Termodynamická analýza procesů v palivových článkách s pevnými oxidy

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Specialization: General mathematics

Prague 2012
Acknowledgements

At first, I would like to thank my advisor prof. Ing. František Maršík, DrSc., who has provided me with a human view of the world through the terms of thermodynamics, as well as he has provided me a lot of valuable remarks and knowledge.

Hereafter, I would like to thank my colleague and friend Mgr. Michal Pavelka, who has helped me a lot with understanding thermodynamic notions and physically complicated issues.

Moreover, I would like to thank colleagues from Institute of Chemical Technology (ICT) for sharing the knowledge and experience with fuel cells, especially my gratitude belongs to my consultant Ing. Roman Kodým, PhD. (ICT), who has given me, amongst other, a practical view on solid oxide fuel cells.

Last but not least I would like to thank my family, my partner and my friends for their endless and unselfish support.

The need to formulate this work has appeared during the solution of the CEN-TEM project, reg. no. CZ.1.05/2.1.00/03.0088, which is co-funded by the ERDF as part of the Ministry of Education, Youth and Sports’ OP RDI programme.
I declare that I carried out this bachelor thesis independently, and only with the cited sources, literature and other professional sources.

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Název práce: Termodynamická analýza procesů v palivových článkách s pevnými oxidy

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Klíčová slova: teorie směsí, palivový článek, pevné oxidy, 1D model

Title: Thermodynamic analysis of processes in the solid oxide fuel cells

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Abstract: The fuel cells are the technology of the future. Although their discovery dates back to the 19th century the nature of how they work hasn’t been adequately explained so far. This thesis focuses on description of solid oxides fuel cells (SOFC) for which ion conductive electrolyte and high operating temperature are distinctive. The mathematical model of SOFC developed in this thesis is formulated in terms of the mixture theory. The model development was constrained and simplified by isothermality, time-stationery and 1D approximation. The model equations characterize gas and ion transport and electric current flow in the fuel cell. Eventually comparison of the thesis model equations with the SOEC (solid oxides electrolysis cell) model [6] developed at the Institute of Chemical Technology in Prague showed that both approaches lead to a similar conclusion. This thesis can be used as a basis for an experimental verification of the mixture theory.

Keywords: mixture theory, fuel cell, solid oxide, 1D model
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Introduction

The production of electric energy is supplied by wide range of power plants nowadays. By \[17\] about 65% of the world electric energy production has origin in the combustion of fossil fuel in 2009. The combustion produces heat, which is propagated to a medium. The heat of the medium is transformed into mechanical energy and finally the mechanical energy is transformed into electric energy. One can realize, that every energy transformation brings a loss of the energy into the electricity generation process, even more, we could realize that combustion is in fact an exchange of electrons between some molecules and so is the electricity! A question arises: whether a combustion enhancement exists, such that the electrons taking part in the combustion could be used as electric current? The answer is not so straightforward as one would wish, but for some specific types of fuel such devices were developed. Such a device is called a fuel cell and in principle the Fuel Cell transforms chemical energy which is accessible by fuel combustion into current directly by some kind of reactants separation. A wide range of fuel cells has been developed, it varies by operational temperature, ion transport principle, used fuel. Most known fuel cells use hydrogen as fuel, whose production neither transport is not very handy. Nevertheless, fuel cells able to combust natural gas or carbon oxide were developed, finally latter mentioned fuel could be steam reformed into the hydrogen \[9\].

The principle of the fuel cell function is known for more than 150 years \[9\], but there is still a lot of space for some improvement of the fuel cell description and consequently an increase of efficiency.

We try to employ a mixture theory for a description of Solid Oxide Fuel Cell (SOFC) operation in this thesis. In brief, the mixture theory we use is a multi-component continuum mechanics enhanced by non-equilibrium thermodynamics. We try to develop a simple SOFC model in terms of this theory.
Mathematical notation

A common mathematical notation, explained below, is used, let $n, k, l \in \mathbb{N}$.

- $\mathbb{R}^n$ denotes a real $n$-dimensional euclidean space with ordinary inner product

  \[ \mathbf{x}, \mathbf{y} \in \mathbb{R}^n : \mathbf{x} \cdot \mathbf{y} = \sum_{i=1}^{n} x_i y_i \]

  and norm

  \[ \mathbf{x} \in \mathbb{R}^n : ||\mathbf{x}||^2 = \sum_{i=1}^{n} x_i^2. \]

- Vector quantities are denoted by boldface and scalar quantities are plane.
- $\Omega \subset \mathbb{R}^n$ denotes an open bounded region.
- $\overline{\Omega}$ denotes the closure of the set $\Omega$ in $\mathbb{R}^n$.
- $\partial \Omega$ denotes the boundary of the set $\Omega$ in $\mathbb{R}^n$.
- $[\mathcal{C}^l(\Omega)]^k$ denotes the set of functions $f \in [\mathcal{C}^l(\Omega)]^k, f : \Omega \to \mathbb{R}^k$, whose arbitrary $l$-th partial derivative is continuous.
- The cross product is defined in $\mathbb{R}^3$ with cartesian coordinates as follows

  \[ \mathbf{x}, \mathbf{y} \in \mathbb{R}^3 : [\mathbf{x} \times \mathbf{y}]_i = \sum_{k=1}^{3} \sum_{j=1}^{3} \epsilon_{ijk} x_j y_k, \]

  where $\epsilon_{ijk}$ is the Levi-Civita symbol. The tensor product of $\mathbf{x}$ and $\mathbf{y}$ in cartesian coordinates is defined followingly

  \[ [\mathbf{x} \otimes \mathbf{y}]_{ij} = x_i y_j. \]

- Gradient and divergence operators are defined below for $f \in \mathcal{C}^1(\mathbb{R}^n)^k$ as follows

  \[ \nabla f = \begin{pmatrix} \frac{\partial f_1}{\partial x_1} & \cdots & \frac{\partial f_1}{\partial x_n} \\ \vdots & \ddots & \vdots \\ \frac{\partial f_k}{\partial x_1} & \cdots & \frac{\partial f_k}{\partial x_n} \end{pmatrix} \quad \text{gradient,} \]

  \[ \text{div} f = \sum_{i=1}^{n} \frac{\partial f_i}{\partial x_i} \quad \text{divergence } n = k. \]

- Let $\mathbf{e}, \mathbf{t}$ be second order tensors on $\mathbb{R}^n$, we define the dyadic product of $\mathbf{e}$ and $\mathbf{t}$ in the cartesian coordinates as

  \[ \mathbf{t} : \mathbf{e} = \sum_{i=1}^{n} \sum_{j=1}^{n} t_{ij} e_{ij}. \]
1. Solid Oxide Fuel Cells

1.1 Composition of the planar model

For simplicity we can imagine that a solid oxide fuel cell is composed of three plates in a sequence

- hydrogen electrode,
- electrolyte,
- oxygen electrode,

where electrodes are made of solid porous material which is electrically and ion conductive. The electrolyte is made of solid material which contains no pores and is ion conductive and as much as possible electrically insulating. Electrodes are connected by a electrically conductive interconnect such as illustrated in the Figure [1.1]. Usually the SOFC operates at a quite high temperature, from 800°C to 1100°C.

1.2 Basic operation scheme

The hydrogen inlet is on the side of the hydrogen electrode which is opposite to the electrolyte, analogously the oxygen inlet is placed on the side of the oxygen electrode opposite to the electrolyte. When the electrodes are connected by a electrically conductive interconnect as in Fig. [1.1] the following chemical reaction appears on the oxygen electrode–cathode:

\[
\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}.
\]

(1.1)

The oxygen ion migrates through the electrolyte which is in ion conductive contact with both electrodes and when appears in hydrogen electrode–anode the hydrogen combustion happens

\[
H_2 + O^{2-} \rightarrow H_2O + 2e^-.
\]

(1.2)

Then the water vapor outlet is managed and electrons are transported through the circuit as a current to the oxygen electrode.

Since the notion about the SOFC was roughly established, we can begin with the detailed description of SOFC operation and construction. However, before we advance in the SOFC description we establish the following nomenclature, which is widely used in the electro-chemistry.

**Anode** is the electrode where an oxidation takes place, in our case it is the hydrogen electrode with the hydrogen oxidation.

Conversely, **cathode** is the electrode where a reduction takes place, for us its the oxygen electrode where oxygen is reduced.
1.3 Materials and requirements

The high operation temperature is necessary, because the most frequently used ion (O$_2$) conductor ZrO$_2$ is not ion-conductive below temperature of about 800°C.

**Anode.** The anode is mostly composed of ion-conduction ceramics and electrically conductive metallic components, the absence of oxygen makes usage of nickel possible as a charge conductor. The zirkonia (ZrO$_2$) stabilised with yttria (Y$_2$O$_3$), abbreviated as YSZ, is commonly used ion-conductor. A porous cermet is made of latter mentioned, which is ion, electrically and gaseous conductive.

