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A new perspective on the electron transfer: Recovering the Butler-Volmer equation in non-equilibrium thermodynamics

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Electron transfer reactions are commonly described by the phenomenological Butler-Volmer equation which has its origin in kinetic theories. The Butler-Volmer equation relates interfacial reaction rates to bulk quantities like the electrostatic potential and electrolyte concentrations. Although the general structure of the equation is well accepted, for modern electrochemical systems like batteries and fuel cells there is still intensive discussion about the specific dependencies of the coefficients. A general guideline for the derivation of Butler-Volmer type equations is missing in the literature.

We derive very general relations of Butler-Volmer structure which are based on a rigorous non-equilibrium thermodynamic model and allow for adaption to a wide variety of electrochemical systems. We discuss the application of the new thermodynamic approach to different scenarios like the classical electron transfer reactions at metal electrodes and the intercalation process in lithium-iron-phosphate electrodes. Furthermore we show that under appropriate conditions also adsorption processes can lead to Butler-Volmer equations. We illustrate the application of our theory by a strongly simplified example of electroplating.

1 Introduction

Energy conversion in batteries, fuel-cells or redox-flow-cells requires electrochemical surface reactions to take place at the contact between electrodes and electrolyte. In electrolysis or electroplating, on the other hand, electrical energy is used to drive a chemical reaction. In all these applications, it is observed that the surface reaction rate $\underset{s}{R}$, or equivalently the electric current density j^{e}, is related to a potential difference at the interface, the *surface overpotential* η_S. The most simple relation of this kind is the empirical Tafel-equation[1]

$$\eta_S = a + b\,\log(j^{\mathrm{e}}), \tag{1}$$

where the coefficient b is called the Tafel-slope and a is a further phenomenological coefficient. A more general relation that accounts for simultaneous anodic (oxidation) reaction and cathodic (reduction) reaction on the same electrode surface is the Butler-Volmer equation[2–4],

$$j^{\mathrm{e}} = i^0_{\mathscr{A}} \exp\left(\frac{\alpha_{\mathscr{A}}\ e_0}{kT}\eta_S\right) - i^0_{\mathscr{C}} \exp\left(-\frac{\alpha_{\mathscr{C}}\ e_0}{kT}\eta_S\right). \tag{2}$$

Herein $i^0_{\mathscr{A}/\mathscr{C}}$ are called anodic and cathodic exchange currents, respectively, which can be general functions of the temperature T and the concentrations of the different chemical species. The transfer coefficients $\alpha_{\mathscr{A}}$ and $\alpha_{\mathscr{C}}$ are considered as phenomenological coefficients. The Boltzmann constant is denoted by k and e_0 is the elementary charge. If the exchange currents are constant, the Butler-Volmer equation predicts constant Tafel-slope at larger overpotentials. Such a behavior can in fact be observed, most pronounced in the case of the hydrogen reduction reaction which shows constant Tafel slopes over a range of several decades of the current[5]. In other reactions a stronger dependence of the Tafel slope on potential and temperature can be observed. These deviations from the linear Tafel behavior are explained within the Marcus-Hush theories[6–10]. We do not consider these theories here in detail and will only briefly remark some relations to our results in the concluding discussion in Sect. 7.

The Butler-Volmer equation is considered to be "the central equation in phenomenological electrode kinetics" (Ref. BRGA01, p. 1053) All the more it is surprising to find in the literature differences in the way the potentials are defined, cf. Ref.[4] vs. Ref.[11] or Ref.[12], and how the exchange currents depend on the concentrations, cf. Ref[4] vs. Ref.[13]. Originally, the derivation of the Butler-Volmer equation is based on kinetic theory[14,15]. Recently some approaches have been made to give the Butler-Volmer equation a thermodynamic justification. A thermodynamic definition

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of an overpotential as a surface excess quantity was introduced by Bedeaux and Kjelstrup[16]. Later on an attempt was taken to give a justification of the Butler-Volmer equation within a mesoscopic thermodynamic theory[17]. Recently a Butler-Volmer equation for oxidation reaction in fuel cells was derived within the GENERIC framework[18], and in the context of phase separating electrode materials, a Butler-Volmer equation in non-equilibrium thermodynamics was derived[19].

In this paper we derive a general Butler-Volmer of the form (2) which is not restricted to a specific application scenario. The derivation is based on a thermodynamic consistent model for electrochemical systems in non-equilibrium and follows from rational arguments. By this procedure we want to clarify characterization of the different quantities in the Butler-Volmer equation and the structure of functional dependencies between them. For the derivation of (2) it is important to bear in mind:

1. The definition of η_S is not evident from modeling based on non-equilibrium thermodynamics where the set of thermodynamic variables contains the electric field $\boldsymbol{E} = -\nabla\varphi$ but not a potential φ itself or some potential difference.
2. The interfacial Maxwell equations require that the electric potential φ is continuous at an interface. Therefore no natural potential difference exists, which can be used to define an overpotential.
3. The generality of $i^0_{\mathscr{A}/\mathscr{C}}$ is restricted by the 2nd law of thermodynamics. In consequence, the forward and backward reaction can not be modeled independently.
4. In order to have a general form of the Butler-Volmer equation that does not depend on a specific experimental setup, the functions have to be expressed in terms of the chemical potential instead of concentrations or particle densities. Usually Butler-Volmer equations seem to implicitly assume that materials are modeled as ideal mixtures (of gases).

The underlying model for electrochemical systems in thermodynamic non-equilibrium was formulated in Ref.[20]. We call this the *complete model* since the diffuse charge layers are spatially resolved. The constitutive laws for the interfacial reaction rates are not of Butler-Volmer type. Under the assumption of appropriate scaling relations, the double layer can asymptotically be considered in equilibrium. This allows the derivation of a locally electroneutral *reduced bulk model* such that all features of the double layer are consistently incorporated into a set of jump conditions at the interfaces[20]. Within this reduced model, we are able to define an overpotential and to recover relations of Butler-Volmer type for the interfacial reaction rates.

Our approach to generalize the Butler-Volmer equation is contrary to those suggested previously. Instead of starting from standard Butler-Volmer equation and then using a-priori assumptions about a specific electrochemical system with its particular double-layer structure to derive new Butler-Volmer equations, we start from a general thermodynamically consistent model and can derive a general Butler-Volmer equation which under appropriate assumptions reduces to the classical variant.

Outline. After the introduction of the notation in the following section, we recapitulate in Section 3 the reduced bulk model of Ref.[20]. In Section 4, we derive a general Butler-Volmer equation and then discuss in Section 5 its application to different relevant scenarios. For illustration of the Butler-Volmer equation and the interaction with the bulk transport, we consider the example of copper deposition and dissolution in Section 6. Finally, in Section 7, we discuss the range of validity of the underlying assumptions, compare our results with the literature and discuss the role of the double layer structure.

2 Description of reacting mixtures

Here we introduce the notation for the description of reacting mixtures in subdomains separated by planar electrochemical interfaces. For simplicity we consider a planar situation where two one-dimensional regions $\Omega^\pm \subseteq \mathbb{R}$ are separated by an interface $I = \partial\Omega^+ \cap \partial\Omega^-$. For quantities defined in the bulk domains there will often be corresponding quantities on the interface I, indicated by a subscript s.

2.1 Constituents and chemical reactions

In each of the two domains $\Omega^\pm$ and on the interface I we consider a mixture of several constituents. The total number of constituents in the subdomains $\Omega^\pm$ is denoted by $N+1$ and the set of constituents is $\mathscr{M} = \{A_0, A_1, \cdots, A_N\}$, usually indexed by $\alpha \in \{0, 1, \cdots, N\}$. In general we have different constituents in Ω^+ and Ω^-, but for the simplicity of notation this fact will only be indicated if necessary. We assume that each constituent of $\Omega^\pm$ is also present on I, but in addition there may be constituents that are exclusively present on I. Accordingly, the number of constituents on I is $N_S \geq N$ and the set of constituents is $\mathscr{M}_S = \{A_0, A_1, \cdots, A_{N_S}\}$.

A constituent A_α has the (atomic) mass m_α and may be carrier of charge $z_\alpha e_0$, where z_α is the charge number and e_0 is the elementary charge. We may have chemical reactions among the constituents. There are M (bulk) reactions and in addition there may be M_S surface reactions of the general form

$$\mathrm{a_0}^{\mathrm{i}}\mathrm{A_0} + \cdots {}^{+}\mathrm{a_N}^{\mathrm{i}}\mathrm{A_N} \underset{R^i_b}{\overset{R^i_f}{\rightleftharpoons}} \mathrm{b_0}^{\mathrm{i}}\mathrm{A_0} + \cdots {}^{+}\mathrm{b_N}^{\mathrm{i}}\mathrm{A_N} \qquad \text{for } i \in \{1, \cdots, M\}, \tag{3a}$$

$$\underset{s}{\mathrm{a}}{}_0{}^{\mathrm{i}}\mathrm{A_0} + \cdots {}^{+}\underset{s}{\mathrm{a}}{}_{\mathrm{N_S}}{}^{\mathrm{i}}\mathrm{A_{N_S}} \underset{\underset{s}{R^i_b}}{\overset{\underset{s}{R^i_f}}{\rightleftharpoons}} \underset{s}{\mathrm{b}}{}_0{}^{\mathrm{i}}\mathrm{A_0} + \cdots {}^{+}\underset{s}{\mathrm{b}}{}_{\mathrm{N_S}}{}^{\mathrm{i}}\mathrm{A_{N_S}} \qquad \text{for } i \in \{1, \cdots, M_S\}. \tag{3b}$$

The constants a^i_α, b^i_α are positive integers and $\gamma^i_\alpha = \mathrm{b}^i_\alpha - \mathrm{a}^i_\alpha$ denote the stoichiometric coefficients of the reactions. The reaction from left to right is called forward reaction with reaction rate $R^i_f > 0$. The reaction in the reverse direction with rate $R^i_b > 0$ is the backward reaction. The net reaction rate is defined as $R^i = R^i_f - R^i_b$. Since charge and mass have to be conserved by every single reaction in the bulk and on the interface, we have

$$\sum_{\alpha=0}^{N} z_\alpha \gamma_\alpha^j = 0 \qquad \text{and} \qquad \sum_{\alpha=0}^{N_S} z_\alpha \underset{s}{\gamma}{}_\alpha^j = 0\,, \tag{4a}$$

$$\sum_{\alpha=0}^{N} m_\alpha \gamma_\alpha^j = 0 \qquad \text{and} \qquad \sum_{\alpha=0}^{N_S} m_\alpha \underset{s}{\gamma}{}_\alpha^j = 0\,. \tag{4b}$$

2.2 Basic quantities

In each point $x \in \Omega^\pm$ and at any time $t > 0$, the state of the mixture is characterized by the number densities $(n_\alpha)_{\alpha=0,1,\cdots,N}$, the barycentric velocity υ, the temperature T and the electric potential φ. On the interface I the mixture is characterized at any $t \geq 0$ by the number densities of the interfacial constituents, $(\underset{s}{n}{}_\alpha)_{\alpha=0,1,\cdots,N_S}$, the velocity w of the interface, the interfacial temperature $\underset{s}{T}$ and electric potential $\underset{s}{\varphi}$.

Multiplication of the number densities n_α by the mass m_α gives the partial mass densities:

$$\rho_\alpha = m_\alpha n_\alpha \qquad \text{and} \qquad \underset{s}{\rho}{}_\alpha = m_\alpha \underset{s}{n}{}_\alpha\,. \tag{5}$$

For the mixtures, the mass density is defined by

$$\rho = \sum_{\alpha=0}^{N} \rho_\alpha \qquad \text{and} \qquad \underset{s}{\rho} = \sum_{\alpha=0}^{N} \underset{s}{\rho}{}_\alpha\,. \tag{6}$$

The free charge densities are defined as

$$n^{\mathrm{F}} = \sum_{\alpha=0}^{N} z_\alpha e_0 n_\alpha \qquad \text{and} \qquad \underset{s}{n}{}^{\mathrm{F}} = \sum_{\alpha=0}^{N} z_\alpha e_0 \underset{s}{n}{}_\alpha\,. \tag{7}$$

2.3 Jumps at interfaces

We introduce the boundary values and the jump of a generic function $u(t,x)$ in $\Omega^\pm$ at the interface I as

$$u|_I^\pm = \lim_{x\in\Omega^\pm \to I} u \qquad \text{and} \qquad [\![u]\!] = u|_I^+ - u|_I^-\,. \tag{8}$$

In case that the function u is not defined in either Ω^+ or in Ω^-, we set the corresponding value in (8) to zero. The normal ν to the interface I always points from Ω^- to Ω^+. In this one-dimensional setting, we have $\nu = \pm 1$.

3 Reduced bulk model for the thin double layer limit

In a previous work[20] we derived a thermodynamic consistent model, which describes the electrochemical interface between two arbitrary mixtures. This model we call the *complete model*, because it spatially resolves the charge layers in the vicinity of the interface, the *double layer*. The characteristic length scale for the charge layers is

$$\lambda L^{ref} = \sqrt{\frac{kT\varepsilon_0}{e_0^2 n^{ref}}}\,, \tag{9}$$

where k is the Boltzmann constant, n^{ref} denotes a characteristic value for the number density and L^{ref} is a characteristic length of the system. For example, L^{ref} can be the distance between two electrodes and n^{ref} can be related to the anion and cation density in an electrolyte. Then, the length λL^{ref} represents the well known Debye length. For a solution of 0.1mol per liter, $\lambda L^{ref} \approx 1.5 \cdot 10^{-10}$m.

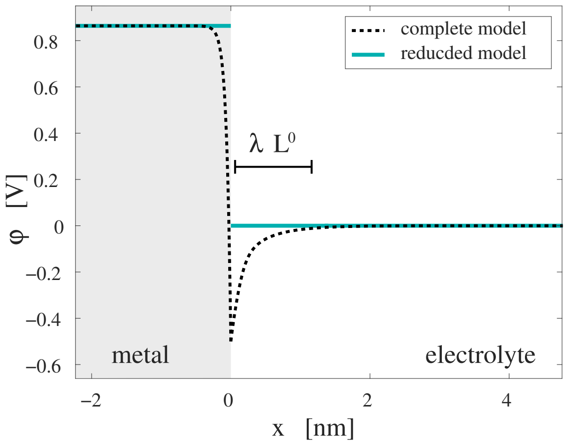

Fig. 1 Electric potential φ at an interface in equilibrium. The complete model resolves the boundary layers and the electric potential is continuous (dashed line). The limit $\lambda \to 0$ yields a reduced model, where the electric potential can be discontinuous at the interface (solid line).

