Mathematical models for electrochemistry: Law of mass action revisited

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Abstract

Chemical reactions move charges. A mathematical model for chemical reactions in electrolytes is developed using an energy variational method consistent with classical thermodynamics. Electrostatics and chemical reactions are included in consistently defined energetic and dissipative functionals. The energy variation method is extended to open systems with inputs and outputs of charge, mass, and energy. Open systems can transform the input energy of one type into the output energy of another type. Models for reactions in the bulk and on boundaries are analyzed with this framework. In particular, we develop a two-domain model for a reaction system with self-regulation, and internal switching, that plays an important role in the electron transport chain of mitochondria that creates the ATP so important for life. Simulations are conducted to study the effects of electric potential on reaction rate and switching within the two-domain system.

Keywords— Open system, Mass action, Electrochemistry

1 Introduction

Theories for chemical reactions based on the law of mass actions often ignore electric effects [9, 29], even though the reactants, catalysts and enzymes of chemistry and biology depend on charge interactions for much of their function [53, 73, 12]. Recently, mathematical models have been developed in the electrochemical tradition [25, 1, 2, 58, 8], some using variational princlies [65, 64].

Here, we extend this work by proposing a general thermodynamics-consistent framework for electrochemical reactions both in the bulk and on the interface in biological systems. Our model naturally fits chemical reactions into the conservation laws of currents and make it possible to use the classical circuit analysis. Classical circuit analysis provides a coarse grain description of electrodynamics that is exact if Kirchhoff's law is applied to the total current, including the displacement current [20]. Specifically, we investigate the electric effects on the rate of chemical reactions using several reduced ('toy') models that show interesting dynamics and interactions between diffusion, reaction, and electric fields of ionic solutions.

Various consistent frameworks have been developed for nonequilibrium systems based on the second law of thermodynamics and Onsager's linear response theory. Onsage's variational principle, which was first proposed in [44, 45] and later generalized by Edwards [16], Doi [15], and Qian [47], is a popular

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approach to irreversible systems. It is based on the maximum dissipation principle proposed by Lord Rayleigh [55] motivated by the analysis of uncharged systems. The principle states that for a system described by variables $\alpha_1, \dots, \alpha_n$ that describe the displacement from thermodynamic equilibrium with the (corresponding) rates $\dot{\alpha}_1, \dots, \dot{\alpha}_n$, and with free energy $F(\alpha_1, \dots, \alpha_n)$, the thermodynamic flux $\dot{\alpha}_i$ follows the dynamic path that minimizes the Rayleigh function. This function is the sum of the dissipation function Φ and the rate of the change of the free energy \dot{F} in an isothermal system. [62] provide a more detailed review. In order to include the fluid kinetic energy [24] for fluid equations, Wang et al. [63, 71] proposed the Generalized Onsager principle (GOP) for both reversible and irreversible processes.

Energetic Variational Approach (EnVarA) is another powerful tool proposed by Liu et al. [49, 19, 68]. The general framework of EnVarA is a combination of statistical physics and nonlinear thermodynamics. All the physics are integrated into the definitions of total energy E and dissipation functional Δ . The Least action principle [23] yields the conservative force F_{con} by taking the variation of the action functional with respect to the flow map in the Lagrange frame of reference. The Maximum principle [44, 45] yields dissipative force F_{dis} by taking the variation of the rate function. The final equation of momentum is achieved by balancing these two forces balance $F_{con} = F_{dis}$. A more detailed review can be found in [64].

Based on the consideration of the second law of thermodynamics, in particular, the requirement that the rate of energy dissipation needs to be non-positive, Ren et al. [48, 75, 74] proposed a more straightforward method built on a concept in [31]. First, the energy functional E is defined according to different physical fields. Based on the laws of conservation, the kinematic assumptions are listed with unknown terms like fluxes and stresses. By taking the time derivative of the total energy $\frac{dE}{dt}$, those unknowns could be described so each term in $\frac{dE}{dt}$ is negative. Following Ren's Method, Shen et al. proposed an energy variation method [51, 52] with predefined energetic and dissipative functionals. The unknown terms in the kinematics assumptions are obtained by matching $\frac{dE}{dt}$ with a predefined dissipative function Δ .

Most existing work focuses on closed systems with no flux entering from the boundary, and flux conditions are added as boundary conditions. However, most biological systems, and all powered devices of engineering, are open systems with flux flowing in and out of the domain under consideration. In this paper, we propose a thermodynamically consistent framework for open systems with both energetic and dissipative components on the boundary as well as in the bulk.

The law of mass action [42] is a fundamental principle in chemistry that relates the concentrations of reactants and products in a chemical reaction to its equilibrium constant. Recently, models have been proposed for the chemical reaction based on thermodynamics laws [30, 72, 39]. Wang et al. [65, 64, 38] extended with the EnVarA framework for a chemical reaction system with general mass action kinetics. The Butler-Volmer equation is a widely used phenomenological equation used to describe the rate of charge transfer carried by ions or electrons [10, 22, 14]. An important question that has not been addressed explicitly is how to fit chemical reactions into the mathematics of Kirchhoff's law and conservation of total current that make possible classical circuit analysis that so reduces the complexity of analysis of electric fields and flows. In this paper, we show one way to describe chemical reactions in ionic solutions with an extension of classical field theory that does not violate the traditions of either chemistry or electrodynamic field theory.

Our methods link the electric field and reaction dynamics as Wang, et al, [65, 64] have for reactions that do not involve charge or electrodynamics. The generalization that combines circuit analysis and chemical reactions allows us to study systems of some importance including all the powered systems of engineering and the electron transport chains that oxidise metabolites to create the chemical power source of life, ATP.

The rest of the paper is organized as follows. In Section 2, we derive the general field theory for open system with flux on the boundary and then the method is use to derive equations for an ionic system with reaction in bulk region, on the boundary and on the interior interface. The simulation results for a bidomain rection system are presented in Section 3. The discussions and conclusions are shown in Section 4.

2 Mathematical Models

For a close system, the First Law of Thermodynamics states that the rate of change of the sum of the kinetic energy \mathcal{K} and the internal energy \mathcal{U} is equal to the sum of the rates of change of work \mathcal{W} and heat \mathcal{Q} , so $\frac{d(\mathcal{K}+\mathcal{U})}{dt} = \frac{d\mathcal{W}}{dt} + \frac{d\mathcal{Q}}{dt}$. From the standard statistical physics, the internal energy \mathcal{U} takes into account the particles interactions. Such interactions can be local, such as hard core interactions and nonlocal, such as Coulomb electrostatic interactions. The Second Law of Thermodynamics, in the isothermal case, is given by, $T\frac{d\mathcal{S}}{dt} = \frac{d\mathcal{Q}}{dt} + \Delta$, where T is temperature, \mathcal{S} is entropy and $\Delta \geq 0$ is entropy production. As a reformulation of the linear response assumption, this entropy production functional can be represented as the sum of various rates such as the velocities and the strain rates. By subtracting the Second Law from the First Law, under the isothermal assumption, assuming both laws are valid for nonequilibrium open systems, we have,

$$\frac{dE}{dt} = \frac{d\mathcal{W}}{dt} - \Delta,\tag{1}$$

where $E = \mathcal{K} + \mathcal{F}$ is the total energy and $\mathcal{F} := \mathcal{U} - \mathcal{T}\mathcal{S}$ is the Helmholtz free energy. In case no external forces or fields are applied, i.e. $\frac{dW}{dt} = 0$, we can derive the dissipation law $\frac{dE}{dt} = -\Delta$. Open systems have some fluxes that flow in or out through the boundary and have distinctive

Open systems have some fluxes that flow in or out through the boundary and have distinctive energy dissipation laws that differ from those of closed systems. In open systems, energy can change both because of the flux across the boundary and also because of the change in dissipation. For open systems, we assume the following energy law

$$\frac{dE}{dt} = \mathcal{P}_{E,\partial\Omega} - \Delta,\tag{2}$$

where $\mathcal{P}_{E,\partial\Omega}$ is the energy exchange rate through energy due to the variation of total particles, energy. It is important to note that both the total energy and dissipation functionals incorporate contributions from both the bulk region and the boundary.

2.1 Bulk reaction

We consider a domain that has reactions in bulk and connects to an infinite large reservoir with fixed chemical potential on the boundary. We focus on elementary reactions containing N species $\{C_1^{z_1}, C_2^{z_2}, \cdots, C_N^{z_N}\}$

where k_f and k_r are the forward and backward reaction rates, C_i is the concentration of i^{th} species, respectively. Here a_i and b_i are the stoichiometric coefficients, and z_i is the valence of i^{th} species. If let $\gamma_i = b_i - a_i$. Charge conservation implies $\sum_{i=1}^{N} \gamma_i z_i = 0$.

Based on the laws of conservation of chemical elements and Maxwell equations, we have the following kinematic assumptions

$$\begin{cases} \frac{\partial C_i}{\partial t} = -\nabla \cdot \boldsymbol{j}_i + \gamma_i \ \mathcal{R}, \\ \nabla \cdot (\boldsymbol{D}) = \sum_{i=1}^N z_i C_i F, \\ \nabla \times \boldsymbol{E} = \boldsymbol{0}, \end{cases}$$
(4)

where $j_i, i = 1, \dots, N$ are the passive fluxes, z_i is the valence of i_{th} particle, F is Faraday constant and $\mathcal{R} = \mathcal{R}_f - \mathcal{R}_r$ is the net reaction rate function with forward and reverse reactions rate \mathcal{R}_f and \mathcal{R}_r . D is Maxwell's electrical displacement field and $D = \varepsilon_0 \varepsilon_r E$ with electric field E, dielectric constant ε_0 and relative dielectric constant ε_r . The equation $\nabla \times E = 0$ implies that there exists a ϕ such that $E = -\nabla \phi$.

The boundary conditions are

$$\begin{cases} \boldsymbol{j}_i \cdot \boldsymbol{n} = j_{i,ex}, i = 1 \cdots, 4, & \text{on } \partial\Omega, \\ \boldsymbol{D} \cdot \boldsymbol{n} = 0, & \text{on } \partial\Omega. \end{cases}$$
(5)

where $j_{i,ex}$ is the flux of i_{th} ion supplied from an external source, n is the unit out normal vector.

