Computationally efficient approach for solving time dependent diffusion equation with discrete temporal convolution applied to granular particles of battery electrodes

Jure Senegačnik\textsuperscript{a}, Gregor Tavčar\textsuperscript{a,}* Tomaž Katrašnik\textsuperscript{a}

\textsuperscript{a}Faculty of Mechanical Engineering, University of Ljubljana

Abstract

The paper presents a computationally efficient method for solving the time dependent diffusion equation in a granule of the Li-ion battery’s granular solid electrode. The method, called Discrete Temporal Convolution method (DTC), is based on a discrete temporal convolution of the analytical solution of the step function boundary value problem. This approach enables modeling concentration distribution in the granular particles for arbitrary time dependent exchange fluxes that do not need to be known a priori. It is demonstrated in the paper that the proposed method features faster computational times than finite volume/difference methods and Padé approximation at the same accuracy of the results. It is also demonstrated that all three addressed methods feature higher accuracy compared to the quasi-steady polynomial approaches when applied to simulate the current densities variations typi-

*Corresponding author, contact address: Aškerčeva 6, 1000 Ljubljana, Slovenia; e-mail: gregor.tavcar@fs.uni-lj.si, phone: 0038614771310
cal for mobile/automotive applications. The proposed approach can thus be considered as one of the key innovative methods enabling real-time capability of the multi particle electrochemical battery models featuring spatial and temporal resolved particle concentration profiles.

Keywords: Li-ion battery, concentration profile in particle, diffusion equation, convolution in time, Bessel functions

1. Introduction

The development of lithium ion battery models emerged in early 90’s[1, 2]. Electrochemical models of the entire cell that are applied in a large variety of applications from the development to the control tasks, e. g. [3, 4, 5, 6, 7, 8], rely on particle models in the electrodes. The transport of lithium ions into, within and out of electrode particles is generally governed by a complex diffusion mechanisms that include phenomena such as phase transition, surface tension, volume changes [9], hysteretic behaviour, particle size and shape variation and other multi-particle effects [10]. However modelling of such complex phenomena comes at great computational costs, which is detrimental for applications where short computational times are needed. Furthermore comprehensive electrode models covering a wide range of operating conditions encountered in the real applications cannot include treatment of most of these phenomena due to a lack of sufficient experimental data needed for their parametrisation and inclusion in such electrode models [9, 10]. Therefore the modelling of the diffusion in the electrode particles typically relies
on two effective simplifications: the assumption of uniform spherical particles and the assumption of Fick’s diffusion within the whole particle. These simplifications are particularly found in models aiming at fast computation, e.g. [3, 4, 5, 6, 7, 8].

As lithium concentration at the surface of the granular particle influences the ion exchange flux and as calculation of this concentration generally requires a considerable CPU share in multi-particle models further enhancements of methods for solving Fick’s diffusion are sought. Presently, several methods are used to predict the surface concentration: finite difference method[11, 12], finite element method [11, 13], polynomial approximation [6, 14], differential quadrature [11], Duhamel’s superposition method [14], diffusion length method [14], analytical methods [8, 15, 16], pseudo steady state methods [14, 15, 17, 18], orthogonal collocation on finite elements [5] and Padé approximation state space method [4, 19].

In this paper a Discrete Temporal Convolution method (DTC) is presented and its results are compared against the results obtained with the following four common methods:

1. analytical method representing the exact solution in a case with a priori defined exchange flux;
2. polynomial approximations representing very computationally fast methods; and
3. finite volume/difference methods representing standard, i.e. benchmark, methods for solving time dependent diffusion equation.
4. Padé approximation state space method as an advanced computationally efficient method

Finite volume/differences methods enable evaluation of spatial and temporal concentration profile by solving the time dependent diffusion equation numerically in both dimensions. As presented in [11, 12] this type of method enables achieving high accuracy of the concentration profile resolution. However, within the field of real-time capable battery models, the computational expenses of finite volume/differences methods mostly limit their application to only the single particle models [11].

A Padé approximation state space method [4, 19] offers faster computational times compared to finite volume/differences methods and will in the present study be used as a benchmark computationally efficient advanced method.

As a computationally much faster alternatives, approximation formulas are widely applied to evaluate the particle surface concentration [6]. The analyses done in this paper show that these approximation formulas return physically plausible results only for low frequencies current variation, which is inherently related to their quasi-steady origin. Additionally, ref. [6] also disputes their accuracy when applied to cycles featuring high charging/discharging currents. These facts significantly limit their use in many applications, e.g. automotive. Deficiencies of the approximation formulas inherently arise from their approximation basis that does not consider physical governing mechanisms.
Alternatively, a fully analytical solution of the time dependent diffusion equation in spatial and temporal dimension is presented in [15, 16]. This method is computationally efficient, however its deficiency in real hardware applications arises from the fact that a priori knowledge of the exchange flux, which must be given in an analytical form, is needed to evaluate the equation. Furthermore, Ref. [3, 8] presents an approximate solution for the spherical diffusion equation that is fully derived and, similarly as in [15, 16], benchmarked with an a priori (i.e.: constant [3, 8] and sinusoidal [8]) molar flux of lithium ions at the particle surface in the radial direction.

This paper presents an approach for solving the time dependent diffusion equation in the form of temporally convoluted analytical solutions of the step function boundary value problem. This approach efficiently tackles the shortcomings of the approaches analyzed above and forms the basis for the method that:

- is capable of accurately solving for the spatial and temporal concentration profile as it is based on time dependent diffusion equation;
- features shorter computational times than finite volume/differences methods and Padé approximation state space method at the same accuracy of the results, which is to a large extend owed to its analytical solution in the spatial dimension;
- is capable or solving for arbitrary time dependent exchange fluxes that do not need to be known a priori as it relies on solution with discrete
temporal convolution.

The proposed method thus opens ways for real-time capable multi particle electrochemical battery models featuring spatially and temporally resolved particle concentration profiles. Furthermore, the DTC’s head principle of temporally convoluted analytical solutions of the step function boundary value problem can be extended to any geometry for which the eigen functions of the Laplace operator can be devised.

2. Theoretical framework

The core principle of the method presented in this paper is the analyti-cal resolution of spatial and temporal concentration distribution of ion concentration in one representative porous granule of the battery’s granular solid electrode. The ion concentration distribution within the granule comes as a solution of time dependent diffusion equation with the boundary condition of given ion molar exchange flux in the radial direction defined at the granule surface. The diffusion equation obeying the Fick’s law is assumed to apply to the whole granule. The modeled granule is assumed ideally spherical and small enough to assume uniform ion surface concentration and uniformly distributed ion exchange flux at the surface leading to the assumption of full spherical symmetry of the problem. (For non-spherical and porous particles that do not feature very significant topology discrepancy compared to spherical geometry, it is reported in [20] that plausible results can be obtained for the particles of the same volume by applying model basis of the spherical
particle and considering surface area difference between spherical particles and non-spherical and porous particles.)

