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 LiPO₄ 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 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 are considerable 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.

**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 LiPO₄. 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

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

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

respectively. The positive electrode generally consists of trivalent cobalt oxide species, in which the lithium ions are intercalated (LiCoO₂) 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 Co⁴⁺/Co³⁺ 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

\[
I_a = FAk_1a_1^{i_{\text{LiCoO}_2}} \quad [3a]
\]

\[
I_c = FAk_{-1}a_e^{i_{\text{LiCoO}_2}} \quad [3b]
\]

where \(F\) is the Faraday constant (96,485 C mol⁻¹), \(A\) is the electrode surface area (m²), and \(a_1\) is the (surface) activity of species \(i\) (mol m⁻³). The reaction rate constants are a function of the electrode potential,¹⁰ according to

\[
k_1 = k_{10}e^{\rho_{\text{LiCoO}_2}(RT)/k_a}a_{\text{LiCoO}_2} \quad [4a]
\]

\[
k_{-1} = k_{-10}e^{-(RT)/k_a}a_{\text{LiCoO}_2} \quad [4b]
\]

where \(R\) is the gas constant (8.314 J mol⁻¹ K⁻¹), \(T\) is the absolute temperature (K), and \(k_{a\text{LiCoO}_2}\) is the charge transfer coefficient for reaction Eq. 1. Introducing these equations into Eqs. 3a and 3b yields

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If an overpotential $\eta_{LiCoO_2}$ is applied to drive the charge transfer reaction at the positive electrode, then Eqs. 5a and 5b can be rewritten as

$$I_a = FA\tilde{a}_{LiCoO_2} \alpha_{LiCoO_2}^a \frac{\rho_{LiCoO_2}}{RT} e^{\eta_{LiCoO_2} / RT}$$

$$I_s = FA\tilde{a}_{LiCoO_2} \alpha_{LiCoO_2}^s \frac{\rho_{LiCoO_2}}{RT} e^{\eta_{LiCoO_2} / RT}$$

Combining the partial cathodic and partial anodic current-potential curves, $I = I_a - I_s$ yields an expression for the kinetics of 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

$$I_{LiCoO_2} = \frac{\rho_{LiCoO_2}}{RT} \left[ \frac{\partial E_{LiCoO_2}}{\partial a_{LiCoO_2}} e^{\eta_{LiCoO_2} / RT} - \frac{\partial E_{LiCoO_2}}{\partial a_{LiCoO_2}} e^{\eta_{LiCoO_2} / RT} \right]$$

Under fully kinetically controlled conditions, $\alpha_{LiCoO_2}^a \alpha_{LiCoO_2}^s = 1$ and $\tilde{a}_{LiCoO_2} \tilde{a}_{LiCoO_2} = 1$ and Eq. 10 can be simplified to the Butler–Volmer equation

$$I_{LiCoO_2} = \frac{\rho_{LiCoO_2}}{RT} \left[ e^{\eta_{LiCoO_2} / RT} - e^{-(1-\eta_{LiCoO_2}) / RT} \right]$$

In a similar way, the kinetics of the second electrode reaction Eq. 2 can be derived. The general expression for the charge transfer reaction at the metallic lithium electrode can be represented by

$$I_{Li} = \frac{\rho_{Li}}{RT} \left[ \frac{\partial E_{Li}}{\partial a_{Li}} \eta_{Li} - \frac{\partial E_{Li}}{\partial a_{Li}} \eta_{Li} \right]$$

where $\tilde{a}_{Li}$ and $\tilde{a}_{Li}$ are the surface and bulk activities of the metallic Li (mol m$^{-3}$), $\alpha_{Li}$ is the charge transfer coefficient for reaction Eq. 2, $\eta_{Li}$ is the overpotential of the charge transfer reaction at the negative electrode, and the exchange current $\tilde{I}_{Li}$ is given by

