

Lithium-ion Battery Design Optimization based on a Dimensionless Reduced-order Electrochemical Model

Luis. D. Couto^a, Mohammad Charkhgard^a, Berke Karaman^b,
Nathalie Job^b, Michel Kinnaert^a

^a*Department of Control Engineering and System Analysis, Universite libre de Bruxelles, Brussels, B-1050, Belgium*

^b*Department of Chemical Engineering - Nanomaterials, Catalysis, Electrochemistry - Universite de Liege (B6a), Liege, B-4000, Belgium*

Abstract

Model-based optimal cell design is an efficient approach to maximize the energy density of lithium-ion batteries. This maximization problem is solved in this paper for a lithium iron phosphate (LFP) cell. We consider half-cells as opposed to full-cells typically considered, which are intermediate steps during battery manufacturing for electrode characterization and they are gaining popularity by themselves as lithium-metal batteries. First, a dimensionless reduced-order electrochemical model is used instead of high-order models. Second, sensitivity equations are analyzed to determine the ranking of the design parameters according to their effect on the energy density, which is often lacking in other contributions. Three parameters, namely electrode thickness, LFP particle radius and electrode cross sectional area, are shown to have the most influential effects. Third, a novel adaptive particle swarm optimization with a specific stopping criterion is used for LIB design optimization. The proposed optimization framework is tested in simulation on a LFP half-cell battery. The results show that the design optimization yields $250 \text{ Wh}\cdot\text{kg}^{-1}$ for an LFP electrode of $310 \mu\text{m}$ thickness, 10 nm particle radius and $2\cdot 10^{-4} \text{ m}^2$ cross-sectional area, which is an increase of energy density of $61 \text{ Wh}\cdot\text{kg}^{-1}$ with respect to an initial design proposed in the literature.

Keywords:

Lithium-ion battery, lithium iron phosphate, reduced-order electrochemical model, optimal cell design, sensitivity analysis, adaptive particle swarm optimization.

1. Introduction

Modern society is surrounded by lithium-ion batteries (LIBs), from small-scale applications like mobile phones and laptops to large-scale applications like electric vehicles and microgrids [1, 2, 3]. The choice of this technology as energy storage device comes from its high energy and power density, relatively safe operation and low self-discharge [4]. However, batteries are typically over-engineered and therefore underused, which is due to limited optimization when it comes to designing a battery along with conservative operation bounds imposed by manufacturers. Battery cells can be optimized in order to maximize either energy or power depending on their intended use. As a simple rule of thumb, for instance, thicker electrode batteries exhibit bigger capacity while thinner electrode batteries resemble more to capacitors and therefore are more suitable for power delivery [5]. Most practical attempts to optimize battery design rely on experimental trial-and-error, meaning that a vast amount of resources and person-hours need to be devoted for this purpose. A cost-effective alternative approach is to rely on battery models for optimization.

Battery modeling is a broad topic that involves different kinds of modeling frameworks in accordance with the target application of such models. Battery models range from data-driven models [6, 7] to equivalent circuit models [8, 9] as well as physical models [10, 11], where the first model type lacks physical interpretability and requires a large amount of data for its identification while the opposite is true for the last model type. In this work we focus on physical models, since we want to optimize the performance of the battery and look at the associated electrochemical variables. Probably the most popular high-fidelity electrochemical model is the so-called Doyle-Fuller-Newman (DFN) or pseudo-two-dimensional (P2D) model [12, 13]. This model has been widely used by the battery scientific community as a digital twin benchmark for physical understanding of electrochemical processes [14, 15], validation of battery management systems (BMSs) [4, 16] as well as battery optimal design [5, 17, 18, 19]. In the last category, the DFN model has been extended with thermal [20] and mechanical dynamics [21] for optimization. These models benefit from a high level of physical description but they suffer from high computational requirements. Alternatively, simpler battery models based on equivalent circuits have been used mainly in BMSs [8]. They are com-

putationally cheap at the expense of unclear relationships between physical properties and circuit equivalences. Therefore, these simple models cannot be used in battery design optimization. A third modeling framework that is midway in terms of complexity is reduced-order electrochemical models. These models can be derived from the DFN model under suitable assumptions of a given electrochemical process dominating over others. That is the case of the single-particle model (SPM) [22, 23], for instance, which considers that the battery operation is limited by active-phase diffusion while neglecting electrolyte dynamics. Other examples include the SPM with thermal [24] and electrolyte (SPMe) [25, 26] dynamics, electrode-average model [27], kinetic battery model [28], reaction-zone model [29], just to name a few. Although physically relevant and computationally efficient, these models have been scarcely used for battery design in favor of the highly descriptive DFN model.

Besides the underlying model, few cost functions have been considered when it comes to battery design optimization. The standard objective is to maximize gravimetric/volumetric energy and/or power density [20, 17, 21], whereas some authors have included constraints such as power requirements [5, 18, 30] or electrode stresses [21], or have also aimed at minimizing degradation [31]. Note that in the latter case, the optimization over hundreds/thousands of cycles could preclude the use of full-order models. Typical design parameters include active material volume fraction, electrode/separator thickness [17] and particle size [21, 31], while other less frequent ones are separator porosity [18, 30], C-rate [20], conductivity [31] and diffusivity [5]. Some of these works prioritized a given subset of possible design parameters during optimization, which was motivated by sensitivity analyses like analysis of variance [18, 20], analysis of means [30] and adjoint sensitivity analysis [21]. Once both the objective function subject to given constraints and the design variables have been defined, then the battery design optimization problems have been solved by different methods such as building cost surfaces [20], nonlinear [21] and sequential quadratic programming [5], sequential approximate optimization [18], direct search method [17] and genetic algorithms [30, 31]. The results obtained in these works are highly dependent on the considered battery chemistries, which includes graphite/lithium iron phosphate (LFP) [20], graphite/lithium manganese oxide (LMO) [5, 17, 18, 30, 31] and lithium (Li)/LMO (i.e. half-cell) [21]. Note that the focus of these optimization efforts has been mainly placed on full-cells including positive and negative electrode design parameters [5, 18, 30],

while single electrode optimization either within a cell [20] or in half-cell configuration [21] is more limited.

The general goal of this work is to optimize the design of a half-cell battery based on a dimensionless reduced-order electrochemical model. The optimization objective is to maximize the gravimetric energy density. The selected design parameters that could be potentially manipulated during battery manufacturing include active material volume fraction, electrode/separator thickness, particle radius and cross-sectional area. The main contributions of this work departing from other studies are the following.

Contributions:

- A dimensionless reduced-order electrochemical model is used. A general modeling framework is first introduced, followed by a particularized one suitable for our needs.
- Analytical sensitivities are derived in order to determine the relative importance of each parameter in the cost function. The resulting most sensitive parameters are retained for optimization.
- An adaptive particle swarm optimization (APSO) with a specific stopping criterion is used as an optimization method. This optimization method belongs to the gradient-free kind of approaches, which are able to avoid getting stuck in local minima.

The motivation behind the research choices associated to these contributions are the following. First, the selected model is able to capture both active- and electrolyte-phase limitations during battery regular operation while keeping a low computational footprint. The dimensionless form of the model allows to have comparable (normalized) quantities as well as to put in evidence relevant group of parameters that define the occurrence/limitation of electrochemical processes. Secondly, analytical sensitivities exhibit less computational load compared to other methods. Finally, a different option to APSO could be genetic algorithms, but they take more time for searching the parameter space, while APSO strikes a good balance between computational burden and efficiency [32, 33].

Regarding the considered battery, a half-cell configuration case is studied, which serves as an intermediate characterization step towards full-cell design and the potential development of lithium-metal batteries. This allows us to focus on the optimization of a single electrode. The LFP electrode chemistry is selected as case study since it is stable, safe to operate, has low cost and it

is environmentally benign [34, 35]. Given these advantages, this chemistry is currently considered by many automakers (e.g. Tesla, Ford Motor or Volkswagen) for their electric vehicles [36]. The downside is their low power and energy density compared to other battery chemistries (e.g. lithium cobalt oxide) due to notably the low voltage plateau, which implies the need of more LFP cells in a pack (also more weight) to provide given energy density and power demand. These batteries are therefore more suitable as standalone energy storage systems for renewable energies. However, the optimization design of a battery is always beneficial from the size and economical perspectives. Here we address the issue of energy density maximization of an LFP electrode in half-cell configuration.

This paper is structured as follows. The electrochemical model considered in this work is presented in Section 2. In Section 3, the battery optimal design is formulated and the tool to solve the optimization problem is also described. Results and associated discussion are presented in Section 4, which is followed by the conclusions in Section 5.

2. Electrochemical modeling

One of the most accurate representations of the electrochemical phenomena occurring in a LIB is the DFN model [15], whose main equations are briefly reported in Table A.1, Appendix A. The interested reader is referred to [15] for more details. The DFN model is based on the porous electrode and concentrated solution theories [12, 15], and it resorts to partial differential equations (PDEs) that are algebraically coupled. The main electrochemical equations and associated state variables are:

- conservation of mass (equation (A.4)) and charge (equation (A.5)) in active phase, describing active-phase lithium concentration $c_a^\pm(x, r, t)$ and electric potential $\phi_a^\pm(x, t)$, respectively;
- conservation of mass (equation (A.6)) and charge (equation (A.7)) in electrolyte phase, describing electrolyte-phase lithium concentration $c_e^{\pm s}(x, t)$ and electric potential $\phi_e^{\pm s}(x, t)$, respectively;
- Butler-Volmer kinetics for solid-electrolyte interphase (equation (A.8)), involving ionic currents $i_e^\pm(x, t)$ and pore-wall molar fluxes $j_n^\pm(x, t)$;
- material balance (equation (A.9)), since moles of lithium n_{Li} are preserved,

where subscripts a and e denote active and electrolyte phases, respectively, while $+$, s and $-$ superscripts represent positive electrode, separator and negative electrode regions, respectively.

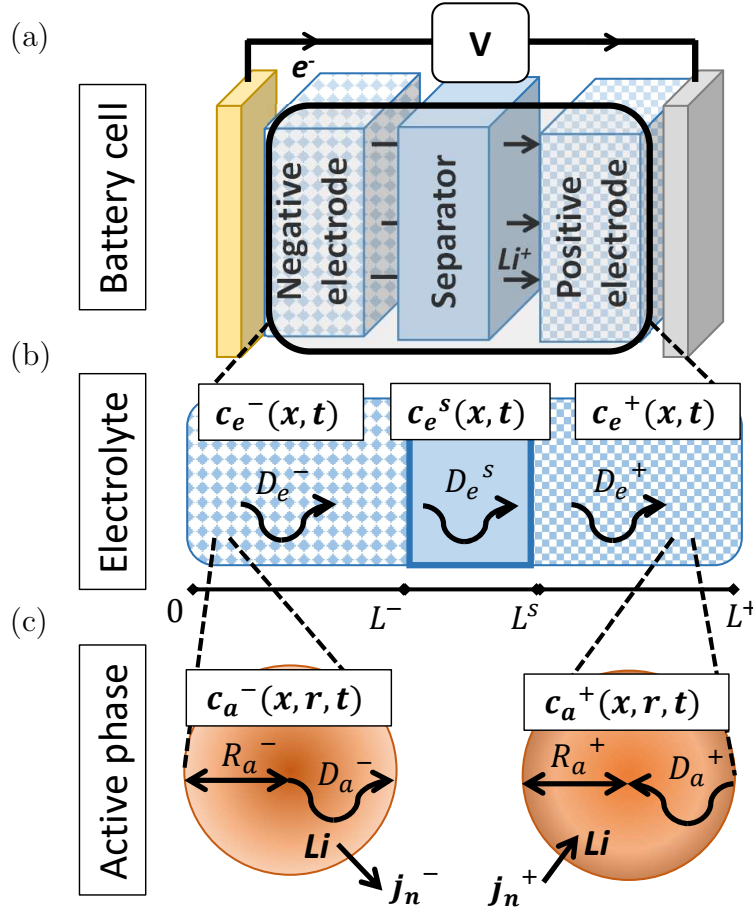


Figure 1: Discharging process of a (full-cell) LIB. a) Longitudinal view of the battery cell with three regions: negative electrode, separator and positive electrode, and two phases: active phase and electrolyte phase. b) An electrolyte-phase representation, and c) an active-phase representation of the spherical particles.

The DFN model mathematically captures the electrochemical processes taking place in a battery (i.e. full-cell). Figure 1 shows a longitudinal view of these processes during battery discharge. When discharging (see Fig. 1a), there is an electrostatic potential difference between the electrodes that drives

the electrochemical phenomena. The lithium contained within spherical-like particles in the active-phase negative electrode diffuses from the bulk to the surface of the particles, where a de-intercalation process occurs (see Fig. 1c). The lithium, now in the form of ions in the electrolyte phase, moves from the negative electrode to the positive electrode by crossing the separator (see Fig. 1b). Simultaneously, the electrons released in the negative electrode after the reaction are forced out of the battery due to the electronically insulated nature of the separator. After performing electrical work, the electrons come back to the battery through the positive electrode. In there, an intercalation process happens at the active-phase spherical particles followed by a diffusion process of lithium from the surface to the bulk of the particle (see Fig. 1c). All these phenomena are encoded in the DFN model, which is considered as a high-fidelity battery model and has been widely used by researchers. However, this model is too complex and computationally intensive for control purposes, which has motivated the derivation of reduced-order electrochemical models. A first attempt to do so is by considering the single spherical particle approximation of the electrode active-phase, the so-called single-particle model (SPM) [37]. This model is valid under low current loads [38, 37], which limits its applicability. In an effort to alleviate this issue, electrolyte dynamics have been added to the SPM giving rise to the SPMe [25, 39]. Indeed, the DFN model has been compared with the SPM and the SPMe in simulation for the same parameter set and it was shown that while the SPM has a reasonable accuracy up to 1C, the SPMe can keep its validity up to c.a. 5C [25]. The present work explores the use of the SPMe for optimal cell design, since it is considered as a physically-meaningful yet relatively simple model that is able to capture a large part of important electrochemical dynamics in LIBs. This simpler modeling framework allows to perform fast simulations of the battery, which contributes to a short computational time during battery optimization and would also be beneficial in case of accounting for battery aging where thousands of cycles are expected.

