. Theory predicts that among different effects, a possible influence of the HERC chip on FC properties can be a change of the temperature of the FC or reactant gases as well (see Section 1.4.1 Activation of fuel cells). Therefore, the results shown in this section can be considered as a preliminary study of influence of the HERC chip on the FC.

In order to test the thermal activation of the fuel cell, the installation had to be prepared with special requirements, that included:

- Continuous working regime for the fuel cell itself to minimize or avoid disruption in power output;
- Stable flow and income of fuel and oxidizer gases;
- Versatility and modularity of installation, if there is need to change, replace or adjust components, to test various schematics;
- Semi-automatic reading of measurements, necessary for logical and complete analysis of testing;

A fuel cell was required to start the experimental part. A rebuildable fuel cell kit from H-TEC Education (USA) was acquired. The kit can be completely disassembled and then reassembled especially for research purposes.

Figure 2.4. H-TEC Education rebuildable PEM fuel cell kit [23]

The fuel cell was built with Nafion 212 membrane [23]. The anode and cathode of FC have the platinum catalyst mixture loading, i.e., 0,5 mg/cm^2 Pt/C 60% / 0,25 mg/cm^2 PtB mix. The electrode area is 16 mm^2. The reactant gases for the work were produced using PEM electrolyser from H-TEC Education (USA). The reactant gases produced by PEM electrolysis was accumulated in store cylinder with 80 cm^3 volume. The gases then moved into the fuel cell by clogged rubber hoses, to ensure no leaks into the system.
Two basic installations were prepared and constructed to test the activation of PEMFC. The first one involved heating only the gas lines without heating the fuel cell itself, as it can be seen in Figure 2.5. The second one involved direct heating of the fuel cell frame and gases, as it is shown in Figure 2.6.

The fuel cell or gas lines were put into the vessel filled with water which in place was put onto the heating plate with temperature control. It was necessary to be able to regulate the temperature since the fuel cell had strong requirements and limitations in working conditions, especially when submerged into water, which is not covered by usage instructions and could easily lead to fuel cell breakdown or damage the membrane or catalyst layers.