Remark 2.1. By multiplying $z_i e$ on both sides of the first equation, we have

$$\frac{\partial}{\partial t} (\nabla \cdot \boldsymbol{D}) = \sum_{i=1}^{N} z_i F \frac{\partial C_i}{\partial t}$$

$$= -\sum_{i=1}^{N} \nabla \cdot (z_i F \boldsymbol{j}_i) + \sum_{i=1}^{N} \gamma_i \mathcal{R}$$

$$= -\sum_{i=1}^{N} \nabla \cdot (z_i F \boldsymbol{j}_i)$$
(6)
(7)

which is consistent with the electrostatic Maxwell equations. Treatment of transient problems, involving displacement currents is needed to deal with some important experimental work [3, 6, 61, 7, 11, 60].

The total energetic functional is defined as the summation of entropies of mixing, internal energy and electrical static energy [57, 65].

$$E = E_{ent} + E_{int} + E_{ele}$$

$$= \sum_{i=1}^{N} \int_{\Omega} RT \left\{ C_i \left(\ln \left(\frac{C_i}{c_0} \right) - 1 \right) \right\} dx + \int_{\Omega} \sum_{i=1}^{N} C_i U_i dx + \int_{\Omega} \sum_{i=1}^{N} z_i F C_i \phi - \int_{\Omega} \frac{\mathbf{D} \cdot \mathbf{E}}{2} dx$$

$$= \sum_{i=1}^{N} \int_{\Omega} RT \left\{ C_i \left(\ln \left(\frac{C_i}{c_0} \right) - 1 \right) \right\} dx + \int_{\Omega} \sum_{i=1}^{N} C_i U_i dx + \int_{\Omega} \frac{\mathbf{D} \cdot \mathbf{E}}{2} dx, \quad (8)$$

where R is universal gas constant, T is temperature, U_i is the internal energy density of i_{th} particle and c_0 is concentration.

Then the chemical potentials can be calculated from the variation of total energy

$$\tilde{\mu}_i = \frac{\delta E}{\delta C_i} = RT \ln \frac{C_i}{c_0} + U_i + z_i \phi F, \ i = 1, \cdots, N.$$
(9)

It is assumed in the present work that the dissipation of the system energy is due to passive diffusion and chemical reaction. Additional dissipations (and energies for that matter) can be included if needed in later applications.

$$\Delta = \int_{\Omega} \left\{ \sum_{j=1}^{N} \frac{RT}{D_i C_i} |\mathbf{j}_i|^2 + RT \mathcal{R} \ln\left(\frac{\mathcal{R}_f}{\mathcal{R}_r}\right) \right\} dx + \sum_{i=1}^{N} \int_{\partial\Omega} \frac{1}{g_i} |j_{i,ex}|^2 dS$$
$$= \int_{\Omega} \left\{ \sum_{j=1}^{N} \frac{RT}{D_i C_i} |\mathbf{j}_i|^2 + RT (\mathcal{R}_f - \mathcal{R}_r) \ln\left(\frac{\mathcal{R}_f}{\mathcal{R}_r}\right) \right\} dx + \sum_{i=1}^{N} \int_{\partial\Omega} \frac{1}{g_i} |j_{i,ex}|^2 dS, \quad (10)$$

where g_i is the conductivity of i_{th} species on the boundary.

The boundary energy communication rate $\mathcal{P}_{E,\partial\Omega}$ is induced by the mass communication flux with energy density μ_{ex}

$$\mathcal{P}_{E,\partial\Omega} = -\sum_{i=1}^{N} \int_{\partial\Omega} \tilde{\mu}_{i,ex} j_{i,ex} dS, \qquad (11)$$

where $\tilde{\mu}_{i,ex}$ is the fixed external chemical potential of i_{th} species.

We need the time derivative of the total energy function (8) to apply the dissipation law, either for open or closed systems.

$$\frac{dE}{dt} = \int_{\Omega} \sum_{i=1}^{N} \left\{ \mu_i \frac{\partial C_i}{\partial t} \right\} dx + \int_{\Omega} \boldsymbol{E} \cdot \frac{\partial \boldsymbol{D}}{\partial t} dx$$

$$= \int_{\Omega} \sum_{i=1}^{N} \left\{ \mu_{i} \frac{\partial C_{i}}{\partial t} \right\} dx - \int_{\Omega} \nabla \phi \cdot \frac{\partial D}{\partial t} dx$$

$$= \int_{\Omega} \sum_{i=1}^{N} \left\{ \mu_{i} \frac{\partial C_{i}}{\partial t} \right\} dx + \int_{\Omega} \phi \nabla \cdot \left(\frac{\partial D}{\partial t} \right) dx$$

$$= \int_{\Omega} \sum_{i=1}^{N} \left\{ \mu_{i} \frac{\partial C_{i}}{\partial t} \right\} dx + \int_{\Omega} \phi F \sum_{i=1}^{N} \left\{ z_{i} \frac{\partial C_{i}}{\partial t} \right\} dx$$

$$= \int_{\Omega} \sum_{i=1}^{N} \left\{ \tilde{\mu}_{i} \frac{\partial C_{i}}{\partial t} \right\} dx$$

$$= -\int_{\Omega} \sum_{i=1}^{N} \left\{ \tilde{\mu}_{i} \nabla \cdot \boldsymbol{j}_{i} \right\} dx + \int_{\Omega} \mathcal{R}(\sum_{i=1}^{N} \gamma_{i} \tilde{\mu}_{i}) dx \qquad (12)$$

$$= \int_{\Omega} \sum_{i=1}^{N} \left\{ \nabla \tilde{\mu}_{i} \cdot \boldsymbol{j}_{i} \right\} dx + \int_{\Omega} \mathcal{R}(\sum_{i=1}^{N} \gamma_{i} \tilde{\mu}_{i}) dx - \int_{\partial \Omega} \sum_{i=1}^{N} (\tilde{\mu}_{i} - \tilde{\mu}_{i,ex}) \boldsymbol{j}_{i} \cdot \boldsymbol{n} dS - \int_{\partial \Omega} \tilde{\mu}_{i,ex} \boldsymbol{j}_{i} \cdot \boldsymbol{n} dS.$$

$$= -\Delta + \mathcal{P}_{E,\partial\Omega}. \qquad (13)$$

By comparing with the dissipation function, we have

$$\begin{cases} \boldsymbol{j}_{i} = -\frac{D_{i}}{RT}C_{i}\nabla\tilde{\mu}_{i}, \ i = 1, \cdots, N \quad \text{in } \Omega\\ \boldsymbol{j}_{i} \cdot \boldsymbol{n} = g_{i}(\tilde{\mu}_{i} - \tilde{\mu}_{i,ex}) & \text{on } \partial\Omega\\ RT\ln\left(\frac{\mathcal{R}_{f}}{\mathcal{R}_{r}}\right) = -\sum_{i=1}^{N}\gamma_{i}\tilde{\mu}_{i} & \text{on } \partial\Omega. \end{cases}$$
(14)

where the last equation is called De Donder relation [50, 1].

At equilibrium, we have

$$\begin{cases} \boldsymbol{j}_i = \nabla C_{i,eq} + \frac{z_i F}{RT} C_{i,eq} \nabla \phi_{eq} = 0, \\ \sum_{i=1}^4 (a_i - b_i) \tilde{\mu}_i^{eq} = 0. \end{cases}$$

The last equation yields

$$0 = RT \ln \left(\frac{\prod_{i=1}^{N} \left(\frac{C_{i,eq}}{c_0} \right)^{a_i}}{\prod_{i=1}^{N} \left(\frac{C_{i,eq}}{c_0} \right)^{b_i}} \right) + \sum_{i=1}^{N} (a_i - b_i) U_i.$$
(15)

According to the definition of equilibrium constant k_{eq} [46],

$$k_{eq} = \left(\frac{C_{i,eq}}{c_0}\right)^{a_i - b_i} = \left(\frac{C_{i,eq}}{c_0}\right)^{-\gamma_i}.$$
(16)

Substituting Eq.(16) into Eq. (15) yields

$$k_{eq} = e^{-\frac{\Delta U}{RT}},\tag{17}$$

with $\Delta U = \sum_{i=1}^{N} (a_i - b_i) U_i$. Then combining the last equation in (14) and (17) yields

$$\ln\left(\frac{\mathcal{R}_f}{\mathcal{R}_r}\right) = \ln\left(\frac{\prod_{i=1}^N \left(\frac{C_i}{c_0}\right)^{a_i}}{\prod_{i=1}^N \left(\frac{C_{i,eq}}{c_0}\right)^{b_i} k_{eq}}\right).$$
(18)

If we assume

$$\mathcal{R}_r = k_{r,ref} \prod_{i=1}^N \left(\frac{C_i}{c_0}\right)^{b_i}$$

then the reaction rate function is

$$\mathcal{R} = \left(k_{f,ref} \prod_{i=1}^{N} \left(\frac{C_i}{c_0}\right)^{a_i} - k_{r,ref} \prod_{i=1}^{N} \left(\frac{C_i}{c_0}\right)^{b_i}\right) = \mathcal{R}_f \left(1 - \frac{\mathcal{R}_r}{\mathcal{R}_f}\right) = \mathcal{R}_{f,ref} \left(1 - e^{\frac{\sum_{i=1}^{N} \gamma_i \tilde{\mu}_i}{\mathcal{R}_T}}\right),$$

where $k_{f,ref} = \frac{k_{r,ref}}{k_{eq}}$ [65]. $k_{f,ref}$ and $k_{r,ref}$ are are forward and backward reaction rate constants with unit $\frac{M}{s} = \frac{Mol}{Ls}$ [46]. If we define a local affinity $A = -\sum_{i=1}^{N} \gamma_i \tilde{\mu}_i = \sum_{i=1}^{N} (a_i - b_i) \tilde{\mu}_i$ [13], the chemical reaction rate equation could be rewritten as

$$\mathcal{R} = \mathcal{R}_f \left(1 - e^{-\frac{A}{RT}} \right). \tag{19}$$

The governing equations for bulk reaction are given as

$$\begin{cases} \frac{\partial C_i}{\partial t} = \nabla \cdot (D_i \nabla C_i + D_i \frac{z_i F}{RT} C_i \nabla \phi) + \gamma_i \mathcal{R}, \\ -\nabla \cdot (\varepsilon_0 \varepsilon_r \nabla \phi) = \sum_{i=1}^N z_i F C_i, \end{cases}$$
(20)

with

$$\mathcal{R} = \left(k_f \Pi_{i=1}^N \left(\frac{C_i}{c_0} \right)^{a_i} - k_r \Pi_{i=1}^N \left(\frac{C_i}{c_0} \right)^{b_i} \right)$$
(21)

and boundary conditions

$$\begin{cases} \boldsymbol{j}_i \cdot \boldsymbol{n} = g_i(\tilde{\mu}_i - \tilde{\mu}_{i,ex}), i = 1 \cdots N, & \text{on } \partial\Omega, \\ \boldsymbol{D} \cdot \boldsymbol{n} = 0, & \text{on } \partial\Omega. \end{cases}$$
(22)