**Cathode.** The high-temperature oxygen presence demands strong oxidation resistivity of the cathode material. Strontium-doped lanthanum manganite (LSM) provides the conduction of ions and charge and is mostly used cathode material.

**Electrolyte.** Because electrolyte has to be only ion-conductive, it is composed purely of YSZ.

Once again we stress that both electrodes are quite porous (20%–40%) and that the electrolyte is gas impermeable. The high temperature is also very troublesome factor for SOFC sealing. Appropriate sealing production is challenging.

1.3.1 Triple phase boundary

The character of the chemical reactions (1.1), (1.2) demands the presence of charge conductive phase, ion-conductive phase and gaseous phase for the reaction occurrence. Hence, the only place where the reaction occurs is the contact of those three phases called the triple phase boundary (TPB). Therefore the presence of TPB is crucial for both electrodes. The TPB surface density $a_{TPB}$, $m^2$ is an important parameter of the electrode material.

1.4 Real SOFC

For our explanation a simplified SOFC has been introduced in the preceding text. The real solid oxide fuel cell construction and operation are more complex.

The effect of hydrogen adsorption mentioned in [3] is neglected in our SOFC model. We also do not specify how the gas is transported to the electrodes, thus implies that we neglect a non–uniform gas distribution at electrodes. Moreover, we assume that the electrolyte is gas impermeable and electrically insulating, in real world none of those properties is achieved.

1.4.1 SOFC shape

Our preferred cell geometry is the planar geometry, however more cell geometries were developed, for example the depicted tubular geometry in the Fig. [1.2]
Figure 1.1: SOFC operation scheme

Figure 1.2: Tubular cell – sectional view.
1.4.2 Stacking

The planar SOFC can easily be stacked and connected to achieve greater voltage. The triple Cathode–Electrode–Anode (CEA) in Fig.1.1 could be repeatably stacked into a stack as shown in Fig. 1.3. Each CAE neighbours with so-called interconnect plate with gas channels. The interconnect plates provide electric conductivity and the gas channels care about fuel inlet and water outlet.

1.5 Thermodynamic performance

The crucial question has not been asked yet. Why do the chemical reactions (1.1), (1.2) happen in SOFC and why is the electric current produced as a consequence? The answer is formulated in the following paragraphs.

1.5.1 Gibbs energy of water formation

The chemical reaction in SOFC can be written in the total form

\[ \text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}. \]  (1.3)

The hydrogen combustion \( (1.3) \) takes place in the nature, because water is much less reactive than hydrogen or oxygen. In terms of thermodynamics, the change in the Gibbs energy of hydrogen combustion is negative. At the standard state (25°C, 101kPa) the hydrogen combustion does not occur naturally because there is a big activation barrier, but the SOFC operates at temperatures of about 1073K or higher. At these temperatures the activation energy decreases rapidly and the Gibbs energy of combustion is still negative, so the reaction takes place in the cell. The Gibbs energy is shown below at the standard pressure for the standard temperature and the operation temperature, when water is vapor, values were obtained in [14].
Gibbs energy of hydrogen combustion at \( p = 101 \text{kPa} \) is

\[
T = 298.15 \text{K} : \quad \Delta^f G \approx -228,582 \frac{\text{kJ}}{\text{mol}}, \quad (1.4)
\]

\[
T = 1100 \text{K} : \quad \Delta^f G \approx -187,033 \frac{\text{kJ}}{\text{mol}}. \quad (1.5)
\]

Because the Gibbs energy of water formation is the maximum amount of non-expansion work that could be extracted from the reaction, apparently the combustion at lower temperature is more effective. The reason why SOFC need high temperature is ion conductivity of used materials. As a consequence, it is no need to use expensive platinum in the electrodes as a catalyst for lowering the reaction activation energy as it is done in the case of low temperature FC.

### 1.5.2 Efficiency

Hereby the question of the definition of the efficiency arises. The total energy that could be extracted from combustion of hydrogen is the formation enthalpy change \( \Delta^f H \), hence it is natural to define the efficiency as the electric work \( W_e \) done by the fuel cell in ratio to the enthalpy change due to the reaction

\[
\frac{\partial W_e}{\partial t} = i_e \cdot \nabla \phi_e, \quad [\text{W}], \quad (1.6)
\]

\[
\eta_{\text{thermal}} = \frac{W_e}{\Delta^f H} \quad (1.7)
\]

where \( i_e, \phi_e \) are electric current and electric potential, respectively. As it is stated in [12], we express the thermal efficiency with usage of the balance of energy

\[
T \Delta^f S = \Delta^f H - W_e \quad \iff \quad \eta_{\text{thermal}} = 1 - \frac{T \Delta^f S}{\Delta^f H} \quad (1.8)
\]

\[
\Delta G = \Delta H - T \Delta S - S \Delta T \quad \iff \quad \eta_{\text{theoretical}} = \frac{\Delta^f G}{\Delta^f H} = \eta_{\text{thermal}} \left( 1 - \frac{S \Delta T}{W_e} \right) \quad (1.9)
\]

Thus the theoretical efficiency has been presented, hence it is obvious that

\[
\eta_{\text{thermal}} \leq \eta_{\text{theoretical}}.
\]

For a better notion about the values of theoretical efficiency we mention the values of \( \text{H}_2\text{O(g)} \) formation enthalpy \( \Delta^f H \) taken from [14].

#### Enthalpy change of hydrogen combustion at \( p = 100 \text{kPa} \) is

\[
T = 298,15 \text{K} : \quad \Delta^f H \approx -241,826 \frac{\text{kJ}}{\text{mol}}, \quad (1.10)
\]

\[
T = 1100 \text{K} : \quad \Delta^f H \approx -248,460 \frac{\text{kJ}}{\text{mol}}. \quad (1.11)
\]

Therefore the theoretical efficiency for these temperatures is

\[
T = 298,15 \text{K} : \quad \eta_{\text{theoretical}} \approx 95\%, \quad (1.12)
\]

\[
T = 1100 \text{K} : \quad \eta_{\text{theoretical}} \approx 75\%. \quad (1.13)
\]

It might imply that the high temperature fuel cells are potentially less efficient than low temperature ones, but experience shows that the difference is not very significant due to the higher activation energy of \( \text{H}_2 \) at lower temperatures.
1.5.3 Theoretical voltage

The terms used in the part about the efficiency are in close connection with the theoretical cell voltage. The relation between the electrical work $W_e$ and the electrical potential $\phi_e$ is stated below

$$W_e = q \cdot \phi_e, \quad (1.14)$$

where $q$ is the exchanged charge. If $n$ moles of H$_2$ are combusted the exchanged charge is equal to the formula below [2]

$$q = 2 \cdot n \cdot N_A q_e = 2 \cdot n \cdot F, \quad (1.15)$$

because molecule of H$_2$ contains two electrons. We have introduced the $N_A = 6,022 \cdot 10^{23} \frac{1}{\text{mol}}$ as the Avogadro’s constant, $q_e = 1,602 \cdot 10^{-19}\text{C}$ as the charge of one electron and their product $F = 96,485\text{C mol}^{-1}$ as the Faraday’s constant. Provided that all the Gibbs energy of the $n$ mole H$_2$ combustion $\Delta^f G$ has been changed into the electrical work $W_e$. The theoretical potential $\phi_{\text{theoretical}}$ get values stated below

$$T = 298,15\text{K} : \quad \phi_{\text{theoretical}} = \frac{n\Delta^f G}{2nF} = 1,18\text{V} \quad (1.16)$$

$$T = 1100\text{K} : \quad \phi_{\text{theoretical}} = \frac{n\Delta^f G}{2nF} = 0,96\text{V}. \quad (1.17)$$
2. Theory of Mixtures

We are going to introduce a part of the Theory of Mixtures in this chapter. This theory provides a framework for the description of the Solid Oxide Fuel Cell (SOFC). The derivation of the theory is going to be quite brief and adapted for the purpose of the SOFC description, for more general, detailed and explained derivation see [11], [10], [12], [8], [18].

Let \( \Omega \subset \mathbb{R}^n, n \in \{1, 2, 3\} \) be bounded region. Let us suppose that there is a material point of mixture in every spatial point of \( \Omega \), so that there is no reason to distinguish between a spatial point and a material point. We define \( \Omega_T := \Omega \times (0, T), T \in (0, \infty) \) for the description of the mixture time-evolution.

