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Bedeaux, Dick; Kjelstrup, Signe; [Öttinger, Hans Christian](#) 

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Dick Bedeaux, Signe Kjelstrup, and Hans Christian Öttinger



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# Nonlinear coupled equations for electrochemical cells as developed by the general equation for nonequilibrium reversible-irreversible coupling

Dick Bedeaux,<sup>1,2,a)</sup> Signe Kjelstrup,<sup>1,2,b)</sup> and Hans Christian Öttinger<sup>1,c)</sup>

<sup>1</sup>Department of Material Science, Swiss Federal Institute of Technology, Zurich, Switzerland

<sup>2</sup>Department of Chemistry, Norwegian University of Science and Technology, Trondheim, Norway

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We show how the Butler-Volmer and Nernst equations, as well as Peltier effects, are contained in the general equation for nonequilibrium reversible and irreversible coupling, GENERIC, with a unique definition of the overpotential. Linear flux-force relations are used to describe the transport in the homogeneous parts of the electrochemical system. For the electrode interface, we choose nonlinear flux-force relationships. We give the general thermodynamic basis for an example cell with oxygen electrodes and electrolyte from the solid oxide fuel cell. In the example cell, there are two activated chemical steps coupled also to thermal driving forces at the surface. The equilibrium exchange current density obtains contributions from both rate-limiting steps. The measured overpotential is identified at constant temperature and stationary states, in terms of the difference in electrochemical potential of products and reactants. Away from these conditions, new terms appear. The accompanying energy flux out of the surface, as well as the heat generation at the surface are formulated, adding to the general thermodynamic basis. © 2014 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4894759>]

## I. INTRODUCTION

The aim of this work is to show how the expressions that are in use for the surface overpotential of an electrode can be connected via a broader thermodynamic basis. The surface overpotential is a central concept in electrochemistry, and it is of utmost importance to have a link between its theoretical description and its various measurements. Before we explain why a better basis is needed, we briefly recapitulate how the surface overpotential,  $\eta$ , is measured and interpreted. The aim is to specify in detail, conditions for which the well-known explicit expressions for  $\eta$  are valid, by providing more general expressions.

The surface overpotential is often obtained<sup>1-3</sup> from a three-electrode set up, see Fig. 1. An electric current is passing the external circuit between the working- (W) and counter (C) electrode. The potential difference  $V$  is measured between W and a currentless reference electrode (R) of the same kind as W. The overpotential is calculated as the difference between the measurement of  $V$  at current density  $j$  and  $j = 0$ . Ohmic potential drops that contribute to the measurement in Fig. 1 are corrected for, for instance, by current interruption techniques. This gives

$$\eta = V_j - V_{j=0}. \quad (1)$$

It is well known that the measurement is sensitive to the positioning of the reference electrode R.<sup>4-6</sup> The measurement has been interpreted as departure of the surface potential jump from the equilibrium potential jump.<sup>1,2</sup> The overpotential is

also routinely determined by impedance experiments, which give the surface resistance  $R_p$  and  $\eta = R_p j$ . The method is used with small amplitudes of the oscillating field, in the presence and absence of a direct current.

The relation between  $j$  and  $\eta$  for large, steady state values of  $j$  is expressed by the Butler-Volmer equation. The equation gives  $j$  as the difference between two exponential functions which can be interpreted as unidirectional rates. For the anode, we have<sup>2</sup>

$$j = j_0 \left[ \exp \left( \frac{n(1-\beta)F\eta}{RT} \right) - \exp \left( \frac{-n\beta F\eta}{RT} \right) \right]. \quad (2)$$

Here  $\beta$  is the symmetry factor or the apparent transfer coefficient, while  $R$ ,  $T$ ,  $n$ , and  $F$  are the gas constant, the absolute temperature, the number of electrons involved in the electrode reaction, and Faraday's constant, respectively. In the derivation of (2),  $\beta$  has been used to indicate the constant position in space of the activation energy barrier in front of the surface. It is 0.5, if the peak is symmetric. The parameter  $j_0$  is the equilibrium exchange current density, expressing the two-way traffic in the absence of an overpotential. The  $j_0$  has an Arrhenius-type behavior. Equation (2) owes its success to the numerous experimental results that follow the predicted relationship.

The electrochemical literature deals with the product  $\eta j$  as a pure heat source at the electrode in question.<sup>1</sup> A scalar chemical reaction rate does not couple to vectorial forces in a homogeneous phase.<sup>7-10</sup> With the word coupling we refer to the direct impact one driving force has on other fluxes in a system.<sup>9</sup> But such coupling is possible at electrode surfaces, leading to work, not dissipation. At the surface, the scalar component of a vectorial force, directed normal to the

<sup>a)</sup>Electronic mail: dick.bedeaux@chem.ntnu.no

<sup>b)</sup>Electronic mail: signe.kjelstrup@ntnu.no

<sup>c)</sup>Electronic mail: hco@math.ethz.ch

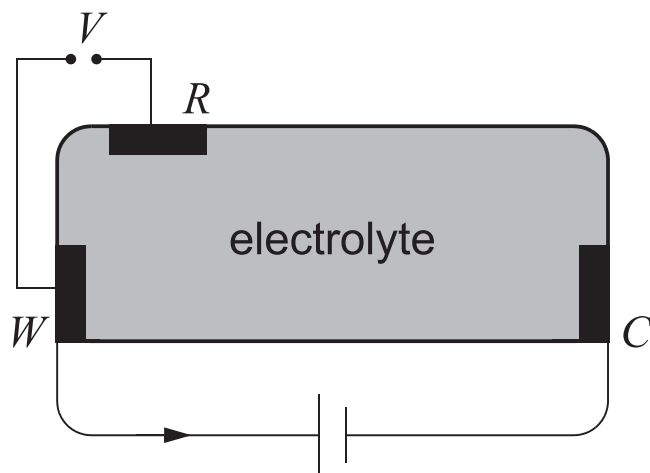


FIG. 1. A sketch of the overpotential measurement. The working electrode W is an anode. Current is passed between W and the counter electrode C. The reference electrode is R (with zero electric current). There is an Ohmic potential drop in the electrolyte to be corrected for. The arrow indicates the direction of the electron current.

surface, can couple to the scalar chemical force.<sup>10,11</sup> In other words, chemical or thermal energy can here be used to produce electrical work, or vice versa.

Equation (2) includes, however, no explicit coupling to other processes. In spite of a predicted large dissipation of energy as heat in the surface due to the product  $\eta j$ , one normally assumes isothermal conditions at the electrode surface. Therefore, one may question whether there is a broader thermodynamic basis for the Butler-Volmer equation that include coupling and can distinguish between reversible and irreversible effects.

Classical nonequilibrium thermodynamics has been used to formulate the coupling of the electric potential at an electrode interface to interface temperature jumps.<sup>7-9</sup> Linear flux-force relations were used, however, while Eq. (2) is clearly nonlinear. A nonlinear current-potential relationship has been derived for an *isothermal* electrode using mesoscopic nonequilibrium thermodynamics.<sup>12</sup> In the mesoscopic branch of nonequilibrium thermodynamics, internal variables are introduced. In order to obtain an expression that applies to the macroscopic level, like the form (2), one has to integrate over the internal variables. The integration depends on the assumption of a quasi-stationary state;<sup>13</sup> an assumption related to the mechanism of transport which may not always hold.<sup>14</sup>

These facts have motivated the present work. We are seeking to give the nonlinear form of (2) a more general thermodynamic basis, avoiding assumptions that restrict its application. We are exploring the possibility for relations to other driving forces, and conditions under which they apply. From this, we aim to derive a well defined expression for the overpotential which can provide insight into the experimental situation.

We shall use a cell with identical electrodes in the first attempt to analyze the problems posed. The electrode is the technically important oxygen electrode of the solid oxide fuel cell, see, e.g., Shao and Haile.<sup>5,15</sup> The symmetrical cell can for convenience be divided into two halves. One half cell may later be combined with another half cell to produce a forma-

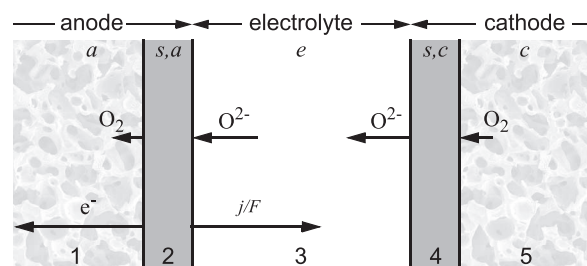
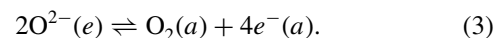


FIG. 2. A sketch the cell with two oxygen electrodes. Subsystems are numbered 1-4. The flux of the oxygen is shown at the anode,  $a$  and cathode,  $c$ , in the stationary state. The electrode surface is denoted by  $s$ , the electrolyte by  $e$ .

tion cell, using the same procedures. We present a procedure, using this example for illustration, and show that we can gain new general insight in this manner.

The system is illustrated in Fig. 2. On the anode side ( $a$ ), electrons and oxygen are produced from oxygen ions coming in this case from the solid state electrolyte:



The reaction at the cathode side ( $c$ ) is the reverse. The fluxes into and out of the anode, corresponding to this reaction are illustrated in Fig. 2. The five subsystems in series are: (1) a porous electron conducting material as anode,  $a$ , (2) the surface of the anode, i.e., the material(s) between the electronic conductor and the electrolyte,  $s, a$ , (3) the electrolyte,  $e$ , (4) the surface of the cathode, i.e., the material(s) between the electrolyte and the electron conducting materials,  $s, c$ , and (5) a porous electron conducting material as cathode,  $c$ . The cell can, in spite of being relatively simple, convert thermal energy into electrical energy, from reversible heat exchange with the surroundings.<sup>16</sup>

## II. PROPERTIES OF GENERIC

GENERIC<sup>17</sup> (general equation for nonequilibrium reversible and irreversible coupling) is designed to test the compatibility of a model with the laws of thermodynamics. Reversible and irreversible contributions to the equation of motion are identified, making it possible to answer questions on dissipative and other phenomena. GENERIC provides expressions for the time-evolution of system variables, grouped in vectors  $x$ . It moreover is a powerful tool for thermodynamic modeling activities, allowing us to digest experimental information, empirical equations, statistical mechanical models, symmetries, and intuition into thermodynamically consistent equations. In compact notation we write

$$\frac{dx}{dt} = L(x) \cdot \frac{\delta E}{\delta x} + M(x) \cdot \frac{\delta S}{\delta x}, \quad (4)$$

where  $x$  is the (sub)system variable vector,  $t$  is the time,  $E$  is the system total energy, and  $S$  is the system total entropy. By writing  $\delta/\delta x$  in front of  $E$  or  $S$ , we mean to perform a functional derivative with respect to all independent variables of the system. Different choices of the vector  $x$  are possible. The symbols  $L(x)$  and  $M(x)$  are also operators on the system

variables called the Poisson and the friction matrix operators, respectively.

The Poisson matrix is an operator which gives the reversible contributions to the time evolution of the system variables. The application to  $\delta S/\delta x$  is zero because there are no entropy changes associated with reversible processes.

The Poisson matrix is always antisymmetric, while the symmetry property of the  $M$ -matrix is not clear from the outset. A symmetric  $M$ -matrix can be expected<sup>17</sup> for ensembles that remain essentially unchanged on the time scale of the observation. When the ensembles differ from that, typically when the process progresses by rare events, the symmetry can be lost. A nonsymmetric  $M$ -matrix was previously found for the GENERIC formulation of the Boltzmann equation.<sup>17</sup> We do not expect a symmetric  $M$ -matrix for the activated processes behind Eq. (2). Also when the  $M$ -matrix is not symmetric, it must be positive semi-definite.

The friction matrix gives the irreversible contributions to the time evolution of the system variables. Energy is conserved, also during dissipation, so the application to  $\delta E/\delta x$  gives also zero. Taking the possible symmetry properties into account, we write

$$\frac{\delta S}{\delta x} \cdot L(x) = 0 = L(x) \cdot \frac{\delta S}{\delta x}, \quad (5)$$

$$\frac{\delta E}{\delta x} \cdot M(x) = 0. \quad (6)$$

These equations are called the *degeneracy* conditions. They have a predictive power in the way that they can be used to rule out forms which do not comply with the laws of thermodynamics, and shall be used here. The derivatives  $\delta E/\delta x$  and  $\delta S/\delta x$  in the degeneracy conditions are transposed. We do not explicitly indicate this, following Ref. 17.

GENERIC can be used with several variable sets, including sets that *do not* belong to classical irreversible thermodynamics. The method can, for instance, handle the variable set proposed by extended irreversible thermodynamics, which includes fluxes as variables. The form of the entropy production will depend on the set. For the set of classical thermodynamic variables used here, the resulting equations obey, as we shall see, local equilibrium. In the context of nonlinear flux-force relations, this is noteworthy.

