Multi-Scale Thermo-Electrochemical Modeling of Performance and Aging of a LiFePO4/Graphite Lithium-Ion Cell

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Lithium-ion batteries show a complex thermo-electrochemical performance and aging behavior. This paper presents a modeling and simulation framework that is able to describe both multi-scale heat and mass transport and complex electrochemical reaction mechanisms. The transport model is based on a 1D + 1D + 1D (pseudo-3D or P3D) multi-scale approach for intra-particle lithium diffusion, electrode-pair mass and charge transport, and cell-level heat transport, coupled via boundary conditions and homogenization approaches. The electrochemistry model is based on the use of the open-source chemical kinetics code CANTERA, allowing flexible multi-phase electrochemistry to describe both main and side reactions such as SEI formation. A model of gas-phase pressure buildup inside the cell upon aging is added. We parameterize the model to reflect the performance and aging behavior of a lithium iron phosphate (LiFePO4, LFP)/graphite (LiC6) 26650 battery cell. Performance (0.1–10 C discharge/charge at 25, 40 and 60 °C) and calendar aging experimental data (500 days at 30 °C and 45 °C and different SOC) from literature can be successfully reproduced. The predicted internal cell states (concentrations, potential, temperature, pressure, internal resistances) are shown and discussed. The model is able to capture the nonlinear feedback between performance, aging, and temperature.

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Mathematical modeling and numerical simulation have become standard techniques in lithium-ion battery research and development—from the atomistic scale up to the system scale. Historically, most lithium-ion cell models are based on the work of John Newman and co-workers who developed a one-dimensional model of electrochemistry and mass and charge transport in porous electrodes on the ~100 μm scale, which was later extended by transport in the active materials particles on the ~1 μm scale, giving rise to 1D + 1D or “pseudo-2D” (P2D) models. This type of model is widely used today. Extensions include solid electrolyte interphase (SEI) formation,9 aging mechanisms,10,11 impedance simulations,12 and multi-phase chemistry in lithium-air13,14 and lithium-sulfur15 cells.

Temperature has a strong influence on the performance and lifetime of a lithium-ion battery. A straightforward approach has been to include heat sources and heat conductivity to the standard P2D type models. However, temperature gradients typically occur on a higher scale, that is, the mm and cm scale of a single cell, as compared to electrode scale described by typical P2D models. Therefore, model extensions to the cell scale are necessary. Consequently, scale-coupling methods have been developed that describe both, electrochemistry on the electrode-pair scale, and heat transport on the cell scale more efficiently. Scale coupling usually uses independent computational domains on the various scales coupled through adequate boundary conditions. As a result, models with various dimensionalities have been presented, for example, 3D + 1D + 1D (cell scale + electrode-pair scale + particle scale),20 3D (cell scale),21 2D + 1D (cell and electrode-pair scale + particle scale),22 3D + 1D (cell scale + electrode-pair scale),23 5D + 2D + 1D (cell scale + electrode-pair scale + particle scale),24 and 1D + 1D + 1D (cell scale + electrode-pair scale + particle scale).25 These studies reveal significant temperature gradients inside the cell, emphasizing the requirement for spatially resolved thermal models.

Limited battery lifetime is today a major cost driver, in particular for stationary energy storage applications where long lifetimes are required.26 Aging mechanisms are complex and consist of coupled chemical, electrochemical and mechanical processes.30–35 Aging mechanisms have been integrated in P2D-type models, for example, SEI formation,9,10,36–38 lithium plating,39,40 capacity loss due to break and repair of the SEI during cycling,41,42 or active material delamination.43,44 Due to the nonlinear temperature dependence of aging mechanisms, temperature gradients inside the cell lead to spatial variations in aging.45

Thermal models on multiple dimensions are computationally expensive and often require parallel computing algorithms. Aging mechanisms are generally complex and require specialized modeling approaches. Still, both, thermal effects and degradation reactions dominantly influence macroscopic cell behavior. Furthermore, they are strongly and nonlinearly coupled in both directions: aging is highly temperature-dependent, while fast aging reactions cause significant heat release, known as thermal runaway. The coupling occurs over multiple scales—aging reaction on the nanoscale (particle), performance on the microscale (electrode), and heat transport on a macroscale (cell). A comprehensive understanding of lithium-ion battery performance, safety and lifetime requires therefore both, the prediction of thermal effects, and the prediction of aging effects, under consideration and coupling of the involved scales. Furthermore, the computational expense should be sufficiently moderate to allow systematic dynamic studies over long simulation times for lifetime prediction. In this article we present a multi-scale model of a lithium-ion battery cell that meets these requirements. The model includes the following features: a) 1D + 1D + 1D multi-scale model of particle scale, electrode-pair scale, and cell scale to capture all relevant transport processes under moderate computational effort; b) flexible multi-phase electrochemistry to describe both main and side reactions, including secondary-phase formation, based on the use of the open-source chemical kinetics code CANTERA,36 c) thermal model capturing the feedback between performance, aging and temperature; d) implementation using a stiff solver that allows both short-term simulation of strong gradients (e.g., during thermal runaway) and long-term simulations (e.g., during calendar aging). We parameterize and test the model with the example of a cylindrical 26650 lithium iron phosphate (LiFePO4, LFP)/graphite cell including SEI formation as aging mechanism.

Modeling and Simulation Approach

1D + 1D + 1D multi-scale transport.—The computational domain of the multi-scale model is shown schematically in Figure 1. It describes transport processes on three distinct scales, each of which is modeled in one dimension, resulting in an overall 1D + 1D + 1D (pseudo-3D or P3D) model.

Macroscopic (cell) scale.—On the macroscopic scale (here: x dimension, centimeter scale, cf. Figure 1), we describe heat transport
due to conduction using energy balance according to
\[
\rho c_p \frac{\partial T}{\partial t} = \text{div}(\lambda \text{grad} T) + \dot{q}^V.
\]

Please refer to the List of Symbols for definition of all symbols and units used throughout this article. We assume that heat conduction takes place along a single through-plane dimension of the cell. In cylindrical cells, this is the radial direction, thus \(\text{div}(\lambda \text{grad} T) = \frac{\lambda}{\rho c_p} \frac{\partial T}{\partial r}\). In flat cells (pouch cells), this is the through-cell direction, thus \(\text{div}(\lambda \text{grad} T) = \frac{\lambda}{\rho c_p} \frac{\partial T}{\partial z}\). We therefore explicitly neglect heat conduction in the axial (in-plane) direction. Although axial heat conduction is known to be more effective due to anisotropic heat conductivity, this assumption is at least partially justified by the fact that typical cell aspect ratios are such that the radial (through-plane) distances are much shorter than axial (in-plane) distances. The full resolution of the cell temperature and assessment of the validity of the 1D assumption for a specific cell geometry would require 3D thermal transport models.

Boundary conditions at the cell center \((x = 0)\) and at the cell/ambient interface \((x = d_{el} / 2, \text{assuming radial symmetry})\) are
\[
J_q = 0,
\]
\[
J_q = \alpha (T - T_{\text{amb}}) + \sigma_{SB} \left( T^4 - T_{\text{amb}}^4 \right),
\]
respectively. The heat source \(\dot{q}^V\) in the energy balance Equation 1 results from physicochemical processes on the mesoscopic (electrode-pair) scale, as will be discussed in the next section, and requires specific attention when upscaling from electrode-pair to cell scale, as will be described in the Upscaling section.

**Mesoscopic (electrode-pair) scale.**—On the mesoscopic scale (here: \(y\) dimension, hundred micron scale, cf. Figure 1), we describe mass and charge transport in the liquid electrolyte as well as charge transport in the electronic phase in through-plane direction of the electrode pair. In the liquid electrolyte, species conservation is given by
\[
\frac{\partial}{\partial t} \left( \rho \frac{\dot{c}_i}{\dot{c}_0} \right) = -\frac{\partial}{\partial y} \left( D_i \frac{\partial \dot{c}_i}{\partial y} \right) + \dot{s}^V_i + \dot{s}^D_i,
\]
and charge conservation follows from assumed local electroneutrality,
\[
0 = -\sum_i z_i F \frac{\partial \dot{c}_i}{\partial y} + \sum_i z_i F \dot{s}^V_i + \sum_i z_i F \dot{s}^D_i.
\]

In these two equations, the three right-hand side terms represent transport fluxes of species \(i\), source term due to (electro-)chemical reactions, and source term due to double layer charging/discharging, respectively. Assuming the presence of an electric double layer at the electrode/electrolyte interface, we describe the electric double layer current as
\[
\dot{i}^V_{\text{DL}} = C_{\text{DL}} \frac{\partial (\Delta \phi)}{\partial t},
\]
where, the electric-potential difference between liquid electrolyte and solid conducting phase is given as
\[
\Delta \phi = \phi_{\text{ele}} - \phi_{\text{elyt}}.
\]

Using Eq. 6, we cast the charge neutrality condition (5) into the form of a differential equation (see Appendix Charge neutrality and double layer capacitance),
\[
C_{\text{DL}} \frac{\partial (\Delta \phi)}{\partial t} = \sum_i z_i F \left( \frac{\partial \dot{c}_i}{\partial y} - \dot{i}^V_i \right),
\]
which we use as governing potential equation.

Convection inside the liquid electrolyte is neglected, thus the species fluxes are given by
\[
J_i = -D_i^{\text{eff}} \frac{\partial \dot{c}_i}{\partial y} - D_i^{\text{migr,eff}} \frac{\partial \phi_{\text{elyt}}}{\partial y},
\]
where, the first and second terms on the right-hand side represent diffusion and migration, respectively. Following porous electrode theory, effective transport coefficients are calculated from bulk properties by correcting for porosity and tortuosity.

\[
D_i^{\text{eff}} = \frac{\epsilon_{\text{elyt}}}{\epsilon_{\text{elyt}}^r} D_i,
\]
The frequently-used Bruggeman approximation, \(D_i^{\text{eff}} = \epsilon_{\text{elyt}}^{1.5} D_i\), is a special case of this general expression, based on the assumption that the tortuosity factor \(\tau' = \tau = \epsilon_{\text{elyt}}^{-0.5}\).