The energy law of this system is

$$\frac{dE}{dt} = -\int_{\Omega} \left\{ \sum_{j=1}^{N} \frac{D_i C_i}{RT} |\nabla \tilde{\mu}_i|^2 + RT \mathcal{R} \ln \left(\frac{\mathcal{R}_f}{\mathcal{R}_r}\right) \right\} dx - \sum_{i=1}^{N} \int_{\partial\Omega} g_i |\tilde{\mu}_i - \tilde{\mu}_{i,ex}|^2 dS$$

$$- \sum_{i=1}^{N} \int_{\partial\Omega} g_i \tilde{\mu}_{i,ex} (\tilde{\mu}_i - \tilde{\mu}_{i,ex}) dS$$

$$= -\Delta + \mathcal{P}_{E,\partial\Omega}$$

$$= -\int_{\Omega} \left\{ \sum_{j=1}^{N} \frac{D_i C_i}{RT} |\nabla \tilde{\mu}_i|^2 + RT \mathcal{R} \ln \left(\frac{\mathcal{R}_f}{\mathcal{R}_r}\right) \right\} dx - \sum_{i=1}^{N} \int_{\partial\Omega} g_i \tilde{\mu}_i (\tilde{\mu}_i - \tilde{\mu}_{i,ex}) dS. \quad (23)$$

Here the boundary condition of concentration is Robin type.

• If the boundary conductivity is zero $g_i = 0$, then we obtain the nonflux boundary condition $j_i \cdot n = 0$; The corresponding energy law is

$$\frac{dE}{dt} = -\int_{\Omega} \left\{ \sum_{j=1}^{N} \frac{D_i C_i}{RT} |\nabla \tilde{\mu}_i|^2 + RT \mathcal{R} \ln\left(\frac{\mathcal{R}_f}{\mathcal{R}_r}\right) \right\} dx = -\Delta.$$
(24)

with zero boundary energy communication rate $\mathcal{P}_{E,\partial\Omega} = 0$.

- If the conductance is infinitely large, the Dirichlet boundary condition is achieved $\tilde{\mu}_i = \tilde{\mu}_{i,ex}$ on the boundary.
- If the conductance is a function of chemical potential, i.e. $g_i = \frac{j_{i,0}}{\tilde{\mu}_i \tilde{\mu}_{i,ex}}$, where $j_{i,0}$ is constant, then we obtain the Neumann boundary condition $j_i \cdot n = j_{i,0}$. In this case, the corresponding energy law is

$$\frac{dE}{dt} = -\int_{\Omega} \left\{ \sum_{j=1}^{N} \frac{D_i C_i}{RT} |\nabla \tilde{\mu}_i|^2 + RT \mathcal{R} \ln\left(\frac{\mathcal{R}_f}{\mathcal{R}_r}\right) \right\} dx - \sum_{i=1}^{N} \int_{\partial \Omega} \tilde{\mu}_i j_{i,0} dS$$

$$= -\Delta + \mathcal{P}_{E,\partial\Omega} \tag{25}$$

where the boundary energy communication rate is $\mathcal{P}_{E,\partial\Omega} = -\sum_{i=1}^{N} \int_{\partial\Omega} \tilde{\mu}_i j_{i,0} dS.$

It is very important to understand this requirement. In reality—in experiments and their models supplying the unknown flux requires specialized instrumentation, for example, a patch clamp amplifier in a voltage clamp setup. Almost always, that flux is supplied at one location in space. In that way a classical voltage clamp can be established. However, if one wishes to "clamp" a field, one must control the potential at many locations. Each location requires a different flux and thus a different amplifier and different electrodes to supply that flux. Without such a complicated apparatus, it is almost impossible to maintain a constant field in space [33]. Indeed, it is nearly impossible to maintain any pre-specified field because it is practically impossible to apply different fluxes at different locations. If one assumes a constant field in a theory, without such apparatus in an experiment, one is in effect introducing flux into the calculation and model that is not present in the experimental setup. One is introducing an artifactual flux likely to produce artifactual conclusions that are not relevant to the original experiment [18, 17].

2.2 Boundary reaction on electrode

In this subsection, we consider the Faradic reactions on the surface of an electrode Γ

$$a_1 C_1^{z_1} + a_2 C_2^{z_2} + \dots + a_N C_N^{z_N} + \Delta z e^{-1} \stackrel{k_f}{\underset{k_r}{\longrightarrow}} b_1 C_1^{z_1} + b_2 C_2^{z_2} + \dots + b_N C_N^{z_N}, \tag{26}$$

where electrons are supplied through Γ and $\sum_{i=1}^{N} \gamma_i z_i + \Delta z = 0$. The electrons are supplied with electric potential equal to the electrode potential ϕ_e . During the derivation, we focus on situations where the oxidized state exists only in the solution and there are no ions inside the electrode.

The conservation law yields the following kinematic assumptions,

$$\begin{cases} \frac{\partial C_i}{\partial t} = -\nabla \cdot \mathbf{j}_i, & \text{in } \Omega\\ -\nabla \cdot (\varepsilon_0 \varepsilon_r \nabla \phi) = \sum_{i=1}^N z_i F C_i, & \text{in } \Omega \end{cases}$$
(27)

with boundary conditions

$$\begin{cases} \boldsymbol{j}_{i} \cdot \boldsymbol{n} = -\gamma_{i} \mathcal{R}, i = 1 \cdots N, & \text{on } \Gamma, \\ F \frac{\partial C_{e}}{\partial t} = \mathbb{C}_{p} \frac{\partial (\phi - \phi_{p})}{\partial t} = j_{ex} F - \Delta z F \mathcal{R}, & \text{on } \Gamma \\ \boldsymbol{j}_{i} \cdot \boldsymbol{n} = 0, & \text{on } \partial \Omega / \Gamma, \end{cases}$$
(28)

where C_e is the density of electrons on the surface of the plate, ϕ_p is the electric potential on the plate, and \mathbb{C}_p is the capacitance, I_{ex} is the current supplied by an external amplifier and the corresponding inlet electron flux is $j_{ex} = -\frac{I_{ex}}{F}$. Here we use the fact that $FC_e = \mathbb{C}_p(\phi - \phi_p)$.

Then the total energy is defined as the sum of mix energy and internal energy of ions, electric static energy in the bulk region, and the energy on the interface induced by electrons and capacitor effect

$$E = E_{tot,bulk} + E_{\Gamma}$$

$$= E_{ent} + E_{int} + E_{ele} + E_{\Gamma}$$

$$= \sum_{i=1}^{N} \int_{\Omega} \left\{ RTC_{i} \left(\ln \left(\frac{C_{i}}{c_{0}} \right) - 1 \right) + C_{i}\mu_{i,0} \right\} dx + \int_{\Omega} \sum_{i} z_{i}FC_{i}\phi dx - \frac{1}{2} \int_{\Omega} \frac{\boldsymbol{D} \cdot \boldsymbol{E}}{2} dx$$

$$+ \int_{\Gamma} \left\{ RTC_{e} \left(\ln \left(\frac{C_{e}}{c_{0}} \right) - 1 \right) + C_{e}\mu_{0,e} \right\} dx + \int_{\Gamma} C_{e}F(\phi - \phi_{p})dS - \frac{1}{2} \int_{\Gamma} \mathbb{C}_{p}(\phi - \phi_{p})^{2}dS,$$

$$= \sum_{i=1}^{N} \int_{\Omega} \left\{ RTC_{i} \left(\ln \left(\frac{C_{i}}{c_{0}} \right) - 1 \right) + C_{i}\mu_{i,0} \right\} dx + \int_{\Omega} \frac{\boldsymbol{D} \cdot \boldsymbol{E}}{2} dx$$

$$+ \int_{\Gamma} \left\{ RTC_{e} \left(\ln \left(\frac{C_{e}}{c_{0}} \right) - 1 \right) + C_{e}\mu_{e,0} \right\} dx + \frac{1}{2} \int_{\Gamma} \mathbb{C}_{p}(\phi - \phi_{p})^{2} dS,$$
(29)



Figure 1: Schematic of reaction on the plate with external electron supply $J_{ex} = \frac{I_{ex}}{F}$.

where $\mu_{i,0}$ is the chemical potential of i_{th} ion at standard state, i.e. 25°C and 1M.

Then the corresponding chemical potentials of ions and electron are

$$\tilde{\mu}_i = \frac{\delta E}{\delta C_i} = \mu_i + z_i F \phi = \mu_{i,0} + RT \ln \frac{C_i}{c_0} + z_i F \phi, \qquad (30)$$

$$\tilde{\mu}_e = \frac{\delta E}{\delta C_e} = \mu_e - F\phi_p = \mu_{e,0} + RT \ln \frac{C_e}{c_0} - F\phi_p.$$
(31)

The dissipation function is defined as

$$\Delta = \int_{\Omega} \sum_{j=1}^{N} \frac{D_i C_i}{RT} |\nabla \tilde{\mu}_i|^2 dx + \int_{\Gamma} RT \mathcal{R} \ln\left(\frac{\mathcal{R}_f}{\mathcal{R}_r}\right) dS + \int_{\Gamma} \frac{g}{F^2} (\tilde{\mu}_e - \tilde{\mu}_{ex}) dS$$
$$= \int_{\Omega} \sum_{j=1}^{N} \frac{D_i C_i}{RT} |\nabla \tilde{\mu}_i|^2 dx + \int_{\Gamma} RT (\mathcal{R}_f - \mathcal{R}_r) \ln\left(\frac{\mathcal{R}_f}{\mathcal{R}_r}\right) dS + \int_{\Gamma} \frac{g}{F^2} (\tilde{\mu}_e - \tilde{\mu}_{ex})^2 dS.$$
(32)

where we used the boundary reaction rate function $\mathcal{R} = \mathcal{R}_f - \mathcal{R}_r$, μ_{ex} is the external electron chemical potential of the reservoir that connects to the boundary.

