Finite difference method of simulation of non-steady-state ion transfer in electrochemical systems with allowance for migration

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Abstract

Finite difference methods of the second order of accuracy are elaborated for numerical calculation of non-steady-state ion transfer, which is caused by diffusion, migration, and convection in the unidimensional electrochemical systems. The methods of decoupling a set of coupled continuity equations of the electrolyte species are proposed, which ensures that the discrete equations are consistent with the initial differential equations and the electroneutrality condition is rigorously met. The methods of approximation of the boundary conditions of the second order temporal and spatial accuracy and the method of decoupling the transfer equations in the boundary nodes are elaborated. The explicit, fully implicit, and semi-implicit finite difference schemes are elaborated. For semi-implicit schemes, two versions of difference equation closure are proposed, which assure the unambiguity of determination of the distribution of electrical potential. Comparison analysis of the accuracy of elaborated finite difference methods of calculation of non-steady-state ion transfer is performed.

Keywords: Finite difference method; Electrochemical systems; Ion transfer; Migration

1. Introduction

To study complex electrochemical systems, which are characterized by a great number of electrolyte components and a complex geometrical shape, with non-steady-state ion transfer processes, the numerical methods are widely used (Newman, 1973; Britz, 1988; Engelhardt and Davydov, 1986, 1988; Karlin, 1992; Feldberg and Goldstein, 1995; Bortels et al., 1996; Georgiadou, 1997; Qiu et al., 1997; Bieniasz, 1999; Nann and Heinze, 1999). The numerical solving involves two steps. (1) Spatial and temporal discretization of equations describing the transfer processes in the electrochemical system. As a result of discretization, the initial set of differential equations with the corresponding boundary conditions is reduced to a set of difference equations, which, in the general case, is non-linear. (2) Solving of a set of difference equations using the direct or iterative methods. Thus, an approximate solution of above problem is determined.

The methods of solving sets of difference equations are well elaborated (Smith, 1985; Ortega and Rheinboldt, 1970), and one can to choice of the most appropriate known method for the numerical solving of non-steady-state ion transfer.

The most popular methods of discretization are as follows (Smith, 1985; Patankar, 1980; Oran and Boris, 1987): the finite difference method, the finite volume method, the finite element method, and the boundary element method. In contrast to the methods of solving the difference equations, the discretization scheme should be chosen with regard to the character of the problem under consideration. The accepted scheme of discretization should assure the consistency of the initial and difference equations, the stability of numerical solution and its required accuracy. Moreover, it should...
be efficient (requiring not too large store size and computing time).

In recent years, much effort has been directed toward elaborating efficient methods of ion transfer simulation (Bieniasz, 1999; Britz and Strutwolf, 2000; Feldberg and Goldstein, 1995). This applies, primarily, to the systems with binary electrolyte or with an excess of supporting electrolyte, where the migration transfer can be ignored or the migration term can be eliminated. For these systems, several finite difference methods of high order of spatial and temporal accuracy, multigrid and adaptive grid techniques on regular and irregular grids are developed, stability and error of numerical solution are obtained. The most efficient methods of ion transfer simulation are Rosenbrock, BDF, extrapolation methods (Bieniasz, 1999; Britz and Strutwolf, 2000; Feldberg and Goldstein, 1995). The systems with homogeneous electrolyte component; ¯

2. Statement of problem

In the unidimensional case, in the approximation of the theory of dilute electrolytes and under the electroneutrality condition, the set of equations of ion transfer in dimensionless form can be written as follows (Newman, 1973):

\[
\frac{\partial C_k}{\partial t} = D_k \frac{\partial^2 C_k}{\partial x^2} + z_k D_k C_k \frac{\partial \varphi}{\partial x} + z_k D_k \frac{\partial C_k}{\partial x} \frac{\partial \varphi}{\partial x} - V \frac{\partial C_k}{\partial x} + R_k, \quad k = 1, \ldots, N_s, \]

\[
\sum_{k=1}^{N_s} z_k C_k = 0. \tag{1}
\]

Here, \(C_k\), \(z_k\), \(D_k\), and \(R_k\) are the concentration, the charge, the diffusion coefficient, and the intensity of the internal source of the \(k\)th electrolyte species, respectively; \(\varphi\) is the electric potential; \(V\) is the hydrodynamic velocity; \(N_s\) is the number of electrolyte species; \(x\) is the coordinate along the normal to the electrode’s surface, which is measured from the surface; and \(t\) is the time.

We passed to the dimensionless form using the following equations:

\[
C_k = \frac{\tilde{C}_k}{\tilde{C}_{1_b}}, \quad x = \frac{x}{\delta}, \quad \varphi = \frac{F \varphi}{RT}, \quad D_k = \frac{\tilde{D}_k}{\tilde{D}_1}, \quad t = \frac{\tilde{t}}{\delta^2}, \quad V = \frac{\tilde{V}}{\tilde{D}_1}, \quad R_k = \frac{\tilde{R}_k}{\tilde{D}_1 \tilde{C}_{1_b}}. \tag{2}
\]

Here, \(\tilde{C}_{1_b}\) is the bulk concentration of the first electrolyte component; \(\delta\) is the diffusion layer thickness (for the forced electrolyte convection, \(\delta\) is the thickness of the Nernst layer; for stagnant electrolyte, \(\delta \geq \sqrt{n/D_1 T}\)); \(F\) is Faraday’s number; \(R\) is the gas constant, and \(T\) is the temperature. The bar identifies the initial dimensional variables.

The initial conditions reduce to the prescribed distribution of electrolyte species concentrations at the initial instant of time.

The boundary conditions at the outer boundary of the diffusion layer are as follows:

\[
C_k(1, t) = C_{k_b}. \tag{3}
\]
At the electrode’s surface, the boundary conditions are determined starting from the type of electrode reaction and the electrolysis conditions. We will consider only the reactions of charge transfer yielding an insoluble product (metal deposit, for example),
\[ S_1^j + n_ee^- \leftrightarrow P, \quad (4) \]
or a soluble product (redox reaction),
\[ S_1^j + n_ee^- \leftrightarrow S_2^j, \quad (5) \]

Here, \( n_e \) is the number of electrons involved in the electrode reaction (\( n_e = z_1 \) for reaction (4) and \( n_e = z_1 - z_2 \) for reaction (5)), \( S_k^j \) is the \( k \)th electroactive electrolyte species; \( P \) is an insoluble product of the electrode reaction.

