

A continuum thermodynamical approach to electrochemical systems

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Abstract This work focuses on formulating constitutive models for the bulk and double layer regions of an electrochemical system based on the fundamentals of modern continuum thermodynamics. Particularly, the constitutive models proposed accounting for transport phenomena in electrochemical systems by emphasizing the possibility of cross-coupling between two or more phenomena. Upon deriving a set of thermodynamic restrictions from the Müller-Liu approach of the second law of thermodynamics and axioms of constitutive theory, non-equilibrium quantities are examined in detail, and constitutive answers of the bulk and double layer regions are discussed. Moreover, the conditions for the thermodynamic equilibrium are evaluated for each region as well as the occurrence of dissipative mechanisms. Besides offering a proper formulation for non-equilibrium electrochemical systems, the approach described in this work can be easily extended to more complex chemical systems.

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1 Introduction

The discovery of electrokinetic phenomena in electrochemical systems by mid-19th century revealed that the metal-electrolyte interface structure was more complex than it had been supposed. Through electrokinetic and electrocapillary experiments, various attempts have been made to build up theoretical models [1,2] of the metal-electrolyte interface. In common, all of them describe the metal-electrolyte interface as a phase boundary carrying an electrical potential difference which arises from opposed charges stored in each phase surface. Then, for example, the electrode holds a positive charge density whereas the electrolyte solution holds a negative one, such as a parallel-plate capacitor. At the phase boundary, these positively and negatively charged layers are at a certain distance from each other, and together they form a double layer.

Of course, this simple physical picture of a double layer could not explain all occurring surface phenomena, in special, the transport phenomena of ions and other chemical species under the influence of external electric fields. Thus, more sophisticated theoretical models for the double layer [3] have been proposed, most of them founded on principles of classical statistical mechanics. Nonetheless, despite their impressive success to provide a framework for understanding the properties of the double layer region, these models require a set of molecular and ionic parameters, which not always are available. Moreover, their results are frequently limited to the structural nature of the double layer. Hence, discussions concerning whether double layer properties affect the drift of species and the fluxes of heat and electric current are frequently neglected.

On the other hand, continuum models provide a framework such that the flows of mass, heat and electric current can be quantitatively analyzed in terms of material properties of the medium. Unlike the microscopic models, the continuum ones do not need molecular and ionic data, but only a few universal principles and macroscopic experimental observations. Besides, according to the modern continuum thermodynamics, the same methodology, particularly, the balance equations and constitutive axioms have been used to investigate the transport phenomena in two different material regions of a system. Some examples can be found e.g. in [4–8].

In this work, a continuum model for the double layer and bulk regions of an electrochemical system is developed. From this model, transport phenomena in the bulk and double layer are investigated and compared. In addition, the implications of material equations on properties of each region are discussed. Although the current model focuses only on electrochemical systems, the results presented can be extended to study the flow of ions and other chemical species across cell membranes, ionic mobility in bio and geological media, and processes whose heat and mass transfers are enhanced by electromagnetic fields.

2 Modern thermodynamics approach

Chemists and chemical engineers frequently deal with methods of equilibrium thermodynamics to describe the many phenomena that take place in systems of chemical

interest. Even though equilibrium thermodynamics has been widely used by them, it is still unsuitable to study more realistic situations involving non-reversible processes. The initial attempts to expand the methods of equilibrium thermodynamics were made by Onsager [9, 10] and Eckart [11, 12], among others [13–15] along the first 60 years of the 20th century. They proposed a non-equilibrium thermodynamic theory, often known as thermodynamics of irreversible processes (TIP), which is founded on the local equilibrium hypothesis, that is, the local and instantaneous relations between thermodynamic quantities in a system out of equilibrium are the same as if the system was in an equilibrium state. While this assumption is well-motivated for small fluctuations of the local equilibrium state, it is not proper for thermodynamic states far from the equilibrium, as pointed out in [16, 17].

In view of the theoretical and practical limitations of both equilibrium thermodynamics and TIP, Truesdell jointly with Coleman and Noll developed a new structure for non-equilibrium thermodynamics without imposing equilibrium neither for the whole system, nor for the point. This new thermodynamic theory [18, 19] shares the same methodology with thermodynamics of irreversible processes, but differs in accounting new premises that are based on more general physical and mathematical principles valid for all types of bodies. Considering its general and analytical nature, this theory created by mid-1950s was coined by its founders as rational thermodynamics and is currently known as continuum thermodynamics.

In this new approach, an essential step is the statement of fundamental laws of Physics, such as the balances of mass, linear and angular momenta, energy, and entropy, as well as the Maxwell's equations of the electrodynamics. These laws concern all bodies, independently of their particularities, but they are not sufficient for uniquely determining the field quantities. Then, other statements—constitutive or material equations—must be used, which not only close the system of equations, but also reflect the constitutive response of each body.

Generally, material equations are based on physical experience and comprise a mathematical description of the material behavior of a certain body. Moreover, since these equations are experimentally motivated, there is a great freedom on postulating them, especially in relation to the number and the choice of the variables to be considered as well as the complexity of the equations. In order to ensure mathematical and physical coherence of the constitutive model, material equations must obey some requirements of constitutive theories, such as material objectivity, material symmetry and the second law of thermodynamics. All these requirements have been extensively discussed in [20, 21], so they will not be detailed in this work. However, due to the different formulations of the second law of thermodynamics, especially concerning its use in continuum mixtures, it is worthwhile to address some comments about the subject.

According to the continuum thermodynamics approach, additionally to the balance equations, the material behavior of a body must also obey the entropy principle, or second law of thermodynamics. In other words, all thermodynamic processes obtained as solutions of the balance laws and constitutive model must be consistent with the second law of thermodynamics. In order to deduce the restrictions put by the entropy principle on the constitutive functions, Coleman and Noll [22] proposed that (i) the supply terms in the linear momentum and energy balance laws do not affect the exploitation of the

second law of thermodynamics and (ii) the entropy flux and the entropy supply are quantities *a priori* given. While these statements are mathematically convenient, they are inconsistent with some results of the gas kinetic theory and inappropriate to treat the diffusion theory of continuum mixtures, as demonstrated by Truesdell in [19].

Thus, Müller [23,24] proposed a weaker formulation of the entropy inequality in which the entropy flux and the entropy supply are considered unspecified constitutive quantities, and the constitutive properties of the material do not depend on external supplies. Nevertheless, as the exploitation of the entropy principle laid down by Müller was too laborious yet, even for simple fluids free of external supplies, Liu [25] proposed to incorporate Lagrange multipliers to the entropy inequality, so it must hold under no constraints for all admissible thermodynamic processes. In the present work, this method will be employed to impose thermodynamic restrictions on the constitutive responses of the bulk and double layer regions.

3 General constitutive assumptions

The electrochemical system is regarded as an apolar material body formed by two regions, being one of ionic electric conduction (bulk) and other of an electrically charged interface (double layer). The former is an isotropic medium whose gradients of species concentration and electric potential are not significant. Consequently, the concentration of any species is virtually constant and the basic phenomena involve ion-solvent and ion-ion interactions. On the other hand, the double layer is an inhomogeneous and anisotropic medium in relation to the fluxes of mass, heat and electric current and comprises the region where the transfer of electrons between the electrode and the ionic solution takes place. For the sake of simplicity, the anisotropy of the double layer is treated as a special case of transverse isotropy, *i.e.*, there is an isotropic plane such that all directions in this plane are equivalent and all constitutive relations keep unchanged under arbitrary rotations of a coordinate system in relation to a major axis [26]. Under these conditions, the fluxes of mass, heat and electric current present a preferred direction that is orthogonal to the isotropic plane.

Furthermore, the separation between the double layer and the bulk is marked by abrupt changes of the electric potential and species concentrations. Mathematically, these changes are accounted for through a singular surface that separates the bulk and double layer. At the singular surface, corresponding jump conditions for balance equations valid in bulk and double layer must be formulated. Nevertheless, the properties of the singular surface are not examined in this work.

In order to study the material behavior of both regions of an electrochemical system, it is supposed that the mixture obeys the postulates of the classical theory of mixtures [19], and the quasi-electrostatic Maxwell's equations [27] are employed according to the Chu formulation of moving media [28]. The mixture is treated as an aqueous diluted solution constituted by chemical species, which carry electric charges and/or dipole moments. A non-specified constituent is denoted by an index a , which assumes values $a = 1, \dots, n$, being the index n reserved for the main fluid (solvent). Accordingly, quantities labeled with an index a , named partial quantities, express physical quantities of the constituent a . All fields are given in the Eulerian description and only Cartesian

tensors are used. The necessary background in non-equilibrium theories and in calculus and tensor analysis is assumed known. In turn, the kinematics and the balance equations used to describe the thermo-electrochemical behavior of the bulk and double layer regions are the same presented in [29], but, for convenience, they are concisely restated.

3.1 Kinematics and balance equations

Let a continuum mixture \mathcal{B} and its constituents \mathcal{B}_a occupy a region in the Euclidean space \mathcal{E} . Besides, let \mathcal{B} and \mathcal{B}_a be continuous sets of particles or material points that are put into a one-to-one correspondence with the points of a region of the physical space. Incidentally, particles in continuum theories do not represent atoms, molecules, ions, nor other classical particles, which can be easily labeled, but rather mathematical points endowed with physical properties, such as mass density, velocity, electric field, internal energy density *etc.*

Each particle of a continuum is identified with its spatial position \mathbf{x} in \mathcal{E} at time t , corresponding to the reference position \mathbf{X} at the initial time $t = 0$. Furthermore, in continuum theories of classical mixtures, \mathcal{B} consists of a set of overlapping \mathcal{B}_a , all occupying the same spatial position in \mathcal{E} at time t . This means that the location \mathbf{x} of a particle of the mixture coincides with the current location \mathbf{x}_a of any constituent. Therefore, there must exist particles of all constituents at every spatial position \mathbf{x} . Despite this assumption is an evident shortcoming in view of the discrete nature of matter, it is physically well-motivated since in single phase mixtures constituents are not macroscopically distinct, but only at the molecular level. Then, any representative volume must always be occupied by some amount of mass of all constituents.

