

Analysis of thermodynamic and material properties assumptions for three-dimensional SOFC modelling

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Abstract In the present work a three-dimensional numerical model of Solid Oxide Fuel Cell (SOFC) is examined. The calculations are performed for geometry similar to the one used earlier by Hirano. Obtained numerical results for different heat and electric coefficients allows to emphasise the fact, how big are the differences between assumed thermodynamics properties for SOFC modeling.

Keywords: Modelling of electrochemical reactions; SOFC; CFD

Nomenclature

A	–	anode surface, m ²
e	–	total energy, kJ/kg
\vec{i}	–	current density, A/m ²
\vec{I}	–	Gibbs idemfactor
LHV	–	lower heating value
$\vec{\tau}_c$	–	total viscous flux of momentum, N/m ²
\vec{q}^c	–	total flux of energy, W/m ²
Y_k	–	species mole fraction
\dot{m}	–	mass flow rate, kg/s
p	–	pressure, Pa
P	–	electric power, W

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R	-	universal gas constant, J/(kmol K)
S_e^f	-	energy source for fluids, W/m ³
S_e^s	-	energy source for solids, W/m ³
S_k	-	species source, kg/(m ³ s)
S_m	-	mass source, kg/(m ³ s)
S_v	-	momentum source
U	-	voltage, V

Greek symbols

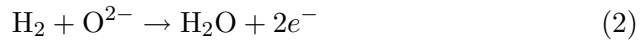
σ	-	electric conductivity coefficient, $\Omega^{-1} \text{ m}^{-1}$
ε	-	porosity factor
ϕ	-	potential, V
ρ	-	density, kg/m ³
λ	-	heat conductivity coefficient, W/(mK)
η_{act}	-	activation losses
η_{conc}	-	concentration losses
η_{ohm}	-	ohmic losses

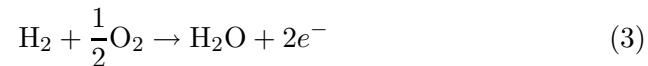
Subscripts

f	-	fluid
s	-	solid
c	-	cathode
e	-	electrolyte
a	-	anode

1 Introduction

The principle of fuel cells is based on the direct energy conversion from the chemical to the electric form. The high temperature solid oxide fuel cell is built of two electrodes separated by a solid electrolyte. The anode is fed with fuel which can be hydrogen, partially reformed natural gas or other gaseous hydrocarbon. Oxygen is fed on the cathode side. Because of one half of electrochemical reaction (1) oxygen ions are generated on the cathode side. Ions diffuse through electrolyte to the anode side. Second half of electrochemical reaction (2) takes place on the anode side where oxygen ions react with hydrogen atoms. The products of this reaction are steam and free electrons transported back on the cathode side by external electric circuit (total reaction is given by (3)).





The advantage of high temperature fuel cells is the possibility of producing hydrogen by internal reforming of methane or methanol after mixing with steam [1],[2]. The internal reforming process generally follows a partial pre-reforming step carried out externally for cracking of higher hydrocarbons. Additionally, since the electrolyte is solid, there is no problem with corrosion, because materials of solids elements are ceramics. Low quantity of pollutants and low noise level make fuel cells environmentally friendly. On the other hand high cost of fuel cells components is a disadvantage.

Single fuel cell generates almost 1 V potential. Since it is very simple to connect fuel cells into the stack, the obtained potential and the power of fuel stacks can be higher. Presently, the maximum nominal power of prototype plants is about 250 kW. The intended power of power plant is higher than 1 MW. The efficiency of fuel cells is about 40 – 50% but combining them in a hybrid cycle with gas turbine increases the efficiency up to 70% and over [3], [4].

Because of high cost of the fuel cell it is necessary to develop an appropriate mathematical and numerical model of SOFC. In the literature it is quite easy to find numerous 0D, 1D, 2D and 3D mathematical models ([1]-[8]). Each model is characterized by different, sometimes inconsistent, assumptions. Therefore in this paper a three-dimensional model is developed and mathematically described. In particular, the discussion and numerical comparison of different closures proposed by Li et al. [5], Fergusson et al. [6] and by Campanari [7] are focused. The model has been implemented into the CFD tool Fluent by means of UDF [11]. The model has been tested by comparison of numerical results with experimental data from the literature [5]. The tubular geometry of SOFC is considered. Presented model does not employ an internal reforming.