Since often $\lambda \ll 1$, we applied[20] the method of formal asymptotic analysis to derive from the complete model a *reduced bulk model* for the limit $\lambda \to 0$. This reduced model is characterized by simplified bulk equations and new surface equations for the (thin double layer) interface. The Figure 1 shows the electrostatic potential at a metal-electrolyte interface given by the complete model and its approximation by the reduced model.

Model assumptions. The reduced model is derived from the complete model under the following assumptions[20]:

1. The parameter λ satisfies the condition $\lambda \ll 1$.
2. The system under consideration can be treated as a one dimensional problem.
3. The electric field is quasi-static, the magnetic field can be ignored.
4. Quasi-static momentum balance, viscosity in the bulk domains is negligible.
5. Isothermal case, the bulk temperature T and surface temperature $\underset{s}{T}$ are constant and satisfy $\underset{s}{T} = T$.

3.1 Bulk and interface equations

The reduced model relies on universal balance equations which are independent of the specific material. In addition we need constitutive equations for the material at hand. In the isothermal case the universal equations are the balance equations of mass and momentum. In addition there is a local electroneutrality condition that is a consequence of Maxwell's equations in the asymptotic limit $\lambda \to 0$.

Bulk equations. In the bulk $\Omega^{\pm}$, the electric potential φ, the velocity υ and the number densities n_α for $\alpha = 0, 1, \cdots, N$ are determined by

$$\partial_t(m_\alpha n_\alpha) + \partial_x(m_\alpha n_\alpha \upsilon + J_\alpha) = \sum_{i=1}^{M} \gamma_\alpha^i m_\alpha R^i \quad \text{for } \alpha = 0, \ldots, N \ , \tag{10a}$$

$$\partial_x \sigma = 0 \ , \tag{10b}$$

$$\sum_{\alpha=0}^{N} z_\alpha e_0 n_\alpha = 0 \ . \tag{10c}$$

The quantities J_α and σ are the mass flux of the constituent A_α and the Cauchy stress tensor, respectively. Note that there are only N independent diffusion fluxes and the flux J_0 is determined by the side condition $\sum_{\alpha=0}^{N} J_\alpha = 0$.

Interface equations. For the interfacial speed w, the electric potential $\underset{s}{\varphi}$ and the number densities $\underset{s}{n}_\alpha$ for $\alpha = 0, 1, \cdots, N_S$ we have

$$[\![m_\alpha n_\alpha(\upsilon - w)\nu + J_\alpha \nu]\!] = \sum_{i=1}^{M_S} \underset{s}{\gamma}_\alpha m_\alpha \underset{s}{R}^i \ , \qquad \alpha = 0, \cdots, N_S \ , \tag{11a}$$

$$[\![\sigma]\!] = 0 \ , \tag{11b}$$

$$\widetilde{q}^{+} + \underset{s}{n}^{\mathrm{F}} + \widetilde{q}^{-} = 0 \ . \tag{11c}$$

The last equation is the electroneutrality condition of the double layer I, which is a consequence of the Maxwell equations in the asymptotic limit $\lambda \to 0$, cf. Ref.[20]. In general the determination of $\widetilde{q}^{\pm}$ requires the solution of an additional system of equations that spatially resolves the layer structure. Therefore the interface equations (11a)-(11c) are not a closed equation system containing exclusively the variables of the reduced system that were introduced above. But in many relevant cases, e.g. for the interface at a metal electrode, an explicit solution of the interface electroneutrality condition (11c) is not necessary. Since it can be decoupled from the rest of the equation system, and then serves only to determine one remaining surface number density within a post processing step.

3.2 Constitutive equations

The universal equations (10a)–(11b) need to be supplemented by constitutive equations for the mass fluxes J_α, the reaction rates R^i, $\underset{s}{R}^i$ and the Cauchy stress tensor σ. The constitutive equations are restricted by the principle of material objectivity and the 2nd law of thermodynamics.

Free energy and chemical potentials. In order to cover a wide class of different materials we use free energy functions of the general form

$$\rho\psi = \rho\hat{\psi}(T, \rho_0, \ldots, \rho_N) \ , \quad \underset{s}{\rho}\underset{s}{\psi} = \underset{s}{\rho}\underset{s}{\hat{\psi}}(\underset{s}{T}, \underset{s}{\rho}_0, \ldots, \underset{s}{\rho}_{N_S}) \ . \tag{12}$$

Note that due to the asymptotic limit, the free energy functions are independent of the electric field[20]. The chemical potentials of the bulk and surface materials are defined by

$$\mu_\alpha = \frac{\partial \rho\psi}{\partial \rho_\alpha} \qquad \text{and} \qquad \underset{s}{\mu}_\alpha = \frac{\partial \underset{s}{\rho}\underset{s}{\psi}}{\partial \underset{s}{\rho}_\alpha} \ . \tag{13}$$

Constitutive equations in bulk. For the diffusion fluxes, the pressure and the reaction rates we choose the following relations that guarantee the consistency with the 2nd law of thermodynamics particularly the non negativeness of the entropy production

$$J_\alpha = -\sum_{\beta=1}^{N} M_{\alpha\beta} \left(\partial_x \Big(\frac{\mu_\beta - \mu_0}{T} \Big) + \frac{e_0}{T} \Big(\frac{z_\beta}{m_\beta} - \frac{z_0}{m_0} \Big) \partial_x \varphi \right) \ , \quad \alpha = 1, \cdots, N \ , \tag{14a}$$

$$\sigma = -p \qquad \text{with} \qquad p = \rho\hat{\psi} - \sum_{\alpha=0}^{N} m_\alpha n_\alpha \mu_\alpha \ , \tag{14b}$$

$$R^i = R_0^i \left[\exp\Big(-\beta^i \frac{A^i}{kT} \sum_{\alpha=0}^{N} \gamma_\alpha^i m_\alpha \mu_\alpha \Big) - \exp\Big((1-\beta^i) \frac{A^i}{kT} \sum_{\alpha=0}^{N} \gamma_\alpha^i m_\alpha \mu_\alpha \Big) \right] . \tag{14c}$$

Here R_0^i and A^i denote positive phenomenological coefficients and $M_{\alpha\beta}$ define the mobility matrix that must be positive definite. Although not required by the 2nd law of thermodynamics, we assume $0 < \beta^i < 1$. The quantity p is the pressure which is given by the Gibbs-Duhem equation $(14\mathrm{b})_2$. All constitutive equations are related to each other since they share the dependency on the chemical potentials and thus on the free energy $\rho\psi$.

Constitutive equations for the interface. As in the volume, the constitutive relations are all related to the surface free energy $\underset{s}{\rho}\underset{s}{\psi}$ and can not be modeled independently of each other. We choose the following thermodynamic consistent constitutive equations for the reaction rates and the mass fluxes on I

$$\begin{aligned} \underset{s}{R}^i = \underset{s}{R}_0^i \Bigg[& \exp\Big(-\underset{s}{\beta}^i \frac{\underset{s}{A}^i}{kT} \sum_{\alpha=0}^{N_S} \underset{s}{\gamma}_\alpha^i m_\alpha \underset{s}{\mu}_\alpha \Big) \\ & - \exp\Big((1-\underset{s}{\beta}^i) \frac{\underset{s}{A}^i}{kT} \sum_{\alpha=0}^{N_S} \underset{s}{\gamma}_\alpha^i m_\alpha \underset{s}{\mu}_\alpha \Big) \Bigg] \ , \end{aligned} \tag{15a}$$

$$\big(\rho(\upsilon - w)\big)\big|_I^{\pm} = \mp \underset{s}{L}^{\pm} \Big(\big(\mu_0 + \tfrac{z_0 e_0}{m_0}\varphi\big)\big|_I^{\pm} - \big(\underset{s}{\mu}_0 + \tfrac{z_0 e_0}{m_0}\underset{s}{\varphi}\big) \Big) \ , \tag{15b}$$

$$\begin{aligned} \big(\rho_\alpha(\upsilon - w)\nu + J_\alpha \nu\big)\big|_I^{\pm} = \mp \underset{s}{M}_\alpha^{\pm} \Big(& \exp\big(\beta_\alpha^{\pm} \tfrac{m_\alpha}{kT} \underset{s}{B}_\alpha^{\pm} D_\alpha^{\pm}\big) \\ & - \exp\big((\beta_\alpha^{\pm} - 1) \tfrac{m_\alpha}{kT} \underset{s}{B}_\alpha^{\pm} D_\alpha^{\pm}\big) \Big) \ . \end{aligned} \tag{15c}$$

where $\underset{s}{R}_0^i$, $\underset{s}{A}^i$, $\underset{s}{L}^{\pm}$, $\underset{s}{M}_\alpha$ and $\underset{s}{B}_\alpha^{\pm}$ denote positive phenomenological coefficients. The coefficients $\underset{s}{\beta}^i$ and $\beta_\alpha^{\pm}$ are usually called symmetry factors. Although not required by the 2nd law of thermodynamics, we assume $0 < \underset{s}{\beta}^i, \beta_\alpha^{\pm} < 1$. By $D_\alpha^{\pm}$ we denote the driving force for adsorption,

$$D^{\pm}_{\alpha} = \Big(\big(\mu_{\alpha} + \tfrac{z_{\alpha}e_0}{m_{\alpha}}\varphi\big)\big|^{\pm}_{I} - \big(\mu_0 + \tfrac{z_0 e_0}{m_0}\varphi\big)\big|^{\pm}_{I} \Big) - \Big(\big(\underset{s}{\mu}_{\alpha} + \tfrac{z_{\alpha}e_0}{m_{\alpha}}\underset{s}{\varphi}\big) - \big(\underset{s}{\mu}_{0} + \tfrac{z_{\beta}e_0}{m_0}\underset{s}{\varphi}\big) \Big) \,. \tag{16}$$

We highlight, that in Ref.[20] linear relations were chosen for all constitutive laws except for the reactions in the volume and on the surface, where an Arrhenius-type exponential form was chosen. Here we also choose the exponential relation for the adsorption in (15c). We note that near to equilibrium, i.e. $|D^{\pm}_{\alpha}| \ll 1$, (15c) can be linearized resulting in the constitutive equation

$$\big(\rho_{\alpha}(\upsilon - w) + J_{\alpha}\big)\big|^{\pm}_{I} = \mp \sum_{\beta=1}^{N_S} \underset{s}{M}^{\pm}_{\alpha\beta} \Big[\Big(\big(\mu_{\beta} + \tfrac{z_{\beta}e_0}{m_{\beta}}\varphi\big)\big|^{\pm}_{I} - \big(\mu_0 + \tfrac{z_0 e_0}{m_0}\varphi\big)\big|^{\pm}_{I} \Big) - \Big(\big(\underset{s}{\mu}_{\beta} + \tfrac{z_{\beta}e_0}{m_{\beta}}\underset{s}{\varphi}\big) - \big(\underset{s}{\mu}_{0} + \tfrac{z_{\beta}e_0}{m_0}\underset{s}{\varphi}\big) \Big) \Big] \tag{17}$$

which coincides with the respective equation in (30) in Ref.[20], if the matrix $\underset{s}{M}^{\pm}_{\alpha\beta}$ is chosen diagonal.

3.3 Remarks

Electrostatic potential. When deriving a strictly thermodynamically consistent model, the proper thermodynamic variables is the electric field $\boldsymbol{E} = -\nabla\varphi$, not the electrostatic potential φ itself[21–23]. The explicit dependence of the constitutive relations (15b) and (15c) on φ is only justified as a consequence of the formal asymptotic approach in Ref.[20]. Moreover, in the reduced model above, φ is not required to be continuous across the interface and hence we have to introduce on I the variable $\underset{s}{\varphi}$ that is in general not an one-sided limit of φ in the bulk.

Electrochemical potential. It is remarkable that the constitutive relations (14a), (15b) and (15c) depend explicitly on the *electrochemical potentials*

$$\mu^{e}_{\alpha} = \mu_{\alpha} + \tfrac{z_{\alpha}e_0}{m_{\alpha}}\varphi \qquad \text{and} \qquad \underset{s}{\mu}^{e}_{\alpha} = \underset{s}{\mu}_{\alpha} + \tfrac{z_{\alpha}e_0}{m_{\alpha}}\underset{s}{\varphi} \,. \tag{18}$$

If we use the electroneutrality condition (10c) and the charge conservation for chemical reactions (4b) we can also express the constitutive equations of the Cauchy stress tensor σ and the reactions rates R^i and R in terms of electrochemical potentials. Such that all constitutive equations (14) and (15) can be expressed in terms of electrochemical potentials instead of chemical potentials.

Electric current. In the reduced model, the electric current is given by the simple relation

$$j^{\mathrm{e}} = \sum_{\alpha=0}^{N} \frac{z_{\alpha}e_0}{m_{\alpha}} J_{\alpha} \,. \tag{19}$$

Moreover, we can derive from (10) and (11) the following stationary balance equation for the electric current j^{e} in the bulk and on the interface

$$\partial_x j^{\mathrm{e}} = 0 \qquad \text{and} \qquad [\![j^{\mathrm{e}} \nu]\!] = 0 \,. \tag{20}$$

The electric current is constant in each subvolume $\Omega^{\pm}$ and continuous at the interface I. Hence j^{e} is even a global constant in the whole electrochemical system.

Electric current – reactions rates. In the reduced model there is a simple relation between the electric current j^{e} and the reaction rates $\underset{s}{R}^{i}$. We introduce the subset $\mathscr{J}^{+} \subseteq \mathscr{M}$ of all species that are present in Ω^{+}. Then multiplying in Ω^{+} the surface balances (11a) for the species $\mathrm{A}_{\alpha} \in \mathscr{J}^{+}$ by $z_{\alpha}e_0/m_{\alpha}$ and subsequent summation together with (10c) yields

$$\sum_{i=1}^{M_S} \Big(\sum_{\alpha \in \mathscr{J}^{+}} \underset{s}{\gamma}^{i}_{\alpha} z_{\alpha} e_0 \Big) \underset{s}{R}^{i} = \sum_{\alpha \in \mathscr{J}^{+}} \big(z_{\alpha} e_0 n_{\alpha} (\upsilon - w) \nu + \tfrac{z_{\alpha}e_0}{m_{\alpha}} J_{\alpha} \nu \big)\big|^{+}_{I} \overset{(10c),(19),(20)}{=} j^{\mathrm{e}} \nu|_{I} \,. \tag{21}$$

If there is only one surface reaction, i.e. $M_S = 1$, we get the direct proportionality

$$j^{\mathrm{e}} \nu|_{I} = \Big(\sum_{\alpha \in \mathscr{J}^{+}} \underset{s}{\gamma}_{\alpha} z_{\alpha} e_0 \Big) \underset{s}{R} \qquad \text{in } \Omega^{\pm} \,, \tag{22}$$

that allows the alternative formulation of the Butler-Volmer equation (2) as a logarithmic relation between electric current and the overpotential.