2.1. Single-particle model with electrolyte dynamics (SPMe)

The main assumption for deriving the SPMe from the DFN model is that the lithium concentration in active phase $c_a^\pm(x, r, t)$, exchange current density $i_0^\pm(x, t)$ and pore-wall molar flux $j_n(x, t)$ are independent of the spatial coordinate x , i.e.

$$c_a^\pm(x, r, t) \approx c_a^\pm(r, t), \quad i_0^\pm(x, t) \approx i_0^\pm(t), \quad j_n^\pm(x, t) \approx j_n^\pm(t).$$

This assumption basically approximates the reaction throughout the cell thickness as uniform, under which the pore-wall molar flux $j_n^\pm(t)$ can be expressed as proportional to the applied current $i(t)$ given by

$$j_n^\pm(t) = \frac{i(t)}{a_a^\pm F L^\pm A} \quad (1)$$

where a_a is the specific interfacial area, F is Faraday's constant, L is the electrode thickness and A is the cross-sectional area. The resulting active-phase and electrolyte-phase diffusion PDEs along with the terminal voltage in the SPMe are reported in Table 1, while all the equation variables and parameters are defined in Table A.2 and Table A.3 in Appendix A.

To reduce model complexity, the nonlinear PDEs associated with the electrolyte dynamics are simplified by assuming that the electrolyte-phase diffusion coefficient is independent of the electrolyte concentration $D_e^{\pm s}(c_e^{\pm s}) \approx D_e^{\pm s}$.

2.2. SPMe for half-cell modeling - Diffusion processes

The optimal cell design is performed for a half-cell configuration (see Fig. 2) in order to focus on one electrode, so the equations in Table 1 for the full-cell model are decomposed into "negative" and "positive" half-cell models. By "positive" we denote the half-cell made of lithium iron phosphate (LiFePO_4 a.k.a. LFP) giving rise to Li/LFP where Li replaces the negative electrode in Fig. 1, see Fig. 2a. On the other hand, by "negative" we denote the half-cell taking the form of graphite/Li, since graphite is typically a negative electrode in full-cell batteries and the associated lithium counter-electrode corresponds to a lithium trap, whatever its physical nature might be. In other words, the term "Li" replaces the positive electrode in the full-cell of Fig. 1, see Fig. 2b. So, we will use the terms positive and negative half-cells (without quotes) in this context from now on, with the understanding that lithium metal is always the negative electrode in half-cells from the physical viewpoint. Under these considerations, the half-cell model retains the equations of active-phase lithium diffusion (2) from the full-cell model, whereas for the electrolyte-phase the PDEs (3) of full-cell model are also kept but the boundary conditions need to be modified to account for the lithium foil counter-electrode. The boundary condition of a graphite/Li half-cell at the separator-lithium foil interface ($x = L$ in Fig. 2b) and the one for the Li/LFP half-cell at the lithium foil-separator interface

Table 1: SPMe model equations for full-cell configuration[†].

Physical Process	Equation
Active-phase diffusion	$\begin{cases} \frac{\partial c_a^\pm}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(D_a^\pm r^2 \frac{\partial c_a^\pm}{\partial r} \right) \\ \frac{\partial c_a^\pm}{\partial r}(x, r, t) \Big _{r=0} = 0 \\ \frac{\partial c_a^\pm}{\partial r}(x, r, t) \Big _{r=R_a^\pm} = -\frac{1}{D_a^\pm} j_n^\pm(x, t) \end{cases} \quad (2)$ with $c_{a,0}^\pm(r) = c_a^\pm(r, 0)$ and $c_{as}^\pm(t) = c_a^\pm(R_a^\pm, t)$
Electrolyte-phase diffusion ^{a,b}	$\begin{cases} \frac{\partial c_e^{\pm s}}{\partial t} = \frac{\partial}{\partial x} \frac{D_{e,\text{eff}}^{\pm s}}{\varepsilon_e^{\pm s}} \frac{\partial c_e^{\pm s}}{\partial x} + \frac{a_a^\pm(1-t_c^0)}{\varepsilon_e^\pm} j_n^\pm \\ \frac{\partial c_e^-}{\partial x}(x, t) \Big _{x=0} = \frac{\partial c_e^+}{\partial x}(x, t) \Big _{x=L} = 0 \\ D_{e,\text{eff}}^- \frac{\partial c_e^-}{\partial x}(x, t) \Big _{x=L^-} = D_{e,\text{eff}}^s \frac{\partial c_e^s}{\partial x}(x, t) \Big _{x=L^-} \\ D_{e,\text{eff}}^s \frac{\partial c_e^s}{\partial x}(x, t) \Big _{x=L^-s} = D_{e,\text{eff}}^+ \frac{\partial c_e^+}{\partial x}(x, t) \Big _{x=L^-s} \\ c_e^-(x, t) \Big _{x=L^-} = c_e^s(x, t) \Big _{x=L^-} \\ c_e^s(x, t) \Big _{x=L^-s} = c_e^+(x, t) \Big _{x=L^-s} \end{cases} \quad (3)$ with $c_{e,0}(x) = c_e^-(x, 0)$, $c_e^0(t) = c_e^-(0, t)$ and $c_e^L(t) = c_e^+(L, t)$
Voltage ^{a,c}	$\begin{cases} v = \eta^+(c_{as}^+, c_e^L, j_n^\pm) - \eta^-(c_{as}^-, c_e^0, j_n^\pm) - F R_f^- j_n^- \\ \quad + U^+(c_{as}^+) - U^-(c_{as}^-) + \Delta\phi_e(c_e^{\{0,L\}}, j_n^\pm) \\ \eta_s^\pm(c_{as}^\pm, c_e^{\{0,L\}}, j_n^\pm) = \frac{R_g T_{\text{ref}}}{\alpha_0 F} \sinh^{-1} \left(\frac{\mp F j_n^\pm}{2i_0^\pm(c_{as}^\pm, c_e^{\{0,L\}})} \right), \\ i_0^\pm(c_{as}^\pm, c_e^{\{0,L\}}) = k_n^\pm \sqrt{c_e^{\{0,L\}} c_{as}^\pm (c_{s,\text{max}}^\pm - c_{as}^\pm)} \\ \Delta\phi_e(c_e^{\{0,L\}}, j_n^\pm) = \frac{L^+ + 2L^s + L^-}{2\kappa_{e,\text{eff}}} i(t) + k_D (\ln(c_e^L) - \ln(c_e^0)) \\ k_D = \frac{2R_g T_{\text{ref}}}{F} (1 - t_c^0) \left(1 + \frac{d \ln f_{c/a}}{d \ln c_e} \right) \end{cases} \quad (4)$

[†]Spatial/temporal dependency of state variables not explicitly indicated for compactness.

^a $\Gamma_{e,\text{eff}}(c_e) = \Gamma_e(c_e) \varepsilon_e^b$ where $\Gamma = \{D, \kappa\}$.

^bFor the separator region, $j_n = 0$ (it is not defined).

^cAssuming $\alpha_0 = 0.5$ [12].

($x = 0$ in Fig. 2a) are given by [14]

$$D_e^s \frac{\partial c_e^s}{\partial x}(\{L, 0\}, t) = -\frac{1 - t_c^0}{FA} i(t) \quad (5)$$

where t_c^0 is the transference number [40].

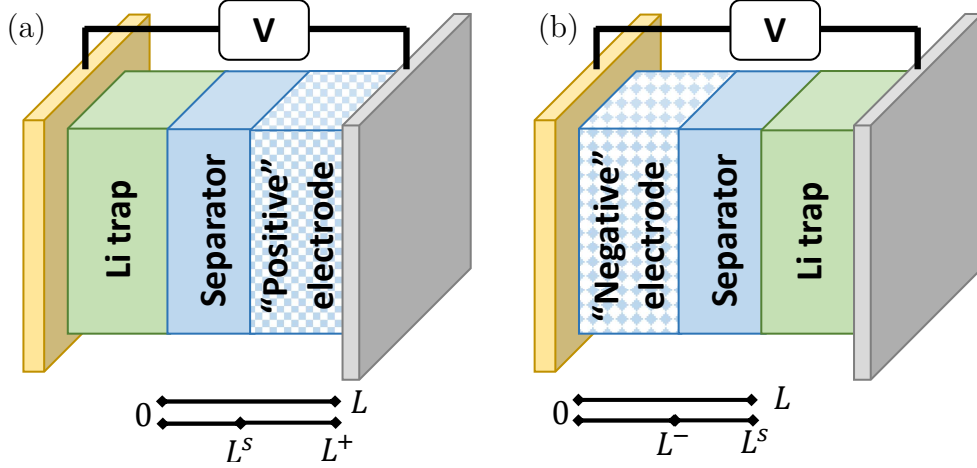


Figure 2: Representation of half-cell configurations for a LIB, where a) is the "positive" half-cell and b) is the "negative" half-cell according to typical positive/negative electrodes in full-cell settings. Note that this notation is used here with the understanding that the Li trap is always the negative electrode in a real experimental half-cell, where all materials (for both positive and negative electrodes in the full cell) are characterized versus a lithium foil (which is always the negative electrode).

Remark 1. *We drop the superscripts $\pm$ in the following to alleviate notation, implicitly considering that the definitions can be associated to either positive or negative half-cell models. Note that in this case, the half-cell model only requires the description of one porous electrode provided that the lithium falls in an infinite reservoir at the Li trap counter-electrode.*

The presented PDE half-cell model is computationally implemented through finite differences as described next.

2.3. Finite difference discretization of half-cell SPMe - Diffusion processes

We discretize in space the PDE-form of the SPMe in Table 1 by resorting to central finite differences for in-domain equations and second-order one-sided finite differences for boundary conditions [25, 41]. The resulting finite difference model for the active-phase equation (2) of a half-cell is given by

$$\frac{d\mathbf{c}_a}{dt}(t) = A_{ca}\mathbf{c}_a(t) + B_{ca}i(t), \quad \mathbf{c}_{a,0} = \mathbf{c}_a(0), \quad (6)$$

$$\mathbf{c}_{as}(t) = C_{ca}\mathbf{c}_a(t) + D_{ca}i(t), \quad (7)$$

where $A_{ca} \in \mathbb{R}^{n_r \times n_r}$, $B_{ca} \in \mathbb{R}^{n_r \times 1}$, $C_{ca} \in \mathbb{R}^{1 \times n_r}$ and $D_{ca} \in \mathbb{R}$ are the state and input matrices of the state equation (6) and output equation (7), respectively, n_r is the number of points used to divide the single spherical particle in the electrode along the particle radius r , the active-phase diffusion state vector is

$$\mathbf{c}_a(t) = [c_{a,1}(t) \ \cdots \ c_{a,n_r}(t)]^\top \in \mathbb{R}^{n_r},$$

and $\mathbf{c}_{as}(t) \in \mathbb{R}$ in (7) denotes the lithium concentration at the surface of the particle.

For the electrolyte-phase equation (3), the resulting finite difference model of a half-cell is given by

$$\frac{d\mathbf{c}_e}{dt}(t) = \frac{D_{e,\text{eff}}}{\varepsilon_e} (A_{ce}\mathbf{c}_e(t) + B_{ce,2}i(t)) + B_{ce}i(t), \quad \mathbf{c}_{e,0} = \mathbf{c}_e(0), \quad (8)$$

$$\mathbf{c}_{e,\text{bc}}(t) = C_{ce}\mathbf{c}_e(t) + D_{ce}i(t). \quad (9)$$

where $A_{ce} \in \mathbb{R}^{n_x \times n_x}$, $B_{ce} \in \mathbb{R}^{n_x \times 1}$, $C_{ce} \in \mathbb{R}^{1 \times n_x}$ and $D_{ce} \in \mathbb{R}$ are the state and input matrices up to constant $D_{e,\text{eff}}/\varepsilon_e$ of the state equation (8) and output equation (9), respectively, while $B_{ce,2} \in \mathbb{R}^{n_x \times 1}$ is the matrix associated to the modified boundary conditions (5) due to half-cell configuration, and n_x is the number of points used to divide the electrolyte phase along the battery thickness x with $n_x = n_x^a + n_x^s$ where n_x^a is associated to the active phase electrode and n_x^s is associated to the separator. The electrolyte-phase lithium concentration state vector is

$$\mathbf{c}_e(t) = [(\mathbf{c}_e^s(t))^\top \ (\mathbf{c}_e^+(t))^\top]^\top \in \mathbb{R}^{n_x} \text{ or } \mathbf{c}_e(t) = [(\mathbf{c}_e^-(t))^\top \ (\mathbf{c}_e^s(t))^\top]^\top \in \mathbb{R}^{n_x},$$

for positive and negative half-cells, respectively, where $\mathbf{c}_e^+(t)$, $\mathbf{c}_e^s(t)$ and $\mathbf{c}_e^-(t)$ represent electrolyte concentration in negative electrode, separator and positive electrode regions, respectively. The output vector in (9) gathers the concentrations at the different half-cell boundaries given by

$$\mathbf{c}_{e,\text{bc}}(t) = [c_{e,\text{bc},1}(t) \ c_{e,\text{bc},2}(t) \ c_{e,\text{bc},3}(t)]^\top \in \mathbb{R}^{3 \times 1},$$

where $c_{e,\text{bc},1}(t)$, $c_{e,\text{bc},2}(t)$ and $c_{e,\text{bc},3}(t)$ in negative half-cells correspond to current collector/negative electrode ($c_e^0(t)$), negative electrode/separator ($c_e^{L-}(t)$) and separator/Li interfaces ($c_e^L(t)$), respectively, and in positive half-cells to Li/separator ($c_e^0(t)$), separator/positive electrode ($c_e^{Ls}(t)$) and positive electrode/current collector interfaces ($c_e^L(t)$), respectively.