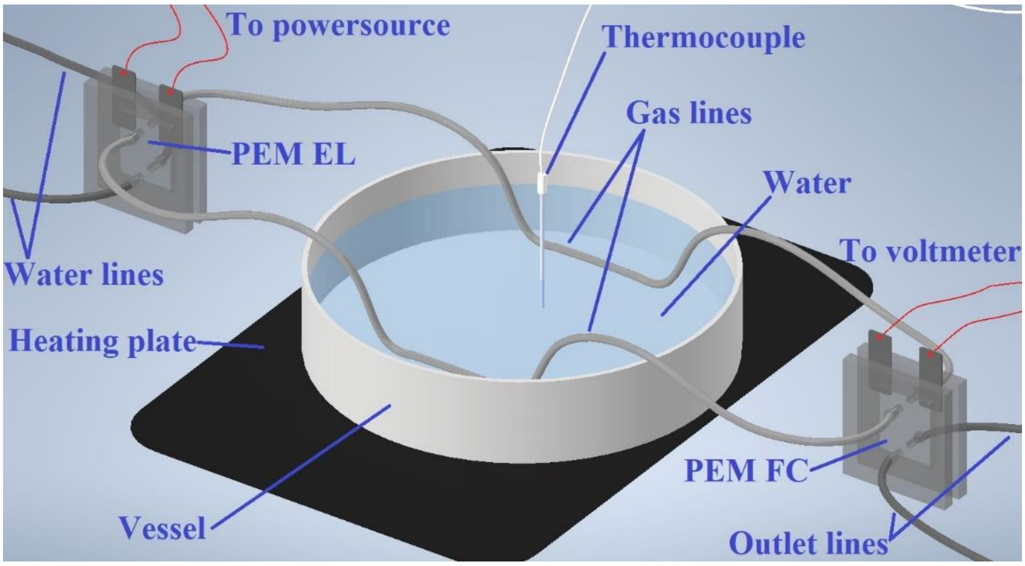

Figure 2.5. PEM fuel cell installation for gas heating

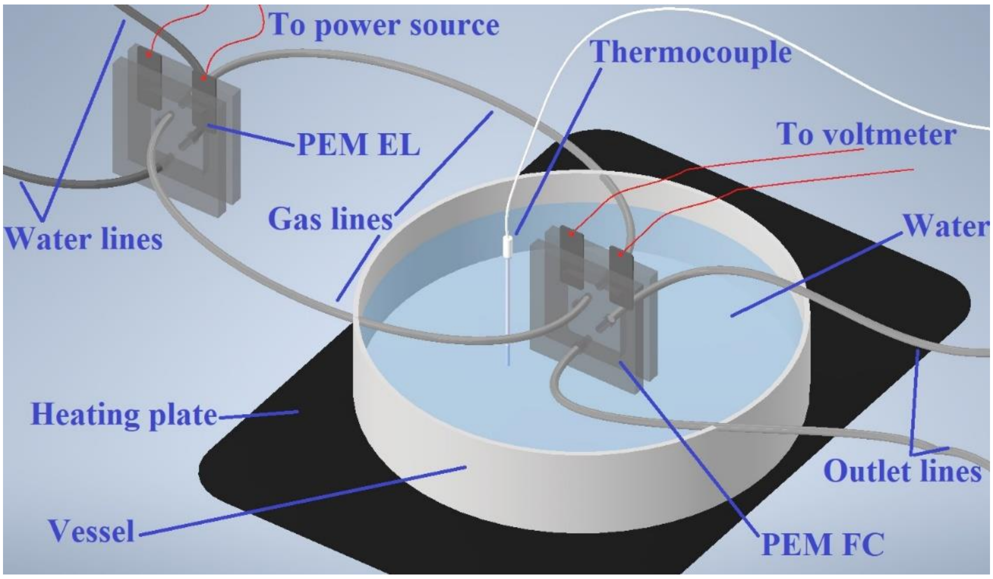

Figure 2.6. PEM fuel cell installation for direct FC heating

3 RESULTS OF EXPERIMENTAL PART

3.1 HERC chip influence on the water temperature

Different types of measurement tests (Types 1-4, see below) were made using HERC chip. In fact, the thermal gradient during the submerging of the chip in hot water can be quite high, i.e. 10-60 °C/sec. In the case of Type 1-3, measurements were made based on supposition that chip work more efficiently if chip is grounded. It was decided to test, whether the order of grounding connection matter for the results. In each type of the test, first the water temperature was measured without the submerging of the chip (see Figure 3.1). In Types 1-4 measurements, in fact, two (or more) thermal cycles heating/cooling tests were carried out during the tests.

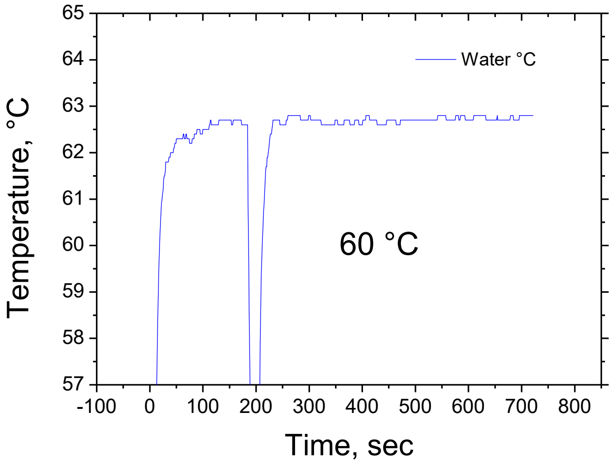

Figure 3.1. Measurement of the water temperature without HERC chip, after 180 sec the thermometer was taken from the water and moved again in water

In total 3 HERC chips were investigated (chips №1, №2 and №3). From the beginning of the measurement it was found that chip №2 did not show expected properties and in the test Type 1 only chips №1 and №3 were investigated. However in following only chip №3 was under investigation as inside of the chip №1 the water was observed.

In Type 1 measurements, the chip was first tested without ground connection (first thermal cycle) and then with ground connection (second thermal cycle). It should be stressed that the drop in the temperature after the chip submerging can be expected, as the cold body (chip) is immersed in the hot water.

