

Research Article

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On the Efficiency of Electrochemical Devices from the Perspective of Endoreversible Thermodynamics

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Abstract: The current work presents a concept that deals with the production of entropy generated by non-equilibrium processes in consequence of mass and energy transfer. The often used concept of endoreversible thermodynamics is based on the non-realistic conjecture that the entire entropy production is realized at the system boundary. In this contribution, an open system in a thermodynamically non-equilibrium state is assumed. Production of entropy is generated due to non-equilibrium processes accompanied by energy conversion. The steady state of the system is maintained by a negative entropy flux. The conclusions for expansion energy conversion, i. e., thermal machines, confirm the general outcomes of the endoreversible thermodynamics. However, the presented conclusions related to non-expansion energy conversion offer a new perspective on the principle of minimum entropy production and the corresponding stability conditions at steady state. The analysis of the energy conversion in closed cycles is presented for fuel cells, i. e., non-expansion energy conversion. The efficiency of the energy conversion is maximal at zero power output. Moreover, the efficiency of the fuel cells, and consequently the efficiency of all non-expansion energy conversion processes, depends on the load and then the maximal possible efficiency can be determined.

Keywords: expansion work, non-expansion work, dynamic equilibrium, endoreversible thermodynamics, efficiency, fuel cells

1 Introduction

Transformation of energy from one form into another can be generally performed in two ways. The first and the most applied way is the transformation of thermal (chemical) energy into mechanical energy by an expansion, expressed via the term $p dV$ [1]. This transformation is used for the thermodynamic analysis of combustion engines, gas and steam turbines, etc. The second possible transformation of energy can be realized by so-called non-expansion, expressed usually via the term $V dp$ [1]. This transformation is applicable in the analysis of hydraulic pumps, by the term $V dp$, or fuel cells and batteries, by the term W_{el} , i. e., devices generating the electric power.

The concept of endoreversible thermodynamics assumes that all irreversibilities may be treated as a transport of heat and/or mass from a source to a sink, as stated in [2, 3, 4, 5, 6] and references therein. The

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presented approach slightly differs from the endoreversibility concept and it is connected with the principle of minimum entropy production and with the attenuation of fluctuations of all thermodynamic quantities. The basic assumption is that, at steady state, the system is stable so that all deviations of the state parameters from this steady state must be reduced. In principle, it is Prigogine's theory [7, 8] extended with the conditions to entropy changes at the system boundaries. This approach allows one to suggest a connection between the efficiency, the transport properties, and the electrolytic membrane properties related to electrochemical devices, e. g., fuel cells and electrolyzers.

The paper is structured in the following way: Firstly, energy balance and entropy balance, necessary for the further analysis, are introduced. Secondly, the conditions of the steady-state stability and the relation to the endoreversibility concept are discussed. The following section deals with principles of the non-expansion work and its application to fuel cell performance. The manuscript ends with a summary and some general conclusions.

2 Balance of energy and balance of entropy

The steady operation has to comply with the balance of energy and balance of entropy expressed via energy fluxes, i. e., the heat flux \mathcal{J}_q and enthalpy flux \mathcal{J}_{Dh} . Transformation of chemical or heat energy into non-expansion work can be formulated by the thermodynamic property enthalpy, H , as [1, 6]

$$\mathcal{J}_q + \mathcal{J}_{Dh} = \dot{H} + \dot{W}_{nexp}, \quad (1)$$

where the non-expansion power is generated during an increase of pressure without changes in volume, i. e., $\dot{W}_{nexp} = -V\dot{p}$, or electric power, i. e., $\dot{W}_{nexp} = \dot{W}_e$ [1]. The total heat and enthalpy fluxes are defined as

$$\mathcal{J}_q = - \int_A \mathbf{j}_q \mathbf{d}\mathbf{a}, \quad \mathcal{J}_{Dh} = - \int_A \sum_{\alpha} \mathbf{j}_{D_{\alpha}} h_{\alpha} \mathbf{d}\mathbf{a}. \quad (2)$$

The enthalpy flux, \mathcal{J}_{Dh} , supplies energy and mass into the system across the system boundary.

The balance of entropy, expressed in terms of the global form of the second law of thermodynamics, serves also as a measure of the steady operation and has the following form:

$$\dot{S} - \mathcal{J}(S) = \mathcal{P}(S) \geq 0, \quad (3)$$

where the entropy flux, $\mathcal{J}(S)$, through the system boundary, A , can be divided into the following partial fluxes:

$$\begin{aligned} \mathcal{J}(S) &= - \int_A \mathbf{j}(s) \mathbf{d}\mathbf{a} = - \int_A \left(\frac{\mathbf{j}_q}{T} + \mathbf{j}_{D_{\alpha}} s_{\alpha} \right) \mathbf{d}\mathbf{a} \\ &= - \int_A \frac{\mathbf{j}_q}{T} \mathbf{d}\mathbf{a} - \int_A \frac{\sum_{\alpha} \mathbf{j}_{D_{\alpha}} h_{\alpha}}{T} \mathbf{d}\mathbf{a} + \int_A \frac{\sum_{\alpha} \mathbf{j}_{D_{\alpha}} \mu_{\alpha}}{T} \mathbf{d}\mathbf{a} \\ &= \mathcal{J}_q(S) + \mathcal{J}_{Dh}(S) - \mathcal{J}_{Dg}(S), \end{aligned} \quad (4)$$

where s denotes the specific entropy, \mathcal{J}_q is the heat flux, \mathcal{J}_{Dh} is the flux of enthalpy H or the specific enthalpy h , and \mathcal{J}_{Dg} is the flux of the Gibbs free energy G , which may be also expressed in term of the chemical potential μ_{α} [7, 9]. The last term of expression (3) is the global production of entropy $\mathcal{P}(S) = \sum_{\alpha} J_{\alpha} X_{\alpha} \geq 0$, usually formulated by the thermodynamic forces X_{α} and thermodynamic fluxes J_{α} , as shown in [8, 9, 10].