In this work we develop for the first time GENERIC (4) for an electrochemical system. GENERIC is used in the outset for isolated systems. This may appear as a problem, as electrochemical cells are always open. We can proceed to lift the restriction, once the results from a time-dependent isolated system are obtained. We proceed to follow the prescriptions of GENERIC for the five subsystems of the cell sketched in Fig. 2. Each subsystem will first be characterized by a set of independent variables. We next give the contributions to  $E$  and  $S$  for each subsystem. The functional derivatives of  $E$  and  $S$  follow, leading to construction of the operators  $L(x)$  and  $M(x)$ . The degeneracy requirements (5) and (6) are used to confirm the correctness of the equations of motion obtained. The GENERIC description of bulk phase phenomena is to a large extent taken from the literature,<sup>17</sup> while the GENERIC description of surface phenomena is new.

The aim is at the end to make connections to the experimental situation, and to see how Eq. (2), the Nernst equation, and thermal coupling (Peltier) effects all can be derived from the same basis.

### III. THERMODYNAMIC VARIABLES OF CELL SUBSYSTEMS

The first step is to specify sets of variables for each of the five subsystems of the total cell. We choose concentrations (molar densities), momentum densities (mass densities times velocities), and internal energy densities as independent variables for all subsystems. As an example take a hydrodynamic flow problem. This set of variables will then render the Euler equations from the  $L(x)$ -operator.<sup>17,18</sup>

The choice of a frame of reference for velocities is simple for the cell in Fig. 2. The interface between a set of the non-moving solid state materials is chosen (see below for further descriptions). Gradients and fluxes along the surfaces play no role for the systems considered, so the transport processes can be regarded as one-dimensional. The  $z$ -axis is taken as the coordinate axis. All density-like variables and fluxes are then average values over the cross-section of the cell and depend only on  $z$ . All but one of the fluxes are in the  $z$ -direction. The exception being the exchange of heat between the pores and the metal in the electrodes, cf. Sec. III B. We start with the simplest phases, the homogeneous phases. The electrochemical energy conversion takes place at the anode and cathode surfaces, and the descriptions of these are more complicated. Analogies with the description of the homogeneous phases are pointed out.

#### A. Subsystem 3: The electrolyte

The electrolyte, subsystem 3, is a homogeneous ceramic material, some hundred  $\mu\text{m}$  thick.<sup>19</sup> Yttria stabilized zirconium oxide has a number of oxygen ion vacancies in the lattice (typically  $60 \text{ mol/m}^3$ ,<sup>20</sup>) and oxygen ions can move in the lattice, jumping between vacancies. The distributions of  $\text{Y}^{3+}$  over the  $\text{Zr}^{2+}$  lattice matches the vacancy distribution, making the material electroneutral. The vacancy concentration is a function of the oxygen pressure. The electrolyte does not allow oxygen molecules to short-circuit the cell.

As thermodynamic variables of the electrolyte, we take the oxygen ion concentration,  $c_{\text{O}^{2-}}$ , the momentum,  $\text{M}_{\text{O}^{2-}}$ , of the *moving* oxygen ions, and the internal energy density,  $u^e$ . The internal energy of the material can be split into contributions from the cation lattice,  $u_{\text{lat}}$ , and its oxygen ion part,  $u_{\text{O}^{2-}}$ , where  $u^e = u_{\text{O}^{2-}} + u_{\text{lat}}$ . The state of subsystem 3 is described by the variable vector  $x = (c_{\text{O}^{2-}}, \text{M}_{\text{O}^{2-}}, u^e)$ .

#### B. Subsystems 1 and 5: The electron conductor and gas supply channel

The bulk of the anode and cathode contains a current collector, normally a metal, and supply channels (pores) for oxygen in the form of air. This part of the system can be described



as two parallel transport systems, one for electrons and the other for oxygen molecules.

The density of conduction electrons in the metal is  $c_{e^-}^m(z)$ , while the oxygen density in the pores is  $c_{O_2}^p(z)$ . These densities refer here to the total cross section of the anode or cathode volumes. The momentum density of electrons is  $M_{e^-}^m(z) \equiv m_{e^-} c_{e^-}^m(z) v_{e^-}(z)$ , while the momentum density of oxygen in the pores is  $M_{O_2}^p(z) \equiv m_{O_2} c_{O_2}^p(z) v_{O_2}(z)$ . Both momenta refer also to the total cross section of the anode or cathode volumes.

The internal energy density in the metal,  $u^m(z)$  in  $J/m^3$ , is the sum of the internal energy density of the metal atoms  $u_m^m(z)$  and the electrons  $u_{e^-}^m(z)$ . The quantities  $u_m^m(z)$  and  $u_{e^-}^m(z)$  are given in terms of the partial internal energies of the metal by

$$u_m^m(z) = c_m^m(z) \frac{\partial u^m(z)}{\partial c_m^m(z)} \quad \text{and} \quad u_{e^-}^m(z) = c_{e^-}^m(z) \frac{\partial u^m(z)}{\partial c_{e^-}^m(z)}. \quad (7)$$

In the channels, the internal energy density  $u^p(z)$  of the air has contributions from nitrogen and oxygen,  $u_{N_2}^p(z)$  and  $u_{O_2}^p(z)$ , respectively. They are given in terms of the partial internal energies of the air by a relation similar to Eq. (7). All internal energies refer to the total anode or cathode volumes. The metal and the pores have their own temperature profiles,  $T^m(z)$  and  $T^p(z)$ , respectively. There is heat exchange between the metal and the pores. We will not consider the possible adsorption and decomposition of oxygen molecules on the surface of the pores.

On this background we choose as variables for the metal phase, the electron concentration,  $c_{e^-}^m$ , its momentum density  $M_{e^-}^m \equiv m_{e^-} c_{e^-}^m v_{e^-} = \rho_{e^-}^m v_{e^-}$  and the internal energy density  $u^m = u_m^m + u_{e^-}^m$ . The variable vector of the metal in subsystems 1 and 5 is thus  $x^m = (c_{e^-}^m, M_{e^-}^m, u^m)$ . For the gas phase, the corresponding variables are  $c_{O_2}^p$ ,  $M_{O_2}^p \equiv m_{O_2} c_{O_2}^p v_{O_2} = \rho_{O_2}^p v_{O_2}$  and  $u^p = u_{N_2}^p + u_{O_2}^p$ . The variable vector for the oxygen channels in subsystems 1 and 5 is thus  $x^p = (c_{O_2}^p, M_{O_2}^p, u^p)$ . We assume that nitrogen is present in the pores with no velocity. It only contributes to the energy density.

### C. Subsystems 2 and 4: The electrode surfaces

The most important subsystems are the electrode surfaces. The material of the electrode surfaces, the catalyst for the electrochemical reaction, is in this case typically a nanoporous perovskite, which adsorbs gas, and conducts electrons (holes) as well as oxygen ions. The material is in contact with the electron conductor, the gas channels (subsystems 1 or 5), and with the electrolyte (subsystem 3). The material adsorbs oxygen gas and contains a large fraction of oxygen vacancies.<sup>20</sup>

The perovskite has a certain thickness, say  $10 \mu\text{m}$ , but we can deal with it as a two-dimensional system, and use as variables the integrals over the variable profiles in the material. Each layer with a finite thickness can be integrated and replaced by a surface in this manner. The alternative is to describe the perovskite layer as 2 surfaces and one homogeneous layer. Coupling between the reaction and the heat

flux will then occur at the 2 surfaces. The outcome would not change, but the analysis becomes considerably more complicated. The perovskite layer is the thinnest layer. It is treated as a single surface because the electrode reaction takes place in this region only. It is impossible to locate the reaction in three-dimensional space. By locating it to a two-dimensional surface we can better describe its interaction with other forces. When densities have their peaks in the interfacial region, the excess densities are in good approximation independent of the precise location of the dividing surface. The equimolar surface of the electrolyte was chosen as the dividing surface for the Gibbs excess variables, see Fig. 3. All surface excess densities are defined relative to this non-moving surface. Figure 3 shows how the oxygen excess density is obtained for the given dividing surface. The densities of the adjoining bulk phases are extrapolated to the dividing surface. The excess density in the plot is the big area to the left minus the small area to the right.

The excess momentum normal to the non-moving surface (which is a scalar quantity) is zero, as the excess mass of the surface is not moving in the chosen frame of reference. This is compatible with a nonzero flux of matter through the surface in this frame of reference. Excess momenta along the surface are not relevant in the one-dimensional formulation of the problem. The only other variable is the excess internal energy. The variable vector for the electrode surface ( $a$  or  $c$ ) is therefore  $x^s = (c_{e^-}^s, c_{O_2}^s, c_{O_2^-}^s, u^s)$ . Superscript  $s$  denotes the surface.

We rewrite the electrochemical reaction for the anode with more precise reference to the sub-processes involved

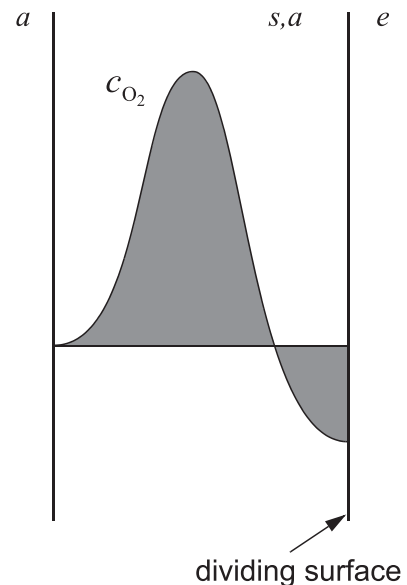
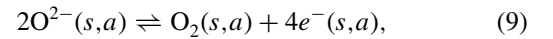
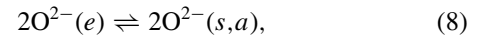
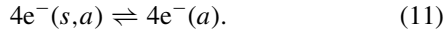
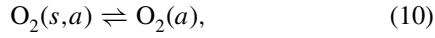


FIG. 3. The surface excess density of oxygen in the anode. The dividing surface is shown on the electrolyte side of the figure. The density is the difference between the big and the small area, obtained by extrapolating the oxygen concentration in the pores to the left to the dividing surface. The electrolyte has no oxygen gas  $e$ .



Here  $s,a$  means the surface of the anode. The first equation describes the adsorption of oxygen ions in the perovskite. The next equation is the reaction in the surface. The transfer of oxygen to the channel, and the transfer of the electron to the conduction band follows. According to the literature,<sup>15,19,20</sup> the chemical reaction (the second step) and the oxygen surface exchange (the third step) are slower than the other two. The second step is an activated electrochemical reaction. The third step, may also be activated, as the oxygen molecule at the surface possibly is dissociated into 2 oxygen atoms. The overall reaction, (3), obtains the combined rate of (9) and (10). On the cathode side, all steps are reversed.

#### IV. THE SYSTEM TOTAL ENERGY AND ENTROPY AND THEIR FUNCTIONAL DERIVATIVES

The next step of GENERIC is to give the system's total energy and entropy. The total energy is found by straight forward summing over the internal, electrostatic, and kinetic energies of each subsystem:

$$\begin{aligned} E = & \int_a \left( u^a + z_{e^-} c_{e^-}^{ma} F \psi^a + \frac{|M_{e^-}^{ma}|^2}{2m_{e^-} c_{e^-}^{ma}} + \frac{|M_{\text{O}_2}^{pa}|^2}{2m_{\text{O}_2} c_{\text{O}_2}^{pa}} \right) dz \\ & + u^{s,a} + (z_{e^-} c_{e^-}^{s,a} + z_{\text{O}_2} c_{\text{O}_2}^{s,a}) F \psi^{s,a} \\ & + \int_e \left( u^e + z_{\text{O}_2} c_{\text{O}_2}^{e} F \psi^e + \frac{|M_{\text{O}_2}^e|^2}{2m_{\text{O}_2} c_{\text{O}_2}^e} \right) dz \\ & + u^{s,c} + (z_{e^-} c_{e^-}^{s,a} + z_{\text{O}_2} c_{\text{O}_2}^{s,a}) F \psi^{s,c} \\ & + \int_c \left( u^c + z_{e^-} c_{e^-}^{mc} F \psi^c + \frac{|M_{e^-}^{mc}|^2}{2m_{e^-} c_{e^-}^{mc}} + \frac{|M_{\text{O}_2}^{pc}|^2}{2m_{\text{O}_2} c_{\text{O}_2}^{pc}} \right) dz. \end{aligned} \quad (12)$$

Charged particles add electrostatic energy  $z_k F \psi$ , where  $z_k$  is the charge number, and  $F$  is Faraday's constant, and  $\psi$  is the electrostatic potential. We have  $z_{e^-} = -1$ ,  $z_{\text{O}_2} = -2$  and  $z_{\text{O}_2} = 0$ . The kinetic energy of the two non-moving surfaces are zero. As said before, all densities are averages over the total cross section of the whole volume in the anode, electrolyte, and cathode, and over the whole surface for the anode and cathode surfaces.

