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 LiCoO$_2$ cathode and a metallic Li anode separated by 1.5 μm Li$_2$PO$_4$ 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 electrolyte 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.

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.10-11 In addition, the degradation (aging) process of Li-ion batteries has also been addressed.11-13 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 LiCoO$_2$ chemistry. The electrodes are separated by a solid-state electrolyte consisting of (either or not N-doped) an amorphous Li$_2$PO$_4$. 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 cobaltate species, in which the lithium ions are intercalated (LiCoO$_2$) to provide electroneutrality. During charging, the trivalent cobalt is oxidized into four-valent cobalt (Co$^4$O$_2$) 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 Co$^{3+/4+}$ 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

$$I_a = FAk_1a_1^{i_a}E_{\text{LiCoO}_2} \quad [3a]$$

$$I_c = FAk_{-1}a_1^{i_c}E_{\text{LiCoO}_2} \quad [3b]$$

where $F$ is the Faraday constant (96,485 C mol$^{-1}$), $A$ is the electrode surface area ($m^2$), and $a_i$ is the (surface) activity of species $i$ (mol m$^{-2}$). The reaction rate constants are a function of the electrode potential,16 according to

$$k_1 = k_1^{E_{\text{LiCoO}_2}}R(T)E_{\text{LiCoO}_2} \quad [4a]$$

$$k_{-1} = k_{-1}^{E_{\text{LiCoO}_2}}R(T)E_{\text{LiCoO}_2} \quad [4b]$$

where $R$ is the gas constant (8.314 J mol$^{-1}$ K$^{-1}$), $T$ is the absolute temperature (K), and $E_{\text{LiCoO}_2}$ 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 $\eta_{LiCoO_2}^{eq} = E_{LiCoO_2} - E_{LiCoO_2}^{\text{eq}}$ is applied to drive the charge transfer ($e^-$) reaction at the positive electrode, then Eqs. 5a and 5b can be rewritten as

$$I_s = F\alpha c_{LiCoO_2}^{eq} \frac{\partial E_{LiCoO_2}}{\partial \alpha Li} e^{(1-\alpha_{LiCoO_2})[e^{(RT/\alpha Li)} - e^{(RT/\alpha Li)}]}$$  \[[9a]\]

$$I_s = F\alpha c_{LiCoO_2}^{eq} \frac{\partial E_{LiCoO_2}}{\partial \alpha Li} e^{(1-\alpha_{LiCoO_2})[e^{(RT/\alpha Li)} - e^{(RT/\alpha Li)}]}$$  \[[9b]\]

Combining the partial cathodic and partial anodic current–potential curves, $I = I_s - I_c$ 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

$$I_{LiCoO_2} = \frac{\partial E_{LiCoO_2}}{\partial \alpha Li} \left[ \frac{\partial E_{LiCoO_2}}{\partial \alpha Li} e^{(1-\alpha_{LiCoO_2})[e^{(RT/\alpha Li)} - e^{(RT/\alpha Li)}]} \right]$$  \[[10]\]

Under fully kinetically controlled conditions, $\alpha c_{LiCoO_2} = \alpha^0_{LiCoO_2}$ and $\partial \alpha_{LiCoO_2} / \partial \alpha Li = 1$ and Eq. 10 can be simplified to the Butler–Volmer equation

$$I_{LiCoO_2} = \frac{\partial E_{LiCoO_2}}{\partial \alpha Li} \left[ e^{(1-\alpha_{LiCoO_2})[e^{(RT/\alpha Li)} - e^{(RT/\alpha Li)}] \alpha^0_{LiCoO_2}} \left[ e^{(RT/\alpha Li)} - e^{(RT/\alpha Li)} \right] \right]$$  \[[11]\]

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

$$I_{Li} = \frac{\partial E_{LiCoO_2}}{\partial \alpha Li} \left[ e^{(1-\alpha_{LiCoO_2})[e^{(RT/\alpha Li)} - e^{(RT/\alpha Li)}] \alpha^0_{LiCoO_2}} \left[ e^{(RT/\alpha Li)} - e^{(RT/\alpha Li)} \right] \right]$$  \[[12]\]

$$I_{Li} = \frac{\alpha^0_{LiCoO_2}}{\alpha Li} \left[ e^{(1-\alpha_{LiCoO_2})[e^{(RT/\alpha Li)} - e^{(RT/\alpha Li)}] \alpha^0_{LiCoO_2}} \left[ e^{(RT/\alpha Li)} - e^{(RT/\alpha Li)} \right] \right]$$  \[[13]\]