We suppose that a thermodynamic system is in a reference state with a total entropy S_0 . This state can be equilibrium or non-equilibrium. Nevertheless, due to interaction with the surrounding and internal non-equilibrium, this entropy changes (fluctuates). We can expand the actual change of the entropy in this reference state as

$$\dot{S} = \dot{S}_0 + \delta \dot{S}_0 + \frac{1}{2} \delta^2 \dot{S}_0 + \dots \quad (5)$$

Similarly we expand the entropy flux, which describes the interaction with the surrounding,

$$\mathcal{J}(S) = \mathcal{J}(S_0) + \delta\mathcal{J}(S_0) + \delta^2\mathcal{J}(S_0), \quad (6)$$

and the entropy production, which demonstrates internal irreversible processes,

$$\mathcal{P}(S) = \mathcal{P}(S_0) + \delta\mathcal{P}(S_0) + \delta^2\mathcal{P}(S_0). \quad (7)$$

Inserting the above expansions in the balance equation (3) we can organize the corresponding terms as follows:

$$\underbrace{\dot{S}_{\text{eq}} - \mathcal{J}(S_{\text{eq}})}_{=0, \mathcal{P}(S_{\text{eq}})=0} + \underbrace{\delta\dot{S}_0 - \delta\mathcal{J}(S_0) - \mathcal{P}(S_0)}_{\geq 0} \quad (8)$$

$$+ \underbrace{\frac{1}{2}\delta^2\dot{S}_0 - \delta^2\mathcal{J}(S_0) - \delta\mathcal{P}(S_0) - \delta^2\mathcal{P}(S_0)}_{\rightarrow 0 \text{ non-equilibrium processes inside}} = 0 \quad (9)$$

with the following physical interpretation:

$$\dot{S}_{\text{eq}} = \mathcal{J}(S_{\text{eq}}), \quad \text{for } \mathcal{P}(S_{\text{eq}}) = 0 \quad \text{for an equilibrium state } S_0 = S_{\text{eq}}, \quad (10)$$

$$\delta\dot{S}_0 - \delta\mathcal{J}(S_0) = \mathcal{P}(S_0) \geq 0, \quad \text{or} \quad (11)$$

$$\dot{S} - \mathcal{J}(S) = \mathcal{P}(S) \geq 0 \quad \text{for a non-equilibrium state } S = S_0.$$

The reference state S_0 is stable under the following conditions:

$$\delta\mathcal{P}(S_0) = 0 \quad \text{and} \quad \delta^2\mathcal{J}(S_0) = 0 \quad (\text{extremum of entropy production}), \quad (12)$$

$$\frac{1}{2}\delta^2\dot{S}_0 = \delta^2\mathcal{P}(S) = \sum_{\alpha} \delta J_{\alpha} \delta X_{\alpha} \geq 0 \quad (\text{condition of minimum}). \quad (13)$$

The extremum (minimum) of the entropy production $\delta\mathcal{P}(S_0) = 0$ was formulated by Prigogine (see, e. g., [8, 11]), and the additional condition for the internal entropy flux $\delta^2\mathcal{J}(S_0) = 0$ can be interpreted as endoreversible entropy flux. The inequality (13) is the condition of the minimum ($\delta^2\mathcal{P}(S) \geq 0$) and its physical interpretation relates to the attenuation of the fluctuations, or in other words, the condition of stability; see [8].

3 Energy conversion through non-expansion work

The energy conversion without volumetric changes is called non-expansion transformation of energy. A general scheme of these processes is depicted in Fig. 1.

As an example of the non-expansion energy conversion, the generation of electric power from chemical energy of hydrogen in a polymer electrolyte membrane fuel cell (PEMFC) will be investigated. The energy fluxes, which are necessary for a theoretical description of the energy conversion in a PEMFC, are schematically depicted in Fig. 2. Note that elementary principles of a PEMFC are shown in Fig. 3.

As shown in Fig. 2, the incoming flux of reactants, \mathcal{J}_{Dh1} , and the outgoing flux of products, \mathcal{J}_{Dh2} , are assumed to be represented by the fluxes

$$\mathcal{J}_{Dh1} = - \int_{A_{in1}} \sum_{\alpha} \mathbf{j}_{Dh\alpha} h_{\alpha} d\mathbf{a}, \quad \mathcal{J}_{Dh2} = \int_{A_{out2}} \sum_{\alpha} \mathbf{j}_{Dh\alpha} h_{\alpha} d\mathbf{a}. \quad (14)$$

The volume V_{in} contains the anode gas diffusion layer (GDL-A) and the anode catalyst layer (CL-A). A reactant enters V_{in} through the surface A_{in1} against the direction of the outer normal. Analogously, the cathodic

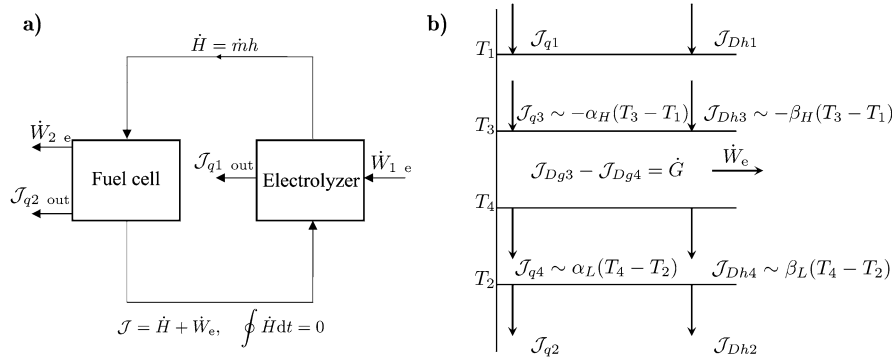


Figure 1: Energy conversion through non-expansion work in closed cycle. (a) Energy conversion in an electrochemical cell. The incoming energy flux contains the energy flux \dot{W}_{1e} needed for the chemical reactions, e. g., water electrolysis, and corresponding heat loss flux $\mathcal{J}_{q1\ out}$, so that $\mathcal{J}_{in} = \mathcal{J}_{q1\ out} + \dot{W}_{1e}$. Outgoing energy flux is $\mathcal{J}_{out} = \mathcal{J}_{q2\ out} + \dot{W}_{2e}$, where \dot{W}_{2e} is the electric power of a fuel cell. (b) Scheme of fluxes in a device generating non-expansion work.

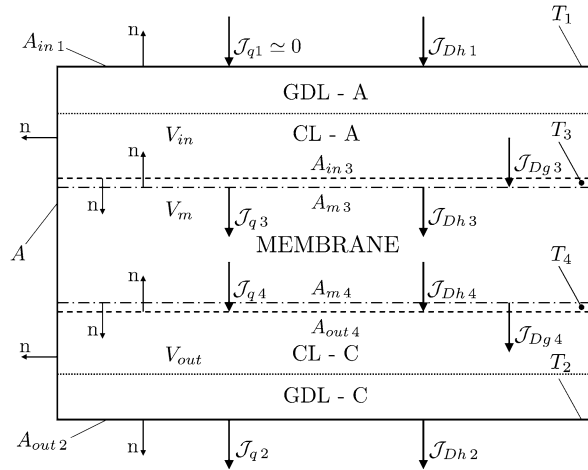


Figure 2: Heat and enthalpy fluxes in fuel cell components and corresponding temperatures. A fuel cell has the whole volume $V = V_{in} \cup V_m \cup V_{out}$ with the surface A . The volume is divided into three components; in the volume V_{in} reactants are transported and activated, in the volume V_m ions are transported due to the generated electric field, and in the volume V_{out} the chemical reaction takes place and products are removed from the fuel cell. Note that the fluxes flow through respective oriented surfaces.