4 Derivation of the Butler-Volmer equation

The above reduced model forms the thermodynamic consistent basis for a derivation of the Butler-Volmer equations. The derivation is not restricted to a single surface reaction. Therefore we derive for each surface reaction a corresponding Butler-Volmer equation. The aim of the derivation is to identify exchange rates $\underset{s}{R}^{0,i}_{f/b}$, coefficients $\alpha^{i}_{f/b}$ and the overpotentials η^{i}_{S} in terms of bulk quantities: number densities n_{α} and electric potential φ. In contrast, the constitutive relation (15a) for the reaction rates depends only on the interfacial quantities: interfacial number densities $\underset{s}{n}_{\alpha}$ and surface electric potential $\underset{s}{\varphi}$. The necessary relation between bulk and interfacial quantities is established by the constitutive relations (15b) and (15c) for the mass fluxes.

Decomposition of the set of bulk constituents. For the derivation of the Butler-Volmer equation, it is necessary to decompose the set of all bulk constituents into two disjoint sets $\mathscr{M} = \mathscr{M}^{+} \cup \mathscr{M}^{-}$, $\mathscr{M}^{+} \cap \mathscr{M}^{-} = \emptyset$, such that all constituents $\mathrm{A}_{\alpha} \in \mathscr{M}^{+}$ are present in Ω^{+} and all constituents $\mathrm{A}_{\alpha} \in \mathscr{M}^{-}$ are present in Ω^{-}. In general, it is possible that a constituent is present in both bulk domains Ω^{+} and Ω^{-}. Then, the decomposition of the set $\mathscr{M}$ into the subsets $\mathscr{M}^{\pm}$ is not uniquely defined.

Assumption of fast adsorption. The constitutive equations (15b) and (15c) for the mass fluxes are the boundary conditions that describe the adsorbtion of the constituents at the interface I. Here we are only interested in the limit case of fast adsorption, i.e. $\underset{s}{L}^{\pm} \to \infty$ and $\underset{s}{M}^{\pm}_{\alpha} \to \infty$. Then, we obtain the continuity of the electrochemical potentials at the interface

$$\big(\mu_{\alpha} + \tfrac{z_{\alpha}e_0}{m_{\alpha}}\varphi\big)\big|^{\pm}_{I} = \big(\underset{s}{\mu}_{\alpha} + \tfrac{z_{\alpha}e_0}{m_{\alpha}}\underset{s}{\varphi}\big) \qquad \text{for } \alpha \in \mathscr{M} \,. \tag{23}$$

Equilibrium, Nernst equation. At first we consider the equilibrium, i.e. $\underset{s}{R}^i = 0$, to show the basic steps for the derivation of the Butler-Volmer equation within the reduced model. We denote all quantities that depend on the equilibrium state by an overbar. For every surface reaction, we deduce from $\underset{s}{R}^i = 0$ and (15a) the law of mass action, viz.

$$0 = \sum_{\alpha\in\mathscr{M}_S} \underset{s}{\gamma}^i_\alpha m_\alpha \underset{s}{\bar{\mu}}_\alpha \, . \tag{24}$$

According to (4a), each reaction conserves electric charge. Therefore

$$0 = \sum_{\alpha\in\mathscr{M}_S} \underset{s}{\gamma}^i_\alpha m_\alpha \big(\underset{s}{\bar{\mu}}_\alpha + \tfrac{z_\alpha e_0}{m_\alpha} \underset{s}{\bar{\varphi}}\big) \, . \tag{25}$$

Next we use the fast adsorption limit (23) to replace the interfacial quantities by bulk quantities,

$$0 = \sum_{\alpha\in\mathscr{M}} \underset{s}{\gamma}^i_\alpha \big(m_\alpha \bar{\mu}_\alpha + z_\alpha e_0 \bar{\varphi}\big)\big|_I^\pm + \sum_{\alpha\in\mathscr{M}_S\setminus\mathscr{M}} \underset{s}{\gamma}^i_\alpha \big(m_\alpha \underset{s}{\bar{\mu}}_\alpha + z_\alpha e_0 \underset{s}{\bar{\varphi}}\big) \, , \tag{26}$$

where in the first sum the bulk value is taken from Ω^+ if $\alpha \in \mathscr{M}^+$ and else is taken from Ω^- . As an abbreviation we define the coefficients

$$\Gamma^i_+ = \sum_{\alpha\in\mathscr{M}^+} \underset{s}{\gamma}^i_\alpha z_\alpha, \qquad \Gamma^i_- = \sum_{\alpha\in\mathscr{M}^-} \underset{s}{\gamma}^i_\alpha z_\alpha, \tag{27a}$$

$$\underset{s}{\Gamma}^i = \sum_{\alpha\in\mathscr{M}_S\setminus\mathscr{M}} \underset{s}{\gamma}^i_\alpha z_\alpha \tag{27b}$$

The conservation of charge (4a) implies $\Gamma^i_+ + \Gamma^i_- + \underset{s}{\Gamma}^i = 0$. Now we obtain for the *i*th reaction the alternative representation of the mass action law

$$0 = \sum_{\alpha\in\mathscr{M}} \underset{s}{\gamma}^i_\alpha m_\alpha \bar{\mu}_\alpha\big|_I^\pm + \sum_{\alpha\in\mathscr{M}_S\setminus\mathscr{M}} \underset{s}{\gamma}^i_\alpha m_\alpha \underset{s}{\bar{\mu}}_\alpha + \Gamma^i_+ e_0 [\![\bar{\varphi}]\!] + \underset{s}{\Gamma}^i e_0 \big(\underset{s}{\bar{\varphi}} - \bar{\varphi}\big|_I^-\big) \, . \tag{28}$$

We observe that by using the constitutive equation (23), we are able to express the surface laws of mass action (24) in terms of bulk quantities. By this we automatically introduce an electric potential difference $[\![\bar{\varphi}]\!]$ across the interface. In the case $\mathscr{M}_S \setminus \mathscr{M} = \emptyset$, and hence $\underset{s}{\Gamma}^i = 0$ and $\Gamma^i_+ \neq 0$, (28) reduces to the well known Nernst-equation

$$\Gamma^i_+ e_0 [\![\bar{\varphi}]\!] = - \sum_{\alpha\in\mathscr{M}} \underset{s}{\gamma}^i_\alpha m_\alpha \bar{\mu}_\alpha\big|_I^\pm \, . \tag{29}$$

Generalized Butler-Volmer equation. Next we consider an arbitrary time dependent state. In order to replace the surface chemical potentials in (15a) by the bulk chemical potentials, we apply the same steps like in the derivation of the Nernst equation in the above version (28). Therefore we first rewrite the driving force of the chemical reactions (15a) as

$$\sum_{\alpha\in\mathscr{M}_S} \underset{s}{\gamma}^i_\alpha m_\alpha \underset{s}{\mu}_\alpha = \sum_{\alpha\in\mathscr{M}} \underset{s}{\gamma}^i_\alpha m_\alpha \mu_\alpha\big|_I^\pm + \sum_{\alpha\in\mathscr{M}_S\setminus\mathscr{M}} \underset{s}{\gamma}^i_\alpha m_\alpha \underset{s}{\mu}_\alpha$$

$$+ \Gamma^i_+ e_0 [\![\varphi]\!] + \underset{s}{\Gamma}^i e_0 \big(\underset{s}{\varphi} - \varphi\big|_I^-\big) \tag{30}$$

Because we want to introduce the overpotential η_S as the deviation from an equilibrium potential, we subtract the law of mass action (28) from (30) to get

$$\sum_{\alpha\in\mathscr{M}_S} \underset{s}{\gamma}^i_\alpha m_\alpha \underset{s}{\mu}_\alpha = \sum_{\alpha\in\mathscr{M}} \underset{s}{\gamma}^i_\alpha m_\alpha \big(\mu_\alpha - \bar{\mu}_\alpha\big)\big|_I^\pm \tag{31}$$

$$+ \sum_{\alpha\in\mathscr{M}_S\setminus\mathscr{M}} \underset{s}{\gamma}^i_\alpha m_\alpha \big(\underset{s}{\mu}_\alpha - \underset{s}{\bar{\mu}}_\alpha\big)$$

$$+ \Gamma^i_+ e_0 [\![\varphi - \bar{\varphi}]\!] + \underset{s}{\Gamma}^i e_0 \Big(\underset{s}{\varphi} - \varphi\big|_I^- - \big(\underset{s}{\bar{\varphi}} - \bar{\varphi}\big|_I^-\big)\Big)$$

For each surface reaction we define its respective overpotential by

$$\eta^i_S := \begin{cases} [\![\varphi - \bar{\varphi}]\!] + \frac{\underset{s}{\Gamma}^i}{\Gamma_+} \Big(\underset{s}{\varphi} - \varphi\big|_I^- - \big(\underset{s}{\bar{\varphi}} - \bar{\varphi}\big|_I^-\big)\Big), & \text{if } \Gamma_+ \neq 0 \\ \underset{s}{\varphi} - \varphi\big|_I^- - \big(\underset{s}{\bar{\varphi}} - \bar{\varphi}\big|_I^-\big), & \text{if } \Gamma_+ = 0 \end{cases} \tag{32}$$

Inserting the identity (31) into (15a) yields net reaction rates $\underset{s}{R}^i$ in the form of a Butler-Volmer equation, viz.

$$\underset{s}{R}^i = R_f^{0,i} \, \exp\Big(-\frac{\alpha^i_f e_0}{kT}\eta^i_S\Big) - R_b^{0,i} \, \exp\Big(+\frac{\alpha^i_b e_0}{kT}\eta^i_S\Big) \, . \tag{33}$$

with the transfer coefficients as

$$\alpha^i_f = \begin{cases} \underset{s}{\beta}^i \underset{s}{A}^i \Gamma^i_+ \, , & \text{if } \Gamma_+ \neq 0 \, , \\ \underset{s}{\beta}^i \underset{s}{A}^i \underset{s}{\Gamma}^i \, , & \text{if } \Gamma_+ = 0 \, , \end{cases} \tag{34a}$$

$$\alpha^i_b = \begin{cases} (1-\underset{s}{\beta}^i) \underset{s}{A}^i \Gamma^i_+ \, , & \text{if } \Gamma_+ \neq 0 \, , \\ (1-\underset{s}{\beta}^i) \underset{s}{A}^i \underset{s}{\Gamma}^i \, , & \text{if } \Gamma_+ = 0 \, , \end{cases} \tag{34b}$$

and the exchange rates

$$R_f^{0,i} = \underset{s}{R}^i_0 \, \exp\Bigg(\quad - \underset{s}{\beta}^i \, \frac{\underset{s}{A}^i}{kT} \Bigg[\sum_{\alpha\in\mathscr{M}} \underset{s}{\gamma}^i_\alpha m_\alpha \big(\mu_\alpha - \bar{\mu}_\alpha\big)\big|_I^\pm$$

$$+ \sum_{\alpha\in\mathscr{M}_S\setminus\mathscr{M}} \underset{s}{\gamma}^i_\alpha m_\alpha \big(\underset{s}{\mu}_\alpha - \underset{s}{\bar{\mu}}_\alpha\big)\Bigg]\Bigg) \, , \tag{35a}$$

$$R_b^{0,i} = \underset{s}{R}^i_0 \, \exp\Bigg((1 - \underset{s}{\beta}^i) \frac{\underset{s}{A}^i}{kT} \Bigg[\sum_{\alpha\in\mathscr{M}} \underset{s}{\gamma}^i_\alpha m_\alpha \big(\mu_\alpha - \bar{\mu}_\alpha\big)\big|_I^\pm$$

$$+ \sum_{\alpha\in\mathscr{M}_S\setminus\mathscr{M}} \underset{s}{\gamma}^i_\alpha m_\alpha \Big(\underset{s}{\mu}_\alpha - \underset{s}{\bar{\mu}}_\alpha\Big)\Bigg]\Bigg) . \tag{35b}$$

Consistency of constitutive equations. Due to the kinetic approach, Butler-Volmer equations in the standard literature usually contain an explicit dependency on the number densities n_α [2–4,14,15]. In contrast, the general Butler-Volmer equation above has only an indirect dependency on n_α because of the chemical potentials. Such a formulation in terms of the chemical potentials can also been found in Butler-Volmer equations which have been proposed recently for specific applications like Li-ion batteries or fuel cells [13,18,19]. We want to emphasize the importance of the chemical potentials for a consistent modeling: In the formulation of the constitutive equations (14) and (15), we followed the approach of non-equilibrium thermodynamics that imposes compatibility constraints. This has the advantage, that the modeling is considerably simplified, because once the free energy density is specified, all constitutive equations are determined uniquely and in a compatible way, up to the choice of phenomenological coefficients. Compared to (15a), surface chemical potentials $\underset{s}{\mu_\alpha}$ have been replaced by bulk chemical potentials μ_α in (33) – (35). By this, we introduced a dependency of the constitutive law for the surface reactions on the bulk free energy $\rho\psi$. Hence the surface reaction rates are also related to the constitutive equations in the bulk (14) and can not be modeled independently of each other. Within our framework, a Butler-Volmer equation formulated in terms of n_α would imply a specific form of the free energy densities and thus impose compatibility constraints for the other constitutive equations in the bulk and the surface.

Simplification in the absence of exclusive surface species. Although most of the surface quantities have been replaced by volume quantities, the general Butler-Volmer equation still contains surface quantities. However, in many electrochemical systems the constituents on the surface are also present in at least one of the bulk phases, i.e. $\mathscr{M}_S \setminus \mathscr{M} = \emptyset$. This leads to a representation of the Butler-Volmer equation that is independent from the surface quantities and we get a single overpotential for all surface reactions as well as simplified reaction coefficients which exclusively depend on bulk quantities,

$$\eta_S = [\![\varphi - \bar{\varphi}]\!] \;, \tag{36}$$

$$R_f^{0,i} = \underset{s}{R_0^i} \, \exp\left(-\underset{s}{\beta^i} \, \frac{\underset{s}{A^i}}{kT} \sum_{\alpha\in\mathscr{M}} \underset{s}{\gamma_\alpha^i} m_\alpha \left(\mu_\alpha - \bar{\mu}_\alpha\right)\Big|_I^\pm \right) \;, \tag{37}$$

$$R_b^{0,i} = \underset{s}{R_0^i} \, \exp\left((1-\underset{s}{\beta^i}) \frac{\underset{s}{A^i}}{kT} \sum_{\alpha\in\mathscr{M}} \underset{s}{\gamma_\alpha^i} m_\alpha \left(\mu_\alpha - \bar{\mu}_\alpha\right)\Big|_I^\pm \right) \;. \tag{38}$$

The potential difference η_S then describes the deviation of the actual potential difference $\varphi|_I^+ - \varphi|_I^-$ from the equilibrium voltage $\bar{\varphi}|_I^+ - \bar{\varphi}|_I^-$ of the bulk phases that is in accordance with usual definitions in electrochemistry[3,4].