2.1 Mixture

Our mixture is composed of \( N \) components, let \( \alpha \) denote a mixture component in the rest of the text, i.e. \( \alpha \in \{1, \ldots, N\} \). In every point of \( \Omega_T \) we define density of an \( \alpha \)-component \( \rho_\alpha \) as a smooth mapping of \( \Omega_T \) into \((0, \infty)\):

\[
\rho_\alpha : \Omega_T \to (0, \infty), \quad \rho_\alpha \in \mathcal{C}^1(\Omega_T), \quad \left[ \frac{\text{kg}}{\text{m}^3} \right].
\]  

Moreover, let us define total density of a mixture \( \rho \) as follows

\[
\rho = \sum_\alpha \rho_\alpha \mathrm{d} \alpha.
\]  

The description of mass distribution in the terms of densities could be easily turned into a molar concentration description if the molar weight is known for every component. The exchange of terms is very useful in an application:

\[
c_\alpha = \frac{\rho_\alpha}{\mathcal{M}_\alpha} \left[ \frac{\text{mol}}{\text{m}^3} \right] = \left[ \frac{\text{kg} \text{ mol}}{\text{m}^3 \text{ kg}} \right], \quad \mathcal{M}_\alpha \in \mathbb{R}, \quad \forall \alpha.
\]  

Furthermore let us define the velocity of a \( \alpha \)-component as a smooth mapping of \( \Omega_T \) into \( \mathbb{R}^n \), where \( n \) is the dimension of \( \Omega \). The velocity \( \mathbf{v}_\alpha \) describes the velocity of an \( \alpha \)-component in a spatial point \( x \in \Omega \) for every time \( t \in (0, T) \):

\[
\mathbf{v}_\alpha : \Omega_T \to \mathbb{R}^n, \quad \mathbf{v}_\alpha \in \mathcal{C}^1(\Omega_T).
\]  

Thus we can introduce the barycentric velocity \( \mathbf{v} \)

\[
\rho \mathbf{v} = \sum_\alpha \rho_\alpha \mathbf{v}_\alpha.
\]  

2.2 Law of Balance

Let \( \Phi \) denote extensive physical quantity represented by a mapping \( \Phi(\mathcal{V}, t) \) and its density \( \phi(x, t) \) that satisfies

\[
\forall \mathcal{V} \subset \Omega \forall t_0 \in (0, T) : \Phi(\mathcal{V}, t_0) = \int_{\mathcal{V}} \phi(x, t_0)dx,
\]  

(2.6)
both are sufficiently smooth. The time change of \( \Phi(V, t) \) for fixed volume \( V \) is
determined by the production of the quantity \( \Phi \) in the \( V \) and by the transport of
the quantity \( \Phi \) through the boundary \( \partial V \)
\[
\frac{d}{dt} \Phi(V, t) = J(\Phi) + S(\Phi).
\] (2.7)
The equation (2.7) is rather symbolic. More rigorous derivation is going to be
done for specific cases below. \[10\]

An application of the Balance Law is going to be done in the following para-
graphs, moreover the integral balance equations will be stated in differential form.
For this transformation the following theorems are necessary.

**Theorem** (Localization Lemma). Let \( \Omega \subset \mathbb{R}^k \) be an open set, let \( f \in C \). Following
assertions hold:

- \( f = 0 \) in \( \Omega \) iff \( \int_\sigma f \, dx = 0 \) for any open bounded set \( \sigma \subset \sigma \subset \Omega \).
- If \( a \in \Omega \), then
  \[
  \lim_{\text{diam}(\sigma) \to 0} \frac{1}{\text{meas}(\sigma)} \int_\sigma f \, dx = f(a) \quad (2.8)
  \]
where the limit is taken over all open sets \( \sigma \subset \sigma \subset \Omega \) such that \( a \in \sigma \) and
\[
\text{diam}(\sigma) := \sup_{x, y \in \sigma} |x - y| \quad x, y \in \sigma
\]
is the diameter of the set \( \sigma \).

**Proof.** For the proof see Feistauer \[5\]. \( \Box \)

**Theorem** (Divergence theorem). Let \( \Omega \subset \mathbb{R}^n \) be a bounded domain with a
Lipschitz-continuous boundary, let \( f \in [C^1(\Omega)]^n \). It holds that
\[
\int_\Omega \text{div} f \, dx = \int_{\partial(\Omega)} f \cdot n \, dS, \quad (2.9)
\]
where \( n \) is outer normal vector to \( \Omega \).

**Proof.** For the proof see Feistauer \[5\]. \( \Box \)

**Theorem** (Derivative of an integral along parameter). Let \( I \subset \mathbb{R} \) be an open
interval, let \( M \subset \mathbb{R}^n \) be a set and let \( f \) be a mapping \( f : I \times M \to \mathbb{R} \). Let the
following be hold:

- there exists an \( \alpha \in I \) such that the Lebesgue integral \( \int_M f(\alpha, x) \, dx \) is convergent,
- for all \( \alpha \in I \) the function \( f(\alpha, \cdot) \) is measurable in \( M \),
- there exists a function \( g : M \to \mathbb{R} \) such that \( g \in L(M) \) and
  \[
  \forall x \in M \forall \alpha \in I \quad \left| \frac{\partial f}{\partial \alpha}(\alpha, x) \right| \leq g(x).
  \]
The integral \( F(\alpha) := \int_M f(\alpha, x) \, dx \) is convergent for all \( \alpha \in I \) and the derivative of \( F \) exists and can be written in the following form

\[
\forall \alpha \in I : \quad \frac{\partial F}{\partial \alpha}(\alpha) = \int_M \frac{\partial f}{\partial \alpha}(\alpha, x) \, dx.
\] (2.10)

**Proof.** For the proof see Černý [4].

### 2.2.1 Balance of mass

Let us have an arbitrary open set \( V \subset \Omega \) with Lipschitz-continuous boundary. Our goal is to calculate a balance of mass of the \( \alpha \)-component in \( V \). Let us assume that the mass of the \( \alpha \)-component can be generated in chemical reactions with other components. Let \( \omega_{\alpha} \) be the density of production of the \( \alpha \)-component, such that the production of the component \( \alpha \) in \( V \) is equal to \( \int_V \rho_{\alpha} \omega_{\alpha} \, dV \). We obtain the mass balance of component \( \alpha \) in the following form

\[
\frac{\partial}{\partial t} \int_V \rho_{\alpha} \, dV = - \int_{\partial V} \rho_{\alpha} v_{\alpha} \cdot n \, dS + \int_V \rho_{\omega_{\alpha}} \, dV.
\] (2.11)

Hence we use the Derivative of an integral (2.10) and switch the partial time derivative with the integral sign on the left side of the equation. After that we employ the Divergence Theorem (2.9) for the first term on the right side of the equation and turn the surface integral into a volume integral and finally we apply the Cauchy localisation lemma (2.8), because the balance is valid for arbitrary set \( V \) with Lipschitz-continuous boundary, so we obtain

\[
\frac{\partial \rho_{\alpha}}{\partial t} = - \text{div} (\rho_{\alpha} v_{\alpha}) + \rho_{\omega_{\alpha}}.
\] (2.12)

We call the latter equation (2.12) Mass balance of the \( \alpha \)-component.

If chemical reactions between the mixture components are known we can express the production term in a way more useful for application

\[
\omega_{\alpha} = \sum_\gamma \frac{\nu_{\alpha \gamma}}{\rho} \zeta_\gamma, \quad \zeta_\gamma = \frac{\zeta_{\alpha}}{\nu_{\alpha \gamma}}, \quad \text{[mol m}^{-3}\text{s]}
\]

where \( \nu_{\alpha \gamma} \) is the stoichiometric number of the component \( \alpha \) in the reaction \( \gamma \) and \( \zeta_\gamma \) is the reaction rate of the reaction \( \gamma \) [1].

For the sake of not repeating the same or very similar arguments all over again. We are not going to derive the following balances in such a detailed way like the balance of mass. Nevertheless we have to mention that the assumption of theorems, necessary for the balance calculation are satisfied by conditions we put on the functions or regions that appear in the equations. Thus the following balances are derived correctly.

\[\text{2} \text{The dot } \dot{()} \text{ means the material derivative: } \dot{\zeta} = \frac{\partial \zeta}{\partial t} + \mathbf{v} \cdot \nabla \zeta.\]
2.2.2 Balance of momentum

From the law of momentum conservation it follows that the balance of momentum for all components is

$$\frac{\partial}{\partial t} \left( \sum_{\alpha} \rho_{\alpha} v_{\alpha} \right) = -\text{div} \left( \sum_{\alpha} \rho_{\alpha} v_{\alpha} \otimes v_{\alpha} - t^T \right) + \sum_{\alpha} \rho_{\alpha} F_{\alpha}, \quad (2.13)$$

where $t^T$ is the Cauchy’s stress tensor and $F_{\alpha}$ represents the external volume forces exerted on the component $\alpha$ such as gravitation force or electric force, expressed in $[\text{m s}^2]$. Hence we suppose that the Cauchy’s stress tensor exists for the mixture [18].