part of the PEMFC has the volume V_{out} containing the cathode gas diffusion layer (GDL-C) and the cathode catalyst layer (CL-C). Through the surface $A_{out\ 2}$ a product, produced water, leaves the system. The additional heat fluxes entering and leaving the system are represented by \mathcal{J}_{q1} and \mathcal{J}_{q2} , as indicated in Fig. 2. So, the heat fluxes can be written as

$$\mathcal{J}_{q1} = - \int_{A_{in\ 1}} \mathbf{j}_q \mathbf{d}\mathbf{a}, \quad \mathcal{J}_{q2} = \int_{A_{out\ 2}} \mathbf{j}_q \mathbf{d}\mathbf{a}. \tag{15}$$

Then, balance of energy, equation (1), is rewritten in the following form:

$$\begin{aligned} \mathcal{J}_{in} - \mathcal{J}_{out} &= \mathcal{J}_{q1} + \mathcal{J}_{Dh1} - (\mathcal{J}_{q2} + \mathcal{J}_{Dh2}) = \dot{H} + \dot{W}_{nexp}, \\ \mathcal{J}_{in} &= \mathcal{J}_{q1} + \mathcal{J}_{Dh1}, \quad \mathcal{J}_{out} = \mathcal{J}_{q2} + \mathcal{J}_{Dh2}. \end{aligned} \tag{16}$$

The energy conversion is achieved in a closed cycle, so the enthalpy as a state variable follows the relation $\oint \dot{H} dt = 0$. This means that the enthalpy of a reactant, i. e., hydrogen for the PEMFC, is zero in the cyclic process. It does not mean that this closed cycle is reversible. Analogously to thermal machines, where the

limiting transformation of energy is given by the Carnot efficiency, transformation of the chemical energy into electric power is limited by the theoretical efficiency $\eta_{th} = \Delta G/\Delta H$.

The steady cyclic process consists of the electrolysis and the electric power generation. So, the change in enthalpy is zero, i. e., $\dot{H} = 0$, and this equation holds even in steady state; see Fig. 1. Then, the balance of energy, equation (16), becomes

$$\mathcal{J}_{in} - \mathcal{J}_{out} = \dot{W}_{nexp} \quad (17)$$

$$\text{and for the efficiency } \eta = \frac{\dot{W}_{nexp}}{\mathcal{J}_{in}} \rightarrow \mathcal{J}_{in} = \frac{\dot{W}_{nexp}}{\eta}, \mathcal{J}_{out} = \frac{1-\eta}{\eta} \dot{W}_{nexp}.$$

The total efficiency is defined as the ratio of the non-expansion power \dot{W}_{nexp} , i. e., the electric power, to the total incoming energy \mathcal{J}_{in} . In fuel cells, the incoming energy is equal to the incoming enthalpy, so $\mathcal{J}_{in} = \dot{H}_{in}$ and hence the incoming heat flux by equation (15) becomes negligible. Then, the definition of the efficiency for the PEMFC takes the form

$$\eta = \dot{W}_{nexp}/\dot{H}_{in} = (\dot{G}_{in}/\dot{H}_{in})(\dot{W}_e/\dot{G}_{in}) \quad (18)$$

for $\mathcal{J}_{in} = \dot{H}_{in}$ and $\mathcal{J}_{q1} \approx 0$, where $\dot{W}_{nexp} = \dot{W}_e \sim -\dot{G}_{in}$.

A reactant is activated and transported to a membrane in the volume V_{in} , as depicted in Fig. 2. There are neither changes of the reactant enthalpy nor substantial sources of heat, so the following relations are valid:

$$\begin{aligned} \mathcal{J}_{Dh1} &= - \int_{A_{in1}} \sum_{\alpha} \mathbf{j}_{Dh\alpha} h_{\alpha} d\mathbf{a} = \int_{A_{in3}} \sum_{\alpha} \mathbf{j}_{Dh\alpha} h_{\alpha} d\mathbf{a} \quad (19) \\ &= - \int_{A_{m3}} \sum_{\alpha} \mathbf{j}_{Dh\alpha} h_{\alpha} d\mathbf{a} = \mathcal{J}_{Dh3}, \end{aligned}$$

$$\mathcal{J}_{q1} = - \int_{A_{in1}} \mathbf{j}_q d\mathbf{a} = \int_{A_{in3}} \mathbf{j}_q d\mathbf{a} = - \int_{A_{m3}} \mathbf{j}_q d\mathbf{a} = \mathcal{J}_{q3}. \quad (20)$$

Note that there is the outer normal of the surface, i. e., $d\mathbf{a}|_{A_{in3}} = -d\mathbf{a}|_{A_{m3}}$. The same assumption is also used in the volume V_{out} , where the reactant (oxygen) is activated and together with the product (water) is transported out of the system. Hence, for the volume V_{out} we can write

$$\begin{aligned} \mathcal{J}_{Dh4} &= \int_{A_{m4}} \sum_{\alpha} \mathbf{j}_{Dh\alpha} h_{\alpha} d\mathbf{a} = - \int_{A_{out4}} \sum_{\alpha} \mathbf{j}_{Dh\alpha} h_{\alpha} d\mathbf{a} \quad (21) \\ &= \int_{A_{out2}} \sum_{\alpha} \mathbf{j}_{Dh\alpha} h_{\alpha} d\mathbf{a} = \mathcal{J}_{Dh2}, \end{aligned}$$

$$\mathcal{J}_{q4} = \int_{A_{m4}} \mathbf{j}_q d\mathbf{a} = - \int_{A_{out4}} \mathbf{j}_q d\mathbf{a} = \int_{A_{out2}} \mathbf{j}_q d\mathbf{a} = \mathcal{J}_{q2}. \quad (22)$$

As shown in Fig. 2, fluxes of the Gibbs free energy through the surfaces A_{m3} of the membrane volume V_m are given by

$$\begin{aligned} \mathcal{J}_{Dg3} - \mathcal{J}_{Dg4} &= -\dot{G}_{in} \quad (23) \\ \text{for } \mathcal{J}_{Dg3} &= - \int_{A_{m3}} \sum_{\alpha} \mu_{\alpha} d\mathbf{a}, \mathcal{J}_{Dg4} = \int_{A_{m4}} \sum_{\alpha} \mu_{\alpha} d\mathbf{a}. \end{aligned}$$

These fluxes relate to changes of the Gibbs free energy in the volume V_m . The reference chemical potential μ_{α}^* of the reactants can be chosen such that the total Gibbs free energy input can be set to zero, i. e., $\mathcal{J}_{Dg3} = 0$. If the incoming Gibbs energy is non-zero, then it has to be respected in equation (23). Equation (23) reflects a decrease of the Gibbs free energy in the volume V_m . More specifically, the Gibbs free energy changes during

the chemical reactions at the electrode in the volume V_{out} and the corresponding electric energy is generated. This results in a change in the enthalpy flux $\mathcal{J}_{Dh3} \neq \mathcal{J}_{Dh4}$ and a change in the heat flux $\mathcal{J}_{q3} \neq \mathcal{J}_{q4}$ between the volumes V_{in} and V_{out} . So, the balances of the heat and enthalpy fluxes between the surfaces A_{in3} and A_{out4} at hypothetical temperatures T_3, T_4 (see Figs. 1 and 2) take the form

$$\begin{aligned} \mathcal{J}_{q3} &= \mathcal{J}_{q1}, & \mathcal{J}_{Dh3} &= \mathcal{J}_{Dh1}, & \mathcal{J}_{Dg3} &= 0, \\ \mathcal{J}_{q4} &= \mathcal{J}_{q2}, & \mathcal{J}_{Dh4} &= \mathcal{J}_{Dh2}, & \mathcal{J}_{Dg4} &= \dot{G}_{in}. \end{aligned} \quad (24)$$