5 Adaption to different electrochemical systems

In this section, we study two scenarios for the application of Butler-Volmer equations: First, we consider a prototypical metal-electrolyte interface like it can be found in many electrochemical applications. Next we turn to the electron transfer reaction in modern lithium-ion-batteries. Here we are interested in the description of the intercalation material $\mathrm{FePO_4}$ that undergoes a phase transition during the intercalation process. Moreover, we discuss the origin of Butler-Volmer type relations in the case of lithium deposition from an electrolyte to a metallic lithium. In particular we demonstrate that Butler-Volmer type equations do not always originate from an electron transfer reaction, but it can result from an intercalation process or a slow adsorption process instead.

5.1 General metal electrode

We consider a metal-electrolyte interface with an electron transfer reaction of the form

$$\mathrm{O} + n\,\mathrm{e}^- \underset{\underset{s}{R_b}}{\overset{\underset{s}{R_f}}{\rightleftharpoons}} \mathrm{R} \;. \tag{39}$$

Here O and R denote the oxidized and the reduced species, respectively, and n is the number of transfered electrons. If $n > 1$ the reaction can be split up into several elementary reaction steps and our derivation of Butler-Volmer equations then corresponds to the “quasi-equilibrium method”[24], see also the discussion in Sect. 7. The backward reaction $\underset{s}{R_b}$ in (39) is the oxidation and the forward reaction $\underset{s}{R_f}$ is the reduction. The stoichiometric coefficients related to (39) are

$$\underset{s}{\gamma_O} = -1 \;, \qquad \underset{s}{\gamma_e} = -n \qquad \text{and} \qquad \underset{s}{\gamma_R} = +1 \;. \tag{40}$$

We describe the metal as a mixture of free electrons e and metal ions M. The electrolyte is a mixture consisting of a solvent S as well as anions and cations. The oxidized species O always is a positively charged cation of the electrolyte. If the reduced species does not coincide with M, then we assume R to be a further cation species of the electrolyte. Because there are no exclusive surface species involved in the reaction (39), we can assume that all species which are present on the metal-electrolyte-interface, are also present in Ω^+ or Ω^-, i.e. $\mathscr{M}_S \setminus \mathscr{M} = \emptyset$, and hence $\underset{s}{\Gamma} = 0$.

Following the convention applied e.g. by Newman[4] (pp. 7), we want the anodic (oxidation) reaction to be dominant for positive overpotential η_S. From (33) and (34) we see that Γ_+ has to be positive and thus we choose Ω^+ to represent the metal electrode. We denote the electric potential in the metal by $\varphi_M = \varphi|_I^+$ and the electric potential on the electrolyte side by $\varphi_E = \varphi|_I^-$. The overpotential is then given by

$$\eta_S = (\varphi_M - \varphi_E) - (\bar{\varphi}_M - \bar{\varphi}_E) \;. \tag{41}$$

Specific bulk material model for metal and electrolyte. To get a fully explicit Butler-Volmer equation we have to specify free energy densities for the metal and the electrolyte. Here we will only introduce the chemical potentials and refer for the corresponding free energy densities to Refs.[25–27].

The elastic model for the metal applied in Ref.[26] implies that the number density of the metallic ions n_M is constant. Then, the electro-neutrality condition (10c) requires that the electron density n_e is also constant. Thus in an isothermal process, also the chemical potentials of the metal ions and electrons in the bulk are constants in space and time, and we set

$$\mu_M = \bar{\mu}_M \qquad \text{and} \qquad \mu_e = \bar{\mu}_e \;. \tag{42}$$

The electrolyte is assumed to be an ideal mixture. Then the chemical potentials of the electrolyte species are given in Ref.[20,25]

$$\mu_\alpha = g_\alpha(T,p) + \tfrac{kT}{m_\alpha} \ln y_\alpha \qquad \text{for } \alpha = \mathrm{A, C, S} \;. \tag{43}$$

Here $y_\alpha = n_\alpha / \sum_\beta n_\beta$ denotes the mole fraction of constituent

A$_\alpha$ and g_α is the Gibbs free energy of the corresponding pure substance. In general the pressure dependence of g_α is of outmost importance in a complete thermodynamic model of electrolytes[25,27]. Here, in the reduced model, the pressure is constant due to the momentum balance equation (10b) and the simple constitutive equation (14b).

Case I: The metal ions are not involved in reaction, i.e. $\mathrm{M} \neq \mathrm{R}$. We obtain the coefficients

$$\Gamma_+ = n \quad \text{and} \quad \alpha_f = \underset{s}{\beta}\underset{s}{A}n, \quad \alpha_b = (1-\underset{s}{\beta})\underset{s}{A}n\,. \tag{44}$$

In equilibrium, i.e. $\underset{s}{R} = 0$, the Nernst equation (28) takes the form

$$\bar\varphi_M - \bar\varphi_E = \frac{kT}{ne_0}\ln\frac{\bar y_O}{\bar y_R} + \frac{1}{ne_0}\left(m_O g_O \;- m_R g_R \;+ n\, m_e \bar\mu_e\right)\,. \tag{45}$$

Since the chemical potentials of the electrons are constant, the equilibrium potential $\bar\varphi_M - \bar\varphi_E$ varies logarithmically with mole fractions $\bar y_O$ and $\bar y_R$ of the ions when pressure p and temperature T are kept fixed.

In Butler-Volmer equation (33) for the reaction (46) the contributions of the electrons vanish due to (42). With $\underset{s}{\gamma_O} = -1$, $\underset{s}{\gamma_R} = 1$ and μ_O and μ_R according to (43), the Butler-Volmer equation reads

$$\begin{aligned}\underset{s}{R} = \underset{s}{R_0}\left(\frac{\bar y_R}{\bar y_O}\,\frac{y_O}{y_R}\right)^{\underset{s}{\beta}\underset{s}{A}} \exp\left(-\frac{\underset{s}{\beta}\underset{s}{A}n\,e_0}{kT}\eta_S\right) \\ - \underset{s}{R_0}\left(\frac{\bar y_O}{\bar y_R}\,\frac{y_R}{y_O}\right)^{(1-\underset{s}{\beta})\underset{s}{A}} \exp\left(\frac{(1-\underset{s}{\beta})\underset{s}{A}n\,e_0}{kT}\eta_S\right)\end{aligned} \tag{46}$$

with the overpotential η_S given by (41). When applying (22), we get a Butler-Volmer equation as a relation between overpotential and electric current, i.e.

$$j^{\mathrm{e}}\nu|_I = j^0_{\mathscr{C}}\exp\left(-\frac{\underset{s}{\beta}\underset{s}{A}n\,e_0}{kT}\eta_S\right) - j^0_{\mathscr{A}}\exp\left(\frac{(1-\underset{s}{\beta})\underset{s}{A}n\,e_0}{kT}\eta_S\right)\,, \tag{47}$$

with the respective anodic and cathodic exchange currents

$$j^0_{\mathscr{C}} = ne_0\underset{s}{R_0}\left(\frac{\bar y_R}{\bar y_O}\,\frac{y_O}{y_R}\right)^{\underset{s}{\beta}\underset{s}{A}} \qquad \text{and} \qquad j^0_{\mathscr{A}} = ne_0\underset{s}{R_0}\left(\frac{\bar y_O}{\bar y_R}\,\frac{y_R}{y_O}\right)^{(1-\underset{s}{\beta})\underset{s}{A}}\,. \tag{48}$$

When $\underset{s}{R} > 0$, then the dominant reaction is the reduction, which depends on the availability of sufficiently many particles of species O. Keeping $\underset{s}{R} > 0$ fixed, then we conclude from (46) that $y_O \to 0$ requires $\eta_S \to -\infty$. Analogously, assuming $\underset{s}{R} < 0$ is a prescribed constant rate, then the oxidation reaction is dominant and $y_R \to 0$ implies $\eta_S \to +\infty$.

Further, for $y_O \ll 1$ we see that already a small overpotential, $0 \le \eta_S \ll kT/e_0$, is sufficient to reach a rate $\underset{s}{R} < 0$. Therefore the Butler-Volmer equation (46) implies the expected behavior that the oxidation is favorable for a low concentration of the oxidized species.

Case II: The meal ions are the reduced species, i.e. $\mathrm{M} = \mathrm{R}$. We obtain the coefficients

$$\Gamma_+ = z_R + n = z_O \quad \text{and} \quad \alpha_f = \underset{s}{\beta}\underset{s}{A}z_O, \quad \alpha_b = (1-\underset{s}{\beta})\underset{s}{A}z_O\,. \tag{49}$$

In equilibrium, i.e. $\underset{s}{R} = 0$, the Nernst equation (28) takes the form

$$\bar\varphi_R - \bar\varphi_E = \frac{kT}{z_O e_0}\ln\bar y_O + \frac{1}{z_O e_0}\left(m_O g_O \;- m_R\bar\mu_R + n\, m_e\bar\mu_e\right)\,. \tag{50}$$

Since the chemical potentials of the metal ions and electrons are constant, there remains only a logarithmic dependence of the equilibrium potential $\bar\varphi_M - \bar\varphi_E$ on $\bar y_O$.

The Butler-Volmer equation (33) for the reaction (46) simplifies considerably because the contributions of the chemical potentials of e and R vanish due to (42). With $\underset{s}{\gamma_O} = -1$ and μ_O according to (43), the Butler-Volmer equation reads

$$\begin{aligned}\underset{s}{R} = \underset{s}{R_0}\left(\frac{y_O}{\bar y_O}\right)^{\underset{s}{\beta}\underset{s}{A}} \exp\left(-\frac{\underset{s}{\beta}\underset{s}{A}z_O\,e_0}{kT}\eta_S\right) \\ - \underset{s}{R_0}\left(\frac{\bar y_O}{y_O}\right)^{(1-\underset{s}{\beta})\underset{s}{A}} \exp\left(\frac{(1-\underset{s}{\beta})\underset{s}{A}z_O\,e_0}{kT}\eta_S\right)\end{aligned} \tag{51}$$

with the overpotential η_S given by (41). From (22), we get

$$j^{\mathrm{e}}\nu|_I = j^0_{\mathscr{C}}\exp\left(-\frac{\underset{s}{\beta}\underset{s}{A}z_O\,e_0}{kT}\eta_S\right) - j^0_{\mathscr{A}}\exp\left(\frac{(1-\underset{s}{\beta})\underset{s}{A}z_O\,e_0}{kT}\eta_S\right), \tag{52}$$

with the respective anodic and cathodic exchange currents

$$j^0_{\mathscr{A}} = z_O e_0\underset{s}{R_0}\left(\frac{\bar y_O}{y_O}\right)^{(1-\underset{s}{\beta})\underset{s}{A}} \qquad \text{and} \qquad j^0_{\mathscr{C}} = z_O e_0\underset{s}{R_0}\left(\frac{y_O}{\bar y_O}\right)^{\underset{s}{\beta}\underset{s}{A}}\,. \tag{53}$$

We highlight two differences to the previous case and (46). First, in (51) there is no mechanism for η_S to blow up if an oxidation at a fixed rate $\underset{s}{R} < 0$ is prescribed. Second, the transfer coefficients in front of η_S differ between (46) and (51) if $z_R \neq 0$ and hence $z_O \neq n$.

5.2 Lithium iron phosphate electrode

The electrode material Li$_y$FePO$_4$ (LFP) is a cheap and safe electrode material for lithium-ion batteries[28]. A LFP electrode consists of a metallic carrier foil, carbon-coated LFP nano-particles, binder and further additives improving the electric and ionic conductivity and the mechanical properties of the battery.

We describe the LFP nano particles as a binary mixture of crystalline FePO$_4$- and Li-atoms. The lithium atoms can move freely through the FePO$_4$ crystal lattice[19,29,30]. Since FePO$_4$ has a low electric conductivity, we can neglect the electron transport inside the nano particles. To establish electric conductivity of the LFP, the LFP particles are coated with a thin carbon layer[31]. Therefore we have free electrons e on the surface, in addition to the electrolyte and electrode species, as well as the non-reacting carbon. The electrolyte consists of an organic solvent S, lithium ions Li$^+$ and the associated anions A.

At the iron phosphate-electrolyte interface, we consider the electron transfer reaction

$$\mathrm{Li}^+ + \mathrm{e}^- \rightleftharpoons \mathrm{Li}\ . \tag{54}$$

The stoichiometric coefficients are

$$\underset{s}{\gamma_{\mathrm{Li}^+}} = -1\ , \qquad \underset{s}{\gamma_{\mathrm{e}}} = -1 \qquad \text{and} \qquad \underset{s}{\gamma_{\mathrm{Li}}} = +1\ . \tag{55}$$

We let Ω^+ represent the domain of the iron phosphate electrode. Accordingly the electrolyte occupies the domain Ω^-. Then we get the coefficients

$$\Gamma_+ = 0, \qquad \Gamma_- = -1, \qquad \text{and} \qquad \underset{s}{\Gamma} = 1\ . \tag{56}$$

For the phenomenological coefficients $\alpha_{f,b}$ we obtain

$$\alpha_f = \beta \underset{s}{A} \qquad \text{and} \qquad \alpha_b = (1-\beta)\underset{s}{A}\ . \tag{57}$$

Since we model the LFP-electrode as mixture of electrically neutral species, there is no space charge layer inside the electrode. In consequence the electric potential is spatially constant and satisfies $\varphi|_I^+ = \underset{s}{\varphi}$. Denoting the electric potential in the electrolyte by $\varphi_{\mathrm{E}} = \varphi|_I^-$ and in the iron phosphate by $\varphi_{\mathrm{LFP}} = \varphi|_I^+$, the overpotential in (32) can be expressed as

$$\eta_S = (\varphi_{\mathrm{LFP}} - \varphi_{\mathrm{E}}) - (\bar{\varphi}_{\mathrm{LFP}} - \bar{\varphi}_{\mathrm{E}})\ . \tag{58}$$

Specific material model. As before, the electrolyte is modeled as a simple mixture with chemical potentials given by the constitutive equations (43). The chemical potential of the surface electrons is assumed to be constant, i.e. $\underset{s}{\mu_e} = \underset{s}{\bar{\mu}_e}$. Lithium-ion batteries with LFP-electrodes are characterized by a phase transition between lithium-poor and lithium-rich phase inside the LFP-electrode[28,32,33]. There are several approaches to model for LFP electrodes taking the phase transition into account[29,30,34–36]. A common feature of all these models is a non-monotone chemical potential of lithium in LFP. The simplest constitutive equation for the chemical potential μ_{Li}, that accounts for heat of solution and the entropy of mixing, is given by

$$\mu_{\mathrm{Li}} = \tfrac{L}{m_{\mathrm{Li}}}(1-2y_{\mathrm{Li}}) + \tfrac{kT}{m_{\mathrm{Li}}}\big(\ln(y_{\mathrm{Li}}) - \ln(1-y_{\mathrm{Li}})\big)\ . \tag{59}$$

Here $y_{\mathrm{Li}} = n_{\mathrm{Li}}/n_{\mathrm{FePO_4}}$ is the mole fraction of lithium and L is the heat of solution. Mechanical contributions due to the volume change of LFP during the lithium intercalation are not considered here.