2.4. Finite difference discretization of half-cell SPMe - Output voltage

Once the diffusion process dynamics have been discretized, the last step is to incorporate an appropriate output equation. The output voltage for the negative half-cell takes the form

$$\begin{aligned} \mathbf{v}(t) = & U_{Li} - U^-(\mathbf{c}_{as}^-) + \eta_{Li}(i) - \eta^-(\mathbf{c}_{as}^-, \mathbf{c}_e^0, i) - \frac{R_f^-}{a_a^- L^- A} i(t) \\ & + \frac{L^- + 2L^s}{2\kappa_{e,\text{eff}} A} i(t) + k_D(\ln(\mathbf{c}_e^L(t)) - \ln(\mathbf{c}_e^0(t))), \end{aligned} \quad (10)$$

while the one for the positive half-cell is given by

$$\begin{aligned} \mathbf{v}(t) = & U^+(\mathbf{c}_{as}^+) - U_{Li} + \eta^+(\mathbf{c}_{as}^+, \mathbf{c}_e^L, i) - \eta_{Li}(i) \\ & + \frac{2L^s + L^+}{2\kappa_{e,\text{eff}} A} i(t) + k_D(\ln(\mathbf{c}_e^L(t)) - \ln(\mathbf{c}_e^0(t))), \end{aligned} \quad (11)$$

where U_{Li} is the equilibrium potential for lithium metal, $U^\pm(c_{as}^\pm)$ are the same as in (4) in Table 1, η_{Li} is given by [35]

$$\eta_{Li}(i) = \frac{R_g T_{\text{ref}}}{\alpha_0 F} \sinh^{-1} \left(\frac{i(t)}{2i_0^{Li}} \right) \quad (12)$$

with i_0^{Li} as the exchange current density for lithium metal [35], $\eta^\pm(c_{as}^\pm, c_e^{\{0,L\}}, i)$ is equivalent to $\eta^\pm(c_{as}^\pm, c_e^{\{0,L\}}, j_n^\pm)$ in (4) where $j_n^\pm(t)$ is written in terms of $i(t)$ using (1), and $\Delta\phi_e$ in (4) is explicitly written out in (10),(11) depending on the considered half-cell. In equations (10) and (11), the voltage variable $\mathbf{v} \in \mathbb{R}$, but we decided to keep the bold notation to differentiate it from the output voltage counterpart of the PDE model (4) in Table 1. The same holds in the derivations below.

In the above equations, model variables like voltage, lithium concentration, and the physical parameters all have different dimensions and variation ranges, which makes hard the comparison and ranking of their impact on the energy density [42]. To alleviate these issues, we made dimensionless the finite difference model equations (6)-(11) as shown next.

2.5. Dimensionless finite difference half-cell SPMe (a.k.a. dSPMe)

In order to transform the finite difference model (6)-(11) into a dimensionless form, we normalize the dimensional variables with respect to a given

maximum/nominal value that characterizes such variables. The considered dimensionless quantities are shown in Table 2 and are denoted by a superscript $*$. In the table, $c_{a,\max}$ is the maximum lithium concentration, i_{typ} is an arbitrary current magnitude that can be set to the equivalent of 1C for instance, t_{ref} is an arbitrary reference time, $c_{e,\text{nom}}$ is a nominal value for the electrolyte concentration and β_T is the so-called thermal voltage to be defined below.

Table 2: Dimensionless variables.

Definition	Symbol	Dimensionless variable
Solid-phase concentration	c_a^*	$c_a/c_{a,\max}$
Current	i^*	i/i_{typ}
Time	t^*	t/t_{ref}
Electrolyte-phase conc.	c_e^*	$c_e/c_{e,\text{nom}}$
Voltage	v^*	v/β_T

By grouping appropriately some of the model parameters, time constants and scaling variables start to emerge which allow to render the model dimensionless. Those grouped parameters are shown in Table 3. Notably, the time constants characterizing diffusion processes are $\tau_d^\pm$ for the active phase and $\tau_{e,d}^{\pm s}$ for the electrolyte phase. Moreover, time scales for (dis)charge processes are $\tau_c^\pm$ for the active phase and $\tau_{e,c}^{\pm s}$ for electrolyte phase, whereas time scales for electrochemical reactions are $\tau_k^\pm$. Other scaling variables include the thermal voltage β_T , a typical ohmic drop in electrolyte $\beta_{\kappa i}$ and an ohmic drop due to a resistive film deposited at the electrode surface (e.g. solid-electrolyte interphase) β_{Ri} .

Table 3: Scaling variables and time constants of the dSPMe.

Definition	Symbol	Expression
Solid-phase (dis)charge	$\tau_c^\pm$	$F c_{a,\max}^\pm L_a^\pm \varepsilon_a^\pm A / i_{\text{typ}}$
Solid-phase diffusion	$\tau_d^\pm$	$(R_a^\pm)^2 / D_a^\pm$
Electrolyte-phase (dis)charge	$\tau_{e,c}^{\pm s}$	$F c_{e,\text{nom}}^\pm L_e^{\pm s} \varepsilon_e^{\pm s} A / ((1 - t_c^0) i_{\text{typ}})$
Electrolyte-phase diffusion	$\tau_{e,d}^{\pm s}$	$(L_e^{\pm s})^2 / D_e^{\pm s}$
Reaction	$\tau_k^{\pm s}$	$R_a^\pm / (k_n^\pm \sqrt{c_{e,\text{nom}}})$
Thermal voltage	β_T	$R_g T_{\text{ref}} / (\alpha_0 F)$
Ohmic drop in electrolyte	$\beta_{\kappa i}$	$(L^+ + 2L^s) / (2\kappa_{e,\text{eff}} A) i_{\text{typ}}$
Ohmic drop in electrode film	β_{Ri}	$R_f^\pm / (a_a^\pm L_a^\pm A) i_{\text{typ}}$

With the definitions from Table 2 to Table 3, the following dimensionless model for the active-phase diffusion process is obtained

$$\frac{d\mathbf{c}_a^*}{dt^*}(t^*) = A_{ca}^* \mathbf{c}_a^*(t^*) + B_{ca}^* i^*(t^*), \quad \mathbf{c}_{a,0}^* = \mathbf{c}_a^*(0), \quad (13)$$

$$\mathbf{c}_{as}^*(t^*) = C_{ca} \mathbf{c}_a^*(t^*) + D_{ca}^* i^*(t^*), \quad (14)$$

where A_{ca}^* , B_{ca}^* and D_{ca}^* are equivalent to A_{ca} , B_{ca} and D_{ca} in (6),(7), respectively, but where the matrices with superscript $*$ notably include the reference time t_{ref} .

Similarly, the dimensionless model for the electrolyte-phase diffusion process is given as follows

$$\frac{d\mathbf{c}_e^*}{dt^*}(t^*) = A_{ce}^* \mathbf{c}_e^*(t^*) + B_{ce,2}^* i^*(t^*) + B_{ce}^* i^*(t^*), \quad \mathbf{c}_{e,0}^* = \mathbf{c}_e^*(0), \quad (15)$$

$$\mathbf{c}_{e,bc}^*(t^*) = C_{ce} \mathbf{c}_e^*(t^*) + D_{ce}^* i^*(t^*), \quad (16)$$

where A_{ce}^* , B_{ce}^* , D_{ce}^* and $B_{ce,2}^*$ are equivalent to A_{ce} , B_{ce} , D_{ce} and $B_{ce,2}$ in (8),(9), respectively, but where the matrices with superscript $*$ notably include the reference time t_{ref} .

Finally, the dimensionless version of the voltage equation is given by

$$\begin{aligned} \mathbf{v}^*(t^*) = & U_{Li}^* - U^{-,*}(\mathbf{c}_{as}^{-,*}) + \eta_{Li}^* - \eta^{-,*}(\mathbf{c}_{as}^{-,*}, \mathbf{c}_e^{0,*}, i) - \frac{\beta_{Ri}}{\beta_T} i^*(t^*) \\ & + \frac{\beta_{\kappa i}}{\beta_T} i^*(t^*) + k_D(\ln(c_{e,\text{nom}} \mathbf{c}_e^{L,*}(t^*)) - \ln(c_{e,\text{nom}} \mathbf{c}_e^{0,*}(t^*))), \end{aligned} \quad (17)$$

for the negative half-cell and

$$\begin{aligned} \mathbf{v}^*(t^*) = & U^{+,*}(\mathbf{c}_{as}^{+,*}) - U_{Li}^* + \eta^{+,*}(\mathbf{c}_{as}^{+,*}, \mathbf{c}_e^{L,*}, i^*) - \eta_{Li}^* \\ & + \frac{\beta_{\kappa i}}{\beta_T} i^*(t^*) + k_D(\ln(c_{e,\text{nom}} \mathbf{c}_e^{L,*}(t^*)) - \ln(c_{e,\text{nom}} \mathbf{c}_e^{0,*}(t^*))), \end{aligned} \quad (18)$$

for the positive half-cell, where $U^{\pm,*} = U^{\pm}/\beta_T$, $\eta_{Li}^* = \eta_{Li}/\beta_T$, and $\eta^{\pm,*} = \eta^{\pm}/\beta_T$ is written in terms of dimensionless variables as

$$\eta^{\pm,*}(c_{as}^{\pm,*}, c_e^{\{0,L\},*}, i^*) = \sinh^{-1} \left(\mp \frac{\tau_k^{\pm}}{6\tau_c^{\pm} \sqrt{c_e^{\{0,L\},*}(t^*) c_{as}^{\pm,*}(t^*) (1 - c_{as}^{\pm,*}(t^*))}} i^*(t^*) \right). \quad (19)$$

Equations (13)-(18) represent the dimensionless equivalent form of the finite difference model (6)-(11). All the variables in this model are dimensionless, which facilitates comparison.

The dimensionless model (13)-(18) can be written in general form as

$$\frac{d\mathbf{x}^*}{dt^*}(t^*) = f(\mathbf{x}^*(t^*), i^*(t^*), \boldsymbol{\theta}) \quad (20)$$

$$\mathbf{v}^*(t^*) = h(\mathbf{x}^*(t^*), i^*(t^*), \boldsymbol{\theta}) \quad (21)$$

where $\boldsymbol{\theta}$ is a parameter vector of interest that parameterizes the model and is defined below, and the state vector is given by $\mathbf{x}^*(t) = [(\mathbf{c}_a^*(t))^\top \ (\mathbf{c}_e^*(t))^\top]^\top$.

3. Optimal design of half-cell lithium-ion batteries

This section is devoted to the formulation of the optimization problem to be solved, i.e. the maximization of the half-cell energy density via the manipulation of some battery design parameters. We first define the objective or cost function to be used. Then, we present the sensitivity equations associated to the cost function with respect to the design parameters to be optimized. Finally, we define the optimization problem to be solved, followed by the optimization algorithm used to find the solution.

3.1. Objective function formulation

In this work we are interested in maximizing the battery specific (gravimetric) energy density. The objective function then takes the form

$$E = \frac{1}{m_{\text{cell}}} \int_0^{t_f} \mathbf{v}(t) i(t) dt \quad (22)$$

where the mass of the cell is defined as $m_{\text{cell}} = m^\pm + m^s + m^{cc}$ which accounts for active materials in electrodes ($m^\pm$), separator (m^s) and current collectors (m^{cc}). The electrode mass is given by $m^\pm = AL^\pm(\rho_e \varepsilon_e^\pm + \rho_a^\pm \varepsilon_a^\pm + \rho_f \varepsilon_f^\pm)$, the separator mass by $m^s = AL^s \rho_e \varepsilon_e^s$ and the current collector mass by $m^{cc} = AL^{cc} \rho_{cc}$, where ρ denotes the density with the same subscript conventions used before together with f and cc standing for filler and current collector, respectively. The time t_f refers to the complete discharging time of the half-cell. The energy density E in (22) is determined from the galvanostatic discharge of a fully charged cell down to a minimum cut-off voltage.

This cost function (22) depends on a set of design parameters that can be adjusted during LIB manufacturing. Some of these physical parameters include: electrode/separator thickness $L^{\pm s}$, particles radius $R_a^{\pm}$, active material volume fraction $\varepsilon_a^{\pm}$ [5, 17, 18, 20, 21, 30, 31] and cross-sectional area A . The parameter vector associated to such parameters in a half-cell model is defined as

$$\boldsymbol{\theta} = [L^s \ L^{\pm} \ R_a^{\pm} \ \varepsilon_a^{\pm} \ A]^{\top} \in \mathbb{R}^{n_{\theta}} \quad (23)$$

for $n_{\theta} = 5$ in this case.

Coming back to the energy density, the form in (22) is dimensional. The dimensionless form of this equation is given by

$$\begin{aligned} E &= \int_0^{t_{\text{ref}} t_f^*} \frac{\beta_T \mathbf{v}^*(t_{\text{ref}} t^*) i_{\text{typ}} i^*(t_{\text{ref}} t^*) t_{\text{ref}}}{\bar{m} m_{\text{cell}}^*} dt^* \\ &= \frac{\beta_T i_{\text{typ}} t_{\text{ref}}}{\bar{m}} \int_0^{t_f^*} \frac{\mathbf{v}^*(t^*) i^*(t^*)}{m_{\text{cell}}^*} dt^*, \end{aligned} \quad (24)$$

for $m_{\text{cell}}^* = m_{\text{cell}}/\bar{m}$ as the dimensionless mass of the cell. We can then write the dimensionless cost function in terms of the dimensional one as

$$E^* = E \left/ \frac{\beta_T i_{\text{typ}} t_{\text{ref}}}{\bar{m}} \right. \Rightarrow E^* = \int_0^{t_f^*} \frac{\mathbf{v}^*(t^*) i^*(t^*)}{m_{\text{cell}}^*} dt^*. \quad (25)$$

As it can be seen, the dimensionless energy density E^* requires the appropriate scaling of (22) with the variables defined in Table (2) and Table (3). Moreover, the coefficient $\beta_T i_{\text{typ}} t_{\text{ref}}/\bar{m}$ is a constant and therefore the dimensionless energy density is just a scaled version of the dimensional one.

Now that the objective function and the design parameters have been specified, we proceed to evaluate the impact of such parameters on the energy density through a sensitivity analysis.

3.2. Sensitivity analysis

The sensitivity of the dimensionless specific energy density E^* with respect to the design parameter vector $\boldsymbol{\theta}$ is denoted as $S_{E^*} = \partial E^*/\partial \boldsymbol{\theta}$ and it is computed from (25) taking the form

$$S_{E^*} = \int_0^{t_f^*} \left(S_{v^*}(t^*) \frac{i^*(t^*)}{m_{\text{cell}}^*} - \frac{1}{(m_{\text{cell}}^*)^2} S_{m^*} i^*(t^*) v^*(t^*) \right) dt^* \quad (26)$$

where the voltage and mass sensitivities are respectively given by

$$S_{v^*}(t^*) = \frac{\partial \mathbf{v}^*}{\partial \boldsymbol{\theta}}(t^*), \quad S_{m^*} = \frac{\partial m^*}{\partial \boldsymbol{\theta}}. \quad (27)$$

While S_{m^*} is a constant row vector, $S_{v^*}(t)$ is time-varying, which can be computed by taking the partial derivatives of (20),(21) with respect to the parameter vector $\boldsymbol{\theta}$. By doing so, the following analytical sensitivity equations are obtained

$$\frac{d}{dt}S_{x^*}(t^*) = \nabla_{x^*}f(\mathbf{x}^*, i^*, \boldsymbol{\theta})S_{x^*}(t^*) + \frac{\partial}{\partial \boldsymbol{\theta}}f(\mathbf{x}^*, i^*, \boldsymbol{\theta}), \quad S_{x^*,0} = S_{x^*}(0), \quad (28)$$

$$S_{v^*}(t^*) = \nabla_{x^*}h(\mathbf{x}^*, i^*, \boldsymbol{\theta})S_{x^*}(t^*) + \frac{\partial}{\partial \boldsymbol{\theta}}h(\mathbf{x}^*, i^*, \boldsymbol{\theta}), \quad (29)$$

with $S_{x^*}(t^*) = \partial \mathbf{x}^*(t^*)/\partial \boldsymbol{\theta}$. The sensitivity system (28),(29) is solved in time and its solution is evaluated in the sensitivity of the cost (26). Therefore, the ranking of the design parameters θ follows directly from (26).

