PREDICTION OF THE BEHAVIOUR OF A HYDROGEN-OXYGEN PEM FUEL CELL BASED ON A SIMPLIFIED MODEL

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This paper's purpose is to build a simplified mathematical model to present the time evolution of studied fuel cell parameters and to facilitate the detection of optimal operation parameters and variables for this fuel cell. We first build a steady state model in order to find steady state variables values to be used in the dynamical model. This paper compares PEM fuel cell behaviour in case of different input flows temperatures and produced current densities. In the final part of the study we chose the appropriate parameters for the fuel cell operation.

INTRODUCTION

Fuel cells are electrochemical energy generators that don't require recharging.[5] The studied Proton Exchange Membrane (PEM) hydrogen-oxygen fuel cell produces electricity, water and heat, using hydrogen and oxygen, and having a solid polymer (NAFION type) as electrolyte.[5,6] PEM has high proton conductivity, is very thin and the fuel cell has little thickness and weight.[21] It is easy to manipulate and does not present leakage danger (only gaseous and solid components are used). Fuel cells are clean and ecological energy generators that ensure between 50% - 90% efficiency, and can be used for long term.

Until now a large number of researchers have developed models for PEM fuel cells (for example: Ceraolo, 2001; Ferguson and Ugursal, 2002; Golbert and Lewin, 2004; Nguyen, 1996; Nguyen and White, 1993; Nguyen, 2003; Perry *et al.*, 1997; Rho *et al*, 1998; Springer *et al*, 1991, 1996; Zhukovsky *et al*, 2003). The research group formed by Oniciu, Agachi and Dumitrescu published PEM fuel cells models already between 1976 and 1986.[25-28]Most of the models are one-dimensional, calculate variables evolution on the anode-cathode direction and are focused on the electrochemical aspects of fuel cells.[24] An exception is the three dimensional Zhukovsky (2003) model, which is concentrated on oxygen transport through the fuel cell electrodes and PEM. For example

Ferguson and Ugursal (2002) have built a quasi steady state parametric model that stresses the electrochemical modelling.

A bibliographic analysis reveals that most of researchers have built models to describe the fuel cells behaviour in steady state conditions, while the dynamic behaviour is avoided in their studies. Dynamic behaviour is very important, especially in case of small fuel cells, where spatial variation of parameters is in narrow intervals. Time evolution is given (Ferguson and Ugursal, 2002; Golbert and Lewin 2004) only for current density, cell voltage, and power density. There is no focus on input compounds quantities or on obtained water flows in the fuel cell. The exception is represented by Golbert and Lewin's (2004) paper that presents a model for PEM hydrogen-oxygen fuel cells which gives out parameters spatial evolution in anode – cathode direction. They study spatial dependencies of current density, power density, solid temperature and water flows in stationary and dynamic conditions.

Considering the bibliographical study and the output of the presented models, we have decided to develop a model in order to present the time dependency of the parameters of a small PEM fuel cell (thickness of 10^{-4}m). The model results will put into evidence how input flows temperature, hydrogen consumption and oxygen consumption influence anode, cathode and solid membrane temperatures and molar flows. Anode hydrogen, cathode oxygen, anode and cathode liquid and

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water vapours are studied. The focus is how parameters modify when the fuel cell functions at different current densities. We have decided to build such a model because it gives parameter time variation, the optimal fuel cell operation interval can be predicted and the behaviour in different real situations also. When external disturbances appear their effect on fuel cell parameters will be known as well as the approximate time to reach a new steady state.

RESULTS AND DISCUSSION

Mathematical model

A deterministic one-dimensional mathematical model was used to investigate the fuel cell behaviour. This model's purpose is to calculate time evolution of components molar flows (hydrogen, oxygen, liquid water and water vapours) and anode, cathode and solid polymer temperatures. The main principles of the model are similar to those used by Golbert, J. and Lewin,

D.R. for their spatial model of the PEM hydrogen-oxygen fuel cell.[7] All used parameters apply only in the considered particular case and have been considered for the purpose of this paper only. Some of the parameters have been proposed by J. Golbert, D.R. Lewin also.[7] The used parameters for the fuel cell, along with their values are presented in table 2.

