

End-of-Life Prediction of a Lithium-Ion Battery Cell Based on Mechanistic Aging Models of the Graphite Electrode

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We present an electrochemical model of a lithium iron phosphate/graphite (LFP/C₆) cell that includes combined aging mechanisms: (i) Electrochemical formation of the solid electrolyte interphase (SEI) at the anode, leading to loss of lithium inventory, (ii) breaking of the SEI due to volume changes of the graphite particles, causing accelerated SEI growth, and (iii) loss of active material due to of loss percolation of the liquid electrolyte resulting from electrode dry-out. The latter requires the introduction of an activity-saturation relationship. A time-upscaling methodology is developed that allows to simulate large time spans (thousands of operating hours). The combined modeling and simulation framework is able to predict calendaric and cyclic aging up to the end of life of the battery cells. The aging parameters are adjusted to match literature calendaric and cyclic aging experiments, resulting in quantitative agreement of simulated nonlinear capacity loss with experimental data. The model predicts and provides an interpretation for the dependence of capacity loss on temperature, cycling depth, and average SOC. The introduction of a percolation threshold in the activity-saturation relationship allows to capture the strong nonlinearity of aging toward end of life ("sudden death").

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The aging of lithium-ion cells, quantified macroscopically in terms of capacity loss and internal-resistance increase, is a complex and nonlinear function of operating parameters, including temperature, state of charge (SOC), cycling depth of discharge (DOD), and current (in-cluding zero current, i.e., resting).¹⁻³ In the macroscopic view, cyclic and calendaric aging are generally distinguished. However, in the microscopic view, both cyclic and calendaric aging result from similar chemical and structural changes of the cell components and cannot be separated mechanistically. Rather, there is a large number of different microscopic degradation mechanisms,^{1,2} which are taking place in parallel, with relative strengths depending on local (microscopic) conditions. Macroscopic cell conditions (ambient temperature, current) nonlinearly influence the microscopic degradation drivers (electric potential, mechanical stress); and resulting structural and chemical changes nonlinearly feed back to the macroscopic cell performance (capacity, internal resistance). The goal of the present paper is to develop and exploit a modeling and simulation framework that captures this two-way nonlinearity. This allows to predict macroscopic aging as function of macroscopic operating conditions, based on an underlying microscopic description of aging mechanisms.

Physically-based models play an important role in supporting lithium-ion cell aging mitigation, firstly because they allow to unravel the complex interdependencies of microscopic and macroscopic behavior,⁴ and secondly because they allow aging predictions over months or years of simulation time within only minutes or hours of wall-clock computation time.⁵ Aging mechanisms have been used extensively within physically-based models, for example, SEI formation,^{6–12} lithium plating,^{13–15} capacity loss due to mechanical break of the SEI during cycling,^{16,17} or active material delamination.^{18,19}

In the present paper we integrate aging mechanisms of the graphite negative electrode (anode) into a pseudo-3D model of a lithium iron phosphate/graphite (LFP/C₆) lithium-ion cell.¹¹ The aging mechanisms studied here are shown schematically in Figure 1. Three mechanisms, running in parallel and depending on each other, are implemented: (a) Electrochemical formation of the solid electrolyte interphase (SEI). SEI formation is believed to be the dominant driver of cell aging²⁰ and has been extensively modeled before.^{6–11} This mechanism leads to a loss of lithium inventory (LLI) and is mainly responsible for calendaric aging. (b) Accelerated SEI formation due to mechanical stresses. Volume changes of the graphite particles during cycling causes mechanical stress both on the particle¹⁷ and on the SEI surrounding the particle,¹⁶ which may lead to cracking of the particle or

the SEI. It has been suggested that these cracks expose fresh graphite surface to the electrolyte, which leads to accelerated SEI growth.^{12,16,17} This mechanism leads, again, to LLI and is mainly responsible for cyclic aging. (c) Dry-out of the electrode. It is well-known experimentally that gas is formed inside the cell during aging, ^{1–3,21} and gaseous species are known products of electrolyte decomposition.¹⁹ Therefore, dry-out has been identified as major capacity-loss mechanism:²² It leads to a contact loss of active material particles with the liquid electrolyte, causing a *loss of active material* (LAM).

A particular feature of lithium-ion cell aging is a strong nonlinearity toward end of life (EOL), that is, accelerated capacity loss when cycling is continued beyond 70–80% state of health (SOH).²³ The mechanistic origin of this behavior is subject of current discussion.²⁴ In this manuscript we postulate that the electrode dry-out



Figure 1. Aging mechanisms of the graphite electrode included in the present model.

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drives liquid-electrolyte saturation below the ionic percolation threshold, leading to fast capacity loss and causing the nonlinearity of aging.

In the next section, we derive a quantitative mathematical description of the aging mechanisms discussed above. Further we present a time-upscaling methodology that allows to simulate long-term aging (thousands of hours) and predict EOL. Then we present and discuss simulation results. Finally, the paper is concluded.

Aging Modeling

Base cell model.—We use the pseudo-3D (P3D) model published before by Kupper and Bessler¹¹ as basis for including aging mechanisms. The base model development, model equations, parameterization strategy, full list of parameters, as well as comparison with experimental data are described in detail in Ref. 11 and are not repeated here for conciseness. Briefly, this model is an extended "Newman-type"²⁵ description of a lithium-ion battery cell. It includes 1D lithium diffusion within the active materials particles on the sub-micrometer scale; 1D mass and charge transport through the electrode pair on the ~200 µm scale; 1D heat transport in the radial direction of the cylindrical cell on the centimeter scale; and a 0D gas reservoir representing the void space inside the cylindrical cell. The scales are coupled to an overall 1D+1D+1D model. The model was parameterized and verified against experimental data of a commercial lithium iron phosphate/graphite (LFP/C₆, 26650-type, 2.3 Ah, 3.3 V) cell.

For the present study, the base P3D cell model serves as platform for introducing physically-motivated aging mechanisms, as shown in Figure 1. These are integrated into the base model in the form of chemical side reactions that run in parallel to the main intercalation reactions. The rate expression of the side reactions will be developed below.

Electrochemical SEI formation.—As main aging mechanism we include SEI formation at the anode/electrolyte interface. We assume a single-step charge-transfer reaction^{8,26–29} according to

$$2 C_{3}H_{4}O_{3} [elyt] + 2 e^{-} + 2 Li^{+} [elyt] \rightleftharpoons (CH_{2}OCO_{2}Li)_{2} [SEI] + C_{2}H_{4} [gas].$$
[1]

where, $C_3H_4O_3$ is ethylene carbonate (EC), main constituent of the assumed electrolyte, $(CH_2OCO_2Li)_2$ is lithium ethylene dicarbonate which was identified as primary product of the electrochemical reduction of EC,³⁰ C_2H_4 is gaseous ethylene, and square brackets are used to indicate the bulk phase the species belongs to. This reaction is assumed to take place in parallel to the main charge-transfer reaction (lithium intercalation/deintercalation), with which it competes for electrons and lithium ions. The reaction is a multi-phase reaction, and the base model¹¹ includes conservation equations for liquid electrolyte, solid SEI, and gas phase volume fractions.

The area-specific rate of the reaction r_{SEI}^{A} (in mol per m² particle surface per second) is modeled with extended Arrhenius-type massaction kinetics,¹¹

$$r_{\rm SEI}^{\rm A}(T,\,\Delta\phi) = k_{\rm f,SEI} \prod_{i=1}^{N_{\rm R}} c_i^{|v_i|} - k_{\rm r,SEI} \prod_{i=1}^{N_{\rm P}} c_i^{|v_i|}$$
[2]

with

$$k_{\rm f} = k_{\rm f}^0 \cdot \exp\left(-\frac{E_{\rm act,f}}{RT}\right) \cdot \exp\left(-\frac{\alpha_{\rm f} zF}{RT}\Delta\phi\right),$$
[3]

where, *T* is the temperature, $\Delta \phi$ the electrical potential difference between electrode and electrolyte, k_f and k_r the forward and reverse rate constants, respectively, c_i the concentration of species *i*, v_i the stoichiometric coefficient of species *i*, k_f^0 and $E_{act,f}$ the preexponential factor and activation energy of the forward reaction, respectively, *R* the ideal gas constant, α_f the symmetry factor, *z* the number of electrons transferred, *F* Faraday's constant, and the sums run over all reactants N_R and products N_P , respectively.

Taking into account the diffusion limitation of SEI growth and the available LiC_6 particle surface area, the homogenized SEI formation

rate $r_{\text{SEI,calendaric}}^{\text{V}}$ (in mol per m³ electrode volume per second) is given by

$$r_{\rm SEI, calendaric}^{\rm V} = A_{\rm LiC_6}^{\rm V} \cdot \frac{1}{\delta_{\rm SEI}} \cdot r_{\rm SEI}^{\rm A}, \qquad [4]$$

where, $A_{\text{LiC}}^{\text{V}}$ is the volume-specific graphite particle surface area and δ_{SEI} is the SEI thickness. SEI growth is known to be diffusion limited,^{6,7,31} which is described by the $1/\delta_{\text{SEI}}$ factor.¹¹ Note that upon time-integration of the species continuity equation, this factor leads to a \sqrt{t} dependence of SEI concentration, as commonly observed experimentally.³² We use the subscript "calendaric" to distinguish from the cyclic-based SEI formation mechanism introduced below. Through the rate coefficients k_f and k_r , the SEI growth depends on temperature and, because it is an electron-transfer reaction, on the potential of electrode and electrolyte.¹¹ As the potential changes with cycling of the battery, calendaric SEI formation depends on SOC.

