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

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ABSTRACT

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

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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 LiCoO_2 (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 $\text{Li}^\oplus$) 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 j_{ct}^p and j_{ct}^n are

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.

used to specify the charge-transfer current densities across both electrode/electrolyte interfaces. In addition, two electrical double layer capacitances (c_{dl}^p 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.

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

respectively. A delithiated LCO positive electrode consists of four-valent cobalt oxide species ($\text{Co}^{\text{IV}}\text{O}_2$). During LCO lithiation, i.e. discharging the battery as shown in Fig. 1, the four-valent cobalt oxide species will be reduced to trivalent cobalt oxide ($\text{LiCo}^{\text{III}}\text{O}_2$) by gaining electrons from the outer electrical circuit in order to maintain electroneutrality. In the present work, it is assumed that

Table 1
List of abbreviations.

Abbreviation	Meaning
AC	Alternating current
ASSB	All-solid-state battery
CCCV	Constant current, constant voltage
DC	Direct current
EMF	Electromotive force
LCO	Lithium cobalt oxide
LiPON	Lithium phosphorus oxynitride
MEMS	Microelectromechanical systems
NDP	Neutron depth profiling
<i>n</i>	The negative electrode
ODE	Ordinary differential equation
<i>p</i>	The positive electrode
PDE	Partial differential equation

Table 2
List of symbols.

Symbol	Description	Dimension
D_i	Diffusion coefficient of species i	m^2s^{-1}
D_i^0	Diffusion scaling constants of species i	m^2s^{-1}
J_i	Flux of species i	$\text{mol m}^{-2}\text{s}^{-1}$
U_{bat}	Battery voltage	V
U_{bat}^*	Battery voltage without Ohmic losses	V
U_{eq}	Voltage under equilibrium conditions	V
$U^i(\cdot)$	Equilibrium voltage function of electrode i	V
U_{prim}	Primary voltage	V
Z_{bat}	Battery impedance	$\Omega \text{ m}^2$
Z_{ct}^i	Charge-transfer impedance electrode i	$\Omega \text{ m}^2$
Z_d^p	Diffusion impedance positive electrode	$\Omega \text{ m}^2$
$Z_{\text{mt}}^{\text{LiPON}}$	Mass-transfer impedance electrolyte	$\Omega \text{ m}^2$
Z_{mt}^p	Mass-transfer impedance positive electrode	$\Omega \text{ m}^2$
Z_s	Total Ohmic series impedance	$\Omega \text{ m}^2$
c_0	Maximum concentration of lithium host sites in electrolyte	mol m^{-3}
c_{dl}^i	Double layer capacity per unit area of electrode i	F m^{-2}
c_{geo}	Geometric capacitance per unit area	F m^{-2}
c_i	Concentration of species i	mol m^{-3}
$\bar{c}_i$	Average bulk concentration of species i	mol m^{-3}
c_i^{eq}	Equilibrium concentration of species i	mol m^{-3}
c_i^{max}	Maximum concentration of species i	mol m^{-3}
c_i^s	Surface concentration of species i	mol m^{-3}
e^-	Electron in LCO electrode	—
j_0^i	Exchange current density of electrode i	A m^{-2}
j_{bat}	Battery current density	A m^{-2}
j_{ct}^i	Charge-transfer current density of electrode i	A m^{-2}
j_{dl}^i	Double layer current density of electrode i	A m^{-2}
j_{geo}	Geometric capacitance current density	A m^{-2}
k_1^s	Standard reaction rate constant for forward reaction in Eq. (1)	$\text{m}^{2.5}\text{s}^{-1}$
k_2^s	Standard reaction rate constant for forward reaction in Eq. (2)	m s^{-1}
k_d	Lithium ion generation reaction rate constant	s^{-1}
k_r	Lithium ion recombination reaction rate constant	$\text{m}^3 \text{mol}^{-1}\text{s}^{-1}$
n^-	Uncompensated negative charge in LiPON electrolyte	—
q_{dl}^i	Charge per unit area in the double layer of electrode i	Ah m^{-2}
q_{geo}	Charge per unit area in geometric capacitance	Ah m^{-2}
z_i	Valence of species i	—
α^i	Charge-transfer coefficient for electrode i	—
η_{bat}	Battery overpotential	V
η_{ct}^i	Charge-transfer overpotential electrode i	V
η_d^p	Diffusion overpotential positive electrode	V
η_i	Potential drop across material i	V
$\eta_{\text{mt}}^{\text{LiPON}}$	Mass-transfer overpotential electrolyte	V
η_{mt}^p	Mass-transfer overpotential positive electrode	V
η_s	Total Ohmic series overpotential	V
ρ_i	Geometrical-area resistance of material i	$\Omega \text{ m}^2$
ρ_s	Total geometrical-area resistance	$\Omega \text{ m}^2$
Li^+	Mobile lithium ion in LiPON electrolyte	—
Li_o	Immobile lithium ion in LiPON electrolyte	—
$\text{Li}^\oplus$	Lithium ion in LCO electrode	—
Li	Lithium	—
Pt	Platinum	—
A	Geometrical surface area	m^2
E	Electric field	V m^{-1}
F	Faraday constant (96485)	As mol^{-1}
K	Thickness of the Pt current collector	m
L	Thickness of the LiPON electrolyte	m
M	Thickness of the LCO electrode	m
N	Thickness of the negative lithium electrode	m
R	Gas constant (8.314)	$\text{J mol}^{-1}\text{K}^{-1}$
T	Absolute temperature	K
V	Vacancy	—
i	Subscript i indicates the type of (active) species/material, which can take values Li, Li^+ , $\text{Li}^\oplus$, Li^0 , LiCoO_2 , CoO_2 , e^- , n^- , or Pt	—
i	Superscript i indicates the positive (p) or negative electrode (n)	—
r	Charge-carrier generation rate	$\text{mol m}^{-3}\text{s}^{-1}$
x	Stoichiometric coefficient of the positive electrode	—
y	Coordinate system of the battery	—
β	Common time- and space-dependent factor for the diffusion coefficients	—
δ	Fraction of Li in LiPON that resides in the mobile state	—

intercalated Li is present inside $\text{LiCo}^{\text{III}}\text{O}_2$ as ions, which will be denoted as $\text{Li}^\oplus$ 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 N , the LiPON layer as L , the LCO layer as M , and that of the Pt current collector as K .

