Modeling all-solid-state Li-ion batteries

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Modeling All-Solid-State Li-Ion Batteries

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A mathematical model for all-solid-state Li-ion batteries is presented. The model includes the charge transfer kinetics at the electrode/electrolyte interface, diffusion of lithium in the intercalation electrode, and diffusion and migration of ions in the electrolyte. The model has been applied to the experimental data taken from a 10 μAh planar thin-film all-solid-state Li-ion battery, produced by radio frequency magnetron sputtering. This battery consists of a 320 nm thick polycrystalline LiCoO2 cathode and a metallic Li anode separated by 1.5 μm Li3PO4 solid-state electrolyte. Such thin-film batteries are nowadays often employed as power sources for various types of autonomous devices, including wireless sensor nodes and medical implants.

Mathematical modeling is an important tool to describe the performance of these batteries in these applications. The model predictions agree well with the galvanostatically measured voltage profiles. The simulations show that the transport limitations in the solid-state Li-ion batteries occur and amounts to at least half of the total overpotential. This contribution becomes even larger when the current density reaches 0.5 mA cm⁻² or higher. It is concluded from the simulations that significant concentration gradients develop in both the positive electrode and the solid-state electrolyte during a high current (dis)charge.

All-solid-state batteries are a quickly growing multimillion-dollar business, which nowadays have a large beneficial impact on many applications, such as autonomous devices for ambient intelligence and medical implants. To describe the performance of these batteries under various conditions, mathematical modeling of the Li-ion system was initiated in the mid-1980s. Simulating discharge voltage curves of Li-ion batteries already dates back to the early 1980s.1 Interesting reviews dealing with the mathematical modeling of Li-ion batteries can be found in the literature.2-5 These models are mainly based on the porous electrode theory developed by Newman.6

Alternatively, equivalent electronic network models have been presented for various types of rechargeable batteries.7-11 All these models are based on the macroscopic descriptions of the fundamental electrochemical and physical processes occurring inside these systems, enabling the quantification of the relevant processes. The electronic network models were elegantly used to visualize these processes. Good agreement between the simulations and experimental results was reported.7-11 In addition, the degradation (aging) process of Li-ion batteries has also been addressed.12,13 However, all these reports did not address thin-film all-solid-state Li-ion batteries.

Solid-state Li-ion batteries represent the state-of-the-art in modern battery technology. Further improvement in the solid-state battery technology requires an in-depth understanding of the electrochemical processes involved, and the ability to simulate these processes is therefore a necessity. The ionically conductive solid-state electrolytes play an important role in the solid-state battery design (see Bates et al.14,15). Construction of a consistent mathematical model describing the conductivity in the solid-state electrolyte therefore forms an essential part of these models. A majority of all-solid-state Li-ion batteries have a flat thin-film design. An example of the cross section of an as-deposited solid-state Li-ion battery is given in Fig. 1a.

The aim of the current paper is to develop a mathematical model for all-solid-state Li-ion batteries, which includes all important physical and electrochemical characteristics and is capable of describing the basic functionality of these devices under a wide variety of operating conditions.

Theoretical Considerations

Electrochemical description.— A conventional solid-state Li-ion battery consists of the following elements (Fig. 1b). The negative electrode comprises metallic lithium. The positive electrode is based on the conventional LiCoO2 chemistry. The electrodes are separated by a solid-state electrolyte consisting of (either or not N-doped) an amorphous Li3PO4. Current collectors are placed on the outer sides of each electrode. Their influence on the electrochemical processes is considered to be negligible. In line with the battery morphology (Fig. 1a), a one-dimensional approach is adopted in the present work.

The basic electrochemical charge transfer reactions at the positive and negative electrodes can be represented by

\[
\text{LiCoO}_2 \rightleftharpoons \text{Li}_{1-x} \text{CoO}_2 + x \text{Li}^+ + xe^{-} \quad (0 \leq x \leq 0.5) \tag{1}
\]

\[
\text{Li}^+ + e^{-} \quad \text{Li} \tag{2}
\]

respectively. The positive electrode generally consists of trivalent cobalt oxide species, in which the lithium ions are intercalated (LiCoO2) for to provide electroneutrality. During charging, the trivalent cobalt is oxidized into four-valent cobalt (Co4+O2) and the excess of positive charge is liberated from the electrode in the form of Li+ ions. The Li+ ions cross the electrolyte and are reduced into metallic Li at the negative electrode. The reverse reactions take place during discharging.