The following **simplifying hypotheses** are considered in order to start building the model: **(1)** One-dimensional variability of parameters (anode – cathode). The parameters vary only in the anode-cathode direction, and do not vary in the transversal section. **(2)** Constant parameters in anode and cathode compartments and in the PEM, in order to study the time dependency of the parameters and not the space dependency. **(3)** Main reaction efficiency is 100%. **(4)** The catalyst is not poisoned and is 100% efficient. Considering these hypotheses, along with the general electrolysis law, the electrolytic processes in the fuel cell, the general gas law and heat and mass transfer processes in the fuel cell, we have obtained the main differential model equations ((1) to (10)).

Table 1

Differential equations of the mathematical model

Equation		Calculated variable
$\dfrac{dN_{H_2,exc}}{dt} = N_{H_2,in} - \dfrac{i_a A_a}{z_a FM_{H_2}}$ (1)	$\dfrac{dN_{O_2,exc}}{dt} = N_{O_2,in} - \dfrac{i_c A_c}{z_c FM_{O_2}}$ (2)	Hydrogen (1) / Oxygen (2) excess at anode / cathode
$\dfrac{dN_{H_2O,a}^l}{dt} = \dfrac{k_c A_a L_a}{RT_a} P_{H_2O,a}^v$ (3)	$\dfrac{dN_{H_2O,c}^l}{dt} = \dfrac{k_c A_c L_c}{RT_c} P_{H_2O,c}^v$ (4)	Liquid water at anode (3) / cathode (4)
$\dfrac{dN_{H_2O,a}^v}{dt} = N_{H_2O,in,a}^v - \dfrac{dN_{H_2O,a}^l}{dt} - \dfrac{\alpha A_a i_a}{z_a FM_{H_2}}$ (5)	$\dfrac{dN_{H_2O,c}^v}{dt} = \dfrac{i_c A_c}{z_c FM_{O_2}} - \dfrac{dN_{H_2O,c}^l}{dt} + \dfrac{\alpha A_a i_a}{z_a FM_{H_2}}$ (6)	Vapour water at anode (5) / cathode (6)
$\dfrac{dT_a}{dt} = \dfrac{C_{P,H_2,in} N_{H_2,in} T_{H_2,in} - C_{p,H_2,a} N_{H_2,exc} T_a - T_a\left(C_{p,HO,a}^v \dfrac{dN_{H_2O,a}^v}{dt} + C_{P,H_2O}^l \dfrac{dN_{H_2O,a}^l}{dt}\right) + K_T A_T (T_s - T_a)}{C_{p,HO,a}^v N_{H_2O,a}^v + C_{P,H_2O}^l N_{H_2O,a}^l}$ (7)		Anode temperature
$\dfrac{dT_c}{dt} = \dfrac{C_{P,O_2,in} N_{O_2,in} T_{O_2,in} - C_{p,O_2,a} N_{O_2,exc} T_c - T_c\left(C_{p,HO,c}^v \dfrac{dN_{H_2O,c}^v}{dt} + C_{P,H_2O}^l \dfrac{dN_{H_2O,c}^l}{dt}\right) + K_T A_T (T_s - T_c)}{C_{p,HO,c}^v N_{H_2O,c}^v + C_{P,H_2O}^l N_{H_2O,c}^l}$ (8)		Cathode temperature
$\dfrac{dT_r}{dt} = \dfrac{K_r A_r (T_s - T_r)}{C_{p,H_2O}^l N_r} + T_{r,in} - T_r$ (9)		Cooling agent temperature
$\dfrac{dT_s}{dt} = \dfrac{(N_{H_2O,a}^l \Delta H_{vap,a} + N_{H_2O,c}^l \Delta H_{vap,c} + \dfrac{L_m A_s \rho_s K_r \Delta H_r}{M_{mu}} - K_T A_T (T_s - T_a) - - K_T A_T (T_s - T_c) - K_r A_r (T_s - T_r)}{c_{p,s} L_m A_s \rho_s}$ (10)		Solid polymer temperature