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

$$U_{bat} = U_{bat}^* + \eta_{Li} + \eta_{Pt} = U^p(c_{\text{LiCoO}_2}^{eq}) + \eta_d^p + \eta_{ct}^p + \eta_{mt}^p - \eta_{mt}^{\text{LiPON}} - \eta_{ct}^n - U^n(c_{\text{Li}}^{eq}) + \eta_{Pt} + \eta_{Li}, \quad (6)$$

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

$$U_{prim} = U^p(c_{\text{LiCoO}_2}^s) - U^n(c_{\text{Li}}^s), \quad (3)$$

where $U^p(\cdot)$ and $U^n(\cdot)$ are equilibrium voltage functions for p and n , accordingly. Note that the equilibrium voltage function $U^p(\cdot)$ is evaluated at $c_{\text{LiCoO}_2}^s$ and $U^n(\cdot)$ at c_{Li}^s , 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 (η_{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 η_{bat} is positive and during discharging η_{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 $\eta_d^p = U^p(c_{\text{LiCoO}_2}^s) - U^p(c_{\text{LiCoO}_2}^{eq})$ is the so-called diffusion

LiPON electrolyte, and η_{mt}^p is the mass-transfer overpotential of $\text{Li}^\oplus$ species in the LCO electrode. The latter four overpotentials will be described in detail in Sections 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 η_{Pt} and η_{Li} are the potential drops across the Pt and Li layers,

respectively. These potential drops follow Ohm's law, according to

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

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

2.2. Charge transfer kinetics and electrical double layers

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

$$j_{ct}^p = j_0^p \left[\frac{c_{\text{LiCoO}_2}^s}{\bar{c}_{\text{LiCoO}_2}} e^{\alpha^p \frac{F}{RT} \eta_{ct}^p} - \frac{c_{\text{CoO}_2}^s c_{\text{Li}^+}^s}{\bar{c}_{\text{CoO}_2} \bar{c}_{\text{Li}^+}} e^{-(1-\alpha^p) \frac{F}{RT} \eta_{ct}^p} \right], \quad (8)$$

where c_i^s are surface concentrations, $\bar{c}_i$ are average bulk concentrations, subscript i denotes the electrochemically active species (LiCoO_2 and CoO_2 in p and Li^+ in the LiPON electrolyte), α^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

$$U_{bat}^* = U_{prim} + \eta_{ct}^p + \eta_{mt}^p - \eta_{mt}^{\text{LiPON}} - \eta_{ct}^n = U^p(c_{\text{LiCoO}_2}^s) + \eta_{ct}^p + \eta_{mt}^p - \eta_{mt}^{\text{LiPON}} - \eta_{ct}^n - U^n(c_{\text{Li}}^s) = U^p(c_{\text{LiCoO}_2}^{eq}) + \eta_d^p + \eta_{ct}^p + \eta_{mt}^p - \eta_{mt}^{\text{LiPON}} - \eta_{ct}^n - U^n(c_{\text{Li}}^{eq}), \quad (5)$$

overpotential for p [22], η_{ct}^p and η_{ct}^n are the charge-transfer overpotentials, η_{mt}^{LiPON} is the mass-transfer overpotential across the

$$j_0^p = Fk_1^s c_{\text{LiCoO}_2}^{\text{max}} \left(1 - \frac{\bar{c}_{\text{LiCoO}_2}}{c_{\text{LiCoO}_2}^{\text{max}}}\right)^{\alpha^p} \left(\frac{\bar{c}_{\text{LiCoO}_2}}{c_{\text{LiCoO}_2}^{\text{max}}}\right)^{(1-\alpha^p)} \bar{c}_{\text{Li}^+}^{\alpha^p}, \quad (9)$$

where k_1^s 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 (η_{ct}^n) and the charge-transfer current density (j_{ct}^n) at the n surface is described by

$$\begin{aligned} j_{ct}^n &= j_0^n \left[\frac{c_{\text{Li}}^s}{\bar{c}_{\text{Li}}} e^{\alpha^n \frac{F}{RT} \eta_{ct}^n} - \frac{c_{\text{Li}^+}^s}{\bar{c}_{\text{Li}^+}} e^{-(1-\alpha^n) \frac{F}{RT} \eta_{ct}^n} \right] \\ &= j_0^n \left[e^{\alpha^n \frac{F}{RT} \eta_{ct}^n} - \frac{c_{\text{Li}^+}^s}{\bar{c}_{\text{Li}^+}} e^{-(1-\alpha^n) \frac{F}{RT} \eta_{ct}^n} \right], \end{aligned} \quad (10)$$

where c_{Li}^s and $\bar{c}_{\text{Li}}$ are surface and bulk molar concentrations of the metallic Li, α^n is the charge-transfer coefficient for the reaction in Eq. (2), η_{ct}^n the charge-transfer reaction overpotential at the negative electrode, and j_0^n the exchange current density, which is given by

$$j_0^n = Fk_2^s \left(\bar{c}_{\text{Li}^+}\right)^{\alpha^n} \left(\bar{c}_{\text{Li}}\right)^{(1-\alpha^n)}, \quad (11)$$

where k_2^s 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

The non-faradaic current (dis)charging the electrical double layers, can be defined in derivative form as

$$j_{dl}^i(t) = \frac{dq_{dl}^i(t)}{dt} = c_{dl}^i \frac{d\eta_{ct}^i(t)}{dt}, \quad (13)$$

where q_{dl}^i and c_{dl}^i are the stored charge and capacity per unit area of the double layer at the electrolyte/electrode interface of electrode i , respectively.

Since the LiPON solid-state electrolyte is an ionic conductor rather than an electronic conductor, it can be considered as an electronic insulator. Assuming that the LCO electrode is also a relatively poor electronic conductor, then the LiPON and LCO can be considered as a dielectric between two electronic conductors, i.e. the Pt current collector and Li electrode. A geometric capacitor is therefore added to the model as shown in Fig. 1. Subsequently, the current density flowing through the geometrical capacitance can be defined as

$$j_{geo}(t) = \frac{dq_{geo}(t)}{dt} = c_{geo} \frac{dU_{bat}^*(t)}{dt}, \quad (14)$$

where q_{geo} and c_{geo} are the stored charge and capacity per unit area of the geometric capacitance, respectively.

Combining Eq. (8) with Eqs. (12)–(14) gives an Ordinary Differential Equation (ODE) in the following form

$$\begin{aligned} j_0^p \left[\frac{c_{\text{LiCoO}_2}^s}{\bar{c}_{\text{LiCoO}_2}} e^{\alpha^p \frac{F}{RT} \eta_{ct}^p(t)} - \frac{c_{\text{CoO}_2}^s c_{\text{Li}^+}^s}{\bar{c}_{\text{CoO}_2} \bar{c}_{\text{Li}^+}} e^{-(1-\alpha^p) \frac{F}{RT} \eta_{ct}^p(t)} \right] + c_{dl}^p \frac{d\eta_{ct}^p(t)}{dt} \\ = j_{bat}(t) - c_{geo} \frac{dU_{bat}^*(t)}{dt}, \end{aligned} \quad (15)$$

for p . Similarly, using Eq. (10) with Eqs. (12)–(14), a similar ODE can be written for n

$$j_0^n \left[\frac{c_{\text{Li}}^s}{\bar{c}_{\text{Li}}} e^{\alpha^n \frac{F}{RT} \eta_{ct}^n(t)} - \frac{c_{\text{Li}^+}^s}{\bar{c}_{\text{Li}^+}} e^{-(1-\alpha^n) \frac{F}{RT} \eta_{ct}^n(t)} \right] + c_{dl}^n \frac{d\eta_{ct}^n(t)}{dt} = j_{bat}(t) - c_{geo} \frac{dU_{bat}^*(t)}{dt}. \quad (16)$$

Fig. 1 [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_{ct}^i) and the other part to (dis)charge the electrical double layers (j_{dl}^i), resulting in the following expression

$$j_{ct}^i + j_{dl}^i = j_{bat} - j_{geo}, \quad (12)$$

where superscript i indicates either the p or n electrode. From Eq. (12) it can be seen that the current density passing the interface ($j_{ct}^i + j_{dl}^i$) is equal to j_{bat} minus the current density (j_{geo}) that flows into the geometric capacitance (c_{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].