$$\tilde{I}_{Li} = FA\tilde{a}_{Li} \alpha_{Li}^a \frac{\rho_{Li}}{RT} \left[ e^{\eta_{Li} / RT} - e^{-(1-\eta_{Li}) / RT} \right]$$

where $\tilde{I}_{Li}$ 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 Li electrode is much larger than that for LiCoO$_2$, and because the electrode areas are exactly the same for planar thin-film batteries it is to be expected that $\eta_{Li}$ is much smaller than $\eta_{LiCoO_2}$. 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$_3$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 the 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 transfer process of immobile, oxygen-binded lithium (indicated by Li(0)) to mobile Li\(^+\) ions leaving uncompensated negative charges (n\(^-\)) behind, which are chemically associated with the closest NBOs.\(^{22}\) In Eq. 14, \(k_d\) is the dissociation rate constant for the ionic generation reaction (s\(^{-1}\)) and \(k_i\) is the rate constant for the inverse recombination reaction (mol\(^{-1}\) s\(^{-1}\)). Both constants obey Arrhenius law. Denoting the activity of mobile Li\(^+\) ions by \(a_{Li^+}\) (mol m\(^{-3}\)), the activity of immobile Li ions by \(a_{Li^0}\) (mol m\(^{-3}\)), the activity of n\(^-\) by \(a_n\) (mol m\(^{-3}\)), the total activity of Li atoms in the Li\(_2\)PO\(_4\) matrix by \(a_0\) (mol m\(^{-3}\)), and the fraction of Li, which resides in equilibrium in the mobile state by \(\delta\), the equilibrium activity of the charge carriers can be represented by \(a^{eq}_{Li^+} = a^{eq}_{Li^0} = \delta a_0\). The equilibrium activity of immobile lithium is consequently given by

\[
a^{eq}_{Li^0} = (1 - \delta) a_0
\]

Under equilibrium conditions, the rates of the forward and backward reactions are equal (\(k_d a^{eq}_{Li^0} = k_i a^{eq}_{Li^+} a_n\)), which implies that \(k_d = k_i a_0^2 / (1 - \delta)\). The overall rate of the charge carrier generation is given by \(r_d = k_d a^{eq}_{Li^0} = k_i a^{eq}_{Li^+} a_n\), and the net rate of the reverse 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 Nerst–Planck equation\(^{26}\)

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

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\(^{-1}\)), \(a_j/\delta y\) 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 \(r_d = r\) and \(r_i = -r\) where \(r = k_d a^{eq}_{Li^0} - k_i a^{eq}_{Li^+} a_n\), 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

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

\[
\frac{\partial a_{Li^0}}{\partial t} = \frac{a_{Li^0}(y,0) - \delta a_0}{z_{Li^0} F A}
\]

\[
J_{Li^+}(0,t) = \frac{I_{LiCoO_2}(t)}{z_{Li^+} F A}
\]

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

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

where \(I_{LiCoO_2}(t)\) and \(I_{Li}(t)\) 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 \(I(t) = I_{LiCoO_2}(t) = I_{Li}(t)\). 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 \(a_{Li^+}(y,t) = a_{Li^0}(y,t)\). The \(Li^+\) ions in the electrolyte are generated from the immobile Li atoms, thus \(a_0 = a_{Li^0}(y,t)\). It can be shown\(^{27}\) that Eqs. 16 and 17 can be reduced to the diffusion equation with respect to \(a(y,t)\), according to

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

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

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

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

and an analytical expression for the electric field is obtained

\[
E(y,t) = \frac{RT}{F} \ln \left( \frac{a(L,t)}{a(0,t)} \right) - \frac{I(t)}{2 F A D_{Li^0}}
\]

The total mass-transfer overpotential across the Li\(_2\)PO\(_4\) electrolyte \(\eta_{Li^+}\) can then be given by

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

The first and the second terms in Eq. 20 define the diffusion and migration components of the total overpotential, respectively.