The functional derivatives with respect to the variables in the electrolyte are

$$\frac{\delta E}{\delta x^e} = \begin{pmatrix} \frac{\delta E}{\delta c_{\text{O}_2}^e} \\ \frac{\delta E}{\delta M_{\text{O}_2}^e} \\ \frac{\delta E}{\delta u^e} \end{pmatrix} = \begin{pmatrix} z_{\text{O}_2} F \psi^e - \frac{1}{2} (v_{\text{O}_2}^e)^2 \\ v_{\text{O}_2}^e \\ 1 \end{pmatrix}. \quad (13)$$

The functional derivatives of  $E$  with respect to the variables in the anode are the same with the superscript  $e$  replaced by  $ma$  in the anode metal and by  $pa$  in the pores. The symbol  $z_{\text{O}_2}$ -

is replaced by  $z_{e^-}$  or  $z_{\text{O}_2}$  in the metal or the pores, respectively. The functional derivatives with respect to the variables in the cathode are the same with superscript  $a$  replaced by  $c$ . The functional derivatives with respect to the variables of the anode surface are

$$\frac{\delta E}{\delta x^{s,a}} = \begin{pmatrix} \frac{\delta E}{\delta c_{e^-}^{s,a}} \\ \frac{\delta E}{\delta c_{\text{O}_2}^{s,a}} \\ \frac{\delta E}{\delta c_{\text{O}_2}^{s,a}} \\ \frac{\delta E}{\delta u^{s,a}} \end{pmatrix} = \begin{pmatrix} z_{e^-} F \psi^{s,a} \\ 0 \\ z_{\text{O}_2} F \psi^{s,a} \\ 1 \end{pmatrix}. \quad (14)$$

For the cathode surface the functional derivatives are the same with the superscript  $s, a$  replaced by  $s, c$ .

The entropy of the total system is the sum of the entropies of the three phases and the surfaces:

$$S = \int_a s^a dz + s^{s,a} + \int_e s^e dz + s^{s,c} + \int_c s^c dz. \quad (15)$$

We assume local equilibrium (validity of Gibbs equation) in order to find the functional derivatives of  $S$  with respect to the variables in the electrolyte:

$$\frac{\delta S}{\delta x^e} = \begin{pmatrix} \frac{\delta S}{\delta c_{\text{O}_2}^e} \\ \frac{\delta S}{\delta M_{\text{O}_2}^e} \\ \frac{\delta S}{\delta u^e} \end{pmatrix} = \begin{pmatrix} -\mu_{\text{O}_2}^e / T^e \\ 0 \\ 1/T^e \end{pmatrix}, \quad (16)$$

where  $\mu_k$  are chemical potentials. The functional derivatives of  $S$  with respect to the variables in the anode are the same with the superscript  $e$  replaced by  $ma$  in the anode metal and by  $pa$  in the pores. The functional derivatives with respect to the variables in the cathode are the same with superscript  $a$  replaced by  $c$ . The functional derivatives with respect to the variables of the anode surface are

$$\frac{\delta S}{\delta x^{s,a}} = \begin{pmatrix} \frac{\delta S}{\delta c_{e^-}^{s,a}} \\ \frac{\delta S}{\delta c_{\text{O}_2}^{s,a}} \\ \frac{\delta S}{\delta c_{\text{O}_2}^{s,a}} \\ \frac{\delta S}{\delta u^{s,a}} \end{pmatrix} = \begin{pmatrix} -\mu_{e^-}^{s,a} / T^{s,a} \\ -\mu_{\text{O}_2}^{s,a} / T^{s,a} \\ -\mu_{\text{O}_2}^{s,a} / T^{s,a} \\ 1/T^{s,a} \end{pmatrix}. \quad (17)$$

For the cathode surface the functional derivatives are the same with the superscript  $s, a$  replaced by  $s, c$ .

#### V. THE POISSON MATRICES

The Poisson matrix is the operator that produces the reversible contributions to the equations of motion from the energy gradient. Taking again hydrodynamic flow as an example, the outcome will lead to the Euler equations. When operating on the entropy gradient the result is zero, as the entropy is not affected by reversible operations. We will first discuss subsystem 3, the electrolyte. With only one moving component this is easier than in the bulk electrodes where there are two moving components.

### A. Subsystem 3: The electrolyte

The variables in the electrolyte are  $x^e = (c_{\text{O}^{2-}}^e, M_{\text{O}^{2-}}^e, u^e)$ . The Poisson matrix is<sup>17</sup>

$$L^e(z, z') = \left( \begin{array}{c|cc} 0 & c_{\text{O}^{2-}}^e(z') \frac{\partial \delta}{\partial z'} & 0 \\ -\frac{\partial \delta}{\partial z} c_{\text{O}^{2-}}^e(z) & M_{\text{O}^{2-}}^e(z') \frac{\partial \delta}{\partial z'} - \frac{\partial \delta}{\partial z} M_{\text{O}^{2-}}^e(z) & -\frac{\partial \delta}{\partial z} [u^e(z) + p^e(z')] \\ 0 & [u^e(z') + p^e(z)] \frac{\partial \delta}{\partial z'} & 0 \end{array} \right), \quad (18)$$

where  $p^e$  is the pressure of the electrolyte and  $\delta = \delta(z - z')$  is the Dirac delta function. By integrating over the  $z'$  coordinate, we can write  $L^e$  as a differential operator

$$L^e(z) = \left( \begin{array}{c|cc} 0 & -\frac{\partial}{\partial z} c_{\text{O}^{2-}}^e(z) & 0 \\ -c_{\text{O}^{2-}}^e(z) \frac{\partial}{\partial z} & -\frac{\partial}{\partial z} M_{\text{O}^{2-}}^e(z) - M_{\text{O}^{2-}}^e(z) \frac{\partial}{\partial z} & -[u^e(z) \frac{\partial}{\partial z} + \frac{\partial}{\partial z} p^e(z)] \\ 0 & -[\frac{\partial}{\partial z} u^e(z) + p^e(z) \frac{\partial}{\partial z}] & 0 \end{array} \right). \quad (19)$$

The product  $L^e(x) \cdot \frac{\delta E}{\delta x^e}$  gives the reversible contribution to the time derivatives of the variables:

$$\frac{\partial c_{\text{O}^{2-}}^e(z)}{\partial t} = -\frac{\partial}{\partial z} c_{\text{O}^{2-}}^e(z) v_{\text{O}^{2-}}^e(z), \quad (20)$$

$$\begin{aligned} \frac{\partial M_{\text{O}^{2-}}^e(z)}{\partial t} &= -z_{\text{O}^{2-}} c_{\text{O}^{2-}}^e(z) F \frac{\partial}{\partial z} \psi^e(z) \\ &\quad - \frac{\partial}{\partial z} M_{\text{O}^{2-}}^e(z) v_{\text{O}^{2-}}^e(z) - \frac{\partial}{\partial z} p^e(z), \end{aligned} \quad (21)$$

$$\frac{\partial u^e(z)}{\partial t} = - \left[ \frac{\partial}{\partial z} u^e(z) + p^e(z) \frac{\partial}{\partial z} \right] v_{\text{O}^{2-}}^e(z). \quad (22)$$

The first two equations are simply the well known balance equations for mass and momentum. These equations correspond to the Euler equations in hydrodynamics. The last equation gives the flow of internal energy density.

The degeneracy requirement is satisfied. We recover the Gibbs-Duhem equation:

$$c_{\text{O}^{2-}}^e(z) \frac{\partial}{\partial z} \frac{\mu_{\text{O}^{2-}}^e(z)}{T^e(z)} - u^e(z) \frac{\partial}{\partial z} \frac{1}{T^e(z)} - \frac{\partial}{\partial z} \frac{p^e(z)}{T^e(z)} = 0. \quad (23)$$

This equation applies for a system in local thermodynamic equilibrium. We have assumed that  $(\mu/T)$  is constant for the electrolyte lattice.

### B. Subsystems 1 and 5: The electron conductor and gas supply channels

The Poisson matrix in the anode metal and in the pores are the same with the superscript  $e$  replaced by  $ma$  in the anode metal and by  $pa$  in the pores. In the expression for the reversible contribution to the time derivative one should use  $z_{e-}$  and  $z_{\text{O}_2}$  in the metal and the pores, respectively. The Gibbs-Duhem relation is also the same, when one uses the proper superscripts, and where we assume that  $\mu/T$  is constant for atoms in the metal and for the nitrogen in the pores.

### C. Subsystems 2 and 4: The electrode surfaces

The  $L$  operators for the anode and the cathode surfaces are zero. There is no reversible contribution to the time rate of change of the excess variables that we use for the surface.

### D. Remarks

We have seen above that the Poisson operator generates equations for the bulk phases that are familiar or taken for granted; namely, the balance equations for mass, momentum, and internal energy. The corresponding Gibbs-Duhem's equations are consequences of the degeneracy requirement. For the surface, there are no reversible contributions. A complete set of equations for reversible transformations of energy can therefore be given using GENERIC.

The appearance of these equations means that any volume element of the cell obeys local equilibrium.<sup>21,23</sup> This applies also to the two-dimensional system, the surface, when it is defined with Gibbs excess variables. In electrochemistry the assumptions of local thermodynamic equilibrium and electroneutrality are commonly used, see, e.g., Ref. 21.

Momentum balances are frequently not considered in electrochemical modeling of solid state cells. Equations like (21) express that the pressure gradient balances the gradient in the electric potential at steady state. We return to these issues in Sec. IX.

## VI. THE FRICTION MATRICES FOR LINEAR-FLUX FORCE RELATIONS

The friction matrix is the operator that produces the irreversible contributions to the equations of motion from the entropy gradient. Taking again hydrodynamic flow as an example, the outcome gives, together with the reversible contributions, the Navier-Stokes equation. The generalized friction of a system is the system's total entropy production:

$$\int \frac{\delta S}{\delta x(z)} \cdot M \cdot \frac{\delta S}{\delta x(z)} dz = \int \sigma(z) dz. \quad (24)$$



Classical nonequilibrium thermodynamics gives the local value of the entropy production as a product sum of independent fluxes and forces:

$$\sigma = \sum_i J_i X_i. \quad (25)$$

The bilinear form of the entropy production applies to linear, as well as nonlinear processes.<sup>17,22,24</sup> GENERIC does not provide a particular form of the flux-force relations, but can provide restrictions via the form of the chosen friction matrix, by requiring that the degeneracy conditions are obeyed.<sup>17</sup> We shall choose the classical form, given by irreversible thermodynamics for the homogeneous phases and for a first approach to the interfaces. The degeneracy requirement of the friction matrix,  $\delta E/\delta x \cdot M = 0$ , means that the total energy is not changed by irreversible operations. This condition shall be shown to be true for all subsystems in the example cell, first for linear and eventually for nonlinear flux-force relations.

### A. Subsystem 3: The electrolyte

The entropy production has two fluxes and conjugate driving forces.<sup>9</sup> With the chosen set of independent variables we have contributions from the total heat flux,  $J_q^e$ , multiplied by the gradient in the inverse temperature of the electrolyte  $\frac{\partial}{\partial z} \frac{1}{T^e}$ , and the oxygen ion flux,  $J_{O^{2-}}^e$ , multiplied with its driving force,  $(\frac{\partial}{\partial z} \frac{\mu_{O^{2-}}^e}{T^e} + z_{O^{2-}} \frac{F}{T^e} \frac{\partial \psi^e}{\partial z})$ :

$$\sigma^e = J_q^e \frac{\partial}{\partial z} \frac{1}{T^e} - J_{O^{2-}}^e \left( \frac{\partial}{\partial z} \frac{\mu_{O^{2-}}^e}{T^e} + z_{O^{2-}} \frac{F}{T^e} \frac{\partial \psi^e}{\partial z} \right). \quad (26)$$

The total entropy production in the electrolyte is equal to the integral of  $\sigma^e(z)$  over the electrolyte. The linear flux-force relations are accordingly:

$$\begin{aligned} J_{O^{2-}}^e &= -\ell_{11}^e \left( \frac{\partial}{\partial z} \frac{\mu_{O^{2-}}^e}{T^e} + z_{O^{2-}} \frac{F}{T^e} \frac{\partial \psi^e}{\partial z} \right) + \ell_{12}^e \frac{\partial}{\partial z} \frac{1}{T^e}, \\ J_q^e &= -\ell_{21}^e \left( \frac{\partial}{\partial z} \frac{\mu_{O^{2-}}^e}{T^e} + z_{O^{2-}} \frac{F}{T^e} \frac{\partial \psi^e}{\partial z} \right) + \ell_{22}^e \frac{\partial}{\partial z} \frac{1}{T^e}, \end{aligned} \quad (27)$$

where the Onsager reciprocal relation is  $\ell_{21}^e = \ell_{12}^e$ . The Onsager coefficients can depend on the variables and depend therefore indirectly on  $z$ . By introducing these relations into

the entropy production, we obtain

$$\begin{aligned} \sigma^e(z) &= \left( - \left( \frac{\partial}{\partial z} \frac{\mu_{O^{2-}}^e}{T^e} + z_{O^{2-}} \frac{F}{T^e} \frac{\partial \psi^e}{\partial z} \right), \frac{\partial}{\partial z} \frac{1}{T^e} \right) \cdot \ell^e \\ &\cdot \left( - \left( \frac{\partial}{\partial z} \frac{\mu_{O^{2-}}^e}{T^e} + z_{O^{2-}} \frac{F}{T^e} \frac{\partial \psi^e}{\partial z} \right), \frac{\partial}{\partial z} \frac{1}{T^e} \right), \end{aligned} \quad (28)$$

where the  $\ell^e$  matrix is

$$\ell^e = \begin{pmatrix} \ell_{11}^e & \ell_{12}^e \\ \ell_{21}^e & \ell_{22}^e \end{pmatrix}. \quad (29)$$