If the partial stress tensor $t_{\alpha}$ for the component $\alpha$ exists and all those satisfy $t = \sum_{\alpha} t_{\alpha}$, a separate balance of the momentum for each component is reachable:

$$\frac{\partial}{\partial t} (\rho_{\alpha} v_{\alpha}) + \text{div} (\rho_{\alpha} v_{\alpha} \otimes v_{\alpha} - t_{\alpha}) = \rho_{\alpha} F_{\alpha} + \rho_{\alpha} \Gamma_{\alpha}. \quad (2.14)$$

The $\Gamma_{\alpha}$ represents the internal interaction force exerted on the component $\alpha$ by other components of the mixture. If we sum the latter equation for all mixture components we obtain the balance of the momentum for the whole mixture, which implies that the internal interaction forces compensate:

$$\rho \Gamma = \sum_{\alpha} \rho_{\alpha} \Gamma_{\alpha} = 0. \quad (2.15)$$

2.2.3 Balance of angular momentum

We also balance the angular momentum for all components of the mixture 4

$$\frac{\partial}{\partial t} \int_{V} \left( x \times \sum_{\alpha} \rho_{\alpha} v_{\alpha} \right) dV = - \int_{\partial V} \left( \sum_{\alpha} x \times \left( \rho_{\alpha} v_{\alpha} (v_{\alpha} \cdot n) - t^T \cdot n \right) \right) dS + \int_{V} \left( \sum_{\alpha} x \times \rho_{\alpha} F_{\alpha} + \rho_{\alpha} M_{\alpha} \right) dV, \quad (2.16)$$

where the $x$ denotes the spatial point, $M_{\alpha}$ is the production of the angular momentum due to the component $\alpha$. As in [18] we assume that $M_{\alpha} = 0$, so we use the mechanics of non-polar continuum. Such a constraint along with (2.13) provides us the symmetry of the Cauchy stress tensor

$$t = t^T. \quad (2.17)$$

Furthermore we are not going to distinguish between $t^T$ and $t$.

---

3For the Cauchy’s stress tensor definition see [11] or [7].

4The stated angular momentum balance [2.16] is valid only for $\mathbb{R}^3$ due to the cross product.
2.2.4 Balance of kinetic energy

From multiplying the Balance of momentum equation (2.13) by the barycentric velocity \( v \) we obtain the balance of kinetic energy of a material point,

\[
\rho \left( \frac{\dot{v}^2}{2} \right) = - \text{div} \, v \cdot \left( \sum \alpha \rho_\alpha v_{D_\alpha} \otimes v_{D_\alpha} - t^T \right) + \left( \sum \alpha \rho_\alpha v_{D_\alpha} \otimes v_{D_\alpha} - t^T \right) : \nabla v + \sum \alpha \rho_\alpha F_\alpha \cdot v.
\]  (2.18)

2.2.5 Balance of total energy

Furthermore we assume that the external volume forces and the internal interaction forces are potential forces

\[
F_\alpha = \nabla \phi_\alpha \, \text{ and } \, \Gamma_\alpha = \nabla \gamma_\alpha
\]  (2.19)

which turn out to be very helpful for the definition of \( \varepsilon_\alpha \)–the specific total energy of component \( \alpha \)

\[
\varepsilon_\alpha = \frac{v_\alpha^2}{2} + u_\alpha + \phi_\alpha + \gamma_\alpha,
\]  (2.20)

\[
\frac{\partial (\rho_\alpha \varepsilon_\alpha)}{\partial t} = \frac{\partial}{\partial t} \left( \rho_\alpha \left( \frac{1}{2} v_\alpha^2 + u_\alpha + \phi_\alpha + \gamma_\alpha \right) \right) = \rho_\alpha \frac{\partial (\phi_\alpha + \gamma_\alpha)}{\partial t} - \text{div} \left( \rho_\alpha v_\alpha \left( \frac{1}{2} v_\alpha^2 + u_\alpha + \phi_\alpha + \gamma_\alpha \right) \right) - \text{div} \left( j_{\eta_\alpha} - t_\alpha \cdot v_\alpha \right) + \sigma(\varepsilon_\alpha)
\]  (2.21)

where \( \gamma_\alpha \) is the mechanical energy of the internal force interaction of the component \( \alpha \), \( \phi_\alpha \) is the energy of the external volume forces exerted on the component \( \alpha \), \( u_\alpha \) is the internal energy of the component \( \alpha \), \( \sigma(\varepsilon_\alpha) \) are other energetic interactions of the rest of the components, \( j_{\eta_\alpha} \) is the heat flux due to the component \( \alpha \).

2.2.6 Balance of internal energy

The balance of internal energy is obtained by the subtraction of the kinetic energy from the total energy. Before we introduce the balance of the internal energy we are going to define component diffusion fluxes \( j_{D_\alpha} \) and diffusion velocities \( v_{D_\alpha} \)

\[
v_{D_\alpha} = v_\alpha - v, \quad j_{D_\alpha} = \rho_\alpha v_{D_\alpha}.
\]  (2.22)

As it is stated in [12] we obtain the balance of internal energy for all components

\[
\rho \dot{u} = - \text{div} \left( \sum \alpha (j_{D_\alpha} u_\alpha - t_\alpha \cdot v_{D_\alpha}) + j_q \right) + t : \nabla v - \sum \alpha \rho_\alpha v_{D_\alpha} \otimes v_{D_\alpha} : \nabla v + \sum \alpha j_{D_\alpha} \cdot (F_\alpha + \Gamma_\alpha) - \sum \alpha \rho_\alpha (\phi_\alpha + \gamma_\alpha),
\]  (2.23)
\[ u = \sum_{\alpha} w_{\alpha} u_{\alpha}, \quad w_{\alpha} = \frac{\rho_{\alpha}}{\rho}, \]  

where \( w_{\alpha} \) is the molar mass fraction of the component \( \alpha \). The equation (2.24) is a particular form of the 1st law of thermodynamics for a material point of the mixture.

### 2.2.7 Balance of entropy

The local form of the 2nd law of thermodynamics is given by the equation below

\[
\frac{\partial (\rho s)}{\partial t} = -\text{div} (\rho \mathbf{v} s + \mathbf{j}(s)) + \sigma(s), \quad (2.25)
\]

\[
\sigma(s) = \rho \dot{s} + \text{div} \mathbf{j}(s), \quad (2.26)
\]

\[
\sigma(s) \geq 0.
\]

In the latter equation were introduced the entropy flux \( \mathbf{j}(s) \) and the entropy production \( \sigma(s) \), those are unknown quantities. Their actual form will be discussed in the following paragraph about the Non-equilibrium linear thermodynamics.

### 2.3 Non-equilibrium thermodynamics

We are going to employ the Classical irreversible thermodynamics (CIT) in the following derivation of the Mixture theory, before this usage we have to make some assumptions. CIT usually describes object called system, whose state is in the thermodynamical equilibrium. Systems in the state of equilibrium are fully characterized by state variables such as temperature, pressure, entropy, enthalpy etc. This requirement of global thermodynamical equilibrium would be rather limiting for our theory, thus we accept that the equilibrium have to be set locally. We mean that the state variables can be defined in local form.

Another possible interpretation of the assumption of the local thermodynamic equilibrium is that every material point represents a number of particles sufficient to be considered a macroscopic thermodynamic system and we assume that such a system is in the thermodynamic equilibrium.

#### 2.3.1 Gibbs definition of entropy

The basic assumption of CIT is the Gibbs definition of entropy [19] which is suitable for ideal mixtures of solid and fluids:

\[
T \dot{s} = \dot{u} - \frac{t_{el}}{\rho} : \dot{\mathbf{e}} - \sum_{\alpha} \mu_{\alpha} \dot{w}_{\alpha}. \quad (2.27)
\]

The symbol \( \mu_{\alpha} \) denotes a specific chemical potential of the component \( \alpha \), \( t_{el} \) is the elastic part of the Cauchy stress tensor, \( \mathbf{e} \) is the Euler deformation tensor, \( T \) is the thermodynamic temperature.

---

5For the Euler deformation tensor definition see [10] or [7].
We introduce the Gibbs energy, an important quantity for the following formulations

\[
g = \sum_{\alpha} w_{\alpha} \mu_{\alpha} = u - \frac{t_{el}}{\rho} : e - T s \tag{2.28}
\]

by application of the Gibbs-Duhem condition [12], we obtain the chemical potential form from Gibbs energy

\[
\mu_{\alpha} = u_{\alpha} - \frac{t_{el}}{\rho} : e_{\alpha} - T s_{\alpha}, \tag{2.29}
\]

\[
s = \sum_{\alpha} w_{\alpha} s_{\alpha} \quad \text{and} \quad e = \sum_{\alpha} w_{\alpha} e_{\alpha}, \tag{2.30}
\]

where \(s_{\alpha}\) is the entropy of the component \(\alpha\) and \(e_{\alpha}\) is the Euler deformation tensor of the component \(\alpha\).

