Jumps in electric potential and in temperature at the electrode surfaces of the solid oxide fuel cell

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Abstract

The electric potential profile and the temperature profile across a formation cell have been derived for the first time, using irreversible thermodynamics for bulk and surface systems. The method was demonstrated with the solid oxide fuel cell. The expression for the cell potential reduces to the classical formula when we assume equilibrium for polarized oxygen atoms across the electrolyte. Using data from the literature, we show for some likely assumptions, how the cell potential is generated at the anode, and how the energy is dissipated throughout the cell. The thermal gradient amounts to $5 \times 10^8 \text{Km}^{-1}$ when the current density is $10^4 \text{Am}^{-2}$ and the thermal resistance of the surface scales like the electrical resistance.

1. Introduction

This work is dedicated to B. Widom, who contributed so much to thermodynamics, on the occasion of his 70th birthday.

We have recently applied the theory of irreversible thermodynamics for surfaces of Albano and Bedeaux [1] to the electrode–electrolyte surface of galvanic cells [2,3]. This theory predicts that there are jumps at the surface, not only in the electric potential and the chemical potential, but also in the temperature; that is in all intensive variables. For electrochemical energy converters, the variation of the electric potential difference, $\Delta \phi$, with the current density, $j$, is central. The classical equation which describes this variation is

$$\Delta \phi = -\frac{1}{nF} \Delta_r G - |\eta^o| - |\eta^c| - rj,$$

(1.1)

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where $F$ is Faraday's constant, $n$ the number of moles of electrons in the chemical reaction and $\Delta r G$ is Gibbs energy of reaction. The overpotentials at the anode and cathode, $\eta^a$ and $\eta^c$, respectively, and the total resistance, $r$ leads to a reduction in cell potential. In the limit $j = 0$ we have the maximum cell potential (emf):

$$\Delta \phi |_{j=0} = -\frac{1}{nF} \Delta r G. \quad (1.2)$$

Knowledge of potential jumps, their variation, origin and magnitude, is important for optimum cell construction and operation. More explicit expressions for $\Delta \phi$ have been obtained by introduction of chemical potentials and the Tafel equation for the overpotentials into Eq. (1.1). It is the aim of this article to give a new method for the construction of $\Delta \phi(j)$, in which the deviations from $-\Delta r G/nF$ are explicitly calculated. This shall be done using irreversible thermodynamics for surfaces and bulk systems. The derivation, which applies in principle to any electrochemical cell, will be demonstrated for the fuel cell. In our first model study [2] we gave equations for the oxygen electrode in the fuel cell. This work is therefore an extension of the previous work to a complete cell.

Fuel cells deliver electricity by electrochemical conversion of gases. Their high efficiencies make them attractive as future energy converters. In addition to resistance losses, the major energy loss in the fuel cell is due to the electrode surfaces. There is a rapid (non-linear) reduction in $\Delta \phi$, observed already for very small $j$, which has been attributed to the overpotentials. We shall describe the fuel cell potential and discuss the losses at the electrodes, using irreversible thermodynamics. Thermodynamic calculations normally assume a continuous temperature across a surface. The current density in fuel cells are now reported to be up to $10^4 \text{A m}^{-2}$ and the electrode reaction involves adsorbed gases. These facts make it likely that the fuel cell electrode surface has high resistances for heat and charge conduction, and therefore can have a jump in the temperature in addition to a jump in the electric potential. We shall discuss this possibility, which may be relevant for material adhesion problems.

A schematic representation of the fuel cell is

$$\text{H}_2(g), \text{H}_2\text{O}(g) |^{s,a}[\text{ZrO}_2\text{Y}_2\text{O}_3(ss)]^{s,c}\text{O}_2(g). \quad (1.3)$$