The resulting  $M^e$ -matrix relates to the number of independent variables of the system, while  $\ell^e$ -matrix relates to the number of processes. GENERIC connects the two via the  $C$ -matrix:

$$M^e = [C^e]^T \cdot \ell^e \cdot C^e, \quad (30)$$

where T as a superscript indicates the transpose of a matrix. The chosen  $M^e$  operator is symmetric in view of the symmetry of the Onsager matrix. One choice of the  $C^e$  operator is such that  $C^e \cdot \delta S/\delta x^e = (-\frac{\partial}{\partial z} \frac{\mu_{O^{2-}}^e}{T^e} + z_{O^{2-}} \frac{F}{T^e} \frac{\partial \psi^e}{\partial z}, \frac{\partial}{\partial z} \frac{1}{T^e})$  and  $\delta E/\delta x^e \cdot C^e = 0$ . The operation  $C^e \cdot \delta S/\delta x^e$  will then produce the driving forces of the system, familiar to classical nonequilibrium thermodynamics. The resulting choice can be written as

$$C^e = \begin{pmatrix} \frac{\partial}{\partial z} v_{O^{2-}}^e & \frac{\partial}{\partial z} & -z_{O^{2-}} F \frac{\partial \psi^e}{\partial z} \\ 0 & 0 & \frac{\partial}{\partial z} \end{pmatrix}. \quad (31)$$

We see that  $C^e$  has three columns (one for each variable) and two rows (one for each process). We verify, using partial integration, that

$$\int_{el} \frac{\delta S}{\delta x^e(z)} \cdot M^e \cdot \frac{\delta S}{\delta x^e(z)} dz = \int_{el} \sigma^e(z) dz \quad (32)$$

gives the total entropy production. The degeneracy requirement is obeyed, because

$$\frac{\delta E}{\delta x^e(z)} \cdot (C^e)^T = (z_{O^{2-}} F \psi^e - \frac{1}{2} (v_{O^{2-}}^e)^2, v_{O^{2-}}^e, 1) \cdot (C^e)^T = 0. \quad (33)$$

The operator  $M^e$  has now all properties asked for by GENERIC. We can then calculate the irreversible contribution to the time rate of change of the variables

$$\begin{aligned} M^e \cdot \frac{\delta S}{\delta x^e} &= -[C^e]^T \cdot \ell^e \cdot C^e \cdot \begin{pmatrix} -\mu_{O^{2-}}^e/T^e \\ 0 \\ 1/T^e \end{pmatrix} \\ &= [C^e]^T \cdot \ell^e \cdot \begin{pmatrix} -\left( \frac{\partial}{\partial z} \frac{\mu_{O^{2-}}^e}{T^e} + z_{O^{2-}} \frac{F}{T^e} \frac{\partial \psi^e}{\partial z} \right) \\ \frac{\partial}{\partial z} \frac{1}{T^e} \end{pmatrix} \\ &= - \begin{pmatrix} \frac{\partial}{\partial z} & 0 \\ \frac{\partial}{\partial z} v_{O^{2-}}^e & 0 \\ z_{O^{2-}} F \frac{\partial \psi^e}{\partial z} & \frac{\partial}{\partial z} \end{pmatrix} \cdot \begin{pmatrix} -\ell_{11}^e \left( \frac{\partial}{\partial z} \frac{\mu_{O^{2-}}^e}{T^e} + z_{O^{2-}} \frac{F}{T^e} \frac{\partial \psi^e}{\partial z} \right) + \ell_{12}^e \frac{\partial}{\partial z} \frac{1}{T^e} \\ -\ell_{21}^e \left( \frac{\partial}{\partial z} \frac{\mu_{O^{2-}}^e}{T^e} + z_{O^{2-}} \frac{F}{T^e} \frac{\partial \psi^e}{\partial z} \right) + \ell_{22}^e \frac{\partial}{\partial z} \frac{1}{T^e} \end{pmatrix} \end{aligned}$$

$$= \left( \begin{array}{c} \frac{\partial}{\partial z} \ell_{11}^e \left( \frac{\partial}{\partial z} \frac{\mu_{\text{O}_2^-}^e}{T^e} + z_{\text{O}_2^-} \frac{F}{T^e} \frac{\partial \psi^e}{\partial z} \right) - \frac{\partial}{\partial z} \ell_{12}^e \frac{\partial}{\partial z} \frac{1}{T^e} \\ \frac{\partial}{\partial z} v_{\text{O}_2^-}^e \left\{ \ell_{11}^e \left( \frac{\partial}{\partial z} \frac{\mu_{\text{O}_2^-}^e}{T^e} + z_{\text{O}_2^-} \frac{F}{T^e} \frac{\partial \psi^e}{\partial z} \right) - \ell_{12}^e \frac{\partial}{\partial z} \frac{1}{T^e} \right\} \\ \frac{\partial}{\partial z} \ell_{21}^e \frac{\partial}{\partial z} \frac{\mu_{\text{O}_2^-}^e}{T^e} + z_{\text{O}_2^-} \frac{F}{T^e} \frac{\partial}{\partial z} \ell_{21}^e \frac{\partial \psi^e}{\partial z} - \frac{\partial}{\partial z} \ell_{22}^e \frac{\partial}{\partial z} \frac{1}{T^e} + z_{\text{O}_2^-} F \frac{\partial \psi^e}{\partial z} \ell_{11}^e \left( \frac{\partial}{\partial z} \frac{\mu_{\text{O}_2^-}^e}{T^e} + z_{\text{O}_2^-} \frac{F}{T^e} \frac{\partial \psi^e}{\partial z} \right) \end{array} \right). \quad (34)$$

## B. Subsystems 1 and 5: The electron conductor and gas supply channels

We do the analysis for the anode. The results for the cathode are the same as for the anode with superscript  $a$  replaced by  $c$ . We remember that  $\delta S/\delta x^{ma} = (-\mu_{e^-}^a/T^{ma}, 0, 1/T^{ma})$  and  $\delta S/\delta x^{pa} = (-\mu_{\text{O}_2}^a/T^{pa}, 0, 1/T^{pa})$ . The entropy production is then

$$\sigma^a = \sigma^{ma} + \sigma^{pa} + \sigma^{mpa}, \quad (35)$$

where<sup>9</sup>

$$\begin{aligned} \sigma^{ma} &= J_q^{ma} \frac{\partial}{\partial z} \frac{1}{T^{ma}} - J_{e^-}^a \left( \frac{\partial}{\partial z} \frac{\mu_{e^-}^a}{T^{ma}} + z_{e^-} \frac{F}{T^{ma}} \frac{\partial \psi^a}{\partial z} \right), \\ \sigma^{pa} &= J_q^{pa} \frac{\partial}{\partial z} \frac{1}{T^{pa}} - J_{\text{O}_2}^a \frac{\partial}{\partial z} \frac{\mu_{\text{O}_2}^a}{T^{pa}}, \\ \sigma^{mpa} &= J_q^{mp} \left( \frac{1}{T^{pa}} - \frac{1}{T^{ma}} \right). \end{aligned} \quad (36)$$

The first contribution  $\sigma^{ma}$  contains the fluxes of heat and electrons in the  $z$  direction in the metal, multiplied with their appropriate driving forces, the second contribution  $\sigma^{pa}$  describes the fluxes of heat and oxygen gas in the  $z$  direction in the pores multiplied with their appropriate driving forces, and the third contribution  $\sigma^{mpa}$  contains the heat flux between the metal and the pore multiplied with the difference in the inverse temperature between the phases.

These three contributions describe processes which do not couple directly since they take place in different locations. Because of this we can discuss their contributions to the friction operator separately. We did not add  $m$  as a superscript to  $\mu_{e^-}^a$  and  $\psi^a$  as these quantities are not affected by the averaging over the cross section of the anode. Similarly, we did not add  $p$  as a superscript to  $\mu_{\text{O}_2}^a$ . Neither did we add  $m$  and  $p$  as superscript to  $J_{e^-}^a$  and  $J_{\text{O}_2}^a$  as these are both averaged over the cross section of the anode.

The friction matrix and all the other relations in the anode metal and in the pores are the same as for the electrolyte in Sec. VI A with the superscript  $e$  replaced by  $ma$  in the anode metal and by  $pa$  in the pores. In the metal and the pores, we use  $z_{e^-}$  and  $z_{\text{O}_2}$ , respectively.

The heat exchange between the metal and the pores is governed by

$$J_q^{mpa} = \ell_q^{mpa} \left( \frac{1}{T^{pa}} - \frac{1}{T^{ma}} \right), \quad (37)$$

By introducing this into the entropy production, we obtain

$$\sigma^{mpa} = \left( \frac{1}{T^{pa}} - \frac{1}{T^{ma}} \right) \ell_q^{mpa} \left( \frac{1}{T^{pa}} - \frac{1}{T^{ma}} \right). \quad (38)$$

For this contribution to the friction matrix we use  $\delta S/\delta x^a = (\delta S/\delta x^{ma}, \delta S/\delta x^{pa}) = (-\mu_{e^-}^a/T^{ma}, 0, 1/T^{ma}, -\mu_{\text{O}_2}^a/T^{pa}, 0, 1/T^{pa})$ . The friction matrix can be written as

$$M^{mpa} = (C^{mpa})^T \cdot \ell_q^{mpa} \cdot C^{mpa} \quad (39)$$

with

$$C^{mpa} = (0, 0, -1, 0, 0, 1). \quad (40)$$

It is now easy to verify that

$$\int_a \frac{\delta S}{\delta x^a} \cdot M^{mpa} \cdot \frac{\delta S}{\delta x^a} dz = \int_a \sigma^{mpa}(z) dz \quad (41)$$

gives the total entropy production for heat exchange between the metal and the pores. We verify also that  $M^{mpa}$  satisfies the degeneracy requirement:

$$\begin{aligned} \frac{\delta E}{\delta x^a(z)} \cdot (C^{mpa})^T \\ = \left( -F\psi^a - \frac{1}{2}(v_{e^-}^a)^2, v_{e^-}^a, 1, -\frac{1}{2}(v_{\text{O}_2}^a)^2, v_{\text{O}_2}^a, 1 \right) \\ \cdot (C^{mpa})^T = 0. \end{aligned} \quad (42)$$

After having constructed the  $M^{mpa}$  operator, we calculate the irreversible contribution to the time rate of change of the variables

$$\begin{aligned} M^{mpa} \cdot \frac{\delta S}{\delta x^a} &= -[C^{mpa}]^T \cdot \ell_q^{mpa} \cdot C^{mpa} \cdot \begin{pmatrix} -\mu_{e^-}^a/T^{ma} \\ 0 \\ 1/T^{ma} \\ -\mu_{\text{O}_2}^a/T^{pa} \\ 0 \\ 1/T^{pa} \end{pmatrix} \\ &= [C^{mpa}]^T \cdot \ell_q^{mpa} \left( \frac{1}{T^{pa}} - \frac{1}{T^{ma}} \right) \\ &= \begin{pmatrix} 0 \\ 0 \\ -\ell_q^{mpa} \left( \frac{1}{T^{pa}} - \frac{1}{T^{ma}} \right) \\ 0 \\ 0 \\ \ell_q^{mpa} \left( \frac{1}{T^{pa}} - \frac{1}{T^{ma}} \right) \end{pmatrix}. \end{aligned} \quad (43)$$

This is exactly the contribution to the time rate of change of the internal energy of the metal and of the pores due to the exchange of heat between the metal and the pores.