Each constituent has its own kinematics. The velocity and acceleration of the constituent a at time t are, respectively,

$$\mathbf{v}_a \equiv \frac{\partial \mathbf{x}_a(\mathbf{X}_a, t)}{\partial t}, \quad \mathbf{a}_a \equiv \frac{\partial^2 \mathbf{x}_a(\mathbf{X}_a, t)}{\partial t^2}. \tag{3.1}$$

Likewise, each \mathcal{B}_a has its own mass and its positive mass density $\rho_a(\mathbf{x}, t)$ at time t . The mass density of the whole mixture, $\rho(\mathbf{x}, t)$, is related to $\rho_a(\mathbf{x}, t)$ by

$$\rho(\mathbf{x}, t) \equiv \sum_{a=1}^n \rho_a. \tag{3.2}$$

At every (\mathbf{x}, t) the mass concentration of \mathcal{B}_a is defined by

$$\xi_a(\mathbf{x}, t) \equiv \frac{\rho_a}{\rho}, \tag{3.3}$$

whence Eqs. (3.2) and (3.3) imply $\sum_{a=1}^n \xi_a = 1$. The mean velocity of \mathcal{B} at time t is defined by

$$\rho \mathbf{v}(\mathbf{x}, t) \equiv \sum_{a=1}^n \rho_a \mathbf{v}_a, \quad (3.4)$$

and the relative velocity of \mathcal{B}_a is

$$\mathbf{u}_a(\mathbf{x}, t) = \mathbf{v}_a - \mathbf{v}. \quad (3.5)$$

Thus, from Eqs. (3.2), (3.4) and (3.5) it follows that $\sum_{a=1}^n \rho \mathbf{u}_a = \mathbf{0}$. Note that \mathbf{u}_a is a generalized relative velocity whose precise definition depends upon specificities of the system and its external supplies.

The governing mechanical and electromagnetic balance equations of an electro-chemical system at every regular point are:

Balance of mass

$$\frac{d\rho}{dt} + \rho \operatorname{div}(\mathbf{v}) = 0, \quad (3.6)$$

Balance of concentration

$$\rho \frac{d\xi_a}{dt} + \operatorname{div}(\mathbf{j}_a) - c_a = 0, \quad (3.7)$$

Balance of linear momentum

$$\rho \frac{d\mathbf{v}}{dt} - \operatorname{div}(\mathbf{T}) - \rho \mathbf{b} - q\mathbf{E} - \mathbf{P} \cdot \nabla \mathbf{E} = 0, \quad (3.8)$$

Balance of angular momentum

$$\mathbf{T} = \mathbf{T}^T, \quad (3.9)$$

Balance of energy

$$\rho \frac{d\varepsilon}{dt} + \operatorname{div}(\mathbf{h}) - \mathbf{T} \cdot \nabla \mathbf{v} - \rho r - \dot{\mathbf{P}} \cdot \mathbf{E} - \mathbf{i} \cdot \mathbf{E} = 0, \quad (3.10)$$

Balance of entropy

$$\rho \frac{d\eta}{dt} + \operatorname{div}(\Phi) - \rho \sigma \geq 0, \quad (3.11)$$

Faraday's law

$$\operatorname{curl}(\mathbf{E}) = \mathbf{0}, \quad (3.12)$$

Ampère's law

$$\operatorname{curl}(\mathbf{H}) = \mathbf{i} + \frac{\partial \mathbf{D}}{\partial t} + \operatorname{curl}(\mathbf{P} \times \mathbf{v}), \quad (3.13)$$

Gauss' law

$$\operatorname{div}(\mathbf{D}) = q, \quad (3.14)$$

Magnetic flux law

$$\operatorname{div}(\mathbf{B}) = 0. \quad (3.15)$$

Here, \mathbf{j}_a is the mass flux, c_a is the mass production, \mathbf{T} is the stress tensor, q is the charge density defined by ρz , being z the charge *per* unit mass, \mathbf{E} and \mathbf{P} respectively are the electric field and the polarization field, \mathbf{b} is the mechanical body force density, ε is the internal energy density, \mathbf{h} is the heat flux, r is the mechanical energy supply density, \mathbf{i} is the electric conduction current density, η is the entropy density, Φ is the entropy flux vector, σ is the entropy supply, \mathbf{H} is the magnetic field, \mathbf{D} is the electric displacement vector, and \mathbf{B} is the magnetic flux. From Eq. (3.12), one exploits the irrotational nature of the quasi-static electric field and defines it in terms of a scalar function. Thus, recalling the Helmholtz theorem, one writes

$$\mathbf{E}(\mathbf{x}, t) = -\nabla\varphi, \quad (3.16)$$

where φ is the electric potential. Expressly, Eq. (3.16) shows that the electric field is completely specified by its scalar source (Gauss law).

4 Constitutive modeling of an electrochemical system

In this section, the entropy inequality is evaluated for constitutive classes that are suitable for the bulk and double layer regions.

4.1 Bulk region

In order to investigate the occurring physical phenomena in the bulk region, the basic fields - mass density of the mixture, $\rho(\mathbf{x}, t)$, mass concentration, $\xi_a(\mathbf{x}, t)$, empiric temperature, $\theta(\mathbf{x}, t)$, electric potential, $\varphi(\mathbf{x}, t)$, and velocity of the mixture, $\mathbf{v}(\mathbf{x}, t)$ - are evaluated by regarding the bulk as a heat and electrical conducting viscous mixture, so that most of its properties are taken into account through the set of independent constitutive variables

$$y \in \{\rho, \xi_a, \theta, \nabla\theta, \varphi, \mathbf{v}, \nabla\mathbf{v}\} \quad (a = 1, \dots, n - 1). \quad (4.1)$$

However, as the material objectivity principle [18,20,21,26] requires that constitutive quantities must not depend on the observer, constitutive functions are independent of

velocity, and they only depend on the gradient of velocity through its symmetric part, represented by the stretching tensor \mathbf{D} . Thus,

$$\mathcal{C} = \hat{\mathcal{C}}(\rho, \xi_a, \theta, \nabla\theta, \varphi, \mathbf{D}) \quad (a = 1, \dots, n-1), \quad (4.2)$$

where $\mathcal{C} \in \{\eta, \Phi, \mathbf{T}, \mathbf{P}, \varepsilon, \mathbf{h}, \mathbf{i}\}$.

The determination of the basic fields proceeds by evaluating the inequality

$$\begin{aligned} \Pi = & \rho \frac{d\eta}{dt} + \operatorname{div}(\Phi) - \rho\sigma - \Lambda^\rho \left(\frac{d\rho}{dt} + \rho \operatorname{div}(\mathbf{v}) \right) - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \left(\rho \frac{d\xi_a}{dt} + \operatorname{div}(\mathbf{j}_a) \right) \\ & - \Lambda^{\mathbf{v}} \cdot \left(\rho \frac{d\mathbf{v}}{dt} - \operatorname{div}(\mathbf{T}) + q\nabla\varphi - \rho\mathbf{b} + \mathbf{P} \cdot \nabla(\nabla\varphi) \right) \\ & - \Lambda^\varepsilon \left(\rho \frac{d\varepsilon}{dt} + \operatorname{div}(\mathbf{h}) - \mathbf{T} \cdot \nabla\mathbf{v} - \rho r + \dot{\mathbf{P}} \cdot \nabla\varphi + \mathbf{i} \cdot \nabla\varphi \right) \\ & - \Lambda^\varphi \left(\operatorname{div}(\mathbf{P}) + \epsilon_o \nabla^2\varphi - q \right) \geq 0, \end{aligned} \quad (4.3)$$

which must be satisfied for any fields $\rho(\mathbf{x}, t)$, $\xi_a(\mathbf{x}, t)$, $\theta(\mathbf{x}, t)$, $\varphi(\mathbf{x}, t)$ and $\mathbf{v}(\mathbf{x}, t)$. Here, the Lagrange multipliers of mass, Λ^ρ , concentration, Λ^{ξ_a} , velocity, $\Lambda^{\mathbf{v}}$, energy, Λ^ε , and electric potential, Λ^φ , are auxiliary constitutive quantities on which thermodynamic restrictions must also be placed.

In addition to the constitutive assumptions presented in the previous section, further hypotheses are necessary to guarantee the adequacy of the constitutive model. These auxiliary hypotheses are valid for both bulk and double layer regions. They are:

1. The Lagrange multiplier of energy is reciprocal of the empiric temperature, $\Lambda^\varepsilon = \frac{1}{\theta}$. As demonstrated by Liu and Müller [30], this expression is appropriate if the time derivative of empiric temperature is not included into the set of independent constitutive variables. Then, Λ^ε can be deduced by considering that, in a ideal material surface separating two heat conducting viscous fluids, temperature is continuous and there is no entropy production. Moreover, Müller [31] also demonstrated that $\Lambda^\varepsilon = \frac{1}{\theta}$ is valid for continuum mixtures because the jump conditions for the empiric temperature and entropy production hold.
2. The definition of the Lagrange multiplier of concentration, Λ^{ξ_a} , can be obtained by using the same arguments employed to deduce the expression for Λ^ε , that is, a heat conducting viscous mixture is brought into contact with one of its constituents through a ideal material surface. In this case, Liu and Müller also demonstrated that Λ^{ξ_a} is continuous across the ideal material surface and is related to the energy and momentum fluxes of a chemical species.
3. Extending the definition of Λ^{ξ_a} provided by Müller [31] to a medium under influence of quasi-electrostatic fields, Λ^{ξ_a} may be decomposed into an intrinsic constitutive part and an electric potential contribution, *viz.* $\Lambda^{\xi_a} = -\theta \Lambda_I^{\xi_a} + q_a \varphi$. The intrinsic part of Λ^{ξ_a} is the chemical potential of a system, $\bar{\mu}_a = -\theta \Lambda_I^{\xi_a}$. On the other hand, $\mu_a = -\theta \Lambda_I^{\xi_a} + q_a \varphi$ is the electrochemical potential since the energy

state of a constituent carrier of charge in any location of the electrolyte solution clearly depends on the chemical environment and its own electric nature. Of course, if the chemical species is not a charge carrier, $\mu_a = \bar{\mu}_a$.