Respecting the flux definitions given in equations (19)–(22), condition (12) takes the form

$$\begin{aligned} d^2 \mathcal{J}(S) &= \mathcal{J}_{q3}(S) + \mathcal{J}_{Dh3}(S) - \\ &- [\mathcal{J}_{q4}(S) + \mathcal{J}_{Dh4}(S)] - \mathcal{J}_{Dg3}(S) + \mathcal{J}_{Dg4}(S) = 0 \\ \text{or} \quad \frac{\mathcal{J}_{q3}}{T_3} + \frac{\mathcal{J}_{Dh3}}{T_3} - \frac{\mathcal{J}_{q4}}{T_4} - \frac{\mathcal{J}_{Dh4}}{T_4} - \frac{\mathcal{J}_{Dg3}}{T_3} + \frac{\mathcal{J}_{Dg4}}{T_4} &= 0. \end{aligned} \quad (25)$$

To satisfy this condition we have introduced the unknown inner temperatures T_3, T_4 , analogously to the zero entropy flux, as it is currently used in the endoreversible concept; see, e. g., [3, 12, 13, 14].

Employing the balance of energy, as given by equations (16) and (17), equation (25) changes to

$$\frac{\mathcal{J}_{in}}{T_3} - \frac{\mathcal{J}_{out}}{T_4} - \frac{\mathcal{J}_{Dg3}}{T_3} + \frac{\mathcal{J}_{Dg3} + \dot{G}_{in}}{T_4} = 0. \quad (26)$$

Thus, a connection between the reactants inlet, products outlet, and efficiency of the system can be qualitatively analyzed via an endoreversibility-like concept [2, 3, 12, 14]. An important form of the condition (12) for systems based on the non-expansion power, e. g., fuel cells, electrolyzers, and batteries, becomes

$$\begin{aligned} \frac{\mathcal{J}_{in}}{T_3} - \frac{\mathcal{J}_{out}}{T_4} + \frac{\dot{G}_{in}}{T_4} &= 0 \\ \text{or} \quad \frac{\mathcal{J}_{in}}{T_3} - \frac{\mathcal{J}_{in}}{T_4} + \frac{\dot{W}_{nexp}}{T_4} + \frac{\dot{G}_{in}}{T_4} &= 0. \end{aligned} \quad (27)$$

In thermodynamic equilibrium, i. e., for reversible processes, the production of entropy is $\mathcal{P}(S) = 0$ and the non-expansion power is equal to the Gibbs free energy, i. e., $\dot{W}_{nexp} = -\dot{G}_{in}$, and equation (27) for $T_3 = T_4$ becomes meaningless. Nevertheless, these conditions are unrealistic and can be realized only for $\dot{W}_{nexp} = -\dot{G}_{in} = 0$. For all systems following non-expansion energy conversion, production of entropy is positive and generated by non-equilibrium processes in the volume $V = V_{in} \cup V_m \cup V_{out}$.

The unknown internal temperatures T_3, T_4 have been introduced to satisfy the condition (12), especially the form (27). Energy fluxes $\mathcal{J}_{in}, \mathcal{J}_{out}$ are continuous at the boundary, but the entropy fluxes have discontinuities. The internal entropy flows compensate for each other at some temperatures T_3, T_4 (12), so that the equation for total entropy production has the usual form (35). The easiest way to implement these additional conditions is the linear relationship

$$\begin{aligned} \mathcal{J}_{in} = \mathcal{J}_{q3} + \mathcal{J}_{Dh3} &= -\gamma_H(T_1 - T_3), & \mathcal{J}_{out} = \mathcal{J}_{q2} + \mathcal{J}_{Dh2} &= \gamma_L(T_4 - T_2) \\ \text{for} \quad \gamma_H &= \alpha_H + \beta_H, & \gamma_L &= \alpha_L + \beta_L, \end{aligned} \quad (28)$$

where γ_H, γ_L are the entropy transfer coefficients with the dimension WK^{-1} ; see Fig. 1. The entropy transfer coefficients are a sum of the transfer coefficients of the heat flux, \mathcal{J}_q , and the flux of enthalpy, \mathcal{J}_{Dh} , i. e., the transfer coefficients α and β , respectively. To ensure that both entropy transfer coefficients γ_H, γ_L are positive, a negative sign before the coefficient γ_H has been placed. This choice corresponds to the fact that the non-equilibrium system is maintained in a dynamic equilibrium by a negative entropy flux; see [7, 8] and references therein.

The temperatures T_3 , T_4 can be eliminated using the balance of energy, equation (17), and additional conditions (28). Then we have

$$\frac{T_4}{T_3} = \frac{\gamma_H [\gamma_L \eta T_2 + (1 - \eta) \dot{W}_{nexp}]}{\gamma_L (\gamma_H \eta T_1 + \dot{W}_{nexp})}. \quad (29)$$

Using the balance of energy according to equation (17) and additional conditions (28), equation (27) is reformulated as

$$\begin{aligned} \frac{T_4}{T_3} \mathcal{J}_{in} - \mathcal{J}_{out} + \dot{G}_{in} &= 0, \\ \left[\frac{\gamma_H [\gamma_L \eta T_2 + (1 - \eta) \dot{W}_{nexp}]}{\gamma_L (\gamma_H \eta T_1 + \dot{W}_{nexp})} - (1 - \eta) \right] \frac{\dot{W}_{nexp}}{\eta} + \dot{G}_{in} &= 0 \end{aligned} \quad (30)$$

and rewritten to

$$\begin{aligned} \frac{(\gamma - 1)(1 - \eta)}{\eta} \frac{\dot{W}_{nexp}^2}{\dot{W}_{nexp,ref}} + \left[\tau + \eta + \frac{\dot{G}_{in}}{\dot{W}_{nexp,ref}} \right] \dot{W}_{nexp} + \eta \dot{G}_{in} &= 0 \\ \text{for } \dot{W}_{nexp,ref} = \gamma_H T_1, \quad \gamma = \frac{\gamma_H}{\gamma_L}, \quad \tau = \frac{T_2}{T_1} - 1. \end{aligned} \quad (31)$$

