Contents

1   Conceptual problems and limitations

Global electroneutrality. It is reasonable to expect the experimental setting to be build from electrically neutral components, e.g. electrolyte and electrodes. However, the electrolyte will in general not maintain global electroneutrality, due to the surface reactions, cf. Fig. 1. The configurations in Fig. 1 differ in the profiles of the related electric potential, in particular in the plateau height of a locally electroneutral bulk region. Thus, if a potential difference is applied to the electrodes, the system will in general respond with a change of the global net charge of the electrolyte. It should be stressed that this charging of the electrolyte is not related to adsorption to the surfaces.
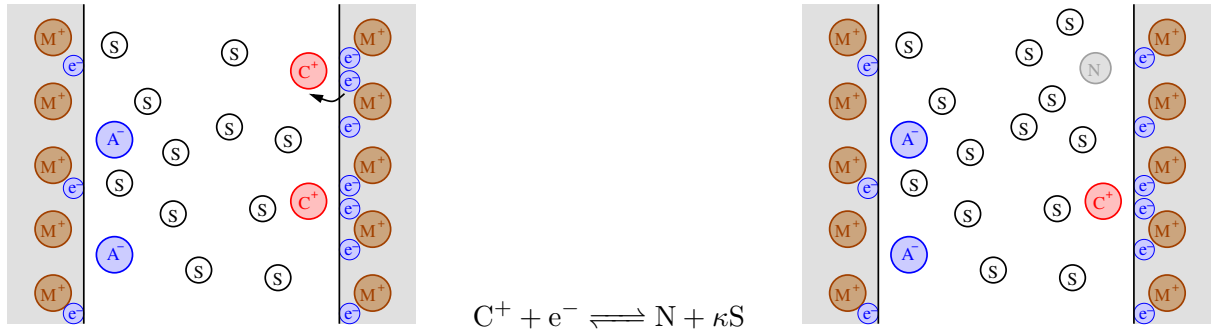

$$C^+ + e^- \rightleftharpoons N + \kappa S$$

Figure 1: Each double layer is elecroneutral, but in the presence of surface reactions, an electrolyte subdomain may be globally charged.

Surface electron density, surface charge. The surface material model relies on a constant chemical potential of electrons, but we do not want to specify the this constant. Thus, we do not want to determine the surface number density of electrons $n_e \atop s$, as well as we do not want to determine the surface free charge $n^{\mathrm{F}} \atop s$. However, the time derivative $\partial_t n^{\mathrm{F}} \atop s$ is determined by the change of the surface jump of the electric field.

Surface velocity and hyperbolic total mass balance. For a single planar surface, the surface velocity can be set to zero by appropriate choice of the coordinate system. By the assumptions that the electrode metal ions are not involved in the surface reaction and that the mass of the electrons can be neglected, the barycentric velocity of the electrolyte at the surface is determined from the net adsorption from the electrolyte to the electrode. This defines one boundary condition for the total mass balance in the electrolyte. If we consider a full cell setting with two surfaces, there is a similar condition to be imposed at the second electrode. Due to the hyperbolic character of the total mass balance, this condition requires the surface velocity to

act as an additional degree of freedom, which can not be specified by a-priori considerations. However, in a stationary state, the surface velocity may be determined by a-priori considerations, e.g. to be the same for both surfaces.

Incompressibility, excess volume and adsorption. The surface reaction necessarily preserves mass and charge, but not volume. Thus, the specific volume of the reaction product may differ from the sum of the specific volumes of the reactants by some excess volume Δv. Incompressibility then defines a relation between the electrolyte composition (the n_α), the amount of adsorption to the surface (the $\underset{s}{n_\alpha}$) and the volume of the electrolyte domain. While in a stationary state of a full cell setting the volume is constant, the size of the volume is not a-priori known. Postulating a domain size of the electrolyte domain would not only have an impact on the transient evolution to the stationary state, but would also impose a condition on the electrolyte composition and adsorption in the stationary state that is reached.