2 SOFC mathematical model

2.1 Geometry

A variety of fuel cell geometries are currently proposed. The most important of them base on a tubular or planar arrangement. In the present paper tubular geometry was examined and it is shown in Fig. 1. This geometry is similar to the one used earlier by Hirano and quoted by Li et al. [5]. In

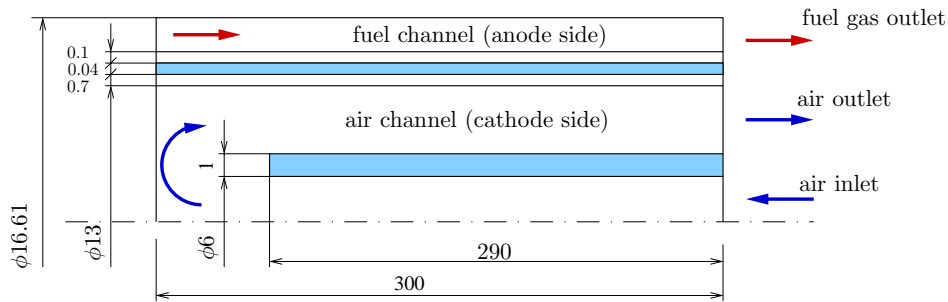


Figure 1. The sketch of geometry of tubular SOFC.

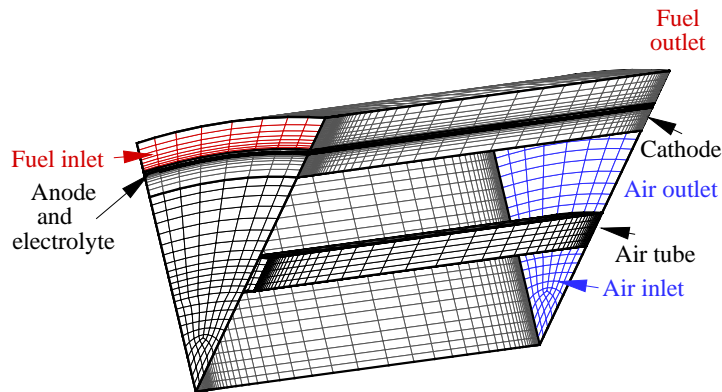


Figure 2. Selected three-dimensional geometry with the mesh of finite volumes for the discretization.

order to simplify the calculations and minimize the time, only 1/12 part of the full geometry is used (Fig.2). Hence, the periodic boundary conditions are employed. It is important to emphasise the fact that fuel cells are connected in the stack by interconnection. When periodic conditions are used it is not possible to take into account local parameter changes caused by the interconnection. This is an additional assumption which should be omitted during further investigations. Structural mesh was applied in the number of 31 000 of finite volumes.

2.2 Governing equations

In this work a mathematical model of SOFC is based on the elementary balance equations solved for fluids: continuity, momentum, energy, and species transport [2]. Additionally, in order to describe electrochemical equation correctly, the equation for current transport is developed and tested. The form of mentioned equations is similar to the one used by: Li et al. [5], Fergusson et al. [6], Lemański and Badur [3]. The differences between described in the literature models base on different forms of electrical and heat resistivities, diffusion coefficients and calculations of potential losses. Balances in solids are restricted only to the equation of energy and the current transport. It is assumed, that the fuel cell consists of two porous electrodes which are separated by solid electrolyte. For porous electrodes in the governing equations porosity should be considered. The porosity factor ε is defined as a parameter that indicates the amounts of fluid volume V_f in the whole volume unit V :

$$\varepsilon = \frac{V_f}{V}.$$

The governing equations for the whole fuel cell model are proposed by Karcz [2] in the following compact form consistent with CFD:

$$\begin{aligned} \frac{\partial}{\partial t} \begin{pmatrix} \varepsilon\rho \\ \varepsilon\rho\vec{v} \\ \varepsilon\rho e + (1-\varepsilon)\rho_s e_s \\ \varepsilon\rho Y_k \\ 0 \end{pmatrix} + \operatorname{div} \begin{pmatrix} \varepsilon\rho\vec{v} \\ \varepsilon\rho\vec{v} \otimes \vec{v} \\ \varepsilon\rho e\vec{v} \\ \varepsilon\rho Y_k\vec{v} \\ 0 \end{pmatrix} + \operatorname{div} \begin{pmatrix} 0 \\ \varepsilon p\vec{I} \\ \varepsilon p\vec{v} \\ 0 \\ 0 \end{pmatrix} = \\ = \operatorname{div} \begin{pmatrix} 0 \\ \varepsilon\vec{\tau}_c \\ \varepsilon\vec{\tau}_c\vec{v} + \vec{q}_c \\ \varepsilon\vec{J}_k \\ \vec{i} \end{pmatrix} + \begin{pmatrix} \varepsilon\rho S_m \\ \varepsilon\rho S_v \\ \varepsilon\rho S_e^f + (1-\varepsilon)\rho S_e^s \\ \varepsilon\rho S_k \\ 0 \end{pmatrix}, \end{aligned} \quad (4)$$

where ρ – density, ε – porosity, S_m – mass source in the mass balance equation, S_v – momentum source in the momentum balance equation, S_e – energy source in the energy balance equation, S_k – species source in the species transport equation, \vec{i} – current density [8].

