Rational modeling of electrochemical double-layers and derivation of Butler-Volmer equations

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Abstract

We derive the boundary conditions for the contact between an electrolyte and a solid electrode. At first we revisit the thermodynamic consistent complete model that resolves the actual electrode–electrolyte interface and its adjacent boundary layers. The width of these layers is controlled by the Debye length that is typically very small, leading to strongly different length scales in the system. We apply the method of asymptotic analysis to derive a simpler reduced model that does not resolve the boundary layers but instead incorporates the electrochemical properties of the layers into a set of new boundary conditions. This approach fully determines the relation of bulk quantities to the boundary conditions of the reduced model. In particular, the Butler-Volmer equations for electrochemical reactions, which are still under discussion in the literature, are rational consequences of our approach. For illustration and to compare with the literature, we consider a simple generic reaction.

1   Introduction

In this paper we derive a thermodynamically consistent model that is capable to give a detailed description of the contact between two different electrochemical systems. Here we consider an electrolyte and a solid electrode. Figure 1 serves to exhibit both the subtleties of the problem and our solution strategies.

The domains of the electrode, the electrolyte and their (actual) interface are indicated by Ω^+, Ω^- and S, respectively. Figure 1_{left} shows the three domains. From left to right we have the electrode (yellow), the interface (black solid line) and the electrolyte (gray). Electrode and electrolyte are described as mixtures consisting of various constituents. The interface S itself also may be a carrier of constituents and is thus considered as a substance. Each of the three substances are described by a mixture model relying on equations of balance for the two bulk domains while on the interface we have jump conditions that are derived from surface balance equations.

Figure 1_{left} shows the possible behavior of a generic field u from our list of state variables. In the bulk domains on the left and right sides of the interface we observe the indicated variation. Across the interface S the field u has a discontinuity described by the double bracket $[\![u]\!]$. Its determination relies mainly on the jump conditions.

The field equations for the variables contain a parameter λ with $0 < \lambda \ll 1$ implying that the variation of u is restricted to a small neighborhood of the interface S. In other words, the parameter λ induces boundary layers on the left and right sides of S. Let L_0 be a typical length scale of the system, then λL_0 characterizes the width of the layers and is known as the Debye length. This fact is indicated in Figure 1_{middle}. Two different expansions of the variable u are introduced: for the approximation inside the boundary layers one defines an expansion $\widetilde{u}$ in terms of rescaled variables. In the bulk part a different approximation is used that by abuse of notation is again denoted by u.

One of the main objectives of this study is the description of the boundary layers in the limit $\lambda \to 0$. The limit procedure will lead to a new interface I with a new jump that we denote by the
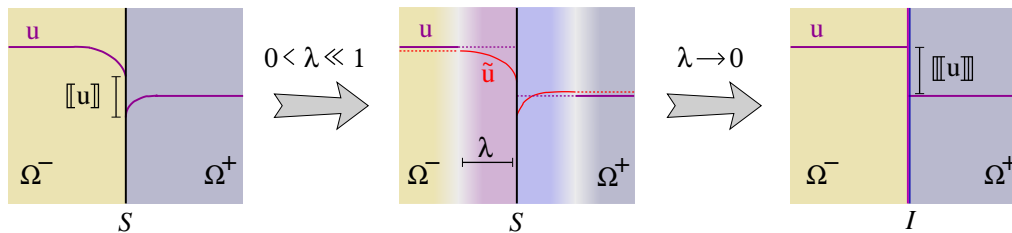
Figure 1: Generic field variable u for an electrochemical system of two substances in contact with the interface S (left). Boundary layers due to a small parameter λ in the model equations (middle). In a simplified model for $\lambda \to 0$, modified jump conditions contain the relevant information of the double layer that is not resolved any more.

triple bracket $[\![u]\!]$. On the scale of the limiting case the original interface S with its discontinuity $[\![u]\!]$ is not resolved anymore, as indicated in Figure 1$_{\text{right}}$.

Among the results of the mathematical limit $\lambda \to 0$ we have in the bulk regions $\Omega^{\pm}$ (i) local charge neutrality in $\Omega^{\pm}$, (ii) a simple relation between the electric current and the electric field (Ohm's law), and (iii) quasi-static mechanical equilibrium. Obviously, this is expected in advance. Moreover the limit $\lambda \to 0$ uniquely determines new jump conditions at the interface I, c.f. Fig. 1$_{\text{right}}$, from the original jump conditions at the interface S, see Fig. 1$_{\text{left}}$. This result is the essential contribution of our approach. In particular, the new jump conditions represent the basis for a rational derivation of the so called Butler-Volmer equations describing interfacial electrochemical reactions.

Outline. In the following section, we introduce thermodynamically consistent models for electrochemical systems in contact with interfaces. The derivation of these models is postponed to the Sections 4 and 5. On the basis of the reduced model, we derive in Section 3 Butler-Volmer equations and discuss differences to the equations found in the literature. The derivation is motivated by a simple prototype of a generic redox reaction and illustrated with different examples. Section 4 contains the derivation of the complete thermodynamically consistent model. Finally, in Section 5 we introduce a scaling in terms of the small parameter λ and carry out the formal asymptotic analysis that leads to the reduced model.

2   Mixture models for an electrochemical interface

This section contains an introduction and a brief summary of two models: on the one hand the *complete model* that is a thermodynamically consistent model for two electrochemical systems that are separated by an interface. On the other hand the *reduced model* that is derived from the complete model by the method of formal asymptotic analysis. Both models are put side by side for comparison and discussion.

In this section we do not give any derivation of the models; this will be the subject of later sections. Herein we assume some preliminary knowledge of the reader. In order to avoid the geometric subtleties of curved interfaces, we restrict ourselves to a plane interface and derive the

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jump conditions under the simplifying assumptions that there is no mass, momentum or energy transport tangential to the interface. We only consider the isothermal case, thus the temperature T features only as a constant in the formulas.

2.1 Description of the mixtures and of the electrochemical interface

First we have to introduce the essential quantities describing electrochemical systems in interaction with interfaces. According to Figure 1 we consider two regions $\Omega^{\pm} \subseteq \mathbb{R}^3$ which are separated by an interface $\partial\Omega^+ \cap \partial\Omega^-$. To emphasize the differences between the models, we denote the interface either by S in the case of the complete model or by I in the reduced model.

Assumptions on the interfaces. For the applications at hand we will consider the one-dimensional case only. For this reason we simplify the geometric properties of S and I by assuming:

   (i) The interfaces S and I are plane and lie parallel to the coordinate plane (x_2, x_3) whose normal vector $\boldsymbol{\nu}$ is oriented in x_1 direction.

   (ii) The interface velocity $\boldsymbol{w}$ lies in normal direction $\boldsymbol{w} = w_\nu \, \boldsymbol{\nu}$.

   (iii) There are no tangential fluxes of mass, momentum, energy or charge.

Given a parametrization $(t, x_2, x_3) \to (x_S(t), x_2, x_3)$ of the interfaces S or I respectively, we have
$$\boldsymbol{w} = w_\nu \, \boldsymbol{\nu} = \frac{dx_S}{dt} \, \boldsymbol{\nu} \; . \tag{1}$$

Jumps at interfaces. Next we introduce the boundary values and the jump of a generic function $u(t, x)$ in $\Omega^{\pm}$ across the interfaces. The Figure 1 suggests that the jumps of $u(t, x)$ are different for the actual interface S and the interface I of the reduced model. In fact, it would be more correct to refer to the function as u^λ in the complete model and as u^0 in the reduced model. For notational convenience we omit the superscript indices and instead highlight the difference between the models by introducing different notations of jump brackets. For S, i.e. in the complete model, we define
$$u|_S^{\pm} = \lim_{\boldsymbol{x} \in \Omega^{\pm} \to S} u \qquad \text{and} \qquad [\![u]\!] = u|_S^+ - u|_S^-, \tag{2}$$

while at the interface I of the reduced model we write
$$u|_I^{\pm} = \lim_{\boldsymbol{x} \in \Omega^{\pm} \to I} u \qquad \text{and} \qquad [\![u]\!] = u|_I^+ - u|_I^-. \tag{3}$$

In case the function u is not defined in either Ω^+ or in Ω^-, we set the corresponding value in (2) and in (3) to zero.

Constituents and chemical reactions. In each of the two domains Ω^+ and Ω^- and –depending on the model– on the interface S or I, we consider a mixture of several constituents. The total number of constituents in the system is denoted by N and the set of constituents is $\mathcal{M} = \{A_1, A_2, \cdots, A_N\}$, usually indexed by $\alpha \in \{1, 2, \cdots, N\}$. In general we have different constituents in Ω^+, Ω^- and on S or I, but for the simplicity of notation this fact will only be indicated if necessary. Then, we use subsets $\mathcal{M}_+, \mathcal{M}_- \subset \mathcal{M}$ for the constituents in Ω^+ and Ω^-, respectively. We assume that each constituent on S or I is also constituent of Ω^+ or Ω^-, for the constituents that are exclusively on the interface we introduce $\mathcal{M}_S = \mathcal{M} \setminus (\mathcal{M}_+ \cup \mathcal{M}_-)$.

For quantities defined in the bulk domains there will often be corresponding quantities on the interfaces S or I, indicated by a subscript s.

Among constituents we may have chemical reactions. There are M (bulk) reactions and in addition there may be M_S surface reactions of the general form

$$a_1^i A_1 + \cdots + a_N^i A_N \underset{R_b^i}{\overset{R_f^i}{\rightleftharpoons}} b_1^i A_1 + \cdots + b_N^i A_N \qquad \text{for } i \in \{1, \cdots, M\}, \qquad (4a)$$

$$\underset{s}{a}_1^i A_1 + \cdots + \underset{s}{a}_N^i \underset{s}{A}_N \underset{\underset{s}{R_b^i}}{\overset{\underset{s}{R_f^i}}{\rightleftharpoons}} \underset{s}{b}_1^i \underset{s}{A}_1 + \cdots + \underset{s}{b}_N^i \underset{s}{A}_N \qquad \text{for } i \in \{1, \cdots, M_S\}. \qquad (4b)$$
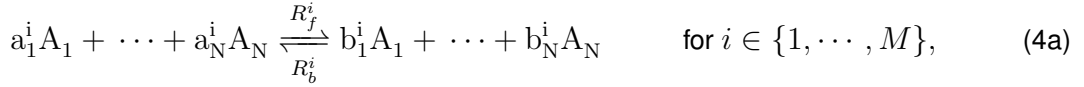
The constants $(a_\alpha^i)_{\alpha=1,2,\cdots,N}$, $(b_\alpha^i)_{\alpha=1,2,\cdots,N}$ are positive integers and $\gamma_\alpha^i = b_\alpha^i - a_\alpha^i$ denote the stoichiometric coefficients of the reactions. The reaction from left to right is called forward reaction with reaction rate $R_f^i > 0$. The reaction in the reverse direction with rate $R_b^i > 0$ is the backward reaction.

The constituents have (atomic) masses $(m_\alpha)_{\alpha=1,2,\cdots,N}$ and may be carrier of charges $(z_\alpha e_0)_{\alpha=1,2,\cdots,N}$. The positive constant e_0 is the elementary charge and z_α are positive or negative integers including the value zero. All constituents may consist of polarizable matter, but magnetization is not considered here.

Basic quantities. At any time $t \geq 0$, the thermodynamic state of $\Omega^\pm$ is described by the number densities $(n_\alpha)_{\alpha=1,2,\cdots,N}$, the velocities $(\boldsymbol{v}_\alpha)_{\alpha=1,2,\cdots,N}$ of the constituents, the electric field $\boldsymbol{E}$ and the temperature T of the mixture. The electric field is often represented by its potential φ. At the same time, the thermodynamic state of the interface S or I is characterized by the number densities of the interfacial constituents, $(\underset{s}{n}_\alpha)_{\alpha \in \{1,2,\cdots,N\}}$, the interface speed $\boldsymbol{w} = (w_\nu, 0, 0)$ and the electric field $\boldsymbol{E}$. Recall that we only consider isothermal processes, so T appears only as a constant parameter in the following equations. Furthermore, the interfacial temperature $\underset{s}{T}$ is also just a constant parameter. Obviously we have $\underset{s}{T} = T$.

In general, the introduced quantities may be functions of time $t \geq 0$ and space $x \in \mathbb{R}^3$. On S and I, the basic variables are functions of time only, due to the assumptions above. Multiplication of the number densities n_α and partial velocities $\boldsymbol{v}_\alpha$ by m_α gives the partial mass densities and

mass fluxes:

$$\rho_\alpha = m_\alpha n_\alpha \qquad \text{and} \qquad \boldsymbol{j}_\alpha = \rho_\alpha \boldsymbol{v}_\alpha \,, \tag{5a}$$

$$\rho_{\alpha \atop s} = m_\alpha n_{\alpha \atop s} \,. \tag{5b}$$

The mass density of the mixture and the barycentric velocity are defined by

$$\rho = \sum_{\alpha=1}^{N} \rho_\alpha \qquad \text{and} \qquad \boldsymbol{v} = \frac{1}{\rho} \sum_{\alpha=1}^{N} \rho_\alpha \boldsymbol{v}_\alpha \,, \tag{6a}$$

$$\rho_{s} = \sum_{\alpha=1}^{N} \rho_{\alpha \atop s} \,. \tag{6b}$$

Total free charge density and total free current are calculated by

$$n^{\mathrm{F}} = \sum_{\alpha=1}^{N} z_\alpha e_0 n_\alpha \qquad \text{and} \qquad \boldsymbol{j}^{\mathrm{F}} = \sum_{\alpha=1}^{N} \frac{e_0 z_\alpha}{m_\alpha} \boldsymbol{j}_\alpha \,, \tag{7a}$$

$$n_{s}^{\mathrm{F}} = \sum_{\alpha=1}^{N} z_\alpha e_0 n_{\alpha \atop s} \,. \tag{7b}$$

The application of Maxwell's theory to continuous matter shows that the total electric charge density n^{e} and the total electric current $\boldsymbol{j}^{\mathrm{e}}$ consist of two additive contributions. We write

$$n^{\mathrm{e}} = n^{\mathrm{F}} + n^{\mathrm{P}} \qquad \text{and} \qquad \boldsymbol{j}^{\mathrm{e}} = \boldsymbol{j}^{\mathrm{F}} + \boldsymbol{j}^{\mathrm{P}} \,, \tag{8a}$$

$$n_{s}^{\mathrm{e}} = n_{s}^{\mathrm{F}} + n_{s}^{\mathrm{P}} \,. \tag{8b}$$

Besides free charge densities and free currents, there are charge densities and currents due to polarization and magnetization but herein we do not consider magnetization. Then the representation of charge and current due to polarization read, c.f. [Mül85],

$$n^{\mathrm{P}} = -\mathrm{div}(\boldsymbol{P}) \qquad \text{and} \qquad \boldsymbol{j}^{\mathrm{P}} = \frac{\partial \boldsymbol{P}}{\partial t} + \mathrm{curl}(\boldsymbol{P} \times \boldsymbol{v}) \,, \tag{9a}$$

$$n_{s}^{\mathrm{P}} = -[\![\boldsymbol{P} \cdot \boldsymbol{\nu}]\!]. \tag{9b}$$

where $\boldsymbol{P}$ denotes the vector of polarization. Polarization embodies phenomena caused by microscopic charges, for example, atomic dipoles within atoms and molecules. Recall that on the interfaces we ignore tangential currents. There are only normal currents across the interface, which leads to the simple law (9b) for the polarization charge.