In a real experiment, pressure and the distance of the electrodes may be kept fixed, but the hight of the electrolyte may change. This setting can not be consistently be described in a simple 1D setting of a full electrolytic cell.

Surface number densities. In a stationary state, the surface coverage of the adsorbed species can be determined a-posteriori from the state in the electrolyte and the Gibbs energies of the adsorption reactions. Since we do not have knowledge about these Gibbs energies, they are treated as model parameters. In a full cell problem, the electrolyte volume and thus the surface velocity (difference between the surfaces) depends on the adsorption and thus on the Gibbs energies. However, we want the voltage-current relation obtained from stationary states not to depend on these unknown Gibbs energies.

Butler-Volmer setting. The Butler-Volmer setting should be understood as asymptotic description for thin double layers, compared to the overall size of the electrolytic cell. Then, volume change due to adsorption is of higher asymptotic order and can be neglected. Nevertheless, the volume change due to a non-vanishing excess volume Δv remains.

Controlled current − controlled voltage. In the asymptotic Butler-Volmer setting, the bulk the total electric charge, as well as the total electric current can be identified with the free charge, free current, respectively. Then, the current can be directly related to the reaction rate In such a context, it is straightforward to apply a current controlled experiment. In the spatially resolved model, it is more natural to prescribe a potential difference.

2 Basic Assumptions

The aim is to model systems that can be well described by Butler-Volmer laws. The asymptotic derivation of Butler-Volmer equations depends on the establishment of quasi-equilibrium in the boundary layer. This in turn, requires vanishing of the velocity gradient, there needs to be a coordinate system, where the barycentric velocity vanishes. This condition can be expected to be approximatively fulfilled if there is only one electron transfer surface reaction. To the contrary, it is not obvious, whether or not this condition can be satisfied in the case of e.g. a lithium intercalation process.
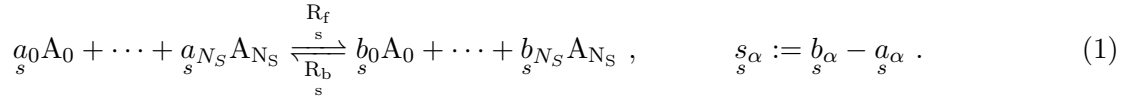
1. **Domain geometry.** We consider a S separating two subdomains $\Omega^\pm \subseteq \mathbb{R}^3$ with $S := \partial\Omega^+ \cap \partial\Omega^-$. The surface is assumed to be asymptotically flat, i.e. curvature is small $k_M \ll 1$. and the normal $\boldsymbol{\nu}$ is chosen to be the inner normal of Ω^+.

2. **Vanishing tangential transport.** We assume that there are no tangential fluxes of mass, momentum, energy or charge. The surface velocity $\underset{s}{\boldsymbol{v}}$ lies in normal direction $\underset{s}{\boldsymbol{v}} = w_\nu \, \boldsymbol{\nu}$.

3. **Isothermal case.** We only consider isothermal processes. Hence the bulk temperature T and surface temperature $\underset{s}{T}$ are constant parameters satisfying $\underset{s}{T} = T$.

4. **Quasi-static electric field.** We consider the quasi-electrostatic approximation, i.e. $|\boldsymbol{B}| \ll c_0 |\boldsymbol{E}|$. Thus, only the electric field is $\boldsymbol{E} = -\nabla \varphi$, while the magnetic field is ignored.

5. **Polarization.** Scale analysis justifies the assumption that polarization relaxation is fast and can be described by a scalar susceptibility χ.

6. **Fast adsorption.** We assume that adsorption to the surface ist fast compared to reaction.

7. **Quasi-static momentum balance.** Asymptotic analysis justifies the assumption of quasi-static momentum balance, if the gradients of the velocity are not too large.

8. **Mobilities.** For simplicity, we choose mobilities according to a Nernst-Planck approach, i.e. as the strong dilution limit of mobilities based on Maxwell-Stefan diffusivities.

