Review of computational parameter estimation methods for electrochemical models

E. Miguel[a,*], Gregory L. Plett[b], M. Scott Trimboli[b], L. Oca[a], U. Iraola[a] and E. Bekaert[c]

[a] *Mondragon Unibertsitatea, Electronic and computing department, 4 Loramendi, Mondragon 20500, Basque Country, Spain*
[b] *Department of Electrical and Computer Engineering, University of Colorado Colorado Springs, Colorado Springs, CO 80918, United States*
[c] *Centre for Cooperative Research on Alternative Energies (CIC energiGUNE), Basque Research and Technology Alliance (BRTA), Alava Technology Park, Albert Einstein 48, 01510 Vitoria-Gasteiz, Spain*

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ABSTRACT

Electrochemical models are an incipient technique for estimation of battery cells internal variables, useful for cells design or state of function optimization. One of the non-trivial procedures that allow the use of this type of models is the estimation of model parameter values. This paper presents a review of the existing computational parameter estimation methods for rocking chair batteries electrochemical models, a crucial step for real case implementation. Physics-based models can not reach accurate predictions if the parameters are not properly estimated, what highlights the necessity of reviewing the validity of these protocols, that are not extensively treated within literature. The gathered methods are explained and analyzed taking into account the accuracy and extent of the presented results, to give the most objective overview of their applicability within real case scenarios. The methods are classified into two different groups: single optimization analysis (using only one optimization procedure to estimate parameters) and multiple optimization analysis (methods using multiple optimizations). In addition, the need for at least some amount of physico-chemical characterization is analyzed as a common procedure for all the parameter estimation methods. The accuracy of each method is determined, taking as reference the best achievements found in literature. The results show that it is possible to estimate parameters with a high accuracy using non-invasive parameter estimation methods. Finally the potential of mixed (non invasive and physico-chemical based) methodologies is presented. These type of estimation procedures can potentially increase the accuracy of the procedures by lightening up the optimizations involved in the processes, and increasing the ability to estimate values for insensitive parameters. These mixed methods could achieve faster and cheaper estimation protocols, making them more efficient in general.

1. Introduction

Generation and transport of energy has become a critical world-level challenge. Different energy-generation methods are used to create a so-called “Energy mix”, with oil, natural gas, and biofuels as the central pillars [28]. Furthermore, energy consumption has passed from the simplicity of illuminating a house to the present complex electric grid. Overall energy demand has increased [29] and transport is now playing an important role in this growth as electric transportation gains traction around the world. In addition, many grid services [2] related to electricity distribution have grown in importance due to the new energy scenario.

Global reliance on fossil fuels to meet the rising energy demand has taken a heavy toll in the last century. CO_2 emissions are primary contributors to the greenhouse effect that is causing climate change. This is a problem of massive proportions that can not be ignored any longer. Other emissions such as CFCs (chlorofluorocarbons) have caused significant damage to the ozone layer [26]. Human health is also affected by air pollution, and related deaths are not isolated events [27].

The energy scenario described above is no longer sustainable, and attention is turning to renewable-energy sources as the most plausible alternative to fossil fuels. These sources do not themselves generate contamination, although their CO_2 footprint is not completely erased because of the production and maintenance of the associated infrastructure. Nevertheless, the intermittent nature of these energy sources (such as wind or solar) presents technical challenges that need to be solved. Energy needs to be delivered to different loads whenever consumption is demanded from those loads, and the timing of this demand is independent of the timing of energy generation. Energy storage is therefore a real and actual need, permitting storage when there is an excess of generation, and delivering energy when it is needed by an application.

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[*] Corresponding author
`emiguel@mondragon.edu` (E. Miguel)
ORCID(s): 0000-0001-8280-5539 (E. Miguel)

Batteries, and specifically Li-ion batteries, are a promising energy-storage technology for a range of applications. Nonetheless, Li-ion batteries are considered to be more dangerous (due to the risk of leakage, fire, or even explosion) than the lead-acid batteries used by the industry for years. It is therefore necessary to adopt some safety measures. If a solution based on Li-ion batteries is to be adopted, a BMS (battery management system) needs to be considered, to ensure that these batteries operate in a safe and efficient manner.

Some difficulties need to be overcome to achieve better battery-based energy-storage system (ESS). The demand for battery systems is increasing due to the penetration of renewable energies and the growth of the electric-transportation market. Nevertheless, lithium and transition-metal resources are finite and future alternatives will be key. One further drawback is that the purchase price of batteries has been high to date, which causes the payback period of lithium battery-based systems to be in the range of years. However, the current trend indicates that the price of Li-ion batteries will continue to drop as the market grows, and production comes online to meet demand. An evident sign of this fact is the cell-manufacturing Gigafactories 1 and 3 that *Tesla Motors* is building [78]. Despite this however, the return-on-investment period will not be negligible if the Li-ion price does not drop lower than expected.

When designing a battery installation where performance must be guaranteed over an operational lifetime, the aging characteristics of the cells must be taken into account. Working temperature, cycling rates, and depth-of-discharge (DOD) range all directly affect the evolution of battery-cell aging. The beginning-of-life capacity of the battery is oversized to ensure end-of-life performance, and this oversizing is usually calculated conservatively because of uncertainty about how quickly cells will age. Those thoughts are being revised and it is believed that with the correct management, battery under/over utilization can be prevented. By understanding and controlling aging, it should be possible to store more energy than presently specified (conservatively) by manufacturers. Furthermore, is believed that the rate of aging can be reduced by smart current limiting. It is therefore necessary to develop improved control strategies to properly limit the utilization window of batteries.

Future generation BMSs then, need to move beyond equivalent-circuit models (ECM). Different alternatives can be found in the literature, artificial intelligence (AI) based techniques can be used to predict the remaining useful life (RUL) of batteries, for example. Nevertheless, physics-based models (PBMs) are one of the most promising techniques to compute accurate SOF estimates, based on cells internal variables, that give insight into the internal processes and operation window of the cells. This presents an advantage over ECMs, which do not provide information about the internal operation of the cell, but rather only predict the voltage and temperature response to an input-current stimulus. Furthermore, combinations of these techniques appear to be a possible alternative to achieving a more profitable battery operation. PBMs are well known, but still pose some challenges before they can be used in current BMSs. Of particular concern is the limiting computational cost of these models. Even if reduced order models (ROMs) have been proven to work, it remains to be seen if they are fully functional when running in real BMSs due to the limited memory and computation power of these systems. In addition, PBMs have parameter values that must be tailored to match the characteristics of particular cells used in a battery design. The process of determining these values is known as the "parameter estimation" problem. This is still a crucial issue, that limits the use of PBMs models. This study therefore, presents a critical review of the techniques found in the literature to address this problem.

The present work: (1) presents an overview of the challenge associated with physics-based battery modeling and parameter estimation; (2) gathers and classifies the optimization based methods found in literature, taking into account the proof of correct determination of parameters; and (3) outlines future trends in the context of the current state of the art.

2. Model characterization and system identification

Model-based strategies for advanced battery management introduce numerous degrees-of-freedom to the battery estimation and control problem and thus open up a wide range of possible performance benefits. Mathematical models of cell-level behavior are able to account for underlying dynamic processes and can be used to generate predictions of future cell behavior. In particular, physics-based models stem from first-principles equations of electrochemistry and can provide valuable insight into the changing internal quantities which govern battery cell performance and long-term health and are thus ideal candidates for future BMS designs.

The selection of a mathematical model and the determination of its descriptors is a non-trivial component of the larger field of system identification and must take into account a number of key considerations. Chief among these is the application for which the model is to be used. For example, a rough estimate of cell state-of-charge can be obtained using a simple single-state integrator, whereas monitoring of cell internal electrode potentials requires an accurate representation of complex electro-chemical dynamics.

Two broad classes of mathematical models are: i) empirical and ii) physics-based. Empirical models are often simplified structures arranged to provide accurate reconstructions of observed input-output behaviors. Physics-based models, on the other hand, derive from underlying phenomenological principles and can, in principle, reproduce expected behaviors throughout a wide operational environment. The focus of this review paper will be on models of the physics-based type.

As mentioned, the complete process of system identification comprises a number of important tasks These include: i) model selection, which establishes the describing parameter set; and ii) parameter estimation, finding the most likely parameter values from possibly noisy data. It is important to note here that all quantities associated to model parameters are estimates of true values. This also includes physical measurements due to inherent measurement uncertainty.

Generating the cell parameter estimates for a physics-based model structure generally involves both cell tear-down to obtain physical measurements (e.g., electrode dimensions, particle sizes, material composition, etc.) and input-output laboratory experiments to find electrochemical parameter values directly linked to dynamic processes. Regarding the first of these, whereas physical teardown is clearly the most reliable method of obtaining highly accurate estimates of certain cell characteristics (e.g., electrode dimensions, particle sizes, etc.), the process is complex and requires highly specialized equipment. Nonetheless, parameters are able to be measured directly through different electrochemical techniques, including galvanostatic or potentiostatic intermittent titration technique, electrochemical impedance spectroscopy (EIS), Hg porosimetry and other direct methods [16, 15, 70, 71]. A related challenge stems from the combination of experimental errors associated with each parameter value determined from independent measurements, which tend to cause the overall error of the cell-level model to be large. Taylor et al., however, studied the error and uncertainty of electrical tests and managed to reduce it from 4 % to 0.6 [77]. On balance, physico-chemical parameter-identification procedures are perhaps best suited for material characterization, battery prototyping, and post-mortem analysis, and less so for finding accurate cell models for battery-management-system applications.