In the bulk, we define diffusion fluxes $\boldsymbol{J}_\alpha$ of constituent A_α as

$$\boldsymbol{J}_\alpha = \rho_\alpha(\boldsymbol{v}_\alpha - \boldsymbol{v}) \quad \text{implying} \quad \sum_{\alpha=1}^{N} \boldsymbol{J}_\alpha = 0 \,. \tag{10}$$

Free energy and chemical potentials. Remarkably, the constitutive behavior is fully determined by the free energy density $\rho\psi$ of the bulk and the free energy density $\underset{s}{\psi}$ of the interface. In order to embody a wide class of different materials we use free energy functions of the general forms

$$\rho\psi = \rho\hat{\psi}(T, \rho_1, \ldots, \rho_N) - \tfrac{1}{2}\varepsilon_0\chi|\boldsymbol{E}|^2 \,, \tag{11a}$$

$$\underset{s}{\psi} = \underset{s}{\hat{\psi}}(\underset{s}{T}, \underset{s}{\rho_1}, \ldots, \underset{s}{\rho_N}) \,. \tag{11b}$$

In isothermal processes, the temperatures T and $\underset{s}{T}$ are identical. The contribution of the electric field to the bulk free energy is made explicit and represents the simplest polarizable matter. The constant parameter χ denotes the electric susceptibility of the material. The chemical potentials of the bulk and surface materials and the polarization vector in the bulk are defined by means of the free energies, i.e.

$$\mu_\alpha = \frac{\partial\rho\psi}{\partial\rho_\alpha} \qquad \text{and} \qquad \boldsymbol{P} = -\frac{\partial\rho\psi}{\partial\boldsymbol{E}} = \varepsilon_0\chi\boldsymbol{E} \,, \tag{12a}$$

$$\underset{s}{\mu_\alpha} = \frac{\partial\underset{s}{\rho}\underset{s}{\psi}}{\partial\underset{s}{\rho_\alpha}} \,. \tag{12b}$$

Note that the assumption of a constant susceptibility χ implies that the chemical potentials in the bulk do not depend on the electric field. Moreover, we ignore tangential dipoles on the interface, therefore there is no electric contribution to $\underset{s}{\psi}$.

2.2 Summary of the mixture models

The models introduced in this section are thermodynamically consistent mixture models for an electrochemical interface between two arbitrary mixtures. The complete model describes bulk materials that exhibit boundary layers at the physical interface. These layers are due to a small dimensionless parameter λ in the model equations that defines a characteristic length scale

$$\lambda L_0 = \sqrt{\frac{kT\varepsilon_0}{e_0^2 n_0}} \tag{13}$$

of the interface. Here k is the Boltzmann constant and L_0 and n_0 denote characteristic values for the number density and a length of the system. For example, L_0 can be the distance between two electrodes and n_0 can be related to the anion and cation density in an electrolyte. Then, the length λL_0 represents the well known Debye length that controls the width of the boundary layers as it is indicated by Figure 1. For solution of $0.1\mathrm{mol}$ per liter $\lambda L_0 \approx 1.5 \cdot 10^{-10}\mathrm{m}$.

In the following the notations $\lambda > 0$ and $\lambda \to 0$ indicate the complete model and the reduced model, respectively. The detailed derivation of the complete model equations is found in Chapter 4 and the limit procedure $\lambda \to 0$ for the reduced model is carried out in Chapter 5.

The objective is the determination of the densities $(n_\alpha)_{\alpha=1,2,\cdots,N}$, the velocity $\boldsymbol{v}$ and the electric potential φ in the bulk and of the densities $(\underset{s}{n_\alpha})_{\alpha=1,2,\cdots,N}$, the speed w and the electric potential

φ on the interface S and I, respectively. Their isothermal evolution in time and space relies on the balance equations for mass and momentum and on the Poisson equation. In addition to the assumptions on the interface we restrict ourselves in the following on the one-dimensional case only.

Poisson equation. The determination of the electric potential φ relies on the Poisson equation which is considerably reduced by the limit $\lambda \to 0$. We have

$$\boxed{\lambda > 0} \qquad\qquad\qquad\qquad\qquad \boxed{\lambda \to 0}$$

$$-\partial_x\big((1+\chi)\varepsilon_0 \partial_x \varphi\big) = n^{\mathrm{F}} \qquad\qquad\qquad 0 = n^{\mathrm{F}} \tag{14}$$

$$[\![(1+\chi)\varepsilon_0 \partial_x \varphi]\!] = \underset{s}{n^{\mathrm{F}}} \qquad\qquad\qquad 0 = \underset{s}{n^{\mathrm{F}}} \tag{15}$$

$$[\![\varphi]\!] = 0, \quad \text{i.e. } \underset{s}{\varphi} = \varphi|_S^{\pm} \tag{16}$$

Observe that the reduced model $\lambda \to 0$ implies local electro-neutrality in the bulk regions and on the interface I. The continuity of φ across S is postulated. In the reduced model, φ will in general be discontinuous.

Mass balances. There are N partial mass balance equations in the bulk regions $\Omega^{\pm}$ that are of the same structure in both the complete and the reduced model. In $\Omega^{\pm}$ we have

$$\partial_t(m_\alpha n_\alpha) + \partial_x(m_\alpha n_\alpha v + J_\alpha) = \sum_{i=1}^{M} \gamma_\alpha^i m_\alpha R^i \quad \text{for } \alpha = 1, \ldots, N , \tag{17}$$

where $R^i = (R_f^i - R_b^i)$ denotes the chemical reaction rates. Also the interfacial mass balances seem to be identical at first glance. Using an analogue definition of the reaction rates on the surfaces, we have for $\alpha = 1, \ldots, N$

$$\boxed{\lambda > 0} \qquad \partial_t(\underset{s}{m_\alpha n_\alpha}) + [\![m_\alpha n_\alpha(v-w)]\!] + [\![J_\alpha]\!] = \sum_{i=1}^{M_S} \underset{s}{\gamma_\alpha} m_\alpha \underset{s}{R^i} , \tag{18a}$$

$$\boxed{\lambda \to 0} \qquad \partial_t(\underset{s}{m_\alpha n_\alpha}) + [\![m_\alpha n_\alpha(v-w)]\!] + [\![J_\alpha]\!] = \sum_{i=1}^{M_S} \underset{s}{\gamma_\alpha} m_\alpha \underset{s}{R^i} . \tag{18b}$$

The essential difference between (18a) and (18b) is indicated by the different notation of the jump brackets $[\![.]\!]$ and $[\![.]\!]$. Recall that taking a generic function u in the complete model and denoting the corresponding function in the reduced model by the same symbol u, we have in general $[\![u]\!] \neq [\![u]\!]$. This fact is visualized in the sequence of picture 1. In many cases (18a) and (18b) are used in a simplified version. If the surface densities $\underset{s}{n_\alpha}$ are constant in time, only the jumps of bulk quantities will remain in (18a) and (18b). Then these equations are often called jump conditions because they determine the discontinuities of bulk quantities.

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Like the mass balances, also the constitutive laws for the diffusion fluxes J^α remain formally unchanged in the limit $\lambda \to 0$. For both models there holds

$$J_\alpha = -\sum_{\beta=1}^{N-1} M_{\alpha\beta} \left(\frac{\partial}{\partial x}\left(\frac{\mu_\beta - \mu_N}{T} \right) + \frac{1}{T}\left(\frac{z_\beta e_0}{m_\beta} - \frac{z_N e_0}{m_N} \right)\frac{\partial\varphi}{\partial x} \right) , \quad \alpha \in \{1, \cdots, N-1\} . \tag{19}$$

Here, $M_{\alpha\beta}$ are the components of the positive definite mobility matrix that might depend on arbitrary combinations of the other variables. Note that there are only $N-1$ diffusion fluxes given by (19) and the Nth diffusion flux is determined by the side condition $\sum_{\alpha=1}^{N} J_\alpha = 0$. Moreover, together with the mass conservation of the chemical reactions, one of the partial mass balances can be replaced by the sum of all mass balances. We obtain the total mass balance of the mixture

$$\partial_t \rho + \partial_x(\rho v) = 0 . \tag{20}$$

In the bulk domains, the constitutive laws for the chemical reaction rates R^i are of the same structure. For both models we get

$$\frac{R_b^i}{R_f^i} = \exp\left(\frac{A^i}{kT} \sum_{\alpha=1}^{N} \gamma_\alpha^i m_\alpha \mu_\alpha \right) , \tag{21}$$

where A^i denote positive kinetic coefficients. Whereas in general it is possible to write the corresponding constitutive relations on the interfaces in the same structure for both models, we introduce a strongly different form for the reduced model, viz.

$$\boxed{\lambda > 0} \quad \frac{\underset{s}{R_f^i}}{\underset{s}{R_b^i}} = \exp\left(-\frac{\underset{s}{A^i}}{kT} \sum_{\alpha \in \mathcal{M}} \underset{s}{\gamma_\alpha^i} m_\alpha \underset{s}{\mu_\alpha} \right) , \tag{22a}$$

$$\boxed{\lambda \to 0} \quad \frac{\underset{s}{R_f^i}}{\underset{s}{R_b^i}} = \exp\left(-\frac{\underset{s}{A^i}}{kT} \sum_{\alpha \in \mathcal{M}_S} \underset{s}{\gamma_\alpha^i} m_\alpha \left(\underset{s}{\mu_\alpha} + \frac{z_\alpha e_0}{m_\alpha}\underset{s}{\varphi} \right) \right.$$
$$\left. -\frac{\underset{s}{A^i}}{kT} \sum_{\alpha \in \mathcal{M}_+ \cup \mathcal{M}_-} \underset{s}{\gamma_\alpha^i} m_\alpha \left(\mu_\alpha|_I^\pm + \frac{z_\alpha e_0}{m_\alpha}\varphi|_I^\pm \right) \right) . \tag{22b}$$

The limit equation (22b) forms the basis of Butler-Volmer equations. The reaction rates (22a) of the complete model $\lambda > 0$ are exclusively dependent on the chemical potentials $\underset{s}{\mu_\alpha}$ defined on the interface S. Thus the reaction rates depend on the particle densities $\underset{s}{n_\alpha}$ but not on the potential $\underset{s}{\varphi}$ of S. The properties of the reaction rates (22b) of the reduced model are quite different. Particularly the second sum in (22b) over the constituents of the bulk regions brings an additional dependence of the reaction rates on the electric potentials $\varphi|_I^+$ and $\varphi|_I^-$ which are unequal in general. This fact gains in importance if there are no constituents exclusively on S. Then, the first sum disappears and reaction rates are fully determined by bulk quantities.

The equations (21)–(22b) alone cannot uniquely determine the evolution of chemical reactions. They are merely sufficient conditions which guarantee thermodynamic consistency of the reaction model. In order to close the system, we need a constitutive law either for the forward or for the backward reaction rate. Then the other reaction rate is already determined by the ratio. In Section 3 we will describe a corresponding ansatz that yields a generalization of the well-known Butler-Volmer equations.

Momentum balance. In the momentum balance we use Σ for a rather general description of all kind of stresses, including Maxwell stresses. We observe that the reduced model $\lambda \to 0$ contains only the quasi-static momentum balance in the bulk and on the surfaces

$$\boxed{\lambda > 0}$$

$$0 = \partial_t(\rho v) + \partial_x(\rho v^2 - \Sigma)$$

$$\boxed{\lambda \to 0}$$

$$0 = \partial_x \Sigma \tag{23}$$

$$0 = \underset{s}{\partial_t}(\rho w) + [\![\rho v(v-w)]\!] - [\![\Sigma]\!] \qquad\qquad 0 = [\![\Sigma]\!] \tag{24}$$

$$\Sigma = \rho\hat\psi - \sum_{\alpha=1}^{N} m_\alpha n_\alpha \mu_\alpha + \tfrac{1}{2}(1+\chi)\varepsilon_0(\partial_x\varphi)^2 \qquad \Sigma = \rho\hat\psi - \sum_{\alpha=1}^{N} m_\alpha n_\alpha \mu_\alpha \tag{25}$$

The limit $\lambda \to 0$ considerably simplifies the constitutive law for the total stress tensor because the Maxwell stress due to the electric field disappears in this limit. Moreover, the quasi-static momentum balance on the surface imply that the interfacial speed w is already uniquely determined by the jump conditions (18b) for the masses.

Kinetic relations. The model is closed by so called kinetic relations which are determined in a thermodynamically consistent way. For simplicity we only consider the quasi-static variant

$$\boxed{\lambda > 0} \qquad\qquad\qquad\qquad \boxed{\lambda \to 0}$$

$$\underset{s}{\mu_\alpha} = \mu_\alpha|_S^{\pm} + \tfrac{1}{2}(v|_S^{\pm} - w)^2 \qquad\quad \underset{s}{\mu_\alpha} + \frac{z_\alpha}{m_\alpha}\underset{s}{\varphi} = \mu_\alpha|_I^{\pm} + \frac{z_\alpha}{m_\alpha}\varphi|_I^{\pm} \tag{26}$$

It will turn out in Section 5 that the reduced kinetic relations $(26)_2$ are of essential importance to derive the representation (22b) of the ratio of reaction rates. Thus they are also of essential importance to formulate the Butler-Volmer equations, which is the subject of Section 3.

2.3 Discussion and Remarks

The presented asymptotic limit $\lambda \to 0$ is intimately connected to the chosen characteristic scales of time, length, diffusion velocity, reaction rates etc. In particular, it is essential how the scales are linked to the parameter λ. Other choices are possible, but would lead to different models. The details of these remarks are found in Chapter 5.

Characterization of the scaling.

(i) The characteristic length of the system is sufficiently large so that charged boundary layers may emerge.

(ii) The characteristic time is of order of seconds.

(iii) Reactions rates and diffusion velocities are of the same order, and they are observable on the chosen time scale.