Due to the electrode reaction (4) or (5), electric current passes through the system. The current density \( i \) in the unidimensional system is independent of the spatial coordinate; therefore, \( i \) can be expressed in terms of electrolyte species fluxes on the electrode’s surface,
\[ i(t) = \sum_{k=1}^N z_k j_k, \quad (6) \]
\[ j_k = -\left( D_k \frac{\partial C_k}{\partial x} + D_k z_k C_k \frac{\partial \varphi}{\partial x} \right)_{x=0}, \quad (7) \]

where \( j_k \) is the flux of the \( k \)th electrolyte species on the electrode’s surface.

The electric potential applied to the system \( U \) is determined as follows:
\[ U(t) = \varphi(1, t) - E(t), \quad (8) \]

where \( E(t) \) is the electrode potential; \( \varphi(1, t) \) is a potential drop in the diffusion layer of solution (we accept \( \varphi(0, t) = 0 \)). If required, the potential drop in the solution beyond the diffusion layer, where the concentrations of all of ions are constant, can be easily taken into consideration.

For reversible electrode reactions, the Nernst equation is valid,
\[ E = E_0 + \frac{1}{n_e} \ln C_1(0, t), \quad (9) \]
\[ E = E_0 + \frac{1}{n_e} \ln \frac{C_1(0, t)}{C_1(0, 0)}, \quad (10) \]

Where \( E_0 \) is the standard electrode potential. Eq. (9) corresponds to reaction (4), and Eq. (10) corresponds to reaction (5).

For non- and quasi-equilibrium electrode reactions, the Butler–Volmer equation will be used,
\[ j_1 = k_2 e^{z_1n_1(E-E_0)} - k_1 C_1(0, t) e^{-z_1n_1(E-E_0)}, \quad (11) \]
\[ j_2 = k_2 C_2(0, t) e^{z_2n_2(E-E_0)} - k_1 C_1(0, t) e^{-z_2n_2(E-E_0)}. \quad (12) \]

Here \( k_2, k_1 \) are constants (\( k_2 = k_1 C_1 \)—for Eq. (11) and \( k_2 C_2 = k_1 C_1 \)—for Eq. (12)); \( z_2, z_1 \) are charge transfer coefficients; \( E_{eq} \) is the equilibrium electrode potential (with respect to the bulk concentration of species, i.e. \( E_{eq} = E_0 + (1/2n_2) \ln C_1/C_2 \) for electrode reaction (4) and \( E_{eq} = E_0 + (1/2n_1) \ln (C_1/C_2) \) for electrode reaction (5)).

For electrode reaction (5), the following relation is valid:
\[ j_1 = -j_2. \quad (13) \]

At the electrode’s surface, the fluxes of species, which are not involved in electrochemical reactions, are zero
\[ j_k = 0. \quad (14) \]

Eqs. (6)–(14) are presented in the dimensionless form, which is obtained using Eq. (2).

Only one of three variables—the current density, the electrode potential, and the applied potential—is independent. Two other dependent variables are determined by Eqs. (6)–(12).

To simulate the processes of non-steady-state ion transfer, a set of non-linear coupled differential–algebraic equations (1) with the corresponding initial and boundary conditions (3)–(14) should be numerically solved for a given operation mode. Here, the method of finite differences is used.

3. Method of solution

3.1. Spatial and temporal discretization

For the numerical solution of set of Eq. (1), we will use the finite difference method (Samarskii and Nikolskii, 1989; Smith, 1985). For the sake of simplicity, we assume that the mesh with nodes in points \( 1, \ldots, l, \ldots, N \) is homogeneous, i.e. \( \Delta x_l = x_l - x_{l-1} = \Delta x = \text{const} \). The node with subscript 1 is located on an electrode’s surface, and the node with subscript \( N \) is located on outer boundary of the diffusion layer.

In the inner nodes of the mesh, for the spatial discretization of equations of electrolyte species transfer (1), we use the central differences. Hence, we obtain:
\[
\frac{dC_k}{dr} = \frac{D_k(C_{k+1} - 2C_k + C_{k-1})}{\Delta r^2} + \frac{z_k D_k C_k(\varphi_{i+1} - 2\varphi_i + \varphi_{i-1})}{\Delta x^2} + \frac{z_k D_k(C_{k+1} - C_{k-1})(\varphi_{i+1} - \varphi_{i-1})}{4\Delta x^2} - \frac{V}{(C_{k+1} - C_{k-1})} \frac{R_k}{2\Delta x} + R_k,
\]

\[
\sum_{k=1}^N z_k C_k = 0, \quad i = 1, \ldots, N - 1.
\]
The use of central differences, as it is known (Smith, 1985), provides the second order of accuracy. The main part of local approximation error with respect to space is expressed by the following equation:

$$E_k = \left( D_k \left[ \frac{\partial^4 C_k}{\partial x^4} \right] + z_k D_k C_k \left[ \frac{\partial^3 \varphi}{\partial x^3} \right] - 2V_j \left[ \frac{\partial C_k}{\partial x} \right] \right) \times \frac{\Delta x^2}{12}.$$  \hspace{1cm} (16)

To realize the boundary conditions at the electrode’s surface to the second order of spatial accuracy, we expand the functions $C_k(x, t)$ and $\varphi(x, t)$ in the Taylor series near to the electrode surface (the node with subscript 1), restricting our consideration to the terms containing up to the second derivatives and using Eqs. (1) and (7), we obtain:

$$\frac{dC_{ki}}{dt} = \frac{2D_k(C_{ki} - C_k)}{\Delta x^2} + 2z_k D_k C_k \frac{(\varphi_2 - \varphi_1)}{\Delta x^2}$$
$$- z_k^2 D_k C_k (\varphi')^2 - z_k D_k \varphi' + \frac{2b_k}{\Delta x} + R_{ki},$$

$$\sum_{k=1}^{N_i} z_k C_k = 0,$$ \hspace{1cm} (17)

where $\varphi'$ is the first derivative of electric potential at the electrode’s surface.