The temporal variation of ion exchange flux at the granule surface (i.e. the boundary condition of the diffusion problem) is treated discretely meaning that for the duration of the chosen computational time-step the influx at the surface is treated as constant and changes discretely only between time-steps. Thus, from the view point of the diffusion equation, the boundary condition is a parameter that varies as a step function. The value of this parameter does not need to be known for every time step prior to the start of simulation (a priori) but can be updated before every time-step by solving the electrochemical equation between time-steps. The diffusion equation reads:

$$\frac{\partial c(\vec{r}, t)}{\partial t} = D \nabla^2 c(\vec{r}, t),$$  \hspace{1cm} (1)

where $c$ is the ion concentration in granule and $\vec{r}$ is the position vector. In spherical symmetry, with the coordinate origin at the centre point of the granule, this is expressed as:

$$\frac{\partial c(r, t)}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c(r, t)}{\partial r} \right) = D \nabla^2_r c(r, t),$$  \hspace{1cm} (2)

where $\nabla^2_r$ is the spherically symmetrical Laplace operator. Let $t = t_i$ denote the beginning of $i^{th}$ time step and $t = t_i + \Delta t = t_{i+1}$ denote the end of that time step and the beginning of the next one. Within the time interval
\( t_i < t < t_{i+1} \) the boundary condition is defined as:

\[
-D \frac{\partial c(r, t)}{\partial r} \bigg|_{r=R} = j_i, \tag{3}
\]

where \( j_i \) is the exchange flux at the surface in the \( i^{th} \) time-step.

A general analytical solution of equation 2 with boundary condition 3 is composed of two parts: the particular integral \( c_{pi}(r, t) \) and the homogeneous part \( c_{hg}(r, t) \):

\[
c(r, t) = c_{pi}(r, t) + c_{hg}(r, t). \tag{4}
\]

The particular integral of equation 2 with boundary condition 3, is a quadratic function of radius and linear function of time:

\[
c_{pi}(r, t) = \frac{j_i}{R} \left( \frac{r^2}{2D} + 3t \right) + C_0, \tag{5}
\]

where \( C_0 \) is a constant term. The time dependence of the concentration distribution of this contribution is limited only to linear translatory shifting with time, with the quadratic shape of the profile remaining constant, thus this part is often refereed to also as the ”quasi steady” [14, 15]. The derivative of \( c_{pi} \) at the granule surface satisfies condition 3 i.e.:

\[
-D \frac{\partial c_{pi}(r, t)}{\partial r} \bigg|_{r=R} = j_i, \tag{6}
\]

which means that the remaining homogeneous part needs to have zero deriva-
tive at the granule surface, i.e. satisfy the homogeneous boundary condition:

$$\frac{\partial c_{hg}(r,t)}{\partial r} \bigg|_{r=R} = 0. \quad (7)$$

The homogeneous part is the solution of equation 2 with homogeneous boundary condition 7 and is a contribution that dies down with time. It is comprised of a series of eigen functions of the $\nabla^2_r$ operator with coefficients that decay with characteristic rates:

$$c_{hg}(r,t) = \sum_{n=1}^{\infty} C_n \Psi_n(r) e^{-k_n^2 D \Delta t}, \quad (8)$$

where $\Psi_n(r)$ are the eigen functions and $k_n^2 D$ their corresponding rates of decay. The eigen functions are the spherical Bessel harmonics of the zeroth order:

$$\Psi_n(r) = \frac{\sin(k_n r)}{k_n r}, \quad (9)$$

having eigenvalues $-k_n^2$. The wavenumbers $k_n$ are chosen so that the eigen functions have zero derivative at granule surface:

$$\frac{\partial \Psi_n(r)}{\partial r} \bigg|_{r=R} = \partial_r \left( \frac{\sin(k_n r)}{k_n r} \right) \bigg|_{r=R} = 0, \quad (10)$$

which is satisfied with the solutions of the transcendent equation:

$$\tan(k_n R) = k_n R. \quad (11)$$
By choosing only eigen functions with zero derivative at the granule surface the boundary condition 3 is met solely by the particular integral.

Any spherically symmetrical function $f(r)$ can be expressed as series expansion of the so constructed eigen functions:

\[ f(r) = \sum_{n=0}^{\infty} f_n \Psi_n(r), \quad (12) \]

where for $n = 0$ additional eigen function is defined: $\Psi_0(r) = 1$ (i.e. a spherical zeroth order Bessel harmonic with wavenumber $k_0 = 0.$) and the coefficients $f_n$ are defined as:

\[ f_n = \frac{3}{R^3} \int_0^R f(r) \Psi_n(r) r^2 dr. \quad (13) \]

Let time $t = t_i$ denote the start of time interval in which the exchange flux at the surface has value $j_i$ and let the concentration profile in the granule be given with: $c(r, t_i) = g(r)$. At this point in time, according to the step function treatment, the value of exchange flux at the surface changes from the old $j_{i-1}$ to the new $j_i$. In case of non a priori knowledge of exchange flux this new exchange flux is calculated by applying electrochemical equation, as for example the Butler-Volmer equation, described in [7], that uses the information on surface ion concentration at that point in time $c(r = R, t_i)$, i.e. $g(R)$. The analytical function $g(r)$ can be expressed in terms of the particular integral and the homogeneous part and this can be done in two
ways: firstly in terms of the *old* current density:

$$c(r, t_i) = g(r) = j_{i-1} - \frac{r^2}{2RD} + \sum_{n=0}^{\infty} C_{i,n} \Psi_n(r)$$  \hspace{1cm} (14)$$

and secondly, in terms of the *new* current density:

$$c(r, t_i) = g(r) = j_i - \frac{r^2}{2RD} + \sum_{n=0}^{\infty} C_{i,n}^* \Psi_n(r).$$  \hspace{1cm} (15)$$

Equating the right-hand sides of equations 14 and 15, rearranging equation 14 and expressing the quadratic function $r^2$ with expansion series yields:

$$\sum_{n=0}^{\infty} C_{i,n} \Psi_n(r) - \Delta j_i - \frac{2}{2RD} \sum_{n=0}^{\infty} A_n \Psi_n(r) = \sum_{n=0}^{\infty} C_{i,n}^* \Psi_n(r),$$  \hspace{1cm} (16)$$

where the change in exchange flux is defined as: $\Delta j_i = j_i - j_{i-1}$ and the series expansion of the quadratic function reads:

$$r^2 = \sum_{n=0}^{\infty} A_n \Psi_n(r), \hspace{0.5cm} A_n = \begin{cases} \frac{3}{5}, & n = 0 \\ (-1)^n \frac{\sqrt{1+k_n^2}}{k_n}, & n > 0, \end{cases}$$  \hspace{1cm} (17)$$

leading to the expression for series $C_{i,n}^*$ in terms of $C_{i,n}$ coefficients:

$$C_{i,n}^* = C_{i,n} - \frac{\Delta j_i}{2RD} A_n.$$  \hspace{1cm} (18)$$

For the duration of the time interval $\Delta t$, i.e. from $t_i$ to $t_{i+1}$, the exchange current at surface has a constant value $j_i$, thus, using equations 5, 8, 15 and
the temporal evolution of concentration profile, expressed at the end of that interval (i.e. at $t = t_{i+1}$), is expressed as:

$$c(r, t_{i+1}) = j_i \left( \frac{r^2}{2RD} + \frac{3D}{R} \right) + \sum_{n=0}^{\infty} C_{i,n}^* \Psi_n(r) e^{-k_n^2 D \Delta t} =$$

$$= j_i \left( \frac{r^2}{2RD} + \frac{3D}{R} \right) + \sum_{n=0}^{\infty} \left( C_{i,n} - \frac{\Delta j_i}{2RD} A_n \right) \Psi_n(r) e^{-k_n^2 D \Delta t}. \quad (19)$$

