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An advanced all-solid-state Li-ion battery model

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A B S T R A C T

A new advanced mathematical model is proposed to accurately simulate the behavior of all-solid-state Li-ion batteries. The model includes charge-transfer kinetics at both electrode/electrolyte interfaces, diffusion and migration of mobile lithium ions in the electrolyte and positive electrode. In addition, electrical double layers are considered, representing the space-charge separation phenomena at both electrode/electrolyte interfaces. The model can be used to simultaneously study the individual overpotential and impedance contributions together with concentration gradients and electric fields across the entire battery stack. Both galvanostatic discharge and impedance simulations have been experimentally validated with respect to 0.7 mAh Li/LiPON/LiCoO2 thin film, all-solid-state, batteries. The model shows good agreement with galvanostatic discharging, voltage relaxation upon current interruption, and impedance measurements. From the performed AC and DC simulations it can be concluded that the overpotential across the LiPON electrolyte is most dominant and is therefore an important rate-limiting factor. In addition, it is found that both ionic and electronic diffusion coefficients in the LiCoO2 electrode seriously influence the battery performance. The present model is generally applicable to all-solid-state batteries where combined ionic and electronic transport takes place and allows for optimizing the battery components to increase the effective energy density, which leads to a decreasing demand for materials and costs.

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1. Introduction

Li-ion batteries are a well-established technology, nowadays widely applied in stationary and mobile energy storage systems. However, conventional Li-ion batteries are based on porous electrodes and liquid electrolytes, and are therefore prone to degradation and serious safety issues. In that respect the application of all-solid-state batteries (ASSB) is a good alternative since these battery systems are based on solid electrolytes, which often combine a better thermal and electrochemical stability and avoids hazardous electrolyte leakage in comparison to their liquid counterpart [1–3]. This makes ASSB ideal devices for implementation in, for example, medical implants and wireless sensor applications [4, 5]. Moreover, ASSB have a low self-discharge rate, and outstanding shelf- and cycle life performance.

Mathematical modelling, which includes all essential physical and electrochemical battery characteristics, can be used to describe the performance of ASSB. Further performance improvement of ASSB technology can be achieved by an in-depth understanding of all essential physical and electrochemical processes involved. The ability to simulate these processes in detail is therefore important. Numerous papers on mathematical modelling of Li-ion batteries with porous electrodes and liquid electrolytes have been published, which are also assessed in various review papers [6–10]. Although several efforts [11–13] have been made to mathematically describe ASSB this research is, however, not so well developed in comparison to liquid-based battery systems. For example, a detailed mathematical model for joined DC and AC simulations with a single set of parameters is still lacking.

Recent reports on mathematical ASSB modelling focus on numerical simulations of the electrochemical-mechanical interaction [14] and the effect of contact area losses between the electrodes and electrolyte [15], leading to battery degradation. Earlier work on electrochemical ASSB modelling has been performed, in which moderately good agreement between the measurements and
simulations has been reported [11,12]. Based on this work, where usually only DC (dis)charges profiles are applied, modelling efforts have also been performed in which highly dynamic battery loads were applied [16]. These dynamic load profiles are very common in microelectromechanical systems (MEMS) [17]. Recently, the model developed by Danilov et al. [11] has been extended with an ionic concentration-dependent diffusion coefficient in the positive electrode [18]. Their model simulations have been experimentally validated. Fabre et al. [12] also used a concentration-dependent ionic diffusion coefficient in their model and also found that this resulted in more accurate ASSB models. In addition, fundamental theoretical ASSB models have been developed but experimental validation is unfortunately often lacking [19,20].

Despite remarkable modelling advances that already have been made in the field of ASSB, the present models still do not capture essential physical and electrochemical processes which are necessary for joined DC and AC simulations. In this work, we therefore extend our previously developed ASSB model [11,18] by introducing additional battery characteristics, such as (i) mixed ionic/electronic conductivity in the positive electrode, (ii) electrical double layers occurring at both electrode/electrolyte interfaces, (iii) variable ionic and electronic diffusion coefficients that depend on the lithium concentration inside the positive electrode, and (iv) including an as-denoted geometric capacitance, which is essential for accurate, high frequency, impedance simulations. The proposed advanced model enables the investigation on the impact of ionic and electronic diffusion coefficients on concentrations profiles during battery operation and provides useful insights in the various loss processes, occurring in ASSB under both DC and AC conditions. After a detailed model description, the simulations are validated with DC voltage discharge curves at various C-rates and AC impedance measurements. It should be emphasized that a single parameter set is used for both the DC and AC simulations. Since both DC and AC impedance measurements are used for model validation, it is to be expected that the model parameters can be determined much more accurately. Although this advanced model focusses on the main physical and electrochemical processes that occur in ASSB, the aging-related processes, such as decomposition of electrolyte and electrode materials as well as contact losses due to electrode deformation are beyond the scope of this work. It is well known that commercial ASSB demonstrate remarkable longevity, with a typical cycle life of many thousands of cycles [21]. Therefore, the changes occurring with the battery on a relatively short-time scale are considered negligible.

2. Theoretical considerations

2.1. Electrochemical description

A schematic representation of an ASSB under discharge conditions is shown in Fig. 1. It consists of a platinum current collector (Pt), onto which the positive electrode material is deposited. In this work, the positive electrode (p) is based on a LiCoO₂ (LCO) chemistry and the negative electrode (n) is metallic lithium (Li). The electrodes are separated by a lithium phosphorus oxynitride (LiPON) solid-state electrolyte. At the left-hand side of Fig. 1 the domain-names are indicated, starting with the position, which indicate the one-dimensional length scales that are being used in the present model, followed by the names (Li, LiPON, LCO, and Pt), which indicate the different materials. The process shows the mobile charge carriers (e⁻, Li⁺, and Li⁰) in each material together with the flow direction (in this example under discharge) indicated by the straight arrows. The (yellow) curved arrows indicate the charge-transfer reactions at both interfaces, while \( i_{ct}^p \) and \( i_{ct}^n \) are used to specify the charge-transfer current densities across both electrode/electrolyte interfaces. In addition, two electrical double layer capacitances \( (c_{dl}^p \text{ and } c_{dl}^n) \) and an as-denoted geometric capacitance \( (c_{geo}) \) are shown. Hence, currents passing the interface can therefore be either faradaic or non-faradaic. It should be noted that the model presented in this work is not an equivalent circuit model. A list of used abbreviations and symbols/dimensions, which are used in the present modelling work can be found in Tables 1 and 2, accordingly.