Therefore the entropy balance is of the following form

\[
\rho T \dot{s} = -\text{div} \left( \mathbf{j}_q + \sum_{\alpha} \mathbf{j}_{D_{\alpha}} \cdot (u_{\alpha} \mathbf{I} - \frac{t_{\alpha}}{\rho}) \right) \tag{2.31}
\]

\[
+ \left( t_{el} + t_{dis} - \sum_{\alpha} \rho_{\alpha} \mathbf{v}_{D_{\alpha}} \otimes \mathbf{v}_{D_{\alpha}} \right) : (d + w)
\]

\[
+ \sum_{\alpha} \mu_{\alpha} \text{div} \mathbf{j}_{D_{\alpha}} - t_{el} : d + \sum_{\alpha} \mathbf{j}_{D_{\alpha}} : (\mathbf{F}_{\alpha} + \Gamma_{\alpha})
\]

\[
- \rho \sum_{\alpha} \omega_{\alpha} (\mu_{\alpha} + \phi_{\alpha} + \gamma_{\alpha}),
\]

where \(\nabla \mathbf{v} = d + w\), \(d\) and \(w\) is the symmetric and the antisymmetric part of \(\nabla \mathbf{v}\), respectively. The symbol \(t_{dis}\) denotes the dissipative part of the Cauchy’s stress tensor \(t\) such that

\[
t = t_{el} + t_{dis} \tag{2.32}
\]

is satisfied.

Hence we introduce the affinity \(A_{\pi}\) associated with the chemical reaction \(\pi\) and the electrochemical potential \(\mu_{\alpha}\) of the component \(\alpha\).

\[
A_{\pi} = -\sum_{\alpha} \nu_{\pi_{\alpha}} M(\mu_{\alpha} + \phi_{\alpha} + \gamma_{\alpha}) = -\sum_{\alpha} \nu_{\pi_{\alpha}} M_{\alpha} \mu_{\alpha}, \tag{2.33}
\]

\[
\mu_{\alpha} = \mu_{\alpha} + \phi_{\alpha} + \gamma_{\alpha}. \tag{2.34}
\]

We assume that only small deformations \(d = \dot{\mathbf{e}}\) occurs.

From all these considerations the entropy production and the entropy flux for
the mixture are derived in a quite satisfying form

\[
\sigma(s) = \left( j_q + \sum_{\alpha} j_{D\alpha} \left( u_{\alpha} I - \frac{t_{\alpha}}{\rho_{\alpha}} \right) \right) \cdot \nabla \left( \frac{1}{T} \right) \\
+ \frac{1}{T} \left( t_{dss} - \sum_{\alpha} \rho_{\alpha} v_{D\alpha} \otimes v_{D\alpha} \right) : d \\
- \sum_{\alpha} j_{D\alpha} \cdot \left( \nabla \left( \frac{\mu_{\alpha}}{T} \right) + \frac{F_{\alpha}}{T} + \frac{\Gamma_{\alpha}}{T} \right) + \sum_{\alpha} \frac{A_{\alpha} S_{\alpha}}{T} \geq 0, \quad (2.35)
\]

\[
j(s) = \frac{1}{T} \left[ j_q + \sum_{\alpha} j_{D\alpha} \mu_{\alpha} + \sum_{\alpha} j_{D\alpha} \left( u_{\alpha} I - \frac{t_{\alpha}}{\rho_{\alpha}} \right) \right]. \quad (2.36)
\]

### 2.3.2 Linear force-flux relations near the equilibrium

Since it is technically possible to achieve that the number of thermodynamic forces is the same as the number of thermodynamic fluxes [11], the entropy production can be formulated as a bilinear function of thermodynamic fluxes \( J_{\gamma} \) and thermodynamic forces \( X_{\gamma} \)

\[
\sigma(s) = \sum_{\gamma} J_{\gamma} X_{\gamma} \geq 0. \quad (2.37)
\]

From constitutive considerations it follows that the thermodynamic fluxes are functions of all thermodynamic forces, temperature, elastic part of stress tensor and molar fractions of all mixture components [11]:

\[
J_{\gamma} = J_{\gamma}(X_1, X_2, \ldots, T, t_{el}, w_1, w_2, \ldots, w_n). \quad (2.38)
\]

Moreover, we assume that the thermodynamical fluxes are sufficiently smooth, thus we can expand them around the equilibrium state. Before we do the expansion we note that at the equilibrium there are neither forces exerted nor fluxes flowing, thus \( X_{eq \gamma} = 0 \) and \( J_{eq \gamma} = 0 \). The expansion is

\[
J_{\gamma} = \sum_{\delta} \left( \frac{\partial J_{\gamma}}{\partial X_{\delta}} \right)_{eq} X_{\delta} + O(X_{\gamma}, X_{\delta}). \quad (2.39)
\]

Terms of order greater than one \( O(X_{\gamma}, X_{\delta}) \) are neglected, thus the linearized constitutive relations

\[
J_{\gamma} = \sum_{\gamma \delta} L_{\gamma \delta}(T, t_{el}, w_{\gamma}) X_{\delta} X_{\gamma} \quad \text{for} \quad L_{\gamma \delta}(T, t_{el}, w_{\gamma}) = \left. \frac{\partial J_{\gamma}(T, t_{el}, w_{\gamma})}{\partial X_{\delta}} \right|_{eq} \quad (2.40)
\]

are obtained. Now the positivity of the entropy production becomes handy

\[
\sigma(s) = \sum_{\gamma} J_{\gamma} X_{\gamma} = \sum_{\delta \gamma} L_{\delta \gamma} X_{\gamma} X_{\delta} \geq 0, \quad (2.41)
\]

because \( L_{\delta \gamma} = \left[ \frac{kg \cdot K \cdot s}{m^3} \right] \) matrix needs to be positive semi-definite bilinear form. Moreover, as in [12] by applying Onsager-Casimir relation we obtain the symmetry of

\[
L_{\delta \gamma} = L_{\gamma \delta}. \quad (2.42)
\]
3. Simple SOFC model

In this chapter the Theory of Mixtures from the preceding chapter is applied and a simple model of SOFC developed. We made the following fundamental simplifications:

- the spatial domain is one-dimensional bounded interval \([h, o] \subset \mathbb{R}\),
- we describe a time-stationary state, i.e. all time derivatives are zero,
- gases in the FC are ideal gases,
- temperature of the cell is constant \(T = 1100\text{K}\).

3.1 Model domain properties and components densities

Neglecting of the gravity force in the momentum balance (2.13) is reasonable, because we are dealing with ideal gases. We also suppose that the velocity of the solid part of our FC is zero. As a consequence we assume that the barycentric velocity is zero, because the weight of the solid parts of the SOFC is much greater than the weight of the moving gases inside the cell, thus it is implied that

\[
\mathbf{v} = 0 \implies \mathbf{v}_{D,\alpha} = \mathbf{v}_\alpha \text{ and } \mathbf{j}_{D,\alpha} = \mathbf{j}_\alpha, \tag{3.1}
\]

\[
g = 0. \tag{3.2}
\]

Nevertheless the gradient of the barycentric velocity is non-zero. Accordingly, we can reasonably fix the FC to the domain as it is shown in the Fig. 3.1. Furthermore we split the model domain into three sub-domains:

- \(A := [h, c]\) denotes the cathode, where the hydrogen oxidation takes part,
- \(E := (c, a)\) denotes the electrolyte, where the ion transport occurs,
- \(C := [a, o]\) denotes the anode, where the oxygen reduction appears,

![Figure 3.1: Position of model domain.](image-url)
where $h < c < a < o; \ a, c, h, o \in \mathbb{R}$. The anode and the cathode are porous, ion and electrically conductive solids. The electrolyte is on-conductive, electrically insulating solid without pores. The electrolyte is in ion-conductive contact with the electrodes. As the division of the domain is in correspondence with the SOFC structure we can apply the equations developed in the preceding chapter.

We have to stress that the solid parts do not take part in the chemical reactions occurring in the FC, even more their velocity is zero so there’s no need to make a mass balance of solid parts anyway. Pores in the electrodes are too small (radius about a micrometer) to be described by the continuum mechanics correctly. Therefore we suppose that each material point contains a lot of pores, thus from the macroscopic point of view the electrodes are homogeneous [18]. Hence we assume that every material point of the electrodes contains gaseous phase and is ion and electrically conductive. Thus it is reasonable to define the densities of hydrogen, oxygen and water vapor at the electrodes, because the diffusion through the electrolyte is negligible, we can define the $O_2, H_2O, H_2O$ density values as zero in $E$. Moreover, we can define the density of the electric charge and the density of ion all over the fuel cell. The enlisted properties below are reflecting the mentioned facts:

$$
\rho_\alpha, \rho_e, \rho_{O_2^-} : (h, o) \rightarrow [0, \infty), \\
\forall x \in A \cup C : \rho_\alpha(x) > 0, \\
\rho_{O_2^-}, \rho_\alpha, \rho_e \in C^1(A \cup E \cup C), \\
\forall x \in E : \rho_\alpha(x) = 0 \& \rho_e(x) = 0.
$$

The letter $\alpha$ denotes $H_2$ or $O_2$ or $H_2O$ vapor, $\rho_e$ is the density of the charge and $\rho_{O_2^-}$ is the density of $O_2^-$ ion.