2.3. Diffusion and migration in the electrolyte

The complex amorphous LiPON structure is schematically shown in Fig. 2a and reveals that two common but different types of nitrogen bonds (indicated in green) can be identified in the LiPON matrix. One type corresponds to triply-coordinated nitrogen and the other to doubly-coordinated nitrogen.

The maximal concentration of host-sites is determined by the stoichiometric composition of the electrolyte material, and is denoted as c_0 . In the ideal case at absolute zero temperature, all available host sites are fully filled with lithium ions, and the ionic conductivity is zero because all ions are immobile. When the temperature is increased, some of the Li ions are thermally excited and a chemical ionization reaction starts to occur, according to

where Li_o denotes the lithium (ionic) bound to the non-bridging oxygen atoms (see Fig. 2), Li^+ is a lithium ion which is transferred

Fig. 2. LiPON matrix with triply- and doubly-coordinated nitrogen (a). Movements of charged particles towards the interstitial space and by means of particle hopping, representing the main ionic conductivity mechanisms in LiPON (b).

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 Li_0 is not a lithium metal and the movement of uncompensated negative charge (n^-) 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_{Li^+} , the concentration of immobile lithium c_{Li_0} , the concentration of uncompensated negative charges (n^-) c_{n^-} , and the fraction of Li that resides in equilibrium in the mobile state δ , then the equilibrium concentration of the charge carriers can be represented by $c_{\text{Li}^+}^{\text{eq}} = c_{n^-}^{\text{eq}} = \delta c_0$. The equilibrium concentration of immobile lithium is then given by $c_{\text{Li}_0}^{\text{eq}} = (1 - \delta)c_0$. Under equilibrium conditions, the

rates of the forward and backward reactions are equal ($k_d c_{\text{Li}_0}^{\text{eq}} = k_r c_{\text{Li}^+}^{\text{eq}} c_{\text{n}^-}^{\text{eq}}$), implying that $k_d = k_r c_0 \delta^2 / (1 - \delta)$. The overall rate of the charge carrier generation under general (dynamic) conditions is given by $r = k_d c_{\text{Li}_0} - k_r c_{\text{Li}^+} c_{\text{n}^-}$ 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

$$\frac{\partial c_{\text{Li}^+}}{\partial t} = -\frac{\partial J_{\text{Li}^+}}{\partial y} + r, \quad (18.1)$$

$$c_{\text{Li}^+}(y, 0) = \delta c_0, \quad (18.2)$$

$$J_{\text{Li}^+}(0, t) = -\frac{j_{\text{ct}}^{\text{n}}(t)}{z_{\text{Li}^+} F} = -\frac{j_{\text{bat}}(t) - j_{\text{geo}}(t) - j_{\text{dl}}^{\text{n}}(t)}{z_{\text{Li}^+} F}, \quad (18.3)$$

$$J_{\text{Li}^+}(L, t) = \frac{j_{\text{ct}}^{\text{p}}(t)}{z_{\text{Li}^+} F} = \frac{j_{\text{bat}}(t) - j_{\text{geo}}(t) - j_{\text{dl}}^{\text{p}}(t)}{z_{\text{Li}^+} F}, \quad (18.4)$$

where J_{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

$$\frac{\partial c_{\text{n}^-}}{\partial t} = -\frac{\partial J_{\text{n}^-}}{\partial y} + r, \quad (19.1)$$

$$c_{\text{n}^-}(y, 0) = \delta c_0, \quad (19.2)$$

$$J_{\text{n}^-}(0, t) = 0, \quad (19.3)$$

$$J_{\text{n}^-}(L, t) = 0. \quad (19.4)$$

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,

$$c_0 = c_{\text{Li}_0}(y, t) + c_{\text{n}^-}(y, t). \quad (20)$$

If, in addition, electroneutrality is assumed, i.e.

$$c_{\text{n}^-}(y, t) = c_{\text{Li}^+}(y, t), \quad (21)$$

then

$$c_{\text{Li}_0}(y, t) + c_{\text{n}^-}(y, t) = c_{\text{Li}_0}(y, t) + c_{\text{Li}^+}(y, t) = c_0. \quad (22)$$

Eq. (22) states that the total lithium concentration in the electrolyte, including immobile and interstitial Li, must be constant and equal to the maximal concentration under all conditions. At the same time, the present modelling work permits the formation of gradients for interstitial (electrochemically active and mobile) lithium, i.e. Li^+ .

When Eqs. (18) and (19) are solved under electroneutrality conditions (Eq. (21)), they can be reduced to the diffusion equation with respect to $c_{\text{Li}^+}(y, t)$, according to

$$\frac{\partial c_{\text{Li}^+}}{\partial t} = \frac{2D_{\text{Li}^+}D_{\text{n}^-}}{D_{\text{Li}^+} + D_{\text{n}^-}} \frac{\partial^2 c_{\text{Li}^+}}{\partial y^2} + r, \quad (23.1)$$

$$c_{\text{Li}^+}(y, 0) = \delta c_0, \quad (23.2)$$

$$\frac{\partial c_{\text{Li}^+}(0, t)}{\partial y} = \frac{j_{\text{ct}}^{\text{n}}(t)}{z_{\text{Li}^+} F} = \frac{j_{\text{bat}}(t) - j_{\text{geo}}(t) - j_{\text{dl}}^{\text{n}}(t)}{2FD_{\text{Li}^+}}, \quad (23.3)$$

$$\frac{\partial c_{\text{Li}^+}(L, t)}{\partial y} = \frac{j_{\text{ct}}^{\text{p}}(t)}{z_{\text{Li}^+} F} = \frac{j_{\text{bat}}(t) - j_{\text{geo}}(t) - j_{\text{dl}}^{\text{p}}(t)}{2FD_{\text{Li}^+}}. \quad (23.4)$$

In addition, an expression for the electric field can be obtained [11,28].

$$E(y, t) = \frac{RT}{F} \frac{1}{c_{\text{Li}^+}(y, t)} \left\{ -\frac{j_{\text{ct}}^{\text{n}}(t)}{2FD_{\text{Li}^+}} + \frac{D_{\text{Li}^+} - D_{\text{n}^-}}{D_{\text{Li}^+} + D_{\text{n}^-}} \left[\frac{\partial c_{\text{Li}^+}(y, t)}{\partial y} - \frac{j_{\text{ct}}^{\text{n}}(t)}{2FD_{\text{Li}^+}} \right] \right\}. \quad (24)$$

The total mass-transfer overpotential across the LiPON electrolyte can then be given by

$$\eta_{\text{mt}}^{\text{LiPON}}(t) = \frac{RT}{F} \ln \left(\frac{c_{\text{Li}^+}(L, t)}{c_{\text{Li}^+}(0, t)} \right) - \int_0^L E(y, t) dy, \quad (25)$$

where the first term on the right-hand side is the as-denoted Nernstian and the second term the Galvanic component.