### C. Subsystems 2 and 4: The electrode surfaces

We do the analysis for the anode surface. The results for the cathode surface are then obtained by replacing superscript  $s, a$  by  $s, c$ . The entropy production is obtained from classical nonequilibrium thermodynamics for surfaces.<sup>9</sup> With the independent variables used here, we obtain seven contributions: the flux of electrons,  $J_{e^-}^{a,e}$ , multiplied with its driving force,  $-(\frac{\mu_{e^-}^{s,a}}{T^{s,a}} - \frac{\mu_{e^-}^{a,e}}{T^{a,e}} + z_{e^-} F \frac{\Delta_{as}\psi}{T^{s,a}})$ , the flux of oxygen gas,  $J_{O_2}^{a,e}$ , multiplied with its driving force,  $(\frac{\mu_{O_2}^{s,a}}{T^{s,a}} - \frac{\mu_{O_2}^{a,e}}{T^{a,e}})$ , the flux of the oxygen ion,  $J_{O_2^-}^{e,a}$ , multiplied with its driving force,  $-(\frac{\mu_{O_2^-}^{e,a}}{T^{e,a}} - \frac{\mu_{O_2^-}^{s,a}}{T^{s,a}} + z_{O_2^-} F \frac{\Delta_{se}\psi}{T^{s,a}})$ , the chemical reaction  $r^{s,a}$  multiplied by its driving force,  $-\frac{\Delta G^{s,a}}{T^{s,a}}$ , the heat flux into the surface from the metal in the anode,  $J_q^{ma,e}$ , multiplied with the difference in the inverse temperature between the relevant phases, the heat flux into the surface from the pores of the anode,  $J_q^{pa,e}$ , multiplied with the difference in the inverse temperature between the relevant phases, and the heat flux from the surface into the electrolyte,  $J_q^{e,a}$ , multiplied with the difference in the inverse temperature between the relevant phases:

$$\begin{aligned} \sigma^{s,a} = & -J_{e^-}^{a,e} \left( \frac{\mu_{e^-}^{s,a}}{T^{s,a}} - \frac{\mu_{e^-}^{a,e}}{T^{a,e}} + z_{e^-} F \frac{\Delta_{as}\psi}{T^{s,a}} \right) \\ & - J_{O_2}^{a,e} \left( \frac{\mu_{O_2}^{s,a}}{T^{s,a}} - \frac{\mu_{O_2}^{a,e}}{T^{a,e}} \right) \\ & - J_{O_2^-}^{e,a} \left( \frac{\mu_{O_2^-}^{e,a}}{T^{e,a}} - \frac{\mu_{O_2^-}^{s,a}}{T^{s,a}} + z_{O_2^-} F \frac{\Delta_{se}\psi}{T^{s,a}} \right) - r^{s,a} \frac{\Delta G^{s,a}}{T^{s,a}} \\ & + J_q^{ma,e} \left( \frac{1}{T^{s,a}} - \frac{1}{T^{ma,e}} \right) + J_q^{pa,e} \left( \frac{1}{T^{s,a}} - \frac{1}{T^{pa,e}} \right) \\ & + J_q^{e,a} \left( \frac{1}{T^{e,a}} - \frac{1}{T^{s,a}} \right), \end{aligned} \quad (44)$$

where  $\Delta_{as}\psi \equiv \psi^{s,a} - \psi^{a,e}$ ,  $\Delta_{se}\psi \equiv \psi^{e,a} - \psi^{s,a}$ , and  $\Delta G^{s,a} \equiv 4\mu_{e^-}^{s,a} + \mu_{O_2}^{s,a} - 2\mu_{O_2^-}^{s,a}$ .

#### 1. The isothermal linear regime

In order to elucidate the essential physics of the processes, we shall first use some drastic simplifications. We assume that the system is unable to maintain temperature differences, in spite of the porous gas filled structure, and that all mass fluxes are related through the stationary state condition:

$$r^{s,a} \equiv -\frac{1}{4} J_{e^-}^{e,a} \equiv -\frac{1}{2} J_{O_2^-}^{e,a} \equiv J_{O_2} \equiv \frac{1}{4F} j. \quad (45)$$

The only term left in the entropy production is the product of the flux,  $j$ , and the conjugate driving force  $X_j^{s,a}$  ( $\sigma^{s,a} = jX_j^{s,a}$ ), giving

$$X_j^{s,a} \equiv -\frac{1}{F} \left[ \mu_{e^-}^{a,e} + \frac{1}{4} \mu_{O_2}^{a,e} - \frac{1}{2} \mu_{O_2^-}^{e,a} + F \Delta_{ae}\psi \right]. \quad (46)$$

By introducing the electrochemical potentials of component  $k$

$$\tilde{\mu}_k \equiv \mu_k + z_k F \psi, \quad (47)$$

the driving force can be written as the difference in electrochemical potentials of the species that enter the reaction:

$$X_j^{s,a} = -\frac{1}{F} \left[ \tilde{\mu}_{e^-}^{a,e} + \frac{1}{4} \mu_{O_2}^{a,e} - \frac{1}{2} \tilde{\mu}_{O_2^-}^{e,a} \right] \equiv -\frac{1}{nF} \Delta \tilde{G}. \quad (48)$$

For reversible conditions  $\sigma^{s,a} = 0$ ,  $X_j^{s,a} = 0$ . The common form of the Nernst equation<sup>1-3</sup> follows from the last parenthesis:

$$\Delta_{ae}\psi_{j=0} = -\frac{1}{F} \left[ \mu_{e^-}^{a,e} + \frac{1}{4} \mu_{O_2}^{a,e} - \frac{1}{2} \mu_{O_2^-}^{e,a} \right]_{j=0}. \quad (49)$$

For small current densities, we have a linear flux-force relationship between the driving force and the flux from  $\sigma^{s,a} = jX_j^{s,a}$ :

$$X_j^{s,a} = R_p j, \quad (50)$$

where  $R_p$  is the Ohmic resistance of the interface. This is exactly the relation used in the impedance measurement, if we identify  $\eta$  with  $X_j^{s,a}$ :

$$\eta = -\frac{1}{F} \left[ \mu_{e^-}^{a,e} + \frac{1}{4} \mu_{O_2}^{a,e} - \frac{1}{2} \mu_{O_2^-}^{e,a} + F \Delta_{ae}\psi \right]. \quad (51)$$

The overpotential describes therefore a deviation from Nernst behavior. It is the net driving force of the electrochemical reaction when divided by  $T/F$ . The relations (50) and (51) confirm the determination of the overpotential from impedance measurements. In more general terms we now have

$$\eta = -\frac{1}{nF} \Delta \tilde{G} = -\frac{1}{nF} [\Delta G + nF \Delta_{a,e}\psi], \quad (52)$$

where  $\Delta \tilde{G}$  was defined above,  $\Delta G$  is the normal reaction Gibbs energy of any electrochemical reaction, and  $n$  is the number of electrons in the electrode reaction (here  $n = 4$ ). This expression was given by Newman and Thomas-Alyea,<sup>1</sup> but not connected to  $\sigma^{s,a}$ .

#### 2. The general linear regime

Consider next a less restrictive regime where the excess oxygen concentration at the surface is allowed to vary. The surface is not isothermal, but still electroneutral, meaning that the electron and oxygen ion fluxes are uniquely related to the electric current density:

$$r^{s,a} \equiv -\frac{1}{4} J_{e^-}^{a,e} \equiv -\frac{1}{2} J_{O_2^-}^{e,a} \equiv \frac{1}{4F} j. \quad (53)$$

On the time scale we consider the exchange of electrons and oxygen ions with the surface is in equilibrium. This implies that

$$\begin{aligned} \frac{\mu_{e^-}^{s,a}}{T^{s,a}} - \frac{\mu_{e^-}^{a,e}}{T^{a,e}} - F \frac{\Delta_{as}\psi}{T^{s,a}} &= 0, \\ \frac{\mu_{O_2^-}^{e,a}}{T^{e,a}} - \frac{\mu_{O_2^-}^{s,a}}{T^{s,a}} - 2F \frac{\Delta_{se}\psi}{T^{s,a}} &= 0. \end{aligned} \quad (54)$$

The reaction and the exchange of oxygen molecules with the surface, cf. Sec. III C, can both be rate-limiting.

By using Eq. (53) or (54), the number of terms in the entropy production becomes smaller

$$\begin{aligned} \sigma^{s,a} = & -J_{O_2}^{a,e} \left( \frac{\mu_{O_2}^{s,a}}{T^{s,a}} - \frac{\mu_{O_2}^{a,e}}{T^{pa,e}} \right) \\ & - r^{s,a} \left( \frac{4\mu_{e^-}^{a,e}}{T^{ma,e}} + \frac{\mu_{O_2}^{s,a}}{T^{s,a}} - \frac{2\mu_{O_2}^{e,a}}{T^{e,a}} + 4F \frac{\Delta_{ae}\psi}{T^{s,a}} \right) \\ & + J_q^{ma,e} \left( \frac{1}{T^{s,a}} - \frac{1}{T^{ma,e}} \right) + J_q^{pa,e} \left( \frac{1}{T^{s,a}} - \frac{1}{T^{pa,e}} \right) \\ & + J_q^{e,a} \left( \frac{1}{T^{e,a}} - \frac{1}{T^{s,a}} \right) \end{aligned} \quad (55)$$

where  $\Delta_{ae}\psi = \Delta_{as}\psi + \Delta_{se}\psi = \psi^{e,a} - \psi^{a,e}$ . It is known that the exchange of oxygen molecules with the surface and the reaction are both activated processes<sup>15</sup> showing an Arrhenius behavior. For ease of notation, we introduce

$$X_r^{s,a} \equiv - \left[ \frac{4\mu_{e^-}^{a,e}}{T^{ma,e}} + \frac{\mu_{O_2}^{s,a}}{T^{s,a}} - \frac{2\mu_{O_2}^{e,a}}{T^{e,a}} + 4F \frac{\Delta_{ae}\psi}{T^{s,a}} \right]. \quad (56)$$

We now have five fluxes and conjugate forces. The normal components of the fluxes are scalar, like the reaction rate  $r^{s,a}$ . Therefore, coupling is possible between all fluxes and forces. The more general linear flux-force relations have therefore, using Onsager's reciprocal relations,  $(5 \times 6)/2 = 15$  independent transport coefficients. This is still very many, with regard to experimental determination, so we would like to reduce the number of unknowns further. Fluxes in the metal and the pores take place at different locations, and we expect that their coupling can be neglected. Similarly, we will neglect the coupling of fluxes on one side of the surface to fluxes on the other side. These approximations,  $\ell_{13} = \ell_{15} = \ell_{34} = \ell_{35} = \ell_{45} = 0$ , reduce the number of independent coefficients to 10.

The resulting linear flux-force relations are

$$\begin{aligned} J_{O_2}^{a,e} = & -\ell_{11}^{s,a} \left( \frac{\mu_{O_2}^{s,a}}{T^{s,a}} - \frac{\mu_{O_2}^{a,e}}{T^{pa,e}} \right) + \ell_{12}^{s,a} X_r^{s,a} \\ & + \ell_{14}^{s,a} \left( \frac{1}{T^{s,a}} - \frac{1}{T^{pa,e}} \right), \\ r^{s,a} = & -\ell_{21}^{s,a} \left( \frac{\mu_{O_2}^{s,a}}{T^{s,a}} - \frac{\mu_{O_2}^{a,e}}{T^{a,e}} \right) + \ell_{22}^{s,a} X_r^{s,a} \\ & + \ell_{23}^{s,a} \left( \frac{1}{T^{s,a}} - \frac{1}{T^{ma,e}} \right) \\ & + \ell_{24}^{s,a} \left( \frac{1}{T^{s,a}} - \frac{1}{T^{pa,e}} \right) + \ell_{25}^{s,a} \left( \frac{1}{T^{e,a}} - \frac{1}{T^{s,a}} \right), \\ J_q^{ma,e} = & \ell_{32}^{s,a} X_r^{s,a} + \ell_{33}^{s,a} \left( \frac{1}{T^{s,a}} - \frac{1}{T^{ma,e}} \right), \end{aligned}$$

$$\begin{aligned} J_q^{pa,e} = & -\ell_{41}^{s,a} \left( \frac{\mu_{O_2}^{s,a}}{T^{s,a}} - \frac{\mu_{O_2}^{a,e}}{T^{pa,e}} \right) + \ell_{42}^{s,a} X_r^{s,a} \\ & + \ell_{45}^{s,a} \left( \frac{1}{T^{s,a}} - \frac{1}{T^{pa,e}} \right), \\ J_q^{e,a} = & \ell_{52}^{s,a} X_r^{s,a} + \ell_{55}^{s,a} \left( \frac{1}{T^{e,a}} - \frac{1}{T^{s,a}} \right), \end{aligned} \quad (57)$$

where the Onsager reciprocal relations,  $\ell_{ij}^{s,a} = \ell_{ji}^{s,a}$  for  $i, j = 1, \dots, 5$ , refer to an  $\ell^{s,a}$ -matrix which is a  $5 \times 5$  matrix. The entropy production can be written as the double contraction of the 5 force elements  $(-\frac{\mu_{O_2}^{s,a}}{T^{s,a}} - \frac{\mu_{O_2}^{a,e}}{T^{pa,e}}, X_r^{s,a}, \frac{1}{T^{s,a}} - \frac{1}{T^{ma,e}}, \frac{1}{T^{s,a}} - \frac{1}{T^{pa,e}}, \frac{1}{T^{e,a}} - \frac{1}{T^{s,a}})$  with the Onsager matrix. The entropy production can also be written with different choices of variables. Linear relations were written with thermal and other driving forces, using (52) as the driving force of the electrochemical reaction.<sup>7,8</sup> The impact of temperature jumps on the electrode potential drop was estimated.<sup>8</sup>

In the present case, the main chemical reaction is coupled to adsorption of oxygen at the surface, and to thermal driving forces from all supply channels. The equations can be used to explain, say, impedance measurements, where the electric field oscillates with small amplitudes, and the condition of electroneutrality applies to the surface.