4. The definition of Λ^ρ comes directly from the evaluation of the equilibrium conditions of a viscous heat conducting fluid. Then, the expression $p = -\rho\theta\Lambda^\rho$ is deduced, where p is the hydrostatic pressure.
5. The supplies of linear momentum, energy, and entropy should not influence the material behavior of the body.
6. The degree of polarization of each region of an electrochemical system is completely determined by a linear and isotropic function of type $\mathbf{P} = -\epsilon_o\chi\nabla\varphi$, where ϵ_o is the permittivity of free space and χ is the electric susceptibility. Hence, thanks to the great excess of solvent mass in relation to the masses of other constituents, the dielectric properties of each region of an electrochemical system are almost exclusively due to the solvent (water).
7. The term c_a only deals with mass production due to electrodic reactions, *i.e.*, reactions that come about at the electrode surface. Thus, $c_a = 0$ for the bulk and $c_a \neq 0$ for the double layer.
8. Because the mixture is diluted, it is assumed that the mixture particles are transported by the aqueous solvent, so that the velocity of the mixture particles is nearly the same as the velocity of the main fluid. Moreover, it is supposed that the constituent particles show the same temperature and electromagnetic fields as the solvent. Then, the dynamics of the mixture is along with that of the main fluid.
9. Since the electric charge density is given in terms of the mass density as stated in the previous section, restrictions are not imposed on both quantities, but either on the electric charge density or mass density.

If the constitutive functions considered in Eq. (4.2) are introduced into Eq. (4.3) and all differentiations are carried out according to the chain rule, Eq. (4.3) is rewritten as

$$\begin{aligned} \Pi = & \frac{d\rho}{dt} \left(\rho \frac{\partial\eta}{\partial\rho} - \Lambda^\rho - \rho\Lambda^\epsilon \frac{\partial\epsilon}{\partial\rho} - \Lambda^\epsilon \nabla\varphi \cdot \frac{\partial\mathbf{P}}{\partial\rho} \right) \\ & + \sum_{a=1}^{n-1} \frac{d\xi_a}{dt} \left(\rho \frac{\partial\eta}{\partial\xi_a} - \rho\Lambda^{\xi_a} - \rho\Lambda^\epsilon \frac{\partial\epsilon}{\partial\xi_a} - \Lambda^\epsilon \nabla\varphi \cdot \frac{\partial\mathbf{P}}{\partial\xi_a} \right) \\ & + \frac{d\theta}{dt} \left(\rho \frac{\partial\eta}{\partial\theta} - \rho\Lambda^\epsilon \frac{\partial\epsilon}{\partial\theta} - \Lambda^\epsilon \nabla\varphi \cdot \frac{\partial\mathbf{P}}{\partial\theta} \right) \\ & + \frac{d\nabla\theta}{dt} \cdot \left(\rho \frac{\partial\eta}{\partial\nabla\theta} - \rho\Lambda^\epsilon \frac{\partial\epsilon}{\partial\nabla\theta} - \Lambda^\epsilon \nabla\varphi \frac{\partial\mathbf{P}}{\partial\nabla\theta} \right) \\ & + \frac{d\varphi}{dt} \left(\rho \frac{\partial\eta}{\partial\varphi} - \rho\Lambda^\epsilon \frac{\partial\epsilon}{\partial\varphi} - \Lambda^\epsilon \nabla\varphi \cdot \frac{\partial\mathbf{P}}{\partial\varphi} \right) \\ & + \frac{d\mathbf{D}}{dt} \cdot \left(\rho \frac{\partial\eta}{\partial\mathbf{D}} - \rho\Lambda^\epsilon \frac{\partial\epsilon}{\partial\mathbf{D}} - \Lambda^\epsilon \nabla\varphi \frac{\partial\mathbf{P}}{\partial\mathbf{D}} \right) + \frac{d\mathbf{v}}{dt} \cdot (-\rho\Lambda^\mathbf{v}) \\ & + \nabla\rho \cdot \left(\frac{\partial\Phi}{\partial\rho} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial\mathbf{j}_a}{\partial\rho} + \Lambda^\mathbf{v} \frac{\partial T}{\partial\rho} - \Lambda^\varphi \frac{\partial\mathbf{P}}{\partial\rho} - \Lambda^\epsilon \frac{\partial\mathbf{h}}{\partial\rho} \right) \end{aligned}$$

$$\begin{aligned}
 & + \sum_{b=1}^{n-1} \nabla \xi_b \cdot \left(\frac{\partial \Phi}{\partial \xi_b} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \xi_b} \Big|_{a \neq b} + \Lambda^v \frac{\partial T}{\partial \xi_b} - \Lambda^\varphi \frac{\partial \mathbf{P}}{\partial \xi_b} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \xi_b} \right) \\
 & + \nabla \theta \cdot \left(\frac{\partial \Phi}{\partial \theta} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \theta} + \Lambda^v \frac{\partial T}{\partial \theta} - \Lambda^\varphi \frac{\partial \mathbf{P}}{\partial \theta} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \theta} \right) \\
 & + \nabla (\nabla \theta) \cdot \left(\frac{\partial \Phi}{\partial \nabla \theta} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \nabla \theta} + \Lambda^v \frac{\partial T}{\partial \nabla \theta} - \Lambda^\varphi \frac{\partial \mathbf{P}}{\partial \nabla \theta} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \nabla \theta} \right) \\
 & + \nabla \varphi \cdot \left(\frac{\partial \Phi}{\partial \varphi} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \varphi} + \Lambda^v \frac{\partial T}{\partial \varphi} - \Lambda^\varphi \frac{\partial \mathbf{P}}{\partial \varphi} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \varphi} - \Lambda^\varepsilon \mathbf{i} \right) \\
 & + \nabla \mathbf{D} \cdot \left(\frac{\partial \Phi}{\partial \mathbf{D}} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \mathbf{D}} + \Lambda^v \frac{\partial T}{\partial \mathbf{D}} - \Lambda^\varphi \frac{\partial \mathbf{P}}{\partial \mathbf{D}} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \mathbf{D}} \right) \\
 & - \Lambda^v \cdot [\mathbf{P} \cdot \nabla (\nabla \varphi)] + \Lambda^\varepsilon \mathbf{T} \cdot \mathbf{D} - \rho \Lambda^\rho \mathbf{1} \cdot \mathbf{D} - \Lambda^\varphi \epsilon_o \nabla^2 \varphi + \Lambda^\varphi q \geq 0,
 \end{aligned}
 \tag{4.4}$$

where ϵ_o is regarded as homogeneous. Eq.(4.4) is alternatively expressed as

$$\Pi = \mathbf{A} (y) \cdot \mathbf{W} + B (y) \geq 0,
 \tag{4.5}$$

where $\mathbf{A} (y)$ and $B (y)$ are respectively vector and scalar functions of y and \mathbf{W} is a constitutive variable not listed in (4.1). Since the inequality above is linear in

$$\mathbf{W} \in \left\{ \frac{d\rho}{dt}, \frac{d\xi_a}{dt}, \frac{d\theta}{dt}, \frac{d\nabla \theta}{dt}, \frac{d\varphi}{dt}, \frac{d\mathbf{D}}{dt}, \frac{d\mathbf{v}}{dt}, \nabla \rho, \nabla \xi_b, \nabla (\nabla \theta), \nabla \varphi, \nabla (\nabla \varphi), \nabla \mathbf{D}, \nabla^2 \varphi \right\},
 \tag{4.6}$$

Liu [26] demonstrated through the principle of local solvability that Eq.(4.5) must hold for arbitrary values of y and \mathbf{W} . Necessary and sufficient condition for this is

$$\mathbf{A} (y) = \mathbf{0}, \text{ and } B (y) \geq 0.
 \tag{4.7}$$

In other terms, Eq.(4.7) indicates that $\mathbf{A} (y)$ must vanish, otherwise Eq.(4.5) could be violated. These arguments lead to the following Liu identities

$$\begin{aligned}
 & \rho \frac{\partial \eta}{\partial \rho} - \Lambda^\rho - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \rho} - \Lambda^\varepsilon \nabla \varphi \cdot \frac{\partial \mathbf{P}}{\partial \rho} = 0, \\
 & \rho \frac{\partial \eta}{\partial \xi_a} - \rho \Lambda^{\xi_a} - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \xi_a} - \Lambda^\varepsilon \nabla \varphi \cdot \frac{\partial \mathbf{P}}{\partial \xi_a} = 0 \quad (a = 1, \dots, n - 1), \\
 & \rho \frac{\partial \eta}{\partial \theta} - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \theta} - \Lambda^\varepsilon \nabla \varphi \cdot \frac{\partial \mathbf{P}}{\partial \theta} = 0, \\
 & \rho \frac{\partial \eta}{\partial \nabla \theta} - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \nabla \theta} - \Lambda^\varepsilon \nabla \varphi \cdot \frac{\partial \mathbf{P}}{\partial \nabla \theta} = \mathbf{0},
 \end{aligned}
 \tag{4.8}$$

$$\begin{aligned} \rho \frac{\partial \eta}{\partial \varphi} - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \varphi} - \Lambda^\varepsilon \nabla \varphi \cdot \frac{\partial \mathbf{P}}{\partial \varphi} &= 0, \\ \rho \frac{\partial \eta}{\partial \mathbf{D}} - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \mathbf{D}} - \Lambda^\varepsilon \nabla \varphi \frac{\partial \mathbf{P}}{\partial \mathbf{D}} &= \mathbf{0}, \\ -\rho \Lambda^\nu &= \mathbf{0}, \quad \Lambda^\varphi = 0, \end{aligned}$$

