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Parameter estimation of an electrochemistry-based lithium-ion battery model using a two-step procedure and a parameter sensitivity analysis

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Summary
Lithium-ion batteries are indispensable in various applications owing to their high specific energy and long service life. Lithium-ion battery models are used for investigating the behavior of the battery and enabling power control in applications. The Doyle-Fuller-Newman (DFN) model is a popular electrochemistry-based model, which characterizes the dynamics in the battery through diffusions in solid and electrolyte and predicts current/voltage response. However, the DFN model contains a large number of parameters that need to be estimated to obtain an accurate battery model. In this paper, a computationally feasible two-step estimation approach is proposed that only uses voltage and current measurements of the battery under consideration. In the two-step procedure, the parameters are divided into 2 groups. The first group contains thermodynamic parameters, which are estimated using low-current discharges, while the second group contains kinetic parameters, which are estimated using a well-designed highly-dynamic pulse (dis-)charge current. A parameter sensitivity analysis is done to find a subset of parameters that can be reliably estimated using current and voltage measurements only. Experimental data are collected for 12 Ah nickel cobalt aluminum pouch lithium-ion cell. The voltage predictions of the identified model are compared with several experimental data sets to validate the model. A root mean square error between model predictions and experimental data smaller than 16 mV is achieved.

KEYWORDS
DFN model, kinetic, lithium-ion battery, parameter estimation, sensitivity analysis, thermodynamic

1 | INTRODUCTION
Lithium-ion (Li-ion) batteries are known to have a high energy density and a long service life. They have been successfully used in the automotive industry, which enables the production of low-emission hybrid vehicles and zero-emission full electric vehicles.\(^1,2\) To facilitate the analysis, design and control of the batteries, models of Li-ion batteries are required. For instance, these models are used in typical functionalities of the battery management system (BMS), such as state-of-charge (SoC) estimation, capacity fade estimation, and real-time control.\(^3,4\) An
accurate model plays a pivotal role in investigation and proper control of the battery.

Among the available battery models, the equivalent circuit model (ECM) and the Doyle-Fuller-Newman (DFN) model are popular ones. The ECM describes the input/output behavior of batteries through an electrical circuit consisting of a voltage source, a series resistance and a parallel connection of a resistor and capacitor, see, eg, Liaw et al, while the DFN model is an electrochemistry-based model, which characterizes the dynamics in Li-ion battery based on concentrations and potentials. Several papers report methods for estimating the parameters of the ECM of Li-ion batteries, see, eg, previous studies, papers presenting methods for estimation the parameters of the DFN model seem to be scarce.

Although some parameters of the DFN model (eg, layer thicknesses and diffusion coefficients) can be determined with direct experiments, it is still complicated and challenging to conduct these measurements. Moreover, since the number of parameters is large and the estimation procedure is computationally complex, it is hard to estimate all parameters in the full DFN model. For this reason, parameter estimation has been mostly applied to simplified DFN models, such as the single particle model. Most of these works relies on Gauss-Newton method for nonlinear optimization to perform parameter estimation, while some have used a homotopy optimization method. Although parameter estimation by a genetic algorithm had been successfully used to estimate parameters in Forman et al, only a few results are available on parameter estimation of the full DFN model. In a number of sources, various parameters are estimated but the parameters choice remains unexplained.

In this paper, the parameter estimation of the full DFN model is considered to obtain a high-fidelity battery model. A computationally feasible two-step estimation approach is developed that uses only voltage and current measurements. In the proposed two-step procedure, the original set of parameters is split into two: thermodynamic parameters and kinetic parameters, which are estimated separately. The thermodynamic parameters are related to the capacity, which are estimated using low-current discharges, while the kinetic parameters are estimated using highly-dynamic pulse (dis-)charge current. A parameter sensitivity analysis based on QR factorization is applied to find a subset of parameters that can be reliably estimated, which leads to a simplified estimation procedure. Additionally, an experimental input current profile is designed for estimation and all data are collected from 12 Ah nickel cobalt aluminum (NCA) li-ion batteries. Giv-

\[ \text{Li}_x\text{MeO}_2 \xrightleftharpoons[]_{\text{ch}} \text{Li}_{x-\Delta x}\text{MeO}_2 + \Delta x\text{Li}^+ + \Delta e^- \quad (1) \]

\*The data belonging to his paper, including a description of it, are available at 4TU.Centre For Research Data at this URL: https://data.4tu.nl/repository/uuid:0d19258e-8fe2-44b7-b390-cfc205669528.

The remainder of this paper is organized as follows. In Section 2, the DFN model is outlined and a numerical computation procedure for implementing the DFN model is given. Two groups of parameters: thermodynamic and kinetic, accompanied with their expected ranges and nominal values will be presented in Section 3. Estimation of the thermodynamic parameters by determining the equilibrium voltage and the capacity of the battery will be done in Section 4. Section 5 deals with identifying the most sensitive subset in the group of kinetic parameters using QR factorization and those parameters are estimated using nonlinear least-square optimization. Finally, the model is validated using different experimental data sets (constant current and pulsed-current discharge) in Section 6 and conclusions will be drawn in Section 7.
can be withdrawn from the cathode, ie, \( x \geq x_{\text{min}} \), for value \( x_{\text{min}} \) close to 0.5. The electrochemical reaction at anode side is given by

\[
\text{Li}_y\text{C}_6 + \Delta y\text{Li}^+ + \Delta y\text{e}^- \xrightleftharpoons{\text{dis}}^\text{ch} \text{Li}_{y+\Delta y}\text{C}_6.
\]  (2)

During discharging, lithium deintercalates from the anode, enters the liquid phase and moves to the cathode through the separator. The reverse process occurs during charging. In the liquid phase, the Li-ions movement is caused by a combination of diffusion and migration across the electrolyte. Therefore, the ionic concentrations and potentials in both electrodes and electrolyte change during the operation of the battery. The DFN model characterizes these dynamics in the Li-ion battery by using the porous electrode theory and the concentrated solution theory.\(^{25}\)

Within the DFN model, the intertemporal response of a cell (in terms of voltage and current) can be predicted from a fundamental characterization of the physical phenomena involved in the process. In particular, thermodynamics (the equilibrium potentials of the electrodes), kinetics (the rate of the charge transfer reactions), and mass/charge transport (the movement of ions through solid and liquid media) are considered.