Mechanical degradation and SEI formation.—As second aging mechanism we include mechanical degradation due to volume changes of the graphite particles during cycling. In particular, we follow here the approach of Laresgoiti et al.¹⁶ These authors assume that volume changes of the particles lead to a breaking of the particle-covering SEI layer. Applying a mechanical model, they use the known graphite expansion coefficient as model input to predict the tangential stress on the SEI layer $\sigma_{t,SEI}$ as function of the Li stoichiometry $X_{Li[C_6]}$. Their results are shown in Figure 2. The relevant aging driver is the derivative $d\sigma_{t,SEI}/dX_{Li[C_6]}$. It shows a minimum around $X_{Li[C_6]} = 0.4$, corresponding to 70% SOC for this particular cell (cf. upper scale in Figure 2). Shallow cycling around $X_{Li[C_6]} = 0.4$ causes little volume changes and therefore little stress on the SEI, while deep cycling or cycling within the outer stoichiometry ranges causes strong volume changes and therefore high stress on the SEI. We apply a fourth-order polynomial fit to these data, yielding

$$\frac{\mathrm{d}\sigma_{\mathrm{t,SEI}}\left(X_{\mathrm{Li}[C_6]}\right)}{\mathrm{d}X_{\mathrm{Li}[C_6]}} = \left(-931 \cdot X_{\mathrm{Li}[C_6]}{}^4 + 1319.96 \cdot X_{\mathrm{Li}[C_6]}{}^3 - 201.684 \cdot X_{\mathrm{Li}[C_6]}{}^2 - 240.56 \cdot X_{\mathrm{Li}[C_6]} + 67.9\right) \,\mathrm{MPa}$$
[5]

as input to our model.

We assume next that breaking of the SEI leads to exposition of fresh particle surface to the electrolyte, causing accelerated formation of new SEI.¹⁶ Simplifying the certainly very complex microstructural features of this process, a first-order description of the SEI formation rate can be formulated as

$$r_{\text{SEI,cyclic}}^{\text{V}} = k_{\text{c}} \cdot A_{\text{LiC}_{6}}^{\text{V}} \cdot i_{\text{chg}}^{\text{V}} \cdot \frac{\text{d}\sigma_{\text{t,SEI}}\left(X_{\text{Li[C_{6}]}}\right)}{\text{d}X_{\text{Li[C_{6}]}}} \cdot r_{\text{SEI}}^{\text{A}}\left(T, \ \Delta\phi\right). \quad [6]$$

The right-hand side of this equation has several terms discussed in the following. The first term k_c is an empirical proportionality constant that includes all microstructural features of the cyclic SEI formation. $A_{LiC_6}^{V}$ is the volume-specific particle surface area. These two constants depend on the individual properties of the graphite electrode and will vary from cell to cell. The third term i_{chg}^{V} is the local faradaic current density of the intercalation reaction when the cell is charged, that is, lithium is intercalated into graphite. Intercalation leads to particle volume increase and tangential stress on the SEI. We assume that SEI breaks only upon tangential stress, while compressive stress upon deintercalation does not lead to aging. i_{chg}^{V} is a local property within the composite electrode and is practically connected to the base model¹¹ as

$$i_{\rm chg}^{\rm V} = \begin{cases} 0 \text{ for } i_{\rm F}^{\rm V} > 0 \text{ (discharge)} \\ -i_{\rm F}^{\rm V} \text{ for } i_{\rm F}^{\rm V} < 0 \text{ (charge)} \end{cases}.$$
[7]

The fourth term $d\sigma_{t,SEI}/dX_{Li[C_6]}$ is the aging driver given by Eq. 5. Finally, r_{SEI}^{A} is the electrochemical SEI formation rate given by Eq. 2.

Eq. 6 describes the complex and nonlinear dependence of cyclic SEI formation on the macroscopic properties current (through i_{chg}^V), voltage (through the $\Delta \phi$ dependence of r_{SFI}^A), SOC (through $\sigma_{t,SEI}$ and,



Figure 2. (a) Tangential stress on the SEI layer as well as (b) its derivative with respect to the Li stoichiometry. Data of the upper panel taken from Laresgoiti et al. 16

because it is a function of potential, through r_{SEI}^A), and temperature (through the Arrhenius factor in r_{SEI}^A). It is thus generally able to capture the influence of these properties on cyclic aging.

Calendaric and cyclic SEI formation, Eqs. 4 and 6, can be combined into a single rate expression,

$$\begin{aligned} r_{\text{SEI}}^{\text{V}} &= r_{\text{SEI,calendaric}}^{\text{V}} + r_{\text{SEI,cyclic}}^{\text{V}} \\ &= A_{\text{LiC}_{6}}^{\text{V}} \cdot \left(\frac{1}{\delta_{\text{SEI}}} + k_{\text{c}} \cdot i_{\text{chg}}^{\text{V}} \cdot \frac{\text{d}\sigma_{\text{t,SEI}}\left(X_{\text{Li[C_{6}]}}\right)}{\text{d}X_{\text{Li[C_{6}]}}} \right) \cdot r_{\text{SEI}}^{\text{A}} \quad [8] \end{aligned}$$

Electrode dry-out and loss of ionic contact.—In the present work, we suggest loss of ionic contact of the active material due to electrode dry-out as key additional degradation mechanism. This mechanism causes "deactivation" of active material particles and hence loss of active material.

The formation of gases during aging of a lithium-ion cell is welldescribed in literature.^{1,3} Dahn and co-workers developed a dedicated experimental setup to investigate gas formation in pouch cells.²¹ Electrode dry-out was identified as dominant capacity-loss mechanism at elevated temperatures by Mao et al.²² An et al. observed increased ohmic resistance in lithium-ion cells when the electrolyte volume was reduced.³³ Despite the experimental evidence of gas formation upon aging, this phenomenon has, to the best of our knowledge, not yet been included in battery aging models. In the present model, we assume that gas formation takes place through reaction Equation 1 only, that is, it is inherently coupled to SEI formation; there are no mechanisms for gas consumption. The base model¹¹ includes continuity equations for the volume fractions ε_i of all bulk phases in the electrode (active material, liquid electrolyte, gas phase) as well as equations of state, thus predicting the decrease of electrolyte volume fraction and increase of gas-phase volume fraction and pressure caused by Eq. 1.

It is reasonable to assume that electrode dry-out leads to a reduction or loss of ionic contact of the active materials particles, thus reducing the active surface area and/or completely deactivating the particle, either because it is not surrounded by liquid electrolyte anymore, or because the liquid electrolyte has lost ionic percolation. In order to quantitatively describe these processes, we introduce two new descriptors of the electrode, that is, *activity* and *saturation*. We include "inactive" graphite (C₆,inactive) as additional bulk phase in the electrode model. The volumetric ratio of "active" over total graphite, called *activity* in the following, is defined as

$$u = \frac{\varepsilon_{\text{LiC}_6}}{\varepsilon_{\text{LiC}_6,\text{inactive}} + \varepsilon_{\text{LiC}_6}},$$
[9]

where, a = 1 means a fully-activated electrode. The dry-out of the electrode depends on the amount and depletion of liquid electrolyte in the composite electrode. This can be quantitatively described in terms of the *liquid saturation s* defined as

$$s = \frac{\varepsilon_{\text{elyt}}}{\varepsilon_{\text{elyt}} + \varepsilon_{\text{gas}}},$$
[10]

where, s = 1 means a fully-electrolyte-flooded pore space and s = 0 a dry electrode. It is reasonable to assume that, in equilibrium, the electrode activity is a function of the saturation, i.e.

$$a^{\rm eq} = f(s). \tag{11}$$

This activity-saturation relationship is a key parameter of the present model. The form of this relationship will be discussed further below in the parameterization section.

In the present model, we use a kinetic ansatz to describe the particle deactivation. Specifically, we describe loss of active material as an additional chemical reaction,

$$\operatorname{Li} [C_6] + V [C_6] \xrightarrow{\prime_{\operatorname{deact}}} \operatorname{Li} [C_6, \operatorname{inactive}] + V [C_6, \operatorname{inactive}]. \quad [12]$$

This ansatz ensures mass conservation and at the same time can be easily implemented into the CANTERA modeling framework (cf. Section on software framework). However, it requires to reformulate the boundary condition for the particle scale in order to ensure mass conservation upon particle deactivation; these modifications are described in the Appendix. The driving force for this reaction is a deviation between the electrode activity a and its equilibrium value given by Eq. 11, thus

$$r_{\text{deact}} = k_d \cdot (a - a^{\text{eq}}) = k_d \cdot (a - f(s)), \qquad [13]$$

where, the kinetic coefficient k_d is chosen such that the deactivation rate is fast and not rate-limiting.

Simulation with Time-Upscaling

Time-upscaling methodology.—Lifetime prediction with physically-based battery models is faced by the challenge of a high computational time. The real-time factor (wall-clock time over simulation time) for the P3D model described above is roughly 10^{-2} (ca. 1 min for one full cycle), which is not sufficiently small to allow practical simulation of months or even years of cell cycling. We therefore apply here a time-upscaling methodology introduced before by Mayur et al. in the context of fuel cells.³⁴



Figure 3. Time-upscaling methodology.

The methodology is shown in Figure 3. The virtual cell is fully described by its state vector y(t), which in our case has a dimension of 240, including mass densities of species and phases, electric potentials, temperatures as function of spatial positions, etc. Taking an initial state before an aging cycle y_0 and a final state after the aging cycle y_1 , the difference between these states reflect the change due to cell aging. Every state variable may be subject to change, but aging will typically induce changes to the SEI and gas-phase mass densities. We linearly interpolate the full state vector for *n* aging cycles according to

$$\mathbf{y}_n = \mathbf{y}_0 + n \cdot (\mathbf{y}_1 - \mathbf{y}_0) \,. \tag{14}$$

The new state vector y_n represents a cell that has been cycled for a time of $n \cdot (t_1 - t_0)$.

It is important to realize that a change in operation state between initial and final state, for example a change in SOC or in cell current, will be also upscaled. Therefore the upscaling must be performed based on cell states under identical operating conditions, for which we use the term reference condition. We use a voltage-based reference condition here 3.329 V (70% SOC). We drive the cell to the reference condition before and after aging cycles by applying first a CV phase (3.329 V/240 h) followed by a rest phase (0 A/240 h), thus defining the states y_0 , y_1 used for upscaling. During the reference protocol, the aging Reaction 1 is switched off. The aging cycle itself is arbitrary and will be discussed below (Cycling protocols section).