where $\alpha^0_{LiCoO_2}$ and $\alpha Li$ are the surface and bulk activities of the metallic Li (mol m$^{-3}$), $\alpha Li$ is the charge transfer coefficient for reaction Eq. 2, $\eta_{LiCoO_2}^{eq}$ is the overpotential of the charge transfer reaction at the negative electrode, and the exchange current $I_{Li}$ is given by

$$I_{Li} = F\alpha c_{LiCoO_2}^{eq} \frac{\partial E_{LiCoO_2}}{\partial \alpha Li} e^{(1-\alpha_{LiCoO_2})[e^{(RT/\alpha Li)} - e^{(RT/\alpha Li)}]}$$  \[[11]\]

The exchange current $I_{LiCoO_2}$ is defined at the equilibrium potential where $I_s = I_c$. Under equilibrium conditions, no concentration profiles are present and all the surface activities are equal to the average bulk activities ($\bar{a}$), i.e., $a^0_i = \bar{a}$. From Eqs. 5a and 5b, it follows that under this condition, $I_{LiCoO_2}$ can be represented by

$$I_{LiCoO_2} = F\alpha c_{LiCoO_2}^{eq} \frac{\partial E_{LiCoO_2}}{\partial \alpha Li} e^{(1-\alpha_{LiCoO_2})[e^{(RT/\alpha Li)} - e^{(RT/\alpha Li)}]}$$  \[[6]\]

An expression for the equilibrium potential ($E_{LiCoO_2}^{eq}$) can then be obtained from Eq. 6

$$E_{LiCoO_2}^{eq} = \frac{RT}{F} \ln \frac{k_0^{eq} a_{LiCoO_2} a_{Li^+}^{1-\alpha_{LiCoO_2}}}{k_0^{eq} a_{LiCoO_2} a_{Li^+}^{1-\alpha_{LiCoO_2}}} = \frac{RT}{F} \ln \frac{k_0^{eq}}{k_0^{eq}} + \frac{RT}{F} \ln \frac{a_{LiCoO_2} a_{Li^+}^{1-\alpha_{LiCoO_2}}}{a_{LiCoO_2} a_{Li^+}^{1-\alpha_{LiCoO_2}}}$$  \[[7]\]

which is recognized as the Nernst equation. The first term on the right-hand side represents the standard redox potential and the second term takes into account the concentration dependence of the electrode potential. Eliminating $E_{LiCoO_2}^{eq}$ in Eq. 6, using Eq. 7, leads to a general expression for $E_{LiCoO_2}^{eq}$

$$E_{LiCoO_2}^{eq} = \frac{F\alpha c_{LiCoO_2}^{eq} \frac{\partial E_{LiCoO_2}}{\partial \alpha Li} e^{(1-\alpha_{LiCoO_2})[e^{(RT/\alpha Li)} - e^{(RT/\alpha Li)}]}}{\alpha Li}$$  \[[8]\]

in which $k_0^i = (k_0^{eq})^{1-\alpha_{LiCoO_2}} / (k_0^{eq})^{1-\alpha_{LiCoO_2}}$ is the standard rate constant for reaction Eq. 1.
describes the transfer process of immobile, oxygen-bound lithium (indicated by Li⁰) to mobile Li⁺ ions leaving uncompensated negative charges (n⁻) behind, which are chemically associated with the closest NBOs.²² In Eq. 14, k₈ is the dissociation rate constant for the ionic generation reaction (s⁻¹) and k₉ is the rate constant for the reverse recombination reaction (mol⁻¹ s⁻¹). Both constants obey Arrhenius law. Denoting the activity of mobile Li⁺ ions by aLi⁺ (mol m⁻³), the activity of immobile Li ions by aLi⁰ (mol m⁻³), the activity of n⁻ by a₈ (mol m⁻³), the total activity of Li atoms in the Li₃PO₄ matrix by a₀ (mol m⁻³), and the fraction of Li, which resides in equilibrium in the mobile state by δ, the equilibrium activity of the charge carriers can be represented by aLi⁺eq = aLi⁺ = δa₀. The equilibrium activity of immobile lithium is consequently given by aLi⁰eq = (1 − δ)a₀. Under equilibrium conditions, the rates of the forward and backward reactions are equal (k₉aLi⁺eq/k₈aLi⁰eq = k₉aLi⁺eq/k₈aLi⁰eq), which implies that k₉ = k₈[1−δ]/δ. The overall rate of the charge carrier generation is given by r₉ = k₈[1−δ][1−δ]a₀, 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 equation²⁰