It should be noted that due to the term $e^{-k_n^2 D \Delta t}$ the series in equation 19 converges quickly (as shown in appendix A). Analogous to equation 14 the concentration profile at time $t = t_{i+1}$ is also expressed as:

$$c(r, t_{i+1}) = j_i \frac{r^2}{2RD} + \sum_{n=0}^{\infty} C_{i+1,n} \Psi_n(r), \quad (20)$$

from which the expression for expansion coefficients $C_{i+1,n}$ as a function of exchange flux density $j_i$, change in the exchange flux density $\Delta j_i$ and the expansion coefficients from previous time-step $C_{i,n}$ is obtained:

$$C_{i+1,n} = \begin{cases} C_{i,0} - \frac{\Delta j_i}{2RD} A_0 + j_i \frac{3D}{R}, & n = 0 \\ (C_{i,n} - \frac{\Delta j_i}{2RD} A_n) e^{-k_n^2 D \Delta t}, & n > 0. \end{cases} \quad (21)$$

Expression 21 is a recursive formula for expansion coefficients. Expressed explicitly as a function of initial conditions and the varying exchange flux it
reads:

\[ C_{i,n} = \begin{cases} 
C_{0,0} - \frac{j_{i-1} - j_0}{2RD} A_0 + \frac{3\Delta t}{R} \sum_{\eta=1}^{i-1} j_{\eta}, & n = 0 \\
C_{0,n}e^{-k_n^2 D_n \Delta t} - A_n \sum_{\eta=1}^{i-1} \Delta j_{\eta} e^{-k_n^2 D(i-\eta)\Delta t}, & n > 0,
\end{cases} \]  

(22)

where \( C_{0,0}, C_{0,n} \) and \( j_0 \) define initial conditions at time \( t = 0 \). The term \( j_i - j_0 \) is simply the sum of changes of exchange flux: \( \sum_{\eta=1}^{i-1} \Delta j_{\eta} \). The expression for the zeroth coefficient (i.e. \( n = 0 \)), which represents the average ionic concentration in the granule, contains the term \( \frac{3\Delta t}{R} \sum_{\eta=1}^{i-1} j_{\eta} \) that reflects the total amount of ionic species that has been exchanged with the granule. The expression for other coefficients contains two parts: the first is the term of temporal evolution of the series expansion of initial concentration profile that dies down with time and the second is discrete convolution between \( \Delta j_i \) and \( e^{-k_n^2 D_n \Delta t} \), i.e. the discrete change in exchange flux and the function of decay. The explicit convolution formula for concentration distribution at time \( t = t_i \) thus reads:

\[ c(r, t_i) = \sum_{n=0}^{\infty} C_{0,n} \Psi_n(r) e^{-k_n^2 D_n \Delta t} + j_i - 1 \frac{r^2}{2RD} + \frac{3\Delta t}{R} \sum_{\eta=1}^{i-1} j_{\eta} - \\
- \sum_{n=0}^{\infty} \left( A_n \Psi_n(r) \sum_{\eta=1}^{i-1} \Delta j_{\eta} e^{-k_n^2 D(i-\eta)\Delta t} \right). \]  

(23)

When taking the limit of infinitesimal time increments, i.e. \( \Delta t \to 0 \), the dis-
crete convolution becomes a continuous convolution as described in appendix B and found in [15].

For calculating current densities it is often sufficient to calculate only the surface concentration of ions in granules, thus, instead of the series expansion of the whole concentration profile, as given by equation 20, a series expansion of the surface concentration can be defined as:

\[
c(r = R, t_{i+1}) = \zeta(t_{i+1}) = j_i \frac{R}{2D} + \sum_{n=0}^{\infty} C_{i+1,n} \Psi_n(R) = j_i \chi + \sum_{n=0}^{\infty} \zeta_{i+1,n}, \quad (24)
\]

where the series terms \(\zeta_{i,n}\) and the constant \(\chi\) are defined as: \(\zeta_{i,n} = C_{i,n} \Psi_n(R)\) and \(\chi = \frac{R}{2D}\). Multiplying equation 21 by the constant \(\Psi_n(R)\) yields the recursive equation for surface concentration expansion terms:

\[
\zeta_{i+1,n} = \begin{cases} 
\zeta_{i,0} - \Delta j_i \alpha_0 + j_i \tau, & n = 0 \\
(\zeta_{i,n} - \Delta j_i \alpha_n) \gamma_n, & n > 0,
\end{cases} \quad (25)
\]

where constants \(\alpha_n, \gamma_n\) and \(\tau\) are defined as: \(\alpha_n = \frac{A_n \Psi_n(R)}{2RD}\), \(\gamma_n = e^{-k^2_n D \Delta t}\) and \(\tau = \frac{3\Delta t}{R}\). Using equations 24 and 25, the surface concentration at the end of the new time step is calculated from: the known expansion terms of the previous time step \(\zeta_{i,n}\), the known surface exchange current density \(j_i\) and the last change in exchange current density \(\Delta j_i\). Inserting equation 23
into 22 thus yields

\[ \zeta(t_{i+1}) = j_i(\chi + \tau) + \sum_{n=0}^{\infty} (\zeta_{i,n} - \Delta j_i \alpha_n) \gamma_n. \] (26)

Equation 26 is the key to the computational efficiency of the method. When taking H number of terms into account in the summation in equation 26 the calculation of all H expansion terms and the evaluation of the surface concentration require only H+1 additions, H subtractions and 2H multiplications.