9. **Electron mass.** We assume that the mass of the electron can be neglected, i.e. $m_e = 0$.

3 Material model

Constituents and chemical reactions. To refer to the individual constituents in Ω^+ and Ω^-, we use index sets $\mathcal{I}^\pm$ and usually denote the index by $\alpha \in \mathcal{I}^\pm$. For the constituents on the surface S, we use the index set $\mathcal{I}_S \supseteq \mathcal{I}^+ \cup \mathcal{I}^-$. Without loss of generality, we assume $\mathcal{I}^+ \cap \mathcal{I}^- = \emptyset$.

We neglect bulk chemical reactions and only one chemical reactions on the surface. Generalization to M bulk reactions and M_S surface reactions is straightforward.

$$\underset{s}{a_0} \mathrm{A}_0 + \cdots + \underset{s}{a_{N_S}} \mathrm{A}_{\mathrm{N_S}} \underset{\underset{s}{\mathrm{R_b}}}{\overset{\underset{s}{\mathrm{R_f}}}{\rightleftharpoons}} \underset{s}{b_0} \mathrm{A}_0 + \cdots + \underset{s}{b_{N_S}} \mathrm{A}_{\mathrm{N_S}} \,, \qquad \underset{s}{s_\alpha} := \underset{s}{b_\alpha} - \underset{s}{a_\alpha} \,. \tag{1}$$

The net reaction rate is the defined as $R = R_f - R_b$.

A constituent A_α has the (atomic) mass m_α and may be carrier of the charge $z_\alpha e_0$, where the positive constant e_0 is the elementary charge and z_α is the charge number of the constituent. Since charge and mass have to be conserved by every single reaction in the bulk and on the surface, we have

$$\sum_{\alpha \in \mathcal{I}_S} z_\alpha \underset{s}{s_\alpha} = 0 \,, \qquad\qquad \sum_{\alpha \in \mathcal{I}_S} m_\alpha \underset{s}{s_\alpha} = 0 \,. \tag{2}$$

We introduce the volume change due to the reaction as $\Delta v = \sum_{\alpha \in \mathcal{I}^-} \underset{s}{s_\alpha} v_\alpha^{ref}$.

Basic quantities. Multiplication of the number densities by m_α gives the partial mass densities $\rho_\alpha = m_\alpha n_\alpha$, $\underset{s}{\rho_\alpha} = m_\alpha \underset{s}{n_\alpha}$. The mass density of the mixture and the barycentric velocity are defined by

$$\rho = \sum_{\alpha \in \mathcal{I}} m_\alpha n_\alpha \,, \qquad\qquad \underset{s}{\rho} = \sum_{\alpha \in \mathcal{I}_S} m_\alpha \underset{s}{n_\alpha} \,. \tag{3a}$$

$$\boldsymbol{v} = \frac{1}{\rho} \sum_{\alpha \in \mathcal{I}} m_\alpha n_\alpha \, \boldsymbol{v}_\alpha \,, \tag{3b}$$

The total free charge density is defined by

$$n^{\mathrm{F}} = e_0 \sum_{\alpha \in \mathcal{I}} z_\alpha n_\alpha \,, \qquad\qquad \underset{s}{n^{\mathrm{F}}} = e_0 \sum_{\alpha \in \mathcal{I}_S} z_\alpha \underset{s}{n_\alpha} \,. \tag{4}$$

Electrolyte material model. The free energy is chosen according to an incompressible ideal mixture with an additional polarization energy term

$$\rho\psi = \rho\psi^{\mathrm{mat}} + \rho\psi^{\mathrm{pol}} \qquad\qquad \mu = \mu^{\mathrm{mat}} + \mu^{\mathrm{pol}} \qquad\qquad p = p^{\mathrm{mat}} + p^{\mathrm{pol}} \tag{5}$$

$$\mu_\alpha^{\mathrm{mat}} = g_\alpha + k_B T \ln(y_\alpha) + v_\alpha^{ref}\left(p^{\mathrm{mat}} - p^{ref}\right) \quad \text{for} \ \alpha \in \mathcal{I} \,, \tag{6}$$

with

$$y_\alpha = \frac{n_\alpha}{\sum_{\beta \in \mathcal{I}} n_\beta} \,, \qquad\qquad \sum_{\alpha \in \mathcal{I}} v_\alpha^{ref} n_\alpha = 1 \,. \tag{7}$$