Set of Eqs. (15) and (17) is unclosed, because the number of unknowns is by unity larger than the number of equations. To obtain a closed set of equations, one more equation should be given; using this equation $\varphi'$ can be determined. In so doing, it is desirable to assure the second order of accuracy.

To determine $\varphi'$, one-sided three point difference can be used, but we prefer using a central difference of the second order. In this case, a behind-the-electrode fictitious node with subscript 0, which is located at a distance of a grid step from the electrode’s surface, is introduced into the consideration (Smith, 1985). Using central-difference approximation of the first-order derivative for concentration in the boundary condition (7), we obtain:

$$C_{k0} = C_{k1} + 2\Delta x z_k C_{k1} \varphi' + \frac{2\Delta x z_k}{D_k}.$$ \hspace{1cm} (18)

From the condition of electroneutrality in the fictitious node, it follows an explicit second-order expression for the determination of $\varphi'$:

$$\varphi' = - \frac{\sum_k z_k D_k}{\sum_k z_k^2 C_{k1}}.$$ \hspace{1cm} (19)

A set of Eqs. (15) and (17) can be written in the matrix form:

$$\frac{dC}{dt} = A_{dif} C + A^n_{migr}(\Phi) C + A^{conv} C + R(C) + F_{bound} I,$$

$$\mathbf{KC} = 0.$$ \hspace{1cm} (20)

Here, $C$ and $\Phi$ are the vectors of species concentrations and the electric potential in the grid nodes, respectively; $A_{dif}$, $A^n_{migr}$, and $A^{conv}$ are the matrices considering the diffusion, migration, and convective transfer, respectively; $R$ and $F_{bound}$ are the matrices considering the homogeneous chemical reactions and the boundary conditions, respectively; $I$ is the vector of species fluxes in the nodes at the boundary of domain (at the electrode’s surface); and $\mathbf{K}$ is the matrix representing the electroneutrality condition.

Matrix $A^n_{migr}(\Phi)$ is linear in $\varphi$; hence:

$$A^n_{migr}(\Phi) C = A^o_{migr}(C) \Phi.$$ \hspace{1cm} (21)

For solving numerically set (20), the temporal discretization should be performed. The most popular schemes are as follows:

The explicit scheme:

$$C^{n+1} = C^n + \Delta t (A_{dif} C^n + A^n_{migr}(\Phi^{n+1/2}) C^n + A^{conv} C^n + R(C^n) + F_{bound} I^n),$$

$$\mathbf{KC}^{n+1} = 0,$$ \hspace{1cm} (22)

the fully implicit scheme:

$$C^{n+1} = C^n + \Delta t (A_{dif} C^{n+1} + A^n_{migr}(\Phi^{n+1}) C^{n+1} + A^{conv} C^{n+1} + R(C^{n+1}) + F_{bound} I^{n+1}),$$

$$\mathbf{KC}^{n+1} = 0,$$ \hspace{1cm} (23)

and also the semi-implicit scheme:

$$C^{n+1} = C^n + \Delta C_{imp}(C^{n+1}, \Phi^{n+1}, I^{n+1}) + \Delta C_{exp}(C^n, \Phi^{n+1/2}, I^n),$$

$$\mathbf{KC}^{n+1} = 0,$$ \hspace{1cm} (24)

where

$$\Delta C_{imp} = \beta \Delta t (A_{dif} C^n + A^n_{migr}(\Phi^{n+1}) C^n + A^{conv} C^n + R(C^n) + F_{bound} I^n),$$

$$\Delta C_{exp} = (1 - \beta) \Delta t (A_{dif} C^n + A^n_{migr}(\Phi^{n+1/2}) C^n + A^{conv} C^n + R(C^n) + F_{bound} I^n).$$

Here, subscript $n$ is correlated with the time instant $t_n = n \Delta t$; $\Delta t = t_{n+1} - t_n$ is the temporal step; $\beta$ is a parameter varying from 0 to 1 and characterizing a degree, to which the scheme is implicit (at $\beta = 0$, the scheme is explicit; at $\beta = 1$, the scheme is fully implicit; and at $\beta = 0.5$, the CN scheme).

For the semi-implicit scheme, it is necessary to prescribe supplementary conditions, because the avail
able equations are inadequate to determine the potential at the time instants \( n+1/2 \) and \( n+1 \). For closure of the system, we can assume that the electroneutrality condition is fulfilled not only for \( C^{n+1} \), but also for \( \Delta C_{\rm exp} \), therefore, instead of \( K C^{n+1} = 0 \), we can use

\[
K \Delta C_{\text{imp}} = 0, \quad K \Delta C_{\text{exp}} = 0. \tag{25}
\]

The second way implies that the electrolyte species transfer is considered at the time instants \( n+1/2 \) and \( n+1 \) under the action of the same averaged electric potential distribution \( \Phi^{n+1/2} \), i.e. Eq. (24) is represented in the following form:

\[
C^{n+1} = C^n + \Delta C_{\text{imp}}(C^{n+1}, \Phi^{n+1}, F^n)
+ \Delta C_{\text{exp}}(C^n, \Phi^{n+1}, F^n),
\]

\[
K C^{n+1} = 0. \tag{26}
\]

Thus derived sets of difference equations are coupled, i.e. it is required to solve simultaneously the full set of difference equations for all of electrolyte species and the electric potential. The presence of migration term is the main reason for the equation coupling. To simplify solving the set of equations, we propose the decoupling algorithm.

### 3.2. Algorithm of decoupling of difference equations

#### 3.2.1. Explicit difference scheme

Substituting the equations for the concentrations at the time instant \( n+1 \) (Eq. (22)) into the electroneutrality condition, we obtain:

\[
K(A_{\text{dif}} C^n + A_{\text{migr}}(C^n) \Phi^{n+1/2} + F_{\text{bound}} F^n) = 0,
\]

\[
C^{n+1} = C^n + \Delta t(A_{\text{dif}} C^n + A_{\text{migr}}(C^{n+1/2}) C^n + A_{\text{conv}} C^n
+ R(C^n) + F_{\text{bound}} F^n). \tag{27}
\]

From the first equation of set (27), the distribution of electric potential can be found. Thereafter, the difference transfer equations for each electrolyte species can be solved independently.