It is necessary to distinguish where individual balance equations and appropriate source terms are employed. For electrodes as well as air and fuel channels equations of continuity, momentum, energy, species and current

transport are solved. Therefore additional terms of sources in Eq. (4) are as follows:

- source of mass in the continuity equation (4)₁, S_m :

– air channel

$$S_{O_2} = -\operatorname{div} \left(\frac{\vec{i}}{4F} M_{O_2} \right), \quad m = O_2, \quad (5)$$

– fuel channel

$$\begin{aligned} S_{H_2} &= -\operatorname{div} \left(\frac{\vec{i}}{2F} M_{H_2} \right), \quad m = H_2, \\ S_{H_2O} &= \operatorname{div} \left(\frac{\vec{i}}{2F} M_{H_2O} \right), \quad m = H_2O; \end{aligned} \quad (6)$$

- source of energy (4)₃, S_e^f :

– cathode – ohmic heating

$$S_c^f = \frac{\vec{i} \cdot \vec{i}}{\sigma_c}, \quad e = \text{cathode}, \quad (7)$$

– anode – ohmic heating and energy from chemical reaction of water creation

$$S_a^f = \frac{\vec{i} \cdot \vec{i}}{\sigma_a} + \operatorname{div} \left(\frac{\vec{i}}{2F} \Delta H_0 \right), \quad e = \text{anode}; \quad (8)$$

- source of species in the species transport equation (4)₄, S_k :

$$\begin{aligned} S_{O_2} &= -\operatorname{div} \left(\frac{\vec{i}}{4F} M_{O_2} \right), \quad k = O_2, \\ S_{H_2} &= -\operatorname{div} \left(\frac{\vec{i}}{2F} M_{H_2} \right), \quad k = H_2, \\ S_{H_2O} &= \operatorname{div} \left(\frac{\vec{i}}{2F} M_{H_2O} \right), \quad k = H_2O \end{aligned} \quad (9)$$

are used [2]. In the above equations $M_k, k = \text{O}_2, \text{H}_2, \text{H}_2\text{O}$, means the molecular weight of species.

For electrolyte and tube elements only energy and current transport equations are employed. In the electrolyte part the energy local source (4)₃ is added in the following form as proposed by Achenbach [1]:

$$S_e^s = \frac{\vec{i} \cdot \vec{i}}{\sigma_e}, \quad (10)$$

where σ_e is the electric conductivity coefficient of electrolyte. The suitable electric conductivity σ forms are presented in Tab. 1.

The current transport equation is taken in the classical Ohm's form:

$$\vec{i} = -\sigma \text{grad } \phi \quad (11)$$

where ϕ means the electric potential.

Table 1. Electrical conductivity coefficient used during calculations.

σ [$\Omega^{-1}\text{m}^{-1}$]	Fergusson et al. [6]	Li et al. [5]	Campanari et al. [7]
σ_c	$\frac{4.2 \cdot 10^7}{T} \cdot e\left(-\frac{1200}{T}\right)$	$12324 \cdot e\left(-\frac{500}{T}\right)$	$12324 \cdot e\left(-\frac{600}{T}\right)$
σ_e	$3.34 \cdot 10^4 \cdot e\left(-\frac{10300}{T}\right)$	$10 \cdot e\left(-10092\frac{1}{T} - 7.854e-4\right)$	$0.340 \cdot 10^5 \cdot e\left(-\frac{10350}{T}\right)$
σ_a	$\frac{9.5 \cdot 10^7}{T} \cdot e\left(-\frac{1100}{T}\right)$	$33557 \cdot e\left(-\frac{1392}{T}\right)$	$33557 \cdot e\left(-\frac{1392}{T}\right)$

Table 2. Heat conductivity coefficient λ used during subsequent calculations.

λ [Wm ⁻¹ K ⁻¹]	Fergusson et al. [6]	Li et al. [5]	Campanari et al. [7]
cathode	3	6	2
electrolyte	2	2.7	2
anode	3	11	2
air channel	-	-	-
fuel channel	-	-	-
air tube	-	1.1	$-0.0096 \cdot T + 17.892$

The heat exchange between fuel cell and environment is not considered. So the adiabatic conditions for fuel cell walls are employed. The energy

balance Eq. (4)₃ consists of two parts which can be separated. First equation involves fluid (12) and the second involves the solid (13) part of fuel cell. In Eq. (12) both heat convection (second term from the left) and conductivity is investigated (second term from the right). For solid (13) only heat conductivity exist (second term from the right). By adding these two equations complete energy equation for porous elements is created (4)₃.