3. Results

In this section the results calculated by DTC (equation 26) are compared to the results calculated by numerical and analytical methods addressed in section 1 in order to analyze its computational efficiency at different variations of exchange fluxes and operational temperatures. Numerical methods comprise the polynomial approximations (appendix C), the Explicit and Implicit Finite Volume methods (EFV and IFV respectively) (appendix D) and Padé approximation state space methods (appendix E). EFV and IFV methods are both analyzed because the first one is computationally faster but limited by stability criteria whereas the second one is not limited by stability criteria but is computationally slower. EFV and IFV methods are integrated using Euler schemes to preserve straightforward comparison of the methods, which is also in-line with other published approaches [21]. The EFV method features less computational operations per time step for equivalent spatial
discretization, i.e. equivalent N, as the IFV method, whereas the maximum time step of the EFV method is limited by the stability criteria as

$$D \frac{\Delta t}{\Delta x^2} < \frac{1}{2},$$

(27)

where $\Delta t$ is the time increment and $\Delta x$ is the grid spacing. At this place it is worth noting that DTC method is also not subjected to any stability criteria as it relies on an the analytical solution in spatial dimensions. Padé approximation state space method is integrated with 4th order explicit Runge-Kutta method as this method performed better than the explicit and implicit Euler method in terms of trade-off between computational time and accuracy of the results in the wide range of the analysed cases. Application of the computationally fast explicit Euler method to integrate Padé approximation function results in very low level of stability of the method, whereas application of implicit methods results in longer computational times. Application of the 4th order explicit Runge-Kutta method to integrate Padé approximation functions inherently result in more computational operations per given time step than application of the explicit Euler method, whereas it should also be considered that exchange flux is updated 4 times per time step thus resulting in a better ratio between accuracy and computational time compared to the application of the explicit Euler method for integrating the Padé approximation functions.

To extensively characterize the DTC an example with sinusoidal exchange
flux is analyzed in section 3.1, followed by an analysis of the non-analytical non a priori exchange flux in section 3.2.

3.1. Sinusoidal exchange flux

First, results of all numerical methods, i.e. DTC, polynomial approximations, finite volume methods and Padé approximation state space methods are compared to the analytic solution of the diffusion equation with a sinusoidal exchange flux as the boundary condition (equation 29). Results are shown for a granule with radius $R = 2 \cdot 10^{-6}$ m and diffusion constant $D = 10^{-14}$ m$^2$s$^{-1}$ representing an average granule in lithium batteries [7]. Initial concentration in the particle is set to 0.5 $c_{max}$, where $c_{max} = 51554$ mol m$^{-3}$ is the maximum concentration in granules [7]. Exchange flux is given as

$$j(t) = Ae^{i\omega t},$$  \hspace{1cm} (28)

where $t$ is time, $A = 1$ mol m$^{-2}$s$^{-1}$ and $\omega$ is frequency. Two frequency values ( $\omega = \pi/10$ s$^{-1}$ and $\omega = \pi/2$ s$^{-1}$) have been analyzed to highlight sensitivity of methods at different exchange current frequencies. For these initial and boundary conditions and particle parameters the analytical solution of equation 2, which is derived in appendix F yields

$$c(r, t) = C_0 + B j_0(\sqrt{i\omega r})e^{i\omega t}. \hspace{1cm} (29)$$
where $j_0$ is spherical Bessel function of zeroth order (not to be confused with exchange flux $j_0$).

A plot of surface concentration as calculated by equation 29 is used to examine convergence of the numerical methods towards the analytical solution, which is per definition the most accurate solution of the concentration profile for the Fick’s diffusion in the spherical particle with a-priori defined analytically given exchange flux. Accuracy of the EFV, IFV, Padé and DTC methods is assessed via the NDRMS (non-dimensional root mean square) which is defined as

$$\text{NDRMS} = \frac{1}{\sqrt{n_t}} \sqrt{\sum_{i=1}^{n_t} \left( \frac{c_{\text{num}}(R, t_i) - c_{\text{analy}}(R, t_i)}{c_{\text{max}}(R) - c_{\text{min}}(R)} \right)^2},$$ (30)

where $n_t$ is the number of time steps and $t_i = i \cdot \Delta t$. $c_{\text{num}}$ is the concentration calculated by the DTC, EFV or IFV method, Padé approximation and $c_{\text{analy}}$ is calculated by equation 29.

3.1.1. Impact of spatial resolution on accuracy of results

In this section the accuracy of four numerical methods, i.e: DTC, both finite volume methods and Padé approximation state space method, is evaluated by comparing the results of these numerical methods to the analytic solution. This comparison is performed for varying levels of numerical resolution, i.e.: varying number of harmonics in case of DTC and varying grid spacing in cases of the finite volume and Padé methods. The angular frequency and the time increment, used with all aforementioned methods in
Fig. 1, is set to $\omega = \frac{\pi}{10}$ s$^{-1}$ and $\Delta t = 0.5$ s respectively, which corresponds to 40 time steps per one sine oscillation. Additionally, also results of the second and third order polynomial approximations are compared to the analytical results. In Fig. 1 results corresponding to the 201$^{st}$ and 202$^{nd}$ sine oscillations are plotted to ensure that the effects of the transition from the initial uniform concentration distribution to the sinusoidally oscillating concentration distribution in the granule have died down. Therefore the time axis was also shifted accordingly to preserve readability and thus 201$^{st}$ cycle starts at time 0 s in Fig. 1. These results are also used in the analysis outlined in section 3.1.2.

Fig. 1d reveals that both polynomial approximations are not able to predict the dimensionless surface concentration $\Theta = \frac{c_s}{c_{s,max}}$ with sufficient accuracy, which is mainly related to their quasi-steady basis. However, results show that the third order polynomial approximation predicts the surface concentration much better than the second order polynomial approximation.

Figs. 1a-1c and 1e confirm the expected trend that increasing the number of harmonics (H), increasing the order of Padé approximation (P) and increasing the number of spatial nodes (N), i.e. decreasing the grid spacing, increases the accuracy of the DTC, both finite volume methods and Padé approximation respectively. Figs. 1a-1c and 1e also confirm that with the increasing number of harmonics, with the increasing number of spatial nodes and with the increasing order of Padé approximation, all methods converge towards the analytical solution.
3.1.2. Trade-off between accuracy and computational speed

In addition to the capability of a method to predict accurate results, the trade-off between accuracy and computational speed is an equally important parameter in system level and/or real-time simulations. This trade-off also clearly shows how computationally efficient a method is. To analyze the trade-off between accuracy and computational speed a reduced time factor (RT) is introduced:

\[
RT = \frac{\text{computational time}}{\text{real time}}.
\]

Computational efficiency of the DTC, both FV methods and Padé approximation is thus examined in terms of RT to NDRMS dependency. Computational times for all methods (equation 31) were obtained using a single core of 3.07 GHz processor. All methods were coded in Mathematica running under Windows.

3.1.2.1 Trade-off at angular frequency \( \omega = \pi/10 \text{ s}^{-1} \)

The plot curves in Fig. 2 calculated by varying H, N and order of Padé approximation P for seven cases of different time increments. The analyzed time increments and the corresponding number of time steps per sine oscillation are given in the figure legend (remark: Padé approximation functions are integrated using 4th order Runge-Kutta method as discussed above). The plot curves are drawn only for the part where increasing the number of harmonics or nodes increases the accuracy of the results i.e. larger values of
H and N leading to smaller values of NDRMS. Explicit Padé approximations are shown only for the cases where computation is stable. For each method, the minimum value of NDRMS is limited by the discrete temporal resolution, with higher sampling rates leading to lower minimum values of NDRMS. The leftmost point of the plot curves represents the solution with the maximum precision for a given time step. Most effective methods are thus characterized by small values of both NDRMS and RT, i.e. most effective methods are found in the lower left end of the graphs in Figs. 2 and 3 or alternatively at the prescribed NDRMS value most effective method is characterized by the smaller RT value.