Here, the quantity $\dot{W}_{nexp,ref}$ is the reference power and depends on the entropy transfer coefficient γ_H . Then, $\gamma \geq 1$ is the ratio of the entropy transfer coefficients and τ is a non-dimensional temperature difference. The change of the Gibbs free energy \dot{G}_{in} , or ΔG for steady-state operations, represents a transformation of the chemical energy into non-expansion power \dot{W}_{nexp} . Furthermore, this transformation is characterized by the so-called second law efficiency η_{II} [15]. Then, equation (31) results in

$$\begin{aligned} \frac{(\gamma - 1)(1 - \eta)}{\eta} \dot{W}_{nexp} + \tau + \eta - \frac{\dot{W}_{nexp}}{\eta_{II}} - \frac{\eta}{\eta_{II}} &= 0 \\ \text{for } \eta = \eta_0 \eta_{II}, \quad \eta_{II} = \frac{-\dot{W}_{nexp}}{\dot{G}_{in}}, \quad \dot{W}_{nexp} = \frac{\dot{W}_{nexp}}{\dot{W}_{nexp,ref}}, \\ \text{and } \eta_0 = -\frac{\dot{G}_{in}}{\dot{H}_{in}}. \end{aligned} \quad (32)$$

Here, the total efficiency may be divided as $\eta = \eta_0 \eta_{II}$, where both efficiencies depend on the normalized power, \dot{W}_{nexp} . The quantity η_0 is named transport or transfer efficiency (see below). Equation (32) leads to the normalized power generated by the device transforming energy by non-expansion work, which may be expressed as

$$\begin{aligned} \dot{W}_{nexp} = \frac{\eta[(1 - \eta_{II})\eta - \tau\eta_{II}]}{(\gamma - 1)(1 - \eta)\eta_{II} - \eta} = \frac{\eta_0 \eta_{II}[(1 - \eta_{II})\eta_0 - \tau]}{(\gamma - 1)(1 - \eta_0 \eta_{II}) - \eta_0} \\ \text{for } \dot{W}_{nexp} = \frac{\dot{W}_{nexp}}{\dot{W}_{nexp,ref}} = \frac{\dot{W}_e}{\gamma_H T_1} = -\frac{\dot{W}_e}{\dot{G}_{in}} \quad \text{and } \gamma = \frac{\gamma_H}{\gamma_L} \geq 1. \end{aligned} \quad (33)$$

If non-expansion power is taken as electric power, i. e., $\dot{W}_{nexp} = \dot{W}_e$, equation (33) will be valid for fuel cells, electrolyzers, batteries, etc. Furthermore, the positive power output given by equation (33) is ensured by

$$\tau = \frac{T_2}{T_1} - 1 > \eta_0(1 - \eta_{II}). \quad (34)$$

The total entropy flux of this system depends on the temperatures T_1 , T_2 . Employing balances of energy given by equations (16) and (17) and by the equation for the normalized power (33), the total entropy flux is

$$\begin{aligned} \mathcal{J}_{tot}(S) = \frac{\mathcal{J}_{in}}{T_1} - \frac{\mathcal{J}_{out}}{T_2} = \frac{\dot{W}_{nexp}}{\eta T_1} \left[1 - \frac{(1 - \eta)T_1}{T_2} \right] \\ = \frac{\dot{W}_{nexp} \dot{W}_{nexp,ref}}{\eta T_1} \frac{\eta + \tau}{1 + \tau} = \frac{\dot{W}_{nexp,ref} [(1 - \eta_{II})\eta_0 - \tau]}{T_1 [(\gamma - 1)(1 - \eta) - \eta_0]} \frac{\eta + \tau}{1 + \tau}. \end{aligned} \quad (35)$$

The total entropy flux is negative if inequality (34) is applied. Moreover, if $\eta_{II} \rightarrow 1$ and $\eta_0 \rightarrow \eta_{th}$, then $\eta \rightarrow \eta_{th}$ and the power output as well as the total entropy flux approaches zero. In the non-equilibrium steady state, $-\mathcal{J}_{tot}(S) = \mathcal{P}(S) > 0$ and the magnitude of the entropy flux depends on the entropy transfer coefficient γ_H , the operation temperature T_1 , and the efficiencies η_0, η_{II} . Note that the production of entropy, $\mathcal{P}(S) > 0$, is generated by transfer processes of energy and matter that accompany energy transformation.

The incoming and outgoing energy fluxes \mathcal{J}_{in} and \mathcal{J}_{out} , equation (28), are related to the reference power, equation (31), i. e., $\dot{W}_{nexp,ref} = \gamma_H T_1$. Thus, values of the hypothetical inner temperatures T_3, T_4 in equation (29) need to be expressed. By the condition already applied in equation (31), the ratio in equation (29) can be rewritten in the following form:

$$\frac{T_4}{T_3} = \frac{\eta(1 + \tau) + (1 - \eta)\gamma\dot{W}_{nexp}}{\eta + \dot{W}_{nexp}} \quad \text{or} \quad \dot{W}_{nexp} = \frac{\eta\left(\frac{T_4}{T_3} - \tau - 1\right)}{\gamma(1 - \eta) - \frac{T_4}{T_3}}. \quad (36)$$

A comparison of equations (33) and (36) leads to the important relation

$$\frac{T_4}{T_3} = 1 + \eta_0(1 - \eta_{II}). \quad (37)$$

Hence, the ratio of the hypothetical temperatures T_3, T_4 is finite in the entire fuel cell operating range; compare with the condition (34). The values of η_0, η_{II} depend on power generation \dot{W}_{nexp} , so these values are not constant.

Note: If we accept the concept of endoreversibility, which physically means that the interior of the system is in thermodynamic equilibrium, then the internal temperatures of T_3, T_4 should be the same. Then it follows from relation (37) that this state occurs only if $\eta_{II} = 1$, i. e., in an idealized case that corresponds to zero power. The same situation also occurs for systems generating expansion work (see, e. g., [12, 13, 14]), but the condition $T_3 = T_4$ gets an unrealistic relation between performance and efficiency. To be more specific, one obtains the following expression:

$$\dot{W}_{exp} = \frac{\alpha_L \alpha_H T_1 \eta (\eta_C - \eta)}{(\alpha_H - \alpha_L)(1 - \eta)} \xrightarrow{T_3=T_4} \frac{\alpha_L \alpha_H T_1 \eta (\eta_C - \eta)}{(\alpha_H - \alpha_L)}. \quad (38)$$

4 Fuel cell efficiency

The efficiency of a fuel cell (see Fig. 3) is defined by the ratio $\eta = \text{electric output}/\text{energy input} = W_e/\Delta H$, where W_e is the electric work,

$$\frac{dW_e}{dt} = \dot{W}_e = V_{cell} I_{cell} \quad (39)$$

is the generated electric power, and V_{cell}, I_{cell} are the cell voltage and produced electric current, respectively.