$$\begin{aligned} \frac{\partial \Phi}{\partial \rho} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \rho} + \Lambda^\nu \frac{\partial \mathbf{T}}{\partial \rho} - \Lambda^\varphi \frac{\partial \mathbf{P}}{\partial \rho} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \rho} &= \mathbf{0}, \\ \frac{\partial \Phi}{\partial \xi_b} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \xi_b} \Big|_{a \neq b} + \Lambda^\nu \frac{\partial \mathbf{T}}{\partial \xi_b} - \Lambda^\varphi \frac{\partial \mathbf{P}}{\partial \xi_b} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \xi_b} &= \mathbf{0} \quad (b = 1, \dots, n-1), \\ \text{sym} \left(\frac{\partial \Phi}{\partial \nabla \theta} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \nabla \theta} + \Lambda^\nu \frac{\partial \mathbf{T}}{\partial \nabla \theta} - \Lambda^\varphi \frac{\partial \mathbf{P}}{\partial \nabla \theta} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \nabla \theta} \right) &= \mathbf{0}, \tag{4.9} \\ \frac{\partial \Phi}{\partial \varphi} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \varphi} + \Lambda^\nu \frac{\partial \mathbf{T}}{\partial \varphi} - \Lambda^\varphi \frac{\partial \mathbf{P}}{\partial \varphi} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \varphi} - \Lambda^\varepsilon \mathbf{i} &= \mathbf{0}, \\ \frac{\partial \Phi}{\partial \mathbf{D}} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \mathbf{D}} + \Lambda^\nu \frac{\partial \mathbf{T}}{\partial \mathbf{D}} - \Lambda^\varphi \frac{\partial \mathbf{P}}{\partial \mathbf{D}} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \mathbf{D}} &= \mathbf{0}, \end{aligned}$$

as well as the residual inequality

$$\begin{aligned} \Pi = \nabla \theta \cdot \left(\frac{\partial \Phi}{\partial \theta} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \theta} + \Lambda^\nu \frac{\partial \mathbf{T}}{\partial \theta} - \Lambda^\varphi \frac{\partial \mathbf{P}}{\partial \theta} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \theta} \right) \\ + \Lambda^\varepsilon \mathbf{T} \cdot \mathbf{D} - \rho \Lambda^\rho \mathbf{1} \cdot \mathbf{D} \geq 0. \end{aligned} \tag{4.10}$$

In obtaining Eq.(4.9)₃, the theorem of Cartesian decomposition of tensors was employed to impose that only the symmetric part of $\nabla(\nabla\theta)$ needs to vanish. Furthermore, in view of the constitutive assumptions previously established, one shows by cross differentiation of Eq.(4.8) that $\eta = \hat{\eta}(\rho, \xi_a, \theta)$, $\varepsilon = \hat{\varepsilon}(\rho, \xi_a, \theta)$, $\Lambda^\rho = \hat{\Lambda}^\rho(\rho, \xi_a, \theta)$, and $\Lambda^{\xi_a} = \hat{\Lambda}^{\xi_a}(\rho, \xi_a, \theta, \varphi)$ for $a = 1, \dots, n$. From the Liu identities (4.8) and $\psi = \varepsilon - \theta\eta + \nabla\varphi \cdot \frac{\mathbf{P}}{\rho}$, one also demonstrates that the thermodynamic relation

$$d\psi = \frac{p}{\rho^2} d\rho + \sum_{a=1}^{n-1} \mu_a d\xi_a - \eta d\theta - \mathbf{P} \cdot d \left(\frac{\nabla\varphi}{\rho} \right) \tag{4.11}$$

holds at every point of the bulk, either in equilibrium or not. Moreover, from Eqs. (4.8) and (4.11), one obtains the integrability conditions,

$$\frac{\partial (p/\rho^2)}{\partial \theta} = -\frac{\partial \eta}{\partial \rho}, \quad \frac{\partial (p/\rho^2)}{\partial \xi_a} = \frac{\partial \mu_a}{\partial \rho}, \quad \frac{\partial \mu_a}{\partial \theta} = -\frac{\partial \eta}{\partial \xi_a}, \quad (4.12)$$

as well as the reduced dependence $\psi = \hat{\psi}(\rho, \xi_a, \theta, \nabla\varphi)$, where it should be recalled that \mathbf{P} is only function of $\nabla\varphi$.

Using the definitions of Lagrange multipliers $\Lambda^{\mathbf{V}}$ and Λ^{φ} , the extra entropy flux $\boldsymbol{\phi} = \boldsymbol{\Phi} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \mathbf{j}_a - \Lambda^{\varepsilon} \mathbf{h}$ is introduced. Then, the Liu identities (4.9) become

$$\begin{aligned} \frac{\partial \boldsymbol{\phi}}{\partial \rho} &= \Lambda^{\varepsilon} \sum_{a=1}^{n-1} \frac{\partial \mu_a}{\partial \rho} \mathbf{j}_a, \\ \frac{\partial \boldsymbol{\phi}}{\partial \xi_b} &= \Lambda^{\varepsilon} \sum_{a=1}^{n-1} \frac{\partial \mu_a}{\partial \xi_b} \mathbf{j}_a \Big|_{a \neq b} \quad (b = 1, \dots, n-1), \\ \text{sym} \left(\frac{\partial \boldsymbol{\phi}}{\partial \nabla \theta} \right) &= \text{sym} \left(\Lambda^{\varepsilon} \sum_{a=1}^{n-1} \frac{\partial \mu_a}{\partial \nabla \theta} \mathbf{j}_a \right), \\ \frac{\partial \boldsymbol{\phi}}{\partial \varphi} &= \Lambda^{\varepsilon} \sum_{a=1}^{n-1} \frac{\partial \mu_a}{\partial \varphi} \mathbf{j}_a + \Lambda^{\varepsilon} \mathbf{i}, \\ \frac{\partial \boldsymbol{\phi}}{\partial \mathbf{D}} &= \Lambda^{\varepsilon} \sum_{a=1}^{n-1} \frac{\partial \mu_a}{\partial \mathbf{D}} \mathbf{j}_a, \end{aligned} \quad (4.13)$$

where the definition of Λ^{ξ_a} was employed. However, as the reduced dependence of Λ^{ξ_a} reflects on μ_a , one has $\mu_a = \hat{\mu}_a(\rho, \xi_a, \theta, \varphi)$ and, from Eq. (4.13), it follows that $\frac{\partial \boldsymbol{\phi}}{\partial \xi_b} = \mathbf{0}$, $\text{sym} \left(\frac{\partial \boldsymbol{\phi}}{\partial \nabla \theta} \right) = \mathbf{0}$, and $\frac{\partial \boldsymbol{\phi}}{\partial \mathbf{D}} = \mathbf{0}$, though $\frac{\partial \boldsymbol{\phi}}{\partial \rho}$ and $\frac{\partial \boldsymbol{\phi}}{\partial \varphi}$ are not null vectors. Then, if one imposes that the extra entropy flux is an isotropic vector, $\boldsymbol{\phi}$ is null since there are no scalar generators for an isotropic vector function. Consequently, Eqs. (4.13)₁ and (4.13)₄ respectively become $\frac{\partial \boldsymbol{\phi}}{\partial \rho} = \mathbf{0}$ and $\mathbf{i} = -\sum_{a=1}^{n-1} \frac{\partial \mu_a}{\partial \varphi} \mathbf{j}_a$. Applying the electrochemical potential definition, the latter can be further simplified to $\mathbf{i} = \sum_{a=1}^{n-1} \mathbf{i}_a$, where $\mathbf{i}_a = -q_a \mathbf{j}_a$ and the electric current sign convention is such that the partial current is negative for the reduction of a cation or for the oxidation of an anion, and positive for the oxidation of a cation or reduction of an anion. This expression implies that (i) the total current in the bulk region is given by the algebraic sum of all flows of charge carrier constituents, also known as faradaic currents, and (ii) the assumption of isotropic material symmetry for the bulk region is physically consistent.

Recalling $\boldsymbol{\phi} = \mathbf{0}$, the definition of mass Lagrange multiplier and $\nabla \mu_a = \frac{\partial \mu_a}{\partial \theta} \nabla \theta$, where $\nabla \mu_a$ is given only in terms of $\nabla \theta$ because $\nabla \rho$, $\nabla \xi_a$ and $\nabla \varphi$ are not independent constitutive variables, the entropy flux takes the form $\boldsymbol{\Phi} = \Lambda^{\varepsilon} \mathbf{h} + \sum_{a=1}^{n-1} \Lambda^{\xi_a} \mathbf{j}_a$ and Eq. (4.10) is rewritten as

$$\Pi = -\frac{\nabla \theta}{\theta} \cdot \mathbf{h} - \sum_{a=1}^{n-1} \mathbf{j}_a \cdot \nabla \mu_a + \mathbf{T} \cdot \mathbf{D} + p \mathbf{1} \cdot \mathbf{D} \geq 0. \quad (4.14)$$

The left-hand side of Eq.(4.14) is the residual entropy production density, a non-negative quantity for arbitrary values of $\{\rho, \xi_a, \theta, \nabla\theta, \varphi, \mathbf{D}\}$. Whenever Π takes the zero value, there is no entropy production and, therefore, there is a local thermodynamic equilibrium state at (\mathbf{x}, t) . Necessary conditions for $\Pi = 0$ at (\mathbf{x}, t) are

$$\left(\frac{\partial \Pi}{\partial y_B}\right)\Big|_E = 0, \quad \left(\frac{\partial^2 \Pi}{\partial y_B \partial y_B}\right)\Big|_E \geq 0, \tag{4.15}$$

where $y_B \in \{\nabla\theta, \nabla\mu_a, \mathbf{D}\}$ and the index E stands for the equilibrium state. Expressly, the heat conduction, the mass transport and the deformations that occur in the bulk are dissipative mechanisms, which contribute to the production of residual entropy density.