$$\frac{\partial}{\partial t} (\epsilon \rho_f e_f) + \text{div} \left[\epsilon \rho_f \left(e_f + \frac{p}{\rho_f} \right) \vec{v} \right] = \text{div} [\epsilon (\vec{q}_f^c + \vec{\tau}_c \vec{v})] + \epsilon \rho S_f, \quad (12)$$

$$\frac{\partial}{\partial t} [(1 - \epsilon) \rho_s e_s] = \text{div} [(1 - \epsilon) (\vec{q}_s^c)] + (1 - \epsilon) \rho S_s. \quad (13)$$

The influence of radiation at the moment is omitted. The works on the choice of the suitable radiation model are in progress. For correct temperature modeling appropriate heat conductivity coefficients of fuel cell elements are distinguished (Tab. 2). In the porous parts the effective heat transfer coefficient λ_{eff} should be investigated. Consequently solid and fluid part of that coefficient must be calculated. It is important to consider total heat conductivity coefficient value ($\lambda_{eff} = \epsilon \lambda_f + (1 - \epsilon) \lambda_s$). This factor should distinguish solid (λ_s) and gas (λ_f) parts of the fuel cell. Therefore, the aim of the work is to evaluate the influence of different heat conductivity coefficients on the reliability of calculations.

Additionally, to the describe mass flux \vec{J}_k in Eq. (4) diffusive mass transport coefficient is employed. It is possible to use the Fick gradient hypothesis or so called Stefan-Maxwell model [9]. The first one does not involved diffusion of one chemical component in another. In present analysis Fick model that do not include a significant error in a binary system (e.i. $\vec{J}_k = D_k \text{grad} Y_k$) was used. The appropriate diffusion coefficients of different species are presented below (D_k in Tab. 3). For porous parts this value is modified due to porosity (ϵ) and tortuosity (τ) of electrodes ($D_k^{eff} = D_k \frac{\epsilon}{\tau}$) [8].

In all fuel cell elements the current transport Eq. (4)₅ together with Eq. (11) is solved. The average current density \vec{i} is assumed to be constant and the electrical potential at the anode (ϕ_a) and cathode (ϕ_c) is calculated. The electrical potential (ϕ) is a function of species concentration and operating medium pressure. The total ideal voltage U_{ideal} of fuel cell

Table 3. Diffusion coefficient used during calculations.

D_k [m ² s ⁻¹]	
oxygen	$0.0000181 \cdot e^{\left(\frac{T}{273}\right)^{1.5}}$
hydrogen	$0.0000753 \cdot e^{\left(\frac{T}{273}\right)^{1.5}}$
nitrogen	$0.0000181 \cdot e^{\left(\frac{T}{273}\right)^{1.5}}$
steam	$0.0000364 \cdot e^{\left(\frac{T}{273}\right)^{1.5}}$

is equal to (in agreement with the Nernst equation):

$$U_{ideal} = \Delta E = -\frac{\Delta G^0}{2F} + \frac{RT}{2F} \ln \left(\frac{X_{H_2} \cdot X_{O_2}^{0.5}}{X_{H_2O}} \right) + \frac{RT}{2F} \ln p_o \quad [\text{V}]. \quad (14)$$

In reality, the following potential losses are considered [2]:

- activation losses

$$\eta_{act} = \frac{2RT}{nF} \operatorname{arc} \sinh \frac{i}{2i_0}, \quad i = |\vec{i}|; \quad (15)$$

- concentration losses

$$\eta_{conc} = \frac{RT}{nF} \ln \left(1 - \frac{i}{i_l} \right), \quad i = |\vec{i}|; \quad (16)$$

- ohmic losses

$$\eta_{ohm} = \frac{i}{\sigma}, \quad i = |\vec{i}|. \quad (17)$$

Hence, the actual cell voltage U is described by:

$$U = \phi_c - \phi_a = \Delta E - \eta_{act} - \eta_{conc} - \eta_{ohm} \quad [\text{V}]. \quad (18)$$

To evaluate the results following factors are calculated:

- fuel cell electric power

$$P = I \cdot U \quad [\text{W}]; \quad (19)$$

- fuel cell efficiency

$$\eta = \frac{P}{\dot{m}_{fuel} \cdot LHV} \quad (20)$$

where $I = i \cdot A$, I – average current A , \dot{m}_{fuel} – fuel mass flow rate, LHV – lower heating value of fuel.

3 Comparison of the different closures

Calculations for all cases were made for the same, boundary, inlet and outlet conditions. The aim of the present work is to evaluate the influence of different values describing material properties (such as electric and thermal coefficient, that are mainly temperature dependent). Changes of heat and electric coefficients result in different temperature fields. Therefore, voltage, efficiency and fuel cell power are different. Calculations are divided into 3 cases (see Tab. 1 and Tab. 2):

- **case 1:** thermal and electric conductivity based on Li work [5];
- **case 2:** thermal and electric conductivity based on Fergusson work [6];
- **case 3:** thermal and electric conductivity based on Campanari work [7].