**Diffusion in the electrode.**—The positive electrode consists of trivalent cobaltoxide species, in which the lithium ions are intercalated (LiCo\(_{0.8}\)O\(_2\)). According to Refs. 28 and 29 Li\(^+\) ions in LiCoO\(_2\) are screened by the mobile electrons, which accompany Li\(^+\) when it moves from one interstitial site to the other. This screening implies that the migration term can be neglected. Assuming, for simplicity reasons, that the rate of phase transition does not play an important role and considering the diffusion coefficients in both phases to be equal, the mass transport of Li ions inside the positive electrode can be described by the standard diffusion equation

\[
\frac{\partial a_{LiCoO_2}}{\partial t} = D_{Li^+} \frac{\partial^2 a_{LiCoO_2}}{\partial y^2}
\]

\[
\frac{\partial a_{LiCoO_2}(y,0)}{\partial y} = 0
\]

\[
\frac{\partial a_{LiCoO_2}(L, t)}{\partial y} = 0
\]

\[
\frac{\partial a_{LiCoO_2}(L + M, t)}{\partial y} = 0
\]

where \(a_{LiCoO_2}(y,t)\) is the Li\(^+\) activity (mol m\(^{-3}\)) in location \(y\) at any moment of time \(t\), \(\partial a_{LiCoO_2}/\partial y\) is the activity of Li\(^+\) (mol m\(^{-3}\)) in the positive electrode at \(t = 0\) (in equilibrium), and \(D_{Li^+}\) is the diffusion
coefficient ($m^2 s^{-1}$) of Li in the electrode. Equation 21a represents how the profile develops as a function of time. Equation 21b reflects the initial conditions and Eq. 21c describes the supply or consumption of the Li$^+$ ions at the electrode interface. Equation 21d reveals 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 $x = a_{LiCoO_2} / a_{LiCoO_2}^{max}$, where $a_{LiCoO_2}^{max}$ is the maximal activity of Li in LiCoO$_2$ ($23.3$ kmol m$^{-3}$). The diffusion overpotential is calculated according to Refs. 28 and 30 as $\eta_{LiCoO_2} = E_{LiCoO_2}^{eq} - E_{LiCoO_2}^D = (x^d - x) (\partial E_{LiCoO_2}^D / \partial x)$, where $x^d = x(L,t)$ is the normalized surface activity, $x$ is the average bulk activity, and $\partial E_{LiCoO_2}^D / \partial x$ is the derivative of the equilibrium potential of the positive electrode at the surface.

Combined effects.— The equilibrium voltage of the Li-ion battery is the difference between the equilibrium voltage of the positive and negative electrodes, i.e., $E_{bat}^{eq} = E_{LiCoO_2}^{eq} - E_{Li}^{eq}$. The total battery overpotential ($\eta_t$) is the difference between the equilibrium voltages and the current-driven voltages ($\eta_t = \eta_{bat} - \eta_{bat}^c$). The total battery overpotential ($\eta_t$) is a sum of three contributions $\eta_t = \eta_{LiCoO_2}^{ct} + \eta_{LiCoO_2}^{d} + \eta_{Li}^{me}$.

Table I. List of symbols.