2.4. Diffusion and migration in the LiCoO₂ electrode

The LiCoO₂ (LCO) electrode consists of trivalent cobalt oxide in which lithium ions are intercalated ($\text{LiCo}^{\text{III}}\text{O}_2$). In the present work it is assumed that intercalated lithium is present inside the electrode in an ionic form (as $\text{Li}^{\oplus}$) and that the electrons can move independently. Motion of both $\text{Li}^{\oplus}$ and e^- obeys the Nernst-Planck flux equation

$$J_j = -D_j(y, t) \frac{\partial c_j}{\partial y} + \frac{z_j F}{RT} D_j(y, t) c_j E, \quad (26)$$

where subscript j represents either $\text{Li}^{\oplus}$ or e^- . The diffusion coefficients $D_{\text{Li}^{\oplus}}$ and D_{e^-} in Eq. (26) are a function of the coordinate y and time t . The reason for this generalization is to make diffusion coefficients dependent on the local concentrations of the electrochemically active species, since solid-state diffusion depends

strongly on the local electrochemical environment [29–31]. In this work, it is assumed that this holds for both $\text{Li}^\oplus$ and e^- . In addition, it will be assumed that changes in local values of diffusion coefficients $D_{\text{Li}^\oplus}$ and D_{e^-} are similarly dependent through a common dimensionless time- and space-dependent factor $\beta(y, t)$, i.e.

$$D_{\text{Li}^\oplus}(y, t) = D_{\text{Li}^\oplus}^0 \beta(y, t) \quad \text{and} \quad D_{e^-}(y, t) = D_{e^-}^0 \beta(y, t), \quad (27)$$

where $D_{\text{Li}^\oplus}^0$ and $D_{e^-}^0$ 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 $\text{Li}^\oplus$ and e^- , can be represented by

$$\frac{\partial c_{\text{Li}^\oplus}}{\partial t} = -\frac{\partial j_{\text{Li}^\oplus}}{\partial y}, \quad (28.1)$$

$$c_{\text{Li}^\oplus}(y, 0) = c_{\text{Li}^\oplus}^{\text{eq}}, \quad (28.2)$$

$$j_{\text{Li}^\oplus}(L, t) = \frac{j_{\text{ct}}^p(t) + j_{\text{dl}}^p(t)}{z_{\text{Li}^\oplus} F}, \quad (28.3)$$

$$j_{\text{Li}^\oplus}(L + M, t) = 0, \quad (28.4)$$

and

$$\frac{\partial c_{e^-}}{\partial t} = -\frac{\partial j_{e^-}}{\partial y}, \quad (29.1)$$

$$c_{e^-}(y, 0) = c_{e^-}^{\text{eq}}, \quad (29.2)$$

$$j_{e^-}(L, t) = 0, \quad (29.3)$$

$$j_{e^-}(L + M, t) = \frac{j_{\text{bat}}(t) - j_{\text{geo}}(t)}{z_{e^-} F}. \quad (29.4)$$

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 $j_{\text{bat}}(t) - j_{\text{geo}}(t) = j_{\text{ct}}^p(t) + j_{\text{dl}}^p(t)$. 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 electro-neutrality conditions, i.e. $c_{\text{LiCoO}_2}(y, t) = c_{\text{Li}^\oplus}(y, t) = c_{e^-}(y, t)$ and performing further derivations (see Refs. [11,28]), this leads to the following diffusion equation with respect to $c_{\text{LiCoO}_2}(y, t)$.

$$\frac{\partial c_{\text{LiCoO}_2}}{\partial t} = D_p^0 \frac{\partial}{\partial y} \left(\beta(y) \frac{\partial c_{\text{LiCoO}_2}}{\partial y} \right) = \frac{\partial}{\partial y} \left(D_p(y) \frac{\partial c_{\text{LiCoO}_2}}{\partial y} \right), \quad (30.1)$$

$$c_{\text{LiCoO}_2}(y, 0) = c_{\text{LiCoO}_2}^{\text{eq}}, \quad (30.2)$$

$$\frac{\partial c_{\text{LiCoO}_2}(L, t)}{\partial y} = \frac{j_{\text{bat}}(t) - j_{\text{geo}}(t)}{2D_{\text{Li}^\oplus}(L, t)F}, \quad (30.3)$$

$$\frac{\partial c_{\text{LiCoO}_2}(L + M, t)}{\partial y} = \frac{j_{\text{bat}}(t) - j_{\text{geo}}(t)}{2D_{e^-}(L + M, t)F}, \quad (30.4)$$

where $D_p^0 = \frac{2D_{\text{Li}^\oplus}^0 D_{e^-}^0}{D_{\text{Li}^\oplus}^0 + D_{e^-}^0}$ and $D_p = \frac{2D_{\text{Li}^\oplus} D_{e^-}}{D_{\text{Li}^\oplus} + D_{e^-}}$. 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

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
L	3.62 ^b	μm
M	8.08 ^b	μm
A	3.36 ^a	cm^2
k_r	$8.00 \cdot 10^{-7}$	$\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$
k_1^s	$1.53 \cdot 10^{-11}$	$\text{m}^{2.5} \text{mol}^{-0.5} \text{s}^{-1}$
k_2^s	$1.09 \cdot 10^{-9}$	m s^{-1}
α^p	0.5 ^c	—
α^n	0.5 ^c	—
$D_{\text{Li}^\oplus}^0$	$1.21 \cdot 10^{-13}$	$\text{m}^2 \text{s}^{-1}$
$D_{e^-}^0$	$5.06 \cdot 10^{-13}$	$\text{m}^2 \text{s}^{-1}$
$D_{\text{Li}^\oplus}$	$1.73 \cdot 10^{-16}$	$\text{m}^2 \text{s}^{-1}$
D_{e^-}	$5.69 \cdot 10^{-16}$	$\text{m}^2 \text{s}^{-1}$
$c_{\text{LiCoO}_2}^{\text{max}}$	$3.22 \cdot 10^{4d}$	mol m^{-3}
$c_{\text{Li}}^s = \bar{c}_{\text{Li}}$	$7.64 \cdot 10^{4c}$	mol m^{-3}
c_0	61141	mol m^{-3}
δ	0.64	—
ρ_s	18.3	Ωcm^2
c_{dl}^p	$5.30 \cdot 10^{-7}$	F cm^{-2}
c_{dl}^n	$1.74 \cdot 10^{-8}$	F cm^{-2}
c_{geo}	$3.24 \cdot 10^{-9}$	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.

