An Inverse Method for Estimating the Electrochemical Parameters of Lithium-Ion Batteries

I. Methodology

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An electrochemical Parameter Estimation (PE) study of lithium-ion batteries for different materials is presented. The PE methodology is developed in Part I of the study and the challenges on the different materials for the positive electrode including LiCoO 2, LiMn 2O 4 and LiFePO 4 are examined in Part II. The most influential electrochemical parameters of the Li-ion battery are estimated by means of an inverse method. The inverse method rests on five elements: the input parameters, a direct model, the reference data, an objective function and an optimizer. Eight electrochemical variables are considered as the target of the PE study. A simplified version of Pseudo-two-Dimensional (P2D) model is developed for the direct model. The P2D model predictions coupled to a random noise function are employed to generate the reference data. The data include the cell potential values with respect to the battery capacity at low and high discharge rates. The least-squared function and Genetic Algorithm are employed as the objective function and its optimizer, respectively. The best time domain for the estimation of each parameter is calculated by using a sensitivity analysis performed for different discharge curves. Results show that the methodology remains accurate and stable at both low and high discharge rates.

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The simultaneous high power and energy density of Lithium-ion (Li-ion) batteries have made it the preferred device for storing electricity. As a result, Li-ion batteries are increasingly used in various applications including electronics and the automotive industry. Regardless of the shape and of the battery pack arrangement, the internal structure of the battery usually comprises four main components: Two electrodes, positive and negative, an electrolyte, and a separator. These components are made of materials that have been gradually modified over the years so as to improve the efficiency, the safety and the performance of the batteries and to reduce their cost. 1–3 A Battery Management System (BMS) is crucial for monitoring the operation of the battery pack. The BMS must interact with all the elements of the system in order to control it and to protect the Li-ion cells. The intelligence of the BMS is based on a mathematical model that simulates and predicts the different operating conditions of the Li-ion battery pack. In high tech and automotive industries, the BMS usually relies on empirical-based models. These models are simple and provide fast response. They cannot however predict the performance of the battery as it ages. Moreover, they are only applicable to a specific cell, i.e., they cannot be transposed to other battery packs without recalibration. 1–6

Electrochemical-based models of Li-ion batteries, on the other hand, overcome these shortcomings. These models rest on chemical/electrochemical kinetics and transport equations. These Li-ion battery models are more complicated and CPU time-consuming than empirical based models. They are, on the other hand, more versatile and they provide reliable and stable responses in a wide range of operating conditions and applications. Among the electrochemical Li-ion battery models, the Pseudo-two-Dimensional (P2D) model and the Single Particle Model (SPM) appear to be the most popular. 2,5,8 The P2D model rests on (1) the porous electrode theory; (2) the concentrated solution theory; and (3) the kinetics equations. Its predictions are accurate and have shown repeatedly good agreement with experimental data. 2,7,9 The SPM, on the other hand, is a simplified version of the P2D model. The SPM ignores the change in the electrolyte properties. As a result, the CPU time of the SPM is much less than that of the P2D model. 7,10

In order to run the electrochemical-based mathematical models, it is imperative to know the different electrochemical parameters of the battery. Experimental measurement of these parameters is a challenging task. Sometimes it requires the dismantling of the battery itself. Also, some parameters need to be monitored continuously due to the fact that they change as the battery ages. In order to overcome the difficulties of experimental measurements, various research strategies for parameter estimation (PE) have been deployed. Table I summarizes the characteristics of the Parameter Estimation (PE) studies that have been applied to Li-ion batteries. 3,4

In 2004, a PE study of a polymer electrolyte membrane fuel cell (PEMFC) cathode was presented by Guo et al. 11 Based on this research, five internal parameters of the Li-ion battery were estimated by Santhanagopalan et al. in 2007. These parameters are the diffusivity of Li + ions in the positive electrode (D s,p), the reaction rate constants at the electrodes/electrolyte interface (K n and K p) and the initial State Of Charge of negative and positive electrodes (SOC n,0 and SOC p,0). The calculation procedure was implemented by minimizing the least squares objective function with the Levenberg-Marquardt (LM) technique. Note that the objective function is defined here as the difference between the predictions of the direct model and the experimental data for the charge/discharge (up to 2C). Both the SPM and the P2D model were employed as the direct model. The PE results showed that the SPM is reliable for low discharge rates (< 1C), while the P2D model remains accurate over the entire range of discharge rates. The CPU time of the PE process for the P2D model is however prohibitive compared to that of the SPM. 12

In 2008, Santhanagopalan et al. made an attempt at estimating some inner parameters of the Li-ion battery in order to quantify its capacity fade. The SPM was used as the direct model to estimate the SOC of the negative and positive electrodes (SOC n,0 and SOC p,0) and the active material loading of electrodes (w n and w p). Experimental data were collected after five charge/discharge cycles (0, 100, 200, 300, 400, and 500) under different temperature conditions. The results showed good agreement with available discharge curves. No predictions were made however for the future battery curves. 13

In 2011, Ramadesigan et al. investigated the effect of five different parameters on the Li-ion battery capacity fade by means of discharge curves of different charge/discharge cycles. These parameters are the diffusion coefficients D s,n and D s,p, and the electrochemical reaction rate constants for negative and positive electrodes (K n and K p).