### 3. Electrode Peltier heats

The linear laws from the entropy production are basis for definition of thermoelectric phenomena.<sup>9</sup> The Peltier coefficient of a conductor,  $\pi^i$ , is the measurable heat flux through a conductor,  $i$ ,  $J_q^i$ , divided by the electric current density over Faraday's constant:

$$\pi^i \equiv \left[ \frac{J_q^i}{j/F} \right]_{\Delta\mu_j=0, \Delta T=0, \eta=0}. \quad (58)$$

The heat flux here is the sum of heat fluxes of parallel conductors  $J_q^a = J_q^{pa} + J_q^{ma}$ . The definition prescribes reversible conditions for heat transfer.

The measurable heat flux was not a variable in the set chosen here. The energy flux, which is continuous and constant through all layers, was more convenient. The energy flux is the measurable heat flux plus the sum of the enthalpy transported by the species. We introduce this definition for the energy flux in the homogeneous phases and obtain

$$\begin{aligned} \frac{du^s}{dt} = 0 = & J_q^{pa,e} + J_q^{ma,e} + j\psi^{a,e} - J_q^{e,a} - j\psi^{e,a} \\ = & J_q^{a,e} + J_{O_2}^{a,e} H_{O_2}^{a,e} + J_{e^-}^{a,e} H_{e^-}^{a,e} + j\psi^{a,e} \\ & - J_q^{e,a} - J_{O_2}^{e,a} H_{O_2}^{e,a} - j\psi^{e,a}. \end{aligned} \quad (59)$$

We can determine the heat produced at the electrode interface at reversible conditions,  $\Pi^a$ , from the jump in the measurable heat fluxes in the equation above:

$$\begin{aligned} \Pi^a = \pi^{e,a} - \pi^{a,e} = & \left[ \frac{J_q^{e,a} - J_q^{a,e}}{j/F} \right]_{\Delta\mu_j=0, \Delta T=0, \eta=0} \\ = & \Delta_{a,e} H - F \Delta_{a,e} \psi = T \Delta_{a,e} S. \end{aligned} \quad (61)$$

In the last step we used the expression for the Nernst potential (49). The electrode Peltier heat is equal to the entropy change of the single electrode reaction. Away from reversible conditions, we can still use Eq. (59), but now with Eqs. (50) and (51). This gives for the stationary state (in the linear regime)

$$\left[ \frac{J_q^{e,a} - J_q^{a,e}}{j/F} \right] = \Delta_{a,e} H - F \Delta_{a,e} \psi = T \Delta_{a,e} S + F \eta. \quad (62)$$

This equation is the same as that derived by Newman and Thomas-Alyea<sup>1</sup> from the energy balance. They use Fourier's law for the heat fluxes, however. This is probably not a good assumption in view of Eq. (57). More detailed descriptions of thermal effects based on the measurable heat flux can be made, but will presently carry to far.

#### 4. The friction matrix for the linear case

From GENERIC we deduce a symmetric  $M^{s,a}$  operator for these sets of conditions:

$$M^{s,a} = [C^{s,a}]^T \cdot L^{s,a} \cdot C^{s,a}. \quad (63)$$

By combining  $\delta S/\delta x^{s,a}$  and  $\delta S/\delta x^{ma}$ ,  $\delta S/\delta x^{pa}$ ,  $\delta S/\delta x^e$  close to the surface into one vector we have  $(\delta S/\delta x^{s,a}$ ,  $\delta S/\delta x^{ma,e}$ ,  $\delta S/\delta x^{pa,e}$ ,  $\delta S/\delta x^{e,a}$ ). Remember that  $\delta S/\delta x^{s,a} = (-\mu_{e^-}^{s,a}/T^{s,a}, -\mu_{O_2}^{s,a}/T^{s,a}, -\mu_{O_2^-}^{s,a}/T^{s,a}, 1/T^{s,a})$ ,  $\delta S/\delta x^{ma,e} = (-\mu_{e^-}^{a,e}/T^{ma,e}, 0, 1/T^{ma,e})$ ,  $\delta S/\delta x^{pa,e} = (-\mu_{O_2}^{a,e}/T^{pa,e}, 0, 1/T^{pa,e})$ ,  $\delta S/\delta x^{e,a} = (-\mu_{O_2^-}^{e,a}/T^{e,a}, 0, 1/T^{e,a})$ . The  $C^{s,a}$  operator is again chosen such that  $C^{s,a} \cdot (\delta S/\delta x^{s,a}$ ,  $\delta S/\delta x^{ma,e}$ ,  $\delta S/\delta x^{pa,e}$ ,  $\delta S/\delta x^{e,a})$  gives the thermodynamic forces while  $C^{s,a} \cdot (\delta E/\delta x^{s,a}$ ,  $\delta E/\delta x^{ma,e}$ ,  $\delta E/\delta x^{pa,e}$ ,  $\delta E/\delta x^{e,a}) = 0$ .

This gives

$$C^{s,a} = \left( \begin{array}{cccc|cccc|cc|ccc} 0 & 1 & 0 & 0 & 0 & 0 & 0 & -1 & -\frac{1}{2}v_{O_2}^a & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & -2F\Delta_{ae}\psi & 4 & 2v_{e^-}^a & 0 & 0 & 0 & 0 & -2 & -v_{O_2^-}^e & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{array} \right). \quad (64)$$

The form of the  $C$ -matrix reflects that there are 13 variables and 5 processes in the surface. The vertical bars are put in as a guide to the eye, to separate between interactions within the surface, between the surface and the metal, between the surface and the oxygen pore, and between the surface and the electrolyte. One can verify that the entropy production is given by

$$\frac{\delta S}{\delta x^{s,a}} \cdot M^{s,a} \cdot \frac{\delta S}{\delta x^{s,a}} = \sigma^{s,a}, \quad (65)$$

and that

$$(\delta E/\delta x^{s,a}, \delta E/\delta x^{ma,e}, \delta E/\delta x^{pa,e}, \delta E/\delta x^{e,a}) \cdot (C^{s,a})^T = 0, \quad (66)$$

so that  $M^{s,a}$  satisfies the degeneracy requirement.

After having constructed the  $M^{s,a}$  operator, we can verify that the fluxes are given by

$$\begin{pmatrix} J_{O_2}^{a,e} \\ r^{s,a} \\ J_q^{ma,e} \\ J_q^{pa,e} \\ J_q^{e,a} \end{pmatrix} = L^{s,a} \cdot C^{s,a} \cdot \begin{pmatrix} \delta S/\delta x^{s,a} \\ \delta S/\delta x^{ma,e} \\ \delta S/\delta x^{pa,e} \\ \delta S/\delta x^{e,a} \end{pmatrix} = L^{s,a} \cdot \begin{pmatrix} -\left(\frac{\mu_{O_2}^{s,a}}{T^{s,a}} - \frac{\mu_{O_2}^{a,e}}{T^{pa,e}}\right) \\ -X_r^{s,a} \\ \frac{1}{T^{s,a}} - \frac{1}{T^{ma,e}} \\ \frac{1}{T^{s,a}} - \frac{1}{T^{pa,e}} \\ \frac{1}{T^{e,a}} - \frac{1}{T^{s,a}} \end{pmatrix}. \quad (67)$$

This operation confirms the consistency of the linear forms of the equations of motions presented above for the electrode surface.

## VII. NONLINEAR CONTRIBUTIONS TO THE EQUATION OF MOTION

We can soon address one of the questions that motivated this work: Can we give the Butler-Volmer equation a better basis in thermodynamics? We first need to discuss how to expand in a consistent manner the linear relations (67) to the nonlinear regime. This will be done here.

An electrochemical reaction has often large driving forces;  $|\Delta G|$  being larger than 100 kJ/mol. The electric potential difference and the reaction Gibbs energy are both large in the surface. This can explain why the electrochemical reaction is nonlinear in its driving forces, like common chemical reactions are.<sup>25</sup> As we argued above, not only the reaction, also the surface adsorption of oxygen can be rate-limiting,<sup>15</sup>



possibly because the molecule has to split into atoms, before the ion is formed. The task is therefore to give a proper description of (at least) two nonlinear coupled processes within the framework of GENERIC.

For simplicity, consider again a matrix with a single diagonal coefficient. The only contribution in Eq. (67) to the electrochemical reaction rate is then

$$r^{s,a} = \ell_{22}^{s,a} X_r^{s,a}. \quad (68)$$

This is the case described above for the linear regime, cf. (49). If  $\ell_{22}^{s,a}$  depends only on state variables, this equation is linear in  $X_r^{s,a}$ . A more complicated expression for  $\ell_{22}^{s,a}$  is used in GENERIC, see Ref. 18,

$$\ell_{22}^{s,a} = -\frac{R\ell_{22,0}^{s,a}}{X_r^{s,a}} \left[ \exp \left( \frac{4\mu_{e^-}^{a,e}}{RT^{ma,e}} + \frac{\mu_{O_2}^{s,a}}{RT^{s,a}} - 4F \frac{\psi^{a,e}}{RT^{s,a}} \right) - \exp \left( \frac{2\mu_{O_2^-}^{e,a}}{RT^{e,a}} - 4F \frac{\psi^{e,a}}{RT^{s,a}} \right) \right]. \quad (69)$$

This expression for  $\ell_{22}^{s,a}$  keeps  $M$  positive definite as required, and leads to a form which is similar to the law of mass action, which we expect

$$r^{s,a} = -R\ell_{22,0}^{s,a} \left[ \exp \left( \frac{4\mu_{e^-}^{a,e}}{RT^{ma,e}} + \frac{\mu_{O_2}^{s,a}}{RT^{s,a}} - 4F \frac{\psi^{a,e}}{RT^{s,a}} \right) - \exp \left( \frac{2\mu_{O_2^-}^{e,a}}{RT^{e,a}} - 4F \frac{\psi^{e,a}}{RT^{s,a}} \right) \right]. \quad (70)$$

The term  $R\ell_{22,0}^{s,a} \exp \left( \frac{4\mu_{e^-}^{a,e}}{RT^{ma,e}} + \frac{\mu_{O_2}^{s,a}}{RT^{s,a}} - 4F \frac{\psi^{a,e}}{RT^{s,a}} \right)$  can be understood as the reverse reaction rate in the electric field (from oxygen molecules and electrons to oxygen ions). The prefactor  $\ell_{22,0}^{s,a}$  contains an Arrhenius-type factor, as the law of mass action does. Close to equilibrium, the nonlinear equation (70) reduces to the linear equation (68) with  $\ell_{22}^{s,a} = \ell_{22,0}^{s,a}$  as expected. By construction we have then obtained a nonlinear flux-force relation for the diagonal contribution. In the present case, there are two activated processes, the oxygen adsorption and the electrochemical reaction.<sup>15</sup> The same procedure must then be used for the diagonal coefficients of the Onsager matrix which are related to oxygen adsorption.

The next important question is how to deal with the off-diagonal coefficients in the matrix. One possibility is to multiply the off-diagonal coefficients also, with the factor

$$-\frac{R}{X_r^{s,a}} \left[ \exp \left( \frac{4\mu_{e^-}^{a,e}}{RT^{ma,e}} + \frac{\mu_{O_2}^{s,a}}{RT^{s,a}} - 4F \frac{\psi^{a,e}}{RT^{s,a}} \right) - \exp \left( \frac{2\mu_{O_2^-}^{e,a}}{RT^{e,a}} - 4F \frac{\psi^{e,a}}{RT^{s,a}} \right) \right] \quad (71)$$

and similar factors from the other diagonal elements. Close to equilibrium these factors reduce to unity, as they should. Such a procedure will make the  $M$ -matrix asymmetric. The multiplication of the columns in the  $\ell$ -matrix with the suggested factors from the diagonal elements, systematically replaces, e.g.,  $X_r^{s,a}$  in the expressions for the fluxes by the nonlinear

“force”

$$-R \left[ \exp \left( \frac{4\mu_{e^-}^{a,e}}{RT^{ma,e}} + \frac{\mu_{O_2}^{s,a}}{RT^{s,a}} - 4F \frac{\psi^{a,e}}{RT^{s,a}} \right) - \exp \left( \frac{2\mu_{O_2^-}^{e,a}}{RT^{e,a}} - 4F \frac{\psi^{e,a}}{RT^{s,a}} \right) \right] \quad (72)$$

and similarly for the other columns. Following this procedure, we obtain for the diagonal and off-diagonal coefficients of the first two columns and rows:

$$\begin{aligned} \ell_{j1}^{s,a} &= R\ell_{j1,0}^{s,a} \frac{\exp \frac{\mu_{O_2}^{s,a}}{RT^{s,a}} - \exp \frac{\mu_{O_2}^{a,e}}{RT^{pa,e}}}{\frac{\mu_{O_2}^{s,a}}{T^{s,a}} - \frac{\mu_{O_2}^{a,e}}{T^{pa,e}}}, \\ \ell_{1k}^{s,a} &= \ell_{k1,0}^{s,a} = \ell_{1k,0}^{s,a} \quad \text{for } k = 3, 4, 5, \\ \ell_{j2}^{s,a} &= -\frac{R\ell_{j2,0}^{s,a}}{X_r^{s,a}} \left[ \exp \left( \frac{4\mu_{e^-}^{a,e}}{RT^{ma,e}} + \frac{\mu_{O_2}^{s,a}}{RT^{s,a}} - 4F \frac{\psi^{a,e}}{RT^{s,a}} \right) - \exp \left( \frac{2\mu_{O_2^-}^{e,a}}{RT^{e,a}} - 4F \frac{\psi^{e,a}}{RT^{s,a}} \right) \right], \\ \ell_{2k}^{s,a} &= \ell_{k2,0}^{s,a} = \ell_{2k,0}^{s,a} \quad \text{for } k = 3, 4, 5. \end{aligned} \quad (73)$$

Close to equilibrium, this reduces to  $\ell_{j1}^{s,a} = \ell_{1j}^{s,a} = \ell_{j1,0}^{s,a} = \ell_{1j,0}^{s,a}$  and  $\ell_{j2}^{s,a} = \ell_{2j}^{s,a} = \ell_{j2,0}^{s,a} = \ell_{2j,0}^{s,a}$ . The symmetry is restored in this limit, but does not exist beyond this limit. The other  $3 \times 3$  coefficients have their normal symmetric form. We see in Eq. (73) that the columns in the nonlinear  $\ell$ -matrix obtain the same nonlinear factor as the diagonal element in the column. As these nonlinear factors are all positive definite, the  $\ell$ -matrix remains positive semi-definite. This ensures that the second law of thermodynamics is valid for the nonlinear case. Similar expressions were obtained in the study of activated transport processes using mesoscopic nonequilibrium thermodynamics.<sup>26</sup> The flux-force relations were then linear on the mesoscopic level, but not after integration to the macroscopic level.