![Fig. 1. Schematic representation of an all-solid-state Li-ion battery under discharge conditions. The positive electrode side is indicated with a p-sign and the negative electrode side with an n-sign.](image)

The basic electrochemical charge-transfer reactions at the p and n surfaces can be represented by

\[
\text{LiCoO}_2 \xrightarrow{k_1 \over k_{-1}} \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^- \quad (0 \leq x \leq 0.5),
\]

\[
\text{Li} \xrightarrow{k_1 \over k_{-2}} \text{Li}^+ + e^-. \quad (2)
\]

respectively. A delithiated LCO positive electrode consists of four-valent cobaltoxide species (Co⁴⁺O₂). During LCO lithiation, i.e. discharging the battery as shown in Fig. 1, the four-valent cobaltoxide species will be reduced to trivalent cobaltoxide (LiCo³⁺O₂) by gaining electrons from the outer electrical circuit in order to maintain electroneutrality. In the present work, it is assumed that

<table>
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<th>Table 1 List of abbreviations.</th>
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Subscript $i$ indicates the type of (active) species/material, which can take values Li, Li$^+$, Li$^0$, Li$^{3+}$, LiCoO$2$, CoO$2$, e$^-$, n$^-$, or Pt

Superscript $i$ indicates the positive ($p$) or negative electrode ($n$)
intercalated Li is present inside LiCoO$_2$ as ions, which will be denoted as Li$^+$ to stress an ionic nature, but to make a distinction with mobile Li$^+$ ions in the LiPON electrolyte. During charging the Li$^+$ ions, released from the p surface, must cross the electrolyte and are reduced into metallic Li at n.

As shown by the coordinate system (position) in Fig. 1, the direction of the y-axis is from n towards p. Note that the y-axis is depicted horizontally in the coordinate system. The origin of the coordinate system is located at the boundary between Li and LiPON. The thickness of the Li electrode is denoted as $L$, the LiPON layer as $M$, and that of the Pt current collector as $K$.

The battery voltage ($U_{bat}$) is determined by the redox reactions

$$U_{bat} = U_{bat}^* + \eta_{Li} + \eta_{Pt} =$$

$$= U^p(c_{LiCoO_2}^{eq}) + \eta_d^p + \eta_{ct}^p + \eta_{mt}^p - U^{p}(c_{Li}^{eq}) + \eta_{Pt} + \eta_{Li}. \quad (6)$$

that release or consume electrons and, furthermore, depends on various energy losses, caused by ionic and electronic transport in the system. The charge-transfer reactions at the surface-positions $y = 0$ and $y = L$ (Fig. 1) are the primary source of energy, which is dissipated in the ionic, inner electronic, and finally the outer electronic circuits. The as-denoted primary voltage between points $y = 0$ and $y = L$, is calculated according to

$$U_{prim} = U^p(c_{LiCoO_2}^i) - U^p(c_{Li}^{eq}), \quad (3)$$

where $U^p(\cdot)$ and $U^{p}(\cdot)$ are equilibrium voltage functions for $p$ and $n$, accordingly. Note that the equilibrium voltage function $U^p(\cdot)$ is evaluated at $c_{LiCoO_2}^{ct}$ and $c_{Li}^{ct}$, which correspond to the surface concentration of lithium at $p$ and $n$, respectively.

The primary voltage (Eq. (3)) will deviate from the battery voltage due to the energy losses in the ionic and electronic domains. These losses generate an overpotential ($\eta_{bat}$), which is defined as

$$\eta_{bat} = U_{bat} - U_{eq}, \quad (4)$$

where $U_{eq}$ is the battery voltage under equilibrium conditions. This implies that during charging $\eta_{bat}$ is positive and during discharging $\eta_{bat}$ is negative.

Losses in the ionic circuit include charge-transfer losses at both electrode/electrolyte interfaces, and energy losses due to mass-transfer across the LiPON electrolyte and in the LCO electrode. We can therefore define voltage $U_{bat}$, which represents the battery voltage without Ohmic losses in the inner electronic circuit, as where $\eta_d^p = U^p(c_{LiCoO_2}^{eq}) - U^p(c_{LiCoO_2}^{ct})$ is the so-called diffusion overpotential for $p$ [22], $\eta_{ct}^p$ and $\eta_{mt}^p$ are the charge-transfer overpotentials, $\eta_{mt}^{LIPON}$ is the mass-transfer overpotential across the LiPON electrolyte, and $\eta_{mt}^{n}$ is the mass-transfer overpotential of Li$^0$ species in the LCO electrode. The latter four overpotentials will be described in detail in Sections 2.2.2-2.4. Voltage $U_{bat}$ is a variable that is important for the theoretical description of the charge-transfer kinetics and electrical double layers in the present modelling work (Section 2.2).

Electrons, generated by the charge-transfer reactions, must pass through the inner electronic circuit(s), i.e. from $y = 0$ and $y = -N$ in the Li electrode, and from $y = L + M$ and $y = L + M + K$ in the Pt current collector. Therefore, the voltage between the terminals of the battery, i.e. the battery voltage, will be equal to where $\eta_{Pt}$ and $\eta_{Li}$ are the potential drops across the Pt and Li layers.

$$\eta_{Pt} = \rho_{Pt} j_{bat} \quad \text{and} \quad \eta_{Li} = \rho_{Li} j_{bat}. \quad (7)$$

where $\rho_{Pt}$ and $\rho_{Li}$ are the geometrical-area resistances of Pt and Li, respectively, and $j_{bat}$ is the current density flowing through the battery. Since $\rho_{Pt}$ and $\rho_{Li}$ cannot be separately identified, they are replaced by $\rho = \rho_{Pt} + \rho_{Li}$, which represents the total Ohmic series resistance of the battery. This results in a total Ohmic series overpotential $\eta_s = \rho j_{bat}$.

### 2.2. Charge transfer kinetics and electrical double layers

The relation between the charge-transfer overpotential ($\eta_{ct}^p$) and the charge-transfer current density ($j_{ct}^p$) at the p surface is defined as

$$j_{ct}^p = j_0 \left[ \frac{c_{LiCoO_2}^{ct} - c_{LiCoO_2}^{eq}}{c_{CoO_2}^{eq} c_{Li}^{eq}} \cdot \frac{c_{LiCoO_2}^{ct} - c_{Li}^{eq}}{c_{CoO_2}^{eq} c_{Li}^{eq}} \cdot (1 - a^p)^2 a^p \eta_{ct}^{eq} \right], \quad (8)$$

where $c_i^s$ are surface concentrations, $\tau_i$ are average bulk concentrations, subscript $i$ denotes the electrochemically active species (LiCoO$_2$ and CoO$_2$ in p and Li$^+$ in the LiPON electrolyte), $a^p$ is the charge-transfer coefficient for the reaction given in Eq. (1), $F$ the Faraday constant, $R$ the gas constant, and $T$ is the absolute temperature. When the pre-exponential concentration fractions are equal to 1, i.e. under full kinetically-controlled conditions, Eq. (8) can be simplified to the classical Butler-Volmer equation. The exchange current density ($j_0^p$) in Eq. (8) is defined as

$$U_{bat} = U_{prim} + \eta_d^p + \eta_{ct}^p - U^{p}(c_{LiCoO_2}^{ct}) + \eta_{ct}^p + \eta_{mt}^p - U^{p}(c_{Li}^{eq}) + \eta_{mt}^{LIPON} - \eta_{ct}^{n} - U^{n}(c_{Li}^{eq}). \quad (5)$$
where $k_1^f$ is the standard reaction rate constant for the forward reaction in Eq. (1) and $c_{\text{LiCoO}_2}^{\text{max}}$ is the maximum lithium concentration in the LCO electrode.