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were estimated from discharge curves under different temperature curve. Second, resistance parameters related to their reduced model of the electrodes were determined by using an open circuit potential
batteries parameters in three steps. First, the composition characteristics
experimental data for the geometry and the material characteristics.
information. The predictive method could be improved with more accurate
to the fact that several Li-ion battery parameters are not identifiable
charge curves and the predicted surface temperature profiles showed
predictions, an objective function is minimized by virtue
model. Based on the difference between the experimental data and
characteristics were determined based on the charge/discharge curves.15 Due
optimization approach was chosen to estimate six parameters, namely
optimization method.
The authors employed a simplified version of the P2D model as the di-
rate. The Gauss-Newton technique was adopted for minimizing the sum-of-squared differences of the objective function. The results revealed that the negative electrode properties are most influential on the battery aging process.14
Forman et al. implemented a full parameter estimation using the P2D model as the forward model and a Genetic Algorithm (GA) as its optimizer. A total of 88 operational parameters and geometric character-
stics were determined based on the charge/discharge curves.15 Due to the fact that several Li-ion battery parameters are not identifiable with performance curves, this method can only provide a rough estimation. The predictive method could be improved with more accurate experimental data for the geometry and the material characteristics.
In 2013, Marcicki et al. used curve fitting to identify the Li-ion bat-
tary parameters in three steps. First, the composition characteristics of the electrodes were determined by using an open circuit potential curve. Second, resistance parameters related to their reduced model were estimated from discharge curves under different temperature conditions. And third, the diffusion coefficients were estimated by tuning the model parameters.16
In 2014, Zhang et al. conducted a multi-objective PE by virtue of the discharge curves and the surface temperatures of Li-ion batteries based on LiCoO2 and LiFePO4. The modified multi-objective genetic algorithm was employed to estimate 25 parameters. The simulated discharge curves and the predicted surface temperature profiles showed good agreement with experimental data for low discharge curves.17
In 2015, Masoudi et al. presented another PE study for Li-ion bat-
tery based on a reduced order model of the P2D model. The homotopy
optimization approach was chosen to estimate six parameters, namely the volume fraction of the separator (εs), the Li+ transference number (t+), the electrical conductivity of the solid phase of the negative electrode (σs), and the initial electrolyte concentration in three regions. The predictions of the P2D model showed good accuracy for low discharge rates.18
Recently, Rahman et al. identified four electrochemical variables of a Li-ion battery based on LiCoO2. A Particle Swarm Optimization (PSO) was used as the optimizer and, a reduced P2D model was employed as the direct model. The PE study was carried out however with a low discharge curve only (1C).19
The present paper extends the aforementioned studies by purposing a new and a general inverse PE method to identify different electrochemical parameters of Li-ion batteries. The method is applicable to both low and high discharge rate curves and to different positive electrode materials. The PE methodology is based on (1) a simpli-
fied version of the P2D model; (2) sensitivity curves of all expected parameters; and (3) an inverse method.
Inverse methods have been applied in many problems of science and engineering. These methods identify the system characteristics by means of specific experimental data and predictions from a direct model. Based on the difference between the experimental data and the model predictions, an objective function is minimized by virtue of an optimizer.20,21 The present inverse methodology comprises five elements: the input electrochemical parameters, the direct model, the reference data, the objective function and the optimizer. These elements are described next.
Eight electrochemical variables were selected as the target for the PE study. These variables are the solid diffusion coefficients (Ds,n and Ds,p), the intercalation/deintercalation reaction-rate constants (Kn and Kp), the initial SOC (SOCn,0 and SOCP,0), and the electroactive surface areas (Sx,n and Sx,p). All these variables are identifiable based on the Li-ion direct models. Their values are required for simulating the battery performance and for predicting the aging process. Also, to improve the accuracy of the predictions, the geometric and the material characteristics were assumed to be known. These parameters are usually available from the manufacturers of Li-ion batteries. They can also be determined experimentally.
To account for low as well as for high discharge curves, it is imperative to rely on a direct model that simulates the experimental data. Moreover, due to the numerous back and forth calls in the PE process, the direct model should be computationally efficient and fast. As a result, a simplified version of the Pseudo-two-Dimensional (P2D) model was developed as the forward model. This model exhibits three main features: (1) It is accurate, i.e., it takes into account the electrolyte properties; (2) it is fast. The calculation procedure has been optimized; and (3) it is flexible. The number of unknown coefficients to be determined in the PE process is variable.
In this work, the reference data for the PE study are generated with the P2D model. These data include the cell potential values with

Table I. Parameter Estimation (PE) studies on Li-ion batteries.

| Author          | Battery Material | Estimated Parameters | Cycle rate | Direct Model | Optimizer | Extra Description                                      |
|-----------------|------------------|----------------------|------------|--------------|-----------|--------------------------------------------------------|
| Zhang et al., 201417 | LiFePO4, LiCoO2 | All related Parameters | C/2, 1C, 1.5C, 2C | P2D | GA | Using Fisher information to improve the accuracy of the predictions, the geometric and the material characteristics were assumed to be known. These parameters are usually available from the manufacturers of Li-ion batteries. They can also be determined experimentally. |
| Masoudi et al., 201518 | - | cε,n,0, cε,p,0, cε,s,0, σs, t+, εs | 1C | Reduced P2D | Homotopy O. M. | Using full-order model outputs as the reference in objective function |
| Rahman et al., 201619 | LiCoO2 | Ds,n, Ds,p, Kn, Kp | 1C | Reduced P2D | PSOb | Using PSO for parameter estimation |

aLevenberg-Marquardt method. bGenetic Algorithm. cParticle Swarm Optimization. dHomotopy optimization method.
Electrolyte