Charge transfer kinetics.— Considering the discrete valence states for the Co3+/Co4+ redox couple, the number of electrons (n) transferred is unity. Denoting \( k_{1} \) and \( k_{-1} \) as the forward and backward reaction rate constants, respectively, the partial anodic \( (I_{a}) \) and cathodic currents \( (I_{c}) \) at the electrode surface can be represented by

\[
I_{a} = FAk_{1}a_{1}^{i}\text{LiCoO}_{2} \tag{3a}
\]

\[
I_{c} = FAk_{-1}a_{4}^{i}\text{CoO}_{2} \tag{3b}
\]

where \( F \) is the Faraday constant (96,485 C mol⁻¹), \( A \) is the electrode surface area (m²), and \( a_{i}^{i} \) is the (surface) activity of species \( i \) (mol m⁻³). The reaction rate constants are a function of the electrode potential,16 according to

\[
k_{1} = k_{1}^{i}e^{-\left(-\frac{\Delta G^{0}(RT)\text{Li}_{1-x}\text{CoO}_{2}}{RT}\right)} \tag{4a}
\]

\[
k_{-1} = k_{-1}^{i}e^{-\left(-\frac{\Delta G^{0}(RT)\text{LiCoO}_{2}}{RT}\right)} \tag{4b}
\]

where \( R \) is the gas constant (8.314 J mol⁻¹ K⁻¹), \( T \) is the absolute temperature (K), and \( \Delta G^{0} \) is the charge transfer coefficient for reaction Eq. 1. Introducing these equations into Eqs. 3a and 3b yields
To determine the charge transfer reaction at the positive electrode, when, in addition, the exchange current, as represented by Eq. 8, is introduced, the following current–potential dependence is obtained

\[ I_{LiCoO_2} = \frac{\alpha_{s}^{i}}{a_{Li}} \left[ e^{\eta_{ct}^{i}/F} - e^{-(1-\eta_{ct}^{i})/F} \right] \frac{\Delta a_{Li}}{\Delta a_{CoO_2}} \Delta L_{1}^{v} \]  

where \( \eta_{ct}^{i} \) and \( \Delta a_{Li} \) are the surface and bulk activities of the metallic Li (mol m\(^{-3}\)), \( \alpha_{Li} \) is the charge transfer coefficient for reaction Eq. 2, \( \eta_{ct}^{i} \) is the overpotential of the charge transfer reaction at the negative electrode, and the exchange current \( I_{Li}^{*} \) is given by

\[ I_{Li}^{*} = FAK \left( \alpha_{Li}^{v} \right)^{i} \eta_{ct}^{i} \]  

where \( K_{Li}^{v} \) is the standard rate constant for reaction Eq. 2. Obviously, the activity of metallic lithium is considered unity. Furthermore, it has been reported that the exchange current density for the metallic lithium electrodes is much larger than that for LiCoO\(_2\). In addition, it is expected that \( \eta_{ct}^{i} \) is much smaller than \( \eta_{ct}^{v} \) for LiCoO\(_2\). For convenience, the charge transfer kinetics of the metallic lithium reaction will therefore be neglected in this work.

**Diffusion and migration in the electrolyte.**—The Li\(_2\)PO\(_4\)-based solid-state electrolyte is a typical ionic conductor in which the conductivity is caused by the transport of Li\(^+\) ions only. Lithium oxide–phosphorus pentoxide (Li\(_2\)O–P\(_2\)O\(_5\)) is a classical glass-forming system. It is known that a quasi-two-dimensional polymeric network of P\(_2\)O\(_5\) is depolymerized in the presence of a modifier, such as Li\(_2\)O. This Li\(_2\)O-induced modification results in converting the bridging oxygen atoms to nonbridging oxygen atoms (nBO’s). The "weak electrolyte" models conclude that Li may reside in two types of states in the glass matrix and assume that the ionic conduction process is dominated by the ions, thermally populating the higher energy (mobile) sites. The chemical reaction of the ionization reaction
describes the transport process of immobile, oxygen-binded lithium (indicated by \( \text{Li}^0 \)) to mobile \( \text{Li}^+ \) ions leaving uncompensated negative charges (\( n^- \)) behind, which are chemically associated with the closest \( \text{NBO}^\circ \).