GENERIC makes it possible to use an asymmetric form of the  $\ell$ -matrix, a form which remains positive semi-definite as it should. In this form, all columns in the symmetric, positive semi-definite  $\ell_0$ -matrix are multiplied with the same nonlinear factor. In the mesoscopic analysis of a transport problem,<sup>26</sup> the corresponding  $\ell_0$  matrix had small deviations in the symmetry. From GENERIC, we learn that this should be corrected.

To summarize this section: An asymmetric friction matrix arises in the nonlinear case. It can be constructed with help from mesoscopic nonequilibrium thermodynamics, and relates fluxes to driving forces in a nonlinear manner. An asymmetric friction matrix has also been found when GENERIC was used for the Boltzmann equation.<sup>17</sup>

## VIII. GENERALIZED BUTLER-VOLMER EQUATIONS

The nonlinear equations presented in Sec. VII gives the most general contributions to the equations of motion for

the electrode surface, under the assumption of local equilibrium. We chose to consider flux equations related to two rate-limiting chemical steps plus the associated transport of energy. The equations describe also nonstationary conditions.

The Butler-Volmer equation applies to stationary states, which allows for a further reduction. In a stationary state, there is also no accumulation of oxygen molecules at the surface. This implies that

$$r^{s,a} = -J_{O_2}^{a,e}. \quad (74)$$

This relation will lead to an equation set with coupling between the reaction rate (the current density) and thermal driving forces. The second activated chemical reaction has a rate equal to the first activated reaction. As a consequence there remains only one equation for the rate in addition to the equations for the energy fluxes. This represents a generalization of the common Butler-Volmer equation (2). The expression for the energy fluxes that accompany the Butler-Volmer equation are new in electrochemistry.

Equation (67) together with Eq. (73) imply for the non-linear case that

$$\begin{aligned} J_{O_2}^{a,e} &= -R\ell_{11,0}^{s,a} \left( \exp \frac{\mu_{O_2}^{s,a}}{RT^{s,a}} - \exp \frac{\mu_{O_2}^{a,e}}{RT^{pa,e}} \right) \\ &\quad - R\ell_{12,0}^{s,a} \left[ \exp \left( \frac{4\mu_{e^-}^{a,e}}{RT^{ma,e}} + \frac{\mu_{O_2}^{s,a}}{RT^{s,a}} - 4F \frac{\psi^{a,e}}{RT^{s,a}} \right) \right. \\ &\quad \left. - \exp \left( \frac{2\mu_{O_2^{e,a}}}{RT^{e,a}} - 4F \frac{\psi^{e,a}}{RT^{s,a}} \right) \right] \\ &\quad + \ell_{13}^{s,a} \left( \frac{1}{T^{s,a}} - \frac{1}{T^{ma,e}} \right) + \ell_{14}^{s,a} \left( \frac{1}{T^{s,a}} - \frac{1}{T^{pa,e}} \right) \\ &\quad + \ell_{15}^{s,a} \left( \frac{1}{T^{e,a}} - \frac{1}{T^{s,a}} \right) \\ r^{s,a} &= -R\ell_{21,0}^{s,a} \left( \exp \frac{\mu_{O_2}^{s,a}}{RT^{s,a}} - \exp \frac{\mu_{O_2}^{a,e}}{RT^{pa,e}} \right) \\ &\quad - R\ell_{22,0}^{s,a} \left[ \exp \left( \frac{4\mu_{e^-}^{a,e}}{RT^{ma,e}} + \frac{\mu_{O_2}^{s,a}}{RT^{s,a}} - 4F \frac{\psi^{a,e}}{RT^{s,a}} \right) \right. \\ &\quad \left. - \exp \left( \frac{2\mu_{O_2^{e,a}}}{RT^{e,a}} - 4F \frac{\psi^{e,a}}{RT^{s,a}} \right) \right] \\ &\quad + \ell_{23}^{s,a} \left( \frac{1}{T^{s,a}} - \frac{1}{T^{ma,e}} \right) + \ell_{24}^{s,a} \left( \frac{1}{T^{s,a}} - \frac{1}{T^{pa,e}} \right) \\ &\quad + \ell_{25}^{s,a} \left( \frac{1}{T^{e,a}} - \frac{1}{T^{s,a}} \right). \quad (75) \end{aligned}$$

In the stationary state the forces have adjusted themselves such that Eq. (74) is true. We use this to eliminate  $\exp(\mu_{O_2}^{s,a}/RT^{s,a})$  in the reaction rate. We also apply the assumptions used before, that certain coupling coefficients are

small (zero). This results in

$$\begin{aligned} j &= 4Fr^{s,a} = -4FR(\ell_{22,0}^{s,a} - B_2(\ell_{12,0}^{s,a} + \ell_{22,0}^{s,a})) \\ &\quad \times \left[ \exp \left( \frac{4\mu_{e^-}^{a,e}}{RT^{ma,e}} + \frac{\mu_{O_2}^{a,e}}{RT^{pa,e}} - 4F \frac{\psi^{a,e}}{RT^{s,a}} \right) \right. \\ &\quad \left. - \exp \left( \frac{2\mu_{O_2^{e,a}}}{RT^{e,a}} - 4F \frac{\psi^{e,a}}{RT^{s,a}} \right) \right] \\ &\quad + 4F\ell_{23}^{s,a}(1 - B_2) \left( \frac{1}{T^{s,a}} - \frac{1}{T^{ma,e}} \right) \\ &\quad + (\ell_{24}^{s,a} - B_2(\ell_{14}^{s,a} + \ell_{24}^{s,a})) \left( \frac{1}{T^{s,a}} - \frac{1}{T^{pa,e}} \right) \\ &\quad + 4F\ell_{25}^{s,a}(1 - B_2) \left( \frac{1}{T^{e,a}} - \frac{1}{T^{s,a}} \right), \quad (76) \end{aligned}$$

where

$$B_j = \frac{\ell_{j1,0}^{s,a} + \ell_{j2,0}^{s,a} \exp \left( \frac{4\mu_{e^-}^{a,e}}{RT^{ma,e}} - 4F \frac{\psi^{a,e}}{RT^{s,a}} \right)}{\ell_{11,0}^{s,a} + \ell_{21,0}^{s,a} + (\ell_{12,0}^{s,a} + \ell_{22,0}^{s,a}) \exp \left( \frac{4\mu_{e^-}^{a,e}}{RT^{ma,e}} - 4F \frac{\psi^{a,e}}{RT^{s,a}} \right)}. \quad (77)$$

For the energy fluxes, three expressions similar to Eq. (76) can be given as

$$\begin{aligned} J_{q,j} &= -R(\ell_{j2,0}^{s,a} - B_j(\ell_{12,0}^{s,a} + \ell_{22,0}^{s,a})) \\ &\quad \times \left[ \exp \left( \frac{4\mu_{e^-}^{a,e}}{RT^{ma,e}} + \frac{\mu_{O_2}^{a,e}}{RT^{pa,e}} - 4F \frac{\psi^{a,e}}{RT^{s,a}} \right) \right. \\ &\quad \left. - \exp \left( \frac{2\mu_{O_2^{e,a}}}{RT^{e,a}} - 4F \frac{\psi^{e,a}}{RT^{s,a}} \right) \right] \\ &\quad + (\ell_{j3}^{s,a} - B_j\ell_{23}^{s,a}) \left( \frac{1}{T^{s,a}} - \frac{1}{T^{ma,e}} \right) \\ &\quad + (\ell_{j4}^{s,a} - B_j(\ell_{14}^{s,a} + \ell_{24}^{s,a})) \left( \frac{1}{T^{s,a}} - \frac{1}{T^{pa,e}} \right) \\ &\quad + (\ell_{j5}^{s,a} - B_j\ell_{25}^{s,a}) \left( \frac{1}{T^{e,a}} - \frac{1}{T^{s,a}} \right), \quad (78) \end{aligned}$$

where  $J_{q,3} = J_q^{ma,e}$ ,  $J_{q,4} = J_q^{pa,e}$ ,  $J_{q,5} = J_q^{e,a}$ .

We find that the reaction has in addition to the usual contribution three additional contributions due to temperature differences in Eq. (76). The same is true for the energy fluxes. Due to the stationary state conditions, we were able to eliminate the thermodynamic force for adsorption of oxygen molecules. The resulting expressions become, on the one hand, simpler in the sense that they contain only four terms due to four driving forces. On the other hand, they obtain more complicated effective coefficients. The coefficients become combinations of the elements in the original  $5 \times 5$   $L$  matrix. In particular the coefficient  $B_j$  depends on coefficients, some of which contain Arrhenius factors in addition to depending on the density of the electrons in the anode, i.e., on  $\exp((\mu_{e^-}^{a,e}/RT^{e,a}) - (F\psi^{e,a}/RT^{s,a}))$ .

The expressions for  $j$  and  $J_{q,j}$  can be said to constitute a generalized set of Butler-Volmer equations. This set has a basis in nonequilibrium thermodynamics, as confirmed by

GENERIC, and can therefore be said to provide a broader thermodynamic basis for the common Butler-Volmer equation (2), as it also contains thermal driving forces. It can be shown in detail below how the common Butler-Volmer equation is contained in the generalized form (Sec. VIII A).

We first note that isothermal conditions at the electrode surface give

$$j = -A_1 \left( \exp \left( \frac{4\tilde{\mu}_{e^-}^{a,e} + \mu_{O_2}^{a,e}}{RT} \right) - \exp \left( \frac{2\tilde{\mu}_{O_2^{2-}}^{e,a}}{RT} \right) \right) \quad (79)$$

and

$$J_{q,j} = -A_j \left( \exp \left( \frac{4\tilde{\mu}_{e^-}^{a,e} + \mu_{O_2}^{a,e}}{RT} \right) - \exp \left( \frac{2\tilde{\mu}_{O_2^{2-}}^{e,a}}{RT} \right) \right). \quad (80)$$

The coefficients  $A_i$  contain the prefactors of the other equations. The energy flux has clearly the same form as the rate of the chemical reaction. It is not possible to obtain the result without starting from the more general basis. This equation is new in electrochemistry.