The kinetics equations.9,26 The P2D model has been extensively used on the porous electrode theory, the concentrated solution theory and most popular electrochemical-based models. The P2D model rests on the battery theory.24,25 Unfortunately, their range of applications is limited. For instance, the equilibrium battery is that they are computationally fast and relatively simple. The battery characterizations are not updated as the battery ages. Also, the empirical model pertaining to a specific battery cannot be transposed to other types of batteries.24,25

Electrochemical models are, on the other hand, more sophisticated. These models are based on chemical/electrochemical kinetics and transport equations. They may be used to simulate the Li-ion battery characteristics and reactions.7 The Pseudo-two-Dimensional (P2D) model and the Single Particle Model (SPM) are among the most popular electrochemical-based models. The P2D model rests on the porous electrode theory, the concentrated solution theory and the kinetics equations.9,20 The P2D model has been extensively used in Li-ion battery investigations.25 Its predictions are accurate and it has shown repeatedly good agreement with experimental data.25,28 In order to reduce the computational times, a simplified version of the P2D model, called the SPM, has been developed. In the SPM, the electrolyte properties are ignored and the transport phenomena are treated in a simple manner.10

In this paper, the PE study is implemented using both low and high discharge curves based on the inverse method. The optimization process is carried out iteratively. On one hand, the P2D model is unquestionably rigorous but it is too complicated and slow. The SPM, on the other hand, provides quick responses but it is inaccurate for simulating high discharge rates and thick electrodes. Therefore, a simplified version of the P2D model is proposed as a compromise between complexity and accuracy for the PE process.

The P2D model.—In 1993, Doyle et al. introduced the Pseudo-Two-Dimensional (P2D) model for Li-ion batteries using a combination of the porous electrode theory and the concentrated solution theory. To this day, this model remains the most popular Li-ion battery model. It has been thoroughly tested and validated.26 Fig. 1 depicts the structure used in this model. The electrodes are considered as a porous matrix. Their behavior is modeled with spherical particles surrounded by the electrolyte. The intercalation and the de-intercalation processes of the Li-ions are performed through the surface area of these particles. Also, the transfer processes are predominantly unidirectional. Consequently, a 1-D mathematical model (x axis) may be applied.29

The governing equations of the P2D model are reported in Table II. The main features of these equations are: (1) The solid-state Li+ ion concentration (ci) in the electrodes is derived from the Fick’s law

![Figure 1. The Li-ion battery P2D model.](image)

| Region            | Eq. no. | Governing equations                                      |
|-------------------|---------|----------------------------------------------------------|
| Electrodes (k = n, p) | [1]     | \( \frac{\partial c_i(x,t)}{\partial t} = \frac{D_{ij}}{r^2} \frac{\partial^2 c_i(x,t)}{\partial r^2} \) |
|                   | [2]     | \( \frac{\partial c_i(x,t)}{\partial r} = \frac{1}{r} \frac{\partial}{\partial r} (D_{ij} \frac{\partial c_i(x,t)}{\partial r}) + \alpha (1 - \phi_i J_i(x,t) \) |
|                   | [3]     | \( \alpha \frac{\partial J_i(x,t)}{\partial x} = \alpha F J_i(x,t) \) |
|                   | [4]     | \( -\alpha \frac{\partial \Phi_i(x,t)}{\partial x} - \kappa \frac{\partial J_i(x,t)}{\partial x} + \frac{2 \alpha J_i R T}{\phi_i (1 - \phi_i)} \ln \phi_i = I \) |
|                   | [5]     | \( J_i(x,t) = K_i (c_{li}^{\max} - c_i^{\text{surf}}) \frac{\partial c_i^{\text{surf}}}{\partial x} + 0.5 \frac{\partial c_i^{\text{surf}}}{\partial x} [\exp(0.5 R T/c_i^{\text{surf}}) - \exp(-0.5 R T/c_i^{\text{surf}})] \) |
|                   | [6]     | \( \frac{\partial c_i(x,t)}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} (D_{ij} \frac{\partial c_i(x,t)}{\partial r}) \) |
|                   | [7]     | \( -\kappa \frac{\partial \Phi_i(x,t)}{\partial x} + \frac{2 \alpha J_i R T}{\phi_i (1 - \phi_i)} \ln \phi_i = I \) |

*Table II. The governing equations of P2D Model.*

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of diffusion for spherical particles; (2) The liquid-phase Li\(^+\) ions concentration \((c_n)\) in the electrolyte and in the separator is based on the conservation of Li\(^+\) ions; (3) The solid-state potential \(\Phi_s\) in the electrodes is derived from Ohm’s law; (4) The liquid-phase potential \(\Phi_l\) in the electrolyte and in the separator is calculated using Kirchhoff’s and Ohm’s laws; (5) The pore wall flux of Li\(^+\) ions \((J)\) in the electrodes is described by the Butler-Volmer kinetics equation.\(^{3,29}\)