As aging is nonlinear for long time scales, the value of n must be chosen small enough as to remain within a piecewise linear range. We then perform repetitive cycling/upscaling steps. Applying a total of msuch steps results in a total aging time of

$$t_{\text{tot}} = m \cdot n \cdot (t_1 - t_0) \,. \tag{15}$$

For the simulations shown below, m = 25, n = 160, $(t_1 - t_0) = 10$ h. In order to account for an initially pronounced nonlinearity in aging, the first four steps are upscaled with reduced n = 10, 20, 40, 80. This protocol represents $t_{tot} = 43.600$ h = 1.400 d = 3.8 years of continuous cycling. Note that, due to capacity loss, $(t_1 - t_0)$ becomes smaller for increasing aging time. The total wall-clock time, including the time for the reference protocols and capacity and impedance simulation after each step, is 2–3 h on a state-of-the-art desktop computer (Intel i7 3.4 GHz) without parallelization. This corresponds to a real-time factor of ca. 5 $\cdot 10^{-5}$.



Figure 4. Exemplary cycling protocols used in the present study. Here, varying DOD is performed for a constant average SOC. A DOD of 0% corresponds to calendaric aging.

Cycling protocols.—The discharge capacity of the fresh virtual cell is determined at 20°C ambient temperature by first CCCV charging (1C CC to 3.6 V, CV until C/20), then 2 h rest, and then 1C CC discharge to 2.0 V. This initial discharge capacity (called nominal capacity $C_{\rm N}$ in the following) is used to determine the current needed for a 1C rate according to $I_{\rm IC} = C_{\rm N}/1$ h, as well as to drive the cell to the desired initial SOC = $Q/C_{\rm N}$ and cycle for the desired DOD = $\Delta Q/C_{\rm N} = I \Delta t/C_{\rm N}$.

We investigate a number of different cycling protocols. In all cases a protocol of 10 h is applied. For model parameterization we follow the cycling protocols of Safari and Delacourt³⁵ because we compare our simulation results to their experimental data. For calendaric aging, the current is simply set to zero after having driven the cell to the desired SOC. For full cycling, the cell was consecutively discharged and charged using 1C CC between 2.2 V and 3.6 V and 10 min rest time after each discharge and after charge phase (no CV phase).

For demonstrating the capability of the model of capturing the influence of cycling depth, we apply 1C CC discharge/charge cycles without rest for different DOD (0% = calendaric, 5%, 10%, 20%, 50%) around 70% average SOC, as well as constant 20% DOD around different average SOC (10%, 30%, 50%, 70%, 90%). The cycling protocol of the former variation is shown in Figure 4. As noted above, the DOD and SOC values are taken with respect to the capacity of a fresh cell. During consecutive aging, the charge phase may reach the 3.6 V cutoff and/or the discharge phase the 2.2 V cutoff. In these cases, the respective charge (or discharge) is stopped and the cycle is continued with the next discharge (or charge).

After each cycling/upscaling phase, the discharge capacity of the virtual cell is determined at 20° C ambient temperature by first CCCV charging (1C CC to 3.6 V, CV until C/20), then 2 h rest, and then 1C CC discharge to 2.0 V. The internal resistance is determined by recharging to 50% SOC, 2 h rest, and then performing an impedance simulation using a potential step/current relaxation method.³⁶ The internal resistance is the absolute value of the complex impedance at 0.3 Hz.

Software framework.—The cell model is implemented in the in-house software code DENIS ("detailed electrochemistry and numerical impedance simulation"), and the reader is referred to Refs. 11,37,38 for all details on this C/C++ code. It implements the P3D transport equations. It also implements a multi-phase continuum electrode model which allows to include an arbitrary number and type of bulk phases (including, for example, solid SEI and gas phase) as well as interfaces between the bulk phases. The transport equations are discretized using a finite-volume approach. The number of grid points is 5, 20 and 6 in *x*, *y*, and *z* dimensions, respectively. Different

Table 1	. Properties	s of phases	s within the	e negative	composite e	electrode.
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Phase	Initial volume fraction ϵ	Density ρ / $kg \cdot m^{-3}$	Species (initial mole fraction <i>X</i>)
Anode active material, graphite (LiC ₆) Deactivated graphite (LiC ₆ ,inactive) Electrolyte SEI Gas phase	0.72 ¹¹ 1 · 10 ⁻⁵ 0.22** ¹¹ 0.01* 0.05**	2540 ¹¹ 2540 ¹¹ 1195 ⁴² 1300 ⁴³ ideal gas law	$\begin{array}{c} \text{LiC}_{6} (0.57), \text{VC}_{6} (0.43) \\ \text{LiC}_{6} (0.5), \text{VC}_{6} (0.5) \\ \text{C}_{3}\text{H}_{4}\text{O}_{3} (0.6), \text{C}_{4}\text{H}_{6}\text{O}_{3} (0.2), \text{Li}^{+} (0.1), \text{PF}_{6}^{-}(0.1) \\ (\text{CH}_{2}\text{OCO}_{2}\text{Li})_{2} (1.0) \\ \text{N}_{2} (0.999), \text{C}_{3}\text{H}_{4}\text{O}_{3} (1.0 \cdot 10^{-8}), \text{C}_{2}\text{H}_{4} (1.0 \cdot 10^{-8}), \\ \text{O}_{2} (1.0 \cdot 10^{-8}), \text{CO}_{2} (1.0 \cdot 10^{-8}), \text{H}_{2}\text{O} (1.0 \cdot 10^{-8}), \\ \text{H}_{4} (1.0 \cdot 10^{-8}), \\ \text{CO}_{2} (1.0 \cdot 10^{-8}), \\ \text{CO}_{3} (1.0 \cdot 10^{-8}), \\ \text{CO}_{4} (1.0 \cdot 10^{-8}), \\ \\ \text{CO}_{4} (1.0 \cdot 1$
			$H_2 (1.0 \cdot 10^{\circ})$

*assumed, corresponds to an initial SEI thickness of 16 nm.

**5% initial gas volume fraction assumed.

Table II. Chemical reactions and rate coefficients taking place at the graphite/electrolyte interface. The interfacial area is $A^{\rm V} = \frac{3e_{\rm LiC_6}}{r_p} = 6.03 \cdot 10^5 \frac{{\rm m}^2}{{\rm m}^3}$.¹¹ We use values of $k_{\rm c} = 27.5 \frac{{\rm m}^3}{{\rm A} \cdot {\rm MPa}}$ and $k_{\rm d} = 10^{-4}$. The expression $\frac{d\sigma_{\rm LSEI}(X_{\rm Li}[C_6])}{dX_{\rm Li}[C_6]}$ is given by Eq. 5. The activity-saturation relationship f(s) is given in Table III.

Reaction	Reaction equation	Rate factor	Pre-exponential factor <i>k</i> _f	Activation energy $E_{act,f}$	Symmetry factor α_f
Intercalation	$\begin{array}{l} \text{Li}^+(\text{elyt}) + e^- + \text{V}[\text{C}_6] \rightleftarrows \\ \text{Li}[\text{C}_6] \end{array}$	а	$3.0\cdot10^{10}\tfrac{A}{m^2}$	53.4 ^{kJ} _{mol}	0.5
SEI formation	$\begin{array}{l} C_{3}H_{4}O_{3}(elyt)+e^{-}+Li^{+}(elyt)\\ \rightleftarrows \frac{1}{2} (CH_{2}OCO_{2}Li)_{2}+\frac{1}{2} C_{2}H_{4} \end{array}$	$\frac{a}{\delta_{\rm SEI}/{\rm m}} + k_{\rm c} \cdot i_{\rm chg}^{\rm V} \cdot \frac{{\rm d}\sigma_{\rm t,SEI}}{{\rm d}X_{\rm Li[C_6]}}$	$1.02 \cdot 10^{-19} \frac{\mathrm{m}^4}{\mathrm{kmol}\ \mathrm{s}}$	55.5 ^{kJ} _{mol}	0.5
Particle deactivation	$\begin{array}{l} \text{Li}[C_6] + V[C_6] \rightarrow \\ \text{Li}[C_6, \text{inactive}] + V[C_6, \text{inactive}] \end{array}$	$k_d \cdot (a - f(s))$	$1 \frac{m^4}{kmol s} *$	0*	-

*Arbitrary values.

to the simulations shown in Ref. 11, we use reduced grid points and only one single representative electrode pair in order to save computational time. Also, we had to reformulate the boundary condition for the particle scale in order to ensure mass conservation upon particle deactivation; these modifications are described in the Appendix.

The DENIS code is interfaced to the open-source chemistry software CANTERA.³⁹ CANTERA is a C++ suite that we use to calculate all reaction rates and species source terms, including those of the aging reactions. The input to CANTERA are thermodynamic parameters (molar enthalpies and entropies) of all species and kinetic parameters (preexponential factors, activation energies, symmetry factors) of all reactions. The CANTERA input file is available from the authors upon request.

The models for the aging side reactions developed above require kinetic rate laws (Eqs. 8 and 13) that are more complex than the standard Arrhenius-type rate laws implemented in CANTERA (Eqs. 2 and 3). We therefore introduce additional rate factors needed for a generalized description of the rate laws. The flexible rate factors are evaluated within DENIS and passed to CANTERA, where the Arrhenius law is evaluated.