The relation between the charge-transfer overpotential ($\eta_{\text{ct}}^n$) and the charge-transfer current density ($j_{\text{ct}}^n$) at the $n$ surface is described by

$$j_{\text{ct}}^n = F k_2^f \left( \tau_{\text{Li}} \right)^{\alpha^n} \left( \tau_{\text{Li}} \right)^{-1} c_{\text{Li}}^{\alpha^n}$$

where $c_{\text{Li}}$ and $\tau_{\text{Li}}$ are surface and bulk molar concentrations of the metallic Li, $\alpha^n$ is the charge-transfer coefficient for the reaction in Eq. (2), $\eta_{\text{ct}}^n$ is the charge-transfer reaction overpotential at the negative electrode, and $j_{\text{ct}}^n$ is the exchange current density, which is given by

$$j_{\text{ct}}^n = F k_3^f \left( \tau_{\text{Li}} \right)^{\alpha^n} \left( \tau_{\text{Li}} \right)^{-1} c_{\text{Li}}^{\alpha^n}$$

where $k_3^f$ is the standard rate constant (Eq. (2)). For a full derivation of the charge-transfer kinetics, we refer to the paper of Danilov et al. [11].

An electrical double layer, also sometimes called space-charge layer, is present at the interface between (solid-state) electrolyte and electrodes as schematically indicated by the dashed lines in [20,23–26]. At the negative electrode/electrolyte interface of solid-state batteries, this layer is formed by mobile Li$^+$ ions in the electrolyte and at the electrolyte/p interface by Li$^+$ vacancies [23]. Current passing an electrode/electrolyte interface can be either faradaic or non-faradaic, implying that a part is used to drive the charge-transfer reactions ($j_{\text{ct}}^f$) and the other part to (dis)charge the electrical double layers ($j_{\text{dl}}$), resulting in the following expression

$$j_{\text{ct}}^f + j_{\text{dl}} = j_{\text{bat}} - j_{\text{geo}}$$

where superscript $i$ indicates either the $p$ or $n$ electrode. From Eq. (12) it can be seen that the current density passing the interface ($j_{\text{ct}}^f + j_{\text{dl}}$) is equal to $j_{\text{bat}}$ minus the current density ($j_{\text{geo}}$) that flows into the geometric capacitance ($c_{\text{geo}}$). In the present work, both the electrical double layers and the geometric capacitance are modelled as electric capacitors in order to reduce the model complexity. However, it is obvious that it is also possible to apply more advanced mathematical models to simulate the space-charge layer formation [20,25,26].
to the meta-stable interstitial state (Fig. 2b), and $n^-$ is a notation for the uncompensated negative charge associated with a vacancy formed in the LiPON matrix at the place where lithium was originally located. Note that $\text{Li}_0$ is not a lithium metal and the movement of uncompensated negative charge ($n^- / C_0$) does not contribute to electronic conductivity; it is known that LiPON electrolytes have a very low electronic conductivity [27].

$k_d$ and $k_r$ are the rate constants for the ionization and recombination reaction, respectively. Denoting the concentration of mobile Li ions by $c_{\text{Li}^+}$, the concentration of immobile lithium $c_{\text{Li}_0}$, the concentration of uncompensated negative charges ($n^- / C_0$), and the fraction of Li that resides in equilibrium in the mobile state $\delta$, then the equilibrium concentration of the charge carriers can be represented by $c_{\text{eq}}^{\text{Li}^+} = c_{\text{eq}}^{\text{Li}_0} = \delta C_0$. The equilibrium concentration of immobile lithium is then given by $c_{\text{eq}}^{\text{Li}_0} = (1 - \delta) C_0$. Under equilibrium conditions, the
rates of the forward and backward reactions are equal \( (k_d c_{\text{eq}}^{\text{n}}) = k_c c_0 \), implying that \( k_d = k_c c_0 \beta^2 / (1 - \delta) \). The overall rate of the charge carrier generation under general (dynamic) conditions is given by \( r = k_d c_{0\text{Li}} - k_c c_{\text{Li}^+} c_n \) and the rate of the inverse reaction is given by the opposite rate.

Fig. 2b illustrates the ionization process at the left-hand side. The encircled letter V that is connected with a negatively charged oxygen atom represents a vacancy, formed by a Li\(^+\) ion that has transferred to an interstitial site. Since Li\(^+\) is a charged particle, it obeys the Nernst-Planck dynamics that can be described by

\[
\frac{\partial c_{\text{Li}^+}}{\partial t} = - \frac{\partial j_{\text{Li}^+}}{\partial y} + r, \tag{18.1}
\]

\[
c_{\text{Li}^+}(y, 0) = \delta c_0, \tag{18.2}
\]

\[
J_{\text{Li}^+}(0, t) = \frac{\rho_{\text{Li}^+}(t)}{z_{\text{Li}^+} F} = \frac{j_{\text{bat}}(t) - j_{\text{geo}}(t) - j_{\text{dl}}(t)}{z_{\text{Li}^+} F}, \tag{18.3}
\]

\[
J_{\text{Li}^+}(L, t) = \frac{\rho_{\text{Li}^+}(t)}{z_{\text{Li}^+} F} = \frac{j_{\text{bat}}(t) - j_{\text{geo}}(t) - j_{\text{dl}}(t)}{z_{\text{Li}^+} F}, \tag{18.4}
\]

where \( J_{\text{Li}^+} \) is the flux of interstitial Li\(^+\) ions at distance \( y \) from the surface of the \( n \) at any moment in time \( t \).

Simultaneously to the ionization reaction (Eq. (17)), vacancies can be occupied by Li\(^+\) ions from neighbouring positions. This process can also be seen in Fig. 2b, where a Li\(^+\) ion hops from a stable position into an available vacancy. Note that the net effect of this reaction is the movement of uncompensated negative charge into the opposite direction. It has been assumed \([11]\) that the movement of \( n^- \) can be approximated by the Nernst-Planck balance equation, according to

\[
\frac{\partial c_n}{\partial t} = - \frac{\partial j_n}{\partial y} + r, \tag{19.1}
\]

\[
c_n(y, 0) = \delta c_0, \tag{19.2}
\]

\[
J_n(0, t) = 0, \tag{19.3}
\]

\[
J_n(L, t) = 0. \tag{19.4}
\]

Eqs. (18.1) and (19.1) represent the mass balances, whereas Eqs. (18.2) and (19.2) reflect the initial concentrations at \( t = 0 \). Eqs. (18.3)-(18.4) and (19.3)-(19.4) represent the fluxes at the left and right boundaries of the electrolyte. Note that the flux for \( n^- \) is zero at both boundaries, while the flux for Li\(^+\) ions is equal to the charge-transfer current density.

If the above described approach is adopted, it imposes some limitations on the system with respect to the concentrations. Indeed, the maximal lithium concentration in LiPON \((c_0)\) corresponds to the total number of locations where lithium can be present in a stable form, i.e. being linked with oxygen. In any state, only some of those locations contain immobile lithium, while some other locations are empty and represent vacancies (Fig. 2b).