The results are presented for constant value of air and fuel utilization factors which are: $U_{air} = 0.25$, $U_{fuel} = 0.80$ (in agreement with Hirano work [5]). These factors affect on the appropriate air and fuel mass flow rate at the cell inlets:

$$\dot{m}_{air} = \frac{iA_{cell}}{2FU_{air}} \cdot \frac{M_{O_2}}{X_{O_2}}, \quad \dot{m}_{fuel} = \frac{iA_{cell}}{2FU_{fuel}} \cdot \frac{M_{H_2}}{X_{H_2}}.$$

The analysis has been performed for different average current values: $i = 1000, 2000, 3000, 4000, 5000$ A/m². It allows to built efficiency and power characteristics of working fuel cell.

Magnitude of the electrical conductivity of electrolyte coefficient from Li [5] paper seems to be incorrect in comparison with the corresponding values from Fergusson [6] and Campanari [7] papers. Therefore the value of this coefficient was replaced with the one used by Campanari. Other values from work of Li are taken as in the original.

In Fig. 3 average static temperature for different heat and electric conductivity coefficients¹ is presented. Temperature values are strongly changing along anode what is presented in Fig. 4. The temperature changes result in different power and efficiency characteristics (Figs. 5a and 5b). Both characteristics are similar to the one from the work by Hirano.

¹The differences result from a different approach to obtain average temperature anode. In the numerical investigations the temperature is calculated as average along anode surface. From experiment there is no knowledge about the way how the temperature was measured.

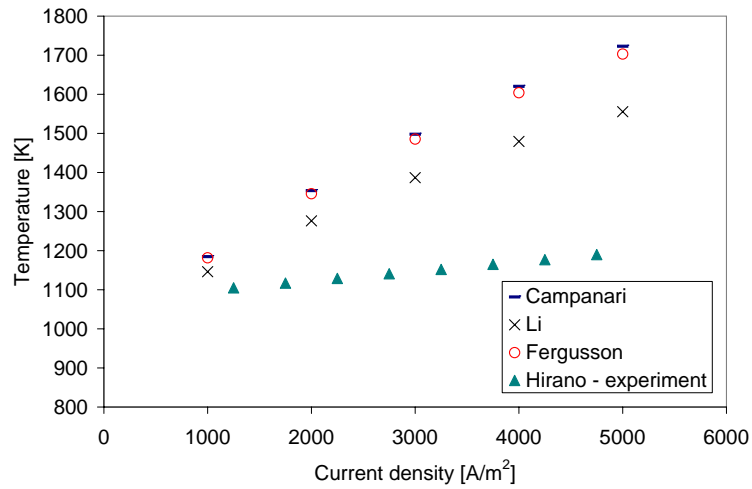


Figure 3. Average temperature of the working SOFC.

Additionally there is no knowledge about another properties describing correct SOFC modeling. In equations (15) and (16) two additional constant values are used: i_0 - exchange current density and i_l limiting current density (which depend on the used electrode materials). Both values can be adjusted to values which can give exactly same power and efficiency characteristics for numerical and experimental data. It is necessary to perform simulation with exactly the same material properties of appropriate fuel cells parts which are used in experiment.

Thermal and electric conductivity coefficients do not influence the species concentration, what is presented in Fig. 6–8 (for two most different cases). Hence, the obtained voltage is only a little bit modified (Fig.9 and 10 - for two most different cases). The voltage changes are compared to the results from the Hirano's experiment in the Fig. 11. The concentration losses have the biggest influence on the potential losses (Fig. 12)².

²The magnitude of the individual potential losses depends on the thickness of fuel cell components. For fuel cells where the electrolyte is much more thicker than electrodes the ohmic losses are the biggest. For other cases the ohmic losses are smaller than activation or concentration losses [10].