The general flux Equation 9 can host both, diluted solution theory (DST) (Nernst-Planck type model) and concentrated solution theory (CST), depending on the choice of diffusion and migration coefficients. In the limit of diluted solution,
\[
D_i^{\text{migr, DST}} = \frac{z_i F \sigma}{RT} c_i D_i,
\]
Concentrated solution theory for a binary electrolyte can be cast into the form of Eq. 9 by selecting (cf. Appendix Transport coefficients from concentrated solution theory)
\[
D_i^{\text{migr, CST}} = \frac{D_0}{z_i F c_i} \cdot \frac{2RT}{F} \sigma(c,T) \cdot \nu(c,T)
\]
where, the index \(i\) refers to the two ions (e.g., Li\(^+\) and PF\(_6^-\)). The diffusion coefficient \(D_0\), electrolyte conductivity \(\sigma\), transference numbers \(t^0(i) = 1 - t^+ i\) and lumped activity parameter \(\nu = (1 - t^0 i)(1 + \frac{2ln(\frac{\nu}{\sigma})}{\xi_{+}^i})\) are the common parameters applied in lithium-ion battery models with concentrated solution theory.

Typical lithium-ion battery electrolytes are concentrated solutions, therefore CST provides a more accurate picture of species transport. However, the parameterization of CST requires specialized and time-consuming experiments. In many cases, parameters may be unavailable, for example because the electrolyte composition of a commercial cell is unknown. Here, DST can be advantageous because the only parameters are the diffusing species’ diffusion coefficients which can be relatively easily derived from cell impedance experiments. Using a correctly-parameterized DST model may give more accurate simulation results than a CST model parameterized to a different type of electrolyte. Also, the DST framework in Equations 9–11 can host electrolytes containing more than two ionic species, for example, polysulfides in lithium/sulfur cells. Here, CST is even more difficult to
parameterize. Therefore, it is advantageous to have a flexible model framework that can host both, CST and DST.

We furthermore assume that the electronic resistance within the electrode is negligible compared to the ionic resistance in the liquid electrolyte, resulting in a spatially constant \( \phi_{elde} \) throughout each electrode. This assumption is valid for typical lithium-ion battery electrode materials. Graphite electrode conductivities are two orders of magnitude higher than that of the electrolyte.\(^52-58\) Although pure lithium iron phosphate is a very bad electron conductor,\(^55-62\) thanks to carbon coating or conductive additives used in commercial LFP batteries the electrode is likely to have one order of magnitude higher conductivity than the electrolyte.\(^51,53-54\)

Boundary conditions for the species conservation are \( J_e = 0 \) at both electrode/current collector interfaces. Electrode-pair voltage follows from

\[
E = \phi_{elde, ca} - \phi_{elde, an} = -i \cdot R_{elde},
\]

where, we assume an additional potential drop due to the electronic resistance \( R_{elde} \) of the current collection system. We set \( \phi_{elde, ca} = 0V \) as potential reference. The externally applied current density \( i \) is given as

\[
i = \int_{x=0}^{L_{electrode}} (\dot{q}_e^y + i_{elde}^y) \, dy. \tag{15}
\]

Heat production takes place within the electrodes. We assume that, on the electrode-pair scale, temperature gradients are small with respect to gradients on the cell scale. Therefore, the electrode pair itself is modeled isothermally, yet with time-dependent temperature as given by the cell model (cf. Upscaling section). The area-specific heat is given by integrating all local heat sources over the electrode-pair length,

\[
\dot{q}^A_e = \int_{y=0}^{L_{EP}} (\dot{q}_{chem}(y) + \dot{q}_{ohm}(y)) \, dy + R_{elde}i^2, \tag{16}
\]

where, reversible and irreversible heating due to all chemical and electrochemical reactions is given by (see Appendix Heat source terms)

\[
\dot{q}_{chem} = \sum_{n=1}^{N_{Li}} (r_n A_n \epsilon_n (-\Delta H_n + F V_{cell} \Delta \phi_n)), \tag{17}
\]

and ohmic (Joule) heating in the liquid electrolyte is given by

\[
\dot{q}_{ohm} = \sigma \cdot \left( \frac{\partial \phi_{elde}}{\partial y} \right)^2. \tag{18}
\]

The last term in Eq. 16 represents ohmic heating due to resistance of the current collection system.

In summary, we have presented governing equations for species concentrations (Eq. 4) and electric potential (Eq. 8) on the electrode-pair scale, as well as the required constitutive equations. We still require a closing relationship between Faradic current and electric-potential difference, \( i_{elde}^y = f(\Delta \phi^{elde}) \). This relationship follows from electrochemistry, as described in the Electrochemistry and multi-phase chemistry section.

**Microscopic (particle) scale.—** On the microscopic scale (here: \( z \) dimension, micrometer scale, cf. Figure 1), we describe diffusive mass transport inside the active materials particles. We assume spherical particles and Fickian diffusion. The mass conservation for lithium inside the active material (Li,AM) is given by

\[
\frac{\partial c_{Li,AM}}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial z} \left( r^2 D_{Li,AM} (c_{Li,AM}) \frac{\partial c_{Li,AM}}{\partial z} \right). \tag{19}
\]

The solid-state diffusion coefficient may depend on the concentration of intercalated lithium \( c_{Li,AM} \). Boundary conditions are \( J_{Li,AM} = 0 \) in particle center and \( J_{Li,AM} = \frac{T_{AM}}{T_{cell}} \dot{q}^V_{Li,AM} \) at particle surface. The geometric factor \( \frac{T_{AM}}{T_{cell}} \) is derived in Appendix Geometric factor.

In some cases, we do not want to model solid-state diffusion on the microscale, for example, if current rates are low (and we want to save computational time); for a model-based sensitivity analysis (where simulations runs with and without solid-state diffusion are compared); or if the active material is showing a phase-change behavior (such as lithium iron phosphate\(^63\)) and therefore requires a different treatment of the microscale. Mass conservation of bulk lithium is then given by

\[
\frac{\partial c_{Li,AM}}{\partial t} \bigg|_{cell} = \dot{q}^V_{Li,AM}, \tag{20}
\]

which can be used instead of Eq. 19.

**Upscaling.—** Each of the three scales described above represents transport processes modeled in one dimension. This section describes the coupling strategy between the scales.

Between macroscale (cell) and mesoscale (electrode pair) we use a homogenization approach, as shown in Figure 2. We use a reduced number of electrode-pair models \( N_{EP} \) (typically, 1 . . . 10) which we distribute along the \( x \) direction. Each electrode-pair model \( m \) thus represents the behavior of a hollow cylinder \( V_m \) of the cell. The cell scale passes the local (on the \( x \)-scale) temperature \( T_m \) down to the electrode-pair scale. In turn, the representative electrode-pair models pass their heat sources \( \dot{q}^V_{Li,AM} \) up to the cell scale, where they are used locally (on the \( x \) scale) within the radial sections represented by the electrode-pair models.

Lithium-ion battery cells consist of stacked or wound sheets of electrode pairs with a total area in the m\(^2\) range (e.g., 0.171 m\(^2\) for the 26650 cell investigated here). This area is referred to as “active electrode area” \( A_e \).\(^11\) Using this parameter, the volumetric (on the \( x \) scale) heat \( \dot{q}^V_{Li,AM} \) is calculated from the area-specific heat \( \dot{q}^A_{Li,AM} \) (Eq. 16) of electrode pair \( m \) according to

\[
\dot{q}^V_{Li,AM} = \frac{A_e}{V_{cell}} \dot{q}^A_{Li,AM}. \tag{21}
\]

The total cell current is given as weighted sum over the representative electrode pairs,

\[
I_{cell} = \frac{A_e}{V_{cell}} \sum_{m=1}^{N_{EP}} V_m \cdot i_m. \tag{22}
\]

while the cell voltage is identical for all electrode pairs due to their parallel connection (assuming negligible potential differences throughout
the current collection system, due to relatively small resistance of the metal foils of about 10 µΩ compared to the full cell resistance in the order of > 1000 µΩ\(^6\).

\[
E_{\text{cell}} = E_1 = E_2 = \cdots = E_{N_p}.
\]  

[23]

Number and size of representative hollow cylinders are typically selected as to resolve the highest temperature gradients. We have empirically observed that even in the limiting case of one single volume section (i.e., one electrode pair represents the complete cell), the thermal cell behavior can be well described. This is due to the fact that, the spatial discretization of the heat transport Equation 1 (indicated as solid line in Figure 2) can be chosen independently from the number of electrode-pair models (indicated as solid points in Figure 2). The latter example would lead to a temperature gradient under a constant heat source along the x-scale.

Between mesoscale (electrode pair) and microscale (particle) we apply the “standard” pseudo-2D (P2D) approach\(^7\,8\) that is, a single particle is modeled at every grid point of the electrodes.

**Electrochemistry and multi-phase chemistry.**—We use a generalized multi-phase chemistry framework that was described in detail in Ref. 13 and that is based on the use of the open-source chemical kinetics code CANTERA\(^6\) (cf. Simulation methodology section). Briefly, the electrode pair (Figure 1, y scale) is assumed to consist of up to seven layers (positive and negative electrode, positive and negative current collectors, separator, positive and negative gas reservoirs). Each layer may host an arbitrary number of bulk phases (solid, liquid, or gaseous) characterized by their respective volume fractions \(\varepsilon\), where each bulk phase may host an arbitrary number of chemical species. Each layer may furthermore host an arbitrary number of interfaces, characterized by their volume-specific surface area \(A_s\), where each interface may host an arbitrary number of interfacial reactions between adjacent bulk phases.

The following Eqs. 24–26 represent the implementation of chemical kinetics in CANTERA. The rate of a single interfacial reaction follows from mass-action kinetics\(^6\,66\)

\[
r = k_i \prod_{i=1}^{N_k} c_i^{n_i} - k_i \prod_{i=1}^{N_p} c_i^{n_i}.
\]  

[24]

where the concentrations \(c_i\) refer to the concentrations at the electrode/electrolyte interface as given by the transport models. The forward rate constant is given by transition state theory through an extended Arrhenius expression\(^6\,65\,66\)

\[
k_f = k_i^0 \cdot \exp\left(-\frac{E_{act,i}}{RT}\right) \cdot \exp\left(-\frac{\alpha_i zF}{RT} \Delta G^{eq}\right) \cdot \exp\left(\frac{(1-\alpha_i) zF}{RT} \Delta G^{act}\right) \right). \]  

[25]

which consists of a thermally-activated part and a potential-dependent part. The reverse rate constant follows from thermodynamic consistency according to

\[
k_i = k_f^0 \cdot \exp\left(-\frac{E_{act,i}}{RT}\right) \cdot \exp\left(\frac{\Delta G^{eq}}{RT}\right) \cdot \exp\left(\frac{\alpha_i zF}{RT} \Delta G^{act}\right) \cdot \prod_{i=1}^{N_k} c_i^{-n_i}. \]  

[26]

where, \(c_i^0\) is the standard concentration (reference state\(^6\)) of species \(i\). CANTERA uses the following definition of standard concentrations: for bulk liquid and solid phases (\textit{ConstDensityThermo} class), \(c_i^0 = \rho/\bar{M}\) (total concentration in the phase); for the gas phase (\textit{IdealGas} class), \(c_i^0 = \frac{N_{\text{mol}}}{N_{\text{mol}}/n_i}\) (total concentration in the phase). The last term in Eq. 26 is required for unit consistency in Eq. 24. Note the interfacial reaction rate \(r\) has units of \(\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}\), while the forward rate preexponential factor \(k_i^0\) has units of \(\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}\) by definition.

