

C – Mathematical reformulation

The following system of partial differential equations with initial and boundary conditions describes problem of electrodiffusion (for the details - see section B)

$$\begin{aligned} \frac{\partial c_i}{\partial t} &= -\frac{\partial}{\partial x} J_i(x, t) \\ \frac{\partial E}{\partial t} &= \frac{1}{\varepsilon} I(t) - \frac{F}{\varepsilon} \sum_{s=1}^r z_s J_s(x, t), \text{ where } J_i := -D_i \frac{\partial c_i}{\partial x} + \frac{F z_i D_i}{RT} c_i E + c_i \nu \\ c_i(x, 0) &= c_i^0(x), \quad E(0, 0) = 0, \quad E(x, 0) = \frac{F}{\varepsilon} \int_0^x \sum_{j=1}^r z_j c_j(y, 0) dy \quad \text{for } x \in [0, d] \end{aligned} \quad (1)$$

$$\begin{aligned} J_i(0, t) &= -\bar{k}_{iL} c_i(0, t) + \bar{k}_{iL} c_{iL} \\ J_i(d, t) &= \bar{k}_{iR} c_i(1, t) - \bar{k}_{iR} c_{iR} \end{aligned}$$

$$\text{where } \nu = \frac{1}{c_{mix}} \sum_{j=1}^r D_j \frac{\partial c_j}{\partial x} - \frac{F}{c_{mix} RT} E \sum_{j=1}^r D_j z_j c_j + \frac{1}{c_{mix}} \sum_{j=1}^r (\bar{k}_{jL} c_{jL} - \bar{k}_{jL} c_j(0, t)) \quad (2)$$

In this section mathematical reformulation of the problem given by eqns. (1)-(2) suitable for obtaining solution to the problem is presented.

Let us introduce the following notation:

$$\begin{aligned} \bar{x} &:= \frac{x}{L}, \quad \bar{t} := \frac{t}{t_c}, \quad \bar{c}_i(\bar{x}, \bar{t}) := \frac{c_i(L\bar{x}, t_c \bar{t})}{c_{max}}, \quad \bar{E}(\bar{x}, \bar{t}) := \frac{E(L\bar{x}, t_c \bar{t})}{E_{max}} \\ \text{where } L, t_c, c_{max}, E_{max} &- \text{characteristic values} \end{aligned} \quad (3)$$

Using (3) we can calculate:

$$\begin{aligned} \frac{\partial c_i}{\partial t} &= \frac{\partial (c_{max} \bar{c}_i)}{\partial \bar{t}} \frac{\partial \bar{t}}{\partial t} = \frac{c_{max}}{t_c} \frac{\partial \bar{c}_i}{\partial \bar{t}} \\ \frac{\partial c_i}{\partial x} &= \frac{\partial (c_{max} \bar{c}_i)}{\partial \bar{x}} \frac{\partial \bar{x}}{\partial x} = \frac{c_{max}}{L} \frac{\partial \bar{c}_i}{\partial \bar{x}} \\ \frac{\partial}{\partial x} &= \frac{\partial}{\partial \bar{x}} \frac{\partial \bar{x}}{\partial x} = \frac{1}{L} \frac{\partial}{\partial \bar{x}} \end{aligned} \quad (4)$$

Using (4) we can rewrite equations (1)

$$\begin{aligned}
\frac{c_{\max}}{t_c} \frac{\partial \bar{c}_i}{\partial \bar{t}} &= -\frac{\partial}{\partial \bar{x}} \left(\frac{J_i(L\bar{x}, t_c \bar{t})}{L} \right) \\
\frac{E_{\max}}{t_c} \frac{\partial \bar{E}}{\partial \bar{t}} &= \frac{1}{\varepsilon} I(t_c \bar{t}) - \frac{F}{\varepsilon} \sum_{s=1}^r z_s J_s(L\bar{x}, t_c \bar{t}) \\
\text{where } J_i(x, t) &= -\frac{c_{\max}}{L} D_i \frac{\partial \bar{c}_i}{\partial \bar{x}} \left(\frac{x}{L}, \frac{t}{t_c} \right) + c_{\max} E_{\max} \frac{F}{RT} z_i D_i (\bar{c}_i \bar{E}) \left(\frac{x}{L}, \frac{t}{t_c} \right) + \\
&+ \sum_{j=1}^r \left\{ \frac{c_{\max}^2}{c_{\max} L} D_j \left(\bar{c}_i \frac{\partial \bar{c}_j}{\partial \bar{x}} \right) \left(\frac{x}{L}, \frac{t}{t_c} \right) \right\} - \sum_{j=1}^r \left\{ \frac{c_{\max}^2 E_{\max} F}{c_{\max} RT} D_j z_j (\bar{c}_i \bar{c}_j \bar{E}) \left(\frac{x}{L}, \frac{t}{t_c} \right) \right\} + \\
&+ \sum_{j=1}^r \left\{ \frac{c_{\max}^2}{c_{\max}} \bar{k}_{jL} \bar{c}_{jL} \bar{c}_i \left(\frac{x}{L}, \frac{t}{t_c} \right) \right\} - \sum_{j=1}^r \left\{ \frac{c_{\max}^2}{c_{\max}} \bar{k}_{jL} \bar{c}_j \left(0, \frac{t}{t_c} \right) \bar{c}_i \left(\frac{x}{L}, \frac{t}{t_c} \right) \right\} \\
\bar{c}_{jL} &:= \frac{c_{jL}}{c_{\max}}
\end{aligned} \tag{5}$$