The second approach consists of collecting input-output (i.e., current/voltage) measurements on intact cells – without performing teardown – and then using computation methods to estimate the parameter values by regressing the data to the model equations. This approach requires less infrastructure but possibly significant computation resources [83]. The experiments required for this task are simpler as only cycling (and similar) data are used. The aim of design of experiment (DOE) techniques, crucial for these methodologies, is to obtain the desired information of the study space with the least number of experiments. The use of DOE techniques helps researchers to choose the samples from the study space, and select representative samples to avoid biased data, which is a matter of much research in the parameter estimation field. In this review, the most relevant studies applied to battery parameter estimation considering DOE are highlighted. The optimal design of experiment is discussed in Sect. 4.4 which is part of the MOA although those techniques could also be applied to SOA and experimental studies to reduce the number of experiments and decrease the experimental or computational cost.

The greatest challenge facing these “nondestructive” experimental methods is the inherent identifiability and informativity of the underlying parameters. These terms refer broadly to the intrinsic connection between the experimental data and the sought-after parameter values. For example, if the model structure has a poorly identified set of parameters forming its description, then no estimation method will be able to find a proper set of estimates for those parameters. This will be discussed in more detail in Sect. 4.2.

2.1. Parameter estimation

Whether using a full-order or reduced-order model to simulate a physical cell, the values of the parameters that describe the model must be properly tuned to match those of the actual cell. Every battery-cell is unique, due to differing physical dimensions, formulations of the electrodes and the electrolyte, separator properties, and so forth. Furthermore, as manufacturing of electrochemical cells is not a simple process, reproducibility is not ideal. Therefore, even batteries of identical design and chemistry from the same batch are never truly equal. In a BMS, algorithms that rely on model accuracy can use observer methods such as Kalman filters [74, 82] to compensate the small differences between individual cells that are supposed to be equal.

Nevertheless, the need for obtaining at least a nominal set of parameters for every cell model is very important in order to achieve accurate predictions. The complete set of parameters that describe a Doyle-Fuller-Newman physics-based model is presented in Table 1. Although this set completely describes the physical properties and dynamic behavior of the lithium-ion cell, there is no guarantee this set is able to be estimated from input-output experiments. Few references are found within the literature dedicated to this specific task, which makes it important to review the

Table 1
List of parameter values required in order to implement the DFN model.

Negative electrode	Separator	Positive electrode
$\sigma^{\mathrm{n}}_{\mathrm{eff}}$		$\sigma^{\mathrm{p}}_{\mathrm{eff}}$
$a^{\mathrm{n}}_{\mathrm{s}}$		$a^{\mathrm{p}}_{\mathrm{s}}$
L^{n}	L^{s}	L^{p}
$\kappa^{\mathrm{n}}_{\mathrm{eff}}$	$\kappa^{\mathrm{s}}_{\mathrm{eff}}$	$\kappa^{\mathrm{p}}_{\mathrm{eff}}$
$D^{\mathrm{n}}_{\mathrm{s}}$		$D^{\mathrm{p}}_{\mathrm{s}}$
$R^{\mathrm{n}}_{\mathrm{s}}$		$R^{\mathrm{p}}_{\mathrm{s}}$
$\varepsilon^{\mathrm{n}}_{\mathrm{e}}$	$\varepsilon^{\mathrm{s}}_{\mathrm{e}}$	$\varepsilon^{\mathrm{p}}_{\mathrm{e}}$
$\varepsilon^{\mathrm{n}}_{\mathrm{s}}$		$\varepsilon^{\mathrm{p}}_{\mathrm{s}}$
$D^{\mathrm{n}}_{\mathrm{e,eff}}$	$D^{\mathrm{s}}_{\mathrm{e,eff}}$	$D^{\mathrm{p}}_{\mathrm{e,eff}}$
k^{n}_{0}		k^{p}_{0}
$c^{\mathrm{n}}_{\mathrm{s,max}}$		$c^{\mathrm{p}}_{\mathrm{s,max}}$
α^{n}		α^{p}
$R^{\mathrm{n}}_{\mathrm{f}}$		$R^{\mathrm{p}}_{\mathrm{f}}$
θ^{n}_{0}		θ^{p}_{0}
$\theta^{\mathrm{n}}_{100}$		$\theta^{\mathrm{p}}_{100}$
A, t^{0}_{+}, $\partial \ln f_{\pm}/\partial \ln c_{\mathrm{e}}$, $c_{\mathrm{e},0}$ span all cell regions		

validity of these methods and the niche for future improvement to them [14, 16, 15, 70, 71, 13, 5].

2.2. Physico-chemical characterization

At this point, it is worth highlighting that the most effective methods for parameter estimation considered in this article are generally mixed methods. Electrode open-circuit-potential (OCP) curves are obtained by cycling half-cells built with samples of the electrodes extracted from the full-cell [16, 70, 6, 31]. Some authors [20] have considered methods to obtain OCP curves computationally however, this makes the optimization process even more complex and can lead to ambiguous results. In addition, since the cell is disassembled to make the half-cells needed to obtain the OCP curves, geometrical parameters of the full-cell can be directly obtained with very little effort and high accuracy. Keeping the optimization problem needed to determine the remaining parameter values simple enough to be solved. For this reason, the remainder of this article focuses on computational parameter-estimation methods, and considers these methods as computational even if they can be considered truly mixed due to the small number of physico-chemical tests used. This is, considering that obtaining OCP curves appears to be a necessary and common pre-step before stepwise parameter estimation, the remainder of this article then focuses on evaluating the differences in the steps of the estimation processes that follow obtaining these curves.

3. The P2D model

The importance of an electrochemical PBM within this scope has been explained. There are many different such models that predict the internal variables of a battery cell, the most common being the "pseudo-two-dimensional" (P2D) or Doyle–Fuller–Newman (DFN) model [12]. This model is based on the porous electrode theory developed by Newman and Tiedemann [47], and states the PDAEs (partial differential algebraic equations) and boundary conditions required to model a cell. It represents three different domains, the two electrodes and the separator (Figure 1). The transport and charge-transfer phenomena are considered to occur in the x axis, while the other two axes are neglected, i.e, the properties are considered uniform across the y and z axes. This is an idealized assumption, but simplification is necessary at this point for practical battery-control algorithms. The distinction between this representation and previous attempts, is that the electrodes are defined as porous composites soaked with electrolyte as shown in Figure 1. This is particularly important because since the late 1990's commercially available cells have been "rocking-chair batteries" manufactured with porous electrodes that improve the rate capabilities of the polymer batteries in use previously.

The DFN P2D model considers all the major electrochemical processes. Electrochemical reaction kinetics can be modeled either with linear, "Tafel" or exponential expressions ("Butler-Volmer" equation). The electron transport

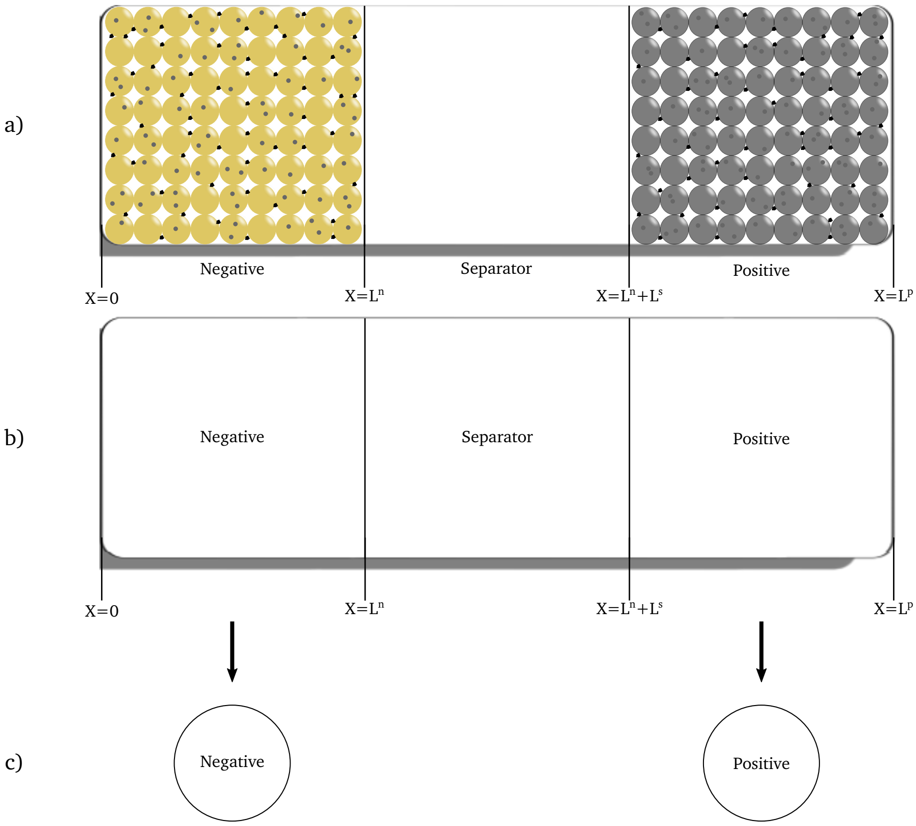

Figure 1: Simplification of the rigorous two-dimensional model (a) to the P2D model (b) and the SP model (c) [66].

in the solid is modeled with "Ohm's law", and based on the effective solid conductivities of each electrode, which are affected by the porosity of the electrodes. The ion transport in the electrolyte is modeled on porous-electrode theory and is affected by the effective electrolyte-phase conductivities. Lithium transport within the solid electrode particles is modeled by Fick's law. The continuum-scale P2D model is derived from a microscale model via volume averaging, which somewhat reduces spatial accuracy, but is usually considered "good enough" for battery-management applications and greatly simplifies computation. The specific equations of this model are:

1. Solid-phase charge conservation:

$$\nabla \cdot (\sigma_{\mathrm{eff}} \nabla \phi_s) = a_s F j,$$

   where $\phi_s(x,t)$ is the solid-phase potential at some spatial location x in the cell at time t, σ_{eff} is the effective conductivity of the solid, a_s is the specific surface area of the solid in the electrode, F is Faraday's constant, and $j(x,t)$ is the flux of lithium leaving the solid and entering the electrolyte. In the negative electrode, $0 \leq x \leq L^{\mathrm{n}}$, in the separator, $L^{\mathrm{n}} \leq x \leq L^{\mathrm{n}} + L^{\mathrm{s}}$, and in the positive electrode $L^{\mathrm{n}} + L^{\mathrm{s}} \leq x \leq L^{\mathrm{n}} + L^{\mathrm{s}} + L^{\mathrm{p}}$.
2. Solid-phase mass-conservation:

$$\frac{\partial c_s}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(D_s r^2 \frac{\partial c_s}{\partial r}\right),$$

   where $c_s(x,r,t)$ is the solid-phase concentration of lithium at radial position $0 \leq r \leq R_s$ within an assumed spherical particle of electrode material, and D_s is the diffusivity of lithium in the solid.
3. Electrolyte-phase charge conservation:

$$\nabla \cdot \left(\kappa_{\mathrm{eff}} \nabla \phi_e + \kappa_{D,\mathrm{eff}} \nabla \ln c_e\right) + a_s F j = 0,$$

where $\phi_e(x,t)$ is the electrolyte-phase potential, $c_e(x,t)$ is the electrolyte-phase concentration of lithium, κ_{eff} is the effective conductivity of the electrolyte, and

$$\kappa_{D,\text{eff}} = 2RT\kappa_{\text{eff}}(t_+^0 - 1)\left(1 + \partial \ln f_\pm / \partial \ln c_e\right)/F$$

scales κ_{eff} to multiply a concentration dependence of ϕ_e, t_+^0 is the transference number of the positive ion in the electrolyte with respect to the solvent, and $f_\pm$ is the mean molar activity coefficient.

4. Electrolyte-phase mass conservation:

$$\frac{\partial(\varepsilon_e c_e)}{\partial t} = \nabla \cdot (D_{e,\text{eff}} \nabla c_e) + a_s(1 - t_+^0)j,$$

where ε_e is the porosity of the electrode, and $D_{e,\text{eff}}$ is the effective diffusivity of the electrolyte. The electrolyte concentration in equilibrium is denoted as $c_{e,0}$.

5. Butler–Volmer kinetics relationship:

$$j = j_0 \left\{ \exp\left(\frac{(1-\alpha)F}{RT}\eta\right) - \exp\left(-\frac{\alpha F}{RT}\eta\right) \right\},$$

where $\eta = \phi_s - \phi_e - U_{\text{ocp}}(c_{s,e}/c_{s,\max}) - FR_{\text{f}}j$ and U_{ocp} is the open-circuit-potential function of the electrode, which in this case is evaluated at the surface concentration $c_{s,e}(x,t) = c_s(x,R,t)$ normalized by the maximum theoretic concentration of lithium $c_{s,\max}$ of the electrode materials. In this relationship, R_{f} is the resistivity of a surface film on the electrode and

$$j_0 = k_0 c_e^{1-\alpha}(c_{s,\max} - c_{s,e})^{1-\alpha} c_{s,e}^{\alpha}$$

where α is an asymmetric charge-transfer coefficient, and k_0 is a kinetic parameter.

During operation, electrode stoichiometry $c_s/c_{s,\max}$ is expected to remain between θ_0 and θ_{100}. Cell electrical current density $i_{\text{app}}(t)/A$ (where A is the current-collector area) drives these equations through a boundary condition on ϕ_s. Cell voltage is the difference between ϕ_s, measured at the positive and negative current collectors.

Many modifications have been made to the standard DFN model over time to describe cell degradation mechanisms. For example, one describes the process of lithium plating [3]; others model solid–electrolyte interphase (SEI) layer growth [60, 59, 58, 65]; another models manganese dissolution in the positive-electrode [10]; and one includes a description of particle fracture [46]. All these degradation models augment the basic DFN framework, hence to predict degradation one must first be able to implement the DFN model.

In addition, many computational simplifications have been made to the standard DFN model to increase its suitability for use in BMS. These include “single-particle models” (SPM) (e.g., [25, 48, 24]) and parabolic approximations of solid concentrations to reduce the complexity of PDE solutions (e.g., [22, 75]). Other approaches such as Padé approximations, residue grouping [73, 18, 61] and using the discrete-time realization algorithm [53, 37] have been considered. As all of these simplified models are based on the DFN model, to implement the reduced-order equations it is necessary to know all the parameter values of the full DFN-model equations as well.

4. Computational parameter esimation methods

Computational parameter-estimation methods estimate battery-cell parameter values based on measured cycling data. This data may be measured from simple constant-current discharges or from more specifically designed profiles. The general idea is to find the combination of parameter values that best fits the DFN model to the measured data in terms of the model’s voltage and/or temperature predictions. Computer-based tools employing a range of optimization methods (e.g., linear, nonlinear, or genetic algorithms) are used to solve the problem in different ways (e.g., series or parallel computing).

4.1. Computational methods in use

Nonlinear-programming methods for optimization seek solutions to a system of equalities and inequalities over a set of unknown real variables (constrained or unconstrained). Within this system, an objective function is maximized or minimized. In the case of finding parameter values for the nonlinear DFN model, nonlinear solvers must be used

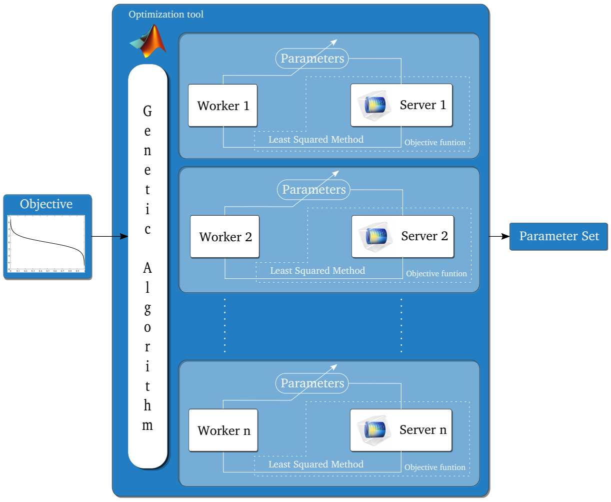

Figure 2: Genetic algorithm optimization with parallel computing structure example.

(e.g, [43]). These solvers are often based on calculus approaches such as gradient descent or different approximations to Newton's method. When the problem can be posed in a nonlinear least-squares form, approaches such as the Levenberg–Marquardt or Gauss–Newton methods can be employed [67, 7].

Genetic algorithms define several candidate parameter sets, and depending on the exact method, these sets can be randomly or deterministically generated. After performing a simulation with each of the candidate parameter sets, the parameters of the simulation achieving the results closest to the experimental dataset are selected, and the remaining sets are discarded. The selected parameters are then randomly mutated to form a new population (as they are called in this method) of candidate parameter sets. This process is repeated continuously until the difference between experimental data and simulation data are admissible; the process can be carried out done in series or in parallel (Figure 2) [85, 19, 20]. A variation of this method is the MOGA (multi objective genetic algorithms) [87], which can optimize more than one objective variable within the same process.

The root-mean-squared (rms) prediction error is generally considered as a way to evaluate the accuracy of the results:

$$\mathrm{rms} = \sqrt{\frac{1}{N}\sum_{n=1}^{N}[y_{\mathrm{simulation}}(t_n) - y_{\mathrm{experimental}}(t_n)]^2}. \tag{1}$$

The minimization of Eq. (1) with respect to model parameter values optimizes a relationship between simulated and experimental data. In this case $y_{\mathrm{simulation}}$ is the output voltage from the simulation of the model that is being adjusted, and $y_{\mathrm{experimental}}$ is the set of voltage data measured when cycling the real cell.

It must be highlighted however, that the selection of an optimization method is only significant once the optimization problem itself is well stated. This means that the choice of solver is key to improving the accuracy of the results and reducing the time taken for optimization. Nonetheless, if the optimization problem itself is not well stated or excessively complicated, all solvers will encounter difficulties in finding a solution. The remainder of this article is therefore focused on evaluating the parameter-estimation methods independent of the solver used. A solver can be chosen and fine-tuned for each case once an optimization problem has been correctly defined, and the specific model equations are fixed.

4.2. Grouping parameters

Before analyzing the computational parameter-estimation methods, we note that there is a drawback common to all. The DFN model is composed of coupled PDAEs, and some of the parameters in these equations are coupled together such that it is mathematically not possible to determine all parameter values correctly and uniquely from input–output data. We refer to this fact by stating that not all parameter values are "identifiable" [30, 31, 9]. Many different combinations of parameter values can lead to the same model output. Even if an optimized set of parameter values fits the experimental input-output data perfectly, the model may not give acceptable results in terms of predictions of cell internal variables [21].

As a simple analogy to this problem, consider the equation $y = (A \times B)x + C$. The parameters of this equation are A, B, and C. If we collect a set of input–output data pairs (x, y), we might attempt to find values for the parameters to fit the equation to the data. But, the problem is that A and B are not independently identifiable. Only the product $M = A \times B$ is identifiable. Many different combinations of A and B arrive at the same product (but perhaps only one of these combinations is physically correct). We see this issue in the DFN model, for example, by observing that solid conductivity σ_{eff} never occurs by itself in the DFN equations. It always occurs as the product $\sigma_{\text{eff}}A/L$. Even though all terms in this expression have direct physical meanings and it is possible to estimate each term by a cell-teardown technique (and so the DFN model is well-posed, in some sense), it is not mathematically possible to estimate a correct value of σ_{eff} from input–output data. However, it is mathematically possible to estimate a correct value for the constant $\sigma_{\text{eff}}^{\text{tot}} = \sigma_{\text{eff}}A/L$.