In an ideal intercalation material, the equilibrium half-cell potential depends on the (concentration-independent) standard Gibbs energy \(\Delta G^{0}\) and the concentrations of the involved species according to the Nernst equation,

\[
\Delta \phi_{\text{eq}}^{\text{bulk}} = -\frac{\Delta G^0}{zF} - \frac{RT}{zF} \ln\left(\prod_{i=1}^{N_k,N_p} \left(\frac{c_i}{c_i^0}\right)^{n_i}\right),
\]  

[27]

which can be derived from Eqs. 24–26 by setting \(r = 0\) and \(\Delta \phi = \Delta \phi^{eq}\). A real intercalation material shows additional concentration dependencies that can be described using a (concentration-dependent) excess Gibbs energy \(\Delta G^{E}\)\(^6\,65\,68\)

\[
\Delta \phi^{E} = -\frac{\Delta G^0 + \Delta G^{E}(c_i)}{zF} - \frac{RT}{zF} \ln\left(\prod_{i=1}^{N_k,N_p} \left(\frac{c_i}{c_i^0}\right)^{n_i}\right).
\]  

[28]

In our simulation approach, we take this into account by using a concentration-dependent Gibbs reaction energy \(\Delta G(c_i) = \Delta G^0 + \Delta G^{E}(c_i)\) in Eq. 26. In CANTERA, the Gibbs reaction energy is calculated from the species molar enthalpies and entropies,

\[
\Delta G(c_i) = \sum_{i=1}^{N_{k,N_p}} v_i \left(h_i(c_i) - T S_i(c_i)\right).
\]  

[29]

We parameterize \(h_i(c_i)\) and \(S_i(c_i)\) of intercalated lithium species from experimental half-cell potentials assuming reference values for the vacancies \(h_v = 0, S_v = 0\).

The effective potential difference between electrode and electrolyte \(\Delta \phi^{E}\) occurring in Eq. 25 follows from its nominal value (Eq. 7) by correcting for a film resistance,

\[
\Delta \phi^{E} = \Delta \phi - R^{\text{film}}V\]  

[30]

representing, for example, the SEI (cf. Calendaric aging section).

The overall (volumetric) bulk species source terms entering the mass balance Eq. 4 are obtained by summing over all interfacial reactions, scaled to the specific area of the respective interface,

\[
\dot{s}_i^V = \sum_{i=1}^{N_i} \left(v_i F A_i^V\right).
\]  

[31]

The faradic current entering the charge balance Eq. 8 is obtained in analogy from the source terms of electrons,

\[
\dot{i}_e^V = F \sum_{i=1}^{N_i} \left(v_i n_i A_i^V\right).
\]  

[32]

The interfacial reactions cause a net mass transfer between bulk phases, leading to a change of volume fractions. Therefore, we introduce additional conservation equations for all bulk phases\(^13\)

\[
\frac{\partial (\rho_i s_i)}{\partial t} = \sum_{i=1}^{N_k,N_p} \left(\frac{N_{\text{mol}}}{n_i}\right) \dot{s}_i^V M_i.
\]  

[33]

Note that the present electrochemistry framework does not use the Butler-Volmer equation. Instead, the more fundamental transition state theory, Eqs. 24–26, is used. In order to cast this theory into Butler-Volmer type kinetics, we additionally multiply the forward rate constant \(k_i\) by a factor \(\exp\left(-\alpha_i \frac{\Delta G^{E}}{RT}\right)\) (see Appendix Mass action kinetics and Butler-Volmer formulation).

In summary, this section has presented complete expressions describing electrochemical thermodynamics and kinetics. It can generally host an arbitrary number of charge-transfer and non-charge-transfer reactions. The required model parameters are the forward rate preexponential factor \(k_f^0\), activation energy \(E_{\text{act},i}\), and symmetry factor \(\alpha_i\) (in case of charge-transfer reactions) of all reactions, as well as molar enthalpies \(h_i\) and molar entropies \(S_i\) of all species. The potential-difference \(\Delta \phi\) enters from the meso-scale transport model.

**Gas pressure inside the cell.**—SEI formation during aging causes gas release, hence, pressure increase inside the cell housing. While a pouch cell can (partially) accommodate pressure increase by volume expansion, in the cylindrical cell studied here the housing is rigid, thus only pressure rise needs to be addressed. In order to quantify this effect, the void spaces of the cell housing are modeled as 0D gas reservoir\(^6\). The governing equations are the continuity equation,

\[
\frac{\partial \rho_{\text{gas}}}{\partial t} = \frac{1}{V_{\text{void}}} \sum_{i=1}^{N_{\text{gas}}} S_i M_i.
\]  

[34]
species conservation,
\[
\frac{\partial (p_{\text{gas}} Y_i)}{\partial t} = \frac{1}{V_{\text{void}}} \frac{\partial}{\partial t} \Sigma_{i=1}^{N_{\text{gas}}} M_i,
\]
and ideal gas law,
\[
p_{\text{gas}} = p_{\text{gas}} RT \sum_{i=1}^{N_{\text{gas}}} Y_i / M_i.
\]

The gas-phase species source term \(\Sigma_{i=1}^{N_{\text{gas}}} \) follows from integration over the complete electrode volume on mesoscale and macroscale, similar to the electrical current (Eqs. 15 and 22), according to
\[
\Sigma_{i=1}^{N_{\text{gas}}} = \frac{A_{\text{cell}}}{V_{\text{cell}}} \sum_{m=1}^{N_{\text{EP}}} \left( \frac{1}{\partial_t} \int_0^{\lambda_{\text{EP}}} \rho_{\text{gas}} \cdot v \, dy \right).
\]

The gas pressure and composition is assumed homogenous throughout the cell, including the gas-filled porosity inside the anode.

**Simulation methodology.**—The governing equations and relationships presented above (except the chemistry, see below) are implemented in the in-house multiphysics software package DENIS (Detailed Electrochemistry and Numerical Impedance Simulation).

DENIS is a C/C++ code with modular structure. Its main functionality is to cast the model equations into the form of a differential-algebraic equation system,
\[
\frac{dy}{dt} = f (y, t), \quad 0 = g (y, t),
\]

based on conveniently editable text input files. The solution vector \(y\) in the particular case presented in the results has a dimension of 1928. We apply the finite-volume method to discretize the partial differential equations for \(T\) (Eq. 1), \(c_i\) (Eq. 4), \(\Delta \phi\) (Eq. 8) and \(c_{\text{LAM}}\) (Eq. 19) using non-equidistant non-adaptive discretization. The number of grid points is 10, 31, and 14 in \(x, y,\) and \(z\) dimensions, respectively. We use \(N_{\text{EP}} = 5\) electrode-pair models distributed unevenly on the \(x\) scale, representing radial sections of 0.5, 4, 4, and 0.5 mm of the cell. The DAE system (38) is numerically solved using the implicit time-adaptive solver LIMEX (version 4.3A,2\textsuperscript{71} The equation system can be either solved for \(\lambda_{\text{EP}}\) when \(E_{\text{cell}}\) is given as independent variable (potentiostatic simulation), or vice versa (galvanostatic simulation).

The complete electrochemistry (thermodynamics and kinetics) is evaluated using the chemical kinetics software CANTERA (version 2.2,\textsuperscript{26}) In particular, CANTERA implements Eqs. 24–26 for reaction mechanisms of arbitrary complexity. The reaction mechanisms as well as all thermodynamic and kinetic data are provided to CANTERA in the form of conveniently editable text input files, which are available from the authors upon request. CANTERA is a C++ code which we interface from DENIS to obtain the reaction rates \(r\) needed in Eqs. 17, 31, 32, and 37, and reaction enthalpies \(\Delta H\) needed in Eq. 17. For all bulk phases we use CANTERA’s ConstDensityThermo (“incompressible solid”) model, except for the gas phase for which we use the IdealGas model. For all interfacial reactions the InterfaceKinetics model, as described by Eqs. 24–26, is used. The stoichiometry-dependent thermodynamics of intercalated lithium species is implemented via an additional DENIS/CANTERA feedback loop.

We use MATLAB (version 2016a) for controlling all DENIS simulations via S-function interfaces, as well as for data evaluation and visualization. Wall-clock computational time is typically 4 hours on a 3.4 GHz Pentium processor desktop computer (single-core simulation) for one discharge curve as shown, for example, in Figure 5. This comparatively long computational time is due to the fact the code was designed for flexibility (including full coupling to CANTERA), not numerical efficiency.

**Results and Discussion**

**Parameterization.**—While the modeling approach presented above is generic in the sense that it can host different types, geometries and chemistries of lithium-ion cells, we here specifically parameterize the model in order to represent a commercially-available cylindrical 26650-size high-power LFP/graphite cell.

The large number of required parameters poses a particular challenge to physically-based battery modeling.\textsuperscript{22} We use the following parameterization approach: (1) Use literature values on the identical or similar cells and components for an initial set of model parameters; (2) use macroscopic experimental data, in particular electrical and thermal behavior upon charge and discharge, to re-parameterize selected performance-sensitive parameters, in particular, rate coefficients (pre-exponential factors the charge-transfer reactions) and thermal parameters (heat transfer coefficient); (3) use macroscopic aging data from literature (capacity as function of calendric aging time) to parameterize the rate coefficients of the aging reaction (pre-exponential factor, activation energy); (4) test the model against macroscopic experimental data over a wide range of conditions (charge/discharge rates from 0.1 C to 10 C, temperatures, SOC). Parameter identification was performed by manually varying values (automated fitting was not possible due to high computational time of the simulation). The resulting full set of model parameters is given in Table I (macroscopic cell scale), Table II (mesoscopic electrode-pair scale), and Table III (microscopic particle scale). In addition, Figure 3 and Figure 4 show the thermodynamics and the transport data of intercalated lithium as function of intercalation stoichiometry. A particular strength of the present modeling approach is the ability to host complex multi-step electrochemical reaction mechanisms. The thermodynamic data of all used species are given in Table V, and the reaction equation and kinetic coefficients are given in Table VI.