Fig. 2 demonstrates that the accuracy of all methods increases with increasing spatial resolution. However, Fig. 2 also clearly indicates that, for all methods, it is computationally most efficient to achieve the desired accuracy, i.e. NDRMS value, with the largest possible time increment. Fig. 2 additionally indicates that for all time increments the smallest NDRMS values can be achieved by the DTC method, which is mainly related to the higher accuracy of the spatial solution that is based on the analytical harmonics. It can also be seen in Fig. 2 that the explicit finite volume method features higher NDRMS values for individual time increments compared to the implicit one, which is mainly related to the fact that the explicit method cannot be used on a spatial grid with a spatial resolution that is higher than that allowed by the stability criteria (equation 27), whereas no such limitation applies to the implicit method.
Fig. 2e and table 1 show comparison of DTC, IFV and EFV methods and Padé approximation for chosen time increments to enable better comparison between the methods, whereas the conclusion drawn below are also generally valid for other time increments. It can be concluded that for the same NDRMS value, the DTC method is computationally significantly faster compared to both finite volume methods and Padé approximation state space methods (proving its higher effectiveness). This very important characteristic of the DTC method mainly originates from the following:

1. It is discernible from figs. 1a, 1c, 1b and table 1 that with the DTC method much less harmonics (H) are needed to achieve similar accuracy compared to the number of spatial nodes (N) needed with the FV methods. This trend is related to the fact that the series of harmonics, which constitute the analytical solution of the diffusion equation (equation 29), converges quickly (appendix A), and thus much smaller number of harmonics (H) is needed for achieving a desired spatial accuracy of the concentration profile compared to the number of spatial nodes N that are used in a pure numerical evaluation of the concentration profile. At the same time slightly less computational operations are needed per each harmonic in the DTC method compared to the computational operations per each spatial node in the EFV (equation 42) and much less than in the IFV method (equation 43).

2. In the case of the Padé approximation method the product of the order of the Padé’s method (P), the number of computational operations
per order (given in Appendix E) and the four Runge-Kutta calculation points in each time step amounts to a greater computational load than in the case of the DTC method when results of similar accuracy are compared as discernible in fig. 2e.

3.1.2.2 Trade-off at angular frequency $\omega = \pi/2 \text{ s}^{-1}$

When analyzing higher frequencies of exchange flux, shorter time steps are needed to sample the exchange flux and concentration. In Fig. 3 time steps are adapted to those shown in Fig. 2 in a way that the number of samples per sine remains the same. Fig. 3 shows that at five times higher frequency methods feature very similar NDRMS vs. RT trends than in Fig. 2 and it is thus clearly seen that the DTC is still computationally faster than other methods at the same NDRMS.

3.2. Non-analytical non a priori exchange flux

In this section an example with non-analytic non a priori exchange flux is analysed to investigate performance of the analysed numerical methods at two different potential loads and two different temperatures. For this purpose a reduced battery model consisting of a single particle model coupled to the SEI model [7] is developed. It is assumed that particle is surrounded by an electrolyte with constant concentration of ions. The simplicity of this reduced model is aimed at highlighting the differences between the different methods for solving the Fick’s diffusion in a spherical particle applied to this analytically unsolvable case.
The analysis compares three versions of this reduced model, where each version employs a different numerical method for computing the concentration profile in the particle. The three methods are based on the following governing equations: DTC (equation 26), IFV (equation 43) and Padé approximation (equation 44). In this section the polynomial approximations and the EFV method are not analysed. The reason for excluding the polynomial approximations is their low accuracy as analyzed in previous sections and the reason for excluding EFV method originates in its subjection to the stability criteria, which either limit the maximum achievable accuracy at a selected time increment or limit the time integration increment of the entire battery model.

Common to the three analysed versions of the reduced model are the equations for exchange flux [7]:

\[ j = -2k_p \sqrt{(c_{s,max} - c_s)c_s c_e \sinh \left( \frac{0.5F}{RT} (\Phi_1 - \Phi_2 - U_p) \right)} , \]  

\[ U_p = \frac{-4.656 + 88.669\Theta^2 - 401.119\Theta^4 + 342.909\Theta^6 - 462.471\Theta^8 + 433.434\Theta^{10}}{-1.0 + 18.933\Theta^2 - 79.532\Theta^4 + 37.311\Theta^6 - 73.083\Theta^8 + 95.96\Theta^{10}} , \]  

where \( c_s \) is the surface concentration of lithium in particles, \( c_{s,max} \) the maximum possible concentration of lithium in particles, \( c_e \) is the concentration of lithium in electrolyte, \( \Phi_1 \) and \( \Phi_2 \) are electric potentials in the liquid and the solid phase respectively, \( U_p \) is the open circuit voltage, \( k_p \) is the constant of the intercalation reaction and \( \Theta \) is the dimensionless surface concentration.

In the analyzed case exchange flux \( j \) is defined by varying the difference
(Φ₁ − Φ₂) according to the profile given in Fig. 4. Initially, the value of (Φ₁ − Φ₂) is selected in a way that exchange flux is zero. This means that (Φ₁ − Φ₂) is equal to \( U_p \) at \( \Theta = 0.5 \), which is selected as initial uniform concentration in the particle. During the course of simulation the variation of (Φ₁ − Φ₂) and the value of \( U_p \) that changes with changing surface concentration (as given in eq. 33) define the exchange flux.

In all figures of Section 3.2 results are shown for the DTC and IFV method with very high spatial discretization (\( H = 100, N = 100 \)) and very small time steps (0.01 s). It is shown in the figures that these curves coincide nearly perfectly and are therefore considered to be numerically converged solutions. These results are thus used to benchmark accuracy of all the other analyzed methods. Figs. 6 - 8 present the results of computationally fast solutions compared to the results of these numerically converged solutions. The computationally fast solutions are obtained by finding such a combination of the spatial and the temporal resolution for each of the three methods (DTC, IFV and Padé) that yields the shortest computational times whilst achieving or surpassing a goal accuracy set at \( \log(\text{NDRMS}) < -3 \). The so obtained fast solutions are, in comparison to the converged solutions, characterised by low spatial resolution, i.e.: \( H, N, P < < 100 \), and low temporal resolution, i.e.: \( dt >> 0.01 \) s.
3.2.1. Lower potential difference at lower temperature

For this simulation case the variation of potential according to fig. 4a and operation temperature $T = 289$ K was used. Firstly, in order to expose the basic characteristics of the DTC method, the results obtained with varying number of harmonics taken into account in the DTC method are analyzed in Fig. 5. If just a few harmonics are taken into account, i.e. $H=3$, a minor discrepancy compared to the numerically converged solution is observed after step change in voltage, however this discrepancy quickly diminishes afterwards. This is related to the fact that higher harmonics die down with the time quickly as they are multiplied by the $e^{-\frac{k^2 T}{D \Delta t}}$ term (equation 26).