We denote $|^{s,a}$ and $|^{s,c}$ as the electrode surface for the anode and cathode, respectively. The surfaces are separate thermodynamic systems, and excess variables must then be used for their thermodynamic description [4,5]. The standard electrolyte, the solid solution of zirconia with 8 w% yttria, conducts oxygen ions above 1273 K. The positions close to the anode and cathode are indicated by superscripts $e,a$ and $e,c$, respectively. The gases are transported to the electrode surface in porous matrices of electronic conductors which constitute the electrode. In our formulation we deal with five thermodynamic systems combined, three bulk systems and two surfaces. The cell reaction is composed of the steps:

$$\frac{1}{2} \text{H}_2(m, a) = \frac{1}{2} \text{H}_2(s, a), \quad (1.4)$$
\[
\begin{align*}
\frac{1}{4} \text{O}_2(m,c) &= \frac{1}{4} \text{O}_2(s,c), \\
\frac{1}{2} \text{H}_2(s,a) + \frac{1}{2} \text{O}^2-(s,a) &= \frac{1}{2} \text{H}_2\text{O}(s,a) + e^-(s,a), \\
\frac{1}{2} \text{O}^2-(s,c) &= \frac{1}{2} \text{O}^2-(s,a), \\
\frac{1}{4} \text{O}_2(s,c) + e^-(s,c) &= \frac{1}{2} \text{O}^2-(s,c), \\
\frac{1}{2} \text{H}_2\text{O}(a,s) &= \frac{1}{2} \text{H}_2\text{O}(m,s).
\end{align*}
\] (1.5) (1.6) (1.7) (1.8) (1.9)

The first steps (1.4) and (1.5) are the adsorption of the reactants on the surface. The next steps are the reaction at the anode surface, (1.6), the conduction of \( \text{O}^2^- \) across the electrolyte, (1.7), and the reaction at the cathode surface, (1.8). Eq. (1.9) is the diffusion of product water away from the surface. We assume at present that diffusion of gases in the pores is not rate-limiting for the cell reaction. The sum of all steps is the total cell reaction; production of water from hydrogen and oxygen in the gas phases close to the anode \((m,a)\) and cathode \((m,c)\). The Gibbs energy of the total reaction, used in Eq. (1.1), is therefore:

\[
\Delta_r G = \frac{1}{2} \mu_{\text{H}_2\text{O}}^{m,a} - \frac{1}{2} \mu_{\text{H}_2}^{m,a} - \frac{1}{4} \mu_{\text{O}_2}^{m,c}.
\] (1.10)

2. Principles

The dissipation function for each separate part determines the flux equations for that part. We write the entropy production in a form which allows us to solve the total set of equations in the most convenient way. Thus we use e.g. the same frame of reference for the fluxes involved, here the positive ion lattice in the electrolyte, which is equal to the non-moving surfaces, at steady state. We consider transport in the \( x \)-direction only. The terminology followed in this paper is according to de Groot and Mazur [6].

2.1. Dissipation functions and flux equations for the bulk phases

The bulk electrolyte transports heat and charge only, so the dissipation function is

\[
T\sigma = -J^q_\theta \frac{\partial \ln T}{\partial x} + jE,
\] (2.1)

where \( \sigma \) is the entropy production rate, \( T \) is the absolute temperature, \( E = -d\phi/dx \) is the electric field, and \( J^q_\theta \) is the measurable heat flux.

Diffusion of gases in the bulk electrodes is taken to be fast in this analysis. This means that there are no chemical contributions to the dissipation function of the bulk electrodes (chemical potential gradients are zero). The flux of gases in the electrodes are constant and given by the electric current density:

\[
2J_{\text{H}_2} = -2J_{\text{H}_2\text{O}} = j/F,
\] (2.2)

\[
4J_{\text{O}_2} = -j/F.
\] (2.3)
For these conditions the dissipation functions for the bulk electrodes take the same form as Eq. (2.1), and the flux equations for all bulk phases are

\[ J_q' = -L_{qq}^i \frac{\partial \ln T}{\partial x} + L_{q\phi}^i E, \]  

(2.4)

\[ j = -L_{\phi q}^i \frac{\partial \ln T}{\partial x} + L_{\phi\phi}^i E, \]  

(2.5)

where \( L_{ij}^i \) are phenomenological coefficients and Onsager reciprocal relation, \( L_{q\phi}^i = L_{\phi q}^i \), holds. Superscript \( i \) means either the bulk anode (\( a \)), the bulk electrolyte (\( e \)) or the bulk cathode (\( c \)). The coefficients of the following transformation of these equations can be directly related to experiment:

\[ \lambda^i = \left( \frac{L_{qq}^i - L_{q\phi}^i L_{\phi q}^i}{L_{\phi\phi}^i} \right) / T \]  