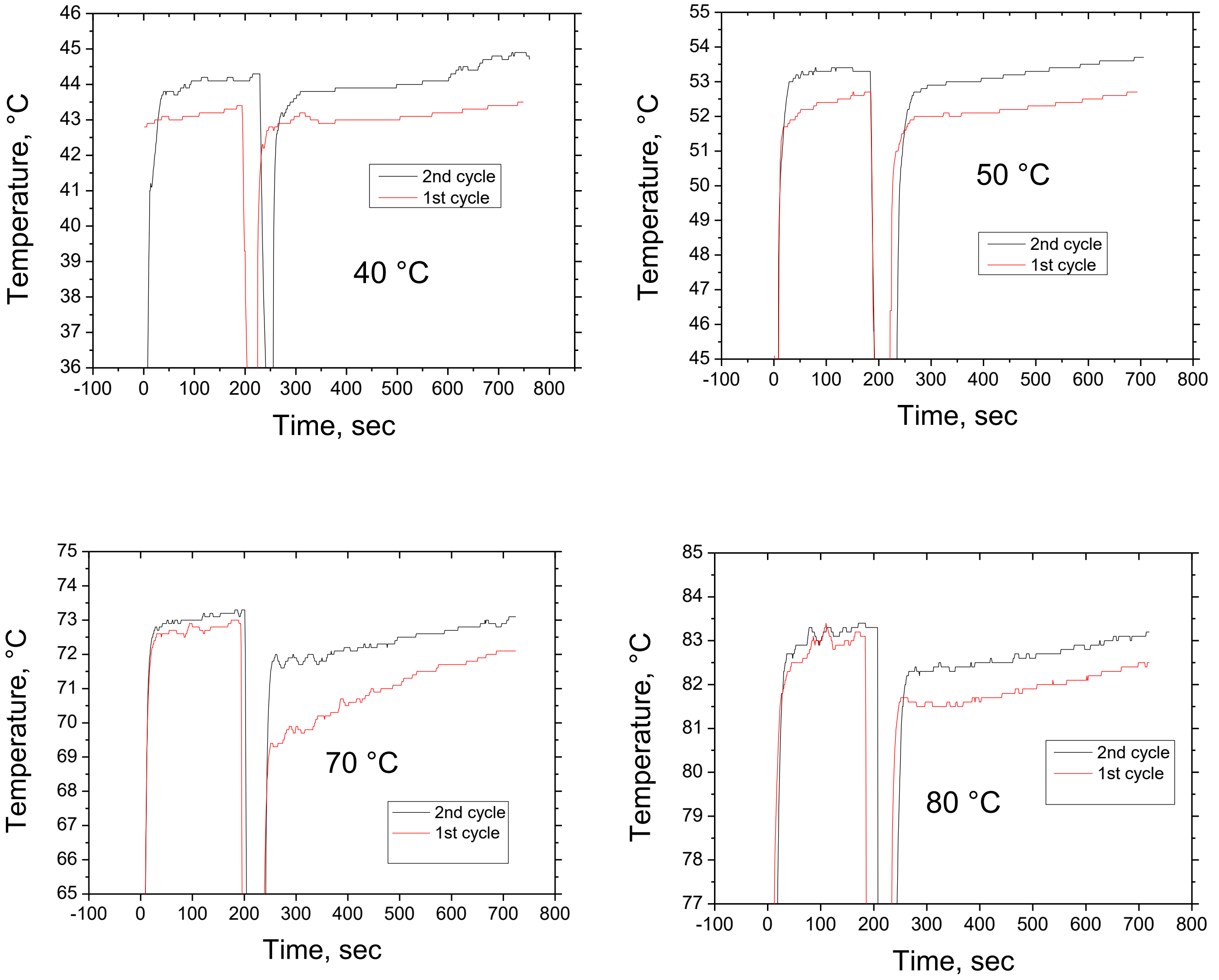

Figure 3.2. Type 1 measurements with HERC chip, in the first thermal cycle (heating/cooling) the chip was submerged into hot water without ground (red) and in second thermal cycle (heating/cooling) chip was submerged into hot water with ground (black)

Type 2 measurements involved reversing the order of measurements, i.e., chip with ground connection were used in the first thermal cycle and measurements with no ground connection went for the second thermal cycle (not shown).

Type 3 measurements were made to with no changes to the chip ground, namely the chip was grounded for the first and second thermal cycles (not shown). During these measurements (Type 3), a water condensate was spotted inside the chip №3 body. It might suggest that vacuum seal at the end of the chips was compromised and water got into the working area. The results might not be relevant as chip most likely failed by that point. Severe conditions under heated water and non-ideal construction might have caused that. Further consideration must be taken in the future about this problem. In conclusion, because of this observation, the results of Types 2 and 3 are not presented in study.

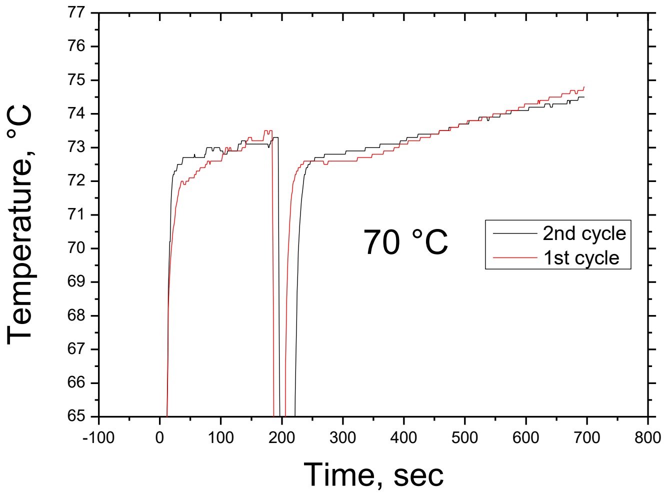

Figure 3.3. Type 4 measurements with dummies

Type 4 measurements involved using dummy chip with the same type of pyroelectric crystals used in standard HERC chip, however with different internal design of chip as compare with standard HERC chip.

Rather unexpected results were observed during the measurements. Calculation in previous chapter 2.1 showed how fast the chip can heat up the water. The results of the Types 1 and 4 measurements (Figures 3.2 and 3.3) were evaluated, i.e., the difference *ΔT* was estimated for each cycle of the tests (Figure 3.4) and the results are shown in Figure 3.5.

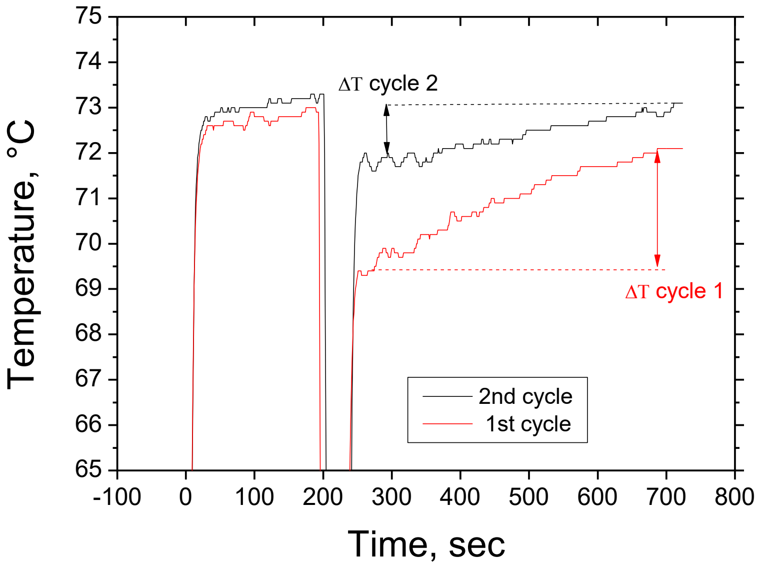

Figure 3.4. Temperature difference *ΔT* for 1 and 2 cycles of measurements

Figure 3.5 shows the results observed after the tests Types 1 and 4. It can be seen that *ΔT* values measured after cycles 1 and 2 (see Figure 3.5) increases with increase in temperature. It can be expected, as the cold body immersed in hot water, therefore the faster increase in temperature *ΔT* during cycle 1 or 2 can be expected if the body immersed in hotter water. Interesting that for the lower temperature range (30 – 60 °C) the difference between the $\Delta T_{total} = \Delta T_{cycle\ 1} - \Delta T_{cycle\ 2}$ for the cycles 1 and 2 is quite similar (see Figure 3.6).

However, for 50 – 60 °C there is tendency that in the case of cycle 1 the temperature increases faster than for the cycle 2. However, for the higher temperatures 70 – 80 °C, there is a reversible dependence, the temperature increase is higher for the cycle 1 in comparison with the cycle 2. Similar behaviour was found for the tests with dummies (see Figure 3.6).

