

# TECHNICAL REPORT

## Modeling of faradaic reactions in electrochemical cell

Enclosed script can be used for dynamical simulations of systems where occur faradaic reactions such as electrochemical cells. Electrochemical interactions play an important role in many fields of science and industry. Reversible electrochemical cells such as rechargeable batteries is one of the most important scopes. Description of electrochemical reactions can be used in micropumps driven by electric field, galvanic cells intended for metal deposition or in electroseparation applications.

Our approach involves kinetic mechanism of electrochemical interactions which assumes fast formation and recombination of electron donors ( $DE^-$ ) and acceptors ( $AE^+$ ) on electrode surfaces. These mediators are continuously formed in the electrode matter by thermal fluctuations. The mediators  $DE^-$  and  $AE^+$  enter electrochemical interactions on the electrode surfaces. Electrochemical dynamics and current-voltage characteristics of a selected electrochemical system can be studied using this approach. The proposed model can be used for studying of fast electrochemical processes in micro and nano systems that are often out of the thermal equilibrium.

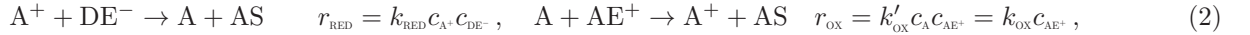
We believe that the proposed model can be useful for dynamical analysis of micro and nano electrochemical systems forced by high-frequency electric fields. Our kinetic mechanism also allows studying and analyzing more complex electrochemical systems by simple adding new kinetic terms into the boundary conditions. Our theory allows description of electrochemical reactions by means of the standard chemical kinetic theory widely accepted in chemical reaction engineering. In this theory, all concentrations are principally non-negative. Electrons are considered to be reactants in the electrochemical reactions. Introduction of the electron donors and acceptors as reactants then avoids negative electron concentrations. Our model is able to simulate cyclic electrochemical processes such as cyclic voltammetry for fast sweep rates together with dynamics of the EDL processes.

### I. MATHEMATICAL MODEL

Here, we study a reversible electrochemical reaction with one electron transfer



We consider that a dilute electrolyte consists of reactive metal cation  $A^+$  and inert ions  $B^-$ ,  $C^+$  that do not participate in electrode reactions. We propose the following reaction mechanism for the reduction and oxidation processes forming overall electrochemical reaction (eq. (1))



where symbols  $DE^-$ ,  $AE^+$  and  $AS$  denote the donor of electrons, the acceptor of electrons (i.e. electron mediators) and active sites on metal surface, respectively. The symbols  $k'_{\text{OX}}$ ,  $k_{\text{RED}}$  are the reaction rate constants. The surface concentration of the metal remains approximately constant and is involved in the rate constant  $k_{\text{OX}}$ . In this particular case (2), the metal  $A$  participates in the electrochemical reaction and simultaneously serves as an mediator (donor, acceptor). Thus, the component  $AS$  is chemically equivalent to the metal  $A$ .

We assume that permanent thermal fluctuations in electrode matter give rise the formation of electron rich atoms (donors of electrons) and electron poor atoms (acceptors of electrons). Schematically, the process is expressed by eq. (3). Formation of the donors and acceptors is considered much faster than the other reaction-transport processes

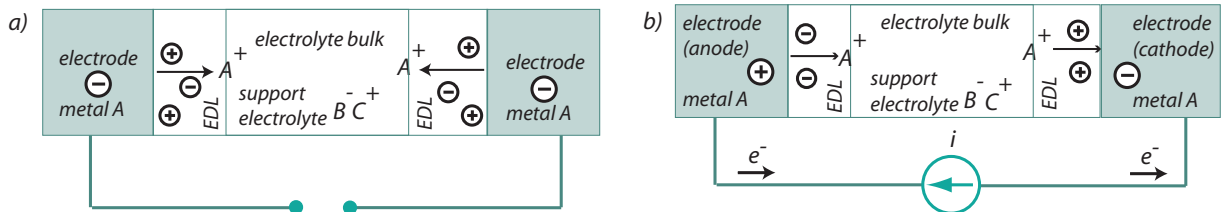
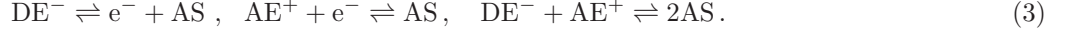


FIG. 1. Scheme of model electrochemical cell. (a) Transient processes when electrodes are immersed into an electrolyte, (b) Cell under a current load.