We analyze a setup (see Fig. 1) with a given current of electrons I_{ex} applied to the plate Γ . This is a flux (really current) boundary condition, of the Neumann type in mathematical language. The other boundaries of the system are controlled in a different way. On the other boundaries, the electric potential is fixed as ϕ_{ref} and no ions enter or leave the system on those other boundaries, i.e. $J_i \cdot n = 0$. The current flow of electrons is only on the left plate and boundary energy power functional is defined as follows

$$\mathcal{P}_{E,\partial\Omega} = \int_{\Gamma} \tilde{\mu}_e j_{ex} dx - \int_{\partial\Omega/\Gamma} \phi_{ref} \frac{\partial \boldsymbol{D} \cdot \boldsymbol{n}}{\partial t} dx$$
(33)

Remark 2.2. Integrating the first equation and using the boundary condition on i_{th} ion yields the law of mass conservation

$$\frac{d}{dt} \int_{\Omega} C_i dt = \int_{\Gamma} \gamma_i \mathcal{R} dS.$$
(34)

To apply the dissipation theorem, we need the derivative of energy with respect to time. All steps are shown because this part of the EnVarA treatment applying the dissipation principle may not be obvious to readers inexperienced with functional and variational methods.

$$\frac{dE}{dt} = \int_{\Omega} \sum_{i=1}^{N} \left\{ \tilde{\mu}_{i} \frac{\partial C_{i}}{\partial t} \right\} dx - \int_{\partial \Omega} \phi \frac{\partial \boldsymbol{D} \cdot \boldsymbol{n}}{\partial t} dS + \int_{\Gamma} \mu_{e} \frac{\partial C_{e}}{\partial t} dS + \int_{\Gamma} (\phi - \phi_{p}) F \frac{\partial C_{e}}{\partial t} dS$$

$$= -\int_{\Omega} \sum_{i=1}^{N} \{\tilde{\mu}_{i} \nabla \cdot \boldsymbol{j}_{i}\} dx - \int_{\partial \Omega} \phi \frac{\partial \boldsymbol{D} \cdot \boldsymbol{n}}{\partial t} dS + \int_{\Gamma} \tilde{\mu}_{e} \frac{\partial C_{e}}{\partial t} dS + \int_{\Gamma} \phi F \frac{\partial C_{e}}{\partial t} dS$$

$$= -\int_{\Omega} \sum_{i=1}^{N} \{\tilde{\mu}_{i} \nabla \cdot \boldsymbol{j}_{i}\} dx - \int_{\Gamma} \phi \frac{\partial}{\partial t} (\boldsymbol{D} \cdot \boldsymbol{n} - FC_{e}) dS + \int_{\Gamma} \tilde{\mu}_{e} (j_{ex} - \Delta z \mathcal{R}) dS$$

$$- \int_{\partial \Omega/\Gamma} \phi \frac{\partial \boldsymbol{D} \cdot \boldsymbol{n}}{\partial t} dS$$

$$= \int_{\Omega} \sum_{i=1}^{N} \{\nabla \tilde{\mu}_{i} \cdot \boldsymbol{j}_{i}\} dx - \int_{\Gamma} \phi \frac{\partial}{\partial t} (\boldsymbol{D} \cdot \boldsymbol{n} - FC_{e}) dS - \int_{\Gamma} \sum_{i}^{N} \tilde{\mu}_{i} \boldsymbol{j}_{i} \cdot \boldsymbol{n} dS + \int_{\Gamma} \tilde{\mu}_{e} (-\Delta z \mathcal{R}) dS$$

$$- \int_{\partial \Omega/\Gamma} \phi \frac{\partial \boldsymbol{D} \cdot \boldsymbol{n}}{\partial t} dS - \int_{\partial \Omega/\Gamma} \sum_{i}^{N} \tilde{\mu}_{i} \boldsymbol{j}_{i} \cdot \boldsymbol{n} dS + \int_{\Gamma} \tilde{\mu}_{e} j_{ex} dS$$

$$= \int_{\Omega} \sum_{i=1}^{N} \{\nabla \tilde{\mu}_{i} \cdot \boldsymbol{j}_{i}\} dx - \int_{\Gamma} \phi \frac{\partial}{\partial t} (\boldsymbol{D} \cdot \boldsymbol{n} - FC_{e}) dS + \int_{\Gamma} \sum_{i}^{N} \tilde{\mu}_{i} \gamma_{i} \mathcal{R} dS - \int_{\Gamma} \tilde{\mu}_{e} (\Delta z \mathcal{R}) dS$$

$$- \int_{\partial \Omega/\Gamma} \phi \frac{\partial \boldsymbol{D} \cdot \boldsymbol{n}}{\partial t} dS - \int_{\partial \Omega/\Gamma} \sum_{i}^{N} \tilde{\mu}_{i} \boldsymbol{j}_{i} \cdot \boldsymbol{n} dS + \int_{\Gamma} (\tilde{\mu}_{e} - \tilde{\mu}_{ex}) j_{ex} dS + \int_{\Gamma} \tilde{\mu}_{e} (\Delta z \mathcal{R}) dS$$

$$= \int_{\Omega} \sum_{i=1}^{N} \{\nabla \tilde{\mu}_{i} \cdot \boldsymbol{j}_{i}\} dx - \int_{\Gamma} (-\sum_{i}^{N} \tilde{\mu}_{i} \gamma_{i} + \tilde{\mu}_{e} \Delta z) \mathcal{R} dS - \int_{\Gamma} \phi \frac{\partial}{\partial t} (\boldsymbol{D} \cdot \boldsymbol{n} - FC_{e}) dS$$

$$+ \int_{\Gamma} (\tilde{\mu}_{e} - \tilde{\mu}_{ex}) j_{ex} dS + \int_{\Gamma} (-\sum_{i}^{N} \tilde{\mu}_{i} \gamma_{i} + \tilde{\mu}_{e} \Delta z) \mathcal{R} dS - \int_{\Omega} \Gamma \phi \frac{\partial}{\partial t} (\boldsymbol{D} \cdot \boldsymbol{n} - FC_{e}) dS$$

$$+ \int_{\Gamma} (\tilde{\mu}_{e} - \tilde{\mu}_{ex}) j_{ex} dS + \int_{\Gamma} \tilde{\mu}_{ex} J_{ex} dS - \int_{\partial \Omega/\Gamma} \phi \frac{\partial \boldsymbol{D} \cdot \boldsymbol{n}}{\partial t} dS - \int_{\partial \Omega/\Gamma} \sum_{i}^{N} \tilde{\mu}_{i} \boldsymbol{j}_{i} \cdot \boldsymbol{n} dS$$

$$= -\Delta + P_{E,\partial\Omega}. \qquad (35)$$

To implement the dissipation principle, we now compare it with the dissipation function. We are dealing with an open system so we include the dissipation (and energy) associated with the boundaries as well as the interior of the system.

$$\begin{cases} \boldsymbol{j}_{i} = -\frac{D_{i}}{RT}C_{i}\nabla\tilde{\mu}_{i}, \ i = 1, \cdots, N, & \text{in}\Omega\\ \boldsymbol{D} \cdot \boldsymbol{n} = FC_{e} & \text{on } \Gamma\\ \boldsymbol{j}_{ex} = \frac{g}{F^{2}}(\tilde{\mu}_{ex} - \tilde{\mu}_{e}), & \text{on } \Gamma\\ RT\ln\left(\frac{\mathcal{R}_{f}}{\mathcal{R}_{r}}\right) = -\sum_{i}^{N}\gamma_{i}\tilde{\mu}_{i} + \tilde{\mu}_{e}\Delta z, & \text{on } \Gamma\\ \boldsymbol{j}_{i} \cdot \boldsymbol{n} = 0, & \text{on } \partial\Omega/\Gamma\\ \boldsymbol{\phi} = \boldsymbol{\phi}_{ref}, & \text{on } \partial\Omega/\Gamma \end{cases}$$
(36)

where the boundary condition is used [2, 5, 70].

The third equation in (36) yields

$$\mathcal{R} = \mathcal{R}_f(1 - e^{\frac{-A_e}{RT}}). \tag{37}$$

with the affinity

$$A_{e} = \sum_{i=1}^{N} (a_{i} - b_{i})\tilde{\mu}_{i} + \Delta z\tilde{\mu}_{e}$$

$$= RT \ln \left(\left(\frac{C_{e}}{c_{0}} \right)^{\Delta z} \frac{\prod_{i=1}^{N} \left(\frac{C_{i}}{c_{0}} \right)^{a_{i}}}{\prod_{i=1}^{N} \left(\frac{C_{i}}{c_{0}} \right)^{b_{i}}} \right) + \Delta \mu_{0} + \sum_{i=1}^{N} (a_{i} - b_{i})z_{i}F\phi - \Delta zF\phi_{p}$$

$$= RT \ln \left(\left(\frac{C_{e}}{c_{0}} \right)^{\Delta z} \frac{\prod_{i=1}^{N} \left(\frac{C_{i}}{c_{0}} \right)^{a_{i}}}{\prod_{i=1}^{N} \left(\frac{C_{i}}{c_{0}} \right)^{b_{i}}} \right) + \Delta \mu_{0} + \Delta zF(\phi - \phi_{p})$$

$$= RT \ln \left(\left(\frac{C_e}{c_0} \right)^{\Delta z} \frac{\prod_{i=1}^N \left(\frac{C_i}{c_0} \right)^{a_i}}{\prod_{i=1}^N \left(\frac{C_i}{c_0} \right)^{b_i} k_{eq}} e^{\frac{\Delta z F}{RT} (\phi - \phi_p)} \right)$$
(38)

where $\Delta \mu_0 = \sum_{i=1}^{N} (a_i - b_i) \mu_{i,0} + \Delta z \mu_{e,0}$ and $k_{eq} = e^{-\frac{\Delta \mu_o}{RT}}$ is used. If we assume

$$\mathcal{R}_f = k_{f,ref} \left(\frac{C_e}{c_0}\right)^{\Delta z} \prod_{i=1}^N \left(\frac{C_i}{c_0}\right)^{a_i} e^{-\frac{\Delta ZF}{RT}\beta(\phi_p - \phi)},\tag{39}$$

then the reaction rate function could be defined as follows

$$\mathcal{R} = \mathcal{R}_{f} \left(1 - e^{-\frac{\sum_{i=1}^{N} (a_{i} - b_{i})\tilde{\mu}_{i} + \Delta z \tilde{\mu}_{e}}{RT}} \right)$$

$$= k_{f,ref} e^{-\frac{\Delta ZF}{RT} \beta(\phi_{p} - \phi)} \left(\frac{C_{e}}{c_{0}} \right)^{\Delta z} \Pi_{i=1}^{N} \left(\frac{C_{i}}{c_{0}} \right)^{a_{i}} - k_{r,ref} e^{\frac{\Delta ZF}{RT} (1 - \beta)(\phi_{p} - \phi)} \Pi_{i=1}^{N} \left(\frac{C_{i}}{c_{0}} \right)^{b_{i}}$$

$$= k_{f,ref} e^{-\frac{\Delta ZF}{RT} \beta(\Delta \phi)} \left(\frac{C_{e}}{c_{0}} \right)^{\Delta z} \Pi_{i=1}^{N} \left(\frac{C_{i}}{c_{0}} \right)^{a_{i}} - k_{r,ref} e^{\frac{\Delta ZF}{RT} (1 - \beta)(\Delta \phi)} \Pi_{i=1}^{N} \left(\frac{C_{i}}{c_{0}} \right)^{b_{i}}$$

$$(40)$$

where we denote $\Delta \phi = \phi_p - \phi$ and β is the so called the transfer coefficient commonly found in the Frumkin-Butler-Volmer Equation [5, 50, 58, 59, 25].