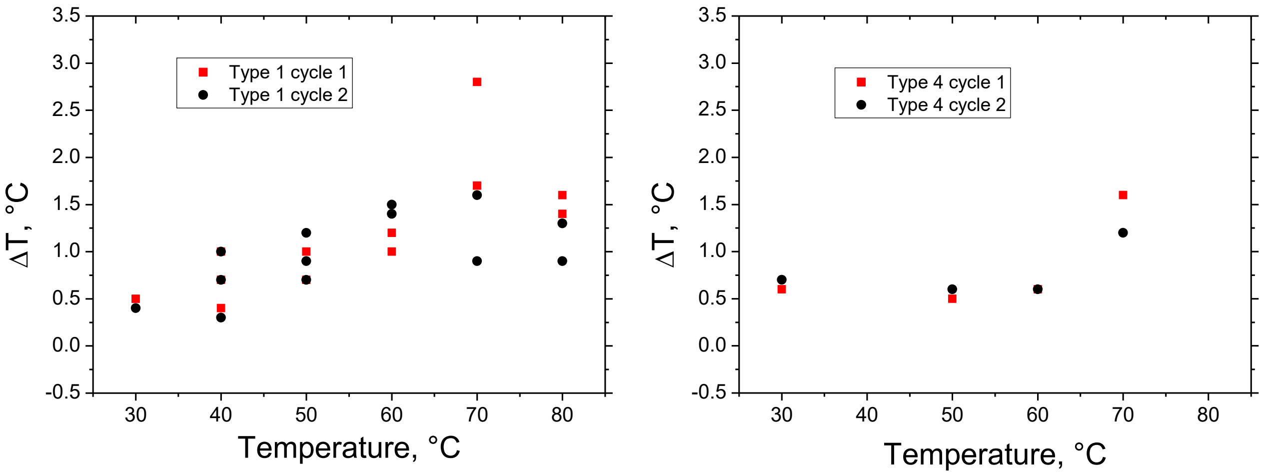

Figure 3.5. ΔT values for each cycle, i.e., for cycle 1 (black) and cycle 2 (red) in case of Types 1 and 4 tests

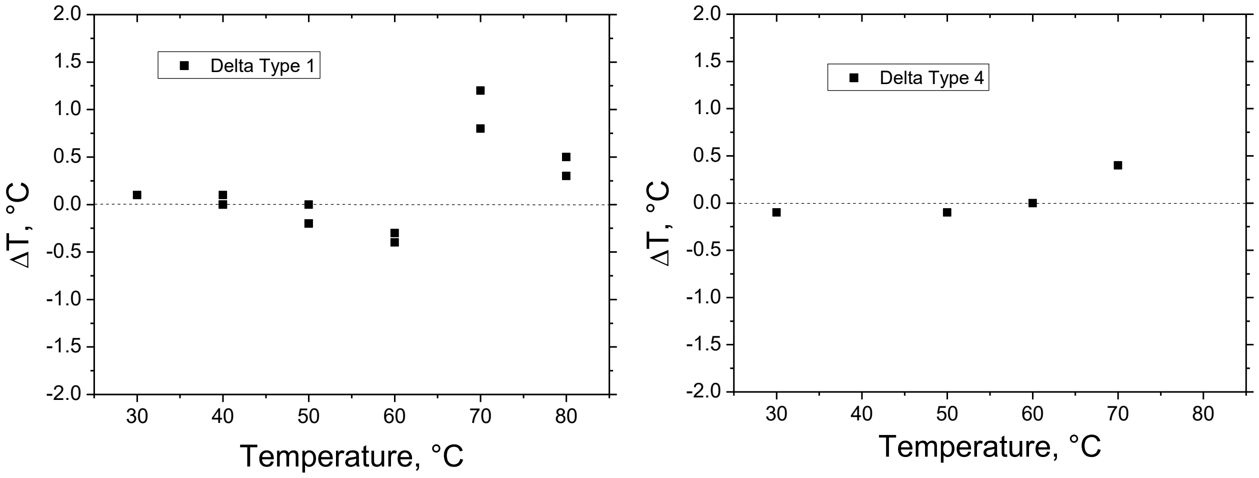

Figure 3.6. ΔT_{total} values in case of Types 1 and 4 tests

It expected that during the test the temperature of the water close to the HERC chip surface can be influenced by HERC effect (see Section 2.1), therefore there are potentially two reasons for increase ΔT in Figure 3.5, namely, due to mentioned above ordinary heating of cold body immersed in hot environment and because of the presence of HERC effect. It should be stressed that dummies used in Type 4 was prepared using the same crystals as for HERC chip, however with different arrangement to supress HERC effect.

Therefore, in principle, as for Type 1 as well for Type 4 some similar effect can take a place resulting in similar results. In addition, one can expect that *ΔT* should be always higher for the cycle 1, as compare with the cycle 2, as a colder body immersed in hot water during the 1 cycle. However, results of the tests Type 1 shows tendency that *ΔT* is higher for the 2 cycles (see Figure 3.6 for 30 – 60 °C), which can be due to influence of HERC effect.

In conclusion, in the present study, the role of the HERC chip in possible heating effect cannot be clearly separated from the ordinary heating of cold body in hot environment, as well as grounding effect cannot be clearly determined from the presented results and an additional study is necessary.

3.4 Thermal behaviour of PEM fuel cell

The results of this part of thesis were used for the preparation of manuscript, which was accepted for publishing in Proceedings of the Estonian Academy of Sciences (see List of Publications).