#### 3.2.2. Fully implicit difference scheme

In the implicit case, the decoupling can be realized by the linearization of set of non-linear equations (23). The following iterative scheme of decoupling is proposed:

\[
K(A_{\text{dif}} C^{n+1,k} + A_{\text{migr}}(C^{n+1,k}) \Phi^{n+1,k+1} + F_{\text{bound}} F^{n+1,k}) = 0,
\]

\[
C^{n+1,k+1} = C^n + \Delta t(A_{\text{dif}} C^n + A_{\text{migr}}(C^{n+1,k}) C^n + A_{\text{conv}} C^n + R(C^n)
+ F_{\text{bound}} F^n).
\]

Here, superscript \( k \) corresponds to the iteration’s number.

For the first iteration, we assume that \( C^{n+1,0} = C^n \).

The electroneutrality condition can be violated due to the linearization of equations. The electroneutrality is restored using the following equation (Volgin and Davydov, 2001):

\[
C^{n+1,0} = C^{n+1,0} + \beta \Delta t(A_{\text{dif}} C^{n+1,k} + A_{\text{migr}}(C^{n+1,k}) C^{n+1,k} + A_{\text{conv}} C^n + R(C^n)
+ F_{\text{bound}} F^n), \tag{29}
\]

\[
\Delta t(A_{\text{dif}} C^{n+1,k} + A_{\text{migr}}(C^{n+1,k}) C^{n+1,k} + A_{\text{conv}} C^n + R(C^n)
+ F_{\text{bound}} F^n) = 0, \tag{30}
\]

For Eq. (26) (the second version of prescribing the supplementary condition), we obtain:

\[
K(A_{\text{dif}} C^n + A_{\text{migr}}(C^n) \Phi^{n+1/2} + F_{\text{bound}} F^n) = 0,
\]

\[
K(A_{\text{dif}} C^{n+1,k} + A_{\text{migr}}(C^{n+1,k}) \Phi^{n+1,k+1} + F_{\text{bound}} F^{n+1,k}) = 0,
\]

\[
C^{n+1,k+1} = C^n + \beta \Delta t(A_{\text{dif}} C^{n+1,k} + A_{\text{migr}}(C^{n+1,k}) C^{n+1,k} + A_{\text{conv}} C^n + R(C^n)
+ F_{\text{bound}} F^n).
\]

\[
\Delta t(A_{\text{dif}} C^{n+1,k} + A_{\text{migr}}(C^{n+1,k}) C^{n+1,k} + A_{\text{conv}} C^n + R(C^n)
+ F_{\text{bound}} F^n) = 0. \tag{31}
\]

In both cases, we obtain the linear sets of difference equations, which can be readily solved. The iterative
process is similar to the above-described one for the fully implicit difference scheme. The electroneutrality is restored by Eq. (29).

3.3. Numerical solutions of difference equations for various types boundary conditions

In the above-described general scheme of splitting of coupled equations of ion transfer, the peculiarities of splitting realization for various types of operation modes and various types of electrode reactions are absent. In this section we will consider in more detail the realization of decoupling technique for the fully implicit scheme (for semi-implicit scheme, a similar procedure can be used).

Taking into account Eq. (15), Eq. (28) for inner mesh nodes can be written as follows:

\[\begin{align*}
    a_j \phi_j^{n+1,m+1} - b_j \phi_{j-1}^{n+1,m+1} + c_j \phi_{j+1}^{n+1,m+1} &= -g_j, \\
    d_k C_{k,j+1}^{n+1,m+1} - e_k C_{k,j}^{n+1,m+1} + f_k C_{k,j-1}^{n+1,m+1} &= -h_k,
\end{align*}\]

where

\[\begin{align*}
    a_j &= \frac{\partial^2 }{\partial x^2} + 4 \frac{\partial }{\partial x} + \frac{1}{4}, \\
    b_j &= 2 \phi_j^{n+1,m}, \\
    c_j &= \frac{\partial^2 }{\partial x^2} + 4 \frac{\partial }{\partial x} + \frac{1}{4}, \\
    g_j &= \sum_k z_k D_k [C_{k,j+1}^{n,m} - 2 C_{k,j}^{n+1,m} + C_{k,j-1}^{n,m}], \\
    d_k &= \frac{\Delta t}{\Delta x^2} [D_k - 0.25 z_k D_k (\phi_j^{n+1,m+1} - \phi_{j-1}^{n+1,m+1}) - 0.5 \Delta x V_j^{n+1}] - e_k = \frac{\partial^2 }{\partial x^2} + 2 \frac{\partial }{\partial x} \frac{\partial }{\partial x} \frac{1}{4}, \\
    h_k &= C_{k,j}^{n+1,m} + \Delta t R_k^{n+1,m}.
\end{align*}\]

In the boundary node, the difference equations will be written in the following form:

\[\phi_j^{n+1,m+1} = - \sum_k \frac{z_k D_k}{D_k} \left\{ \frac{1}{\sum_k z_k^2 C_k^{n+1,m}} \right\},\]

\[\begin{align*}
    -\Delta x^2 \sum_k D_k z_k^2 C_k^{n+1,m} (\phi_j^{n+1,m+1})^2 &= 0, \\
    -\Delta x^2 \sum_k z_k D_k \phi_j^{n+1,m+1} + 2 \Delta x \sum_k z_k D_k \phi_j^{n+1,m+1} &= 0, \\
    \tilde{C}_{j,k}^{n+1,m+1} &= C_{j,k}^{n+1,m}, \\
    + \frac{2 D_k \Delta t}{\Delta x^2} [C_{j,k}^{n+1,m+1} - C_{j,k}^{n+1,m+1} + 2 z_k C_{j,k}^{n+1,m+1} \phi_j^{n+1,m+1}] + \Delta t \left[ -D_k z_k^2 C_{j,k}^{n+1,m+1} (\phi_j^{n+1,m+1})^2 \right. \\
    z_k D_k \phi_j^{n+1,m+1} + 2 z_k D_k \phi_j^{n+1,m+1} + R_k^{n+1,m} \right].
\end{align*}\]

Let us consider the procedure of solving the set of difference equations Eqs. (32) and (33) for various types of boundary conditions: a prescribed current density, a prescribed electrode potential, and a prescribed applied potential (Eq. (8)).