(2.6)

\[ \rho^i = \frac{1}{L_{i\phi}^i} \]  

(2.7)

Here \( \lambda^i = (L_{qq}^i - L_{q\phi}^i L_{\phi q}^i)/T \) is the Fourier thermal conductivity of phase \( i \), \( \rho^i = 1/L_{i\phi}^i \) is the electric resistance, and \( \pi^i = L_{q\phi}^i/L_{\phi\phi}^i \) is the Peltier coefficient. The Peltier coefficients can be identified as

\[ \pi^a = T^a \left[ S_e^k + \frac{1}{2} (S_{H_2} - S_{H_2O}) \right] / F, \]

(2.8)

\[ \pi^e = -\frac{1}{2} T^a S_{O_2}^k / F, \]

(2.9)

\[ \pi^c = -T^a \left( -S_e^k + \frac{1}{2} S_{O_2} \right) / F, \]

(2.10)

where \( S_i \) is the entropy and \( S_i^k \) is the transported entropy of \( i \), and \( T^a \) is the temperature of the anode.

We shall find the profile of the intensive variables \( \phi \) and \( T \) across the cell, for given \( j \), temperature border values, transport coefficients, Joule heat production, and a temperature difference between the outer part of the electrodes. In these calculations, the electrode surfaces play, as we shall see, an important role.

2.2. The dissipation function and flux equations for the anode surface

The dissipation function for the anode surface is

\[ T^{s,a}_m, s,a = -J^{m}_{q} T^{s,a} - T^{m,a} - J^{e}_{q} T^{e,a} - T^{s,a} - J^{m}_{H_2} (\mu_{H_2,T}^{s,a} - \mu_{H_2,T}^{m,a}) \]

\[ -J^{m}_{H_2O} (\mu_{H_2O,T}^{s,a} - \mu_{H_2O,T}^{m,a}) + J^{m}_{e} T^{s,a} v^{s,a} A^{s,a}. \]

(2.11)

There are two heat fluxes, one into the surface from the anode, \( J^{m}_{q} \), and one out of the surface into the electrolyte, \( J^{e}_{q} \). The two mass fluxes \( J^{m}_{H_2} \) and \( J^{m}_{H_2O} \) are both in the porous bulk anode. The chemical forces are \( \Delta \mu_{H_2,T}^{s,a} = \mu_{H_2,T}^{s,a} - \mu_{H_2,T}^{m,a} \) and \( \Delta \mu_{H_2O,T}^{s,a} = \mu_{H_2O,T}^{s,a} \).
where superscript $T$ means constant temperature. There is no equilibrium between the surface and the adjacent phase when these forces are non-zero. The molar fluxes are given by Eq. (2.2) in the steady state. The electric current density, $j$, through the surface, has the conjugate force $E^{s,a}$. The last term is the product of the electrode reaction rate, $v^{s,a}$, and the affinity, $A^{s,a}$, of the electrochemical reaction at the anode. In addition to Eq. (2.2) we have

$$v^{s,a} = j/2F.$$  

(2.12)

The reaction rate refers to two mole electrons (one faraday) produced. According to Eq. (1.6) the affinity is

$$A^{s,a} = \mu_{H_2O}^{s,a} - \mu_{H_2}^{s,a} - \left( \mu_{O_2}^{s,a} - 2\mu_{e}^{s,a} \right).$$  

(2.13)

The chemical potentials in this equation are not taken at constant temperature. For the oxygen atom, which can be stable at the surface, we define:

$$\mu_0^{s,a} \equiv \mu_{O_2}^{s,a} - 2\mu_{e}^{s,a}.$$  

(2.14)

The combination $\left( \mu_{O_2}^{s,a} - 2\mu_{e}^{s,a} \right)$ is the chemical potential of the polarized oxygen atom at the electroneutral surface, $\mu_0^{s,a}$. We assume that the surface has a constant polarization in the steady state. Its displacement current is then zero, and there is no contribution to $T^{s,a}$ from the displacement current. By introducing the flux dependencies of Eqs. (2.2) and (2.12) into Eq. (2.11) we have:

$$T^{s,a} = -J_q^{m,a} \frac{\Delta T^{m,a}}{T^{m,a}} - J_q^{e,f} \frac{\Delta T^{e,a}}{T^{e,a}} + j \left( -\frac{\Delta \mu_T^{s,a}}{2F} + E^{s,a} - \frac{A^{s,a}}{2F} \right),$$  