In Eq. 14, \( k_4 \) is the dissociation rate constant for the ionic generation reaction (\( s^{-1} \)) and \( k_j \) is the rate constant for the reverse recombination reaction (\( m^{-1} s^{-1} \)). Both constants obey Arrhenius law. Denoting the activity of mobile \( \text{Li}^+ \) ions by \( a_{\text{Li}^+} \) (mol m\(^{-3} \)), the activity of immobile \( \text{Li} \) ions by \( a_{\text{Li}^0} \) (mol m\(^{-3} \)), the total activity of \( \text{Li} \) atoms in the \( \text{Li}_2\text{P}_2\text{O}_7 \) matrix by \( a_0 \) (mol m\(^{-3} \)), and the fraction of \( \text{Li} \), which resides in equilibrium in the mobile state by \( \delta \), the equilibrium activity of the charge carriers can be represented by \( a_{\text{Li}^+}^{\text{eq}} = a_{\text{Li}^0} = \delta a_0 \). The equilibrium activity of immobile \( \text{Li} \) is consequently given by \( a_{\text{Li}^0}^{\text{eq}} = (1 - \delta)a_0 \). Under equilibrium conditions, the rates of the forward and backward reactions are equal (\( k_4 a_{\text{Li}^0}^{\text{eq}} = k_j a_{\text{Li}^+} a_{\text{Li}^0} \)), which implies that \( k_4 = k_j \delta a_0^2 / (1 - \delta) \). The overall rate of the charge carrier generation is given by \( r_4 = k_4 a_{\text{Li}^0}^{\text{eq}} \), & \( k_j a_{\text{Li}^+} \), and the net rate of the inverse reaction is given by the opposite number.

The net current passing the electrode/electrolyte interface induces an ionic mass and charge transport in the electrolyte. In the case of a flat geometry, it is reasonable to assume that the ionic transport in the electrolyte is also a one-dimensional process, which can be described by the Nernst–Planck equation:

\[
J_j = -D_j \frac{\partial a_j}{\partial y} + \frac{z_j F E}{RT} D_j \frac{\partial}{\partial t} a_j
\]

where \( J_j(y,t) \) is the flux of species \( j \) (mol m\(^{-2} s^{-1} \)) at a distance \( y \) from the surface of the negative electrode at any moment in time \( t \), \( D_j \) is the diffusion coefficient of \( j \) (m\(^{-2} s^{-1} \)), \( \partial a_j / \partial y \) is the concentration gradient (mol m\(^{-3} \)), \( E \) is the potential gradient (V m\(^{-1} \)), \( z_j \) is the valence (dimensionless), and \( a_j \) is the activity (mol m\(^{-3} \)) of species \( j \). The two terms on the right-hand side of Eq. 15 represent the diffusion and migration contributions to the ionic flux.

Denoting \( r_4 = r \) and \( r_5 = -r \) where \( r = k_4 a_{\text{Li}^0}^{\text{eq}} - k_j a_{\text{Li}^+} a_{\text{Li}^0} \), it can be shown that the two partial differential equations, describing the diffusion–migration process combined with the generation/ recombination reaction Eq. 14, can be represented by the following equations:

\[
\frac{\partial a_{\text{Li}^0}}{\partial t} = - \frac{\partial a_{\text{Li}^+}}{\partial y} + r
\]

\[
a_{\text{Li}^0}(y,0) = \delta a_0
\]

\[
J_{\text{Li}^0}(0,t) = \frac{I(t)}{z_{\text{Li}^0} F A}
\]

\[
J_{\text{Li}^0}(L,t) = \frac{I_{\text{LiCoO}_2}(t)}{z_{\text{Li}^0} F A}
\]

and

\[
\frac{\partial a_{\text{Li}^+}}{\partial t} = - \frac{\partial a_{\text{Li}^0}}{\partial y} + r
\]

\[
a_{\text{Li}^+}(y,0) = \delta a_0
\]

\[
J_{\text{Li}^+}(0,t) = 0
\]

\[
J_{\text{Li}^+}(L,t) = 0
\]