Remark concerning the electrochemical potentials.   In the derivation of the reduced model, the *electrochemical potentials* play an essential role. They are defined as a combination of chemical potentials and electric potential, i.e.

$$\mu_\alpha^{\mathrm{e}} = \mu_\alpha + \frac{z_\alpha e_0}{m_\alpha} \varphi. \tag{27}$$

The electrochemical potentials occur twice. Their gradient is the driving force of the diffusion fluxes in the bulk regions. Moreover, the electrochemical potential represents the essential quantity in the boundary layers. According to the asymptotic procedure and the chosen scaling, see Chapter 5, the electrochemical potential is a constant with respect to the normal distance to the interface S. This is the essential property leading to the kinetic relations (26)$_2$ and the representation (22b) of the reaction rates.

Remarks on the electric current.   A further crucial quantity in electrodynamics is the electric current j^{e} as defined by the equations (7a)–(9a). For the complete model and the reduced model respectively, we obtain the following representations:

$$\boxed{\boldsymbol{\lambda > 0}} \qquad\qquad\qquad \boxed{\boldsymbol{\lambda \to 0}}$$

$$j^{\mathrm{e}} = \sum_{\alpha=1}^{N} \frac{z_\alpha e_0}{m_\alpha}(m_\alpha n_\alpha v + J_\alpha) - \varepsilon_0 \chi \frac{\partial^2 \varphi}{\partial t \partial x} \qquad\Bigg\| \qquad j^{\mathrm{e}} = \sum_{\alpha=1}^{N} \frac{z_\alpha e_0}{m_\alpha} J_\alpha \ . \tag{28}$$

In the limit $\lambda \to 0$ the leading contribution to the electric current is due to the diffusion of the charged constituents. For the chosen scaling, the polarization current $\varepsilon_0 \chi \frac{\partial^2 \varphi}{\partial t \partial x}$ and the convective current $z_\alpha e_0 n_\alpha v$ do not contribute in the limiting case. This result is also a consequence of the chosen scaling, see Section 5. Particularly, the choice of the characteristic time of the system, which is in the order of seconds, is essential. If the characteristic time were given due to a high frequent alternating current, the polarization current would contribute to j^{e}.

Moreover, the representations (28)$_2$ of the electric current and the mass fluxes (19) in the reduced model imply

$$\boxed{\boldsymbol{\lambda \to 0}}$$

$$j^{\mathrm{e}} = -\sum_{\alpha,\beta=1}^{N-1} M_{\alpha\beta} \left(\frac{z_\alpha e_0}{m_\alpha} - \frac{z_N e_0}{m_N} \right) \left(\frac{\partial}{\partial x} \left(\frac{\mu_\beta - \mu_N}{T} \right) + \frac{1}{T} \left(\frac{z_\beta e_0}{m_\beta} - \frac{z_N e_0}{m_N} \right) \frac{\partial \varphi}{\partial x} \right) \ . \tag{29}$$

In a system where the gradients of the chemical potentials and of the temperature are zero, we obtain Ohm's law, $j^{\mathrm{e}} = -\kappa \partial_x \varphi$ with the conductivity κ.

Finally, we observe that due to electro-neutrality of the reduced model $(14)_2$

$$\boxed{\boldsymbol{\lambda > 0}} \qquad\qquad \boxed{\boldsymbol{\lambda \to 0}}$$

$$\partial_t n^{\mathrm{e}} + \partial_x(n^{\mathrm{e}} v + j^{\mathrm{e}}) = 0 \qquad\qquad \partial_x j^{\mathrm{e}} = 0 \tag{30}$$

Thus for $\lambda \to 0$ the electric current is spatially constant in the bulk but might be time dependent.

Remarks on the chemical equilibrium. The necessary conditions for chemical equilibrium are $R^i_{sf} = R^i_{sb}$, so from (22a) we obtain for the interface S and from (22b) for the interface I

$$\boxed{\boldsymbol{\lambda > 0}} \quad 0 = \sum_{\alpha \in \mathcal{M}} \gamma^i_{s\alpha} m_\alpha \bar{\mu}_\alpha, \tag{31a}$$

$$\boxed{\boldsymbol{\lambda \to 0}} \quad 0 = \sum_{\alpha \in \mathcal{M}_S} \gamma^i_{s\alpha} m_\alpha \left(\bar{\mu}_\alpha + \frac{z_\alpha e_0}{m_\alpha} \bar{\varphi} \right) + \sum_{\alpha \in \mathcal{M}_+ \cup \mathcal{M}_-} \gamma^i_{s\alpha} m_\alpha \left(\bar{\mu}_\alpha|^\pm_I + \frac{z_\alpha e_0}{m_\alpha} \bar{\varphi}|^\pm_I \right) . \tag{31b}$$

The algebraic equations (31a) and (31b) are the laws of mass action for the interfaces S and I, respectively.

3 Butler-Volmer equations

The above models form the basis to develop a rational derivation of general Butler-Volmer equations for interfacial electrochemical reactions. Here the notion Butler-Volmer equation refers to an equation that determines an interfacial reaction rate $\underset{s}{R}$ by the temperature, the particle densities n_α at the interface, and a potential difference η_S. We write

$$\underset{s}{R_f} - \underset{s}{R_b} = \underset{s}{R}(T, n_\alpha, \eta_S) . \tag{32}$$

Existing Butler-Volmer equations have one principle in common. The forward as well as the backward reaction rates are given by Arrhenius-type laws leading to the general structure

$$\underset{s}{R} = R^0_f \exp\left(\frac{\alpha_f e_0 \eta_S}{kT} \right) - R^0_b \exp\left(\frac{-\alpha_b e_0 \eta_S}{kT} \right) . \tag{33}$$

Herein $R^0_{f/b}$ are called exchange rates. The parameter α_f and α_b are considered as phenomenological coefficients, sometimes restricted by the condition $\alpha_f + \alpha_b = 1$. Frequently, (33) is used to establish a relation between the potential difference η_S and the electric current density j^{e} instead of $\underset{s}{R}$. Then, the coefficients $R^0_{f/b}$ are replaced by the exchange current densities $i^0_{b/f}$. The literature provides a variety of Butler-Volmer equations, a generally accepted representation is missing. Even if the Butler-Volmer equations look similar to (33), they crucially differ in the way functions for the exchange rates and exchange currents or the potentials are defined. For

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an overview over the literature see e.g. textbooks like [BRGA01, NTA04] and the survey in [BVSB09].

The potential difference η_S plays a crucial role in the general Butler-Volmer equation. For some controversial discussion of different explicit definitions we refer to [BCB05, LZ11, LZ13]. Often η_S is called driving force of the electrochemical reaction. According to Newman[NTA04], see also [BRGA01], η_S represents the deviation from the equilibrium potential, and the exchange rates $R_{b,f}^0$ and exchange currents $i_{b,f}^0$ are considered as general functions of temperature and particle densities.

The design of the function $\underset{s}{R}$ or the coefficients $R_{f/b}^0$ presupposes a careful attention of two facts:

1. The ratio of $\underset{s}{R}_f$ and $\underset{s}{R}_b$ is given by (22b), which restricts the generality of $\underset{s}{R}$. Thus only one of the two reaction rates $\underset{s}{R}_f$ and $\underset{s}{R}_b$ is available for a thermodynamically consistent constitutive modeling.

2. The definition of the potential difference η_S is a priori not given in the complete model. It requires some connection between variables of the bulk regions and the surface reactions.

From our point of view, the essential criticism of the treatment in the existing literature has to be that it ignores the dependence between those functions appearing in the Butler-Volmer equation and the corresponding functions in the bulk regions. That connection is enforced by the equations of balance and the 2nd law of thermodynamics. In our model this fact is highlighted by the relations (22a) and (22b). Thus our objective is a rational grounded derivation of this explicit dependence in the definition of the exchange rates and the identification of the relevant potential difference.

Remark on the relation of the complete model to the reduced model. The general Butler-Volmer equation (33) relates the reaction rate to a potential difference η_S. If we compare (33) with our relation (22a) of the complete model $\lambda > 0$, we observe that the electric potential φ does not explicitly appear in (22a). Moreover, according to (16) the electric potential is continuous across the interface S. We are thus confronted with the question, which potential difference drives the the chemical reaction at the interface? For these reasons it becomes evident that the model $\lambda > 0$ does not imply the general Butler-Volmer relation (33). Rather it can be deduced only within the setting of the reduced model $\lambda \to 0$. Only in the limit $\lambda \to 0$ and with respect to the new interface I we observe a dependence of the reaction rate (22b) from the electric potentials $\varphi|_I^\pm$ of the bulk regions.

In the following sections we consider at first a simple chemical reaction to describe the essential steps of a thermodynamically consistent modeling of the reaction rates. Hereafter we generalize our results within the reduced model $\lambda \to 0$. Then, for further illustration, we apply the results to the electroplating of metals and to the charging-discharging process of a lead-acid battery.

3.1 Motivation – a simple reaction

To illustrate the strategy, we consider a simple generic redox reaction of the form

$$O + n\,e^- \underset{R_b}{\overset{R_f}{\rightleftharpoons}} R\,. \tag{34}$$

The constituents R and e^- may represent the metallic ions and free electrons of electrodes, $n \in \mathbb{N}$ and O are cations that exist in an electrolyte. The stoichiometric coefficients of the reduced and oxidized constituents and the electron are $\underset{s}{\gamma_O} = -1$, $\underset{s}{\gamma_e} = -n$ and $\underset{s}{\gamma_R} = +1$.

The condition (22b), which restricts the interfacial reaction rates, reads for the given reaction

$$\frac{\underset{s}{R_f}}{\underset{s}{R_b}} = \exp\left(-\frac{\underset{s}{A}}{kT}\Big[\Gamma e_0\,(\varphi_E - \varphi_S) + \sum_{\alpha=e^-,R,O} \underset{s}{\gamma_\alpha} m_\alpha \mu_\alpha\Big]\right)\,. \tag{35}$$

To indicate the electric potentials of the electrode (E) and the electrolytic solution (S), we have used the notations φ_E and φ_S. The quantity Γ is defined as $\Gamma = \sum_{\alpha=e^-,R} \underset{s}{\gamma_\alpha} z_\alpha = -\underset{s}{\gamma_O} z_O$. For an equilibrium state with the corresponding potentials $\bar\varphi_E$, $\bar\varphi_S$ and $\bar\mu_\alpha$, we use the law of mass action (31b) for the interface I to calculate the equilibrium potential

$$U_0 := \bar\varphi_E - \bar\varphi_S = -\frac{1}{\Gamma e_0} \sum_{\alpha\in e^-,R,O} \underset{s}{\gamma_\alpha} m_\alpha \bar\mu_\alpha\,. \tag{36}$$

Then, we may write (35) as

$$\frac{\underset{s}{R_f}}{\underset{s}{R_b}} = \exp\left(-\frac{\underset{s}{A}}{kT}\Big[\Gamma e_0\,(\varphi_E - \varphi_S - U_0) + \sum_{\alpha=e^-,R,O} \underset{s}{\gamma_\alpha} m_\alpha(\mu_\alpha - \bar\mu_\alpha)\Big]\right)\,. \tag{37}$$

General Form. Next we model one of the two reaction rates, either $\underset{s}{R_f}$ or $\underset{s}{R_b}$, then the other rate is determined by the condition (37) that guarantees thermodynamic consistency. Motivated by the Arrhenius-law we propose the following ansatz for the forward rate and calculate the backward rate from (37):

$$\underset{s}{R_f} = \underset{s}{R_0} \exp\left(\frac{\underset{s}{A}}{kT}\Big[(\beta-1)\,\Gamma e_0(\varphi_E - \varphi_S - U_0) + \sum_{\alpha=e^-,R,O} (\beta_\alpha - 1)\,\underset{s}{\gamma_\alpha} m_\alpha(\mu_\alpha - \bar\mu_\alpha)\Big]\right) \tag{38a}$$

$$\underset{s}{R_b} = \underset{s}{R_0} \exp\left(\frac{\underset{s}{A}}{kT}\Big[\beta\,\Gamma e_0(\varphi_E - \varphi_S - U_0) + \sum_{\alpha=e^-,R,O} \beta_\alpha\,\underset{s}{\gamma_\alpha} m_\alpha(\mu_\alpha - \bar\mu_\alpha)\Big]\right)\,. \tag{38b}$$

Herein $\underset{s}{R_0}$, β and $(\beta_\alpha)_{\alpha=e^-,R,O}$ are introduced as phenomenological coefficients for the reaction components. To write the result according to the general Butler-Volmer structure (33), we

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introduce the definitions

$$R_f^0 = R_0 \exp\left(\frac{A}{kT} \sum_{\alpha=e^-,R,O} (\beta_\alpha - 1)\, \gamma_\alpha m_\alpha (\mu_\alpha - \bar{\mu}_\alpha)\right), \qquad \alpha_f = A(\beta - 1)\, \Gamma \quad \text{(39a)}$$

$$R_b^0 = R_0 \exp\left(\frac{A}{kT} \sum_{\alpha=e^-,R,O} \beta_\alpha\, \gamma_\alpha m_\alpha (\mu_\alpha - \bar{\mu}_\alpha)\right), \qquad \alpha_b = -A\,\beta\,\Gamma \qquad \text{(39b)}$$

and identify the potential difference by

$$\eta_S = \varphi_E - \varphi_S - U_0 \,. \tag{39c}$$

Note that the exchange reaction rates $R_{f/b}^0$ depend on the particle densities, according to (12a), but they do not depend on the electric potential.

Specific material model.   We consider the reaction (34) for a metallic electrode consisting of ions, R, and free electrons, e^-. The oxidized species O represents the cations of an electrolyte. In addition the electrolyte consists of anions, A, and the solvent, S.

At first we discuss the chemical potentials for the metal which is described as a binary mixture. The electro-neutrality condition $(14)_2$ and the plausible assumption that the particle density of the metallic ions does not depend on space, implies that also the electron density n_{e^-} is a constant. Thus in an isothermal process, the chemical potentials are constants in space and time

$$\mu_\alpha = \bar{\mu}_\alpha \qquad \text{for } \alpha = e^-, R \,. \tag{40}$$

The same assumptions are also made for hydrogen fuel cells in [BVSB09]. We assume that the electrolyte is a ternary ideal mixture. In this case the chemical potentials are represented by

$$\mu_\alpha = g_\alpha + \frac{kT}{m_\alpha} \ln y_\alpha \qquad \text{for } \alpha = O, A, S \,. \tag{41}$$

Here $y_\alpha = n_\alpha/n$ denotes the mole fraction of constituent α and g_α is the Gibbs free energy of the corresponding pure substance. The quantity $n = \sum_\alpha n_\alpha$ is the total particle density of the mixture. Note that g_α may depend on temperature and pressure. In general the pressure dependence is of outmost importance, see [DGM13], which contains more information on the thermodynamic modeling of electrolytes.