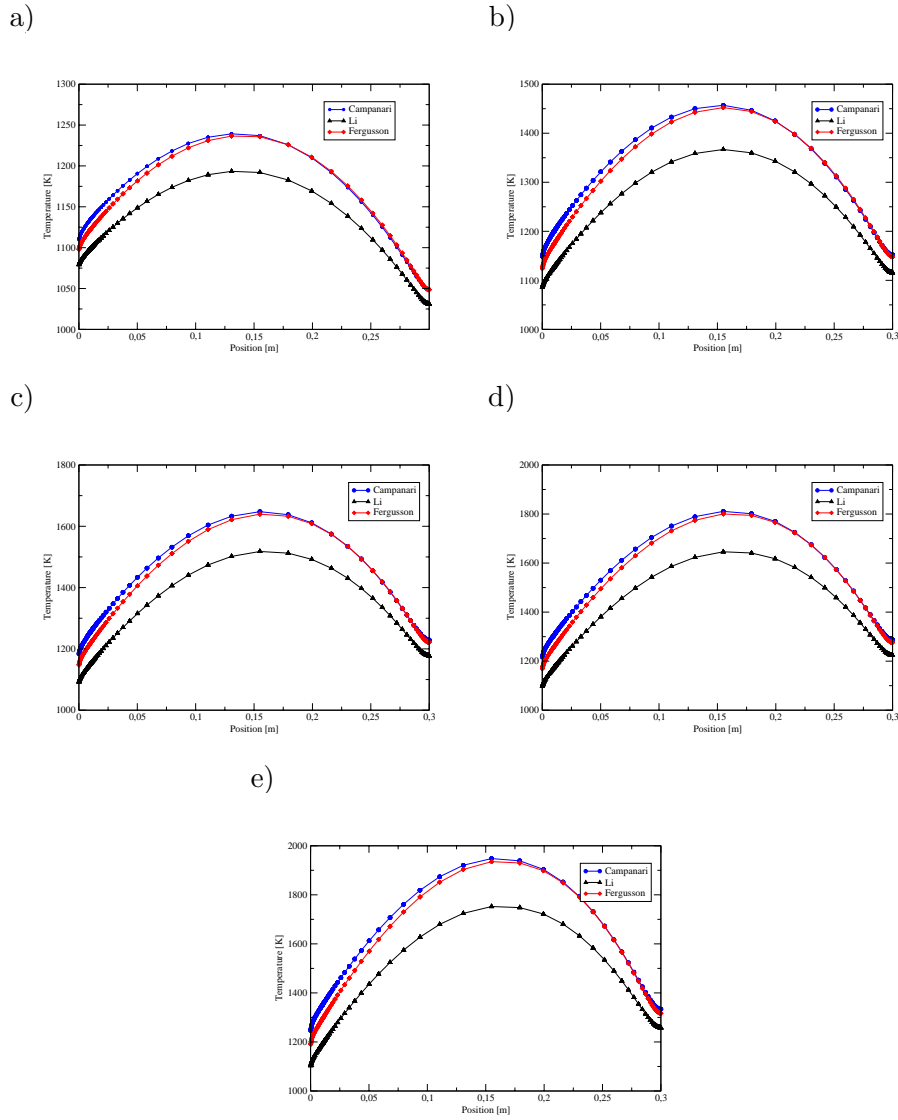


Figure 4. Average temperature calculated along the anode for different current densities: a) 1000, b) 2000, c) 3000, d) 4000, e) 5000 A/m^2 involved different calculated cases.

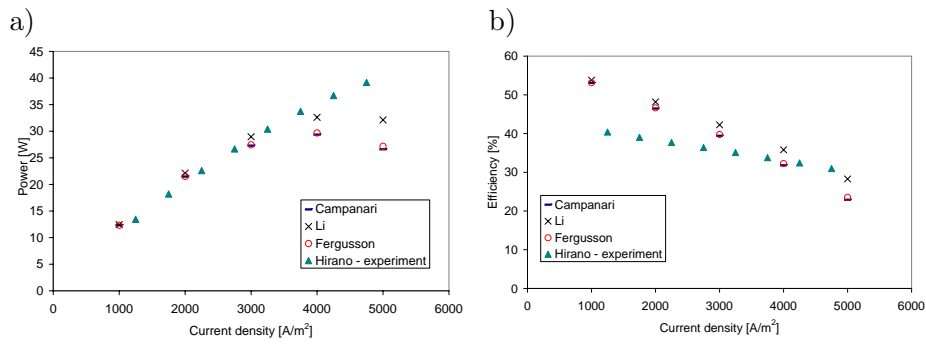


Figure 5. Power (a) and efficiency (b) characteristic of working fuel cell.

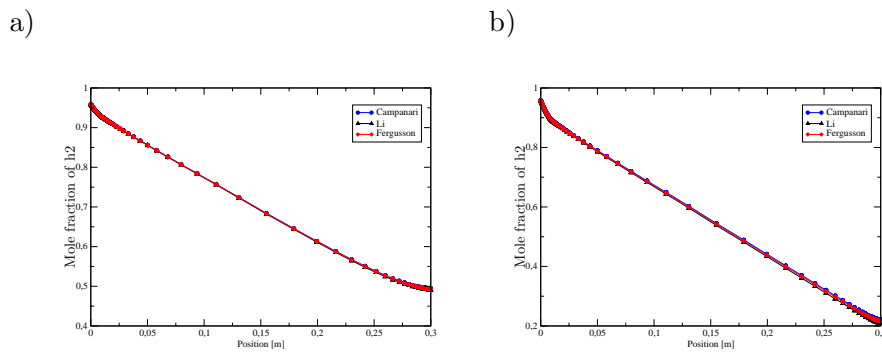


Figure 6. Hydrogen mole fraction Y_{h_2} for different current densities: a) 1000, b) 5000 A/m^2 involved different calculated cases.