Butler-Volmer equation for LFP. The Butler-Volmer equation for the reaction (54) at the iron phosphate-electrolyte interface is given by

$$\underset{s}{R} = R_f^0 \exp\left(-\frac{\beta \underset{s}{A} e_0}{kT}\eta_S\right) - R_b^0 \exp\left(\frac{(1-\beta)\underset{s}{A} e_0}{kT}\eta_S\right) \tag{60}$$

with the coefficients

$$R_f^0 = \underset{s}{R_0}\left(\frac{y_{\mathrm{Li}^+}}{\bar{y}_{\mathrm{Li}^+}}\,\frac{1-y_{\mathrm{Li}}}{1-\bar{y}_{\mathrm{Li}}}\,\frac{\bar{y}_{\mathrm{Li}}}{y_{\mathrm{Li}}}\exp\Big(+\tfrac{2L}{kT}\big(y_{\mathrm{Li}}-\bar{y}_{\mathrm{Li}}\big)\Big)\right)^{\beta \underset{s}{A}}, \tag{61a}$$

$$R_b^0 = \underset{s}{R_0}\left(\frac{\bar{y}_{\mathrm{Li}^+}}{y_{\mathrm{Li}^+}}\,\frac{1-\bar{y}_{\mathrm{Li}}}{1-y_{\mathrm{Li}}}\,\frac{y_{\mathrm{Li}}}{\bar{y}_{\mathrm{Li}}}\exp\Big(-\tfrac{2L}{kT}\big(y_{\mathrm{Li}}-\bar{y}_{\mathrm{Li}}\big)\Big)\right)^{(1-\beta)\underset{s}{A}}. \tag{61b}$$

Compared to the Butler-Volmer equation (46) for the metal-electrolyte interface, the structure of the exchange rates is more complex because of the dependency on the lithium mole fraction y_{Li}.

For intercalation electrodes, the overpotential should blow up if the electrode is completely filled or empty, cf. Ref.[13]. This requirement is satisfied by the Butler-Volmer equation (60): During the intercalation of lithium in the electrode, the reduction is the dominating reaction and thus the reaction rate in (60) has to be positive. Assume an intercalation process with a fixed positive rate $\underset{s}{R} > 0$. For $y_{Li} \to 1$, the exchange rates yield $R_f^0 \to 0$ and $R_b^0 \to +\infty$. Then, the Butler-Volmer equation (60) implies $\eta_S \to -\infty$. Analogously, for deintercalation process with a constant negative reaction rate $\underset{s}{R} < 0$, the overpotential has to increase $\eta_S \to +\infty$ for $y_{Li} \to 0$.

5.3 Lithium electrode

The metallic lithium electrode in contact with a lithium conducting electrolyte serves as an example where the Butler-Volmer equation does not originate from an electron transfer reaction. Instead, the Butler-Volmer equation here can result from two different processes: i) surface reaction without charge transfer and ii) adsorption. Let the domain Ω^+ represent the metallic lithium electrode and Ω^- represent the electrolyte domain. The electrolyte consists of lithium ions Li^+, the associated anions A and a solvent S. As already described in Section 5.1, the metal electrode consists of positive metal ions Li_M^+ and free electrons e^-. Since Li^+ and Li_M^+ have the same charge number, an electric current can not originate from an electron transfer reaction between these two species. However measurements show, that also this process generates an exponential relationship of Butler-Volmer type between the overpotential of the lithium-electrolyte interfaces and electric current[37]. Therefore this behavior has to originate from one of the three mechanism:

1. Adsorption of the lithium ions from the electrolytic solution to the metal-electrolyte interface.

2. Intercalation of lithium from the electrolyte phase to the metal phase, i.e.

$$\mathrm{Li}_\mathrm{M}^+ \rightleftharpoons \mathrm{Li}^+ \qquad \text{at} \quad I\ . \tag{62}$$

3. Adsorption of lithium ions and electrons from the metal to the metal-electrolyte interface.

In general the third mechanism is assumed fast compared to the other, and therefore cannot be the origin of the non-linear relationship between overpotential and current. The fast adsorption is modeled by $\underset{s}{L^+} \to \infty$ in (15b) and $\underset{s}{M_e^+} \to \infty$ in (15c). We obtain on the lithium metal side the equations

$$(\mu_{Li_M^+} + \tfrac{e_0}{m_{Li_M^+}}\varphi)\big|_I^+ = (\underset{s}{\mu}_{Li_M^+} + \tfrac{e_0}{m_{Li_M^+}}\underset{s}{\varphi}), \tag{63a}$$

$$(\mu_e - \tfrac{e_0}{m_e}\varphi)\big|_I^+ = (\underset{s}{\mu}_e - \tfrac{e_0}{m_e}\underset{s}{\varphi}) \ . \tag{63b}$$

We denote the potential in the lithium metal with $\varphi_M = \varphi|_I^+$ and in the electrolyte with $\varphi_E = \varphi|_I^-$. Accordingly, we define the overpotential as $\eta_S = \varphi_M - \varphi_E - (\bar{\varphi}_M - \bar{\varphi}_M)$. Now we show that both cases, a slow reaction and a slow adsorption, result in a Butler-Volmer equation of the same type.

We use the same constitutive relations for the metal and the electrolyte as in Section 5.1.

Case 1: Slow reaction and fast adsorption. Let the reaction (62) be the limiting process. We can assume that the fast adsorption assumption (23) is satisfied, i.e.

$$(\mu_\alpha + \tfrac{z_\alpha e_0}{m_\alpha}\varphi)\big|_I^+ = (\underset{s}{\mu}_\alpha + \tfrac{z_\alpha e_0}{m_\alpha}\underset{s}{\varphi}) \qquad \alpha = Li^+, A, S \ , \tag{64}$$

and the results of Section 4 are applicable. In particular we can use the results of Section 5.1, since the derivation holds also in the case where no electrons are involved in the reaction (39). We have

$$j^{\mathrm{e}}\nu|_I = j^0_{\mathscr{C}} \exp\left(-\frac{\underset{s}{\beta}\underset{s}{A} z_{Li^+}e_0}{kT}\eta_S\right) - j^0_{\mathscr{A}} \exp\left(\frac{(1-\underset{s}{\beta})\underset{s}{A} z_{Li^+}e_0}{kT}\eta_S\right), \tag{65}$$

with anodic and cathodic exchange currents

$$j^0_{\mathscr{A}} = z_{Li^+}e_0\underset{s}{R}_0\left(\frac{\bar{y}_{Li^+}}{y_{Li^+}}\right)^{(1-\beta)\underset{s}{A}} \qquad \text{and} \qquad j^0_{\mathscr{C}} = z_{Li^+}e_0\underset{s}{R}_0\left(\frac{y_{Li^+}}{\bar{y}_{Li^+}}\right)^{\beta\underset{s}{A}} . \tag{66}$$

Case 2: Fast reaction and slow adsorption. The reaction (62) is fast compared to the adsorption. We can assume that the kinetic parameter for the reaction rate meet $\underset{s}{R}_0 \to \infty$ in (15a). Then the law of mass action reads

$$\underset{s}{\mu}_{Li^+} = \underset{s}{\mu}_{Li_M^+} \ . \tag{67}$$

To simplify the argumentation in the following, we assume that the adsorption of the solvent $S(=A_0)$ to the metal-electrolyte interface is fast, i.e. $\underset{s}{L}^- \to +\infty$ in (15b), and we have

$$\mu_S|_I^- = \underset{s}{\mu}_S \ . \tag{68}$$

Further, we assume that the anions cannot adsorb at the metal surface, i.e. $\underset{s}{M}_A^- = 0$ in (15c), and we obtain from the constitutive relation (15c)

$$\big(\rho_A(\upsilon - w)\nu + J_A\nu\big)\big|_I^- = 0 \ . \tag{69}$$

These assumptions yield that the electric current j^e at the interface is given by the lithium flux

$$j^e\nu|_I^- = \tfrac{e_0}{m_{Li^+}}\big(\rho_{Li^+}(\upsilon - w)\nu + J_{Li^+}\nu\big)\big|_I^- \ . \tag{70}$$

This relation follows from the simple relation (19) for the electric current, the local electroneutrality condition (10c) and the equation (69).

The lithium flux in (70) is given by the constitutive relation for the adsorption, equation (15c),

$$\begin{aligned}&\big(\rho_{Li^+}(\upsilon - w)\nu + J_{Li^+}\nu\big)\big|_I^- \\ =&\underset{s}{M}^-_{Li^+}\Big(\exp\big(\beta^-_{Li^+}\tfrac{m_{Li^+}}{kT}\underset{s}{B}^-_{Li^+}D^-_{Li^+}\big) - \exp\big((\beta^-_{Li^+} - 1)\tfrac{m_{Li^+}}{kT}\underset{s}{B}^-_{Li^+}D^-_{Li^+}\big)\Big) \ .\end{aligned} \tag{71}$$

Here, the driving force is defined as

$$D^-_{Li^+} = \Big((\mu_{Li^+} + \tfrac{z_{Li^+}e_0}{m_{Li^+}}\varphi)\big|_I^-\Big) - \Big((\underset{s}{\mu}_{Li^+} + \tfrac{z_{Li^+}e_0}{m_{Li^+}}\underset{s}{\varphi})\Big) \ . \tag{72}$$

Using the relation $(63)_1$ we can write the driving force as

$$D^-_{Li^+} = \Big((\mu_{Li^+} + \tfrac{z_{Li^+}e_0}{m_{Li^+}}\varphi)\big|_I^-\Big) - \Big((\mu_{Li_M^+} + \tfrac{z_{Li^+}e_0}{m_{Li^+}}\varphi)\big|_I^+\Big) \ . \tag{73}$$

As in the derivation of the Butler-Volmer equation, we introduce an equilibrium state in which the driving force vanishes, leading to $(\bar{\mu}^-_{Li^+} + \tfrac{z_{Li^+}e_0}{m_{Li^+}}\bar{\varphi})\big|_I^- = (\bar{\mu}_{Li_M^+} + \tfrac{z_{Li^+}e_0}{m_{Li^+}}\bar{\varphi})\big|_I^+$. The driving force (73) can be written as

$$D^-_{Li^+} = (\mu_{Li^+} - \bar{\mu}_{Li^+})\big|_I^- - (\mu_{Li^+} - \bar{\mu}_{Li^+})\big|_I^+ - \tfrac{z_{Li^+}e_0}{m_{Li^+}}\eta_S \ , \tag{74}$$

where we have replaced the electric potentials by the overpotential $\eta_S = (\varphi - \bar{\varphi})|_I^+ - (\varphi - \bar{\varphi})|_I^-$. With the chemical potentials (43) for the lithium ions of the electrolyte and the constant chemical potential for lithium metal according to (42), we get for the current

$$\begin{aligned}j^e\nu|_I = {}& j^0_{\mathscr{C}}\exp\left(-\frac{\beta^-_{Li^+}\underset{s}{B}^-_{Li^+}z_{Li^+}e_0}{kT}\eta_S\right) \\ &- j^0_{\mathscr{A}}\exp\left(\frac{(1-\beta^-_{Li^+})\underset{s}{B}^-_{Li^+}z_{Li^+}e_0}{kT}\eta_S\right)\end{aligned} \tag{75}$$

with the exchange coefficients

$$j^0_{\mathscr{A}} = \underset{s}{M}^-_{Li^+}\frac{z_{Li^+}e_0}{m_{Li^+}}\left(\frac{\bar{y}_{Li^+}}{y_{Li^+}}\right)^{(1-\beta^-_{Li^+})\underset{s}{B}^-_{Li^+}} , \tag{76a}$$

$$j^0_{\mathscr{C}} = \underset{s}{M}^-_{Li^+}\frac{z_{Li^+}e_0}{m_{Li^+}}\left(\frac{y_{Li^+}}{\bar{y}_{Li^+}}\right)^{\beta^-_{Li^+}\underset{s}{B}^-_{Li^+}} . \tag{76b}$$

These relations are identical to the Butler-Volmer equation (65) resulting from the surface reaction. This is remarkable, because of the thermodynamic origin of the non-linear relations, which are derived in one case from an adsorption process and in the other case from an surface reaction. Therefore we can not conclude from a Tafel-plot whether the adsorption or the surface reaction is the limiting surface process.

6 Example Electroplating

The electroplating of metals serves as a simple example of an electrochemical process with a surface reaction that can be described by a steady state. We consider an aqueous copper sulfate solution between two parallel copper plates, as shown in Figure 2. The domain of the electrolyte is Ω^- and we let Ω^+ denote both electrodes. We model copper electrodes as a binary mixture of free

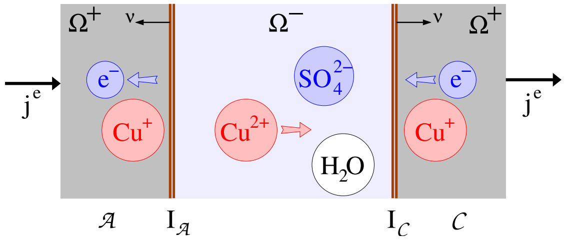

Fig. 2 Experimental setup for electroplating: aqueous copper sulfate solution bounded by two copper electrodes. The surface normal ν always points to the electrodes. The role of the electrodes as anode or cathode depends on the direction of the imposed current $j^e\nu$.

electrons e and cuprous ions Cu^+. The electrolyte consists of water H_2O as the solvent S, the anions $SO_4{}^{2-}$ and the cations Cu^{2+}, in the following also denoted by A and C, respectively.