### 2.2 Governing equations

The DFN model is a pseudo two-dimensional model and consists of a set of coupled partial differential equations, ordinary differential equations, and algebraic equations. The model describes the transport of Li-ions is determined by diffusion in solid phase and in the liquid phase and charge conservation in both electrodes described by Ohm’s law. A brief summary of the model’s governing equations is given below.

- The concentration of Li-ions in solid phase \( C_{\kappa}(x, r, t) \) in the negative \((k = n)\) and the positive electrode \((k = p)\) electrode depends on the particle position \( x \in [0, \delta_-] \) for positive electrode and \( x \in [L - \delta_+ , L] \) for negative electrode, where \( \delta_- \) and \( \delta_+ \) are the thickness of negative and positive electrode, respectively, and the radial position within a particle \( r \in [0, R_s] \), where \( R_s \) is the radius of particles, and time \( t \in \mathbb{R}_+ \). The ionic concentration inside a single spherical active material particle is described by Fick’s law of diffusion, ie,

\[
\frac{\partial C_{\kappa}}{\partial t} = \frac{D_{\kappa}}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C_{\kappa}}{\partial r} \right),
\]  (3a)

with boundary conditions

\[
\frac{\partial C_{\kappa}}{\partial r} \bigg|_{r=0} = 0, -D_{\kappa} \frac{\partial C_{\kappa}}{\partial r} \bigg|_{r=R_s} = \frac{J_{\kappa} F}{a_{\kappa}}
\]  (3b)

where \( k \in \{ n, p \} \), represents negative or positive electrode. In this expression, \( D_{\kappa} \) are the diffusion coefficients in solid phase, \( J_{\kappa} \) is the volume-specific rate of the electrochemical reaction, which will be defined below, \( F \) is Faraday’s constant \((96487 \text{ C.mol}^{-1})\) and the specific interfacial active surface area \( a_{\kappa} = 3 \epsilon_{\kappa} \) in which \( \epsilon_{\kappa} \) is the volume fraction of active particles in both electrodes.

- The concentration of Li-ions in the liquid phase \( C_{e}(x, t) \), where \( x \in [0, L] \), is governed by Fick’s law of linear diffusion combined with an intercalation current density term \( J_{Li} \), transferring ions between the solution and the solid, ie,

\[
\epsilon_{e} \frac{\partial C_{e}}{\partial t} = \frac{\partial}{\partial x} \left( D_{e}^{\text{eff}} \frac{\partial C_{e}}{\partial x} \right) + 1 - \frac{t_+}{F} J_{Li}.
\]  (4a)

with zero-flux boundary conditions at the current collectors

\[
\frac{\partial C_{e}}{\partial x} \bigg|_{x=0} = \frac{\partial C_{e}}{\partial x} \bigg|_{x=L} = 0.
\]  (4b)

In these expressions, \( \epsilon_{e} \) is electrolyte phase volume fraction, \( t_+ \) is the transference number of Li ions, \( D_{e}^{\text{eff}} \) denotes the effective diffusion coefficient in
the electrolyte phase, which is calculated from a reference coefficient using the Bruggeman relation, i.e., $D_c^{\text{eff}} = D_c e^{\kappa}$, where $p$ is Bruggeman porosity exponent, given by $p = 1.5$.

- The potentials in the solid phase $\phi_{s,k}(x,t)$ is given by
  \[
  \frac{\partial}{\partial x}(\sigma_k^{\text{eff}} \frac{\partial \phi_{s,k}}{\partial x}) = j_{l,k},
  \]
  with boundary conditions
  \[
  -\sigma_k^{\text{eff}} \frac{\partial \phi_{s,k}}{\partial x} \Bigg|_{x=0} = \frac{I_{\text{app}}}{A}, \quad \frac{\partial \phi_{s,k}}{\partial x} \Bigg|_{x=L} = 0,
  \]
  \[
  \frac{\partial \phi_{s,p}}{\partial x} \Bigg|_{x=L-\delta_s} = 0, -\sigma_p^{\text{eff}} \frac{\partial \phi_{s,p}}{\partial x} \Bigg|_{x=L} = \frac{I_{\text{app}}}{A},
  \]
  where $k \in \{n,p\}$, denotes the negative or positive electrode. In this expression, $\sigma_k^{\text{eff}} = \sigma_k^{\text{eff},s,k}$ denotes the effective electrical conductivity, in which $\sigma_k$ represents the electrical conductivity in solid active material, $A$ is the electrode plate area and $I_{\text{app}}(t)$ is the applied current, as an input of the model.

- The potential in the electrolyte phase $\phi_e(x,t)$ is described by
  \[
  \frac{\partial}{\partial x}(k^{\text{eff}} \frac{\partial \phi_e}{\partial x} + k^D \frac{\partial \ln C_s}{\partial x}) = -j_{l,k},
  \]
  with boundary conditions
  \[
  \frac{\partial \phi_e}{\partial x} \Bigg|_{x=0} = \frac{\partial \phi_e}{\partial x} \Bigg|_{x=L} = 0.
  \]

In the above equations, $k^{\text{eff}} = \kappa c_e^{\rho}$ denotes effective ionic conductivity, with $\kappa = 15.8C_s^{\text{exp}}(0.85(1000C_s)^{-1})$. Moreover, the effective diffusional conductivity $k^D$ is derived from concentrated solution theory and given by
\[
  k^D = \frac{2RT\kappa^{\text{eff}}(T_e - 1)}{F} \left( 1 + \frac{\partial \ln f_\pm}{\partial \ln C_e} \right),
\]
where $R$ is the universal gas constant (8.3143 J·mol$^{-1}$K$^{-1}$), $T$ is the absolute temperature and $f_\pm$ is the activity coefficient, which is assumed to be constant in the present work, leading to the simplified expression
\[
  k^D = \frac{2RT\kappa^{\text{eff}}}{F}(T_e - 1).
\]