Reactions occurring in the fuel cell are spontaneous and do not usually require any additional driving force except the catalyst. First, a stability of FC at room temperature was estimated (Figure 3.7), as can be seen at the beginning of the test there is a small drop in voltage (0.005 V), which stabilizes after approximately 120 minutes. This data serves as reference point to the following measurements.

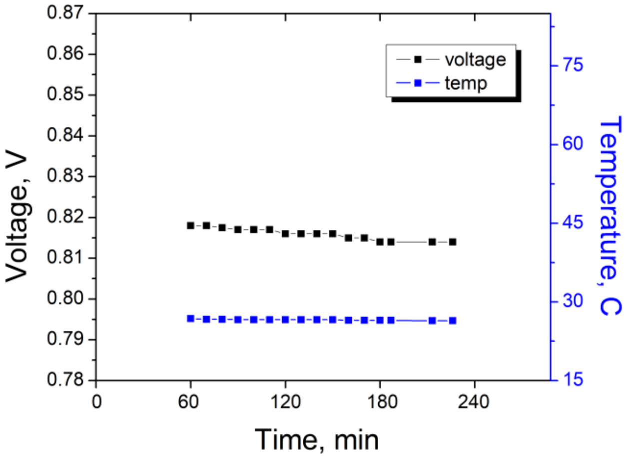

Figure 3.7. Relation between the voltage and temperature at room temperature for the PEM FC

With the reference point given, the effect of temperature on the activation of fuel cell can be studied. Two different kinds of fuel cell installations were tested: gas heating and direct heating (see Section 2.2). The results have brought two distinctive patterns in a behaviour of the PEM FC, the following graphs show the results where the effects were the most prominent.

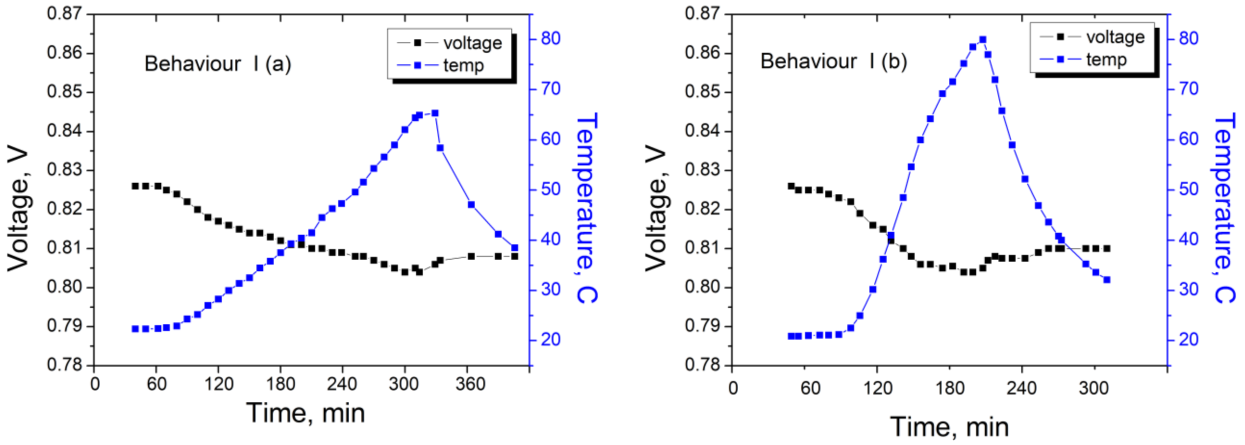

Figure 3.8. Results of experiments leading to behaviour I between the voltage and temperature

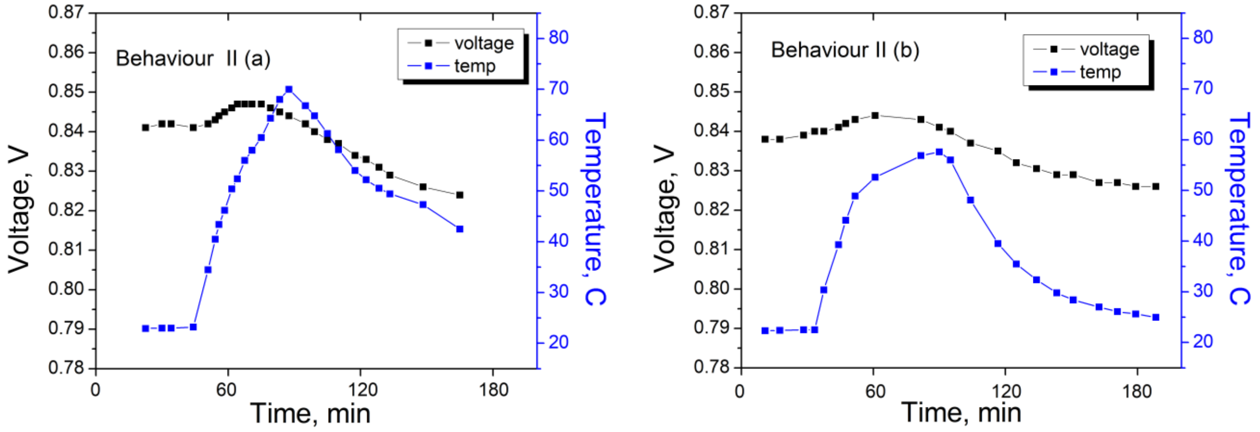

Figure 3.9. Results of experiments leading to behaviour II between the voltage and temperature

Figure 3.8 shows the results of experiments when only gases were heated (later called Behaviour I). The main tendency of the behaviour I is the inverse dependence between the voltage and temperature, i.e., with increasing of temperature the voltage decreases and vice versa. In contrast, in the case of behaviour II (shown in Figure 3.9 and set-up of the experiment in Figure 2.6), the voltage increases with the temperature increase.