The details of electron flow are not described in our model Fig. 1 and 2 because those details are not well known in the biological case which remains our main focus. Those details are significantly different in each of the many (quite different) systems that are described by the Butler-Volmer equation of electrode reactions [25].

At equilibrium, i.e. $\mathcal{R}_f = \mathcal{R}_r$, we have

$$\Delta \phi_{eq} = \phi_p - \phi_{eq} = \frac{RT}{\Delta zF} \ln \left(\left(\frac{C_{e,eq}}{c_0} \right)^{\Delta z} \frac{k_{f,ref} \prod_{i=1}^N \left(\frac{C_{i,eq}}{c_0} \right)^{a_i}}{k_{r,ref} \prod_{i=1}^N \left(\frac{C_{i,eq}}{c_0} \right)^{b_i}} \right)$$

$$= \frac{RT}{\Delta zF} \ln \left(\frac{k_{f,ref}}{k_{r,ref}} \right) + \frac{RT}{\Delta zF} \ln \left(\left(\frac{C_{e,eq}}{c_0} \right)^{\Delta z} \frac{\prod_{i=1}^N \left(\frac{C_{i,eq}}{c_0} \right)^{a_i}}{\prod_{i=1}^N \left(\frac{C_{i,eq}}{c_0} \right)^{b_i}} \right)$$

$$= \frac{\Delta \mu_o}{\Delta zF} + \frac{RT}{\Delta zF} \ln \left(\left(\frac{C_{e,eq}}{c_0} \right)^{\Delta z} \frac{\prod_{i=1}^N \left(\frac{C_{i,eq}}{c_0} \right)^{a_i}}{\prod_{i=1}^N \left(\frac{C_{i,eq}}{c_0} \right)^{b_i}} \right)$$
(41)

which is call the Nernst equation.

In summary, we have the following system

$$\begin{cases} \frac{\partial C_i}{\partial t} = -\nabla \cdot \mathbf{j}_i, & \text{in } \Omega\\ -\nabla \cdot (\varepsilon_0 \varepsilon_r \nabla \phi) = \sum_{i=1}^N z_i F C_i, & \text{in } \Omega \end{cases}$$
(42)

with boundary conditions

$$\begin{cases} \boldsymbol{j}_{i} \cdot \boldsymbol{n} = -\gamma_{i} \mathcal{R}, i = 1 \cdots N, & \text{on } \Gamma, \\ \mathbb{C}_{p} \frac{d(\phi - \phi_{p})}{dt} = -I_{ex} - \Delta z F \mathcal{R} = \frac{g}{F} (\tilde{\mu}_{ex} - \tilde{\mu}_{e}) - \Delta z F \mathcal{R}, & \text{on } \Gamma \\ \mathcal{R} = k_{f,ref} e^{-\frac{\Delta ZF}{RT} \beta(\Delta \phi)} \left(\frac{C_{e}}{c_{0}}\right)^{\Delta z} \Pi_{i=1}^{N} \left(\frac{C_{i}}{c_{0}}\right)^{a_{i}} - k_{r,ref} e^{\frac{\Delta ZF}{RT}(1-\beta)(\Delta \phi)} \Pi_{i=1}^{N} \left(\frac{C_{i}}{c_{0}}\right)^{b_{i}}, & \text{on } \Gamma \\ \boldsymbol{D} \cdot \boldsymbol{n} = \mathbb{C}_{p} (\phi - \phi_{p}), & \text{on } \Gamma \\ \boldsymbol{j}_{i} \cdot \boldsymbol{n} = 0, \phi = \phi_{ref}, & \text{on } \partial \Omega / \Gamma. \end{cases}$$
(43)

The reaction rate function could be written as

$$\mathcal{R} = k_f \left(\frac{C_e}{c_0}\right)^{\Delta z} \prod_{i=1}^N \left(\frac{C_i}{c_0}\right)^{a_i} - k_r \prod_{i=1}^N \left(\frac{C_i}{c_0}\right)^{b_i},\tag{44}$$

where we denote

$$k_f = k_{f,ref} e^{-\frac{\Delta ZF}{RT}\beta(\Delta\phi)},\tag{45}$$

$$k_r = k_{r,ref} e^{\frac{\Delta ZF}{RT} (1-\beta)(\Delta\phi)},\tag{46}$$

to include the effects of electric potential on the reaction rates.

If we choose $g = \frac{I_0 F}{\tilde{\mu}_e - \tilde{\mu}_{ex}}$, then the input current is constant I_0 and the condition is changed to be $\mathbb{C}_p \frac{d(\phi - \phi_p)}{dt} = -I_0 - \Delta z F \mathcal{R}$ which is the set of boundary condition found widely in the literature [40, 58, 41, 8].

Remark 2.3. Since $C_e^s = \mathbb{C}_p(\phi^s - \phi_p^s)$ is the charge density, it should be nonegative during evolution, which means $\phi^s > \phi_p^s \ge 0$ for $\forall t \ge 0$.

Remark 2.4. If there is no chemical reaction on the surface Γ , the model degenerates to

$$\begin{cases} \frac{\partial C_i}{\partial t} = -\nabla \cdot \boldsymbol{j}_i, & \text{in } \Omega\\ -\nabla \cdot (\varepsilon_0 \varepsilon_r \nabla \phi) = \sum_{i=1}^N z_i F C_i, & \text{in } \Omega \end{cases}$$
(47)

with boundary conditions

$$\begin{cases} \boldsymbol{j}_{i} \cdot \boldsymbol{n} = 0, & i = 1 \cdots N, & on \partial \Omega, \\ \mathbb{C}_{p} \frac{d(\phi - \phi_{p})}{dt} = -I_{ex}, & on \Gamma, \\ \boldsymbol{D} \cdot \boldsymbol{n} = \mathbb{C}_{p}(\phi - \phi_{p}), & on \Gamma, \\ \phi = \phi_{ref}, & on \partial \Omega / \Gamma. \end{cases}$$
(48)

2.3**Bi-reaction** system

We now apply these general principles to a specific system of considerable interest in biological applications like the electron transport chain (ETC) on the mitochondrial membrane [32, 76, 67, 66], and red blood cell (RBC) membrane [37, 4]. The electron transport chain (ETC) is a series of biochemical reactions that occur in the inner mitochondrial membrane of eukaryotic cells or the plasma membrane of prokaryotic cells. It plays a key role in cellular respiration, which is the process by which cells convert nutrients (such as glucose) into energy (in the form of ATP). During the ETC, electrons are transferred from electron donors (such as NADH and FADH2) to electron acceptors (such as oxygen) through a series of redox reactions. This transfer of electrons is accompanied by the pumping of protons (H+) across the inner mitochondrial membrane or the plasma membrane, creating an electrochemical gradient that is used to generate ATP. The oxidation is carried out by a sequence of chemical reactions catalyzed by membrane proteins that link electron flow on one side of a membrane to a chemical reaction on the other. The general scheme is shown in Fig. 2.

In this section, we consider the case that two compartments Ω_s , s = l, r are separated by the plate Γ . The thickness of the plate is negligible compared with the domain size. There are total N species $\{C_1^{z_1}, C_2^{z_2}, \cdots, C_N^{z_N}\}$ in two compartments $\Omega_s, s = l, r$.

$$a_1^s C_1^{z_1} + a_2^s C_2^{z_2} + \dots + a_N^s C_N^{z_N} + \Delta z^s e^{-1} \underset{k_r^s}{\overset{k_f^s}{\longleftrightarrow}} b_1^s C_1^{z_1} + b_2^s C_2^{z_2} + \dots + b_N^s C_N^{z_N}.$$
(49)

In the left region Ω_l , the forward reaction is oxidation the process that produces electrons ($\Delta z^l <$ 0); In the right compartment Ω_r , the forward reaction is a reduced process that consumes electrons $(\Delta z^r > 0)$. In the electrolyte region Ω_s , we have the following kinematic assumption

$$\begin{cases} \frac{\partial C_i^s}{\partial t} = -\nabla \cdot \boldsymbol{j}_i^s, \\ -\nabla \cdot (\varepsilon_0 \varepsilon_r \nabla \phi^s) = \sum_{i=1}^N z_i F C_i^s \end{cases}$$
(50)



Figure 2: Schematic of Bi-reaction system. On the right side of the plate, the reduction reaction consumes the electrons that are produced by the oxidation reaction on the left side of the plate.

for the boundary conditions

$$\begin{cases} \boldsymbol{j}_{i}^{s} \cdot \boldsymbol{n}_{s} = -\gamma_{i} \mathcal{R}^{s}, & \text{on } \Gamma, \\ \mathbb{C}_{p} \frac{d(\phi^{l} - \phi_{p}^{l})}{dt} = -\Delta z^{l} F \mathcal{R}_{l} + I_{ex}, \mathbb{C}_{p} \frac{\phi^{r} - \phi_{p}^{r}}{dt} = -\Delta z^{r} \mathcal{R}_{r} F - I_{ex}, & \text{on } \Gamma, \\ \boldsymbol{j}_{i}^{s} \cdot \boldsymbol{n} = 0, & \text{on } \partial\Omega \setminus \Gamma. \end{cases}$$
(51)

