

Short communication

Heat balance in the catalyst layer and the boundary condition for heat transport equation in a low-temperature fuel cell

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Abstract

We consider heat balance in the catalyst layer of a low-temperature fuel cell. Based on the heat transport equation in the layer, the exact boundary condition for the problem of heat transport in the cell is obtained. The limits of validity of the resulting expression are discussed.

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1. Introduction

The rates of virtually all transport and kinetic processes in low-temperature fuel cells (PEFCs and DMFCs) exponentially depend on temperature. Local overheat by several Kelvin degrees may change the rate of electrochemical reactions, shift liquid–vapor equilibrium and enhance diffusion transport of reactants and products [1]. Clearly, heat balance is an essential issue in fuel cell operation. Proper heat management is even more difficult in fuel cell stacks, where dense packing of cells retards heat removal.

Cell warming is due to heat generated in the electrochemical reactions and due to the electric power dissipated by currents. Fuel cell “sandwich” supports two types of currents: electron current transported through the carbon threads in the catalyst and backing layers and proton current in the bulk membrane and in the membrane phase dispersed in the catalyst layer (CL).

In the CL, the electron conductivity of the carbon phase is several orders of magnitude larger, than the proton conductivity of the electrolyte phase. Since maximal electron and proton current densities in the CL are equal, the vast majority of electric heat there is released in the electrolyte phase.

Furthermore, typical proton conductivity of the CL is at least several times lower than the conductivity of bulk membrane [2,3] and thus the dissipation of electric power in the CL exceeds that

dissipation in the bulk membrane. Taking into account that the reaction heat is released also in the CLs we conclude, that these layers are the major source of heat in the fuel cell.¹

Numerical models usually ignore the details of heat transport in the CLs and assume that these layers are infinitely thin interfaces generating heat [5–7,1]. This approach requires the expression for the heat flux from the CL, which is used as the boundary condition for the problem of heat transport in the other parts of the cell (backing layers, flow fields, etc.).

In this work we consider the sources of heat in the CL. We show how heat balance equation in the layer can be reduced to the boundary condition for the problem of heat transport in the fuel cell. This procedure gives exact expressions and makes it possible to establish their limits of validity.

2. Heat balance in the catalyst layer

Consider for definiteness the cathode catalyst layer (CCL) of a hydrogen or direct methanol fuel cell (Fig. 1). The “thermodynamic” heat (J mol^{-1}) generated in the oxygen reduction reaction (ORR) is given by

$$Q_{\text{ORR}} = T\Delta S \quad (1)$$

¹ Electron current in the backing layers tends to concentrate near the edges of the current collector ribs [4]. This concentration may lead to local overheat. However, these effects are out of the scope of the present work.

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Nomenclature

b	Tafel slope (V)
c_p	specific heat ($\text{J g}^{-1} \text{K}^{-1}$)
C	molar concentration (mol m^{-3})
C_{ref}	reference molar concentration (mol m^{-3})
F	Faraday constant ($9.6495 \times 10^4 \text{ C mol}^{-1}$)
i_*	exchange current density per unit volume (A m^{-3})
j_e	local electron current density in the catalyst layer (A m^{-2})
j_p	local proton current density in the catalyst layer (A m^{-2})
j_0	current density in the cell (A m^{-2})
j_*	characteristic current density (A m^{-2})
l	thickness of the catalyst layer (m)
n	number of electrons transferred in the electrochemical reaction ($n = 4$ for ORR and $n = 6$ for methanol oxidation)
q_j	rate of heat production due to currents (W m^{-3})
q_S	rate of thermodynamic heat production due to entropy change (W m^{-3})
q_n	rate of heat production in the electrochemical reaction due to proton transfer through the potential barrier (W m^{-3})
Q	total thermodynamic heat produced in the reaction (J mol^{-1})
R	rate of the electrochemical reaction (A m^{-3})
ΔS	entropy change in the electrochemical reaction ($\text{J mol}^{-1} \text{K}^{-1}$)
T	temperature (K)
x	coordinate across the catalyst layer (m)
\sim	marks dimensionless variables

