

State of Health Estimation for Lithium Ion Batteries based on an Equivalent-Hydraulic Model: An Iron Phosphate Application

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Abstract

A two-step approach for state-of-health (SOH) estimation of a lithium-ion (Li-ion) battery is developed. In the first step, state-of-charge (SOC) estimation is performed by a constrained extended Kalman filter (EKF) based on the so-called equivalent-hydraulic model. The latter model allows to characterize the internal battery state and main physical parameters while being suitable for on-line computation. The internal battery states are further exploited in the second step of the approach to obtain parameter-based SOH indicators that characterize the long term evolution of the diffusion and charge transfer processes associated to aging. Capacity and power fade indicators are determined by using notably an instrumental variable method in order to obtain unbiased parameter estimates in the presence of heteroscedastic colored noise. The methodology is validated on both simulation and experimental data for a lithium iron phosphate (LFP) half battery cell. This also provides insight on the properties of the LFP electrodes.

Keywords: Li-ion battery, state estimation, state-of-charge, state-of-health, system identification.

1. Introduction

Renewable energies have been proposed as clean alternative sources for energy generation. Nevertheless, these sources are unpredictable and a mismatch exists between energy supply and consumption periods. To tackle these issues, lithium-ion batteries comprise a suitable solution to store energy, given their high efficiency and energy/power density. However, they come associated with safety concerns. This drawback can be addressed by using a battery-management system (BMS) to monitor internal state evolution, such as state-of-charge (SOC) and state-of-health (SOH). This paper introduces a two-step procedure to estimate SOH based on a generic reduced-order electrochemical model.

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The SOH has not been formally defined by industry [1], but any variable that changes with battery usage can be considered as a SOH indicator [2]. In this way, the SOH could be generally defined as

$$\text{SOH} = \frac{\delta\theta_0}{\theta_0} \quad (1)$$

where $\delta\theta_0$ is the variation of any chosen variable from its initial value θ_0 (brand new battery cell), i.e. $\delta\theta_0 = \hat{\theta} - \theta_0$ where $\hat{\theta}$ denotes the current parameter estimate. The larger this variation is, the older the battery.

The SOH estimation can be performed resorting to two different approaches, namely experimental-based and model-based [3]. The former approach is simple from the computational standpoint, but it might require specific measurements only available in controlled environments. Besides access to the entire cycling history of the battery might be needed. The second approach requires to link degradation to specific parameters to start with, to develop an accurate model with such parameters embedded in it, and to devise a suitable procedure to estimate them from standard on-line measurements. The challenge with this approach lies in the limited available measurements (current and voltage). Roughly speaking, the experimental burden of the first approach is translated into model and estimator design efforts in the second. The payoff is a method that provides SOH estimation in real time during battery daily regular operation.

Two widely used notions to characterize SOH are capacity and power fade. The identification of a meaningful parameter set that captures SOH degradation is difficult due to the multiple root causes behind it and its dependency on battery chemistry [4, 5, 6] and operating conditions. Nevertheless, some general sources of capacity and power loss have been reported in the literature, which could be associated to specific parameters. For instance, side reactions involving lithiated carbon, the electrolyte and the solvent produce a passive film surrounding the electrode material. If this resistive film is diffusion limiting [7], the solid-phase diffusion time constant $\tau_s = D_s^{-1}R_s^2$ increases, where D_s and R_s are the solid-phase diffusion coefficient and the electrode particle radius, respectively. A larger τ_s is caused by a decrease in the value of D_s as battery ages. Now, in a charge process, the maximum voltage is reached when the electrode surface layer is saturated with lithium. A smaller D_s value due to aging makes this layer to be saturated sooner by preventing the lithium to travel from the surface to the bulk of the electrode as fast as in a less aged battery. Thus, this degradation mechanism limits battery capacity and induces capacity fade. The solid-phase diffusion process can be slowed down for multiple reasons, such as electrode particles cracking due to mechanical stress [8, 9] or the plugging of pores of the porous electrode material [10]. If the resistive film is kinetic limiting, the

contact resistance R_c at the electrode surface increases [11]. This internal resistance rise translates into power fade. Magnitude changes of these parameters have been estimated to be a 100% drop for D_s and 400% increase for R_c when a lithium cobalt oxide battery cell was subjected to 500 charge/discharge cycles of maximum 1C [12]. Similar degradation trends have been reported for other lithium-ion batteries [13, 14, 15].

A suitable battery model is needed for the second type of approaches to SOH estimation. Several battery cell models have been proposed in the literature, such as data-driven [16], equivalent-circuit [17] and electrochemical models. The first type of models has the drawback of requiring a large amount of data for training. Equivalent-circuit models (ECM) rely on the analogy between battery systems and electrical systems. However, the former systems involve lithium diffusion and intercalation, just to name a few other processes besides the electrical ones, which cannot be modeled by the latter type of systems. Therefore, ECM variables suffer from lack of interpretability preventing its link to e.g. the physics of battery degradation. In contrast, electrochemical models (EChM) do not exhibit the latter inconveniences. The so-called Doyle-Fuller-Newman (DFN) model [18, 19, 20] is the most popular EChM. The high accuracy of the DFN model makes it ideal for simulation, although its complexity prohibits its use in on-line applications. Moreover, the DFN framework might not be enough to capture additional specific features of some electrode materials as the LFP, which has promoted the development of chemistry-oriented models.

Lithium iron phosphate (LiFePO_4) electrodes exhibit high capacity, low price and environmental impact, and remarkable stability [21, 22], which makes them stick out among other chemistries. Despite the great interest aroused by this material since its candidacy as cathode material [23], there is still speculation about its operation mechanism. The controversy lies in its outstanding performance for high-power applications, which is in opposition to the two-phase process widely accepted to occur during lithium intercalation/deintercalation [23]. The latter physical description yielded a core-shell model [24], where the two phases are separated by a moving interface for each electrode particle. Lithium diffuses through a Li-rich growing shell surrounding a Li-poor shrinking core [24, 25]. This model has been extended to consider resistive-reactant effects [26], multiple two-phase boundaries [27, 28] and multiple scales [29]. These phase-change models are computationally expensive and thermodynamically inconsistent. In contrast to a two-phases particle, experiments show that each phase is simultaneously present in different particles that interact with each other forming a mosaic, which has given rise to many-particle [30] and mesoscopic [31] models. However, other results based on more complex phase-field models show that small particles subject to discharge currents suppress phase separation [32, 33], which is aligned with the LFP carbon coating and particle size reduction to improve its intrinsic low conductivity and diffusivity. Regular solid-solution

models, i.e. that neglect phase transformations, have also been proposed, such as a multi-particle resistive-reactant model with interparticle resistance distribution [22, 34], a variable solid-state diffusivity model with particle-size distribution [21, 22], and a model that enhances the last one with electrolyte dynamics [35]. Most of these LFP models seek to provide insight into the limiting electrochemical processes that govern LFP electrode dynamics. Given their complexity, they might not be suitable for battery real-time monitoring in contrast to other more generic reduced-order EChMs [36, 37, 38, 39, 40, 41, 42, 43, 44].

SOH indicators deduced from models vary depending on the model choice. The following discussion focuses on contributions exploiting EChMs, deliberately leaving aside the rich body of literature dealing with other model types such as ECMs. The interested reader is referred to more extensive reviews on the subject [1, 2, 3, 45, 46] covering different SOH estimation methods. Model-based SOH indicators have been built resorting to two main tools, namely parameter estimation techniques and adaptive state observers. Within the first category lie optimization-based techniques, such as Levenberg-Marquardt method [47] and Gauss-Newton method [13, 48], as well as recursive parameter update laws such as gradient method [49]. Within the second category are state observers with recursive parameter estimation update laws based on least-squares [50, 51, 52], cascaded estimation resorting to sliding mode [53, 54], Lyapunov-based [55] and proportional-integral observers [56], as well as lumped parameter/state estimation via Kalman filters (KF) [41, 57, 58, 59, 60], particle filters [60, 61] and nonlinear geometric observers [62]. Most of the parameter estimation techniques state a least-squares estimation problem, which induces two drawbacks: 1) the initialization of these methods requires some a priori knowledge of the unknown parameters, and 2) they produce biased estimates in presence of colored noise. Moreover, SOH assessment during real time operation requires access to the battery internal state, besides monitoring specific model parameters. This leads to joint state/parameters estimation [41, 57, 58, 62]. However, as aging is a slow phenomenon, it has to be handled at a different time-scale than state estimation, and it even suffices to evaluate the aging level periodically without necessarily performing a permanent monitoring. This is not well recognized in the indicated references except for [60, 61], and it can lead to SOH indicators that are overly sensitive to noise or operating point changes. To avoid the above pitfalls, the work reported here resorts to instrumental variable (IV) methods [63, 64, 65], which provide unbiased estimates regardless of the noise type and are robust to initial parameter uncertainty when used with suitable pre-filtering operations. Besides, we introduce a two-step procedure to ensure time separation between states and aging dynamics hence guaranteeing that the SOH indicators are not subject to short term transients and only capture the monotonic variation due to aging pointed out in [49].

This procedure is represented in Figure 1. Step 1 exploits an equivalent-hydraulic model (EHM) [43] to design a constrained extended Kalman filter for battery state estimation. The state vector comprises SOC and surface concentration (c_{ss}). This state estimation is a prerequisite for parameter estimation in Step 2. Two parameter estimation procedures are used, namely the simplified refined instrumental variable for continuous time-systems (SRIVC) method based on a Padé approximation model, and a least-squares (LS) method based on an output model. Resorting to continuous-time identification allows keeping the physical meaning of the estimated parameters. The SRIVC and LS methods generate capacity and power fade SOH indicators, respectively. The proposed methodology is validated through simulation and experimental studies. Although the considered battery corresponds to a LFP half battery cell, the proposed approach was devised for an easy extension to full battery cells of other chemistries.