To address this problem, two different solution approaches can be found in the literature. Some authors opt to reformulate the models so new lumped parameters are used (similar to the lumping that produced $\sigma_{\text{eff}}^{\text{tot}}$ as above) as will be explained more extensively in the following [30, 31, 9]. In the simple example, the ambiguous parts of the model are reformulated as $y = Mx + C$ and the data pairs would be used to determine M and C uniquely; no attempt would be made to determine A and B.

The second alternative groups parameters based on the sensitivity of the measured voltage, or voltage and temperature, to their values. Parameters to which the voltage is very sensitive are called "sensitive" parameters and the remaining are called "insensitive" parameters. The authors choose to estimate the sensitive parameters (or group parameters creating "sensitive" groups) and either use nominal values for the insensitive parameters or delete portions of the model equations in which the insensitive parameters occur (an example is SPM, which often completely discards electrolyte dynamics from the cell model since the parameters that describe electrolyte potential and concentration are relatively insensitive to the voltage curve).

There is however a drawback to both of these solutions that remains unsolved. Aging models are often linked to PBMs so the most benefit of these models is obtained. These aging models use some parameters included in the PBMs which are lumped together or even discarded during the optimization process. This involves some difficulties. If the model has been lumped there can be two solutions, the aging model can be reformulated accordingly, or the set of lumped parameters can be freed using additional tests (either cycling or physico-chemical). On the other hand, if some parameters have been discarded, or even if nominal values are used because voltage is insensitive to the parameters, there is a risk that the internal variables are not correctly estimated [21]. This can lead to a poor response of the aging model, since internal variables are used to feed aging models. Errors in, or omission of these "insensitive" parameters could lead therefore to an important lack of accuracy in an aging model. To the knowledge of the authors, there is no published solution to this problem, and it remains a research gap worthy of further investigation.

4.3. Comparison of computational methods

All computational parameter-estimation methods can be classified into two groups based on the definition of the optimization problem: single-optimization analysis (SOA) and multi-optimization analysis (MOA). Single optimization methods use data obtained experimentally (charges, discharges, or different types of cycles), and optimize the whole set of parameters so that the model output fits the data. Multi-optimization methods also use data sets or differentiated sections of them, then, single parameters or groups of parameters are optimized independently to fit experimental data.

In the following subsections, we identify SOA and MOA approaches from the literature. Since most authors present their own unique reformulations of the P2D or SPM models, there is not room in this survey to present each reformulation and to explore all the differences between every reformulation. Instead, we wish to compare the ability of each method to determine the values required to parameterize the employed models. The interested reader is referred to the references presented in the following subsections for more details.

4.3.1. Single optimization analysis (SOA)

To implement a single-optimization analysis, a single set of experimental data is normally used (typical profiles include constant-current discharges). Either a single discharge, discharges at different rates, or other cycles can be employed. The shared characteristic of these methods is that the load profiles are not specifically designed to isolate the effect of individual parameters, or sets of parameters, in the input–output data. All parameter values are jointly optimized to fit the experimental data. After the data is collected, each author uses a specific model and/or model-reduction in addition to a solving method. Nevertheless, this approach can lead to a loss of accuracy due to a highly complex optimization scheme. For this reason it is important to differentiate the accuracy of the obtained results, even if the model parameters are lumped.

Table 2
Summary of the literature references.

Reference	Model	Parameters		Validation data			Profiles	
		Full	Partial	Voltage	Temp.	Param.	SOA	MOA
[55]	P2D^{re}		X	X			X	
[7]	P2D/P2D^{re}		X	X			X	
[33, 57, 32, 62]	P2D		X	X			X	
[54]	P2D^{s}		X	X			X	
[67, 68, 79]	P2D		X	X	X		X	
[56]	SPM^{e}		X	X		X	X	
[42]	SPM		X	X		X	X	
[11]	SPM^{ve,v,r}/P2D^{v}		X^{LS}	X		X	X	
[20]	P2D	X		X				X
[4]	P2D		X	X				X
[80]	P2D^{ve}		X	X				X
[39]	SS	X^{R}		X				X
[49]	P2D	X^{LS}		X				X
[64]	P2D^{r}	X^{R}		X	X			X
[72]	SPM^{e}	X^{LS}		X	X			X
[81]	P2D		X	X	X			X
[41]	SPM^{e}	X		X	X			X
[51]	P2D	X^{LS}				X		X
[45]	SPM^{re}/P2D^{v}	X^{L}		X		X		X
[38]	P2D^{ve,r,re}	X^{L}		X	X	X		X
[31, 30, 9, 8]	P2D^{re}	X^{L}		X	X	X		X
[83, 85, 86, 84]	P2D	X^{LS}		X	X	X		X
[76]	P2D	X		X		X		X

s: state space; r: reduced order; re: reformulated; e: extended; v: used for voltage observation ; ve: own version or similar; L: lumped parameters; LS: parameters lumped using sensitivity analysis; R: ROM parameters.

All authors identified in the literature using SOA chose either the P2D or SPM model (sometimes small variations or reformulations are made, Table 2). The choice of model determines the sets of parameters that must be estimated; for example, since SPM models predict fewer phenomena occurring inside the cell than P2D models, they require fewer parameters. Nevertheless this aspect is not crucial, as all the authors using SOA methods obtain a partial set of parameters. It is also worth noting that the coupling of parameters explained in section 4.2 is not fully addressed when using partial sets of parameters, but it is still important to evaluate the potential of these parameter-estimation techniques.

State of the art results can be validated using three different approaches based on voltage, temperature, and the parameter values themselves. Voltage validation refers to evaluating the voltage response of the cell versus the parameterized cell model (this can be done with the same cycles used for the validation, or with others, e.g., UDDS cycles). Temperature can also be taken into account, as it has a significant influence on battery behavior. These two methods can be implemented with real cycling data or with virtual data obtained from a full-order electrochemical model [11]. The last validation strategy directly compares the estimated parameter values to the true parameter values. To implement this strategy, the true values must be known, which is not generally the case. However, it is still useful to initially determine whether the parameter-estimation methods are able to produce reasonable results. This is achieved by generating synthetic simulated cell-test data from a cell model (e.g., simulating the P2D model for some input-current profile), then using the simulated cell-test data to determine parameter values, and finally comparing the

Table 3
Parameters estimated by authors using SOA. r:Rajabloo *et al.* [56] estimated parameters, m:Masoudi *et al.* [42] estimated parameters, d:Deng *et al.* [11] estimated parameters.

Negative electrode		**Separator**		**Positive electrode**	
$\sigma^{\mathrm{n}}_{\mathrm{eff}}$	m			$\sigma^{\mathrm{p}}_{\mathrm{eff}}$	
$a^{\mathrm{n}}_{\mathrm{s}}$				$a^{\mathrm{p}}_{\mathrm{s}}$	
L^{n}		L^{s}		L^{p}	
$\kappa^{\mathrm{n}}_{\mathrm{eff}}$		$\kappa^{\mathrm{s}}_{\mathrm{eff}}$		$\kappa^{\mathrm{p}}_{\mathrm{eff}}$	
$D^{\mathrm{n}}_{\mathrm{s}}$	d/r			$D^{\mathrm{p}}_{\mathrm{s}}$	d/r
$R^{\mathrm{n}}_{\mathrm{s}}$				$R^{\mathrm{p}}_{\mathrm{s}}$	
$\varepsilon^{\mathrm{n}}_{\mathrm{e}}$	d/r	$\varepsilon^{\mathrm{s}}_{\mathrm{e}}$	m	$\varepsilon^{\mathrm{p}}_{\mathrm{e}}$	d/r
$D^{\mathrm{n}}_{\mathrm{e,eff}}$		$D^{\mathrm{s}}_{\mathrm{e,eff}}$		$D^{\mathrm{p}}_{\mathrm{e,eff}}$	
k^{n}_{0}	d			k^{p}_{0}	d
$c^{\mathrm{n}}_{\mathrm{s,max}}$	d			$c^{\mathrm{p}}_{\mathrm{s,max}}$	d
α^{n}				α^{p}	
$R^{\mathrm{n}}_{\mathrm{f}}$				$R^{\mathrm{p}}_{\mathrm{f}}$	
θ^{n}_{0}	r			θ^{p}_{0}	r
$\theta^{\mathrm{n}}_{100}$				$\theta^{\mathrm{p}}_{100}$	
A, t^0_+[m], $\partial \ln f_\pm / \partial \ln c_{\mathrm{e}}$, $c_{\mathrm{e},0}$ [d/m] span all cell regions					

estimated parameter values to the true values used in the simulation.

It is therefore necessary to analyse these validation methods and their viability. Some authors have demonstrated that cell voltage is not sensitive to some model parameters [11, 17], which is a key conclusion as it negates the concept that voltage validation is sufficient to ensure correct estimation of model parameters. This could be true, because parameters are fundamentally not identifiable, as discussed in Sect. 4.2. This problem can be solved by grouping parameters together into "lumped parameters". It might also be correct because parameters are identifiable in principle, but the signal-to-noise ratio available in the measured data is not sufficient to allow accurate parameter estimates. In this second case the use of enormous data sets could provide a solution, but the nonlinear optimization methods required to find the parameter values are not guaranteed to find the uniquely correct values in that case. Furthermore Zhang *et al.* [83, 85, 86, 84] reported the same conclusion when implementing an MOA method based on different temperature and rates constant current cycles (this method is presented in section 4.4). For this reason, the present paper focuses on the references that report reliable proof of proper parameter estimation, i.e., based on parameter values (reporting the error of the estimated parameters towards compared to virtual data). The work of Rajabloo *et al.*, Masoudi *et al.*, and Deng *et al.* [56, 42, 11] is therefore studied in this section.

Rajabloo *et al.* [56] used a SPM that was improved with a state of charge linear dependency (for which they also found parameter values) and solved in COMSOL(R). The selected parameter values were then estimated linking COMSOL(R) with MATLAB(R) through the COMSOL LiveLink for MATLAB(R). The Matlab Optimization toolbox ran the optimization routine, and more specifically, a solver dedicated to constrained nonlinear multivariable problems based on the Newton's method.