Greek symbols

α	dimensionless parameter
η	polarization voltage of the CL (overpotential, V)
λ_{eff}	thermal conductivity of the catalyst layer ($\text{W m}^{-1} \text{K}^{-1}$)
σ_e	electron conductivity of the carbon phase ($\Omega^{-1} \text{m}^{-1}$)
σ_p	proton conductivity of the electrolyte phase ($\Omega^{-1} \text{m}^{-1}$)
φ_e	carbon phase potential in the catalyst layer (V)
φ_p	electrolyte phase potential in the catalyst layer (V)

Subscripts

e	carbon phase (electron-conducting)
ORR	oxygen reduction reaction
p	electrolyte phase (proton-conducting)
0	at the membrane surface (at $x = 0$)
*	characteristic value

Superscripts

w	water
ox	oxygen

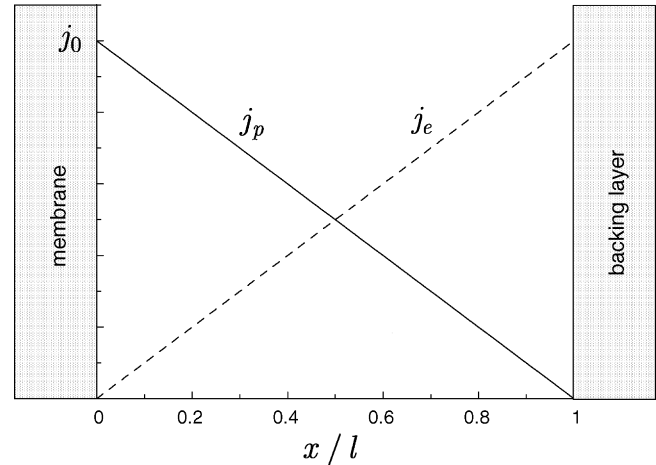


Fig. 1. Sketch of the cathode catalyst layer and the shapes of electron j_e and proton j_p current densities. Note that $j_p(0) = j_0$ is the total current density in the cell.

where ΔS ($\text{J mol}^{-1} \text{K}^{-1}$) is the change in entropy in ORR. Generally, ΔS depends on pressure and temperature [13]. We will assume that pressure variation due to the reaction is negligible.² At constant pressure the change in entropy due to the ORR is [13]:

$$\Delta S(T) = \Delta S_0 + \int_{T_0}^T \frac{c_p^w - c_p^{\text{ox}}}{T} dT \approx \Delta S_0 + (c_p^w - c_p^{\text{ox}}) \ln \left(\frac{T}{T_0} \right) \quad (2)$$

where $\Delta S_0 \equiv \Delta S(T_0)$ is the change in entropy at the standard temperature T_0 , c_p^w and c_p^{ox} are specific heats of water and oxygen, respectively. Note that due to small mass, the contribution of protons and electrons to the second term in (2) is negligible.

Simple estimate shows that in the typical for fuel cell operation temperature range (300–380 K) the second term on the right side of (2) is much smaller, than the first one. Physically, the change in entropy due to creation of new molecules (water) is much larger, than the change in entropy due to species heating. In the following we thus will take $\Delta S = \Delta S_0 = \text{const}$.

The local rate of thermodynamic heat production q_S (W m^{-3}) in the catalyst layer is

$$q_S = \frac{T \Delta S}{4F} R_{\text{ORR}} \quad (3)$$

where R_{ORR} is the local rate of electrochemical reaction (the proton charge consumed in the reaction per second per unit volume, A m^{-3}).