(2.15)

where $\Delta T^{m,a} = T^{s,a} - T^{m,a}$ and $\Delta T^{e,a} = T^{e,a} - T^{s,a}$ and $\Delta \mu_T^{s,a} = (\Delta \mu_H^{s,a} - \Delta \mu_{H_2O}^{s,a})$. According to Eq. (2.15), the flux equations are now:

$$J_q^{m,a} = -l_{nm}^{s,a} \frac{\Delta T^{m,a}}{T^{m,a}} - l_{me}^{s,a} \frac{\Delta T^{e,a}}{T^{e,a}} + \pi^{m,a} j,$$  

(2.16)

$$J_q^{e,f} = -l_{em}^{s,a} \frac{\Delta T^{m,a}}{T^{m,a}} - l_{ee}^{s,a} \frac{\Delta T^{e,a}}{T^{e,a}} + \pi^{e,a} j,$$  

(2.17)

$$E^A = \pi^{m,a} \frac{\Delta T^{m,a}}{T^{m,a}} + \pi^{e,a} \frac{\Delta T^{e,a}}{T^{e,a}} + r^{s,a} j.$$  

(2.18)

The effective electrical force at the anode surface is

$$E^A = E^{s,a} = \frac{1}{2F}(\Delta \mu_T^{s,a} + A^{s,a})$$  

(2.19)

so that the electric potential jump at the surface becomes:

$$E^{s,a} = \frac{1}{2F}(\Delta \mu_T^{s,a} + A^{s,a}) + \pi^{m,a} \frac{\Delta T^{m,a}}{T^{m,a}} + \pi^{e,a} \frac{\Delta T^{e,a}}{T^{e,a}} + r^{s,a} j.$$  

(2.20)

The diagonal phenomenological coefficients in the matrix above are excess properties of the anode surface. It is reasonable that the surface has an excess electric resistance.
In the bulk phase, collisions are usually obstructions to charge transfer. In the surface, however, collisions are necessary to accomplish charge transfer. The excess coefficients may depend on the state of surface polarization. Coupling coefficients are largely unknown, and we shall neglect the coefficients, \( l_{em}^s = l_{me}^s \). The Peltier coefficients are, with the convention given by Kjelstrup et al. [7]:

\[
\pi_{m,a}^e = T^a \left[ S_{e^-}^* + \frac{1}{2} (S_{H_2} - S_{H_2O}) \right] / F,
\]

\[
\pi_{s,a}^e = -\frac{1}{2} S_{O^2-}^* T^a / F.
\]

Eqs. (2.11)–(2.18) relate the jumps in the intensive variables to the surface (for \( T \) and \( \mu \)) and across the surface, \( E^{s,a} \), to one another. Once hydrogen is adsorbed, it reacts with oxygen ion and diffuses away from the surface as water at the same speed. The reaction is not in chemical equilibrium, when the affinity is different from zero. There is always local thermodynamic equilibrium at the surface, however, for the components of Eq. (2.13). The heat flux varies across the surface. There are sink and source terms which accompany the chemical reaction at the surface (the Peltier terms), and there is thermal conduction away from the surface. The direction of the conduction will depend on boundary conditions and other sources for heat (i.e. Joule heat). The energy flux across the surface is conserved, however. At stationary state, we have:

\[
J_{q,e}^{m,a} = J_{q}^{m,a} + \frac{j}{2F} (h_{H_2}^{m,a} - h_{H_2O}^{m,a}),
\]

where \( h_{H_2}^{m,a} \) and \( h_{H_2O}^{m,a} \) are enthalpies of formation for \( H_2 \) and \( H_2O \), respectively. The enthalpy difference and the entropy difference of the above equations are converted into electric energy at the anode surface.