The time-upscaling methodology, cycling protocols, as well as data post-processing are implemented in MATLAB (revision 2016a) which we couple to DENIS via a MATLAB S-function. The differentialalgebraic equation system is numerically solved using the implicit time-adaptive solver LIMEX (version 4.3A).^{40,41}

Results and Discussion

Parameterization and activity-saturation relationship.—We use the base model from Ref. 11; this reference describes the parameterization of the performance part (discharge and charge behavior as function of C-rate and temperature), which is not repeated here for conciseness. In the following, only the aging-relevant parameters are discussed. Table I shows the bulk phases assumed in the composite negative electrode, and Table II shows the interfaces and reactions assumed in the negative electrode. Note that we scale the rate of the intercalation reaction with the electrode activity *a*. Thus, as graphite particles are gradually deactivated by electrode dry-out, the interfacial area for electrochemical reaction decreases. This increases the internal resistance. The same applies for the calendaric SEI formation.

A key parameter of the dry-out model is the activity-saturation relationship a(s). It describes the loss of ionic contact of the active material, either due to complete dry-out of the pore space directly surrounding the particle, or due to loss of percolation of the liquid electrolyte (cf. Figure 1c). There is, to the best of our knowledge, no literature data available on this phenomenon in the context of lithiumion batteries. In order to study the influence of a(s) on aging behavior, for the present work we assume four different generic analytical relationships and compare the resulting end-of-life simulation results. The relationships are summarized in Table III and shown in Figure 5. Assuming a = 1 throughout corresponds to a model without dryout. A linear relationship a = s is used as first-order assumption. Additionally, we include two nonlinear relationships that account for a sudden drop of activity below a percolation threshold. The most complex expression no. 4 is motivated by providing a good agreement of resulting capacity loss with experimental data, as will be shown below.

The model has a number of further unknown parameters that directly influence calendaric and cyclic aging behavior: $k_{\rm f,SEI}$ (preexponential factor of SEI formation, directly influencing both calendaric and cyclic aging rate), $E_{\rm act,f,SEI}$ (activation energy of SEI formation, influencing the temperature dependence of aging), and $k_{\rm c}$ (cyclic aging factor, accounting for the cyclic aging rate relative to the calendaric aging rate). We developed a set of these parameters by comparing simulated SOH vs. aging time to experimental data by Safari and Delacourt on the same cell type at two temperatures (25 and 45°C) and two aging protocols (calendaric aging at 100% SOC and cyclic aging with 100% DOD).³⁵ We selected the nonlinear asymmetric a(s)

Table III. Assumed activity-saturation relationships investigated in the present study.

No.	Relationship	Comment
1	a = 1	Particle deactivation disabled
2	a = s	Linear relationship
3	$a = 0.5 \cdot \tanh(10 \cdot (s - 0.5)) + 0.5$	Nonlinear, symmetric at $s = 0.5$
4	$a = (0.5 \cdot s + 0.5) \cdot (0.5 \cdot \tanh(15 \cdot (s - 0.4)) + 0.5)$	Nonlinear, asymmetric



Figure 5. Assumed activity-saturation relationships investigated in the present study. The analytical expressions are given in Table III.

relationship (no. 4 in Table III and Figure 5) as basis and then fitted the kinetic parameters by hand. In particular, $k_{\rm f,SEI}$ and $E_{\rm act,f,SEI}$ were fitted by using two data points from calendaric aging (100% SOC, 25 and 45°C, 4400 h aging); and $k_{\rm c}$ was fitted by using a single data point from cyclic aging (100% SOC, 45°C, 4400 h aging).

It should be emphasized that the set of parameters developed in this way is not unique, as the choice of the a(s) relationship strongly influences aging behavior, which can be partially compensated by changing the kinetic parameters.

Calendaric and cyclic aging: comparison to experiments.—Simulated (this work) and experimental (Safari and Delacourt³⁵) aging data are shown in Figure 6. Panel a) shows calendaric aging results at two temperatures (25 and 45°C) and two SOC (50 and 100 %). Panel b) shows cyclic aging results (full cycles) at two temperatures (25 and 45°C). The simulation shows a quantitative agreement with the experiments over the complete data set. This includes the temperature dependence, the SOC/DOD dependence, and the nonlinearity both at high SOH (\sqrt{t} type behavior) and at low SOH (accelerated aging). The simulation is also able to predict the long-term behavior beyond the available experimental data. Here we simulated ca. 1.400 days (ca. 3.8 years) aging time.

Figure 6 also shows the three experimental data points used for model parameterization, as discussed above. Based on these three calibration points, the complete remaining data is predicted by the model. It should be emphasized that all simulations are based on a single set of model parameters without adjustment for the individual experimental conditions.

Two discrepancies between model and experiment may still be noted. The influence of SOC on calendaric aging is overpredicted by the model. The physical aging driver in this case is the anode half-cell potential ($\Delta \phi$ in Eq. 3), which depends on SOC. An incorrect SOC dependency of aging might indicate an incorrect choice of SEI thermodynamics (equilibrium potential). Furthermore, the influence of temperature on cyclic aging is also overpredicted. In the model, the temperature influences both calendaric and cyclic aging in the same way



Figure 6. Comparison of simulated capacity loss to experimental data from Safari and Delacourt.³⁵ (a) Calendaric aging at 50 and 100% SOC and 25 and 45°C. (b) Cyclic aging (100% DOD) at 25 and 45°C. The arrows indicate the calibration points used for fitting the parameters $k_{\rm f,SEI}$, $E_{\rm act,f,SEI}$ and $k_{\rm c}$. Every small filled symbol corresponds to one cycling-upscaling step.

(Arrhenius term in Eq. 3), as k_c is assumed temperature-independent. A refined cyclic aging model might include a temperature-dependent k_c . These adjustments are beyond the scope of the present article, and would also require more detailed experimental data.

Cell performance and internal states.—We further analyze the data for cyclic aging (100% DOD) at 45° C. Figure 7a shows simulated discharge curves at 1C rate at each upscaling step. The data illustrate well the capacity loss and the internal-resistance increase. Panel b) shows capacity (same data as in Figure 6b) and internal resistance at 50% SOC. Each point in panel b) corresponds to one curve of panel a). Both capacity decrease and internal-resistance increase are nonlinear, and follow different shapes.

While Figure 7 shows electrical performance data that are wellaccessible experimentally, the model allows to analyze internal states that are not (easily) measurable. A selection of internal states is shown in Figure 8. Panel a) shows volume fractions of the different components of the composite anode. The fresh electrode consists mainly



Figure 7. Simulated cell performance during cyclic aging with 100% DOD at 45° C. (a) 1C discharge curves. (b) Capacity and internal resistance at 50% SOC.

of active material and electrolyte. During aging, the SEI formation reaction consumes electrolyte and forms SEI (Eq. 1). As the density of SEI is higher than that of electrolyte (cf. Table I), this reaction is associated with an overall volume decrease of these (incompressible) phases. This is compensated by the (compressible) gas phase, which also takes up the formed ethylene. Note that we assume a 0D gas reservoir above the electrodes, representing the void spaces inside the cylindrical cell;¹¹ this gas reservoir and the electrode pore space take up the formed gas, leading to a simulated in-cell pressure of 32.7 bar after 800 days. The electrode dryout is clearly visible through the decrease in electrolyte volume fraction and increase in gas-phase volume fraction. This causes consecutive loss of active material, which is visible from the decrease of active graphite and increase of inactive graphite volume fraction.

Figure 8b shows the concentrations of species within the electrolyte. The fresh electrolyte is composed of EC:DMC (assumed ratio 3:1) and LiPF₆ as conducting salt. During aging, EC is consumed in the SEI formation reaction (Eq. 1). EC is almost completely consumed after 700 d cycling time. At the same time, DMC concentration increases. Note that this does not contradict mass conservation, because concentration is given in moles per volume of liquid phase, and this volume decreases simultaneously (cf. panel a). The concentration of LiPF₆ stays essentially constant (the lithium ions that are lost to the SEI according to Eq. 1 are immediately replenished from the graphite active material).

Panel c) shows the saturation (following from the volume fractions) and the corresponding activity (following from the activity-saturation relationship). The SEI thickness is shown as function of aging time in Figure 8d. Starting from an assumed initial thickness of 16 nm, it grows to almost 200 nm. The growth slows down with increasing cycling time mainly due to the consumption of EC (cf. panel b), which is a reactant in the SEI formation reaction. The simulated SEI thickness is in agreement with literature. Theoretical work predicted a thickness of 100 nm after about 34 days of cycling.⁴⁴ Measured thickness can even extend to 111 nm – 315 nm depending on the degree of degradation.⁴⁵ Colclasure et al.⁴⁶ predicted thicknesses between 10–100 nm. On the other hand, several publications mention smaller SEI thicknesses.⁴⁷⁻⁴⁹ This apparent contradiction may be caused by a layered structure of the SEI; for example, Andersson et al. show an



Figure 8. Results of cyclic aging (100% DOD) simulations at 45° C. (a) Volume fractions, (b) electrolyte concentration, (c) activity and saturation, (d) SEI thickness, (e) physical SOC of the individual electrodes at end of charge, and (f) loss of active material (LAM) and loss of lithium inventory (LLI) as function of cycling time.

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almost 100 nm thick outer porous layer of polymers (polyethylene oxide) and an about 2 nm thin inner dense layer, composed amongst others of lithium carbonate.⁵⁰ The present model does not include the two-layer structure.

Panel e) shows the individual physical SOC of the two electrodes after fully charging the cell (CCCV) to 3.6 V. These data follow from lithium stoichiometry according to

$$SOC_{i} = \frac{X_{\text{Li}[i]} - X_{\text{Li}[i]}^{\text{SOC}=0}}{X_{\text{Li}[i]}^{\text{SOC}=1} - X_{\text{Li}[i]}^{\text{SOC}=0}},$$
[16]

where, $i = \{ca, an\}$ is the index for the electrode, and $X_{\text{Li},i}^{\text{SOC}=00\%}$ and $X_{\text{Li},i}^{\text{SOC}=100\%}$ are the lithium stoichiometries for a fresh empty and full cell, respectively. The data show the de-balancing of the electrodes upon consecutive cycling. In particular, the graphite anode loses capacity relative to the LFP cathode. The cathode stoichiometry remains constant up to ca. 400 h (corresponding to an SOH of ca. 50%). This is consistent with the experiments of Mao et al.²² where the LFP lower lithium stoichiometry remained unchanged, while the graphite upper stoichiometry considerably decreased (both corresponding to a fully-charged cell); note that their aging data does not go below ca. 50% SOH.

