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)

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

$$
where \ \ \upsilon = \frac{1}{c_{mix}}\sum_{j=1}^{r} D_j \frac{\partial c_j}{\partial x} - \frac{F}{c_{mix} RT} E \sum_{j=1}^{r} D_j z_j c_j + \frac{1}{c_{mix}}\sum_{j=1}^{r}\left(\vec{k}_{jL} c_{jL} - \overleftarrow{k}_{jL} c_j(0,t)\right) \tag{2}
$$

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:

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

Using (3) we can calculate:

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

Using (4) we can rewrite equations (1)

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

After rearrangements we get:

$$
\begin{aligned}
&\frac{\partial \overline{c}_i}{\partial \overline{t}} = -\frac{\partial}{\partial \overline{x}}\left(\frac{t_c}{c_{max}L}J_i\right) = -\frac{\partial}{\partial \overline{x}}\overline{J}_i\\
&\frac{\partial \overline{E}}{\partial \overline{t}} = \frac{t_c}{E_{max}\varepsilon}I(t_c\overline{t}) - \frac{t_cF}{E_{max}\varepsilon}\sum_{s=1}^{r}z_sJ_s = \overline{I}(\overline{t}) - \lambda\sum_{s=1}^{r}z_s\overline{J}_s\\
&where\\
&\lambda := \frac{c_{max}LF}{E_{max}\varepsilon},\;\; \overline{I}(\overline{t}) := \frac{t_c}{E_{max}\varepsilon}I(t_c\overline{t})\\
&\overline{J}_i(\overline{x},\overline{t}) := \frac{t_c}{c_{max}L}J_i(L\overline{x}, t_c\overline{t}) = -\frac{t_c}{L^2}D_i\frac{\partial \overline{c}_i}{\partial \overline{x}}\left(\overline{x},\overline{t}\right) + \frac{t_cE_{max}}{L}\frac{F}{RT}z_iD_i\left(\overline{c}_i\overline{E}\right)\left(\overline{x},\overline{t}\right) +\\
&\qquad +\sum_{j=1}^{r}\left\{\frac{t_cc_{max}}{c_{mix}L^2}D_j\left(\overline{c}_i\frac{\partial \overline{c}_j}{\partial \overline{x}}\right)\left(\overline{x},\overline{t}\right)\right\} - \sum_{j=1}^{r}\left\{\frac{t_cc_{max}E_{max}}{Lc_{mix}}\frac{F}{RT}D_jz_j\left(\overline{c}_i\overline{c}_j\overline{E}\right)\left(\overline{x},\overline{t}\right)\right\} +\\
&\qquad +\sum_{j=1}^{r}\left\{\frac{t_cc_{max}}{c_{mix}L}\vec{k}_{jL}\overline{c}_{jL}\overline{c}_i\left(\overline{x},\overline{t}\right)\right\} - \sum_{j=1}^{r}\left\{\frac{t_cc_{max}}{c_{mix}L}\overleftarrow{k}_{jL}\overline{c}_j\left(0,\overline{t}\right)\overline{c}_i\left(\overline{x},\overline{t}\right)\right\}
\end{aligned}
\tag{6}
$$

Boundary conditions:

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

Finally we get:

$$
\begin{cases}
\dfrac{\partial \bar{c}_i}{\partial \bar{t}} = -\dfrac{\partial}{\partial \bar{x}} \bar{J}_i \\
\dfrac{\partial \bar{E}}{\partial \bar{t}} = \bar{I}(\bar{t}) - \lambda \sum_{s=1}^{r} z_s \bar{J}_s \\
\bar{c}_i(\bar{x},0) = \bar{c}_i^0(\bar{x}) \quad for \quad \bar{x} \in [0,1] \\
\bar{E}(0,0) = 0, \;\; \bar{E}(\bar{x},0) = \dfrac{F c_{\max}}{\varepsilon E_{\max}} \displaystyle\int_0^{\bar{x}} \sum_{j=1}^{r} z_j \bar{c}_j(y,0)\, dy \quad for \quad \bar{x} \in [0,1] \\
\bar{J}_i(0,\bar{t}) = -\overleftarrow{\bar{k}}_{iL} \bar{c}_i(0,\bar{t}) + \overrightarrow{\bar{k}}_{iL} \bar{c}_{iL} \quad for\; i = 1, \ldots r \\
\bar{J}_i(1,\bar{t}) = \overleftarrow{\bar{k}}_{iR} c_i(1,\bar{t}) - \overrightarrow{\bar{k}}_{iR} \bar{c}_{iR} \quad for\; i = 1, \ldots r-1 \\
\bar{J}_r(1,\bar{t}) = \bar{J}_r(0,\bar{t}) - \sum_{j=1}^{r-1} \left(\bar{J}_j(0,\bar{t}) - \bar{J}_j(1,\bar{t}) \right)
\end{cases}
\tag{8}
$$