2.3. The dissipation function and flux equations for the cathode surface

The dissipation function for the cathode surface is

\[
T^{s,c} \sigma^{s,c} = -J_{q}^{m,c} \frac{T^{m,c} - T^{s,c}}{T_{e,a}} - J_{q}^{e,c} \frac{T^{s,c} - T^{e,c}}{T_{e,c}}
- J_{O_2}^{m} (\mu_{O_2}^{s,c} - \mu_{O_2}^{c}) + jE^{s,c} - v^{s,c} A_{s,a}^{c}.
\]

The symbols have the same meaning as described above for the anode surface, they refer now, however, to the cathode surface. There is only one chemical flux, \( J_{O_2}^{m} \), in the bulk cathode. The chemical reaction Eq. (1.6) has the affinity:

\[
A^{s,c} = \mu_{O_2}^{s,c} - \frac{1}{2} h_{O_2}^{s,c}
\]
and the steady state reaction rate
\[ v^{s,c} = j/2F. \] (2.26)

Using Eqs. (2.3) and (2.25), the dissipation function becomes:
\[ T^{s,c} \sigma^{s,c} = -J^{m} \frac{T^{m,c} - T^{s,c}}{T^{e,a}} - J^{e} \frac{T^{s,c} - T^{e,c}}{T^{e,c}} + jE^{c} \] (2.27)

with the effective electric force
\[ E^{c} = E^{s,c} + \frac{1}{4F}(\mu_{H_{2},T}^{e,c} - \mu_{O_{2},T}^{s,c}) - \frac{1}{2F} \Delta A^{s,c}. \] (2.28)

The heat flux equations and \( E^{c} \) are
\[ J_{q}^{m} = -J_{mm}^{s,c} A T^{m,c} + \pi^{m,c} j, \] (2.29)
\[ J_{q}^{e} = -J_{ee}^{s,c} A T^{e,c} + \pi^{e,c} j, \] (2.30)
\[ E^{c} = \pi^{m,c} A T^{m,c} + \pi^{e,c} A T^{e,c} + \nu^{s,c} j. \] (2.31)

The Peltier coefficients are:
\[ \pi^{m,c} = T^{c} \left(-S_{s}^{*} + \frac{1}{4} S_{O_{2}}^{*}\right) / F, \] (2.32)
\[ \pi^{e,c} = -\frac{1}{2} S_{O_{2}}^{*} - T^{c} / F. \] (2.33)

A different sign convention was used in our first work at this electrode [2]. The equations which govern the heat transport has been presented before, but the electric force is described in a more general way here.

3. Reduction to the classical expression

The cell potential is minus the integral of \( E \) across the cell:
\[ \Delta \phi = -\int_{a}^{m,a} E \, dx - E^{s,a} - \int_{e,a}^{e,c} E \, dx - E^{s,c} - \int_{m,c}^{c} E \, dx. \] (3.1)

The integration is carried out over the bulk anode, the anode surface, the electrolyte, the cathode surface, and the bulk cathode. By introducing the appropriate expressions, we obtain the general result:
\[ \Delta \phi = \frac{1}{F} \left(S_{e}^{*} + \frac{1}{2} (S_{H_{2}} - S_{H_{2}O}) \right) (T^{s,a} - T^{m,a}) - \frac{1}{2F} S_{O_{2}}^{*} (T^{s,c} - T^{s,a}) \]
\[ -\frac{1}{F} \left(\frac{1}{2} S_{O_{2}} - S_{c}^{*}\right) (T^{m,c} - T^{s,c}) \]
\[
-\frac{1}{2F}(\mu_{H_2}^{s,a} - \mu_{H_2}^{m,a} - \mu_{H_2O,T}^{s,a} + \mu_{H_2O,T}^{m,a}) - \frac{1}{4F}(\mu_{O_2,T}^{m} - \mu_{O_2,T}^{s,c})
\]

\[
-\frac{1}{2F}(A^{s,a} + A^{s,c}) - j \sum_{k=1}^{5} r^k,
\]

where the last summation is carried out over all integrated ohmic resistances in the circuit.

We shall see how this expression compares to Eq. (1.1) with (1.10). We first put \( \Delta T = 0 \), and assume that there is chemical equilibrium at both surfaces \( (A^{s,a} = 0, A^{s,c} = 0) \). The expression reduces to:

\[
\Delta \phi = -(E^{s,a} + E^{s,c}) - (r^a + r^c + r^c)j
\]

\[
= -\frac{\Delta r G}{F} + \frac{1}{2F} \left( \mu_{H_2O,T}^{s,a} - \mu_{H_2O,T}^{s,c} - \frac{1}{2} \mu_{O_2,T}^{s,c} \right) + j \sum_{k=1}^{5} r^k
\]

\[
= -\frac{\Delta r G}{F} + \frac{1}{2F}(\mu_{O_2,T}^{s,a} - \mu_{O_2,T}^{s,c}) + j \sum_{k=1}^{5} r^k.
\]

We see that the classical expression for \( \text{emf} \) is obtained by setting \( \mu_{O_2,T}^{s,a} = \mu_{O_2,T}^{s,c} \) at \( j = 0 \).