Finally, panel f) shows the commonly-used aging indicators LAM and LLI, which are directly accessible from the physical model according to

$$LAM = 1 - a,$$
[17]

LLI

$$= \frac{n_{(CH_2OCO_2Li)_2}}{2n_{(CH_2OCO_2Li)_2} + n_{Li[C_6]} + n_{Li[C_6,inactive]} + n_{Li[cathode]} + n_{Li^+[elyt]}},$$
[18]

where, n_i is the total number of moles species *i* present in the cell.

Influence of activity-saturation relationship.—Due to the influence of electrode dry-out on the cell performance, the assumed activity-saturation relationship a(s) has a strong influence on the simulation results. Figure 9 shows calendaric and cyclic aging data as well as selected internal states for the different a(s) shown in Figure 5 and Table III. Notably, the shape of a(s) dominantly translates into the shape of SOH vs. aging time, which is a superposition of the a(s) behavior and the aging kinetics resulting from Eq. 8. When particle deactivation is not considered (relationship 1), cyclic aging (panel b) seems to stop after ca. 8000 cycles at an SOH of 88%, despite the fact that essentially the complete EC is consumed (panel d). This demonstrates the requirement for integrating dry-out as additional degradation mechanism. It is also notable that the SEI growth (panel c) is comparatively insensitive to the assumed a(s) relationship.

The simulations presented above and below have been carried out using the most complex a(s) relationship 4. This choice was governed through the empirical observation that it shows best agreement with experimental aging data (Figure 6). Obviously, an independent validation or determination of a(s) would be desirable. However, to the best of our knowledge, there is no literature data available. Yet, some insight can be obtained from related fields.

Two-phase flow and the influence of saturation on performance is well-known in the field of PEM fuel cells,⁵¹ where both liquid and gas-phase water are present in the gas diffusion layers and catalyst layers. Models are available both on the continuum level⁵² and with microstructural resolution.⁵³ Although liquid-phase percolation is not relevant for PEM fuel cell (only gas-phase percolation is⁵⁴), the existing broad body of literature is a good entry point to the topic. Saturation strongly depends on the wettability (contact angle) of the porous material by the liquid, and this parameter is available for some lithium-ion battery materials and electrolytes.⁵⁵

Electrode wetting is a key process during lithium-ion battery manufacturing, taking place during filling of the cell with electrolyte. This



Figure 9. Simulated aging behavior for different a(s) relationships according to and. (a) Calendaric aging at 100% SOC and 45°C. (b) Cyclic aging (100% DOD) at 45°C. (c) SEI thickness during cyclic aging. (d) EC concentration during cyclic aging.

can be seen as reverse process to the electrode dry-out studied here. Due to its technical relevance, there are a number of modeling studies on electrode wetting.^{56,57} A recent study investigates solvent drying from the electrodes, another manufacturing step.⁵⁸ Again, liquid percolation is not assessed in these studies.

Percolation theory has been used in the context of solid powder mixtures.⁵⁹ Here, a distinct percolation threshold is observed when de-



Figure 10. Cyclic aging for 20% DOD around different average SOC at 298 K. (a) SOH, (b) SEI thickness.

creasing the volume fraction of a solid constituent. The theory has been applied to the ionic conduction in solid-oxide fuel cell electrodes.⁶⁰ In the context of lithium-ion batteries, solid-state percolation theory has been applied to conductive additives.⁶¹

The potentially most relevant field to the present topic is that of lithium-air batteries. Here, the air electrode is a two-phase system (liquid electrolyte and gas-phase oxygen) requiring ionic percolation of the electrolyte. Danner et al. presented a Lattice-Boltzmann simulation study of an aqueous lithium-air cathode, showing loss of percolation below ca. 40% liquid saturation.^{62,63} Wang et al. modeled the discharge performance of an organic lithium-oxygen cell as function of saturation, showing lower performance for decreasing saturation, however not explicitly studying the percolation region.⁶⁴

This short discussion shows that the computational methodology for predicting a(s) is well-developed in other fields, but has not yet been applied to the electrode dry-out of lithium-ion batteries.

Influence of cycling DOD and SOC.—Cycling depth is known to strongly and nonlinearly influence the aging behavior.²³ We carried out simulations for 20% DOD around different average SOC; and for an average SOC of 70% with different DOD (cf. Figure 4). The results of the first study are shown in Figure 10. Although the cycling depth is identical for all data sets, the capacity loss is quite different, following no clear trend and in fact increasing according to 70% < 10% < < $90\% \approx 50\% << 30\%$ average SOC. Analyzing the physics behind the aging model, these results follow from a superposition of three effects: (i) magnitude of the $d\sigma_{t,SEI}/dX_{Li[C_6]}$ relationship (Figure 2b) according to Eq. 6, (ii) potential dependence of the SEI formation according to Eq. 3, and (iii) debalancing of the electrode upon con-



Figure 11. Cyclic aging at 70% average SOC for different DOD at 298 K. (a) SOH, (b) SEI thickness.

secutive aging. The minimum at $X_{\text{Li}[C_6]} = 0.4$ corresponds to an SOC of 70% within our model, consequently this data set shows the least aging. As $d\sigma_{\text{t,SEI}}/dX_{\text{Li}[C_6]}$ increases toward higher and lower SOC, aging increases (50%, 90% SOC) until it reaches a maximum at 30% SOC. A further decrease of SOC to 10% decreases $\Delta \phi$, which nonlinearly decreases SEI formation rate and therefore compensates further increasing $d\sigma_{\text{t,SEI}}/dX_{\text{Li}[C_6]}$. The data at SOC 50% and 90% cross each other. This is due to the debalancing of the electrodes, pushing the graphite toward lower $d\sigma_{\text{t,SEI}}/dX_{\text{Li}[C_6]}$ at SOC 50% and lower $d\sigma_{\text{t,SEI}}/dX_{\text{Li}[C_6]}$ at SOC 90%.

Figure 11 shows data for varying DOD around an average SOC of 70%. This average SOC was chosen because it corresponds to the minimum of the $d\sigma_{t,SEI}/dX_{Li[C_6]}$ relationship (cf. Figure 2). A DOD of 0% means calendaric aging. The aging systematically accelerates according to $0\% < 5\% \approx 10\% < 20\% < 50\% < 100\%$ DOD. The least capacity loss occurs for calendaric aging, and cycling with increasing cycling depth increases capacity loss. The behavior is nonlinear, reflecting again the combined influences of (i) the $d\sigma_{t,SEI}/dX_{Li[C_6]}$ relationship and, (ii) the potential dependence of the SEI formation.

It is interesting to compare the predicted behavior to experimental data. Due to the significant effort of long-term cycling experiments, the availability of literature data with cycling protocols other than 100% DOD is scarce. Figure 12 compares results from the present study with aging experiments from five different sources.^{10,23,65–68} All data sets represent different cell types (cathode chemistries, geometries, internal electrode balancing) and cycling conditions (temperature, C-rate); the key differences are given in the figure legends. Given the strong scatter of the data, it is difficult to draw meaningful conclusions. Still, a few observations merit further discussion. Figure



Figure 12. Comparison of the present results to available literature experimental data. (a) cyclic aging for fixed DOD around different average SOC, 10,23,65 (b) cyclic aging for different DOD at fixed average SOC. $^{23,66-68}$

12a shows the influence of average cycling SOC on capacity loss. The data by Ecker et al. show a distinct maximum at 50% SOC. Our own data also show a maximum; the shift to 70% SOC can be explained by the different balancing of the graphite, such that the minimum in the $d\sigma_{t,SEI}/dX_{Li[C_6]}$ relationship corresponds to different SOC. The studies by Wu et al. and Watanabe et al. were carried out with considerably larger DOD, therefore a smaller influence of average SOC is expected. Figure 12b shows the influence of DOD on capacity loss. There is no consistent trend even with respect to the question if capacity loss decreases or increases with increasing DOD. The present study includes degradation mechanisms of the graphite anode only; although all data sets shown in Figure 12 were obtained from graphite-based cells, cathode degradation may influence or even dominate the cell behavior.

This comparison clearly shows that the influence of SOC and DOD on long-term aging is still very little understood. The present study may contribute to the understanding by providing a knowledge-based interpretation of the simulated aging behavior. However, in the light of the data shown in Figure 12, systematic experimental validation is not possible at the present stage.

Conclusions

We have presented a mechanistic aging model for graphite-based lithium-ion cells. The model combines three aging mechanisms:

- 1. Electrochemical formation of the solid electrolyte interphase (SEI), modeled as charge-transfer reaction taking place in parallel to the main intercalation reaction.
- 2. Breaking of the SEI due to volume changes of the graphite particles, causing accelerated SEI growth, modeled by scaling the SEI formation rate with a tangential stress/stoichiometry relationship.
- 3. Electrode dry-out and resulting loss of active material due to loss of percolation of the liquid electrolyte, modeled by introducing an empirical activity-saturation relationship.

The aging mechanisms are based on physicochemical concepts and were cast into quantitative rate expression for chemical side reactions, which were included into an existing pseudo-3D transport model. The required parameterization was empirical, that is, main parameters of all three processes were obtained by fitting to experimental aging data. In particular, the parameterization used three calibration points from capacity vs. cycling time measurements (half-year calendaric aging at two temperatures and cylic aging at one temperature) and assumed an activity-saturation relationship for the electrode. It should be noted that the developed parameter set is not unique; for example, a change in the assumed activity-saturation relationship can be partially compensated by a change in reaction rate coefficients.