R_{ORR} is the rate of conversion of proton current into electron current. Generally, R_{ORR} is a function of x [8,9]. The equation, which describes the decay of proton current along x (Fig. 1) is

$$\frac{\partial j_p}{\partial x} = -R_{\text{ORR}} \quad (4)$$

² The electrochemical reactions in cells considered occur on the surface of catalyst particles immersed in Nafion®. To our knowledge the variation of pressure in polymer electrolyte due to the reactions has not been studied in literature.

Integrating (4) from $x = 0$ to $x = l$ and taking into account that $j_p(l) = 0$, we get

$$\int_0^l R_{\text{ORR}} dx = j_0 \quad (5)$$

where l is the CL thickness, $j_0 \equiv j_p(0)$ is the local current in the cell. Note that Eq. (5) expresses the conservation of charge and thus it is valid regardless of the actual relation for R_{ORR} .³

ORR occurs at the catalyst surface, which has potential φ_e (the potential of electron-conducting phase in the CL). Protons, however, move in the polymer electrolyte phase, which has potential φ_p . To reach the catalyst surface the proton has to be transported through the double layer at the catalyst/electrolyte interface, i.e., through the potential jump $\eta = \varphi_p - \varphi_e$ (overpotential). The power dissipated in this process is

$$q_\eta = \eta R_{\text{ORR}} \quad (6)$$

Another source of heat in the CL is electric power dissipated due to currents. Since CL supports electron and proton currents, the total dissipated power is

$$q_j = -j_e \frac{\partial \varphi_e}{\partial x} + j_p \frac{\partial \varphi_p}{\partial x} \quad (7)$$

where j_e and j_p are electron and proton current densities, respectively. Here, we assume that heat transfer between the two phases is infinitely fast.

Taking into account Ohm's law $j_e = -\sigma_e \partial \varphi_e / \partial x$, $j_p = \sigma_p \partial \varphi_p / \partial x$ we may rewrite (7) as

$$q_j = \frac{j_e^2}{\sigma_e} + \frac{j_p^2}{\sigma_p} \quad (8)$$

Here, σ_e , σ_p are electron conductivity of the carbon phase and proton conductivity of the electrolyte phase, respectively.

Velocity of gas flow in the CL is very small. This allows us to neglect convective term in the heat transport equation. Heat balance in the CL is, therefore, given by

$$-\frac{\partial}{\partial x} \left(\lambda_{\text{eff}} \frac{\partial T}{\partial x} \right) = q_s + q_\eta + q_j$$

or, taking into account (3), (6) and (7):

$$-\frac{\partial}{\partial x} \left(\lambda_{\text{eff}} \frac{\partial T}{\partial x} \right) = \left(\frac{T \Delta S}{4F} + \eta \right) R_{\text{ORR}} + \frac{j_e^2}{\sigma_e} + \frac{j_p^2}{\sigma_p} \quad (9)$$

Here, λ_{eff} is the thermal conductivity of the CL ($\text{W m}^{-1} \text{K}^{-1}$). This is the general equation, which determines heat transport in the cathode CL of a hydrogen or direct methanol fuel cell.

³ Usually, for R_{ORR} the Tafel equation is used:

$$R_{\text{ORR}} = i_* \left(\frac{C_{\text{ox}}}{C_{\text{ref}}} \right) \exp \left(\frac{\eta}{b} \right)$$

Here, i_* is the volumetric exchange current density (A m^{-3}), C_{ox} and C_{ref} local oxygen concentration and the reference oxygen concentration, respectively, $\eta = \varphi_p - \varphi_e$ overpotential, φ_e and φ_p potentials of electron and electrolyte phase, respectively, b is Tafel slope. However, for the present analysis the explicit expression for R_{ORR} is not required.

Eq. (9) does not take into account the heat due to phase transformation of water in the CL. This process can, in principle, be accounted for as described in Refs. [10,11], though evaporation/condensation requires to consider mass transfer between the liquid and vapor phases [12].