where \( I_{\text{LiCoO}_2}(t) \) and \( I_{\text{Li}^0}(t) \) are the charge transfer currents at the positive and negative electrodes, respectively. Equations 16a and 17a represent the mass balances, Eqs. 16b and 17b reflect the fact that at \( t = 0 \) no concentration profiles have been developed yet and hence that the activities of the charge carriers are equal to their equilibrium activities. Equations 16c, 16d, 17c, and 17d represent the flux conditions at the left and right boundaries of the electrolyte (see also Fig. 1b). Assuming that no side reactions take place, the current flowing through the battery can simply be represented by \( I(t) = I_{\text{LiCoO}_2}(t) = -I_{\text{Li}^0}(t) \). Equations 16 and 17 accommodate diffusion and migration of both charge carriers. In line with Eq. 15, the flux of each charge carrier is considered independently. Equations 16 and 17 are solved under the electroneutrality condition \( a_{\text{Li}^+}(t) = a_{\text{Li}^0}(0,t) = a_{\text{Li}^0}(y,t) + a(y,t) \). It can be shown that Eqs. 16 and 17 can be reduced to the diffusion equation with respect to \( a(y,t) \), according to

\[
\frac{\partial a}{\partial t} = \frac{2D_{\text{Li}^+} D_{\text{Li}^0}}{D_{\text{Li}^+} + D_{\text{Li}^0}} \frac{\partial^2 a}{\partial y^2} + r
\]

\[
a(y,0) = \delta a_0
\]

\[
\frac{\partial a(0,t)}{\partial y} = \frac{I(t)}{2F D_{\text{Li}^0}}
\]

\[
\frac{\partial a(L,t)}{\partial y} = \frac{I(t)}{2F D_{\text{Li}^+}}
\]

and an analytical expression for the electric field is obtained

\[
E(y,t) = \frac{RT}{F} \ln \left[ \frac{a(L,t)}{a(0,t)} \right] - \int_0^L E(y,t) dy
\]

The total mass-transfer \( \text{(mol)} \) overpotential across the \( \text{Li}_2\text{P}_2\text{O}_7 \) electrolyte \( \eta_{\text{Li}^+}^{\text{mt}} \) can then be given by

\[
\eta_{\text{Li}^+}^{\text{mt}}(t) = \frac{RT}{F} \ln \left[ \frac{a(L,t)}{a(0,t)} \right] - \int_0^L E(y,t) dy
\]
coefficient (m² s⁻¹) of Li in the electrode. Equation 21a represents how the profile develops as a function of time. Equation 21b reflects the insulating condition at the electrode/current collector interface (y = L + M in Fig. 1b) through which no Li⁺ ions can pass. Note that the normalized activity of Li in the electrode can be defined as x = aLiCoO₂/aLiCoO₂, max where aLiCoO₂, max is the maximal activity of Li in LiCoO₂ (23.3 kmol m⁻³). The diffusion overpotential is calculated according to the three main processes occurring inside the battery: charge transfer reaction at the positive electrode, the ionic flow through the solid-state electrolyte, and the diffusion in the intercalation electrode. Herewith, it is indeed assumed that ηLI⁺ at the metallic lithium electrode is negligibly low. Table I lists all model parameters.

Experimental

A 10 µAh planar thin-film all-solid-state Li-ion battery was deposited using an in-house built equipment, comprising a radio frequency sputtering tool with 2 in. targets (13.56 MHz) and thermal/E-beam evaporation, both placed in a glove box containing an inert argon atmosphere. Care was taken that the base pressure before deposition was always less than 10⁻⁶ mbar. Hard masks were used for the definition of each of the active battery layers. As substrate, silicon covered with a bilayer of TiO₂/Pt (50 nm/250 nm) was used. For the cathode (LiCoO₂ target), a power of 60 W and a pressure of 8 × 10⁻⁶ bar O₂/Ar (4:6) were used to deposit 320 nm. Hereafter, the cathode was thermally annealed at 800°C for 10 min using rapid thermal anneal at a 60°C/min heating rate in order to obtain the high-T crystalline phase. Hereafter, a 1.5 µm thick
Li$_3$PO$_4$ layer was deposited using a power of 30 W using a Li$_3$PO$_4$ target (at a pressure of 15 $\times$ 10$^{-6}$ bar Ar). Finally, 150 nm cobalt was deposited as the current collector at $-5$ Å/s via E-beam evaporation. The as-prepared battery was charged and discharged according to the following regime: constant current constant voltage (CCCV) charging with a 1.6 C-rate till the maximum voltage level of 4.2 V was reached, followed by a 30 min relaxation period and a current constant (CC) discharge. The following discharge rates were successively applied: 1.6, 3.2, 6.4, 12.8, 25.6, and 51.2 C. Cycling was performed on an 8-channel Biologic VMP3 battery tester equipped with a low current and impedance boards. The experimental data are obtained at room temperature, i.e., 25°C, the same temperature as used for the simulations.