Masoudi *et al.* [42] also used SPM, but employed Maplesim to solve the equations. For parameter estimation, the "Homotopy optimization method" was utilized to prevent inaccurate results arising from local minima solutions.

Deng *et al.* [11] used their own version of the SPM to generate a reduced order model and estimate parameters. In addition P2D and SPM models were used for voltage response observation.

Nevertheless, the models described above are not so trivial, since all of these authors estimate partial sets of parameters, i.e., few parameters values are estimated to validate the estimation method itself (Table 3).

The results obtained by these authors are presented in Figures 3 and 4. The error of the estimated parameters vary widely (between 0% and 42.8%), which can be attributed to the difference in sensitivity between individual parameters. Additionally, in the case of Deng *et al.* [11], even when using different cycles, parametric sensitivity gave rise to different results (Figure 4a).

Reduced order, P2D and SPM models were studied using different optimization methods and experimental cycling profiles to estimate various sets of parameters. Nevertheless, the parametric errors obtained in these works were not negligible . This could be due to poor parameter identifiability as explained before, which can be addressed in MOA methods by lumping parameters. Furthermore dedicated input profiles or specific fitting procedures designed for each parameter or parameter group can be an alternative to improve estimation accuracy, as presented in the next section.

4.4. Multi optimization analysis (MOA)

In the same vein as single-optimization analysis, the idea behind multi-optimization analysis is to fit model parameters using optimization routines and obtain output variables similar to experimental data. However, instead of using generic input-current profiles to collect a data set, MOAs make a more advanced attempt to design profiles to isolate specific parameters or groups of parameters. This does not change the fundamental identifiability of the model; however, careful design of experiments can improve the informativity of the collected data to determining accurate estimation of values for certain parameters. Electrochemical impedance spectroscopy (EIS) tests, charge and discharge tests conducted at different rates, pulse tests, tests at different temperatures, tests around different cell states of charge, sensitivity analysis, or any combination of these can be used [31, 45, 38, 83, 85, 86, 84, 51].

In all the new identification sequences proposed in the literature, a proper design of experiment (DOE) is conducted. Optimal experiment design (OED) has become a topic of much research for parameter identification for batteries with different modeling approaches [63, 44, 36, 40, 1, 50], and these studies optimize the experimental profile to maximize parameter sensitivity. There are widely known identifiability metrics (Fisher information) in which the shape of battery experimental profiles can be optimized to improve the battery identification process in terms of speed and accuracy [63]. Some of the examples of the application of OED for identification of battery parameters are presented in the next lines: using the full set of model parameters [63, 84], adding thermal parameters into the study [44, 83] and for ageing analysis [36, 1]. Rothenberg et al. [63], presented a battery cycling procedure in which the signal to noise ratio and the parameter estimation through the 4 hour experiment was improved compared to other works for an equivalent circuit model. Mendoza et al. [44] optimized the design of a thermal cycle to estimate the entropy coefficient of a battery cell at 20% state of charge in a 24 hour experiment, complementing the work proposed by [63]. Additional studies were conducted for ageing analysis with optimal designs [36, 1].

In the identification of electrochemical model parameters, the electrochemical impedance spectroscopy (EIS) technique plays an inportant role, as it can isolate the contributions of certain parameters. Mechanisms occurring inside a cell are differently excited using this technique, when the input profile (typically a sinusoidal signal) is changed in frequency (as shown in Figure 5). Consequently the contribution of each mechanisms to the cell terminal voltage is different. This isolates the influence of the mechanism, and in turn, the influence of the model equations (intended to model mechanisms) [34]. This effect also alters the influence of the equation parameter on the voltage response,

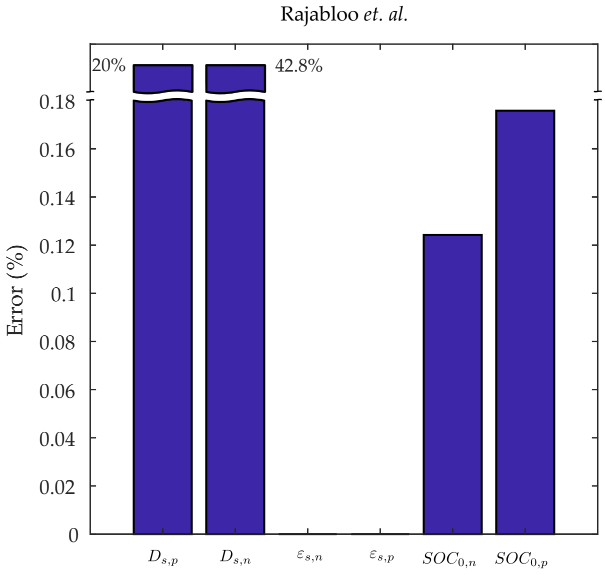

Figure 3: Parametric errors adapted from [56].

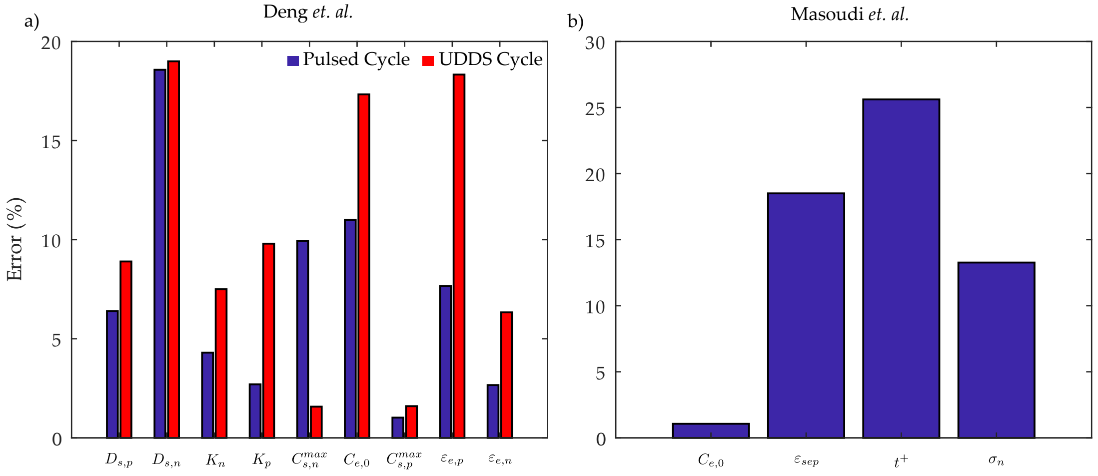

Figure 4: Parametric errors adapted from [11](a) and [42](b).

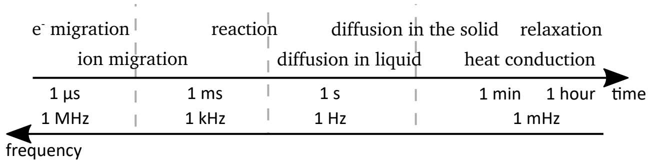

Figure 5: Cell mechanisms related to their typical time constants, adapted from [35].

allowing the design of more precise parameter identification methods. Some of the following works consider EIS in their methodologies, and the interested reader can also find a more detailed discussion about EIS technique in [35, 69, 70, 71].

Moreover, is worth mentioning that the optimal set of experiments given by OED is model dependent. This means that while an optimal design is best for parameter estimation of an equivalent circuit model, it may not be the most appropriate for electrochemical models.

Most of the authors in the literature using MOA (shown in Table 2) have used P2D, SPM or similar models. There are however, some exceptions which have reduced the models leading to a state-space or equation-based simpler model [64, 39]. Nevertheless the validation methods used for these reductions are based on voltage and temperature because the set of parameters that is used in those models is related to the specific model, discarding parameters that are not used due to the reduction or losing the physical meaning in the case of a state-space model. As a result, validation cannot be taken as proof of good parameter estimation, because the parameters can not be compared to those of a full-order model. The validity of this type of model should therefore be oriented to online system implementation, and can be developed once a reliable set of parameters has been previously obtained.

At this point it is important to review at the validation results reported by authors using P2D or SPM models as in section 4.3.1 for SOA. The rest of the section is then focused on the studies presenting reliable proof of parameter estimation (reporting the error of the estimated parameters against virtual data). In Table 4 an overview of the parameter groups and experimental profiles or sequences that are proposed in the studied works for parameter estimation are presented.

Zhang *et al.* [83, 86, 84, 82] reported an estimation methodology for the full set of parameters of a thermal-electrochemical P2D model. The methodology includes three steps, and is introduced in [84]. First of all, the maximum voltage sensitivity point for each parameter is searched based on benchmark parameter values ("Best Condition for Identification (BCI)". Then the results are normalized and weighted to be comparable. Finally, the Fuzzy-C-Means method for parameter clustering is used. The parameters estimated by this methodology are set out in Table 4, and two parameter clusterings were proposed by the authors [84, 83]. [84] In this same study, 28 parameters were examined, from which five were considered insensitive to voltage, three could not be clustered as the degree of membership was

Table 4
MOA: Parameter groups and experimental sequences.