After rearrangements we get:

$$\begin{aligned}
\frac{\partial \bar{c}_i}{\partial \bar{t}} &= -\frac{\partial}{\partial \bar{x}} \left(\frac{t_c}{c_{\max} L} J_i \right) = -\frac{\partial}{\partial \bar{x}} \bar{J}_i \\
\frac{\partial \bar{E}}{\partial \bar{t}} &= \frac{t_c}{E_{\max} \varepsilon} I(t_c \bar{t}) - \frac{t_c F}{E_{\max} \varepsilon} \sum_{s=1}^r z_s J_s = \bar{I}(\bar{t}) - \lambda \sum_{s=1}^r z_s \bar{J}_s \\
\text{where } \lambda &:= \frac{c_{\max} L F}{E_{\max} \varepsilon}, \quad \bar{I}(\bar{t}) := \frac{t_c}{E_{\max} \varepsilon} I(t_c \bar{t}) \\
\bar{J}_i(\bar{x}, \bar{t}) &:= \frac{t_c}{c_{\max} L} J_i(L\bar{x}, t_c \bar{t}) = -\frac{t_c}{L^2} D_i \frac{\partial \bar{c}_i}{\partial \bar{x}} (\bar{x}, \bar{t}) + \frac{t_c E_{\max}}{L} \frac{F}{RT} z_i D_i (\bar{c}_i \bar{E}) (\bar{x}, \bar{t}) + \\
&+ \sum_{j=1}^r \left\{ \frac{t_c c_{\max}}{c_{\max} L^2} D_j \left(\bar{c}_i \frac{\partial \bar{c}_j}{\partial \bar{x}} \right) (\bar{x}, \bar{t}) \right\} - \sum_{j=1}^r \left\{ \frac{t_c c_{\max} E_{\max}}{L c_{\max}} \frac{F}{RT} D_j z_j (\bar{c}_i \bar{c}_j \bar{E}) (\bar{x}, \bar{t}) \right\} + \\
&+ \sum_{j=1}^r \left\{ \frac{t_c c_{\max}}{c_{\max} L} \bar{k}_{jL} \bar{c}_{jL} \bar{c}_i (\bar{x}, \bar{t}) \right\} - \sum_{j=1}^r \left\{ \frac{t_c c_{\max}}{c_{\max} L} \bar{k}_{jL} \bar{c}_j (0, \bar{t}) \bar{c}_i (\bar{x}, \bar{t}) \right\}
\end{aligned} \tag{6}$$

Boundary conditions:

$$\begin{aligned}
\bar{J}_i(0, \bar{t}) &= \frac{t_c}{c_{\max} L} J_i(0, t_c \bar{t}) = -\frac{t_c}{L} \bar{k}_{iL} \frac{c_i(0, t_c \bar{t})}{c_{\max}} + \frac{t_c}{L} \bar{k}_{iL} \frac{c_{iL}}{c_{\max}} = -\frac{t_c}{L} \bar{k}_{iL} \bar{c}_i(0, \bar{t}) + \frac{t_c}{L} \bar{k}_{iL} \frac{c_{iL}}{c_{\max}} \\
\text{for } i &= 1, \dots, r \text{ and} \\
\bar{J}_i(1, \bar{t}) &= \frac{t_c}{c_{\max} L} J_i(1, t_c \bar{t}) = \frac{t_c}{L} \bar{k}_{iR} \frac{c_i(d, t_c \bar{t})}{c_{\max}} - \frac{t_c}{L} \bar{k}_{iR} \frac{c_{iR}}{c_{\max}} = \frac{t_c}{L} \bar{k}_{iR} \bar{c}_i(1, \bar{t}) - \frac{t_c}{L} \bar{k}_{iR} \frac{c_{iR}}{c_{\max}} \\
\text{for } i &= 1, \dots, r-1 \\
\bar{J}_r(1, \bar{t}) &= \bar{J}_r(0, \bar{t}) - \sum_{j=1}^{r-1} (\bar{J}_j(0, \bar{t}) - \bar{J}_j(1, \bar{t}))
\end{aligned} \tag{7}$$