The total fuel cell efficiency is then given, as the efficiency in equation (17), by

$$\begin{aligned} \eta &= \frac{\dot{W}_{e,act}}{\dot{H}_{in}} = \left(\frac{-\dot{G}_{in}}{\dot{H}_{in}} \right) \left(\frac{\dot{W}_{e,act}}{-\dot{G}_{in}} \right) = \eta_0 \eta_{II} = \\ &= \frac{V_{cell}}{V_{th}} \frac{\dot{N}_{H_2,in}}{\dot{N}_{H_2,act}} = \frac{V_{cell}}{V_{th}} \frac{I_{cell}}{\underbrace{z_e F \dot{N}_{H_2,act}}_{\text{fuel utilization}}}. \end{aligned} \quad (40)$$

Here, $W_{e,act}$ is the actual produced work, V_{th} is the maximal theoretical electrochemical cell voltage at temperature T and pressure p , and $\dot{N}_{H_2,in}$ and $\dot{N}_{H_2,act}$ are the fluxes of the incoming enthalpy and the actually

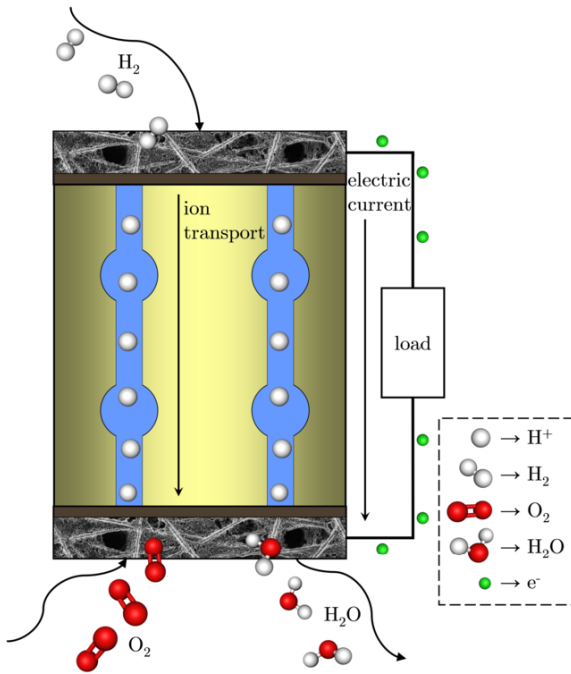


Figure 3: Schematic of a polymer electrolyte membrane fuel cell (PEMFC). The fuel cell consists of three different layers, i. e., porous media (gas diffusion layer), catalyst layers, and polymer electrolyte membrane. Hydrogen and oxygen, or air, are consumed at the anode and cathode, respectively. From the cathode it is necessary to remove the produced water.

consumed enthalpy, respectively. The quantities z_e and F are the valency number of ions and the Faraday constant, respectively.

The total fuel cell efficiency is defined as

$$\eta = \eta_0 \eta_{II}, \quad \text{where} \quad \eta_0 = \frac{-\dot{G}_m}{\dot{H}_{in}} \quad \text{and} \quad \eta_{II} = -\frac{\dot{W}_{e,act}}{\dot{G}_m}. \quad (41)$$

Here, η_0 is the transport or transfer efficiency and η_{II} is the second law efficiency describing, as mentioned above, the transformation of chemical energy into non-expansion power. The corresponding theoretical efficiency is $\eta_{th} = V_{eq}/1.482 = 0.7989 \approx 0.8$. The value of 1.482 V is the potential related to hydrogen's higher heating value, or the thermoneutral potential [16].

As an example of the typical dependency, the efficiency vs. generated power curve of a fuel cell is depicted in Fig. 4. Here, preliminary outcomes of the presented theoretical approach are confronted with a simple experiment represented by the polarization curve measurement. The investigated membrane electrode assembly (MEA) was provided by ElectroChem and has an active area of 50 cm^2 , 20% Pt/C catalyst, a platinum catalyst loading of 1 mg cm^{-2} , and a membrane thickness of $50 \text{ }\mu\text{m}$. Focusing only on the PEMFC operating under fully humidified conditions, the temperature of the cell, the temperature of the inlet gases, and the relative humidity of the inlet gases were kept at constant values during the test, i. e., $T_{cell} = 353 \text{ K}$, $T_{gas} = 353 \text{ K}$, $RH = 100\%$, respectively. The simple test consisted of several steps [17]. Thus, heating the cell up to the temperature 353 K; humidifying the cell for 2 hours at the temperature 353 K and relative humidity $RH = 100\%$; keeping a constant load of 20 A, i. e., current density = 0.4 A cm^{-2} , for 24 hours. The anode hydrogen flow was set to 0.21 nlpm (normal litres per minute) and the cathode air flow was set to 0.66 nlpm; measurement of the polarization curve for the mentioned constant reactants flows was carried out according to JRC Scientific and Technical Reports Test Module PEFC SC 5-2 Polarisation curve for a PEFC single cell [18]. This test was conducted via the TP50 research cell provided by Tandem Technologies connected to the Greenlight Innovation test stand G20.

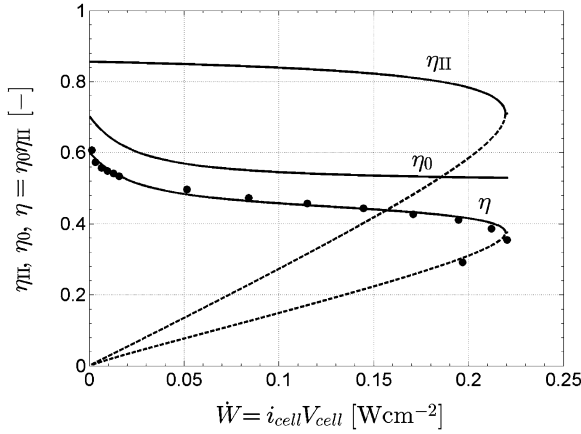


Figure 4: Dependency of the total efficiency on the electric power output given by (33). Used parameters are $\eta_{th} = 0.798$, $\eta_{0,min} = 0.513$, $\eta_{II,0} = 0.89$, $\dot{W}_{nexp,ref} = \gamma_H T_1 = 0.723 \text{ W cm}^{-2}$, $T_1 = 353 \text{ K}$, $\gamma_H = 0.00205 \text{ W cm}^{-2} \text{ K}^{-1}$, $\gamma = 1.95$, $\tau = 0.074$; see Appendix A.

In the described experiment, the anode hydrogen flow $\dot{m}_{H_2} = 1.561 \cdot 10^{-4} \text{ mol s}^{-1}$ represents a corresponding molar flow of hydrogen. The change in enthalpy and the change in Gibbs free energy of a PEMFC working at $T_1 = 353 \text{ K}$ are equal to $\Delta H = -284.18 \text{ kJ mol}^{-1}$ and $\Delta G = -231.63 \text{ kJ mol}^{-1}$, respectively, if a PEMFC produces liquid water [16]. Thus, the total incoming energy flux is given by the flux of the Gibbs free energy, so that $\dot{W}_{nexp,ref} = \gamma_H T_1 = -\dot{G}_{in} = -\Delta G \dot{m}_{H_2} = 0.723 \text{ W cm}^{-2}$, which is also used to obtain curves in Fig. 4.