LFP is known to be a two-phase material with charge/discharge equilibrium-potential hysteresis.\textsuperscript{72,73} In the present model we neglect the hysteresis and assume that charge and discharge thermodynamics are described by the same data (Figure 3). More sophisticated models that are able to capture the equilibrium-potential hysteresis have been published\textsuperscript{75} and may be integrated into the present framework in future, but are out of scope of the present study. As LFP shows a two-phase behavior during charge and discharge, the model of spherical diffusion used for the graphite anode is not applicable here\textsuperscript{55,76,77} and requires a more complex mathematical description like the core-shell model used in Dargaville et al.\textsuperscript{26} or the multi-particle model of Farkhondeh et al.\textsuperscript{78} Again, these may be integrated into the present framework in future, but are out of scope of the present study. Therefore, bulk diffusion is not modeled at the cathode, recognizing that the model starts to become less reliable for high C-rates (>5 C), as will also be shown below.

The present framework is able to host both, DST and CST transport models of the electrolyte (cf. Mesoscopic (electrode-pair) scale section). While we have investigated both models, the simulation results show rather small differences (results not shown). As the CST parameters are not known for the electrolyte of the investigated cells, the results shown in the remainder of this section are based on DST. It should be noted that a number of other parameters have to be considered as “preliminary”, either because the true materials and

| Table I. Macroscale: Thermal and geometrical parameters of the cell scale. |
|-----------------|-----------------|-----------------|---------------|
| Parameter       | Value           | Reference       |
| Thermal conductivity \(\kappa\) | 1.02 W·m\(^{-1}\)·K\(^{-1}\) | From similar cell\textsuperscript{97} |
| Heat capacity \(pcp\) | 3.2·10\(^5\)J/(m\(^3\)K) | From similar cell\textsuperscript{97} |
| Heat transfer coefficient \(\alpha\) | 32 W·m\(^{-2}\)·K\(^{-1}\) | Fitted to temperature decay of hot cell |
| Emissivity of the cell surface \(\epsilon\) | 0.8 | Assumed |
| Diameter of battery \(d_{\text{cell}}\) | 2.6 cm | Measured |
| Active electrode area \(A_{e}\) | 0.171 m\(^2\) | Measured\textsuperscript{98} |
| Void (gas-filled) volume within the cell housing \(V_{\text{void}}\) | 4.1·10\(^{-6}\) m\(^3\) | Estimated from CT data\textsuperscript{99} |
Table II. Mesoscale: Geometry and transport parameters of the electrode-pair scale.

| Parameter | Value      | Reference |
|-----------|------------|-----------|
| Thickness of cathode \((y\text{-scale})\) | 79.5 μm | Measured\(^98\) |
| Thickness of separator \((y\text{-scale})\) | 20.0 μm | Measured\(^98\) |
| Thickness of anode \((y\text{-scale})\) | 35.5 μm | Measured\(^98\) |
| Tortuosity of cathode \(\tau\) | 1.2 | Assumed |
| Tortuosity of separator \(\tau\) | 1.0 | Assumed |
| Tortuosity of anode \(\tau\) | 1.2 | Assumed |
| Diffusion coefficients \(D_{Li^{+}\text{(solv)}}, D_{PF_{6}^{-}\text{(solv)}}\) | 7.7·10^{-2} m^2 s^{-1} \cdot e^{-\frac{50kJ}{RT}} | Value at 25°C from Newman et al.\(^{100}\), activation energy assumed |
| Anode double layer capacitance \(C_{DLA}\) | 2.0·10^{4} F·m^{-3} | Fitted to EIS data\(^98\) |
| Cathode double layer capacitance \(C_{DLC}\) | 1.0·10^{3} F·m^{-3} | Fitted to EIS data\(^98\) |
| Ohmic resistance of current collection system \(R_{cc}\) | 1.1 mΩ·m² | Fitted to EIS data\(^{101}\) |
| Electrical conductivity of the SEI-layer \(\sigma_{SEI}\) | 5.0·10^{-6} S/m | From similar cell\(^{102}\) |
| Anode stoichiometry range \(X_{Li[6]} (0\ldots100\% \text{SOC})\) | 0.01–0.57 | Determined from discharge curves\(^{101}\) |
| Cathode stoichiometry range \(X_{Li[FePO_{4}] (0\ldots100\% \text{SOC})}\) | 0.99–0.01 | Determined from discharge curves\(^{101}\) |

composition of the commercial cells used for this study are not known, or because there is no experimental data available for these materials. In this case, available data from similar materials and composition were used. By fitting selected model parameters to experimental data on the investigated cells, deviations of "preliminary" parameters from their true values and deviations due to simplified modeling assumptions (two-phase behavior, DST) are implicitly included in the fits. Note that fitted parameters may still not be unique, in particular when parameters show similar sensitivities to cell behavior (e.g., pre-exponential factors of cathode and anode charge-transfer reaction). Still, our parameterization approach is justified by the fact that the thermal and electrical cell performance and aging behavior can be successfully reproduced over a wide range of operating conditions, as will be shown in the following.

Discharge and charge characteristics.—Using the multi-scale model as described in the Modeling and simulation approach section and parameterized in the Parameterization section, charge and discharge behavior was simulated over a wide range of C-rates (0.1 C, 1 C, 5 C, 10 C) and ambient temperatures (25°C, 40°C, 60°C). The comparison of the simulations to experimental data\(^{79}\) is shown in Figure 5 (cell voltage) and Figure 6 (cell surface temperature). In Figure 5 and Figure 6 both, simulations and experiments used constant-current constant-voltage (CCCV) discharge to 2.0 V and CCCV-charge to 3.6 V with C/10 final current. The model is able to quantitatively reproduce the experimental electrical and thermal behavior over the complete range of investigated conditions. Going into detail, there are a number of aspects where simulation and experiment deviate, as discussed in the following. (a) The simulated cell capacity shows lesser dependence on C-rate than the experiments. We believe that this is an artefact of the experiment, as the data at 0.1 C and 1 C were carried out

Table III. Microscale: Transport parameters of particle scale.

| Parameter | Value | Reference |
|-----------|-------|-----------|
| Radius of anode particles \(r_{p}\) \((z\text{-scale})\) | 3.58 μm | Measured\(^98\) |
| Diffusion coefficient of anode active material \(D_{Li,AM,AN}\) | see Figure 4 | Measured\(^{103}\) |
| Radius of cathode particles \(r_{p}\) \((z\text{-scale})\) | 37.0 nm | Measured\(^98\) |

Figure 3. Thermodynamic data (molar enthalpies and entropies) of intercalated lithium in the negative electrode (upper panel, data from Reynier et al.\(^{111}\) and Safari et al.\(^{88}\)) and the positive electrode (lower panel, data from Dodd\(^{108}\) and Safari et al.\(^{88}\)) as function of intercalation stoichiometry.

Figure 4. Solid-state diffusion coefficient of lithium in graphite as function of intercalation stoichiometry, data from Levi et al.\(^{103}\) (with extrapolation for \(x \rightarrow 0\)).
with a different individual cell than the data at 5 C and 10 C; note the model parameters were fitted to the data at 0.1 C and 1 C. (b) At 5 C and 10 C, simulations show an increasingly different voltage than the data at 5 C and 10 C; note the concentrations of Li and PF6– ions in the electrolyte is shown in Figure 8a. The state of charge (SOC) at the center (x = 0) and surface (x = 13 mm) of the cell. While the surface temperature increases from 25°C to 40.3°C during discharge, the core temperature increases to 43.5°C. The temperature difference between surface and core remains relatively low but still significant. Erhard et al.26 have simulated and measured temperature differences within an LFP/graphite cell. Their highest C-rate (2 C) showed a maximum core temperature of about 40°C and a maximum temperature difference to the surface of about 5°C. They have emphasized the strong influence of this relatively small temperature difference on local cell properties like voltage or current density.

The spatiotemporal behavior of the internal states on the mesoscopic (electrode pair) scale is shown in Figure 8. These profiles were taken at the center of the cell (macroscale x = 0). The concentration of Li⁺ and PF6– ions in the electrolyte is shown in Figure 8a. Note the concentrations of Li⁺ and PF6– are identical, as enforced by charge neutrality (cf. Mesoscopic (electrode-pair) scale section). They both show a gradient between negative electrode (high concentration) and positive electrode (low concentration), consistent with the location of formation and consumption of Li⁺, respectively. The gradient becomes smaller for progressing discharge. This is due to the increas-

### Table IV. Properties of layers within the electrode pair.

| Layer      | Phase                      | Initial volume fraction \( \varepsilon \) | Density \( \rho \) kg \cdot m\(^{-3}\) | Species (initial mole fraction \( X \))                                      |
|------------|----------------------------|------------------------------------------|------------------------------------------|----------------------------------------------------------------------------|
| Cathode    | Cathode active material    | 0.67 \( ^{101} \)                          | 1510 \( ^{101} \)                        | Li[LiF] (0.01), V[LiF] (0.99)                                              |
| Electrolyte|                             | 0.28 \( ^{101} \)                           | 1130 \( ^{101} \)                        | C\(_2\)H\(_2\)O\(_3\)(1) (0.6), Li\(_2\)H\(_2\)O\(_3\) (0.2), Li\(^+\) (0.1), PF\(_6\)– (solv) (0.1) |
| Gas phase cathode |                       | 0.05 \( ^{102} \)                          | 1.14 \( ^{104} \)                        | N\(_2\) (0.999), C\(_2\)H\(_2\)O\(_3\)(g) (1.0 \(
\times\) 10\(^{-5}\)), C\(_2\)H\(_4\) (1.0 \(
\times\) 10\(^{-5}\)), O\(_2\) (1.0 \(
\times\) 10\(^{-5}\)), CO\(_2\) (1.0 \(
\times\) 10\(^{-5}\)), H\(_2\) (1.0 \(
\times\) 10\(^{-5}\))          |
| Separator  | Separation                 | 0.5 \( ^{105} \)                           | 200 \( ^{106} \)                         | Separator (1.0)                                                            |
| Electrolyte|                             | 0.5 \( ^{105} \)                           | 1130 \( ^{101} \)                        | C\(_2\)H\(_2\)O\(_3\)(1) (0.6), Li\(_2\)H\(_2\)O\(_3\) (0.2), Li\(^+\) (solv) (0.1), PF\(_6\)– (solv) (0.1) |
| Anode      | Anode active material      | 0.72 \( ^{101} \)                          | 2540 \( ^{101} \)                        | Li[LiF] (0.57), V[LiF] (0.43)                                              |
| Electrolyte|                             | 0.22 \( ^{101} \)                          | 1130 \( ^{101} \)                        | C\(_2\)H\(_2\)O\(_3\)(1) (0.6), Li\(_2\)H\(_2\)O\(_3\) (0.2), Li\(^+\) (solv) (0.1), PF\(_6\)– (solv) (0.1) |
| SEI        |                            | 0.01*                                      | 1300 \( ^{107} \)                        | (CH\(_2\))O\(_2\)C\(_2\) (1.0)                                             |
| Gas phase anode |                   | 0.05 \( ^{102} \)                          | 1.14 \( ^{104} \)                        | N\(_2\) (0.999), C\(_2\)H\(_2\)O\(_3\)(g) (1.0 \(
\times\) 10\(^{-5}\)), C\(_2\)H\(_4\) (1.0 \(
\times\) 10\(^{-5}\)), O\(_2\) (1.0 \(
\times\) 10\(^{-5}\)), CO\(_2\) (1.0 \(
\times\) 10\(^{-5}\)), H\(_2\) (1.0 \(
\times\) 10\(^{-5}\))          |

*\( ^{*} \) assumed, corresponds to an initial SEI thickness of 16 nm.  
**\( ^{**} \) 5% gas volume fraction assumed.