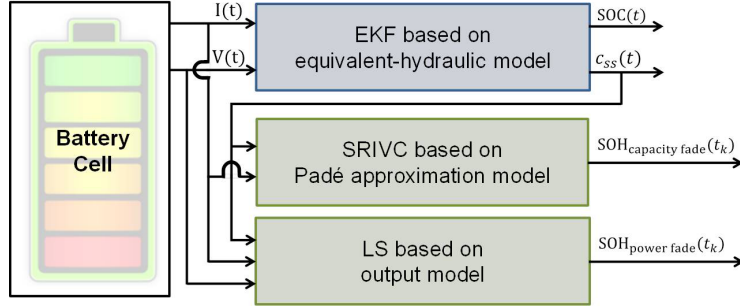


Figure 1: Block diagram of the estimation scheme, where EKF stands for extended Kalman filter, SRIVC for simplified refined instrumental variable for continuous-time systems and LS for least-squares.

This contribution departs from previous works in the following ways:

- It uses a generic model to describe a system with LFP as an electrode in contrast to other approaches that develop chemistry specific models [21, 24, 34]. Besides, it considers two parameters as uncertain by specifying them as slowly time-varying, instead of keeping nominal parameters [50] or using spatially distributed [34] or linearly time-varying parameters [66] for describing the LFP electrode. This parameter adaptation accounts for the change in battery operating conditions.
- It includes a systematic tuning procedure for the constrained EKF applied to a battery.
- It exploits for the first time the SRIVC procedure for the parameter identification of batteries. In contrast to widely used least-squares estimation [49, 50, 51], the SRIVC provides unbiased estimates while properly handling noise and parameter initialization.
- It introduces both simulation and experimental validations to assess state/parameter estimation.
- It provides insight on the properties of LFP electrodes through the experimental studies.

This article is structured as follows. The DFN model used for simulation along with reduced-order models exploited for estimation are introduced in Section 2. The estimation procedure developed to generate capacity and power fade SOH indicators is explained in Section 3. Simulation and experimental studies are presented in Sections 4 and 5, respectively.

2. Modeling

The knowledge of the battery cell type is fundamental for model selection. Lithium iron phosphate (LFP) electrode is the working porous electrode considered here, while a lithium metal foil acts as a counter-electrode. Despite using a half battery cell setup here, the proposed approach can be implemented with full battery cells by considering the limiting electrode as the only one for estimation/control [51].

Within the half battery cell, both working and counter electrodes (system solid phase) are ionically connected through a separator and electronically connected via current collectors placed at their boundaries. An electrolytic media (system solution phase) fills up the entire battery cell and allows the exchange of lithium ions between electrodes. The current collectors link the electrodes to the external electric circuit. During battery discharge, the lithium at the negative electrode undergoes an oxidation reaction that produces lithium ions, which cross the entire battery cell up to the positive electrode, where a reduction reaction takes place. Battery charge corresponds to the exact opposite mechanism. Two relevant processes can be distinguished within a porous electrode, namely a bulk process and an interfacial process. The former corresponds to the solid-phase diffusion of lithium throughout the active electrode material and it defines the capacity of the battery. The latter takes place at the solid-electrolyte interface corresponding to the electrochemical reaction, and it defines the power of the battery.

A general framework for modeling lithium-ion batteries corresponds to the Doyle-Fuller-Newman (DFN) model [18, 19, 20]. Even though each battery chemistry is different, any specific feature of a given battery can be added to this model.

2.1. The DFN model

The DFN model is used in this work for the LFP half battery cell simulator. For a thorough description of model equations together with the initial and boundary conditions, the references [18, 19, 20] may be consulted. The DFN model describes the phases of the system via porous electrode and concentrated solution theories for the solid and solution phases, respectively [20]. The LFP electrode active material is assumed to be made up of spherical particles, while the material exchange between electrodes is assumed to be one

dimensional. The solid concentration of the lithium metal foil counter-electrode is considered to be constant [67]. The model consists of five independent governing equations for five dependent variables, namely the porous solid-phase concentration and electric potential (c_s and ϕ_s , respectively), the electrolyte solution phase concentration and electric potential (c_e and ϕ_e , respectively) and the pore-wall molar flux (j_n). All the variables are time and space dependent.

In order to account for LFP electrode specific features, two parameter variations have been introduced into the original DFN model. On the one hand, a C-rate¹ dependent solid-phase diffusion coefficient [24, 68] represents a variable solid-phase diffusion coefficient [21, 22]. On the other hand, a contact-resistance distribution [22, 34] reflects resistive-reactant effects [24, 26, 34]. This distribution is uniform over the interval $[0.835, 1.660] \Omega \cdot \text{m}^2$, and it was introduced in a discrete way into the DFN model by associating to each considered spherical particle a contact-resistance sampled from the distribution.

The DFN model described above consists of a coupled set of algebraic nonlinear partial-differential equations (PDEs). Although highly accurate for simulation, such model structure is not amenable for on-line purposes of estimation/control. Therefore model reduction is addressed in the following subsections.

2.2. The single-particle model

The single particle model is an intermediate step towards the rational transfer function model and the state space model used in the methodology for SOH estimation.

2.2.1. Diffusion equation

First, the DFN model is simplified by considering a single particle whose surface area is equivalent to the active area of the porous electrode, i.e. single particle model (SPM) framework. The dynamics of the spherical diffusion process are governed by Fick's law with Dirichlet and Robin boundary conditions, given by

$$\left\{ \begin{array}{l} \frac{\partial \bar{c}_s}{\partial t}(t, r) = D_s \frac{\partial^2 \bar{c}_s}{\partial r^2}(t, r), t \geq 0, r \in [0, R_s] \\ \bar{c}_s(t, r) = 0 \quad t \geq 0, r = 0 \\ R_s \frac{\partial \bar{c}_s}{\partial r}(t, r) - \bar{c}_s(t, r) = \frac{R_s^2}{D_s} j_n(t), t \geq 0, r = R_s \\ \bar{c}_s(t, r) = r c_s(t, r) \end{array} \right. \quad (2)$$

where $c_s(t, r)$ and D_s are the solid-phase concentration and diffusion coefficient, respectively, R_s is the particle radius and $\bar{c}_s(t, r)$ is a transformed state [51]. Assuming that the reaction rate is uniform, the pore-wall molar

¹C-rate: normalization of the battery current [A] with respect to the battery nominal capacity [Ah].

flux $j_n(t)$ is a function dependent on the input current $I(t)$ given by

$$j_n(t) = \frac{1}{Fa_s l} I(t) \quad (3)$$

where F is Faraday's constant, l is the thickness of the electrode region and a_s is the specific interfacial area of each electrode. By using the Laplace transform with respect to the time variable, solving the resulting ordinary-differential equation and setting r to R_s , the following solid-phase diffusion impedance [69] is obtained from Eq. (2)

$$\frac{C_{ss}(s)}{I(s)} = \frac{1}{Fa_s l} \frac{R_s \sinh(\alpha)}{D_s (\alpha \cosh(\alpha) - \sinh(\alpha))} \quad (4)$$

with $\alpha = R_s \sqrt{\frac{s}{D_s}}$. $C_{ss}(s)$ and $I(s)$ denote the Laplace transforms of $c_{ss}(t)$ and $I(t)$ respectively, where $c_{ss}(t) = c_s(t)|_{r=R_s}$ is the solid surface concentration and s is the Laplace variable. Given the non integer order of the system, the corresponding transfer function is irrational. Moreover, it has an infinite number of zeros $-(k\pi \sqrt{D_s} R_s^{-1})^2$ with $k \in \mathbb{N}$ and poles $-(\alpha_k \sqrt{D_s} R_s^{-1})^2$ with α_k the roots of $\tanh \alpha_k = \alpha_k$. From the viewpoint of linear time invariant (LTI) system identification, this infinite-dimensionality means that an infinite number of parameters has to be estimated. In order to deal simultaneously with both issues, a Padé's expansion is used to truncate the transfer function (TF) Eq. (4).

2.2.2. Padé approximation model (transfer function)

Considering a third-order Padé approximation, the reduced-order model obtained for TF Eq. (4) corresponds to

$$\frac{C_{ss}(s)}{I(s)} \approx \frac{1}{Fa_s l} \frac{21R_s^3 s^2 + 1260R_s D_s s + 10395R_s^{-1} D_s^2}{s(R_s^4 s^2 + 189R_s^2 D_s s + 3465D_s^2)} \quad (5)$$

This model can be leveraged to estimate capacity fade SOH through the batch identification of the constant lumped parameter $D_s^{-1} R_s^2$. This parameter dictates the diffusion time constant, which is expected to increase as the battery ages. The input/output relationship in TF Eq. (4) links the current $I(t)$ and the surface concentration $c_{ss}(t)$, respectively. However, the only measurements that can be directly taken during regular battery operation are current and voltage. One way to overcome this obstacle is to generate pseudo-measurements of $c_{ss}(t)$ through its estimation from voltage and current signals. Moreover, model adaptation might be advisable when parameter changes are foreseen. These issues motivate the transformation of the TF Eq. (5) into the state-space model shown below.

2.2.3. Equivalent-hydraulic model (state space)

A straightforward state space representation of the TF Eq. (5) is the controllable canonical form [70]. Nevertheless, such form induces the state to pass through a linear transformation based on diffusion parameters to reconstruct the solid particle concentration profile [70]. An alternative parameterization that yields a physically meaningful state equation is known as equivalent-hydraulic model (EHM) [43]. In contrast with the second-order EHM used for SOC/SOH estimation [71, 72], a third-order EHM is developed here to ensure coherency with model Eq. (5). This EHM is augmented to account for time-varying uncertain parameters and it is used for $c_{ss}(t)$ estimation.