The first two equations present the oxygen and hydrogen excess at anode and cathode, which are calculated by extracting consumed quantities at electrode from the inlet molar flow. Equations (3)

and (4) calculate anode and cathode liquid water, considering that water vapours will partially condense, depending on electrode temperature, water vapours partial pressure and the

condensation constant (K_c). The next two equations, (5) and (6), calculate water vapours in the fuel cell compartments, as a function of partial pressure and temperature at electrode. Water diffusion through membrane and that water dragging through the membrane from anode to cathode by protons in the electrochemical process is also taken into account. In steady state liquid water at cathode has a value of $0.5742 \ 10^{-5}$ mol/s, the vapours molar flow is $1.312 \ 10^{-5}$ mol/s at anode and $1.312 \ 10^{-5}$ mol/s at cathode. And the hydrogen and oxygen excess are both around 10^{-15} mol/s.

The last three differential equations calculate temperature evolution for the anode (7), cathode (8), membrane (10) and the cooling agent (9). The cooling agent is water, which flows into a network of channels through the solid polymer.[7] The fuel cell is fed with 368 K water vapours and hydrogen at anode, and with 353 K oxygen at cathode. The cooling agent input flow temperature is 333 K. In steady state conditions the fuel cell functions at 356.758 K, anode temperature; 355.43 K, cathode temperature and 354.31 K for the PEM.

Table 2

Used fuel cell parameters and their values

Parameter	Parameter name	Used value
A_a	Anode surface [m^2]	$8.8 \ 10^{-4}$
A_c	Cathode surface [m^2]	$8.8 \ 10^{-4}$
A_s	PEM surface [m^2]	$6 \ 10^{-4}$
A_r	Cooling area [m^2]	$5 \ 10^{-4}$
A_T	Heat exchange area [m^2]	$2 \ 10^{-4}$
Cp_s[7]	PEM molar heat [J/(g K)]	1
$C^l p_{H2O}$[11]	Liquid water molar heat [J/(g K)]	75.31
densmu[7]	Dry membrane density [g/m^3]	$2 \ 10^6$
ΔH_r[7,11]	Reaction enthalpy [J/mol]	$2.41 \ 10^5$
F[11]	Faradays number [As/Eg]	96480
k_c	Water condensation rate constant [s^{-1}]	10^{-9}
K_T[7]	Heat transfer coefficient [W/(m^2 K)]	250
K_r	Reaction rate constant [s^{-1}]	10^{-5}
L_m	PEM thickness [m]	$2 \ 10^{-4}$
L_a	Anode thickness [m]	$8.07 \ 10^{-4}$
L_c	Cathode thickness [m]	$8.07 \ 10^{-4}$
M_{mu}[7]	Dry membrane molecular weight [g/mol]	1100
M_{H2}	Hydrogen molecular weight [g/mol]	2
M_{O2}	Oxygen molecular weight [g/mol]	32
M_{H2O}	Water molecular weight [g/mol]	18
N_r	Cooling agent molar flow [mol/s]	0.003
P_a[7]	Anode pressure [atm]	1
P_c[7]	Cathode pressure [atm]	1
R[11]	General gas constant [m^3 atm/(mol K)]	8.314
$T_{r,in}$	Cooling agent input temperature [K]	333
z_a	Number of exchanged electrons at anode	2
z_c	Number of exchanged electrons at cathode	4

Simulation results

Equations (1) – (10) are implemented in Matlab/Simulink, obtaining a 5 input and 10 output system. The input variables and their values are: anode input hydrogen molar flow ($1.14 \ 10^{-5}$ mol/s), cathode input oxygen molar flow ($5.7 \ 10^{-6}$ mol/s), current density (4999.418 A/m^2), anode input flow temperature (368 K), cathode input flow temperature (353 K). And the output variables are calculated using formulas from table 1. The model shows a simplified behaviour for the fuel cell, considering molar flows and temperatures. The fuel cell system dynamic behaviour is studied by applying disturbances.[1] Firstly we present the influence of hydrogen and oxygen modified consumption on the output variables and in the second part the input flows temperature influence.