Finally we get:

$$\left\{ \begin{array}{l} \frac{\partial \bar{c}_i}{\partial \bar{t}} = -\frac{\partial}{\partial \bar{x}} \bar{J}_i \\ \frac{\partial \bar{E}}{\partial \bar{t}} = \bar{I}(\bar{t}) - \lambda \sum_{s=1}^r z_s \bar{J}_s \\ \bar{c}_i(\bar{x}, 0) = \bar{c}_i^0(\bar{x}) \text{ for } \bar{x} \in [0, 1] \\ \bar{E}(0, 0) = 0, \bar{E}(\bar{x}, 0) = \frac{F c_{\max}}{\varepsilon E_{\max}} \int_0^{\bar{x}} \sum_{j=1}^r z_j \bar{c}_j(y, 0) dy \text{ for } \bar{x} \in [0, 1] \\ \bar{J}_i(0, \bar{t}) = -\bar{k}_{iL} \bar{c}_i(0, \bar{t}) + \bar{k}_{iL} \bar{c}_{iL} \text{ for } i = 1, \dots, r \\ \bar{J}_i(1, \bar{t}) = \bar{k}_{iR} \bar{c}_i(1, \bar{t}) - \bar{k}_{iR} \bar{c}_{iR} \text{ for } i = 1, \dots, r-1 \\ \bar{J}_r(1, \bar{t}) = \bar{J}_r(0, \bar{t}) - \sum_{j=1}^{r-1} (\bar{J}_j(0, \bar{t}) - \bar{J}_j(1, \bar{t})) \end{array} \right. \quad (8)$$

where

$$\begin{aligned} \bar{J}_i &= -a_i \frac{\partial \bar{c}_i}{\partial \bar{x}} + b_i \bar{c}_i \bar{E} + \sum_{j=1}^r \left(g_j \bar{c}_i \frac{\partial \bar{c}_j}{\partial \bar{x}} \right) - \sum_{j=1}^r (\alpha_j \bar{c}_i \bar{c}_j \bar{E}) + \beta \bar{c}_i - \sum_{j=1}^r \gamma_j \bar{c}_j(0, \bar{t}) \bar{c}_i \\ a_i &:= \frac{t_c}{L^2} D_i, \quad b_i := \frac{t_c E_{\max}}{L} \frac{F}{RT} z_i D_i, \quad g_j := \frac{t_c c_{\max}}{c_{\max} L^2} D_j, \quad \alpha_j := \frac{t_c c_{\max} E_{\max}}{c_{\max} L} \frac{F}{RT} z_j D_j, \\ \beta &:= \frac{c_{\max}}{c_{\max}} \sum_{j=1}^r (\bar{k}_{jL} \bar{c}_{jL}), \quad \gamma_j := \frac{c_{\max}}{c_{\max}} \bar{k}_{jL}, \quad \bar{c}_i^0(\bar{x}) := \frac{c_i^0(L\bar{x})}{c_{\max}}, \quad \bar{c}_{iL} := \frac{c_{iL}}{c_{\max}}, \quad \bar{c}_{iR} := \frac{c_{iR}}{c_{\max}} \\ \bar{k}_{iL} &:= \frac{t_c}{L} \bar{k}_{iL}, \quad \bar{k}_{iL} := \frac{t_c}{L} \bar{k}_{iL}, \quad \bar{k}_{iR} := \frac{t_c}{L} \bar{k}_{iR}, \quad \bar{k}_{iR} := \frac{t_c}{L} \bar{k}_{iR} \end{aligned} \quad (9)$$

In the further part of the text for simplicity we will omit “bars” in the equation (8) and we will analyze the numerical solution of the following problem

$$\left\{ \begin{array}{l}
 \frac{\partial c_i}{\partial t} = -\frac{\partial}{\partial x} J_i \\
 \frac{\partial E}{\partial t} = I(t) - \lambda \sum_{s=1}^r z_s J_s \\
 c_i(x, 0) = c_i^0(x) \text{ for } x \in [0, 1] \\
 E(0, 0) = 0, \quad E(x, 0) = \frac{F c_{\max}}{\varepsilon E_{\max}} \int_0^x \sum_{j=1}^r z_j c_j(y, 0) dy \text{ for } x \in [0, 1] \\
 J_i(0, t) = -\bar{k}_{iL} c_i(0, t) + \vec{k}_{iL} c_{iL} \text{ for } i = 1, \dots, r \\
 J_i(1, t) = \bar{k}_{iR} c_i(1, t) - \vec{k}_{iR} c_{iR} \text{ for } i = 1, \dots, r-1 \\
 J_r(1, t) = J_r(0, t) - \sum_{j=1}^{r-1} (J_j(0, t) - J_j(1, t))
 \end{array} \right. \quad (10)$$