The 4 governing Equations 3 to 6 are coupled with the volume-specific rate of reaction $j_{l,k}$, which satisfies Butler-Volmer electrochemical kinetic expression
\[
  j_{l,k} = a_k i_{0,k} \left( \exp \left( \frac{\alpha_k F}{RT} \eta_k \right) - \exp \left( -\frac{(\alpha_k - 1)F}{RT} \eta_k \right) \right),
\]
where $a_k$ is charge transfer coefficient for $k$-th electrode. In this expression, $i_{0,k}$ is the exchange current density given by
\[
  i_{0,k} = k_0 C_s^{\text{max}} C_{\text{surf}}^{\text{max}}(C_{\text{surf}}^{\text{max}})^{-n_k},
\]
where $k_0$ is a kinetic rate constant, $C_s^{\text{max}}$ denotes the maximum concentration in the solid phase and $C_{\text{surf}}(x,t) = C_{s,k}(R_e, x, t)$ is the concentration at the particle surface. Moreover, $\eta_k$ represents the overpotential at both electrodes, which is related to the potentials in 2 phases and the equilibrium potential as
\[
  \eta_k = \phi_{s,k} - \phi_e - U_k,
\]
where $U_k, k \in \{p,n\}$, is the equilibrium potential in electrodes, which is always evaluated as a predefined function of the solid phase concentration at the particle surface $C_{s,k}(R_e, x, t)$, written as
\[
  U_p = U_p(x), \quad U_n = U_n(y),
\]
where $x(t) = C_{s,p}(R_e, x, t)/C_{s,p}^{\text{max}}$ and $y(t) = C_{s,n}(x, R_e, t)/C_{s,n}^{\text{max}}$ are the normalized concentrations at the surface of the positive and negative electrodes accordingly. Finally, the terminal voltage is calculated by the difference between the solid phase potential at the 2 current collectors, minus an Ohmic drop due to contact resistance, given by
\[
  V(t) = \phi_s(L, t) - \phi_s(0, t) - \frac{R_f}{A} I_{\text{app}}(t),
\]
where $R_f$ denotes the contact resistance.

### 2.3 Model implementation

To obtain the predicted output of the DFN model for proper parameter estimation, a reliable numerical implementation of the model is needed. The implementation method used in this paper is based on a numerical procedure proposed by Xia et al.\textsuperscript{26} The main idea for implementing the DFN model can be summarized into the following 3 steps. The first step is a spatial discretization of 3 to 6, by approximating the $\frac{\partial}{\partial x}$ term in these equations using a finite-volume or finite-difference method, leading to a set of nonlinear differential algebraic equations (DAE) of the form:
\[
  \left\{ \begin{array}{l}
  \frac{dC}{dt} = f(C, \phi, P) \\
  0 = g(C, \phi, I_{\text{app}}, P),
  \end{array} \right.
\]
where $C$ denotes the spatially discretized concentrations, $\phi$ denotes the spatially discretized potentials, $I_{\text{app}}$ is the applied current and $P$ is the vector of all the model
parameters. The functions \( f \) and \( g \) are nonlinear functions resulting from the spatially discretized modelling equations.

The second step in the numerical implementation is a backward Euler discretization over time, leading to

\[
\begin{align*}
C(t_{n+1}) &= C(t_n) + (t_{n+1} - t_n)f(C(t_{n+1}), \phi(t_{n+1}), P) \\
0 &= g(C(t_{n+1}), \phi(t_{n+1}), I_{\text{app}}(t_{n+1}), P),
\end{align*}
\]

which is a set of purely algebraic equations. Equation 15 is finally solved using an iterative numerical procedure based on Gauss-Newton's method, which represents the third step. After obtaining the solution of the dependent variables of the model (\( C, C_e, \phi, \phi_e \)), the cell terminal voltage \( V(t) \), as the output of the DFN model can be calculated by (13). More details on the model implementation can be found in Xia et al.\textsuperscript{26}

3 | PARAMETERS GROUPING AND RANGING

The DFN model contains a large number of parameters related to design, size, and electrochemistry of the battery. Various physical parameters have different influence on the behavior of the battery and they can be divided into 2 groups: thermodynamic parameters and kinetics parameters. In this section, the 2 groups of parameters will be described, and the ranges and nominal values of the parameters will be given.

3.1 | Thermodynamic parameters

The thermodynamic parameters describe the system in equilibrium, when all concentration profiles and potentials are stable over the time and all net reaction currents are zero. For a battery, this means that the thermodynamic parameters are related to the equilibrium voltage and the battery's maximum capacity, since both of them are obtained when the applied current is zero. While the equilibrium potential is given by nonlinear equation that depends on the normalised concentrations, see (12), the reversible maximum capacities of the negative and positive electrodes are given by

\[
\begin{align*}
Q_n &= A \delta_\epsilon \epsilon_{s,n} \epsilon_{s,n}^\text{max}(y_{100\%} - y_{0\%})F, \\
Q_p &= A \delta_\epsilon \epsilon_{s,p} \epsilon_{s,p}^\text{max}(x_{0\%} - x_{100\%})F,
\end{align*}
\]

where \( x_{100\%}, y_{100\%}, x_{0\%}, \) and \( y_{0\%} \) are stoichiometry at 100% and 0% SOC, respectively, in both electrodes. According to these equations, the thermodynamic parameters are estimated and listed in Table 1.

Generally, batteries are manufactured with similar geometry and composition, while different capacities are obtained through altering the plate area \( A \) of batteries. Therefore, the values of the remaining thermodynamic parameters presented in Table 1 are adopted from Smith et al.\textsuperscript{27} The only parameter that is not directly taken from Smith et al\textsuperscript{27} is plate area \( A \). The real capacity of the battery used in the present work can be determined by specific estimation procedure, based on voltage extrapolation towards zero current, which will be described in Section 4. The value for plate area \( A \) is estimated by the proportional relationship between the capacity reported in Smith et al\textsuperscript{27} and the measured capacity in the present work.