**Results and Discussion**

Figure 2 shows the charge and discharge voltage curves as a function of time where, for convenience reasons, $t = 0$ corresponds to the start of each discharge cycle. It is remarkable to see that these thin-film batteries can be discharged with extremely high currents up to 51.2 C-rate.

Figure 3 shows the same discharge curves but now plotted as a function of the amount of extracted charge ($Q_{out}$), i.e., capacity density, together with the extrapolated equilibrium voltage curve (green line). Note that the equilibrium voltage of the battery is equal to that of the positive electrode as the voltage of the metallic Li electrode is 0 V vs Li/Li$^+$. The equilibrium voltage has been determined by regression extrapolation (see Chap. 4 in Ref. 31). The regression extrapolation was applied separately on the flat and steep parts of the equilibrium voltage curve. Figure 4 shows, as an example, the dependence of the voltage on the applied discharge current for six different values of $Q_{out}$. A linear relationship between the current density and voltage is found for the low $Q_{out}$ values up to 8 $\mu$Ah cm$^{-2}$. At low state-of-charge, a nonlinear dependence is found, which can be well approximated by a quadratic regression model. The steep part of the equilibrium voltage curve has been obtained by applying a regression model to the set of $Q_{out}$ and current densities. By extrapolating the currents to zero, the equilibrium voltage can be determined. Figure 5 shows the dependence of $Q_{out}$

---

**Figure 2.** (Color online) Experimentally measured voltage profiles during CCCV charging (CC = C-rate; $V_{max} = 4.2$ V), relaxation and discharging at various C-rates (3.2, 6.4, 12.8, 25.6, and 51.2 C-rate).

**Figure 3.** (Color online) Equilibrium voltage (green) obtained from extrapolation and experimentally measured discharge curves (1.6, 3.2, 6.4, 12.8, 25.6, and 51.2 C-rate).

**Figure 4.** (Color online) The red symbols are measured voltages at various values of $Q_{out}$; The blue symbols are measured voltages at various values of $Q_{out}$; The red line is the regression interpolation; The red dots represent the extrapolated equilibrium voltage. The curves were obtained at $Q_{out} = 0, 2, 4, 8, 9.25, $ and $9.50 \mu$Ah cm$^{-2}$.

**Figure 5.** (Color online) The blue symbols are measured $Q_{out}$ values as a function of discharge current; The red line is the regression interpolation; The red symbols represent the extrapolated $Q_{out}$ values. The curves are obtained at $V = 3.0, 3.2, 3.4, 3.6, $ and $3.8$ V.
on the applied discharge current at five different voltages. For all voltages, nonlinear dependencies between \( Q_{\text{out}} \) and the applied current are found, which have been approximated by a quadratic regression. \( Q_{\text{out}} \) can then be found by extrapolating toward zero current. The difference between the equilibrium voltage and the discharge voltage is the overpotential. The dependence of the total experimental overpotential as a function of \( Q_{\text{out}} \) at various discharge rates is shown in Fig. 6. For all currents, a wide flat plateau is followed by a sharp decrease at the end of the discharge process.

Figure 7 shows the optimized simulations obtained with the applied model. Good agreement is obtained between the experimental results (blue dots) and the theoretical prediction (red lines) for all (dis)charge currents. The optimized parameters are listed in Table II.