Fig. 4. Measured (symbols) and simulated (lines) voltage discharge and relaxation curves at various C-rates: 0.2C (a), 0.5C (b), 1.0C (c), 2.0C (d), 4.0C (e), and 6.0C (f). Note that the voltage discharge curves are shown as a function of extracted charge and the relaxation periods after current interruption as a function of time.

$$E(y, t) = \frac{RT}{F} \frac{1}{\beta(y, t) c_{\text{LiCoO}_2}(y, t)} \left\{ \frac{D_{\text{Li}^+}^0 - D_{e-}^0}{D_{\text{Li}^+}^0 + D_{e-}^0} \frac{\partial c_{\text{LiCoO}_2}(y, t)}{\partial y} - \frac{2D_{\text{Li}^+}^0}{D_{\text{Li}^+}^0 + D_{e-}^0} \frac{j_{\text{bat}}(t) - j_{\text{geo}}(t)}{F} \right\} \quad (31)$$

The mass-transfer overpotential for Li^+ ions across p is then given by

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

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 μm , 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 μm . 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 $\text{Li}^{\oplus}$ (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 LiCoO_2 electrode. It can be seen that at low to medium lithium concentrations ($0.5 \leq x \leq 0.75$), representing the so-called second hexagonal phase [34], the diffusion coefficients are relatively constant. In the two-phase coexistence region ($0.75 \leq x \leq 0.92$), 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 $\text{Li}^{\oplus}$ 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, Li_xCoO_2 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 (c_{Li^+}) 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 (c_0) 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 1 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 ($\partial c_{\text{Li}^+}(y, t)/\partial y$), 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 $1/c_{\text{Li}^+}(y, t)$ 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 1 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

Fig. 5. Optimized diffusion coefficients of $\text{Li}^{\oplus}$ (solid line) and e^- (dotted line) as a function of lithium stoichiometry in the positive electrode material.

Fig. 6. Mobile Li^+ concentration (c_{Li^+}) in the LiPON electrolyte (a, d) and electric field (b, e) as a function of time and position across the electrolyte. Development of the individual electrolyte overpotentials as a function of time (c, f). The time axis represents the complete constant current discharge and successive current interruption period for a 1C (a–c) and 4C discharge rate (d–f).

C-rates.

4.3. Positive electrode

Fig. 7a shows the development of the $\text{Li}^{\oplus}$ 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^+ concentration in the positive electrode as a function of time and position (a, e); Li^+ 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).

Fig. 8. EMF voltage curve as a function of x in Li_xCoO_2 including voltages in the bulk (crosses) and at the surface (circles) at the end of discharging at 1 (red) and 4C (green). The diffusion overpotentials (η_d^p) at the end of discharging are also indicated. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

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. Fig. 7h shows these overpotentials at a 4C-rate. 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 . Fig. 8 also shows the voltages related to the bulk (crosses) and surface (circles) concentrations at the end of 1C (red) and 4C (green) discharging. It should be noted that the bulk-related voltages are equal to the voltages observed after long-term current interruption. As explained in Section 2.1, the diffusion overpotential (η_d^p) has been defined as the difference between the voltage at the electrode surface under current loading conditions and at equilibrium. 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 ($x \approx 1$). 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 (η_{ct}^p) and by the diffusion losses inside p (η_d^p) (red). In particular, the diffusion losses in p increase significantly at the end of discharging because the ionic concentrations differences increase between the electrode surface and bulk, as discussed above. The same also holds for the mass-transfer overpotential (η_{mt}^p) 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 η_s) and charge-transfer at the n /electrolyte surface (magenta area representing η_{ct}^n) 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 (η_{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 charge-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. $D_{\text{Li}^+} = D_{e^-}$. 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

Fig. 9. Discharge EMF curve, including the various simulated overpotential contributions (a, d); all overpotentials during discharge (b, e); all overpotentials during relaxation after discharge (c, f). Fig. 9a–c represent the 1C-rate discharge and Fig. 9d–f the 4C-rate discharge. The insets in (c) and (f) show an enlargement of the start of the relaxation period.

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 (η_d^p) 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

Fig. 10. Simulated diffusion coefficients and ionic concentration profiles for three different cases: $D_{Li^+} < D_{e^-}$ (a, b); $D_{Li^+} = D_{e^-}$ (c, d) and; $D_{Li^+} > D_{e^-}$ (e, f). The insets in a, c, and e show the EMF voltage (black line), the measured voltage curve at 1C (symbols), and simulated voltage (blue line) curve at 1C. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

simulations, i.e. $D_{Li^+} > D_{e^-}$. 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 $D_{Li^+} < D_{e^-}$ (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 $LiFePO_4$ 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_{mt}^{LiPON}). 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_{mt}^{LiPON}). 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,

Fig. 11. (a) Measured (line with squares) and simulated (line with circles) battery impedance; (b) all individual simulated impedance contributions, including the total battery impedance (black); (c) enlargement of the smallest impedance contributions shown in (b).

applications in which mid-to-high frequency dynamic loads are applied, such as microelectromechanical systems (MEMS) [16].

The diffusion (Z_d^p) and mass-transfer (Z_{mt}^p) 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° . 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.

The Ohmic series resistance (Z_s) is also clearly visible in Fig. 11c, which obviously is a frequency-independent real value.

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/LiCoO₂ 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_{LiCoO_2} is substituted by c to economize notations:

$$\frac{\partial c}{\partial t} = D_p^0 \frac{\partial}{\partial y} \left(\beta(y) \frac{\partial c}{\partial y} \right) = \frac{\partial}{\partial y} \left(D_p(y) \frac{\partial c}{\partial y} \right), \quad (\text{A.1.1})$$

$$c(y, 0) = c_0, \quad (\text{A.1.2})$$

$$\frac{\partial c(L, t)}{\partial y} = \frac{j_{bat}(t) - j_{geo}(t)}{2D_{Li^+}(L, t)F}, \quad (A.1.3)$$

$$\frac{\partial c(L + M, t)}{\partial y} = -\frac{j_{bat}(t) - j_{geo}(t)}{2D_{e^-}(L + M, t)F}, \quad (A.1.4)$$

where $D_p^0 = \frac{2D_{Li^+}^0 D_{e^-}^0}{D_{Li^+}^0 + D_{e^-}^0}$ and $D_p = \frac{2D_{Li^+} D_{e^-}}{D_{Li^+} + D_{e^-}}$. For the sake of brevity, the boundary conditions in Eq. (A.1.3) and Eq. (A.1.4) are further used as

$$g_0(t) = \frac{j_{bat}(t) - j_{geo}(t)}{2D_{Li^+}^0 F}, \quad (A.2.1)$$

$$g_L(t) = -\frac{j_{bat}(t) - j_{geo}(t)}{2D_{e^-}^0 F}. \quad (A.2.2)$$

Substituting Eq. (A.2.1) and (A.2.2), into Eq. (A.1) yields

$$\frac{\partial c(x, t)}{\partial t} = D_p^0 \frac{\partial}{\partial y} \left(\beta(x) \frac{\partial c}{\partial x} \right) = \frac{\partial}{\partial y} \left(D_p(y) \frac{\partial c}{\partial y} \right), \quad (A.3.1)$$

$$c(x, 0) = c_0, \quad (A.3.2)$$

$$\beta(x) \frac{\partial c(x, t)}{\partial x} \Big|_{x=0} = g_0(t), \quad (A.3.3)$$

$$\beta(x) \frac{\partial c(x, t)}{\partial x} \Big|_{x=L} = g_L(t). \quad (A.3.4)$$

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 Δt 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

$$\beta(x_i + h/2, t) \frac{\partial c(x_i + h/2, t)}{\partial x} \approx \beta(x_i + h/2, t) \frac{c(x_i + h, t) - c(x_i, t)}{h} \quad (A.4.1)$$

and

$$\beta(x_i - h/2, t) \frac{\partial c(x_i - h/2, t)}{\partial x} \approx \beta(x_i - h/2, t) \frac{c(x_i, t) - c(x_i - h, t)}{h}, \quad (A.4.2)$$

respectively.