\[
J_j = -D_j \frac{\partial a_j}{\partial y} + \frac{z_j F}{RT} D_j a_j E \quad \text{[15]}
\]

where \(J(y,t)\) 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 \(j\) (m² s⁻¹), \(a_j/\delta y\) is the concentration gradient (mol m⁻⁴), \(E\) 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 \(r₉ = r\) and \(r₈ = −r\) where \(r = k₈[1−δ][1−δ]a₀\), 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

\[
\frac{\partial a_{Li⁺}}{\partial t} = - \frac{\partial J_{Li⁺}}{\partial y} + r \quad \text{[16a]}
\]

\[
a_{Li⁺}(y,0) = \delta a₀ \quad \text{[16b]}
\]

\[
J_{Li⁺}(0,t) = \frac{I(t)}{z_{Li⁺} F A} \quad \text{[16c]}
\]

\[
J_{Li⁺}(L,t) = I_{LiCoO₂(t)} \quad \text{[16d]}
\]

and

\[
\frac{\partial a_{Li⁰}}{\partial t} = - \frac{\partial J_{Li⁰}}{\partial y} + r \quad \text{[17a]}
\]

\[
a_{Li⁰}(y,0) = \delta a₀ \quad \text{[17b]}
\]

\[
J_{Li}(0,t) = 0 \quad \text{[17c]}
\]

\[
J_{Li}(L,t) = 0 \quad \text{[17d]}
\]

where \(I_{LiCoO₂(t)}\) 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 \(I(t) = I_{LiCoO₂(t)}(t) = I_{Li}(t)\). 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 \(a(y,t) = a_{Li⁺}(y,t) + a_{Li⁰}(y,t)\). The Li⁺ ions in the electrolyte are generated from the immobile Li atoms, thus \(a_0 = a_{Li⁺}(y,t) + a_{Li⁰}(y,t) = a_{Li⁺}(y,t) + a(y,t)\). It can be shown²⁷ that Eqs. 16 and 17 can be reduced to the diffusion equation with respect to \(a(y,t)\), according to

\[
\frac{\partial a}{\partial t} = \frac{2D_{Li⁺}D_{Li⁰}}{D_{Li⁺} + D_{Li⁰}} \frac{\partial^2 a}{\partial y^2} + r
\]

\[
a(y,0) = \delta a₀ \quad \text{[18]}
\]

and an analytical expression for the electric field is obtained

\[
E(y,t) = \frac{RT}{F} \frac{1}{a(y,t)} \left( \frac{I(t)}{2FAD_{Li⁺}} + \frac{D_{Li⁺} - D_{Li⁰}}{D_{Li⁺} + D_{Li⁰}} \frac{\partial a(y,t)}{\partial y} \right) \left( E(0) \right) \quad \text{[19]}
\]

The total mass-transfer \(m(t)\) overpotential across the Li₃PO₄ electrolyte \(\eta_{Li}^{mt}\) can then be given by

\[
\eta_{Li}^{mt}(t) = \frac{RT}{F} \ln \left( \frac{a(L,t)}{a(0,t)} \right) - \int_0^L E(y,t)dy \quad \text{[20]}
\]

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 (LiCoO₂). According to Refs. 28 and 29 Li⁺ ions in LiCoO₂ 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

\[
\frac{\partial a_{LiCoO₂}}{\partial t} = D_{Li⁺} \frac{\partial^2 a_{LiCoO₂}}{\partial y^2} \quad \text{[21a]}
\]

\[
a_{LiCoO₂}(y,0) = a₀_{LiCoO₂} \quad \text{[21b]}
\]

\[
D_{Li⁺} \frac{\partial a_{LiCoO₂}(L,t)}{\partial y} = \frac{I(t)}{F A} \quad \text{[21c]}
\]

\[
D_{Li⁺} \frac{\partial a_{LiCoO₂}(L + M,t)}{\partial y} = 0 \quad \text{[21d]}
\]