### 3.2 Mass balance

In the case of the time-stationary situation the mass balance equation for an arbitrary component $\alpha$ has the form

$$
\text{div} \ j_\alpha = \sum_\gamma \nu_{\gamma\alpha} M_\alpha \dot{\zeta}_\gamma, \quad (3.3)
$$

where $j_\alpha = \rho_\alpha v_\alpha$ is the flux of the $\alpha$ component. Now we can specify the chemical reactions taking place in the fuel cell

$$
cathode: \quad H_2 + O_2^- \rightarrow H_2O + 2e, \quad (3.4) \\
anode: \quad O_2 + 2e \rightarrow O_2^- . \quad (3.5)
$$
3.2.1 Linear force-flux relation

The fluxes are determined by (2.40) hence for our model they give

\[ j_{O^2^-} = -\frac{L_{O^2^-}}{T} \nabla \mu_{O^2^-} - \frac{z_{O^2^-}}{T} \frac{F}{M_{O^2^-}} \nabla \phi_{\text{ion}}, \]  
(3.6)

\[ j_e = -L_{ee} \frac{F}{T} \nabla \phi_e, \]  
(3.7)

\[ j_{O_2} = -\frac{L_{O_2}}{T} \nabla \mu_{O_2}, \]  
(3.8)

\[ j_{H_2} = -\frac{L_{H_2}}{T} \nabla \mu_{H_2} - \frac{L_{H_2}}{T} \nabla \mu_{H_2O}, \]  
(3.9)

\[ j_{H_2O} = -\frac{L_{H_2O}}{T} \nabla \mu_{H_2O} - \frac{L_{H_2O}}{T} \nabla \mu_{H_2}. \]  
(3.10)

In the ion flux (3.6) the \( \phi_{\text{ion}}, [V] \), the Galvani potential of the ion-conductive phase, is introduced and \( z_\gamma \) is the number of the electrons exchanged by the \( O^2^- \) ion.

However the Onsager reciprocal relations (2.42) are valid, thus \( L_{\gamma\alpha} = L_{\alpha\gamma} \).

The coefficients \( \forall \alpha \in \{O_2, H_2, H_2O\} : L_{O^2^- \alpha} = 0 \) are equal to zero because the transport of the \( O^2^- \) ion is bounded to ion conductive solid. A similar argument is used for the charge flux

\[ \forall \alpha \in \{O_2, H_2, H_2O\} : L_{e \alpha} = 0. \]

And finally the coefficients

\[ L_{O_2H_2} = 0 \quad \& \quad L_{O_2H_2O} = 0 \]

are zero because the oxygen is not present in the anode, and vice versa hydrogen and water vapor are not present in the cathode hence their diffusive fluxes do not interfere. The final form of the \( L_{\gamma\phi} \) coefficient will be discussed later.

3.2.2 Butler-Volmer equation

Now we are going to focus on the source terms on the right-hand side in the equation (3.3). Generally the reaction rate \( \dot{\zeta}_\gamma \) is a function of the source/product concentration and reaction kinetic constant which is determined experimentally for each reaction mechanism and reaction environment [13]. We are going to characterize reaction rates in the following text. Our approach will result in Butler-Volmer equation (BVE) for the anode and the cathode. Let us change the notation of reaction rate to \( \dot{\zeta} = j \).

This approach seems to be the most natural in the case of the electric charge transport. The BVE for electric current at the triple phase boundary (TPB) is going to be derived similarly in Barbir [2] for proton exchange membrane (PEM) cell.

The electric charge passing through the SOFC has to be transported via \( O^2^- \) ions, hence all transported charge has to pass through the TPB and take place in the reactions occurring at the TPB. We have to realize that always there
are forward and backward chemical reactions are present in the FC, therefore the reaction rate is the difference between the rate of the forward reaction and the rate of the backward reaction. Let us focus on the anode environment, the forward reaction is the hydrogen oxidation with electron release

\begin{align}
\text{anode: } \quad \text{O}_2^{-} + H_2 & \xrightarrow{\text{forward - oxidation}} H_2O + 2e, \quad (3.11) \\
\text{cathode: } \quad \frac{1}{2}\text{O}_2 + 2e & \xrightarrow{\text{backward - reduction}} \text{O}^2-, \quad (3.12)
\end{align}

the opposing backward reaction is the water decomposition, i.e. hydrogen reduction and electron consummation. Overall reaction rate \( j \) per unit area is equal to

\[ j = j_f - j_b, \quad \text{[mol m}^{-2}\text{s}] \quad (3.13) \]

From the Faraday’s Law it follows how the electric current density is proportional to the overall reaction rate per area, i.e. charge transferred through the unit of TPB surface

\[ j_e = z_{\gamma} F j_{\gamma}, \quad \text{[A m}^{-2} \text{]} = \text{[C m}^{-2}\text{s]} \quad (3.14) \]

where \( F \) is the Faraday’s constant and \( z_{\gamma} \) is the number of the electrons involved in the reaction \( \gamma \) and \( j_{\gamma} \) is the reaction rate per unit area \([\text{mol m}^{-2}\text{s}]\). As it is suggested in [2] we accept that the rate of the reaction is in the following relation with the reactant concentration at the TPB

\[ j_f = k_f C_{H_2} \quad j_b = k_b C_{H_2O}, \quad (3.15) \]

where \( k_f, k_b \) are forward and backward reaction rate coefficient, respectively and \( C_{H_2O}, C_{H_2} \) are the surface concentrations of \( H_2O, H_2 \) powered to their stoichiometric coefficients. In the case of ideal gases, which are the only ones we assume in this model, surface concentrations in the equation (3.15) can be substituted by partial pressures as it is done below.

The Transition State Theory [2] implies that the latter coefficients are functions of Gibbs free energy of the reaction for the electrochemical reaction in FC

\[ k_{f/b} = k_{0, f/b} \exp \left[ \frac{\Delta G_{f/b}}{RT} \right]. \quad (3.16) \]

Here we use \( \Delta G_{f/b} \) as the Gibbs energy of the formation change of the forward/backward reaction. The change of the Gibbs free energy for electrochemical reaction is composed of two terms

\[ \Delta G_{\text{red}} = \Delta^f G_{\text{ch}} + \alpha_{\text{red}} F \eta_{\text{an}} \quad \text{and} \quad \Delta G_{\text{ox}} = \Delta^f G_{\text{ch}} - \alpha_{\text{ox}} F \eta_{\text{an}}, \quad (3.17) \]

where \( \eta_{\text{an}} = \phi_e - \phi_{\text{ion}} - \phi_{\text{eq}}^{\text{an}} \) is the anode overpotential and \( \phi_{\text{eq}}^{\text{an}} \) is the anode equilibrium potential, which is defined as a net potential of the anode TPB in the equilibrium, hence no fluxes are present. Both latter mentioned variables can be defined for the cathode too. Therefore \( j_{e, \text{an}} = 0 \) when \( \phi_{\text{eq}}^{\text{an}} \) is measured as net
potential. This $\phi_{\text{eq}}^{\text{an}}$ is the Nernst potential which is specified by Nernst equation [13], stated for the anode

$$\phi_{\text{eq}}^{\text{an}} = -\frac{\Delta G_{\text{an}}(T_{\text{eq}})}{2F} - \frac{RT_{\text{eq}}}{2F} \log \left( \frac{p_{H_2}^{\text{eq}}}{p_{H_2O}^{\text{eq}}} \right), \quad (3.18)$$

By subtraction of $j_0^e$ (3.19) from $j_e$ in (3.13) and employing equations (3.15), (3.16), (3.17), (3.14) we obtain the Butler–Volmer equation. Butler–Volmer equation is formulated for the anode (3.22) and the cathode (3.23) separately, where $j_0^\text{an/cat}$ the exchange current density at the state of the equilibrium, $p^{\text{eq}}$ are the pressures measured at this state, $\eta$ is the overpotential of whole cell:

$$\eta = \phi_e - \phi_{\text{ion}} - \phi_{\text{eq}}, \quad (3.20)$$

$$\phi_{\text{eq}}^{\text{an}} = \phi_{\text{eq}}^{\text{an}} - \phi_{\text{eq}}^{\text{cat}} = -\frac{\Delta f G_{\text{ch}}(T_{\text{eq}})}{2F} - \frac{RT_{\text{eq}}}{2F} \log \left( \frac{p_{H_2}^{\text{eq}}}{p_{H_2O}^{\text{eq}} \sqrt{p_{O_2}^{\text{eq}}/p_{\text{st}}^{\text{eq}}}} \right), \quad (3.21)$$

**Butler-Volmer equation**

$$j_{e, \text{an}} = j_0^e (3.19) \exp \left( \frac{\Delta f G_{\text{ch}}(T_{\text{eq}})}{RT_{\text{eq}}} \right) p_{H_2}^{\text{eq}} = k_{f, 0} \exp \left( \frac{\Delta f G_{\text{ch}}(T_{\text{eq}})}{RT_{\text{eq}}} \right) p_{H_2O}^{\text{eq}}. \quad (3.19)$$

$$j_{e, \text{cat}} = j_0^e \exp \left( \frac{\Delta f G_{\text{ch}}(T_{\text{eq}})}{RT_{\text{eq}}} \right) \sqrt{\frac{p_{O_2}^{\text{eq}}}{p_{\text{st}}^{\text{eq}}}} = k_{b, 0} \exp \left( \frac{\Delta f G_{\text{ch}}(T_{\text{eq}})}{RT_{\text{eq}}} \right) p_{H_2O}^{\text{eq}}. \quad (3.23)$$

The $\Delta f G(T_{\text{eq}})$ in the Gibbs energy of the water formation measured at the temperature $T_{\text{eq}}$ and the pressure $p^{\text{eq}}$. The referential pressure $p_o^{\text{eq}}$ represents the pressures at which the net current density was measured and it is are mostly chosen as the standard pressure 101kPa. Values of the anodic and the cathodic current exchange densities $j_0^\text{an/cat}$ can be obtained from Ni's article [15]. Values of the $\alpha_{o_x/o_y}$ coefficients are mostly taken as 1, −1, see [2]. The reaction rates are zero in the electrolyte, because there are no chemical reactions in the electrolyte.