where

$$
\bar{J}_i = -a_i \frac{\partial \bar{c}_i}{\partial \bar{x}} + b_i \bar{c}_i \bar{E} + \sum_{j=1}^{r} \left(g_j \bar{c}_i \frac{\partial \bar{c}_j}{\partial \bar{x}} \right) - \sum_{j=1}^{r} \left(\alpha_j \bar{c}_i \bar{c}_j \bar{E} \right) + \beta \bar{c}_i - \sum_{j=1}^{r} \gamma_j \bar{c}_j \left(0,\bar{t}\right) \bar{c}_i
$$

$$
a_i := \frac{t_c}{L^2} D_i, \;\; b_i := \frac{t_c E_{\max}}{L} \frac{F}{RT} z_i D_i, \;\; g_j := \frac{t_c c_{\max}}{c_{mix} L^2} D_j, \;\; \alpha_j := \frac{t_c c_{\max} E_{\max}}{c_{mix} L} \frac{F}{RT} z_j D_j, \tag{9}
$$

$$
\beta := \frac{c_{\max}}{c_{mix}} \sum_{j=1}^{r} \left(\overrightarrow{\bar{k}}_{jL} \bar{c}_{jL} \right), \;\; \gamma_j := \frac{c_{\max}}{c_{mix}} \overleftarrow{\bar{k}}_{jL}, \;\; \bar{c}_i^0(\bar{x}) := \frac{c_i^0(L\bar{x})}{c_{\max}}, \;\; \bar{c}_{iL} := \frac{c_{iL}}{c_{\max}}, \;\; \bar{c}_{iR} := \frac{c_{iR}}{c_{\max}}
$$

$$
\overleftarrow{\bar{k}}_{iL} := \frac{t_c}{L} \overleftarrow{k}_{iL}, \overrightarrow{\bar{k}}_{iL} := \frac{t_c}{L} \overrightarrow{k}_{iL}, \;\; \overleftarrow{\bar{k}}_{iR} := \frac{t_c}{L} \overleftarrow{k}_{iR}, \overrightarrow{\bar{k}}_{iR} := \frac{t_c}{L} \overrightarrow{k}_{iR}
$$

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

$$
\begin{cases}
\dfrac{\partial c_i}{\partial t} = -\dfrac{\partial}{\partial x} J_i \\
\dfrac{\partial E}{\partial t} = I(t) - \lambda \sum_{s=1}^{r} z_s J_s \\
c_i(x,0) = c_i^0(x) \quad for \quad x \in [0,1] \\
E(0,0) = 0, \;\; E(x,0) = \dfrac{F c_{\max}}{\varepsilon E_{\max}} \int_0^x \sum_{j=1}^{r} z_j c_j(y,0)\, dy \quad for \quad x \in [0,1] \\
J_i(0,t) = -\overleftarrow{k}_{iL} c_i(0,t) + \overrightarrow{k}_{iL} c_{iL} \quad for \; i = 1, \ldots r \\
J_i(1,t) = \overleftarrow{k}_{iR} c_i(1,t) - \overrightarrow{k}_{iR} c_{iR} \quad for \; i = 1, \ldots r-1 \\
J_r(1,t) = J_r(0,t) - \sum_{j=1}^{r-1} \left(J_j(0,t) - J_j(1,t) \right)
\end{cases}
\tag{10}
$$