The influence of is going to be discussed in the next paragraphs modified consumption.

Increasing the fuel cell hydrogen and oxygen consumption, the fuel cell produced current density will also increase in proportion. Fuel cell temperatures will first decrease (for 1 to 5 seconds), depending on step amplitude, as shown in figures 1, 2 and 3. If the step is higher, the temperature variation will be higher. After those first seconds, temperatures begin to increase slowly until the new steady state installs (after approximately 10 to 15 minutes).

Fig. 1 presents temperatures versus time evolution after 20% positive (left) and negative

(right) step on hydrogen and oxygen consumption. In the case of a positive disturbance the new steady state is established at 1710s after applying the input step. Cathode temperature stabilizes first, at 1250s, and anode temperature the last one, at 1690s. After a 20% negative consumption step temperatures stabilization is complete 1590s after applying the step, the cathode temperature is still the first one, at 1260s, and anode temperature the last one at 1810s.
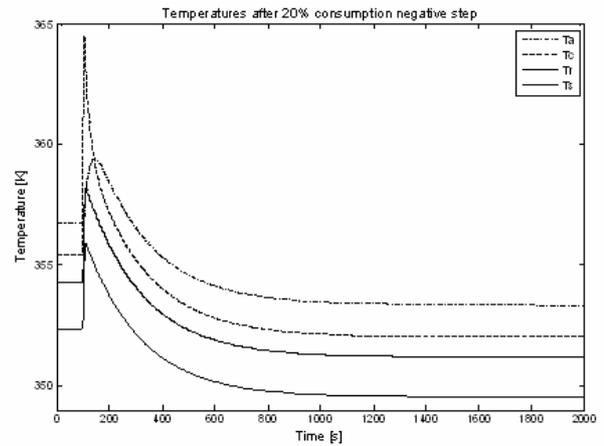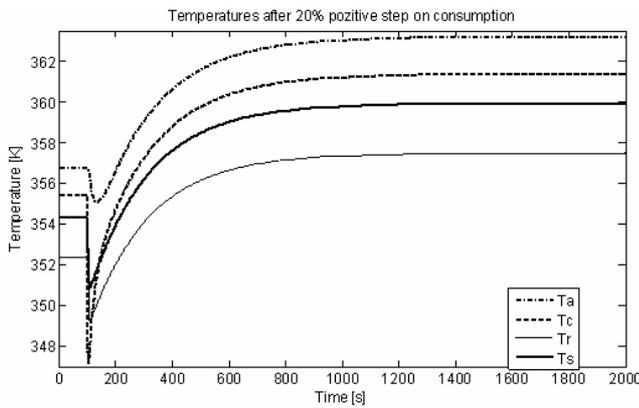

Fig. 1 – Temperatures behaviour after 20% consumption perturbation applied at 100s.

If the same 5%, 10% and 20% negative perturbations are applied (fig. 2) to the input hydrogen and oxygen molar flows, temperatures will have a similar behaviour, increasing the first seconds, and slowly decreasing after, until stabilization. Comparing anode and cathode answer to negative and positive steps, presented in