Based on the parameterized aging mechanisms, the model was able to quantitatively reproduce experimental aging data over a wide range of conditions, in particular:

· Both calendaric and cyclic aging behavior

• The nonlinearity of aging both at BOL (\sqrt{t} type behavior) and toward EOL (strong decrease of capacity toward "sudden death")

• The dependence of aging on temperature

The results can be interpreted and understood by analyzing the predicted internal physical states, including electrode de-balancing, loss of active material (LAM) and loss of lithium inventory (LLI). The model also allows to predict the dependence of capacity loss on cycling depth and cycling SOC; a validation of these data is not possible at present due to the large scatter in available experimental literature.

Despite its remarkable level of predictivity, the present model is based on a number of assumptions and empirical parameters that open broad room for further investigations:

• The used activity-saturation relationship a(s) is so far a mere assumption (albeit showing very good agreement with experimental aging behavior). Independent models could provide the required information; as discussed, a large body of relevant literature is available from the related fields of PEM fuel cells, solid oxide fuel cells, lithiumair cells, and electrolyte wetting during lithium-ion cell production. Experiments on ionic percolation behavior as function of saturation could be carried out on laboratory coin cells with varying electrolyte load.

• The loss of EC and electrode dry-out are likely to strongly influence conductivity behavior of the electrolyte, which is currently not considered in the model.

• Transport of solvent in between the two electrodes, a likely consequence of anode dry-out, is not considered in the model.

• The tangential stress on the SEI, origin of cyclic aging and its dependence on SOC and DOD, is based on a static $d\sigma_{t,SEI}/dX_{Li[C_6]}$ relationship with particle-averaged $X_{Li[C_6]}$. We expect that the stress should have a dynamic component and depend on the spatial lithium distribution inside the particle.

• SEI formation is modeled as simple one-step reaction. All nanoscopic details of SEI formation, growth, break-up and reformation are neglected and included in only two semiempirical rate constants.

• The aging mechanisms are restricted to the graphite electrode. Therefore, the aging model is representative of cells with graphite electrode, and the specific LFP-cathode-based cylindrical cell is used as example. Although out of scope of the present study, additional phenomena are known to contribute to cell aging. These include, but are not limited to, loss of electronic contact of the active material, 1,3,69,70 iron dissolution from the positive electrode and chemical cross-talk between the electrodes, $^{12,71-74}$ particle break-up, $^{16,67,75-77}$ delamination of electrodes, 2,67,71,78,79 electrolyte salt decomposition $^{27,80-82}$ and lithium plating. 2,3,27,69,83,84

The refinement of the model parameters and the addition of other aging mechanisms has to be subject of future studies.

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Appendix

Boundary condition for particle scale.—When describing loss of active material as chemical reaction, particular care has to be taken with respect to the transport model on the particle scale (z scale).¹¹ The deactivation reaction

$$Li [C_6] + V [C_6] \rightarrow Li [C_6, inactive] + V [C_6, inactive]$$
[A1]

provides sink terms for lithium and vacancies of the active material; it therefore leads to a change in volume fraction of active material, but not to deintercalation. On the other hand, the charge-transfer reaction

$$\operatorname{Li}[C_6] \rightleftharpoons \operatorname{Li}^+[\operatorname{elyt}] + e^- + V[C_6],$$
 [A2]

leads to deintercalation, but not to loss of active material. Based on the source term for $Li[C_6]$ alone, the homogenized (continuum) electrode model¹¹ cannot distinguish between particle deactivation (Eq. A1) and lithium deintercalation (Eq. A2). We therefore rederive the mass conservation equation for intercalated lithium and the boundary condition for the microscale diffusion model.

We use the lithium density $\rho_{Li[AM]}$ as conservative state variable, where AM stands for active material. In order to derive a consistent governing equation for this state, we start with the mass conservation of the electrode-homogenized lithium density $\rho_{Li[AM]}\epsilon_{AM}$, given by

$$\frac{\partial \left(\rho_{\text{Li}[AM]} \varepsilon_{\text{AM}}\right)}{\partial t} = \dot{s}_{\text{Li}[AM]}^{\text{V}} \cdot M_{\text{Li}[AM]}, \qquad [A3]$$

The total differential of the left-hand side is

$$\frac{\partial \left(\rho_{\text{Li}[AM]}\varepsilon_{AM}\right)}{\partial t} = \varepsilon_{AM}\frac{\partial \rho_{\text{Li}[AM]}}{\partial t} + \rho_{\text{Li}[AM]}\frac{\partial \varepsilon_{AM}}{\partial t}.$$
 [A4]

Combining yields an expression for our desired state variable $\rho_{Li[AM,i]}$,

$$\frac{\partial \rho_{\text{Li}[AM]}}{\partial t} = \frac{1}{\varepsilon_{\text{AM}}} \dot{s}^{\text{V}}_{\text{Li}[AM]} \cdot M_{\text{Li}[AM]} - \frac{\rho_{\text{Li}[AM]}}{\varepsilon_{\text{AM}}} \frac{\partial \varepsilon_{\text{AM}}}{\partial t}.$$
 [A5]

Note the last term is missing in the original model:¹¹ this last term accounts for volume changes and therefore, for example, for particle deactivation. The last term can be substituted by using the total mass density conservation of the active material,

$$\frac{\partial \left(\rho_{AM}\varepsilon_{AM}\right)}{\partial t} = \sum_{k=1}^{N_s} \dot{s}_k^{\rm V} \cdot M_k = \dot{s}_{\rm Li[AM]}^{\rm V} \cdot M_{\rm Li[AM]} + \dot{s}_{\rm V[AM]}^{\rm V} \cdot M_{\rm V[AM]}.$$
 [A6]

Again, the total differential is

$$\frac{\partial \left(\rho_{AM} \varepsilon_{AM}\right)}{\partial t} = \varepsilon_{AM} \frac{\partial \rho_{AM}}{\partial t} + \rho_{AM} \frac{\partial \varepsilon_{AM}}{\partial t}, \qquad [A7]$$

and for an incompressible solid (used CANTERA phase type),

$$\frac{\partial \rho_{\rm AM}}{\partial t} = 0. \tag{[A8]}$$

Combining Eqs. A5-A8 yields

$$\frac{\partial \rho_{\text{Li}[AM]}}{\partial t} = \frac{1}{\varepsilon_{\text{AM}}} \left(\left(1 - \frac{\rho_{\text{Li}[AM]}}{\rho_{\text{AM}}} \right) \dot{s}^{\text{V}}_{\text{Li}[AM]} \cdot M_{\text{Li}[AM]} - \frac{\rho_{\text{Li}[AM]}}{\rho_{\text{AM}}} \dot{s}^{\text{V}}_{\text{V}[AM]} \cdot M_{\text{V}[AM]} \right).$$
[A9]

This is the new and generalized governing equation for lithium mass density. It subsitutes Eq. A2 of Ref. 11. In particular, it involves source terms for both lithium and vacancies and is therefore able to host both, intercalation and loss of active material.

If we include micro-scale transport, the mass conservation is given by Fick's second law,

$$\frac{\partial \rho_{\text{Li}[AM]}}{\partial t} = \frac{1}{z^2} \frac{\partial}{\partial z} \left(z^2 D_{\text{Li},AM} \left(X_{\text{Li}[AM]} \right) \frac{\partial \rho_{\text{Li}[AM]}}{\partial z} \right).$$
 [A10]

The change of lithium density given by Eq. A9 is now occurring as boundary condition to this PDE at the particle surface,

$$j_{\text{Li},\text{AM}} = \frac{1}{A_{\text{AM}}^{\text{V}}} \cdot \frac{1}{\varepsilon_{\text{AM}}} \left(\left(1 - \frac{\rho_{\text{Li}[\text{AM}]}}{\rho_{\text{AM}}} \right) \dot{s}_{\text{Li}[\text{AM}]}^{\text{V}} \cdot M_{\text{Li}[\text{AM}]} - \frac{\rho_{\text{Li}[\text{AM}]}}{\rho_{\text{AM}}} \dot{s}_{\text{V}[\text{AM}]}^{\text{V}} \cdot M_{\text{V}[\text{AM}]} \right),$$
[A11]

where, the active material specific surface area A_{AM}^{V} is given as

$$A_{\rm AM}^{\rm V} = \frac{A_{\rm P}}{V_{\rm P}} = \frac{4\pi r^2}{\frac{4}{3}\pi r^3} = \frac{3}{r}.$$
 [A12]

The simulations presented in this article use Eqs. A10-A12 and thereby substitute Eq. A1 in Ref. 11.