The reason in different behaviour can be due to difference in the range of the heating intensity, i.e., likely the heating of gases was not intensive in the case of behaviour I.

On the other hand, in experiments leading to the results with the behaviour II, the whole FC frame and gases were more intensively heated.

The both types of experiments can be compared with theoretically predicted behaviour for the reversible FC. It should be stress that the theory of the reversible FC is based on the equilibrium thermodynamics of gases assuming temperature increase or decrease is as slow as it allows to finish relaxation process after each step of the temperature increase or decrease.

In the case of the reversible FC, the dependence of the voltage on temperature is the straight line with the inverse dependence between the voltage and temperature, see Section 1.2.

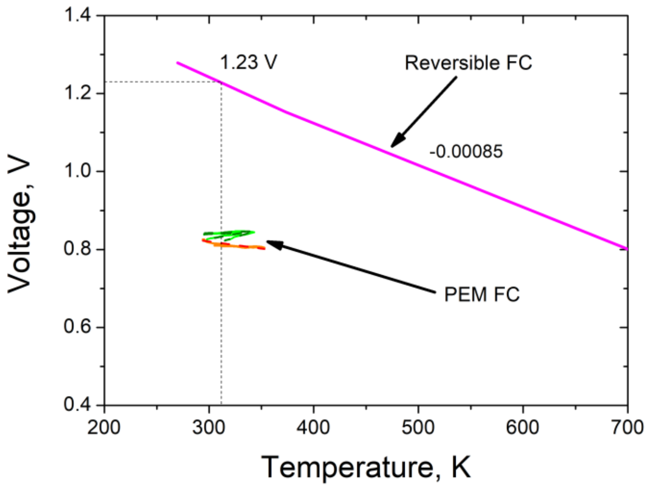

Figure 3.10. Relation between voltage and temperature for PEM FC and reversible FC

The slope for reversible FC is equal to -0,00085 (Figure 1.4). The straight line passes the reference point 1,23 V at 25 °C.

The results of both types of experiments on PEM FC are also shown in Figure 3.10 for comparison with the behaviour of the reversible FC. It can be stated that the results corresponding to the behaviour I look very similar to ones for the reversible FC. The curves observed in the experiments are shown in more details in Figure 3.11. The slopes of the curves observed in experiments with behaviour I and II were evaluated and shown in Figure 3.11, as well.

A good agreement between the results of experiments with behaviour I and ones for the reversible FC points to the fact that conditions during the measurements resembles the conditions of the equilibrium thermodynamics mentioned above. The reversible-like behaviour of FC, with inverse proportionality between voltage and temperature and almost no hysteresis can be seen in Figure 3.11, see two curves corresponding to behaviour Ia and Ib.

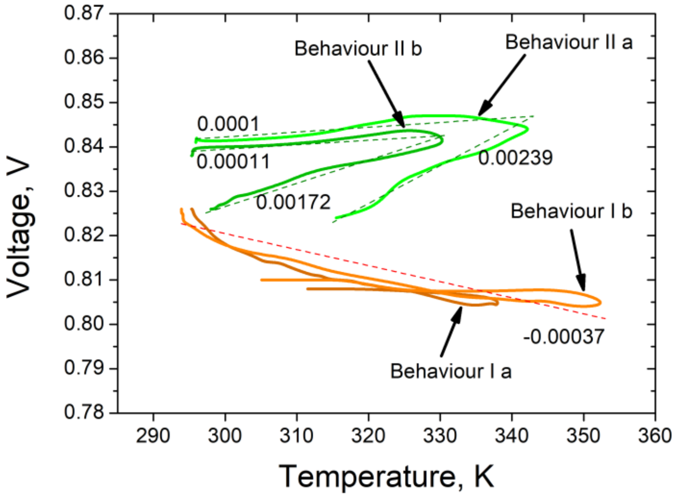

Figure 3.11. Relation between voltage and temperature for PEMFC

In the case of experiments with immersing of the FC in water tank (behaviour II), the hysteresis was observed (Figure 3.11). Although, the both lines slope (behaviour IIa and IIb) during heating up period was about 0,0001, during cooling the line slopes were different, with the higher line slope for the case when max heating temperature was higher, i.e., 70 °C in comparison with 55 °C.

It can be stated from this study that the line slope of the PEM FC differs from the ideal reversible FC depending on the power of divergence of experimental conditions from the ideal equilibrium ones. The slope changes from -0,00085 to more positive value. In other words, the relation between the voltage and temperature changes from inverse to direct proportionality.

Thermal activation by direct heating brought Behaviour II (Figure 3.9). In behaviour II, the hysteresis was observed. This behaviour resembles more scientifically established normal behaviour of PEM fuel cell that is also specified by the manufacturers, see Figure 1.13. An increase in open-circle voltage at about 0,05 V can be seen as well, indicating an effect of activation of FC. Interesting that increase in voltage was found for temperature range about 35 – 50 °C, for higher temperature the activation effect disappeared. The voltage rises with the temperature, reaches maximum and then drops.

Such activation was not observed in the case of Behaviour I (Figure 3.8), however, interestingly, that an increase in voltage was observed during the FC cooling.

SUMMARY

The aims of this study were to investigate methods for efficient energy conversion for the fuel cells and electrolysers. Numerous practical implementations of activation methods were discussed as a part of literature review. The potential advantages of different installations were discussed. In particular, implementation of pyroelectric effect and x-ray radiation generators into the fuel cell and electrolysers systems was proposed. It was stressed that one of the expected influences of HERC effect is the change of the temperature of surrounding environment.