It is discernible from Figure 6a and c that globally methods behave similarly, which is mainly due to the relatively high goal accuracy that was set for the ”fast” methods. Analysing the zoomed-in Figure 6 b in conjunction with table 2 it is discernible that although the DTC method features the lowest value of NDRMS (being the most accurate) it concurrently also features the shortest computational times thus proving to be the most computationally efficient.

3.2.2. Higher potential difference at lower temperature

For this simulation case the variation of potential according to fig. 4b and operation temperature $T = 289$ K was used. Fig. 7 shows a similar case as shown in Figure 6 but with a higher potential difference used in the potential variation (temperature remaining the same). This higher potential
difference yields, according to eq. (32), a higher exchange flux and thus a higher rate of surface concentration variation. This faster variation of surface concentration requires a more frequent update of the calculation of exchange flux (eq. (32)), i.e. shorter integration time steps. As clearly discernible from fig. 7b and table 2 the DTC method again features higher accuracy than the IFV method and the Padé approximation whilst also achieving the shortest computational times.

3.2.3. **Higher potential load at higher temperature** $T = 323$ K

For this simulation case the variation of potential according to fig. 4b and operation temperature $T = 323$ K was used. Fig. 8 shows a similar case as shown in fig. 7 but with a higher temperature used ($323$ K instead of $289$ K). Higher temperature leads to a higher diffusion constant in eq. 1 and higher constant of reaction $k$ in eq. 32 ($D_{T=323K} = 12.69D_{T=289K}$ and $k_{p,T=323K} = 3.56k_{p,T=289K}$ according to in [3]). The increase in reaction constant prevails over the effects of the decreased argument of the “sinh” function in eq. (32) yielding larger exchange currents. Compared to the case analysed in Section 3.2.2 the rate of surface concentration variation due to higher exchange currents being driven by higher temperature is less pronounced due to higher diffusivity. Namely, a higher diffusivity decreases concentration gradient within a particle. Following the same reasoning as in sections 3.2.1 and 3.2.2, Figure 8b and Table 2 again confirm the highest computational efficiency of the DTC method.
4. Summary

A method for modelling concentration in electrode granules is presented in this paper. The diffusion equation is solved by discretely convolving the analytical solution of the step-function boundary value problem in the granule. Owing to its analytical spatial solution and exponentially decreasing factors, a smaller number of harmonics is needed to achieve the same accuracy of results at a given time increment compared to the number of spatial nodes of the finite volume methods. Additionally, the DTC method features slightly less computational operations compared to the EFV method, whereas it features significantly less computational operations compared to the IFV method, which is similarly to DTC method, not limited by stability criteria. DTC also turns out to be faster than Padé approximation state space method at the same accuracy of the results and more accurate at the same computation time. Results confirm that the DTC method enables predicting concentration profile with high accuracy and that it is capable of predicting highly accurate results at very short computational times. Additionally, it is demonstrated in the paper that unlike the methods based on pure analytical solution or solutions with continuous convolution the DTC method is capable of solving for non-analytical, non-a priori known exchange fluxes as it relies on numerical temporal integration. DTC can therefore be integrated into any simulation model featuring arbitrarily varying exchange fluxes. Due to these characteristics DTC can be considered a very promising approach for
system level and real-time battery simulation models. Finally, it should be mentioned that the applicability of the DTC model extends beyond modeling ion concentration in battery electrode granules. It can be used for solving the time dependent diffusion equation in all geometries for which eigen functions of the Laplace operator can be devised and thus serves as a computationally efficient replacement for the conventional computational methods.
5. Nomenclature

### Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Unit</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A )</td>
<td>mol m(^{-2})s(^{-1})</td>
<td>amplitude of exchange flux</td>
</tr>
<tr>
<td>( A_n )</td>
<td>-</td>
<td>coefficient of ( r^2 ) expansion</td>
</tr>
<tr>
<td>( c )</td>
<td>mol m(^{-3})</td>
<td>concentration</td>
</tr>
<tr>
<td>( C_{i,n} )</td>
<td>-</td>
<td>coefficients of expansion of concentration</td>
</tr>
<tr>
<td>( D )</td>
<td>m(^2)s(^{-1})</td>
<td>diffusion constant</td>
</tr>
<tr>
<td>( f )</td>
<td>-</td>
<td>spherically symmetrical function</td>
</tr>
<tr>
<td>( F )</td>
<td>As mol(^{-1})</td>
<td>Faraday constant</td>
</tr>
<tr>
<td>( H )</td>
<td>-</td>
<td>number of harmonics</td>
</tr>
<tr>
<td>( j )</td>
<td>mol m(^{-2})s(^{-1})</td>
<td>current through particle surface</td>
</tr>
<tr>
<td>( j_0 )</td>
<td>-</td>
<td>Bessel function of zeroth order</td>
</tr>
<tr>
<td>( j_1 )</td>
<td>-</td>
<td>Bessel function of first order</td>
</tr>
<tr>
<td>( k_n )</td>
<td>-</td>
<td>wavenumber of Bessel functions</td>
</tr>
<tr>
<td>( k_p )</td>
<td>mol(^{-1/2})m(^{5/2})s(^{-1})</td>
<td>constant of the reaction</td>
</tr>
<tr>
<td>( N )</td>
<td>-</td>
<td>number of FV nodes</td>
</tr>
<tr>
<td>( r )</td>
<td>m</td>
<td>radial variable</td>
</tr>
<tr>
<td>( R )</td>
<td>m</td>
<td>radius of electrode particle</td>
</tr>
<tr>
<td>( R_g )</td>
<td>J mol(^{-1})K(^{-1})</td>
<td>gas constant</td>
</tr>
<tr>
<td>( t )</td>
<td>s</td>
<td>time</td>
</tr>
<tr>
<td>( T )</td>
<td>K</td>
<td>temperature</td>
</tr>
<tr>
<td>( \Theta )</td>
<td>-</td>
<td>dimensionless concentration</td>
</tr>
<tr>
<td>( \Phi_1 )</td>
<td>V</td>
<td>solid-phase potential</td>
</tr>
<tr>
<td>( \Phi_2 )</td>
<td>V</td>
<td>electrolyte phase potential</td>
</tr>
<tr>
<td>( \Psi )</td>
<td>-</td>
<td>eigen function</td>
</tr>
<tr>
<td>( \omega )</td>
<td>s(^{-1})</td>
<td>angular frequency</td>
</tr>
</tbody>
</table>
APPENDIX

A. Convergence of series in DTC method

As defined in equation 11 the wave vector $k_n$ is bound by:

$$\frac{(2n+1)\pi}{2} < k_n < \frac{(2n+3)\pi}{2},$$

thus the term $e^{-k_n^2 D \Delta t}$ is bound by two Gaussian expressions:

$$e^{-\left(\frac{(2n+3)\pi}{2}\right)^2 D \Delta t} < e^{-k_n^2 D \Delta t} < e^{-\left(\frac{(2n+1)\pi}{2}\right)^2 D \Delta t}.$$

Since, according to equations 14 and 17, the two finite series $\sum_{n=0}^{H} C_{i,n} \Psi_n(r)$ and $\sum_{n=0}^{H} A_n \Psi_n(r)$ converge towards analytical functions with increasing value of $H$, the series in equation 19 converges even quicker due to the additional term $e^{-k_n^2 D \Delta t}$ that decreases with increasing $n$ in a Gaussian fashion.