In general, the EHM can be parameterized with an arbitrary number of sections, starting from one single section that renders a pure integrator. A representation of the single spherical particle discretized in 3 sections is given in Figure 2. The outer section is the shell of the particle that is directly in contact with the current density $I(t)$. The two inner sections correspond to the cores of the particle, inner and outer cores. The lithium concentration in each section is represented by the following state variables: the solid concentration at the surface (c_{ss}), at the outer core (c_{so}) and at the inner core (c_{si}). The latter was replaced in the model by the total normalized solid concentration of the spherical particle, i.e. the SOC, obtained from material balance $\text{SOC} = (\beta_s c_{ss} + \beta_i c_{si} + \beta_o c_{so}) / c_{s,\max}$ where β_j is the ratio of the sphere volume section j to the total volume and $c_{s,\max}$ is the maximum solid concentration. Indeed, the SOC is directly relevant for a BMS. The rate of material exchange between contiguous particle sections is described by $\gamma_i \omega$, where $\gamma_i, i = 1, 2$ are constants and ω is the inverse of the unknown diffusion time constant τ_s given by $\omega = \tau_s^{-1} = R_s^{-2} D_s$.

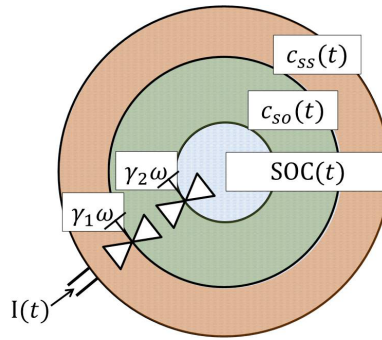


Figure 2: Equivalent-hydraulic model representing the spherical particle.

After discretization to account for the sampled data used in the BMS, the following equation is obtained to describe the above dynamic system

$$\mathbf{x}(k+1) = f(\mathbf{x}(k), \mathbf{I}(k)) \quad (6)$$

where $k \in \mathbb{N}$ stands for the number of sampling periods, $\mathbf{x}(k) \in \mathbb{R}^3$ is the state vector, that takes the form $\mathbf{x}(k) = [c_{ss}(k), c_{so}(k), \text{SOC}(k)]^T$. Setting the sampling period $T_s = 1$ s yields a function f of the form

$$\begin{cases} f_1(\mathbf{x}(k), \mathbf{I}(k)) = \frac{\gamma_2}{\beta_i} \omega \frac{c_{so}(k)}{c_{s,\max}} + \left(1 - \frac{\gamma_2}{\beta_i} \omega\right) \frac{c_{ss}(k)}{c_{s,\max}} + \frac{1}{\beta_i c_{s,\max}} \frac{1}{F \varepsilon_s l} \mathbf{I}(k) \end{cases} \quad (7a)$$

$$\begin{cases} f_2(\mathbf{x}(k), \mathbf{I}(k)) = \frac{\gamma_1}{\beta_s \beta_o} \omega \text{SOC}(k) + \left(1 - \left(\frac{\gamma_1}{\beta_s} + \frac{\gamma_1 + \gamma_2}{\beta_o}\right) \omega\right) \frac{c_{so}(k)}{c_{s,\max}} + \left(\frac{\gamma_2}{\beta_o} - \frac{\beta_i \gamma_1}{\beta_s \beta_o}\right) \omega \frac{c_{ss}(k)}{c_{s,\max}} \end{cases} \quad (7b)$$

$$\begin{cases} f_3(\mathbf{x}(k), \mathbf{I}(k)) = \text{SOC}(k) - \frac{1}{c_{s,\max}} \frac{1}{F \varepsilon_s l} \mathbf{I}(k) \end{cases} \quad (7c)$$

In order to account for the variable solid-phase diffusion coefficient of LFP electrodes [21, 22] the parameter ω is considered as slowly time-varying. Therefore, the state vector is augmented as² $\mathbf{x}(k) = [c_{ss}(k), c_{so}(k), \text{SOC}(k), \omega(k)]^T$ and f_4 takes the form

$$f_4(\mathbf{x}(k), \mathbf{I}(k)) = \omega(k) \quad (8)$$

2.2.4. Output model

The state space representation Eq. (6) of the solid-phase diffusion process has to be completed with an output equation describing the charge transfer process, which gives rise to the voltage across the half battery cell. This output equation relies on the Butler-Volmer equation and the open-circuit voltage (OCV) function, and it will be used for power fade SOH estimation. The discrete-time nonlinear equation can be written as

$$y(k) = h(\mathbf{x}(k), \mathbf{I}(k)) \quad (9)$$

where $y(k) \in \mathbb{R}$. The nonlinear function h is given by

$$h(\mathbf{x}(k), \mathbf{I}(k)) = \eta_s^+(k) - \eta_s^-(k) - \Delta\phi_e(k) + U^+(k) - U^- - \frac{R_c}{a_s l} \mathbf{I}(k) \quad (10)$$

The superscripts (+) and (−) are introduced in this subsection to account for the potential response of both LFP and lithium counter electrodes, respectively. The surface overpotentials $\eta_s^\pm$, the voltage drop throughout the electrolyte phase $\Delta\phi_e$ and the equilibrium potential U^+ for the LFP electrode are functions

²The same notation is used for the three dimensional and higher-dimensional state vectors for sake of simplicity.

of the state and the input as shown in Table A1 in the Appendix. For the lithium metal foil electrode U^- is considered as zero [18].

The last term in Eq. (10) corresponds to an ohmic voltage drop caused by a contact resistance. In LFP electrodes, such a resistive contribution is described by a distribution of contact resistances and it is known as resistive-reactant feature [24, 26, 34]. This feature is accounted for by considering the parameter R_c as time-varying. Therefore, the state vector is further augmented as $\mathbf{x}(k) = [c_{ss}(k), c_{so}(k), \text{SOC}(k), \omega(k), R_c(k)]^T$ and f_5 that complements Eqs. (7) and (8) is given by

$$f_5(\mathbf{x}(k), \mathbf{I}(k)) = R_c(k) \quad (11)$$

3. SOH estimation

The aim is to determine both capacity and power fade SOH. To this end, slow parameter changes characteristic of aging have to be monitored. This is achieved by periodically recording a data set over a sufficiently long time horizon to achieve precise estimation of the relevant parameters. Some physical parameters related to battery aging are the diffusion time constant τ_s and the contact resistance R_c , both increase with time and they respectively reflect capacity and power fade. The estimation problem will be solved successively for each parameter.

3.1. Capacity fade

The determination of $\tau_s = D_s^{-1}R_s^2$ will be based on model Eq. (5), as the relevant parameters D_s and R_s show up in its parameterization. A continuous time parameter estimation approach will be used in order to keep the link between the estimated parameters and the physical parameters. However, as the solid surface concentration c_{ss} is not measured, it has to be determined first. Therefore, a two step approach is followed below:

1. Estimation of $c_{ss}(t)$
2. Estimation of τ_s in order to monitor capacity fade.

As the estimation of $c_{ss}(t)$ turns out to provide an estimate of the state-of-charge $\text{SOC}(t)$ as a byproduct, it is performed on-line, contrary to the capacity fade estimation which processes a batch of data.

3.1.1. Estimation of the solid surface concentration

We rely on the equivalent-hydraulic model (augmented with parameters ω and R_c) to estimate $c_{ss}(t)$. Such model introduced above takes the form

$$\begin{aligned} \mathbf{x}(k+1) &= f(\mathbf{x}(k), \mathbf{I}(k)) + \mathbf{v}_1(k) \\ y(k) &= h(\mathbf{x}(k), \mathbf{I}(k)) + v_2(k) \end{aligned} \quad (12)$$

where $\mathbf{x}(k) \in \mathbb{R}^5$ is the augmented state vector. The function f is given by Eqs. (7), (8) and (11) and the function h is given by Eq. (10). The process and measurement noises have been added and are ascribed to $\mathbf{v}_1(k)$ and $v_2(k)$, respectively. $\mathbf{v}_1(k) \in \mathbb{R}^5$ and $v_2(k) \in \mathbb{R}$ are zero-mean white noise sequences that are mutually uncorrelated such that

$$\mathbb{E} \left[\begin{bmatrix} \mathbf{v}_1(k) \\ v_2(k) \end{bmatrix} \begin{bmatrix} \mathbf{v}_1(m)^T & v_2(m)^T \end{bmatrix} \right] = \begin{bmatrix} \mathbf{Q} & 0 \\ 0 & R \end{bmatrix} \delta_{km} \quad (13)$$

where $\mathbb{E}[\cdot]$ is the mathematical expectation operator, δ_{km} is the Kronecker delta, $\mathbf{Q}$ and R are the process and measurement noise variances, respectively.