where \(a_{LiCoO₂}(y,t)\) is the Li⁺ activity (mol m⁻³) in location \(y\) at any moment of time \(t\), \(a₀_{LiCoO₂}\) is the activity of Li⁺ (mol m⁻³) in the positive electrode at \(t = 0\) (in equilibrium), and \(D_{Li⁺}\) is the diffusion
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 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 $a_{LiCoO_2}$ is the maximal activity of Li in LiCoO₂ (23.3 kmol m⁻³). The diffusion overpotential is calculated according to Refs. 28 and 30 as $\eta_{LiCoO_2} = E_{LiCoO_2}^{eq}(x) - E_{LiCoO_2}(x) = (x - x')(aE_{LiCoO_2}^{eq}/\alpha)$, where $x' = x(L,t)$ is the normalized surface activity, $x$ is the average bulk activity, and $aE_{LiCoO_2}^{eq}/\alpha$ 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., $E^{eq}_{bat} = E_{LiCoO_2}^{eq} - E_{Li}^{eq}$. The total battery overpotential ($\eta$) is the difference between the equilibrium voltages and the current-driven voltages ($\eta = \eta_{bat} - \eta_{Li}^{d}$). The total battery overpotential ($\eta_{bat}$) is a sum of three contributions

\[\eta = \eta_{LiCoO_2}^{eq} + \eta_{LiCoO_2}^{d} + \eta_{Li}^{me} \quad [22]\]

giving the three main processes occurring inside the battery: the charge transfer reaction at the positive electrode, the ionic flow through the solid-state electrolyte, and the diffusion in the intercalation electrode. Herein, it is indeed assumed that $\eta_{Li}^{eq}$ 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 hystack of TiO₂/Pt (50 nm/250 nm) was used. For the cathode (LiCoO₂ target), a power of 60 W and a pressure of 8 x 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 60°C/min heating rate in order to obtain the high-T crystalline phase. Hereafter, a 1.5 μm thick

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<tr>
<td>$\eta_{LiCoO_2}^{d}$</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 × 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 constant current (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 2.** (Color online) Experimentally measured voltage profiles during CCCV charging (CC = C-rate; $V_{\text{max}}$ = 4.2 V), relaxation and discharging at various C-rates (3.2, 6.4, 12.8, 25.6, and 51.2 C-rate).

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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 (\( \eta_{\text{diff}} \)) 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 (\( \eta_{\text{mt}} \)) of the electrolyte is the second in magnitude at the beginning of discharging, but dominates in the end. The charge transfer overpotential (\( \eta_{\text{ct}} \)) 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 (\( \eta_{\text{mt}} \)), 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 (\( \eta_{\text{diff}} \)) 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

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**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(^3)</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>( \alpha_0 )</td>
<td>mol m(^-3)</td>
<td>( 6.01 \times 10^4 )</td>
<td>Total activity of Li atoms in Li,PPO matrix(^d)</td>
</tr>
<tr>
<td>( k_v )</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>( 9.0 \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>( 5.1 \times 10^{-15} )</td>
<td>Diffusion coefficient for n(^-) in the electrolyte</td>
</tr>
<tr>
<td>( D_{LiCoO2} )</td>
<td>m(^2) s(^{-1})</td>
<td>( 1.76 \times 10^{-15} )</td>
<td>Maximal activity of Li in the positive electrode</td>
</tr>
<tr>
<td>( k_{LiCoO2} )</td>
<td>—</td>
<td>0.6</td>
<td>Diffusion coefficient for Li in the positive electrode</td>
</tr>
<tr>
<td>( k_{1} )</td>
<td>m(^3) mol(^{-0.6}) s(^{-1})</td>
<td>( 5.1 \times 10^6 )</td>
<td>Charge transfer coefficient for the positive electrode</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 Li+-concentration is found at the metallic Li/electrolyte interface from a flat concentration profile at equilibrium, a steep increase is observed upon high current discharging. The diffusion coefficient for Li in the electrode has been analyzed to be $1.76 \times 10^{-15} \text{ m}^2 \text{s}^{-1}$, 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 LiCoO2 electrode upon discharging at a high 51.2 C-rate 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 (at $y = 0$, 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 ($\eta$) and the individual contributions of diffusion (red line) and migration (blue line) at 51.2 C-rate discharging. The equilibrium situation ($\tau < 0$) 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 thicknesses of the electrode ($M$) and the electrolyte ($L$) have been determined by scanning electron microscopy (SEM). The total number of Li in the Li$_3$PO$_4$ electrolyte has been analyzed by neutron depth profiling (NDP) to be $a_0 = 6.01 \times 10^4 \text{ mol m}^{-3}$. 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 ($k_r = 0.9 \times 10^{-8} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$). Both diffusion coefficients are estimated to be of the order of $10^{-15} \text{ m}^2 \text{ s}^{-1}$.

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

Figure 10. (Color online) Development of the Li-concentration profile inside the positive electrode during 51.2 C discharge.

Figure 9. (Color online) Development of the Li-concentration profile inside the electrolyte layer during 51.2 C discharge.
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 \(\Omega\) 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 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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