B. Limit of infinitesimal time increment

In this section the expression for the continuous convolution is derived by taking the limit of infinitesimal time increment.
Let two points in time, denoted by \( t \) and \( \tau \) coincide with the end of \( i \)-th and \( \eta \)-th time-step interval respectively, i.e. \( t = t_i \) and \( \tau = t_\eta \). According to the discrete treatment this occurs after \( i \) and \( \eta \) time-step intervals, i.e. \( t = i \Delta t \) and \( \tau = \eta \Delta t \). Taking the limit of \( i \to \infty \) and \( \Delta t \to 0 \) whilst preserving their product the discrete sums become integrals:

\[
\lim_{i \to \infty} \sum_{\eta=1}^{i-1} j_\eta \Delta t = \int_0^t j(\tau) d\tau 
\]

(36)

\[
\lim_{i \to \infty} \sum_{\eta=1}^{i-1} \Delta j_\eta = \int_0^t j'(\tau) d\tau = j(t) - j(0),
\]

(37)

and the discrete temporal convolution becomes continuous temporal convolution:

\[
\lim_{i \to \infty} \sum_{\eta=1}^{i-1} \Delta j_\eta e^{-k_n^2 D(i-\eta)\Delta t} = \int_0^t j'(\tau) e^{-k_n^2 D(t-\tau)} d\tau = j'(t) * e^{-k_n^2 D(t)} 
\]

(38)

In the limit of infinitesimal time-step increments equation 25 thus becomes:

\[
c(r, t) = \sum_{n=0}^{\infty} C_{0,n} \Psi_n(r) e^{k_n^2 D t} + \frac{j(t) r^2}{2RD} + \frac{3}{R} \int_0^t j(\tau) d\tau - \sum_{n=0}^{\infty} \left( \frac{A_n \Psi_n(r)}{2RD} \int_0^t j'(\tau) e^{-k_n^2 D(t-\tau)} d\tau \right)
\]

(39)
C. Polynomial approximation formulas

Polynomial approximations to predict surface concentration in the particles were recapitulated from [6].

C.1. Second order polynomial approximation

Equations for second order polynomial approximation are:

\[ c(r, t) = -\frac{3}{2} c_s(t) + \frac{5}{2} \bar{c}(t) + \left( \frac{5}{2} c_s(t) - \frac{5}{2} \bar{c}(t) \right) \frac{r^2}{R^2} \]
\[ \frac{d}{dt} \bar{c}(t) + 3 \frac{j}{R} = 0 \]
\[ \frac{D}{R} [c_s(t) - \bar{c}(t)] = -\frac{j}{5}, \quad (40) \]

where \( \bar{c} \) is average concentration in particles and \( c_s \) is surface concentration.

C.2. Third order polynomial approximation

For third order polynomial approximation equations are

\[ c(r, t) = \frac{39}{4} c_s(t) - 3\bar{q}R - \frac{35}{4} \bar{c}(t) + \]
\[ + (35c_s(t) + 10\bar{q}R + 35\bar{c}(t)) \frac{r^2}{R^2} + \]
\[ + \left( \frac{105}{4} c_s(t) - 7\bar{q}R - \frac{105}{4} \bar{c}(t) \right) \frac{r^4}{R^4} \]
\[ \frac{d}{dt} \bar{c}(t) + 3 \frac{j}{R} = 0 \]
\[ \frac{d}{dt} \bar{q}(t) + 30 \frac{D}{R^2} \bar{q}(t) + \frac{45}{2} \frac{j}{R^2} = 0 \]
\[ 35 \frac{D}{R} [c_s(t) - \bar{c}(t)] - 8D \bar{q}(t) = -j, \quad (41) \]
where in addition to the symbols presented with equation 40, $\bar{q}$ is volume averaged flux.

D. Finite volume formulas

Explicit and implicit finite volume formulas for modeling concentration profile using equation 2 and boundary conditions 3 are recapitulated from [21]. Index $i$ stands for spatial discretization and $k$ for temporal. In systems of equations 42 and 43, first equation is used to model the concentration in the central volume of spherical particles, the last for the concentration in the volume at the surface, and the second for the concentration in the intermittent volumes. Index $i$ runs from 1 to N-1.

D.1. Explicit finite volume method

\[
\begin{align*}
\frac{c^{k+1}_0 - c^k_0}{\Delta t} &= 6D \frac{(c_1^k - c_0^k)}{\Delta r^2} \\
\frac{c^{k+1}_i - c^k_i}{\Delta t} &= D \frac{r_{i+\frac{1}{2}}(c_{i+1}^k - c_i^k) - r_{i-\frac{1}{2}}(c_i^k - c_{i-1}^k)}{r_i^2 \Delta r^2} \\
\frac{c^{k+1}_N - c^k_N}{\Delta t} &= \frac{r_{N+\frac{1}{2}}(c_{N+\frac{1}{2}}^k) - D r_{N-\frac{1}{2}}(c_N^k - c_{N-1}^k)}{r_N^2 \Delta r} 
\end{align*}
\] (42)
D.2. Implicit finite volume method

\[
\frac{c_{0}^{k+1} - c_{0}^{k}}{\Delta t} = 3D \left( \frac{c_{1}^{k} - c_{0}^{k}}{\Delta r^{2}} + \frac{c_{1}^{k+1} - c_{0}^{k+1}}{\Delta r^{2}} \right) \\
\frac{c_{i}^{k+1} - c_{i}^{k}}{\Delta t} = \frac{1}{2} D \frac{r_{i+\frac{1}{2}}^{2} (c_{i+1}^{k} - c_{i}^{k}) - r_{i-\frac{1}{2}}^{2} (c_{i}^{k} - c_{i-1}^{k})}{r_{i}^{2} \Delta r^{2}} + \\
\frac{1}{2} D \frac{r_{i+\frac{1}{2}}^{2} (c_{i+1}^{k+1} - c_{i}^{k+1}) - r_{i-\frac{1}{2}}^{2} (c_{i}^{k+1} - c_{i-1}^{k+1})}{r_{i}^{2} \Delta r^{2}} \\
\frac{c_{N}^{k+1} - c_{N}^{k}}{\Delta t} = \frac{1}{2} r_{N+\frac{1}{2}}^{2} j (c_{N+\frac{1}{2}}^{k}) - D r_{N-\frac{1}{2}}^{2} \frac{(c_{N}^{k} - c_{N-1}^{k})}{\Delta r} + \\
\frac{1}{2} r_{N+\frac{1}{2}}^{2} j (c_{N+\frac{1}{2}}^{k+1}) - D r_{N-\frac{1}{2}}^{2} \frac{(c_{N}^{k+1} - c_{N-1}^{k+1})}{\Delta r} \tag{43}
\]