Therefore,

\[
c_0 = c_{\text{Li}^+}(y, t) + c_n(y, t). \tag{20}
\]

If, in addition, electroneutrality is assumed, i.e.
In line with Eq. (26), the accommodation of diffusion and migration of both charge carriers, i.e. $c_{Li}^+$ and $e^-$, are represented by the following Partial Differential Equations (PDE), describing the diffusion-migration process of $Li^{10}$ and $e^-$, can be shown that two Partial Differential Equations (PDE),

$$\frac{\partial c_{Li}^+}{\partial t} = -\frac{\partial D_{Li}^+ \beta}{\partial y},$$  

$$\frac{\partial c_e^-}{\partial t} = -\frac{\partial D_e^- \beta}{\partial y},$$  

where $D_{Li}^+$ and $D_e^-$ are individual scaling constants. This leads to constant transport numbers as a function of lithium concentration. Deriving expressions similar to those presented in Section 2.3, it can be shown that two Partial Differential Equations (PDE), describing the diffusion-migration process of $Li^{10}$ and $e^-$, can be represented by

$$J_Li^+(L, t) = \frac{\beta_{Li}^+}{c_{Li}^+} \frac{\partial c_{Li}^+}{\partial y}$$  

$$J_e^-(L, t) = \frac{\beta_e^-}{c_e^-} \frac{\partial c_e^-}{\partial y},$$

and

$$\frac{\partial c_{Li}^+}{\partial t} - \frac{\partial c_e^-}{\partial t} = \frac{\partial c_{Li}^+}{\partial y} \frac{\partial c_e^-}{\partial y}$$

Eqs. (28.1) and (29.1) represent the mass balances, whereas Eqs. (28.2) and (29.2) reflect the fact that at $t = 0$ no concentration profiles have been developed yet and, hence, that the concentrations of charge carriers are equal to their equilibrium concentrations. Eqs. (28.3)-(28.4) and (29.3)-(29.4) represent the flux conditions at the left and right electrode boundaries of the LCO electrode, respectively (see Fig. 1). Following Eq. (12) and assuming that no side reactions take place, the current density flowing through the interfaces at positions $L$ and $L + M$ can simply be represented by $j_{bat}(t) - j_{geo}(t) = \frac{\partial c_{Li}^+}{\partial y} + \frac{\partial c_e^-}{\partial y}$. Eqs. (28) and (29) accommodate the diffusion and migration of both charge carriers. In line with Eq. (26), the flux of each charge carrier is considered to occur independently. Solving Eqs. (28) and (29) under electroneutrality conditions, i.e. $c_{LiCoO_2}(y, t) = c_{Li}^+(y, t) = c_e^-(y, t)$ and performing further derivations (see Refs. [11,28]), this leads to the following diffusion equation with respect to $c_{LiCoO_2}(y, t)$.

$$\frac{\partial c_{LiCoO_2}(L, t)}{\partial t} = \frac{\partial}{\partial y} \left( \beta(y) \frac{\partial c_{LiCoO_2}}{\partial y} \right) = \frac{\partial}{\partial y} \left( D_{LiCoO_2} \frac{\partial c_{LiCoO_2}}{\partial y} \right).$$  

$$\frac{\partial c_{LiCoO_2}(y, 0)}{\partial y} = c_{eq}^{LiCoO_2},$$

$$\frac{\partial c_{LiCoO_2}(L + M, t)}{\partial y} = -\frac{\partial c_{LiCoO_2}(L + M, t)}{\partial y} = \frac{\partial c_{LiCoO_2}(L + M, t)}{\partial y} = \frac{\partial c_{LiCoO_2}(L + M, t)}{\partial y}.$$  

$$\frac{\partial c_{LiCoO_2}(y, t)}{\partial y} = -\frac{\partial c_{LiCoO_2}(y, t)}{\partial y} = \frac{\partial c_{LiCoO_2}(y, t)}{\partial y} = \frac{\partial c_{LiCoO_2}(y, t)}{\partial y}.$$  

where $D_p^L$ and $D_p^M$ and $D_p$ are similarly dependent through a common $D_p$. In Appendix A the finite difference approximation for flat solid-state diffusion in $p$ is described, which has been used for the implementation in Matlab. Similar as described in Section 2.3, an expression for the electric field can be obtained, which after derivations (see Refs. [11,28]) results in

$$\text{Fig. 3. Measured (symbols) and simulated (lines) voltage discharge curves as a function of extracted charge at various C-rates. The extrapolated EMF voltage curve is also shown.}$$

| Table 3 |
| Model parameter values. |
| Symbol | Value | Dimension |
| $T$ | 293$^a$ | K |
| $\kappa$ | 3.62$^a$ | $\mu$m |
| $M$ | 8.08$^a$ | $\mu$m |
| $A$ | 3.36$^a$ | cm$^2$ |
| $k_1$ | 8.00$ \times 10^{-7}$ | m$^3$ s$^{-1}$ |
| $k_2$ | 1.53$ \times 10^{-11}$ | m$^3$ mol$^{-1}$ s$^{-1}$ |
| $K_3$ | 1.09$ \times 10^{-9}$ | m$^{-1}$ |
| $\delta$ | 0.5 | $\mu$m |
| $\phi^e$ | 0.5 | $\mu$m |
| $D_Li^+$ | 1.21$ \times 10^{-13}$ | m$^2$ s$^{-1}$ |
| $D_e^-$ | 5.06$ \times 10^{-13}$ | m$^2$ s$^{-1}$ |
| $D_LiCoO_2$ | 1.73$ \times 10^{-16}$ | m$^2$ s$^{-1}$ |
| $D_{LiCoO_2}^{max}$ | 5.69$ \times 10^{-16}$ | m$^2$ s$^{-1}$ |
| $c_{LiCoO_2}^{eq}$ | 3.22$ \times 10^{10}$ | mol m$^{-3}$ |
| $\phi_0$ | 7.64$ \times 10^{10}$ | mol m$^{-3}$ |
| $\delta$ | 0.64 | $\mu$m |
| $h_Li$ | 18.3 | $\Omega$ cm$^2$ |
| $\phi_{Li}$ | 5.30$ \times 10^{-7}$ | F cm$^{-2}$ |
| $\phi_{LiCoO_2}$ | 1.74$ \times 10^{-8}$ | F cm$^{-2}$ |
| $\phi_{geo}$ | 3.24$ \times 10^{-9}$ | F cm$^{-2}$ |

$^a$ Identified by direct measurements.
$^b$ Measured with Scanning Electron Microscope.
$^c$ Predefined (non-optimized) parameters.
$^d$ Calculated from the EMF voltage curve.
E(y, t) = \frac{RT}{F} \frac{1}{\beta(y, t) c_{\text{LiCoO}_2}(y, t)} \left\{ \frac{D_{\text{Li}^+}^0}{D_{\text{Li}^+}^0 + D_e^0} \frac{\partial \gamma_{\text{LiCoO}_2}(y, t)}{\partial y} - \frac{2D_{\text{Li}^+}^0}{D_{\text{Li}^+}^0 + D_e^0} j_{\text{bat}}(t) - j_{\text{geo}}(t) \right\}. \quad (31)

The mass-transfer overpotential for Li\(^{\text{+}}\) ions across \( p \) is then given by

\[ \psi_{\text{mt}}^p = \frac{RT}{F} \ln \left( \frac{c_{\text{LiCoO}_2}(L + M, t)}{c_{\text{LiCoO}_2}(L, t)} \right) - \int_L^{L+M} E(y, t) dy. \quad (32) \]

3. Experimental

Commercial all-solid-state thin-film batteries with a capacity of 0.7 mAh were used for the experiments. The positive electrode is a layer of LiCoO\(_2\) with a thickness of 8.08 \( \mu \)m, which is deposited on a platinum substrate while Lithium metal is used as negative electrode. The electrolyte is a layer of LiPON with a thickness of 3.62 \( \mu \)m. The surface area of the deposited electrodes is 3.36 cm\(^2\).