The diffusion fluxes and the reaction rates are

$$\boldsymbol{J}_\alpha = -m_\alpha n_\alpha D_{\alpha\alpha}\left(\nabla\left(\mu_\alpha - \tfrac{m_\alpha}{m_0}\mu_0\right) + e_0 z_\alpha \nabla\varphi\right) \,, \qquad \alpha \in \mathcal{I} \setminus \{0\} \,. \tag{8}$$

$$\underset{s}{R} = \underset{s}{R_0}\left(\exp\left(-\beta\underset{s}{\mathcal{A}}\right) - \exp\left((1-\beta)\underset{s}{\mathcal{A}}\right)\right) \,, \qquad \text{with } \mathcal{A} := \frac{1}{k_B T}\sum_{\alpha \in \mathcal{I}_S} \underset{s}{s_\alpha}\underset{s}{\mu_\alpha} \,, \tag{9}$$

We consider the cases of either constant or concentration dependent susceptibility. Let χ_α be constant for $\alpha \in \mathcal{I}$. We set

$$\chi = \begin{cases} \chi_0, \\ \sum_{\alpha \in \mathcal{I}} v_\alpha^{ref} n_\alpha \cdot \chi_\alpha \,, \end{cases} \qquad\qquad \rho\psi^{\mathrm{pol}} = -\chi\frac{\varepsilon_0}{2}|\nabla\varphi|^2, \tag{10}$$

$$\mu^{\mathrm{pol}} = \begin{cases} 0 \\ -\chi\frac{\varepsilon_0}{2}|\nabla\varphi|^2, \end{cases} \qquad\qquad p^{\mathrm{pol}} = \begin{cases} -\rho\psi^{\mathrm{pol}}, \\ 0 \end{cases} \tag{11}$$

In the 1D setting, the total stress tensor simplifies to

$$\Sigma = \begin{cases} -p^{\mathrm{mat}} + \frac{(1+\chi)\varepsilon_0}{2}|\partial_x\varphi|^2, \\ -p^{\mathrm{mat}} + \frac{(1+2\chi)\varepsilon_0}{2}|\partial_x\varphi|^2. \end{cases} \tag{12}$$

Surface material model. We define

$$\underset{s}{n} = \frac{a_M^{ref}}{a_V^{ref}}\underset{s}{n_M^{ref}} \tag{13}$$

$$\underset{s}{y_\alpha} = \frac{a_V^{ref}}{a_M^{ref}}\frac{\underset{s}{n_\alpha}}{\underset{s}{n_M^{ref}}} \qquad\qquad \underset{s}{y_V} = 1 - \sum_{\alpha \in \mathcal{I}} \frac{a_\alpha^{ref}}{a_V^{ref}}\underset{s}{y_\alpha} \tag{14}$$

The chemical potentials are

$$\underset{s}{\mu_\alpha} = \underset{s}{\psi_\alpha^{ref}} + k_B T \ln(\underset{s}{y_\alpha}) - \frac{a_\alpha^{ref}}{a_V^{ref}}k_B T \ln(\underset{s}{y_V}) \tag{15}$$

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4   Boundary value problem with planar surface

Consider a metal electrode in the domain $\Omega^+ = \{(x,y,z) : x < 0\}$ such that the surface velocity vanishes and the surface normal at $x = 0$ is $\boldsymbol{\nu} = -\boldsymbol{e_x}$. We assume that in y and z direction the system is either infinite and homogeneous, or can be periodically extended. In a half cell setting, the electrolyte domain is $\Omega^+ = \{(x,y,z) : x < 0\}$. This can be approximated by a restriction to $0 < x < L/2$, for some L large enough. For a full cell problem, Ω^+ is extended by the domain $\{(x,y,z) : L(t) < x\}$.