The Butler-Volmer equation gives relation between the overpotential $\eta$ and the current density via description of the chemical reaction kinetics. Firstly the BVE is useful for the electric charge transport description, but we can also realize that the reverse usage of Ohm’s Law gives us the reaction rates for both chemical reactions on the TPB surface, hence when the TPB surface density $\alpha_{\text{TPB}}$, $[\text{m}^{-2}]$ is known we can easily deal with the source terms in the material balance equations (3.24).

$$\dot{\zeta}_{\text{an/cat}} = j_{e, \text{an/cat}} \frac{\alpha_{\text{TPB}}}{z_{\text{an/cat}} F}. \quad (3.24)$$

### 3.3 System of equations

Mass balance equations are going to be presented in a detailed form below. We don’t assume the $\mu_{O^2-}$ effect in the ion flux $j_{O^2-}$ (3.6), thus it can be neglected,
since its effect is much smaller than the effect of the ion potential $\phi_{\text{ion}}$.

$$\text{div} \ j_e = \nu_e, \gamma \frac{M_e}{F} j_e a_{\text{TPB}},$$  \quad (3.25)  

$$\text{div} \ j_{O_2^-} = \nu_{\text{ion}}, \gamma \frac{M_{O_2^-}}{2F} j_e a_{\text{TPB}},$$  \quad (3.26)  

$$\text{div} \ j_{H_2} = \nu_{H_2}, \gamma \frac{M_{H_2}}{2F} j_e a_{\text{TPB}},$$  \quad (3.27)  

$$\text{div} \ j_{H_2O} = \nu_{H_2O}, \gamma \frac{M_{H_2O}}{2F} j_e a_{\text{TPB}},$$  \quad (3.28)  

$$\text{div} \ j_{O_2} = \nu_{O_2}, \gamma \frac{M_{O_2}}{2F} j_e a_{\text{TPB}},$$  \quad (3.29)  

where $\gamma$ is the function of space $x$ and indicates which reaction is occurring, and is specified in the table (3.1). The symbol $j_e$ we also covers the current density at the cathode and the anode, in the electrolyte this term is zero, because we don’t assume any sources or sinks of anything in the electrolyte.

For further development the following chemical potential $\mu_\alpha$ formulation for ideal gases is used as it is derived in [16] for ideal mixture of ideal gases

$$\mu_\alpha(T, p_{st}, p_\alpha) = \mu_\alpha^0(T, p_{st}) + RT \log \frac{p_\alpha}{p_{st}},$$  \quad (3.30)  

$$\nabla \mu_\alpha(T, p_{st}, p_\alpha) = \frac{RT}{p_\alpha} \nabla p_\alpha, \quad \left[ \frac{\text{mol}}{\text{m}^3} \right]$$  due to isothermality, \quad (3.31)  

$$\nabla \mu_\alpha(T, p_\alpha) = \frac{RT}{M_\alpha p_\alpha} \nabla p_\alpha, \quad \left[ \frac{\text{J}}{\text{kg}} \right]$$  \quad (3.32)  

where $\mu_\alpha^0(T, p_{st})$ is the chemical potential of the component $\alpha$ measured at the temperature $T$ and the standard pressure $p_{st}$. The final form of the mass balance equations is reached by employing the latter equation (3.32) in (3.6), (3.7), (3.8), (3.9), (3.10) and substitution of these flux terms in the latter mentioned mass balance equations.

$$- \text{div} \left( L_{O_2} \frac{R}{M_{O_2}} \nabla p_{O_2} \right) = \nu_{O_2}, \gamma \frac{M_{O_2}}{2F} j_e a_{\text{TPB}},$$  \quad (3.33)  

$$- \text{div} \left( L_{\text{lee}} \frac{F}{M_e T} \nabla \phi_e \right) = \nu_e, \gamma \frac{M_e}{F} j_e a_{\text{TPB}},$$  \quad (3.34)  

$$- \text{div} \left( L_{O_2^-} \frac{2F}{TM_{O_2^-}} \nabla \phi_{\text{ion}} \right) = \nu_{\text{ion}}, \gamma \frac{M_{O_2^-}}{2F} j_e a_{\text{TPB}},$$  \quad (3.35)  

$$- \text{div} \left( L_{H_2} \frac{R}{M_{H_2}} \nabla p_{H_2} + L_{H_2} \frac{R}{M_{H_2O}} \nabla p_{H_2O} \right) = \nu_{H_2}, \gamma \frac{M_{H_2}}{2F} j_e a_{\text{TPB}},$$  \quad (3.36)  

$$- \text{div} \left( L_{H_2O} \frac{R}{M_{H_2O}} \nabla p_{H_2O} + L_{H_2} \frac{R}{M_{H_2}} \nabla p_{H_2} \right) = \nu_{H_2O}, \gamma \frac{M_{H_2O}}{2F} j_e a_{\text{TPB}},$$  \quad (3.37)  

Let us specify the force-flux coefficients. The $L_{\text{lee}}$ coefficient is proportional to the electric conductivity of the material, the $L_{\text{ion}}$ coefficient is conversely.
### 3.3.1 Diffusion coefficients and boundary conditions

Firstly the $L_{H_2O}$, $L_{H_2}$, $L_{H_2O}$ coefficients are zero in the electrolyte and the cathode, conversely for the $L_{O_2}$ is zero at the electrolyte and the anode. Moreover, the $L_{ee}$ is zero in the electrolyte, nevertheless we assume that the $L_{\gamma \alpha}$ coefficients are smooth functions. Hitherto, we have obtained 5 equations with 5 unknown functions.

We choose the inlet pressure of hydrogen and oxygen as natural boundary conditions

$$p_{H_2}(h) = p_{H_2}^{in}, \quad \frac{\partial p_{H_2}(o)}{\partial x} = 0,$$

$$p_{O_2}(o) = p_{O_2}^{in}, \quad \frac{\partial p_{O_2}(h)}{\partial x} = 0,$$

$$p_{H_2O}(h) = p_{H_2O}^{in}, \quad \frac{\partial p_{H_2O}(o)}{\partial x} = 0,$$

because the inlet pressures are easily adjustable parameters. The following boundary conditions are also reasonable

$$\phi_e(h) = \phi_{app}, \quad \phi_e(o) = 0,$$

$$\frac{\partial \phi_{ion}(h)}{\partial x} = 0, \quad \frac{\partial \phi_{ion}(o)}{\partial x} = 0,$$

because there are neither sinks nor source of $O^{2-}$ in the electrodes and the voltage needed by the load is also adjustable.

From the mathematical point of view the question of existence or uniqueness of a solution is very difficult to answer, even in 1D approximation, because the second derivative cannot be stripped of first derivative in the case of the hydrogen and the water vapor partial pressure.

---

**Table 3.1: Stoichiometric coefficients**

<table>
<thead>
<tr>
<th>$\gamma$</th>
<th>anode</th>
<th>electrolyte</th>
<th>cathode</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_{O_2 \gamma}$</td>
<td>0</td>
<td>0</td>
<td>$-\frac{1}{2}$</td>
</tr>
<tr>
<td>$\nu_{H_2 \gamma}$</td>
<td>-1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\nu_{H_2O \gamma}$</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$j_e \gamma$</td>
<td>$j_e, \text{ an}$</td>
<td>0</td>
<td>$j_e, \text{ cat}$</td>
</tr>
</tbody>
</table>

proportional to the ion conductivity of the material, which can be considered complementary to the electric conductivity coefficient. Proceeding with $\alpha$, $\alpha \in \{O_2, H_2O, H_2O\}$, these are proportional to $\alpha \ (\text{gas})$ self-diffusion coefficients and finally the $L_{H_2} \ H_2O$ coefficient is proportional to binary diffusion coefficient of the hydrogen in water vapor. In gas diffusion coefficients the porosity of the material is going to be counted in.

For further discussion about this system of equations we have to make few assumptions.