3.3. Optimization problem for half-cell battery design

The problem of maximizing the specific energy density (25) by manipulating the battery design parameters (23) can be formalized in the following way

$$\max_{\boldsymbol{\theta}} \quad E^* = \frac{1}{m_{\text{cell}}^*} \int_0^{t_f} \mathbf{v}^*(t^*) i^*(t^*) dt^* \quad (30)$$

$$\text{s.t. equations (20), (21),} \quad (31)$$

$$i^*(t^*) = H(t^*), \quad (32)$$

$$v^*(0) = v_{\text{max}}^*, \quad (33)$$

$$v^*(t_f) = v_{\text{min}}^*, \quad (34)$$

$$\boldsymbol{\theta}_{\text{min}} \preceq \boldsymbol{\theta} \preceq \boldsymbol{\theta}_{\text{max}}, \quad (35)$$

where $H(t^*)$ is the Heaviside step function and the operator $\preceq$ represents component-wise inequality between vector elements and the solution space is constrained with upper and lower bounds for the considered parameters. The evaluation of the energy density is done by imposing the equivalent of a normalized 1C discharge current (32) starting from a fully charged state (33) of the half-cell battery and finishing when it is empty (34). Notice that in this case, the battery power is intrinsically accounted for by imposing an applied

current that is equivalent to 1C rate since the battery is discharged in 1 h, and therefore maximizing the power $P = E/t_f$ is equivalent to maximizing the energy E for the same discharging time t_f .

The optimization problem (30)-(35) is solved here by resorting to an adaptive particle swarm optimization with a specific stopping criterion, which is explained next.

3.4. Particle swarm optimization algorithm

The particle swarm optimization (PSO) algorithm works based on social behavior simulation, in contrast with population-based evolutionary algorithms like genetic algorithms. In social simulations, each member of the group represents a so-called problem solution i.e. a position, and it has an associated velocity. The members are known as particles that explore the search space.

First, a population of desired number of particles is generated, which does not change during exploration. Then, the position and velocity of each particle are adjusted based on its experience i.e. track of its associated objective value and the best experiment (best objective value) of companion particles in the population. The goal of the particles is to go towards the best location of the search space. Each particle is associated with a value of objective function which should be devised based on problem targets. In this paper, the objective function is the dimensionless specific energy density $F(\cdot) = E^*$, as defined in (25). At each iteration, the velocity and new position of the particles considered given the dimensionless model, design physical parameter vector $\boldsymbol{\theta}$ and associated dimensionless energy density are updated by the following laws [33, 43]

$$\mathbf{v}_i^{n+1} = \omega_i^n \mathbf{v}_i^n + c_1 r_1 (\boldsymbol{\theta}_{p,i}^n - \boldsymbol{\theta}_i^n) + c_2 r_2 (\boldsymbol{\theta}_g^n - \boldsymbol{\theta}_i^n), \quad (36)$$

$$\boldsymbol{\theta}_i^{n+1} = \boldsymbol{\theta}_i^n + \mathbf{v}_i^{n+1}, \quad (37)$$

where $\boldsymbol{\theta}_i^n$ and $\mathbf{v}_i^n$ are the position and velocity of the i -th particle in step n , respectively, $\boldsymbol{\theta}_{p,i}^n$ and $\boldsymbol{\theta}_g^n$ represent the best position of i -th particle in the n_θ -dimensional parameter space and all particles up to step n , respectively, which should be stored at each iteration, ω_i^n is inertia weight of the i -th particle in step n , c_1 and c_2 are acceleration coefficients whose sum should not be more than 4, and they are known as cognitive and social parameters, respectively. Moreover, r_1 and r_2 are two random variables in the range of $[0,1]$. In this work, an adaptive version of the PSO (i.e. APSO) is used based

on which ω_i^n should be adjusted at each step. To do so, at first, the adjacency index (AI) should be calculated as follows [33]

$$AI_i^n = \frac{E^*(\boldsymbol{\theta}_{p,i}^n) - F_{KN}}{E^*(\boldsymbol{\theta}_g^n) - F_{KN}} - 1, \quad (38)$$

where, $E^*(\boldsymbol{\theta}_g^n)$ and $E^*(\boldsymbol{\theta}_{p,i}^n)$ represent the maximum dimensionless energy density of all particles and particle i , respectively, up to step n , and F_{KN} is the maximum value of the objective function. Because the exact maximum value of the dimensionless energy density cannot be determined in advance, after some simulation trials of the model and the calculation of the dimensionless energy density, F_{KN} is set to five times of the maximum calculated dimensionless energy density value. The latter choice was based on multiple simulation runs. With the value of adjacency index AI_i^n at hand, ω_i^n can be determined as follows:

$$\omega_i^n = \frac{1}{1 + \exp(-(\alpha AI_i^n)^{-1})}, \quad (39)$$

where α is a positive coefficient in the range of $(0,1]$. Based on (39), ω_i^n changes in the range of $[0.5,1)$. The other important aspect in PSO implementation is the stopping criterion, i.e. the specific condition based on which the algorithm stops searching. In this paper, a new stopping criterion is implemented, which yields a fast convergence rate and suitable accuracy. It is based on the normalized swarm radius defined as follows

$$R_{\text{norm}}^\theta(n) = \frac{\|\Theta^n\| - \|\Theta^{n-N}\|}{\|\Theta^n\|} = 1 - \frac{\|\Theta^{n-N}\|}{\|\Theta^n\|}, \Theta^n = [\boldsymbol{\theta}_1^n \ \boldsymbol{\theta}_2^n \ \cdots \ \boldsymbol{\theta}_{n_s}^n]^\top, \quad (40)$$

$$\|\Theta^n\| = \sigma_{\max}(\Theta^n),$$

where n_s is the number of particles in the population, and N represents the previous N -th sample from which the normalization is calculated. As it can be seen from (40), the norm of the swarm, i.e. the matrix of all particles in each iteration Θ^n , is the maximum singular value of the population matrix. For determining the stopping condition, R_{norm}^θ should have a deviation close to zero for a number of steps, namely

$$\max(R_{\text{norm}}^\theta(n - N : n)) - \min(R_{\text{norm}}^\theta(n - N : n)) \leq \epsilon, \quad (41)$$

$$R_{\text{norm}}^\theta(n - N : n) = (R_{\text{norm}}^\theta(n - N) \ R_{\text{norm}}^\theta(n - N + 1) \ \cdots \ R_{\text{norm}}^\theta(n)). \quad (42)$$

Table 4: Summary of the APSO algorithm.

Initialization:
Determination of search space boundaries $\theta_{\min} \preceq \theta \preceq \theta_{\max}$
Random initialization of n_s -dimensional particle population
While stopping criterion (41),(42) not fulfilled, do:
For each particle, $i = 1, \dots, n_s$
Restrict the particles to the search space: $\theta_{\min} \preceq \theta \preceq \theta_{\max}$
Set the best position:
If $(F(\theta_i^n) \geq F(\theta_{p,i}^n))$ then $\theta_{p,i}^n = \theta_i^n$
Set the global best position:
If $(F(\theta_{p,i}^n) \geq F(\theta_{g,i}^n))$ then $\theta_{g,i}^n = \theta_{p,i}^n$
Update the velocity and position using equation (36),(37)
End

The APSO algorithm implemented in this work is reported in Table 4 and the obtained results are discussed in the next section.

For restricting the particles to the search space as indicated in Table 4, if any element of the particles goes beyond the determined upper and lower bounds, it is equated to the associated upper or lower bound, respectively. This is illustrated in the flowchart of the algorithm in Fig. 3, for instance, which is presented for the sake of clarity.

4. Results and discussion

We now test the proposed optimization framework in the light of simulation studies, where the optimal design of a half-cell LIB is considered with LFP as positive electrode material. This is without loss of generality, since the framework can also consider a half-cell LIB with a negative electrode material. The dSPMe model discretized with finite differences is used. The model parameters come from the literature and are reported in Table A.3 in the Appendix A. The interested reader is referred to the Supplementary material for insights on the validity of the model choice coming from the model identification using LFP half-cell impedance data.

Figure 4 shows the results obtained from a sensitivity analysis of the voltage with respect to each design parameter. It is interesting to see the dynamic behavior of these sensitivities as they are the main contributor for the overall cost function sensitivity given in (25). The equivalent of a 1C

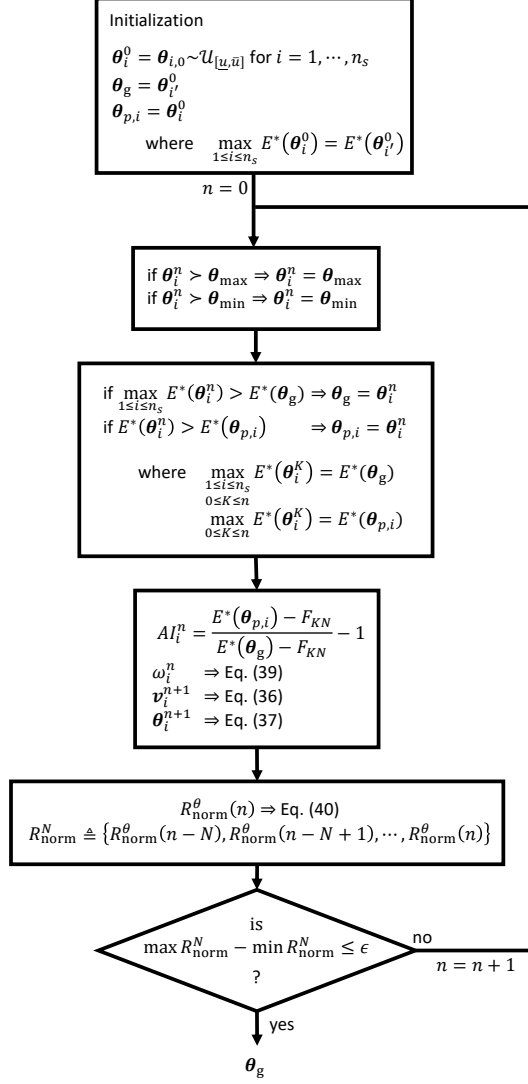


Figure 3: Flowchart of the APSO algorithm.

input current profile used to discharge the considered LFP half-cell is depicted in Fig. 4a. The plots are built with respect to SoC for convenience, where the SoC is defined in terms of electrochemical variables for an SPM-type of model as[44, 25]

$$\text{SoC}(t) = \frac{3}{c_{a,\max} R_a^3} \int_0^{R_a} r^2 c_a(r, t) dr. \quad (43)$$

Note that the SoC goes from 0 to 1 for a discharging LFP half-cell given that the LFP electrode is actually being charged or lithiated, i.e. the concentration of lithium in the electrode increases upon discharge of the half-cell. The sensitivities are shown in Fig. 4b to Fig. 4f for separator/electrode thickness, particle radius, volume fraction and cross-sectional area, respectively. Most sensitivities exhibit a flat region in the mid-SoC range (from 10% to 90%) which follows from the typically flat OCV characteristics of LFP electrodes. Moreover, the separator thickness has the lowest sensitivity magnitude among the considered design parameters, whereas electrode thickness, particle radius and area are the most sensitive parameters. On the other hand, the voltage is sensitive to different parameters in different SoC ranges. For instance, separator thickness is important at low SoC whereas electrode thickness, particle radius and area are more relevant at high SoC.

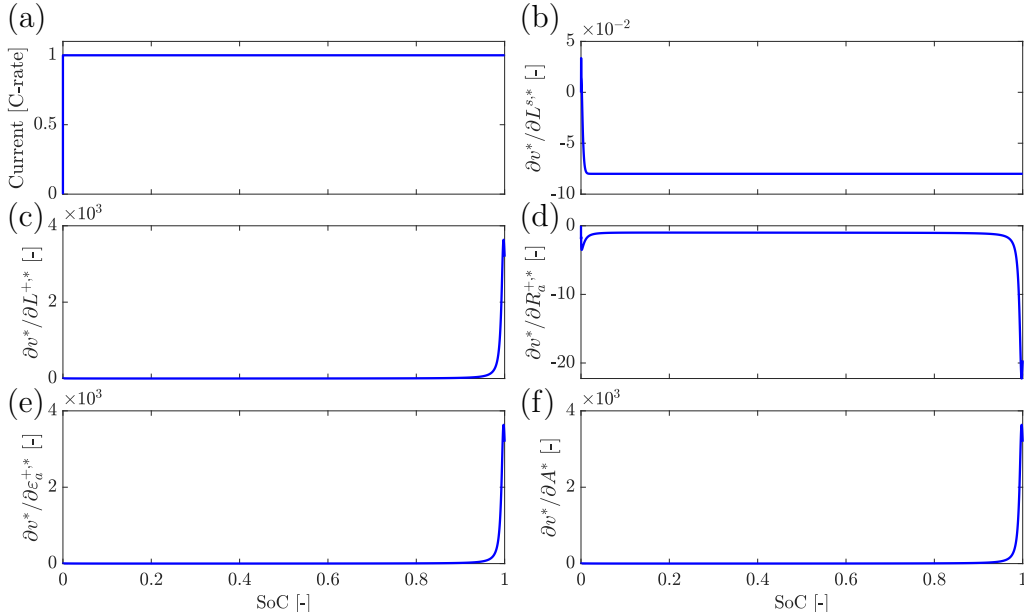


Figure 4: Sensitivity trajectories of the voltage with respect to the design parameters. Plot a) shows the discharge current, whereas plots b) to f) portray the voltage sensitivity with respect to separator/electrode thickness, particle radius, volume fraction and area, respectively.