### A. The common Butler-Volmer equation

We return to the empirical form of Butler-Volmer's equation (2). Again, we note that the Butler-Volmer equation applies at isothermal, stationary state conditions (no charge or mass accumulation at or in the electrode surface). This means that we should be able to recover the equation from (76), by neglecting contributions from thermal driving forces. We obtain

$$j = j' \left[ \exp \left[ (2\tilde{\mu}_{O_2^{2-}}^{e,a})/RT \right] - \exp \left[ (4\tilde{\mu}_{e^-}^{a,e} + \mu_{O_2}^{a,e})/RT \right] \right], \quad (81)$$

where  $j'/F = 4R(\ell_{22,0}^{s,a} + B_2(\ell_{12,0}^{s,a} + \ell_{22,0}^{s,a}))$ , and the electrochemical potentials were defined in (47). We label reactants with ( $r$ ) and products with ( $p$ ) and write more generally:

$$\begin{aligned} \tilde{G}_r &= 2\tilde{\mu}_{O_2^{2-}}^{e,a}, \\ \tilde{G}_p &= 4\tilde{\mu}_{e^-}^{a,e} + \mu_{O_2}^{a,e}, \end{aligned} \quad (82)$$

where  $\Delta\tilde{G} = \tilde{G}_p - \tilde{G}_r = \Delta G + nF\Delta_{a,e}\psi$  as in Eq. (52) with  $n = 4$ . The last identity gives again the Nernst equation, at reversible conditions, when the net driving force is zero. We can now write Eq. (81) in the form

$$j = j' [\exp[\tilde{G}_r/RT] - \exp[\tilde{G}_p/RT]]. \quad (83)$$

In the same manner as before,<sup>12</sup> we subtract the value of the electrochemical potential at reversible conditions (equilibrium),  $\tilde{G}_{j=0} = \tilde{G}_{r,\text{eq}} = \tilde{G}_{p,\text{eq}}$  from the chemical potentials of reactants ( $r$ ) and products ( $p$ ) and define

$$\begin{aligned} \tilde{G}_r - \tilde{G}_{j=0} &\equiv 4(1 - \beta)F\eta, \\ \tilde{G}_p - \tilde{G}_{j=0} &\equiv -4\beta F\eta. \end{aligned} \quad (84)$$

The difference of these equations gives the identification used before  $\Delta\tilde{G} = -nF\eta$ , cf Eq. (51). The overpotential of the oxygen anode becomes

$$\eta = -\frac{1}{F} \left( \tilde{\mu}_{e^-}^{a,e} + \frac{1}{4}\mu_{O_2}^{a,e} - \frac{1}{2}\tilde{\mu}_{O_2^{2-}}^{e,a} \right) = X_j^{s,a}. \quad (85)$$

This is the same expression as derived in the linear regime, demonstrating the robustness of the definition.

By introducing the identities (84) into the flux equation (83), we obtain the Butler-Volmer equation that was given in Eq. (2). We can identify the exchange current density by  $j_0 = j' \exp(\tilde{G}_{j=0}/RT)$ , which contains an Arrhenius factor as expected. In this case, it gives the overall result of two slow steps. We have seen that it is restricted to isothermal conditions.

In the small current regime, we obtain using  $n = 4$

$$j = j_0 \frac{4\eta F}{RT} \quad (86)$$

giving the identification of the resistance  $R_p = RT/(4Fj_0)$  obtained from impedance measurements at small current densities.

For a single rate-limiting reaction at isothermal conditions the product  $j\eta$  will describe pure dissipation of the electrochemical energy as heat into the surroundings. In the presence of temperature differences or chemical potential differences (electrolysis conditions) this is no longer true. The general expression (76) showed that work terms are involved.<sup>7,8</sup>

We can now return to the interpretation of the measurements in Fig. 1.<sup>1,2</sup> We write for the two experiments

$$\begin{aligned} \Delta_{a,e}\psi_j &= -\frac{1}{F} \left[ \mu_{e^-}^{a,e} + \frac{1}{4}\mu_{O_2}^{a,e} - \frac{1}{2}\mu_{O_2^{2-}}^{e,a} \right]_j + R_p j, \\ \Delta_{a,e}\psi_{j=0} &= -\frac{1}{F} \left[ \mu_{e^-}^{a,e} + \frac{1}{4}\mu_{O_2}^{a,e} - \frac{1}{2}\mu_{O_2^{2-}}^{e,a} \right]_{j=0}. \end{aligned} \quad (87)$$

We subtract the last from the first, introduce  $R_p j = \eta$ , and obtain

$$\begin{aligned} \Delta_{a,e}\psi_j - \Delta_{a,e}\psi_{j=0} &= \eta + \frac{1}{F} \left[ \mu_{e^-}^{a,e} + \frac{1}{4}\mu_{O_2}^{a,e} - \frac{1}{2}\mu_{O_2^{2-}}^{e,a} \right]_{j=0} \\ &\quad - \frac{1}{F} \left[ \mu_{e^-}^{a,e} + \frac{1}{4}\mu_{O_2}^{a,e} - \frac{1}{2}\mu_{O_2^{2-}}^{e,a} \right]_j. \end{aligned} \quad (88)$$

If we make the identification  $V_j - V_{j=0} = \Delta_{a,e}\psi_j - \Delta_{a,e}\psi_{j=0}$  there is an assumption involved in the interpretation of the measurement in terms of a the jumps in the Maxwell potential at the surface. The two last terms, both are large, must cancel in order to obtain the wanted interpretation of  $\eta$ .

## IX. DISCUSSION

### A. GENERIC's contributions

This is the first time GENERIC has been used to develop equations of motion for an electrochemical cell.

#### 1. The reversible contributions

It is comforting to first see in Sec. V that the familiar balance equations appear. The energy balance for the interface, has the same form as that used by Newman<sup>1</sup> to describe

the energy flux between the surface and the bulk. The results are presented mainly to show how these equations can be developed using GENERIC. There are interesting details to the picture given by the balance equations. One of them gives the momentum balance. It may be useful to have a momentum balance on the same footing as the other equations for an electrochemical cell. A balance of forces, created at all interfaces, might well have an impact on the lifetime of electrochemical systems, e.g., of Li-batteries.

## 2. The irreversible contributions

In addition to the conservation laws, nonequilibrium thermodynamics offers yet an equation for the energy flux for our example, here represented by Eq. (80) and its forerunners. GENERIC confirms that this extra equation is essential for agreement with the second law of thermodynamics. This is a new theoretical addition to electrochemistry; obtained from the search for a more general thermodynamic basis for the Butler-Volmer equation. It becomes clear that other driving forces than the electrochemical one, can contribute to the description in the linear as well as the nonlinear regime.

In our search for contributions from the friction operator, we always use linear flux-force relations for the homogeneous phases. The mechanism for transport of energy, mass, and charge is by diffusion in these materials, and classical nonequilibrium thermodynamics therefore applies. This is no longer true in the electrode regions. The electrochemical reactions are activated (rare events), motivating the use of nonlinear flux-force relations. We construct a plausible form of this nonlinearity. The relevant friction matrix becomes asymmetric, but remains positive semi-definite. This is crucial for the validity of the second law. The constructed form of the nonlinearity is supported by results from mesoscopic nonequilibrium thermodynamics and its form is restricted by GENERIC. (The asymmetric friction matrix satisfies the degeneracy requirement of GENERIC.) We were not able to find this result in the mesoscopic analysis. GENERIC adds therefore a firm basis to all equations.

In the linear regime (classical nonequilibrium thermodynamics), we associate Onsager symmetry with time-reversal invariance. The nonlinear flux-force relations do not disagree with time-reversal invariance. In the mesoscopic analysis we consider a finer scale (a mesoscopic scale). By integrating across this scale, which has linear relations, we find nonlinear relations.<sup>12,26</sup> An asymmetric  $M$ -matrix, which is also found when one formulates the Boltzmann equation in the context of GENERIC, is therefore not in contradiction with time-reversal invariance. This point will be further discussed later.

## B. Assumptions

Several types of assumptions have been made in the development. We distinguish between assumptions specific to GENERIC, to nonequilibrium thermodynamic theory, and to the particular problem that is used as an example.

Input to GENERIC are the sets of independent variables for each subsystem. Different sets can be chosen, but no assumption about their relationships are needed. We have used

validity of normal thermodynamic relations in the construction of the expressions for  $E$  and  $S$ , in Sec. IV. In this sense we have used the assumption of local equilibrium. To then find the Gibbs-Duhem equation for the bulk phases by GENERIC, is in agreement with this postulate. Validity of linear flux-force relations has also been taken as a sign that the hypothesis of local equilibrium applies.

Nonlinear flux-force relations have been taken as a sign of being far from equilibrium. It is necessary to specify the system in this context. Interfaces, which are autonomous thermodynamic systems, have been found to be in local equilibrium even under severe gradients.<sup>23,25</sup> We expect this to be true also here, arguing that this assumption is essential in mesoscopic nonequilibrium thermodynamics, which also gives nonlinear flux-force relations.

Assumptions used with the example cell, inspired by the solid oxide fuel cell materials, are of a different character. Based on literature reports, we have assumed a set of four steps connected with the oxidation of oxygen in the anode. The steps can be simplified or changed. Changing the assumptions behind the model will have an impact on the precise form of the equations obtained in Sec. VIII. The equations presented here are only “general” as far as our description is a good model of reality. When this is said, it is clear that other “general” sets of equations can be found for other descriptions. The results are general in the sense that they include all possible coupling effects. It remains to be seen by experiments, whether these coupling effects are large or can be neglected.

One motivation for the choice of an example with a porous electrode was that temperature gradients are more likely around this electrode than in metal electrodes in contact with liquid electrolytes. This makes an elaborate model possibly more relevant. We have seen in Sec. VIII A how the general set of equations simplify drastically by introducing isothermal conditions, an assumption that is always used in connection with overpotential measurements. The equations presented in Sec. VIII A are still more general than Eq. (2), because they derive from a more general basis.

## C. Coupled transport processes

Nonequilibrium thermodynamics predicts coupling of transport processes in the bulk phases and at the interface. The coupling terms are well established for transport in the bulk phase. Special for the interface is the possibility for coupling of the reaction with scalar normal components of vectorial fluxes.<sup>9</sup> For example, a chemical reaction, which cannot couple to heat transport in the bulk phase, will have a coupling coefficient with this flux at the interface. For the interface, these coupling terms are not yet in regular use, and it is difficult to predict their magnitude in the absence of experiments. In the simpler case of (energy) heat and mass transport, coupling coefficients have been shown to be essential.<sup>11</sup> GENERIC supports the existence of these coefficients and gives the proper form of the asymmetric friction matrix for the nonlinear description.



We observe that the existence and inclusion of such terms lead to a generalized form of the Butler-Volmer equation, represented by Eq. (76). The results can be said to expand on earlier results.<sup>7,8,12</sup> In addition to the electrochemical driving force, also thermal driving forces contribute to the reaction rate, cf. Eq. (76). The new equations for the interface can, both in the linear and nonlinear form, be used to describe impedance measurements, thermoelectric phenomena, concentration or formation cell potentials.

The generalized Butler-Volmer equation contains possibilities for work through the coupling terms. This means that the equations do not describe purely dissipative phenomena. Given a set of  $n$  thermodynamic forces and fluxes, it is always possible to diagonalize the  $\ell$ -matrix. This gives  $n$  eigenvalues and eigenvectors corresponding to  $n$  independent, purely dissipative processes. But given the symmetry of the linear case, there are  $n(n + 1)/2$  independent matrix elements. The  $n(n - 1)/2$  degrees of freedom that arise, can give transfer of energy from one form to another. Electric work can, for instance, be taken from a concentration cell (in reverse electro dialysis cells). Another example is the Soret effect, where a temperature gradient creates a concentration gradient which can also be used to do separation work.

#### D. The overpotential and the energy flux

This study reinforces the definition (52) used for the overpotential in the electrochemical literature, and its determination via impedance measurements. There is a clear connection of this expression to the expression in the Butler-Volmer equation, via Eqs. (84) and (85). This means that one can also trust the generalized forms given in Sec. VIII. The equations in this section give new expressions for the overall reaction, where all rate-limiting steps contribute, in addition to thermal driving forces. Moreover, the same definition can be used for the overpotential in the linear as well as the nonlinear case. As shown by (88), the interpretation of the measured overpotential in terms of electrostatic potential differences is not straight forward. The determination from impedance measurements is to be preferred, and can be done in the linear as well as the nonlinear regime.

The energy flux (80) has not been described in connection with the overpotential before and deserves a special comment. It gives additional information on the energy flux into and out of the electrode surface, additional to the energy conservation equation obtained from the Poisson operator.

Three contributions were ascribed to the energy flux in the  $z$ -direction in the present case. There were energy flux contributions from the oxygen pore, from the metal, and from the electrolyte. The coupling terms are specific to each flux. In the case of good thermal conductivity at the interface (no thermal driving forces), the expression reduces and we obtain a Butler-Volmer-like expression also for the energy flux. It is in all directions driven by the same effective electrochemical driving force for the two superimposed activated processes. The equation provides a strong link between the overpotential and the energy flux.

## X. CONCLUSIONS

We have developed a description of a simple electrochemical cell using GENERIC.<sup>17,18</sup> We find that it gives a more general thermodynamic basis to the Butler-Volmer and Nernst equations, including also Peltier effects. A multitude of possibilities arise for coupling between the electrochemical driving force, chemical driving forces and thermal driving forces in the nonlinear regime, extending the postulate of the linear to the nonlinear regime.<sup>7,8</sup> GENERIC, which contains NET at its center, ensures that the more general expression obeys the laws of thermodynamics. The friction matrix is no longer symmetric, a result anticipated from the mesoscopic derivation of analogous equations.<sup>26</sup>

This is the first time GENERIC is used for an electrochemical cell. Formation cells have different electrodes; a description of them will follow the same procedure as used here. GENERIC can set all relevant phenomena on the same basis, and is therefore suited to deal with all relevant effects, including hydrodynamic effects. Like in classical nonequilibrium thermodynamics, a prescription is found on how to integrate across the cell. The local dissipation can then be found, which is essential for electrode optimization discussions. Electrochemical science is a vast field, with numerous applications. Experimental evidence for the ideas proposed here may help a further development.

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