Before describing the state estimation procedure for model Eqs. (12), (13), the model has to be completed to account for physical constraints, namely:

$$\begin{aligned} 0 &\leq c_{ss}(k)/c_{s,\max} \leq 1 \\ 0 &\leq R_c(k) \\ 0 &\leq \omega(k) \end{aligned} \quad (14)$$

To perform state estimation while enforcing constraints Eq. (14) on the estimated state, a constrained extended Kalman filter with estimate projection is used. This is a direct extension of the Kalman filter with state constraints presented in [73]. To apply this method, first note that, given the definition of the state variables in Eq. (12), the constraints Eq. (14) can be rewritten in the form

$$D\mathbf{x}(k) \leq d \quad (15)$$

with matrix D and vector d defined as:

$$D = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & -1 \end{bmatrix}, \quad d = \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \end{bmatrix}.$$

Now, at any time instant, only a subset of the constraints Eq. (15) will be active. In particular, only one of the first two constraints can be active at a given time. Let $\tilde{D}$ and $\tilde{d}$ denote the matrix and vector made of the rows of D and d corresponding to the active constraints. Furthermore, let $\hat{\mathbf{x}}(k)$ denote the state estimate at time k given measurements up to time $k - 1$, and let $\tilde{\mathbf{x}}(k)$ denote its constrained counterpart. Then the projection step in the Kalman filter amounts to solving the following optimization problem:

$$\begin{aligned} \tilde{\mathbf{x}}(k) = \operatorname{argmin}_{\mathbf{x}} & (\mathbf{x} - \hat{\mathbf{x}}(k))^T (\mathbf{x} - \hat{\mathbf{x}}(k)) \\ \text{subject to} & \\ & \tilde{D}\mathbf{x} = \tilde{d}. \end{aligned} \tag{16}$$

This yields the following solution

$$\tilde{\mathbf{x}}(k) = \hat{\mathbf{x}}(k) - \tilde{D}^T (\tilde{D}\tilde{D}^T)^{-1} (\tilde{D}\hat{\mathbf{x}}(k) - \tilde{d}).$$

The complete extended Kalman filter (EKF) algorithm with state projection is summarized in Table 1.

Table 1: Extended Kalman filter with state constraints.	
Initialization:	$\hat{\mathbf{x}}(0) = \hat{\mathbf{x}}_0 = \mathbb{E}[\mathbf{x}_0], \quad \Sigma(0) = \Sigma_0 = \mathbb{E}[(\mathbf{x}_0 - \hat{\mathbf{x}}_0)(\mathbf{x}_0 - \hat{\mathbf{x}}_0)^T]$
At each time instant compute:	
Kalman gain	$K(k) = F(k)\Sigma(k)H(k)^T (H(k)\Sigma(k)H(k)^T + R)^{-1}$
State estimate update	$\hat{\mathbf{x}}(k+1) = f(\hat{\mathbf{x}}(k), \mathbf{I}(k)) + K(k)(\mathbf{y}(k) - h(\hat{\mathbf{x}}(k), \mathbf{I}(k)))$
Projection	$\tilde{\mathbf{x}}(k) = \hat{\mathbf{x}}(k) - \tilde{D}^T (\tilde{D}\tilde{D}^T)^{-1} (\tilde{D}\hat{\mathbf{x}}(k) - \tilde{d})$
Covariance update	$\Sigma(k+1) = F(k)\Sigma(k)F(k)^T + Q - K(k)(H(k)\Sigma(k)H(k)^T + R)K(k)^T$
where	$F(k) = \left. \frac{\partial f(\mathbf{x}(k), \mathbf{u}(k))}{\partial \mathbf{x}(k)} \right _{\mathbf{x}(k)=\hat{\mathbf{x}}(k)}, \quad H(k) = \left. \frac{\partial h(\mathbf{x}(k), \mathbf{u}(k))}{\partial \mathbf{x}(k)} \right _{\mathbf{x}(k)=\hat{\mathbf{x}}(k)}$

The initialization step in Table 1 involves setting the state estimate $\hat{\mathbf{x}}_0 = [\hat{c}_{ss,0}, \hat{c}_{so,0}, \widehat{\text{SOC}}_0, \hat{\omega}_0, \hat{R}_{c,0}]^T$ and the covariance of the state estimation error Σ_0 . Initialization of the state elements comprising the solid concentration is straightforward by assuming that the battery cell was at rest (zero current) during a long enough period of time before its use. This condition ensures equilibrium where $c_{ss,0} = c_{so,0} = \text{SOC}_0 \times c_{s,\max} =$

$c_{s,0}$, which can be estimated by inverting the open circuit voltage (OCV) function. Initialization of the uncertain parameters ω and R_c relies on the knowledge of the battery chemistry. ω can be initialized with a reasonable a priori estimate of the diffusion time constant τ_s , whereas R_c can be initialized e.g. with a value around $1 \text{ } \Omega\text{m}^2$. Finally, Σ_0 is chosen as a diagonal matrix. Its diagonal elements are taken as tuning parameters in order to ensure an appropriate trade-off between convergence speed and "noise level" on the estimate. The covariance matrix Q is also used as a tuning parameter, since it accounts for model inaccuracies that are difficult to quantify.

Although the constrained EKF is designed here based on the EHM with output Eqs. (9),(10), it can be used with whatever model able to represent battery dynamics. However, electrochemical models such as the EHM are rooted in the physical phenomena taking place inside a battery cell, which makes them more descriptive than e.g. equivalent-circuit models. For instance, the former models can capture lithium concentration gradients and electrolyte diffusion limitations that the latter models cannot. This fact might explain the higher accuracy of an electrochemical SPM when compared to a two resistance-capacitance ECM in terms of output voltage mean absolute error [74]. This improved accuracy of the SPM with respect to the ECM is at the expense of a tenfold larger execution time, which is still as low as in the order of $10 \text{ } \mu\text{s}$ [74]. Now that an estimate of c_{ss} is available, capacity fade estimation can be addressed.

3.1.2. Estimation of the diffusion time constant

The estimation problem now consists in estimating parameters R_s and D_s in

$$\frac{C_{ss}(s)}{I(s)} \approx \frac{1}{Fasl} \frac{21R_s^3s^2 + 1260R_sD_ss + 10395R_s^{-1}D_s^2}{s(R_s^4s^2 + 189R_s^2D_ss + 3465D_s^2)} \quad (17)$$

given the measurements

$$\hat{c}_{ss}(t_k) = c_{ss}(t_k) + v(t_k)$$

with $t_k = kT_s$, T_s the sampling period, and $v(t_k)$ an heteroscedastic³ noise accounting for the estimation error of the EKF notably. This noise is assumed to be uncorrelated with the input data. Moreover, as the model Eq. (12) used in the EKF method is nonlinear, the additive noise of the state estimation is not granted to be white. Special attention to this feature will be necessary.

Note that the above parameter estimation problem does not directly lend itself to standard continuous-time parameter estimation in the prediction error framework for the following reasons:

³An heteroscedastic noise is a noise whose variance varies with time.

1. The transfer function (TF) has a pole at the origin.
2. The parameters of interest D_s and R_s appear nonlinearly in Eq. (17).

To overcome these issues, in the following the unstable part of the TF is removed by prefiltering the data with a state-variable-filter (SVF). The resulting TF is identified by using instrumental variable (IV) techniques, and finally the nonlinear function in the coefficients D_s and R_s is turned into a linear form to obtain the capacity fade SOH indicator.

The SVF yields the filtered quantities $C_{ss,f}$, I_f , $\hat{c}_{ss,f}$ and ν_f defined as

$$C_{ss,f} = \frac{s}{s + \nabla} C_{ss} \quad \text{and} \quad I_f = \frac{1}{s + \nabla} I, \quad (18)$$

$$\hat{c}_{ss,f} = \frac{s}{s + \nabla} \hat{c}_{ss} \quad \text{and} \quad \nu_f = \frac{1}{s + \nabla} (\hat{c}_{ss} - c_{ss}). \quad (19)$$

The cutoff frequency ∇ should be properly chosen to keep the relevant frequency range with respect to the third-order Padé approximation. Based on Eq. (17) and the new set of signals Eqs. (18) and (19), the filtering operation transforms model Eq. (17) and the associated measurement equation into:

$$\frac{C_{ss,f}(s)}{I_f(s)} = \frac{1}{Fa_s l} \frac{21R_s^3 s^2 + 1260R_s D_s s + 10395R_s^{-1} D_s^2}{R_s^4 s^2 + 189R_s^2 D_s s + 3465D_s^2} \quad (20)$$

$$\hat{c}_{ss,f}(t_k) = c_{ss,f}(t_k) + \nu_f(t_k) \quad (21)$$

The knowledge of the pole at the origin has been accounted for a priori through the filtering operation so that Eq. (20) corresponds to a stable system. Similarly to ν , ν_f is an heteroscedastic colored noise.

To estimate the parameters D_s and R_s in Eq. (20), the model is first rewritten as:

$$C_{ss,f}(s) = \frac{B(s, \theta)}{A(s, \theta)} \tilde{I}_f(s) \quad (22)$$

where $A(s, \theta)$ and $B(s, \theta)$ respectively stand for

$$\begin{cases} B(s, \theta) = b_2 s^2 + b_1 s + b_0 \\ A(s, \theta) = s^2 + a_1 s + a_0 \end{cases} \quad (23a)$$

$$\quad (23b)$$

with $\theta = [a_1 \ a_0 \ b_2 \ b_1 \ b_0]^T$ and $\tilde{I}_f(s) = I_f(s)/(Fa_s l)$. The constant $Fa_s l$ involves geometric parameters that are assumed to be known, but the method could be extended to the case where they are unknown.

Comparing Eq. (22) and Eq. (20) directly yields the expressions for the unknown parameters:

$$a_1 = 189R_s^{-2}D_s, \quad a_0 = 3465R_s^{-4}D_s^2, \quad b_2 = 21R_s^{-1}, \quad b_1 = 1260R_s^{-3}D_s \quad \text{and} \quad b_0 = 10395R_s^{-5}D_s^2 \quad (24)$$

The identification of the vector parameter θ from Eqs. (21), (22) cannot be solved by the least squares approach because the output measurements are corrupted by colored noise. The least squares approach would result in a biased estimate [64]. Therefore, an instrumental variable (IV) method for continuous-time model is used, namely the so-called simplified refined instrumental variable for continuous-time systems (SRIVC) method [65]. The corresponding algorithm is summarized in Table 2. It returns both an estimate of θ , $\hat{\theta}$, and of the variance of this estimate, $\hat{\sigma}_\theta^2 = \text{diag}(P_\theta)$ [75].