Figure 8a shows the contributions of the various overpotential components during discharging at 3.2 C-rate. It is evident that the diffusion overpotential at the LiCoO\(_2\) electrode (\( \eta_{\text{LiCoO}_2}^{0} \)) provides the largest contribution at the beginning of discharging, but reduces toward zero, except at the very end of the discharge process where it increases sharply due to the steep concentration gradient of Li ions in the cathode. The mass-transfer overpotential (\( \eta_{\text{me}} \)) of the electrolyte is the second in magnitude at the beginning of discharging, but dominates in the end. The charge transfer overpotential (\( \eta_{\text{Li}}^{0} \)) is initially small but is growing significantly toward the end of the discharge process.

Similarly, a high discharge rate of 51.2 C (Fig. 8b) induces a high mass-transfer overpotential (\( \eta_{\text{me}} \)), which is slowly increasing upon discharging. This overpotential across the electrolyte is responsible for at least half of the total overpotential starting from the second half of the discharge process. The diffusion overpotential at the cathode (\( \eta_{\text{LiCoO}_2}^{0} \)) contributes significantly in the beginning and at the very end of the discharge process. This behavior is in-line with the definition of the diffusion overpotential which is proportional to the derivative of the equilibrium voltage (see Diffusion in the electrode). Consequently, the overpotential is small in the second half of the discharge process, where the corresponding equilibrium voltage curve is rather flat and explodes sharply at the very end of the discharge process, where the equilibrium voltage drops rapidly. The simulated total overpotential agrees well with the experimentally determined overpotentials plotted in Fig. 5: in the case of a 51.2 C-rate discharge simulation, a wide overpotential plateau at about -0.2 V is calculated which is in good agreement with the experimentally determined overpotential in Fig. 6 (black line). By carefully checking the various overpotential contributions at the end

![Figure 6.](image1)  
Experimental overpotentials as a function of \( Q_{\text{out}} \) at various C-rates (from 1.6 to 51.2 C-rate).

![Figure 7.](image2)  
Overall performance of the model during discharges with various C-rates. The blue symbols are measurements and, the red lines are the model predictions.

**Table II. Model parameters.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Dimension</th>
<th>Estimated value</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( L )</td>
<td>nm</td>
<td>1500</td>
<td>Thickness of the electrolyte(^{a})</td>
</tr>
<tr>
<td>( M )</td>
<td>cm(^{2})</td>
<td>320</td>
<td>Thickness of the electrode(^{a})</td>
</tr>
<tr>
<td>( A )</td>
<td>cm(^{2})</td>
<td>1</td>
<td>Geometrical surface area(^{a})</td>
</tr>
<tr>
<td>( a_{0} )</td>
<td>mol m(^{-3})</td>
<td>6.01 \times 10(^{6})</td>
<td>Total activity of Li atoms in Li,Po matrix(^{b})</td>
</tr>
<tr>
<td>( k_{r} )</td>
<td>m(^{3}) mol(^{-1}) s(^{-1})</td>
<td>0.90 \times 10(^{-4})</td>
<td>Li(^{+})-ion recombination reaction rate</td>
</tr>
<tr>
<td>( \delta )</td>
<td></td>
<td>0.18</td>
<td>Fraction of free Li(^{+}) ions in equilibrium</td>
</tr>
<tr>
<td>( D_{Li^{+}} )</td>
<td>m(^{2}) s(^{-1})</td>
<td>0.90 \times 10(^{-15})</td>
<td>Diffusion coefficient for Li(^{+}) ions in the electrolyte</td>
</tr>
<tr>
<td>( D_{n^{-}} )</td>
<td>m(^{2}) s(^{-1})</td>
<td>5.10 \times 10(^{-15})</td>
<td>Diffusion coefficient for n(^{-}) in the electrolyte</td>
</tr>
<tr>
<td>( \sigma_{\text{LiCoO}_2}^{\text{max}} )</td>
<td>mol m(^{-3})</td>
<td>2.33 \times 10(^{10})</td>
<td>Maximal activity of Li in the positive electrode</td>
</tr>
<tr>
<td>( D_{Li^{+}} )</td>
<td>m(^{2}) s(^{-1})</td>
<td>1.76 \times 10(^{-15})</td>
<td>Diffusion coefficient for Li in the positive electrode</td>
</tr>
<tr>
<td>( \sigma_{\text{LiCoO}_2} )</td>
<td></td>
<td>0.6</td>
<td>Charge transfer coefficient for the positive electrode</td>
</tr>
<tr>
<td>( k_{1}^{t} )</td>
<td>m(^{3}) mol(^{-0.6}) s(^{-1})</td>
<td>5.1 \times 10(^{-6})</td>
<td>Standard rate constant for positive electrode charge transfer reaction</td>
</tr>
</tbody>
</table>

\(^{a}\) Design parameters.  
\(^{b}\) Outcome of NDP analysis.  
\(^{c}\) Estimated from the design parameters and maximal capacity of the battery. All the remaining parameters are obtained from model optimization.
of the discharge process, it becomes clear that diffusion inside the LiCoO₂ electrode is the leading process, inducing the current interruption at the battery cutoff voltage of 3.0 V.