When the full cost function, and not only the voltage contribution, is considered in the sensitivity analysis, the sensitivity of the cost with respect to the different parameters can be ranked in accordance to the impact of each design parameter. This parameter ranking is shown in Fig. 5. The

most sensitive parameter is particle radius followed by separator thickness, electrode thickness and area, whereas the least sensitive parameter is the active material volume fraction. The reason why the latter parameter with relatively large voltage sensitivity (see Fig. 2e) became the least sensitive parameter for the dimensional cost is because the nominal parameter ε_a^+ is the largest among the others by at least three orders of magnitude. Since transforming the dimensionless cost into a dimensional one involves the division by the nominal parameter following from $\theta^* = \theta/\bar{\theta}$, smaller nominal parameters increase the value of the sensitivity cost.

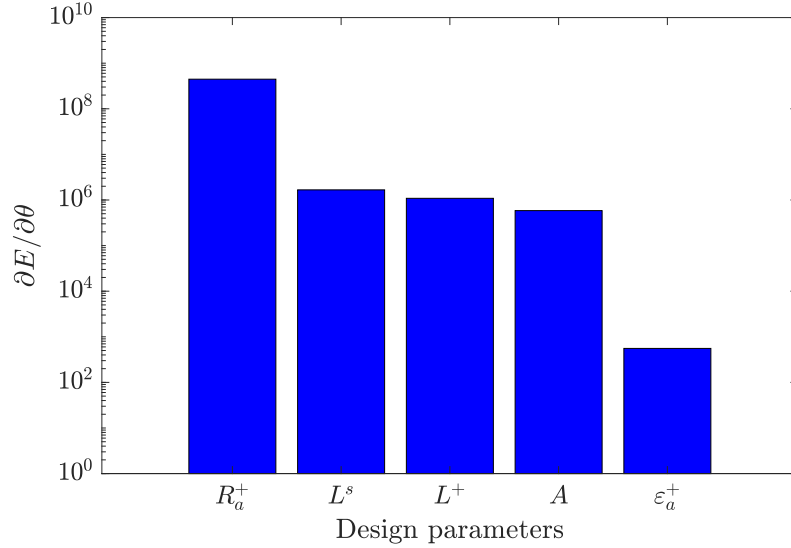


Figure 5: Ranking of the sensitivity of the cost function for each design parameter.

From a sensitivity analysis, three design parameters were found to have the most influential effects on the energy density E , namely electrode thickness L^+ , particle radius R_a^+ and cell cross-sectional area A . The remaining possible design parameters include active material volume fraction and separator thickness, but the former has a small sensitivity and it can be difficult to manipulate during manufacturing while the latter cannot be arbitrarily reduced since too low thickness would lead to internal short-circuits. Therefore, L^+ , R_a^+ and A are taken as the design parameters for maximizing cell specific (gravimetric) energy density.

Let us first explore the shape of the cost surface for two of the design parameters. Figure 6 shows the surface of the specific energy density over the space of L^+ and R_a^+ within the range of $[10, 350] \mu\text{m}$ and $[10, 300] \text{nm}$,

respectively, and for an area of $A = 2.43 \cdot 10^{-4} \text{ m}^2$. As it can be seen, the maximum energy density is around $249 \text{ Wh}\cdot\text{kg}^{-1}$ at the point of $L^+ = 305 \text{ }\mu\text{m}$ and $R_a^+ = 10 \text{ nm}$ approximately. The optimal solution indicating the minimum radius is expected, since smaller particle sizes imply shorter diffusion paths for the lithium in the active phase (less diffusion limitations) and therefore larger energy density.

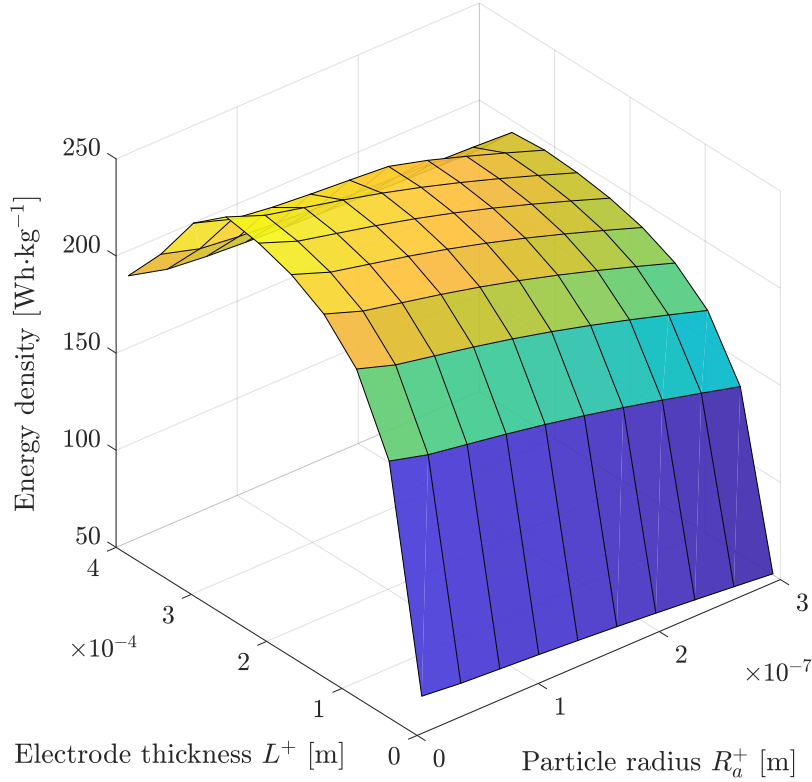


Figure 6: Surface of specific energy density over two of the selected design parameters.

In order to validate the APSO algorithm, we compare the attained maximum with the one obtained from the exhaustive search method in the case of two design parameters L^+ and R_a^+ of the cost surface in Fig. 6. The optimization problem (30)-(35) was solved using the APSO algorithm (see Table 4) in a 2.6 GHz 6-core laptop with 64GB of RAM using Matlab R2021b[®]. The resulting optimal values are $250 \text{ Wh}\cdot\text{kg}^{-1}$ at the point $L^+ = 307 \text{ }\mu\text{m}$ and $R_a^+ = 10 \text{ nm}$, which are in accordance with the depicted surface. The optimization time to solve this problem was c.a. 137 s. We then enlarge the

design parameter space to three parameters as stated above, namely L^+ , R_a^+ and A , and investigate the resulting optimal design. Now the maximum specific energy density is $250 \text{ Wh}\cdot\text{kg}^{-1}$ with optimal parameters as given in Table 5, and optimization time of c.a. 133 s. It can be seen how the optimal design features a thicker electrode together with a smaller spherical particle, and the area is also reduced. It is worth highlighting that while both the particle size and the area hit their lower bounds, the electrode thickness does not go up to its upper bound. This is likely to be the result of the trade-off between having a thicker electrode that provides more half-cell capacity at the expense of increasing the associated weight as discussed next.

Table 5: Results of the optimization based on APSO algorithm.

Design parameters	Lower bound	Upper bound	Initial design	Optimal design
$L^+ [\mu\text{m}]$	10	390	70	309
$R_a^+ [\text{nm}]$	10	300	36.5	10
$A [\text{m}^2]$	$1.8\cdot 10^{-4}$	$3.0\cdot 10^{-4}$	$2.4\cdot 10^{-4}$	$1.8\cdot 10^{-4}$
$E [\text{Wh}\cdot\text{kg}^{-1}]$			188	250

Figure 7 presents the discharge profile of current (Fig. 7a) and voltage (Fig. 7b) for the initial design (id) and optimal design (od) of the battery as reported in Table 5. The signals are reported in appropriate dimensions. The discharge current for both designs corresponded to 1C discharge, i.e. the current required to discharge the half-cell battery from maximum to minimum cut-off voltage in one hour, as it can be corroborated by the voltage profile. However, since the design parameters change, the current magnitude equivalent to the 1C current also changes. In this case, the optimal design corresponds to a smaller area and a thicker electrode compared to the initial design. Since the current corresponding to 1C is larger for the optimal design (see Fig. 7a), this means that the half-cell is effectively bigger which translates in the electrode thickness overweighting the area reduction. In terms of voltage (Fig. 7b), both designs depict a similar response. Regarding mass, the optimal design is heavier than the initial one as illustrated by Fig. 7c. However, the overall computation of specific energy density involves the integral of the product between current and voltage, and the division by the cell mass (see (30)-(35)). This results in the optimal design having $61 \text{ Wh}\cdot\text{kg}^{-1}$ more specific energy than the initial one, i.e. from $188 \text{ Wh}\cdot\text{kg}^{-1}$ to $250 \text{ Wh}\cdot\text{kg}^{-1}$.

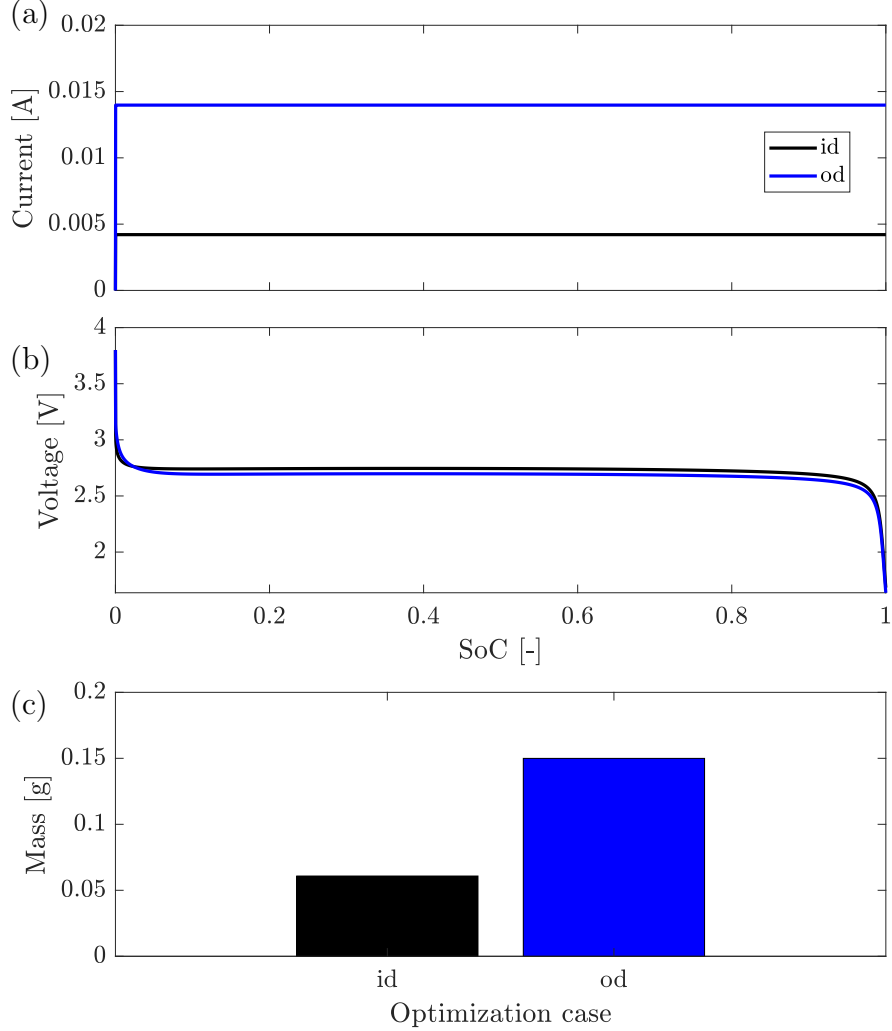


Figure 7: Discharge profile with respect to the SoC for the initial (id) and optimal (od) LFP half-cell design presented in Table 5. The plots show a) the discharge current, b) voltage response and c) resulting cell masses.

Just to have more physical insight into the optimal cell design, we look now at the internal states of the simulated LFP half-cell for both initial and optimal cases. Figure 8 shows the obtained results in terms of temporal evolution of normalized concentrations, with the active phase in Fig. 8a, the electrolyte phase in the separator in Fig. 8b and the electrolyte-phase in the positive electrode in Fig. 8c. Instead of showing the entire concentration profile for a given spatial discretization, we show the upper (ub) and lower

(lb) bounds for these concentrations. These bounds are obtained at given boundary positions within the half-cell (e.g. surface of the spherical particle or positive electrode-current collector interface), and enclose all the other internal concentration dynamics for a constant discharge profile as the one used here. Note that, in the optimal design, the utilization of the half-cell is higher since the concentration values are closer to 1 (Fig. 8a). Moreover, since the effectively applied equivalent to 1C current is larger for the optimal design than for the initial one, the electrolyte concentrations in both separator and positive electrode regions exhibit a larger gradient, as reflected by the lower and upper bounds in Fig. 8b and Fig. 8c. These aspects contribute to a larger overpotential of the cell, which explains why the voltage plateau of the optimal design is slightly lower than the one of the initial design (see Fig. 7b).