In the absence of chemical equilibrium at the surface, the surface potential jumps are

\[
E^{s,a} = \frac{1}{2F} \left( \mu_{H_2O}^{m} - \mu_{H_2O}^{m,c} - \frac{1}{2} \mu_{O}^{s,c} \right) + \mu_{O_2}^{s,c} j,
\]

\[
E^{s,c} = \frac{1}{4F}(\mu_{O}^{m} - 2\mu_{O}^{m,c}) + r^{s,a} j.
\]

Also these expressions, when introduced into Eq. (2.34), give the classical emf when the assumption

\[
\mu_{O_2,T}^{s,a} = \mu_{O_2,T}^{s,c}
\]

is valid. This assumption is then required for the classical expression to be valid. The experimental observation in most solid oxide fuel cells, that \( \Delta \phi \) is about 0.2 V less than the theoretical value of Eq. (1.2) even for small \( j \) can now possibly be explained by a lack of validity of this condition.

There is electronic contact between the electrodes through the outer circuit. This gives \( \mu_{e}^{m,a} = \mu_{e}^{m,c} \). The electrolyte consists of a homogeneous material having a constant oxygen vacancy concentration. For this reason, it is likely that the chemical potential of oxygen ion of the electrolyte is constant. But, it is not necessarily true that the equalities in chemical potentials pertain into the surface, to give \( \mu_{e}^{m,a} = \mu_{e}^{s,a} = \mu_{e}^{s,c} = \mu_{e}^{m,c} \) and likewise that \( \mu_{O_2,T}^{s,a} = \mu_{O_2,T}^{s,c} \). Therefore, it may well happen that the surface chemical potentials \( \mu_{O_2,T}^{s,a} \) and \( \mu_{O_2,T}^{s,c} \) are not equal to one another. This may explain why even at \( j = 0 \), that the theoretical result for emf has not been observed.
The surface chemical potential of oxygen may likely vary with the current density (the polarization of the electrode). As soon as current is drawn from the cell, also $A_{s,a}$ and $A_{c,s}$ may differ from zero and vary with the current density. More experiments are needed to find the chemical potentials of Eq. (2.41).

4. Calculations

The relative importance of the various terms in the equations above was studied for the condition $\mu_{O,T}^{s,a} = \mu_{O,T}^{s,c}$, that is for the ideal cell. The cell potential is then a linear function of the current density, see Eq. (3.5). The electrolyte thickness was 200 $\mu$m, and the electrode thicknesses were both 150 $\mu$m in the calculation. We used as boundary conditions, first that the end temperatures of the electrode plates were the same, $T^a = T^c = T_0 = 1273$ K, and next that there was a temperature difference $\Delta T = T^a - T^c = 5$ K with $T^c = 1273$ K.

Electric potential profiles and temperature profiles across the fuel cell were then calculated using data from Table 1 and 2. Transport coefficients for the bulk phases and thermodynamic data in the tables are mainly taken from Bossel and Ferguson (see Ref. [8]). Peltier coefficients were calculated using data from Kjelstrup Ratkje and Tomii [9]. The coefficient $\pi_e$ was previously neglected by us [2]. The current density was 0, $10^3$, $5 \times 10^3$ and $10^4$ A m$^{-2}$, respectively. The oxygen and hydrogen pressures were 1 bar, and the water pressure was 0.01 bar. Faraday’s constant was 96500 C mol$^{-1}$.

The excess surface conductivities, $l^s$, or resistivities, $r^s$, were estimated from the relations:

$$l^s = l^b \frac{k}{\delta}; \quad r^s = \rho^b \frac{\delta}{k}, \quad (4.1)$$

where $l^b$ is the corresponding bulk coefficient, $\delta$ is the surface thickness and $k$ is a coefficient which scales the surface property to the bulk property. The surface thickness was set to 2 nm. For the electric resistance, we found $k = 10^{-5}$, a value consistent with the experimental resistance loss in the cell for this surface thickness. The $k$-values for the thermal conductivities were chosen equal to this value, see Table 2.