In exploiting the first-order derivative of Π in relation to y_B , constraints are imposed on the static parts of constitutive quantities. Thus, immediate consequences of (4.15)₁ are

$$\left(\frac{\partial \Pi}{\partial \nabla\theta}\right)\Big|_E = -\frac{1}{\theta} \mathbf{h} = \mathbf{0}, \tag{4.16}$$

$$\left(\frac{\partial \Pi}{\partial \nabla\mu_a}\right)\Big|_E = -\mathbf{j}_a = \mathbf{0}, \tag{4.17}$$

and

$$\left(\frac{\partial \Pi}{\partial \mathbf{D}}\right)\Big|_E = \mathbf{T} + p\mathbf{1} = \mathbf{0}, \tag{4.18}$$

$$\mathbf{T} = -p\mathbf{1}.$$

Restrictions on the dynamic parts of constitutive functions come from the second-order derivative of Π in relation to y_B . Supposing an isotropic Newtonian fluid and following the theorem of representation of isotropic functions [32,33], one writes in component form

$$\begin{aligned} T_{ij} &= -p\delta_{ij} + \left(\alpha + \frac{2}{3}\beta\right) D_{nm}\delta_{ij} + 2\beta\bar{D}_{ij} + O(2), \\ h_i &= \kappa_1\theta_{,i} + \kappa_2\mu_i^a + O(2), \\ j_i^a &= C_1^a\mu_{,i}^a + C_2^a\theta_{,i} + O(2), \end{aligned} \tag{4.19}$$

where $\bar{\mathbf{D}} = \mathbf{D} - \frac{1}{3}\text{tr}(\mathbf{D})\mathbf{1}$ is the deviatoric part of \mathbf{D} and all phenomenological coefficients are material functions of type

$$\mathcal{P}_B = \hat{\mathcal{P}}_B(\rho, \xi_a, \theta, \varphi, \nabla\theta \cdot \nabla\theta, \text{tr}\mathbf{D}). \tag{4.20}$$

With Eq. (4.19), the residual entropy inequality becomes

$$\begin{aligned} \Pi = & -\kappa_1 \frac{\theta_{,i}}{\theta} \theta_{,i} - \sum_{a=1}^{n-1} C_1^a \mu_{,i}^a \mu_{,i}^a - \left(\frac{\kappa_2}{\theta} + \sum_{a=1}^{n-1} C_2^a \right) \theta_{,i} \mu_{,i}^a \\ & + \left(\alpha + \frac{2}{3} \beta \right) D_{nn}^2 + 2\beta \bar{D}_{ij} \bar{D}_{ij} \geq 0, \end{aligned} \quad (4.21)$$

which implies the following restrictions on phenomenological parameters

$$\frac{\kappa_1}{\theta} \leq 0, \quad \sum_{a=1}^{n-1} C_1^a \leq 0, \quad \sum_{a=1}^{n-1} C_2^a - \frac{\kappa_2}{\theta} \leq 0, \quad \alpha + \frac{2}{3} \beta \geq 0, \quad \beta \leq 0, \quad (4.22)$$

where κ_1 is the thermal conductivity coefficient, C_1^a is the mass transport coefficient, C_2^a and κ_2^a are phenomenological coefficients related to thermophoresis, and β and $\alpha + \frac{2}{3} \beta$ are the shear and bulk viscosities, respectively. Physically, the inequalities above evidence that the heat flux vector opposes the temperature gradient (Fourier's law) as well as the diffusive flux vector is opposed to the gradient of electrochemical potential. Moreover, the transport of matter through bulk is also caused by the coupling of heat and mass flows, and the particles of the electrolyte bulk flow in the direction of shearing forces.

4.2 Double layer region

It has been long recognized that the introduction of an electrode under potential control into an electrolyte solution disrupts the bulk solution structure, modifying the interactions that occur between the ions/molecules in solution and the electrode surface. As a result, different physical and chemical phenomena arise in the electrochemical system, and a new constitutive class should be formulated.

In the double layer, one is interested in determining the same basic fields accounted in the bulk region, but, unlike there, one assumes that the double layer is a viscous heat and electrical conducting mixture with chemical reactions and mass transport caused by sources different than those in the bulk. Thus, the constitutive response of double layer depends on

$$w \in \{\rho, \theta, \nabla \theta, \xi_a, \nabla \xi_b, \varphi, \nabla \varphi, \mathbf{v}, \nabla \mathbf{v}, \mathbf{n}\} \quad (\forall a, b = 1, \dots, n-1), \quad (4.23)$$

where \mathbf{n} is a vector that characterizes the preferred direction of the double layer in an undistorted configuration. At this point, it is worth mentioning that the representation theorem of anisotropic invariants [34] has been used to write constitutive relations $\mathcal{C} = \hat{\mathcal{C}}(w)$, where $\mathcal{C} \in \{\mathbf{j}_a, c_a, \mathbf{T}, \varepsilon, \mathbf{h}, \mathbf{P}, \mathbf{i}, \eta, \Phi\}$.

Axioms of constitutive theory require that all variables listed in (4.23) are objective scalars, vectors and tensors. In addition, all constitutive equations must obey the principle of material objectivity. Then, \mathcal{C} does not depend explicitly on \mathbf{v} , but it depends

on $\nabla \mathbf{v}$ only through its symmetric part \mathbf{D} , that is,

$$w \in \{\rho, \theta, \nabla\theta, \xi_a, \nabla\xi_b, \varphi, \nabla\varphi, \mathbf{D}, \mathbf{n}\} \quad (\forall a, b = 1, \dots, n - 1). \quad (4.24)$$

According to the method of Lagrange multipliers for exploitation of entropy inequality, there exist Lagrange multipliers $\Lambda^\rho, \Lambda^{\xi_a}, \Lambda^{\mathbf{v}}, \Lambda^\varepsilon$ and Λ^φ that, whenever multiplied by their corresponding balance laws, they produce an inequality

$$\begin{aligned} \Pi = & \rho \frac{d\eta}{dt} + \text{div}(\Phi) - \rho\sigma - \Lambda^\rho \left(\frac{d\rho}{dt} + \rho \text{div}(\mathbf{v}) \right) - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \left(\rho \frac{d\xi_a}{dt} + \text{div}(\mathbf{j}_a) - c_a \right) \\ & - \Lambda^{\mathbf{v}} \cdot \left(\rho \frac{d\mathbf{v}}{dt} - \text{div}(\mathbf{T}) + q\nabla\varphi - \rho\mathbf{b} + \mathbf{P} \cdot \nabla(\nabla\varphi) \right) \\ & - \Lambda^\varepsilon \left(\rho \frac{d\varepsilon}{dt} + \text{div}(\mathbf{h}) - \mathbf{T} \cdot \nabla\mathbf{v} - \rho r + \dot{\mathbf{P}} \cdot \nabla\varphi + \mathbf{i} \cdot \nabla\varphi \right) \\ & - \Lambda^\varphi \left(\text{div}(\mathbf{P}) + \varepsilon_o \nabla^2\varphi - q \right) \geq 0 \end{aligned} \quad (4.25)$$

which is valid for any solution $\{\rho(\mathbf{x}, t), \xi_a(\mathbf{x}, t), \theta(\mathbf{x}, t), \varphi(\mathbf{x}, t), \mathbf{v}(\mathbf{x}, t)\}$ of field equations. After introducing constitutive equations into (4.25) and all differentiations are performed in accordance with the chain rule, the entropy inequality becomes

$$\begin{aligned} \Pi = & \frac{d\rho}{dt} \left(\rho \frac{\partial\eta}{\partial\rho} - \Lambda^\rho - \rho \Lambda^\varepsilon \frac{\partial\varepsilon}{\partial\rho} - \Lambda^\varepsilon \nabla\varphi \cdot \frac{\partial\mathbf{P}}{\partial\rho} \right) \\ & + \sum_{a=1}^{n-1} \frac{d\xi_a}{dt} \left(\rho \frac{\partial\eta}{\partial\xi_a} - \rho \Lambda^{\xi_a} - \rho \Lambda^\varepsilon \frac{\partial\varepsilon}{\partial\xi_a} - \Lambda^\varepsilon \nabla\varphi \cdot \frac{\partial\mathbf{P}}{\partial\xi_a} \right) \\ & + \sum_{b=1}^{n-1} \frac{d\nabla\xi_b}{dt} \cdot \left(\rho \frac{\partial\eta}{\partial\nabla\xi_b} - \rho \Lambda^\varepsilon \frac{\partial\varepsilon}{\partial\nabla\xi_b} - \Lambda^\varepsilon \nabla\varphi \cdot \frac{\partial\mathbf{P}}{\partial\nabla\xi_b} \right) \\ & + \frac{d\theta}{dt} \left(\rho \frac{\partial\eta}{\partial\theta} - \rho \Lambda^\varepsilon \frac{\partial\varepsilon}{\partial\theta} - \Lambda^\varepsilon \nabla\varphi \cdot \frac{\partial\mathbf{P}}{\partial\theta} \right) \\ & + \frac{d\nabla\theta}{dt} \cdot \left(\rho \frac{\partial\eta}{\partial\nabla\theta} - \rho \Lambda^\varepsilon \frac{\partial\varepsilon}{\partial\nabla\theta} - \Lambda^\varepsilon \nabla\varphi \cdot \frac{\partial\mathbf{P}}{\partial\nabla\theta} \right) \\ & + \frac{d\varphi}{dt} \left(\rho \frac{\partial\eta}{\partial\varphi} - \rho \Lambda^\varepsilon \frac{\partial\varepsilon}{\partial\varphi} - \Lambda^\varepsilon \nabla\varphi \cdot \frac{\partial\mathbf{P}}{\partial\varphi} \right) \\ & + \frac{d\nabla\varphi}{dt} \cdot \left(\rho \frac{\partial\eta}{\partial\nabla\varphi} - \rho \Lambda^\varepsilon \frac{\partial\varepsilon}{\partial\nabla\varphi} - \Lambda^\varepsilon \nabla\varphi \cdot \frac{\partial\mathbf{P}}{\partial\nabla\varphi} \right) \\ & + \frac{d\mathbf{D}}{dt} \cdot \left(\rho \frac{\partial\eta}{\partial\mathbf{D}} - \rho \Lambda^\varepsilon \frac{\partial\varepsilon}{\partial\mathbf{D}} - \Lambda^\varepsilon \nabla\varphi \cdot \frac{\partial\mathbf{P}}{\partial\mathbf{D}} \right) \\ & + \frac{d\mathbf{n}}{dt} \cdot \left(\rho \frac{\partial\eta}{\partial\mathbf{n}} - \rho \Lambda^\varepsilon \frac{\partial\varepsilon}{\partial\mathbf{n}} - \Lambda^\varepsilon \nabla\varphi \cdot \frac{\partial\mathbf{P}}{\partial\mathbf{n}} \right) + \frac{d\mathbf{v}}{dt} \cdot (-\rho \Lambda^{\mathbf{v}}) \end{aligned}$$