Inserting the constitutive laws into (39a) and (39b) yield explicit representations of the exchange rates. We obtain (with $\gamma_O = -1$ as above and $\gamma_A = \gamma_S = 0$)

$$R_f^0 = R_0 \left(\frac{y_O}{\bar{y}_O}\right)^{A(1-\beta_O)} \qquad \text{and} \qquad R_b^0 = R_0 \left(\frac{y_O}{\bar{y}_O}\right)^{-A\beta_O} \,. \tag{42}$$

In summary, the Butler-Volmer equation for the reaction (34) with a specific material model (40), (41) is

$$R = R_0 \left(\frac{y_O}{\bar{y}_O}\right)^{A(1-\beta_O)} \exp\left(\frac{A(\beta-1)\,\Gamma e_0 \eta_S}{kT}\right) - R_0 \left(\frac{y_O}{\bar{y}_O}\right)^{-A\beta_O} \exp\left(\frac{-A\,\beta\,\Gamma e_0 \eta_S}{kT}\right) \,.$$
$$\tag{43}$$

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3.2 Discussion.

At first, let us compare our representation of the Butler-Volmer equation with the corresponding equation (8.16) from the textbook by J. Newman and K. E. Thomas-Alyea, [NTA04]. In our notation the authors write:

$$\text{Newman \& Thomas-Alyea}: \quad R_s = R^0 \left[\exp\left(\frac{(1-\beta)ne_0\eta_S}{kT} \right) - \exp\left(-\frac{\beta ne_0\eta_S}{kT} \right) \right].$$
(44)

There is only a single exchange rate in (44) and it is given by

$$R^0 = k_f^\beta k_b^{1-\beta} n_R^\beta n_O^{1-\beta} .$$
(45)

Newman and Thomas-Alyea call the parameter β symmetry factor. Moreover they introduce $k_{f/b}$ as to constants related to the forward and backward reaction, respectively. The potential difference η_S is defined identical to (39c).

A comparison of the general Butler-Volmer equation (33) with the coefficients from (39) shows essential differences. The two exchange rates $R^0_{f/b}$ in (44) are equal, $R^0_f = R^0_b = R^0$. However, this violates the condition (35), which we introduced to guarantee thermodynamic consistency. Moreover, the form how the exchange rates in (45) depend on the particle densities n_R and n_O assumes already a specific constitutive model like (41). In contrast, our version (39) is more general since the exchange rates depend on the particle densities via the chemical potentials. But even in this simple case of (42) where we consider the electrolyte as an ideal mixture and have constant chemical potentials in the metal, we observe essential differences between (42) and the exchange rates according (45).

Another concept is used for the generalized Frumkin-Butler-Volmer equation (gFBV), see [BVSB09]. There, the potential difference is defined as the voltage over the Stern-layer. This definition was motivated by the aim to include effects of diffusive polarization layers at the electrodes into the equations. Since diffuse layers are not resolved in standard models based on local electro-neutrality, the combination of this gFBV with a microscopic model that resolves space charge layers was proposed in [IKV77] and analyzed in in detail in [BCB05]. There, also asymptotic limit equations for thin diffuse layers are derived and analyzed. This limiting procedure corresponds to the formal asymptotic analysis in Chapter 5 below.

We did not introduce a Stern layer into our models because –contrary to the standard Poisson-Nerst-Planck model– the complete model of Section 2 is already fully capable to describe diffuse layers correctly, including boundedness of the concentrations and pressure effects that becomes most important in the layers [DGM13]. For saturation effects at the electrodes see [DGL13]. Moreover, there is not a problem of missing boundary conditions for the Poisson equation that would require the introduction of a Stern layer condition. On the other hand, the reduced model fulfills local electro-neutrality in the bulk but the boundary conditions incorporate all effects of the diffusive space charge layers. Moreover the bulk variables are linked to the interface reactions in a thermodynamically consistent way.

3.3 General Butler-Volmer equation

Now we consider the general chemical reaction (4b) to generalize our results of the last section. We start with a summary of the two essential steps that lead to the Butler-Volmer equation for the simple reaction (34):

1. We choose a suitable reference state to characterize an equilibrium. Then we use (31b) to introduce in (22b) the potential difference η_S^i between the actual state and the equilibrium state. It follows

$$
\frac{R_f^i}{\underset{s}{R_b^i}} = \exp\left(-\frac{A_s^i}{kT}\left(\Gamma^i e_0 \eta_S^i + \sum_{\alpha \in \mathcal{M}_S} \gamma_\alpha^i m_\alpha \left(\underset{s}{\mu_\alpha} - \underset{s}{\bar{\mu}_\alpha} \right) \right.\right.
$$
$$
\left.\left. + \sum_{\alpha \in \mathcal{M}_+ \cup \mathcal{M}_-} \gamma_\alpha^i m_\alpha \left(\mu_\alpha|_I^\pm - \bar{\mu}_\alpha|_I^\pm \right) \right) \right) . \tag{46}
$$

Herein the potential difference is given by

$$
\eta_S^i = \left(\varphi|_I^+ - \varphi|_I^- - (\bar{\varphi}|_I^+ - \bar{\varphi}|_I^-) \right) - \frac{1}{\Gamma^i} \sum_{\alpha \in \mathcal{M}_S} \gamma_\alpha^i z_\alpha \left(\varphi|_I^- - \underset{s}{\varphi} - (\bar{\varphi}|_I^- - \underset{s}{\bar{\varphi}}) \right), \tag{47}
$$

where the coefficient Γ^i is introduced as an abbreviation, $\Gamma^i = \sum_{\alpha \in \mathcal{M}_+} \gamma_\alpha^i z_\alpha$. Due to charge conservation in every reaction we have

$$
\Gamma^i = -\sum_{\alpha \in \mathcal{M}_- \setminus \mathcal{M}_+} \gamma_\alpha^i z_\alpha - \sum_{\alpha \in \mathcal{M}_S} \gamma_\alpha^i z_\alpha. \tag{48}
$$

Note that in general the potential difference η_S^i depends on the surface potential $\underset{s}{\varphi}$. Only if there are no pure interfacial constituents, i.e. $\mathcal{M}_S = \emptyset$, or if the total charge of the pure interfacial constituents is zero, i.e. $\sum_{\alpha \in \mathcal{M}_S} \gamma_\alpha^i z_\alpha = 0$, the second term in (47) disappears so that η_S becomes the same for all surface reactions $i = 1, 2..., M_S$. In this case the potential difference η_S describes the deviation of the actual potential difference $\varphi|_I^+ - \varphi|_I^-$ from the equilibrium voltage $U_0 = \bar{\varphi}|_I^+ - \bar{\varphi}|_I^-$ of the bulk phases.

2. In this step we propose a forward and backward reaction rates so that the exponential condition (22b) between the rates and the potential remains preserved. Then the net reaction rate $\underset{s}{R^i}$ can be written as a generalized Butler-Volmer equation,

$$
\underset{s}{R^i} = R_f^{0,i} \exp\left(\frac{\alpha_f^i e_0 \eta_S}{kT} \right) - R_b^{0,i} \exp\left(\frac{-\alpha_b^i e_0 \eta_S}{kT} \right) . \tag{49}
$$

The newly introduced coefficients are

$$
\alpha_f^i = \underset{s}{A^i}(\beta^i - 1)\Gamma^i \quad \text{and} \quad \alpha_b^i = \underset{s}{A^i}\beta^i \Gamma^i , \tag{50}
$$

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and the exchange rates are identified as

$$R_f^{0,i} = R_0^i \exp \left(\frac{A_s^i}{kT} \left[\sum_{\alpha \in \mathcal{M}_S} (\beta_\alpha^i - 1) \gamma_\alpha^i m_\alpha \left(\mu_\alpha - \bar{\mu}_\alpha \right) \right. \right.$$

$$\left. \left. + \sum_{\alpha \in \mathcal{M}_+ \cup \mathcal{M}_-} (\beta_\alpha^i - 1) \gamma_\alpha^i m_\alpha \left(\mu_\alpha|_I^\pm - \bar{\mu}_\alpha|_I^\pm \right) \right] \right) \tag{51}$$

$$R_b^{0,i} = R_0^i \exp \left(\frac{A_s^i}{kT} \left[\sum_{\alpha \in \mathcal{M}_S} \beta_\alpha^i \gamma_\alpha^i m_\alpha \left(\mu_\alpha - \bar{\mu}_\alpha \right) \right. \right.$$

$$\left. \left. + \sum_{\alpha \in \mathcal{M}_+ \cup \mathcal{M}_-} \beta_\alpha^i \gamma_\alpha^i m_\alpha \left(\mu_\alpha|_I^\pm - \bar{\mu}_\alpha|_I^\pm \right) \right] \right). \tag{52}$$

Thus in this step we have introduced the new phenomenological coefficients R_0^i, β^i and $(\beta_\alpha^i)_{\alpha \in \mathcal{M}}$.

The equations (49)–(52) represent a thermodynamically consistent formulation of interfacial reaction rates R^i. The rates explicitly depend on the electric potentials of the bulk phases. Moreover they additionally depend via the chemical potentials on the bulk concentrations.

A further important observation that is often ignored in the literature is this: The reaction rates (49), the diffusion fluxes (19), the chemical potentials and the stress tensor (25) are related to each other, hence they cannot be chosen independent of each other. The three quantities follow from the same free energy function $\rho\psi$. Once this function is given, only the phenomenological coefficients in the diffusion fluxes and the reaction rates can be still independently chosen. In particular, if the diffusion equations are explicitly given, the reaction rates are also fixed in the above sense.

3.4 Example I – Electroplating

The electroplating of metals serves as a simple example of an electrochemical process with a surface reaction of the type (34). Moreover it has the advantage that it can be described by a steady state.

We consider a situation with an aqueous copper sulfate solution in the domain Ω, bounded by two parallel copper plates $\mathcal{A}$ and $\mathcal{C}$ as shown in Figure 2. If the plates are sufficiently large the process is one dimensional and stationary. When a current is applied to the electrodes, copper is oxidized at the anode $\mathcal{A}$ and the copper ions are dissolved from the the anode interface $I_\mathcal{A}$ into the electrolyte. On the other side, at the interface $I_\mathcal{C}$, the copper ions for Ω are reduced and incorporated into cathode $\mathcal{C}$. The reactions at both electrodes can be written as

$$\mathrm{Cu}_{\mathrm{aq}}^{2+} + \mathrm{e}^- \rightleftharpoons \mathrm{Cu}^+ \quad \text{at } I_\mathcal{A} \text{ and } I_\mathcal{C} , \tag{53}$$
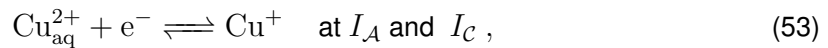
where the forward reaction is dominant at the cathode $\mathcal{C}$ and the backward reaction at the anode $\mathcal{A}$. We model copper electrodes as a binary mixture of free electrons e^- and copper ions
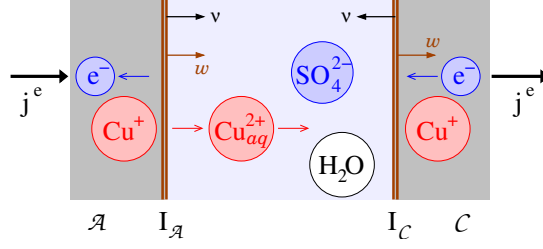
Figure 2: Experimental setup for electroplating: aqueous copper sulfate solution bounded by two copper electrodes. The role of the electrodes as anode or cathode depends on the sign of the applied current j^{e}. The surface normal ν always points to the electrolyte.

Cu^+ which are the reduced species R. The electrolyte consists of the ions $\mathrm{Cu}^{2+}_{\mathrm{aq}}$, that form the oxidized species O and sulfate ions SO_4^{2-} and water $\mathrm{H_2O}$, in the following denoted by A and S, respectively.

R: Cu^+	e^-	A: SO_4^{2-}	O: $\mathrm{Cu}^{2+}_{\mathrm{aq}}$	S: $\mathrm{H_2O}$
$\underset{s}{\gamma_R} = +1$	$\underset{s}{\gamma_e} = -1$	$\underset{s}{\gamma_A} = 0$	$\underset{s}{\gamma_O} = -1$	$\underset{s}{\gamma_S} = 0$
$z_R = +1$	$z_e = -1$	$z_A = -2$	$z_O = +2$	$z_S = 0$

Table 1: Stoichiometric coefficients and charge numbers for the chemical species at the interfaces.

