Investigations of the proton exchange membrane fuel cell at the change of oxygen concentration

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Abstract. The article considers the peculiarities of functioning of proton exchange membrane fuel cells (PEMFC). The mathematical model of the fuel cell, describing its electrical properties and dynamic characteristics is studied. A simulation model of power system with fuel cell as power source in the software environment Matlab/Simulink is developed. The study analyzed the reaction of the PEMFC output characteristics concerning the change in the concentration of oxygen in the oxidizer and the corresponding dependences.

Keywords: fuel cell, PEMFC, simulation

1. Introduction
Every year the amount of electric power generation through alternative sources increases in the modern world. This trend is a result of the large number of harmful emissions from traditional energy sources, which affect negatively the ecosystem of the planet. Besides, the fact of the limited hydrocarbon resources for traditional energy supply is important. The power distribution to consumers at the expense of hydrogen fuel cells is a promising area of alternative energy. Although they operate using non-renewable resources, fuel cells differ from the traditional sources as they are highly environmentally friendly and their power resource is inexhaustible, because hydrogen is one of the most abundant elements on the planet. Generation of electric and thermal energy by fuel cells has been used relatively recently that requires additional studies on the analysis of the modes of the elements and parameters that affect its output characteristics. This will improve the performance of fuel cells, and as a consequence, reduce the cost of equipment and energy produced by them [1-2].

2. Problem Statement
To reduce the cost of fuel cells, to increase their efficiency, to reduce power tariffs, it is necessary to study and analyze the operating modes and parameters of the fuel cells affecting their output characteristics.
One of the factors is the influence of changes in the percentage of oxygen in the oxidizer, a fuel cell proton exchange membrane on its output power parameters of current, voltage and power. To determine the nature of this influence, it is required to develop mathematical and simulation model of the fuel cell. The study and subsequent analysis of the obtained simulation data will allow to estimate the character and degree of impact of the parameter, to draw conclusions and make recommendations.

3. Theory
A fuel cell is an electrochemical energy source. A chemical reaction occurs on the porous electrodes. Atoms of hydrogen-containing substances, acting in response to fuel, flow to the anode and are divided into protons and electrons. The electrons motion to the cathode is carried out through the external circuit, which creates a constant electric current. The protons motion to the cathode is carried out through the electrolyte. At the cathode reduction reaction occurs. Protons and electrons are combined with oxygen-containing mixture. A byproduct of this process are heat and water vapor.

The figure shows a schematic diagram of the FC with proton exchange membrane [3].

![Schematic diagram of proton exchange membrane fuel cell](image)

**Figure 1.** Schematic diagram of proton exchange membrane fuel cell

Reactions occurring in the cell are described by the following expressions:

On the anode:

\[ \text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- \]  \hspace{1cm} (1)

On the cathode:

\[ \frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O} \]  \hspace{1cm} (2)

The overall reaction in PEMFC:

\[ \text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O} \]  \hspace{1cm} (3)

A detailed mathematical model of the fuel cell allows to explore the impact of changes in its input parameters such as pressure, temperature, concentration of reactants and flow rate of fuel and oxidant to the change of open circuit voltage \((E_{OC})\), the exchange current \((i_0)\) and the Tafel slope \((A)\).

\(E_{OC}\), \(i_0\) and \(A\) are modified as follows:

\[ E_{OC} = K_e E_n, \]  \hspace{1cm} (4)

\[ i_0 = \frac{zFk(P_{H2} + P_{O2})}{R_h} e^{-\frac{\Delta G}{RT}}, \]  \hspace{1cm} (5)