$$\begin{aligned}
& + \nabla \rho \cdot \left(\frac{\partial \Phi}{\partial \rho} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \rho} + \Lambda^v \frac{\partial T}{\partial \rho} - \Lambda^\varphi \frac{\partial \mathbf{P}}{\partial \rho} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \rho} \right) \\
& + \sum_{b=1}^{n-1} \nabla \xi_b \cdot \left(\frac{\partial \Phi}{\partial \xi_b} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \xi_b} \Big|_{a \neq b} + \Lambda^v \frac{\partial T}{\partial \xi_b} - \Lambda^\varphi \frac{\partial \mathbf{P}}{\partial \xi_b} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \xi_b} \right) \\
& + \sum_{b=1}^{n-1} \nabla (\nabla \xi_b) \cdot \left(\frac{\partial \Phi}{\partial \nabla \xi_b} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \nabla \xi_b} \Big|_{a \neq b} + \Lambda^v \frac{\partial T}{\partial \nabla \xi_b} - \Lambda^\varphi \frac{\partial \mathbf{P}}{\partial \nabla \xi_b} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \nabla \xi_b} \right) \\
& + \nabla \theta \cdot \left(\frac{\partial \Phi}{\partial \theta} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \theta} + \Lambda^v \frac{\partial T}{\partial \theta} - \Lambda^\varphi \frac{\partial \mathbf{P}}{\partial \theta} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \theta} \right) \\
& + \nabla (\nabla \theta) \cdot \left(\frac{\partial \Phi}{\partial \nabla \theta} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \nabla \theta} + \Lambda^v \frac{\partial T}{\partial \nabla \theta} - \Lambda^\varphi \frac{\partial \mathbf{P}}{\partial \nabla \theta} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \nabla \theta} \right) \\
& + \nabla \varphi \cdot \left(\frac{\partial \Phi}{\partial \varphi} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \varphi} + \Lambda^v \frac{\partial T}{\partial \varphi} - \Lambda^\varphi \frac{\partial \mathbf{P}}{\partial \varphi} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \varphi} - \Lambda^\varepsilon \mathbf{i} \right) \\
& + \nabla (\nabla \varphi) \cdot \left(\frac{\partial \Phi}{\partial \nabla \varphi} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \nabla \varphi} + \Lambda^v \frac{\partial T}{\partial \nabla \varphi} - \Lambda^v \cdot \mathbf{P} - \Lambda^\varphi \frac{\partial \mathbf{P}}{\partial \nabla \varphi} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \nabla \varphi} \right) \\
& + \nabla \mathbf{D} \cdot \left(\frac{\partial \Phi}{\partial \mathbf{D}} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \mathbf{D}} + \Lambda^v \frac{\partial T}{\partial \mathbf{D}} - \Lambda^\varphi \frac{\partial \mathbf{P}}{\partial \mathbf{D}} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \mathbf{D}} \right) \\
& + \nabla \mathbf{n} \cdot \left(\frac{\partial \Phi}{\partial \mathbf{n}} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \mathbf{n}} + \Lambda^v \frac{\partial T}{\partial \mathbf{n}} - \Lambda^\varphi \frac{\partial \mathbf{P}}{\partial \mathbf{n}} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \mathbf{n}} \right) \\
& + \Lambda^\varepsilon \mathbf{T} \cdot \mathbf{D} - \rho \Lambda^\rho \mathbf{1} \cdot \mathbf{D} - \Lambda^\varphi \epsilon_o \nabla^2 \varphi + \Lambda^\varphi q + \sum_{a=1}^{n-1} \Lambda^{\xi_a} c_a \geq 0, \tag{4.26}
\end{aligned}$$

where ϵ_o is homogeneous. In the same way that Eq. (4.4), Eq. (4.26) can be expressed as

$$\Pi = \mathbf{A}(w) \cdot \mathbf{Z} + B(w) \geq 0,$$

which is linear in

$$\mathbf{Z} \in \left\{ \frac{d\rho}{dt}, \frac{d\xi_a}{dt}, \frac{d\nabla \xi_b}{dt}, \frac{d\theta}{dt}, \frac{d\nabla \theta}{dt}, \frac{d\varphi}{dt}, \frac{d\nabla \varphi}{dt}, \frac{d\mathbf{D}}{dt}, \frac{d\mathbf{n}}{dt}, \frac{d\mathbf{v}}{dt}, \nabla \rho, \nabla (\nabla \xi_b), \nabla (\nabla \theta), \nabla (\nabla \varphi), \nabla \mathbf{D}, \nabla \mathbf{n}, \nabla^2 \varphi \right\}. \tag{4.27}$$

Hence, according to the principle of local solvability, the coefficients of \mathbf{Z} in Eq. (4.26) must vanish, otherwise the entropy inequality could be violated. These arguments lead to the Liu identities

$$\begin{aligned}
 &\rho \frac{\partial \eta}{\partial \rho} - \Lambda^\rho - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \rho} - \Lambda^\varepsilon \nabla \varphi \cdot \frac{\partial \mathbf{P}}{\partial \rho} = 0, \\
 &\rho \frac{\partial \eta}{\partial \xi_a} - \rho \Lambda^{\xi_a} - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \xi_a} - \Lambda^\varepsilon \nabla \varphi \cdot \frac{\partial \mathbf{P}}{\partial \xi_a} = 0, \\
 &\rho \frac{\partial \eta}{\partial \nabla \xi_b} - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \nabla \xi_b} - \Lambda^\varepsilon \nabla \varphi \frac{\partial \mathbf{P}}{\partial \nabla \xi_b} = \mathbf{0}, \quad (b = 1, \dots, n - 1) \\
 &\rho \frac{\partial \eta}{\partial \theta} - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \theta} - \Lambda^\varepsilon \nabla \varphi \cdot \frac{\partial \mathbf{P}}{\partial \theta} = 0, \\
 &\rho \frac{\partial \eta}{\partial \nabla \theta} - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \nabla \theta} - \Lambda^\varepsilon \nabla \varphi \frac{\partial \mathbf{P}}{\partial \nabla \theta} = \mathbf{0}, \\
 &\rho \frac{\partial \eta}{\partial \varphi} - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \varphi} - \Lambda^\varepsilon \nabla \varphi \cdot \frac{\partial \mathbf{P}}{\partial \varphi} = 0, \\
 &\rho \frac{\partial \eta}{\partial \nabla \varphi} - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \nabla \varphi} - \Lambda^\varepsilon \nabla \varphi \frac{\partial \mathbf{P}}{\partial \nabla \varphi} = \mathbf{0}, \\
 &\rho \frac{\partial \eta}{\partial \mathbf{D}} - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \mathbf{D}} - \Lambda^\varepsilon \nabla \varphi \frac{\partial \mathbf{P}}{\partial \mathbf{D}} = \mathbf{0}, \\
 &\rho \frac{\partial \eta}{\partial \mathbf{n}} - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \mathbf{n}} - \Lambda^\varepsilon \nabla \varphi \frac{\partial \mathbf{P}}{\partial \mathbf{n}} = \mathbf{0}, \\
 &-\rho \Lambda^\nu = \mathbf{0}, \quad \Lambda^\varphi = 0,
 \end{aligned}
 \tag{4.28}$$

$$\begin{aligned}
 &\frac{\partial \Phi}{\partial \rho} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \rho} + \Lambda^\nu \frac{\partial \mathbf{T}}{\partial \rho} - \Lambda^\varphi \frac{\partial \mathbf{P}}{\partial \rho} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \rho} = \mathbf{0}, \\
 &\text{sym} \left(\frac{\partial \Phi}{\partial \nabla \xi_b} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \nabla \xi_b} \Big|_{a \neq b} + \Lambda^\nu \frac{\partial \mathbf{T}}{\partial \nabla \xi_b} - \Lambda^\varphi \frac{\partial \mathbf{P}}{\partial \xi_b} \right. \\
 &\quad \left. - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \nabla \xi_b} \right) = \mathbf{0}, \quad (b = 1, \dots, n - 1) \\
 &\text{sym} \left(\frac{\partial \Phi}{\partial \nabla \theta} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \nabla \theta} + \Lambda^\nu \frac{\partial \mathbf{T}}{\partial \nabla \theta} - \Lambda^\varphi \frac{\partial \mathbf{P}}{\partial \nabla \theta} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \nabla \theta} \right) = \mathbf{0}, \tag{4.29} \\
 &\text{sym} \left(\frac{\partial \Phi}{\partial \nabla \varphi} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \nabla \varphi} + \Lambda^\nu \frac{\partial \mathbf{T}}{\partial \nabla \varphi} - \Lambda^\nu \cdot \mathbf{P} - \Lambda^\varphi \frac{\partial \mathbf{P}}{\partial \nabla \varphi} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \nabla \varphi} \right) = \mathbf{0}, \\
 &\frac{\partial \Phi}{\partial \mathbf{D}} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \mathbf{D}} + \Lambda^\nu \frac{\partial \mathbf{T}}{\partial \mathbf{D}} - \Lambda^\varphi \frac{\partial \mathbf{P}}{\partial \mathbf{D}} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \mathbf{D}} = \mathbf{0}, \\
 &\frac{\partial \Phi}{\partial \mathbf{n}} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \mathbf{n}} + \Lambda^\nu \frac{\partial \mathbf{T}}{\partial \mathbf{n}} - \Lambda^\varphi \frac{\partial \mathbf{P}}{\partial \mathbf{n}} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \mathbf{n}} = \mathbf{0},
 \end{aligned}$$