Figure 9 shows in more detail the development of the Li-ion concentration profile in the LiCoO₂ electrode upon discharging at a high 51.2 C-rate. Starting at t = 0, the system is at equilibrium and no concentration gradient has been built up yet. As soon as a discharge current is applied, a concentration profile is built up across the LiCoO₂ electrode, increasing more rapidly at the electrode/electrolyte interface. This is in good agreement with the Li-intercalation reaction Eq. 1, which indeed reveals an influx of Li ions into the positive electrode during discharging. The diffusion coefficient for Li in the electrode has been analyzed to be 1.76 × 10⁻¹⁵ m² s⁻¹, which also agrees well with the reported experimental results.

After about 1 min, the current is switched off and the concentration profile quickly relaxes toward the equilibrium.

The evolution of the concentration profile of Li⁺ ions across the electrolyte upon high current discharging is shown in Fig. 10. Starting from a flat concentration profile at equilibrium, a steep increase of the Li⁺-concentration is found at the metallic Li/electrolyte interface (y = 0, see also Fig. 1b), while at the LiCoO₂/electrolyte interface (y = L) the concentration becomes rather low. When the discharge current is switched off after 1 min, the concentration profiles rapidly relax to their equilibrium value of 11 kmol m⁻³.

Figure 11 shows the development of the total overpotential (pink line) and the individual contributions of diffusion (red line) and migration (blue line) at 51.2 C-rate discharging. The equilibrium situation (r < 0) corresponds to a zero overpotential. When the current is switched on, a 40 mV voltage drop is instantaneously formed, which is fully carried by the electric field as no concentration gradient has been built up yet. This rapid initial increase is followed by a more steady increase of both migration and diffusion, in total amounting to 110 mV at the end of discharging. The thickness of the electrode (Mt) and the electrolyte (L) have been determined by scanning electron microscopy (SEM). The total number of Li in the LiₓPO₄ electrolyte has been analyzed by neutron depth profiling (NDP) to be a₀ = 6.01 × 10⁴ mol m⁻³. The simulations show that, in equilibrium, only about 18% of the Li atoms are mobile and that the Li-ion recombination reaction rate is moderately large (kₗ = 0.9 × 10⁻⁸ m⁴ mol⁻³ s⁻¹). Both diffusion coefficients are estimated to be of the order of 10⁻¹⁵ m² s⁻¹.

Figure 12 reviews the concentration profiles across the entire battery stack at three moments in time: directly preceding constant current-discharging (blue line), 20 s after 51.2 C-rate discharging has been commenced (red line), and after 50 s (pink line) just before discharging will be terminated. It can be concluded that before discharging no concentration profiles are present in both the electrode
and the electrolyte, indeed implying that the battery is in the equilibrium state. However, as soon as the current is switched on, significant concentration gradients in both the electrode and the electrolyte are established, with significant accumulation at the metallic lithium electrode (y = 0) and depletion at the electrolyte/cathode interface (y = L). The lithium concentration in the positive electrode, conversely, is growing with time, in agreement with the main storage reaction Eq. 1. The simulated total overpotential corresponds to charge transfer resistances of the order of 50–100 Ω at the voltage plateau but obviously increases at the end of discharging. This is also in good agreement with the reported experimental results.18,19

Conclusions

A one-dimensional model has been applied to simulate the performance of all-solid-state Li-ion batteries. The model describes the electrode, electrolyte, and the interface between these elements. The proposed model provides a detailed information about the various diffusion and migration fluxes, concentration profiles, and the corresponding overpotential contributions, occurring across the electrode and electrolyte. The model provides good fits with the measurements, including discharge curves with high C-rates.

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