\[ A = \frac{RT}{z\alpha F^2}, \]  \hspace{1cm} (6)
where, $R$ is equal to $8.3145 \text{ J/(mol K)}$; $F$ is $96485 \text{ C/mol}$, $z$ is the number of moving electrons, $E_n$ is the Nernst voltage, which is the thermodynamics voltage of the cells and depends on the temperature and partial pressure of reactants and products inside the stack ($V_B$); $\alpha$ is the coefficient of charge transfer, which depends on the type of electrodes and catalysts; $P_{H_2}$ is the partial pressure of hydrogen inside the stack (ATM); $P_{O_2}$ is the partial pressure of oxygen inside the stack (ATM); $K$ is the Boltzmann constant - $1.38 \times 10^{-23} \text{ J/K}$; $h$ is the Planck constant - $6.626 \times 10^{-34} \text{ J s}$; $\Delta G$ is the size of the activation barrier which depends on the type of electrode and the catalyst used, $T$ is the operation temperature (K); $K_c$ is a constant voltage at the nominal operating conditions.

The rates of conversion of hydrogen ($U_{H_2}$) and oxygen ($U_{O_2}$) are calculated using the following expressions:

$$U_{fH_2} = \frac{n_{H_2}^n}{n_{H_2}^i} = \frac{60000RT_{fC}}{zFP_{fuel}V_{lpm(fuel)}x\%}$$  \hspace{2cm} (7)$$

$$U_{fO_2} = \frac{n_{O_2}^n}{n_{O_2}^i} = \frac{60000RT_{fC}}{2zFP_{air}V_{lpm(air)}y\%},$$  \hspace{2cm} (8)$$

where, $P_{fuel}$ is the absolute fuel supply pressure (ATM); $P_{air}$ is the absolute air supply pressure (ATM); $V_{lpm(fuel)}$ is the fuel consumption (l/min); $V_{lpm(air)}$ is the air flow (l/min); $x$ is the percentage of hydrogen in the fuel ($\%$); $Y$ is the percentage of oxygen in the oxidant ($\%$); $N$ is the number of cells.

Constant 60000 comes from the conversion from flow speed l/min used in the model, to the dimensionality of m$^3$/s (1 liter / min = 1/60000 m$^3$/sec).

Partial pressure and the Nernst voltage are determined as follows:

$$P_{H_2} = (1 - U_{fH_2})x\%P_{fuel},$$ \hspace{2cm} (9)$$

$$P_{H_2O} = (w + 2y\%U_{fO_2})P_{air},$$ \hspace{2cm} (10)$$

$$P_{O_2} = (1 - U_{fO_2})y\%P_{air},$$ \hspace{2cm} (11)$$

$$E_{ernst} = \begin{cases} 1.229 + (T - 298) \frac{-44.43}{zF} + \frac{RT}{zF} \ln(P_{H_2}P_{O_2}^{1/2}) & \text{при } T \leq 100^\circ C \\ 1.229 + (T - 298) \frac{-44.43}{zF} + \frac{RT}{zF} \ln \left( \frac{P_{H_2}P_{O_2}^{1/2}}{P_{H_2O}} \right) & \text{при } T > 100^\circ C \end{cases},$$  \hspace{2cm} (12)$$

where $P_{H_2O}$ is the partial pressure of water vapor inside the stack (ATM); $W$ is the percentage of water vapor in the oxidant ($\%$).

The partial gases pressures and the Nernst voltage can be used to calculate the new values of open circuit voltage ($E_{OC}$), the exchange current ($i_0$) and the Tafel slope ($A$).

The parameters $\alpha$, $\Delta G$ and $K_c$ are calculated based on the polarization curve at nominal conditions of fuel cell operation along with some additional parameters, such as the low efficiency of the calorific value of the stack, composition of fuel and air, gas pressure and temperature. These values are specified in the manufacturer’s specifications of the fuel cell.