as well as the residual inequality

$$\begin{aligned}
 \Pi &= \sum_{b=1}^{n-1} \nabla \xi_b \cdot \left(\frac{\partial \Phi}{\partial \xi_b} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \xi_b} \Big|_{a \neq b} + \Lambda^v \frac{\partial T}{\partial \xi_b} - \Lambda^\varphi \frac{\partial \mathbf{P}}{\partial \xi_b} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \xi_b} \right) \\
 &+ \nabla \theta \cdot \left(\frac{\partial \Phi}{\partial \theta} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \theta} + \Lambda^v \frac{\partial T}{\partial \theta} - \Lambda^\varphi \frac{\partial \mathbf{P}}{\partial \theta} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \theta} \right) \\
 &+ \nabla \varphi \cdot \left(\frac{\partial \Phi}{\partial \varphi} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \varphi} + \Lambda^v \frac{\partial T}{\partial \varphi} - \Lambda^\varphi \frac{\partial \mathbf{P}}{\partial \varphi} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \varphi} - \Lambda^\varepsilon \mathbf{i} \right) \\
 &+ \Lambda^\varepsilon \mathbf{T} \cdot \mathbf{D} - \rho \Lambda^\rho \mathbf{1} \cdot \mathbf{D} - \Lambda^\varphi \epsilon_o \nabla^2 \varphi + \Lambda^\varphi q + \sum_{a=1}^{n-1} \Lambda^{\xi_a} c_a \geq 0. \tag{4.30}
 \end{aligned}$$

Further conclusions can be drawn from the Liu identities above. Since \mathbf{P} is an isotropic and linear function of $\nabla \varphi$ and Λ^ε depends exclusively on θ , by the cross differentiation of identities (4.28) one proves that $\eta = \hat{\eta}(\rho, \theta, \xi_a)$, $\varepsilon = \hat{\varepsilon}(\rho, \theta, \xi_a)$, $\Lambda^\rho = \hat{\Lambda}^\rho(\rho, \theta, \xi_a)$, $\Lambda^{\xi_a} = \hat{\Lambda}^{\xi_a}(\rho, \theta, \xi_a, \varphi)$, and

$$\frac{\partial (p/\rho^2)}{\partial \theta} = -\frac{\partial \eta}{\partial \rho}, \quad \frac{\partial (p/\rho^2)}{\partial \xi_a} = \frac{\partial \mu_a}{\partial \rho}, \quad \frac{\partial \mu_a}{\partial \theta} = -\frac{\partial \eta}{\partial \xi_a}, \tag{4.31}$$

where (4.31) are the integrability conditions for thermodynamic potential $\psi = \varepsilon - \theta \eta + \frac{\mathbf{P}}{\rho} \cdot \nabla \varphi$. Thus, one has the thermodynamic relation

$$d\psi = \frac{p}{\rho^2} d\rho + \sum_{a=1}^{n-1} \mu_a d\xi_a - \eta d\theta - \mathbf{P} \cdot d \left(\frac{\nabla \varphi}{\rho} \right), \tag{4.32}$$

whence $\psi = \hat{\psi}(\rho, \theta, \xi_a, \nabla \varphi)$.

In turn, from the Liu identities (4.29) one introduces the extra entropy flux $\phi = \Phi - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \mathbf{j}_a - \Lambda^\varepsilon \mathbf{h}$, where $\Lambda^v = \mathbf{0}$ and $\Lambda^\varphi = 0$ were used. Substituting the expression for the extra entropy flux into (4.29) and making use of definition of Λ^{ξ_a} , it follows that

$$\begin{aligned}
 \frac{\partial \phi}{\partial \rho} &= \Lambda^\varepsilon \sum_{a=1}^{n-1} \frac{\partial \mu_a}{\partial \rho} \mathbf{j}_a, \\
 \text{sym} \left(\frac{\partial \phi}{\partial \nabla \xi_b} \right) &= \text{sym} \left(\Lambda^\varepsilon \sum_{a=1}^{n-1} \frac{\partial \mathbf{j}_a}{\partial \nabla \xi_b} \Big|_{a \neq b} \right), \quad (\forall b = 1, \dots, n-1) \\
 \text{sym} \left(\frac{\partial \phi}{\partial \nabla \theta} \right) &= \text{sym} \left(\Lambda^\varepsilon \sum_{a=1}^{n-1} \frac{\partial \mu_a}{\partial \nabla \theta} \mathbf{j}_a \right),
 \end{aligned}$$

$$\begin{aligned}
 \frac{\partial \boldsymbol{\phi}}{\partial \nabla \varphi} &= \Lambda^\varepsilon \sum_{a=1}^{n-1} \frac{\partial \mu_a}{\partial \nabla \varphi} \mathbf{j}_a, \\
 \frac{\partial \boldsymbol{\phi}}{\partial \mathbf{D}} &= \Lambda^\varepsilon \sum_{a=1}^{n-1} \frac{\partial \mu_a}{\partial \mathbf{D}} \mathbf{j}_a, \\
 \frac{\partial \boldsymbol{\phi}}{\partial \mathbf{n}} &= \Lambda^\varepsilon \sum_{a=1}^{n-1} \frac{\partial \mu_a}{\partial \mathbf{n}} \mathbf{j}_a.
 \end{aligned}
 \tag{4.33}$$

Nevertheless, as μ_a should present the same reduced dependence of Λ^{ξ_a} , one has from Eq. (4.33) that $\text{sym} \left(\frac{\partial \boldsymbol{\phi}}{\partial \nabla \xi_b} \right) = \mathbf{0}$, $\text{sym} \left(\frac{\partial \boldsymbol{\phi}}{\partial \nabla \theta} \right) = \mathbf{0}$, $\frac{\partial \boldsymbol{\phi}}{\partial \nabla \varphi} = \mathbf{0}$, $\frac{\partial \boldsymbol{\phi}}{\partial \mathbf{D}} = \mathbf{0}$ and $\frac{\partial \boldsymbol{\phi}}{\partial \mathbf{n}} = \mathbf{0}$. Note that only the derivative of the extra entropy flux in relation to mass density is different of zero and, consequently, $\boldsymbol{\phi}$ should depend on ρ . Nevertheless, as $\boldsymbol{\phi}$ is an isotropic vector function of its arguments, from the theorem of representation of transversely isotropic functions [34] one has $\boldsymbol{\phi} = \mathbf{0}$ and the entropy flux can be rewritten as $\boldsymbol{\Phi} = \Lambda^\varepsilon \mathbf{h} + \sum_{a=1}^{n-1} \Lambda^{\xi_a} \mathbf{j}_a$ or $\boldsymbol{\Phi} = \Lambda^\varepsilon \mathbf{h} - \Lambda^\varepsilon \sum_{a=1}^{n-1} \mu_a \mathbf{j}_a$. Here, it is worth remembering that, unlike the total current in the bulk region, the total current \mathbf{i} is not exclusively given by partial faradaic currents. In fact, the total current in double layer is due to non-faradaic currents associated with the charging of the electrical double layer at an electrode-solution interface, as well as the faradaic currents corresponding to the reduction or oxidation of some chemical substance. Consequently, the expression $\mathbf{i} = \sum_{a=1}^{n-1} \mathbf{i}_a$ is not valid in the double layer region.

In view of the restrictions above, and by recalling that $\nabla \rho$ is not an independent constitutive variable, one uses $\nabla \mu_a = \sum_{b=1}^{n-1} \frac{\partial \mu_a}{\partial \xi_b} \Big|_{a \neq b} \nabla \xi_b + \frac{\partial \mu_a}{\partial \theta} \nabla \theta + \frac{\partial \mu_a}{\partial \varphi} \nabla \varphi$ and $\sum_{a=1}^{n-1} c_a \mu_a = \sum_{r=1}^R \bar{U}_r \gamma_r$, where γ_r and \bar{U}_r respectively are the reaction extent and the chemical affinity of a chemical reaction r , to write down Eq. (4.30) as

$$\begin{aligned}
 \Pi &= - \sum_{a=1}^{n-1} \mathbf{j}_a \cdot \nabla \mu_a + \left(\sum_{a=1}^{n-1} \mathbf{j}_a \mu_a - \mathbf{h} \right) \cdot \frac{\nabla \theta}{\theta} + \mathbf{T} \cdot \mathbf{D} \\
 &+ p \mathbf{1} \cdot \mathbf{D} - \sum_{r=1}^R \bar{U}_r \gamma_r - \mathbf{i} \cdot \nabla \varphi \geq 0.
 \end{aligned}
 \tag{4.34}$$

Eq. (4.34) evidences that some dissipative mechanisms in an electrochemical system, e.g. thermal diffusion, electrodic reactions and Joule’s effect, take place only in the double layer. Moreover, observe that the gradient of electrochemical potential is given in terms of $\nabla \xi_a$, $\nabla \varphi$ and $\nabla \theta$, unlike the bulk. Therefore, one expects that the mass transport in the double layer region is associated with the gradient of species concentration (diffusive flux) and the gradient of electric potential (migration flux). As consequence, the thermodynamic equilibrium state at point (\mathbf{x}, t) in the double layer requires a more complex set of conditions than in the bulk.