Table 2: Simplified refined instrumental variable method for continuous-time systems (SRIVC).

Initialization:	
Given the data sequences $I(t_k)$ and $\hat{C}_{ss}(t_k)$ for $k = 0, \dots, N$	
Compute the LS-SVF estimation	$\hat{\theta}_0 = \left(\sum_{k=0}^N \varphi(t_k)^T \varphi(t_k) \right)^{-1} \left(\sum_{k=0}^N \varphi(t_k)^T Y(t_k) \right)$ $\text{with } \varphi(t_k) = \frac{1}{(s + \nabla)^2} \begin{bmatrix} \frac{s^2}{Fa_s l} I_f & \frac{s}{Fa_s l} I_f & \frac{1}{Fa_s l} I_f & -s\hat{C}_{ss,f} & -\hat{C}_{ss,f} \end{bmatrix}_{t=tk}$ $\text{and } Y(t_k) = \frac{s^2}{(s + \nabla)^2} \hat{C}_{ss,f} \Big _{t=tk}$
Initialization of $j = 0$	
At iteration j :	
Determine the auxiliary output	$\tilde{C}_{ss,f}(s) = \frac{1}{Fa_s l} \frac{B(s, \hat{\theta}_j)}{A(s, \hat{\theta}_j)} I_f(s)$
Instrumental vector update	$\zeta(t_k) = \frac{1}{A(s, \hat{\theta}_j)} \begin{bmatrix} \frac{s^2}{Fa_s l} I_f & \frac{s}{Fa_s l} I_f & \frac{1}{Fa_s l} I_f & -s\tilde{C}_{ss,f} & -\tilde{C}_{ss,f} \end{bmatrix}_{t=tk}$
Regressor vector update	$\varphi(t_k) = \frac{1}{A(s, \hat{\theta}_j)} \begin{bmatrix} \frac{s^2}{Fa_s l} I_f & \frac{s}{Fa_s l} I_f & \frac{1}{Fa_s l} I_f & -s\hat{C}_{ss,f} & -\hat{C}_{ss,f} \end{bmatrix}_{t=tk}$
IV estimation	$\hat{\theta}_{j+1} = \left(\sum_{k=0}^N \zeta(t_k)^T \varphi(t_k) \right)^{-1} \left(\sum_{k=0}^N \zeta(t_k)^T Y(t_k) \right)$ $\text{with } Y(t_k) = \frac{s^2}{A(s, \hat{\theta}_j)} \hat{C}_{ss,f} \Big _{t=tk}$
If convergence occurs according to a user-specified criterion, for example $\frac{\ \theta_{j+1} - \theta_j\ }{\ \theta_j\ } \rightarrow 0$, or the maximum number of iterations is reached, then stop, else set $j = j + 1$	
Output:	
An estimate of the parameter vector θ , $\hat{\theta}$, and the associated error covariance matrix:	
Error covariance matrix	$P_\theta = \sigma_v^2 \left(\sum_{k=0}^N \zeta(t_k)^T \zeta(t_k) \right)^{-1}$

The last step consists in recovering the physical parameter estimate $\hat{\theta}_{\text{PHYS}} = [\hat{R}_s \ \hat{D}_s]$. From Eq. (24), the

following equation is deduced by taking the logarithm of θ component-wise:

$$\log_{10} \hat{\theta} = M \log_{10}(\hat{\theta}_{\text{PHYS}}) + L \quad (25)$$

with M and L defined as

$$M = \begin{bmatrix} -2 & 1 \\ -4 & 2 \\ -1 & 0 \\ -3 & 1 \\ -5 & 2 \end{bmatrix} \quad \text{and} \quad L = \begin{bmatrix} \log_{10}(189) \\ \log_{10}(3465) \\ \log_{10}(21) \\ \log_{10}(1260) \\ \log_{10}(10395) \end{bmatrix} \quad (26)$$

A least-squares (LS) estimate of θ_{PHYS} (in logarithmic scale) can be determined as:

$$\log_{10}(\hat{\theta}_{\text{PHYS}}) = (M^T M)^{-1} M^T (\log_{10} \hat{\theta} - L) \quad (27)$$

From Eq. (27) estimates of D_s and R_s are obtained, whose respective variances $\hat{\sigma}_{D_s}^2$ and $\hat{\sigma}_{R_s}^2$ are provided by the error propagation of $\hat{\sigma}_{\theta}^2$. Both estimates can be lumped together in order to have an estimate of τ_s . Although R_s might be known a priori from physical characterization of the electrode, its simultaneous estimation along with D_s is convenient. Indeed, it was observed that it reduces the estimation error while providing an accuracy indication of the overall estimation.

The solid-phase diffusion coefficient D_s might change in the short term with operating conditions and in the long term with aging [76]. To distinguish operation-induced and aging-induced parameter changes in a given battery, the following approach could be used. First parameter estimates are determined at the beginning of the battery life for a set of operating conditions that covers the operating range. This yields a set of values $\hat{\tau}_{s0,i}, i = 1, \dots, n_{oc}$ where n_{oc} stands for the number of operating conditions. Next, new parameter estimates $\hat{\tau}_{sc,j}$ are determined regularly from current data in a given operating condition, say the j^{th} one. A suitable SOH indicator is then deduced as $\frac{\hat{\tau}_{sc,j} - \hat{\tau}_{s0,j}}{\hat{\tau}_{s0,j}}$.

3.2. Power fade

The identification of R_c is simpler than the previous identification of τ_s since it involves the static electrochemical reaction process in contrast with the dynamic solid-phase diffusion process (see Figure 1).

The output voltage equation given in Eqs. (10), (12) can be rewritten in the following linear form

$$z(t_k) = R_c \phi(t_k) + v_2(t_k) \quad (28)$$

where

$$\begin{cases} z(t_k) = y(t_k) - \eta_s^+(t_k) + \eta_s^-(t_k) - U^+(t_k) + \Delta\phi_e(t_k) \\ \phi(t_k) = -\frac{1}{a_s l} \mathbf{I}(t_k) \end{cases}$$

The stated estimation problem can be solved within the output error minimization framework through a least-squares (LS) method. The parameter estimate for the contact resistance $\hat{R}_c$ is given by

$$\hat{R}_c = \left(\sum_{k=0}^N \phi^T(t_k) \phi(t_k) \right)^{-1} \left(\sum_{k=0}^N \phi^T(t_k) z(t_k) \right) \quad (30)$$

whose variance can be computed through

$$\hat{\sigma}_{R_c}^2 = \sigma_{v_2}^2 \left(\sum_{k=0}^N \phi^T(t_k) \phi(t_k) \right)^{-1} \quad (31)$$

where $\sigma_{v_2}^2$ is the residual variance.

4. Simulation studies

During regular operation, the information available from a battery cell is limited to current and voltage. Therefore, before applying the proposed approach using experimental data from a LFP half battery cell, synthetic data coming from a simulator is exploited to validate the proposed methodology. In this way, all the battery cell internal state and parameters are perfectly known.

The model used for simulation is the DFN model briefly described in Section 2.1. The solid-phase diffusion process is implemented through a fifth-order Padé approximation while discretizing all the other PDEs with a central difference method. The system of nonlinear equations is solved using Newton's method at each time step. Table A3 in the Appendix shows the parameters used to set up the simulator. The current profile consists of a series of galvanostatic charge/discharge consecutive steps with three different C-rates: C/5, C/2 and 1C (see upper left plot of Figure 3). For convenience, the charge/discharge cycles that share the same C-rate are called here cycle blocks and each set of charge/discharge cycles within each block is denoted as a period. Therefore, the considered input profile has three cycle blocks made of 3, 5 and

10 periods respectively. The voltage sequence obtained from the simulator (see upper right plot of Figure 3, black solid line) was corrupted with a white noise sequence with variance $\sigma^2 = 1 \text{ mV}^2$.

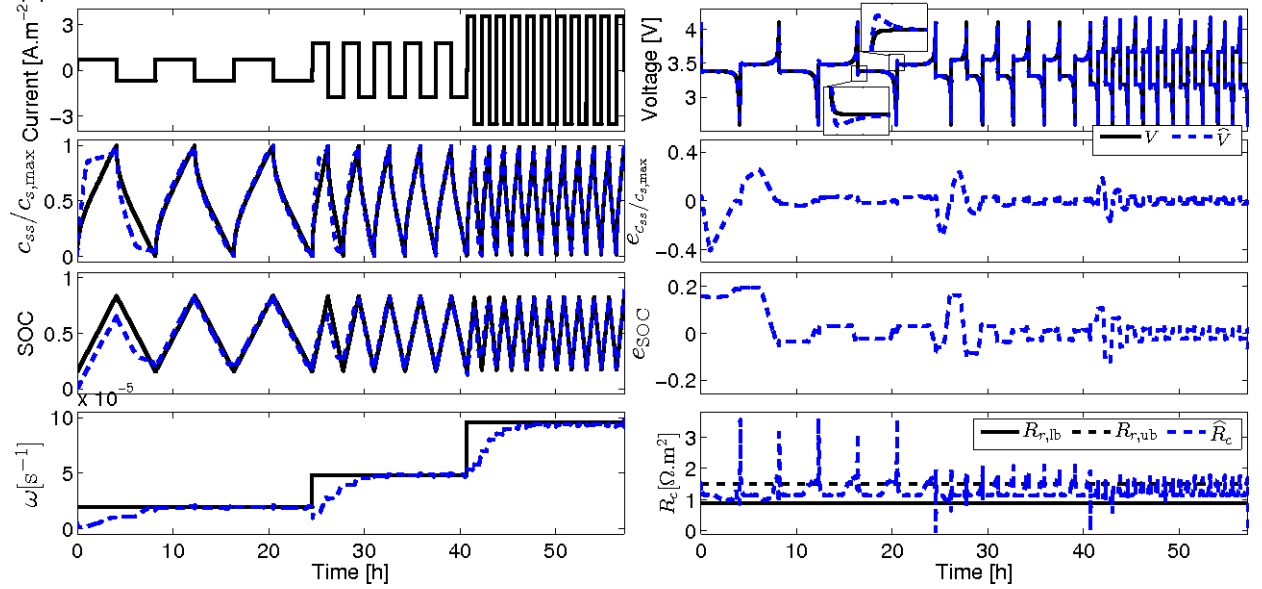


Figure 3: Upper plots: left, series of galvanostatic charge/discharge current profile and right, simulated voltage (noise free) and predicted voltage, middle plots: left, simulated and predicted $c_{ss}/c_{s,max}$ and SOC, and right, $c_{ss}/c_{s,max}$ and SOC estimation error, lower plots: left, fixed and predicted ω , and right, solid and dashed black lines are respectively the lower and upper bound of the contact-resistance distribution R_r , while dashed blue line is the predicted R_c .