<table>
<thead>
<tr>
<th>Notation</th>
<th>Dimension</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L$</td>
<td>m</td>
<td>Thickness of the electrolyte</td>
</tr>
<tr>
<td>$M$</td>
<td>m</td>
<td>Thickness of the electrode</td>
</tr>
<tr>
<td>$A$</td>
<td>m$^2$</td>
<td>Geometrical surface area</td>
</tr>
<tr>
<td>$a^i$</td>
<td>mol m$^{-3}$</td>
<td>Generic notation for surface activity</td>
</tr>
<tr>
<td>$a$</td>
<td>mol m$^{-3}$</td>
<td>Generic notation for bulk activity</td>
</tr>
<tr>
<td>$a_{LiCoO_2}$</td>
<td>mol m$^{-3}$</td>
<td>Activity of Li in the positive (LiCoO$_2$) electrode (generic)</td>
</tr>
<tr>
<td>$a_{LiCoO_2}^{max}$</td>
<td>mol m$^{-3}$</td>
<td>Activity of Li in the negative (metallic Li) electrode (generic)</td>
</tr>
<tr>
<td>$a_{Li}$</td>
<td>mol m$^{-3}$</td>
<td>Activity of Li$^+$ in the electrolyte (generic)</td>
</tr>
<tr>
<td>$a_{\sigma}$</td>
<td>mol m$^{-3}$</td>
<td>Activity of $\sigma$ in the electrolyte (generic)</td>
</tr>
<tr>
<td>$a_{LiPS}$</td>
<td>mol m$^{-3}$</td>
<td>Activity of immobile lithium in Li$_3$PO$_4$ matrix</td>
</tr>
<tr>
<td>$a_L$</td>
<td>mol m$^{-3}$</td>
<td>Total activity of Li atoms in Li$_3$PO$_4$ matrix</td>
</tr>
<tr>
<td>$k_i$</td>
<td>m s$^{-1}$</td>
<td>Positive electrode charge transfer anodic reaction rate constant</td>
</tr>
<tr>
<td>$k_i^+$</td>
<td>m$^4$ mol$^{-4}$ s$^{-1}$</td>
<td>Positive electrode charge transfer cathodic reaction rate constant</td>
</tr>
<tr>
<td>$k_i^-$</td>
<td>m$^2$ s$^{-1}$</td>
<td>Standard rate constant for positive electrode charge transfer reaction</td>
</tr>
<tr>
<td>$k_i$</td>
<td>m s$^{-1}$</td>
<td>Negative electrode charge transfer anodic reaction rate constant</td>
</tr>
<tr>
<td>$k_i^-$</td>
<td>m s$^{-1}$</td>
<td>Negative electrode charge transfer cathodic reaction rate constant</td>
</tr>
<tr>
<td>$k_i$</td>
<td>m$^1$ mol$^{-1}$ s$^{-1}$</td>
<td>Standard rate constant for negative electrode charge transfer reaction</td>
</tr>
<tr>
<td>$k_i$</td>
<td>m$^1$ mol$^{-1}$ s$^{-1}$</td>
<td>Li$^+$ ion recombination reaction rate constant</td>
</tr>
<tr>
<td>$k_i$</td>
<td>m$^1$ mol$^{-1}$ s$^{-1}$</td>
<td>Li$^+$ ion generation reaction rate constant</td>
</tr>
<tr>
<td>$\beta$</td>
<td>--</td>
<td>Net rate of Li$^+$ ion generation/recombination</td>
</tr>
<tr>
<td>$\delta$</td>
<td>--</td>
<td>Fraction of mobile Li$^+$ ions in the electrolyte</td>
</tr>
<tr>
<td>$D_{Li^+}$</td>
<td>m$^2$ s$^{-1}$</td>
<td>Diffusion coefficient for Li$^+$ ions in the electrolyte</td>
</tr>
<tr>
<td>$D_{\sigma}$</td>
<td>m$^2$ s$^{-1}$</td>
<td>Diffusion coefficient for $\sigma$ in the electrolyte</td>
</tr>
<tr>
<td>$D_L$</td>
<td>m$^2$ s$^{-1}$</td>
<td>Diffusion coefficient for Li in the positive electrode</td>
</tr>
<tr>
<td>$J_i$</td>
<td>mol m$^{-2}$ s$^{-1}$</td>
<td>Flux of species $j$ in the electrolyte</td>
</tr>
<tr>
<td>$z_j$</td>
<td>--</td>
<td>Valence of species $j$</td>
</tr>
<tr>
<td>$I_{LiCoO_2}$, $I_L$</td>
<td>A</td>
<td>Main storage reaction currents for the positive and negative electrode correspondingly</td>
</tr>
<tr>
<td>$I_L$</td>
<td>A</td>
<td>Current flowing through the battery</td>
</tr>
<tr>
<td>$I_{LiCoO_2}$</td>
<td>A</td>
<td>Exchange currents for the positive and negative electrodes correspondingly</td>
</tr>
<tr>
<td>$E_{LiCoO_2}$, $E_{Li}$</td>
<td>V</td>
<td>Voltage and equilibrium voltage of the positive electrode</td>
</tr>
<tr>
<td>$E_{bat}$</td>
<td>V</td>
<td>Voltage and equilibrium voltage of the battery</td>
</tr>
<tr>
<td>$E_{bat}$</td>
<td>V</td>
<td>Electric field (electric potential gradient)</td>
</tr>
<tr>
<td>$\eta_{LiCoO_2}$</td>
<td>V</td>
<td>Total overpotential of the battery</td>
</tr>
<tr>
<td>$\eta_{Li}$</td>
<td>V</td>
<td>The charge transfer overpotential for the positive electrode</td>
</tr>
<tr>
<td>$\eta_{LiCoO_2}$</td>
<td>V</td>
<td>The mass-transfer overpotential across the electrolyte</td>
</tr>
<tr>
<td>$\eta_{Li}^{me}$</td>
<td>V</td>
<td>The diffusion overpotential for the positive electrode</td>
</tr>
<tr>
<td>$T$</td>
<td>K</td>
<td>Temperature</td>
</tr>
<tr>
<td>$t$</td>
<td>s</td>
<td>Time</td>
</tr>
</tbody>
</table>
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 ($Q_{\text{out}}$), 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$^+$, i.e., $E_{\text{bat}}^{eq} = E_{\text{bat}}^{eq}$. 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 $Q_{\text{out}}$. A linear relationship between the current density and voltage is found for the low $Q_{\text{out}}$ values up to 8 µAh cm$^{-2}$. At low state-of-charges, 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 $Q_{\text{out}}$ and current densities. By extrapolating the currents to zero, the equilibrium voltage can be determined. Figure 5 shows the dependence of $Q_{\text{out}}$
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 ($\eta_{\text{LiCoO}_2}^d$) 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 ($\eta_{\text{Li}}^m$) of the electrolyte is the second in magnitude at the beginning of discharging, but dominates in the end. The charge transfer overpotential ($\eta_{\text{Li}}^c$) 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 ($\eta_{\text{Li}}^m$), 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 ($\eta_{\text{LiCoO}_2}^d$) 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](image_url)  
**Figure 6.** (Color online) Experimental overpotentials as a function of $Q_{\text{out}}$ at various C-rates (from 1.6 to 51.2 C-rate).