The DC (dis)charge experiments were performed with an automatic cycling device (Maccor 2300). Before performing characterization to obtain the electromotive force (EMF) voltage curves, five activation cycles were applied. During characterization a constant-current constant-voltage (CCCV) charge mode was used. CC-charging was performed at 1 C-rate (0.7 mA) up to a voltage of 4.2 V, followed by CV-charging at 4.2 V, using a cut-off current of 0.1 C-rate (0.07 mA). A wide range of discharge currents (0.1, 0.2, ...
0.5, 1.0, 2.0, 4.0, and 6.0 C-rates) with a cut-off voltage of 3.0 V was applied after each CCCV charging cycle to obtain a complete set of voltage discharge curves. On the basis of this set the EMF voltage curve was determined by mathematical extrapolation, of which the details can be found in previous publications [32,33]. After both charging and discharging a relaxation period of 2 h was applied.

Potentiostatic impedance measurements were performed at a voltage of 3.9 V for 50 logarithmically distributed frequencies in the range of 10 mHz–800 kHz with an Autolab PGSTAT302 N (Metrohm). The applied AC excitation voltage was set to 10 mV in order to obtain a good signal-to-noise ratio and a linear response.

Both the DC and impedance measurements were performed under a temperature-controlled condition of 20 °C, which is also the temperature used in the simulations.

4. Results and discussion

4.1. Total battery

Fig. 3 shows the measured (symbols) and optimized simulated (lines) discharge curves as a function of extracted charge together with the corresponding extrapolated EMF (upper black line). It can be seen that the agreement between the measurements and simulations is good across the wide range of investigated C-rates. The optimized model parameters are listed in Table 3. Obviously, the extracted charge decreases with increasing C-rate due to the higher overpotentials. For example, at a discharge rate of 6C less than half of the full discharge capacity can be extracted.

The measured (symbols) and simulated (lines) voltage discharge and relaxation curves at various C-rates are shown in Fig. 4. Note that the voltage discharge curves are shown as a function of extracted charge, while the relaxation curves are shown as a function of measurement time. From these results it can be concluded that the simulations are not only in good agreement during constant current discharging but also after current interruption during the entire relaxation time under all conditions.

Fig. 5 shows the optimized diffusion coefficients of Li⁺ (solid line) and e⁻ (dotted line) as a function of lithium stoichiometry in p. Since both diffusion coefficients are proportional to each other (Eq. (27)), their dependence as a function of lithium concentration in the electrode is the same, which indeed implies that the transport number is constant. The results show that the magnitude of the electronic diffusion coefficient is higher than that of the ionic diffusion coefficient, indicating that ionic diffusion is a limiting factor in the LiCoO₂ electrode. It can be seen that at low to medium lithium concentrations (0.5 ≤ x ≤ 0.75), representing the so-called second hexagonal phase [34], the diffusion coefficients are relatively constant. In the two-phase coexistence region (0.75 ≤ x ≤ 0.92), the diffusion coefficients decrease more than one order of magnitude. For values of x > 0.92, which represent the first hexagonal phase, the diffusion coefficients are constant again. The optimized diffusion coefficient for Li⁺ is in agreement with measurement and simulation results published in the literature for similar ASSB [12,35].

In this study both the ionic and electronic diffusion coefficient are used to model mixed ionic/electronic diffusion. In the literature, the electronic diffusion coefficient is often referred to as electronic conductivity/mobility. According to the Nernst-Einstein equation, the electronic conductivity is proportional to the diffusion coefficient at constant temperature [20,36]. It is therefore reasonable to compare the behavior of the optimized electronic diffusion coefficient in Fig. 5 with electronic conductivity data of LCO electrodes reported in the literature: it has been frequently found that for values of x between 0.50 and about 0.75, LiₓCoO₂ behaves like a metal, which shows good electronic conductivity properties. For higher values of x the conductivity decreases rapidly [37–39], which is in good agreement with the optimized electronic diffusion coefficient shown in Fig. 5.

4.2. Electrolyte

Fig. 6a and d shows the mobile lithium concentration (cLi⁺) development in the LiPON electrolyte at a 1C and 4C discharge rate, respectively. The mobile Li⁺ concentration in the bulk of the electrolyte is about 39 kmol m⁻³, which is in close agreement with the estimated value of 40 kmol m⁻³ reported by Put et al. [40]. This value depends on the maximal concentration (c₀) and the fraction of Li⁺ that resides in the mobile state (δ). The optimized parameter values are reported in Table 3. Fig. 6a and d also show that at both outer sides of the electrolyte strong concentrations gradients are build up, while the profile in the bulk remains constant. At position 0 (interface with n in Fig. 1), the concentration of mobile Li⁺ is higher than at position L (interface with p) as Li⁺ ions are inserted into the electrolyte at 0 and removed from the electrolyte at L during discharge.

The development of the electric field (Eq. (24)) in the LiPON electrolyte at a 1C and 4C discharge rate is shown in Fig. 6b and e, respectively. The electric field immediately develops when the current is applied and quickly reduces to zero if the current is switched off. The electric field at both electrolyte interfaces is stronger in comparison to that in the bulk of the electrolyte where it takes a non-zero, constant, value under current flowing conditions. From Eq. (24) it can be derived that the electric field increases with an increasing concentration gradient (κcLi⁺ (y,t)/∂y), which is indeed the case at the electrode/electrolyte boundaries. In addition, it can be seen that the electric field is asymmetric, i.e. the magnitudes at both outer sides (0 and L) are not equal. This becomes apparent from the 1/cLi⁺ (y,t) term in Eq. (24), from which it can be seen that the electric field has a decreasing tendency for increasing concentrations.

Fig. 6c and f shows the individual overpotentials in the LiPON electrolyte at 1C and 4C discharge rates, respectively. These results are calculated according to Eq. (25). The figures reveal that the overpotentials are dominated by migration (dashed red lines), while the diffusive component (dotted green lines) only has a minor contribution. Obviously, all overpotentials are higher at higher...
C-rates.

4.3. Positive electrode

Fig. 7a shows the development of the \( \text{Li}^+ \) concentration in the LCO electrode as a function of time and position at a 1C discharge rate. The same results are shown in Fig. 7e for a 4C discharge rate. In both figures it can be seen that the concentration increases as a function of discharge time, which is in agreement with the Li-intercalation reaction of Eq. (1). Particularly for the 4C-rate, the concentration profiles increase more rapidly at the electrode/electrolyte interface than in the bulk of the electrode. This can also be clearly seen from Fig. 7b and f, where the surface and average bulk concentrations are plotted as a function of time. Due to the low diffusion coefficients at the end of discharging (Fig. 5), the concentrations at the surface largely increase with respect to the bulk, especially at the 4C discharge rate. After discharging, the concentration profiles converge towards equilibrium, as expected. Furthermore, from Fig. 7b and f it can be concluded that the concentrations at the end of the measurement are higher at 1C-rate in comparison to 4C-rate, indicating that less capacity can be extracted at higher discharge rates.