3.3.1. Mode of prescribed current density

In this case, the fluxes of electrolyte species at the electrode’s surface, are determined immediately from the prescribed current density. For electrode reaction (4), we obtain

\[f_j^{n+1,m+1} = \frac{n_1^{n+1}}{n_e}, \quad f_k^{n+1,m+1} = 0, \quad k > 1,\]

and for electrode reaction (5),

\[f_j^{n+1,m+1} = \frac{n_1^{n+1}}{n_e}, \quad f_k^{n+1,m+1} = -f_j^{n+1,m+1}, \quad f_k^{n+1,m+1} = 0, \quad k > 2.\]

At every time step, the fluxes are determined by Eq. (34) or Eq. (35); then, from the first and the second equations of set (33), \(\phi_j^{n+1,m+1}\) and \(\phi_j^{n+1,m+1}\) are calculated. The first equation of set (32) is solved by the Tomas algorithm; as a result, the distribution of electric potential \(\phi_j^{n+1,m+1}\) is found. Then, sequentially and independently of one another, \(C_{j,k}^{n+1,m+1}\) are calculated using the Tomas algorithm by the second equation of set (32); thereafter, the electroneutrality condition is restored by Eq. (29); as a result, the next approximation for species concentrations \(C_{j,k}^{n+1,m+1}\) is calculated. The iteration process is repeated up to reaching a required accuracy. The applied potential \(U\) and the electrode potential \(E\) can be determined by Eqs. (8)–(12).

3.3.2. Mode of prescribed electrode potential

In this case, the calculation should be performed by different methods depending on the type of electrode reaction (4) or (5) and a degree of its reversibility.
3.3.2.1. Equilibrium electrode reaction. In this case, the electrode potential $E$ and the species fluxes are not immediately interrelated leading to the necessity of changing the calculation procedure. The calculation should be performed in different ways for electrode reactions (4) and (5).

3.3.2.1.1. Insoluble product (electrode reaction (4)). In the case of electrode reaction (4), the electrode potential immediately defines the electroactive species concentration on the electrode’s surface,

$$C_{n}^{+1} = e^{n(E^{+1} - E_{b})} = \theta^{n+1}. \quad (36)$$

Taking into account this equation, set of Eq. (33) will take the following form:

$$\varphi^{n+1,m+1} = -\frac{2N_{k=1} D_{k} \left(C_{k}^{n+1,m} - C_{k}^{n+1,m}\right)}{D_{k}} + 2N_{k=2} D_{k} \left(C_{k}^{n+1,m} - C_{k}^{n+1,m}\right)$$

$$+ 2N_{k=2} D_{k} z_{k} C_{k}^{n+1,m} \varphi_{k}^{n+1,m+1}$$

$$- \Delta x^{2} \sum_{k=2}^{N_{k}} D_{k} z_{k} C_{k}^{n+1,m} \left(\varphi^{n+1,m+1}\right)^{2}$$

$$+ \Delta x^{2} \sum_{k=2}^{N_{k}} \left(\varphi^{n+1,m+1} - \varphi^{n,m+1}\right) = 0,$$

$$\theta^{n+1} = \theta^{n} + \frac{2D_{k} \Delta t}{\Delta x^{2}} \left[C_{k}^{n+1,m} - \theta^{n+1}\right]$$

$$+ 2N_{k=1} \left[C_{k}^{n+1,m} - \theta^{n+1}\right]$$

$$+ \Delta t \left[-D_{k} z_{k} \varphi^{n+1,m+1}\right]$$

$$- \Delta x \left[\varphi^{n+1,m+1} + \frac{2N_{k=1} \left[C_{k}^{n+1,m} - \theta^{n+1}\right]}{\Delta x} + R_{n+1,m}\right]. \quad (37)$$

Solving set (37), we obtain $\varphi^{n+1,m+1}$, $\varphi_{k}^{n+1,m+1}$, $\varphi_{k}^{n+1,m+1}$, and $R_{n+1,m+1}$. Further calculation is performed similarly to the case of prescribed current density.

3.3.2.1.2. Soluble product (electrode reaction (5)). From Eq. (10) we obtain,

$$C_{1}^{n+1} / C_{2}^{n+1} = e^{n(E^{+1} - E_{b})} = \theta^{n+1} \quad \text{or} \quad \frac{C_{1}^{n+1}}{C_{2}^{n+1}} = \theta^{n+1} \frac{C_{2}^{n+1}}{C_{2}^{n+1}}. \quad (38)$$

Taking into account Eq. (38), set (33) will take the following form:

$$\varphi^{n+1,m+1} = -\frac{2N_{k=1} D_{k} \left(C_{k}^{n+1,m} - C_{k}^{n+1,m}\right)}{D_{k}} + 2N_{k=2} D_{k} \left(C_{k}^{n+1,m} - C_{k}^{n+1,m}\right)$$

$$+ 2N_{k=2} D_{k} z_{k} C_{k}^{n+1,m} \varphi_{k}^{n+1,m+1}$$

$$- \Delta x^{2} \sum_{k=1}^{N_{k}} D_{k} z_{k} C_{k}^{n+1,m} \left(\varphi^{n+1,m+1}\right)^{2}$$

$$- \Delta x^{2} \left(z_{1} - z_{2}\right) \varphi^{n+1,m+1} + 2\Delta x n_{f_{1}} \varphi^{n+1,m+1} = 0,$$

$$C_{1}^{n+1} - \theta^{n+1} C_{2}^{n+1}$$

$$+ \frac{2\Delta t}{\Delta x^{2}} \left[D_{1} C_{1}^{n+1,m} - C_{1}^{n+1,m}\right]$$

$$- \theta^{n+1} D_{2} C_{2}^{n+1,m} - C_{2}^{n+1,m}\right]$$

$$+ \frac{2\Delta t}{\Delta x^{2}} \left(z_{1} D_{1} C_{1}^{n+1,m} - \theta^{n+1} z_{2} D_{2} C_{2}^{n+1,m}\right) \varphi_{2}^{n+1,m+1}$$

$$- \Delta t \left(z_{1} - \theta^{n+1} z_{2}\right) \varphi^{n+1,m+1} + f_{1}^{n+1,m+1} = 0. \quad (39)$$

Solving set (39), we obtain $\varphi^{n+1,m+1}$, $\varphi_{k}^{n+1,m+1}$, $\varphi_{k}^{n+1,m+1}$. Further calculation is performed similarly to the case of prescribed current density.