Ref.	Grouped parameters	Experimental profiles
[85]	4 clusters: (A) σ^{p}, c_{e}, κ, k_0^{p}, $E_{act}^{\mathrm{n}}k_0$, $E_{act}^{\mathrm{p}}k_0$, $E_{act}^{\mathrm{n}}D_e$, $E_{act}^{\mathrm{n}}\kappa_e$; (B) $\varepsilon_{\mathrm{e}}^{\mathrm{n}}$, $\varepsilon_{\mathrm{s}}^{\mathrm{n}}$; (C) $R_{\mathrm{s}}^{\mathrm{n}}$, $R_{\mathrm{s}}^{\mathrm{p}}$, $D_{\mathrm{s}}^{\mathrm{n}}$, $D_{\mathrm{s}}^{\mathrm{p}}$, $\varepsilon_{\mathrm{s}}^{\mathrm{p}}$, D_e, $\varepsilon_{\mathrm{e}}^{\mathrm{p}}$, $E_{act}^{\mathrm{n}}D_s$; (D) $R_{\mathrm{f}}^{\mathrm{n}}$, R_{ext}; (NC) θ_0^{n}, θ_0^{p}, k_0^{n}; (IS) σ^{n}, $R_{\mathrm{f}}^{\mathrm{p}}$, ρ_e, $\varepsilon_{\mathrm{e}}^{\mathrm{s}}$, $E_{act}^{\mathrm{p}}D_s$	Five different temperatures (-5, 10, 25, 40, 55) °C and five different discharge rates (0.2, 0.5, 1, 2, 4) C.
[83]	3 clusters: (A) $R_{\mathrm{s}}^{\mathrm{p}}$, $D_{\mathrm{s}}^{\mathrm{p}}$, c_{e}, R_{ext}, $\varepsilon_{\mathrm{e}}^{\mathrm{p}}$, k_0^{n}, k_0^{p}, $E_{act}^{\mathrm{n}}k_0$, $E_{act}^{\mathrm{p}}k_0$, $E_{act}^{\mathrm{n}}D_s$, $E_{act}^{\mathrm{p}}D_s$, λ; (B) $R_{\mathrm{s}}^{\mathrm{n}}$, $D_{\mathrm{s}}^{\mathrm{n}}$, σ^{p}, θ_0^{n}, $\varepsilon_{\mathrm{s}}^{\mathrm{n}}$, κ, $E_{act}^{\mathrm{n}}D_e$, h; (C) $\varepsilon_{\mathrm{s}}^{\mathrm{p}}$, $R_{\mathrm{f}}^{\mathrm{n}}$, D_e, $\varepsilon_{\mathrm{e}}^{\mathrm{n}}$, $\varepsilon_{\mathrm{e}}^{\mathrm{s}}$; (NC) θ_0^{p}, $E_{act}^{\mathrm{n}}\kappa_e$; (IS) σ^{n}, $R_{\mathrm{f}}^{\mathrm{p}}$, ρ_e	Five different temperatures (-5, 10, 25, 40, 55) °C and five different discharge rates (0.2, 0.5, 1, 2, 4) C.
[31]	Non-lumped parameters grouped according to the optimization groups (*1): (A) Related to OCV testing: $\theta_{0,coin}^{\mathrm{n}}$, $\theta_{100,coin}^{\mathrm{n}}$, $\theta_{0,coin}^{\mathrm{p}}$, $\theta_{100,coin}^{\mathrm{p}}$; (B) Related to pulse testing: $\kappa_{\mathrm{eff}}^{\mathrm{n}}$, $\kappa_{\mathrm{eff}}^{\mathrm{s}}$, $\kappa_{\mathrm{eff}}^{\mathrm{p}}$, $\sigma_{\mathrm{eff}}^{\mathrm{n}}$, $\sigma_{\mathrm{eff}}^{\mathrm{p}}$, k_0^{n}, k_0^{p}, $R_{\mathrm{f}}^{\mathrm{n}}$, $R_{\mathrm{f}}^{\mathrm{p}}$, θ_0^{n}, θ_0^{p}, $\theta_{100}^{\mathrm{n}}$, $\theta_{100}^{\mathrm{p}}$; (C) Related to frequency testing: $c_{\mathrm{e},0}^{n}$, $c_{\mathrm{e},0}^{s}$, $c_{\mathrm{e},0}^{p}$, $D_{\mathrm{e,eff}}^{\mathrm{n}}$, $D_{\mathrm{e,eff}}^{\mathrm{s}}$, $D_{\mathrm{e,eff}}^{\mathrm{p}}$, $D_{\mathrm{s}}^{\mathrm{n}}$, $D_{\mathrm{s}}^{\mathrm{p}}$, t_+^0	Experimental procedure (i) Half-Cell OCP data (coin cells) C/30 CC process; (ii) OCV/Rss data (full-cell) C/30 CC process; (iii) Full-cell frequency data; (iv) Full-cell R0 data (0.1 s pulses at different Crates). At different temperatures (0, 10, 25, 30, 40) °C.
[45]	SPM grouped parameters (*2): (A) Related to low-rate testing: Q^n, Q^p; (B) Related to pulse testing: $k_0^{*,\mathrm{n}}$, $k_0^{*,\mathrm{p}}$, R_{cell}; (C) Related to GITT testing: $D_{\mathrm{s}}^{*,\mathrm{n}}$, $D_{\mathrm{s}}^{*,\mathrm{p}}$	(i) Low rate tests; (ii) Pulse tests; (iii) Galvanostatic Intermittent Titration Technique (GITT) tests.
[38]	Grouped parameters: (A) Related to OCV testing:θ_0^{n}, θ_0^{p}, $\theta_{100}^{\mathrm{n}}$, $\theta_{100}^{\mathrm{p}}$, Q^n, Q^p; (B) Related to ohmic resistance and reaction polarization: P_{act}; (C) Related to diffusion processes: P_{con}, τ_s	Special operating condition with constant current charge/discharge of 6 minutes and 15 minute rest.
[51]	Grouped parameters: (A) $R_{\mathrm{s}}^{\mathrm{n}}$, $R_{\mathrm{s}}^{\mathrm{p}}$; (B) $D_{\mathrm{s}}^{\mathrm{n}}$, $D_{\mathrm{s}}^{\mathrm{p}}$, $\varepsilon_{\mathrm{e}}^{\mathrm{n}}$, κ, D_e, $\partial \ln f_{\pm}/\partial \ln c_{\mathrm{e}}$; (C) $R_{\mathrm{f}}^{\mathrm{n}}$, $R_{\mathrm{f}}^{\mathrm{p}}$, k_0^{n}, $\varepsilon_{\mathrm{e}}^{\mathrm{p}}$, $c_{\mathrm{e},0}$; (D) k_0^{p}, σ^{n}, σ^{p}, $\varepsilon_{\mathrm{e}}^{\mathrm{s}}$, t_+^0; Fixed parameters: L^{n}, L^{s}, L^{p}, A	738 different profiles: pulses, sinusoids and driving cycles.
[85]	2 clusters: (A) σ^{p},σ^{n},$\varepsilon_{\mathrm{e}}^{\mathrm{s}}$,$c_{\mathrm{e}}$ (B) rest of parameters	EIS and CC-CV

R_{ext}: extra resistance; E_{act}: activation energy; ρ_e: electrolyte density; λ: thermal conductivity; h: heat transfer coefficient; (NC): Not clustered, (IS): insensitive; (*1) For better understanding of the studied works, the original non-lumped parameters are presented in the table. However, to apply Jobman's methodology, parameters should be lumped as specified in (*2) $Q = FR_sa_sc_{s,max}$; $k_0^* = (k_0c_e^{0.5})/R_s$; $D_s^* = D_s/R_s$; R_{cell}: cell resistance. P_{act}: coefficient of anode reaction polarization; P_{con}: proportional coefficient of liquid-phase diffusion; τ_s: solid-phase diffusion time constant.

less than 0.6, and the remaining parameters were clustered into four groups. The authors concluded that the remaining 20 parameters are changeless during cycling or can be obtained directly (geometrical or material characteristics) and therefore were not included in the analysis. They grouped the parameters as a function of their sensitivity towards constant-current discharges at different temperatures. Among the studied experimental profiles they found that three profiles can be used as the "Best practicable Conditions" for parameter estimation: very low temperature/very high rate, room temperature/medium rate, and very high temperature/very high rate. To reduce the computation time, parallelized genetic estimation was proposed [84, 82]. [83] was based on [84], but several improvements in the methodology and the model were included. The thermal-electrochemical model (P2D) was coupled to a thermal impedance model, so as to simulate the thermal distribution in the radial direction of the cylindrical battery. A sensitivity analysis was performed for both voltage and temperature, and two additional parameters (related to thermal properties) were added to the analysis. Zhang et al. [83] grouped 30 parameters into three clusters as specified in Table 4. In this case, the degree of membership of non-clustered parameters was less than 0.5. The authors undertook a further step, using an MOA to implement a stepwise estimation process based on the results of the sensitivity analysis to decrease the computational time and overcome difficulties of low sensitivity parameter estimation. This stepwise experimental design consists of three steps, and the starting point values of the parameters was taken from the literature. In the first step, highly sensitive parameters are estimated based on the "Best Practicable Condition (BPC)", which corresponds to the condition that makes a cluster of parameters most sensitive (based on BCI results). The second step estimates the sensitive parameters in another BPC point, while highly sensitive parameters are taken from step 1, and low sensitivity