Fig. 7c and g shows the development of the electric field in the LCO electrode at 1C and 4C-rate, respectively. The electric field is calculated using Eq. (31) and it only increases to significant levels at those places where a strong concentration gradient develops, such as at the end of discharging. The electric field contributes to the...
Fig. 7. Li$_4$ concentration in the positive electrode as a function of time and position (a, e); Li$_4$ concentration at the LCO/electrolyte interface and in the electrode bulk as a function of time (b, f); electric field in the positive electrode as a function of time and position (c, g); overpotentials at the positive electrode as a function of time (d, h). The time axis represents a full discharge and successive relaxation period at 1C (a–d) and 4C-rate (e–h).
mass-transfer overpotential (Eq. (32)) in the LCO electrode. The mass-transfer overpotential, together with the diffusion and charge-transfer overpotentials at 1C-rate discharging are shown in Fig. 7d and h. From Fig. 7d and h, it can be seen that the mass-transfer overpotential has the smallest contribution during discharging. In general, the charge-transfer overpotential at p/electrolyte interface is most dominant. The diffusion overpotential also contributes significantly at the beginning of discharge, but then slowly decreases in magnitude towards the end of discharging. However, at the very end of discharging, all overpotentials significantly increase in magnitude due to the increasing concentration gradients.

Remarkably, the diffusion overpotential at 1C-rate (Fig. 7d) is larger at the end of discharging than at 4C-rate (Fig. 7h). This difference can be best explained with the help of Fig. 8, which shows the EMF voltage curve as a function of x in Li_xCoO_2. From Fig. 8 it can be clearly seen that the surface voltage at the end of 1C-rate discharging is much lower than that at 4C-rate discharging, which explains the large difference between the diffusion overpotentials in Fig. 7d and h. Apparently, the surface concentration at 4C does not reach the level of that at 1C, although Fig. 7b and f shows that the surface concentrations at the end of discharging are about the same (x ≈ 1). However, because the EMF curve is almost vertical at the end of discharging (Fig. 8), small changes in concentration can lead to large changes in voltage. From Fig. 7b and f, and Fig. 8 it also becomes clear that at the end of discharging the difference in bulk concentrations between 1C and 4C is much larger than the difference in surface concentrations. However, the EMF curve is almost flat at the bulk concentration levels (see crosses in Fig. 8), leading to much smaller voltage differences.

4.4. Overpotential contributions

In Fig. 9a and d the EMF curve (upper black line) and the various overpotential contributions (colored areas) are shown for 1 and 4C-rate discharging, respectively. Each overpotential contribution is shown separately in distinct colors in order to emphasize the differences. From this figure it becomes immediately apparent that the electrolyte overpotential (green area) has the largest contribution. Other important overpotential contributions, though much smaller than the electrolyte overpotentials, are caused by the charge-transfer losses (cyan) at the p/electrolyte interface (\( \eta_p^{ct} \)) and by the diffusion losses inside p (\( \eta_p^{ct} \)) (red). In particular, the diffusion losses in p increase significantly at the end of discharging because the ionic concentration differences increase between the electrode surface and bulk, as discussed above. The same also holds for the mass-transfer overpotential (\( \eta_{mt}^{ct} \)) for Li^+ ions across p (Eq. (32)), which is represented by the yellow area. The remaining overpotentials, due to the Ohmic series resistance (blue area representing \( \eta_o \)) and charge-transfer at the n/electrolyte surface (magenta area representing \( \eta_n^{ct} \)) have the smallest contributions. The charge-transfer overpotential at p is larger than at n because the reaction rates are faster at n. All individual overpotentials, including the total battery overpotential (\( \eta_{bat} \)) are shown in Fig. 9b and e for a 1 and 4C-rate, respectively.

All overpotentials increase with increasing currents. Based on the overpotential analysis, it can be concluded that the electrolyte is the dominating factor in the performance limitations of ASSB. Obviously, the performance of this particular ASSB with LiPON as solid-state electrolyte can be improved by, for example, substantially decreasing the electrolyte layer thickness, increasing the ionic conductivity of the electrolyte or by using another solid-state electrolyte with improved ionic conductivity.

The simulated relaxation overpotentials are shown in Fig. 9c as a function of time after 1C-rate discharging. The inset of Fig. 9c shows an enlargement of the start of the relaxation period up to 1 min. Fig. 9f shows the relaxation results after 4C-rate discharging. Both Fig. 9c and f reveal that the voltage relaxation of the investigated batteries is mainly caused by the processes in p, such as diffusion, mass- and charge-transfer. Although the applied current is interrupted, the charge-transfer overpotential can still be identified in the relaxation process. The reason is because the pre-exponential concentration fractions (Eq. (8)) are unequal to 1 during relaxation. As soon as they are converged, the change-transfer overpotential will be absent.

4.5. Influence of diffusion coefficients

In order to investigate the influence of both the ionic and electronic diffusion coefficients, a small sensitivity study is performed of which the results are shown in Fig. 10a. The inset shows the EMF (black line), the measured voltage curve at 1C (symbols), and simulated voltage curve at 1C (blue line). Note again the excellent agreement between the simulation and experiment. Fig. 10b shows the simulated ionic concentration profiles of mobile Li^+ ions in the LiPON electrolyte and Li^+ ions in the LCO electrode for three time instants: at the start of discharging (blue), midway discharging (green), and at the end of discharging (red). The results shown in Fig. 10a–b are obtained from the optimized simulations (see Table 3 for the optimized parameters).

Fig. 10c–d shows the situation that both diffusion coefficients are taken exactly the same in the simulation, i.e. \( D_{Li^+} = D_{e^-} \). In this specific case, the electronic diffusion coefficient has been reduced to make it equal to the ionic diffusion coefficient (Fig. 10c). The other parameters were kept the same as for the optimized...
simulations. From this latter simulation result using the same diffusion coefficients, it can immediately be seen that the concentration profile in the LCO electrode has become fully symmetric (Fig. 10d). Due to this symmetry there is no electric field development inside the electrode and, moreover, the concentrations at both LCO interfaces are identical. This favorably results in the absence of a mass-transfer overpotential, which is according to Eq. (32) indeed equal to zero. In addition, the diffusion overpotential ($\eta_d$) is also lower because the difference between the surface and equilibrium concentration is smaller. This results in a lower total overpotential and more capacity can therefore be extracted from the battery as can be concluded from the inset of Fig. 10c. These simulation results show that if both the ionic and electronic diffusion coefficients are identical, the battery performance increases significantly with respect to the case of unbalanced diffusion coefficients.

An interesting, but rather rare situation, is obtained when the diffusion coefficients are reversed with respect to the optimized
simulations, i.e. $D_{L_{i}^{+}} > D_{e}$. The simulation results of this specific case are shown in Fig. 10e–f. The concentration profiles in Fig. 10f are mirrored with respect to the situation where $D_{L_{i}^{+}} < D_{e}$ (Fig. 10b). Because the ionic mobility is now higher than the electronic one, a higher concentration of $Li^{+}$ ions is built up at the current collector side upon discharging. Similar unusual concentration profiles have indeed been demonstrated experimentally in LiFePO4 powder electrodes in recent Neutron Depth Profiling (NDP) studies [41].