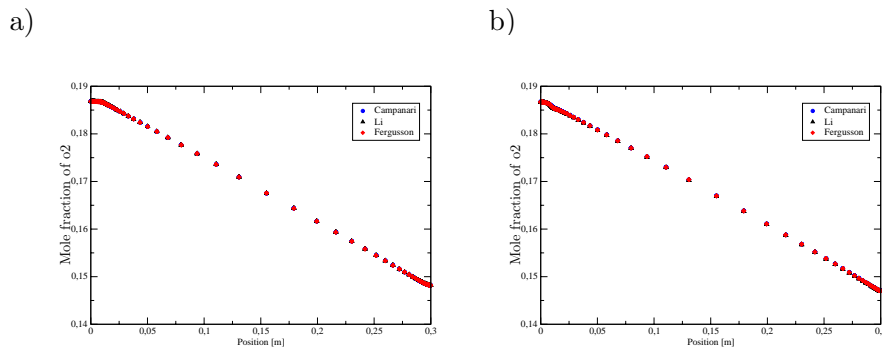


Figure 7. Oxygen mole fraction Y_{o_2} for different current densities: a) 1000, b) 5000 A/m^2 involved different calculated cases.

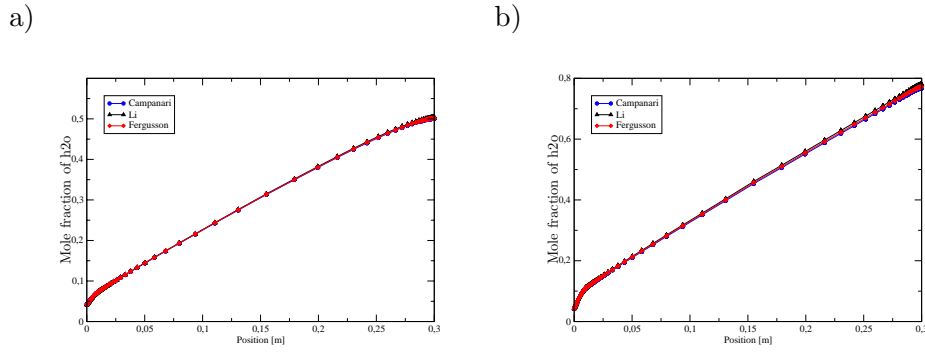


Figure 8. Steam mole fraction Y_{H_2O} for different current densities: a) 1000, b) 5000 A/m² involved different calculated cases.

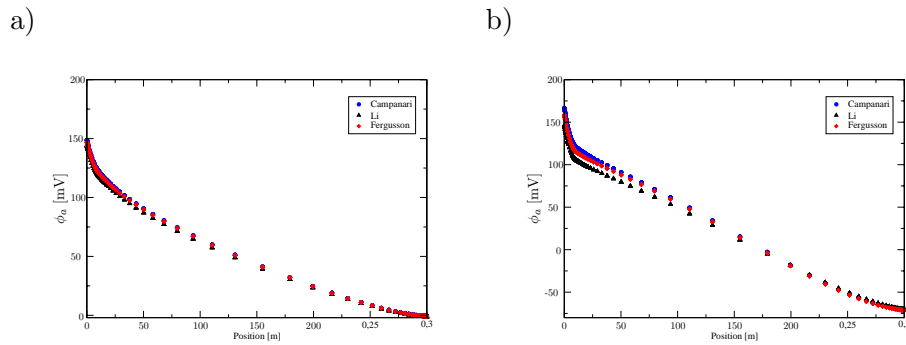


Figure 9. Potential distribution on the anode surface for different current densities: a) 1000, b) 5000 A/m² involved different calculated cases.