Nominal levels of gases conversion are calculated as follows:
\[
U_{fH_2} = \frac{\eta_{nom}\Delta h^0(H_2O_{(gas)})N}{2FP_{nom}}, \\
U_{fO_2} = \frac{60000RT_{nom}V_{nom}}{2FP_{air_{nom}}V_{pma(air)_{nom}}^{0.21}}.
\]

where \(\eta_{nom}\) is the nominal stack efficiency of STC (%), \(\Delta h^0 (H_2O_{(gas)}) - 241.83 \times 10^3 j/mol\); \(V_{nom}\) is the nominal voltage (V); \(I_{nom}\) is the nominal current (A); \(V_{pma(air)_{nom}}\) is the nominal air flow (l/min); \(P_{air_{nom}}\) is the rated absolute supply pressure of air (PA); \(T_{nom}\) is the nominal operating temperature (K).

The nominal partial pressure of gases and the Nernst voltage can be obtained from these rate values. Under certain \(E_{DC}, i_0\) and \(A\), and also under the condition that the stack operates with a constant rate of conversion or in the nominal mode \(\alpha\), \(\Delta G\) and \(K_c\) can be determined [7 - 10].

To study the operation of the fuel cell and analysis of the impact on performance of concentration of oxygen in the oxidant changes, we have developed a calculation of the quantitative simulation model in the software environment MATLAB/Simulink. The developed model is shown in Figure 2.

**Figure 2.** A simulation model of the fuel cell.

The nominal voltage of the fuel cell 45 V_{dc} is applied to the voltage converter. The transformer increases the voltage to 100 V_{dc}, then the voltage is applied to a constant load, with interval time of 1 sec. The nominal capacity of the unit is 6 kW [3-6].

4. Experimental results

In contrast to the quality of the mixture of the hydrogen fuel cell, an oxidizing agent fuel cell proton exchange membrane is not subject to particularly strict requirements. In the model under consideration, the nominal percentage content of oxygen in the oxidizer is equal to 21%. This means that it is possible to use air as an oxidizer. As the air is the simplest and cheapest option of an oxidizer, it is advisable to explore only increase in the oxygen percentage in the oxidizer. Figure 3 shows an example of changing a driving signal of the oxygen percentage throughout the entire simulation.
Figure 3. Reference-input signal that characterizes the oxygen concentration in the oxidizer in the simulation.

A number of the experimental values showed that PEMFC is workable even if the concentration of oxygen in the oxidant increases to a level when the oxidizer agent is pure oxygen (99.7 %) Figures 4-7 show graphs of currents and voltages corresponding to the change in the concentration of oxygen in oxidizer.

Figure 4. Dependence of the PEMFC output voltage on the time when the concentration of oxygen in the oxidizer is equal to 99.7 %
Figure 5. Dependence of the PEMFC current on the time when the concentration of oxygen in the oxidizer is equal to 99.7 %

Figure 6. Dependence of the output voltage of the voltage converter on the time when the concentration of oxygen in the oxidizer is equal to 99.7 %
Figure 7. Dependence of the output current of the voltage converter on the time when the concentration of oxygen in the oxidizer is equal to 99.7%.

Figures 8-9 show the dependence of the output currents and voltages on the changes in oxygen concentration in oxidizer from the nominal to the maximum value.

Figure 8. Voltage curve depending on the oxygen concentration.
5. Results and discussion
The result of simulation revealed that the change of oxygen concentration in the oxidizer is possible in a wide range from the nominal value equal to 21% (normal air) up to a value of 99.7% (pure oxygen). It should be noted that at these changes range emergency and critical PEMFC modes do not occur. The regulation of hydrogen concentration in the fuel, Safe to the fuel cell, is possible only in the range of 5%. Going beyond this limit will create an emergency operation mode and increase of current up to 2.5 kA. The change in the concentration of oxygen in the oxidant has a significant influence on the output characteristics, but the values of current and voltage do not reach emergency values.

6. Conclusion
• The PEMFC simulation model is developed.
• The influence of changes of oxygen concentration on output PEMFC characteristics is analyzed.
• It is revealed that the change of oxygen concentration in the oxidizer PEMFC has a significant impact on its output characteristics.
• It is determined that the change of oxygen concentration does not lead to emergency modes of PEMFC operation.

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