The derivation of Eq. (9) employs only the general laws of heat and charge conservation. The only detail in (9) specific to the ORR is stoichiometry coefficient $4F$. Clearly, Eq. (9) can be generalized to describe the heat balance in any CL as follows:

$$-\frac{\partial}{\partial x} \left(\lambda_{\text{eff}} \frac{\partial T}{\partial x} \right) = \left(\frac{T \Delta S}{nF} + \eta \right) R + \frac{j_e^2}{\sigma_e} + \frac{j_p^2}{\sigma_p} \quad (10)$$

Here, R is the local rate of the electrochemical reaction, ΔS the respective entropy change and n is the number of electrons transferred in the reaction ($n = 4$ for ORR and $n = 6$ for methanol oxidation).

3. Reduction to the boundary condition

Calculations show that in a wide range of parameters the variation of temperature across the CL is vanishingly small (see Appendix A).⁴ Thus, in many situations an attractive option would be to replace the CL with a thin interface generating heat. Formally this means that in the "external" problems (e.g. in the problems of heat transport in the backing layers, flow fields, etc.) the active layer is replaced with the boundary condition, which represents the total heat flux emitted from the CL. This approach is widely used in numerical simulations; however, the relations for heat flux used in many works have no proper justification. Moreover, the limits of validity of these relations are usually not clear.

The exact boundary condition can be obtained from Eq. (10) using the following assumptions. If the concentration of feed molecules does not vary significantly across the CL and if cell current:

$$j_0 \ll j_* \quad (11)$$

where

$$j_* = \frac{2\sigma_p b}{l} \quad (12)$$

then the electron and proton current densities vary linearly with the distance across the CL (Fig. 1):

$$j_p = j_0 \left(1 - \frac{x}{l} \right) \quad (13)$$

$$j_e = j_0 \frac{x}{l} \quad (14)$$

Here, b is the Tafel slope and σ_p is the proton conductivity of the CL (for the detailed discussion please see Ref. [8]). Furthermore, if (11) is fulfilled, η does not vary significantly across the CL and we, therefore, may put in (10) $\eta \simeq \text{const}$.

Temperature variation across the CCL is small (see Appendix A); thus on the right side of Eq. (10) we put $T \simeq \text{const}$. Inte-

⁴ This, however, does not mean that the temperature gradient in the CL is small (see below).

grating this equation over the CL thickness we get

$$-\lambda_{\text{eff}} \frac{\partial T}{\partial x} \Big|_l + \lambda_{\text{eff}} \frac{\partial T}{\partial x} \Big|_0 = \left(\frac{T\Delta S}{nF} + \eta \right) j_0 + \frac{j_0^2 l}{3} \left(\frac{1}{\sigma_e} + \frac{1}{\sigma_p} \right) \quad (15)$$

where (5), (13) and (14) are taken into account.

In the CL σ_e is several orders of magnitude larger, than σ_p . Thus, $1/\sigma_e$ on the right side of (15) can be neglected. Physically, Joule heat in the active layer is generated mainly in the electrolyte phase.

The left side of (15) is the sum of the two one-sided heat fluxes leaving the CL in the opposite directions: the first one is directed to the backing layer and the other to the membrane (Fig. 1). Our goal is to derive expression for the total heat flux from the CL. Clearly, the total flux is a sum of one-sided fluxes and we, therefore, may write

$$-\lambda_{\text{eff}} \frac{\partial T}{\partial x} \Big|_{\text{tot}} = \left(\frac{T\Delta S}{nF} + \eta \right) j_0 + \frac{j_0^2 l}{3\sigma_p} \quad (16)$$

Eq. (16) is the desired boundary condition for external problems. The sign “minus” on the left side means that the temperature drops along x and the heat flux is directed towards the backing layer (Fig. 1); this sign should be chosen in accordance with the formulation of the external problem.

The first term on the right side of (16) represents the heat flux due to the electrochemical reaction. The second term is the heat flux due to Joule heating in the proton-conducting phase. Generally, all terms in (16) are of the same order of magnitude and no one can be neglected.