Constituents and reaction.   Let the index sets for the constituents of the metal be $\mathcal{I}^+ = \{\mathrm{M}, \mathrm{e}^-\}$. The electrolyte consists of the solvent, solvated anions and cations and the reaction product B, such that $\mathcal{I}^- = \{\mathrm{A}, \mathrm{B}, \mathrm{C}, \mathrm{S}\}$. We consider the reaction

$$\mathrm{C} + \mathrm{e}^- \rightleftharpoons \mathrm{B} + \kappa\mathrm{S} , \tag{16}$$

such that

$$\underset{s}{s_A} = 0, \qquad \underset{s}{s_B} = 1, \qquad \underset{s}{s_C} = -1, \qquad \underset{s}{s_S} = \kappa, \qquad \underset{s}{s_e} = -1. \tag{17}$$

Thus, the affinity is

$$k_B T \, \mathcal{A} = \underset{s}{\mu_B} - \underset{s}{\mu_C} + \kappa\underset{s}{\mu_S} - \underset{s}{\mu_e^{ref}} \tag{18}$$

Depending on the charge number of the cation, the reaction product may be charged or not, but in any case $z_B - z_C = -1$.

Gibbs energies and adsorption.   Instead of the surface chemical potential of the electrons, we use the Gibbs energy related to the surface reaction equilibrium as a parameter.

$$\mathcal{A} = \left. \left(\ln(y_B) - \ln(y_C) + \kappa \ln(y_S) + \frac{\Delta v}{k_B T} \left(p^{\mathrm{mat}} - p^{ref} \right) \right) \right|_S + \frac{\Delta g}{k_B T} , \tag{19}$$

with $\Delta g = g_B - g_C + \kappa g_S - \frac{1}{k_B T}\underset{s}{\mu_e^{ref}}$. The adsorption

$$\underset{s}{y_\alpha} = \left(\underset{s}{y_V} \right)^{\frac{a_\alpha^{ref}}{a_V^{ref}}} \cdot y_\alpha|_S \cdot \exp\left(\frac{\Delta g_\alpha}{k_B T} + \frac{v_\alpha^{ref}}{k_B T} \left(p^{\mathrm{mat}}|_S - p^{ref} \right) \right) \tag{20}$$

with $\Delta g_\alpha = g_\alpha - \underset{s}{\psi_\alpha^{ref}}$

Full cell 1D BVP.   In the electrolyte domain $\Omega^-(t) = \{0 < x < L(t)\}$, the variables $n_A, n_B, n_C, v, \varphi, L(t)$ are for $t > 0$ determined by initial conditions and the PDEs

$$\partial_t n_A + \mathrm{div}(n_A v + J_A) = 0 , \tag{21a}$$
$$\partial_t n_B + \mathrm{div}(n_B v + J_B) = 0 , \tag{21b}$$
$$\partial_t n_C + \mathrm{div}(n_C v + J_C) = 0 , \tag{21c}$$
$$\partial_t \rho + \mathrm{div}(\rho \boldsymbol{v}) = 0 , \tag{21d}$$
$$- \mathrm{div}((1 + \chi)\varepsilon_0 \nabla\varphi) = n^{\mathrm{F}} , \tag{21e}$$

together with the incompressibility condition and the integrated momentum equation

$$v_A^{ref} n_A + v_B^{ref} n_B + v_C^{ref} n_C + v_S^{ref} n_S = 0 \tag{22a}$$

$$p^{\mathrm{mat}} - p^{ref} = \begin{cases} \frac{(1+\chi)\varepsilon_0}{2}|\partial_x\varphi|^2 \ , \\ \frac{(1+2\chi)\varepsilon_0}{2}|\partial_x\varphi|^2 \ , \end{cases} \tag{22b}$$