3.3.2.2. Non-equilibrium electrode reaction. In the case of non-equilibrium (quasi-equilibrium) electrode reaction, the electrode potential and fluxes of the electroactive species are related by the Butler–Volmer equations Eqs. (11) and (12).

For electrode reaction (4), the flux $f_{1}^{n+1,m+1}$ is determined by the following equation:

$$f_{1}^{n+1,m+1} = k_{2} e^{n_{2} e^{(E^{+1} - E_{b})}} - k_{1} C_{1}^{n+1,m} e^{-z_{2} n_{2} e^{(E^{+1} - E_{b})}}, \quad (40)$$

and for electrode reaction (5), the fluxes are as follows:

$$f_{1}^{n+1,m+1} = k_{2} C_{2}^{n+1,m} e^{n_{2} e^{(E^{+1} - E_{b})}}$$

$$- k_{1} C_{1}^{n+1,m} e^{-z_{2} n_{2} e^{(E^{+1} - E_{b})}}$$

$$f_{2}^{n+1,m+1} = -f_{1}^{n+1,m+1}. \quad (41)$$

Further calculation is performed similarly to the case of prescribed current density.

3.3.3. Mode of prescribed applied potential

In this case, as well as in the case of prescribed electrode potential, equilibrium and non-equilibrium electrode reactions (4) and (5) should be considered individually.

3.3.3.1. Equilibrium electrode reaction.

3.3.3.1.1. Insoluble product. Due to the fact that electrode potential is not prescribed, Eq. (9) can be presented as follows:
\[ C_{n+1}^{m+1} = e^{\phi_{n+1}^m - E_n - U_{n+1}^m} = \theta^{n+1,m+1}. \]  

(42)

Substituting Eq. (42) into set Eq. (33) and using the first equation of set (32), we obtain the following set of non-linear equations:

\[
\phi^{n+1,m+1} = -\frac{z_D v_{n+1,m+1}}{D_1} + \left( \sum_{k=1}^{N_L} \frac{z_k^2 C_{n+1,m+1}^{k}}{D_k} \right),
\]

\[
2 \sum_{k=2}^{N_L} z_k D_k (C_{n+1,m}^{k} - C_{n+1,m}^{k_1}) + \Delta \sum_{k=2}^{N_L} D_k z_k^2 C_{n+1,m}^{k_1} \phi_2^{n+1,m+1} \\
- \Delta \sum_{k=2}^{N_L} D_k z_k^2 C_{n+1,m}^{k_1} (\phi_{n+1,m+1} - \frac{R_{n+1,m+1}}{C_{n+1,m+1}}) \\
= \alpha_t C_{n+1,m+1} - \frac{2 \Delta t}{\Delta \chi} \left[ \left( \frac{R_{n+1,m+1}}{C_{n+1,m+1}} + \sum_{j=1}^{N} f_j \right) \right],
\]

(43)

Solving set of Eq. (43) by Newton’s method, we determine \( \phi_{n+1,m+1} \), \( \phi_{n+1,m+1} \), \( j_{1+1,m+1} \), \( j_{1+1,m+1} \), \( \phi^{n+1,m+1} \). Then, the concentrations are calculated and the electroneutrality of solution is restored.

3.3.3.3.1. Soluble product. From Eqs. (8) and (10), we obtain

\[
\phi^{n+1,m+1} = e^{\phi_{n+1}^m - E_n - U_{n+1}^m} = \theta^{n+1,m+1}.
\]

(44)

As well as in the previous case, from Eqs. (32) and (33), with regard to Eq. (44), we obtain

\[
\phi^{n+1,m+1} = -\left( \frac{z_D}{D_1} - \frac{z_2^2}{D_2} \right) f_{1+1,m+1} + \left( \sum_{k=1}^{N_L} \frac{z_k^2 C_{n+1,m+1}^{k}}{D_k} \right),
\]

\[
2 \sum_{k=1}^{N_L} z_k D_k (C_{n+1,m}^{k} - C_{n+1,m}^{k_1}) + \Delta \sum_{k=2}^{N_L} D_k z_k^2 C_{n+1,m}^{k_1} \phi_2^{n+1,m+1} \\
- \Delta \sum_{k=2}^{N_L} D_k z_k^2 C_{n+1,m}^{k_1} (\phi_{n+1,m+1} - \frac{R_{n+1,m+1}}{C_{n+1,m+1}}) \\
= \alpha_t C_{n+1,m+1} - \frac{2 \Delta t}{\Delta \chi} \left[ \left( \frac{R_{n+1,m+1}}{C_{n+1,m+1}} + \sum_{j=1}^{N} f_j \right) \right],
\]

(45)

Solving set of Eq. (45) by Newton’s method, we determine \( \phi_{n+1,m+1} \), \( \phi_{n+1,m+1} \), \( j_{1+1,m+1} \), \( j_{1+1,m+1} \), \( \phi^{n+1,m+1} \).

Then, the concentrations are calculated and the electroneutrality of solution is restored.

3.3.3.3.2. Non-equilibrium electrode reaction.

3.3.3.3.2.1. Insoluble product.

\[
f_{1+1,m+1} = k_2 e^{z_{1,n} (E_{1+1,m+1} - E_0)},
\]

\[
- k_1 C_{1+1,m} e^{z_{1,n} (E_{1+1,m+1} - E_0)},
\]

(46)

3.3.3.3.2.2. Soluble product.

\[
f_{2+1,m+1} = k_2 C_{2+1,m} e^{z_{2,n} (E_{2+1,m+1} - E_0)},
\]

\[
- k_1 C_{2+1,m} e^{z_{2,n} (E_{2+1,m+1} - E_0)},
\]

(47)

For both cases of soluble and insoluble products, further calculation is performed similarly to the case of prescribed current density.