3.2 | Kinetic parameters

The kinetic parameters are determined by the rate of charge transfer reactions and the speed of charge/mass transport by migration and diffusion. Furthermore, the voltage drop, caused by current flow in the current collectors is included in kinetic parameters. A summary of the kinetic parameters in the DFN model is given in the Table 1.

The range of every kinetic parameter presented in Table 1 is obtained by gathering different values for every parameter from the literature\textsuperscript{9,10,17-20,27-34} and setting the minimum and maximum value as the boundary of each kinetic parameter. Within the range, every parameter can be expressed on a linear or a logarithmic scale, ie,

\[
p_i = \beta p_i + (1 - \beta)\overline{p_i}, \tag{17a}
\]

or

\[
\log p_i = \beta \log p_i + (1 - \beta)\overline{p}, \tag{17b}
\]

where \( \beta \in [0, 1] \), \( p_i \in \mathbf{p} \) denotes every kinetic parameter, \( p_i \) and \( \overline{p_i} \) represent minimum and maximum value of the parameter, respectively. For the parameters whose range is in the same order of magnitude, (17a) is used, while (17b) is used to express the parameters whose range differ in orders of magnitude. This is shown in the last column in Table 1. The nominal values for each parameter are calculated by substituting \( \beta = 0.5 \) into either (17a) or (17b).

4 | THERMODYNAMIC MODELLING

The output voltage of a Li-ion battery depends strongly on the equilibrium potentials of cathode and anode, which, in turn, depend on temperature and amount of lithium stored in each electrode. Therefore, the equilibrium potential functions of the cell have to be estimated in accordance with measured data. As discussed in Section 3, the thermodynamic parameters are related to the equilibrium potentials of the battery. Hence, the equilibrium potential
functions for both electrodes will be determined based on the estimated values of thermodynamic parameters.

The methodology proposed in this paper for determining the equilibrium potentials for both electrodes is as follows. First, an equilibrium voltage (EMF) of the complete battery is estimated, which also yields the maximal capacity of the battery. The method to estimate the EMF is described in Danilov et al.\textsuperscript{35} Subsequently, the thermodynamic parameter $A$ is estimated using the available maximal capacity. Finally, the function describing the negative electrode potential $U_n$ is derived from Smith et al\textsuperscript{27} and the function describing the positive potential $U_p$ is determined on the basis of total EMF and the thermodynamic parameters.

| Thermodynamic parameters | Nominal value | Range | Scaling |
|--------------------------|---------------|-------|---------|
| $\delta_-$ | $\mu$m | Negative electrode thickness | 50 | |
| $\delta_+$ | $\mu$m | Positive electrode thickness | 36.4 | |
| $\epsilon_{x,n}$ | | Active particles volume fraction in negative electrode | 0.58 | |
| $\epsilon_{x,p}$ | | Active particles volume fraction in positive electrode | 0.5 | |
| $C_{s,n}^{\text{max}}$ | mol·m$^{-3}$ | Maximum solid phase concentration in negative electrode | $16.1 \cdot 10^3$ | |
| $C_{s,p}^{\text{max}}$ | mol·m$^{-3}$ | Maximum solid phase concentration in positive electrode | $23.9 \cdot 10^3$ | |
| $y_{0\%}$ | | Stoichiometry at $0\%$ state of charge in negative electrode | 0.126 | |
| $x_{0\%}$ | | Stoichiometry at $0\%$ state of charge in positive electrode | 0.936 | |
| $y_{100\%}$ | | Stoichiometry at $100\%$ state of charge in negative electrode | 0.676 | |
| $x_{100\%}$ | | Stoichiometry at $100\%$ state of charge in positive electrode | 0.442 | |
| $A$ | m$^2$ | Electrode plate area | 1.84 | |

**Kinetic Parameters**

| Parameter | Dimension | Description | Nominal value | Range | Scaling |
|-----------|-----------|-------------|---------------|-------|---------|
| $\epsilon_{e,n}$ | | Electrolyte volume fraction in negative electrode | 0.21 | [0, 0.42] | (17a) |
| $\epsilon_{e,\text{sep}}$ | | Electrolyte volume fraction in separator | 0.5 | [0, 1] | (17a) |
| $\epsilon_{e,p}$ | | Electrolyte volume fraction in positive electrode | 0.25 | [0, 0.48] | (17a) |
| $D_e$ | m$^2$·s$^{-1}$ | Li-ion diffusion coefficient in electrolyte | $2.6 \cdot 10^{-11}$ | [2.6 · $10^{-12}$, 2.6 · $10^{-10}$] | (17b) |
| $D_{s,n}$ | m$^2$·s$^{-1}$ | Li-ion diffusion coefficient in negative electrode | $2 \cdot 10^{-14}$ | [2 · $10^{-18}$, 2 · $10^{-10}$] | (17b) |
| $D_{s,p}$ | m$^2$·s$^{-1}$ | Li-ion diffusion coefficient in positive electrode | $3.7 \cdot 10^{-16}$ | [1.7 · $10^{-20}$, 8 · $10^{-12}$] | (17b) |
| $\delta_+$ | | Transference number | 0.35 | [0.3, 0.4] | (17a) |
| $R_s$ | $\mu$m | Radius of electrode material particle | 1 | [0.1, 10] | (17a) |
| $\alpha_n$ | | Charge transfer coefficients in negative electrode | 0.5 | [0.3, 0.7] | (17a) |
| $\alpha_p$ | | Charge transfer coefficients in positive electrode | 0.5 | [0.3, 0.7] | (17a) |
| $k_{0,n}$ | A·m$^{3/2}$·mol$^{-3/2}$ | Kinetic constant in negative electrode | $1.38 \cdot 10^{-5.5}$ | [1.38 · $10^{-7}$, 1.38 · $10^{-4}$] | (17b) |
| $k_{0,p}$ | A·m$^{3/2}$·mol$^{-3/2}$ | Kinetic constant in positive electrode | $6.4 \cdot 10^{-5.5}$ | [0.64 · $10^{-7}$, 0.64 · $10^{-4}$] | (17b) |
| $\sigma_n$ | S·m$^{-1}$ | Electrical conductivity in negative electrode | 1000 | [10, $10^5$] | (17b) |
| $\sigma_p$ | S·m$^{-1}$ | Electrical conductivity in positive electrode | 0.003 | [3 · $10^{-7}$, 30] | (17b) |
| $C_{e,0}$ | mol·m$^{-3}$ | Initial electrolyte concentration | $1.2 \cdot 10^4$ | [10$^3$, 1.5 · $10^5$] | (17b) |
| $R_f$ | $\Omega$·m$^2$ | Contact resistance | $2 \cdot 10^{-3}$ | [2 · $10^{-4}$, 2 · $10^{-2}$] | (17b) |
FIGURE 2  Set of discharge curves (0.1, 0.2, 0.3, 0.5, 0.75 and 1.00 C-rate) together with estimated $U_{bat}$ and fitting result according to (19b) [Colour figure can be viewed at wileyonlinelibrary.com]