Another way to look at these results is by inspecting the spatial distribution of the internal state of the half-cell at given time instants. Figure 9 shows the radial distribution $r^* = r/R_a$ of the normalized active-phase concentration c_a^* every 10 min (Fig. 9a), followed by the electrolyte-phase profiles along the x dimension at the separator $c_e^{s,*}$ (Fig. 9b, where $x^{s,*} = x^s/L^s$) and the positive electrode regions $c_e^{+,*}$ every 10 s (Fig. 9c, where $x^{+,*} = x^+/L^+$). For simplicity, we define x dimensions in the separator x^s and positive electrode regions x^+ . The time differences reflect the speed of each process, where electrolyte dynamics tend to be faster than active-phase dynamics [39]. In Fig. 9a it can be seen how the initial concentration is uniform and close to the minimum value. As the time elapses, the concentration profile increases towards the maximum value of one, and it tends to bend with the maximum concentration in the $r^* = 1$ boundary and the minimum one in the $r^* = 0$ boundary (see Fig. 9a.1), representing the surface and the center of the spherical particle respectively. Note that the optimal design incurs in a smaller concentration gradient compared to the initial design, which is due to the smaller particle sizes suggested by the optimization algorithm. A similar trend can be found when analyzing the electrolyte profiles (see Fig. 9b and Fig. 9c) as the discharge of the electrode proceeds, where the concentration in the electrolyte starts from a uniform position around 1 and is displaced to higher values. Given that the effective current is larger for the optimal design, the resulting electrolyte concentration gradients are larger compared to the initial design. Moreover, a thicker electrode also contributed to have larger concentration gradients in the positive electrode region. The maximum electrolyte concentrations appear in the $x^{s,*} = 0$ boundary of the separator

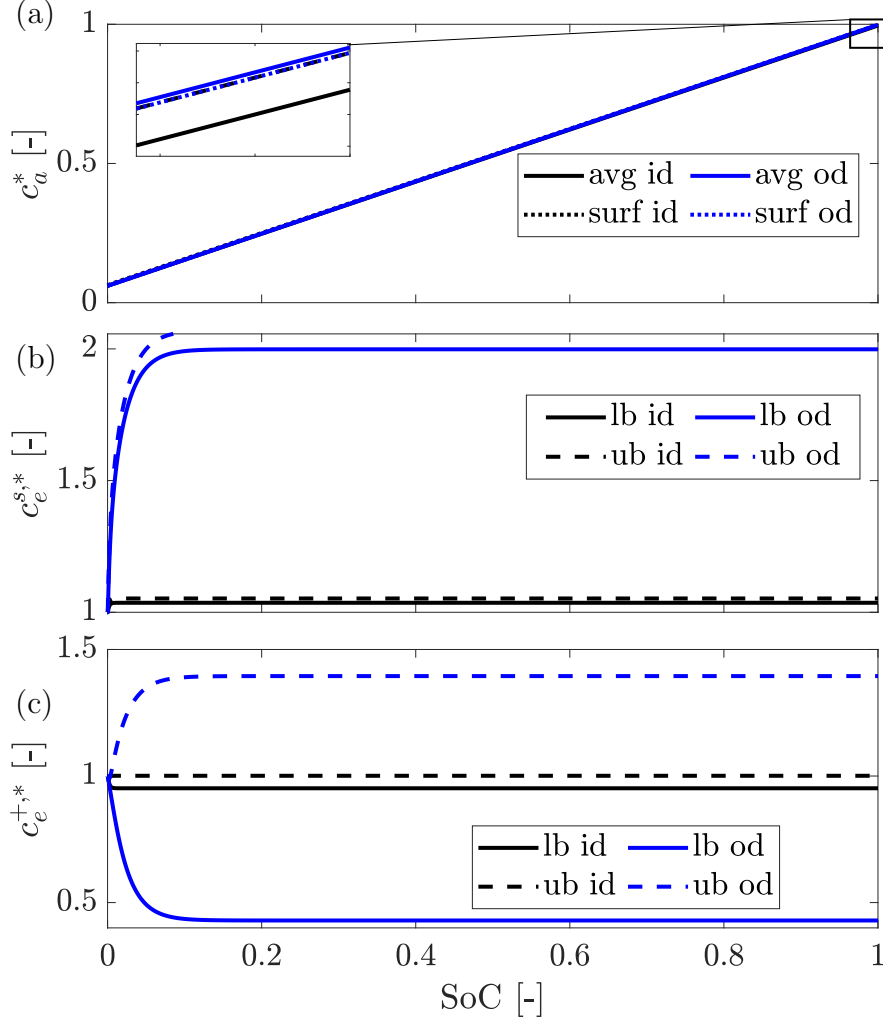


Figure 8: Temporal evolution of normalized concentrations for the simulated LFP half-cell with initial (id) and optimal design (od). Plot a) shows the average (avg) and surface (surf) active-phase concentration, whereas plots b) and c) show the upper (ub) and lower bounds (lb) for the electrolyte-phase concentration in the separator and the positive electrode regions, respectively.

(see Fig. 9b) corresponding to the lithium foil-separator interface (see Fig. 2a), whereas the minimum electrolyte concentrations are in the $x^{+,*} = 1$ boundary of the positive electrode (see Fig. 9c) associated to the positive

electrode-current collector interface (see Fig. 2a).

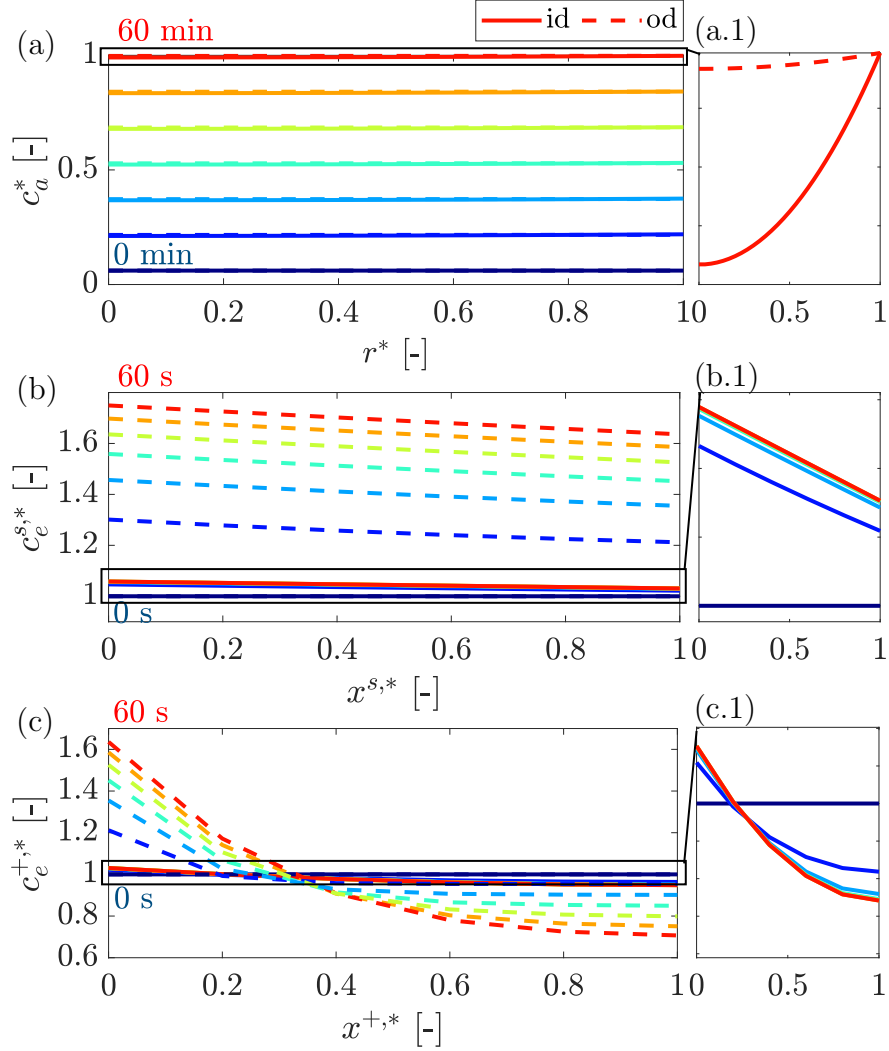


Figure 9: Temporal evolution of normalized concentrations with respect to the normalized space for the simulated LFP half-cell with initial (id) and optimal design (od). Plot a) shows the active-phase concentration (with $r^* = r/R_a$), whereas plots b) and c) show the electrolyte-phase concentration in the separator (with $x^{s,*} = x^s/L^s$) and the positive electrode regions (with $x^{+,*} = x^+/L^+$), respectively. The color gradient of the curves from blue to red corresponds to initial and final times, respectively. While the active-phase results are shown every 10 min up to 60 min, the electrolyte-phase ones are every 10 s up to 60 s.

Additionally, we can also look at the different time constants that govern the electrochemical processes of the considered LFP half-cell battery. Table 6 shows the resulting time-constant values for both initial and optimal design. From the table follows that the (dis)charge time scales in both active and electrolyte phase as well as the diffusion time constant for the electrolyte-phase have increased for the optimal design with respect to the initial design. While the larger time scales validate the notion of having a bigger half-cell in both phases requiring larger absolute currents for full discharge (see Fig. 7a), the larger electrolyte-phase time constant can be verified in Fig. 8b,c where the electrolyte subsystem for the optimal design is slower than for the initial design. Contrarily, the diffusion time constant for the active phase and the reaction kinetics time scale are lower for the optimal design with respect to the initial design. The shorter diffusion time is the result of having shorter diffusion paths due to particle size reduction, whereas faster kinetics facilitates the transfer of charges from the electrolyte to the active phase. Finally, while the initial design was limited by the reaction kinetics given the large value of τ_k^+ , the optimal design shifted the limiting step to the electrode (dis)charge capacity due to the large value of τ_c^+ .

Table 6: Values for the time constants/scalings of the considered LFP half-cell.

Constants	Values i.d.	Values o.d.
τ_c^+ [s]	4603	22827
τ_d^+ [s]	167	13
$\tau_{e,c}^+$ [s]	233	1156
$\tau_{e,d}^+$ [s]	18	432
τ_k^+ [s]	37757	10344

The results of the APSO algorithm during the searching procedure of optimal solutions are shown in Fig. 10. As it can be seen, after 20 iterations the algorithm stops and reaches the best solution. Figure 10a depicts the best cost function at the end of each iteration, and it seems that after 8 iterations it reaches the maximum point. However, the value of the swarm norm (i.e. swarm radius $\|\Theta^n\|$) indicates a non-homogenous space distribution of the particle population (see Fig. 10b), meaning that they have not concentrated around the optimal solution. By checking the normalized swarm radius $R_{\text{norm}}^\theta(n)$ (see Fig. 10c) and considering the stopping criteria in (41),(42), it can be seen that around iteration 20, most of the particles

have gathered around a specific solution and so the deviation of the swarm norm is the least, which led to accept the stopping condition of the search process.

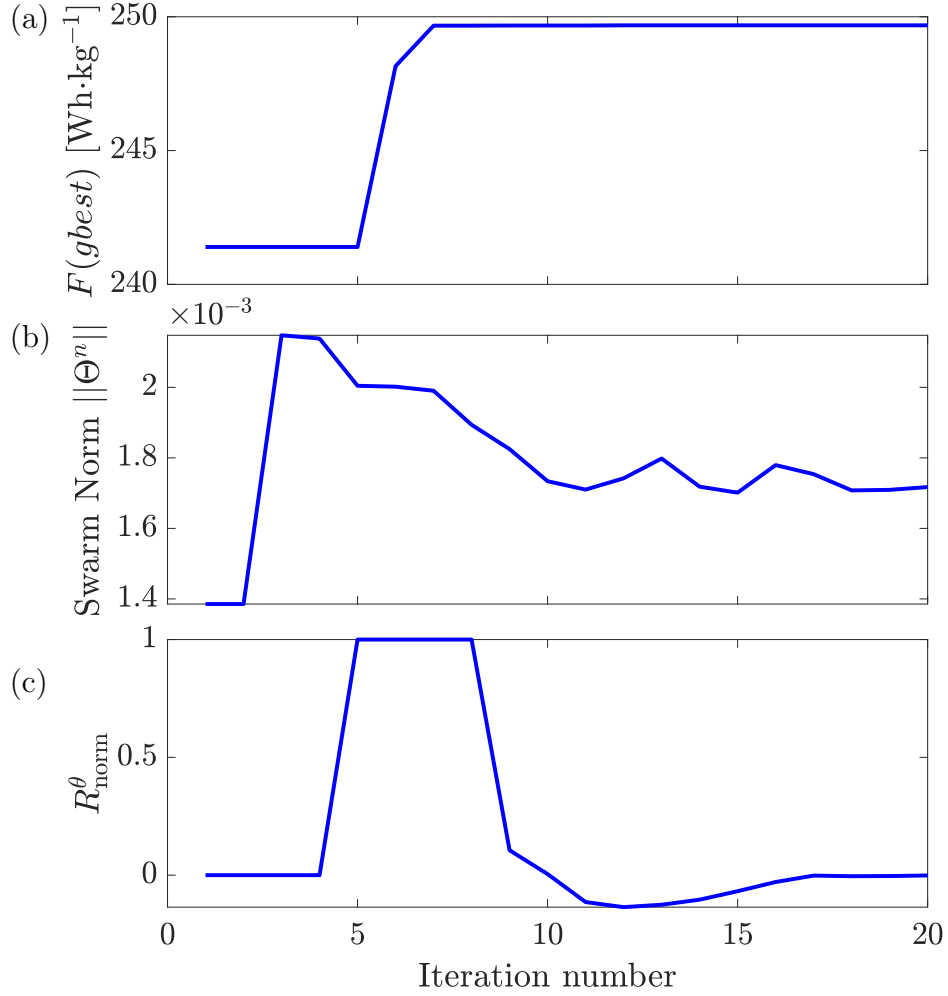


Figure 10: Results of the APSO algorithm optimal search in the design space. a) Best cost function in each iteration, b) swarm norm $\|\Theta^n\|$, and c) normalized swarm radius $R_{norm}^\theta(n)$.

5. Conclusion

The maximization of the specific (gravimetric) energy density of a LIB (LFP half-cell configuration) was proposed based on a reduced-order model. The dSPMe was considered, which is an approximation of the DFN model that allowed us to reduce computational complexity. The dimensionless form of the SPMe shed light on limiting processes, like the fact that a standard battery was limited by reaction kinetics while the optimal design shifted the limitation to the (dis)charge time scale. On the basis of a sensitivity analysis, the most relevant design parameters affecting the energy density were particle radius, electrode thickness and cross-sectional area. An adaptive particle swarm optimization algorithm tuned for fast convergence was used to solve the LIB optimal design problem. The optimal design resulted in an energy density of $250 \text{ Wh}\cdot\text{kg}^{-1}$ for an LFP electrode of $310 \text{ }\mu\text{m}$ thickness, 10 nm particle radius and $2\cdot 10^{-4} \text{ m}^2$ cross-sectional area. This corresponds to an increase of energy density of $61 \text{ Wh}\cdot\text{kg}^{-1}$ with respect to an initial standard design obtained from the literature. This highlights the importance of the proposed framework for optimizing battery performance.

An evident limitation of the half-cell battery optimal design of this work is that it relies on a reduced-order electrochemical model, making it valid for low current rates typically found in standalone energy storage applications, for instance. Given the model simplicity, one could solve the optimization problem over multiple charge-discharge cycles of the battery in order to e.g. minimize capacity loss. Another possible extension of this work is to consider a full-cell lithium-ion battery and properly dimension both positive and negative electrodes simultaneously. Finally, ongoing work concerns the experimental validation of the proposed approach.

Acknowledgments

This work is supported by the Fonds de la Recherche Scientifique - FNRS under grant n°T.0142.20. The first author would also like to thank the Wiener-Anspach Foundation for its financial support.