![Figure 7](image_url)  
**Figure 7.** (Color online) 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>
<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>nm</td>
<td>320</td>
<td>Thickness of the electrode(^b)</td>
</tr>
<tr>
<td>$A$</td>
<td>cm$^2$</td>
<td>1</td>
<td>Geometrical surface area(^c)</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$_3$PO$_4$ matrix(^b)</td>
</tr>
<tr>
<td>$k_r$</td>
<td>m$^3$ mol$^{-1}$ s$^{-1}$</td>
<td>$9.0 \times 10^{-4}$</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>$0.90 \times 10^{-13}$</td>
<td>Diffusion coefficient for Li$^+$ ions in the electrolyte</td>
</tr>
<tr>
<td>$D_n^m$</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>$\alpha_{LiCoO_2}^m$</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>$\alpha_{LiCoO_2}^d$</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>$\kappa_1^c$</td>
<td>—</td>
<td>0.6</td>
<td>Charge transfer coefficient for the positive electrode</td>
</tr>
<tr>
<td>$k_{1}^{c}$</td>
<td>m$^{-3}$ mol$^{-0.6}$ s$^{-1}$</td>
<td>$5.1 \times 10^{-4}$</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 LiCoO$_2$ 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 LiCoO$_2$ 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 LiCoO$_2$ 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 $\times$ $10^{-15}$ m$^2$ 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.

Figure 10 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 layer during 51.2 C discharge.

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 those 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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