4.1  EMF (equilibrium voltage) and capacity of the cell

To estimate the equilibrium voltage, or EMF voltage, the battery is discharged several times at a constant current at different C-rates, where discharging is terminated at 2.7 V. The following C-rates has been used for discharging: 0.1, 0.2, 0.3, 0.5, 0.75, 1.00, and 1.25 C-rate. The results of these measurements are used to determine the EMF based on the voltage extrapolation towards zero current\textsuperscript{35,36} Figure 2 shows the measured discharge curves as functions of the amount of extracted charge $Q_{\text{out}}$ (solid colored lines), together with the extrapolated equilibrium voltage curve (dashed black line).

The capacity of the battery is the maximal extracted charge $Q_{\text{out}}^{\text{max}}$. From the extrapolated EMF curve in Figure 2, it can be seen that the capacity $Q_{\text{out}}^{\text{max}} = 12.7$ Ah. Thus, the plate area $A$ is calculated as 1.84 m$^2$ according to the proportional relationship $Q_{\text{out}}^{\text{max}}/Q_1 = A/A_1$, where $Q_1$ and $A_1$ are the capacity and plate area of battery used in Smith et al.\textsuperscript{27}

4.2  Positive electrode equilibrium potential function

As mentioned above, the function describing the equilibrium potential of the negative electrode $U_n$ is taken from Smith et al.\textsuperscript{27} while the function describing the equilibrium potential of the positive electrode $U_p$ is computed using the equilibrium voltage $U_{bat}$. Namely, it holds that

$$U_{bat} = U_p - U_n,$$  \hspace{1cm} (18)

where $U_{bat}$ is the equilibrium voltage. The rationale behind this approach is based on the fact that the potential of the negative electrode contributes much less to total battery voltage than the potential of the positive electrode (see also Figure 3). Moreover, much of the variation in equilibrium potentials of various cells types is due to differences in cathode chemistries, while there is much less variation in composition of graphite anodes, which makes their equilibrium potential almost standard. By that reason, an equilibrium voltage of anode $U_n$ is taken from Smith et al.\textsuperscript{27}

After the total battery EMF $U_{bat}$ has been estimated by extrapolation towards zero current, and the negative electrode equilibrium potential is assumed to be given by (see Smith et al.\textsuperscript{27})

$$U_n(y) = \sum_{i=0}^{5} \gamma_{n,i} y^i + \gamma_{n,6} \exp(\gamma_{n,7} y) + \gamma_{n,8} \exp(\gamma_{n,9} y),$$  \hspace{1cm} (19a)

the positive electrode equilibrium potential $U_p$ can be computed using (18), which is then captured by the following expression:

$$U_p(x) = \sum_{i=0}^{7} \gamma_{p,i} \left( \frac{x - x_0 \%}{x_{100\%} - x_0 \%} \right)^i + \gamma_{p,8} \exp \left( \gamma_{p,9} \left( \frac{x - x_0 \%}{x_{100\%} - x_0 \%} \right)^{10} \right),$$  \hspace{1cm} (19b)

where $\gamma_{k,i}$, $i \in \{1, \ldots, 9\}$, $k \in \{n,p\}$, are coefficients parameterizing these functions. Coefficients $\gamma_{k,i}$ are estimated by fitting the experimental data, while $\gamma_1$ in $U_n$ are obtained from Smith et al.\textsuperscript{27} All coefficients are listed in Table 2.

The dashed red line in Figure 2 is the fitted result of total equilibrium (EMF) voltage, and Figure 3 displays the resulting equilibrium potentials in the negative and posi-
tive electrodes, as functions of SoC. The dashed red line in Figure 3 is the total EMF.

5 | KINETICS MODELLING

After determining the thermodynamic parameters, the kinetic parameters have to be estimated. Identifying a large number of kinetic parameters from measurements leads to the question: which model properties can be estimated reliably from the available measurement data? To answer this question, the sensitivity of the battery voltage with respect to changes in the parameters can be investigated. If only some of the parameters are sensitive, then it is possible to reduce the complexity of the parameter estimation procedure and avoid large uncertainties in estimates, because only the sensitive parameters can be reliably estimated. Since the parameter sensitivity of the battery voltage depends on the choice of the current drawn from the battery, this current input design is an imperative premise of the followed sensitivity analysis and estimation.

5.1 | Input design

An essential preparation for the sensitivity analysis and the parameter estimation is the design of a suitable input. The objective of input design is to generate informative data while experimentation effort is reduced. As the input of the model, the cell current has to excite the battery at various C-rates to cover different charging or discharging conditions. The design of input current is based on the following considerations:

- **Both charging and discharging**: The output voltage may reveal different dynamics when charging and discharging the battery since the response of the DFN model might not be symmetric.
- **Different C-rates**: The voltage response of the DFN model might depend nonlinearly on magnitude of the exciting current.
- **Relaxation**: To capture the voltage relaxation behavior of the cell, the (dis-)charging periods should be followed by zero current periods.