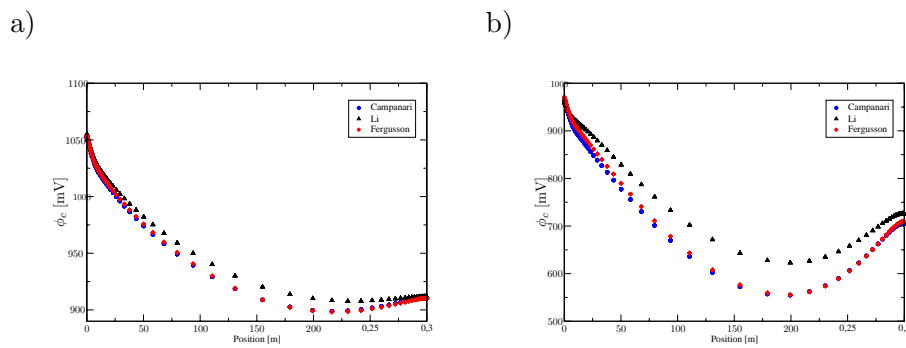


Figure 10. Potential distribution on the cathode surface for different current densities: a) 1000, b) 5000 A/m² involved different calculated cases

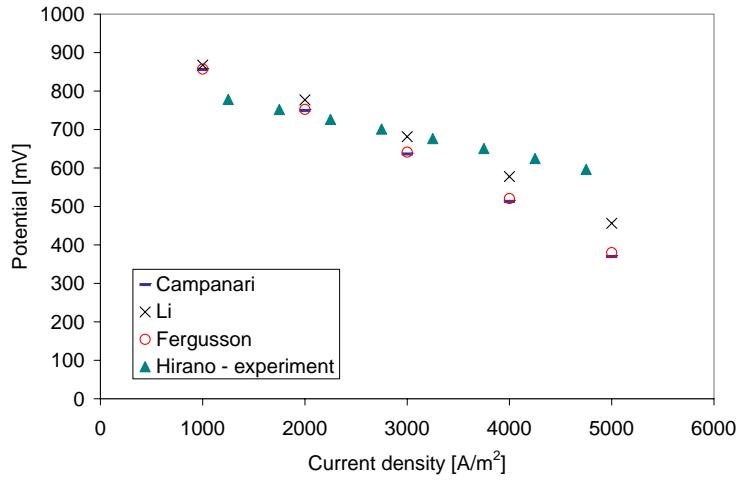


Figure 11. Obtained average potential U in the function of current density for working fuel cell.

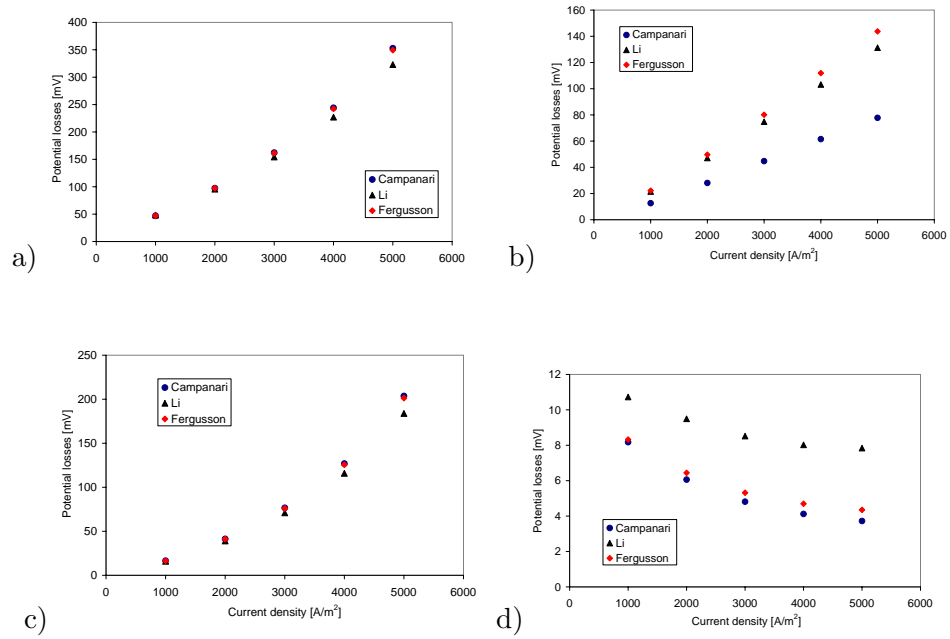


Figure 12. Potential losses for working fuel cell: a) sum of all losses, b) activation losses, c) concentration losses, d) ohmic losses.

4 Conclusions

The presented results show the differences between numerical and experimental data. It is necessary to make calculation and experiment for the same conditions. As a result it is possible to evaluate implemented mathematical model. Because authors of the paper do not have sufficient knowledge about experimental data it was necessary to use the data found in literature.

The temperature changes for all considered cases are similar. It increases for higher current densities. The character of temperature plot along the anode is also similar. Moreover the local species mole fraction along electrodes are the same. Obtained power and fuel cell efficiency keep the comparable shape for different cases. It allows to evaluate the implemented model. Despite the fact that there are changes in obtained temperature and potential values the model seems to be well prepared for further investigations. The obtained efficiency and power characteristics for different closures show how important is to use correct thermodynamical and material properties.

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