Table 1

<table>
<thead>
<tr>
<th>Entropies, $S$, and transported entropies, $S^*$, for the solid oxide fuel cell in J K$^{-1}$ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{O_2}$</td>
</tr>
<tr>
<td>$S_{H_2}$</td>
</tr>
<tr>
<td>$S_{H_2O}$</td>
</tr>
<tr>
<td>$S^*_{O_2}$</td>
</tr>
<tr>
<td>$S^*_{e^-}$</td>
</tr>
</tbody>
</table>
Table 2
Transport properties of materials for the solid oxide fuel cell

<table>
<thead>
<tr>
<th>Phase</th>
<th>Coefficient</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrodes</td>
<td>$\lambda_a = \lambda_c$</td>
<td>2 W K$^{-1}$ m$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$\tau_a = \tau_c$</td>
<td>$10^{-5}$ Ω m$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$\pi^a/T_0$</td>
<td>$-5.4 \times 10^{-4}$ JK$^{-1}$ C$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$\pi^c/T_0$</td>
<td>$-6.2 \times 10^{-4}$ JK$^{-1}$ C$^{-1}$</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>$\lambda_e$</td>
<td>3 W K$^{-1}$ m$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$\tau_e$</td>
<td>$0.1$ Ω m$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$\pi^e/T_e$</td>
<td>$-2.1 \times 10^{-4}$ JK$^{-1}$ C$^{-1}$</td>
</tr>
<tr>
<td>Anode surface</td>
<td>$k_a^e = k_n^e$</td>
<td>$10^{-2}$, $10^{-3}$ and $10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>$\delta^a$</td>
<td>$2 \times 10^{-9}$ m</td>
</tr>
<tr>
<td></td>
<td>$\pi^{m,a}/T_0$</td>
<td>$-5.4 \times 10^{-4}$ JK$^{-1}$ C$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$\pi^{c,a}/T_0$</td>
<td>$-2.1 \times 10^{-4}$ JK$^{-1}$ C$^{-1}$</td>
</tr>
<tr>
<td>Cathode surface</td>
<td>$k_c^e = k_n^e$</td>
<td>$10^{-2}$, $10^{-3}$ and $10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>$\delta^c$</td>
<td>$2 \times 10^{-9}$ m</td>
</tr>
<tr>
<td></td>
<td>$\pi^{m,c}/T_0$</td>
<td>$-6.5 \times 10^{-4}$ JK$^{-1}$ C$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$\pi^{c,c}/T_0$</td>
<td>$-2.1 \times 10^{-4}$ JK$^{-1}$ C$^{-1}$</td>
</tr>
</tbody>
</table>

5. Results and discussions

5.1. The electric potential profile

The electric potential difference, $\Delta \phi$, is always linear in $j$, as expected from the assumption applied, see Eqs. (3.5) and (3.8). The electric potential profile, which refers to the bulk anode at $x = 0$, always has its major jump at the anode surface. In the emf-calculation of the isothermal cell, which gives $(\Delta \phi)_{i=0} = 1.171$ V, the total potential jump is at this surface. When the cell starts to deliver electric current, the jump at the anode is lowered by the resistance losses. When, for instance, $\Delta \phi = 0.569$ for $10^4$ A m$^{-2}$, the jump at the anode surface is from 0.0004 to 0.971 V. The first number is higher than zero because of the Peltier effect in the electrode, the second is reduced compared to 1.171 V, mainly because of the ohmic resistance of the surface. The potential level in the electrolyte proceeds to decline across the electrolyte, until it jumps again at the cathode surface from 0.771 to 0.570. Fig. 1 shows the potential profile across the electrolyte, cathode surface and cathode for $10^3$ A m$^{-2}$. The reductions from the ideal values are then smaller.

Even at high current densities, there is only a negligible effect on the potential in the isothermal cell by Peltier effects of the electrode surfaces. This means that the electrode surface potential is not sensitive to the temperature of the electrode surface once the bulk electrode is thermostatted.