When a current j^e is applied to the electrodes, copper is oxidized at the anode $\mathscr{A}$ and cupric ions are dissolved from the the anode interface $I_{\mathscr{A}}$ into the electrolyte. On the other side, at the interface $I_{\mathscr{C}}$, the cupric ions are reduced and incorporated into cathode $\mathscr{C}$. If the plates are sufficiently large the process is one dimensional. The overall dissolution/deposition process can be split into several steps, see also the discussion in Sect. 7:

- adsorption/desorption of Cu^+ between electrode bulk and surface,
- electron transfer reaction

$$Cu^{2+} + e^- \rightleftharpoons Cu^+ \ . \tag{77}$$

- adsorption/desorption of Cu^{2+} between surface and cations of the electrolyte.

The adsorption in the first and third step is considered inherently fast compared to (77) such that assumption (23) is valid.

Bulk transport. The momentum balance (10b) implies that the pressure in Ω^+ and Ω^- is constant $p = p_0$. To simplify the presentation, we do not consider solvated ions[25,26] here. Thus, we may assume that all particles are of the same size. Then the constitutive model for an incompressible simple mixture[20,25] together with global electroneutrality according to (10c) leads to the relations

$$n_A + n_C + n_S = n_0^{ref} \ , \tag{78a}$$

$$z_A n_A + z_C n_C = 0 \ , \tag{78b}$$

where n_0^{ref} is constant total number density of particles. The species A, C and S of the electrolyte satisfy the stationary version of the mass balance equations (10a). In the absence of bulk reactions we have to solve in Ω^-

$$\partial_x \left(m_A n_A \upsilon + J_A \right) = 0 \ , \tag{79a}$$

$$\partial_x \left(m_C n_C \upsilon + J_C \right) = 0 \ , \tag{79b}$$

$$\partial_x \left(\rho\, \upsilon \right) = 0 \ , \tag{79c}$$

where we replaced the partial balance of S by the total mass balance. In addition there are two more constraints. First, we have to specify the total amount of copper sulphate dissolved into the water by prescribing the average number density n_C^0 of cations in the electrolyte. Second, an absolute reference value for φ has to be defined, e.g. $\varphi = 0$ at $I_{\mathscr{C}}$.

The boundary conditions (11a) for the species A, C and S at the interfaces are

$$m_\alpha \underset{s}{\gamma_\alpha} \underset{s}{R}_{\mathscr{A}/\mathscr{C}} = -\left(m_\alpha n_\alpha \left(\upsilon - w_{\mathscr{A}/\mathscr{C}} \right) \nu + J_\alpha \nu \right)\big|^-_{I_{\mathscr{A}}/I_{\mathscr{C}}} \ , \tag{80}$$

where $\underset{s}{R}_{\mathscr{A}/\mathscr{C}}$ and $w_{\mathscr{A}/\mathscr{C}}$ denotes the reaction rates and the interfacial speed at $I_{\mathscr{A}}$ and $I_{\mathscr{C}}$, respectively. For the reaction (77) we have $\underset{s}{\gamma_C} = -1$ and $\underset{s}{\gamma_A} = \underset{s}{\gamma_S} = 0$. We multiply (80) with $z_\alpha e_0 / m_\alpha$ for each α. Then summation and the electroneutrality (78b) yields

$$-z_C e_0 \underset{s}{R}_{\mathscr{A}/\mathscr{C}} = -\sum_{\alpha \in \{A,C,S\}} \left(\tfrac{z_\alpha e_0}{m_\alpha} J_\alpha \nu \right)\big|^-_{I_{\mathscr{A}/\mathscr{C}}} \ , \tag{81}$$

With (21) we conclude that $z_C e_0 \underset{s}{R}_{\mathscr{A}/\mathscr{C}} = j^e \nu$ and get the boundary conditions

$$m_\alpha \underset{s}{\gamma_\alpha}\, j^e = -z_C e_0 \left(m_\alpha n_\alpha \left(\upsilon - w_{\mathscr{A}/\mathscr{C}} \right) + J_\alpha \right)\big|^-_{I_{\mathscr{A}/\mathscr{C}}} \qquad \text{for } \alpha \in \{\mathrm{A,C,S}\} \ . \tag{82}$$

Summing the boundary conditions (82) for $\alpha = \mathrm{A,C,S}$ shows

$$m_C \underset{s}{\gamma_C}\, j^e = -z_C e_0 \left(\rho \left(\upsilon - w_{\mathscr{A}/\mathscr{C}} \right) \right)\big|^-_{I_{\mathscr{A}/\mathscr{C}}} \ . \tag{83}$$

From (79c) we conclude $w_{\mathscr{A}} = w_{\mathscr{C}}$. Thus we can choose a coordinate system such that $w_{\mathscr{A}} = w_{\mathscr{C}} = 0$. The explicit form of the boundary conditions (82) is

$$-\left(m_A n_A \, \upsilon + J_A \right) = 0 \ , \tag{84a}$$

$$-z_C e_0 \left(m_C n_C \, \upsilon + J_C \right) = m_C \underset{s}{\gamma_C}\, j^e \ , \tag{84b}$$

$$-z_C e_0 \, \rho \, \upsilon = m_C \underset{s}{\gamma_C}\, j^e \ . \tag{84c}$$

The boundary conditions can be extended to hold in the whole electrolyte domain Ω^- by applying (79). We emphasize the direct proportionality between the electric current j^e and the barycentric velocity υ in the electrolyte in (84c). For this reason as long a electric current flows, the barycentric velocity can not be neglected, as it usually is done in the literature.

To solve the system (84) it is not necessary to specify any Butler-Volmer equation. Moreover we stress that there is not the problem of a missing boundary condition[11]. For a numerical solution of (84) we choose a diagonal mobility matrix with $M_{\alpha\alpha} = B_\alpha T m_\alpha^2 n_\alpha$ leading to the diffusive fluxes

$$J_\alpha = -kT\, B_\alpha m_\alpha \left(\partial_x n_\alpha - \tfrac{m_\alpha}{m_0} \tfrac{n_\alpha}{n_0} \partial_x n_0 + n_\alpha z_\alpha \tfrac{e_0}{kT} \partial_x \varphi \right) \ , \quad \alpha = \mathrm{A,C} \ . \tag{85}$$

Note that there is no pressure dependence in (85) because $\partial_x p = 0$. Simulation for Ω^- of length $L = 1$cm and using material parameter according to Table 1 yields solutions n_C and φ as plotted in figures 3 and 4. We observe a nearly linear spatial distribution

	A: SO_4^{2-}	C: Cu^{2+}_{aq}	S: H_2O
$m_\alpha/\,[\mathrm{u}]$	96.078	63.546	18.015
$B_\alpha/\,[\mathrm{s/kg}]$	3.36×10^{11}	5.61×10^{11}	–

Table 1 Material parameters used for the calculations[38].

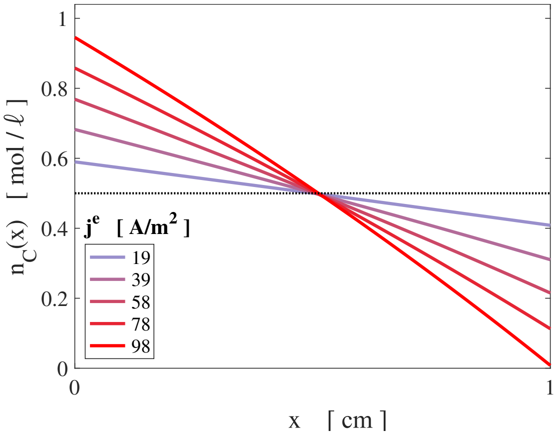

Fig. 3 Solution of (84) over space for different applied currents and a salt concentration of $0.5\,\mathrm{mol}/\ell$. We observe almost linear concentration profiles n_C with a slope proportional to j^e.

of the cations with a slope that is proportional to the imposed current j^e. With increasing current, we observe a nonlinear behavior of the electrostatic potential φ near the cathode, where the cation concentration gets low.

Butler-Volmer equation. A Butler-Volmer equation for the reaction (77) can be derived in the context of case II of Sect. 5.1. The choice of Ω^+ above and (77) imply $\Gamma_+ = z_C = 2$. Experimental measurements[39] show that $\alpha_{\mathscr{A}} \approx 1.5$ and $\alpha_{\mathscr{C}} \approx 0.5$. We thus choose $\underset{s}{A} = 1$ and $\beta = 1/4$ to get from (51) at $I_{\mathscr{A}}$ and $I_{\mathscr{C}}$

$$\underset{s}{R} = R_0 \left(\frac{n_C}{\bar{n}_C}\right)^{1/4} \exp\left(-\frac{1}{2}\frac{e_0}{kT}\eta_S\right) \quad - R_0 \left(\frac{n_C}{\bar{n}_C}\right)^{-3/4} \exp\left(\frac{3}{2}\frac{e_0}{kT}\eta_S\right) . \tag{86}$$

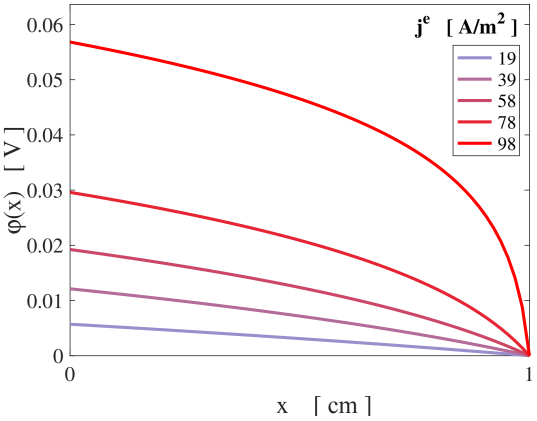

Fig. 4 Electrostatic potential φ over space for different applied currents and a salt concentration of $0.5\,\mathrm{mol}/\ell$.

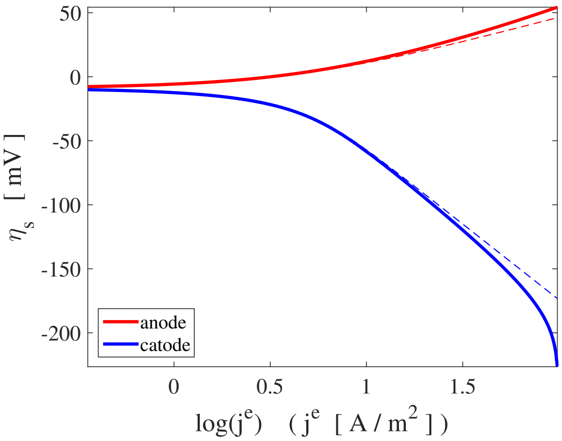

Fig. 5 Tafel plot from the reaction (77) and the computed electrolyte concentrations at $I_{\mathscr{A}}$ and $I_{\mathscr{C}}$ according to (84) with $n_C^0 = 0.5\mathrm{mol}/\ell$. Dashed lines for fixed cation concentration $n_C = n_C^0$ at $I_{\mathscr{A}}$ and $I_{\mathscr{C}}$ show the linear Tafel slope in the large overpotential regime.

Using the electrolyte concentrations at the interfaces from the previous computation, we can determine from (86) the overpotential at the anode and cathode, see Figure 5. In the Tafel plot we observe a nearly linear slope over one decade of the imposed current densities. When j^e gets larger, the Tafel plots deviate from the linear behavior. This effect is due to the dependency of the exchange currents on the concentration of the species. The observed deviation is much more pronounced at the cathode, where $n_C \to 0$ for larger imposed current densities.

Polarographic curves. From the computed overpotential we can not directly infer the potential difference $[\![\varphi]\!]$ over the double layer, since by definition η_S also depends on the chosen equilibrium values. But, since in the experimental setup considered here the electrodes consist of the same material, the equilibrium potential $[\![\bar{\varphi}]\!]$ is the same at $I_{\mathscr{A}}$ and $I_{\mathscr{C}}$. We denote the electrostatic potential in the bulk of the electrode $\mathscr{A}$ and $\mathscr{C}$ by $\varphi_{\mathscr{A}}$ and $\varphi_{\mathscr{C}}$, respectively. Then the voltage over the complete electrochemical cell is

$$\varphi_{\mathscr{A}} - \varphi_{\mathscr{C}} = \eta_S^{\mathscr{A}} + \varphi|^-_{I_{\mathscr{A}}} - \varphi|^-_{I_{\mathscr{C}}} - \eta_S^{\mathscr{C}} \ , \tag{87}$$

where $\eta_S^{\mathscr{A}/\mathscr{C}}$ denotes the overpotential at $I_{\mathscr{A}/\mathscr{C}}$, respectively. At a certain imposed current where n_C approaches 0 at $I_{\mathscr{C}}$, the overpotential at the cathode, and thus also $\varphi_{\mathscr{A}} - \varphi_{\mathscr{C}}$, has to blow up, as discussed in Sect. 5.1. Motivated by the diffusion limited current in Ref.[40], we define

$$j_d^e := \frac{4 z_C e_0 kT B_C n_C^0}{L} \ . \tag{88}$$

For a diluted electrolytes, we observe that the blow up of the cell voltage occurs close to $j^e = j_d^e$, see Figure 7. Increasing the salt concentration, i.e. increasing n_C^0, the characterization of the limiting current by j_d^e gets less and less sharp, as the blow up of the cell voltage occurs at higher imposed currents. This discrepancy has to attributed to the simpler bulk model in Ref.[40], where $\upsilon = 0$ is assumed in Ω^- and the ion–solvent interaction is neglected.

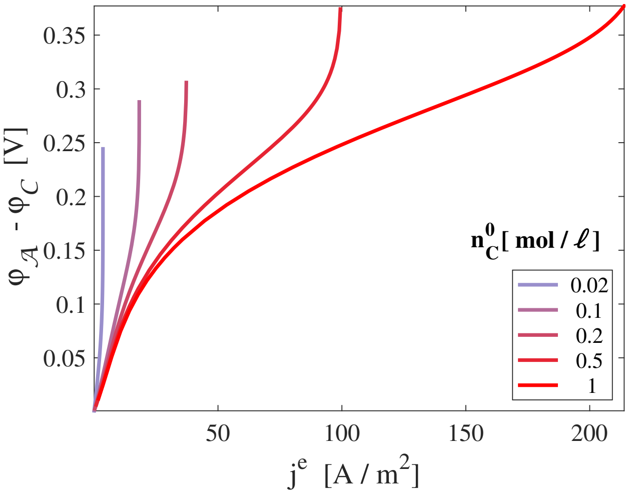

Fig. 6 Limiting current causing a blow up of the cell voltage. Left: polarographic curves for different salt concentrations. we observe a blow up of the cell voltage for different applied current j^e.