In a steady state, the boundary conditions (18b) at the interfaces $I_{\mathcal{A}}$ and $I_{\mathcal{C}}$ reduce to

$$m_\alpha \underset{s}{\gamma_\alpha} \underset{s}{R_{\mathcal{A}/\mathcal{C}}} = [\![m_\alpha n_\alpha (v - w_{\mathcal{A}/\mathcal{C}}) + J_\alpha]\!] . \tag{54}$$

Taking a linear combination of these conditions for the electrode species R and e^-, it turns out that reaction rates $\underset{s}{R_{\mathcal{A}/\mathcal{C}}}$ are related to the electric current j^{e}. We set $\underset{s}{R} := \underset{s}{R_{\mathcal{A}}} = -\underset{s}{R_{\mathcal{C}}}$ and get

$$\underset{s}{R} = -\frac{1}{\underset{s}{\gamma_e} z_e e_0 + \underset{s}{\gamma_R} z_R e_0} j^{\mathrm{e}} = -\frac{1}{2e_0} j^{\mathrm{e}} . \tag{55}$$

The species A, O and S of the electrolyte satisfy the stationary version of the mass balance equations (17) where we replaced the partial balance of S by the total mass balance (20). In the bulk region we have

$$\partial_x (m_A n_A v + J_A) = 0 , \tag{56a}$$
$$\partial_x (m_O n_O v + J_O) = 0 , \tag{56b}$$
$$\partial_x (\rho v) = 0 , \tag{56c}$$

together with $n^{\mathrm{F}} = e_0 z_A n_A + e_0 z_O n_O = 0$ according to (14). As in [DGM13], we get from the momentum balance (23) that the pressure is constant $p = p_0$ and moreover, for an ideal mixture of compressible fluids, $n = n_A + n_O + n_S$ can be related to p and hence n is also constant. With these relations, n_A and n_S can be expressed as functions of n_O. Summing (54) for $\alpha = \mathrm{A, O, S}$ and using (56), it follows that $w_{\mathcal{A}} = w_{\mathcal{C}} =: w$. Choosing a coordinate system

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that moves with the interface $I_\mathcal{A}$, we have $w = 0$. Then we easily derive from a combination of (54) and (56) that

$$\rho\, v = m_O \gamma_O \underset{s}{R} \quad = \frac{m_O}{2e_0} j^{\mathrm{e}} \,. \tag{57}$$

This identity can be used to reduce (56) to a system of two nonlinear coupled second order differential equations for the variables n_O and φ, viz.

$$\partial_x\left(-\frac{z_O}{z_A} m_A n_O\, v(n_O) + J_A(n_O, \varphi) \right) = 0 \,, \tag{58a}$$

$$\partial_x\left(m_O n_O\, v(n_O) + J_O(n_O, \varphi) \right) = 0 \,. \tag{58b}$$

For the diffusive fluxes we choose a diagonal mobility matrix with $M_{\alpha\alpha} = B_\alpha T m_\alpha^2 n_\alpha$. With chemical potentials of the form (41) we have

$$J_A(n_O, \varphi) = \frac{z_O}{z_A} B_A\left(\partial_x n_O - \frac{m_A}{m_S}\frac{n_O}{n_S(n_O)}\partial_x n_S(n_O) + z_A\, n_O\, \partial_x \varphi \right) , \tag{59a}$$

$$J_O(n_O, \varphi) = -B_O\left(\partial_x n_O - \frac{m_O}{m_S}\frac{n_O}{n_S(n_O)}\partial_x n_S(n_O) + z_O\, n_O\, \partial_x \varphi \right) . \tag{59b}$$

The explicit boundary conditions (54) for the particle fluxes $n_\alpha v + J_\alpha$, $\alpha = A, O$ are

$$\frac{z_O}{z_A} m_A n_O v(n_O) + J_A(n_O, \varphi) = 0 \qquad\qquad \text{at } I_\mathcal{A}\,, \tag{60a}$$

$$m_O n_O v(n_O) + J_O(n_O, \varphi) = \frac{m_O}{2e_0} j^{\mathrm{e}} \qquad\qquad \text{at } I_\mathcal{A}\,, \tag{60b}$$

$$-\frac{z_O}{z_A} m_A n_O v(n_O) + J_A(n_O, \varphi) = 0 \qquad\qquad \text{at } I_\mathcal{C}\,, \tag{60c}$$

$$m_O n_O v(n_O) + J_O(n_O, \varphi) = -\frac{m_O}{2e_0} j^{\mathrm{e}} \qquad\qquad \text{at } I_\mathcal{C}\,. \tag{60d}$$

In addition there are two more constraints. First, we have to specify the total amount N_O of cations in the electrolyte. Second, an absolute reference value for φ has to be define, e.g. $\varphi = 0$ at $I_\mathcal{C}$. For the Butler-Volmer equation we have $\Gamma = 2$ and $\gamma_O = -1$. We choose $\underset{s}{A} = 1$ and $\beta = 1/2$ to get

$$\underset{s}{R} = R_0\left(\frac{n_O}{\bar{n}_O} \right)^{(1-\beta_O)} \exp\left(\frac{1}{2}\frac{2e_0}{kT}\eta_S \right) \quad - R_0\left(\frac{n_O}{\bar{n}_O} \right)^{-\beta_O} \exp\left(-\frac{1}{2}\frac{2e_0}{kT}\eta_S \right) \tag{61}$$

where $\eta_S = \varphi_E - \varphi_S - U_0$ with the equilibrium potential $U_0 = \bar{\varphi}_E - \bar{\varphi}_S = 0.16\,\mathrm{V}$, c.f. [Hay10].

The system (58)–(61) can be solved numerically, solutions are plotted in Figure 3. The voltage $\varphi_\mathcal{A} - \varphi_\mathcal{C}$ of the galvanic cell is defined as the difference between the potentials on the electrode side of $I_\mathcal{A}$ and $I_\mathcal{C}$. For very low cation concentrations, i.e. strongly diluted electrolytes, the convective flux $n_O v$ and the influence of the solvent S can be neglected in (58). This approximation leads to a linear spacial distribution of n_O with a slope proportional to the imposed current j^{e}.

A: SO_4^{2-}		O: Cu_{aq}^{2+}		S: H_2O	
m_A	$= 96.078\,\mathrm{u}$	m_O	$= 63.546\,\mathrm{u}$	m_S	$= 18.015\,\mathrm{u}$
B_A	$= 3.36 \times 10^{11}\,\mathrm{s/kg}$	B_O	$= 5.61 \times 10^{11}\,\mathrm{s/kg}$		–

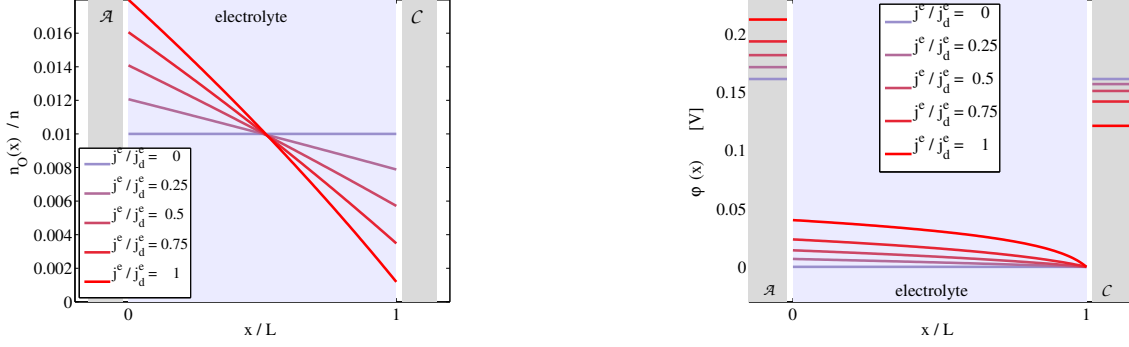Table 2: Material parameters used for the calculations, c.f. [Hay10].

Figure 3: Solution of (58)–(61) over space for different applied currents. Left: We observe almost linear concentration profiles n_O with slope related to j^{e}. Right: Electrostatic potential φ in the electrolyte and the jump across the Interfaces $I_{\mathcal{A}}$ and $I_{\mathcal{C}}$ according to (61).

When n_O approaches 0 at the cathode, the voltage $\varphi_{\mathcal{A}} - \varphi_{\mathcal{C}}$ has to blows up. This motivates the definition of a limiting current as in [BCB05]

$$ \overset{\cdot}{j}_d^{\mathrm{e}} := \frac{4 z_O e_0 \, kT \, B_O \, N_O}{L} \ . \tag{62} $$

In fact, for strongly diluted electrolytes with a very low total amount N_O of cations, we observe a blow up of the cell voltage that occurs close to $j^{\mathrm{e}} = j_d^{\mathrm{e}}$, see Figure 4. For less diluted electrolytes it is possible to increase the applied current beyond j_d^{e}. This is due to fact that convective fluxes and the influence of the solvent, can no longer be ignored as N_O is increased.

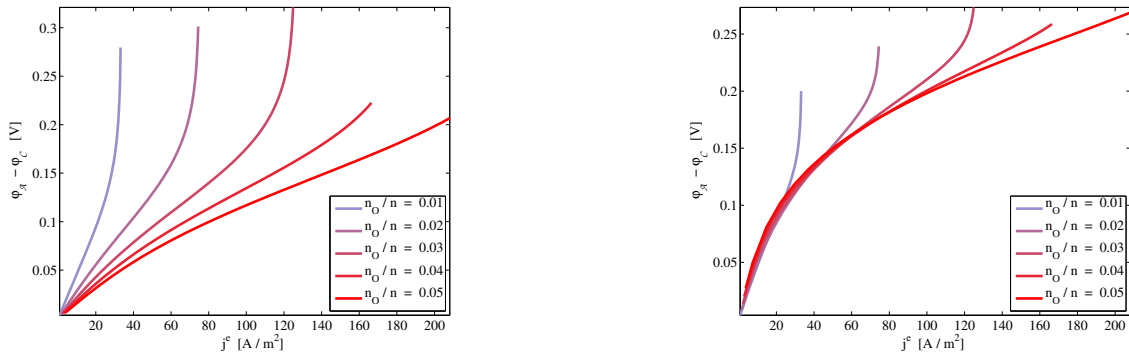For the choice $\beta_O = 0$, the Butler-Volmer equation (61) has a similar structure as the generalized

Figure 4: Polarographic curves for different choices of the parameter β_O. Left: $\beta_O = 0$; right: $\beta_O = 1$. Independent of β_O but depending on the ion concentration N_O, we observe a blow up of the cell voltage for different applied current j^{e}.
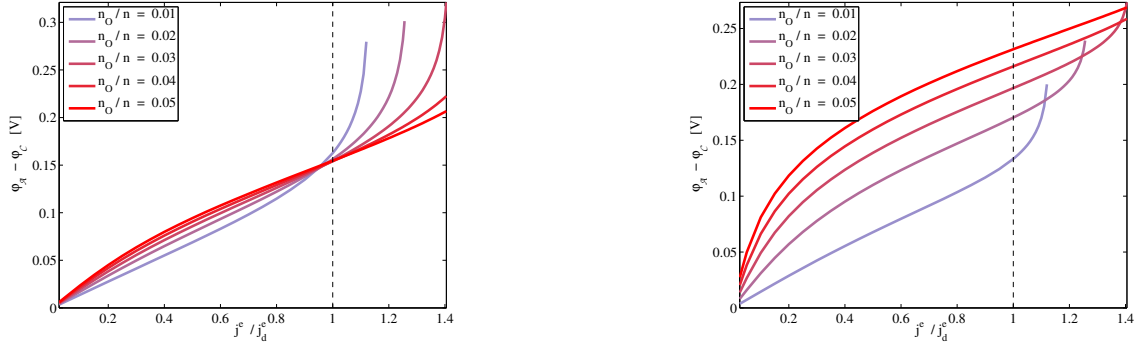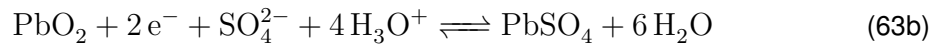
Figure 5: Polarographic curves for the same situation as in Fig. 4 but this time the current is scaled by the limiting current j_d^e defined in (62). Left: $\beta_O = 0$; right: $\beta_O = 1$.

Frumkin-Butler-Volmer equation used in [BCB05, BVSB09], c.f. the discussion at the end of Section 3.1. But for a comparison of the results one has to keep in mind that the bulk equations used there differ from (58), because convective fluxes and the solvent are neglected and the potential difference is taken at the Stern layer. Nevertheless, there is some overlap: in the Helmholtz limit of infinite Stern layer capacitance, the potential difference over the Stern layer coincides with the potential difference at an interface I. Then, for a strongly diluted electrolyte and applying a *thin layer limit* that corresponds to our asymptotic analysis below, the models and results become similar. There are also other choices of a Stern layer analyzed in [BCB05] that can not be justified by derivation of the models proposed here. E.g. there is also the Gouy-Chapman limit of vanishing Stern layer capacitance. This singular limit gives raise to a different limiting current in case of small reaction rates at the interfaces. Neither the Helmholtz limiting model nor our model show a comparable reaction limited current.

3.5   Example II – Lead acid battery

With a second example, we want to suggest that the proposed reduced model and the Butler-Volmer equations are capable to model and simulate by far more complex situations than the simple reaction of Section 3.1. To describe a lead acid battery, we use the same one–dimensional geometric setting but now consider two electrodes of different material. The lead electrode is modeled by a mixture of Pb^{2+} and free electrons e^-. The other electrode consists of lead oxide PbO_2. In between we have a solution of sulfuric acid H_2SO_4 water H_2O. The species are label by E and S respective. The sulfuric acid dissociates into anions SO_4^{2-} and cations H_3O^+, denoted by A and C respective. From the surface reactions

$$Pb^{2+} + SO_4^{2-} \rightleftharpoons PbSO_4 \tag{63a}$$

$$PbO_2 + 2\,e^- + SO_4^{2-} + 4\,H_3O^+ \rightleftharpoons PbSO_4 + 6\,H_2O \tag{63b}$$

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we derive the Butler-Volmer equations. At the lead electrode we have $U_0 = 0.35\,\text{V}$, $\gamma_A = -1$, $z_A = -2$ and hence $\Gamma = -2$. We choose $\underset{s}{A} = 1$ and $\beta = 1/2$ to get

$$\underset{s}{R} = R_0 \left(\frac{n_A}{\bar{n}_A}\right)^{(1-\beta_A)} \exp\left(-\frac{e_0}{kT}\eta_S\right) \quad - R_0 \left(\frac{n_A}{\bar{n}_A}\right)^{-\beta_A} \exp\left(\frac{e_0}{kT}\eta_S\right) . \tag{64a}$$

At the lead oxide electrode we have $U_0 = -1.67\,\text{V}$, $\gamma_A = -1$, $z_A = -2$, $\gamma_C = -4$, $z_A = 1$ and hence $\Gamma = 2$. With the same choice of $\underset{s}{A}$ and β we get

$$\underset{s}{R} = R_0 \left(\frac{n_A}{\bar{n}_A}\right)^{(1-\beta_A)} \left(\frac{n_C}{\bar{n}_C}\right)^{4(1-\beta_C)} \exp\left(\frac{e_0}{kT}\eta_S\right) \quad - R_0 \left(\frac{n_A}{\bar{n}_A}\right)^{-\beta_A} \left(\frac{n_C}{\bar{n}_C}\right)^{-4\beta_C} \exp\left(-\frac{e_0}{kT}\eta_S\right) .$$
$$\tag{64b}$$

If the electrodes are not connected by an outer circuit the system will reach an equilibrium where $\underset{s}{R} = 0$ and the ion concentrations are constant in space. Combing both equations (64a) and (64b), one can calculate the open circuit voltage (OCV) for for given concentration n_E and n_C of sulfuric acid (E) that has partially dissociated into cations (C) and anions, see Figure 6.