The experiments with the effect of x-ray emission into the water were conducted with the help of the HERC chips produced by Efenco OÜ. It was estimated HERC chip influence on the water temperature, namely an increase in temperature of the water surrounding the chip. The achieved results suggest that some influence of HERC chip on the water temperature increase can be expected, however, it was difficult to clearly separate this influence from the natural temperature increase of water surrounding cold body immersed in hot environment.

Second part of experimental study involved investigation of the thermal behaviour and thermal activation of the PEM FC. The aim of this part was investigation of the thermodynamic behaviour of PEM FC and comparison with the theoretical behaviour of ideal reversible fuel cell. The thermal behaviour and thermal activation of the PEM FC was shown experimentally and an interesting phenomenon was observed, namely an increase in open-circuit voltage during FC heating and as well as cooling, i.e., PEM FC performance can indeed benefit from controlling the thermal treatment of the installation. It was also shown that PEM fuel cell can exhibit a behaviour similar to the reversible fuel cell, which solely relies on theoretical effects of thermodynamics of PEM FC and rarely achieved in practice. That would depend on the techniques and methods at which operating parameters, such as temperature change gradient. Procedure, in a best-case scenario, must be adjusted to different fuel cell.

It is important to also mention that the experimental procedures for the fuel cell were made with only one particular type of the PEM fuel cell. Although, operating principles remain the same, some other parameters, including the deterioration of the catalysts or membrane, handling of the fuel cell, reactivation procedures, might be different for different types of FC.

KOKKUVÕTTE

Selle töö eesmärk oli uurida kütuseelementide ja elektrolüsaatorite tõhusa energia muundamise meetodeid. Kirjanduse ülevaate raames käsitleti arvukalt aktiveerimismeetodite praktilisi rakendusi. Arutati erinevate paigalduste võimalikke eeliseid. Eelkõige pakuti välja püroelektrilise efekti ja röntgenkiirguse generaatorite rakendamine kütuseelementide ja elektrolüüsiseadmete süsteemidesse. Rõhutati, et HERC efekti üheks eeldatavaks mõjutajaks on ümbritseva keskkonna temperatuuri muutus.

Katsed vette röntgenikiirguse mõjuga viidi läbi Efenco OÜ poolt toodetud HERC kiipide abil. Hinnanguliselt oli HERC kiibi mõju veetemperatuurile, nimelt kiipi ümbritseva vee temperatuuri tõus. Saavutatud tulemused viitavad sellele, et HERC kiibi mõningast mõju veetemperatuuri tõusule võib eeldada, kuid seda mõju oli raske selgelt eraldada kuuma keskkonda sukeldatud külma keha ümbritseva vee loomulikust temperatuuritõusust.

Eksperimentaaluuringu teine osa hõlmas PEM FC termilise käitumise ja termilise aktiveerimise uurimist. Selle osa eesmärk oli uurida PEM FC termodünaamilist käitumist ja võrrelda ideaalse pööratava kütuseelemendi teoreetilise käitumisega. Katseliselt näidati PEM FC termilist käitumist ja termilist aktiveerimist ning täheldati huvitavat nähtust, nimelt avatud vooluahela pinge suurenemist FC kuumutamise ja jahutuse ajal, st PEM kütuseelemendi jõudlus võib paigalduse termotöötluse juhtimisest tõepoolest kasu saada. Samuti näidati, et PEM-kütuseelement võib käituda sarnaselt pööratava kütuseelemendiga, mis tugineb ainult PEM-kütuseelemendi termodünaamika teoreetilistele mõjudele ja mida praktikas harva saavutatakse. See sõltuks tööparameetrite, näiteks temperatuurimuutuse gradiendi, tehnikatest ja meetoditest. Parimal juhul tuleb protseduur kohandada erinevatele kütuseelementidele.

Samuti on oluline mainida, et kütuseelemendi eksperimentaalsed protseduurid tehti ainult ühe konkreetse PEM-kütuseelemendi tüübiga. Kuigi tööpõhimõtted jäävad samaks, võivad mõned muud parameetrid, sealhulgas katalüsaatorite või membraani riknemine, kütuseelemendi käsitsemine, taasaktiveerimisprotseduurid, olla erinevat tüüpi FC puhul erinevad.

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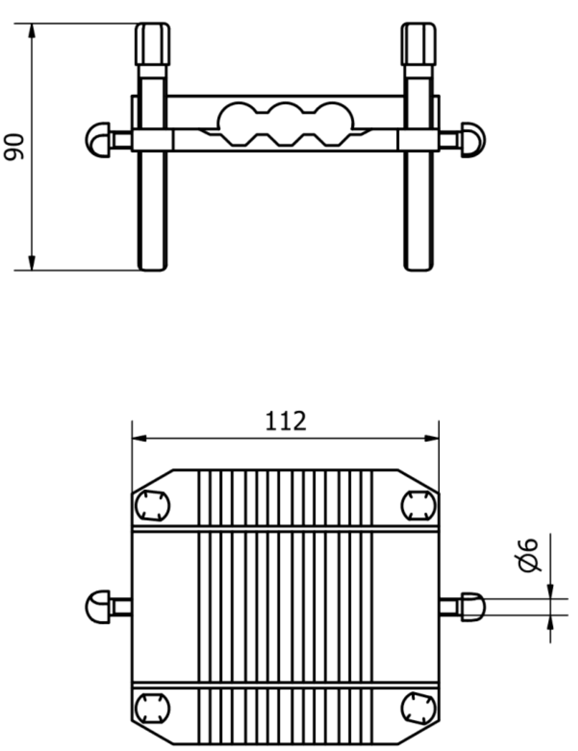
APPENDICES