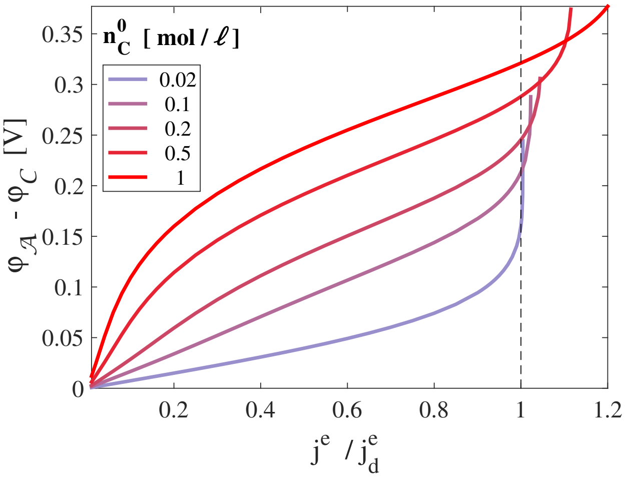

Fig. 7 Limiting current causing a blow up of the cell voltage. Polarographic curves of Fig. 6, but with the current rescaled by j_d^e defined in (88).

7 Discussion

7.1 General non-equilibrium thermodynamics framework

Complex real world electrochemical system like batteries couple various phenomena of very different type and on very different scales. Mathematical models are useful to understand these processes. But to gain more insight into their interplay, there is a need for a physically consistent and structured theory, which guides the development of electrochemical models. Non-equilibrium thermodynamics is such a powerful theory on the continuum level. While continuum models are well accepted on the macro scale, their applicability for the finer scales is often questioned. However, recent results[26] demonstrate impressively that it is possible to resolve details of double layer structure within the nanometer range.

A particular advantage of non-equilibrium thermodynamics is that it provides a systematic way for the derivation of constitutive relations such that compatibility with the 2nd law of thermodynamics is guaranteed. It simplifies the modeling procedure by restricting the modeling effort to constitutive equations for the surface and bulk free energy densities and the minimal required set of phenomenological coefficients. But, the formulation of explicit free energy densities as functions of the thermodynamics state is not obvious and may be a difficult task, because thermodynamics does not tell anything about their explicit form. In general one has to rely on extrinsic theories, usually from some underlying microscopic model, to derive free energy functions. The same holds true for the phenomenological coefficient. For example, to model the reaction rates, kinetic theories can be used to motivate the structure of the coefficients, as discussed in Sect. 7.4. For the constitutive relations, most often linear relations between (generalized) driving forces and fluxes are applied. But for processes far from equilibrium, also nonlinear relations can be found, like for example for reactions or in certain situations also for adsorption. Non-equilibrium thermodynamics does not provide any specific structure of these relations and we choose an exponential relation of Arrhenius type that is compatible with 2nd law of thermodynamics.

Another advantage of non-equilibrium thermodynamics is that, it automatically ensures the consistent coupling of different phenomena. For example the inclusion of elastic properties in a model of electrochemical cells can be done in a first step by inclusion of deformation gradients in the free energy functions. Then the elastic contribution appears in all constitutive equation, in particular in those for the stress tensor and the reaction rates. Thereby the consistent coupling of deformation and chemical reactions is established. This advantage of coupling different phenomena might on the other hand lead to equation systems that are very complex, difficult to analyze and hard to solve. Then, asymptotic methods can be used for the derivation of the reduced models of simpler mathematical structure. This process can be assumed to preserve the thermodynamic consistency but leads to some limitations of the range of validity of these reduced models, cf. Sect. 7.2.

In summary, non-equilibrium thermodynamics provides a general structure for the mathematical model and couples different phenomena in a consistent way. But to model a particular electrochemical system, additional input from microscopic theories is needed. The complex coupling of different phenomena then often requires some model reduction before successful application to real world problems is possible.

7.2 Validity of the Butler-Volmer equation

The Butler-Volmer equation is not a universal natural law but its validity is limited to certain application scenarios. Our general Butler-Volmer equation (33) can only be valid as long as the assumptions of the underlying reduced bulk model hold. First of all, the reduced bulk model requires that "the Debye length is small". That means, we choose a characteristic length scale L^{ref} for the electrochemical system under consideration, such that the overall size of the system is comparable to L^{ref} and the curvature of surfaces is less than $1/L^{ref}$. Then the Debye length, which controls the width of boundary layers, has to be smaller than L^{ref} by some orders of magnitude. In consequence, the Butler-Volmer equation (33) can not be applied in the context of nano-systems. Second, the derivation of the reduced bulk model is based on quasi-equilibrium of the boundary layer. For this, it is necessary that relaxation times of the layer are small compared to the macroscopic experimental timescales. In Ref.[20], a macroscopic time scale of $t^{ref} = 10s$ was used. This certainly rules out the application of (33) in processes where excitations by short pulses or medium to high frequencies are applied. Moreover in the reduced model, we assumed isothermal systems. If the surface reactions are strongly endothermic or exothermic, the energy balance can not be neglected and the procedure of the asymptotic analysis of Ref.[20] has to be applied to the larger system of equations and might possibly lead to different relations. Finally, we remark that in some cases it might be more appropriate to assume that the number densities of the surface species are comparable to those in the volume. This would necessitate the inclusion of a material model for the surface species and lead to different coupling conditions of the surface species to the bulk equations.

The Marcus-Hush theory is often used in situations where the classical Butler-Volmer equations fails. In particular, the Marcus-Hush theory is able to describe curved Tafel slopes which are interpreted as a dependency of the transfer coefficients on the overpotential. Curved Tafel slopes have been reported[41], but usually this requires non-steady state techniques. Experimental conditions to observe curved Tafel slopes under steady-state conditions were described in Ref.[42] and experimental results have been reported for a "redox couple that has a pathologically small rate constant"[43]. We note that because the Butler-Volmer equation (33) is formulated in terms of chemical potentials instead of number densities, it seems possible that applying a material model different from the simple mixture would allow for curved Tafel behavior. The same also holds true for temperature dependence of Tafel slope. In a series of comparative studies[44–46], experimental data of square wave voltammetry and cyclic voltammetry was fitted to Marcus-Hush and Butler-Volmer theory. The results indicate some quantitative weakness of the Marcus-Hush theory. We remark that cyclic voltammetry or square-wave voltammetry require the inclusion of a time scale into the model equations that is at least one order of magnitude lower than the $t^{ref} = 10s$ considered here. Thus, in our point of view, a simulation of these processes should be based on the complete model of Ref.[20].

7.3 Comparison with textbook literature

General metal electrode. The textbook literature provides Nernst- and the Butler-Volmer equations for the electron transfer reaction (39) at a metal electrode which we can compare with the respective equations in Sect. 5.1. For the Nernst equation, we find

$$\text{Newman}^{4}\ (8.20): \qquad \bar{\varphi}_M - \bar{\varphi}_E = \frac{kT}{ne_0} \ln\left(\frac{k_{\mathscr{C}}}{k_{\mathscr{A}}}\,\frac{\bar{y}_O}{\bar{y}_R}\right) . \tag{89}$$

Here $k_{\mathscr{A}/\mathscr{C}}$ are the rate constants related to the anodic and cathodic reaction, respectively. The same structure of the Nernst equations can be found in the books by Bockris[3] (7.40) and Bard and Faulkner[2] (3.2.2), only the rate constants are replaced by a reference potential. All these equations show the same logarithmic dependency on the equilibrium concentrations $\bar{y}_O$ and $\bar{y}_R$ as (45).

For the Butler-Volmer equation, the overpotential η_S defined by Newman[4] (8.21) is identical to (41) and in our notation the authors state the Butler-Volmer equation:

$$\text{Newman}^{4}\ (8.24): \quad j^{\mathrm{e}} \nu|_I = j^0 \exp\left(-\frac{\beta n e_0}{kT}\eta_S\right) - j^0 \exp\left(\frac{(1-\beta) n e_0}{kT}\eta_S\right) . \tag{90}$$

The same structure of the equation can be found in Ref.[3] (7.23). We observe that the exchange currents are the same for the anodic and the cathodic current, i.e. $j^0_{\mathscr{A}} = j^0_{\mathscr{C}} = j^0$, what is not compatible with our approach to guarantee the consistency with the 2nd law of thermodynamics. Moreover $j^{\mathrm{e}} \to 0$ then always implies $\eta_S \to 0$. In contrast, the overpotential defined in Section 4 depends on the chosen equilibrium state with its respective electrolyte concentrations at the interface. A deviation from the concentrations of the reference state then implies a non-vanishing overpotential even for $j^{\mathrm{e}} = 0$.

The dependency on the concentrations is specified as

$$\text{Newman}^{4}\ (8.23): \qquad j^0 = ne_0\, k^{\beta}_{\mathscr{A}}\, k^{1-\beta}_{\mathscr{C}}\ y^{\beta}_R\, y^{1-\beta}_O\ . \tag{91}$$

As a consequence, for a low amount of the oxidized species $y_O \ll 1$, the Butler-Volmer equation (90) implies that a high overpotential $\eta_S \gg 0$ is required in order to maintain an oxidation reaction, i.e. current $j^e \nu|_I > 0$ and $\underset{s}{R} > 0$ respectively. This is contrary to the expected behavior of an electron transfer reaction at an metal-electrolyte interface. Our Butler-Volmer equations predicts the behavior correctly, see Sect. 5.1. Moreover, the transfer coefficients in (90) coincide with the coefficients in (47), but in general are different from those in (52). Thus, (90) can not directly be applied, if the reduced species is the electrode metal or the current is caused by a combination of adsorption and electron transfer like in Sect. 6. Finally, we note that in (46) and (51) there is an additional coefficient $\underset{s}{A}$ that can be used for further modeling.

Copper dissolution. For a macroscopic description of the copper dissolution process, the reactions at the electrode surfaces are often given in the form[4,39]

$$\mathrm{Cu}^{2+} + 2\mathrm{e}^- \rightleftharpoons \mathrm{Cu}\ . \tag{92}$$

Moreover, this simple reaction is then decomposed into the two elementary steps

$$\mathrm{Cu}^{+} + \mathrm{e}^- \rightleftharpoons \mathrm{Cu}\ , \qquad \text{(fast)} \tag{93a}$$

$$\mathrm{Cu}^{2+} + \mathrm{e}^- \rightleftharpoons \mathrm{Cu}^{+}\ . \qquad \text{(slow)} \tag{93b}$$

At first glance these descriptions of the copper dissolution might seem fundamentally different to the one in Sect. 6. Whereas there is a two electron reaction in (92) and two single electron reactions in (93), there is only a single electron transfer reaction in (77). But since the electrodes consist of cupric ions Cu^{+} and free electrons e^{-}, rather than of neutral copper atoms, we may replace in (92) and (93a) Cu by $\mathrm{Cu}^{+}+\mathrm{e}^{-}$. Then, the first step in (93) takes the form of an adsorption, instead of an electron transfer reaction. As outlined in Sect. 5.3, also this adsorption step is related to a charge transfer that causes an electric current. Since the first step (93a) is inherently fast[39] compared to (93b), assumption (23) is appropriate for the derivation of a Butler-Volmer equation. This derivation then is in full accordance with the “quasi-equilibrium method”[24].

Another problem might arise when trying to apply standard Butler-Volmer equations from the literature, e.g. (8.24) of Ref.[4]. There the transfer coefficients depend on the number of transfered electrons and this number seems to differ between (77) and (92). But one has to keep in mind that (8.24) of Ref.[4] is derived for a reaction where the electrode metal is not involved (case I of Sect. 5.1). For the copper dissolution, we have to apply case II of Sect. 5.1 instead. There, the transfer coefficients depend on the charge number of the cations which does not differ between (77), (92) and (93b).

Lithium iron phosphate electrode. A main aspect of Ref.[19] by Bazant is the formulation of a consistent Butler-Volmer equations for electron transfer reaction at the interface between a LFP particle and an electrolyte. A phasefield model of Cahn-Hilliard type is used to describe the phase transition within the LFP particles. For this purpose, the constitutive equations are extended to include higher derivatives of the lithium concentration, scaled by a small parameter. Since the phase transition mainly takes place in the interior of the LFP particle and not at the particle surface where the Butler-Volmer equation has to be applied, it is possible to compare our theory with the Butler-Volmer equation of Ref.[19] when the small parameter is set to 0. Moreover, we neglect the elastic contributions considered in[19].

The Butler-Volmer equation (71-72) in Ref.[19] for a single reaction of the general form (3b) reads in our notation

$$\underset{s}{R}=\underset{s}{R}_0\Big(\exp\big(-\tfrac{\beta e_0}{kT}\widetilde{\eta}\big)-\exp\big(\tfrac{(1-\beta)e_0}{kT}\widetilde{\eta}\big)\Big)\ . \tag{94}$$

In contrast to our notation $\widetilde{\eta}$ is the activation potential, (69) of Ref.[19]. It is defined as

$$\widetilde{\eta}=\sum_{\alpha=0}^{N_S}\tfrac{\gamma_\alpha m_\alpha}{e_0}\big(\mu_\alpha+\tfrac{z_\alpha e_0}{m_\alpha}\varphi\big)\big|_I^{\pm}\ . \tag{95}$$

If we consider a single surface reaction and we assume that all surface species exist in the bulk, then the Butler-Volmer equation (94) is consistent with our general Butler-Volmer equation (33)–(35b).

For the reaction $\mathrm{Li}^{+}+\mathrm{e}^{-}\rightleftharpoons\mathrm{Li}$, the properties of double layer are neglected for the derivation of the Butler-Volmer equation in Ref.[19]. Nonetheless, the Butler-Volmer equation in (78)-(86) of Ref.[19] is consistent with our Butler-Volmer equation (60), if we assume i) a constant chemical potential for the lithium ions μ_{Li^+} in the electrolyte, ii) $\beta=1/2$, and iii) the phenomenological coefficient $\underset{s}{R}_0$ is defined as

$$\underset{s}{R}_0=(1-y_{Li}|_I^{+})\exp\big(\tfrac{\beta e_0}{kT}\mu_{Li}|_I^{+}\big)\underset{s}{\widetilde{R}}_0\ . \tag{96}$$

This coincidence can be explained by the fact that M. Bazant has correctly recognized that the driving force of electron transfer reactions are the bulk electrochemical potentials and not the bulk chemical potentials. Note that using the bulk electrochemical potentials in the formulation of the Butler-Volmer equations implies that the absorption on the surface of bulk species is implicitly assumed in equilibrium.