### The Single Particle Model (SPM).

In 2000, Zhang et al. proposed a simplified version of the P2D model known as the Single Particle Model (SPM) for Li-ion batteries. The SPM rests on two main assumptions: First, each electrode is modeled as a spherical particle in which intercalation and de-intercalation phenomena occur. Second, variations of the electrolyte concentration and potential are ignored.\(^{30}\) Equations 1 and 5 of Table II are the governing equations of the SPM. These equations comprise the solid-state concentration and the Butler-Volmer kinetics equations at both negative and positive electrodes. By using these equations, the cell potential function of the Li-ion batteries can be determined as:\(^{31}\)

\[
V_{cell} = (U_p - U_n) + \frac{2RT}{F} \ln\left(\frac{m_n^+ + m_p^+}{2}\right)
+ \frac{2RT}{F} \ln\left(\frac{m_n^- + m_p^-}{2}\right) \tag{8}
\]

\[
m_p = \frac{I}{FK_p} S \frac{c_{p,x}^{\text{max}}}{\epsilon} \left(1 - SOC_p\right) \left(SOC_p\right)^{\alpha-5} \tag{9}
\]

\[
S_p = \frac{3\epsilon_p V_p}{R_p}, \quad SOC_p = \frac{c_{p,x}^{\text{surf}}}{c_{p,x}^{\text{surf}} + c_{p,x}^{\text{diff}}} \tag{10}
\]

\[
SOC_k = SOC_{k,0} - \frac{J_k}{c_{k,x}^{\text{max}}} \left[ \frac{3}{2} \frac{D_{k,0}}{R_k^2} \tau_k + 1 + \frac{2}{\lambda_k^2} \exp\left(-\frac{\lambda_k^2 D_{k,0} t}{R_k^2}\right) \right];
\sin(\lambda_k) - \lambda_k \cos(\lambda_k) = 0 \tag{11}
\]

The main advantages of the SPM are: (1) it is a simple model; (2) its solution requires minimal computational effort; (3) it can serve many purposes such as online estimation\(^{19}\) and life modeling\(^{32}\) of Li-ion batteries. Its main drawback is that it must be fine-tuned according to the electrolyte properties in thick electrodes and at high discharge rates.\(^7\)

### The simplified P2D model.

Several efforts have been deployed in the development of simplified models of Li-ion batteries. The complex governing equations of P2D model are reduced by using different mathematics- and physics-based techniques.\(^{3,33}\) In this paper, a reduced Li-ion battery model for the PE process is proposed. Two assumptions are made: first, the wall flux value in the electrodes \((J_k, I_k, L_p, L_s)\) is considered constant like in the SPM; second, a linear function (Eq. 12) is employed to describe the electrolyte concentration behavior as respect to the operation time and the position in three regions: the cathode, the separator, and the anode.

\[
c_{e,x}(x, t) = A_{1k}(t) x + A_{2k}(t); \quad k = p, s, n, \quad 0 \leq x \leq L \tag{12}
\]

\(A_{1k}\) and \(A_{2k}\) are assumed to be the time-dependent coefficients. The lengths \(L_p, L_s, L_n\) are illustrated in Fig. 1. Applying the first assumption to the solid potential equation (Eq. 3) and to its boundary conditions, the constant wall fluxes may be calculated as follows:

\[
J_p = \frac{I}{a_p L_p}; \quad 0 \leq x \leq L_p \tag{13}
\]

\[
J_s = \frac{-I}{a_p L_p}, \quad L_p < x \leq L \tag{14}
\]

Moreover, the first derivative of the solid potential function with respect to \(x\) are determined as follows:

\[
\frac{d\Phi_s(x, t)}{dx} = \frac{I}{a_p L_p} \left( x \left( L_p - 1 \right) \right); \quad 0 \leq x \leq L_p \tag{15}
\]

\[
\frac{d\Phi_s(x, t)}{dx} = \frac{I}{a_p L_p} \left( -x + L_p + L_s \right); \quad L_p < x \leq L \tag{16}
\]

Eqs. 17 to 19 are immediately obtained by substitution of the second assumption into Eqs. 2 and 6, that is,

\[
\frac{dA_{1k}}{dt} = 0; k = p, s, n, \tag{17}
\]

\[
\frac{dA_{2k}}{dt} = \frac{a_p (1 - t_n) J_k}{\epsilon_k}; k = p, s, n \tag{18}
\]

By using the boundary conditions of the electrolyte concentration profiles given by Eqs 20 and 21, the values of the \(A_{1k}\) are equal to zero as shown in Eq. 22.

\[
-D_p \frac{dc_{e,p}(x, t)}{dx} \bigg|_{x=0} = -D_p \frac{dc_{e,n}(x, t)}{dx} \bigg|_{x=L} = 0 \tag{20}
\]

\[
-D_p \frac{dc_{e,p}(x, t)}{dx} \bigg|_{x=L_p} = -D_p \frac{dc_{e,s}(x, t)}{dx} \bigg|_{x=L'_s} = 0 \tag{21}
\]

\[
A_{1k} = 0; k = p, s, n \tag{22}
\]

Therefore, the electrolyte concentration profiles are computed by substituting Eqs. 18, 19 and 22 into Eq. 12.