The input current designed according to the conditions above is shown in Figure 4A. The excitation signal is composed of several periods, and different constant currents are applied in each period. The designed input \( I_{\text{app}}(t) \) includes charge and discharge pulses at 1C-rate and 0.5 C-rate; each pulse is followed by relaxation phase. The duration of each pulse and relaxation phase is 5 minutes, which is enough to capture the dynamics of the battery when current flows and during relaxation period.

5.2 | Sensitivity analysis

The idea of estimating only a subset of the parameter set in the DFN model has been proposed before in other works. In particular, all the aforementioned papers propose to estimate some of the parameters, see Table 3, while keeping the others at some nominal value. It can be observed from Table 3 that no consensus exist on which parameter should be estimated. Moreover, a systematic approach for selecting which parameters can be reliably estimated does not seem to be present in these papers. In this paper, such a systematic approach is developed in the form of a parameter sensitivity analysis. The parameter sensitivity analysis determines how sensitive is the output of the model with respect to variation in values of parameters. Since the output of the DFN model depends nonlinearly on the parameters, this is a local analysis. Besides presenting a formal mathematical model, the method is illustrated numerically.

5.2.1 | Parameter ranking by QR factorization

In this paper, the sensitive analysis is done using a QR factorization with column permutation of a to-be-defined sensitivity matrix. To define this sensitivity matrix, let us write the predicted voltage output of the DFN model using the following nonlinear function:

\[
\hat{V} = h(I_{\text{app}}, p; C_0, \phi_0),
\]

where \( \hat{V} = [\hat{V}(t_1), \hat{V}(t_2), \ldots, \hat{V}(t_N)]^T \), is a prediction of output voltage measurements of the battery stacked over time, and \( h(I_{\text{app}}, p; C_0, \phi_0) \) represents the solution to the DFN governing equations (15), where \( I_{\text{app}} = [I_{\text{app}}(t_1), I_{\text{app}}(t_2), \ldots, I_{\text{app}}(t_N)]^T \), is the input current stacked over time. Finally, \( p = [p_1, p_2, \ldots, p_m]^T \in \mathbb{P} \) is the parameter vector which contains all kinetic parameters and \( C_0, \phi_0 \) are the initial state vectors of concentrations and potentials.

Making a first-order Taylor expansion of the output of the model \( \hat{V} \) around its nominal parameters \( \hat{p} \) leads to

| \( \gamma_{k,0} \) | \( \gamma_{k,1} \) | \( \gamma_{k,2} \) | \( \gamma_{k,3} \) | \( \gamma_{k,4} \) | \( \gamma_{k,5} \) | \( \gamma_{k,6} \) | \( \gamma_{k,7} \) | \( \gamma_{k,8} \) | \( \gamma_{k,9} \) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| \( U_p(k = p) \) | \(-2.49 \cdot 10^3\) | 14.56 | -1.86 \cdot 10^2 | 8.14 \cdot 10^2 | -2.56 \cdot 10^3 | 4.63 \cdot 10^3 | -4.51 \cdot 10^3 | 1.90 \cdot 10^3 | 2.49 \cdot 10^3 | -0.052 |
| \( U_n(k = n) \) | -8.63 \cdot 10^{-4} | 0 | 8.00 | -12.58 | 5.07 | 2.18 \cdot 10^{-5} | 0.019 | 15 | -5.19 | -2.43 |
\[ \dot{V}(p) = \dot{\hat{V}} + \frac{\partial \dot{V}}{\partial p} (p - \hat{p}), \] (21)\

where the sensitivity matrix \( S = \frac{\partial \dot{V}}{\partial p} \) for the model output \( \dot{V} \) with respect to the kinetic parameters \( p \) is given by the \( N \times m \) matrix

\[
S(p,t) = \begin{bmatrix}
    s_1(p,t_1) & s_2(p,t_1) & \cdots & s_m(p,t_1) \\
    s_1(p,t_2) & s_2(p,t_2) & \cdots & s_m(p,t_2) \\
    \vdots & \vdots & \ddots & \vdots \\
    s_1(p,t_N) & s_2(p,t_N) & \cdots & s_m(p,t_N)
\end{bmatrix},
\] (22)

where \( N \) is a number of measurements, which is equal to the length of designed input, and \( m = 16 \), is the number of kinetic parameters. \( s_j(p,t_i) = \frac{\partial \dot{V}(t_i)}{\partial p_j} \) denotes the sensitivity of output \( V(t_i) \) to parameter \( p_j \), approximated using a finite-difference method. The output \( \dot{V} \) is obtained by supplying the designed input \( I_{app}(t_i) \) (cf Figure 4) to the model, while being at 50% SoC and given certain nominal parameter value \( \hat{p} = [\hat{p}_1, \hat{p}_2, \cdots, \hat{p}_m] \) (obtained by substituting \( \beta = 0.5 \) in (17a) or (17b)).

Each column of sensitivity matrix \( S \) expresses the output sensitivity to every kinetic parameter. The norm of each column indicates the size of sensitivity while the linear dependence between 2 columns indicates the degree of similar effect on the output if changing these parameters. To allow comparing different parameters that have different orders of magnitude, the sensitivity matrix is normalized by multiplying with \( \Gamma_0 \):

\[
S(p,t)_{\text{norm}} = S(p,t) \Gamma_0.
\] (23)

where \( \Gamma_0 = \text{diag}(\hat{p}_1, \hat{p}_2, \cdots, \hat{p}_m) \) represents the diagonal matrix of nominal parameter values.