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References

- J. Vetter, P. Novák, M. R. Wagner, C. Veit, K.-C. Möller, J. O. Besenhard, M. Winter, M. Wohlfahrt-Mehrens, C. Vogler, and A. Hammouche, "Ageing mechanisms in lithium-ion batteries," *J. Power Sources*, 147, 269 (2005).
- A. Barré, B. Deguilhem, S. Grolleau, M. Gérard, F. Suard, and D. Riu, "A review on lithium-ion battery ageing mechanisms and estimations for automotive applications," *J. Power Sources*, 241, 680 (2013).
- M. Broussely, P. Biensan, F. Bonhomme, P. Blanchard, S. Herreyre, K. Nechev, and R. J. Staniewicz, "Main aging mechanisms in Li ion batteries," *J. Power Sources*, 146, 90 (2005).
- A. A. Franco, M. L. Doublet, and W. G. Bessler, eds., *Physical Multiscale Modeling* and Numerical Simulation of Electrochemical Devices for Energy Conversion and Storage. From Theory to Engineering to Practice, (Springer, 2016).
- B. Weißhar and W. G. Bessler, "Model-based lifetime prediction of an LFP/graphite lithium-ion battery in a stationary photovoltaic battery system," *J. Energy Storage*, 14, 179 (2017).
- A. M. Colclasure, K. A. Smith, and R. J. Kee, "Modeling detailed chemistry and transport for solid-electrolyte-interface (SEI) films in Li-ion batteries," *Electrochim. Acta*, 58, 33 (2011).
- J. Christensen and J. Newman, "A Mathematical Model for the Lithium-Ion Negative Electrode Solid Electrolyte Interphase," J. Electrochem. Soc., 151, A1977 (2004).
- N. Tanaka and W. G. Bessler, "Numerical investigation of kinetic mechanism for runaway thermo-electrochemistry in lithium-ion cells," *Solid State Ionics*, 262, 70 (2014).
- M. Safari, M. Morcrette, A. Teyssot, and C. Delacourt, "Life-Prediction Methods for Lithium-Ion Batteries Derived from a Fatigue Approach," *J. Electrochem. Soc.*, 157, A713 (2010).
- R. Fu, S.-Y. Choe, V. Agubra, and J. Fergus, "Development of a physics-based degradation model for lithium ion polymer batteries considering side reactions," *J. Power Sources*, 278, 506 (2015).
- C. Kupper and W. G. Bessler, "Multi-Scale Thermo-Electrochemical Modeling of Performance and Aging of a LiFePO₄/Graphite Lithium-Ion Cell," *J. Electrochem. Soc.*, 164, A304 (2017).
- D. Li, D. L. Danilov, B. Zwikirsch, M. Fichtner, Y. Yang, R.-A. Eichel, and P. H. L. Notten, "Modeling the degradation mechanisms of C6/LiFePO₄ batteries," *Journal of Power Sources*, 375, 106 (2018).
- S. Tippmann, D. Walper, L. Balboa, B. Spier, and W. G. Bessler, "Low-temperature charging of lithium-ion cells part I: Electrochemical modeling and experimental investigation of degradation behavior," *J. Power Sources*, 252, 305 (2014).
- N. Legrand, B. Knosp, P. Desprez, F. Lapicque, and S. Raël, "Physical characterization of the charging process of a Li-ion battery and prediction of Li plating by electrochemical modelling," *J. Power Sources*, 245, 208 (2014).
- P. Arora, R. E. White, and M. Doyle, "Capacity fade mechanisms and side reactions in Lithium-ion batteries//Capacity Fade Mechanisms and Side Reactions in Lithium-Ion Batteries," J. Electrochem. Soc., 145, 3647 (1998).
- I. Laresgoiti, S. K\u00e4bitz, M. Ecker, and D. U. Sauer, "Modeling mechanical degradation in lithium ion batteries during cycling. Solid electrolyte interphase fracture," *J. Power Sources*, 300, 112 (2015).
- J. Purewal, J. Wang, J. Graetz, S. Soukiazian, H. Tataria, and M. W. Verbrugge, "Degradation of lithium ion batteries employing graphite negatives and nickel– cobalt–manganese oxide + spinel manganese oxide positives. Part 2, chemical– mechanical degradation model," *J. Power Sources*, 272, 1154 (2014).
- S. Pal, S. S. Damle, S. H. Patel, M. K. Datta, P. N. Kumta, and S. Maiti, "Modeling the delamination of amorphous-silicon thin film anode for lithium-ion battery," *J. Power Sources*, 246, 149 (2014).

- S. Pal, S. S. Damle, P. N. Kumta, and S. Maiti, "Modeling of lithium segregation induced delamination of a-Si thin film anode in Li-ion batteries," *Comput. Mater. Sci.*, 79, 877 (2013).
- P. Verma, P. Maire, and P. Novák, "A review of the features and analyses of the solid electrolyte interphase in Li-ion batteries," *Electrochim. Acta*, 55, 6332 (2010).
- D. J. Xiong, L. D. Ellis, R. Petibon, T. Hynes, Q. Q. Liu, and J. R. Dahn, "Studies of Gas Generation, Gas Consumption and Impedance Growth in Li-Ion Cells with Carbonate or Fluorinated Electrolytes Using the Pouch Bag Method," *J. Electrochem. Soc.*, 164, A340 (2017).
- Z. Mao, M. Farkhondeh, M. Pritzker, M. Fowler, and Z. Chen, "Calendar Aging and Gas Generation in Commercial Graphite/NMC-LMO Lithium-Ion Pouch Cell," J. *Electrochem. Soc.*, 164, A3469 (2017).
- M. Ecker, N. Nieto, S. Käbitz, J. Schmalstieg, H. Blanke, A. Warnecke, and D. U. Sauer, "Calendar and cycle life study of Li(NiMnCo)O2-based 18650 lithiumion batteries," *J. Power Sources*, 248, 839 (2014).
- E. Sarasketa-Zabala, F. Aguesse, I. Villarreal, L. M. Rodriguez-Martinez, C. M. López, and P. Kubiak, "Understanding Lithium Inventory Loss and Sudden Performance Fade in Cylindrical Cells during Cycling with Deep-Discharge Steps," *J. Phys. Chem. C*, **119**, 896 (2015).
- M. Doyle, T. F. Fuller, and J. Newman, "Modeling of Galvanostatic Charge and Discharge of the Lithium/Polymer/Insertion Cell," *J. Electrochem. Soc.*, 140, 1526 (1993).
- R. Spotnitz and J. Franklin, "Abuse behavior of high-power, lithium-ion cells," J. Power Sources, 113, 81 (2003).
- V. A. Agubra and J. W. Fergus, "The formation and stability of the solid electrolyte interface on the graphite anode," *J. Power Sources*, 268, 153 (2014).
- Y. Ein-Eli, "A New Perspective on the Formation and Structure of the Solid Electrolyte Interface at the Graphite Anode of Li-Ion Cells," *Electrochem. Solid-State Lett.*, 2, 212 (1999).
- G. Ning, R. E. White, and B. N. Popov, "A generalized cycle life model of rechargeable Li-ion batteries," *Electrochim. Acta*, 51, 2012 (2006).
- G. V. Zhuang, K. Xu, H. Yang, T. R. Jow, and P. N. Ross, "Lithium Ethylene Dicarbonate Identified as the Primary Product of Chemical and Electrochemical Reduction of EC in 1.2 M LiPF 6/EC:EMC Electrolyte," *J. Phys. Chem. B*, 109, 17567 (2005).
- H. J. Ploehn, P. Ramadass, and R. E. White, "Solvent diffusion model for aging of Lithium-ion battery cells," (2004).
- D. A. Stevens, R. Y. Ying, R. Fathi, J. N. Reimers, J. E. Harlow, and J. R. Dahn, "Using High Precision Coulometry Measurements to Compare the Degradation Mechanisms of NMC/LMO and NMC-Only Automotive Scale Pouch Cells," *J. Electrochem. Soc.*, 161, A1364 (2014).
- S. J. An, J. Li, D. Mohanty, C. Daniel, B. J. Polzin, J. R. Croy, S. E. Trask, and D. L. Wood, "Correlation of Electrolyte Volume and Electrochemical Performance in Lithium-Ion Pouch Cells with Graphite Anodes and NMC532 Cathodes," *J. Electrochem. Soc.*, **164**, A1195 (2017).
- M. Mayur, S. Strahl, A. Husar, and W. G. Bessler, "A multi-timescale modeling methodology for PEMFC performance and durability in a virtual fuel cell car," *International Journal of Hydrogen Energy*, 40, 16466 (2015).
- C. Delacourt and M. Safari, "Simulation-Based Analysis of Aging Phenomena in a Commercial Graphite/LiFePO₄ Cell," *J. Electrochem. Soc.*, **158**, A1436 (2011).
- W. G. Bessler, "Rapid Impedance Modeling via Potential Step and Current Relaxation Simulations," J. Electrochem. Soc., 154, B1186 (2007).
- J. P. Neidhardt, D. N. Fronczek, T. Jahnke, T. Danner, B. Horstmann, and W. G. Bessler, "A Flexible Framework for Modeling Multiple Solid, Liquid and Gaseous Phases in Batteries and Fuel Cells," *J. Electrochem. Soc.*, **159**, A1528 (2012).
- W. G. Bessler, S. Gewies, and M. Vogler, "A New Framework For Physically Based Modeling of Solid Oxide Fuel Cells," *Electrochim. Acta*, 53, 1782 (2007).
- D. G. Goodwin, H. K. Moffat, and R. L. Speth, "Cantera: An Object-Oriented Software Toolkit For Chemical Kinetics, Thermodynamics, And Transport Processes. https://www.cantera.org, 2018. Version 2.3.0.
- P. Deuflhard, E. Hairer, and J. Zugck, "One-step and extrapolation methods for differential-algebraic systems," *Numer. Math.*, 51, 501 (1987).
- R. Ehrig, U. Nowak, L. Oeverdieck, and P. Deuflhard, "Advanced Extrapolation Methods for Large Scale Differential Algebraic Problems," in *High performance scientific and engineering computing. Lecture notes in computational science and engineering*, Vol. 8, H.-J. Bungartz, F. Durst, and C. Zenger, eds. (Springer, 1999), pp. 233.
- 42. T. B. Reddy, Linden's Handbook of Batteries, 4th ed. (McGraw-Hill, 2010).
- K. Kwon, F. Kong, F. McLarnon, and J. W. Evans, "Characterization of the SEI on a Carbon Film Electrode by Combined EQCM and Spectroscopic Ellipsometry," *J. Electrochem. Soc.*, 150, A229 (2003).
- 44. E. Rejovitzky, C. V. Di Leo, and L. Anand, "A theory and a simulation capability for the growth of a solid electrolyte interphase layer at an anode particle in a Li-ion battery," *Journal of the Mechanics and Physics of Solids*, 78, 210 (2015).
- J. T. Lee, N. Nitta, J. Benson, A. Magasinski, T. F. Fuller, and G. Yushin, "Comparative study of the solid electrolyte interphase on graphite in full Li-ion battery cells using X-ray photoelectron spectroscopy, secondary ion mass spectrometry, and electron microscopy," *Carbon*, 52, 388 (2013).
 A. M. Colclasure and R. J. Kee, "Thermodynamically Consistent Modeling of El-
- A. M. Colclasure and R. J. Kee, "Thermodynamically Consistent Modeling of Elementary Electrochemistry in Lithium-Ion Batteries," *Electrochim. Acta*, 55, 8960 (2010).
- E. Peled, D. Bar Tow, A. Merson, A. Gladkich, L. Burstein, and D. Golodnitsky, "Composition, depth profiles and lateral distribution of materials in the SEI built on HOPG-TOF SIMS and XPS studies," *Journal of Power Sources*, 97–98, 52 (2001).