(electrode reactions, diffusion and electromigration transports in the electrolyte). Hence, the thermal equilibrium can be expected in the form of equation.



In this equilibrium, the overall reaction rate is equal to zero and we can write

$$k_d c_{\text{AS}}^2 = k_a c_{\text{AE}^+} c_{\text{DE}^-}, \quad k_d c_{\text{AS}}^2 / k_a = c_{\text{AE}^+} c_{\text{DE}^-} = K_{\text{D}}, \quad (4)$$

where symbols  $k_a$ ,  $k_d$  and  $K_{\text{D}}$  denote the donor-acceptor association rate constant, the active site dissociation rate constant, and the equilibrium constant of the donor-acceptor recombination, respectively. If the active sites are in high surplus, their concentration can be considered constant. Alternatively, we can assume a total concentration of the active sites as a sum of concentration of the free active sites, electron donors, and electron acceptors. However, this approach brings a higher complexity to the proposed model.

The difference between concentrations of donors and acceptors on an electrode is equal to the concentration of the electric charge  $Q$  available on the electrode

$$c_{\text{AE}^+} - c_{\text{DE}^-} = Q/F \equiv 2b. \quad (5)$$

The combination of equations (4) and (5) leads to explicit expressions for the concentration of donors and acceptors

$$c_{\text{AE}^+} = b + \sqrt{b^2 + K_{\text{D}}}, \quad c_{\text{DE}^-} = -b + \sqrt{b^2 + K_{\text{D}}}. \quad (6)$$

If we assume the presence of a dilute electrolyte in the electrochemical cell, the local ion concentrations  $c_i$  are given by the molar balances,

$$\frac{\partial c_i}{\partial t} = -\frac{\partial J_i}{\partial x}, \quad J_i = -D_i \frac{\partial c_i}{\partial x} - \frac{z_i D_i F}{RT} c_i \frac{\partial \phi}{\partial x}, \quad i = \text{A}^+, \text{B}^-, \text{C}^+. \quad (7)$$

where the molar flux of ion  $J_i$  is given by the Nernst-Planck equation. The symbols  $D_i$  and  $z_i$  are the diffusivity and the ion charge number.

Distribution of the electric potential  $\phi$  satisfies the Poisson equation

$$\frac{\partial}{\partial x} \left( \varepsilon \frac{\partial \phi}{\partial x} \right) = -q = -F \sum_i z_i c_i. \quad (8)$$

where  $q$  is the electric charge density,  $\varepsilon$  is the electric permittivity of the electrolyte (here assumed constant).

As we consider two electrodes, both made from the same material, the same boundary conditions were used for both the electrode-solution interfaces. The zero molar fluxes are used for ions which do not participate in the electrode reactions. The molar flux of the reactive cation  $J_{\text{A}^+}$  is equal to the release or consumption via the electrochemical reactions

$$J_{\text{A}^+} \Big|_{x=0, L} = r_{\text{An, Cat}} = k_{\text{OX}} c_{\text{AE}^+} - k_{\text{RED}} c_{\text{A}^+} c_{\text{DE}^-}. \quad (9)$$

Actual electric charge concentration  $Q$  on the electrode boundaries (An - anode at  $x = 0$ , Cat - cathode at  $x = L$ ) has to be evaluated in order to compute the donor and acceptor concentrations

$$\frac{\partial Q_{\text{An}}}{\partial t} \Big|_{x=0} = i - F r_{\text{An}}, \quad \frac{\partial Q_{\text{Cat}}}{\partial t} \Big|_{x=L} = -i - F r_{\text{Cat}}, \quad (10)$$

where  $i$  denotes the external electric current load - the principal parameter of the model.