\[
c_{e,p}(t) = \frac{a_p (1 - t_n) J_p t}{\epsilon_p} \left( \frac{1 - t_s}{\epsilon_p F L_p} \right); \quad 0 \leq x \leq L_p \tag{23}
\]

\[
c_{e,s}(t) = \text{Constant}; \quad L_p \leq x \leq L_p + L_s \tag{24}
\]

\[
c_{e,n}(t) = \frac{a_n (1 - t_n) J_n t}{\epsilon_n} \left( \frac{1 - t_s}{\epsilon_n F L_n} \right); \quad L_p + L_s \leq x \leq L \tag{25}
\]

With the help of Eqs. 12 to 24 and the electrolyte potential governing equations (Eqs. 4 and 7), we get:

\[
\Phi_{e,p}(x, t) = \Phi_e(0) - I \left( \frac{x^2}{2k_{eff,p} L_p} \right); \quad 0 \leq x \leq L_p \tag{26}
\]

\[
\Phi_{e,s}(x, t) = \Phi_e(0) - I \left( \frac{x - L_p}{2k_{eff,s}} + \frac{L_p}{2k_{eff,s}} \right); \quad L_p \leq x \leq L_s + L_p \tag{27}
\]

\[
\Phi_{e,n}(x, t) = \Phi_e(0) - I \left( \frac{L_p}{2k_{eff,n}} + \frac{L_s}{2k_{eff,n}} - \frac{(x - L_p)^2 + L_s^2}{2k_{eff,n} L_n} \right); \quad L_s + L_p \leq x \leq L \tag{28}
\]
The conductivity for the liquid/salt/polymer is approximated with a polynomial function of the form:\textsuperscript{34}
\[
\kappa_{eff,s}(x, t) = \exp\left( a_0 + \sum_{j=1}^{L} a_j x_j \right); \ 0 \leq x \leq L
\]
where \( a_j \) are constant coefficients for all regions. By incorporating Equations 15 to 28, the following electrolyte potential drop function between the positive and the negative electrodes is proposed:
\[
(\Phi_+ - \Phi_-)(0, t) \approx IR_{cell} + \epsilon
\]
where \( I \) is the current, \( R_{cell} \) is the cell resistance, and \( \epsilon \) represents the additional potential drop not accounted for by the cell resistance. The new constant coefficients \( (a_j) \) are determined by the PE procedure and the simulated annealing method.\textsuperscript{36}

**Parameter Estimation Process**

**Inverse method.**—Inverse methods are used for the PE of a system or for its functional identification. In the former, the unknown parameters can be estimated by means of experimental data. In the latter, the unknown functions can be determined in a finite or an infinite dimensional space.\textsuperscript{20} The solution methods for inverse problems are usually more complicated than for direct problems. Direct problems are well-posed problems. The conditions that must be satisfied in a well-posed problem are that (1) the solution must exist; (2) it is unique and (3) it must be a continuous function. Inverse problems are, on the other hand, ill-posed problems. The solution of most inverse problems is highly dependent on the initial condition and on the boundary conditions as well as on the measured signals. There have been numerous attempts to tackle these difficulties and to convert inverse problems into well-posed problems.\textsuperscript{20,21,35}

In PE problems, the experimental signals play a key role in finding the expected parameters. These parameters must be measurable and accurate when compared with the direct model. In the identification of the Li-ion battery parameters, the time-varying cell potential values can be measured during the charge/discharge process. Fig. 2 illustrates the relationship between the different elements of a PE study based on an inverse method. The objective function is defined here as the difference between the experimental data and the predictions of the direct model. A mathematical optimizer is employed to minimize the objective function so as to find the best values of the expected parameters.

**PE equations.**—The inverse problem of the Li-ion battery can be defined as a “whole time domain” approach. This means that the experimental data can be measured in the small time interval between zero to cutoff time \((0 < t \leq t_c)\). The experimental data vector \( \mathbf{V}_{cell,m} \) relates to one charge/discharge process with \( N \) time intervals as shown in Eq. 32:
\[
\mathbf{V}_{cell,m} = \begin{bmatrix} V_{cell,1}^* \\
V_{cell,2}^* \\
\vdots \\
V_{cell,N}^* \end{bmatrix} ; t = t_1, t_2, \ldots, t_N
\]

The measurement of random errors is always a concern in the solution of inverse problems. The stability of the inverse method is sensitive to these errors. The solution technique for the inverse problem should be stable with the measurement errors and for small time intervals.\textsuperscript{20,35} In order to develop the mathematics for the inverse method, it is assumed that the measurement error \( (\epsilon_t) \) is a random and additive variable:
\[
\epsilon_t = \mathbf{V}_{cell,m}^* - \mathbf{V}_{cell,m} ; t = t_1, t_2, \ldots, t_N
\]

The objective function (S) is defined as the ordinary least-squares function of the measured data \( \mathbf{V}_{cell,m}^* \) and the calculated values \( \mathbf{V}_{cell} \):\textsuperscript{20}
\[
S = (\mathbf{V}_{cell,m}^* - \mathbf{V}_{cell}^*)^T (\mathbf{V}_{cell,m}^* - \mathbf{V}_{cell}^*) = \sum_{i=1}^{N} (\mathbf{V}_{cell,m,i}^* - \mathbf{V}_{cell,i}^*)^2
\]

The objective function 28 is usually stable when only few parameters are unknown. It may become unstable when the inverse process involves a larger number of unknown parameters. The instability is then reduced by adding regularization terms to the least-square objective function like Tikhonov’s regularization and Alifanov’s iteration regularization methods.\textsuperscript{39} The expected parameters are estimated by solving the following optimization problem:
\[
\min S = S(\mathbf{P}) \text{ subject to } P_{j,\text{low}} \leq P_j \leq P_{j,\text{high}} \quad \text{[36]}
\]

\( P_{j,\text{low}} \) and \( P_{j,\text{high}} \) are the minimum and maximum of the \( P_j \) values respectively. Eq. 36 is solved for the unknown vector \( \mathbf{P} \) as the system parameters. This process is implemented with an appropriate optimizer that finds the problem global minimum.