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

$$\frac{c(x_i, t_j + \Delta t) - c(x_i, t_j)}{\Delta t} = \frac{D_p^0}{h} \left[\beta(x_i + h/2, t) \frac{c(x_i + h, t) - c(x_i, t)}{h} - \beta(x_i - h/2, t) \frac{c(x_i, t) - c(x_i - h, t)}{h} \right]. \quad (A.5)$$

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

$$\frac{c(x_i, t_j + \Delta t) - c(x_i, t_j)}{\Delta t} = \frac{D_p^0}{2h^2} \left[(\beta(x_i, t) + \beta(x_i + h, t))(c(x_i + h, t) - c(x_i, t)) - (\beta(x_i - h, t) + \beta(x_i, t))(c(x_i, t) - c(x_i - h, t)) \right]. \quad (A.6)$$

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

$$\begin{aligned} \frac{c_i^{j+1} - c_i^j}{\Delta t} &= D_p^0 \frac{(\beta_i^j + \beta_{i+1}^j)(c_{i+1}^j - c_i^j) - (\beta_{i-1}^j + \beta_i^j)(c_i^j - c_{i-1}^j)}{2h^2} \\ &= D_p^0 \frac{(\beta_i^j + \beta_{i+1}^j)c_{i+1}^j - (\beta_{i+1}^j + 2\beta_i^j + \beta_{i-1}^j)c_i^j + (\beta_{i-1}^j + \beta_i^j)c_{i-1}^j}{2h^2}, \end{aligned} \quad (A.7)$$

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

$$\frac{\beta_1^j (c_2^j - c_0^j)}{2h} = g_0^j, \quad (A.8.1)$$

$$\frac{\beta_n^j (c_{n+1}^j - c_{n-1}^j)}{2h} = g_L^j. \quad (A.8.2)$$

Note that the concentrations at locations c_0^j and c_{n+1}^j 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

$$\begin{aligned} c_i^{j+1} &= c_i^j + \frac{D_p^0 \Delta t}{h} \frac{(\beta_i^j + \beta_{i+1}^j)(c_{i+1}^j - c_i^j) - (\beta_{i-1}^j + \beta_i^j)(c_i^j - c_{i-1}^j)}{2h}, \\ \text{for } i &= 1 \dots n \end{aligned} \quad (A.9.1)$$

$$c_0^j = c_2^j - 2g_0^j \frac{h}{\beta_1^j}, \quad (A.9.2)$$

$$c_{n+1}^j = c_{n-1}^j + 2g_L^j \frac{h}{\beta_n^j}. \quad (A.9.3)$$

Substituting Eq. (A.9.2) and (A.9.3) into Eq. (A.9.1) for $i = 1$ and $i = n$, accordingly and assuming $\beta_0^j \approx \beta_1^j$ and $\beta_{n+1}^j \approx \beta_n^j$, finally produces

the following set of finite difference equations

$$c_1^{j+1} = c_1^j + D_p^0 \frac{\Delta t}{h} \left\{ \frac{(\beta_2^j + \beta_1^j)(c_2^j - c_1^j)}{2h} - \frac{\beta_1^j}{h} \left(c_1^j - c_2^j + \frac{2hg_0^j}{\beta_1^j} \right) \right\}, \text{ for } i = 1 \quad (\text{A.10.1})$$

$$c_i^{j+1} = c_i^j + D_p^0 \frac{\Delta t}{h} \frac{(\beta_i^j + \beta_{i+1}^j)(c_{i+1}^j - c_i^j) - (\beta_{i-1}^j + \beta_i^j)(c_i^j - c_{i-1}^j)}{2h}, \text{ for } i = 2 \dots n-1 \quad (\text{A.10.2})$$

$$\mathbf{c}^{j+1} = \mathbf{c}^j + D_p^0 \frac{\Delta t}{h^2} \mathbf{H}^j \mathbf{c}^j + D_p^0 \frac{\Delta t}{h} \mathbf{b}^j, \quad (\text{A.12})$$

where.

$$\mathbf{c}^j = \begin{pmatrix} c_1^j \\ c_2^j \\ \vdots \\ c_n^j \end{pmatrix}, \quad (\text{A.13.1})$$

$$\mathbf{H}^j = \frac{1}{2} \begin{pmatrix} -(3\beta_1^j + \beta_2^j) & (3\beta_1^j + \beta_2^j) & 0 & \dots & 0 \\ (\beta_1^j + \beta_2^j) & -\beta_1^j - 2\beta_2^j - \beta_3^j & (\beta_2^j + \beta_3^j) & \dots & 0 \\ 0 & (\beta_2^j + \beta_3^j) & -\beta_2^j - 2\beta_3^j - \beta_4^j & \dots & 0 \\ 0 & \dots & 0 & (3\beta_n^j + \beta_{n-1}^j) & -(3\beta_n^j + \beta_{n-1}^j) \end{pmatrix}, \quad (\text{A.13.2})$$

$$c_n^{j+1} = c_n^j + D_p^0 \frac{\Delta t}{h} \left\{ \frac{\beta_n^j}{h} \left(c_{n-1}^j - c_n^j + 2g_L^j \frac{h}{\beta_n^j} \right) - \frac{(\beta_n^j + \beta_{n-1}^j)(c_n^j - c_{n-1}^j)}{2h} \right\}, \text{ for } i = n. \quad (\text{A.10.3})$$

$$\mathbf{b}^j = \begin{pmatrix} -2g_0^j \\ 0 \\ \vdots \\ 0 \\ 2g_L^j \end{pmatrix}. \quad (\text{A.13.3})$$