A QR factorization with column pivoting is a method that determines an orthogonal matrix \( Q \), an upper triangular matrix \( R \), with a decreasing magnitude of diagonal entries \(|r_{11}| \geq |r_{22}| \geq \cdots \geq |r_{mm}|\), and a permutation matrix \( \Pi \), so that

\[
S_{\text{norm}} \Pi = QR,
\] (24)

The permutation matrix \( \Pi \) determines a new order of columns for matrix \( S_{\text{norm}} \) so that the most sensitive parameters appear in the first entries of the parameter vector \( p \). The new ordering of parameters from most sensitive to least sensitive can be computed using

\[
[1 \ 2 \ \cdots \ m] \Pi,
\] (25)

where \([1 \ 2 \ \cdots \ m]\) is the initial order of parameters. A detailed explanation of sensitivity analysis based on the QR decomposition is given in Golub\(^{37}\) and some examples using this method are given in Lund et al and Fink et al.\(^{22,38}\)

When applying the QR factorization to the sensitivity matrix obtained by applying the current input \( I_{app} \) (cf Figure 4A) at 50% SOC, the order of parameters ranking from the most sensitive to the least is given by

\[
[1 \ 2 \ \cdots \ 16] \Pi = [8 \ 14 \ 4 \ 6 \ 16 \ \cdots].
\] (26)

To assess how many parameter are sufficiently sensitive, the diagonal entries in \( R \) are considered, which are shown in Figure 4B. From this figure, it can be seen that the first 5 values are much larger than the others. This means that 5 parameters are sufficiently sensitive. The extremely small values correspond to the directions in the parameter space in which varying the parameters has very limited influence on the output, leading to an unreliable parameter estimation, and these parameters will be kept at their nominal values. Hence, only the parameters cor-
TABLE 4 Parameters ranking in the DFN model using QR

| Rank | Parameter | Description                                      |
|------|-----------|--------------------------------------------------|
| 1    | Rs        | Radius of electrode material particle            |
| 2    | σ_p       | Solid phase electrical conductivity in positive electrode |
| 3    | De        | Li-ion diffusion coefficient in electrolyte       |
| 4    | D_{s,p}   | Li-ion diffusion coefficient in positive electrode |
| 5    | R_f       | Contact resistance                               |

responding to the first 5 indices will be estimated, which are \([8, 14, 4, 6, 16]\). By looking up the number in the kinetic parameters in Table 1, this corresponds to the parameters \(p_s = [Rs, \sigma_p, De, D_{s,p}, R_f]^T\), which are listed in Table 4, ranking from the most sensitive parameter to the least sensitive one. It should be noted that the conclusions presented here are based on the current input \(I_{app}\) given in Figure 4A at 50% SOC. However, the analysis has been done at 20% (an almost empty battery) and 80% SOC (an almost full battery), and for other current inputs, and the conclusions on the sensitive parameters remained the same.

5.2.2 Numerical illustration

To illustrate that the method based on the QR factorization indeed properly captures the sufficiently sensitive parameters, a numerical illustration is given. To illustrate the sensitivity of the parameters, a perturbation is given to every nominal kinetic parameter to see whether these changes influences the model output.

Consider the battery at 50% SOC, apply \(I_{app}(t)\) as given in Figure 4A to the model and substitute \(\beta = 0.4\) in (17a) or (17b) to increase each parameter by the same extent based on its nominal value. The model output is compared with that derived by using nominal values \(p\). The same is done for decreasing the parameters by replacing \(\beta = 0.6\). It turns out that \(Rs, \sigma_p, De, D_{s,p},\) and \(R_f\) are sensitive parameters since the variation in model output \(\hat{V}(t)\) is obvious when changing these parameters, which is reflected in the first 5 plots in Figure 5. However, for the transference number \(t_+\), which is the first nonidentifiable parameter (ranking sixth in sensitivity), the output of the model is non-sensitive to the deviation of \(t_+\) from its nominal value, as the last plot in Figure 5 shows.

5.3 Parameter estimation

After selecting parameters which can be properly estimated using the dynamic current input of Figure 4A, the kinetic parameters are now estimated by minimizing the sum of the squared error between experimental voltage and predicted one, ie,

\[
\hat{p}_s := \arg \min_{p_s} \sum_{i=1}^{N} (V_{exp}(t_i) - \hat{V}(p_s, t_i))^2,
\]

where \(V_{exp}(t_i)\) denotes the measurement of voltage, \(\hat{V}(p_s, t_i)\) is the predicted output voltage and \(p_s\) is a vector of identifiable parameters.

In this paper, a nonlinear least-squares regression technique called the Levenberg-Marquardt method\(^{24}\) is used to solve (35) and to obtain parameter estimates. The
TABLE 5 Estimated values of first 5 most sensitive parameters using Levenberg-Marquardt method

| Parameter | Dimension | Initial value | Optimized value |
|-----------|-----------|---------------|-----------------|
| $R_s$     | $\mu m$  | 1             | 0.834           |
| $\sigma_p$ | S$^{-1}m$ | $3 \cdot 10^{-3}$ | $2 \cdot 10^{-3}$ |
| $D_e$     | m$^3s^{-1}$ | $2.6 \cdot 10^{-11}$ | $1.66 \cdot 10^{-11}$ |
| $D_h$     | m$^3s^{-1}$ | $3.7 \cdot 10^{-16}$ | $8.38 \cdot 10^{-16}$ |
| $R_f$     | $\Omega m^2$ | $2 \cdot 10^{-3}$ | $2.4 \cdot 10^{-3}$ |

Levenberg-Marquardt algorithm is implemented in Matlab by the function *nonlsq* and it actually consists of a combination of 2 minimization methods: the gradient descent method and the Gauss-Newton method. The update rule is given by

$$\hat{p}_{s,\ell+1} = \hat{p}_{s,\ell} + (J_f^T J_f + \lambda_\ell I)^{-1} J_f^T f_\ell,$$  

(36)

where $\ell \in \mathbb{N}$ is the iteration index, $\lambda_\ell > 0$ is a well-chosen damping factor, $f_\ell = V_{exp} - \hat{V}(\hat{p}_{s,\ell})$, $V_{exp} = [V_{\exp}(t_1), \ldots, V_{\exp}(t_N)]^T$ and $\hat{V}(\hat{p}_{s,\ell}) = [\hat{V}(\hat{p}_{s,\ell}, t_1), \ldots, \hat{V}(\hat{p}_{s,\ell}, t_N)]^T$. The matrix $J_\ell$ is a Jacobian matrix of the partial derivatives of the output voltage $\hat{V}(\hat{p}_{s,\ell})$ with respect to all the parameters $p_s$, and is evaluated in local parameter $\hat{p}_{s,\ell}$ at each iteration, ie, $J_f = \frac{\partial \hat{V} (\hat{p}_{s,\ell})}{\partial p_s} |_{\hat{p}_{s,\ell}}$.