---
4. SOEC and SOFC model relation

This thesis was carried out in co-operation with the Faculty of Technology of the Institute of Chemical Technology in Prague (ICT). ICT research among other concerns about solid oxide electrolysis cells (SOEC). In fact, there is not a big difference between SOFC and SOEC simple models, hence we use a ICT experimental data in our model. The data which we use were extracted from Fischer’s Bachelor Thesis [6], where SOEC model is develop, here we are going to compare our and Fischers’ approach.

Firstly, we have to say, that apart from boundary conditions, models are, in fact, suitable for both kinds of solid oxide devices: electrolysers and cells. In general, the phenomenological description is common to both models. The next used method common for both models is the description of the relation of chemical kinetics and potential via Butler–Volmer equation. The first main difference is in flux terms where Fischers model do not a priori concern any relation of fluxes on other forces, but a posteriori it is fixed by usage of very complicated diffusion coefficients. The second main difference and advantage of Fischers model, is the non-isothermality, so the effects of temperature are better counted in.
Conclusion

Achieved goals

We have analysed thermodynamic processes in the solid oxide fuel cell. With this basis we have developed a time stationary 1D model of the SOFC in terms of mixture theory. Our approach is based on well verified Gibbs entropy definition which makes our model more general then the SOEC model developed at the ICT [6].

Undone goals

Unfortunately we have not solved the model equations neither analytically nor numerically due to limited time horizon and difficulties with the diffusion coefficient determination.

Future goals

We would like to continue with the SOFC model development in master thesis in this way

- specification of diffusion coefficients,
- variable temperature and consequences to force–flux relations,
- numerical solution of a such model equations,
- mathematical analysis of linearized model equations,
- improvement to 2D and real geometry, numerical solution.

The developed model has a potential to be expanded into a more sophisticated and precise form which would describe a real SOFC. Such a model could be used for predicting a real SOFC performance and more detailed inside processes for different SOFC geometries. Furthermore, the comparison of the model equations solution with experimental data can support the validity of Mixture theory. The model equations will be analyzed like a real example by PDE methods.


List of Tables

3.1 Table of stoichiometric coefficient due to location .................25
### List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tr>
<td>FC</td>
<td>fuel cell</td>
</tr>
<tr>
<td>SOFC</td>
<td>solid oxides fuel cell</td>
</tr>
<tr>
<td>SOEC</td>
<td>solid oxides electrolyser cell</td>
</tr>
<tr>
<td>CIT</td>
<td>classical irreversible thermodynamics</td>
</tr>
<tr>
<td>TPB</td>
<td>triple phase boundary</td>
</tr>
<tr>
<td>CEA</td>
<td>cathode–electrolyte–anode</td>
</tr>
<tr>
<td>ICT</td>
<td>Institute of Chemical Technology in Prague</td>
</tr>
<tr>
<td>PEM</td>
<td>proton exchange membrane</td>
</tr>
</tbody>
</table>
**Nomenclature**

**Greek symbols**

- $\Delta G_{\text{red/ox}}$: Gibbs free energy change due to the reduction/oxidation
- $\Delta f G$: Gibbs energy change of formation
- $\Delta f G_{\text{ch}}$: Gibbs free energy change due to the chemical reaction
- $\Delta f H$: enthalpy change of formation
- $\dot{\gamma}$: rate reaction of the reaction $\gamma$
- $\eta$: efficiency
- $\eta_{\gamma \alpha}$: stoichiometric coefficient of the component $\alpha$ in the reaction $\gamma$
- $\gamma_{\alpha}$: mechanical energy of the internal force interaction of the component $\alpha$
- $\mathcal{M}_{\alpha}$: molar mass of the component $\alpha$
- $\mu_{\alpha}$: chemical potential of the component $\alpha$
- $\mu_{\text{ea}}$: electrochemical potential of the component $\alpha$
- $\nu$: overpotential
- $\Omega$: bounded region
- $\omega_{\alpha}$: density of the production of the component $\alpha$
- $\Omega_T$: bounded region
- $\phi_{\alpha}$: energy of the external volume forces exerted on the component $\alpha$
- $\phi^{\text{eq}}$: net potential of the fuel cell in the equilibrium
- $\phi_e$: electric potential
- $\phi_{\text{ion}}$: Galvani potential in the ion conductive phase
- $\phi_{\text{theoretical}}$: theoretical voltage of the fuel cell
- $\rho$: density
- $\rho_{\alpha}$: density of the component $\alpha$
- $\sigma$: set
- $\sigma(\epsilon_{\alpha})$: other energetic interactions of the rest components
- $\sigma(s)$: production of the entropy
- $\varepsilon_{\alpha}$: specific total energy of the component $\alpha$
\( \Gamma_\alpha \) internal interaction force exerted on the component \( \alpha \)

Latin symbols

\( \mathcal{A}_\pi \) affinity of the chemical reaction \( \pi \)

\( \mathcal{C} \) set of continuous functions

\( \mathcal{V} \) volume

\( \mathbf{d} \) symmetric part of the velocity gradient \( \nabla \mathbf{v} \)

\( \mathbf{e} \) Euler tensor of the deformation

\( \mathbf{e}_\alpha \) Euler deformation tensor of the component \( \alpha \)

\( \mathbf{f} \) function

\( \mathbf{F}_\alpha \) external volume force exerted on the component \( \alpha \)

\( \mathbf{g} \) density of the gravity force

\( \mathbf{i}_e \) electric current

\( \mathbf{j}(s) \) entropy flux

\( \mathbf{j}_\alpha \) flux of the component \( \alpha \)

\( \mathbf{j}_{D\alpha} \) diffusion flux of the component \( \alpha \)

\( \mathbf{J}_\gamma \) thermodynamic flux

\( \mathbf{j}_{qs} \) heat flux due to the component \( \alpha \)

\( \mathbf{j}_q \) heat flux

\( \mathbf{J}_{eq\gamma} \) \( \gamma \)-th thermodynamical flux in state of the equilibrium

\( \mathbf{M}_\alpha \) production of the angular momentum due to the component \( \alpha \)

\( \mathbf{n} \) outer normal vector

\( \mathbf{t} \) Cauchy’s stress tensor

\( \mathbf{t}_{\text{dis}} \) dissipative part of the Cauchy’s stress tensor

\( \mathbf{t}_{\text{el}} \) elastic part of the Cauchy’s stress tensor

\( \mathbf{v} \) barycentric velocity

\( \mathbf{v}_\alpha \) velocity of the component \( \alpha \)

\( \mathbf{v}_{D\alpha} \) diffusion velocity of the component \( \alpha \)

\( \mathbf{w} \) antisymmetric part of the velocity gradient \( \nabla \mathbf{v} \)

\( \mathbf{X}_\gamma \) thermodynamic force
$X_{eq \gamma}$  \(\gamma\)-th thermodynamical force in state of the equilibrium

$a_{TPB}$ density of the triple phase boundary surface

$c_\alpha$ molar concentration of the component $\alpha$

$C_{H_2/H_2O}$ surface concentration of the $H_2/H_2O$

$F$ Faraday constant

$g$ Gibbs energy

$I$ interval

$j$ reaction rate

$j^0$ current exchange density

$j_b$ backward reaction rate

$j_f$ forward reaction rate

$j_{e \text{ an/cat}}$ current density at the anode/cathode

$k_{0/f/b}$ reaction rate constant due to the forward/backward reaction

$k_{f/b}$ reaction rate coefficient of the forward/backward reaction

$L_{\gamma\delta}$ linear constitutive relation coefficient

$M$ subset of $\mathbb{R}^n$

$N_A$ Avogadro number

$p_\alpha$ partial pressure of the gas $\alpha$

$p^{\text{in}}_\alpha$ inlet pressure of the gas $\alpha$

$p^{\text{out}}_{H_2O}$ hydrogen outlet pressure

$p^{\text{ref}}_\alpha$ referential pressure of the gas $\alpha$

$q$ charge

$q_e$ elementary charge

$R$ molar gas constant

$S$ entropy

$s$ specific entropy

$s_\alpha$ entropy of the component $\alpha$

$T$ thermodynamic temperature

$t$ time
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$u$</td>
<td>internal energy</td>
</tr>
<tr>
<td>$u_\alpha$</td>
<td>internal energy of the component $\alpha$</td>
</tr>
<tr>
<td>$w_\alpha$</td>
<td>molar mass fraction of the component $\alpha$</td>
</tr>
<tr>
<td>$W_e$</td>
<td>electric work</td>
</tr>
<tr>
<td>$z_\gamma$</td>
<td>number of the electrons exchanged by the reaction $\gamma$</td>
</tr>
<tr>
<td>$\mathbf{C}^n$</td>
<td>set of functions with continuous $n$-th partial derivatives</td>
</tr>
<tr>
<td>diam</td>
<td>diameter</td>
</tr>
<tr>
<td>meas</td>
<td>Lebesgue measure</td>
</tr>
</tbody>
</table>