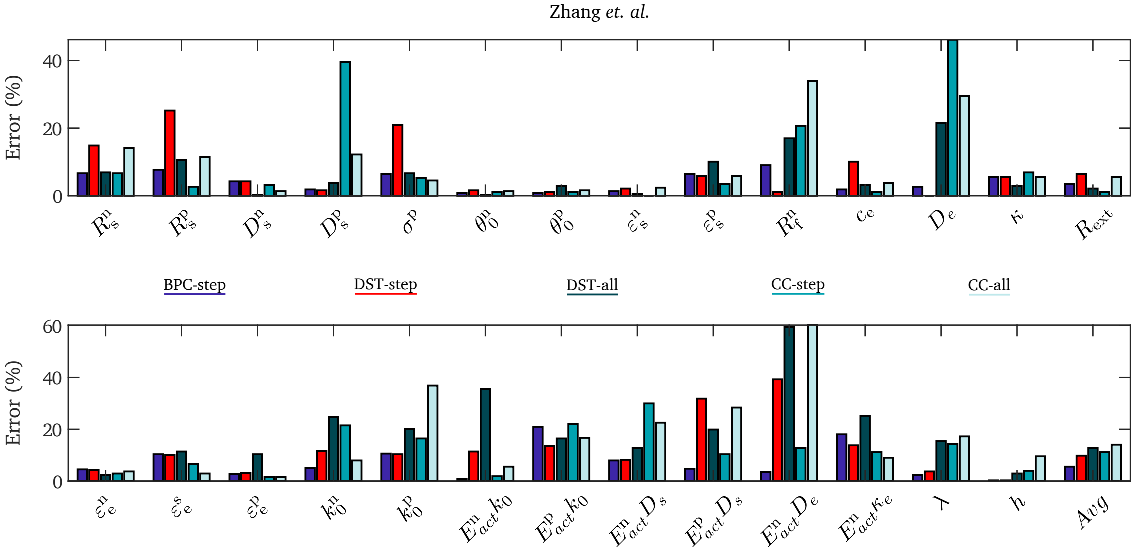

Figure 6: Comparison of relative errors in parameter estimation from [83] using best practicable conditions (BPCs) which corresponds to the conditions that make a cluster of parameters most sensitive, dynamic stress test (DST), or constant current (CC) experimental profiles. Stepwise (step) or non-stepwise estimation (all) are differentiated making reference to all in one and stepwise optimization procedures for the estimation sequence.

parameters are assigned benchmark values. Finally, in the third step, low sensitivity parameters are estimated. The best optimization results were obtained with this method. Except for two parameters with a maximum error of 20.86 %, the remaining parameter estimation error was 10 % or lower. The authors reported a comparison of the relative errors using different experimental profiles (shown in Figure 6). Furthermore, in [86] a multi-objective optimization approach based on genetic algorithms was proposed. DST profile at 15 and 30°C was used for estimation without parameter grouping or sequencing.

Jobman *et al.* [31, 30] and Chu *et al.* [9, 8] proposed an estimation process performed in a P2D model that was reformulated using lumped parameters. This makes parameter estimation possible and minimizes the number of independent parameters to the minimum. The lumped parameters were obtained by incorporating the influence of design adjustable parameters (L, A, a_s, ε_e, ε_s, R_s) into the remaining parameters so as to prevent crosslinked interactions in the parameter estimation process. The parameters were sequentially estimated using four steps, which use only cell voltage and current relationships. The sequenced experimental profiles used in this methodology are described in Table 4. The first set of tests collects slow C/30 dis/charge data from the electrodes and full-cell to determine open-circuit-potential and open-circuit-voltage relationships. The second set of tests obtains pulse responses from the cell at different initial SOC setpoints and pulse magnitudes, exploiting the nonlinearity of the instantaneous voltage response predicted by the cell model to determine 15 of the model parameter values. The third set of tests captures frequency-response data from the cell around different SOC setpoints, and uses electrochemical impedance spectroscopy (EIS) to determine the remaining model parameter values. A final set of tests gathers constant-current dis/charge data from the cell at different (slow) rates to exploit the nonlinearity of the steady-state response to refine the parameter values (especially those describing the electrolyte dynamics, which are technically identifiable, but which in practice quite insensitive). These tests are repeated for several temperatures, and Arrhenius relationships are fit to parameter values to create a model that describes the cell across the entire operating range. The reported errors for the full parameter set estimation are set out in Figure 7. All of the parameters were kept below 10.1% of error, except the $n_{e,0}$ terms (the lumped initial electrolyte concentration term). The author reported that this error could be refined further with a better optimization method. Chu *et al.* [8] further developed the work proposed by Jobman *et al.* using a reference electrode. In this way, the influence of negative and positive electrodes could be decoupled, allowing further isolation of equations (related to cell processes), and achieving a better determination of parameters. The results reported by Chu *et al.* (shown in Figure 8) significantly reduced the maximum errors observed by Jobman *et al.*: the error of parameter $n_{e,0}$ decreased from 114.7% to 18.6%. In addition, the accuracy obtained for a number of other parameters increased considerably.

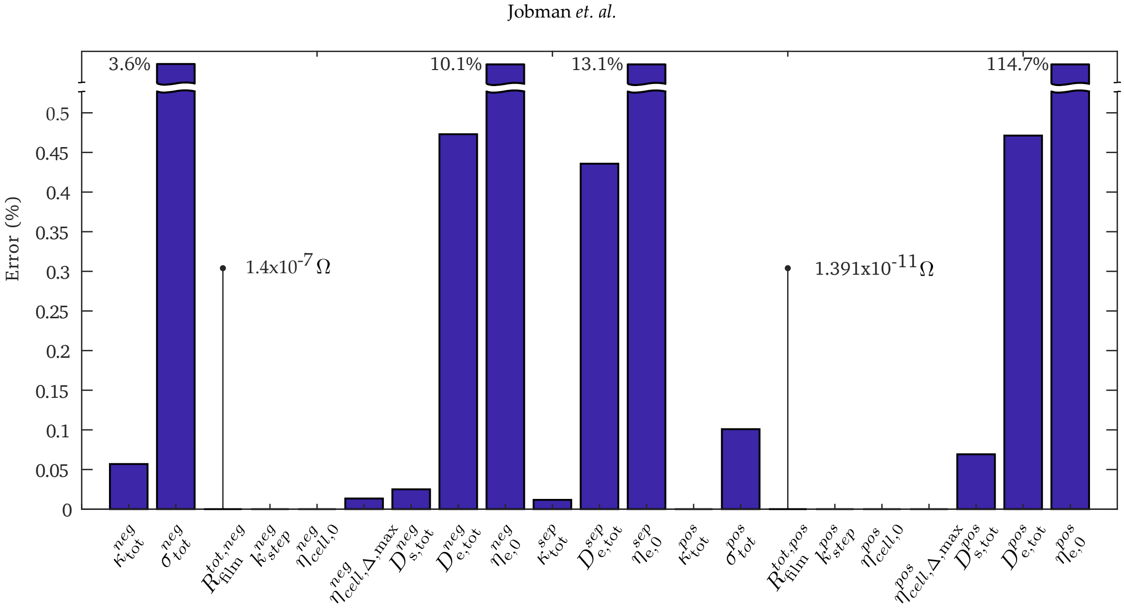

Figure 7: Parametric errors adapted from [31]. Note that parameters are labeled as in the reference.

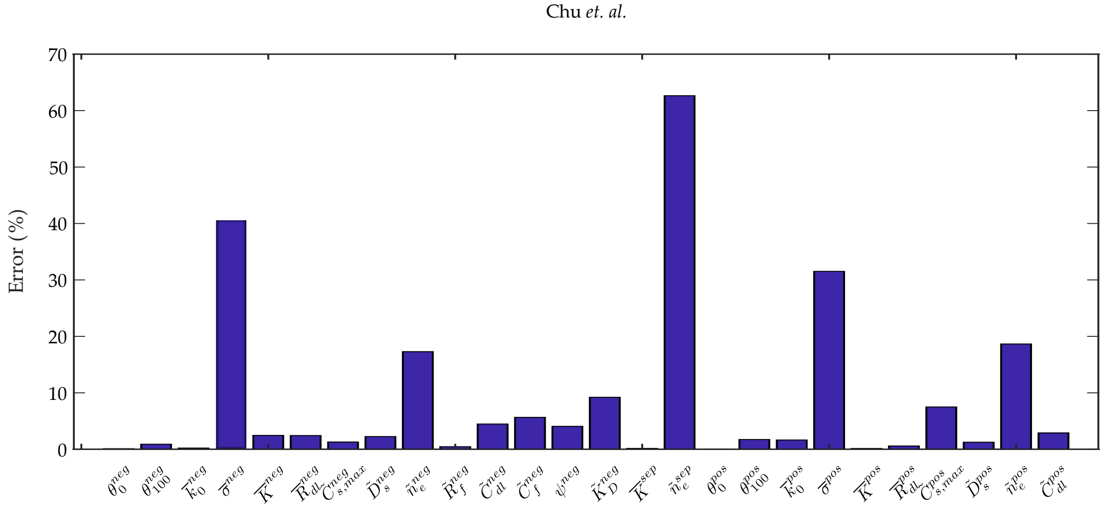

Figure 8: Parametric errors adapted from [8].

Namor et al. [45] performed a parameter estimation in a single-particle model using non-invasive testing (see Table 4). The SPM parameters were normalized and grouped reducing, the number of parameters to be estimated from 14 to 7. Three parameter groups were then defined, and each group was estimated separately based on the experimental test set out in Table 4. The maximum error was maintained below 22%, as illustrated in Figure 9.

Li *et al.* [38] adopted a simplified model with regrouped and reduced parameters based on SPM and their previous work. They grouped the parameters as presented in Table 4,in accordance with their proposed parameter estimation process. Three steps are defined in the methodology, in which 9 parameters are estimated with a specific pulsed profile. The stepwise procedure consist of estimation of parameters related to the open-circuit potential, ohmic resistance and reaction polarization, and diffusion processes. The fitting errors (shown in Figure 10a) remained below 20% for the worst case, and most parameter errors were negligible. The reduction of the model makes the optimization problem easier, due to the smaller number of parameters and the simpler model itself. However some information is lost, as the

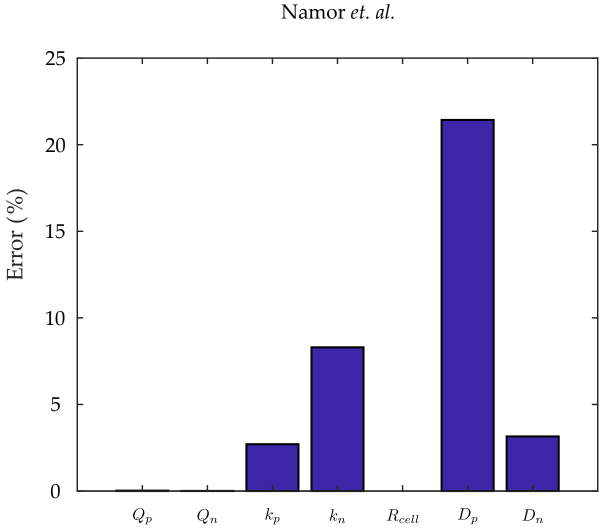

Figure 9: Parametric errors adapted from [45].