**Table V. Properties of present species.**

| Species      | Molar enthalpy \( h_i /kJ \cdot mol^{-1} \) | Molar entropy \( s_i /J \cdot mol^{-1} \cdot K^{-1} \) | Reference |
|--------------|---------------------------------------------|-----------------------------------------------------|-----------|
| Li[LiF]      | See Figure 3                                 | See Figure 3                                         | 88,108    |
| V[LiF]       | 0                                           |                                                     | 109       |
| C\(_2\)H\(_2\)O\(_3\)(l) | \(-578^{*}\)                              | 175^{*}                                              |           |
| Li\(^+\) (solv) |                                                  | 0                                                   |           |
| Li[LiF]      | See Figure 3                                 | See Figure 3                                         | 110       |
| V[LiF]       | 0                                           |                                                     |           |
| (CH\(_2\))O\(_2\)C\(_2\) | \(-1370\)                               | 88.8                                                 | Calculated assuming SEI formation potential of 0.8 V vs. Li/Li\(^+\) |
| N\(_2\)      | 0.00143^{*}                                 | 191^{*}                                              |           |
| C\(_2\)H\(_2\)O\(_3\)(g) | \(-503^{*}\)                             | 314^{*}                                              |           |
| C\(_2\)H\(_4\) | 52.5^{*}                                   | 219^{*}                                              |           |
| O\(_2\)      | 1.63 \times 10^{-5}^{*}                  | 205^{*}                                              |           |
| CO\(_2\)     | \(-394^{*}\)                                | 214^{*}                                              |           |
| H\(_2\)O     | \(-242^{*}\)                                | 189^{*}                                              |           |
| H\(_2\)      | 5.20 \times 10^{-6}^{*}                   | 131^{*}                                              |           |

*\( ^{*} \) Values are assumed \( T \)-dependent, here given at 298.15 K.
Figure 5. Simulated and experimental\textsuperscript{79} cell voltage as function of capacity for different C-rates and ambient temperatures during CCCV charge (left column) and CCCV discharge (right column).

The results shown in the previous section were obtained with a fresh (non-aged) cell. In the present section, we use the model to investigate calendaric aging. We assume that aging is due to SEI formation at the anode/electrolyte interface according to discharging cell temperature (cf. Figure 7), increasing the ion diffusivity of the electrolyte.

Figure 8b shows the normalized electric-potential distribution in the electrolyte. Its absolute value (not shown) changes by around 1 V during discharge due to the changing electrode potential. For Figure 8b, we have normalized the potential to the value at separator center to make the small potential gradient (ca. 10 mV) visible. The potential drop is decreasing with progressing discharge because of the increasing cell temperature, increasing the ionic conductivity of the electrolyte. The potential is increasing from the positive to the negative electrode. This drives a migration flux of Li\textsuperscript{+} from the negative to the positive electrode, which adds to the diffusive flux due to the concentration gradient (Figure 8a) in the same direction. For PF\textsubscript{6}–, migration flux is in the opposite direction, i.e., from positive to negative electrode. It is cancelled by diffusive flux, resulting in a net zero flux for the PF\textsubscript{6}– ion. The combined fluxes satisfy both, charge neutrality and net Li\textsuperscript{+} transport.

Finally, on the microscopic (particle) scale, the distribution of lithium stoichiometry in the graphite anode particle is shown in Figure 9. These data were taken at the center of the cell (\(x = 0 \text{ mm}\)) for a representative particle close to the anode/separator interface (\(y = 100 \mu\text{ m}\)). The stoichiometry continuously decreases during discharge, starting at the particle surface (\(z = 0 \mu\text{ m}\)). The wave-like shape of the profiles is a result from the non-constant solid-state diffusion coefficient (cf. Figure 4). The diffusion coefficient has a minimum at a stoichiometry of ca. 0.3, corresponding to the strongest gradient in the stoichiometry profiles.

Calendaric aging.—The results shown in the previous section were obtained with a fresh (non-aged) cell. In the present section, we use the model to investigate calendaric aging. We assume that aging is due to SEI formation at the anode/electrolyte interface according to
Figure 6. Simulated and experimental\textsuperscript{79} cell surface temperature as function of time for different C-rates and ambient temperatures during CCCV charge (left column) and CCCV discharge (right column). The corresponding electrical data are shown in Figure 5.

a single-step charge-transfer reaction\textsuperscript{37,80–83} (cf. Table VI),

\[2\text{C}_3\text{H}_4\text{O}_3\text{(l)} + 2\text{e}^- + 2\text{Li}^+ \rightarrow (\text{CH}_2\text{OCO}_2\text{Li})_2\text{(s)} + \text{C}_2\text{H}_4\text{(g)}.\] \textsuperscript{[39]}

This reaction takes place in parallel to the main charge-transfer reaction (intercalation/deintercalation). Note that SEI formation was also included in all simulations shown in the previous sections, however did not affect the results shown there due the short time scales of simulation.

The film resistance entering Eq. 30 is given by (see Appendix SEI film resistance and formation rate)

\[R_{\text{SEI}}^V = \frac{1}{3} \frac{r_{\text{SEI}}^2}{\sigma_{\text{SEI}} \cdot \varepsilon_{\text{AM}}} \left( \sqrt{1 + \frac{\varepsilon_{\text{SEI}}}{\varepsilon_{\text{AM}}}} - 1 \right).\] \textsuperscript{[40]}

SEI film growth is known to be diffusion-limited, resulting in a growth rate proportional to \(1/\delta_{\text{SEI}}\) (see Appendix SEI film resistance and formation rate). We include this into the model by scaling the pre-exponential factor of the SEI formation reaction with a factor of \(1/\delta_{\text{SEI}}\) (cf. Table VI). The details of the complex multi-step SEI formation mechanism\textsuperscript{86} are not resolved here, but are assumed to be implicitly included in the fit of the rate coefficients to experimental ageing data. Additionally the typical dry-out of the cell during aging due to electrolyte consumption is considered by multiplying the specific area of the anode active material surface with the aging factor \(\varepsilon_{\text{elyt}}(t)\) (cf. Table VI).

In order to simulate calendaric aging, all parameters were initialized and the electrode stoichiometries were set to 100% SOC, representing a fresh fully-charged cell. The cell was virtually aged
by carrying out a transient simulation with zero-current boundary condition for different times up to 500 days. After aging, the capacity of the virtual cell was determined by first fully charging (1 C, CCCV, 3.6 V cutoff, C/10 break, 1 h resting time) and then fully discharging (1 C, CC, 2.0 V). The same types of simulations were carried out for different initial SOC and ambient temperature. Note the wall-clock time for 500 days aging simulation is only 10 min.

Figure 10 shows simulated (this work) and experimental (Grolleau et al.\textsuperscript{84}) state of health (SOH) as function of aging time for three different states of charge at 30°C ambient temperature. Here, the SOH is defined as

\[
\text{SOH} = \frac{C_{\text{aged cell}}}{C_{\text{fresh cell}}}. \tag{41}
\]

Within the scatter of the experimental data, the simulation is able to reproduce capacity loss both qualitatively and quantitatively for 30°C. Capacity loss is up to 5% for 500 days calendaric aging under the investigated conditions. At 45°C, the experiments show a stronger linearity than the simulation, which follow a $\sqrt{t}$ behavior as expected from diffusion-limited film growth.\textsuperscript{85,86} The data indicate that additional degradation mechanisms not considered in the model become relevant at elevated temperature, for example, cathode decomposition due to precipitation of iron particles.\textsuperscript{87} It should be noted that only two fit parameters of the model are associated with aging, that is, pre-exponential factor and activation energy of the SEI formation reaction (cf. Table VI). The SOC dependence results from the simulated internal potential distribution (cf. Figure 8b) driving the charge-transfer SEI formation reaction. Note that the fitted activation energy (106 kJ/mol) is higher than that reported before (43 kJ/mol).\textsuperscript{88,89} The origin for this difference may be associated with the different types of investigated cells and different chemical ageing models.

In order to further investigate aging behavior, we have simulated the internal resistance of a fresh cell and an aged cell (500 days, 65% SOC, 30°C). The internal resistance of the virtual cell was determined following a typical experimental protocol:\textsuperscript{90-92} Perform complete charge/discharge cycle to determine the reference capacity for SOC and SOH definition; full charge using a CCCV protocol; discharge with 1 C rate for 15 min, corresponding 25% of the SOC; rest for 15 min; discharge at 0.1 C rate for 30 s; current step to 1 C and discharge for 30 s; rest for 15 min. The internal resistance was determined from the current and voltage values before and 3 s after the step according to

\[
R_{\text{int, total}} = -\frac{\Delta E_{\text{cell}}}{\Delta I_{\text{cell}}}. \tag{42}
\]

In addition, we have used the simulated internal cell states to quantify the contributions of the different cell components to the internal resistance, in particular, anode, cathode, separator, and current collector. Results of this analysis are shown in Figure 11, where a fresh cell and an aged cell are compared. The internal resistance of the fresh cell shows a distinct SOC dependence well-known from experiments,\textsuperscript{30,92} with a minimum at intermediate SOC and maxima for both full and empty cells. This shape is a result from anode and cathode, while separator and current collector show SOC-independent behavior. The aged cell shows an increased internal resistance due to SEI film resistance (cf. Eq. 30 and Eq. 40). Interestingly, internal resistance increase is pronounced at 0% SOC, while at the same time internal resistance of the cathode decreases. This is caused by electrode imbalancing during aging.\textsuperscript{45} In our simulations the stoichiometry range at the cathode ($x$ in Li$_x$PO$_4$) changes from 0.012–0.990 (fresh cell) to 0.012–0.915 (aged cell) and that of the anode ($x$ in Li$_x$C$_6$) from 0.010–0.590 (fresh cell) to 0.0064–0.562 (aged cell). Activation overpotential and therefore electrode internal resistance strongly increase toward high and low intercalation stoichiometries.\textsuperscript{93} An SOC of 0% corresponds to the upper $x$ value in Li$_x$PO$_4$, which is decreasing upon ageing, and
to the lower x value in Li$_x$C$_6$, which is also decreasing upon ageing, therefore causing the observed variation in electrode resistances.