To simulate charging and discharging of the lead acid battery one has to solve the full system of instationary equations (14), (17) and (23). In addition to the surface reactions above, one also has to consider dissociation reactions in the bulk

$$\text{H}_2\text{SO}_4 + 2\,\text{H}_2\text{O} \rightleftharpoons 2\,\text{H}_3\text{O}^+ + \text{SO}_4^{2-} . \tag{65}$$
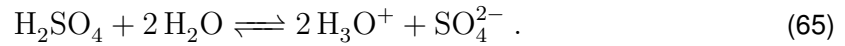
The results of the simulation show the qualitative behavior as expected from experiments, see Figure 6. For more details of the system and the numerical solution we refer to [DGM14].
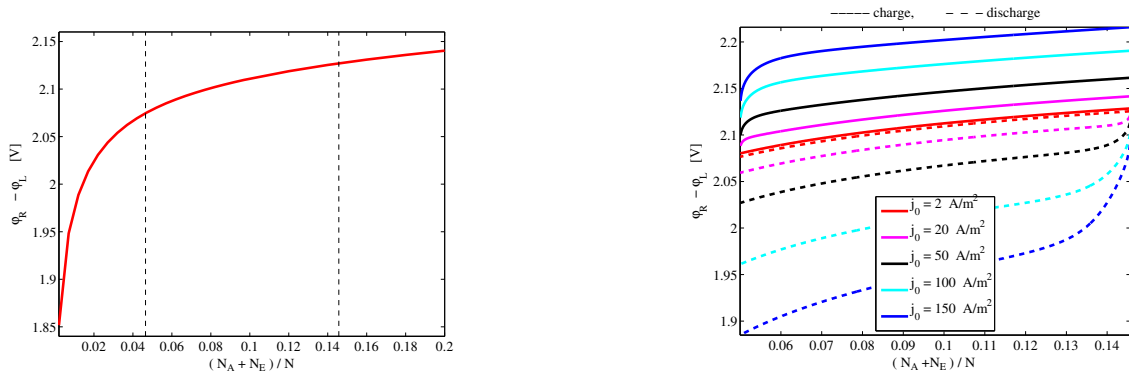

Figure 6: Left: OCV of a lead acid battery over the electrolyte concentration calculated from (64). The dashed lines mark the range within that a battery is operated. Right: Cell voltage during charge–discharge cycles for different imposed currents. When the imposed current is increased we observe a larger gap between the curves for charging and discharging.

4 Thermodynamically consistent modeling of mixtures separated by an electrochemical interface

In this section we describe the thermodynamical consistent derivation of the *complete model* from Section 2. For notation and the assumptions we refer to Section 2.1. The coupled system of equations for the basic variables rely on partial equations of balance, i.e. on the conservation laws for the mass of the constituents and the balance equations for the momentum of the mixture. Recall that we do not take into account tangential fluxes on the interfaces, see section 2.1.

Equations for the electric field. We consider quasi-static electric fields only. In this case the Maxwell equations in the bulk regions and for interfaces reduce to

$$\varepsilon_0 \operatorname{div}(\boldsymbol{E}) = n^{\mathrm{e}} , \qquad\qquad \boldsymbol{E} = -\nabla\varphi , \tag{66a}$$

$$[\![\varepsilon_0\boldsymbol{E}]\!] = (n^{\mathrm{F}}_s + n^{\mathrm{P}}_s)\boldsymbol{\nu} . \tag{66b}$$

The interfacial charge density due to polarization is determined by the jump condition

$$\boldsymbol{\nu} \times [\![\boldsymbol{P} \times \boldsymbol{v}]\!] - [\![\boldsymbol{P}]\!]w_\nu = n^{\mathrm{P}}_s w_\nu \boldsymbol{\nu} . \tag{67}$$

Later on we will derive further interface conditions where the electric potential φ explicitly appears. For this reason we also need a jump condition for φ. We choose

$$[\![\varphi]\!] = 0 , \tag{68}$$

which is only possible if interfacial polarization charges, n^{P}_s are exclusively induced due to different polarizations of the bulk phases. Thus we assume that the interface itself is not a double layer, i.e. there is no surface density of dipoles on S. Finally, in accordance with (68) we introduce the definition

$$\varphi_s = \varphi|^{\pm}_S . \tag{69}$$

Equations of balance. With the definitions (10) and (7a) we can split the mass flux of species α into $\rho_\alpha \boldsymbol{v}_\alpha = \rho_\alpha \boldsymbol{v} + \boldsymbol{J}_\alpha$. In each of the subdomains $\Omega^\pm$ as well as on the interface S, the partial mass balances may be written as

$$\partial_t \rho_\alpha + \operatorname{div}(\rho_\alpha \boldsymbol{v} + \boldsymbol{J}_\alpha) = r_\alpha , \qquad \text{for } \alpha = 1, 2, \cdots, N \tag{70a}$$

$$\partial_t \rho_\alpha_s + [\![\rho_\alpha(\boldsymbol{v} - \boldsymbol{w}) \cdot \boldsymbol{\nu}]\!] + [\![\boldsymbol{J}_\alpha \cdot \boldsymbol{\nu}]\!] = r_\alpha_s , \qquad \text{for } \alpha = 1, 2, \cdots, N . \tag{70b}$$

Herein r_α and r_α_s denote the mass production rate of constituent A_α or A_α_s respective. Forward and backward reactions contribute to the mass production rate of the constituent. The corresponding reactions rates give the number of forward and backward reactions per time and per volume respective per surface area. We write

$$r_\alpha = \sum_{i=1}^{M} m_\alpha \gamma^i_\alpha (R^i_f - R^i_b) , \qquad\qquad r_\alpha_s = \sum_{i=1}^{M_S} m_\alpha \gamma^i_\alpha_s (R^i_f_s - R^i_b_s) . \tag{71}$$

The conservation laws of charge and mass for every single reaction $i \in \{1, 2, \cdots, M\}$ in the bulk read

$$\sum_{\alpha=1}^{N} z_\alpha \gamma_\alpha^i = 0 \quad \text{and} \quad \sum_{\alpha=1}^{N} m_\alpha \gamma_\alpha^i = 0 \;, \quad \text{implying} \quad \sum_{\alpha=1}^{N} r_\alpha = 0 \;. \tag{72}$$

Analogous relations hold for the surfaces. The balance equations for momentum read

$$\partial_t \rho \boldsymbol{v} + \operatorname{div}(\rho \boldsymbol{v} \otimes \boldsymbol{v} - \boldsymbol{\Sigma}) = \rho \boldsymbol{b} \;, \tag{73a}$$

$$\partial_t (\rho w_\nu) + [\![\rho \boldsymbol{v} \cdot \boldsymbol{\nu} (\boldsymbol{v} - \boldsymbol{w}) \cdot \boldsymbol{\nu}]\!] - [\![\boldsymbol{\nu}^T \cdot \boldsymbol{\Sigma} \cdot \boldsymbol{\nu}]\!] = \rho \underset{s}{\boldsymbol{b}} \;, \tag{73b}$$

where $\boldsymbol{\Sigma} := \boldsymbol{\sigma} + \varepsilon_0 (\boldsymbol{E} \otimes \boldsymbol{E} - \frac{1}{2}|\boldsymbol{E}|^2 \mathbf{1})$ is the total stress consisting of a part given by the Cauchy stress tensor $\boldsymbol{\sigma}$ and the Maxwell stress due to quasi-static Lorentz forces. $\mathbf{1}$ denotes the unit matrix. The force densities $\rho \boldsymbol{b}$ and $\rho \underset{s}{\boldsymbol{b}}$ are due to gravitation and inertia. In the following we set $\boldsymbol{b} = \underset{s}{\boldsymbol{b}} = 0$.

Variants of the equations of balance. For explicit calculations there are useful alternatives of the equations of balance. Instead of the N partial mass balances we use the mass balance for the total mass density of the mixture and the remaining $N - 1$ mass balances serve as the basis for the diffusion equations.

$$\partial_t \rho_\alpha + \operatorname{div}(\rho_\alpha \boldsymbol{v} + \boldsymbol{J}_\alpha) = r_\alpha \quad \text{for} \;\; \alpha = 1, 2, \cdots, N - 1 \;, \tag{74a}$$

$$\partial_t \rho + \operatorname{div}(\rho \boldsymbol{v}) = 0 \;. \tag{74b}$$

Summing up the partial mass balances yields the interfacial balance for the total mass density,

$$\partial_t \rho_\alpha + [\![\rho_\alpha (\boldsymbol{v} - \boldsymbol{w}) \cdot \boldsymbol{\nu}]\!] + [\![\boldsymbol{J}_\alpha \cdot \boldsymbol{\nu}]\!] = \underset{s}{r_\alpha} \quad \text{for} \;\; \alpha = 1, 2, \cdots, N - 1 \;, \tag{74c}$$

$$\partial_t \rho + [\![\rho (\boldsymbol{v} - \boldsymbol{w}) \cdot \boldsymbol{\nu}]\!] = 0 \;. \tag{74d}$$

Constitutive model in $\Omega^\pm$. The variables $(\rho_\alpha)_{\alpha=1,2,\cdots,N}$, $\boldsymbol{v}$ and $\boldsymbol{E}$ are not the only quantities in the equations of balance. There are further quantities that must be given by thermodynamically consistent constitutive equations, so that the equations of balance become system of partial differential equations for the variables. Our constitutive model describes a viscous and reacting polarizable mixture with volume changes and diffusion under isothermal conditions.

The corresponding constitutive model starts from a free energy density function of the general form

$$\rho \psi = \rho \widetilde{\psi}(T, \rho_1, \rho_2, \cdots, \rho_N, \boldsymbol{E}) \;. \tag{75}$$

At first we present the results of the 2$^{\text{nd}}$ law of thermodynamics, that are based on the general function (75),[dM63, MR59, Mül85]:

1. Chemical potentials and polarization:

$$\mu_\alpha = \frac{\partial \rho \psi}{\partial \rho_\alpha} \;, \quad \boldsymbol{P} = -\frac{\partial \rho \psi}{\partial \boldsymbol{E}} \;. \tag{76}$$

2. The stress can be decomposed into elastic and viscous parts. We write $\boldsymbol{\sigma} = \boldsymbol{\sigma}^{\mathrm{E}} + \boldsymbol{\sigma}^{\mathrm{NS}}$ and call the viscous part the Navier-Stokes stress. The representation of the elastic stress reads:

$$\boldsymbol{\sigma} = \Big(\rho\psi - \sum_{\alpha=1}^{N} \rho_\alpha \mu_\alpha \Big) \, \mathbf{1} + \boldsymbol{E} \otimes \boldsymbol{P} \,. \tag{77}$$

3. Representation and sign of the entropy production due to (i) diffusion, (ii) chemical reactions and (iii) viscous flow:

$$\xi = -\sum_{\alpha=1}^{N} \boldsymbol{J}_\alpha \Big(\nabla\Big(\frac{\mu_\alpha}{T}\Big) + \frac{1}{T}\frac{z_\alpha}{m_\alpha}\nabla\varphi \Big) - \frac{1}{T}\sum_{i=1}^{M} \Big(\sum_{\alpha=1}^{N} m_\alpha \gamma_\alpha^i \mu_\alpha \Big) \big(R_f^i - R_b^i \big) + \frac{1}{T}\boldsymbol{\sigma}^{\mathrm{NS}} : \nabla\boldsymbol{v} \,. \tag{78}$$

The entropy production must be non negative for every solution of the balance equations, $\xi \geq 0$. Equilibrium is a solution of the balance equations with $\xi = 0$.

The representation of ξ is important because it allows to formulate constitutive relations for the diffusion flux, the reaction rates and the viscous part of the stress tensor that guarantee $\xi \geq 0$. In this case we say that the constitutive functions are compatible with the 2$^{\mathrm{nd}}$ law of thermodynamics.

The simplest choice of constitutive functions for $(N-1)$ diffusion fluxes $(\boldsymbol{J}_\alpha)_{\alpha=1,2,\cdots,N-1}$ are

$$\boldsymbol{J}_\alpha = -\sum_{\beta=1}^{N-1} M_{\alpha\beta} \Big(\nabla\Big(\frac{\mu_\beta - \mu_N}{T}\Big) - \frac{1}{T}\Big(\frac{z_\beta}{m_\beta} - \frac{z_N}{m_N}\Big) \boldsymbol{E} \Big) \,, \quad \alpha = 1, 2, \cdots, N-1 \,. \tag{79}$$

The kinetic matrix $M_{\alpha\beta}$ must be positive definite.

It is important to note that only $(N-1)$ diffusion fluxes are given by constitutive laws. Due to the side condition (7a), the flux $\boldsymbol{J}_N$ is expressed by the other $(N-1)$ fluxes according to $\boldsymbol{J}_N = -\sum_{\alpha=1}^{N-1} \boldsymbol{J}_\alpha$.

The constitutive for the Navier-Stokes stress is constructed in an analogous manner [Mül85],

$$\boldsymbol{\sigma}^{NS} = \nu\mathrm{div}\,\boldsymbol{v}\,\mathbf{1} + \eta\Big(\nabla\boldsymbol{v} + \nabla\boldsymbol{v}^T\Big) \quad \text{with} \quad \nu + \frac{2}{3}\eta \geq 0 \quad \text{and} \quad \eta \geq 0 \,. \tag{80}$$

Bulk viscosity ν and shear viscosity η are considered as constants here.

Finally we read off from (78) an ansatz for the reaction rates guaranteeing a non-negative entropy production.

$$\frac{R_f^i}{R_b^i} = \exp\Big(-\frac{A^i}{kT}\sum_{\alpha=1}^{N} \gamma_\alpha^i m_\alpha \mu_\alpha \Big) \quad \text{with} \quad A^i \geq 0. \tag{81}$$

Herein A^i are introduced as a further phenomenological constants. It is crucial to recognize that the ratio of forward and backward reaction is determined by (81). Further constitutive assumptions can only be introduced in agreement with (81). For a more detailed discussion of chemical reactions in the context of the 2$^{\mathrm{nd}}$ law of thermodynamics we refer the reader to [BD13].

Up to now the constitutive model is quite general. The special material properties for the mixture at hand are embodied in the free energy function (75). In the following we restrict the generality of that function by assuming a simple dependence on the electric field, viz.

$$\rho\psi = \rho\hat{\psi}(T, \rho_1, \rho_2, \cdots, \rho_N) - \frac{1}{2}\varepsilon_0\chi\boldsymbol{E}^2, \tag{82}$$

with a constant susceptibility χ. This law implies a simple polarization model where the polarization is proportional to the electric field because from (76)$_2$ we obtain $\boldsymbol{P} = \varepsilon_0\chi\boldsymbol{E}$. The constancy of χ implies that the combination $\rho\hat{\psi} - \sum_{\alpha=1}^{N}\rho_\alpha\mu_\alpha$ does not depend on the electric field. Therefore the quantity

$$p = -\rho\hat{\psi} + \sum_{\alpha=1}^{N}\rho_\alpha\mu_\alpha \tag{83}$$

is called the material part of the elastic pressure and (83) is called the Gibbs-Duhem equation.

Concerning the density dependence of the free energy function we still remain in the general setting.

Constitutive model on S. As in the bulk, the interfacial variables are not the only quantities in the equations of balance. There are further quantities that must be given by thermodynamically consistent constitutive equations. Our interfacial constitutive model describes a reacting polarizable mixture under isothermal conditions.