**The optimization process.**—Due to the numerous parameters used in the objective function of the present PE study, there may be several local minimums in the vicinity of the global minimum. As a result, the optimization process for the inverse problem is mathematically challenging, slow to converge and computationally expensive.\textsuperscript{21} Colaço et al. presented detailed description and comparison between different solution methods for inverse problems using the steepest descent method, the conjugate gradient method, the Newton-Raphson method, the quasi-Newton method, the Levenberg-Marquardt method (LM), Genetic Algorithms (GA), differential evolutions, the particle swarm method and the simulated annealing method.\textsuperscript{36} In general, these optimization tools can be divided into two categories: the deterministic techniques and the stochastic methods. If deterministic methods are
usually faster than the stochastic methods, they easily fall into system local extremums and have complex structures. Stochastic-based optimization methods employ, on the other hand, random-based operation functions ideally suited for reaching the system global extremum. Therefore, in this paper, a stochastic technique called the Genetic algorithm (GA) will be applied to the objective function in order to estimate the large number of electrochemical parameters of the Li-ion batteries.

The Genetic algorithm (GA) is by far the most popular stochastic optimization technique used in all engineering fields. This method was officially introduced by Holland in the 1970s. The GA originates from natural selection mechanisms. It starts from a strong random database, namely an initial population, and moves upward to many extremum points. Inspired by the living organism’s structure, each member of the initial population is called chromosome containing some genes. Each chromosome represents a probabilistic answer of the optimization problem in which the number of variables is equivalent to the number of genes.

In the GA, more fitted new populations replace older populations. Therefore, the algorithm requires a fitness function, which refers to the cost of each chromosome and its chance for selection.

1. The pairing operator: This operator chooses the suitable parent chromosomes from the current population for pairing. The objective function determines the cost of each chromosome and its chance for selection.
2. The mating operator: This operator produces one or more offspring from the selected pairs. After selecting the pairs, they are being mated by a random function and two children are produced.
3. The mutation operator: This operator applies a random change in a small percent of genes in all chromosomes. Mutation results in being mated by a random function and two children are produced. In the GA, a small percent of genes in all chromosomes. Mutation results in introducing new characteristics to the chromosomes that did not exist in the previous ones. This operator avoids quick convergence to a local minimum especially for objective functions which have many local minima.

Fig. 3 shows the GA flowchart with the relationships between all GA operators.

**Parameters and Reference Data**

**Expected parameters.**—The effective variables of the Li-ion battery performance can be classified into three groups: the geometric, the material and the operational parameters. The geometric and material parameters can be easily obtained from direct measurements or from the datasheets provided by the manufacturer. The operational properties are, on the other hand, not easily available. Furthermore, some of them may vary according to the measurement techniques or the battery’s age. And sometimes, the measurement of these parameters requires the dismantling of the battery itself. Therefore, eight electrochemical parameters, as the operational properties, were selected for the present PE study. These parameters are the solid diffusion coefficients (Ds,n and Ds,p), the intercalation/deintercalation reaction-rate constants (Kn and Kp), the initial SOC (SOCn,0 and SOCp,0), and the electroactive surface areas (Sn and Sp). All these variables are identifiable based on the Li-ion direct models. Their values are needed to simulate the battery’s performance and to predict its aging process. Table III provides the range for each parameter for a typical Li-ion battery with a LiCoO2 positive electrode.

Reference data.—To identify the electrochemical parameters for the Li-ion battery, the reference data must be compared to the predictions of the direct model. In the present study, the reference data were generated with the P2D model available in COMSOL® Inc. Multiphysics 5.1. The reference data is composed of the cell potential values with respect to the battery capacity for low and high discharge rates, namely C/10, C/2, 1C, 2C, 5C. Moreover, to mimic real experimental data, random noise was added to the reference data (Eq. 37). The error profile is generated by a normal distribution random function multiply by the accuracy of the measurement tools (0.001 V). The mean value and the standard deviation of the normal distribution are chosen zero and one, respectively. Due to the high accuracy of the experimental setup, the deviation value should even be lower. This means that the added error profile represents the worst case scenario. Fig. 4 illustrates noisy reference data for different discharge curves. The error profile is defined as the first order partial derivatives of the calculated cell potential (Vcell) with respect to the unknown parameters.