The electric potential boundary conditions were considered in the following form:

$$\frac{\partial \phi}{\partial x} \Big|_{x=0} = -\frac{Q_{\text{An}}}{\varepsilon}, \quad \phi \Big|_{x=L} = 0. \quad (11)$$

Spatially uniform concentrations of  $\text{B}^-$  and  $\text{C}^+$  ions and zero concentration of the reactive ion  $\text{A}^+$  were considered as the initial condition for dynamical simulations

$$c_{\text{B}^-, \text{C}^+} \Big|_{x, t=0} = c_0, \quad c_{\text{A}^+} \Big|_{x, t=0} = 0. \quad (12)$$

The model equations were transformed into a dimensionless form used in the enclosed script.

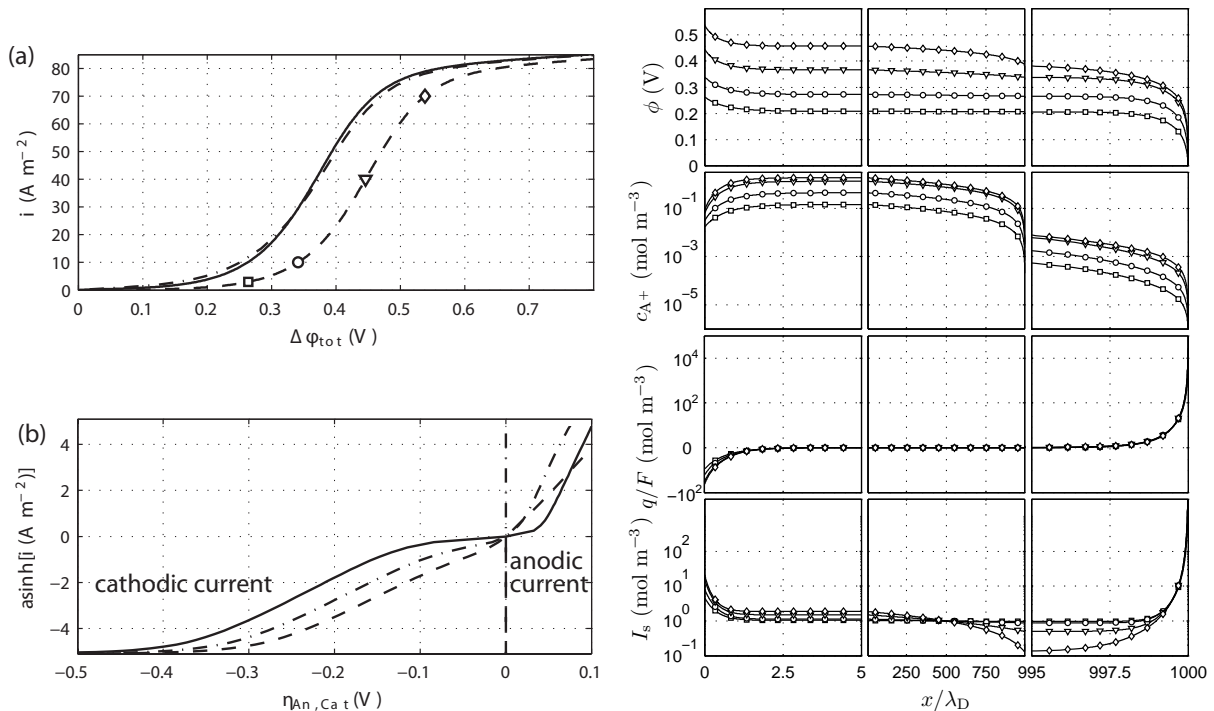


FIG. 2. The CV characteristics of (a) the whole electrochemical cell, (b) half-cells. Values of the model parameters: dash-dotted line -  $L = 1000 \lambda_D$ ,  $k_{\text{RED}} = D/\lambda_D^2 \times 10^2 \text{ m}^3 \text{ mol}^{-1}$ ,  $k_{\text{OX}} = D/\lambda_D^2 \times 10^2$ ,  $K_D = (c_0 \lambda_D)^2$ , solid line -  $L = 1000 \lambda_D$ ,  $k_{\text{RED}} = D/\lambda_D^2 \times 10^2 \text{ m}^3 \text{ mol}^{-1}$ ,  $k_{\text{OX}} = D/\lambda_D^2 \times 10^2$ ,  $K_D = 1000 (c_0 \lambda_D)^2$ , dashed line -  $L = 1000 \lambda_D$ ,  $k_{\text{RED}} = D/\lambda_D^2 \times 10^5 \text{ m}^3 \text{ mol}^{-1}$ ,  $k_{\text{OX}} = D/\lambda_D^2 \times 10^2$ ,  $K_D = (c_0 \lambda_D)^2$ .

(c) Stationary behavior of the whole electrochemical cell under a current load. Electric current density: square  $3 \text{ A m}^{-2}$ , circle  $10 \text{ A m}^{-2}$ , triangle  $40 \text{ A m}^{-2}$ , diamond  $70 \text{ A m}^{-2}$ . Values of the model parameters -  $L = 1000 \lambda_D$ ,  $k_{\text{RED}} = D/\lambda_D^2 \times 10^5 \text{ m}^3 \text{ mol}^{-1}$ ,  $k_{\text{OX}} = D/\lambda_D^2 \times 10^2$ ,  $K_D = (c_0 \lambda_D)^2$ , where  $L$  is the length of the system, the Debye length ( $\lambda_D$ ) can be written as  $\lambda_D^2 = \frac{\epsilon RT}{2 c_0 F^2}$  and  $c_0 = 1 \text{ mol m}^{-3}$ .