4.1 Maximal fuel cell efficiency

For $\eta_{II} \rightarrow 1$ and $\eta_0 \rightarrow \eta_{th}$, the temperature difference τ , equation (34), complying the inequality $\tau \geq \eta_{th}(1 - \eta_{II}) > \eta_0(1 - \eta_{II})$, is equal to zero. Furthermore, the temperature difference slightly depends on the fuel cell power and hence on its actual efficiency. Because of negligible changes in the temperature difference, the following empirical interpolation can be used:

$$\tau = \frac{T_2}{T_1} - 1 \approx \frac{(2\eta_{th} + \eta_{0,min})(1 - \eta_{II,0})}{3}. \quad (42)$$

This formula contains two unknown parameters $\eta_{0,min}$, $\eta_{II,0}$ whose initial values are determined by the following procedure. To obtain a relation for the maximal value of the efficiency, the condition $d\dot{w}/d\eta = 0$ needs to be analyzed. Provided that the transport efficiency depends on the second law efficiency, the following relation can be derived:

$$\left\{ \left[\frac{\partial \dot{w}(\eta_0, \eta_{II})}{\partial \eta_0} \right]_{\eta_{II}} \frac{d\eta_0}{d\eta_{II}} + \left[\frac{\partial \dot{w}(\eta_0, \eta_{II})}{\partial \eta_{II}} \right]_{\eta_0} \right\} d\eta_{II} = 0, \quad (43)$$

so that

$$\frac{d\eta_0}{d\eta_{II}} = - \frac{\left[\frac{\partial \dot{w}(\eta_0, \eta_{II})}{\partial \eta_{II}} \right]_{\eta_0}}{\left[\frac{\partial \dot{w}(\eta_0, \eta_{II})}{\partial \eta_0} \right]_{\eta_{II}}}. \quad (44)$$

Then, the extremum condition $d\eta_0/d\eta_{II} = 0$, by employing the relation (34), results in the following implicit equation for the maximal power:

$$\dot{w}_{max} = \frac{\eta_0(\dot{w}_{max})[2\eta_{II}(\dot{w}_{max}) - 1] + \tau}{\gamma - 1}. \quad (45)$$

Note that the expressions for the derivatives in equation (44) are given in Appendix B.

Expressions for the derivatives (50) lead to the extremum values of both the transport efficiency, η_0 , and the second law efficiency, η_{II} . The extremum transport efficiency and the extremum second law efficiency are given by the condition $(\partial\eta_0/\partial\dot{w})_{\eta_{II}} = (\partial\eta_{II}/\partial\dot{w})_{\eta_0} = 0$. Thus, the minimal value of the transport efficiency adopts the form

$$\begin{aligned}\eta_{0,min} &= \frac{\gamma - 1}{1 + (\gamma - 1)\eta_{II}(\dot{w}_{max})} \Big|_{\dot{w}_{max} \rightarrow 0} = \\ &= \frac{\gamma - 1}{1 + (\gamma - 1)\eta_{II,0}} \Big|_{\eta_{II,0} \rightarrow 1} = 1 - \frac{1}{\gamma},\end{aligned}\quad (46)$$

where $\eta_{II,0}$ is the second law efficiency at zero power output. Thus, there is an explicit relation between the minimal transport efficiency $\eta_{0,min}$ and the entropy transfer coefficient γ for $\eta_{II,0} = 1$.

Similarly, the second law efficiency at maximal power is given by

$$\eta_{II,max} = \left[\frac{1}{\eta_0(\dot{w}_{max})} - \frac{1}{\gamma - 1} \right]_{\dot{w} \rightarrow 0} = \eta_{II,0} \quad (47)$$

and is indeed equal to the second law efficiency at zero power output used in equation (46). Hence, the estimated efficiencies (46) and (47) are used to determine the explicit dependency of the total efficiency $\eta(\dot{w})$ on the power output \dot{w} in the first approximation, as also shown in Appendix A. In order to find the most precise approximation of the polarization curve, iterative process and knowledge of at least three of its points determined by the experiment are necessary. All the parameters γ (activation losses, resistance, catalyst quality, etc.), $\eta_{0,min}$, $\eta_{II,0}$ (membrane conductivity with adequate water supply, membrane thickness, etc.) are for given FC constant in all regimes of operations. By determining these constants, the exchange current density [17] can also be calculated by this method. The introduced interpolation was also utilized to fit experimental data plotted in Fig. 4; see Appendix A.

5 Conclusion

Application of a modified concept of endoreversible thermodynamics to the transformation of energy in expansion and non-expansion processes is investigated and briefly summarized. Conditions for the highest efficiency of transformation of chemical energy into electrical energy are introduced and discussed. From detailed thermodynamic analysis based on the principles of linear non-equilibrium thermodynamics, the following outcomes can be highlighted:

- Production of entropy contains all relevant processes, including diffusion processes, electric and thermal conductivity, and the chemical reaction. The steady-state is maintained by a negative entropy flux.
- Transport coefficients for reactants inlet, i. e., hydrogen and air, and for the products outlet, i. e., water, are suggested. The calculated efficiency qualitatively corresponds to the experimentally obtained values. Further research shall focus on the dependency of the parameter $\eta_{II,0}$, characterizing the membrane, and the parameter γ , characterizing the transport of reactants and products, on the power output.
- The total efficiency of the fuel cell and the second law efficiency are analyzed in detail and the conditions for their maxima are formulated.

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Appendix A. Calculation of the membrane and transport efficiency

The curves plotted in Fig. 4 are calculated by the following interpolation:

- To evaluate experimental data of the fuel cell operating at the temperature T_1 with the hydrogen consumption \dot{m}_{H_2} , the reference non-expansion power may be given as $\dot{W}_{\text{exp,ref}} = -\Delta G \dot{m}_{\text{H}_2}$. For given η_{th} , the entropy transfer coefficient $\gamma \in (1.5, 1/(1 - \eta_{\text{th}}))$ and the second law efficiency at zero power output $\eta_{\text{II},0} \in (1, 0.8)$ are estimated. For the chosen values of γ and $\eta_{\text{II},0}$, the minimal transport efficiency $\eta_{0,\text{min}}$ and the temperature difference τ are calculated by relations (42) and (46), respectively. The entropy transfer coefficient γ , the minimal transport efficiency $\eta_{0,\text{min}}$, and consequently the temperature difference τ are taken as constant in the first iteration. Nevertheless, these parameters are generally dependent on the actual power \dot{w}_e . Furthermore, the second law efficiency is determined by equation (33) rewritten to the explicit quadratic expression

$$\eta_{\text{II},1,2}(\dot{w}_e) = \frac{-b_{\text{II}} \pm \sqrt{b_{\text{II}}^2 - 4a_{\text{II}}c_{\text{II}}}}{2a_{\text{II}}}, \text{ for } a_{\text{II}} = \eta_{0,\text{min}}^2, \quad (48)$$

$$b_{\text{II}} = \eta_{0,\text{min}}[\tau - (\gamma - 1)\dot{w}_e - \eta_{0,\text{min}}], \quad c_{\text{II}} = \dot{w}_e(\gamma - 1) - \eta_{0,\text{min}}.$$