4.6. Impedance simulations

Impedance measurements (blue) and simulations (red) are shown in Fig. 11. The impedance simulations are performed with exactly the same model and parameter set (Table 3) that was used for the DC simulations. However, instead of applying a DC current to the ASSB an AC current has been applied with a zero DC bias. The resulting time-domain signals have then been transformed to the frequency domain by Fourier transformation, which makes it possible to calculate the impedance spectra. Performing impedance simulations in addition to DC simulations results in much more accurate parameter estimation since more measurement information has been made available. Moreover, it should be noted that when only the DC simulations are used for parameter optimization, the impedance simulations do not agree with the impedance measurements. It is therefore important that both the AC and DC behavior are simulated.

In Fig. 11a the total measured (blue line) and simulated (black line) battery impedances are shown, including indicated highest (800 kHz) and lowest (10 mHz) frequencies. There is a reasonable agreement between the measurement and simulation along the entire frequency range. The individual simulated impedance contributions, including the total battery impedance ($Z_{bat}$), are shown in Fig. 11b. It immediately becomes apparent that the LiPON electrolyte has the largest impedance contribution ($Z_{LiPON}^{mt}$). This is in good agreement with the results shown in Fig. 9, in which the electrolyte overpotential is also dominating. In Fig. 11b it can be seen that the total battery impedance ($Z_{bat}$) at the highest frequencies is lower than the electrolyte impedance ($Z_{LiPON}^{mt}$). The reason is because the geometric capacitance ($C_{geo}$) 'short-circuits' the battery at high frequencies and the relatively high impedances of the LCO electrode and the LiPON electrolyte are therefore shunted.

An enlargement of the other, smaller, impedance contributions is shown in Fig. 11c. It can be seen that the charge-transfer, including the electrical double layer impedance of $p$ ($Z_{ct}^{p}$), is larger in comparison to that of $n$ ($Z_{ct}^{n}$), which is in line with the investigated overpotentials of Fig. 9. The combination of the electrical double layer capacitance and charge-transfer resistance, theoretically described in Section 2.2, results in the characteristic semicircles in the high to middle frequency range for the $p$ and $n$. At low frequencies in the $p$ and $n$ impedance, another semicircle appears due to the changing ionic concentrations. The pre-exponential concentration fractions in Eqs. (8) and (10) are responsible for this behavior. Apparently, the (interface) concentrations develop in such a way that this leads to a reduction in impedance and to an uncommon (inductive) semicircle in the low frequency range for the negative electrode. In the case when the pre-exponential concentration fractions are equal to one, only one semicircle appears due to the combination of electrical double layer and charge-transfer.

The high-to middle-frequency range is the range where the double layer capacitors play a role. This suggests that the space-charge layers in this particular ASSB do not have a large influence on the static (DC) discharge curves and, thus, on the overall performance, which has also been concluded by others [26,42]. However, this might be different for ASSB that are used in, for example,
applications in which mid-to-high frequency dynamic loads are applied, such as microelectromechanical systems (MEMS) [16].

The diffusion \( \left( Z_{p}^{d} \right) \) and mass-transfer \( \left( Z_{p}^{mt} \right) \) impedances in \( p \), which are visible in Fig. 11c, are only developing at low frequencies and show the typical diffusive line with an angle of approximately \( 45^\circ \). As with the overpotentials, which are shown in Fig. 9, diffusion (red line) has a larger impedance than mass-transfer (yellow line) because at the lowest frequencies the diffusion impedance is larger.

5. Conclusions

A new advanced one-dimensional model has been developed in order to simulate thin-film all-solid-state Li-ion batteries. The model describes all relevant processes occurring in the electrodes, electrolyte, and at the interfaces. Those processes include charge-transfer kinetics at both electrode/electrolyte interfaces, diffusion and migration of mobile lithium ions in the electrolyte, and diffusion and migration of lithium ions and electrons in the positive electrode. The LiPON and LCO layers can be considered as a dielectric barrier between two electronic conductors, i.e., the Pt current collector and metallic Li electrode. Therefore, a geometric capacitor is added to the model. In addition, double layer capacitors are applied at both electrode/electrolyte interfaces to describe the space-charge effect.

The model parameter values have been optimized such that both DC and AC model simulations are in a good agreement with measurements on 0.7 mAh Li/LiPON/LiCoO\(_2\) all-solid-state batteries. It should be emphasized that the parameter set for the DC simulations is exactly equal to that of the AC simulations. From both the DC and AC simulations it turns out that the overpotential across the electrolyte layer has the largest contribution. Charge-transfer, including electrical double layer losses at the positive electrode/electrolyte interface, and diffusion in the positive electrode are causing the second major losses in the battery. The charge-transfer kinetics and double layer losses at the negative electrode/electrolyte interface, mass-transfer in the positive electrode, and series resistance have only minor contributions to the total overpotential.

In addition, the simulations suggest that the space-charge layers in this particular ASSB do not have a large influence on the static discharge curves and, thus, on the overall performance.

The model has also been used to investigate the influence of ionic and electronic diffusion coefficients in the positive electrode. It turns out that concentration profiles are highly dependent on these diffusion coefficients and that the battery performance increases significantly if the ionic and electronic diffusion coefficients are identical.

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Appendix A

In this Appendix the finite differences for flat solid-state diffusion in the positive electrode are described. These are used for the calculations in Matlab. For convenience, Eq. (30) is reproduced here as a starting point for further derivations, where \( c_{\text{LiCoO}_2} \) is substituted by \( c \) to economize notations:

\[
\frac{\partial c}{\partial t} = D_p \frac{\partial}{\partial y} \left( \beta(y) \frac{\partial c}{\partial y} \right) = \frac{\partial}{\partial y} \left( D_p(y) \frac{\partial c}{\partial y} \right). \tag{A.1.1} \]

\[ c(y, 0) = c_0. \tag{A.1.2} \]
\( \frac{\partial c(x, t)}{\partial t} = D_p \frac{\partial^2 c(x, t)}{\partial x^2} \) \quad (A.3.1)

Consider a uniform grid in the interval \([0, L]\) with \(n\) steps, i.e. sequence \(x_i = (i - 1)h\), where \(h = L/(n-1)\), then \(x_1 = 0\) and \(x_n = L\). A similar grid in the time domain is defined by \(t_j = (j - 1)\Delta t\), \(j \geq 1\), where \(\Delta t\) is the time step. A central finite-difference approximation for differential operator \(\beta(x, t) \frac{\partial c(x, t)}{\partial x}\) (Eq. (A.3.3)) and (A.3.4)) in points \((x_i + h/2, t)\) and \((x_i - h/2, t)\) can then be defined as

\[ \beta(x_i + h/2, t) \frac{\partial c(x_i + h/2, t)}{\partial x} = \beta(x_i - h/2, t) \frac{\partial c(x_i - h/2, t)}{\partial x} \]

\[ \frac{c(x_i + h/2, t) - c(x_i - h/2, t)}{h} \]

and

\[ \beta(x_i + h/2, t) \frac{\partial c(x_i - h/2, t)}{\partial x} = \beta(x_i - h/2, t) \frac{\partial c(x_i + h/2, t)}{\partial x} \]

\[ \frac{c(x_i + h/2, t) - c(x_i - h/2, t)}{h} \]

respectively.