Since different information will be obtained when starting (dis-)charging a nearly empty or a full battery, the experimental data $V_{exp}$ are collected by giving the designed input $I_{app}(t)$ (Figure 4A) to the battery at both 20% and 80% SoC. The initial sensitive parameter vector $\hat{p}_{s,0}$ is chosen as the nominal values, as given by Table 1, and the final identifiable parameter estimates $\hat{p}_{s}$ are obtained via an iterative procedure using (36) until it has converged and provides a solution to (35). The obtained parameter estimates are given in Table 5. The predicted and experimental voltages at different initial SoC (80% and 20%) after the parameter estimation procedure are shown Figure 6B,C. The solid blue and red lines represent the measured voltage and output of the identified model, respectively. It can be observed that the optimized parameter estimates lead to a model prediction that agrees quite well with the measured voltages at both SoC. It also worthwhile to note that

![Current and Voltage Graphs](image)
the optimized parameter values deviate not too much from the initial guess. In fact, those are well within “rationality ranges” derived from available publications and listed in the rightmost column of Table 1. That confirms, from one side, validity of the initial guess of sensitive kinetic parameters, but from another side, good quality of estimation in thermodynamic part. Estimation of kinetic part, therefore, plays a role of fine-tuning step and does not impair robustness of overall estimation scheme.

6 VALIDATION

In this section, the model with the optimized values of the parameters will be validated on different data sets. Constant currents and pulsed current profiles will be used in the model validation.

6.1 Static discharge experiments

The constant discharge reveals how the battery performs in the whole process from the full to the empty. Substitute the estimated parameters into the model and give the constant currents 12A, 6A, and 1.2A, as inputs to the model, to discharge the battery at 1C-rate, 0.5C-rate, and 0.1C-rate, respectively. Figure 7 presents the comparison of the model predictions to the experimental data when discharging the battery in various C-rates. The solid colored lines represent measured data and the symbols stand for the predicted voltage of the model. It can be seen that the model output is in good agreement with the measured data in the static discharges.

6.2 Pulses experiments

Besides the constant currents, the validation is also done on pulsed (dis-)charge inputs to assure that the estimated model is able to capture the dynamics of battery. In Section 5, the experimental data sets at 20% and 80% SoC are used for estimation, so it is sensible to validate on the measured voltage at 50% SoC (the middle of the entire range of SoC). The input profile is the same as that used in parameter estimation, but the initial SoC has changed to 50%. Figure 6D shows the simulation result compared to the measured data when starting at 50% SoC. Additionally, another input with shorter pulses and longer relaxation periods is used for validation. The input is characterized by several pulses last 2 minutes, each is followed by 10 minutes relaxation period. Figure 8 displays the validation result on this input profile.

From Figure 6D and Figure 8, it can be observed that the prediction of voltage for the identified model agrees with the experimental ones well. The root mean square error (RMSE) between the predictions and various experimental data sets is calculated and reported in Table 6. The error at 80% SoC is the smallest, RMSE is 5.6 mV, while RMSE at 20% SoC is the largest, 15.5 mV. Regardless of what initial SoC the battery start at and what durations of the pulses and relaxation periods are in the input, RMSE values are small, which indicates the identified battery model is in good agreement with real behavior of the battery in pulses (dis-)charge. It also should be noted that RMSE-s achieved in validation phase, ie, third and fourth lines in Table 6, are in range of RMSE-s obtained in estimation stage. That fact, together with good performance on static discharges, indicate successful validation of model. Attained accuracy
TABLE 6 Root mean square error between predictions and various experimental data sets

| Input [A] | RMSE [mV] |
|-----------|-----------|
| Figure 6B | 5.6       |
| Figure 6C | 15.5      |
| Figure 6D | 7.2       |
| Figure 6B | 5.9       |

is comparable with accuracy of previously published DFN modeling results, ie, Masoudi et al\textsuperscript{18} or Smith et al.\textsuperscript{27}

7 | CONCLUSIONS

The DFN model is one of the most popular models in describing the behavior of the Li-ion battery and contains a large number of parameters. It is important to estimate parameters in the DFN model to obtain an accurate model for simulation or solving control-oriented problems. In this paper, a computationally feasible two-step estimation approach is developed in which the original set of parameters is split into two. The first set contains thermodynamically determined parameters, which have been estimated on the set of static discharge curves by extrapolating towards zero current. The second set contains kinetic parameters, which have been estimated using a designed highly-dynamic pulse (dis-)charge current. A sensitivity analysis based on QR factorization with column pivoting has been done to find out the most sensitive kinetic parameters. Estimating only the sufficiently sensitive parameters leads to a more reliable estimation result.

The sufficiently sensitive parameters have been estimated through minimizing the sum of square error between experimental data and predicted voltage using the Levenberg-Marquardt method, which was selected for the parameter estimation due to its fast convergence. The result was illustrated by comparing the model outputs with the battery measurements, and a quite well fit was achieved. Finally, the estimated model has been validated on several specifically designed validation data sets. Validation results reveal an error in output voltage of less than 16 mV RMSE of magnitude which is comparable with majority of cited DFN model estimation results. Therefore, a good performance of the identified model in predicting the experiment results is demonstrated. Estimated parameter values agree well with ranges expected from the literature.

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