- Explicit quadratic expression for the transport efficiency follows as well from equation (33), i. e.,

$$\eta_{0,1,2}(\dot{w}_e) = \frac{-b_0 \pm \sqrt{b_0^2 - 4a_0c_0}}{2a_0} \quad \text{for } a_0 = \eta_{\text{II},0}(1 - \eta_{\text{II},0}), \quad (49)$$

$$b_0 = \dot{w}_e[\eta_{\text{II},0}(\gamma - 1) + 1] - \tau\eta_{\text{II},0}, \quad c_0 = -\dot{w}_e(\gamma - 1).$$

- The total efficiency is given by the relation used in (32), i. e., $\eta = \eta(\dot{w}_e) = \eta_0(\dot{w}_e)\eta_{\text{II}}(\dot{w}_e)$.

Note that the upper parts of the curves presented in Fig. 4 correspond to relations (48) and (49). To improve the fit of the experimental data, the initial guesses of the γ and $\eta_{\text{II},0}$ may be changed. At least three experimental points are required to determine the entire polarization curve for a particular FC. This procedure was used for fitting the experiment in Fig. 4.

Appendix B. Maximal fuel cell efficiency – derivatives

The expressions for derivatives used in equation (44) are derived from equation (33) and may be written as follows:

$$\left[\frac{\partial \dot{w}(\eta_0, \eta_{\text{II}})}{\partial \eta_0} \right]_{\eta_{\text{II}}} = \frac{\eta_{\text{II}}[(\gamma - 1)\dot{w} + 2\eta_0(1 - \eta_{\text{II}}) - \tau] + 1}{(\gamma - 1)(1 - \eta_{\text{II}}\eta_0) - \eta_0}, \quad (50)$$

$$\left[\frac{\partial \dot{w}(\eta_0, \eta_{\text{II}})}{\partial \eta_{\text{II}}} \right]_{\eta_0} = \frac{\eta_0[(\gamma - 1)\dot{w} + \eta_0 - 2\eta_0\eta_{\text{II}} - \tau]}{(\gamma - 1)(1 - \eta_{\text{II}}\eta_0) - \eta_0}.$$

Nomenclature

H	Enthalpy
S	Entropy
$\mathcal{P}(S)$	Entropy production
G	Gibbs free energy
h	Specific enthalpy
s	Specific entropy
\mathcal{J}_{in}	Incoming heat flux

\mathcal{J}_{out}	Outgoing heat flux
$\mathcal{J}(S)$	Entropy flux
\mathcal{J}_q	Heat flux
\mathcal{J}_{Dh}	Flux of the enthalpy
\mathcal{J}_{Dg}	Flux of the Gibbs free energy
W_{exp}	Expansion work
W_{nexp}	Non - expansion work
\dot{W}_e	Generated electric power
\dot{w}_{nexp}	Normalised generated power
$\alpha_{L,H}$	Entropy transfer coefficients
$\beta_{L,H}$	Entropy transfer coefficients
γ	Entropy transfer coefficient
η	Total efficiency
η_c	Carnot efficiency
η_{th}	Theoretical efficiency
η_0	Transport efficiency
η_{II}	Second law efficiency
μ	Chemical potential
τ	Non-dimensional temperature difference

References

- [1] P. Atkins and J. de Paula, *Physical Chemistry*, Eighth ed., Oxford University Press, Oxford, 2006.
- [2] A. Bejan, Entropy generation minimization: The new thermodynamics of finite-size devices and finite-time processes, *J. Appl. Phys.* **79** (1996), 1191–1218.
- [3] A. De Vos, Endoreversible thermodynamics and chemical reactions, *J. Phys. Chem.* **95** (1991), no. 11, 4534–4540.
- [4] K. Wagner and K. H. Hoffmann, ETA-graphics – an interface to endoreversible thermodynamics, *Eur. J. Phys.* **36** (2015), 025010.
- [5] K. Wagner and K. H. Hoffmann, Endoreversible modeling of a PEM fuel cell, *J. Non-Equilib. Thermodyn.* **40** (2015), 283–294.
- [6] K. Wagner and K. H. Hoffmann, Chemical reactions in endoreversible thermodynamics, *Eur. J. Phys.* **37** (2015), 015101.
- [7] F. Marsik, P. Novotny and M. Tomas, What is entropy ? – A generalized outlook and application to living systems, in: J. Sestak, P. Hubik and J. J. Mares (eds.), *Thermal Physics and Thermal Analysis*, Hot Topics in Thermal Analysis and Calorimetry 11, Springer, Cham (2017).
- [8] P. Glandsdorff and I. Prigogine, *Thermodynamic Theory of Structure, Stability and Fluctuations*, Wiley-Interscience, New York, 1971.
- [9] S. R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics*, North-Holland, Amsterdam, 1962.
- [10] M. Pavelka and F. Marsik, Detailed thermodynamic analysis of polymer electrolyte membrane fuel cell efficiency, *Int. J. Hydrog. Energy* **38** (2013), 7102–7113.
- [11] P. Vagner, M. Pavelka and F. Marsik, Pitfalls of exergy analysis, *J. Non-Equilib. Thermodyn.* **42** (2017), 201–216.
- [12] A. De Vos, *Endoreversible Thermodynamics of Solar Energy Conversion*, Oxford University Press, Oxford, 1992.
- [13] I. I. Novikov, The efficiency of atomic power stations, *J. Nucl. Energy* **7** (1958), no. 1-2, 125–128.
- [14] F. L. Curson and B. Ahlborn, Efficiency of a Carnot engine at maximum power output, *Am. J. Phys.* **43** (1975), 22–24.
- [15] E. Chen, Thermodynamics and electrochemical kinetics, in: G. Hoogers (ed.), *Fuel Cell Technology Handbook*, CRC Press, Boca Raton (2003).
- [16] F. Barbir, *PEM Fuel Cells: Theory and Practice*, Elsevier, Amsterdam, 2005.
- [17] F. Marsik, P. Novotny, M. Pavelka and V. Klika, Thermodynamic analysis of the fuel cells efficiency – Thermodynamic stability approach, in: *20th World Hydrogen Energy Conference (WHEC 2014)*, Curran Associates, Inc., Red Hook, (2014). ISBN: 978-1-63439-655-4.
- [18] FCTestNet/FCTes^{QA}. Test module PEFC SC 5-2. Testing the voltage and the power as a function of the current density. Polarisation curve for a PEFC single cell, Technical report, European Commission Joint Research Centre, Institute for Energy, 2010.