The total energy is defined as

$$E = E_{l} + E_{r} + E_{\Gamma}$$

$$= \sum_{i=1}^{N} \int_{\Omega^{l}} \left\{ RTC_{i}^{l} \left(\ln \left(\frac{C_{i}^{l}}{c_{0}} \right) - 1 \right) + C_{i}^{l} \mu_{0,i} \right\} dx + \int_{\Omega^{l}} \frac{D^{l} \cdot E^{l}}{2} dx$$

$$+ \sum_{i=1}^{N} \int_{\Omega^{r}} \left\{ RTC_{i}^{r} \left(\ln \left(\frac{C_{i}^{r}}{c_{0}} \right) - 1 \right) + C_{i}^{r} \mu_{0,i} \right\} dx + \int_{\Omega^{r}} \frac{D^{r} \cdot E^{r}}{2} dx$$

$$+ \int_{\Gamma} \left\{ RTC_{e}^{l} \left(\ln \left(\frac{C_{e}^{l}}{c_{0}} \right) - 1 \right) + C_{e}^{l} \mu_{0,e}^{l} \right\} dx + \frac{1}{2} \int_{\Gamma} \mathbb{C}_{p} (\phi^{l} - \phi_{p}^{l})^{2} dS$$

$$+ \int_{\Gamma} \left\{ RTC_{e}^{r} \left(\ln \left(\frac{C_{e}^{r}}{c_{0}} \right) - 1 \right) + C_{e}^{r} \mu_{0,e}^{r} \right\} dx + \frac{1}{2} \int_{\Gamma} \mathbb{C}_{p} (\phi^{r} - \phi_{p}^{r})^{2} dS.$$
(52)

The dissipative function is defined as

$$\Delta = \Delta_l + \Delta_r + \Delta_{\Gamma}$$

$$= \int_{\Omega^l} \sum_{j=1}^N \frac{D_i C_i^l}{RT} |\nabla \tilde{\mu}_i^l|^2 dx + \int_{\Gamma} RT \mathcal{R}^l \ln\left(\frac{\mathcal{R}_f^l}{\mathcal{R}_r^l}\right) dx$$

$$+ \int_{\Omega^r} \sum_{j=1}^N \frac{D_i C_i^r}{RT} |\nabla \tilde{\mu}_i^r|^2 dx + \int_{\Gamma} RT \mathcal{R}^r \ln\left(\frac{\mathcal{R}_f^r}{\mathcal{R}_r^r}\right) dx$$

$$+ \int_{\Gamma} \frac{g(C_e^l)}{F^2} (\tilde{\mu}_e^l - \tilde{\mu}_e^r)^2 dS.$$
(53)

For the boundary input energy power, it is assumed to be

$$\mathcal{P}_{E,\partial\Omega} = -\int_{\partial\Omega} \phi_{ref} \frac{\partial \mathbf{D} \cdot \mathbf{n}}{\partial t} dx.$$
(54)

Taking the time derivative of the total energy yields

$$\frac{dE}{dt} - \mathcal{P}_{E,\partial\Omega} = \frac{dE_l}{dt} + \frac{dE_r}{dt} + \frac{dE_\Gamma}{dt} - \int_{\partial\Omega} \phi_{ref} \frac{\partial \mathbf{D} \cdot \mathbf{n}}{\partial t} dx$$

$$= \int_{\Omega_l} \sum_{i=1}^N \nabla \tilde{\mu}_i^l \cdot \boldsymbol{j}_i^l dx - \int_{\Gamma} \sum_{i=1}^N \tilde{\mu}_i^l \boldsymbol{j}_i^l \cdot \boldsymbol{n}^l dS - \int_{\Gamma} \phi_l \frac{\partial}{\partial t} (\boldsymbol{D}^l \cdot \boldsymbol{n}^l - FC_e^l) dS + \int_{\Gamma} \tilde{\mu}_e^l (-\Delta z^l \mathcal{R}_l - J_e)$$

$$\begin{split} &\int_{\Omega_{r}} \sum_{i=1}^{N} \nabla \tilde{\mu}_{i}^{r} \cdot \boldsymbol{j}_{i}^{r} dx - \int_{\Gamma} \sum_{i=1}^{N} \tilde{\mu}_{i}^{r} \boldsymbol{j}_{i}^{r} \cdot \boldsymbol{n}^{r} dS - \int_{\Gamma} \phi_{r} \frac{\partial}{\partial t} (\boldsymbol{D}^{r} \cdot \boldsymbol{n}^{r} - FC_{e}^{r}) dS + \int_{\Gamma} \tilde{\mu}_{e}^{r} (-\Delta z^{l} \mathcal{R}_{r} + J_{e}) \\ &- \int_{\partial\Omega} (\phi - \phi_{ref}) \frac{\partial \boldsymbol{D} \cdot \boldsymbol{n}}{\partial t} dS \\ = \int_{\Omega_{l}} \sum_{i=1}^{N} \nabla \tilde{\mu}_{i}^{l} \cdot \boldsymbol{j}_{i}^{l} dx + \int_{\Gamma} \sum_{i=1}^{N} \tilde{\mu}_{i}^{l} \gamma_{i} \mathcal{R}^{l} dS - \int_{\Gamma} \phi_{l} \frac{\partial}{\partial t} (\boldsymbol{D}^{l} \cdot \boldsymbol{n}^{l} - FC_{e}^{l}) dS + \int_{\Gamma} \tilde{\mu}_{e}^{l} (-\Delta z^{l} \mathcal{R}_{l} - J_{e}) \\ &\int_{\Omega_{r}} \sum_{i=1}^{N} \nabla \tilde{\mu}_{i}^{r} \cdot \boldsymbol{j}_{i}^{r} dx + \int_{\Gamma} \sum_{i=1}^{N} \tilde{\mu}_{i}^{r} \gamma_{i} \mathcal{R}^{r} dS - \int_{\Gamma} \phi_{r} \frac{\partial}{\partial t} (\boldsymbol{D}^{r} \cdot \boldsymbol{n}^{r} - FC_{e}^{l}) dS + \int_{\Gamma} \tilde{\mu}_{e}^{r} (-\Delta z^{l} \mathcal{R}_{l} - J_{e}) \\ &- \int_{\partial\Omega} (\phi - \phi_{ref}) \frac{\partial \boldsymbol{D} \cdot \boldsymbol{n}}{\partial t} dS \\ = \int_{\Omega_{l}} \sum_{i=1}^{N} \nabla \tilde{\mu}_{i}^{l} \cdot \boldsymbol{j}_{i}^{l} dx - \int_{\Gamma} (-\sum_{i=1}^{N} \tilde{\mu}_{i}^{l} \gamma_{i} \mathcal{R}^{l} + \tilde{\mu}_{e}^{l} \Delta z^{l}) \mathcal{R}_{l} dS - \int_{\Gamma} \phi_{l} \frac{\partial}{\partial t} (\boldsymbol{D}^{l} \cdot \boldsymbol{n}^{l} - FC_{e}^{l}) dS \\ &+ \int_{\Omega_{r}} \sum_{i=1}^{N} \nabla \tilde{\mu}_{i}^{r} \cdot \boldsymbol{j}_{i}^{r} dx - \int_{\Gamma} \left(-\sum_{i=1}^{N} \tilde{\mu}_{i}^{l} \gamma_{i} \mathcal{R}^{l} + \tilde{\mu}_{e}^{l} \Delta z^{l}) \mathcal{R}_{l} dS - \int_{\Gamma} \phi_{r} \frac{\partial}{\partial t} (\boldsymbol{D}^{r} \cdot \boldsymbol{n}^{r} - FC_{e}^{l}) dS \\ &+ \int_{\Omega_{r}} \sum_{i=1}^{N} \nabla \tilde{\mu}_{i}^{r} \cdot \boldsymbol{j}_{i}^{r} dx - \int_{\Gamma} \left(-\sum_{i=1}^{N} \tilde{\mu}_{i}^{r} \gamma_{i} + \Delta z^{r} \tilde{\mu}_{e}^{r} \right) \mathcal{R}^{r} dS - \int_{\Gamma} \phi_{r} \frac{\partial}{\partial} (\boldsymbol{D}^{r} \cdot \boldsymbol{n}^{r} - FC_{e}^{l}) dS \\ &+ \int_{\Gamma} (\tilde{\mu}_{e}^{r} - \tilde{\mu}_{e}^{l}) J_{e} - \int_{\partial\Omega} (\phi - \phi_{ref}) \frac{\partial \boldsymbol{D} \cdot \boldsymbol{n}}{\partial t} dS \\ &= -\Delta. \end{split}$$

$$(55)$$

Matching terms yield

$$\begin{pmatrix} \boldsymbol{j}_{i}^{s} = -\frac{D_{i}^{s}C_{i}^{s}}{RT}\nabla\tilde{\mu}_{i}^{s}, & \text{in }\Omega^{s} \\ \mathcal{R}^{l} = k_{f,ref}e^{-\frac{\Delta ZF}{RT}\beta(\eta + \Delta\phi_{eq}^{l})}\Pi_{i=1}^{N}\left(\frac{C_{i}^{l}}{c_{0}}\right)^{a_{i}} - k_{r,ref}e^{\frac{\Delta z^{l}F}{RT}(1-\beta)(\eta + \Delta\phi_{eq}^{l})}\Pi_{i=1}^{N}\left(\frac{C_{e}^{r}}{c_{0}}\right)^{-\Delta z^{l}}\left(\frac{C_{i}^{l}}{c_{0}}\right)^{b_{i}} & \text{on }\Gamma^{l} \\ \frac{\Delta ZF}{2}e^{(\omega + \Delta + \Gamma_{i})}\left(\frac{CT}{2}\right)^{\Delta z^{r}} = N - \left(\frac{CT}{2}\right)^{a_{i}} - \frac{\Delta z^{r}F}{2}(1-\beta)(\eta + \Delta\phi_{eq}^{l})\Pi_{i=1}^{N}\left(\frac{CT}{c_{0}}\right)^{b_{i}} & \text{on }\Gamma^{l} \end{cases}$$

$$\mathcal{R}^{r} = k_{f,ref} e^{-\frac{\Delta Z T}{RT} \beta(\eta + \Delta \phi_{eq}^{r})} \begin{pmatrix} \frac{C_{e}}{c_{0}} \end{pmatrix}^{-r} \Pi_{i=1}^{N} \begin{pmatrix} \frac{C_{i}}{c_{0}} \end{pmatrix}^{-r} - k_{r,ref} e^{\frac{\Delta Z T}{RT} (1-\beta)(\eta + \Delta \phi_{eq}^{r})} \Pi_{i=1}^{N} \begin{pmatrix} \frac{C_{i}}{c_{0}} \end{pmatrix}^{r} \quad \text{on } \Gamma^{r}$$
$$\boldsymbol{D}^{s} \cdot \boldsymbol{n}^{s} = C_{e}^{s} F = \mathbb{C}_{p} (\phi^{s} - \phi_{p}^{s}), \qquad \text{on } \Gamma$$
$$J_{e} = -\frac{g}{F^{2}} (\tilde{\mu}_{e}^{r} - \tilde{\mu}_{e}^{l}), \qquad \text{on } \Gamma$$