Apart from the macroscopic electrical behavior in terms of capacity and internal resistance, the physically-based model allows insight into internal cell states that are difficult to access experimentally. Figure 12 shows the volume fractions of the phases of the negative electrode as function of time for a 500-day calendaric aging simulation. SEI volume fraction continuously increases from its initial value of 1.0% to 4.68%. The latter value corresponds to a film thickness of 75.6 nm. At the same time, electrolyte volume fraction decreases by 5.11% due to its decomposition (cf. Reaction 39). The reaction product SEI has an overall higher density than the reactant electrolyte (cf. Table IV). The resulting “void” volume increases by 1.69%, which can be directly interpreted as drying-out of the cell. The “void” volume in the electrode is actually filled with the formed gaseous ethylene. The gas also fills the “void” volume of the cell beyond the wound electrode pairs (cf. Table IV). As a result of the formed gas, the pressure inside the cell increases. Pressure as function of time is shown on the right axis of Figure 12. The simulation predicts a pressure increase to over 6 bar after 500 days aging time. This value is in the same order of magnitude compared to values from literature where cells with graphite anode and similar electrolyte reached 3 to 5.5 bars at 60°C and 100% SOC after just 50 days of aging.31 The high value might be due to one or several shortcomings in the model: (a) the initial void volume fraction inside the cell and/or the electrodes might have been underestimated; (b) the mechanical expansion of the cell housing and/or compression of the cell components due to increasing gas-phase pressure is not considered in the model; (c) potential follow-up reactions of the gaseous ethylene are not considered.

The multi-scale model is able to reproduce all expected physico-chemical changes inside the cell at least qualitatively, including

![Figure 9](image1.png)

**Figure 9.** Microscale: Simulated distribution of intercalated lithium concentration inside the negative active materials particle for a 5C discharge at 25°C ambient temperature at the center of the cell (x = 0 mm) the electrode/separator interface (y = 100 μm).

![Figure 10](image2.png)

**Figure 10.** Simulated (this work) and experimental (Grolleau et al.84) calendaric aging behavior: State of health as function of the square root of aging time at different ambient temperatures and SOC.

![Figure 11](image3.png)

**Figure 11.** Simulated internal resistance for a fresh cell and an aged cell (500 days at 30°C and 65% SOC) as function of state of charge (SOC).

| Table VI. Interfacial chemical reactions and rate coefficients. |
|---------------------------------------------------------------|
| Interface          | Specific area $A^1/m^2$  | Reaction                                                                 | Pre-exponential factor $A$  | Activation energy $E_{act}$/kJ/mol$^{-1}$  | Symmetry factor $a_1$  |
|--------------------|--------------------------|---------------------------------------------------------------------------|-----------------------------|---------------------------------------------|--------------------------|
| LFP/Electrolyte    | 5.43 $\times$ 10$^7$**   | Li$^+$ (solv) + e$^−$ + V[LFP] $\Leftrightarrow$ Li[LFP]                  | $7.0 \cdot 10^4$ $\frac{mol}{m^2 s}$** | 41.4$^101$                                | 0.5$^****$               |
| Graphite/Electrolyte| 6.03 $\times$ 10$^5$*     | Li$^+$ (solv) + e$^−$ + V[C$_6$] $\Leftrightarrow$ Li[C$_6$]               | $3.0 \cdot 10^1$ $\frac{mol}{m^2 s}$* | 53.4$^101$                                | 0.5$^****$               |
| Graphite/Electrolyte| 6.03 $\times$ 10$^5$*     | 2 C$_3$H$_4$O$_3$(l) + 2 e$^−$ + 2 Li$^+$ (solv) $\Leftrightarrow$ (CH$_2$OCO$_2$Li)$_2$ + C$_2$H$_4$ | $7.0 \cdot 10^{-11}$ $\frac{mol}{s m^2}$*** | 106***                                   | 0.5$^****$               |

*initial values equal to $\frac{3xAM}{rP}$ (see Appendix Geometric factor)
**fitted to discharge/charge curves (Figure 5)
***fitted to aging data (Figure 10)
****assumed
capacity loss, internal resistance increase, electrolyte decomposition, SEI formation, and pressure buildup. Quantitative conclusions are subject to the uncertainty of the model parameters (cf. Parameterization section). Further validation, in particular of the internal cell behavior, is beyond the scope of the present study, but will be subject of future investigations.

Conclusions

Lithium-ion batteries show a complex thermo-electrochemical performance and aging behavior. We have presented a modeling and simulation framework that is able to describe both multi-scale heat and mass transport and complex electrochemical reaction mechanisms. The transport model is based on a 1D + 1D + 1D (pseudo-3D or P3D) multi-scale approach. Heat transport in the radial cell direction (1D, macroscopic) is modeled as conductive process. Mass and charge transport on the electrode-pair scale (1D, mesoscopic) is modeled as diffusion and migration. The charge neutrality condition is cast into a time-dependent partial differential equation by including double layer charging/discharge, allowing stable numerical simulation. Intra-particle transport of lithium atoms (1D, microscopic) is modeled as Fickian diffusion with concentration-dependent diffusion coefficient. A 0D model of the void cell volume was added, allowing to describe gas-phase species concentration and pressure buildup during aging.

The electrochemistry model is based on the use of the open-source chemical kinetics code CANTERA, which is coupled to the transport model via the chemistry source terms. In this approach, charge-transfer reaction kinetics are not modeled with Butler-Volmer equations, but with more fundamental relationships based on mass-action kinetics and transition state theory. The framework allows to describe multi-reaction multi-phase thermo-electrochemistry. In the present study we couple the main reactions (intercalation at the particle surface) to SEI formation as parallel side reaction at the anode.

We have parameterized the model to reflect the performance and aging behavior of an LFP/graphite 26650 battery cell. The model was demonstrated against cell voltage and surface temperature (0.1–10°C) as well as calendric aging experimental data (500 days at 30°C) with a detailed internal cell state (concentrations, potential, pressure, internal resistance) during SCE discharge and during calendric aging was shown and discussed. The model is able to capture the nonlinear feedback between performance, aging, and temperature.

Future work will address the further parameterization and validation of the model using an extended experimental data base; and the application of the model to various scenarios, including sensitivity analyses, thermal runaway, and lifetime prediction.

Acknowledgments

CK acknowledges financial support from the state of Baden-Württemberg through the cooperative graduate college DENE (Dezentrale Erneuerbare Energiesysteme). This work has been partially funded by the German Ministry of Education and Research (BMBF, grant no. 03FH013PX3). The authors thank Michael Danzer and Harry Döring (Zentrum für Sonnenenergie und Wasserstoffforschung, ZSW, Ulm) for providing experimental data of lithium-ion battery cells as part of a project founded by the Volkswagen Foundation. WB thanks Timo Danner, Michael Hedwig, Birger Horstmann, Christian Hellwig, Manik Mayur, Wolfgang Mielke, Sundar Sathyamoorthy, Svenja Spitznagel, and Nanako Tanaka for their various contributions to model development, implementation, and parameterization.

Appendix

Charge neutrality and double layer capacitance.—In the following we describe the reformulation of the charge-neutrality Equation 5 into a differential equation for the local potential difference, Eq. 6. We assume that the electric current due to double layer charging and discharging is described as (Eq. 6)

\[ \dot{\phi}_{DL} = \frac{\partial \phi}{\partial t} \]  

Mass and charge conservation within the double layer requires that the electronic double layer current entering the electronic phase (solid-conductive matrix) is counterbalanced by specific adsorption/desorption of ions from/to the ionic phase (liquid electrolyte). This results in an additional species source term in the continuity Equation 4,

\[ \sum_{i} z_{i} F \dot{c}_{i}^{e} = \dot{\phi}_{DL} \]  

In the present study, we assign the double layer current to one single ionic species, that is, \( i = \text{Li}^{+} \).

The faradic current \( i_{f} \) follows from the production rate of electrons in the electronic phase due to charge-transfer reactions \( \dot{i}_{f}^{e} \).

\[ i_{f}^{e} = i_{f} \]  

Due to overall charge neutrality of all (electro) chemical reactions,

\[ F \dot{c}_{i}^{e} = \sum_{i} z_{i} F \dot{c}_{i}^{e} \]  

Inserting Eqs. A1–A4 into the charge neutrality Equation 5 yields a new governing equation for the electric potential difference \( \Delta \phi \),

\[ \dot{c}_{\text{eff}}^{-} = \sum_{i} z_{i} F \dot{c}_{i}^{e} - \dot{i}_{f}^{e} \]  

This is the governing potential equation that we solve for. It has the advantage of being a differential equation instead of an algebraic equation 5, allowing a more straightforward numerical implementation and numerically more stable simulations.