4. Results of simulation

Using the above-elaborated finite difference methods of calculating the non-steady-state ion transfer, we
performed the computing experiments. The aim of experiments was to determine spatial and temporal accuracy of proposed methods, and also to demonstrate the potentialities of these methods under various electrolysis conditions.

When elaborating the methods, we used the approximation of spatial derivative of the second-order accuracy, which will assure the second-order spatial accuracy and the first-order temporal accuracy of the methods for explicit and fully implicit schemes and the second-order temporal accuracy for the CN scheme. However, the iterative solution of decoupled set of difference equations involving the stage of electrolyte electroneutrality restoration can affect the order of accuracy of proposed methods.

To check the adequacy of elaborated numerical methods of ion mass-transfer calculation, we performed the calculations for an electrochemical system with binary electrolyte \((z_1 = 1, z_2 = -1, C_1 = 1, C_2 = 1, D_1 = D_2 = 1)\) under the galvanostatic conditions \((i = 1.5)\). It was assumed that the electrochemical reaction Eq. (4) proceeds at the electrode’s surface.

An exact solution of this problem was derived by Rosenberg and Miller (Vetter, 1961):

\[
C_1(x, t) = C_{1_0} - \frac{\varepsilon_2}{(z_1 - z_2)z_1} \left[ 1 - x - \frac{8}{\pi^2} \sum_{m=1}^{\infty} \frac{1}{(2m - 1)^2} \frac{\pi^2}{(2m - 1)^4} e^{-((2m - 1)^2/4) t} \right] \cos \left( \frac{(2m - 1)\pi}{2} x \right),
\]

\[(48)\]

where \(D = (D_1D_2(z_1 - z_2))/(D_1z_1 - D_2z_2)\) is the effective diffusion coefficient of electrolyte.

To examine the spatial accuracy, we performed calculations at \(\Delta x = 0.02, 0.01\) and 0.005 for time 0.01 (Table 1). For the explicit scheme, the temporal step is \(10^{-5}\); for fully implicit and CN schemes, it is \(10^{-4}\). We compute the root mean square differences \((E_{av})\) and maximum differences \((E_{max})\) of the simulation results and exact solution Eq. (48).

As is seen from Table 1, for explicit and CN schemes, nearly second-order error convergence rate with respect to spatial grid step is observed for \(E_{max}\) and a higher convergence rate is observed for \(E_{av}\). For fully implicit scheme, the second-order convergence rate is observed for \(E_{av}\), and for \(E_{max}\) the convergence rate is somewhat lower; this can be associated with the peculiarities of iteration algorithm of solution of splitted set of difference equations. The accuracy of CN method is comparable to that of explicit method at a 10 times larger temporal grid step \((\Delta t = 1E-4)\) for the CN scheme and \(\Delta t = 1E-5\) for explicit scheme, pointing to its higher accuracy. The CN method with both versions of prescribing the supplementary conditions demonstrated similar results; therefore, from here on, we will consider only the second version of the method, which takes a shorter computing time.

To estimate the temporal accuracy, we performed the calculations for fully implicit and CN schemes at \(\Delta x = 0.01\) with temporal grid steps \(\Delta t = 2E-3, 1E-3\) and \(5E-4\) (Table 2). As it should be expected, for fully implicit scheme, the linear convergence rate (order of accuracy) with respect to temporal grid step is observed,
and for the CN scheme, the second-order convergence rate is observed (Table 2).

An alternative approach to the estimation of the orders of spatial and temporal accuracy of elaborated methods enabling one to estimate the errors in the absence of exact solution. In this case, the simulation is performed for three different temporal or spatial grid steps, and the results of simulation enable one to estimate the order of accuracy. Using this approach, the accuracy of proposed methods was studied under the galvanostatic and potentiodynamic conditions for electrolyte concentrations (Eq. 4). The conditions of calculation: \(C_{1h} = C_{3h} = C_{3b} = 1, z_1 = z_3 = 1, z_2 = -2, D_1 = 1, D_2 = 0.5, D_3 = 2\). The orders of accuracy were determined for electrolyte components \(n_{C_1}\) and electric potential \(n_p\). To investigate the order of spatial accuracy, we perform the simulations at \(\Delta x = 0.02, 0.01\) and \(0.005\) and \(\Delta t = 10^{-6}\) for explicit scheme, at \(\Delta t = 10^{-3}\) for fully implicit scheme, and \(\Delta t = 10^{-4}\) for CN scheme at \(t = 0.01\). The calculations were performed at \(i = -1\) (Table 3) for the galvanostatic conditions and at a potential scan rate \(V = 10\) for the potentiodynamic conditions (Table 5). Both for the electrolyte concentrations and the electric potential, the results are in good agreement with the theoretical value: the second-order of accuracy. For the potentiodynamic conditions, the order of accuracy is somewhat lower, and a larger number of iterations should be performed at each temporal grid step to solve the decoupled set of difference equations. For the CN method, approximately two times smaller number of iterations is required to achieve a given accuracy.

To study the order of temporal accuracy, we perform simulations at \(\Delta x = 0.02\) and \(\Delta t = 10^{-6}, 5 \times 10^{-7}, 2.5 \times 10^{-7}\) for explicit scheme, \(\Delta t = 10^{-3}, 5 \times 10^{-4}, 2.5 \times 10^{-4}\) for fully implicit scheme, and \(\Delta t = 10^{-4}, 5 \times 10^{-4}, 2.5 \times 10^{-4}\) for CN scheme at \(t = 0.01\). For explicit scheme, the first-order of accuracy was obtained for both the galvanostatic (Table 4), and the potentiodynamic (Table 6) conditions corresponding to the theoretical value. For the fully implicit scheme, the order of temporal accuracy was found to be slightly smaller than one; this can be explained by the peculiarities of realization of proposed splitting algorithm. For the CN scheme, the order of accuracy for concentrations is close to two, while the order of accuracy for the electric potential appeared to be close to one. This can be due to the fact that, in the second version of CN method, at each temporal grid step in each node, only one averaged electric potential is determined. The estimated orders of temporal accuracy are rather close for the galvanostatic and potentiodynamic conditions.