After rearrangements, Eq. (A.10) can be reduced to

$$c_1^{j+1} = c_1^j + D_p^0 \frac{\Delta t}{h} \left\{ \frac{(\beta_2^j + 3\beta_1^j)(c_2^j - c_1^j)}{2h} - 2g_0^j \right\}, \text{ for } i = 1 \quad (\text{A.11.1})$$

$$c_i^{j+1} = c_i^j + D_p^0 \frac{\Delta t}{h} \frac{(\beta_i^j + \beta_{i+1}^j)(c_{i+1}^j - c_i^j) - (\beta_{i-1}^j + \beta_i^j)(c_i^j - c_{i-1}^j)}{2h}, \text{ for } i = 2 \dots n-1 \quad (\text{A.11.2})$$

$$c_n^{j+1} = c_n^j + D_p^0 \frac{\Delta t}{h} \left\{ \frac{(3\beta_n^j + \beta_{n-1}^j)(c_{n-1}^j - c_n^j)}{2h} + 2g_L^j \right\}, \text{ for } i = n. \quad (\text{A.11.3})$$

It is convenient to write Eq. (A.11) in matrix form as

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

$$\mathbf{H}^j = \beta \begin{pmatrix} -2 & 2 & 0 & \dots & 0 \\ 1 & -2 & 1 & \dots & 0 \\ 0 & 1 & -2 & \dots & 0 \\ 0 & \dots & 0 & 2 & -2 \end{pmatrix}. \quad (\text{A.14})$$

References

- [1] J.G. Kim, B. Son, S. Mukherjee, N. Schuppert, A. Bates, O. Kwon, M.J. Choi, H.Y. Chung, S. Park, A review of lithium and non-lithium based solid state batteries, *J. Power Sources*. 282 (2015) 299–322, <https://doi.org/10.1016/j.jpowsour.2015.02.054>.
- [2] K. Takada, Progress in solid electrolytes toward realizing solid-state lithium batteries, *J. Power Sources*. 394 (2018) 74–85, <https://doi.org/10.1016/j.jpowsour.2018.05.003>.
- [3] F. Zheng, M. Kotobuki, S. Song, M.O. Lai, L. Lu, Review on solid electrolytes for all-solid-state lithium-ion batteries, *J. Power Sources* 389 (2018) 198–213, <https://doi.org/10.1016/j.jpowsour.2018.04.022>.
- [4] P.H.L. Notten, F. Roozeboom, R.A.H. Niessen, L. Baggetto, 3-D integrated all-solid-state rechargeable batteries, *Adv. Mater.* 19 (2007) 4564–4567, <https://doi.org/10.1002/adma.200702398>.
- [5] Y. Wang, B. Liu, Q. Li, S. Cartmell, S. Ferrara, Z.D. Deng, J. Xiao, Lithium and lithium ion batteries for applications in microelectronic devices: a review, *J. Power Sources* 286 (2015) 330–345, <https://doi.org/10.1016/j.jpowsour.2015.02.054>.