$$e_{e} = -\frac{g}{F^{2}} (\tilde{\mu}_{e}^{r} - \tilde{\mu}_{e}^{l}), \qquad \text{on } \Gamma$$

$$\phi = \phi_{ref}, \qquad \text{on } \partial\Omega/\Gamma.$$

In summary, the bidomain reaction system is

$$\begin{cases} \frac{\partial C_i^s}{\partial t} = \nabla \cdot \left(\frac{D_i^s C_i^s}{RT} \nabla \tilde{\mu}_i^s\right), & \text{in } \Omega^s \\ -\nabla \cdot \left(\varepsilon_0 \varepsilon_r \nabla \phi^s\right) = \sum_{i=1}^N z_i F C_i^s, & \text{in } \Omega^s \end{cases}$$
(56)

for the boundary conditions

$$\begin{cases} \boldsymbol{j}_{i}^{s} \cdot \boldsymbol{n}_{s} = -\gamma_{i} \mathcal{R}^{s}, & \text{on } \boldsymbol{\Gamma}, \\ \mathcal{R}^{l} = k_{f,ref} e^{-\frac{\Delta ZF}{RT}\beta(\eta + \Delta \phi_{eq}^{l})} \boldsymbol{\Pi}_{i=1}^{N} \left(\frac{C_{i}^{l}}{c_{0}}\right)^{a_{i}} - k_{r,ref} e^{\frac{\Delta z^{l}F}{RT}(1-\beta)(\eta + \Delta \phi_{eq}^{l})} \boldsymbol{\Pi}_{i=1}^{N} \left(\frac{C_{e}^{r}}{c_{0}}\right)^{-\Delta z^{l}} \left(\frac{C_{i}^{l}}{c_{0}}\right)^{b_{i}} & \text{on } \boldsymbol{\Gamma}^{l} \\ \mathcal{R}^{r} = k_{f,ref} e^{-\frac{\Delta ZF}{RT}\beta(\eta + \Delta \phi_{eq}^{r})} \left(\frac{C_{e}^{r}}{c_{0}}\right)^{\Delta z^{r}} \boldsymbol{\Pi}_{i=1}^{N} \left(\frac{C_{i}^{r}}{c_{0}}\right)^{a_{i}} - k_{r,ref} e^{\frac{\Delta z^{r}F}{RT}(1-\beta)(\eta + \Delta \phi_{eq}^{r})} \boldsymbol{\Pi}_{i=1}^{N} \left(\frac{C_{i}^{r}}{c_{0}}\right)^{b_{i}} & \text{on } \boldsymbol{\Gamma}^{r} \\ \mathbb{C}_{p} \frac{d(\phi^{l} - \phi_{p}^{l})}{dt} = -\Delta z^{l} F \mathcal{R}^{l} + \frac{g}{F} (\tilde{\mu}_{e}^{r} - \tilde{\mu}_{e}^{l}), \mathbb{C}_{p} \frac{d(\phi^{r} - \phi_{p}^{r})}{dt} = -\Delta z^{r} F \mathcal{R}^{r} - \frac{g}{F} (\tilde{\mu}_{e}^{r} - \tilde{\mu}_{e}^{l}), & \text{on } \boldsymbol{\Gamma}, \\ \boldsymbol{D}^{s} \cdot \boldsymbol{n}^{s} = \mathbb{C}_{p} (\phi^{s} - \phi_{p}^{s}), & \text{on } \boldsymbol{\Gamma}, \\ \boldsymbol{j}_{i}^{s} \cdot \boldsymbol{n} = 0, \phi = \phi_{ref} & \text{on } \boldsymbol{O} \boldsymbol{\Gamma}. \end{cases}$$

Remark 2.5. At equilibrium, we have

$$\Delta z^{l} \mathcal{R}^{l} F = -\Delta z^{r} \mathcal{R}^{r} F = g(\tilde{\mu}_{e}^{r} - \tilde{\mu}_{e}^{l}).$$
(58)

Remark 2.6. If there is no reaction, the model degenerates to

$$\begin{cases} \frac{\partial C_i^s}{\partial t} = \nabla \cdot \left(\frac{D_i^s C_i^s}{RT} \nabla \mu_i^s\right), & \text{in } \Omega^s \\ -\nabla \cdot \left(\varepsilon_0 \varepsilon_r \nabla \phi^s\right) = \sum_{i=1}^N z_i F C_i^s, & \text{in } \Omega^s \end{cases}$$
(59)

for the boundary conditions

$$\begin{cases} \boldsymbol{j}_{i}^{s} \cdot \boldsymbol{n}_{s} = 0, & \text{on } \partial\Omega, \\ \mathbb{C}_{p} \frac{d(\phi^{l} - \phi_{p}^{l})}{dt} = g(\tilde{\mu}_{e}^{r} - \tilde{\mu}_{e}^{l}) = -\mathbb{C}_{p} \frac{d(\phi^{r} - \phi_{p}^{r})}{dt} & \text{on } \Gamma, \\ \boldsymbol{D}^{s} \cdot \boldsymbol{n}^{s} = \mathbb{C}_{p}(\phi^{s} - \phi_{p}^{s}), & \text{on } \Gamma, \\ \phi = \phi_{ref} & \text{on } \partial\Omega \setminus \Gamma. \end{cases}$$
(60)

Let $c_0, t^* = \frac{L^2}{D^*}, D^*, L, \frac{RT}{F}$ be the characteristic concentration, time, diffusion constant, length, and electric potential. Then the equations could be written as in Ω_s

$$\begin{cases} \frac{\partial C_i^s}{\partial t} = \nabla \cdot (D_i^s (\nabla C_i^s + z_i C_i^s \nabla \phi^s)), \\ -\nabla \cdot (\delta^2 \nabla \phi^s) = \sum_{i=1}^N z_i C_i^s, \end{cases}$$
(61)

with the boundary conditions

$$\begin{cases} \boldsymbol{j}_{i}^{s} \cdot \boldsymbol{n}_{s} = -\gamma_{i} \zeta \mathcal{R}^{s}, & \text{on } \Gamma, \\ \boldsymbol{D}_{s} \cdot \boldsymbol{n}_{s} = \lambda_{s} (\phi^{s} - \phi_{p}^{s}), & \text{on } \Gamma \\ \frac{\partial}{\partial t} (\boldsymbol{D}_{l} \cdot \boldsymbol{n}_{l}) + \frac{\zeta}{\delta^{2}} \Delta z_{l} \mathcal{R}_{l} = g(C_{e}^{l}, \phi_{p}^{l}, \phi_{p}^{r}) (\tilde{\mu}_{e}^{r} - \tilde{\mu}_{e}^{l}) = g(C_{e}^{l}, \phi_{p}^{l}, \phi_{p}^{r}) (\ln(\frac{C_{e}^{r}}{C_{e}^{l}}) + \phi_{p}^{l} - \phi_{p}^{r})), & \text{on } \Gamma \\ \frac{\partial}{\partial t} (\boldsymbol{D}_{r} \cdot \boldsymbol{n}_{r}) + \frac{\zeta}{\delta^{2}} \Delta z_{r} \mathcal{R}_{r} = -g(C_{e}^{l}) (\tilde{\mu}_{e}^{r} - \tilde{\mu}_{e}^{l}) = -g(C_{e}^{l}) (\ln(\frac{C_{e}^{r}}{C_{e}^{l}}) + \phi_{p}^{l} - \phi_{p}^{r}), & \text{on } \Gamma. \\ \boldsymbol{j}^{s} \cdot \boldsymbol{n} = 0, \phi^{s} = 0, & \text{on } \partial\Omega/\Gamma \end{cases}$$

where $\mathbf{D}_s = -\epsilon_s \nabla \phi_s$, $\mathcal{R}^l = \prod_{i=1}^N (C_i^l)^{a_i} k_{f,ref}^l e^{-\Delta Z_l \beta(\phi_p^l - \phi^l)} - k_{r,ref}^l (C_e^l)^{-\Delta z^l} \prod_{i=1}^N (C_i^l)^{b_i} e^{\Delta Z_l (1-\beta)(\phi_p^l - \phi^l)}$, $\mathcal{R}^r = (C_e^r)^{\Delta z^r} \prod_{i=1}^N (C_i^r)^{a_i} k_{f,ref}^r e^{-\Delta Z_r \beta(\phi_p^r - \phi^r)} - k_{r,ref}^r \prod_{i=1}^N (C_i^r)^{b_i} e^{\Delta Z_r (1-\beta)(\phi_p^r - \phi^r)}$. Here $\delta = \frac{\lambda_D}{L}$ is the ratio between Debye length $\lambda_D = \sqrt{\frac{RT\epsilon_0\epsilon_r}{F^2c_0}}$ and macroscale length; $\zeta = \frac{k_f^* L}{D^*c_0}$ is the ratio between reaction time and diffusion time; $\lambda_s = \frac{C_s L}{\epsilon_0\epsilon_r}$ is the ratio between macroscale length and effective width for the Stern layer; and $g = \frac{gt^* L}{\epsilon_0\epsilon_r}$ is the ratio between diffusion time and electric conduction time. To consider the gating phenomena, the conductance g is modeled with a hard threshold θ_0

$$g = \begin{cases} g_0 & \text{if } \phi_p^r - \phi_p^l > \theta_0; \\ 0 & \text{otherwise,} \end{cases}$$
(63)

or a soft one

$$g = g_0 \tanh\left(\frac{(\phi_p^r - \phi_p^l) - \theta_0}{\epsilon}\right),\tag{64}$$

with relaxation ϵ . When the difference of potential between two sides of plates is large enough, then the plate becomes conductive and the electron is transported.

Alternating Access and Switches. We turn now to an extra process that is crucial in the actual function of coupled systems such as shown in Fig. 2. Such systems include a switch that allows alternating access to the reactions on either side of the membrane [26, 27].