and the boundary conditions

$$\underline{x = 0, \quad (\nu = -\boldsymbol{e}_x)}: \qquad\qquad \underline{x = L(t), \quad (\nu = +\boldsymbol{e}_x)}:$$

$$\partial_t n_A + (n_A v + J_A) = 0 \ , \qquad\qquad \partial_t n_A - (n_A v + J_A) = 0 \ , \tag{23a}$$

$$\partial_t n_B + (n_B v + J_B) = R \ , \qquad\qquad \partial_t n_B - (n_B v + J_B) = R \ , \tag{23b}$$

$$\partial_t n_C + (n_C v + J_C) = -R \ , \qquad\qquad \partial_t n_C - (n_C v + J_C) = -R \ , \tag{23c}$$

$$\partial_t \rho + \rho v = 0 \ , \qquad\qquad \partial_t \rho - \rho(v - v) = 0 \ , \tag{23d}$$

$$\varphi = \varphi_0(t) \ , \qquad\qquad \varphi = 0 \ , \tag{23e}$$

For the surface variables, we have

$$n_A = \frac{a_M^{ref}}{a_V^{ref}} n_M^{ref} \left(y_V\right)^{\frac{a_A^{ref}}{a_V^{ref}}} \cdot y_A|_S \cdot \exp\left(\frac{\Delta g_A}{k_B T} + \frac{v_A^{ref}}{k_B T} (p^{\mathrm{mat}}|_S - p^{ref}) \right) \tag{24a}$$

$$n_B = \frac{a_M^{ref}}{a_V^{ref}} n_M^{ref} \left(y_V\right)^{\frac{a_B^{ref}}{a_V^{ref}}} \cdot y_B|_S \cdot \exp\left(\frac{\Delta g_B}{k_B T} + \frac{v_B^{ref}}{k_B T} (p^{\mathrm{mat}}|_S - p^{ref}) \right) \tag{24b}$$

$$n_C = \frac{a_M^{ref}}{a_V^{ref}} n_M^{ref} \left(y_V\right)^{\frac{a_C^{ref}}{a_V^{ref}}} \cdot y_C|_S \cdot \exp\left(\frac{\Delta g_C}{k_B T} + \frac{v_C^{ref}}{k_B T} (p^{\mathrm{mat}}|_S - p^{ref}) \right) \tag{24c}$$

$$n_S = \frac{a_M^{ref}}{a_V^{ref}} n_M^{ref} \left(y_V\right)^{\frac{a_S^{ref}}{a_V^{ref}}} \cdot y_S|_S \cdot \exp\left(\frac{\Delta g_S}{k_B T} + \frac{v_S^{ref}}{k_B T} (p^{\mathrm{mat}}|_S - p^{ref}) \right) \tag{24d}$$

$$y_V = 1 - \sum_{\alpha \in \mathcal{I}} \frac{a_\alpha^{ref}}{a_M^{ref}} \frac{n_\alpha}{n_M^{ref}} \tag{24e}$$

Half cell problem. For the half cell problem, we choose a constant numerical domain size L and replace (23) by

$$\underline{x = 0, \quad (\nu = -\boldsymbol{e}_x)}: \qquad\qquad \underline{x = L, \quad (\nu = +\boldsymbol{e}_x)}:$$

$$\partial_t n_A + (n_A v + J_A) = 0 \ , \qquad\qquad n_A = n_A^{\mathrm{bulk}} \ , \tag{25a}$$

$$\partial_t n_B + (n_B v + J_B) = R \ , \qquad\qquad n_B = n_B^{\mathrm{bulk}} \ , \tag{25b}$$

$$\partial_t n_C + (n_C v + J_C) = -R \ , \qquad\qquad n_C = n_C^{\mathrm{bulk}} \ , \tag{25c}$$

$$\partial_t \rho + \rho v = 0 \ , \tag{25d}$$

$$\varphi = \varphi_0(t) \ , \qquad\qquad \varphi = 0 \ , \tag{25e}$$

In particular, there in no second boundary condition for the total mass balance.