Transport coefficients from concentrated solution theory.—The electrolyte transport model described in the Mesoscopic (electrode-pair) scale section can host CST as shown in the following. We compare here to the CST model of a binary electrolyte as originally developed by Newman and co-workers, where the solvent is used as reference species and its velocity is taken to be zero (i.e., convection is neglected). The transfer number is considered with respect to solvent velocity. For a binary electrolyte described by concentrated solution theory, Eq. 9 reads

\[ j_{i} = -D_{i}^{\text{CST,eff}} \frac{\partial \tilde{c}_{i}}{\partial y} - D_{i}^{\text{prop,CST,eff}} \frac{\partial \phi_{\text{ele}}}{{\partial y}} \]  

Using expressions (12)–(13) and assuming effective transport parameters, the transport coefficients are expressed by

\[ D_{i}^{\text{CST,eff}} = D_{i}^{\text{prop}} \left( 1 - \frac{\nu}{\nu_{\text{ele}}} + \frac{2RT}{\nu_{\text{ele}} F} \sigma^{\text{eff}} (c, T) \right) \nu (c, T), \]  

\[ D_{i}^{\text{prop,CST,eff}} = \frac{\nu_{\text{ele}}}{\nu} \sigma^{\text{eff}} (c, T), \]  

where the index \( i \) refers to the two ions (e.g., \( \text{Li}^{+} \) and \( \text{PF}_{6}^{-} \)) denoted by subscripts + and − in the following, and

\[ \nu (c, T) = (1 - t_{0}) \left( 1 + \frac{d \ln f_{i}}{d \ln c} \right), \]
\[ f = 1 - f^0, \quad c = c^0, \quad c = c^0, \quad z = -z. \]

Inserting A7–A9 into Eq. A6 yields

\[ J_i = -D_i \frac{\partial \phi}{\partial y} + \frac{\partial}{\partial y} \left( \frac{RT}{z_i F} \partial \phi \right) \frac{\partial \kappa_i}{\partial y} - \frac{\partial}{\partial y} \left( \frac{RT}{z_i F} \partial \phi \right) \frac{\partial \rho_{\text{tot}}}{\partial y}. \]

We first derive the governing equation for the ionic potential. The ionic current density \( i_i \) (in \( \text{A/m}^2 \)) in the electrolyte is given by \[ A10 \]

\[ i_i = F \sum z_i J_i. \]

In our case,

\[ i_i = F z_i J_s + F z_r J_r. \]

Inserting Eq. A13 and using Eqs. A10–A12 yields

\[ i_i = \frac{2RT}{F} \frac{\partial \phi}{\partial (c, T)} (c, T) \frac{\partial \kappa}{\partial y} - \frac{\partial}{\partial y} \left( \frac{RT}{z_i F} \partial \phi \right) \frac{\partial \rho_{\text{tot}}}{\partial y}. \]

Finally, inserting into Eq. A9 gives the potential equation,

\[ \frac{\partial \phi_{\text{tot}}}{\partial y} = -\frac{i_i}{F} + \frac{2RT}{F} \frac{1}{\partial (c, T)} (1 - \alpha) \left( 1 + \frac{\partial \ln F}{\partial \ln c} \right) \frac{\partial \kappa}{\partial y}. \]

This is the standard expression used in literature for a concentrated binary electrolyte solution.\(^{11}\)

We next derive the governing equation for the ionic concentration. We start from Eq. 4 for the cation (in the following, \( \kappa = \kappa_{\text{Li}^+} \) and \( J = J_{\text{Li}^+} \)).

\[ \frac{\partial \kappa_{\text{Li}^+}}{\partial t} = -\frac{\partial}{\partial y} \left( \frac{F \kappa_{\text{Li}^+} \partial \kappa_{\text{Li}^+}}{\partial y} - \frac{\partial}{\partial y} \left( \frac{RT}{z_{\text{Li}^+} F} \partial \phi \right) \right) + \eta_{\text{Li}^+}. \]

Inserting Eq. A13, using Eq. A11 and A16, and assuming concentration-independent \( t_{\text{Li}^+} \) gives

\[ \frac{\partial \kappa_{\text{Li}^+}}{\partial y} = \frac{\partial}{\partial y} \left( \frac{F \kappa_{\text{Li}^+} \partial \kappa_{\text{Li}^+}}{\partial y} - \frac{\partial}{\partial y} \left( \frac{RT}{z_{\text{Li}^+} F} \partial \phi \right) \right) + \eta_{\text{Li}^+}. \]

This is the standard literature expression for a concentrated binary electrolyte solution.\(^{66,68}\) If we recognize that \( \eta_{\text{Li}^+} = \frac{1}{F \kappa_{\text{Li}^+}} \), the right-hand side modifies to

\[ \frac{\partial \kappa_{\text{Li}^+}}{\partial y} = \frac{\partial}{\partial y} \left( \frac{F \kappa_{\text{Li}^+} \partial \kappa_{\text{Li}^+}}{\partial y} + \left( 1 - \alpha \right) \frac{\partial i_i}{\partial y} \right), \]

which is the standard literature expression for a concentrated binary electrolyte solution with source term in a porous electrode.\(^{11}\) Note that, in the absence of a source term (e.g., in the separator), \( \frac{\partial i_i}{\partial y} = 0 \) and so the second term on the right vanishes. We have therefore shown that our formalism introduced in Eqs. 4, 9, 12, 13 is identical to the standard literature formalism, Eqs. A17 and A19.

**Heat source terms.**—We apply here a spatially-resolved (on the mesoscopic scale) description of heat sources. The total energy released by an interfacial chemical reaction is given by its reaction enthalpy,

\[ \phi_{\text{react}} = \phi_{\text{react}} + \phi_{\text{dissociation}} = -r \Delta H. \]

and, in a case of a charge-transfer reaction, is distributed among thermal and electrical energy release. The released electrical energy is given by the work of the electron during its movement over the electrode/electrolyte potential step according to

\[ \phi_{\text{dissociation}} = \frac{1}{F} \partial \phi. \]

Therefore,

\[ \phi_{\text{react}} = \phi_{\text{react}} - \phi_{\text{dissociation}} = -r \Delta H + i_i \Delta \Phi. \]

We can further reformulate this expression by recognizing that \( i_i \Delta \Phi = F V \alpha \Delta N \), yielding

\[ \phi_{\text{react}} = r \Delta N - \Delta H + F V \alpha \Delta \Phi. \]

Generally, an arbitrary number of chemical and electrochemical reactions can take place at different interfaces within the electrode. The released heat follows as sum over all reactions,

\[ \phi_{\text{react}} = \sum_{\text{reactant}} \left( r_i \Delta N_i \cdot \Delta H_i + F \gamma_i \Delta \Phi \right), \]

which is the expression used in our model (Eq. 17). It is valid for both electrochemical and thermochemical reactions, as for the latter, \( \gamma_i = 0 \).

Eq. A24 implicitly includes both reversible and irreversible heat contributions. We will next show that it can explicitly be cast into a function of these contributions. The activation overpotential is defined as,

\[ \eta_{\text{act}} = \Delta \phi - \Delta \phi^0, \]

where, the equilibrium half-cell potential difference follows from thermodynamics according to

\[ \Delta \phi^0 = \frac{\Delta G}{\Delta F} = \frac{\Delta H - T \Delta S}{\Delta F}. \]

We convert Eq. A24 to a function of current according to

\[ \phi_{\text{heat}} = i_i \left( \frac{\Delta H}{z_F} + \Delta \phi \right). \]

Inserting Eqs. A26 and A27 and recognizing \( \gamma_i = -z \) for a charge-transfer reaction written in standard reduction direction yields

\[ \phi_{\text{heat}} = i_i \left( \frac{\Delta H}{z_F} + \eta_{\text{act}} \right). \]

With the temperature derivative of Eq. A27 this can be further converted to

\[ \phi_{\text{heat}} = i_i \left( \frac{T \Delta S}{z_F} + \eta_{\text{act}} \right). \]

In this expression, the first and second terms on the right-hand side represent reversible and irreversible heat, respectively. Eq. A30 is often used in thermal models of lithium-ion batteries.\(^{16,18,20,23}\) In our physically-based modeling approach, we use instead the implicit form of Eq. A24.

**Geometric factor.**—Volume-specific interfacial area and volume fraction of an active material particle in a composite electrode are defined as

\[ A' = A_{\text{AM}} V/V_{\text{eff}}. \]

where, \( V \) is the electrode volume. Assuming a spherical particle, volume and surface area are given by

\[ V_{\text{AM,LP}} = 4/3 \pi r_{\text{AM}}^3, \]

\[ A_{\text{AM,LP}} = 4 \pi r_{\text{AM}}^2, \]

respectively. Inserting Eqs. A32–A34 into Eq. A31 yields an expression for the specific area as function of volume fraction,

\[ A' = \frac{3 A_{\text{AM}}}{r_{\text{TP}}} \]

Upon intercalation, the volumetric source term \( i_i' \) is converted to a surface flux via

\[ J_{i,\text{AM}} = \frac{1}{A'} i_i' A_{\text{AM}}. \]

Inserting Eq. A35 into Eq. A36 yields the geometric factor introduced in the Microscopic (particle) scale section.

**Mass action kinetics and Butler-Valmer formulation.**—The Butler-Valmer equation can be derived from transition state theory\(^{50,53}\) by inserting Eqs. 25–26 into Eq. 24, substituting the absolute potential difference \( \Delta \phi^0 \) with the activation overpotential,

\[ \eta_{\text{act}} = \Delta \phi^0 - \Delta \phi^0, \]

and converting the reaction rate to current via

\[ i = z F \tau. \]

Extensive algebraic manipulation results in the Butler-Valmer form

\[ i = i_0 \exp \left( -\frac{E_{\text{react}}}{RT} \eta_{\text{act}} \right) \left( 1 - \frac{\ln (1 - \alpha) \Delta F}{RT} \eta_{\text{act}} \right) \]

with the exchange current density

\[ i_0 = \frac{z F}{\Delta F} \exp \left( \frac{E_{\text{react}}}{RT} \right) \prod_{k=1}^{n_k} \left( \frac{\gamma_k}{\gamma_k} \right)^{n_k} \left( \frac{\gamma_k}{\gamma_k} \right)^{n_k} \]

and the exchange current density factor

\[ i_0 = z F \cdot k_0 \exp \left( \frac{\Delta G}{RT \Delta F} \right) \prod_{k=1}^{n_k} \left( \frac{\gamma_k}{\gamma_k} \right)^{n_k}. \]

Eq. A41 shows that \( i_0 \) is a function of \( \Delta G \), which, in lithium-ion batteries, is a function of SOC (cf. Electrochemistry and multi-phase chemistry section). In order to ensure SOC independent \( i_0 \), we multiply \( k_0 \) with a factor of \( \exp(-\alpha \Delta F \eta_{\text{act}}) \), as implemented in CANTERA (exchange_current_density_formulation in the interfaceKinetics class).
SEI film resistance and formation rate.—The film resistance in Eq. 30 depends on the thickness of the SEI layer. Starting from the area-specific resistance of the SEI layer according to

$$R^A_{\text{SEI}} = \frac{\rho_{\text{SEI}}}{\sigma_{\text{SEI}}}. \quad [A42]$$

the volume-specific film resistance is obtained by dividing with the specific surface area,

$$R^V_{\text{SEI}} = \frac{R^A_{\text{SEI}}}{\epsilon_{\text{AM}}}. \quad [A43]$$

Inserting Eq. A35 and A42 into Eq. A43 yields

$$R^V_{\text{SEI}} = \frac{r_D \rho_{\text{SEI}}}{3 \, \epsilon_{\text{SEI}}}. \quad [A44]$$