The switch usually provides **alternating** access to an occluded state that is not connected (or accessible) to either side of the protein. The occluded state blocks the conduction path (and incidentally often traps ions in the 'middle' of the transporter) and thus prevents backward flux. Alternating access mechanisms create flux across the transporter protein without allowing backward flux which would seriously degrade the efficiency of the transporter. Transporters were first thought to use quite different mechanisms from channels [56, 34]. However, recent work [21] shows otherwise. Alternating access is apparently created by correlated motions of gates that account for activation and inactivation in classical voltage-activated sodium channels [26, 28]. The physical basis of the gates is not discussed in the classical literature. The gate is usually described as a conformational change and left at that without discussing what conformation one is dealing with (distribution of mass? distribution of potential? distribution of charge? etc.) or the physics of how that conformation changes.

Alternating access might arise in other ways, for example, from bubbles in the conduction pathway, as are widely thought to form gates in ion channels [43]. Another possibility is that the gate in the

oxidase is like the switch in a semiconductor (diode) rectifier. The switches might be rectifiers produced by spatial distributions of permanent charge, of opposite signs, as rectification (and switching) is produced in PN diodes and bipolar transistors. Diode rectifiers depend on changes in the shape (i.e., conformation) of the electric field, not changes in the distribution (i.e., conformation) of mass. In the next, we are going to study how the switch functions affect electron transportation.

3 Results

In the simulation, we consider the 1D computation domain [0, 1] and the plate is in the middle, at x = 0.5. On the left side of the plate, we have

$$A^+ + B^{2-} \stackrel{k_f^l}{\underset{k_r^l}{\rightleftharpoons}} C + e^-.$$

On the right side of the plate,

$$D^{2+} + E^- + e^- \stackrel{k_f^r}{\underset{k_r^r}{\rightleftharpoons}} F.$$

The initial concentrations and dimensionless parameters are set to be $C_1(t=0) = 1$, $C_2(t=0) = \frac{1}{2}$, $C_3(t=0) = 0$, $C_4(t=0) = \frac{1}{2}$, $C_5(t=0) = 1$, $C_6(t=0) = 0$, $\delta = 0.1$, g = 0.1, $k_{r,ref}^l = k_{r,ref}^r = 0.001$.

3.1 Left and right with equal reaction rates

We first consider that the left and right reactions with the same reaction rate, $k_{f,ref}^l = k_{f,ref}^r = 1$. Fig. 3 shows the results of the dynamics of reaction rates, electron density, concentrations of substances, and conductance over time with different cases $\zeta = 0.1$ (diffusion dominates), $\zeta = 1$ (diffusion-reaction equal), $\zeta = 10$ (reaction dominates). As ζ increases, the reaction rate also increases (Fig. 3a). The substances on the left plates are consumed much faster (Fig. 3c left) and more electrons accumulate on the left side of the plates (Fig. 3b). The electric potential difference between two sides of the plates $\phi_p^r - \phi_p^l$ increases and opens the gate so that electrons are transported to the right side of the plate (Fig. 3b,d). Then the right reaction starts 3c right). Due to the transport of electrons, the difference in potential between two sides of the plate decreases. The switch then turns off producing the gating dynamics shown in Fig. 3d. Since the total amounts of reactants on the left region are limited, the left reaction stops after a period of time because it runs out of electrons. Without a supply of electrons, the switch turns and the right-side reaction stops. The larger ζ is, the earlier the reaction stops and the switch turns off.

In Fig. 4, we show the phase diagram of potential difference and forward reaction rate function k_f in Eq.(45). The squares and triangles are the start points and end points of the phase diagrams, respectively. $k_{f,ref}$ is the reference constant shown as the solid back line in the figure. When the electric potentials variate with time, the forward reaction rates on the plate variate correspondingly. since $\Delta z_l < 0$ and $\phi_p^l < \phi_s^l$, then the reaction rate on the left plate is smaller that the reference value $k_{f,ref}$. On the right plate, since $\Delta z_r > 0$, so the reaction rate is always greater than the reference value.

The space distributions of electric potential and substances in two regions at equilibrium are shown in Fig. 5. For different ζ , the equilibrium is almost same. The electric potentials on two sides of the plate ϕ_p^s are lower than the potentials of the electrolyte ϕ^s due to the existence of capacitors. And the left plate potential is lower than the potential on the right plate due to the accumulation of electrons. Since C_3 and C_6 are neutral particles, they are spacial uniformly distributed. The distributions of cations and anions are effected by the electric field.

In Fig. 6 and Fig. 7, we compare the results with different effective capacitance λ_s . The reaction rate increases as the capacitance increases. And more electron could be stored on the capacitors. At the equilibrium, due to larger capacitance, the electric potential difference between two sides electrolyte decreases. The effect on the spacial distributions of substances at the equilibrium is mainly on the left region due to the decrease of electric potential difference.



Figure 3: Results with same reaction rate. (a) Reaction rates on both sides of the plate over time; (b) Electron Density on both sides of the plate over time; (c) Substance concentrations on both sides of the plate over time; (d) Conductance function over time.

In Fig. 8, we show the results when the switch function (64) is used with $\epsilon = 0.001$. Compared with the hard switch, the reaction rate function \mathcal{R} is more smooth, especially for larger capacitance $\lambda_s = 0.1$. When capacitance is $\lambda_s = 0.01$, as ζ increases, the switch could maintain an open state for a longer time due to the accumulation of electrons on the left plate (Panel c red dot line).



Figure 4: Phase diagram of Reaction rate k_f^l and electric potential difference $\phi_p^l - \phi_s^l$. Left: left plate; Right: right plate. The black line the reference forward reaction rate value $k_{f,ref} = 1$. The squares are the start points and the triangles are the end points of the phase diagrams.



Figure 5: Results with same reaction rate space distribution at equilibrium. (a) Electric potential; (b) Substance concentrations.

3.2 Reaction Rates

In this subsection, we consider the case when the left and the right reaction rate is different, i.e. $k_{f,ref}^l \neq k_{f,ref}^r$. Here we fix the effective capacitance $\lambda_s = 0.1$ and diffusion-reaction time scale ratio $\zeta = 1$. The results are shown in Fig.9 where the solid lines are for the left-fast-right-slow case



Figure 6: Results with same reaction rate different λ_s . (a) Reaction rate; (b) Electron density; (c) Substance concentrations.

 $k_{f,ref}^l = 1, k_{f,ref}^r = 0.1$, the dash-dot lines are for the left-slow-right-fast case $k_{f,ref}^l = 0.1, k_{f,ref}^r = 1$ case and the dot lines are for the equal reaction case $k_{f,ref}^l = 1, k_{f,ref}^r = 1$. When the left forward reaction rate constant is faster than the right one, electrons accumulate on the left plate more and faster in the beginning. As a consequence, the left plate reaction slows down compared to the equal reaction case $k_{f,ref}^l = k_{f,ref}^r = k_{f,ref}^r = 1$. The accumulated electron active the gate earlier than the slower one (Fig.9d). When the substances run out in the left region in a very short time (Fig.9c), then the switch is closed. Since the right side forward reaction is slow $k_{f,ref}^r = 0.1$, electrons accumulate on the right plates (Fig.9d) and maintain the right plates reaction smoothly even after the gate is closed (Fig.9a). In contrast, when the left forward reaction rate constant is slower than the right one, the electron density on the left plate increases slowly. When the gate is open, the electrons are transported to the right plate and start the reaction on the right later than the other two cases (Fig.9a). At the same time, since the right forward reaction rate is large, the electron is consumed very fast which induces high oscillation of reaction function on the right plate and high-frequency gating.

4 Discussion and Conclusion

This paper seeks to combine the classical description of chemical reactions with a general variational treatment of forces and flows taking care to use a treatment of current flow in circuits beyond the usual electrostatic approach. Based on the first and second laws of thermodynamics, we generalized the energy variation method [51, 52] for an open system with flux communication on the boundary. Then the framework is used to study the chemical reaction in electrolytes where the charges are taken into consideration. When the reaction is in the bulk region, the obtained model is a Poisson-Nernst-Planck



Figure 7: Results with same reaction rate different λ_s space distribution at equilibrium. (a) Electric potential; (b) Substance concentrations.

(PNP) system with reaction terms that could be taken as a generalized version of the diffusion-reaction model in [65]. Then we consider the reactions on the boundary with the external current supply and on the interface of the self-regulation bidomain reaction system. The effect of electric potential on the reaction rate is consistently modeled by the Frumkin-Butler-Volmer Equation [5, 50, 58, 59, 25]. Then, we proposed a bidomain model for electron transportation across the interface with oxidation on the left side that produces electrons and reduction on the right that consumes electrons. The electron transportation process plays an important role in ATP production and the transport of oxygen/carbon dioxide. Any disruption in these reactions can lead to a range of health problems, including anemia, sickle cell disease, and other blood disorders. The simulation results are used to illustrate the diffusion-reaction competition and how the electric potential affects the reaction rate function. In order to model the gating phenomena, we presented simple both hard switch and soft switch models that assume the conductivity of the interface depends on the electric potential difference like the Hodgkin-Huxley model [36, 35].

Our treatment, however, uses only the simplest representations of the chemical reactions themselves and we are quite aware that the specifics of the reactions that have been so exhaustively analyzed in the electrochemistry literature will need to be introduced to our current based models as more realism is sought. In this regard, it will be of particular interest to biologists to consult the literature on proton-electron reactions in inorganic systems [25]. In the future, with more detailed information on the reactions and biological structure, our model could be used to study the full electron transport chain during the ATP production or blood clotting cascade process [69, 54]. Chemical reactions can also play an important role in the active motion of soft matter. For example, in some active gels, chemical reactions between the gel components can generate mechanical stress that drives the motion of the gel. Similarly, chemical reactions can be used to generate motion in droplets or other active soft matter systems. Also, in the current work, the fluid is neglected temporarily for simplicity. By adding the kinetic energy of the fluid to the total energy E and constitutive relation, our model could be used to study the active rheology of soft matter [62].

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Figure 8: Results with soft switch function. (a) Reaction rate with $\lambda_s = 0.01$; (b) Reaction rate with $\lambda_s = 0.1$; (c) Electron density with $\lambda_s = 0.01$; (d) Electron density with $\lambda_s = 0.1$; (e) Conductance with $\lambda_s = 0.01$; (f) Conductance with $\lambda_s = 0.1$.



Figure 9: Results with different reaction rates. (a) Reaction rates on both sides of the plate over time; (b) Electron Density on both sides of the plate over time; (c) Substance concentrations on both sides of the plate over time; (d) Conductance function over time.