The coefficient $1/3$ in the second term on the right side of (16) arises due to linear dependence $j_p(x)$ (13). In the case of $j_0/j_* \gg 1$, $j_p(x)$ strongly deviates from linear law. The respective coefficient in Eq. (16) can then be calculated using the relations [8]. Note also, that if $j_0/j_* \gg 1$, overpotential is no longer constant across the CL and integration of Eq. (10) with $\eta(x)$ from Ref. [8] leads to a more complicated expression. Physically, in a CL with poor proton conductivity peak of reaction rate at the membrane interface would lead to a larger overheat, especially when the thermal conductivity of the CL is not large.

It should be noted that the Joule term in (16) is proportional to the square of local current density. The distribution of local current in a cell is usually very non-uniform [14] and we may expect the effects due to temperature variation along the cell surface. Furthermore, in stacks with poor heat management these thermal non-uniformities may further enhance. Though temperature variation across the CL in the stack is still small, the absolute temperatures at different points of the cell surface may differ quite strongly. The respective temperature fields and effects should be studied with the models of a higher dimensionality. These models may utilize the boundary condition (16), where T , η and j_0 should be considered as local values.

4. Conclusions

We consider the sources and transport of heat in the catalyst layers of low-temperature polymer electrolyte fuel cells. Heat

balance equation contains the terms, which describe the thermodynamic heat generated or lost in the electrochemical reaction, the “irreversible” heat due to transport of protons through the electric double layer at the catalyst particle/electrolyte interface and the Joule heat dissipated in the membrane phase due to proton current.

The exact solution to the heat transport equation shows that in typical conditions the temperature variation across the catalyst layer is negligibly small. The heat flux from the layer is, however, not small. If proton current density varies linearly with the distance across the layer, the heat balance equation can be integrated once to yield the expression for the heat flux generated in the CL. This expression can be used as a boundary condition for “external” problems, which treat CL as an infinitely thin interface. The limits of validity of the resulting expression are discussed.

Appendix A. Solution to heat transport equation

In this section we return to the general Eq. (10). Above we have shown that heat in the CL is generated mainly in the electrolyte phase. Therefore, the term j_c^2/σ_e in (10) can be neglected.

Linear shape of proton current density in the CL (13) is equivalent to the constancy of the rate R across the layer [8]; thus Eq. (5) reduces to $j_0 = Rl$. Taking into account this relation and Eq. (13) we may rewrite Eq. (10) as

$$-\frac{\partial}{\partial x} \left(\lambda_{\text{eff}} \frac{\partial T}{\partial x} \right) = \left(\frac{T\Delta S}{nF} + \eta \right) \frac{j_0}{l} + \frac{j_0^2}{\sigma_p} \left(1 - \frac{x}{l} \right)^2 \quad (17)$$

Assuming that λ_{eff} is constant and introducing dimensionless variables:

$$\tilde{x} = \frac{x}{l}, \quad \tilde{j}_0 = \frac{j_0}{j_*} \quad (18)$$

Eq. (17) transforms to

$$-\frac{\partial^2 T}{\partial \tilde{x}^2} = \left(T + \frac{nF\eta}{\Delta S} \right) \left[\frac{\Delta S j_* l}{nF \lambda_{\text{eff}}} \right] \tilde{j}_0 + \left(\frac{j_*^2 l^2}{\lambda_{\text{eff}} \sigma_p} \right) \tilde{j}_0^2 (1 - \tilde{x})^2 \quad (19)$$

The left side of (19) has dimension of temperature (K); therefore, the expression in square brackets on the right side is dimensionless parameter:

$$\alpha = \frac{j_* l \Delta S}{nF \lambda_{\text{eff}}} = \frac{2\sigma_p b \Delta S}{nF \lambda_{\text{eff}}} \quad (20)$$

where Eq. (12) is used.