### Table III. Range of the electrochemical parameters for a Li-ion battery with LiCoO2.

| Symbol     | Unit      | Low value | High value |
|------------|-----------|-----------|------------|
| Da,n       | m²/s      | 1.5e-14   | 4.5e-14    |
| Da,p       | m²/s      | 0.5e-14   | 1.5e-14    |
| Kn         | m²/s/mol⁰.⁵ s | 0.9e-11   | 2.7e-11    |
| Kp         | m²/s/mol⁰.⁵ s | 3.3e-11   | 10e-11     |
| SOCn,0     |           | 0.65      | 0.85       |
| SOCp,0     |           | 0.4       | 0.6        |
| Sn         | m²        | 0.6       | 1.3        |
| Sp         | m²        | 0.6       | 1.3        |
Figure 4. Noisy reference data for various discharge curves.

Figure 5. Sensitivity curves (a-e) and best time domain (f) for estimating the electrochemical parameters.

The governing equations for the SPM (Eqs. 8–11) are employed to calculate the sensitivity values. Due to the different order of magnitudes for these values, the dimensionless sensitivity coefficients are estimated as

$$ J_{P_j} = P_j \frac{\partial V_{cell}}{\partial P_j} \quad [39] $$

It should be noted that the mean values of each parameter, extracted from Table III, have been used to determine the sensitivity coefficients. Figs. 5a to 5e show the sensitivity curves related to different discharge curves. The higher the Jacobian value, the better the estimation. The Jacobian values for each parameter vary with the discharge time and the discharge rate. Fig. 5f presents a schematics of the best time domain for estimating of electrochemical parameters for
Li-ion batteries based on Graphite/LiCoO2. Regardless of the discharge rates, the discharge curves may be divided into three distinct regions for the best time domain including (1) the beginning of the discharge process; (2) the discharge cell voltage plateau; and (3) the end of the process with decreasing cell potential. Note that due to the various open circuit potentials, these results would be affected by the positive electrode materials, which will be shown in the next paper. According to the sensitivity analysis curves, the best time domain for the PE of different electrochemical parameters is as follows:

- **D_s,n, k_n**: For both low and high discharge rates, region 2 appears to be the best time domain to estimate these electrochemical parameters.
- **D_s,p**: Region 2 is best for identifying D_s at low discharge rates. However, by using the SPM as the direct model, the region 3 seems more appropriate for identifying D_s at high discharge rates. This change is because of the dramatic increase of the first derivative of the cathode open circuit potential function (U_p) with respect to D_s at the end of the discharge process in high C-rates. Since (∂U_p/∂D_s) profile is a material characteristic, its behavior may change with using other cathode materials. This effect will be shown in the next part of this paper.
- **S_n, SOC_n,0**: Region 3 is the best time range for estimating both these parameters for all discharge rates.
- **S_p, SOC_p,0**: The best time domain for these parameters are in regions 1 and 3 for both low and high discharge rates.

### Results

Six different scenarios for the PE study were investigated. Two scenarios were examined at low discharge rates (C/10), with and without a sensitivity analysis. Four additional scenarios were simulated for discharge curves of C/2, 1C, 2C and 5C.

**Sensitivity analysis effects.**—It is observed, for low battery discharge rates (in the present case C/10), that the changes in the electrolyte properties are negligible along the x-direction. As a result, the SPM is accurate enough to be the direct model. The PE process was performed for two different scenarios, with and without a sensitivity analysis. Figs. 6a, 6b illustrate the flow chart of both these scenarios.

The objective function used in both scenarios is defined in Eqs. 34 and 36. It means that the Least-squared objective function is applied to only one discharge curve. The parameter constraints for the optimization process are provided in Table III. The characteristics and the main results of these simulations are reported in Table IV. The specific error function is defined as

$$
es = \left( \frac{1}{N} \right) \sum_{i=1}^{N} \left( V_{cell,i}^{*,m} - V_{cell,i}^{*} (P) \right)^2 \quad [40]
$$

Examination of Table IV reveals that the sensitivity analysis in the first scenario increases the accuracy of the predicted cell potential function as compared to the reference data. Moreover, the order of

| Parameter | Unit | 1st | 2nd |
|-----------|------|-----|-----|
| Initial population | - | 800 | 800 |
| Mutation Rate | % | 5 | 5 |
| GA iteration | - | 100 | 100 |
| Specific error | V^2 | 5.19e-6 | 3.56e-5 |
Table V. The characteristics and results of different scenarios of PE study.

| Sc. | Data Discharge Rate | Direct Model | Sensitivity Analysis | Initial population | Mutation Rate (%) | GA iteration | No. of Parameters |
|-----|---------------------|--------------|----------------------|--------------------|------------------|-------------|-------------------|
| 3   | C/2, 1C, 2C, 5C     | Reduced model (one unknown variable $a_0$) | No                  | 800                | 5                | 100         | 9                 |
| 4   | Yes                 | Reduced model (two unknown variables $a_0, a_1$) | No                  | 800                | 5                | 100         | 10                |
| 5   | Yes                 | Reduced model (two unknown variables $a_0, a_1$) | No                  | 800                | 5                | 100         | 10                |

Figure 7. PE results using both normal and noisy data.

The following conclusions may be drawn from Fig. 7:

1. The computational methodology remains stable and accurate in all cases, including the worst case scenario with noisy data.
2. The magnitude of the specific errors for scenarios 3 and 5 and scenarios 4 and 6 shows that the higher the number of unknown parameters, the lower the error. Also, as expected, the performance of a sensitivity analysis improves the accuracy of the predictions.
3. The last scenario, scenario no. 6, is the best for the PE study of the Li-ion battery. It is based on the simplified model with two unknown parameters and it relies simultaneously on the sensitivity analysis.