A forward finite-difference approximation of Eq. (A.3.1) takes the form

\[ c(x_i, t_j + \Delta t) - c(x_i, t_j) = \]

\[ \frac{D_p^0}{h} \beta(x_i + h/2, t) \frac{c(x_i + h, t) - c(x_i, t)}{h} - \beta(x_i - h/2, t) \frac{c(x_i, t) - c(x_i - h, t)}{h} \]

Approximating \(\beta(x_i + h/2, t)\) by \(\frac{\beta(x_i + h/2, t)}{2}\) and \(\beta(x_i - h/2, t)\) by \(\frac{\beta(x_i - h/2, t)}{2}\) gives

\[ c(x_i, t_j + \Delta t) - c(x_i, t_j) = \]

\[ \frac{D_p^0}{h^2} \left[ \beta(x_i + h, t) - \beta(x_i, t) \right] \]

\[ \frac{d}{dt} \left[ \beta(x_i + h, t) - \beta(x_i, t) \right] \]

After denoting \(c_i = c(x_i, t_j)\) and \(\beta_i = \beta(x_i, t_j)\), Eq. (A.6) can be reduced to

\[ c_{i+1} - c_i = \frac{D_p^0}{h^2} \left( \beta_{i+1} + \beta_{i-1} \right) \left( c_{i+1} - c_i \right) - \left( \beta_{i+1} + \beta_i \right) \left( c_i - c_{i-1} \right) \]

\[ = \frac{D_p^0}{h^2} \left( \beta_{i+1} + \beta_i \right) c_{i+1} - \left( \beta_{i+1} + 2\beta_i + \beta_{i-1} \right) c_i + \left( \beta_{i-1} + \beta_i \right) c_{i-1} \]

where subscript \(i\) corresponds to the space argument and superscript \(j\) indicates the time moment.

The boundary conditions in Eq. (A.3.3) and (A.3.4) are approximated by central differences with step \(2h\) across the boundary point as

\[ \frac{\beta_0 (c_1 - c_0)}{2h} = g_0 \]

\[ \frac{\beta_n (c_{n+1} - c_{n-1})}{2h} = g_n \]

Note that the concentrations at locations \(c_0\) and \(c_{n+1}\) are 'virtual'. Adopting Eq. (A.7) and resolving Eq. (A.8.1) and (A.8.2) with respect to virtual concentrations gives the following formulas

\[ c_{i+1} = c_i + \frac{D_p^0 \Delta t}{h} \left( \beta_{i+1} + \beta_i \right) \frac{c_{i+1} - c_i}{2h} - \left( \beta_{i+1} + 2\beta_i + \beta_{i-1} \right) \frac{c_i - c_{i-1}}{2h} \]

for \(i = 1 \ldots n\)

\[ c_0 = c_2 - \frac{2\beta_0 h}{\beta_1} \]

\[ c_{n+1} = c_{n-1} + \frac{2\beta_n h}{\beta_{n-1}} \]

Substituting Eq. (A.9.2) and (A.9.3) into Eq. (A.9.1) for \(i = 1\) and \(i = n\), accordingly and assuming \(\beta_0 = \beta_1\) and \(\beta_n = \beta_n\), finally produces

\[ c_{i+1} = c_i + \frac{D_p^0 \Delta t}{h} \left( \beta_{i+1} + \beta_i \right) \frac{c_{i+1} - c_i}{2h} - \left( \beta_{i+1} + 2\beta_i + \beta_{i-1} \right) \frac{c_i - c_{i-1}}{2h} \]

the following set of finite difference equations

\[ \frac{\partial c(x, t)}{\partial t} = \]

\[ D_p \frac{\partial^2 c(x, t)}{\partial x^2} \]
After rearrangements, Eq. (A.10) can be reduced to

\[
c_{i+1}^c = c_i^c + D_p^c \frac{\partial t}{h} \left\{ \left( \frac{3 \beta_1^c + \beta_2^c}{2h} \right) \left( c_{i-1}^c - c_i^c \right) \right\}, \quad \text{for } i = 1
\]

\[
c_{i+1}^c = c_i^c + D_p^c \frac{\partial t}{h} \left\{ \left( \frac{3 \beta_1^c + \beta_2^c}{2h} \right) \left( c_{i-1}^c - c_i^c \right) \right\}, \quad \text{for } i = 2 \ldots n - 1
\]

(A.10.1)

\[
c_{i+1}^d = c_i^d + D_p^d \frac{\partial t}{h} \left\{ \left( \frac{\beta_1^d + \beta_1^d}{2h} \right) \left( c_{i-1}^d - c_i^d \right) \right\}, \quad \text{for } i = 1
\]

\[
c_{i+1}^d = c_i^d + D_p^d \frac{\partial t}{h} \left\{ \left( \frac{\beta_1^d + \beta_1^d}{2h} \right) \left( c_{i-1}^d - c_i^d \right) \right\}, \quad \text{for } i = 2 \ldots n - 1
\]

(A.11.1)

\[
c_{n+1}^c = c_n^c + D_p^c \frac{\partial t}{h} \left\{ \left( \frac{3 \beta_1^c + \beta_2^c}{2h} \right) \left( c_{n-1}^c - c_n^c \right) + 2g_L^c \right\}, \quad \text{for } i = n
\]

\[
c_{n+1}^d = c_n^d + D_p^d \frac{\partial t}{h} \left\{ \left( \frac{\beta_1^d + \beta_1^d}{2h} \right) \left( c_{n-1}^d - c_n^d \right) + 2g_L^d \right\}, \quad \text{for } i = n
\]

(A.11.2)

(A.11.3)

where

\[
\mathbf{c}^t = \begin{pmatrix} c_1^t & c_2^t & \cdots & c_n^t \end{pmatrix}
\]

\[
H^t = \begin{pmatrix}
-3 \beta_1^t & -3 \beta_1^t & \cdots & 0 \\
\beta_2^t + \beta_3^t & -2 \beta_2^t - \beta_3^t & \cdots & 0 \\
0 & \beta_2^t + \beta_3^t & \cdots & 0 \\
0 & 0 & \cdots & 0
\end{pmatrix}
\]

(A.13.1)

\[
\mathbf{b}^t = \begin{pmatrix} -2g_0^t \\
0 \\
0 \\
2g_L^t
\end{pmatrix}
\]

(A.13.3)

In case of a constant diffusion coefficient, i.e. \( \beta_{n+1}^d = \beta_n^d = \beta \), matrix \( H \) is reduced to

\[
H^t = \beta \begin{pmatrix}
-2 & 0 & \cdots & 0 \\
1 & -2 & \cdots & 0 \\
0 & 1 & -2 & \cdots & 0 \\
0 & \cdots & 0 & -2
\end{pmatrix}
\]

(A.14)

References