- K. Edström, M. Herstedt, and D. P. Abraham, "A new look at the solid electrolyte interphase on graphite anodes in Li-ion batteries," *Journal of Power Sources*, 153, 380 (2006).
- S. Bhattacharya and A. T. Alpas, "Micromechanisms of solid electrolyte interphase formation on electrochemically cycled graphite electrodes in lithium-ion cells," *Carbon*, 50, 5359 (2012).
- A. M. Andersson, A. Henningson, H. Siegbahn, U. Jansson, and K. Edström, "Electrochemically lithiated graphite characterised by photoelectron spectroscopy," *Journal* of *Power Sources*, 119–121, 522 (2003).
- A. Z. Weber, R. L. Borup, R. M. Darling, P. K. Das, T. J. Dursch, W. Gu, D. Harvey, A. Kusoglu, S. Litster, M. M. Mench, R. Mukundan, J. P. Owejan, J. G. Pharoah, M. Secanell, and I. V. Zenyuk, "A Critical Review of Modeling Transport Phenomena in Polymer-Electrolyte Fuel Cells," *J. Electrochem. Soc.*, 161, F1254 (2014).
- C. Ziegler, H. M. Yu, and J. O. Schumacher, "Two-Phase Dynamic Modeling of PEM-FCs and Simulation of Cyclo-Voltammograms," *J. Electrochem. Soc.*, 152, A1555 (2005).
- N. Zamel, X. Li, J. Becker, and A. Wiegmann, "Effect of liquid water on transport properties of the gas diffusion layer of polymer electrolyte membrane fuel cells," *International Journal of Hydrogen Energy*, 36, 5466 (2011).
- A. Grosman and C. Ortega, "Capillary condensation in porous materials. Hysteresis and interaction mechanism without pore blocking/percolation process," *Langmuir:* the ACS journal of surfaces and colloids, 24, 3977 (2008).
- Y. Sun, C. J. Radke, B. D. McCloskey, and J. M. Prausnitz, "Wetting behavior of four polar organic solvents containing one of three lithium salts on a lithium-ion-battery separator," *Journal of Colloid and Interface Science*, **529**, 582 (2018).
 M.-S. Wu, T.-L. Liao, Y.-Y. Wang, and C.-C. Wan, "Assessment of the Wettability of
- M.-S. Wu, T.-L. Liao, Y.-Y. Wang, and C.-C. Wan, "Assessment of the Wettability of Porous Electrodes for Lithium-Ion Batteries," *J Appl Electrochem*, 34, 797 (2004).
- S. G. Lee, D. H. Jeon, B. M. Kim, J. H. Kang, and C.-J. Kim, "Lattice Boltzmann Simulation for Electrolyte Transport in Porous Electrode of Lithium Ion Batteries," *J. Electrochem. Soc.*, 160, H258 (2013).
- N. Susarla, S. Ahmed, and D. W. Dees, "Modeling and analysis of solvent removal during Li-ion battery electrode drying," *Journal of Power Sources*, 378, 660 (2018).
- D. Bouvard and F. F. Lange, "Relation between percolation and particle coordination in binary powder mixtures," *Acta metall. mater*, **39**, 3083 (1991).
- S. Gewies and W. G. Bessler, "Physically based impedance modeling of Ni/YSZ cermet anodes," J. Electrochem. Soc., 155, B937 (2008).
- M. Cerbelaud, B. Lestriez, A. Videcoq, R. Ferrando, and D. Guyomard, "Understanding the Structure of Electrodes in Li-Ion Batteries: A Numerical Study," *J. Electrochem. Soc.*, 162, A1485 (2015).
- Timo Danner, Modeling and experimental investigation of transport processes in the porous cathode of aqueous Li-air batteries, Stuttgart University, 2015.
 D. Grübl, T. Danner, V. P. Schulz, A. Latz, and W. G. Bessler, "Multi-Methodology
- D. Grübl, T. Danner, V. P. Schulz, A. Latz, and W. G. Bessler, "Multi-Methodology Modeling and Design of Lithium-Air Cells with Aqueous Electrolyte," *ECS Transactions*, **62**, 137 (2014).
- F. Wang and X. Li, "Pore-Scale Simulations of Porous Electrodes of Li-O2 Batteries at Different Saturation Levels," ACS applied materials & interfaces, 10, 26222 (2018).
- 65. S. Watanabe, M. Kinoshita, and K. Nakura, "Capacity fade of LiNi_(1-x-y)Co_xAl_yO₂ cathode for lithium-ion batteries during accelerated calendar and cycle life test. I. Comparison analysis between LiNi_(1-x-y)Co_xAl_yO₂ and LiCoO₂ cathodes in cylindrical lithium-ion cells during long term storage test," *Journal of Power Sources*, 247, 412 (2014).
- N. Omar, M. A. Monem, Y. Firouz, J. Salminen, J. Smekens, O. Hegazy, H. Gaulous, G. Mulder, Peter Van den Bossche, T. Coosemans, and J. van Mierlo, "Lithium iron phosphate based battery – Assessment of the aging parameters and development of cycle life model," *Applied Energy*, **113**, 1575 (2014).
- E. Sarasketa-Zabala, I. Gandiaga, L. M. Rodriguez-Martinez, and I. Villarreal, "Calendar ageing analysis of a LiFePO₄/graphite cell with dynamic model validations: Towards realistic lifetime predictions," *J. Power Sources*, **272**, 45 (2014).
- J. Wang, P. Liu, J. Hicks-Garner, E. Sherman, S. Soukiazian, M. Verbrugge, H. Tataria, J. Musser, and P. Finamore, "Cycle-life model for graphite-LiFePO₄ cells," *J. Power Sources*, **196**, 3942 (2011).
- M. Bauer, C. Guenther, M. Kasper, M. Petzl, and M. A. Danzer, "Discrimination of degradation processes in lithium-ion cells based on the sensitivity of aging indicators toward capacity loss," *Journal of Power Sources*, 283, 494 (2015).
- M. Safari and C. Delacourt, "Aging of a Commercial Graphite/LiFePO₄ Cell," J. Electrochem. Soc., 158, A1123 (2011).
- M. Kassem, J. Bernard, R. Revel, S. Pélissier, F. Duclaud, and C. Delacourt, "Calendar aging of a graphite/LiFePO₄ cell," *J. Power Sources*, 208, 296 (2012).
- M. Dubarry, C. Truchot, and B. Y. Liaw, "Cell degradation in commercial LiFePO₄ cells with high-power and high-energy designs," *Journal of Power Sources*, 258, 408 (2014).
- D. Li, D. L. Danilov, L. Gao, Y. Yang, and P. H. L. Notten, "Degradation Mechanisms of C₆/LiFePO₄ Batteries. Experimental Analyses of Cycling-induced Aging," *Electrochim. Acta*, 210, 445 (2016).
- Y. Zhang, C.-Y. Wang, and X. Tang, "Cycling degradation of an automotive LiFePO₄ lithium-ion battery," *J. Power Sources*, **196**, 1513 (2011).
- R. D. Deshpande and D. M. Bernardi, "Modeling Solid-Electrolyte Interphase (SEI) Fracture. Coupled Mechanical/Chemical Degradation of the Lithium Ion Battery," J. Electrochem. Soc., 164, A461 (2017).
- C. Veth, D. Dragicevic, R. Pfister, S. Arakkan, and C. Merten, "3D Electro-Thermal Model Approach for the Prediction of Internal State Values in Large-Format Lithium Ion Cells and Its Validation," *J. Electrochem. Soc.*, **161**, A1943 (2014).
- D. Aurbach, B. Markovsky, I. Weissman, E. Levi, and Y. Ein-Eli, "On the correlation between surface chemistry and performance of graphite negative electrodes for Li ion batteries," *Electrochimica Acta*, 45, 67 (1999).

- S. Grolleau, A. Delaille, H. Gualous, P. Gyan, R. Revel, J. Bernard, E. Redondo-Iglesias, and J. Peter, "Calendar aging of commercial graphite/LiFePO₄ cell – Predicting capacity fade under time dependent storage conditions," *J. Power Sources*, 255, 450 (2014).
- P. Liu, J. Wang, J. Hicks-Garner, E. Sherman, S. Soukiazian, M. Verbrugge, H. Tataria, J. Musser, and P. Finamore, "Aging Mechanisms of LiFePO₄ Batteries Deduced by Electrochemical and Structural Analyses," *J. Electrochem. Soc.*, **157**, A499 (2010).
- P. G. Balakrishnan, R. Ramesh, and T. Prem Kumar, "Safety mechanisms in lithiumion batteries," *J. Power Sources*, 155, 401 (2006).
- J. Christensen, D. Cook, and P. Albertus, "An Efficient Parallelizable 3D Thermoelectrochemical Model of a Li-Ion Cell," *J. Electrochem. Soc.*, 160, A2258 (2013).
- K. Tasaki, A. Goldberg, J.-J. Lian, M. Walker, A. Timmons, and S. J. Harris, "Solubility of Lithium Salts Formed on the Lithium-Ion Battery Negative Electrode Surface in Organic Solvents," *J. Electrochem. Soc.*, **156**, A1019 (2009).
- V. Agubra and J. Fergus, "Lithium Ion Battery Anode Aging Mechanisms," *Materials*, 6, 1310 (2013).
- I. Baghdadi, O. Briat, P. Gyan, and J. M. Vinassa, "State of health assessment for lithium batteries based on voltage-time relaxation measure," *Electrochimica Acta*, 194, 461 (2016).