Appendix A. DFN model equations and dSPMe model parameters

This appendix lists the main equations associated to the DFN model in Table A.1. Then, the main electrochemical variables of the dSPMe are reported in Table A.2, followed by the nomenclature and model parameters of the dSPMe model in Table A.3. The equations adopted for the OCV as a function of the normalized active phase concentration as well as the ionic conductivity and activity coefficient as functions of the normalized electrolyte phase concentration are respectively given by

$$U^+(c_{as}^*) = 3.5796 + 0.55163 \tan^{-1}(23.54 - 408.95c_{as}^*) \\ + 0.46309 \tan^{-1}(-203.36c_{as}^* + 202.43), \quad (\text{A.1})$$

$$\kappa(c_e^*) = 0.0911 + 1.9101 \cdot 10^{-3}c_e^* - 1.052 \cdot 10^{-6}(c_e^*)^2 \\ + 0.1554 \cdot 10^{-9}(c_e^*)^3, \quad (\text{A.2})$$

$$\nu(c_e^*) = 0.601 - 0.24(c_e^*)^{0.5} + 0.982(c_e^*)^{1.5}, \quad (\text{A.3})$$

where $\nu = (1 - t_c^0) \left(\frac{d \ln f_{c/a}}{d \ln c_e} \right)$.

Table A.1: DFN model equations[†].

Physical Process	Equation
Active phase:	
Conservation of Li	$\frac{\partial c_a^\pm}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(D_a^\pm r^2 \frac{\partial c_a^\pm}{\partial r} \right) \quad (\text{A.4})$
Conservation of charge	$\frac{\partial^2 \varphi_a^\pm}{\partial x^2} = \frac{a_a^\pm F}{\sigma_a^\pm} j_n^\pm \quad (\text{A.5})$
Electrolyte phase:	
Conservation of Li ^b	$\frac{\partial c_e^{\pm s}}{\partial t} = \frac{\partial}{\partial x} \frac{D_{e,\text{eff}}^{\pm s}}{\varepsilon_e^{\pm s}} \frac{\partial c_e^{\pm s}}{\partial x} + \frac{a_a^\pm (1 - t_c^0)}{\varepsilon_e^\pm} j_n^\pm \quad (\text{A.6})$
Conservation of charge ^{a,b}	$\frac{\partial^2 \varphi_e^{\pm s}}{\partial x^2} = -\frac{a_a^\pm F}{\kappa_{e,\text{eff}}^\pm} j_n^\pm + \kappa_D^{\pm s} \frac{\partial^2 c_e^{\pm s}}{\partial x^2} \quad (\text{A.7})$
Electrode kinetics:	
Intercalation reaction ^c	$j_n^\pm = \frac{2}{F} i_0^\pm \sinh \left(\frac{\alpha_0 F}{RT} \eta_s^\pm \right) \quad (\text{A.8})$
where $\eta_s^\pm = \varphi_a^\pm - \varphi_e - U^\pm - R_f^\pm j_n^\pm$	
Moles of Li	$n_{Li} = \sum_{j \in \{\pm\}} \frac{3\varepsilon_a^j}{(R_a^j)^3} \int_0^{L^j} \int_0^{R_a^j} r^2 c_a^j dr dx \quad (\text{A.9})$

[†]Spatial/temporal dependency of state variables not explicitly indicated for compactness, as well as boundary conditions not reported.

^aLinearized equation [45].

^bFor the separator region, $j_n = 0$ (it is not defined).

^cAssuming $\alpha_0 = 0.5$ [12].

Table A.2: Electrochemical states/variables, inputs and outputs in the dSPMe.

Variable	Symbol
Li concentration in active phase [$\text{mol}\cdot\text{m}^{-3}$]	$c_a^\pm$
Li concentration at active particle surface [$\text{mol}\cdot\text{m}^{-3}$]	$c_{as}^\pm$
Li concentration in electrolyte phase [$\text{mol}\cdot\text{m}^{-3}$]	$c_e^{\pm s}$
Li concentration in electrolyte phase boundaries [$\text{mol}\cdot\text{m}^{-3}$]	$c_{e,bc}^{\pm s}$
Active-phase electric potential [V]	$\phi_s^\pm$
Electrolyte electric potential [V]	$\phi_e^{\pm s}$
Ionic current [$\text{A}\cdot\text{m}^{-2}$]	$i_e^\pm$
Pore-wall molar flux [$\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$]	$j_n^\pm$
Exchange current density [$\text{A}\cdot\text{m}^{-2}$]	$i_0^\pm$
Surface/lithium over-potential [V]	$\eta_s^\pm/\eta_{Li}$
Applied current [A]	i
Terminal voltage [V]	v

Table A.3: Definition of dSPMe parameters and values used in the LFP half-cell simulation.

Definition [units]	Symbol	Value	Reference
Active-phase parameters			
Specific interfacial area [m^{-1}]	a_a	$3.53 \cdot 10^7$	[35]
Maximum lithium conc. [$\text{mol} \cdot \text{m}^{-3}$]	$c_{a,\text{max}}$	$2.298 \cdot 10^4$	[46]
Active-phase diffusion coefficient [$\text{m}^2 \cdot \text{s}^{-1}$]	D_a	8e-18	[46]
Exchange current density [$\text{A} \cdot \text{m}^{-2}$]	i_0^L	19.0	[35]
Reaction rate [$\text{m}^{2.5} \cdot \text{mol}^{0.5} \cdot \text{s}^{-1}$]	k_n	$3.05 \cdot 10^{-14}$	[35]
LFP electrode thickness [μm]	L^+	70	[35]
Current collector thickness [μm]	L^{cc}	25	[46]
Particle radius [nm]	R_a	36.5	[35]
Film resistance [$\Omega \cdot \text{m}^2$]	R_f	0.001	^a
Open circuit voltage (OCV) of LFP, Li [V]	U^+, U_{Li}	Eq. (A.1), 0	[47, 35]
Charge transfer coefficient [-]	α_0	0.5	[35]
Volume fraction in active-phase electrode [-]	ε_a	0.43	[35]
Volume fraction of filler [-]	ε_f	0.27	^a
Mass density of active phase [$\text{kg} \cdot \text{m}^{-3}$]	ρ_a	3600	[46]
Mass density of filler [$\text{kg} \cdot \text{m}^{-3}$]	ρ_f	1800	[46]
Mass density of current collector [$\text{kg} \cdot \text{m}^{-3}$]	ρ_{cc}	2707	[46]
Electrical conductivity [$\Omega^{-1} \cdot \text{m}^{-1}$]	σ	$7.4 \cdot 10^{-3}$	[46]
Electrolyte-related parameters			
Electrolyte-phase diffusion coefficient [$\text{m}^2 \cdot \text{s}^{-1}$]	D_e	$2.7877 \cdot 10^{-10}$	[40]
Activity coefficient [-]	$\frac{d \ln f_c/a}{d \ln c_e}$	Eq. (A.3)	[48]
Separator thickness [μm]	L^s	25	^a
Transference number [-]	t_c^0	0.4	[40]
Volume fraction in electrolyte-phase electrode [-]	ε_e^+	0.3	^a
Volume fraction in electrolyte-phase separator [-]	ε_e^s	0.5	^a
Ionic conductivity [$\Omega^{-1} \cdot \text{m}^{-1}$]	κ	Eq. (A.2)	[40]
Mass density of electrolyte phase [$\text{kg} \cdot \text{m}^{-3}$]	ρ_e	1200	[46]
Cell-level parameters			
Cross-sectional area [m^2] ^a	A	$2.43 \cdot 10^{-4}$	^a
Bruggeman exponent [-]	b	1.5	[14]
Electrolyte nominal conc. [$\text{mol} \cdot \text{m}^{-3}$]	$\bar{c}_e$	1000	[46, 35]
Faraday's constant [$\text{C} \cdot \text{mol}^{-1}$]	F	96487	[14]
Universal gas constant [$\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$]	R_g	8.31	[14]
Reference temperature [K]	T_{ref}	298.15	^a

^aUsed in this work.

^bFunctional form coming from the cited reference.

References

- [1] R. Georgious, R. Refaat, J. Garcia, A. A. Daoud, Review on energy storage systems in microgrids, *Electronics* 10 (17) (2021) 2134.
- [2] I. González, A. J. Calderón, F. J. Folgado, Iot real time system for monitoring lithium-ion battery long-term operation in microgrids, *Journal of Energy Storage* 51 (2022) 104596.
- [3] W. Cao, J.-W. Xiao, S.-C. Cui, X.-K. Liu, An efficient and economical storage and energy sharing model for multiple multi-energy microgrids, *Energy* 244 (2022) 123124.
- [4] N. A. Chaturvedi, R. Klein, J. Christensen, J. Ahmed, A. Kojic, Algorithms for advanced battery-management systems, *IEEE Control Systems* 30 (3) (2010) 49–68.
- [5] N. Xue, W. Du, A. Gupta, W. Shyy, A. Marie Sastry, J. R. R. A. Martins, Optimization of a single lithium-ion battery cell with a gradient-based algorithm, *Journal of The Electrochemical Society* 160 (8) (2013) A1071–A1078.
- [6] S. Wang, S. Jin, D. Bai, Y. Fan, H. Shi, C. Fernandez, A critical review of improved deep learning methods for the remaining useful life prediction of lithium-ion batteries, *Energy Reports* 7 (2021) 5562–5574.
- [7] S. Wang, P. Takyi-Aninakwa, S. Jin, C. Yu, C. Fernandez, D.-I. Stroe, An improved feedforward-long short-term memory modeling method for the whole-life-cycle state of charge prediction of lithium-ion batteries considering current-voltage-temperature variation, *Energy* 254 (2022) 124224.
- [8] X. Hu, S. Li, H. Peng, A comparative study of equivalent circuit models for li-ion batteries, *Journal of Power Sources* 198 (2012) 359–367.
- [9] Y. Wang, H. Fang, L. Zhou, T. Wada, Revisiting the state-of-charge estimation for lithium-ion batteries: A methodical investigation of the extended kalman filter approach, *IEEE Control Systems Magazine* 37 (4) (2017) 73–96.

- [10] C. Zou, C. Manzie, D. Nešić, A framework for simplification of pde-based lithium-ion battery models, *IEEE Transactions on Control Systems Technology* 24 (5) (2016) 1594–1609.
- [11] D. Zhang, S. Dey, L. D. Couto, S. J. Moura, Battery adaptive observer for a single-particle model with intercalation-induced stress, *IEEE Transactions on Control Systems Technology* (2019) 1–15.
- [12] M. Doyle, T. Fuller, J. Newman, Modeling of galvanostatic charge and discharge of the lithium/ polymer/insertion cell, *Journal of The Electrochemical Society* 140 (6) (1993) 1526–1533.
- [13] T. F. Fuller, M. Doyle, J. Newman, Simulation and optimization of the dual lithium ion insertion cell, *Journal of The Electrochemical Society* 141 (1) (1994) 1–10.
- [14] K. E. Thomas-Alyea, J. Newman, R. M. Darling, *Mathematical Modeling of Lithium Batteries*, 1st Edition, Springer US, New York, 2002, book section 12, pp. 345–392.
- [15] J. Newman, K. Thomas-Alyea, *Electrochemical Systems*, 3rd Edition, John Wiley & Sons, Inc., Hoboken, New Jersey, 2004.
- [16] V. Ramadesigan, P. W. C. Northrop, S. De, S. Santhanagopalan, R. D. Braatz, V. R. Subramanian, Modeling and simulation of lithium-ion batteries from a systems engineering perspective, *Journal of The Electrochemical Society* 159 (3) (2012) R31–R45.
- [17] Y. Dai, V. Srinivasan, On graded electrode porosity as a design tool for improving the energy density of batteries, *Journal of The Electrochemical Society* 163 (3) (2016) A406–A416.
- [18] J.-S. Kim, D.-C. Lee, J.-J. Lee, C.-W. Kim, Optimization for maximum specific energy density of a lithium-ion battery using progressive quadratic response surface method and design of experiments, *Scientific Reports* 10 (1) (2020) 15586.
- [19] M. Astaneh, J. Andric, L. Löfdahl, P. Stopp, Multiphysics simulation optimization framework for lithium-ion battery pack design for electric vehicle applications, *Energy* 239 (2022) 122092.

- [20] E. Hosseinzadeh, J. Marco, P. Jennings, Electrochemical-thermal modelling and optimisation of lithium-ion battery design parameters using analysis of variance, *Energies* 10 (1278) (2017) 1–22.
- [21] S. Golmon, K. Maute, M. L. Dunn, Multiscale design optimization of lithium ion batteries using adjoint sensitivity analysis, *International Journal for Numerical Methods in Engineering* 92 (5) (2012) 475–494.
- [22] G. Ning, B. N. Popov, Cycle life modeling of lithium-ion batteries, *Journal of The Electrochemical Society* 151 (10) (2004) A1584–A1591.
- [23] S. Santhanagopalan, Q. Guo, P. Ramadass, R. E. White, Review of models for predicting the cycling performance of lithium ion batteries, *Journal of Power Sources* 156 (2) (2006) 620–628, c.
- [24] M. Guo, G. Sikha, R. E. White, Single-particle model for a lithium-ion cell: Thermal behavior, *Journal of The Electrochemical Society* 158 (2) (2011) A122–A132.
- [25] S. J. Moura, F. B. Argomedeo, R. Klein, A. Mirtabatabaei, M. Krstic, Battery state estimation for a single particle model with electrolyte dynamics, *IEEE Transactions on Control Systems Technology* 25 (2) (2017) 453–468.
- [26] T. R. Tanim, C. D. Rahn, C.-Y. Wang, State of charge estimation of a lithium ion cell based on a temperature dependent and electrolyte enhanced single particle model, *Energy* 80 (2015) 731–739.
- [27] D. Di Domenico, A. Stefanopoulou, G. Fiengo, Lithium-ion battery state of charge and critical surface charge estimation using an electrochemical model-based extended kalman filter, *Journal of Dynamic Systems, Measurement, and Control* 132 (6) (2010) 061302.1–061302.11.
- [28] J. F. Manwell, J. G. McGowan, Lead acid battery storage model for hybrid energy systems, *Solar Energy* 50 (5) (1993) 399–405.
- [29] J. Newman, Optimization of porosity and thickness of a battery electrode by means of a reaction-zone model, *Journal of The Electrochemical Society* 142 (1) (1995) 97–101.