The first step of the proposed procedure (EKF in Figure 1) aims to estimate c_{ss} and SOC from current and voltage measurements while accounting for parameter uncertainty. The initial conditions and tuning parameters used for setting the EKF correspond to

$$\begin{aligned}\hat{\mathbf{x}}_0 &= [4.33, 4.33] \times 10, 0.19 \times 10^{-2}, 6.40 \times 10^{-6}, 1.30]^T \\ \text{diag}(\Sigma_0) &= [10^{-10}, 10^{-10}, 10^{-10}, 10^{-17}, 10^{-9}] \\ \text{diag}(\mathcal{Q}) &= [10^{-13}, 10^{-19}, 10^{-21}, 10^{-21}, 10^{-10}]\end{aligned}\tag{32}$$

where $[\hat{c}_{ss,0}, \hat{c}_{so,0}, \widehat{\text{SOC}}_0]$ were obtained by inverting the OCV function taken from [68]. Regarding the parameters, $\omega (= R_s^{-2} D_s)$ was initialized with a value of $D_s = 10^{-17} \text{ m}^2 \cdot \text{s}^{-1}$ within the range reported in the literature, i.e. $[10^{-22}, 10^{-14}] \text{ m}^2 \cdot \text{s}^{-1}$ [34], along with a particle radius of $R_s = 1.25 \times 10^{-6} \text{ m}$ provided by the manufacturer. For its part, R_c was initialized by comparing the voltage drop at the onset of the voltage-capacity curve of the synthetic data with that obtained from the EHM combined with the output Eqs. (9), (10). The measurement noise variance R was set to 10^{-2} mV^2 , which is two orders of magnitude less than the actual noise value, to improve convergence speed.

Some guidelines coming from the physics of the problem were followed in order to set the process noise

variance matrix. First of all, the solid phase concentration state estimates within each charge/discharge cycle have to be smooth; no abrupt changes are allowed. Moreover, the $c_{ss}/c_{s,\max}$ estimate has to cover all its possible range, from 0 to 1, since this ensures that the battery-cell voltage achieves the maximum and minimum cut-off voltages. The transient of these state estimates should vanish in one period. The ω estimate has to slowly vary between cycles and blocks, and to exhibit some convergence trend at the end of each block. The R_c estimate is responsible for the ohmic drop of the voltage within the intermediate composition region, and therefore it has to ensure that the filtered output voltage is as close as possible to the measured voltage.

Figure 3 shows in the upper right plot the predicted voltage coming from the EKF based on the EHM with output Eqs. (9),(10). The middle plots on the left provide the simulated and predicted c_{ss} (normalized as $c_{ss}/c_{s,\max}$) and SOC, while the ones on the right provide the associated estimation error. Finally, the lower plots show the fixed values of the parameters considered within the simulation framework, as well as the time evolution of the considered parameters within the estimation framework. The lower left plot corresponds to ω , whereas the lower right plot corresponds to the bounds (minimum and maximum values) on the contact-resistance distribution R_r (simulator) and R_c (EKF). Black lines correspond to known variables coming from the simulator, while dashed blue lines are the estimated counterparts.

Regarding state estimation, this figure shows an overall good match after transient between simulated and predicted battery internal states, namely $c_{ss}/c_{s,\max}$ and SOC. Most of the transient dynamics of the filter appear in the first period of each cycle block. After this first period per C-rate, the estimation error starts to converge towards zero for both states. During the first periods of C/5, C/2 and 1C, the estimation errors are as large as [0.41, 0.29, 0.18] for $c_{ss}/c_{s,\max}$ and [0.20, 0.17, 0.12] for SOC, respectively, but they remain smaller than 0.09 for both states for subsequent periods (after transient).

Regarding time-varying parameters estimation, $\hat{\omega}$ exhibits a monotonic increase within the considered time horizon and in turn within each cycle block. Within each block, the ω estimate moves towards its true value stated in the simulator ($\omega = R_s^{-2}D_s$, see Table A3), but it requires more periods as the C-rate increases. For its part, two resistive contributions can be ascribed to $\hat{R}_c$. The first one is a constant resistance along the considered time horizon, whereas the second one is a resistance that increases non-linearly (in contrast with the proposition in [66]) in the extreme composition regions at each charge/discharge cycle, i.e. where the nonlinearities prevail. The former and the latter contributions can be associated to a film resistance and the LFP resistive reactant feature, respectively. While the film resistance contribution remains within the R_r bounds (0.835, 1.660) $\Omega.m^2$, the resistive-reactant contribution tends to overstep these bounds by forming

the spikes clearly observed in the figure. These spikes are artifacts that cause a small overpotential in the filtered output (inset plot), but it is corrected within seconds (less than 10 s). These artifacts might be avoided by modifying the tuning parameters of the filter, but it would render a slower convergence.

The c_{ss} estimate coming from the EKF is then used in the second step of the proposed procedure to obtain a refined estimate parameter set $\hat{\theta}_{\text{PHYS}} = [\hat{D}_s, \hat{R}_s]$ (SRIVC in Figure 1) and $\hat{R}_c$ (LS in Figure 1) for each C-rate. The SRIVC estimation was carried out using the available data after removing the transient, i.e. the first 1, 2 and 4 periods for C/5, C/2 and 1C, respectively. The need to account for longer transient periods as the current rate increases comes from the fact that both current and diffusion coefficient are approximately doubled simultaneously.

Table 3 shows the D_s and R_s refined estimates, along with their standard deviation. By comparing these results with the true values (Table A3), it is observed that the diffusion coefficient exhibits relative errors of 15%, 9% and 13%, while the particle radius presents relative errors of 10%, 4% and 9% for C/5, C/2 and 1C, respectively. This error level is acceptable in the considered framework aiming at SOH monitoring as will be justified below. It can be ascribed to the use of a state estimate prediction coming from a third-order model of a single particle to fit a fifth-order system with a particle distribution (the simulator), while relying on a limited noisy data set.

Table 3: Results obtained using the SRIVC method for the estimation of D_s and R_s , and the LS method for the estimation of R_c on each cycle block of simulated data.

C-rate	$\hat{D}_s \times 10^{17}$ [m ² .s ⁻¹]	$\hat{\sigma}_{D_s} \times 10^{19}$	$\hat{R}_s \times 10^6$ [m]	$\hat{\sigma}_{R_s} \times 10^9$	$\hat{R}_c$ [Ω.m ²]	$\hat{\sigma}_{R_c} \times 10^5$
C/5	2.55	1	1.127	3	1.2951	10
C/2	6.83	5	1.201	5	1.26830	4
1C	13.0	14	1.357	8	1.23295	2

In spite of the gap between estimated and true parameters, their standard deviations do not reflect such a difference. This issue can be explained in terms of modeling error. Indeed, the parameter estimation procedure relies on a 3rd order model (both in the Kalman filter and in the SRIVC method), while the simulator relies on a higher order model (5th order model). In order to exhibit that the misfit stems from modeling uncertainties, the fit, defined by the following metric, is evaluated:

$$\text{Fit} = 100 \left(1 - \frac{\| c_{ss} - \tilde{c}_{ss} \|}{\| c_{ss} - \mu_{c_{ss}} \|} \right) \quad (33)$$

where $\| \cdot \|$ denotes the 2-norm, c_{ss} is the EKF estimate of the surface concentration, $\mu_{c_{ss}}$ is the mean of c_{ss}

and $\tilde{c}_{ss}$ is captured from the 3rd order Padé approximation Eq. (17). $\tilde{c}_{ss}$ is evaluated twice, respectively with the estimated parameters $\hat{\theta}$ from Table 3 and with the true parameters θ from Table A3, which results in the values of the fit reported in Table 4. In both cases the fit has the same order of magnitude, demonstrating that modeling uncertainties rather than parameter estimation is the main source of misfit.

Table 4: Fit results obtained from comparing the EKF estimation with the Padé Approximation model using the true (θ) and estimated ($\hat{\theta}$) parameters.

C-rate [h^{-1}] \ Fit [%]	θ	$\hat{\theta}$
C/5	81	86
C/2	79	84
1C	79	72

Finally, although the relative error can be as big as 15% for D_s at C/5, the variance is still small indicating a good model fit. Given the simplicity of the third-order model compared to the target system, the obtained results are satisfactory. Meanwhile, the R_c refined estimates are within the considered contact-resistance range (Table A3).