E. Padé approximation formulas

Padé approximation state space representation formulas in controllable canonical form [4] for modeling concentration profile using equation 2 and
boundary conditions 3.

\[
\begin{pmatrix}
0 & 1 & 0 & 0 & \cdots & 0 \\
0 & 0 & 1 & 0 & \cdots & 0 \\
0 & 0 & 0 & \ddots & \ddots & \ddots \\
\vdots & \vdots & \vdots & \ddots & 1 & 0 \\
0 & 0 & 0 & \cdots & 0 & 1 \\
0 & \frac{1}{b_2} & \frac{b_2}{b_2} & \frac{b_3}{b_2} & \cdots & \frac{b_{Q-1}}{b_2} \\
\end{pmatrix}
\begin{pmatrix}
x \\
u
\end{pmatrix}
\]

\[
y = \begin{bmatrix}
c_s \\
\bar{c}
\end{bmatrix} = \begin{bmatrix}
a_0 & a_1 & a_2 & \cdots & a_{Q-1} \\
a_0 & a_0b_2 & \cdots & a_0b_{Q-1} & -a_0b_Q
\end{bmatrix} x
\]

The transfer function is:

\[
\frac{C_s}{U}(s; Q) = \frac{a_0 + a_1 s + a_2 s^2 + \cdots + a_{Q-1} s^{Q-1}}{(1 + b_2 s + b_3 s^2 + \cdots + b_Q s^{Q-1})} \left( \frac{1}{s} \right)
\]

F. Derivation of the analytical solution for the sinusoidal exchange flux

This appendix gives the derivation of the analytical solution of the time dependant diffusion equation (2) with boundary condition:

\[
- D \frac{\partial c(r,t)}{\partial r} \bigg|_{r=R} = A e^{i\omega t},
\]
where \( A \) is the amplitude of the oscillating current density. The concentration distribution is expressed as:

\[
c(r, t) = C_0 + c_{hg}(r, t) + Bjo(kr)e^{i\omega t},
\]

where \( c_{hg}(r, t) \) is the homogeneous part that solves the homogeneous boundary condition and \( Bjo(kr)e^{i\omega t} \) is the ansatz for the particular integral (spherical Bessel function \( j_0 \) is not to be confused with ion exchange current density). The homogeneous part is defined by equation 8 and all its terms die down with time. Thus, after the homogeneous part has subsided the expression for concentration distribution reads:

\[
c(r, t) = C_0 + Bjo(kr)e^{i\omega t}.
\]

Inserting equation 48 into differential equation 2 yields:

\[
i\omega Bjo(kr) = D\nabla_r^2 Bjo(kr),
\]

which is recognised as Bessel differential equation that is solved by \( j_0 \), i.e. the spherical Bessel harmonic of the zeroth order with \( B \) being a constant term. The dependency of wave number \( k \) on frequency \( \omega \) is obtained as:

\[
i\omega Bjo(kr) = DB\nabla_r^2 j_0(kr) = Dh^2 Bjo(kr)
\Rightarrow k^2 = i\omega \Rightarrow k = \sqrt{\frac{i\omega}{\sqrt{2}}}.
\]
By inserting equation 48 into boundary condition 46 the expression for the constant $B$ is obtained:

$$\left.- D \frac{\partial c(r, t)}{\partial r} \right|_{r=R} = - DB \frac{\partial j_0(kr)}{\partial r} \left|_{r=R} e^{i\omega t} = Ae^{i\omega t}\right.$$

$$\Rightarrow B = \frac{A}{Dk_1(kR)} = \frac{A}{D\sqrt{i\omega}j_1(\sqrt{i\omega}R)},$$  \hspace{1cm} (51)

where $j_1$ is the spherical Bessel harmonic of the first order. The constant term is obtained following the requirement that the initial concentration is uniform with value $c(r, t = 0) = c_{\text{init}}$:

$$c(r, t = 0) = C_0 + c_{hg}(r, t) + B j_0(kr) = c_{\text{init}}$$

$$C_0 + c_{hg}(r, t) = c_{\text{init}} - B j_0(kr).$$  \hspace{1cm} (52)

From equations 12, 13 and the definition of $\Psi_0 = 1$ it follows that:

$$\sum_{n=0}^{\infty} C_n \Psi_n(r) = c_{\text{init}} - B j_0(kr) \Rightarrow C_0 = c_{\text{init}} - \frac{3}{R^2} \int_0^R B j_0(kr)r^2 dr.$$  \hspace{1cm} (53)


Table 1: Method accuracy in dependence to method spatial resolution. The value of Log(NDRMS) is given for various number of harmonics H (DTC), spatial nodes N (IFV) and Padé order P (Padé) for the case plotted in fig. 1.

<table>
<thead>
<tr>
<th></th>
<th>DTC</th>
<th>IFV</th>
<th>Padé</th>
</tr>
</thead>
<tbody>
<tr>
<td>H=3</td>
<td>-0.82</td>
<td>-0.38</td>
<td>P=2</td>
</tr>
<tr>
<td>H=5</td>
<td>-1.52</td>
<td>-0.52</td>
<td>P=3</td>
</tr>
<tr>
<td>H=10</td>
<td>-2.95</td>
<td>-0.97</td>
<td>P=5</td>
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</table>
Table 2: Comparison of computational efficiency of computationally fast methods. Methods are not compared at exactly the same NDRMS because only integer orders of H, P and N are possible.

<table>
<thead>
<tr>
<th>method</th>
<th>case 3.2.1</th>
<th>case 3.2.2</th>
<th>case 3.2.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Log(NDRMS)</td>
<td>-4.25</td>
<td>-3.41</td>
<td>-3.36</td>
</tr>
<tr>
<td>Average Log(RT)</td>
<td>-3.20</td>
<td>-3.17</td>
<td>-3.26</td>
</tr>
<tr>
<td>times slower than DTC</td>
<td>2.2</td>
<td>2.6</td>
<td>3.3</td>
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1 Method accuracy in dependence to method spatial resolution. The value of Log(NDRMS) is given for various number of harmonics H (DTC), spatial nodes N (IFV) and Padé order P (Padé) for the case plotted in fig. 1. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 41

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Figure 1
(a) DTC

(b) EFV method

(c) IFV method

(d) Padé approximation

(e) Comparison of methods

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(a) Lower potential difference  
(b) Higher potential difference

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(b) Zoom-in of the second change of potential difference

(c) Li ion exchange flux

Figure 6
(a) Dimensionless Li concentration  
(b) Zoom-in of the second change of potential difference  
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Figure 7
(a) Dimensionless Li concentration

(b) Zoom-in of the second change of potential difference

(c) Li ion exchange flux

Figure 8