The corresponding constitutive model starts from an interfacial free energy density function of the general form

$$\underset{s}{\rho}\underset{s}{\psi} = \underset{s}{\rho}\underset{s}{\psi}(T, \underset{s}{\rho_1}, \underset{s}{\rho_2}, \cdots, \underset{s}{\rho_N}). \tag{84}$$

In contrast to the bulk, see (75), the electric field does not appear in (84). This reflects our assumption that interfacial polarization charges are exclusively induced due to different polarizations of the bulk phases as it is described by the jump condition (67).

The exploitation of the general function (84) by the axioms of the 2nd law of thermodynamics for interfaces implies the following constitutive model, [Mül85, Dre03, DG13]:

1. Interfacial chemical potentials:

$$\underset{s}{\mu_\alpha} = \frac{\partial \underset{s}{\rho}\underset{s}{\psi}}{\partial \underset{s}{\rho_\alpha}} \qquad \alpha = 1, \ldots, N\,. \tag{85}$$

2. Representation and sign of the interfacial entropy production:

$$\underset{s}{\xi} = -\frac{1}{T}\sum_{\alpha=1}^{N}\left[\!\left[\left(\underset{s}{\mu_\alpha} - \mu_\alpha - \tfrac{1}{2}\big((\boldsymbol{v} - \boldsymbol{w})\big)^2 - \tfrac{1}{\rho}\boldsymbol{\nu}^T \cdot \boldsymbol{\sigma}^{NS} \cdot \boldsymbol{\nu}\right)\dot{m}_\alpha\right]\!\right]$$

$$-\frac{1}{T}\sum_{i=1}^{M_S}\left(\sum_{\alpha=1}^{N} \underset{s}{m_\alpha}\underset{s}{\gamma_\alpha^i}\underset{s}{\mu_\alpha}\right)\left(\underset{s}{R_f^i} - \underset{s}{R_b^i}\right) \geq 0\,. \tag{86}$$

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where the normal mass flux across S is abbreviated as $\dot{m}_\alpha = \big(\rho_\alpha(\boldsymbol{v} - \boldsymbol{w}) + \boldsymbol{J}_\alpha\big) \cdot \boldsymbol{\nu}$. The interfacial entropy production $\underset{s}{\xi}$ must be non negative for every solution of the balance equations. Interfacial equilibrium is a solution of the balance equations with $\underset{s}{\xi} = 0$.

Because the isothermal interface S is not equipped with viscous flow, there are only two dissipative mechanisms, namely adsorption/desorption of species on the interface S and chemical reaction on S. Moreover, we assume that on S the adsorption reactions are much faster established than chemical reaction on S. As a good approximation we then have at any time the two conditions

$$\underset{s}{\mu_\alpha} - \mu_\alpha^\pm - \frac{1}{2}\big((\boldsymbol{v} - \boldsymbol{w}) \cdot \boldsymbol{\nu}\big)^2 - \frac{1}{\rho^\pm}\boldsymbol{\nu}^T \cdot \boldsymbol{\sigma}^{NS,\pm} \cdot \boldsymbol{\nu} = 0 \, . \tag{87}$$

The general case with dynamical adsorption reactions where the left side of (87) is not zero but related to the corresponding mass fluxes $\dot{m}_\alpha^\pm$ is treated in [Dre03, DG13].

The chemical contribution to the interfacial entropy production (86) is formally the same as in the bulk. Hence in analogy to (81) we conclude that

$$\frac{\underset{s}{R_f^i}}{\underset{s}{R_b^i}} = \exp\left(-\frac{\underset{s}{A^i}}{kT}\sum_{\alpha=1}^N \underset{s}{\gamma_\alpha} m_\alpha \underset{s}{\mu_\alpha}\right) \quad \text{with} \quad \underset{s}{A^i} \geq 0 \, . \tag{88}$$

is compatible with a non-negative entropy inequality. The quantities $\underset{s}{A^i}$ are phenomenological coefficients.

5 Derivation of the leading order problem

It is well known that the adjacent regions of an interface between two different electrochemical mixtures form thin layers, where the electric potential and the particle densities exhibit variations with steep gradients. The method of formal asymptotic analysis is well established in electrochemistry to analyze the boundary layers at an interface, [BCB05, New65]. In [DGM13] we used this method to describe the electrochemical phenomena within the layers. However, in that paper we only considered equilibria and moreover we ignored chemical reactions. In the current study we remove these limitations and apply the method of asymptotic analysis to the model of Section 4.

In preparation of the formal asymptotic analysis it is necessary to transform the equations into a dimensionless quantities and to identify the small parameters of the system.

Dimensionless quantities. To this end we introduce scaling constants L_0, t_0, n_0, R_0, p_0, M_0, m_0 and ν_0 that are related to characteristic length, time, particle density, reaction rate, pressure, mobility, molecular weight and viscosity. With the Boltzmann constant k and the temperature T

of the isothermal system we substitute in the bulk regions $\Omega^{\pm}$:

$$
\begin{aligned}
\boldsymbol{x} &\rightarrow L_0\boldsymbol{x} \,, & t &\rightarrow t_0t \,, & \boldsymbol{v} &\rightarrow \tfrac{L_0}{t_0}\boldsymbol{v} \,, \\
m_\alpha &\rightarrow m_0m_\alpha \,, & n_\alpha &\rightarrow n_0n_\alpha \,, & \rho &\rightarrow n_0m_0\rho \,, \\
\boldsymbol{\sigma} &\rightarrow \tfrac{\nu_0}{t_0}\boldsymbol{\sigma} \,, & \nu &\rightarrow \nu_0\nu \,, & \eta &\rightarrow \nu_0\eta \,, \\
\rho\psi &\rightarrow n_0kT\rho\psi \,, & \mu_\alpha &\rightarrow \tfrac{kT}{m_\alpha}\mu_\alpha \,, & \boldsymbol{\Sigma} &\rightarrow p_0\boldsymbol{\Sigma} \,, \\
\boldsymbol{E} &\rightarrow \tfrac{kT}{e_0L_0}\boldsymbol{E} \,, & \varphi &\rightarrow \tfrac{kT}{e_0}\varphi \,, & \boldsymbol{P} &\rightarrow \tfrac{\varepsilon_0kT}{e_0L_0}\boldsymbol{P} \,, \\
M_{\alpha\beta} &\rightarrow M_0M_{\alpha\beta} \,, & R^i_{f/b} &\rightarrow R_0R^i_{f/b} \,, & n^{\mathrm{F}} &\rightarrow n_0e_0n^{\mathrm{F}} \,, \\
\boldsymbol{j}^{\mathrm{e}} &\rightarrow \tfrac{e_0kTn_0M_0}{L_0}\boldsymbol{j}^{\mathrm{e}} \,, & \boldsymbol{J}_\alpha &\rightarrow \tfrac{m_\alpha kTn_0M_0}{L_0}\boldsymbol{J}_\alpha \,.
\end{aligned}
\tag{89}
$$

On the interface S we introduce a dimensionless constant δ to relate bulk and corresponding surface quantities to each other. Then, we substitute:

$$
\begin{aligned}
w &\rightarrow \tfrac{L_0}{t_0}w \,, & \underset{s}{\mu}_\alpha &\rightarrow \tfrac{kT}{m_\alpha}\underset{s}{\mu}_\alpha, \\
\underset{s}{n}_\alpha &\rightarrow \delta L_0n_0\underset{s}{n}_\alpha \,, & \underset{s}{\rho} &\rightarrow \delta L_0n_0m_0\underset{s}{\rho} \,, \\
\underset{s}{n}^{\mathrm{F/P}} &\rightarrow \delta L_0n_0e_0\underset{s}{n}^{\mathrm{F/P}} & \underset{s}{R}^i_{f/b} &\rightarrow \delta L_0R_0\underset{s}{R}^i_{f/b} \,, & \underset{s}{\rho}\underset{s}{\psi} &\rightarrow \delta L_0n_0kT\underset{s}{\rho}\underset{s}{\psi} \,.
\end{aligned}
\tag{90}
$$

The scalings (89) generate the following six characteristic dimensionless numbers:

$$
\begin{aligned}
\lambda^2 &= \frac{kT\varepsilon_0}{e_0^2n_0L_0^2} \,, & a^2 &= \frac{p_0}{n_0kT} \,, & \kappa^2 &= \frac{kTt_0M_0}{L_0^2} \,, \\
\tau^2 &= \frac{m_0L_0^2}{t_0^2kT} \,, & \zeta^2 &= \frac{\nu_0}{t_0n_0kT} \,, & \omega^2 &= \frac{t_0R_0}{n_0} \,.
\end{aligned}
\tag{91}
$$

Summary of model equations in dimensionless form. From now on we study for simplicity the one-dimensional version of the model. We agree that space dependent functions exclusively depend on the coordinate $x_1 = x$ which is normal to the interface S. After introduction of the dimensionless numbers in the model equations of section 4 we are then lead to the following model. In the subdomains $\Omega^{\pm}$ we have

$$
\partial_t n_\alpha + \partial_x(n_\alpha v) + \kappa^2\partial_x J_\alpha = \omega^2\sum_{i=1}^{M}\gamma^i_\alpha R^i \qquad \alpha = 1,\ldots,N \,,
\tag{92a}
$$

$$
\tau^2\partial_t(\rho v) + \partial_x(\tau^2\rho v^2 - a^2\Sigma) = 0 \,,
\tag{92b}
$$

$$
-\lambda^2(1 + \chi)\partial_{xx}\varphi = n^{\mathrm{F}},
\tag{92c}
$$

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where the constitutive equations read in dimensionless form

$$J_\alpha = -\sum_{\beta=1}^{N-1} M_{\alpha\beta}\frac{\partial}{\partial x}\left(\mu_\beta - \frac{m_\beta}{m_N}\mu_N + \left(z_\beta - z_N\frac{m_\beta}{m_N}\right)\varphi\right), \quad \alpha = 1,\cdots,N-1, \tag{93a}$$

$$J_N = -\sum_{\alpha=1}^{N-1} J_\alpha , \tag{93b}$$

$$a^2\Sigma = \rho\hat{\psi} - \sum_{\alpha=1}^{N} n_\alpha\mu_\alpha + \zeta^2(\nu+2\eta)\partial_x v + \lambda^2\tfrac{1}{2}(1+\chi)(\partial_x\varphi)^2 , \tag{93c}$$

$$R^i = (R_f^i - R_b^i) \quad \text{with} \quad \frac{R_f^i}{R_b^i} = \exp\left(-A^i\sum_{\alpha=1}^{N}\gamma_\alpha^i\mu_\alpha\right). \tag{93d}$$

The dimensionless jump conditions on the interface S read

$$\delta\partial_t n_\alpha + [\![n_\alpha(v-w)]\!] + \kappa^2[\![J_\alpha]\!] = \delta\omega^2\sum_{i=1}^{M_S}\gamma_{\alpha}^i R^i_{\ s} \quad \alpha = 1,\cdots,N , \tag{94a}$$

$$\delta\tau^2\partial_t(\rho w) + \tau^2[\![\rho v(v-w)]\!] - a^2[\![\Sigma]\!] = 0 , \tag{94b}$$

$$[\![\varphi]\!] = 0 , \tag{94c}$$

$$\lambda^2[\![(1+\chi)E]\!] = \delta n^{\mathrm{F}}_{\ s} , \tag{94d}$$

$$\frac{1}{m_\alpha}\left(\mu_\alpha - \mu_\alpha^\pm\right) - \frac{\tau^2}{2}(v^\pm - w)^2 - \frac{\zeta^2}{\rho^\pm}(\nu+2\eta)(\partial_x v)^\pm = 0 , \tag{94e}$$

which are supplemented by the dimensionless constitutive equations for surface reaction rates

$$R^i_{\ s} = (R^i_{\ sf} - R^i_{\ sb}) \quad \text{with} \quad \frac{R^i_{\ sf}}{R^i_{\ sb}} = \exp\left(-A^i_{\ s}\sum_{\alpha=1}^{N}\gamma_\alpha\mu_\alpha_{\ s\ s}\right). \tag{95}$$

Characteristic numbers. In order to determine the six dimensionless numbers (91) appearing in the model equations we fix the following quantities:

$$\begin{aligned}
L_0 &= 10^{-2}\,\mathrm{m}, & t_0 &= 10\,\mathrm{s}, & n_0 &= 10^{28}\,\tfrac{1}{\mathrm{m}^3}, \\
m_0 &= 1.66\times10^{-27}\,\mathrm{kg}, & R_0 &= 10^{23}\,\tfrac{1}{\mathrm{m}^3\mathrm{s}}, & M_0 &= 10^{12}\,\tfrac{\mathrm{s}}{\mathrm{kg}}, \\
\nu_0 &= 8.91\times10^{-4}\,\tfrac{\mathrm{kg}}{\mathrm{m\,s}}, & T &= 298.15\,\mathrm{K}, & p_0 &= 10^5\,\mathrm{Pa}.
\end{aligned} \tag{96}$$

Then the dimensionless numbers assume the values

$$\begin{aligned}
\lambda &= 1.19\times10^{-9}, & a &= 4.93\times10^{-2}, & \kappa &= 2.03\times10^{-2}, \\
\tau &= 6.35\times10^{-7}, & \zeta &= 1.47\times10^{-6}, & \omega &= 1.00\times10^{-2}.
\end{aligned} \tag{97}$$

We observe that the parameter λ, τ and ζ are much smaller than a, κ and ω. We already know from [DGM13] that λ generates the boundary layers, and because we prefer to deal with a single smallness parameter only, we set

$$\tau = \lambda\bar{\tau} \quad \text{and} \quad \zeta = \lambda\bar{\zeta} \, . \tag{98}$$

Finally we use a surface parameter δ with the property

$$\delta \gg \lambda. \tag{99}$$

5.1 Method of asymptotic analysis

The main idea of the formal asymptotic analysis is to assume for a generic function u^λ the existence of two different expansions. The *outer expansion* approximates u^λ in the bulk of the domain without the boundary layers. For the *inner expansion* to approximate u^λ inside the boundary layer, a rescaled space variable is used that is related to the width λ of the layer. Then the expansions are entered into the equations and terms related to the same powers of λ are connected with matching conditions. A detailed description of the method of asymptotic analysis can be found in [CF88]. Using the equations in the layers and the original interface conditions at the interface S it is possible to formulate new jump conditions that model the behavior of physical quantities across boundary layers including the interface S.

Expansions of outer and inner solutions. We denote the solutions of (92a)-(95) by φ^λ, n_α^λ, $\boldsymbol{v}^\lambda$, n_α^λ and x_S^λ, and we assume that these solutions can be expanded into power series with respect to λ. According to [DGM13] we expect boundary layers where the solutions have very steep gradients.