A temperature difference across the cell alters the potential profile. When the temperature is higher on the cathode side by 5 K, the emf increases 2 mV compared to
the emf of the isothermal cell. When the temperature is higher on the anode side by 5 K, the emf decreases 5 mV. These changes are due to the Peltier effects, (we did not take the temperature dependence of the entropies into account), and can be understood as follows. The Peltier coefficients at the cathode give a larger energy change than in the anode, mainly due to the reduction in gas molecules at this side. This means that heating of the anode will be more effective in raising the cell potential.

The dissipation of electric energy is by Joule heat. The potential jumps at the surfaces which originate from changes in chemical potentials do not lead to any dissipation. In the classical formulation, reaction overpotentials leads to dissipation of energy. In our theory, only the resistive contributions are dissipative.

5.2. The temperature profile

When the electrodes of the fuel cell are thermostatted, the typical temperature profile looks like the one plotted in Fig. 2. The electrolyte has a higher temperature than the bulk electrodes. The main finding is that a temperature gradient arises at both electrode surfaces. It is as high as $5 \times 10^8 \text{Km}^{-1}$ for the highest current density, and decreases almost proportionally with $j$ as $j$ is reduced. The temperature difference across the surface may appear negligible in absolute value, but the gradient is tremendous
comparing to what is normal in bulk phases. It seems likely that this may cause difficulties for material adhesion etc. The large temperature drop at the surfaces of the cell with thermostatted bulk electrodes, is largely due to a combination of Joule heat production in the electrolyte and at the surfaces, plus a low thermal conductivity, which prevents heat conduction. One may question whether the scaling factor $k = 10^{-5}$, which is partly responsible for the gradient, is a realistic choice. The value was determined by scaling the (known) electric resistance of the surface to the electrolyte values. Thermal conduction does not have the same obstruction as electrical conduction, and it might well be that the value of $k$ is higher. Still, the temperature gradient that will be obtained is considerable. We have chosen the lower value, also because kinetic theory [10] supports this.

The temperature profile in the bulk electrodes is always linear, due to their low electric resistance. In the electrolyte the temperature profile becomes parabolic at high current densities. The curving is not apparent in Fig. 2, which has $j = 10^3 \text{ A m}^{-2}$.

A peculiarity is that the surface temperature of the anode can be higher than both the temperature of the adjacent bulk anode and of the bulk electrolyte, see Fig. 2. This is most striking at low current densities, when the Peltier heat effect is comparable to the Joule heat production. The results are understood as follows: The Peltier coefficients at the anode surface express that net heat is released by disappearance of H$_2$, production
of H$_2$O and heat transported to the surface associated with O$^{2-}$ conduction in the electrolyte. The peak in temperature is connected with reduction in net cell potential, see discussion above. At the cathode surface, there is a release of heat due to disappearance of O$_2$. This effect is partly compensated by the reversible heat transport away from the surface by O$^{2-}$.

5.3. Theoretical aspects

This work is a derivation of the cell potential of a concentration cell using irreversible thermodynamics for all bulk phases and electrode surfaces. The derivation was done for a fuel cell, but the theoretical apparatus can be used for any cell. We have previously presented the equation for emf of an electrode concentration cell. New, more accurate expressions can be derived for any electrochemical cell by following that procedure and the present one.

We have obtained our results as an interplay of several effects on a local scale. This is the strength of the present method; it allows the precise localization of particular effects, and can determine their relative importance by a set of interacting phenomena. This was not possible in previous estimates [11].

The first important features of the new method is the introduction of well defined boundary conditions for the surfaces, i.e., the dissipation function, the flux equations and the Onsager relations for these two-dimensional thermodynamic systems. The boundary conditions allow the precise integration of Maxwell’s electric field across the cell. The second important point of the method, is the new formulation for electric potential jumps at very small current densities. It is shown that such losses need not be due to lack of chemical equilibrium at the electrode surface. Expressions like the ones we have derived may offer alternatives to the empirical Tafel equation for the overpotential.

The nonlinear voltage–current dependence seen in electrochemical cells in operation has so far always been interpreted by the cell being far from equilibrium. The present analysis implies that this is not necessarily so. The non-linear dependence is fully compatible with a system which is everywhere in local equilibrium, and which can be described by linear flux–force relations. The non-linearity arises in our description through the dependence of surface chemical potentials on e.g. the polarizability of the electrode.

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References