In fact, one has the same necessary conditions to ensure $\Pi = 0$ at any (\mathbf{x}, t) in the double layer,

$$\left(\frac{\partial \Pi}{\partial w_{DB}} \right) \Big|_E = 0, \quad \left(\frac{\partial^2 \Pi}{\partial w_{DB} \partial w_{DB}} \right) \Big|_E > 0,$$

but w_{DB} is given by $w_{DB} \in \{\nabla \mu_a, \nabla \theta, \nabla \varphi, \Upsilon_r, \mathbf{D}\}$. Performing the first-order derivative in relation to w_{DB} , one obtains

$$\left(\frac{\partial \Pi}{\partial \nabla \mu_a} \right) \Big|_E = -\mathbf{j}_a = \mathbf{0}, \quad (4.35)$$

$$\left(\frac{\partial \Pi}{\partial \nabla \theta} \right) \Big|_E = \frac{1}{\theta} \left(\sum_{a=1}^{n-1} \mathbf{j}_a \mu_a - \mathbf{h} \right) = \mathbf{0},$$

$$\mathbf{h} = \mathbf{0}, \quad (4.36)$$

$$\left(\frac{\partial \Pi}{\partial \nabla \varphi} \right) \Big|_E = -\mathbf{i} = \mathbf{0}, \quad (4.37)$$

$$\left(\frac{\partial \Pi}{\partial \Upsilon_r} \right) \Big|_E = -\mathcal{U}_r = 0, \quad (4.38)$$

$$\left(\frac{\partial \Pi}{\partial \mathbf{D}} \right) \Big|_E = \mathbf{T} + p\mathbf{1} = \mathbf{0},$$

$$\mathbf{T} = -p\mathbf{1}. \quad (4.39)$$

whence it concludes that, at the thermodynamic equilibrium state, the mass flux, the heat flux and the electric current flux vanish as well as the chemical reactions, and the stress tensor is given by the hydrostatic pressure.

In order to evaluate the constraints on the dynamic part of constitutive quantities listed in (4.24), one restricts to the simplest linear forms for the constitutive relations. If the gradients of temperature, chemical potential and electric field and the strains are not very large, linear constitutive equations are adequate for the treatment of constitutive answers of the double layer. Although, as it has been pointed out in the literature [14], linear constitutive functions for chemical affinity are only suitable close to chemical equilibrium, otherwise \mathcal{U}_r presents a highly non-linear relation with the reaction extent. In view of these arguments, the constitutive relation for the chemical affinity of a reaction r is not discussed in this work.

Under these conditions, one considers the symmetry group \mathcal{G}_2 , which characterizes transversely isotropic material bodies,

$$\mathcal{G}_2 = \{Q \in \mathcal{O}(\mathcal{E}), Q\mathbf{n} = \mathbf{n}\},$$

where Q is an orthogonal transformation in a 3D-Euclidean space and \mathcal{O} is the orthogonal group of \mathcal{E} , and next uses the theorem of representation of constitutive functions to set

$$T_{ij} = -p\delta_{ij} + \left(\lambda + \frac{2}{3}\tau \right) D_{mm}\delta_{ij} + 2\tau \bar{D}_{ij} + O(2),$$

$$h_i = \kappa_1 \theta_{,i} + \kappa_2 \varphi_{,i} + \kappa_3 \mu_{,i}^a + \kappa_4 n_i + O(2),$$

$$\begin{aligned}
 i_i &= \iota_1 \theta_{,i} + \iota_2 \varphi_{,i} + \iota_3 \mu_{,i}^a + \iota_4 n_i + O(2), \\
 j_i^a &= C_1^a \theta_{,i} + C_2^a \varphi_{,i} + C_3^a \mu_{,i}^a + C_4^a n_i + O(2),
 \end{aligned}
 \tag{4.40}$$

where \bar{D}_{ij} is the deviatoric part of \mathbf{D} and all phenomenological coefficients are functions of

$$\mathcal{P}_{DB} = \hat{\mathcal{P}}_{DB}(\rho, \theta, \varphi, \xi_a, \nabla\theta \cdot \nabla\theta, \nabla\xi_a \cdot \nabla\xi_a, \nabla\varphi \cdot \nabla\varphi, \text{tr}\mathbf{D}), \tag{4.41}$$

such that the scalar product $\mathbf{n} \cdot \mathbf{n}$ has been eliminated because is equal to a unit constant. Here, the influence of unit vectors on the stress tensor is omitted since it was considered that only transport phenomena has a preferred direction. Moreover, observe that the same phenomenological coefficients may be numerically different in bulk and double layer (compare Eqs. 4.20 and 4.41). Furthermore, all phenomenological coefficients are not constants that depend only on the chemical species or medium under question, but constitutive functions that suffer the influence of temperature, electric potential, viscosity among others.

Inserting Eq. (4.40) into Eq. (4.34), one obtains

$$\begin{aligned}
 \Pi &= - \sum_{a=1}^{n-1} (C_1^a \theta_{,i} + C_2^a \varphi_{,i} + C_3^a \mu_{,i}^a + C_4^a n_i) \mu_{,i}^a \\
 &\quad + \sum_{a=1}^{n-1} (C_1^a \theta_{,i} + C_2^a \varphi_{,i} + C_3^a \mu_{,i}^a + C_4^a n_i) \mu^a \frac{\theta_{,i}}{\theta} \\
 &\quad - (\kappa_1 \theta_{,i} + \kappa_2 \varphi_{,i} + \kappa_3 \mu_{,i}^a + \kappa_4 n_i) \frac{\theta_{,i}}{\theta} + \left(\lambda + \frac{2}{3} \tau \right) D_{mm}^2 \\
 &\quad + 2\tau \bar{D}_{ik} \bar{D}_{ik} - \sum_{r=1}^R \psi_r \gamma_r \\
 &\quad - (\iota_1 \theta_{,i} + \iota_2 \varphi_{,i} + \iota_3 \mu_{,i}^a + \iota_4 n_i) \varphi_{,i} \geq 0,
 \end{aligned}
 \tag{4.42}$$

and by carrying out the second-order derivatives of Π in relation to w_{DB} it results in

$$\begin{aligned}
 \sum_{a=1}^{n-1} C_3^a &\leq 0, & \sum_{a=1}^{n-1} C_1^a \frac{\mu^a}{\theta} - \frac{\kappa_1}{\theta} &\geq 0, & \iota_2 &\leq 0, \\
 \lambda + \frac{2}{3} \tau &\geq 0, & \tau &\geq 0, & \sum_{a=1}^{n-1} C_4^a &\leq 0, \\
 \sum_{a=1}^{n-1} C_4^a \frac{\mu^a}{\theta} - \frac{\kappa_4}{\theta} &\geq 0, & \iota_4 &\leq 0, & \sum_{a=1}^{n-1} C_2^a + \iota_3 &\leq 0, \\
 \sum_{a=1}^{n-1} C_2^a \frac{\mu^a}{\theta} - \frac{\kappa_2}{\theta} - \iota_1 &\geq 0, & \sum_{a=1}^{n-1} C_1^a + \sum_{a=1}^{n-1} C_3^a \frac{\mu^a}{\theta} + \frac{\kappa_3}{\theta} &\leq 0.
 \end{aligned}
 \tag{4.43}$$

The proposed phenomenological equations in Eq. (4.40) incorporate many cross phenomena that are impossible to happen in the bulk region, such as thermoelectric and electrophoretic effects, and thermal diffusion. These effects are due to the coupling of fields, which interfere in a reciprocal way in the heat, mass and electric current flows. For example, $C_2^a \neq 0$ and $t_3 \neq 0$, both constrained by the condition (4.43)₉, evidence that the gradient of electric potential opposes the electrochemical potential gradients of all ions. This thermodynamic condition recalls an important non-equilibrium phenomenon observed in electrolyte solutions: the development of a diffusion potential. Whenever an electrolyte is brought into contact with water, a gradient of electrochemical potential arises both for the positive and negative ions and, therefore, they started flowing away. Then, because of the difference of ionic mobility, there appears a tendency for segregation of cations and anions, so that a gradient of electric potential develops across the inter-phase that marks the local separation of ions. It is precisely this gradient of electric potential that inhibits the charge segregation as the accelerated cations face resistance to their motion whereas the slower anions are pushed up by the gradient of electric field. Similar conclusions can be obtained for the remaining phenomenological coefficients, where $C_1^a \neq 0$ and $\kappa_1 \neq 0$ are related to the thermal diffusion, $C_2^a \neq 0$ and $\kappa_2 \neq 0$ to thermoelectric phenomena and $C_3^a \neq 0$ and $\kappa_3 \neq 0$ to electrophoretic effects.

5 Concluding remarks

A continuum thermodynamical description for the regions of bulk and double layer of an electrochemical system is presented. Comparing the residual entropy inequalities obtained for each region, it was shown that some dissipative mechanisms develop only in the double layer, such as thermal diffusion, and thermoelectric and electrophoretic phenomena. Then, the thermodynamic equilibrium state in the double layer requires stricter conditions than in the bulk.

Even though the constitutive equations are the simplest possible, the constitutive models proposed to the double layer and bulk regions are physically consistent, and more comprehensive than the usual models since the emerging results do not constrain themselves to equilibrium or close-equilibrium conditions, neither to limiting conditions. Furthermore, the approach used has the advantages of clearness and generality over the traditional non-equilibrium theory because the set of fundamental postulates adopted are physically motivated and less restrictive. Hence, the thermodynamic description provided in this work may stimulate chemists and chemical engineers to take advantage of it to describe other non-equilibrium phenomena in more complex chemical systems.

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