In order to have a benchmark to compare the simulation results on SOH estimation obtained from the SRIVC method, the widely popular least-squares estimation method is now used to estimate the same parameter set $\theta_{\text{PHYS}} = [D_s, R_s]$. This method has been already used to tackle similar battery parameter identification problems as the one considered here [49, 50, 51]. The parameter estimates obtained from the LS method are denoted as $\hat{D}_s^{\text{LS}}$ and $\hat{R}_s^{\text{LS}}$, which are shown in Table 5 together with their associated standard deviation. In contrast to the SRIVC method, the LS parameter estimates for D_s and R_s exhibit a bigger error with respect to the true values (Table A3). The diffusion coefficient shows relative errors of 62%, 88% and 96% whereas the particle radius incurs in 25%, 40% and 100% of relative error for C/5, C/2 and 1C, respectively. Not only these estimates are more biased than the ones obtained through SRIVC method, but they are also inconsistent since the wrong trend can be seen as the magnitude of the current applied to the battery becomes larger. It is worth recalling that the true value of D_s increases with battery current while R_s is constant throughout the simulation studies, which are trends revealed by the SRIVC method despite some offset in the actual value of the estimated parameters. Indeed, in presence of noise on the output data, the LS method applied to continuous-time systems is known to provide biased estimated parameters [64].

The above results demonstrate that the proposed approach is able to detect parameter changes in the order of 100% with less than 15% of relative error once the transient has vanished. Even though the results focus on parameter changes of a LFP battery cell during regular operation, the considered parameters are directly related with aging processes and their evolution reflects the SOH of most lithium-ion batteries.

Table 5: Results obtained using the LS method for the estimation of D_s and R_s on each cycle block of simulated data.

C-rate	$\hat{D}_s^{\text{LS}} \times 10^{17}$ [m ² .s ⁻¹]	$\hat{\sigma}_{D_s^{\text{LS}}} \times 10^{19}$	$\hat{R}_s^{\text{LS}} \times 10^6$ [m]	$\hat{\sigma}_{R_s^{\text{LS}}} \times 10^9$
C/5	1.15	5	0.933	20
C/2	0.88	4	0.755	20
1C	0.66	1	0.002	0.01

Indeed, magnitude changes of more than 70% and 400% are expected for D_s and R_c , respectively, after 360-500 operating cycles [12, 13, 14, 15]. Therefore the methodology is suitable for SOH monitoring.

Notice that the order of the original EHM is three, which is in line with the model order selected in [66] for the same positive electrode chemistry. Such model order selection results from the frequency response of the model and the frequency content of the input signal, which happens to be driving cycles in [66]. This model size is the same as a third-order ECM with two resistance-capacitance pairs. Moreover, the original EHM is augmented with two unknown parameters and an EKF is designed based on this model, which is also traditionally done with ECMs [77, 78]. Finally, periodic tracking of aging-related parameters prevents the computational burden to explode if compared to continuous tracking. Therefore, the proposed SOH estimation strategy is expected to have a similar computing load as the traditional ECM-based strategies. Next, the accuracy of the proposed approach is tested in the light of experimental data in the next section.

5. Experimental studies

5.1. Setup and testing conditions

The considered positive electrode consists of lithium iron phosphate, LiFePO₄ (LFP), as active material provided by beLife/Prayon (Pholicat FE100). Slurries containing LFP, binder and conducting carbon (Timcal C-nergy Super C65) in weight ratios 75:5:20 respectively were coated on Al acting as current collector. After drying at 60°C overnight, the coated electrodes were weighted, giving access to the mass of active material with good accuracy ($\approx 2 \text{ mg.cm}^{-2}$). These electrodes were then dried under vacuum ($2 \times 10^3 \text{ Pa}$) during 2 h and introduced in a glovebox (M-Braun) under argon atmosphere for half-cell assembly.

To evaluate the electrochemical behavior, the formed electrodes were assembled in CR2032 coin-cells, with 2 Celgard® separators (25 μm thickness and 16 mm diameter each) soaked with 80 μL of electrolyte (lithium hexafluorophosphate, LiPF₆ 1 mol.L⁻¹ in an ethylene carbonate:diethyl carbonate – 1:1 mixture). 15-mm diameter metallic lithium disks were used as reference- and counter-electrode (half-cell design). The half-cells were then tested in galvanostatic cycling mode on a BioLogic VMP3 multichannel potentiostat

at 25°C in a temperature-controlled climate chamber. Galvanostatic charge/discharge was carried out at C-rates of C/5, C/2 and 1C between 2.0 and 4.2 V vs. Li⁺/Li. The equilibrium potential of the material was obtained from the average of charge and discharge curves at a C-rate of C/100. The maximum experimental capacity of the material was 155 mAh.g⁻¹.

5.2. Results and Discussion

A set of current and voltage data was gathered from the above introduced experiment. Both simulated data of the previous section and real data of the current section share the same type of input current profile, but the last cycle block of the experimental data is comprised of five periods instead of ten (see upper left plot of Figure 4). The initial conditions and tuning parameters considered for setting the constrained EKF in the first step of the proposed procedure were the following

$$\begin{aligned}\hat{\mathbf{x}}_0 &= \left[[1.92, 1.92] \times 10, 8.41 \times 10^{-4}, 6.40 \times 10^{-6}, 1.00 \right]^T \\ \text{diag}(\Sigma_0) &= \left[10^{-10}, 10^{-10}, 10^{-10}, 10^{-17}, 10^{-9} \right] \\ \text{diag}(\mathbf{Q}) &= \left[10^{-14}, 10^{-13}, 10^{-12}, 10^{-22}, 10^{-12} \right].\end{aligned}\tag{34}$$

The same initialization procedure used in the simulation framework was followed in the experimental framework. Nevertheless, the OCV function used with experimental data was the one obtained from LFP half battery-cell measurements at C/100. The measured OCV was fitted using a nonlinear least-squares method and its functional form is given by Eq. (A1) in the Appendix. While the variance of the measured voltage was found to be between $(1.1, 14.2) \times 10^{-1}$ mV² according to the considered cycle block, the measurement noise variance was set to a smaller value of 10^{-2} mV² to improve convergence speed. The tuning parameters (Σ_0 and $\mathbf{Q}$) were set following the same procedure as for the simulation.

Figure 4 shows in the upper right plot the measured voltage coming from the LFP half battery-cell, along with the voltage predicted by the filter. The middle plots present the predicted c_{ss} (normalized as $c_{ss}/c_{s,\max}$) on the left, and on the right both the SOC computed through a rightly initialized Coulomb-counting method and the one predicted by the filter. Although the c_{ss} estimate covers the entire range of allowed values (minimum to maximum normalized concentrations of 0 and 1, respectively), the SOC estimate exhibits a smaller operating range (from approximately 0.2 to 0.8). This cyclic behavior can be ascribed to the slow diffusion dynamics of the LFP chemistry, which results in a difference between the lithium concentration at the outer shell and the inner core of the spherical particle. The SOC estimated by the EKF tends to converge to the value reported by the current integration after the transient is overcome.

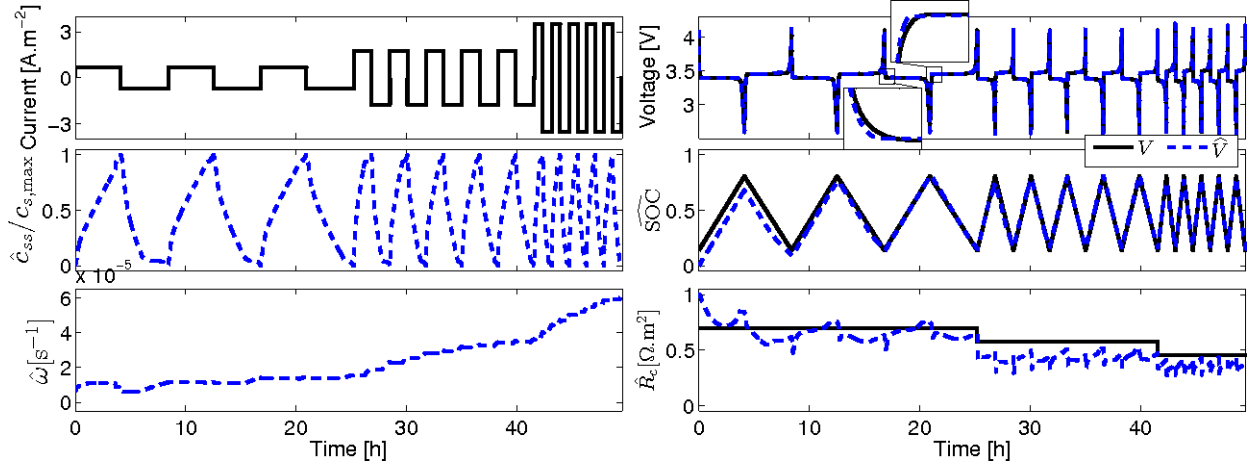


Figure 4: Upper plots: left, series of galvanostatic charge/discharge current profile and right, experimental and predicted voltage, middle plots: left and right, predicted $c_{ss}/c_{s,max}$ and SOC, respectively, with solid black line as Coulomb-counting SOC, lower plots: left and right, predicted ω and R_c , respectively, with solid black line as experimentally determined contact resistance mean $\bar{R}_r$.

The same figure shows the tracking of the uncertain parameters, namely ω and R_c in the lower left and right plot, respectively, whereas the latter plot also portrays the mean value of a contact resistance determined experimentally $\bar{R}_r$. In contrast with other modeling efforts, the EHM combined with the output Eqs. (9), (10) used here does not embed any special feature or mechanism limitation, such as bulk-related rate [21, 22] or resistive-reactant rate limitations [24, 26, 34]. This model relies on few assumptions and gives "freedom" to these parameters, that in turn govern the controversial electrochemical mechanism of LFP electrode operation. The slowly time-varying parameters are expected to adjust their values to the considered data, revealing the underlying electrochemical mechanism instead of imposing it. This is only possible in a state/parameter estimation setting.