Using the estimated parameters for the best scenario, the discharge curves for the Li-ion battery were determined by running the simplified model. Figs. 8a and 8b show the simulation results for the normal and the noisy reference data respectively. It is seen that the predictions remain accurate for all discharge curves and for noisy reference data.

The relative errors were obtained by comparing with the real parameters ($P_{j,real}$) which are used to generate the reference data with the P2D COMSOL model.

$$e_r = \left| \frac{P_{j,PE} - P_{j,real}}{P_{j,real}} \right| \times 100$$  \hspace{1cm} [41]

Fig. 9 reveals that the relative errors for the constant rates ($K_p$ and $K_n$) are higher than those for the other parameters. On other hand, according to Figs. 5a–5e their sensitivity coefficients are very low when compared to others. As a result, their effect on the cell potential function of the battery remains insignificant.
The final values of the expected electrochemical parameters are presented in Table VI. It is seen that all parameters are in the expected range and compatible with the data available in the open literature.

### Conclusions

An electrochemical Parameter Estimation (PE) of a Li-ion battery was conducted with an inverse method. The numerical procedure identifies eight key internal parameters of the Li-ion battery. The PE study was conducted by means of a sensitivity analysis for all parameters with respect to the cell potential. A least square function and the Genetic Algorithm (GA) are chosen as the objective function and the optimizer for the inverse method, respectively.

Using this methodology, six comparative scenarios are examined. In the 1st and 2nd scenarios, the effect of the sensitivity analysis on the PE process is investigated by using C/10 discharge curve. The results reveal that the sensitivity analysis increases the accuracy of the predicted cell potential function as compared to the reference data. Moreover, the order of magnitude of the specific error for the scenario with considering sensitivity analysis is 10 times lower than that for the regular scenario. In the other four scenarios, the effect of the developed simplified model and of the sensitivity analysis on the identification process is simultaneously examined for both low and high discharge rates. Results show that the larger the number of unknown coefficients in the simplified model, the lower the error. The best PE predictions are obtained when the reduced model calculations are coupled to a sensitivity analysis.

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### List of Symbols

- $a_k$: Specific surface area of electrode $k (k = p,n)$, m²/m³
- $c_{e,k}$: Electrolyte concentration in region $k (k = p,s,n)$, mol/m³
- $c_{e,k,0}$: Initial condition of electrolyte concentration in region $k (k = p,s,n)$, mol/m³
- $c_{e,k}$: Solid-state concentration of electrode $k (k = p,n)$, mol/m³
- $c_{e,k,\max}$: Maximum concentration of Li⁺ in the particle of electrode $k (k = p,n)$, mol/m³
- $\epsilon_{\text{Li}}$: Concentration of Li⁺ on the surface of the particles of the electrode $k (k = p,n)$, mol/m³
- $D_{\text{eff},k}$: Effective diffusion coefficient of Li⁺ in electrolyte for region $k (k = p,s,n)$, m²/s
- $D_{k}$: Li⁺ diffusion coefficient in the particle of electrode $k (k = p,n)$, m²/s
- $e_1$: Measurement error function of the cell potential, V
- $e_2$: Relative error, %
- $e_s$: Specific error function of the cell potential, V²
- $F$: Faraday’s constant, C/mol
- $J$: Applied current density, A/m²
- $J_{\text{ref}}$: Wall flux of Li⁺ on the particle of Li (k = p,n), mol/m²s
- $J_{\text{ref}}$: Dimensionless sensitivity coefficient, V
- $K_{r}$: Reaction rate constant of electrode $k (k = p,n)$, mol/m³s
- $L$: Total thickness, m
- $L_k$: Thickness of region $k (k = p,s,n)$, m
- $n$: Negative electrode
- $P$: Unknown parameter matrix
- $p$: Positive electrode
- $R$: Universal gas constant, J/mol K
- $R_{\text{pd}}$: Solution phase resistance, Ω
- $R_{k}$: Radius of the particle of electrode $k (k = p,n)$, m
- $r$: Radial coordinate, m
- $S$: Objective function, V²
- $S_k$: Total electroactive area of electrode $k$, m²
- $S_{O,C_k}$: State Of Charge of electrode $k (k = p,n)$
- $S_{O,C_{k,0}}$: Initial State Of Charge of electrode $k (k = p,n)$
- $s$: Separator
- $T$: Absolute temperature, K
- $t$: Time, s
- $t_{\text{Li}}$: Li⁺ transference number in the electrolyte
- $U_k$: Open-circuit potential of electrode $k (k = p,n)$, V
- $w_k$: Weight of the active material of electrode $k, g$
- $x$: Spatial coordinate, m

### Greek

- $\varepsilon_k$: Porosity of region $k (k = p,s,n)$
- $\kappa_{\text{eff},k}$: Effective ionic conductivity of the electrolyte in region $k (k = p,s,n)$, S/m
- $\mu_{k}$: Overpotential of electrode $k (k = p,n)$, V
- $\sigma_{\text{eff},k}$: Effective electronic conductivity of the solid phase of electrode $k (k = p,n)$, S/m
- $\Phi_k$: Solid-phase potential of electrode $k (k = p,n)$, V
- $\Phi_{\text{Li}}$: Electrolyte potential in region $k (k = p,s,n)$, V

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