- [30] D.-C. Lee, K.-J. Lee, C.-W. Kim, Optimization of a lithium-ion battery for maximization of energy density with design of experiments and micro-genetic algorithm, *International Journal of Precision Engineering and Manufacturing-Green Technology* 7 (4) (2020) 829–836.
- [31] C. Liu, L. Liu, Optimal design of li-ion batteries through multi-physics modeling and multi-objective optimization, *Journal of The Electrochemical Society* 164 (11) (2017) E3254–E3264.
- [32] F. Wang, H. Zhang, A. Zhou, A particle swarm optimization algorithm for mixed-variable optimization problems, *Swarm and Evolutionary Computation* 60 (2021) 100808.
- [33] A. Alfi, H. Modares, System identification and control using adaptive particle swarm optimization, *Applied Mathematical Modelling* 35 (3) (2011) 1210–1221.
- [34] V. Srinivasan, J. Newman, Discharge model for the lithium iron-phosphate electrode, *Journal of The Electrochemical Society* 151 (10) (2004) A1517–A1529.
- [35] M. Safari, C. Delacourt, Modeling of a commercial graphite/lifepo4 cell, *Journal of The Electrochemical Society* 158 (5) (2011) A562–A571.
- [36] M. Wayland, Tesla will change the type of battery cells it uses in all its standard-range cars, <https://tinyurl.com/yc58nxh8> (2021).
- [37] S. J. Moura, N. A. Chaturvedi, M. Krstić, Adaptive partial differential equation observer for battery state-of-charge/state-of-health estimation via an electrochemical model, *Journal of Dynamic Systems, Measurement, and Control* 136 (1) (2014) 011015–1–011015–11.
- [38] L. Couto, Electrochemical Modeling, Supervision and Control of Lithium-Ion Batteries, Ph.D. thesis, École Polytechnique de Bruxelles, ULB, Brussels, Belgium (2018).
- [39] S. G. Marquis, V. Sulzer, R. Timms, C. P. Please, S. J. Chapman, An asymptotic derivation of a single particle model with electrolyte, *Journal of Power Sources* (2019).

- [40] J. Christensen, Modeling diffusion-induced stress in li-ion cells with porous electrodes, *Journal of The Electrochemical Society* 157 (3) (2010) A366–A380.
- [41] J. C. Strikwerda, *Finite Difference Schemes and Partial Differential Equations*, 2nd Edition, Finite Difference Schemes and Partial Differential Equations, Second Edition, 2004.
- [42] C. Gommès, T. Gilet, Combine dimensional analysis with educated guessing, *Chemical Engineering Progress* 114 (2) (2018) 49–54.
- [43] A. Engelbrecht, *Computational Intelligence: An Introduction*, John Wiley & Sons, 2007.
- [44] R. Klein, N. A. Chaturvedi, J. Christensen, J. Ahmed, R. Findeisen, A. Kojic, Electrochemical model based observer design for a lithium-ion battery, *IEEE Transactions on Control Systems Technology* 21 (2) (2013) 289–301.
- [45] C. D. Rahn, C.-Y. Wang, *Governing Equations*, John Wiley & Sons Ltd, 2013, pp. 23–48.
- [46] S. Stewart, P. Albertus, V. Srinivasan, I. Plitz, N. Pereira, G. Amatucci, J. Newman, Optimizing the performance of lithium titanate spinel paired with activated carbon or iron phosphate, *Journal of The Electrochemical Society* 155 (3) (2008) A253–A261.
- [47] P. Albertus, J. Coutts, V. Srinivasan, J. Newman, Ii. a combined model for determining capacity usage and battery size for hybrid and plug-in hybrid electric vehicles, *Journal of Power Sources* 183 (2) (2008) 771–782.
- [48] L. O. Valoen, J. N. Reimers, Transport properties of LiPF_6 -based Li-ion battery electrolytes, *Journal of The Electrochemical Society* 152 (5) (2005) A882.

S. Supplementary material

This supplementary material includes a procedure for manufacturing LFP half-cell batteries, the collection of data through experiments and the use of this data to indentify the grouped model parameters of the SPM_e.

S.1. Electrode and half-cell manufacturing

LFP electrodes were produced via robotic spray coating by adaptation of a previously published method [S.9] that used airbrush to spray. The mixture has been prepared by using 12 wt% solids including LFP (Prayon), xanthan gum (Sigma-Aldrich) and conducting carbon (Timcal C-nergy Super C65) in a weight ratio of 75 : 20 : 5 (active material:conducting carbon:binder). The mixture was stirred by using magnetic stirrer for 3 h prior to spraying. The prepared ink was sprayed on pre-weighted stainless-steel discs (Type 304, 15.5 mm, MTI corp.) current collectors and dried overnight at 60°C. The coated discs were weighted and dried in an oven for 2 h under vacuum at 110°C before being introduced into the glovebox. The cell assembly was conducted by using LFP electrode as positive electrode, metallic Li disc (PI-KEM) as counter and reference electrode, two Celgard[®] separators and 80 μ L of electrolyte (1 M in an ethylene carbonate:diethyl carbonate:dimethylcarbonate – 1:1:1 mixture, Sigma Aldrich). Prepared half-cells were then used for electrochemical characterization.

S.2. Electrochemical characterization

Produced LFP half-cells were characterized using a BioLogic VMP3 multichannel potentiostat. EIS was conducted in the 10-2-106 Hz frequency range. Prior the electrochemical impedance spectroscopy, cells were submitted to formation cycles between 2.0 and 4.2 V vs. Li⁺/Li by using galvanostatic charge and discharge mode and applied current densities were calculated based on the theoretical capacity of 170 mA.h/g for LFP. The cycling sequence of formation cycles were designed as 10 cycles at C/5 and 10 cycles at 1C rate. The State of Charge (SOC) for EIS was selected as 40% SOC, the SOC point being calculated by using the total capacity observed at 1C C-rate during the formation cycles. Following completion of the formation cycles, half-cells were discharged to 0% SOC and let to rest until the potential change rate decreased down to 0.5 mV/h, at which point the electrode was assumed to be stable. The half-cell was charged to 40% SOC and let rest until it reaches to 0.5 mV/h potential change rate before conducting the EIS.

S.3. SPMe impedance model

The model to be identified is the SPMe in frequency domain in order to obtain its parameters from electrochemical impedance spectroscopy data. Hence, the SPMe model in Table 1 needs to be converted from time-domain to frequency-domain. In order to achieve this, the next steps are followed:

- (i) take the Laplace transform of the diffusion PDE,
- (ii) solve the resulting ODE to get the general solution,
- (iii) find the unknown constants by substituting the ODE solution in the boundary conditions,
- (iv) evaluate the obtained transfer function at the desired spatial point.

We used this procedure to transform the time-domain PDE models of the SPMe (notably active-phase and electrolyte-phase lithium concentration dynamics in (2) and (3), respectively, of Table 2 in the paper) into frequency-domain, similarly as it has been presented in the literature (see e.g. [S.1-S.3]). On the other hand, the voltage equation as expressed in (18) assumes that the high-frequency dynamics associated to e.g. double-layer effects are much faster than diffusion dynamics in active- and electrolyte phases, i.e. the kinetics are technically instantaneous and can be neglected [S.4] . For electrochemical impedance spectroscopy, this is not a valid assumption since clear double-layer effects can be seen in the impedance response of batteries which manifest as high-frequency semicircles (see [S.5,S.6]). To properly model the impedance of batteries, double-layer dynamics have to be accounted for. In this sense, we also derived two impedance double-layer models to be able to capture the two high-frequency semicircles in LFP half-cell battery. These models are based on the work reported in [S.2,S.4,S.7,S.8] . The impedance model made of a set of transfer functions can be written as

$$H_v(s, \boldsymbol{\nu}) = H_{as}(s, \boldsymbol{\nu}) + H_e(s, \boldsymbol{\nu}) + H_{dl}(s, \boldsymbol{\nu}) + H_{rc}(s, \boldsymbol{\nu}) + H_i(s, \boldsymbol{\nu}) \quad (\text{A.1})$$

where s is the Laplace variable and $\boldsymbol{\nu}$ is the vector of grouped parameters to be identified, $H_{as}(s)$ corresponds to the potential transfer function of the active-phase lithium surface concentration, $H_e(s)$ is for the electrolyte-phase concentration, $H_{dl}(s)$ is for the first double-layer dynamics that are physically modelled, $H_{rc}(s)$ is for the second double-layer dynamics that are modelled as an RC-pair, and $H_i(s)$ is for the ohmic drop. This frequency-domain

SPMe model with two double layers (A.1) was used to identify the grouped model parameters $\boldsymbol{\nu}$ from electrochemical impedance spectroscopy data. Notice that some of these parameters involve the active-phase diffusion time constant, kinetic reaction time scale or the double-layer time constant given by

$$\tau_d = \frac{R_a^2}{D_a}, \quad \tau_k = \frac{R_a}{k_n \sqrt{c_{e,\text{nom}}}}, \quad \tau_{dl} = a_a C \left(\frac{1}{\sigma_{\text{eff}}} + \frac{1}{\kappa_{\text{eff}}} \right) (L^+)^2 \quad (\text{A.2})$$

where most physical parameters have been defined in the paper except C that is double-layer capacitance.

S.4. Model identification

The measured impedance of a cell at a given frequency ω_i is given by the complex number $Z(\omega_i) = Z'(\omega_i) + iZ''(\omega_i)$, where Z' and Z'' denote the real and imaginary part respectively. The optimal parameter estimate can be obtained by solving the following optimization problem [S.3]

$$\min_{\boldsymbol{\nu}} J(\boldsymbol{\nu}) = \min_{\boldsymbol{\nu}} \sum_{i=1}^{N_\omega} |Z(\omega_i) - H_v(\omega_i, \boldsymbol{\nu})|^2 \quad (\text{A.3})$$

where N_ω is the number of evaluated frequencies. This optimization problem (A.3) is solved to find the best values of the parameter vector $\boldsymbol{\nu}$.

S.5. Identification results

The results are shown in the Nyquist plot of Fig. S.1, where the impedance data is depicted as black dots, the model response with the parameter initialization is the solid blue curve and the model response with the optimal parameter set is the dashed red curve. From the figure follows that the proposed model is able to capture the typical response of LFP half-cell batteries including the two semi-circles at high frequency and the low-frequency content associated to diffusion in active and electrolyte phases.

The presented curves show that the proposed electrochemical model can be adjusted to fit the measured impedance data coming from a LFP half-cell battery, which validates the model choice. However, there are still some issues, notably when attempting to link the transfer function parameters to the physical battery parameters. Taking for instance the time constants in (A.2), it is still unclear how to optimize with respect to R_a if only τ_d and

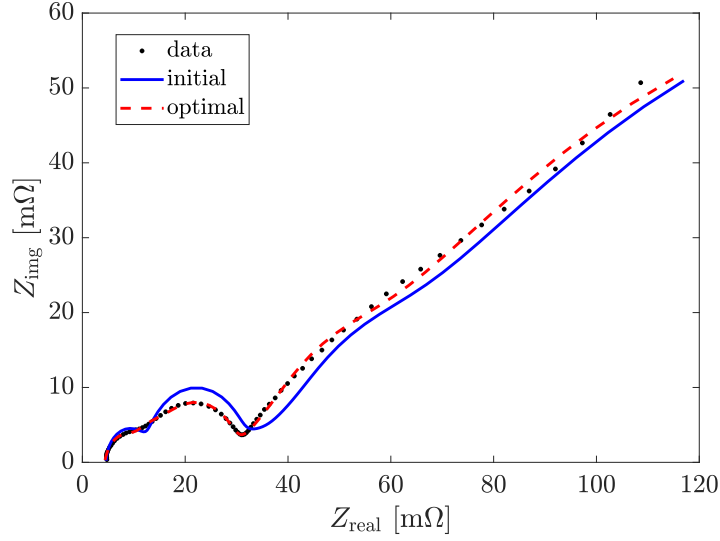


Figure S.1: Nyquist plots of impedance response of a LFP half-cell battery.

τ_k are known, or how to link the double-layer effects to the kinetic reaction, both of which being fast dynamics. These are nontrivial issues that we are currently exploring, which need to be solved before being able to make the link with the experimental validation. Once this has been done, the next step is to use the identified model to optimize the cell performance using the framework proposed in this paper, which will complete the experimental validation part of the work.

References:

- [S.1] T. Jacobsen, K. West, Diffusion impedance in planar, cylindrical and spherical symmetry, *Electrochimica Acta* 40 (2) (1995) 255-262.
- [S.2] R. Drummond, S. R. Duncan, Structural identifiability of a pseudo-2D Li-ion battery electrochemical model, *IFAC-PapersOnLine* 53 (2) (2020) 12452-12458.
- [S.3] A. M. Bizeray, J. Kim, S. R. Duncan, D. A. Howey, Identifiability and parameter estimation of the single particle lithium-ion battery model, *IEEE Transactions on Control Systems Technology* 27 (5) (2019) 1862 - 1877.

- [S.4] I. J. Ong, J. Newman, Double-layer capacitance in a dual lithium ion insertion cell, *Journal of The Electrochemical Society* 146 (12) (1999) 4360-4365.
- [S.5] U. Westerhoff, K. Kurbach, F. Lienesch, M. Kurrat, Analysis of lithium-ion battery models based on electrochemical impedance spectroscopy, *Energy Technology* 4 (12) (2016) 1620-1630.
- [S.6] J. P. Schmidt, T. Chrobak, M. Ender, J. Illig, D. Klotz, E. Ivers-Tiffée, Studies on LiFePO₄ as cathode material using impedance spectroscopy, *Journal of Power Sources* 196 (12) (2011) 5342-5348.
- [S.7] R. Drummond, A. M. Bizeray, D. A. Howey, S. R. Duncan, A feedback interpretation of the Doyle-Fuller-Newman lithium-ion battery model, *IEEE Transactions on Control Systems Technology* 28 (4) (2019) 1284 - 1295.
- [S.8] R. Drummond, C. Cheng, P. S. Grant, S. R. Duncan, Modelling the impedance response of graded LiFePO₄ cathodes for Li-ion batteries, *Journal of The Electrochemical Society* 169 (1) (2022) 010528.
- [S.9] A. F. Léonard, N. Job, Safe and green Li-ion batteries based on LiFePO₄ and Li₄Ti₅O₁₂ sprayed as aqueous slurries with xanthan gum as common binder, *Materials Today Energy* 12 (2019) 168-178.