7.4 Alternative constitutive relations for reaction rates

The Butler-Volmer equations in this work are based on the specific choice of the constitutive relations for the reaction rates $\underset{s}{R}$, viz. equation (15a). In the following we want to specify and discuss three alternative constitutive relations for the reaction rates and their implications for the derivation of Butler-Volmer equations. For simplicity we consider a single surface reaction,

$$\underset{s}{\mathrm{a}}_0\mathrm{A}_0+\cdots{}^{+}\underset{s}{\mathrm{a}}_{\mathrm{N_S}}\mathrm{A}_{\mathrm{N_S}}\underset{\underset{s}{R_b}}{\overset{\underset{s}{R_f}}{\rightleftharpoons}}\underset{s}{\mathrm{b}}_0\mathrm{A}_0+\cdots{}^{+}\underset{s}{\mathrm{b}}_{\mathrm{N_S}}\mathrm{A}_{\mathrm{N_S}}\ . \tag{97}$$

The entropy production for a single surface reaction is[20],

$$-\tfrac{1}{kT}D\underset{s}{R}\geq 0\ , \tag{98}$$

where D is the driving force for the surface reaction,

$$D=\sum_{\alpha=0}^{N_S}\underset{s}{\gamma}_\alpha m_\alpha\underset{s}{\mu}_\alpha\ . \tag{99}$$

An Arrhenius ansatz of the form

$$\underset{s}{R}=\underset{s}{L}_0\Big(1-\exp\big(\tfrac{\underset{s}{A}}{kT}D\big)\Big)\qquad\text{with}\qquad\underset{s}{A},\underset{s}{L}_0>0\ , \tag{100}$$

satisfies the entropy inequality. From a mathematical point of view only the sign of the phenomenological coefficients $\underset{s}{A}$ and $\underset{s}{L}_0$ is restricted by the entropy inequality (98). However the coefficients $\underset{s}{A}$ and $\underset{s}{L}_0$ can be arbitrary functions of the fields of matter and the electromagnetic fields as long as they are positive and satisfy the principle of material frame indifference. This gives us some freedom for the formulation of different kinds of constitutive relations for the reaction rate. Independent of the specific choice of $\underset{s}{L}_0$ below, the relation (100) for the reaction rates always implies $D=0$ and $\underset{s}{R}=0$ in thermodynamic equilibrium. Next we discuss three different choices of $\underset{s}{L}_0$.

Case I. For the derivation of the consitituive relations (15a) used in this work, it was assumed in Ref.[20] that the phenomenological coefficient $\underset{s}{L}_0$ is a function of the driving force D, i.e.

$$\underset{s}{L}_0=\underset{s}{R}_0\exp\big(-\underset{s}{\beta}\tfrac{\underset{s}{A}}{kT}D\big)\quad\text{with}\quad\underset{s}{R}_0>0\ . \tag{101}$$

Here the exchange rate $\underset{s}{R}_0$ and the symmetry factor $\underset{s}{\beta}$ are assumed to be constant. Note the entropy inequality does not restrict the sign of $\underset{s}{\beta}$. The coefficient $\underset{s}{L}_0$ is choosen such that the reaction rate $\underset{s}{R}$ yields symmetric terms for the forward reaction $\underset{s}{R}_f$ and backward reaction $\underset{s}{R}_b$,

$$\underset{s}{R} = \underset{s}{R}_f - \underset{s}{R}_b = \underset{s}{R}_0 \Big(\exp\big(-\underset{s}{\beta} \tfrac{\underset{s}{A}}{kT} D\big) - \exp\big((1-\underset{s}{\beta}) \tfrac{\underset{s}{A}}{kT} D\big) \Big) \ . \tag{102}$$

The corresponding Butler-Volmer equation (33) is derived in Section 4, and reads

$$\underset{s}{R} = R_f^0 \exp\big(-\frac{\alpha_f e_0}{kT} \eta_S\big) - R_b^0 \exp\big(+\frac{\alpha_b e_0}{kT} \eta_S\big) \ . \tag{103}$$

The choice leads to transfer coefficients $\alpha_{f/b}$ and the exchange rates $R^0_{f/b}$ that are independent of the overpotential η_S, see (34) and (35).

Case II. In the first case the forward and the backward reaction are driven by the same driving force D. But sometimes it could be favorable that the forward reaction is driven by the educts and the backward reaction is driven by the products only[2]. To this end we decompose the driving force D into educts and products according to

$$D = D_b - D_f \qquad \text{with} \quad D_f = \sum_{\alpha=0}^{N_S} \underset{s}{\mathrm{a}}_\alpha m_\alpha \underset{s}{\mu}_\alpha \quad \text{and} \quad D_b = \sum_{\alpha=0}^{N_S} \underset{s}{\mathrm{b}}_\alpha m_\alpha \underset{s}{\mu}_\alpha \ . \tag{104}$$

Then we choose

$$\underset{s}{L}_0 = \underset{s}{R}_0 \exp\big(\tfrac{1}{kT} D_f\big) \ . \tag{105}$$

Inserting (105) into (100) leads to

$$\underset{s}{R} = \underset{s}{R}_0 \Big(\exp\big(\tfrac{\underset{s}{A}}{kT} D_f\big) - \exp\big(\tfrac{\underset{s}{A}}{kT} D_b\big) \Big) \ . \tag{106}$$

This choice leads to some difficulties in the derivation of a Butler-Volmer equation. To illustrate that we consider the simple surface reaction $\mathrm{O} + n\mathrm{e}^- \rightleftharpoons \mathrm{R}$ at a metal-electrolyte interface. We set $\underset{s}{A} = 1$ and follow the notation of Section 5.1. When carrying out the same steps as in the Section 4, we obtain

$$\begin{aligned} \underset{s}{R} =& \underset{s}{R}_0 \left(\frac{y_O}{\bar{y}_O} \right) \exp\left(-\frac{e_0}{kT} \big((\varphi_E + n\varphi_M) - (\bar{\varphi}_E + n\bar{\varphi}_M) \big) \right) \\ & - \underset{s}{R}_0 \left(\frac{y_R}{\bar{y}_R} \right) \exp\left(\frac{e_0}{kT} \big(\varphi_E - \bar{\varphi}_E \big) \right) \ . \end{aligned} \tag{107}$$

We observe that the forward reaction depends only on the oxidized species, whereas the backward reaction depends on the reduced species. This is in agreement with the formulation of the Butler-Volmer equation (3.4.10) in Ref.[2]. However, a definition of an overpotential is not that obvious from (107). One could define the overpotential as $\eta_S = (\varphi_M - \varphi_E) - (\bar{\varphi}_M - \bar{\varphi}_E)$, and then shift the remaining terms depending on the potentials into the definitions of the transfer coefficients or exchange rates. But then we have exchange rates or transfer coefficients that are functions of the electric potentials, what is in contrast to (3.4.10) of Ref.[2].

Case III. An common concept in chemistry is the introduction of reaction paths and transition states. From this concept microscopic models for the reaction rates are derived. Important contributions in this field are the theories of Marcus and Hush[2,6,7,9,19]. From our point of view reaction path as well as the transition state must be considered as new objects in non-equilibrium thermodynamics. They are called internal variables and need new evolution equations. However, we can include some aspects of Marcus and Hush in our concept by taking into account a quadratic contribution of the driving force D in (101). We choose for the phenomenological coefficient

$$L_0 = \underset{s}{R}_0 \exp\big(-\tfrac{\underset{s}{A}}{kT} (\beta + \tfrac{D}{\lambda}) D\big) \ . \tag{108}$$

The newly introduced parameter λ represent the reorganization energy, which is a microscopic energy contribution. The great achievement of Marcus and Hush was to link the reorganization energy to measurable quantities, such that the predictions of reaction mechanisms were possible. Insertion of (108) in (100) yields

$$\underset{s}{R} = \underset{s}{R}_0 \left(\exp\Big(\tfrac{\underset{s}{A}}{kT} \big(-\underset{s}{\beta} D - \tfrac{D^2}{\lambda} \big) \Big) - \exp\Big(\tfrac{\underset{s}{A}}{kT} \big((1-\underset{s}{\beta}) D - \tfrac{D^2}{\lambda} \big) \Big) \right) \ . \tag{109}$$

The resulting Butler-Volmer equation from this choice is derived in analogous way to Section 4. We obtain

$$\underset{s}{R} = R_f^0 \exp\big(-\frac{\alpha_f e_0}{kT} \eta_S\big) - R_b^0 \exp\big(+\frac{\alpha_b e_0}{kT} \eta_S\big) \ . \tag{110}$$

The overpotential is defined as in Section 4, equation (32). In contrast to the first case the definitions of the transfer coefficients and the exchange rates are function of the overpotential,

$$\alpha_f = \underset{s}{\beta} \underset{s}{A} \Gamma + \tfrac{D^* + \Gamma e_0 \eta_S}{\lambda} \qquad \text{and} \quad \alpha_b = (1 - \underset{s}{\beta} \underset{s}{A}) \Gamma - \tfrac{D^* + \Gamma e_0 \eta_S}{\lambda} \tag{111}$$

and

$$R_f^0 = \underset{s}{R}_0 \ \exp\Big(\big(-\underset{s}{\beta} \ \tfrac{\underset{s}{A}}{kT} - \tfrac{1}{\lambda} \tfrac{(D^* + e_0 \eta_S)}{kT} \big) D^* \Big) \ , \tag{112}$$

$$R_b^0 = \underset{s}{R}_0 \ \exp\Big(\big((1 - \underset{s}{\beta}) \ \tfrac{\underset{s}{A}}{kT} - \tfrac{1}{\lambda} \tfrac{(D^* + e_0 \eta_S)}{kT} \big) D^* \Big) \ . \tag{113}$$

D^* is an abbreviation for

$$D^* = \sum_{\alpha \in \mathscr{M}} \underset{s}{\gamma}^i_\alpha m_\alpha \big(\mu_\alpha - \bar{\mu}_\alpha \big) \big|_I^\pm + \sum_{\alpha \in \mathscr{M}_S \setminus \mathscr{M}} \underset{s}{\gamma}^i_\alpha m_\alpha \Big(\underset{s}{\mu}_\alpha - \underset{s}{\bar{\mu}}_\alpha \Big) \tag{114}$$

and the constant Γ is defined as

$$\Gamma = \begin{cases} \Gamma_+ \ , & \text{if } \Gamma_+ \neq 0 \ , \\ \underset{s}{\Gamma} \ , & \text{if } \Gamma_+ = 0 \ . \end{cases} \tag{115}$$

The dependency of the transfer coefficients on η_S is identical to that, which is proposed in (3.6.15b) of Ref.[2]. However, the dependency of the exchange rates on the overpotential is missing in Ref.[2].

The dependency of the transfer coefficients on the overpotential, more precisely the quadratic dependency of L_0 on the driving force D, leads to curved Tafel slopes[8]. When the reaction rates are moderate, such that $D \gg D^2$ than the quadratic contribution of D in (109) is approximately small compared to the linear one, such that the first and the third case behave identical.

7.5 Inclusion of double layer effects

The constitutive law (15a) gives a thermodynamically consistent relation between the surface reaction rates and the chemical potentials at the surface. A drawback of this relation is that the involved quantities are not directly measurable but only their according bulk values. Bridging this gap is the exceptional value of Butler-Volmer equation (33).

In contrast, the literature starts from measurable bulk values "just in front of the double layer" and derives a Butler-Volmer equation for the surface reaction rates based on kinetic arguments. According to the standard model of the double layer, one has to pass from the bulk through the "diffuse part of the double layer" to reach to so called *outer Helmholtz plane* where the reaction is supposed to take place. For the diffuse layer, the validity of Gouy-Chapman model is postulated resulting in an exponential relation between the species concentration and the electrostatic potential. This motivates a modification of the overpotential attributed to Frumkin[47] [4,48]. There are two mayor objections: first one should note the critics by Newman[4] (p. 227) that microscopic double layer modeling lacks a "firm macroscopic basis" in thermodynamics, and thus "can-not be applied with any certainty to solid electrodes". Second, we emphasize, that instead of postulating a double layer structure, the structure should be a consequence of the model equations. As demonstrated in Refs.[25,27], a dilute solution assumption in general is not valid in boundary layers and thus the Gouy-Chapman model is not applicable there. For a correct description of the complete layer it is of outmost importance to account for the coupling of electric and mechanical effects.

The combination of a Poisson-Nernst-Planck model (PNP) that resolves space charge layers with a generalized Frumkin-Butler-Volmer equation (gFBV) was proposed in Refs.[40,49] and analyzed in detail by Bazant and coworkers[11,40]. Again, there is a specific double layer structure postulated: a Stern-layer structure consisting of a compact layer in front of the reaction plane followed by a diffuse layer. The compact layer is characterized by a linear spatial profile of the electrostatic potential. The overpotential which enters the gFBV is then defined as the voltage drop over the compact layer whereas the diffuse layer has to be resolved by the bulk equations. Compared to the standard models there is an advantage that with the combination of the gFBV approach and the PNP system, it is possible to apply more realistic boundary conditions for the electric potential. Moreover one might argue that this concept is superior to the standard approach with a locally electroneutral bulk model since no quasi-equilibrium for the diffuse part of the double layer is assumed. Nevertheless there is a specific Stern layer structure postulated with a constant compact layer. But instead the diffuse layer is constant whereas the saturation layer varies with the potential drop over the double layer and the spatial profile of the potential is not linear there[26].

In Ref.[40] there are also asymptotic limit equations derived for thin double layers. This limiting procedure corresponds to the formal asymptotic analysis used in Ref. [20] to derive reduced bulk model of Sect. 3. But there are differences: The underlying PNP system in[40] is missing the pressure dependence of the chemical potentials and the momentum balance. Both are indispensable for correct description of boundary layers. For the postulated Stern layer structure there is an additional parameter controlling the partition of the double layer into the compact and the diffuse part. In the one extreme case, the "Gouy-Chapman limit", there is no potential drop over the compact layer. This means that the Nernst-Planck flux has to be applied up to the reaction plane leading to the well known problems of possibly negative concentrations and thus leading to a reaction limited current. In the other limit, the "Helmholtz limit", there is only the compact but no diffuse layer. That means that the complete double layer has been replaced by an ad-hoc postulated structure with a linear profile of the potential.

To summarize our point of view about the role of the double layer structure for the Butler-Volmer equation: when the assumptions of the reduced model are appropriate, i.e. the double layer is asymptotically in quasi-equilibrium, then the Butler-Volmer equation (33) already gives an exact description of the situation at the reaction plane and we can not get better by "correcting" the bulk values according to any kind of assumed double-layer structure. On the other hand, if the scaling that was used in the asymptotic analysis is not appropriate, then the Butler-Volmer equation should not be used at all but instead the complete model of Ref.[20] in combination with the original constitutive laws (15a) for the reactions at the surface.

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