## II. RESULTS

The simulations of the electrochemical cell under a current load was carried out, Fig. 2. We constructed current-voltage (CV) characteristics of the entire electrochemical cell, Fig. 2a, and a half-cell, Fig. 2b. The symbol  $\Delta\phi_{\text{tot}}$  in Fig. 2a represents the total potential difference imposed on the electrochemical cell. The anodic/cathodic overpotentials  $\eta_{\text{An,Cat}}$  (Fig. 2b) are defined as  $\eta_{\text{An,Cat}} = \Delta\phi_h - \Delta\phi_e$ , where  $\Delta\phi_h$  is the potential difference between the electrode surface and the cell centre, and  $\Delta\phi_e$  is the established equilibrium electrode potential.

The CV dependencies of the whole electrochemical cell are characterized by exponential current growth for small potential differences. When the system becomes limited by the transport, the exponential growth is suppressed. For high potential differences, the limiting current is reached. The shift of the system from the electrochemically limited regime (exponential growth) to the transport limited regime was studied in detail. Four steady state profiles, that correspond to four marked points in Fig. 2a, are plotted in Fig. 2c. The two steady states obtained for low current densities (square and circle markers) can be characterized by almost constant ionic strength and negligible electric charge density in the electrolyte bulk. As the voltage increases, the system shifts to the transport limited regime (triangle and diamond markers). The  $\text{A}^+$  ions are the only electric charge carriers at any steady states. Growing supply of electrons to the cathode results in massive formation of the electron donors and in a decrease of the electric potential. The  $\text{A}^+$  ions are then intensively consumed on the cathode and, simultaneously, attracted to the electrode surface from the electrolyte bulk. The electric field strength in the cathode vicinity becomes high. Hence, the other electrolyte components ( $\text{B}^-$  and  $\text{C}^+$ ) are electrostatically expelled from this region and the ionic strength decreases. With growing electric current, the depleted zone extends far from the cathode. The obtained CV characteristics of the electrochemical system are in good qualitative agreement with those given by the classical theory.