- j.jpowsour.2015.03.164.
- [6] Y. Zhao, P. Stein, Y. Bai, M. Al-siraj, Y. Yang, B. Xu, A review on modeling of electro-chemo-mechanics in lithium-ion batteries, *J. Power Sources*. 413 (2019) 259–283, doi:S0378775318313624.
 - [7] A.A. Franco, Multiscale modelling and numerical simulation of rechargeable lithium ion batteries: concepts, methods and challenges, *RSC Adv.* 3 (2013) 13027–13058, <https://doi.org/10.1039/c3ra23502e>.
 - [8] A. Fotouhi, D.J. Auger, K. Propp, S. Longo, M. Wild, A review on electric vehicle battery modelling: from Lithium-ion toward Lithium-Sulphur, *Renew. Sustain. Energy Rev.* 56 (2016) 1008–1021, <https://doi.org/10.1016/j.rser.2015.12.009>.
 - [9] A. Jokar, B. Rajabloo, M. Desilets, M. Lacroix, Review of simplified Pseudo-two-Dimensional models of lithium-ion batteries, *J. Power Sources* 327 (2016) 44–55, <https://doi.org/10.1016/j.jpowsour.2016.07.036>.
 - [10] A.A. Franco, A. Rucci, D. Brandell, C. Frayret, M. Gaberscek, P. Jankowski, P. Johansson, Boosting rechargeable batteries R&D by multiscale modeling: myth or reality? *Chem. Rev.* 119 (2019) 4569–4627, <https://doi.org/10.1021/acs.chemrev.8b00239>.
 - [11] D.L. Danilov, R.A.H. Niessen, P.H.L. Notten, Modeling all-solid-state Li-ion batteries, *J. Electrochem. Soc.* 158 (2011) A215–A222, <https://doi.org/10.1149/1.3521414>.
 - [12] S.D. Fabre, D. Guy-Bouysson, P. Bouillon, F. Le Cras, C. Delacourt, Charge/Discharge simulation of an all-solid-state thin-film battery using a one-dimensional model, *J. Electrochem. Soc.* 159 (2012) A104, <https://doi.org/10.1149/2.041202jes>.
 - [13] A. Bates, S. Mukherjee, S. Schuppert, B. Son, J.G. Kim, S. Park, Modeling and simulation of 2D lithium-ion solid state battery, *Int. J. Energy Res.* 39 (2015) 1505–1518, <https://doi.org/10.1002/er.3344>.
 - [14] R. Behrou, K. Maute, Numerical modeling of damage evolution phenomenon in solid-state lithium-ion batteries, *J. Electrochem. Soc.* 164 (2017) A2573–A2589, <https://doi.org/10.1149/2.1101712jes>.
 - [15] H.-K. Tian, Y. Qi, Simulation of the effect of contact area loss in all-solid-state Li-ion batteries, *J. Electrochem. Soc.* 164 (2017) E3512–E3521, <https://doi.org/10.1149/2.0481711jes>.
 - [16] K. Teichert, K. Oldham, Modeling cyclic capacitive loading of thin-film batteries, *J. Electrochem. Soc.* 164 (2017) A360–A369, <https://doi.org/10.1149/2.1141702jes>.
 - [17] K. Teichert, K. Oldham, Simulation of thin-film battery response to periodic loading by a transition matrix approximation using boundary and nonlinearity error analysis, *J. Energy Storage*. 14 (2017) 94–105, <https://doi.org/10.1016/j.est.2017.09.014>.
 - [18] N. Kazemi, D.L. Danilov, L. Haverkate, N.J. Dudney, S. Unnikrishnan, P.H.L. Notten, Modeling of all-solid-state thin-film Li-ion batteries: accuracy improvement, *Solid State Ion.* 334 (2019) 111–116, <https://doi.org/10.1016/j.ssi.2019.02.003>.
 - [19] K. Becker-Steinberger, S. Funken, M. Landstorfer, K. Urban, A mathematical model for all solid-state lithium ion batteries, *ECS Trans.* 25 (2010) 285–296, <https://doi.org/10.1149/1.3393864>.
 - [20] M. Landstorfer, S. Funken, T. Jacob, An advanced model framework for solid electrolyte intercalation batteries, *Phys. Chem. Chem. Phys.* 13 (2011) 12817–12825, <https://doi.org/10.1039/c0cp02473b>.
 - [21] N.J. Dudney, Solid-state thin-film rechargeable batteries, *Mater. Sci. Eng. B.* 116 (2005) 245–249, <https://doi.org/10.1016/j.mseb.2004.05.045>.
 - [22] K.J. Vetter, *Electrochemical Kinetics: Theoretical and Experimental Aspects*, Academic Press, New York, NY, 1967.
 - [23] Y. Aizawa, K. Yamamoto, T. Sato, H. Murata, R. Yoshida, C.A.J. Fisher, T. Kato, Y. Iriyama, T. Hirayama, In situ electron holography of electric potentials inside a solid-state electrolyte: effect of electric-field leakage, *Ultramicroscopy* 178 (2017) 20–26, <https://doi.org/10.1016/j.ultramic.2016.07.015>.
 - [24] K. Yamamoto, Y. Iriyama, T. Asaka, T. Hirayama, H. Fujita, C.A.J. Fisher, K. Nonaka, Y. Sugita, Z. Ogumi, Dynamic visualization of the electric potential in an all-solid-state rechargeable lithium battery, *Angew. Chem. Int. Ed.* 49 (2010) 4414–4417, <https://doi.org/10.1002/anie.200907319>.
 - [25] S. Braun, C. Yada, A. Latz, Thermodynamically consistent model for space-charge-layer formation in a solid electrolyte, *J. Phys. Chem. C* 119 (2015) 22281–22288, <https://doi.org/10.1021/acs.jpcc.5b02679>.
 - [26] N.J.J. de Klerk, M. Wagemaker, Space-charge layers in all-solid-state batteries: important or negligible? *ACS Appl. Energy Mater.* 1 (2018) 5609–5618, <https://doi.org/10.1021/acs.aem.8b01141>.
 - [27] L. Le Van-Jodin, A. Claudel, C. Secouard, F. Sabary, J.P. Barnes, S. Martin, Role of the chemical composition and structure on the electrical properties of a solid state electrolyte: case of a highly conductive LiPON, *Electrochim. Acta* 259 (2018) 742–751, <https://doi.org/10.1016/j.electacta.2017.11.021>.
 - [28] D. Danilov, P.H.L. Notten, Mathematical modelling of ionic transport in the electrolyte of Li-ion batteries, *Electrochim. Acta* 53 (2008) 5569–5578, <https://doi.org/10.1016/j.electacta.2008.02.086>.
 - [29] H. Xia, L. Lu, G. Ceder, Li diffusion in LiCoO₂ thin films prepared by pulsed laser deposition, *J. Power Sources* 159 (2006) 1422–1427, <https://doi.org/10.1016/j.jpowsour.2005.12.012>.
 - [30] J. Barker, R. Pynenburg, R. Koksang, M.Y. Saidi, An electrochemical investigation into the lithium insertion properties of Li_xCoO₂, *Electrochim. Acta* 41 (1996) 2481–2488, [https://doi.org/10.1016/0013-4686\(96\)00036-9](https://doi.org/10.1016/0013-4686(96)00036-9).
 - [31] J. Xie, N. Imanishi, T. Matsumura, A. Hirano, Y. Takeda, O. Yamamoto, Orientation dependence of Li-ion diffusion kinetics in LiCoO₂ thin films prepared by RF magnetron sputtering, *Solid State Ion.* 179 (2008) 362–370, <https://doi.org/10.1016/j.ssi.2008.02.051>.
 - [32] D. Li, D.L. Danilov, J. Xie, L. Raijmakers, L. Gao, Y. Yang, P.H.L. Notten, Degradation mechanisms of C₆/LiFePO₄ batteries: experimental analyses of calendar aging, *Electrochim. Acta* 190 (2016) 1124–1133, <https://doi.org/10.1016/j.electacta.2015.12.161>.
 - [33] D. Li, D. Danilov, L. Gao, Y. Yang, P.H.L. Notten, Degradation mechanisms of C₆/LiFePO₄ batteries: experimental analyses of cycling-induced aging, *Electrochim. Acta* 210 (2016) 445–455, <https://doi.org/10.1016/j.electacta.2016.05.091>.
 - [34] J.N. Reimers, J.R. Dahn, Electrochemical and in situ X-ray diffraction studies of lithium intercalation in Li_xCoO₂, *J. Electrochem. Soc.* 139 (1992) 2091–2097, <https://doi.org/10.1149/1.2221184>.
 - [35] S. Larfaillou, D. Guy-Bouysson, F. Le Cras, S. Franger, Comprehensive characterization of all-solid-state thin films commercial microbatteries by Electrochemical Impedance Spectroscopy, *J. Power Sources* 319 (2016) 139–146, <https://doi.org/10.1016/j.jpowsour.2016.04.057>.
 - [36] J.C. Bachman, S. Muy, A. Grimaud, H. Chang, N. Pour, S.F. Lux, O. Paschos, F. Maglia, S. Lupat, P. Lamp, L. Giordano, Y. Shao-Horn, Inorganic solid-state electrolytes for lithium batteries: mechanisms and properties governing ion conduction, *ACS Chem. Rev.* 116 (2016) 140–162, <https://doi.org/10.1021/acs.chemrev.5b00563>.
 - [37] J. Molenda, A. Stoklosa, T. Bak, Modification in the electronic structure of cobalt bronze Li_xCoO₂ and the resulting electrochemical properties, *Solid State Ion.* 36 (1989) 53–58, [https://doi.org/10.1016/0167-2738\(89\)90058-1](https://doi.org/10.1016/0167-2738(89)90058-1).
 - [38] M. Ménétrier, I. Saadoun, S. Lecasseur, C. Delmas, The insulator – metal transition upon lithium deintercalation from LiCoO₂: electronic properties and ⁷Li NMR study, *J. Mater. Chem.* 9 (1999) 1135–1140, <https://doi.org/10.1039/A900016j>.
 - [39] N. Imanishi, M. Fujiyoshi, Y. Takeda, O. Yamamoto, M. Tabuchi, Preparation and ⁷Li-NMR study of chemically delithiated Li_{1-x}CoO₂ (0 < x < 0.5), *Solid State Ion.* 118 (1999) 121–128, [https://doi.org/10.1016/S0167-2738\(98\)00441-X](https://doi.org/10.1016/S0167-2738(98)00441-X).
 - [40] B. Put, P.M. Vereecken, A. Stesmans, On the chemistry and electrochemistry of LiPON breakdown, *J. Mater. Chem. A* 6 (2018) 4848–4859, <https://doi.org/10.1039/c7ta07928a>.
 - [41] X. Zhang, T.W. Verhallen, F. Labohm, M. Wagemaker, Direct observation of Li-ion transport in electrodes under nonequilibrium conditions using Neutron depth profiling, *Adv. Energy Mater.* 5 (2015) 1–8, <https://doi.org/10.1002/aenm.201500498>.
 - [42] M. Haruta, S. Shiraki, T. Suzuki, A. Kumatani, T. Ohsawa, Y. Takagi, R. Shimizu, T. Hitosugi, Negligible “negative space-charge layer effects” at oxide-electrolyte/electrode interfaces of thin-film batteries, *Nano Lett.* 15 (2015) 1498–1502, <https://doi.org/10.1021/nl5035896>.