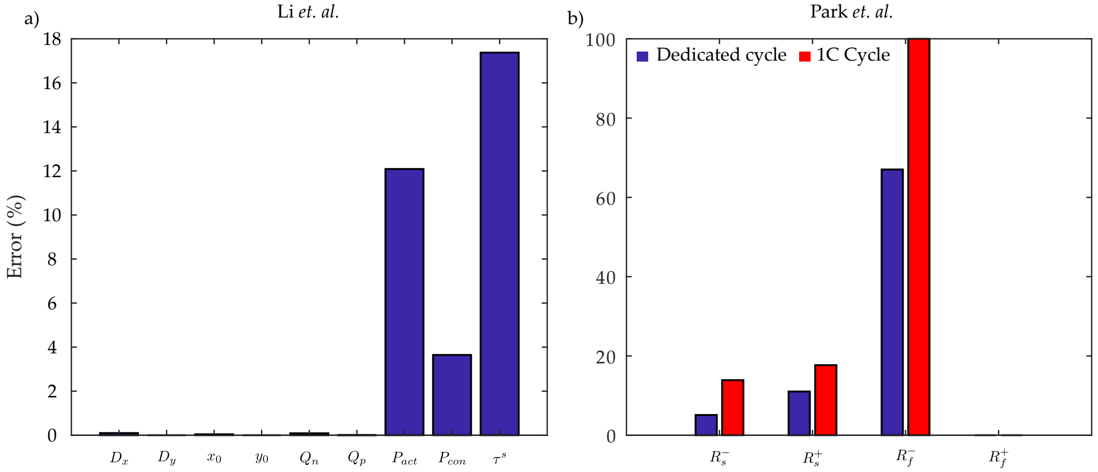

Figure 10: Parametric errors adapted from [38] (a) and [51] (b).

SPM is less rigorous than the P2D model.

Park *et al.* [51] used a similar methodology to [84, 83] in which the general P2D model was used [12]. First, a sensitivity analysis is performed across a variety of profiles including pulses, sinusoids and driving cycles. They generated a library gathering different input profiles oriented to maximize the sensitivity of model parameters. Then, a normalization is applied, and the linear dependence and sensitivity ranking is calculated. The parameter grouping is shown in Table 4. Finally, parameter fitting is obtained via a gradient-based algorithm. Figure 10b shows the error percentage using two different cycles (one dedicated and one typical 1C constant current [51]), with similar results. This work only reports the validation of estimation for four parameters, in which some errors are non-trivial.

Talukdar *et al.* [76] proposed a method based on EIS and cycling data. In this work the authors developed a two step procedure, in which a subset of parameters (Table 4) is first identified from EIS data. Then, CC-CV cycling data together with a suite of electrochemical models is used to fit the remaining parameters. As the electrochemical suite contains EIS and ROMs, a sensitivity analysis is used to fit each model to the most sensitive parameters. It is important to note that ROMs are a very useful tool, despite the fact that accuracy can be affected or some information compared to the P2D lost (depending on the authors terminology simplified models can also be presented as ROMs, what would imply a loss of information) these models are much faster. ROMs can be considered a very useful tool in that they

Talukdar *et. al.*

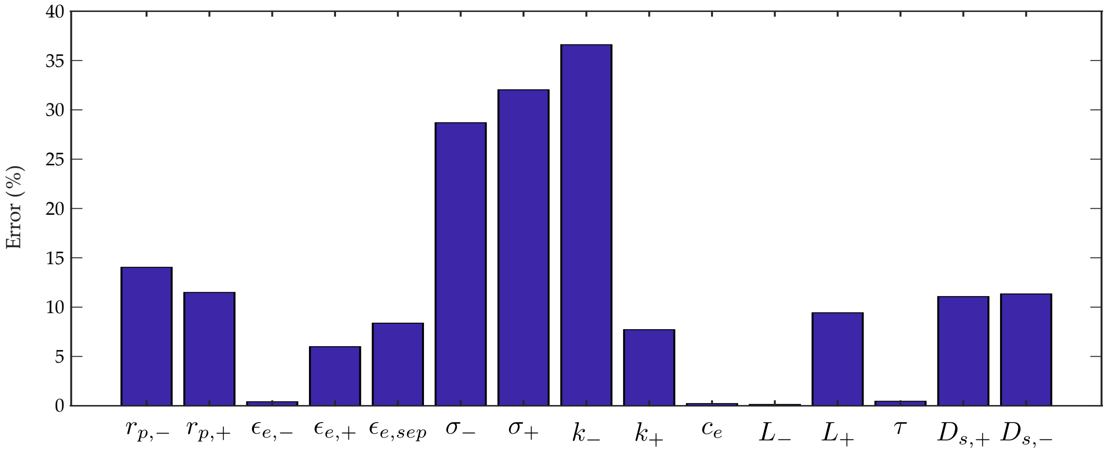

Figure 11: Parametric errors adapted from [76].

are much faster. However they do present drawbacks when compared to P2Ds: accuracy can be affected or some information lost. It should be noted however, that some simplified models can also be presented in the literature as ROMs, which would imply a loss of information. The speed of ROMs enables more simulated scenarios at the same time, or faster optimization procedures, which can subsequently be refined with full order models (FOMs) [23]. Figure 11 shows the results reported by Talukdar *et al.*, the identified parameters are in line with the reference values overall, with a maximum estimation error of 14.06% and a minimum of 0.14%.

5. Conclusions and avenues for future investigation

The present paper highlights the potential use of PBMs to control cell degradation in BMSs. To achieve accurate predictions however, proper parameter estimation of these models is critical. For this reason a review of current approaches to paramater identification is presented.

Parameter estimation approaches based on computational methods have been classified within two different groups: single-optimization analysis and multi-optimization analysis (SOA and MOA). Studies with reliable proof of parameter estimation were analysed for both groups, and significant differences were found depending on the method used. Some of the SOA methods reported good accuracy, but did not fully parameterize a P2D model (only partial sets of parameter values were estimated). On the other hand, authors using MOA obtained accurate parameter estimations for both SPM and P2D models. These latter either reformulated the models using analytic parameter lumping, or used optimization routines to group parameters based on sensitivity tests. The analytic method would appear to deliver more accurate results than the sensitivity based method, but is only able to find values for groups of parameters and not for every individual parameter.

If the objective of parameter estimation is to develop a cell model that can predict cell internal states and voltage, then there is no need to de-lump parameters that have been identified in a lumped form. Simulations of the lumped model will give identical predictions of internal states and voltage to simulations of the de-lumped model. However, if there is also a desire to understand cell design characteristics, then an interesting future avenue of investigation would be to develop methods to de-group lumped sets of parameters. This might involve introducing physico-chemical tests, introducing different sensors (e.g., magnetic in the case of iron-phosphate cells, reference electrodes in a commercial cell [52], or stress/strain in a more general setting) to obtain a richer dataset. One further approach could be to design more specific identification tests (perhaps based on observed rates of aging) to estimate key parameters that can be used to free the full set. Furthermore the definition of mixed methods, comprising physico-chemical tests and model-based fitting identification could also prove to be an effective approach. Not only to de-group lumped parameter models but to define more efficient methodologies, reducing the time and cost of the identification procedure while increasing the accuracy.

Additionally, there do not appear to be proofs in the literature even that models that perfectly match the input–output dynamics of a lithium-ion cell will actually match the input–state dynamics. That is, models may predict voltage and/or temperature well, but we are not aware of literature that guarantees that the parameter estimates are non-ambiguous and that the internal electrochemical variables (e.g., lithium concentrations and internal potentials) are correctly estimated. Mixed methodologies can be in this context a very useful tool, since not only precise parameters estimation, but also accurate state and voltage prediction is considered. These methodologies then, would be more robust to error caused by both, parameters and model assumptions. It is important to have assurance that these internal variables are being correctly modeled before PBMs can be used with confidence in BMS applications.

6. List of symbols

Table 5
Symbols and descriptions.

Symbol	Description
L^s, L^n, L^p	Length of the separator, negative and positive electrodes
A	Total cell area
R_s^n, R_s^p	Particle radius negative and positive electrode
σ_{eff}^n, σ_{eff}^p	Negative and positive solid phase conductivity
$\kappa_{eff}^n, \kappa_{eff}^s, \kappa_{eff}^p$	Electrolyte conductivity
ε_e^n, ε_e^s, ε_e^p	Separator, negative and positive liquid phase volume fraction
ε_s^n, ε_s^p	Negative and positive solid phase volume fraction
a_s^n, a_s^p	Negative and positive specific surface area
D_s^n, D_s^p	Li-diffusivity in negative and positive matrix
k_0^n, k_0^p	Negative and positive reaction rate coefficient
α^n, α^p	Charge transfer coefficient
E_{act}	Activation energies
$D_{e,eff}^n, D_{e,eff}^s, D_{e,eff}^p$	Salt diffusivity in the electrolyte
t_+^0	Transport number
$c_{e,0}$	Initial electrolyte concentration
$c_{s,max}^n$, $c_{s,max}^s$, $c_{s,max}^p$	Initial, max and min solid phase concentrations
R_f^n, R_f^p	Film resistance of negative and positive electrode
θ_0^n, θ_{100}^n	Initial and final negative electrode state of lithiation
θ_0^p, θ_{100}^p	Initial and final positive electrode state of lithiation
$\partial \ln f_\pm / \partial \ln c_\mathrm{e}$	Electrolyte activity coefficient ln derivative

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