In the bulk regions of $\Omega^\pm$ we approximate a generic function u^λ by

$$u^\lambda(t, x) = u^{(0)}(t, x) + u^{(1)}(t, x)\lambda + \mathcal{O}(\lambda^2) \, . \tag{100}$$

Within the boundary layers we introduce a new coordinate z such that for $x \in \Omega^\pm$

$$z = \frac{x - x_S^\lambda}{\lambda} \, . \tag{101}$$

We define inner solutions $\widetilde{u}^\lambda$ by

$$\widetilde{u}^\lambda(t, z) = u^\lambda(t, x_S^\lambda + \lambda z) \, . \tag{102}$$

As in the bulk regions we likewise assume the existence of power series of the inner solutions,

$$\widetilde{u}^\lambda(t, z) = \widetilde{u}^{(0)}(t, z) + \widetilde{u}^{(1)}(t, z)\lambda + \mathcal{O}(\lambda^2) \, . \tag{103}$$

Moreover we assume that also the surface densities n_α^λ and the parametrization x_S^λ of S can be expanded,

$$n_\alpha^\lambda = n_\alpha^{(0)} + n_\alpha^{(1)}\lambda + \mathcal{O}(\lambda^2) \, , \tag{104}$$

$$x_S^\lambda = x_S^{(0)} + x_S^{(1)}\lambda + \mathcal{O}(\lambda^2) \, . \tag{105}$$

Matching conditions. The relation (102) between inner and outer solutions and the expansions imply so called matching conditions. In [CF88, Peg89] the matching conditions are introduced as asymptotic expansions that are formally achieved by (i) inserting the corresponding expansions into the left and right hand sides of (102) and (ii) a subsequent comparison of powers of λ. The result is

$$\widetilde{u}^{(0)}(t,z) \overset{z\to\pm\infty}{\to} u^{(0),\pm}(t,x_S^{(0)}) \,, \tag{106a}$$

$$\partial_z \widetilde{u}^{(0)}(t,z) \overset{z\to\pm\infty}{\to} 0 \,, \tag{106b}$$

$$\partial_{zz} \widetilde{u}^{(0)}(t,z) \overset{z\to\pm\infty}{\to} 0 \,, \tag{106c}$$

$$\widetilde{u}^{(1)}(t,z) - \partial_x u^{(0),\pm}(t,x_S^{(0)})(z + x_S^{(1)}) \overset{z\to\pm\infty}{\to} u^{(1),\pm}(t,x_S^{(0)}) \,, \tag{106d}$$

$$\partial_z \widetilde{u}^{(1)}(t,z) \overset{z\to\pm\infty}{\to} \partial_x u^{(0),\pm}(t,x_S^{(0)}) \,, \tag{106e}$$

$$\widetilde{u}^{(2)}(t,z) - \partial_x u^{(1),\pm}(t,x_S^{(0)})(z + x_S^{(1)}) \overset{z\to\pm\infty}{\to} u^{(2),\pm}(t,x_S^{(0)}) \,. \tag{106f}$$

The bulk equations in the leading orders. The equations (92a)–(92c) yield in the leading order

$$\partial_t \rho^{(0)} + \partial_x(\rho^{(0)} v^{(0)}) = 0 \,, \tag{107a}$$

$$\partial_t n_\alpha^{(0)} + \partial_x(n_\alpha^{(0)} v^{(0)}) + \kappa^2 \partial_x J_\alpha^{(0)} = \omega^2 \sum_{i=1}^M \gamma_\alpha^i R^{i,(0)} \quad \text{for} \quad \alpha \in \{1,\ldots,N-1\} \,, \tag{107b}$$

$$\partial_x \Sigma^{(0)} = 0 \,, \tag{107c}$$

$$0 = n^{F,(0)} \,. \tag{107d}$$

The mass fluxes and the total stress tensor have the following expansions:

$$J_\alpha^{(0)} = -\sum_{\beta=1}^{N-1} M_{\alpha\beta} \frac{\partial}{\partial x}\left(\left(\mu_\beta^{(0)} - \frac{m_\beta}{m_N}\mu_N^{(0)}\right) + \left(z_\beta - z_N \frac{m_\beta}{m_N}\right)\varphi^{(0)}\right)$$

$$\alpha = 1, \cdots, N-1 \,, \tag{108a}$$

$$a^2 \Sigma^{(0)} = p^{(0)} \,. \tag{108b}$$

The leading order of the reaction rates is represented by

$$R^{i,(0)} = (R_f^{i,(0)} - R_b^{i,(0)}) \qquad \text{with} \qquad \frac{R_f^{i,(0)}}{R_b^{i,(0)}} = \exp\left(-A^i \sum_{\alpha=1}^N \gamma_\alpha^i \mu_\alpha^{(0)}\right) \,. \tag{109}$$

The inner equations in the leading order. The relevant equations of the boundary layers result from the equations (92a)–(92c) in the inner coordinate (101). In the leading order we obtain

$$\partial_z\big(\widetilde{\rho}^{(0)}(\widetilde{v}^{(0)} - w^{(0)})\big) = 0 \tag{110a}$$

$$\partial_z\widetilde{J}_\alpha^{(-1)} = 0 \qquad \alpha = 1,\ldots,N-1 , \tag{110b}$$

$$\partial_z\widetilde{\Sigma}^{(0)} = 0 , \tag{110c}$$

$$-(1+\chi)\partial_{zz}\widetilde{\varphi}^{(0)} = \widetilde{n}^{\mathrm{F},(0)} , \tag{110d}$$

with the corresponding constitutive laws

$$\widetilde{J}_\alpha^{(-1)} = -\sum_{\beta=1}^{N-1} M_{\alpha\beta}\frac{\partial}{\partial z}\left(\left(\widetilde{\mu}_\beta^{(0)} - \frac{m_\beta}{m_N}\widetilde{\mu}_N^{(0)}\right) + \left(z_\beta - z_N\frac{m_\beta}{m_N}\right)\widetilde{\varphi}^{(0)}\right)$$
$$\alpha = 1,\cdots,N-1 \tag{111a}$$

$$a^2\widetilde{\Sigma}^{(0)} = \widetilde{p}^{(0)} + \tfrac{1}{2}(1+\chi)(\partial_z\widetilde{\varphi}^{(0)})^2 . \tag{111b}$$

These equations are exploited as follows. At first we combine the momentum equation (110c), the Poisson equation (111b) and the constitutive law (111b) with the Gibbs-Duhem equation (83) to obtain the important identity

$$0 = -\sum_{\alpha=1}^N \widetilde{n}_\alpha^{(0)}\partial_z\left(\widetilde{\mu}_\alpha^{(0)} + z_\alpha\widetilde{\varphi}^{(0)}\right) \tag{112}$$

Next the matching conditions (106a) and (106b) are used to derive from (110b) with (111a) the identities

$$0 = \frac{\partial}{\partial z}\left(\widetilde{\mu}_\alpha^{(0)} + z_\alpha\widetilde{\varphi}^{(0)}\right) - \frac{m_N}{m_\alpha}\frac{\partial}{\partial z}\left(\widetilde{\mu}_N^{(0)} + z_N\widetilde{\varphi}^{(0)}\right) \qquad \alpha = 1,\ldots,N-1 . \tag{113}$$

We immediately observe that the equations (112) and (113) imply the constancy of the electrochemical potentials $\widetilde{\mu}_\alpha^{(0)} + z_\alpha\widetilde{\varphi}^{(0)}$ within the boundary layers. The integration constants are determined by the matching conditions (106a) and we obtain

$$\widetilde{\mu}_\alpha^{(0)} + z_\alpha\widetilde{\varphi}^{(0)} = \mu_\alpha^{(0),\pm} + z_\alpha\varphi^{(0),\pm} \qquad \alpha \in \{1,\ldots,N\} . \tag{114}$$

We have already used the constancy of the leading order of the total stress. The corresponding integration constant follows likewise from the matching conditions (106a),

$$\widetilde{\Sigma}^{(0)} = \Sigma^{(0),\pm} . \tag{115}$$

Finally we derive from (110a) by means of (106a) and (106b) the conservation law of mass within the boundary layers. It reads

$$\widetilde{\rho}^{(0)}(\widetilde{v}^{(0)} - w^{(0)}) = \rho^{(0),\pm}(v^{(0),\pm} - w^{(0)}) . \tag{116}$$

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The inner equations in higher orders. Further useful relations within the boundary layers are achieved when we consider higher orders of the equations (92a) and (92b).

At first we study the equation (92a) in the order λ^{-1}. Application of the matching conditions yields after some simple but cumbersome calculations the relation

$$\widetilde{n}_\alpha^{(0)}\big(\widetilde{v}^{(0)} - w^{(0)}\big) + \kappa^2 \widetilde{J}_\alpha^{(0)} = n_\alpha^{(0),\pm}\big(v^{(0),\pm} - w^{(0)}\big) + \kappa^2 J_\alpha^{(0),\pm} \tag{117}$$

Its detailed derivation is not of value here. The interested reader is referred to [DG13, DGK13] where the necessary steps can be found. Moreover, the explicit constitutive function that relates inner flux $\widetilde{J}_\alpha^{(0)}$ to the variables is not need in further development of the theory. It is therefore omitted here.

Leading order jump conditions at the interface S. Finally we use the asymptotic expansions (104) and (105) to achieve from the jump conditions (94a)–(95) the following results in the leading order:

$$\delta\partial_t \underset{s}{n_\alpha^{(0)}} = \delta\omega^2 \sum_{i=1}^{M_S} \underset{s}{\gamma_\alpha^i} \underset{s}{R^{i,(0)}} - [\![\widetilde{n}_\alpha^{(0)}(\widetilde{v}^{(0)} - w^{(0)})]\!] - \kappa^2[\![\widetilde{J}_\alpha^{(0)}]\!] \qquad \alpha = 1, \cdots, N , \tag{118a}$$

$$0 = [\![\widetilde{\Sigma}^{(0)}]\!] , \tag{118b}$$

$$0 = [\![\widetilde{\varphi}^{(0)}]\!] , \tag{118c}$$

$$0 = \underset{s}{n^{\mathrm{F},(0)}} , \tag{118d}$$

$$0 = \underset{s}{\mu_\alpha^{(0)}} - \widetilde{\mu}_\alpha^{(0),\pm} , \tag{118e}$$

and the constitutive equation for interfacial reaction rate is given by

$$\underset{s}{R^{i,(0)}} = \big(\underset{s}{R_f^{i,(0)}} - \underset{s}{R_b^{i,(0)}}\big) \qquad \text{with} \qquad \frac{\underset{s}{R_f^{i,(0)}}}{\underset{s}{R_b^{i,(0)}}} = \exp\Big(-\underset{s}{A^i} \sum_{\alpha=1}^N \underset{s}{\gamma_\alpha^i} \underset{s}{\mu_\alpha^{(0)}}\Big) . \tag{119}$$

Interface conditions at the new interface I. The original jump conditions (118a)–(119) across the interface S and the inner equations (110a)–(117) for the boundary layers form the basis for the new jump conditions across the interface I from Figure 1$_{\mathrm{right}}$.

To this end we introduce new jump brackets. For a generic function u of the regions $\Omega^\pm$ we define

$$u^{(0)}|_I^\pm = \lim_{z \to \pm\infty} \widetilde{u}^{(0)} = \lim_{x \to I^\pm} u^{(0)} \qquad \text{and} \qquad [\![u^{(0)}]\!] = u^{(0)}|_I^+ - u^{(0)}|_I^- . \tag{120}$$

In an analogous manner to (2)$_2$ we agree on the following. If the function u is only defined either in Ω^+ or in Ω^-, we set the corresponding value in (120)$_2$ equal to zero.

It is important to note: The new jump bracket $[\![u^{(0)}]\!]$ represents the jump of a quantity u across the double layer while the original bracket $[\![u]\!]$ is a jump across the actual interface S.

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There are four different kinds of interface conditions at the new interface I. At first we have the jump conditions arising from the balance equations for mass and momentum, (118a)–(118b). By means of the inner equations (115)–(117) we obtain

$$\delta \partial_t \underset{s}{n}_\alpha^{(0)} = \delta \omega^2 \sum_{i=1}^{M_S} \underset{s}{\gamma}_\alpha^i \underset{s}{R}^{i,(0)} - [\![n_\alpha^{(0)}(v^{(0)} - w^{(0)})]\!] - \kappa^2 [\![J_\alpha^{(0)}]\!] \quad \text{for } \alpha \in \{1, \cdots, N\} \,,$$

(121a)

$$0 = [\![\Sigma^{(0)}]\!] \,,$$

(121b)

The following conditions require the introduction of three groups of constituents, $\mathcal{M}_+$, $\mathcal{M}_-$ and $\mathcal{M}_S$, defined in section 2.1. Then, due to the continuity of the electrical potential across S, (69), the inner equations (118e) and (114) can be written as

$$\underset{s}{\mu}_\alpha^{(0)} + z_\alpha \underset{s}{\varphi}^{(0)} = \mu_\alpha^{(0),\pm} + z_\alpha \varphi^{(0),\pm} \qquad \text{for} \qquad \alpha \in \mathcal{M}_+, \mathcal{M}_- \,.$$

(122)

The third kind of conditions concerns the interfacial reaction rates (119). As before we use (114) and (118e) to rewrite the exponential term in $(119)_2$. Furthermore we take into account that chemical reactions conserve the electric charge, i.e. $\sum_{\alpha=1}^N \underset{s}{\gamma}_\alpha^i z_\alpha = 0$, to obtain $\underset{s}{R}^{i,(0)} = (\underset{s}{R}_f^{i,(0)} - \underset{s}{R}_b^{i,(0)})$ with

$$\frac{\underset{s}{R}_f^i}{\underset{s}{R}_b^i} = \exp\left(-\underset{s}{A}^i \Big(\sum_{\alpha \in \mathcal{M}_S} \underset{s}{\gamma}_\alpha (\underset{s}{\mu}_\alpha^{(0)} + z_\alpha \underset{s}{\varphi}^{(0)}) + \sum_{\alpha \in \mathcal{M}_- \cup \mathcal{M}_+} \underset{s}{\gamma}_\alpha (\mu_\alpha^{(0),\pm} + z_\alpha \varphi^{(0),\pm}) \Big) \right) \,.$$

(123)

Hence the reaction rates on the interface S depend on the bulk values of potentials at the boundaries of the layers.

Finally equation (118d) yields that the total interfacial charge density is zero,

$$\underset{s}{n}^{\mathrm{F},(0)} = 0 \,.$$

(124)

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