fig. 2, it can be observed that the electrode temperatures have similar behaviour. For disturbances having the same absolute value, anode temperature stabilizes quicker after a positive perturbation, then after a negative one. And stabilizes first for the smallest absolute perturbation value.
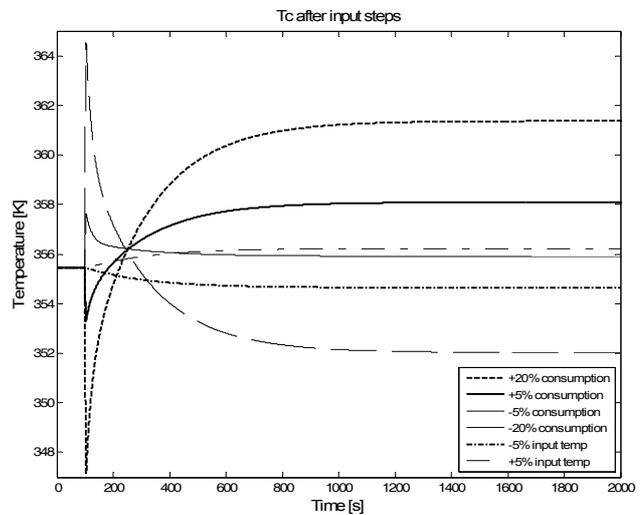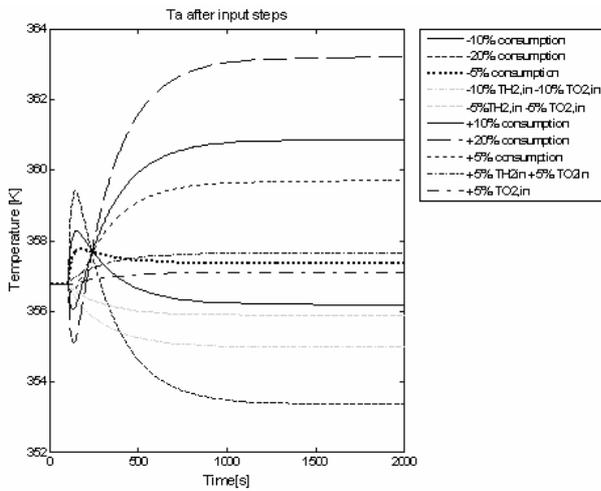

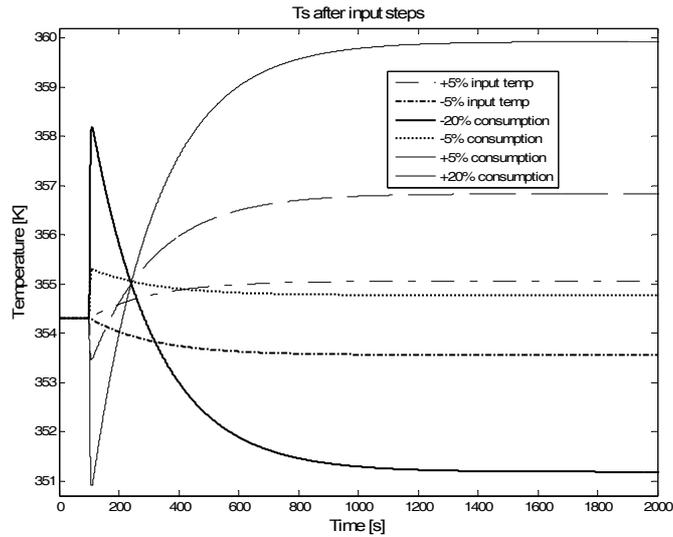Fig. 2 –Electrode temperatures after perturbations applied at 100s.

Fig. 3 – Solid polymer temperatures behaviour after perturbations applied at 100s.

In figures 1 and 2 it can be observed that after the disturbance, in the first seconds, anode temperature decreases less (for the positive disturbance) than cathode temperature, causing a faster anode temperature stabilization (distinguished in fig. 1). Both temperatures, and also solid polymer temperature (fig. 3) increase in proportion when current density increases because of fuel cell species consumption increase, and decrease with species consumption in the electrochemical process.

When hydrogen and oxygen input flows are modified, water molar flows in the fuel cell also modify, as shown in fig. 4. For example, if fuel cell species consumption at electrode increases, the electrochemically produced water will also increase in proportion. At anode the water dragged by protons through the PEM will also increase.