For the proposed methods, the number of operations \(N_0\), which are performed at each temporal grid step for the modes of prescribed current density and prescribed electrode potential, can be preliminary estimated as follows:

\[
N_0 = \begin{cases} O(N(N_i + 1)) & \text{for explicit scheme} \\ O(N_{\text{iter}} N^p(N_i + 1)) & \text{for fully implicit and CN schemes} \end{cases}
\]

where \(N_{\text{iter}}\) is the number of iterations for solving the decoupled set of difference equations and \(p\) is the coefficient characterizing the number of operations for solving the set of linear algebraic equations (\(p = 3\) for the Gauss elimination).

For the mode of prescribed applied potential, a somewhat larger number of iterations is required due to the necessity of solving the non-linear set of equations of \(N + 2\) order for equilibrium electrode reaction.

Simultaneous solution of complete set of difference equations for fully implicit and CN schemes by known methods requires \(N_0 = O(N_{\text{iter}}(N(N_i + 1))^2)\) iterations at each temporal grid step. The number of iterations \(N_{\text{iter}}\), which are performed at each temporal grid step for the proposed method (CN scheme) and the known methods, are approximately equal; consequently, the realization of decoupled algorithm is more efficient, especially at

### Table 3

Order of spatial accuracy and number of iterations under the galvanostatic conditions

<table>
<thead>
<tr>
<th>Method</th>
<th>Order of spatial accuracy</th>
<th>Number of iterations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(n_{C_1})</td>
<td>(n_{C_2})</td>
</tr>
<tr>
<td>Explicit</td>
<td>2.0026</td>
<td>2.0037</td>
</tr>
<tr>
<td>Fully implicit</td>
<td>2.0031</td>
<td>2.0039</td>
</tr>
<tr>
<td>Crank–Nicolson</td>
<td>2.0026</td>
<td>2.0036</td>
</tr>
</tbody>
</table>

### Table 4

Order of temporal accuracy under the galvanostatic conditions

<table>
<thead>
<tr>
<th>Method</th>
<th>Order of temporal accuracy</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(n_{C_1})</td>
<td>(n_{C_2})</td>
</tr>
<tr>
<td>Explicit</td>
<td>1.0000</td>
<td>1.0000</td>
</tr>
<tr>
<td>Fully implicit</td>
<td>0.9742</td>
<td>0.9677</td>
</tr>
<tr>
<td>Crank–Nicolson</td>
<td>1.9999</td>
<td>2.0004</td>
</tr>
</tbody>
</table>
high parameter $p$ and for the multicomponent electrolytes.

To illustrate the potentialities of proposed methods, we performed the simulations of non-steady-state transfer processes for various conditions of electrolysis and various kinetics of electrode reactions (Figs. 1–5). The calculations were performed by the CN scheme at $\Delta x = 0.02$. The temporal grid step was determined from the condition of the absence of fictitious oscillations in the numerical solution. For electrode reaction Eq. (4) yielding insoluble product (metal deposition), the dependences of the current density on the electrode potential were obtained for reversible (Fig. 1) and irreversible (Fig. 2) conditions. For electrode reaction Eq. (5), yielding a soluble product, the dependences of the current density on the electrode potential were obtained for reversible (Fig. 3) and irreversible (Figs. 4 and 5) conditions.

### Table 5

<table>
<thead>
<tr>
<th>Method</th>
<th>$n_{C_1}$</th>
<th>$n_{C_2}$</th>
<th>$n_{C_3}$</th>
<th>$n_o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Explicit</td>
<td>1.9977</td>
<td>1.9991</td>
<td>1.9975</td>
<td>2.0029</td>
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<tr>
<td>Fully implicit</td>
<td>1.8040</td>
<td>2.2128</td>
<td>1.8751</td>
<td>1.8726</td>
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<tr>
<td>Crank–Nicolson</td>
<td>1.9940</td>
<td>2.0021</td>
<td>1.9953</td>
<td>2.0027</td>
</tr>
</tbody>
</table>

### Table 6

<table>
<thead>
<tr>
<th>Method</th>
<th>Order of temporal accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Explicit</td>
<td>1.0000 1.0000 1.0000 1.0000</td>
</tr>
<tr>
<td>Fully implicit</td>
<td>0.9711 0.9670 0.9681 0.9996</td>
</tr>
<tr>
<td>Crank–Nicolson</td>
<td>1.9388 1.9460 1.9455 1.0030</td>
</tr>
</tbody>
</table>

### 5. Conclusions

The decoupled finite difference schemes of the second-order accuracy for the numerical calculation of non-steady-state ion transfer, which is due to the diffusion, migration, and convection are elaborated. The methods of approximation of the boundary conditions of the second-order accuracy providing the decoupling of the difference equations in the grid nodes located at the electrode’s surface are created. The algorithms were proposed for simulating various conditions of electro-

![Fig. 2](image)

**Fig. 2.** Voltammograms for binary electrolyte $C_{1b} = 1$, $z_1 = 1$, $D_1 = 1$, $C_{2b} = 1$, $z_2 = -1$, $D_2 = 1$, $E_0 = 0$ in the case of irreversible electrode reaction (4) with $k_2 = 10$ (1–3) and $k_2 = 1$ (4–6) at various scan rates: (1, 4) 10; (2, 5) 5; (3, 6) 1.

![Fig. 3](image)

**Fig. 3.** Cyclic voltammograms for electrolyte containing three types of ions ($C_{1b} = 1$, $z_1 = 1$, $D_1 = 1$, $C_{2b} = 10^{-1}$, $z_2 = 0$, $D_2 = 1$, $C_{3b} = 1$, $z_3 = -1$, $D_3 = 1$, $E_0 = 0$) in the case of reversible electrode reaction (5) at various scan rates: (1) 100; (2) 50; (3) 10.
ysis: the modes of prescribed current density, prescribed electrode potential, and prescribed applied potential. The computational experiments confirmed the second-order of spatial accuracy for all of proposed methods and the second-order of temporal accuracy for the proposed CN method. The potentialities of the proposed methods for simulation of non-steady-state processes of ion transfer are shown for various electrolysis conditions. Further, we will extend the proposed methods to two-dimensional electrochemical systems and realize the splitting algorithms simultaneously with the finite difference schemes of high-order accuracy.

References