In the following an explicit relationship between SEI resistance and SEI volume fraction is developed. In analogy to Eq. A33, the volume of the SEI layer on one particle is equal to

$$V_{\text{SEI},p} = \frac{4}{3} \pi ((r_D + \delta_{\text{SEI}})^3 - r_D^3). \quad [A45]$$

which, solved for the layer thickness, yields

$$\delta_{\text{SEI}} = \sqrt[3]{\frac{3 V_{\text{SEI},p}}{4 \pi}} - r_D. \quad [A46]$$

The particle-related volumes are related to the macroscopic volume fractions via

$$\frac{V_{\text{SEI},p}}{V_{\text{AM},p}} = \frac{\epsilon_{\text{SEI}}}{\epsilon_{\text{AM}}}. \quad [A47]$$

Inserting Eqs. A34 and A47 into Eq. A46 yields

$$\delta_{\text{SEI}} = \sqrt[3]{\frac{V_{\text{SEI},p}}{V_{\text{AM},p}}} - 1 \cdot r_D. \quad [A48]$$

Finally, Eq. A48 can be cast into Eq. A44, yielding the formula of the volume fraction dependent SEI resistance,

$$R^V_{\text{SEI}} = \frac{1}{3} \frac{r_D^2}{\epsilon_{\text{SEI}}} \left(1 + \frac{\epsilon_{\text{SEI}}}{\epsilon_{\text{AM}}} - 1\right). \quad [A49]$$

For diffusion-limited film growth, the film formation rate $r$ is proportional to the diffusion flux (Fick’s first law) of the limiting species (here: electron $^-$) with concentration $c$,

$$r = D \frac{dc}{dx} \approx D \frac{\Delta c}{\delta_{\text{SEI}}} \sim \frac{1}{\delta_{\text{SEI}}}. \quad [A50]$$

### List of Symbols

| Symbol | Unit       | Meaning                                      | Introduced in          |
|--------|------------|----------------------------------------------|------------------------|
| $A$    | $1$        | Pre-exponential factor                        | Table VI               |
| $A_D$  | $m^2$      | Active electrode area                         | Upscaling section      |
| $A^V$  | $m^2$      | Volume-specific surface area                  | Eq. A19                |
| $A_n$  | $m^2$      | Volume-specific surface area of reaction $n$  | Eq. 17                 |
| $A_{\text{AM},p}$ | $m^2$  | Surface area of active material particle     | Eq. A31                |
| $C$    | F          | Capacity                                      | Eq. 41                 |
| $c_i$  | mol $\cdot m^{-3}$ | Concentration of species $i$ in a bulk phase | Eq. 4                  |
| $c_{+}$ | mol $\cdot m^{-3}$ | Concentration of cation $i$                  | Eq. A11                |
| $c_{-}$ | mol $\cdot m^{-3}$ | Concentration of anion $i$                  | Eq. A11                |
| $c_{Li+}$ | mol $\cdot m^{-3}$ | Concentration of solved Li-ions               | Eq. A11                |
| $c_L$  | mol $\cdot m^{-3}$ | Concentration of solution $i$                | Eq. A14                |
| $D^0$  | $m^2$ $\cdot s^{-1}$ | Diffusion coefficient used in CST | Eq. 12                 |
| $D^{DST,\text{eff}}$ | $m^2$ $\cdot s^{-1}$ | Effective diffusion coefficient of species $i$ under CST | Eq. A6                 |
| $D^{\text{migr,}\text{DST}}$ | mol $\cdot V^{-1} \cdot m^{-1} \cdot s^{-1}$ | Migration coefficient of species $i$ for DST | Eq. 11                 |
| $D^{\text{migr,}\text{CST}}$ | mol $\cdot V^{-1} \cdot m^{-1} \cdot s^{-1}$ | Effective migration coefficient of species $i$ for CST | Eq. A6                 |
| $D^{\text{CST,eff}}$ | mol $\cdot V^{-1} \cdot m^{-1} \cdot s^{-1}$ | Effective migration coefficient of species $i$ | Eq. 9                  |
| $D_{\text{eff}}$ | $m^2$ $\cdot s^{-1}$ | Diffusion coefficient of lithium in active material | Eq. 19                 |
| $E$    | V          | Electrode-pair voltage                        | Eq. 14                 |
| $E_{\text{cell}}$ | V          | Cell voltage                                  | Eq. 23                 |
| $E_{\text{NXP}}$ | V          | Cell voltage of the $\text{Nth}$ electrode pair | Eq. 23                 |
| $E_{\text{act},f}$ | J $\cdot mol^{-1}$ | Activation energy of forward reaction | Eq. 25                 |
| $F$    | C $\cdot mol^{-1}$ | Faraday’s constant                           | Eq. 5                  |
| $f_\pi$ | mol$^{-1}$ | CST activity coefficient                      | Mesoscopic (electrode-pair) scale section |
| $h_1$  | J $\cdot mol^{-1}$ | Molar enthalpy of species $i$                 | Eq. 29                 |
| $h_{Li}$ | J $\cdot mol^{-1}$ | Molar enthalpy of intercalated lithium         | Electrochemistry and multi-phase chemistry section |
| $h_V$  | J $\cdot mol^{-1}$ | Molar enthalpy of vacancy                     | Electrochemistry and multi-phase chemistry section |
| $i$    | 1          | Index of species                              | Eq. 4                  |
| $i$    | A $\cdot m^{-2}$ | Area-specific current (with respect to $A_D$) | Eq. 14                 |
| $i_0$  | A $\cdot m^{-2}$ | Exchange current density                      | Eq. A40                |
| $i_{00}$ | A $\cdot m^{-2}$ | Exchange current density factor               | Eq. A41                |
| $i_l$  | A $\cdot m^{-2}$ | Ionic current density of binary solution under CST | Eq. A14                |
| Symbol | Unit | Description |
|--------|------|-------------|
| $i_m$ | A·m⁻³ | Area-specific current of representative electrode pair |
| $i_{DL}$ | A·m⁻³ | Volume-specific current due to double layer |
| $i_e$ | A·m⁻³ | Volume-specific faradaic current |
| $j$ | 1 | Index of bulk phases |
| $I_{cell}$ | A | Current of the cell |
| $I_q$ | W·m⁻² | Heat flux from cell surface |
| $J_i$ | mol·m⁻²·s⁻¹ | Molar flux of species $i$ |
| $J_e$ | mol·m⁻²·s⁻¹ | Molar flux of cation |
| $J_\text{Li}^+$ | mol·m⁻²·s⁻¹ | Molar flux of anion |
| $J_{Li^+}$ | mol·m⁻²·s⁻¹ | Molar flux of solved Li-ion |
| $J_{LLAM}$ | mol·m⁻²·s⁻¹ | Molar flux of lithium over particle surface |
| $k_i$ | mol, m, s (*) | Reaction rate constant of forward reaction |
| $k_i^0$ | mol, m, s (*) | Pre-exponential factor of forward reaction |
| $k_r$ | mol, m, s (*) | Reaction rate constant of reverse reaction |
| $L_{EP}$ | m | Thickness of electrode pair |
| $L_{e, electrode}$ | m | Thickness of electrode |
| $M_i$ | kg·mol⁻¹ | Molar mass of species $i$ |
| $M$ | kg·mol⁻¹ | Average molar mass of phase |
| $m$ | 1 | Index of electrode pair |
| $n$ | 1 | Index of chemical reactions |
| $N_{EP}$ | 1 | Number of electrode pairs |
| $N_{gas}$ | 1 | Number of gas-phase species |
| $N_p$ | 1 | Number of products participating in reaction |
| $N_R$ | 1 | Number of reactants participating in reaction |
| $N_e$ | 1 | Number of reactions |
| $p_{gas}$ | kg·m⁻¹·s⁻² | Pressure of gas phase |
| $\dot{q}_V$ | W·m⁻³ | Volume-specific heat source |
| $\dot{q}_m$ | W·m⁻³ | Volume-specific heat source of hollow cylinder $V_m$ |
| $\dot{q}^A$ | W·m⁻² | Heat source specific to active electrode area |
| $\dot{q}_0^A$ | W·m⁻² | Area-specific heat source of a cells hollow cylinder $V_m$ |
| $\dot{q}_{chem}$ | W·m⁻² | Heat source due to chemical reactions |
| $\dot{q}_{ohm}$ | W·m⁻² | Heat source due to ohmic losses |
| $\dot{q}_{tot}$ | W·m⁻³·s⁻¹ | Total heat source rate |
| $r$ | mol·m⁻²·s⁻¹ | Interfacial reaction rate |
| $r_n$ | mol·m⁻²·s⁻¹ | Interfacial reaction rate of reaction $n$ |
| $r_p$ | m | Radius of active material particle |
| $R$ | J·K⁻¹·mol⁻¹ | Ideal gas constant |
| $R_{\text{cell}}$ | Ω·m² | Area-specific ohmic resistance of current collection system |
| $R_{\text{tot}}$ | Ω | Total internal resistance |
| $R^\text{SEI}$ | Ω·m³ | Area-specific ohmic resistance of SEI film |
| $R^\text{SEI}_{\text{total}}$ | Ω·m³ | Volume-specific ohmic resistance of SEI film |
| $\dot{\xi}_V$ | mol·m⁻³·s⁻¹ | Volumetric species source term |
| $\dot{\xi}_e$ | mol·m⁻³·s⁻¹ | Volumetric species source term of electrons |
| $\dot{\xi}^V_{DL}$ | mol·m⁻³·s⁻¹ | Volumetric species source term due to double layer charge/discharge |
| $s_i^\text{gas}$ | J·mol⁻¹·K⁻¹ | Volumetric species source term of gas phase |
| $s_i^\text{Li}$ | J·mol⁻¹·K⁻¹ | Molar enthalpy of species $i$ |
| $s_i^\text{Li}$ | J·mol⁻¹·K⁻¹ | Molar enthalpy of intercalated lithium |
| $s_V$ | J·mol⁻¹·K⁻¹ | Molar enthalpy of vacancy |
| $T$ | K | Temperature |
| $T_{\text{amb}}$ | K | Ambient temperature |
| $T_m$ | K | Temperature of hollow cylinder $V_m$ of the cell |
| $V$ | m³ | Volume of electrode |
| $V_{\text{cell}}$ | m³ | Volume of cell |
| $V_{\text{AM}}$ | m³ | Volume of representative electrode pair |
| $V_{\text{void}}$ | m³ | Volume of SEI shell |
| $x$ | m | Spatial position along battery thickness |
| $X_{\text{Li}[Ca]}$ | l | Macroscopic (cell) scale section |

*Table II*