Introducing the dimensionless temperature and overvoltage:

$$\tilde{T} = \frac{T}{T_*}, \quad \tilde{\eta} = \frac{\eta}{b} \quad (21)$$

where

$$T_* = \frac{nFb}{\Delta S}$$

Eq. (19) transforms to

$$-\frac{\partial^2 \tilde{T}}{\partial \tilde{x}^2} = \alpha \tilde{j}_0 (\tilde{T} + \tilde{\eta}) + 2\alpha \tilde{j}_0^2 (1 - \tilde{x})^2 \quad (22)$$

Table A.1
Parameters for the calculations

Parameter	Value	Reference
Proton conductivity of the electrolyte phase, σ_p (S m^{-1})	1	[2]
Tafel slope, b (V)	0.05	[2]
Entropy change in the ORR, ΔS ($\text{J mol}^{-1} \text{K}^{-1}$)	326.36	[13]
Thermal conductivity of water, λ_w ($\text{W m}^{-1} \text{K}^{-1}$)	0.58	[15]
Current density, j_0 (A m^{-2})	10^4	Assumed
Overpotential, η (V)	0.5	Assumed

To qualitatively illustrate the solutions to Eq. (22) we will assume that heat flux to the membrane is negligible, i.e., $\partial \tilde{T} / \partial \tilde{x} |_{\tilde{x}=0} = 0$; heat flux at $\tilde{x} = 1$ (GDL interface) is then the total heat flux from the CL. At $\tilde{x} = 1$ we fix the temperature: $\tilde{T}(1) = \tilde{T}_1$. Note that the actual value of \tilde{T}_1 should be determined from solution of an external problem.

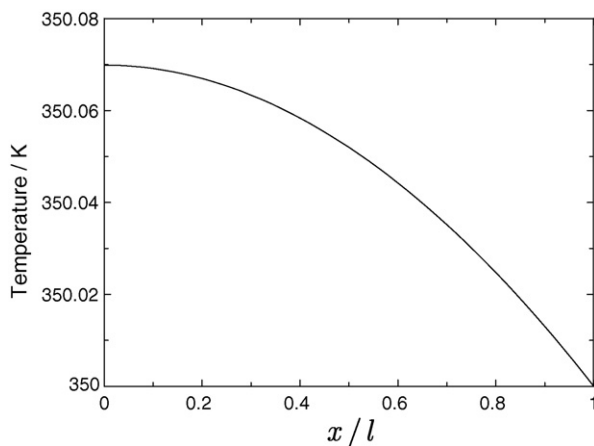


Fig. A.1. Temperature profile across the catalyst layer.

Solution to (22) subject to these boundary conditions is

$$\tilde{T}(\tilde{x}) = \frac{(\tilde{T}_1 + \tilde{\eta}) \cos(\omega \tilde{x})}{\cos \omega} - \tilde{\eta} - 2(1 - \tilde{x})^2 \tilde{j}_0 + \frac{4\tilde{j}_0[\omega \sin(\omega(1 - \tilde{x})) - \cos(\omega \tilde{x}) + \cos \omega]}{\omega^2 \cos \omega} \quad (23)$$

where

$$\omega \equiv \sqrt{\alpha \tilde{j}_0}$$

Plot of (23) with the parameters from Table A.1 is shown in Fig. A.1.⁵ Temperature variation across the CL is less than 0.1 K and can safely be ignored.⁶ However, temperature gradient at $\tilde{x} = 1$ is not small. This gradient (given by Eq. (16)) determines the heat flux from the CL to the backing layer.

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⁵ Parameter ω is small; for numerical calculations it is useful to expand (23) in terms of ω retaining only linear term.

⁶ CCL generates water; thus we may expect that in typical situations thermal conductivity of the CCL does not differ much from that of water and for the estimate we put $\lambda_{\text{eff}} \simeq \lambda_w$. In dry catalyst layer, due to lower thermal conductivity the temperature variation can be larger.