The water will cross the PEM in anode and cathode direction, mostly towards cathode. Therefore the quantity of water at cathode will increase. At cathode and anode a part of this water will condense because of water partial pressure at electrodes and PEM and electrodes temperature. One of the reasons is, as Golbert and Lewin (2004) showed, that in the PEM-cathode direction temperature decreases.[7] At the cathode more liquid water will exist then at the anode, because anode input flow contains vapour water at a higher temperature (368 K) than PEM temperature (354.31 K). Differences between water quantities at electrodes is also caused by mass transfer processes, on anode-cathode direction. Protons drag water through the membrane (from anode to cathode) and water diffusion through the solid membrane also occurs.
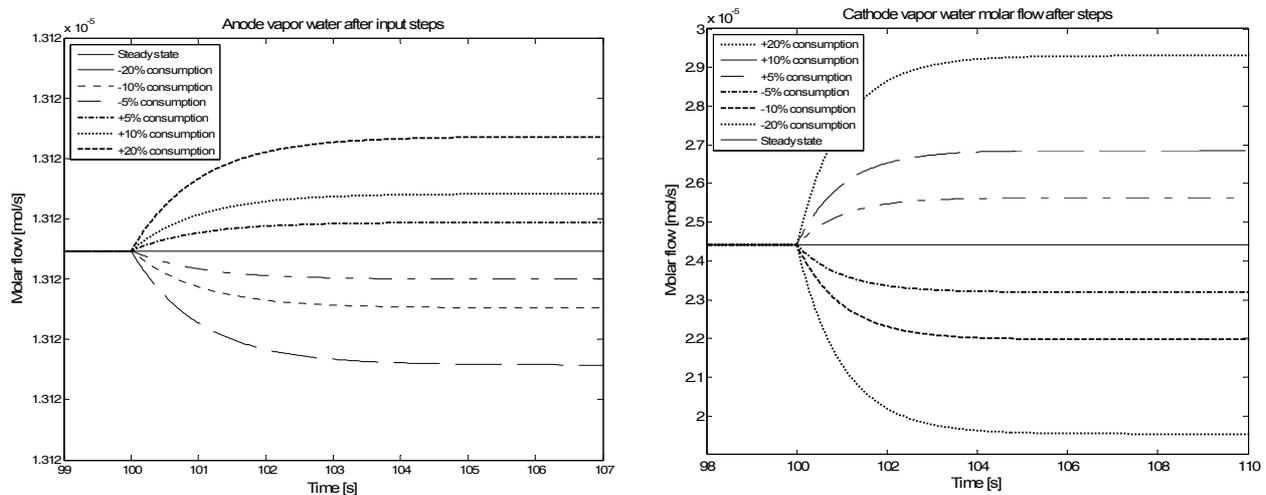

Fig. 4 –Vapour water molar flow behaviour after current density perturbations applied at 100s.

Molar flows response at perturbations is faster than the response of fuel cell temperatures. The longest molar flow stabilization time is 7.2s for cathode vapour water molar flow after 20% consumption decrease (fig. 4) while the smallest temperatures stabilization time is 650s for cathode temperature after 5% input flows temperature increase (fig. 2).

In the following paragraph the influence of the impact flows temperature disturbances is presented.

If input flows temperature modifies, the fuel cell temperatures will modify, but not the compounds quantities. Component quantities modify only when input molar flows and current density are modified. Anode, cathode and solid polymer temperatures modify because of the electrochemical processes and transfer heat to the cooling agent through the cooling network crossing PEM. Temperatures in the fuel cell decrease in proportion when input flows temperature decrease and increase when a positive perturbation appears in the input flows temperature (see fig. 2 and 3).

The model can be used to predict hydrogen-oxygen fuel cells behaviour, in steady state and dynamic conditions. It calculates molar flows and temperature evolution in dynamic conditions, providing the user the possibility to detect the optimal operating parameters and variables for the fuel cell. The studied fuel cell optimal behaviour is in steady state conditions and in dynamic ones when small perturbations appear. Between -5% and +5% input parameter disturbances the new steady state is reached after approximately 12 minutes.

CONCLUSIONS

A deterministic one-dimensional mathematical model was developed, in order to predict hydrogen-oxygen PEM fuel cells behaviour, in steady state and non steady state conditions. The model has been implemented in the MATLAB/SIMULINK environment. We have used the model to detect fuel cell temperatures and molar flows evolution when disturbance on input flows temperature and fuel consumption appear. The optimal operating parameters and variables for the studied PEM fuel cell have been determined. The model can also be used to find parameter values and to make dimensioning calculations and optimization for the fuel cell. Further work starting from this simplified model is to be carried out in order to elaborate a more complex model to simulate the real time behaviour of this type of fuel cells, by eliminating the simplifying hypotheses. The final goal is to work out a control strategy for electrical and water production.

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