From the figure it can be noticed that the ω estimate follows a similar trend as for the simulation framework. Considering a constant particle radius, it can be argued that the diffusion coefficient changes not only with C-rate but even within each cycle block. Nevertheless, simulation showed that ω time-variation within each block is due to the convergent trend of the estimate and not because of an actual parameter variation.

With regard to the other parameter, the contact resistance, there are multiple ways to obtain a reference value from experimental data [79, 80]. Here, this experimental value was computed using the following expression:

$$\bar{R}_r = a_s l \frac{\Delta V}{\Delta I}, \quad (35)$$

where ΔV is the first potential drop at the onset of the discharge voltage curve as soon as a current is

applied, and ΔI is the current magnitude that causes such a voltage change. The R_c estimate coming from the filter underestimates the contact resistance with respect to the reference value $\bar{R}_r$. However, $\bar{R}_r$ might be larger than the real impedance of the battery since it was computed just after the current flip from charge to discharge. Therefore, effects such as concentration gradients might be included in $\bar{R}_r$. Even if $\bar{R}_r$ is an overestimation, its order of magnitude and decreasing trend as the current rate increases coincides with those ones of the $\hat{R}_c$. The same two contributions observed in the simulation framework are exhibited by the R_c estimate, namely the film resistance and the resistive reactant feature. Moreover, this estimate also shows similar spikes as the ones observed in simulation. Nonetheless, these spikes have smaller magnitude than in simulation, which also reduces the fictitious overpotential in the filtered output (inset plot). Again, the spikes are artifacts made up by the filter given the tuning parameters.

The SRIVC method is now used to split $\hat{\omega}$ into its contributions $\hat{D}_s$ and $\hat{R}_s$. The data was pretreated similarly as in simulation, by removing the first 1, 2 and 4 transient periods for C/5, C/2 and 1C, respectively. The obtained refined estimates are shown in Table 6. As expected, $\hat{D}_s$ increases for each cycle block, whereas $\hat{R}_s$ can be considered as constant. Therefore, the $\hat{\omega}$ dynamics can be mainly ascribed to the D_s . This further motivates the notion of a C-rate dependent diffusion coefficient [24] to describe the rate capability of LFP electrodes. Given these results, it seems clear that the electrochemical reaction is facilitated at the bulk diffusion level with higher current densities.

Table 6: Results obtained using the SRIVC method for the estimation of D_s and R_s , and the LS method for the estimation of R_c on each cycle block of experimental data.

C-rate	$\hat{D}_s \times 10^{17}$ [m ² .s ⁻¹]	$\hat{\sigma}_{D_s} \times 10^{19}$	$\hat{R}_s \times 10^6$ [m]	$\hat{\sigma}_{R_s} \times 10^8$	$\hat{R}_c$ [Ω.m ²]	$\hat{\sigma}_{R_c} \times 10^5$
C/5	1.15	4	2.42	1	0.5961	10
C/2	5.09	3	2.19	2	0.38591	4
1C	28.0	20	2.3	10	0.31090	3

Regarding R_s , the particle radius refined estimate is c.a. 2.30×10^{-6} m in contrast with the value of 1.25×10^{-6} m provided by the manufacturer. This discrepancy can be explained in terms of the real infinite-dimensional system and the considered reduced-order model. While LFP electrodes are comprised by a particle-size distribution within a range of c.a. $(0.1, 2.0) \times 10^{-6}$ m, the reduced-order model is based on a single-particle approach. Therefore, the particle radius estimate should be considered as an apparent one describing LFP crystals agglomeration. Considering the radius of agglomerates as the characteristic diffusion length renders larger values of diffusion coefficient [44].

Finally, the contact resistance parameter variation is obtained using the LS method and it is shown in

Table 6. The overall trend of the contact resistance estimate is to decrease its value as the C-rate increases, suggesting that the reaction becomes easier at the surface reaction level besides the bulk diffusion level assessed above.

6. Conclusions

A two-step procedure for capacity/power fade SOH estimation of a LFP half battery-cell has been presented. In the first step, the SOC estimation was performed on-line with the aid of a constrained extended Kalman filter designed from an equivalent-hydraulic model with voltage equation. The simple structure of this model provides some insight of the electrochemical processes occurring within a battery-cell once the experimental data is processed with a suitable estimation procedure. Instead of imposing any mechanism into the model structure, the model is allowed to adapt by accounting for the uncertainty of the main relevant cyclic time-varying parameters that describe the process itself. This allows the convergence of the estimates within the first charge/discharge cycles for each considered C-rate, which is specially convenient for the SOH estimation.

In the second step of the proposed procedure, capacity/power fade SOH indicators were developed based on parameters that are correlated with aging mechanisms. In contrast with the SOC estimation, the SOH estimation neglects the fast variations of the parameters and is performed in a batch setup. Thus, refined estimates of the considered parameters were obtained by using notably instrumental variable techniques suitable for handling whatever initial conditions and noise.

The proposed method was successfully validated on simulation and against experimental data. Precise SOC estimation is obtained after the Kalman filter transient has vanished and the parameters related to SOH are determined with sufficient precision to exhibit the aging phenomena.

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Appendix

This appendix lists functions and parameters that define properties of the considered LFP half battery-cell setup.

Table A1: Functions associated to the model introduced in Section 2. The nomenclature for this table is shown in Table A2

Variable	Function
U^+	$ \begin{aligned} & -0.01284y + 0.2766(1 + \exp(896y))^{-1} \\ & + 0.7715(1 + \exp(113.3(y - 0.002127)))^{-1} \\ & - 0.192(1 + (\exp(-107(y - 0.015))))^{-1} \quad (A1) \\ & + 0.4515(1 + \exp(-108.7((1 - y) - 0.03279)))^{-1} \\ & + 0.8637(1 + \exp(-90.71(1 - y)))^{-1} + 2.312 \end{aligned} $
SOC^+	$\rho SOC(k) + \sigma \quad (A2)$
CSC^+	$\rho CSC(k) + \sigma \quad (A3)$
ρ, σ	$ \rho = \frac{R_s^- L^- a_s^-}{c_{s,\max}^+ R_s^+ L^+ a_s^+}, \quad \sigma = \frac{3n_s^{Li}}{c_{s,\max}^+ R_s^+ L^+ a_s^+} \quad (A4) $
$\eta_s^\pm$	$ \frac{R_g T}{\alpha_0 F} \sinh^{-1} \left(\frac{\mp 1}{2a_s^\pm L^\pm j_{n,0}^\pm} I(k) \right) \quad (A5) $
$j_{n,0}^+$	$k_n^+ c_{s,\max}^+ \sqrt{\bar{c}_e CSC(k) (1 - CSC(k))} \quad (A6)$
$\Delta\phi_e$	$\frac{1}{2\kappa} (l + 2l^s) I(k)$
κ^a	$ \begin{aligned} & 0.0911 + 1.9101\bar{c}_e \times 10^{-3} - 1.052(\bar{c}_e \times 10^{-3})^2 \\ & + 0.1554(\bar{c}_e \times 10^{-3})^3 \quad (A7) \end{aligned} $

^aTaken from [24]

Table A2: Nomenclature for Table A1.

Symbol	Parameter
R_g	Universal gas constant ($=8.31 \text{ J.mol}^{-1}\text{K}^{-1}$)
T	Constant temperature (K)
l	Electrode/separator thickness (m)
A	Cross-sectional battery cell area (m^2)
n^{Li}	Total amount of lithium (mol)
α_0	Apparent transfer coefficient
k_n	Reaction rate constant ($\text{A.m}^{2.5}.\text{mol}^{-1.5}$)
$\bar{c}_e$	Average electrolyte concentration (mol.m^{-3})
κ	Electrolyte phase ionic conductivity (S.m^{-1})
y	Stoichiometry of lithium

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Table A3: List of parameters used for setting up the DFN-based simulator used in Section 4.

Parameter	Symbol	Value
Design adjustable parameters		
Electrode area ^b (m ²)	A	1.13×10^{-4}
Electrode thickness ^b (m)	l	5×10^{-5}
Active material volume fraction ^b	ε_s	0.14
Particle radius ^b (m)	R_s	1.25×10^{-6}
Specific interfacial area ^b (m ⁻¹)	a_s	3.36×10^5
Initial state-of-charge ^a	SOC ₀	15.78×10^{-2}
Initial surface concentration ^a (mol.m ⁻³)	$c_{ss,0}$	93.50×10^2
Average electrolyte concentration ^a (mol.m ⁻³)	$\bar{c}_e$	1×10^3
Separator thickness ^b (m)	l^s	5×10^{-5}
Electrode parameters		
Diffusion coefficient ^d (m ² .s ⁻¹)	$D_s(I(t))$	3×10^{-17}
		7.5×10^{-17}
		15×10^{-17}
Maximum solid concentration ^c (mol.m ⁻³)	$c_{s,max}$	22806
Reaction rate constant ^a (A.m ^{2.5} .mol ^{-1.5})	k_n^+	4×10^{-5}
Exchange current density ^c (A.m ²)	$j_{n,0}^-$	19.0
Apparent transfer coefficient ^a	α_0	0.5
Conductivity ^b (S.m ⁻¹)	σ	6.75
Contact-resistance range (Ω .m ²)	R_r	(0.835, 1.660)
Open-circuit voltage ^c (V)	U^+	[68]

^aAssumed ^bMeasured ^cTaken from [68]^dSet according to the C-rate (C/5, C/2 and 1C, successively)

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