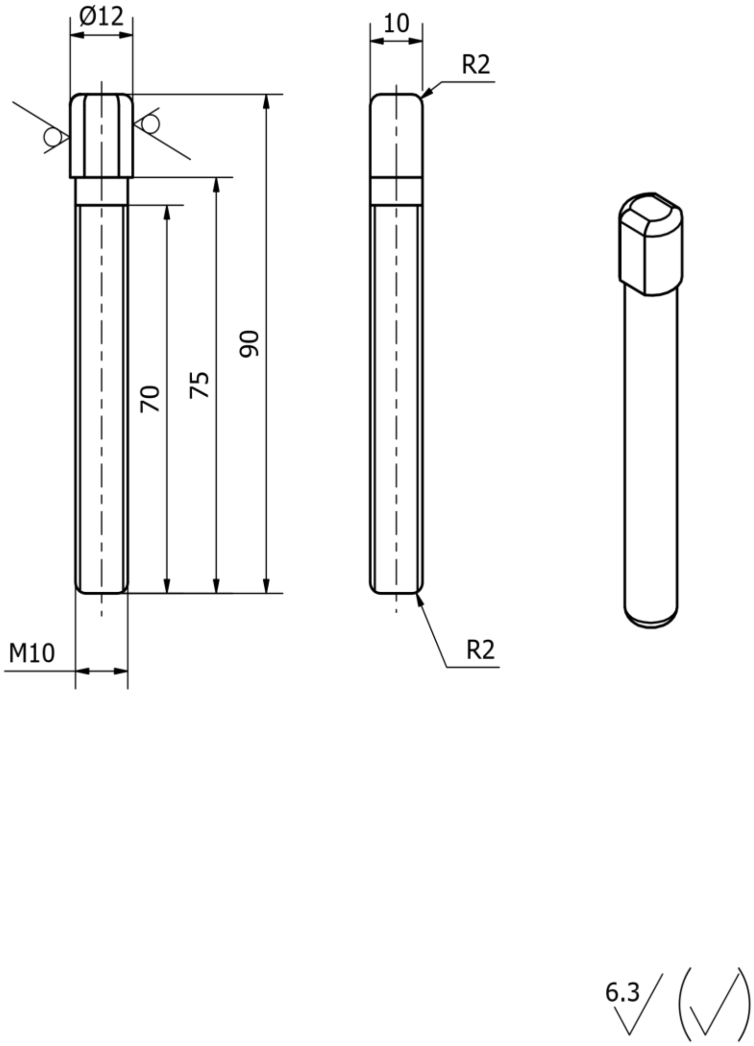
Appendix 1 Drawing of HERC chip stand with fixator



Designer	Date	Blank part	Weight	Material	Scale 1 : 2
TTÜ					
	Base			Rev. 1	Sheet 1 / 1

Appendix 2 Drawing of HERC chip stand screw #1

General tolerances (ISO 2768 medium)	
Nom. size, mm	Tolerance, mm
0.5 … 3	±0.1
> 3 … 6	±0.1
> 6 … 30	±0.2
> 30 … 120	±0.3
> 120 … 400	±0.5
> 400 … 1000	±0.8

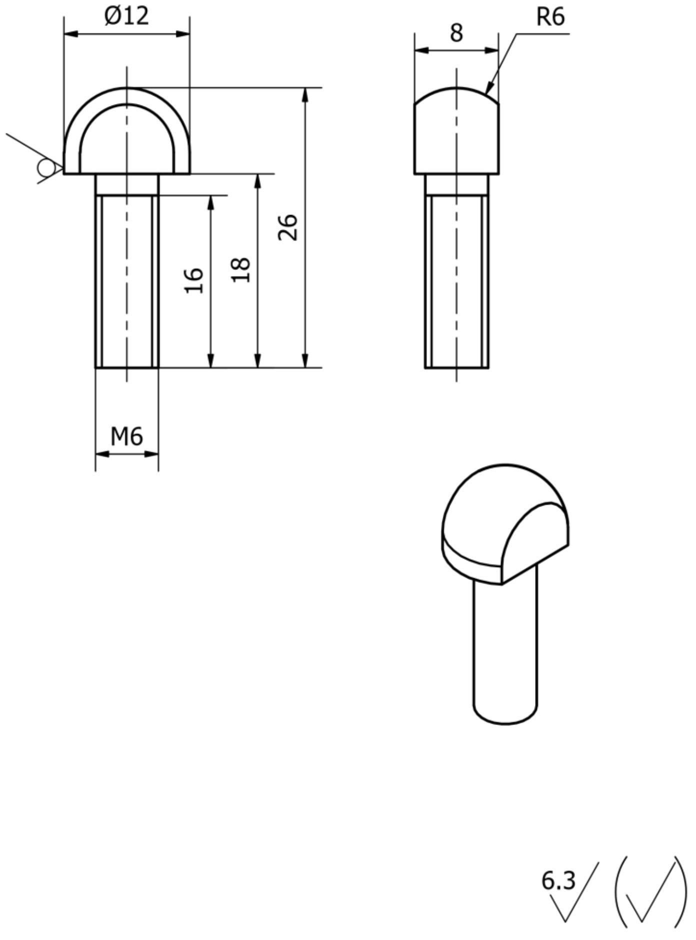


Designer	Date	Blank part	Weight	Material PTFE	Scale 1 : 1
TTÜ		Screw screw		Rev. 1	Sheet 1 / 1

Appendix 3 Drawing of HERC chip stand screw #2

General tolerances (ISO 2768 medium)

Nom. size, mm	Tolerance, mm
0.5 … 3	±0.1
> 3 … 6	±0.1
> 6 … 30	±0.2
> 30 … 120	±0.3
> 120 … 400	±0.5
> 400 … 1000	±0.8



Designer	Date	Blank part	Weight	Material PTFE	Scale 2 : 1
TTÜ	Screw				
	SA-115			Rev. 1	Sheet 1 / 1